

Room temperature hydrogen production via electro-dehydrogenation of amines into nitriles: advancements in Liquid Organic Hydrogen Carriers

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S1. General Methods

All working solutions were prepared, and all glassware cleaned using deionized water (Millipore MilliQ, 18.2 M Ω cm).

S1.1. Materials

All reagents were used from the commercial suppliers without further purification. Na₂SO₄ (Sigma Aldrich, 99.0%), NiCl₂·6 H₂O (Sigma Aldrich, 99.999%), Ti (Sigma Aldrich, 99.7%), Ni (<150 μ m, Sigma Aldrich 99.99%), PGR (4B hardness, 2.0 mm diameter and 13.0 mm length, ©STAEDTLER mars GmbH & CO, KG, made in Germany), KOH (Sigma Aldrich, 99.99%), Nafion 117 membrane (Sigma Aldrich), Ni foam (GoodFellow, 99.5%, thickness 6 mm).

S1.2. Electrode preparation

NiNF: This electrode was prepared through electrodeposition of Ni onto nickel foam (NF), using NiCl₂. The electrodeposition process was carried out using cyclic voltammetry in a one-compartment cell with a three-electrode configuration. In a typical experiment, a 2 cm² nickel foam working electrode was immersed in a 0.1 M Na₂SO₄ and 0.02 M NiCl₂·6 H₂O solution. Reference and counter electrodes were Ag/AgCl and Pt wire, respectively. The cyclic voltammetry conditions for the electrodeposition involved 25 cycles ranging from -1.3 to 0 V vs Ag/AgCl, at a scan rate of 50 mV·s⁻¹, under magnetic stirring.

NiPGR: This electrode was prepared through electrodeposition of Ni pencil graphite rod (PGR). Electrodeposition process as previously described for NiNF.

Ni45: This electrode was prepared using a previously reported method¹ by mixing 550 mg of Ti (100 mesh) and 450 mg of Ni (< 150 μ m), powders in a pestle and mortar. The powder was introduced into a die equipped with a set of screws and nuts to be able to retain the pressure. An axial pressure of 5 ton was applied to the punch. Then, the electrode obtained was introduced into an oven and heated at 500 °C during 3 h.

S1.3. Electrochemical measurements

S1.3.1. Cyclic voltammetry

Cyclic Voltammetry experiments were performed in a one-compartment cell with three electrodes, using a Gamry (Reference 3000tm) potentiostat/galvanostat. A Pt wire and Ag/AgCl (3 M KCl) were used as counter and reference electrodes, respectively. Nickel electrodes were employed as working electrodes.

Measurements were done in a 20 mL of 0.25 to 1 M solution of KOH with magnetic stirring. Cyclic voltammeteries in the absence and presence of amines were measured at a scan rate of 10 mV/s from 0 to 1 V vs Ag/AgCl.

S1.3.2. Impedance Spectroscopy (IS)

Impedance Spectroscopy (IS) experiments were performed in a one-compartment cell with three electrodes, using a Biologic Science Instruments VSP. The NiNF (2 cm²) electrode was used as working electrode with 20 mL of 0.5 M KOH solution and 50 mM 1,6-hexanediamine in one-compartment cell. The measurements of IS were done in the potential range of 0 to 1 V (vs Ag/AgCl), at steps of 25 mV and 50 mV. The frequency used ranged from 400 kHz to 3 mHz.

S1.3.3. Chronocoulometry analysis

Chronocoulometry experiments were carried out in a glass cell with two compartments using a three-electrode assembly for electrochemical dehydrogenation of primary amines at room temperature, pressure and under magnetic stirring on the anode compartment. Current density and voltage dependence were measured with a Gamry (Reference 3000^{mm}). 20 mL of 0.5 M KOH was used as electrolyte at pH 13.6, as obtained after saturation with N₂. Pt wire was used as a counter electrode and was separated from the working electrode (NiNF) using a proton exchange Nafion 117 membrane. Ag/AgCl in 3 M aqueous KCl solution was used as a reference electrode and potentials were corrected with reference to the Reversible Hydrogen Electrode (RHE) scale after the experiments. *J-V* curves and chronoamperometry measurements were recorded and the organic products formation were analyzed by ¹H-NMR spectroscopy and gas chromatography (GC-FID).

S1.4. Product Characterization

S1.4.1. Nuclear Magnetic Resonance (NMR) Spectroscopy

¹H-NMR spectra were collected on a 400 MHz Bruker spectrometer. All samples were prepared taking 100 μL of sample and adding 500 μL of deuterated water (D₂O), using ethylene glycol (EG) as internal integration standard.

S1.4.2. Gas Chromatography (GC)

GC analyses of the reaction liquid products were obtained on a Shimadzu GC-2010 apparatus equipped with a FID detector, and using a Teknokroma column (TRB-5MS, 30 m x 0.25 mm x 0.25 μm). Gaseous products generated in the reaction were analyzed using an Agilent micro-GC 490, equipped with a molecular sieve (MS5) column and a TCD detector. Argon was used as the carrier gas at 19.9 mL min⁻¹.

S1.4.3. Microscopy Electrode Characterization (SEM)

The scanning electron microscopy (SEM) measurements were carried out in a JEOL 7001F equipment operating at 15 kV.

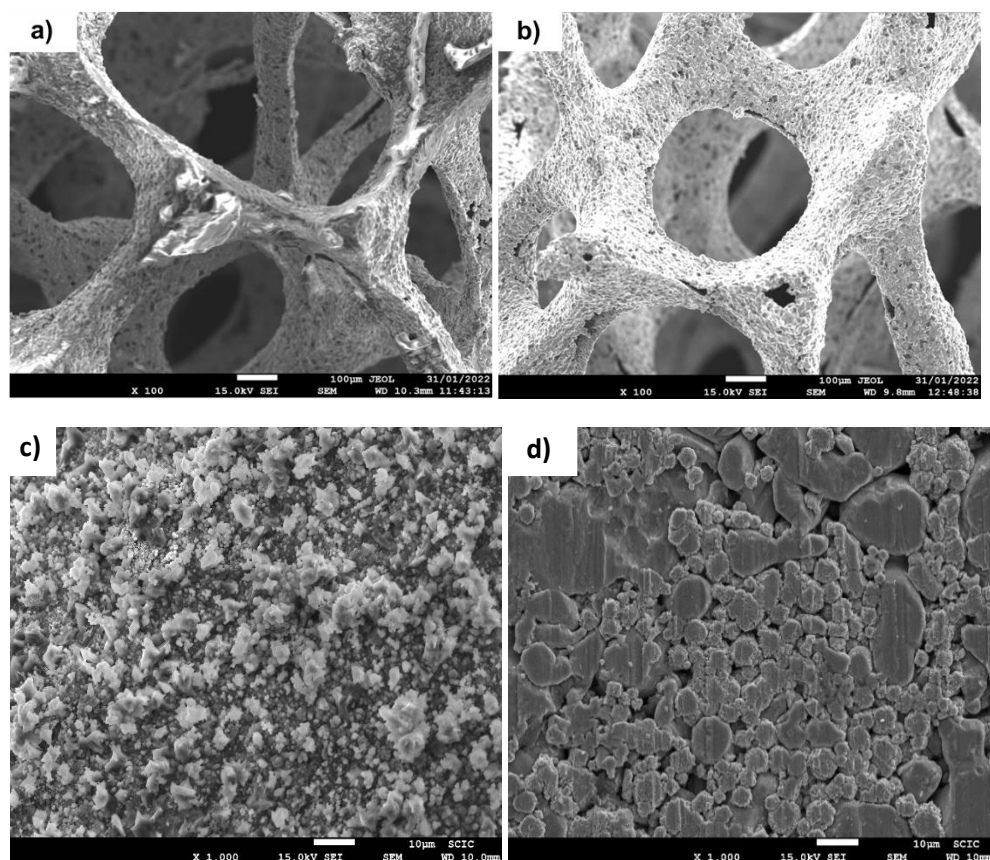


Figure S1. SEM images of **a)** commercial Nickel Foam (NF), **b)** commercial Nickel Foam after nickel electrodeposition (NiNF), **c)** Pencil graphite rods with after nickel electrodeposition (NiPGR) and **d)** Ni45.

S2. Experimental Procedures

S2.1. Electrode activation

The activation of nickel electrodes was performed by CV in 1 M KOH, performing 10 cycles in each case, under magnetic stirring. This methodology was used to increase the amount of electroactive species on the surface of the electrodes. The reversible redox peak observed during the activation process by CV shows the transformation of α/β -Ni(OH)₂ (Ni²⁺) to catalytically active β -NiOOH (Ni³⁺).

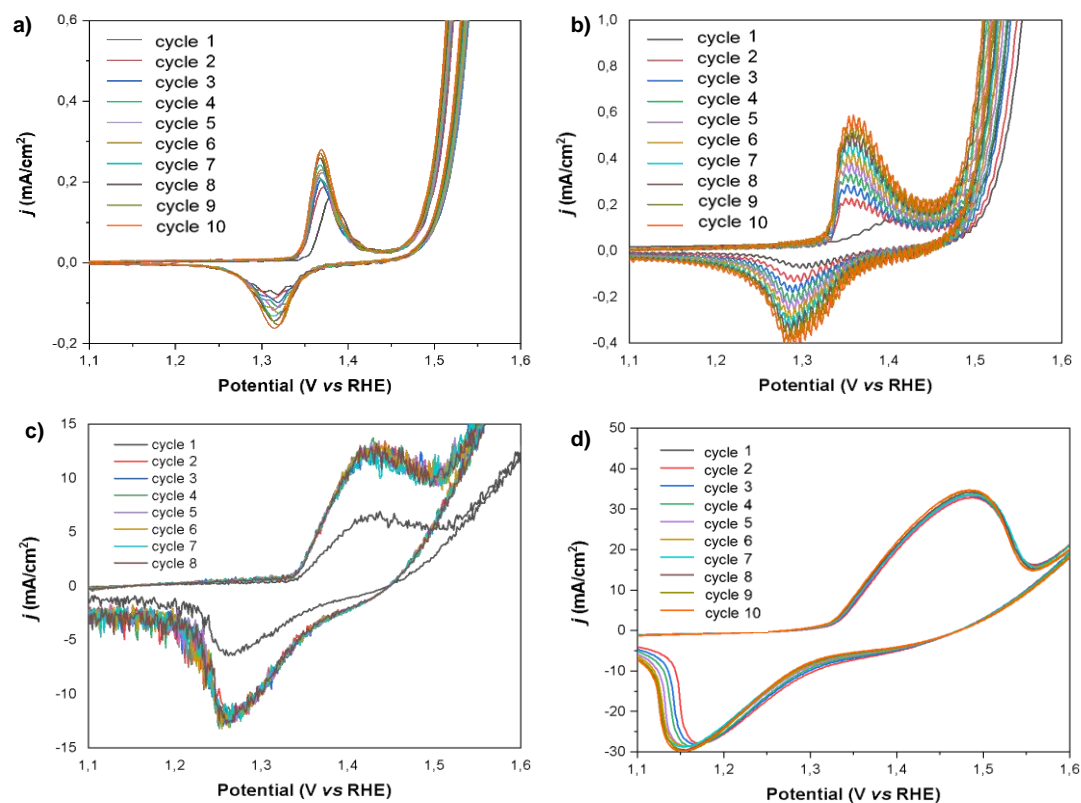


Figure S2. Activation of the nickel electrodes by CV in 1 M KOH, at a scan rate of $10 \text{ mV} \cdot \text{s}^{-1}$. **a)** Ni foil, **b)** Ni foam, **c)** NiPGR, **d)** NiNF

S2.2. Temperature Effect

Table S1. Temperature effect on the electrochemical oxidation of 1a to 2a .				
Entry	Temperature (°C)	% Conversion 1a	% Yield 2a	
			% Yield	% FE
1	25	99	90	95
2	40	96	91	81
3	60	100	24	24

Reaction conditions: 25 mM **1a** in 0.5 M KOH, under magnetic stirring in the anode compartment with NiNF as working electrode.

S2.3. Stability of NiNF electrodes

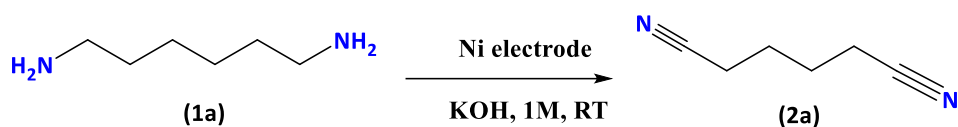
Table S2. Results in the stability test for the electrooxidation of 1a to 2a using the same electrode.				
Entry	Run	% Conversion 1a	% Yield	% FE
			2a	
1	1	99	84	84
2	2	100	85	85
3	3	100	82	82
4	4	97	89	89
5	5	100	83	83

Reaction conditions: 25 mM **1a** in 0.5 M KOH, under magnetic stirring in the anode compartment with NiNF as working electrode.

S2.4. ^1H -NMR Spectra

Following figures show ^1H -NMR spectra recorded before ($t = 0$) and after the chronoamperometry experiments

S2.4.1. ^1H -NMR spectra for the electro-dehydrogenation of **1a** using different Ni-bases electrodes in 1 M KOH



Scheme S1. Electrodehydrogenation of **1a** using Ni-based electrodes in 1 M KOH

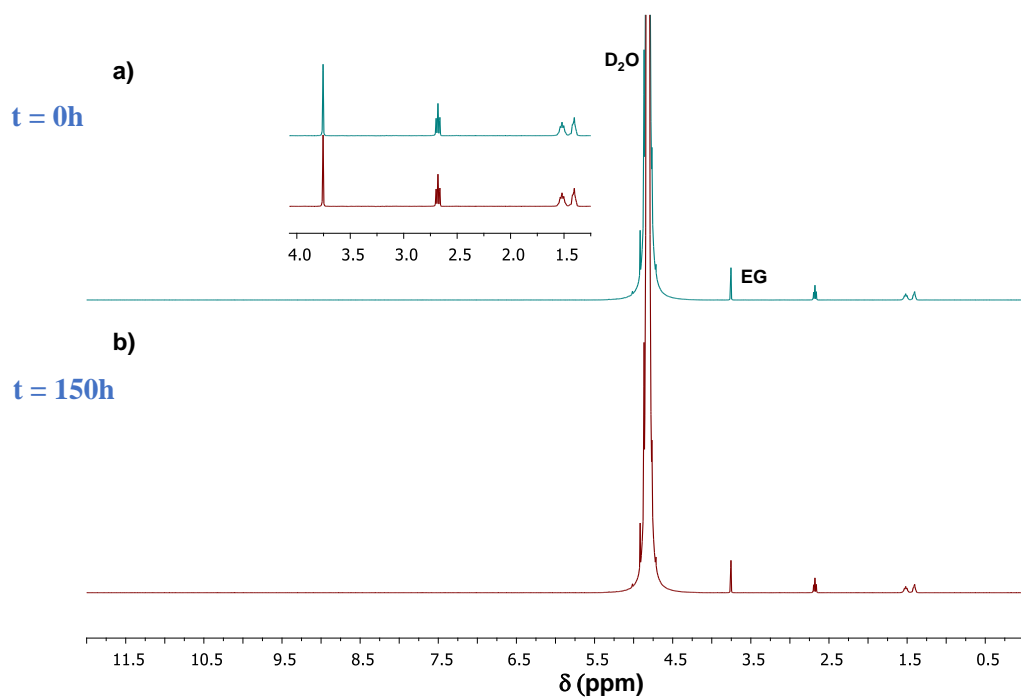


Figure S3. a) ^1H -NMR spectrum of **1a** before starting the reaction. b) ^1H -NMR spectrum of the liquid products at $t = 150\text{h}$.

Ethylene glycol (EG) as internal standard. Inset: Zoom of ^1H NMR spectrum in the region of 1 to 4 ppm. Electro-dehydrogenation conditions: 25mM **1a** in a 1 M KOH solution at 1.55 V vs RHE using Ni foil.

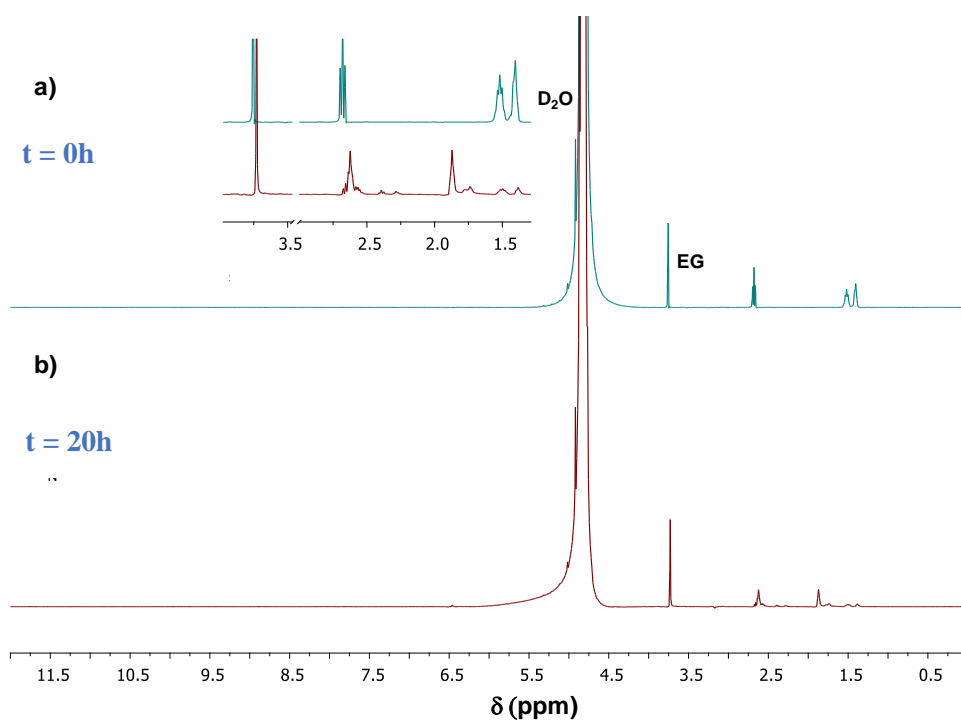


Figure S4. a) $^1\text{H-NMR}$ spectrum of **1a** before starting the reaction. **b)** $^1\text{H-NMR}$ spectrum of the liquid products at $t = 20\text{h}$. Ethylene glycol (EG) as internal standard. Inset: Zoom of $^1\text{H NMR}$ spectrum in the region of 1 to 4 ppm. Electro-dehydrogenation conditions: 25mM **1a** in a 1 M KOH solution at 1.55 V vs RHE using NiF.

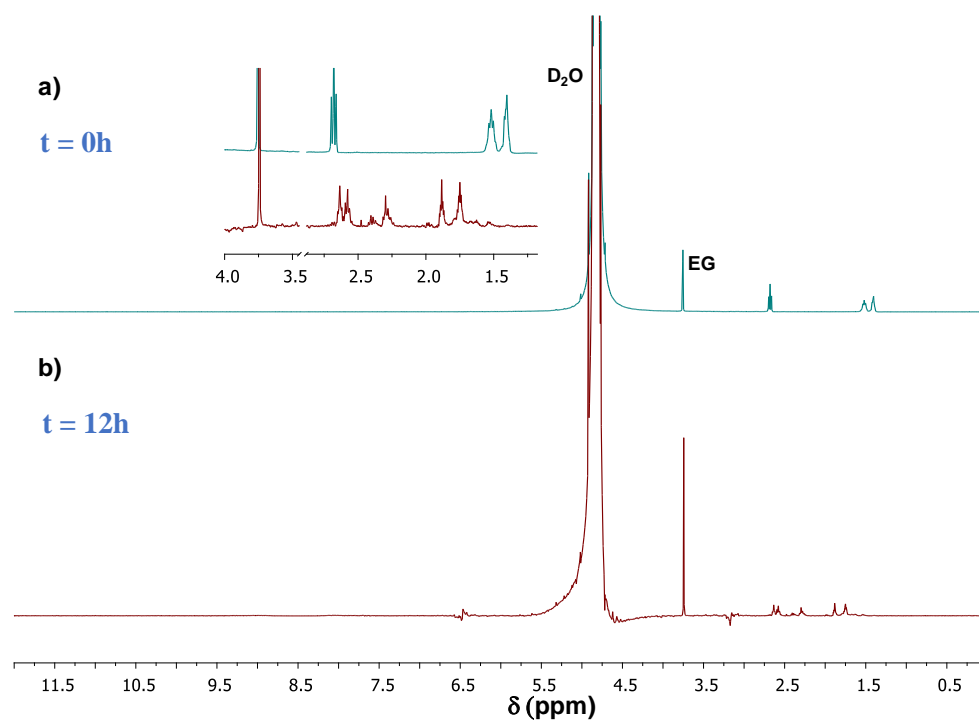


Figure S5. a) $^1\text{H-NMR}$ spectrum of **1a** before starting the reaction. **b)** $^1\text{H-NMR}$ spectrum of the liquid products at $t = 12\text{h}$. Ethylene glycol (EG) as internal standard. Inset: Zoom of $^1\text{H NMR}$ spectrum in the region of 1 to 4 ppm. Electro-dehydrogenation conditions: 25mM **1a** in a 1 M KOH solution at 1.55 V vs RHE using NiPGR.

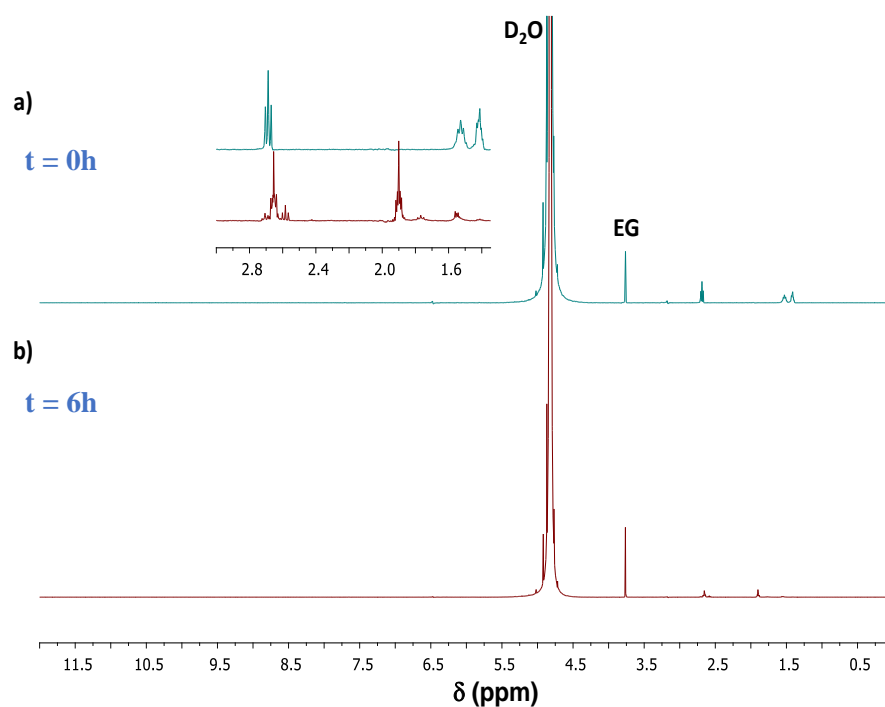


Figure S6. a) $^1\text{H-NMR}$ spectrum of **1a** before starting the reaction. b) $^1\text{H-NMR}$ spectrum of the liquid products at $t = 6\text{h}$. Ethylene glycol (EG) as internal standard. Inset: Zoom of $^1\text{H NMR}$ spectrum in the region of 1.5 to 3 ppm. Electro-dehydrogenation conditions: 25mM **1a** in a 1 M KOH solution at 1.55 V vs RHE using Ni45.

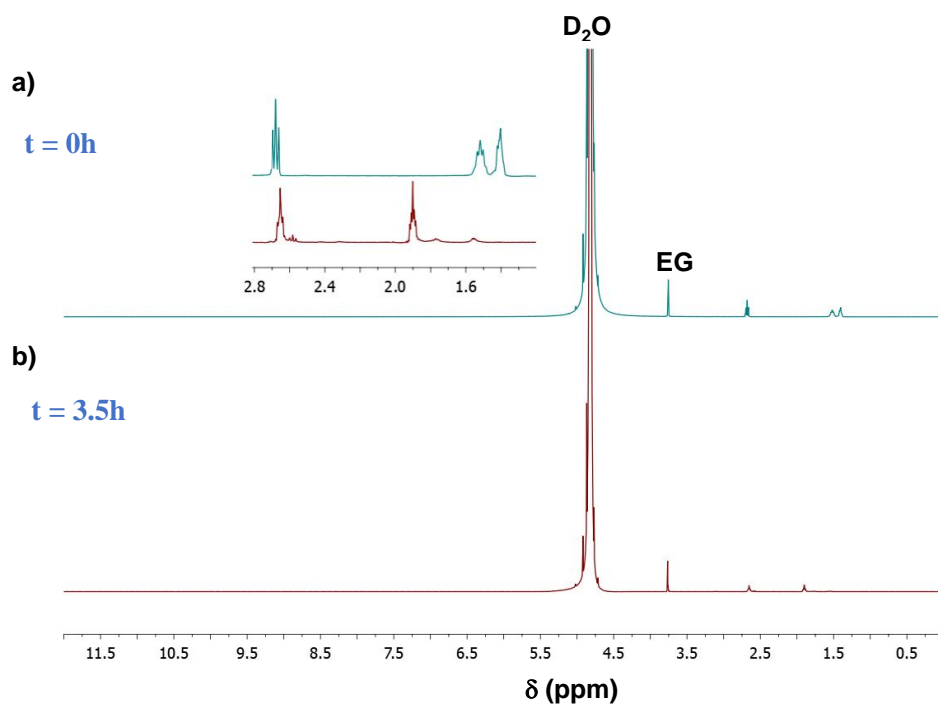
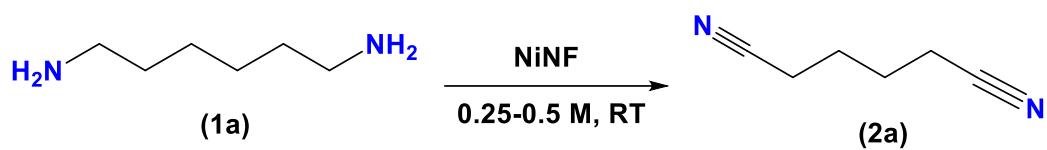


Figure S7. a) $^1\text{H-NMR}$ spectrum of **1a** before starting the reaction. b) $^1\text{H-NMR}$ spectrum of the liquid products at $t = 3.5\text{h}$. Ethylene glycol (EG) as internal standard. Inset: Zoom of $^1\text{H NMR}$ spectrum in the region of 1.3 to 3.8 ppm. Electro-dehydrogenation conditions: 25mM **1a** in a 1 M KOH solution at 1.55 V vs RHE using NiF.

S2.4.2. Influence of KOH amount in electro-dehydrogenation of **1a** using NiNF



Scheme S2. Electrodehydrogenation of **1a** using NiNF in 0.25 and 0.5 M KOH

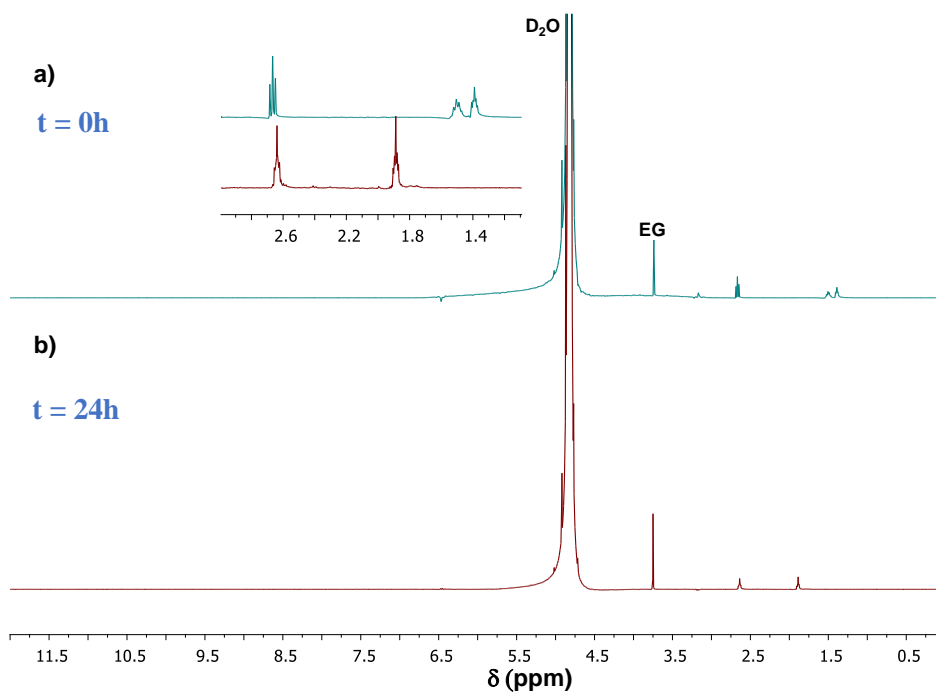


Figure S8. a) ^1H -NMR spectrum of **1a** before starting the reaction. b) ^1H -NMR spectrum of the liquid products at $t = 24\text{h}$. Inset: Zoom of ^1H NMR spectrum in the region of 1 to 3 ppm. Electro-dehydrogenation conditions: 25mM **1a** in a 0.25 M KOH solution at 1.55 V vs RHE.

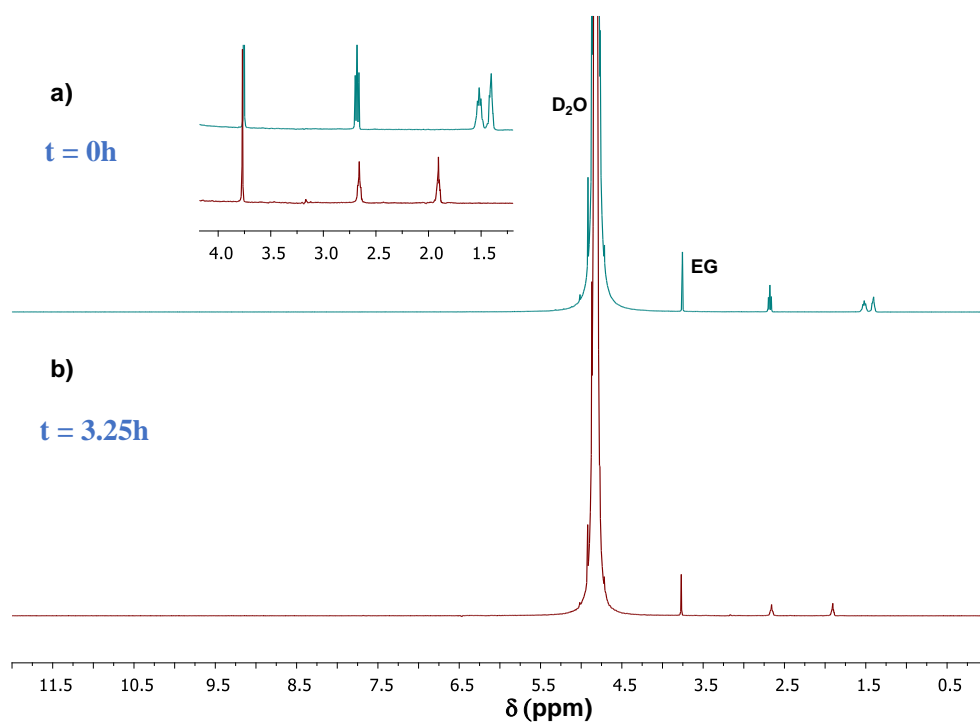
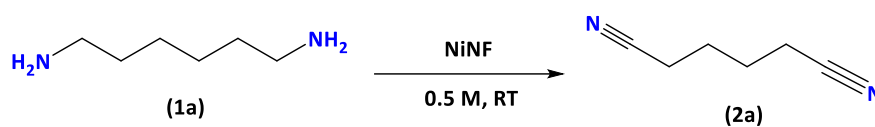


Figure S9. a) ¹H-NMR spectrum of **1a** before starting the reaction. b) ¹H-NMR spectrum of the liquid products at $t = 3.25\text{h}$. Inset: Zoom of ¹H NMR spectrum in the region of 1 to 3 ppm. Electro-dehydrogenation conditions: 25mM **1a** in a 0.50 M KOH solution at 1.55 V vs RHE.

S2.4.3. ^1H -NMR spectra of the electro-dehydrogenation of different amines using NiNF electrode in 0.5 M of KOH



Scheme S3. Electro-dehydrogenation of **1a** using NiNF.

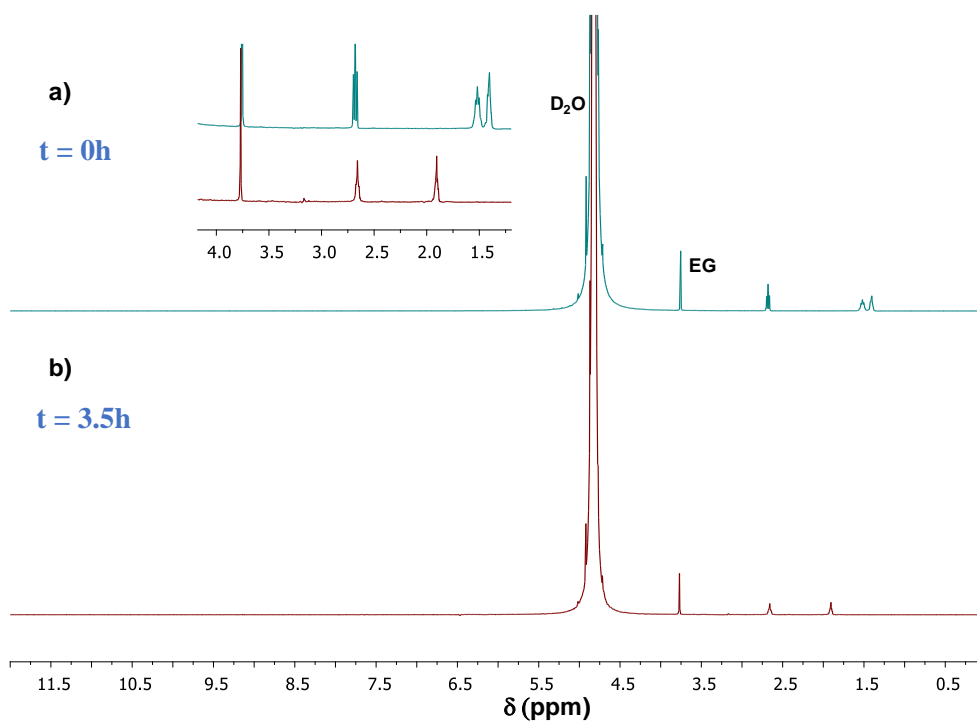
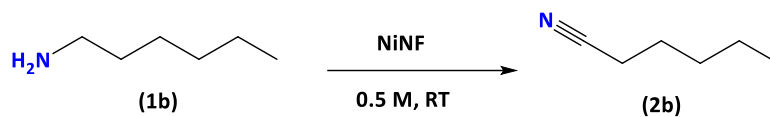


Figure S10. a) ^1H -NMR spectrum of **1a** before starting the reaction. b) ^1H -NMR spectrum of the liquid products at $t = 3.25\text{h}$. Inset: Zoom of ^1H NMR spectrum in the region of 1 to 3 ppm. Electro-dehydrogenation conditions: 25mM **1a** in a 0.50 M KOH solution at 1.55 V vs RHE.



Scheme S4. Dehydrogenation of **1b** using NiNF.

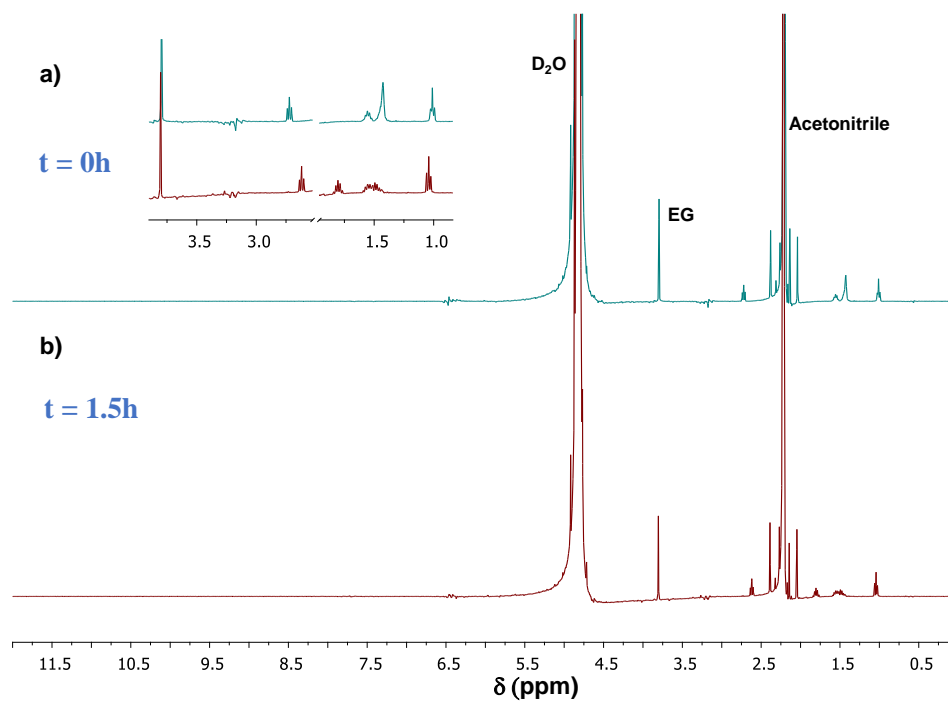
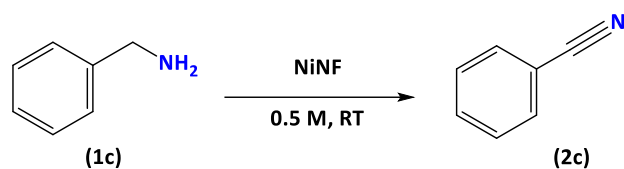


Figure S11. a) $^1\text{H-NMR}$ spectrum of **1b** before starting the reaction. b) $^1\text{H-NMR}$ spectrum of the liquid products at $t = 1.5\text{h}$. Inset: Zoom of $^1\text{H-NMR}$ spectrum in the region of 0.9 to 4 ppm. Electro-dehydrogenation conditions: 25mM **1b** in a 0.50 M KOH solution at 1.55 V vs RHE.



Scheme S5. Dehydrogenation of **1c** using NiNF.

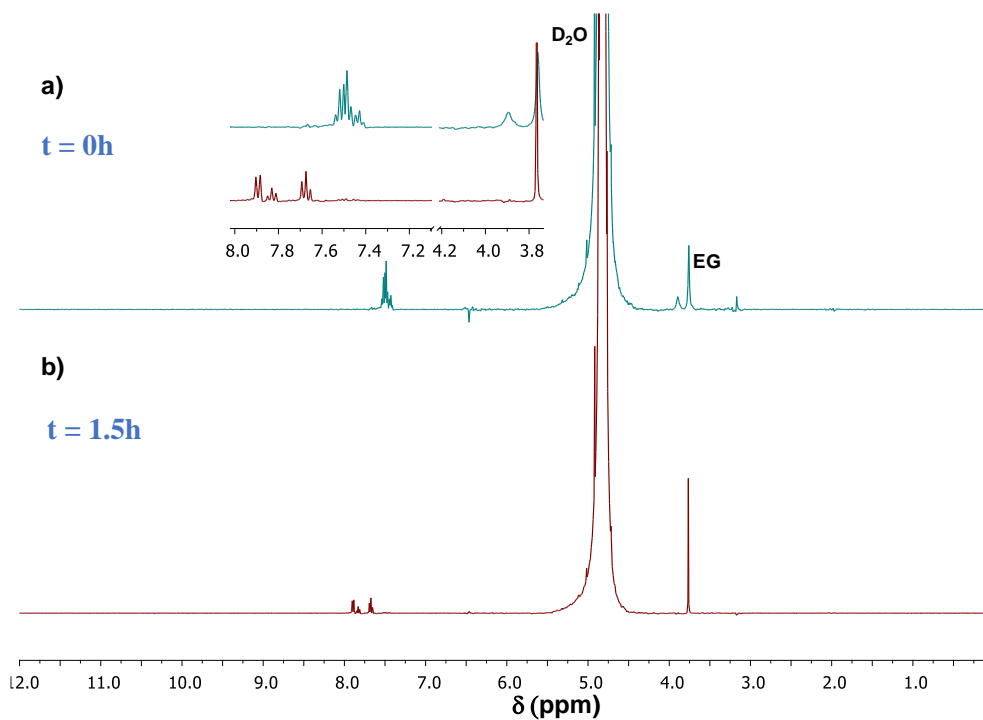
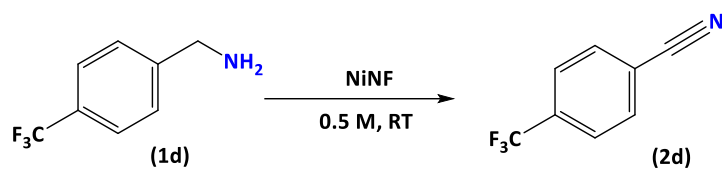


Figure S12. a) ^1H -NMR spectrum of **1c** before starting the reaction. b) ^1H -NMR spectrum of the liquid products at $t = 1.5\text{h}$. Inset: Zoom of ^1H NMR spectrum in the region of 3.5 to 8 ppm. Electro-dehydrogenation conditions: 25mM **1c** in a 0.50 M KOH solution at 1.55 V vs RHE.



Scheme S6. Dehydrogenation of **1d** using NiNF.

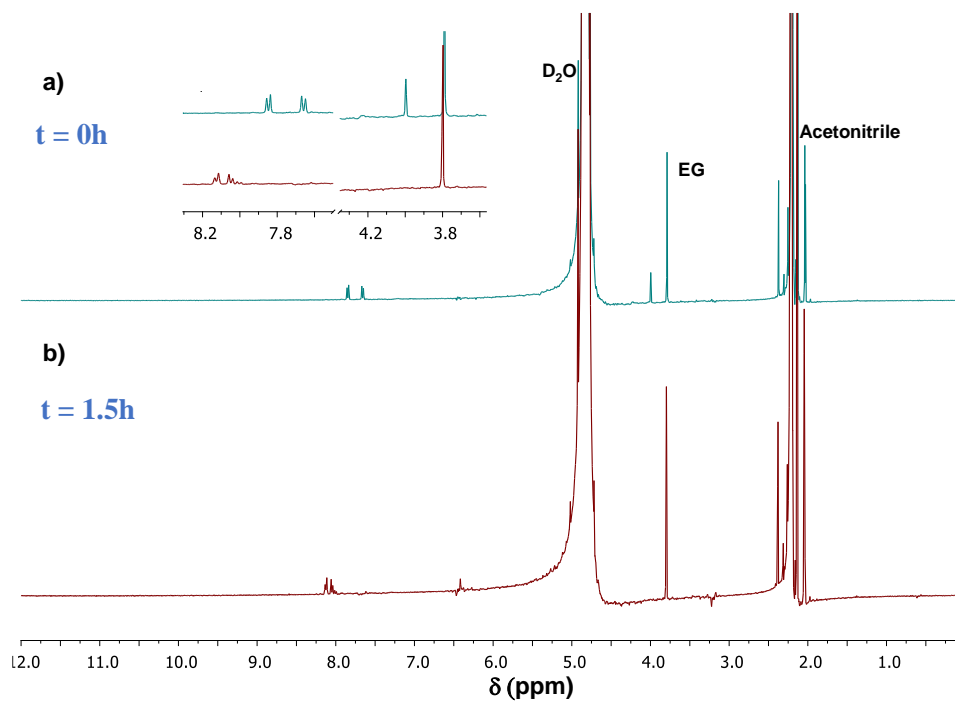
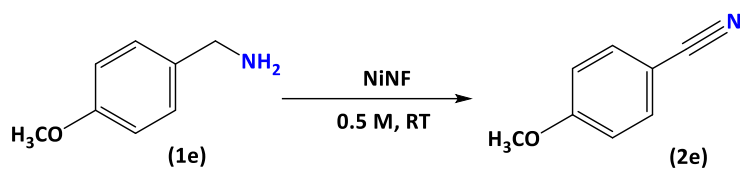


Figure S13. a) $^1\text{H-NMR}$ spectrum of **1d** before starting the reaction. b) $^1\text{H-NMR}$ spectrum of the liquid products at $t = 1.5\text{h}$. Inset: Zoom of $^1\text{H NMR}$ spectrum in the region of 3.5 to 8.3 ppm. Electro-dehydrogenation conditions: 25mM **1d** in a 0.50 M KOH solution at 1.55 V vs RHE.



Scheme S7. Dehydrogenation of **1e** using NiNF.

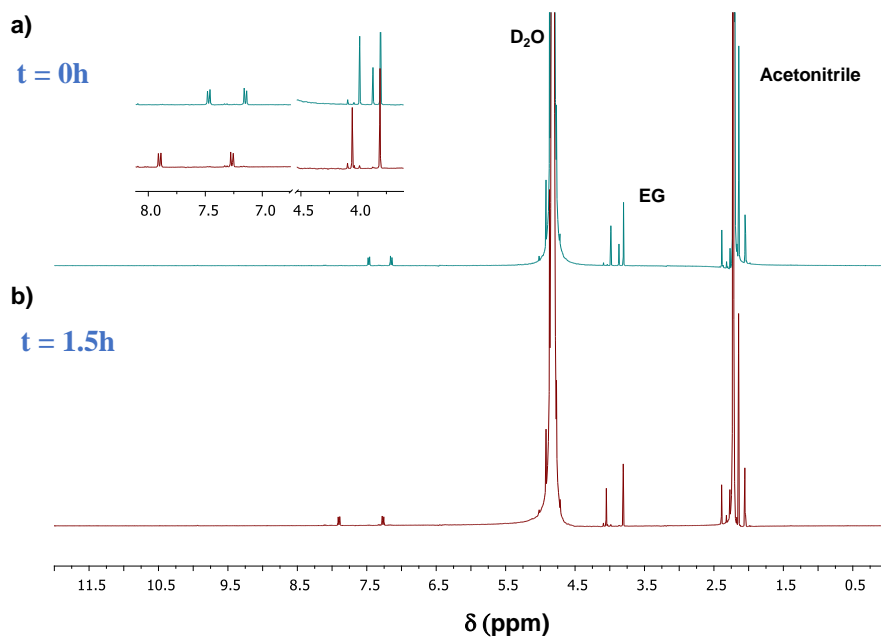


Figure S14. a) ¹H-NMR spectrum of **1e** before starting the reaction. b) ¹H-NMR spectrum of the liquid products at $t = 1.5\text{h}$. Inset: Zoom of ¹H NMR spectrum in the region of 3 to 8 ppm. Electro-dehydrogenation conditions: 25mM **1e** in a 0.50 M KOH solution at 1.55 V vs RHE.

S2.5. Adiponitrile stability

A 25 mM solution of adiponitrile in aqueous media with KOH was stirred at room temperature for 20 hours. The solution was extracted in CH₂Cl₂/H₂O (3 x 20ml), and the organic phase was dried under vacuum. Subsequently, it was analysed by ¹H-NMR spectroscopy using 1,3,5-trimethoxybenzene (TMB) as internal standard. The spectrum indicates a 30% loss of the starting material (Figure S16). Following this, the aqueous phase was neutralized and extracted in CH₂Cl₂/H₂O once again undergoing the same procedure. In this case, the ¹H-NMR spectrum reveals the formation of amide-based subproducts, which contribute to previous losses of the starting material. (Figure S17).

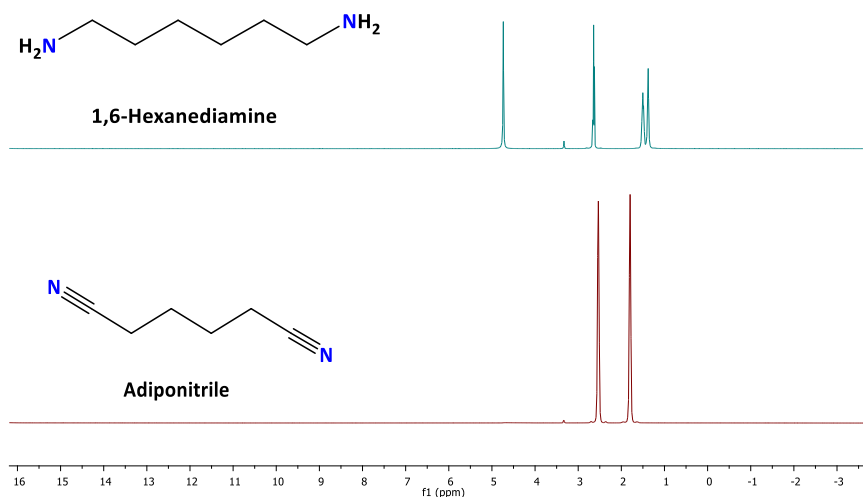


Figure S15. ¹H-NMR spectra of **1a** (top) and **2a** (bottom) commercially available in MeOD.

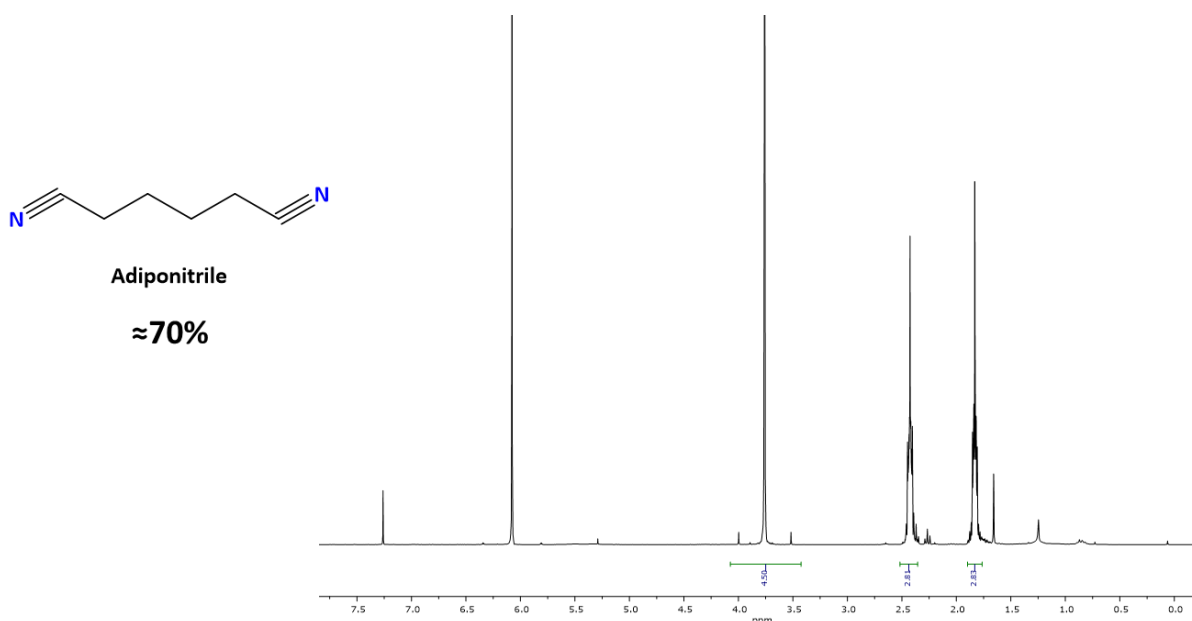


Figure S16. $^1\text{H-NMR}$ spectrum of organic phase in CDCl_3 . TMB as internal standard (signals at 3.75 and 6.2 ppm).

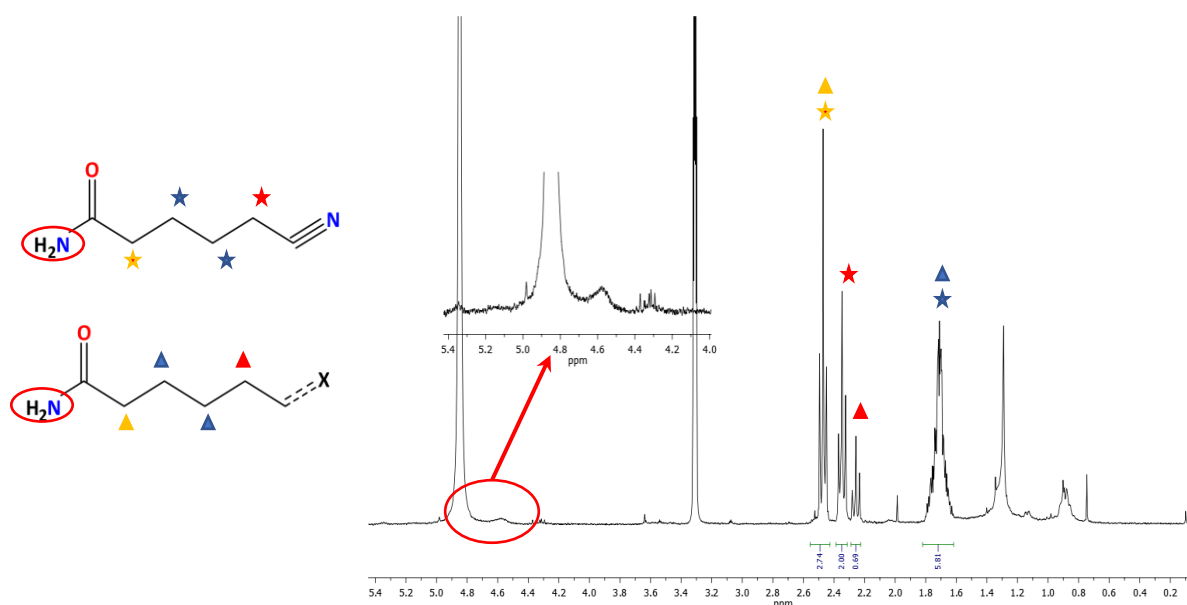


Figure S17. Zoom $^1\text{H-NMR}$ spectrum in MeOD of the second organic phase extracted.

S2.6. Hydrogen detection

To identify the gases produced during the catalytic electro-oxidation of **1a**, we conducted two chronoamperometry experiments in the presence and in the absence of **1a**. Chronoamperometries were performed in a one-compartment cell utilizing a three-electrode setup at room temperature and ambient pressure. Prior to experimentation, the cell was purged with argon for 3 hours. Current density and voltage dependence were measured using a potentiostat/galvanostat (AUTOLAB PGSTAT302N). A 20 mL solution of 0.5 M KOH at pH 13.6 served as the electrolyte, with a Pt wire as the counter electrode,

Ag/AgCl in 3 M KCl as the reference electrode, and NiNF as the working electrode. The applied voltage was set at 0.55 V vs Ag/AgCl, and argon was bubbled during the whole experiment.

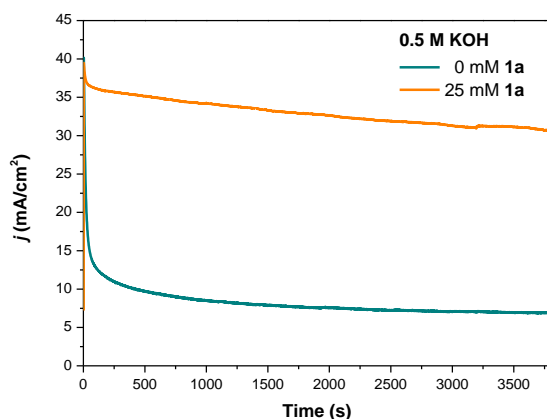


Figure S18. Chronoamperometry using NiNF as working electrode at a constant voltage of 1.5 V vs RHE with and without **1a**.

With the aim to identify the generated gas products, the cell was connected to a gas chromatograph (Agilent micro-GC 490), equipped with a molecular sieve (MS5) column and a TCD detector, has been used. Argon was used as the carrier gas at 19.9 mL min⁻¹ Figure S18 show three chromatograms after 1h reaction. Black line is the response of the detector where we don't see the presence of any gas. Green line shows the reaction without **1a**, where we can observe hydrogen and traces of oxygen, due to the OER. Orange line corresponds to the reaction in the presence of **1a**, showing an increase of the intensity signal of hydrogen gas and no oxygen detection, suggesting that OER reaction was avoided and oxidation of amine into nitrile was achieved.

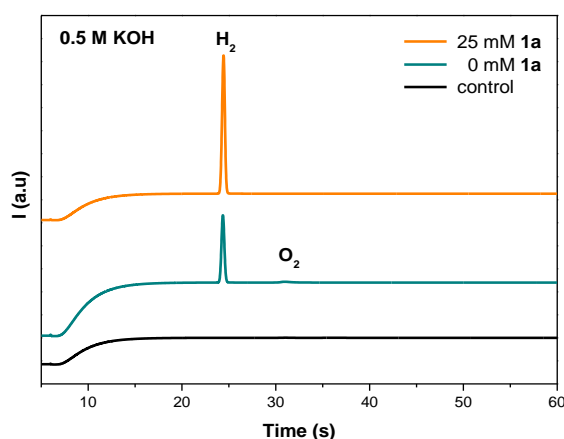
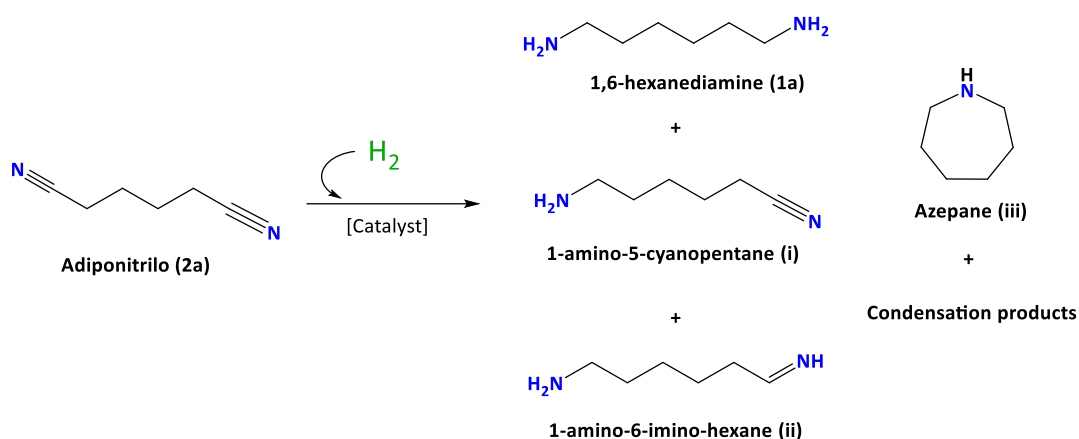


Figure S19. Detection of molecular hydrogen with (orange line) and without (green line) **1a**.

S2.7. Hydrogenation experiments



Scheme S8. Possible products for the hydrogenation of adiponitrile.

In a general catalytic experiment, a 2 mL vial equipped with a stirring bar was charged with the catalyst, 0.15 mmol of nitrile, 1 mL of isopropanol and the specified amount of 28% aqueous NH₄OH solution as additive. The charged vial was then introduced in a high-pressure autoclave. The reactor was purged 3 times with H₂ before pressurizing at 20 bars. The system was heated at 80 °C for 6 h. After this time, the reactor was left to reach room temperature and H₂ was released. Yields and conversions were determined by GC and/or ¹H-NMR analysis using anisole as an internal standard.

Table S3. Optimization of reaction conditions in the hydrogenation of adiponitrile							
Entry	Catalyst (mol%)	Solvent	H ₂ (bar)	T (°C)	Additive	Conv. (%)	Selectivity (1a/i/ii/iii/cp)
1	Pd/C (1)	Toluene	10	80	-	-	-
2	Pd/C (1)	MeOH	10	80	-	-	-
3	Pd/C (1)	<i>i</i> PrOH	20	80	NH ₄ OH (100μL)	76	0/9/0/0/91
4	Pd/Al ₂ O ₃ (1)	<i>i</i> PrOH	20	80	NH ₄ OH (100μL)	53	0/9/1/3/87
5	Pt/Al ₂ O ₃ (1)	<i>i</i> PrOH	20	80	NH ₄ OH (100μL)	63	4/58/5/15/18
6	Ru/Al ₂ O ₃ (1)	<i>i</i> PrOH	20	80	NH ₄ OH (100μL)	58	16/75/4/5/0
7	Ru/Al ₂ O ₃ (2,5)	<i>i</i> PrOH	20	80	NH ₄ OH (100μL)	76	17/70/7/16/0
8	Ru/Al ₂ O ₃ (2,5)	<i>i</i> PrOH	20	80	NH ₄ OH (200μL)	100	80/0/5/15/0
9	Ru/C (1)	<i>i</i> PrOH	20	80	NH ₄ OH (100μL)	59	36/49/5/8/2
10	Ru/C (2,5)	<i>i</i> PrOH	20	80	NH ₄ OH (100μL)	100	57/5/1/32/5
11	RaneyNi (100μL)	<i>i</i> PrOH	20	80	NH ₄ OH (100μL)	60	25/68/1/6/0
12	RaneyNi (200μL)	<i>i</i> PrOH	20	80	NH ₄ OH (100μL)	100	94/0/0/5/1

Reaction conditions: adiponitrile (0.15mmol), catalyst (1-2.5 mol%), 80 °C, 6h. Yields and conversions were determined by GC/FID and ¹H-NMR spectroscopic analysis using anisole as external standard.

S3. References

- (1) Guenani, N.; Barawi, M.; Villar-García, I. J.; Bisquert, J.; De La Peña O'Shea, V. A.; Guerrero, A. Highly Porous Ti-Ni Anodes for Electrochemical Oxidations. *Sustain Energy Fuels* **2020**, *4* (8), 4003–4007. <https://doi.org/10.1039/d0se00242a>.