

Supporting Information

Electrochemical Reductive N-Methylation with CO₂ Enabled by A Molecular Catalyst

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Materials

All chemicals were purchased and used as received unless otherwise stated. Gas cylinders of CO₂ (99.99%) and Ar (99.999%) were purchased from Airgas. Cobalt phthalocyanine (>95%) was purchased from Alfa Aesar. KHCO₃ (99.7%), paraformaldehyde (95%, powder), and hydrazine (35 wt.% in water) were purchased from Sigma Aldrich. NH₄HCO₃ (99%) and hydroxylamine hydrochloride (>99%) were purchased from Acros. KOH (45 wt.%) was purchased from Ricca. All amines and nitro-compounds were purchased from Sigma Aldrich: methylamine (40 wt.% in water), dimethylamine (40 wt.% in water), diethylamine (40 wt.% in water), morpholine (>99%), piperidine (>99.5%), aniline (>99.5%), nitrobenzene (>99%), 2-nitroethanol (97%), triethylamine (>99.5%), 4-methyl morpholine (99%), N-methyl piperidine (99%), N-methyl aniline (98%), N-methyl(ethanol)amine (>98%). Deionized water used in all experiments was purified through a Millipore water purification system to reach a resistivity of 18.2 mΩ cm (at 25 °C).

Electrolyte purification

500 mL of 0.1 M KHCO₃ (or 0.5 M KHCO₃) aqueous solution was electrochemically purified using a two-electrode set-up with two parallel 10 × 5 cm² titanium sheets. A voltage of 2.5 V was applied until the current dropped to 150 μA, and then a current of 150 μA was maintained for 24 hours. The titanium plates were then removed from the solution before stopping the electrochemical experiment to prevent dissolution of removed impurities. An appropriate quantity, typically 20 mM, of nitrogenous reagent was added to the electrolyte solution post-purification.

Preparation of CoPc/CNT and CoPc-NH₂/CNT electrodes

The synthesis of CoPc-NH₂, the purification of as-received multi-walled CNTs (FT 9100, C-Nano), and the loading of CoPc and CoPc-NH₂ onto purified CNTs were all carried out as detailed in our previous work (Nature, 2019, 575, 639-642), in which structural characterization results are available. The weight percentage of CoPc and CoPc-NH₂ in their respective CNT hybrid catalysts was about ~3%, as measured by inductively coupled plasma mass spectrometry (ICP-MS). Catalyst ink was prepared by dispersing 2 mg of CoPc (or CoPc-NH₂) in 2 mL of ethanol with 6 μL of 5 wt.% Nafion solution and sonicating for 1 hour. Once well-dispersed, 4 × 100 μL of catalyst ink was drop-casted onto a 1.0 cm² section of a 1 × 3 cm² piece of carbon fiber paper (Toray 030, 30% polytetrafluoroethylene) and dried under an IR lamp. The carbon fiber paper was cut in half to prepare working electrodes with a catalyst-covered geometric area of 0.5 cm² and a catalyst mass loading of 0.4 mg/cm².

Controlled potential electrolysis

Controlled potential electrolysis experiments were carried out using a Bio-Logic VMP3 Potentiostat and a custom-made gas-tight two-compartment H-cell. The anodic and cathodic compartments were separated by an anion exchange membrane (Selemion DSV). Each compartment contained 12 mL of electrolyte and 18 mL of gas headspace. For all experiments, the purified 0.1 M KHCO_3 was used as the electrolyte in the anodic compartment, and the purified 0.1 M KHCO_3 + nitrogenous reagent was used as the electrolyte in the cathodic compartment. The concentration of nitrogenous reagent was typically 20 mM, unless otherwise stated. A graphite rod was used as the counter electrode and placed in the anodic compartment. The reference electrode was Ag/AgCl (saturated KCl) and placed in the cathodic compartment near the working electrode. The cathodic compartment included two-tubing ports: the in-tubing was placed in the electrolyte and connected to a flowmeter, whereas the out-tubing was placed in the headspace and connected to the gas chromatograph (GC). Before the start of each electrolysis, the electrolyte was pre-saturated with CO_2 (or Ar for control experiments) by bubbling for at least 20 min. During all electrolyses, gas was flowed continuously at a rate of 20 standard cubic centimeters per minute. The Ohmic drop between the working electrode and the reference electrode was determined using potentiostatic electrochemical impedance spectroscopy at -0.5 V vs Ag/AgCl between 200 kHz and 1 Hz with an amplitude of 10 mV. The resistance was determined as the intersection of the curve with the real axis of the Nyquist plot. The internal resistance was corrected during all electrolysis experiments with 100% iR compensation. Current densities were calculated with respect to the catalyst-covered geometric area of the working electrode. All potentials were converted to the RHE scale using the following equation:

$$V_{\text{RHE}} = V_{\text{Ag/AgCl}} + (0.1976 \text{ V}) + (0.0592 \text{ V}) \times \text{pH}$$

Gas product quantification

The gas products of electrocatalysis were analyzed by a GC (MG #5, SRI Instruments) equipped with a flame ionization detector and a thermal conductivity detector. Argon was used as the carrier gas. Typically, the in-line GC was programmed to sample the headspace every 10 minutes, and therefore the gas products were quantified six times during a 1-hour controlled potential electrolysis. The peak areas were converted to gas volumes using a calibration curve created with known concentrations of H_2 and CO. The FEs and partial current densities of gas products were reported as the average of three or more independent measurements.

Liquid product quantification

Liquid products of electrocatalysis were detected using a Bruker 400 MHz NMR spectrometer. ^1H NMR spectra were collected using a water suppression mode ($d1 = 20$ s, 32 scans). NMR samples were prepared by adding 450 μL of electrolyte taken from the cathode compartment immediately post-electrolysis into an NMR tube containing 50 μL of an internal standard dissolved in D_2O (99.9 atom%, Sigma Aldrich). The internal standard employed depended on the peak positions of the analytes; it was either 10.00 mM potassium benzoate (99%, Alfa Aesar) or 10.00 mM dimethyl malonic acid (*TraceCERT*, Sigma Aldrich). The peak(s) corresponding to the internal standard were integrated to equal the concentration in mM of protons that they represent in the sample. The Faradaic efficiency and partial current density for each analyte was then calculated according to the below equation (example for N-methyl piperidine).

$$\text{FE}_{\text{NMP}} = (\text{peak area at 2.73 ppm}) \times \frac{(0.01 \text{ M I.S.})(12 \text{ g electrolyte})(5 \times 10^{-5} \text{ L})(6 \text{ mol e}^{-})(96485.33 \text{ C})}{(3 \text{ mol protons})(4.5 \times 10^{-4} \text{ L})(1 \text{ mol e}^{-})(1004.6 \frac{\text{g}}{\text{mol}})(Q_{\text{total}})} \times 100$$

$$j_{\text{NMP}} = \frac{FE_{\text{NMP}} \times Q_{\text{total}} \times 1000}{3600 \text{ s} \times 0.5 \text{ cm}^2}$$

For quantifying the co-reduction products of nitrobenzene and CO₂, we used calibration curves of known concentrations of standards, since we discovered that our quantitative NMR procedure under-estimated the concentration of some aromatic protons in the electrolyte (Figure S9). For control experiments in argon, the electrolyte was saturated with CO₂ post-electrolysis to adjust the pH to near-neutral for more direct comparison of the ¹H NMR features.

To confirm the identity of liquid products, we prepared standard solutions of the chemical in the CO₂-saturated 0.1 M KHCO₃ electrolyte and compared their ¹H NMR features with that of the post-electrolysis electrolyte. The stacked spectra are reported in this work. Additionally, we used the peak augmentation method, in which a known amount of the standard solution was added to the post-electrolysis solution to ensure that the signals of interest were augmented and not bifurcated. We note two exceptions in which a chemical standard of the product of interest was not available: methyl hydrazone and N-methyl phenyl hydroxylamine. In the case of methyl hydrazone, the features we attribute to methyl hydrazone in the post-electrolysis electrolyte from CO₂ reduction with hydrazine match well with features attributed to methyl hydrazone in the literature (Carcinogenesis, 1988, Jan 9(1):65-70) as well as those from a reaction of hydrazine with formaldehyde in the 0.1 M KHCO₃ electrolyte. The methyl signal we assign to N-methyl phenyl hydroxylamine at 3.03 ppm matches well with a simulated spectrum (MestReNova). Additionally, we rule out the possibility of the peak at 3.03 ppm being *N,N*-dimethylaniline (Figure S14). We also note that hydrazine and methyl hydrazone react with the 0.1 M KHCO₃ electrolyte, which changes its ¹H NMR features (Figure S5).

Turnover Frequency Calculation

TOF was reported as the number of product molecules per CoPc (or CoPc-NH₂) molecule per hour of electrolysis duration. The molecular catalyst loading was determined by inductively coupled plasma mass spectrometry (ICP-MS) analysis performed with an Agilent Technologies 7700 series instrument, which showed a 0.27 wt.% of cobalt in both the CoPc/CNT and CoPc-NH₂/CNT materials, which corresponds to 18.3 nmol/cm² of cobalt active sites per geometric electrode area (catalyst loading on the electrodes was 0.4 mg/cm²).

Example calculation of TOF for N-methyl morpholine:

$$\text{TOF}_{N-\text{methyl morpholine}} = 4.83 \times 10^{-4} \frac{\text{A}}{\text{cm}^2} \times 3600 \text{ s} \times \frac{1 \text{ mol e}^-}{96485.3 \text{ C}} \times \frac{1 \text{ mol N - methyl morpholine}}{6 \text{ mol e}^-} \times \frac{1 \text{ cm}^2}{1.83 \times 10^{-8} \text{ mol Co}}$$

$$\text{TOF}_{N-\text{methyl morpholine}} = 164 \text{ hr}^{-1}$$

Supplementary tables

Entry	Nitrogenous reagent	Total Current Density (mA/cm ²)	FE (H ₂)	FE (CO)	FE (CH ₃ OH)	C-N Coupled Product(s)				
						Structure(s)	FE	Turnover Frequency (hr ⁻¹)	Selectivity	Conversion
1	20 mM NH ₄ HCO ₃	20.8 ± 1.6	13.5% ± 4.7%	54.3% ± 9.5%	28.6% ± 1.4%	CH ₃ NH ₂	0%	0	0%	0%
2	20 mM CH ₃ NH ₂	19.6 ± 1.0	20.4% ± 2.4%	57.5% ± 5.3%	21.3% ± 2.5%		1.0% ± 0.4%	63 ± 27	100%	0.24%
3	20 mM (CH ₃) ₂ NH	19.9 ± 1.7	19.8% ± 5.3%	52.7% ± 17%	20.5% ± 2.2%		3.4% ± 0.7%	226 ± 48	100%	0.86%
4	20 mM (CH ₃ CH ₂) ₂ NH	21.7 ± 2.7	20.9% ± 2.2%	56.1% ± 8.3%	21.6% ± 1.9%		2.9% ± 0.4%	212 ± 33	100%	0.81%
5	20 mM Piperidine	20.6 ± 1.1	27.4% ± 1.3%	47.3% ± 4.2%	17.2% ± 1.1%		7.5% ± 0.6%	524 ± 44	100%	2.00%
6	20 mM Aniline	20.4 ± 2.5	12.8% ± 3.0%	67% ± 4.1%	22% ± 2.0%		0.6% ± 0.2%	41 ± 11	100%	0.16%
7	20 mM Morpholine	19.7 ± 2.0	21.8% ± 3.4%	53.9% ± 7.5%	19.7% ± 1.0%		2.5% ± 0.4%	164 ± 28	100%	0.63%
8	0.2 M Hydrazine	48.5 ± 3.5	65% ± 10%	16.2% ± 3.8%	5.4% ± 1.3%	CH ₂ NNH ₂	8.6% ± 0.2%	2130 ± 50	86%	0.94%
						CH ₃ NHNH ₂	0.6% ± 0.1%	99 ± 16	4%	
						CH ₃ NH ₂	2.0% ± 0.1%	247 ± 12	10%	
9	50 mM Hydroxylamine	25.5 ± 2.2	24% ± 2.7%	64% ± 5.5%	2.7% ± 0.5%	CH ₂ NOH	2.8% ± 0.4%	367 ± 52	31%	1.79%
						CH ₃ NHOH	1.9% ± 0.4%	166 ± 34	14%	
						CH ₃ NH ₂	9.8% ± 1.3%	637 ± 85	54%	

Table S1. List of nitrogenous reagents (amines, hydroxylamine, hydrazine) tested for C-N coupling on the CoPc/CNT electrocatalyst along with the total current density, Faradaic efficiencies for all detected products, TOF and selectivity for each C-N coupled product, and conversion of nitrogenous reagent. Table entries correspond to Table 1. The reaction condition was 1-hour CPE at -0.93 V vs RHE. Listed errors are standard deviations for three independent measurements.

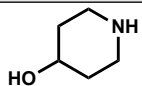
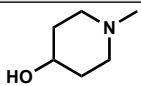
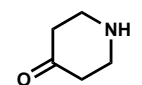
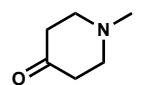
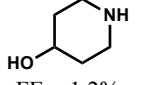
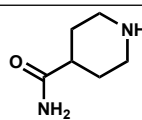
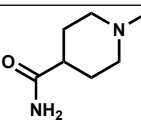
Entry	Nitrogenous reagent	Total Current Density (mA/cm ²)	FE (H ₂)	FE (CO)	FE (CH ₃ OH)	C-N Coupled Product		Nitrogenous Side Product?
						Structure	FE	
1		19.4	37.4%	32.3%	22.6%		2.6%	None
2		20.2	20.0%	63.8%	11.7%		<i>Not detected</i>	 FE = 1.2%
3		27.1	52.7%	29.2%	12.4%		0.70%	None

Table S2. Functional group tolerance results for piperidine derivatives tested for C-N coupling on the CoPc-NH₂/CNT electrocatalyst along with the total current density and Faradaic efficiencies for all detected products from a 12-hour CPE at -1.0 V vs RHE.

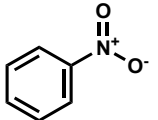
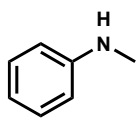
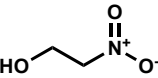
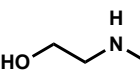
Entry	N source	Potential V vs RHE (Duration)	N-methyl Amine Product		Electrolyte (Aqueous)
			Structure	FE & <i>j</i>	
1		-0.93 (1 h)		6.0% ± 0.5% 1.2 mA/cm ²	10 mM PhNO ₂ + 0.1 M KHCO ₃
2		-0.93 (1 h)		14% ± 0.4% 5.5 mA/cm ²	20 mM HO(CH ₂) ₂ NO ₂ + 0.1 M KHCO ₃

Table S3. List of nitro-compounds tested for cascade reductive N-methylation with CO₂ on the CoPc/CNT electrocatalyst and yield of the N-methyl amine product. Error is the standard deviation for either two or three independent measurements.

Supplementary figures

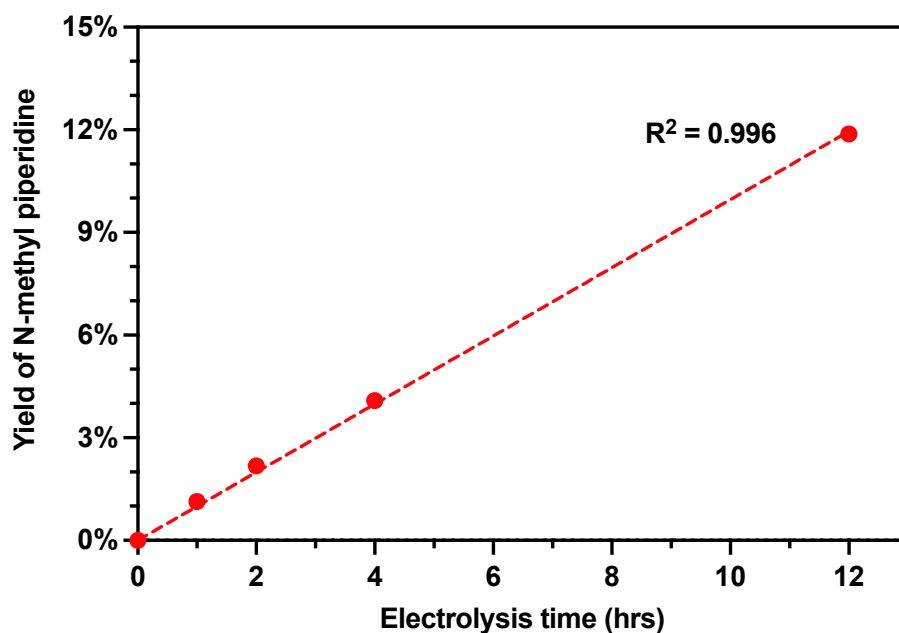
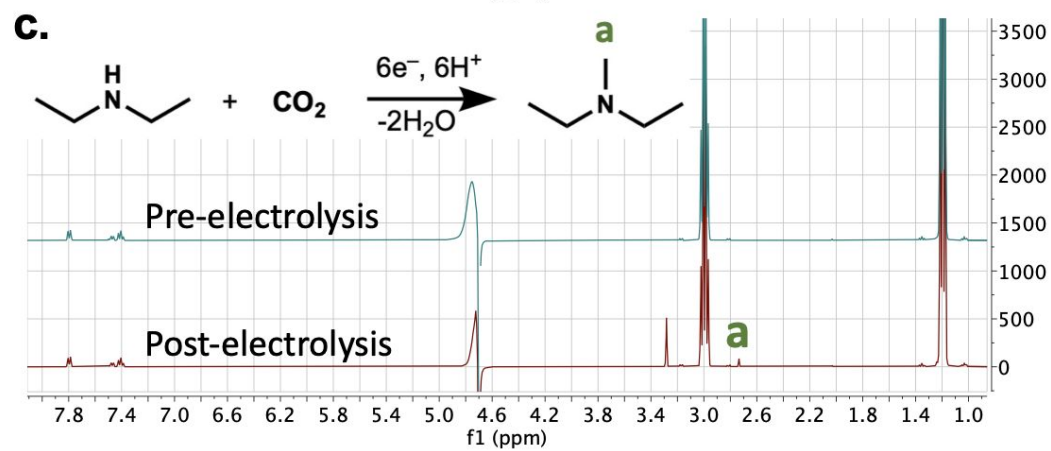
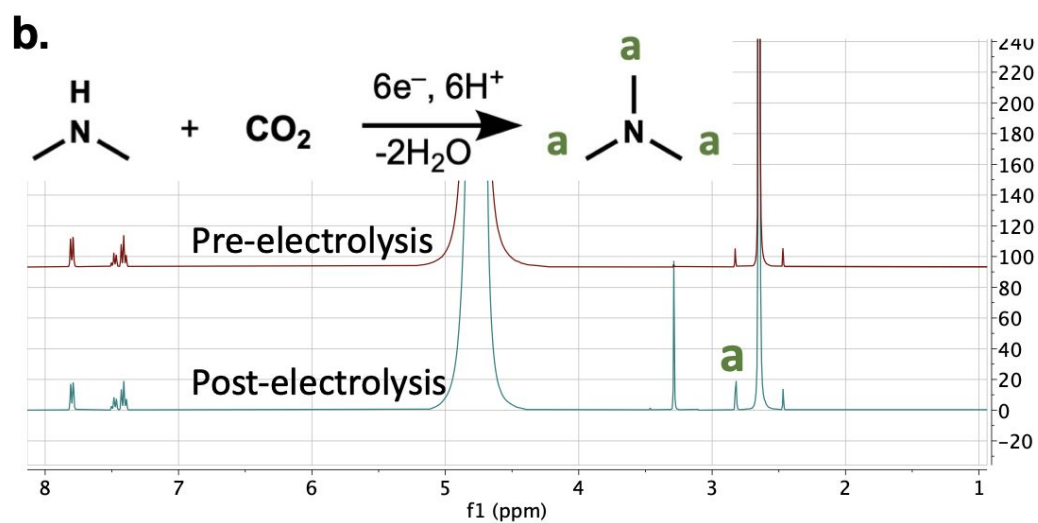
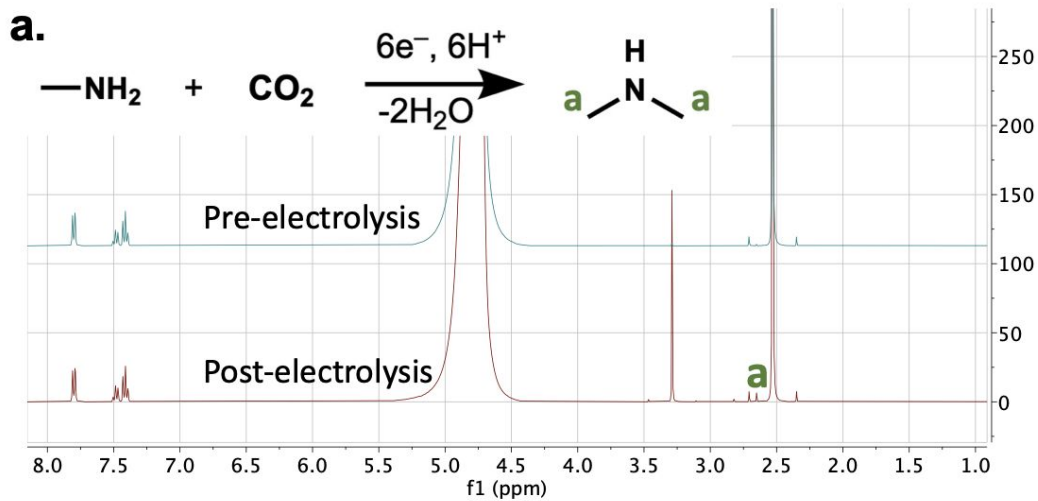


Figure S1. Percent yield of N-methyl piperidine over the same working electrode (loaded with the CoPc-NH₂/CNT electrocatalyst) for reaction cycles of varying durations. The electrode was rinsed with water and let dry between reaction cycles. The percent yield is linear with respect to electrolysis time indicating no performance decay between reaction cycles.



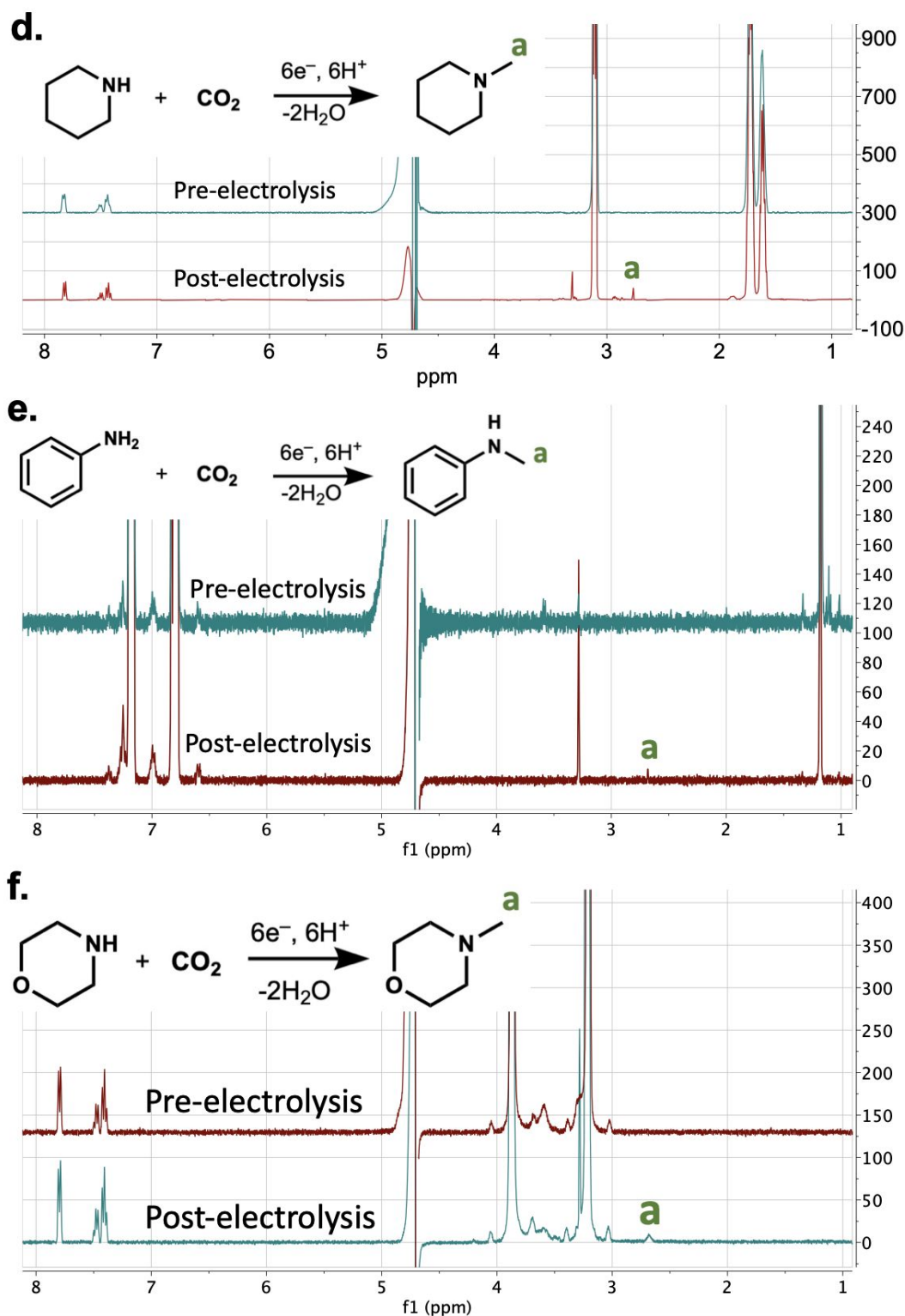


Figure S2. Reaction schemes and ^1H NMR spectra before and after the reductive N-methylation reaction for the amine reactants: a) methylamine, b) dimethylamine, c) diethylamine, d) piperidine, e) aniline, and f) morpholine. The reactions were 1-hour controlled potential electrolyses at -0.93 V vs RHE over the CoPc/CNT catalyst with 20 mM of amine dissolved in the cathode electrolyte. The ^1H NMR signal for the appended methyl group is labelled in the post-electrolysis spectra.

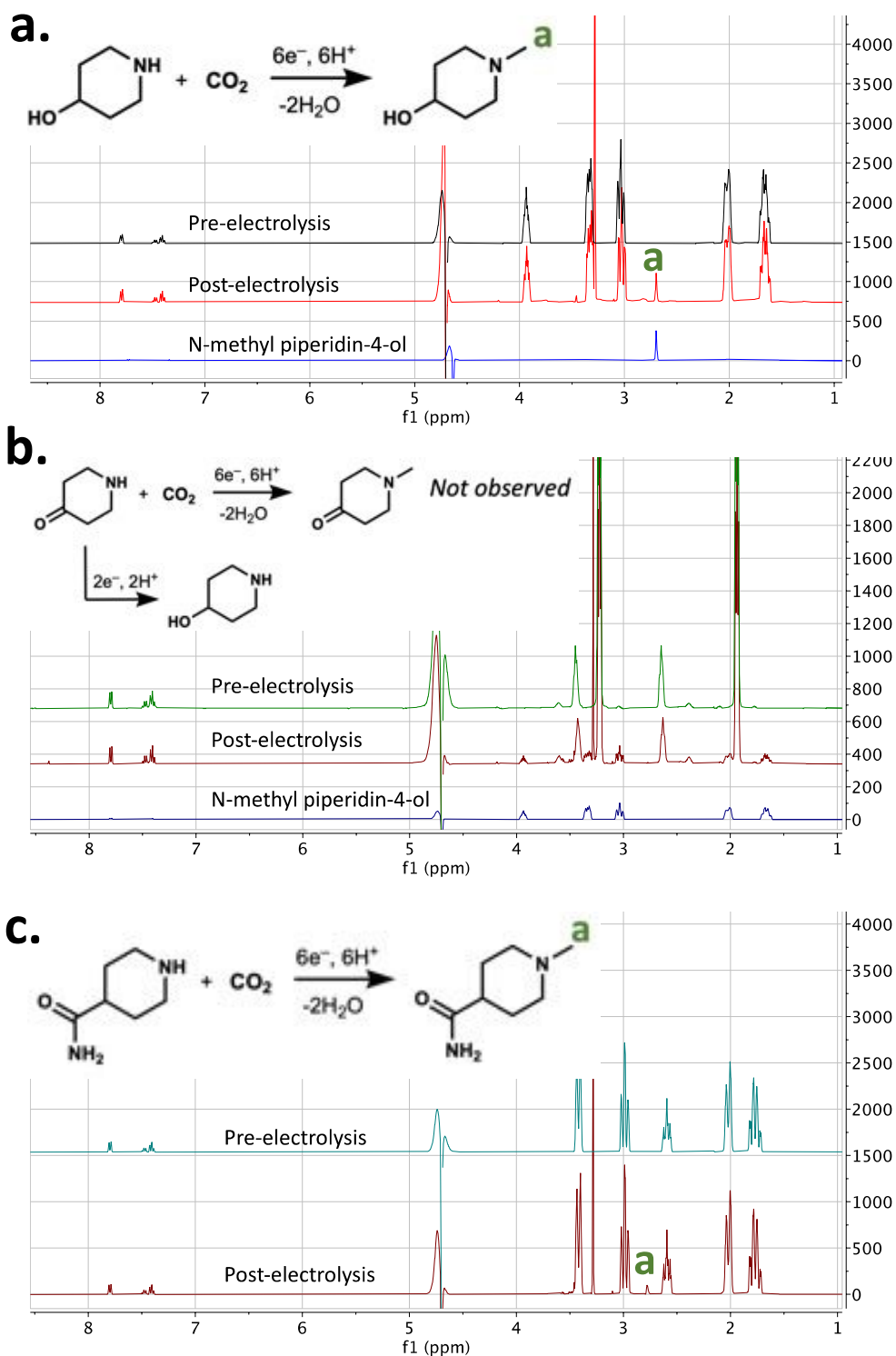


Figure S3. Reaction schemes and ^1H NMR spectra before and after the reductive N-methylation reaction for the amine reactants: a) piperidin-4-ol, b) piperidin-4-one, and c) piperidine-4-carboxamide. The reactions were 12-hour controlled potential electrolyses at -1.0 V vs RHE using the CoPc-NH₂/CNT catalyst with 20 mM of amine dissolved in the cathode electrolyte. The ^1H NMR signal for the appended methyl group is labelled in the post-electrolysis spectra.

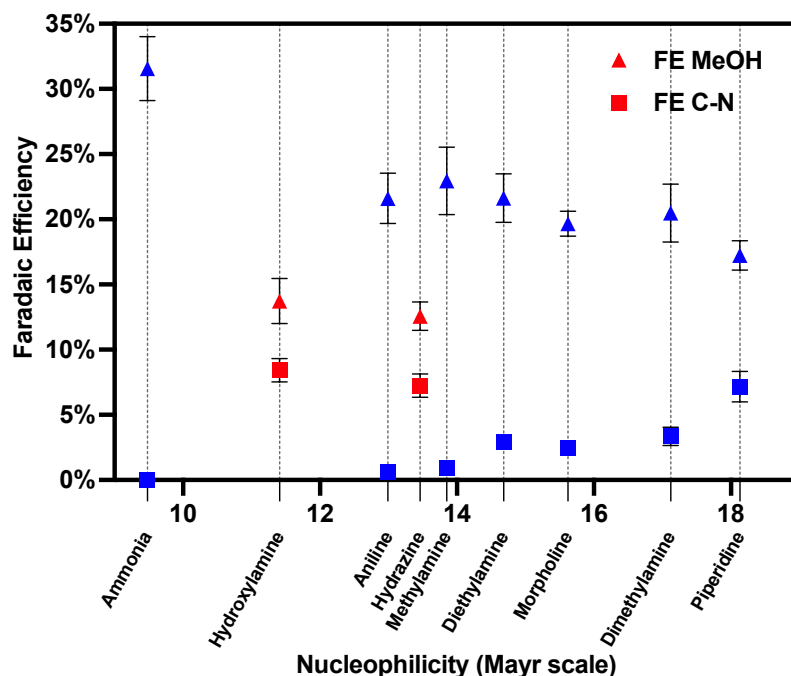


Figure S4. Faradaic efficiencies for methanol (triangle data symbols) and C-N products (square data symbols) as a function of nucleophilicity of the nitrogenous reactant. Data points are averages of three measurements and error is their standard deviation. Error bars are omitted when smaller than the data symbols.

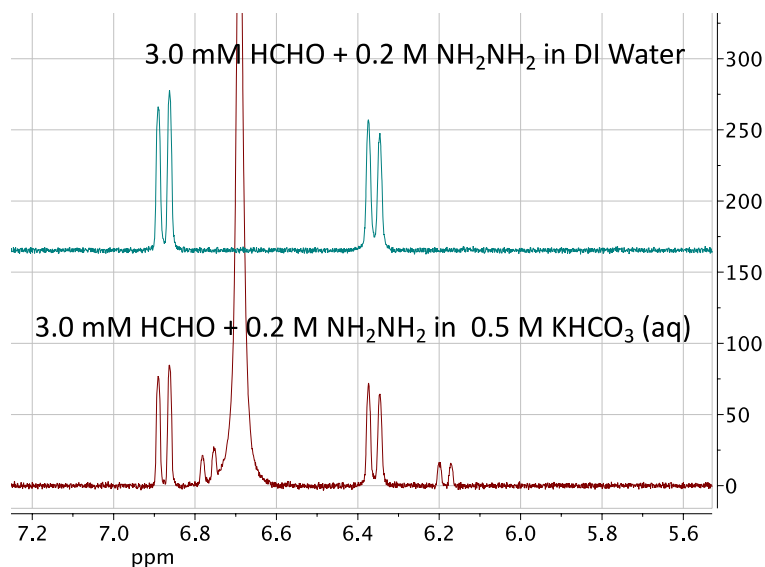


Figure S5. ^1H NMR spectra of the chemical reaction between 3.0 mM formaldehyde and 0.2 M hydrazine in DI water (blue) and the CO_2 -saturated 0.5 M KHCO_3 electrolyte (red) performed in an NMR tube (500 μL) and measured after 10 minutes. Formaldehyde hydrazone is the major product in both cases, with the cis (6.88 ppm) and trans (6.35 ppm) protons giving characteristic doublets. The two other doublets (6.76 ppm, 6.19 ppm) that appear in the bicarbonate electrolyte are believed to be from the hydrazone- CO_2 adduct. The large peak at 6.69 ppm is attributed to the hydrazine- CO_2 adduct.

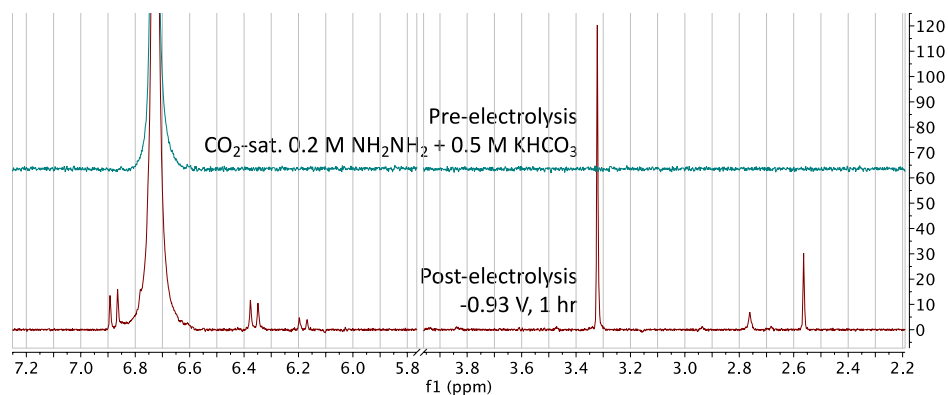


Figure S6. ^1H NMR spectra of CO_2 -saturated $0.2\text{ M NH}_2\text{NH}_2 + 0.5\text{ M KHCO}_3$ electrolyte prior to CO_2 -electrolysis and post CO_2 -electrolysis. The large peak at 6.72 ppm in both spectra is attributed to the hydrazine carbamate. The other peaks are assigned to electrolysis products as detailed in the main text.

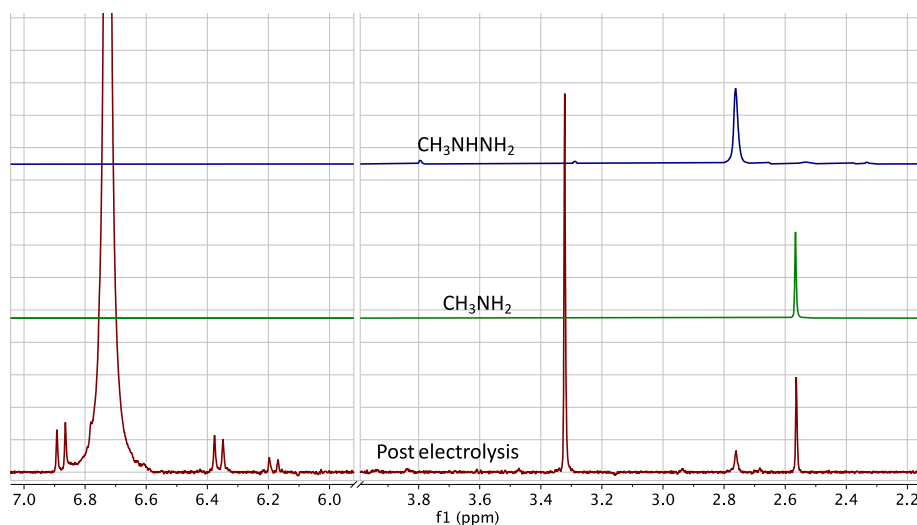


Figure S7. ^1H NMR spectra of methyl hydrazine and methylamine standards compared to the post CO_2 -electrolysis (-0.93 V , 1 hr) $0.2\text{ M NH}_2\text{NH}_2 + 0.5\text{ M KHCO}_3$ electrolyte. The singlet at 2.56 ppm corresponds to methylamine and the broad singlet at 2.76 ppm corresponds to methyl hydrazine.

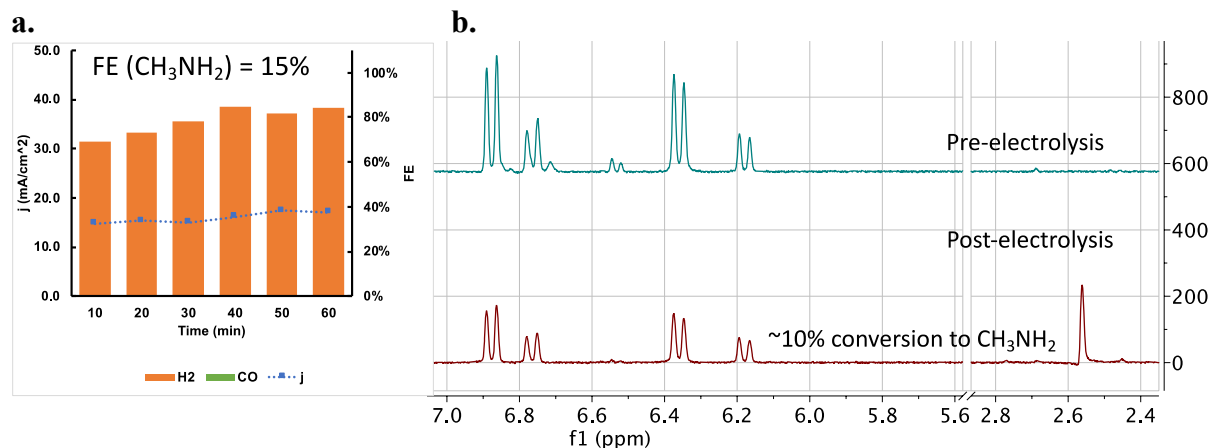


Figure S8. a) Total current density and Faradaic efficiency for gas and liquid products from a 1 hr controlled potential electrolysis at -0.93 V with continuous argon flow of 6 mM formaldehyde hydrazine (prepared from 6 mM formaldehyde and 20 mM NH_2NH_2) in 0.1 M KHCO_3 electrolyte. b) ¹H NMR spectra of pre- and post-electrolysis electrolyte. The singlet at 2.56 ppm is methylamine, confirmed via peak augmentation.

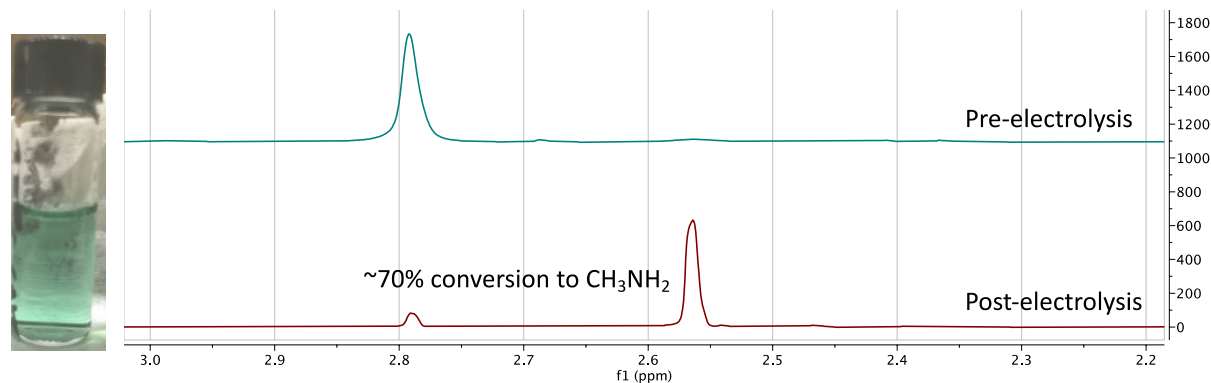


Figure S9. ¹H NMR spectra of 5 mM methyl hydrazine (purchased from Sigma Aldrich) in 0.1 M KHCO_3 electrolyte (blue), and the same electrolyte after 1 hr electrolysis at -0.93 V with continuous argon flow (red). The methyl hydrazine peak diminishes, and the methylamine peak appears in the post-electrolysis trace, as confirmed via peak augmentation. Qualitative colorimetric analysis via the salicylate test shows the characteristic blue color attributed to ammonia.

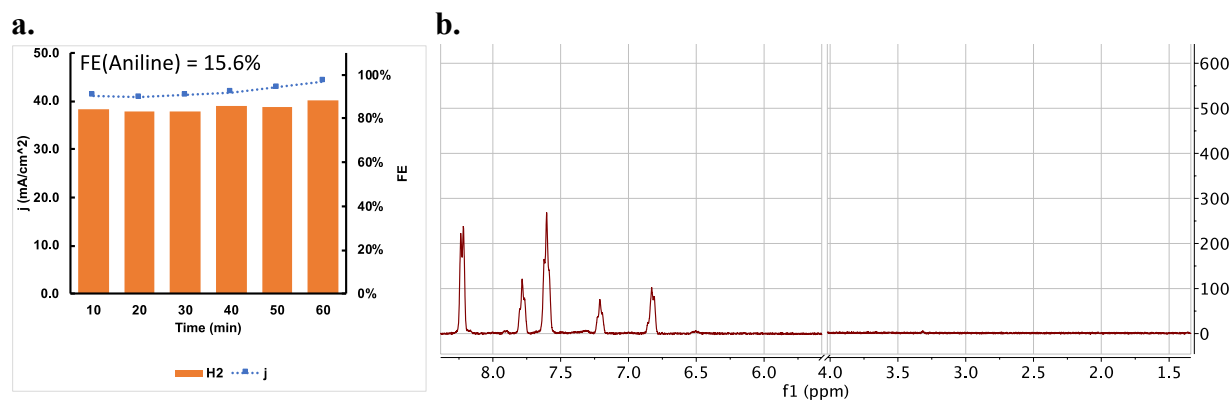


Figure S10. a) Total current density and product Faradaic efficiencies for the reduction of nitrobenzene to aniline using CoPc/CNT in 10 mM nitrobenzene + 0.1 M KHCO₃ electrolyte under argon flow conditions. b) ¹H NMR spectrum of post-electrolysis electrolyte. The three most downfield peaks correspond to the nitrobenzene starting material and the two most upfield peaks correspond to aniline, as described in Figure S8.

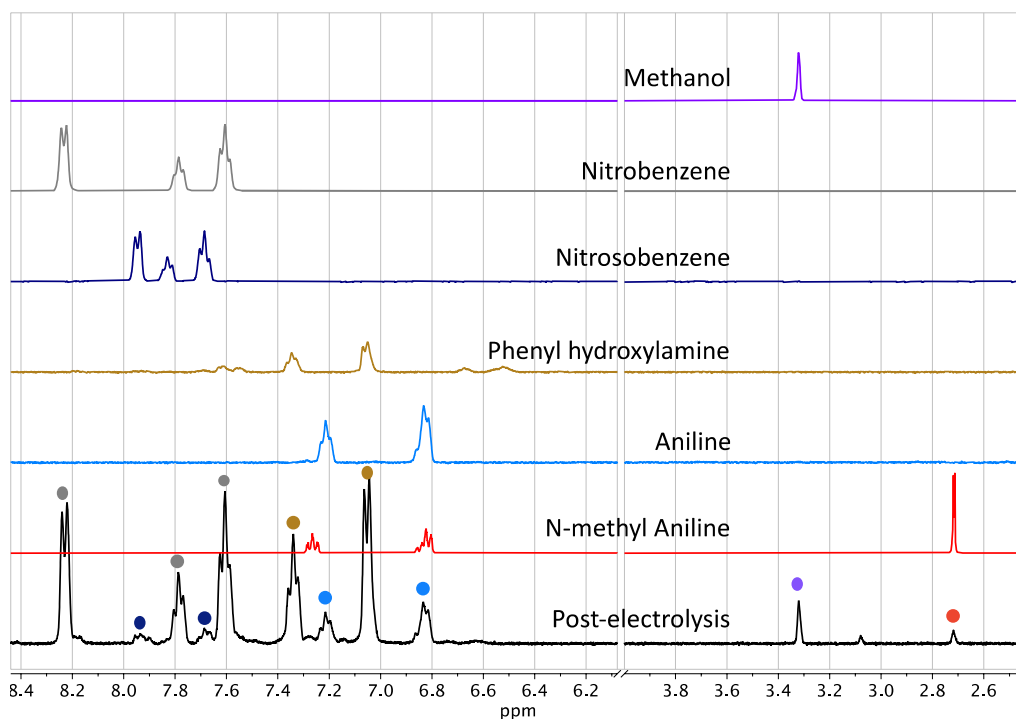


Figure S11. ¹H NMR spectrum of post CO₂-electrolysis catholyte (10 mM nitrobenzene + 0.1 M KHCO₃, 1 hr at -0.93 V vs RHE) stacked below the spectra of chemical standards (purchased from Sigma-Aldrich) in CO₂-saturated 0.1 M KHCO₃. All identified co-reduction products and their respective peaks are marked with colored dots. The singlet at 3.08 ppm is assigned to the methyl group on N-methyl phenyl hydroxylamine, however a standard of this chemical was not prepared due its unavailability.

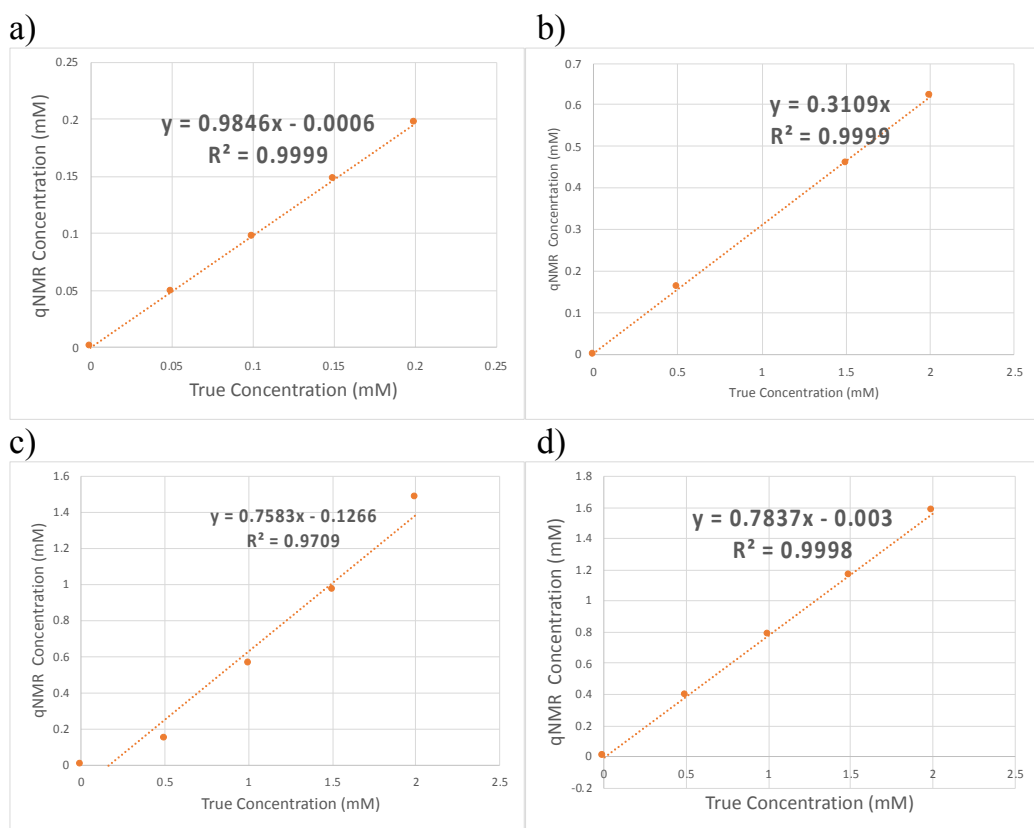


Figure S12: Quantitative NMR calibration curves for nitrobenzene/CO₂ co-reduction liquid product quantification. a) N-methyl aniline, b) nitrosobenzene, c) phenyl hydroxylamine, and d) aniline. The internal standard was 1.0 mM dimethyl malonic acid. Phenyl hydroxylamine quantification gives larger error due to its instability in the aqueous electrolyte.

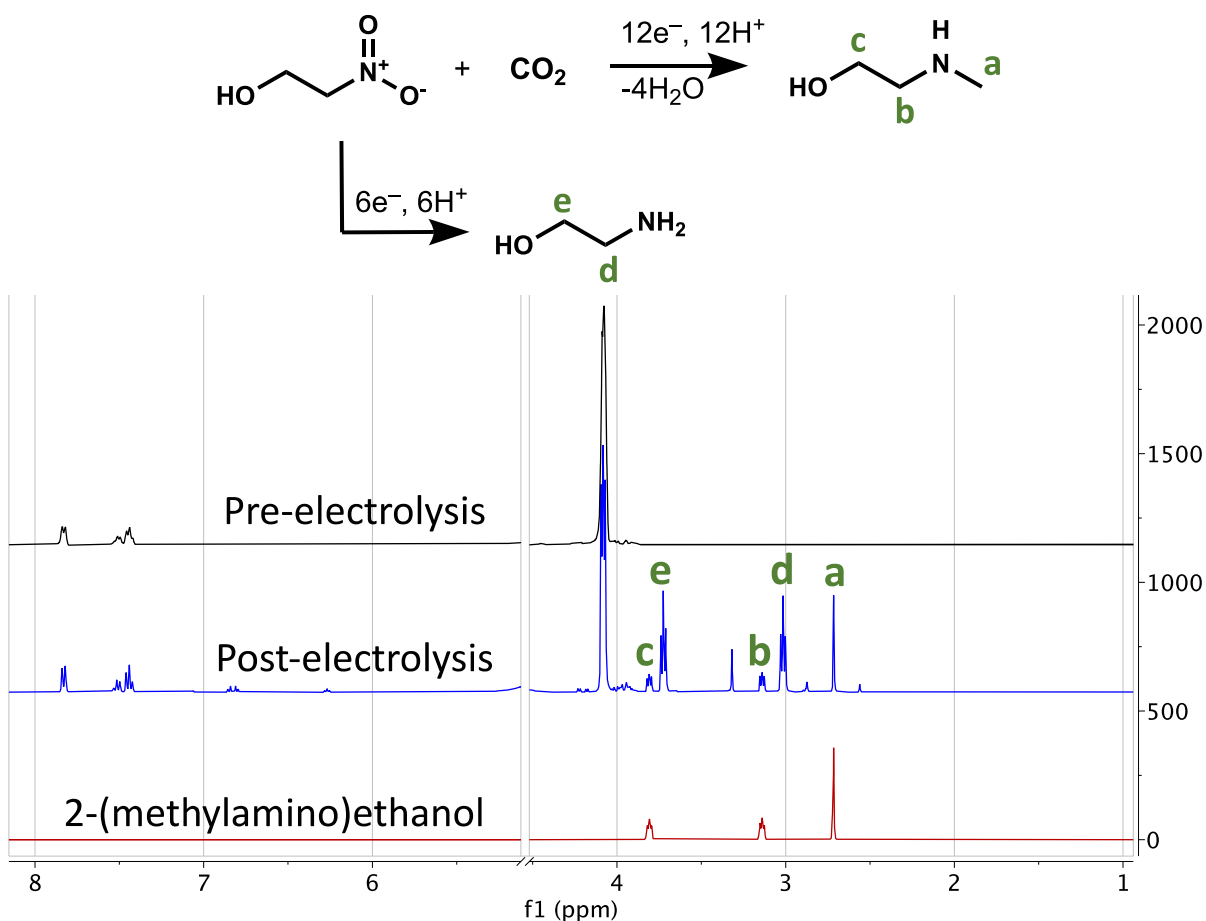


Figure S13. Reaction scheme and ¹H NMR spectra before and after the cascade reductive N-methylation reaction with 2-nitroethanol. The reaction was a 1-hour controlled potential electrolysis at -0.93 V vs RHE with CO₂ gas flow and 20 mM 2-nitroethanol dissolved in the 0.1 M KHCO₃ electrolyte. The ¹H NMR signal for the N-methyl(ethanol)amine product is labelled in the post-electrolysis spectrum and compared to a prepared standard. The other major electrolysis products are MeOH (3.30 ppm) and ethanolamine (3.02 ppm and 3.72 ppm). Ethanolamine is the six-electron reduction product of 2-nitroethanol.

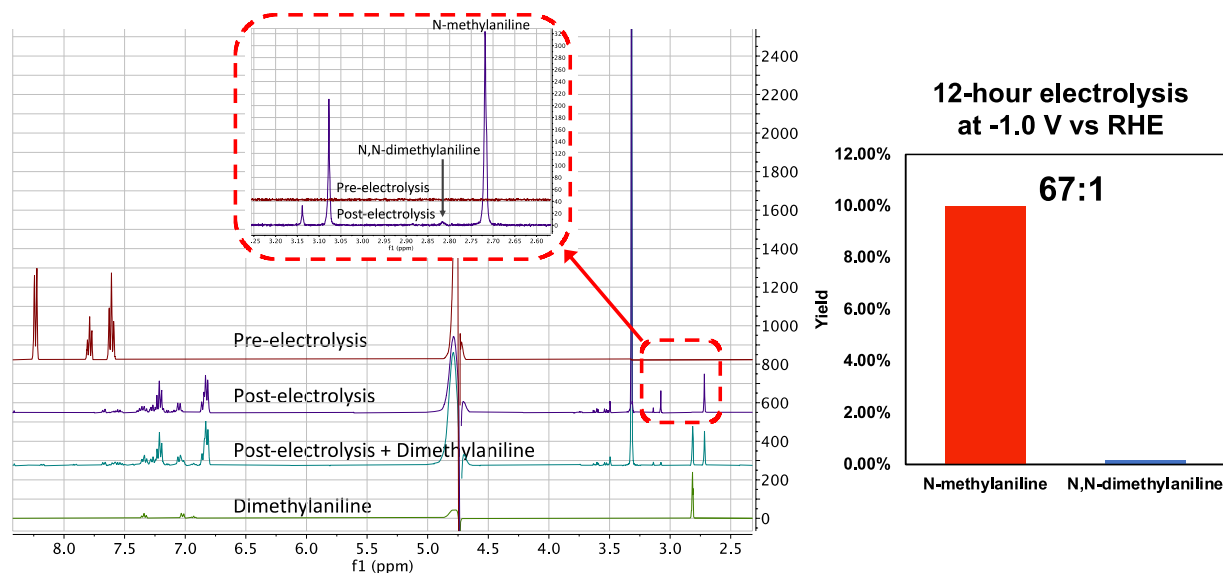


Figure S14. ¹H NMR spectra before and after the reductive N-methylation reaction of nitrobenzene. The reaction was a 12-hour controlled potential electrolysis at -1.0 V vs RHE using the CoPc-NH₂/CNT catalyst with 10 mM nitrobenzene dissolved in the cathode electrolyte. Inset shows the peak positions of N-methylaniline and N,N-dimethylaniline. Bar graph shows the percent yield of N-methylaniline and N,N-dimethylaniline from the 12-hour electrolysis.