## Supplementary Experimental Procedures

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Supplementary Experimental Procedures

Materials

Anhydrous methanol, 99.8+% (Alfa Aesar, 42311-AK). Molecular sieves 3Å, 4 to 8 mesh (Acros Organics, AC19724). Benzaldehyde, 99.5+% (Sigma Aldrich, 418099-100ML). Benzyl amine, ReagantPlus 99% (Sigma Aldrich, 185701-100G). Dibenzyl amine, 97.0+% (TCI, D0152). (1R,2R)-(+)-1,2-diphenylethlenediamine, 98.0+% (TCI, D2176). (1S,2S)-(−)-1,2-diphenylethlenediamine, 98.0+% (TCI, D2175). Tetrabutylammonium tetrafluoroborate (TCI, T0914). Trifluoroacetic acid (Sigma-Aldrich, T6508-100ML). Anhydrous ammonia gas (Airgas, AM AH80N705). Glassy carbon plate, 2mm thick, type 1 (Alfa Aesar, 38025). Platinum foil, 0.025mm thick, 99.99% trace metals basis (Beantown Chemical, 213815). Rhodium Foil, 0.025mm thick, 99.9% trace metals basis (Sigma-Aldrich, 357340). Silver foil, 0.1mm thick, Premion 99.998% trace metals basis (Alfa Aesar, 12126). Gold foil, 0.127mm thick, Premion 99.99% trace metals basis (Alfa Aesar, 00132). Copper foil, 0.025mm thick, 99.9% (Strem Chemical Inc., 93-2970). Nickel foil, 0.1 mm thick, Puratronic 99.994% trace metals basis (Alfa Aesar, 12046). Iron foil, 0.1mm thick, 99.995% trace metals basis (Alfa Aesar, 11381). Cobalt foil, 0.1mm thick 99.9965% trace metals basis (Alfa Aesar 11455). Zinc Foil, 0.5mm thick, Puratronic 99.994% trace metals basis (Alfa Aesar 11914). Palladium foil, 0.1mm thick, 99.9% trace metals basis (Beantown Chemical, 135850). Nitric acid, TraceMetal grade (Fisher Chemical, A509). Leak-free Ag/AgCl reference electrodes (Innovative Instruments, LF-2). Ferrocene, 99% (Alfa Aesar, 87202). Polishing pad and alumina (CH Instruments Inc, CH1 120). Argon UHP grade 5.0 gas (Airgas, AR UHP300). Deuterium Oxide, 99.9% D (Cambridge Isotope Laboratories, Inc, DLM-4-100). Hydrochloric Acid, 36.5-38% (VWR BDH Chemicals, BDH3028-2.5LG). Dimethyl sulfoxide, GC Headspace >99.9%(Fisher Chemical, D139-1). Celgard Li-ion battery separator film, 25 μm thick (MTI Corporation, EQ-bsf-0025-60C).

Electrolyte preparation

General
Anhydrous methanol was used as the electrolyte. It was stored in ~25 vol% molecular sieves for at least 48 hours before usage. The molecular sieves were dried by first rinsing with acetone and then drying at 400°C for 4 hours. Throughout this work, all methanol used was prepared in this way.

A typical procedure involved preparing electrolyte solution for multiple experiments and one (1) ferrocene calibration, with each experiment requiring 3.5 mL of electrolyte solution (details provided below). In a typical day, five (5) experiments were performed, requiring a prepared solution volume of 21 mL (including the 3.5 mL for a ferrocene calibration). First, a fixed amount of tetrabutylammonium tetrafluoroborate (TBA-BF₄) was measured and placed in a glass vial or centrifuge tube (enough so that the final solution would be 1 M, or 6.91g for 21 mL). Next, anhydrous methanol was added to the solution. Due to non-ideal mixing between methanol, TBA-BF₄, and ammonia, the exact amount of methanol required depends on the quantity of solution being prepared (in the case of 21 mL final solution volume, 12.5 mL of methanol is enough).
To saturate with ammonia, anhydrous ammonia was bubbled through the solution for 30-60 minutes. We generally used an Alicat flow meter to bubble ammonia gas at a rate of ~80 standard cubic centimeters per minutes (SCCM) into the methanol. Initially, no bubbling is observed because the ammonia dissolves instantly. After ~30-60 minutes, the solution is saturated and vigorous bubbling is observed.

The electrolyte solutions were divided into glass vials (3.5 mL per vial) and benzaldehyde (and trifluoroacetic acid for the proton dependence experiments) were added, depending on the experiment. Trifluoroacetic acid was chosen for the proton dependence experiments due to its purity (no additional water), the stability of the anion, the high solubility of ammonium trifluoroacetate, and the low pK\textsubscript{a} (~0.5 in water), suggesting it will be fully dissociated. The lids were sealed with parafilm to prevent any ammonia leakage. The electrolyte solutions were left to sit overnight in the dark before use to guarantee that the imine formation reaction had equilibrated. In general, the solutions were used between 12 and 36 hours after preparation.

One of the most important parts of saturating the solution with ammonia is the speed used when preparing the solutions. The ammonia will quickly leave the solution if left open, particularly at saturation, so the solutions must be prepared and sealed as rapidly as possible. Because ammonia is corrosive and toxic, all experiments should be conducted in a fume hood. Additionally, an ammonia sensor is recommended so that potentially dangerous leaks can be avoided.

**Electrode preparation**

Glassy carbon (GC) was used as the anode electrode for ferrocene calibration and for reference experiments. The GC was polished for one minute with 0.05 micron alumina, then rinsed with MilliQ water to remove visible particulates. The electrode was then sonicated in DI water. The GC was dried at 80 °C afterwards to remove all water before usage. The anode electrode was a Pt foil that is stored overnight in 10% nitric acid after every day of experiments, rinsed with MilliQ water, and then dried for at least 15 minutes at 80 °C before usage.

For metal foil cathodes, the foils were polished using 400 grit sand paper for >1.5 minutes, sonicated for at least 5 minutes in DI water, and then dried at 80 °C to remove all water. This was done before every experiment unless specified otherwise. Due to the thinness of Pt and Rh foils, these foils were not polished with sand paper. Instead, they were dipped in 10% nitric acid for at least a minute and then sonicated in DI water and dried as described above.

**Cell setup**

*Cleaning and preparation*

All PEEK cell parts and Idex connectors were soaked in 10% nitric acid overnight after every day of experiments. Before usage, the cell parts were removed from the nitric acid, rinsed with MilliQ water, and then dried for at least 30 minutes at 80 °C before usage. At the end of each day, the cell parts were disassembled, rinsed with acetone and MilliQ water and placed in the nitric acid bath.
Experimental setup
The cell consisted of a two-compartment cell with a Celgard separator. A leak-free, Ag/AgCl reference (Innovative Instruments, LF-2) was used as a pseudo-reference and calibrated against ~5 mM Fc/Fc\(^+\) in electrolyte (methanol, TBA-BF\(_4\), benzaldehyde) at the start of each day (Figure S2). To avoid ferrocene contamination, a different set of PEEK cell parts was used for the calibration. Aluminum foil current collectors were used behind the electrodes. 1.75 mL of electrolyte solution was placed in each half of the cell, and the top was sealed so that only one vertical opening was available for gas to evolve from each compartment. This was done to minimize ammonia loss during the experiment. See Figure S1 for a picture of the setup.

Electrochemical experiments
All electrochemical experiments were performed using a Biologic VMP3 potentiostat. Electrolyte solutions were only used after conversion of benzaldehyde to the imine overnight (at least 12 hours); i.e., the electrolyte solutions added to the cell have already sat in the dark for at least 12 hours to fully equilibrate the ammonia and benzaldehyde. Each experiment started with a PEIS test. All electrochemical steps used 85% IR Compensation. In general, an experiment consists of a constant potential hold until 2 Coulombs have been passed. Data was collected every 1 second. After an experiment, the solution was removed from the cell, and each compartment was rinsed with 0.5 mL of anhydrous methanol which was then added to the removed solution (~4.5 mL of solution expected).

For the intentional product doping, specific amounts of the products were added to the catholyte immediately prior to testing. For the primary amine, 30 μmol was added. For the secondary amine, 2 μmol was added. For the diamine, 1 μmol was added. In general, due to the small quantities required for doping, a stock solution of between 0.1 and 0.5 M was made of each product so that pipetting was possible without loss of accuracy.

Unless otherwise stated, all experiments were conducted at -1.9 V vs Fc/Fc\(^+\) with 85% IR compensation. Manual compensation for the remaining 15% (< 5Ω for a typical run) was used when appropriate, e.g. for Tafel analysis. Substrate dependence and proton dependence experiments were conducted at -1.74 V vs Fc/Fc\(^+\).

To verify that the intended cathode was not being affected by potential contaminants from the counter electrode (Pt foil) or from small amounts of nitrogen reduction to ammonia at the cathode, trials were run using a glassy carbon counter electrode and under an Ar atmosphere over the catholyte (in practice, Ar was flowed at 5 SCCM over the catholyte headspace to exclude nitrogen).
Table S1. Comparison of different control experiments

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Total I (mA/cm²)</th>
<th>FE toward primary amine</th>
<th>Partial current toward primary amine (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical (as per above)</td>
<td>4.2 ± 0.6</td>
<td>75%</td>
<td>3.3 ± 0.5</td>
</tr>
<tr>
<td>Ar over catholyte</td>
<td>3.8 ± 0.5</td>
<td>74%</td>
<td>3.1 ± 0.4</td>
</tr>
<tr>
<td>GC Anode</td>
<td>3.4 ± 0.7</td>
<td>65%</td>
<td>2.4 ± 0.5</td>
</tr>
</tbody>
</table>

From this table, we can see first that an Argon atmosphere had almost no effect on the system. Additionally, we see that the GC anode experiments had a little lower total current and FE toward the primary amine. However, this lower current and FE is likely from experimental error; if the Pt anode in the typical experiments were being stripped and then plated onto the cathode, we would expect the GC anode to increase the current and FE toward our desired product since we know that the Pt cathode is worse at amination in our system. Moreover, while in theory Pt stripping could happen, in practice this is thermodynamically almost impossible. First, our solution is saturated with ammonia, making it basic. Platinum is very stable in basic solutions; a Pourbaix diagram of platinum reveals that extremely acidic (< 0 pH) and oxidative potentials (> 0.9 V vs. SHE) are necessary to strip platinum.¹ Second, since methanol is our solvent, we expect that the anode potential is relatively close to methanol’s oxidation potential. Methanol oxidation has been performed successfully on anodes containing platinum without stripping in a variety of previous research.² Last, even if platinum were to strip from the anode, over the course of an hour it would only diffuse ~0.2 cm, less than the width of our unstirred anode compartment. Because Pt is such a poor cathode catalyst for our system (Figure 2), we expect it would be obvious if there was Pt being plated on the cathode electrode.

Hydrogen Quantification

Hydrogen quantification was done using an SRI gas chromatograph. A thermal conductivity detector with nitrogen gas as the carrier was used to detect hydrogen gas. Reaction conditions are the same as in other experiments, namely a 1 M tetrabutylammonium tetrafluoroborate (TBA-BF₄) in methanol electrolyte with 0.1 M benzaldehyde and saturated with ammonia at 1 bar of ammonia initially. The cell was set up as described above, with the addition of 5 standard cubic centimeters per minute (SCCM) of Ar gas bubbled through the catholyte. A pre trap of methanol to keep the flow saturated with methanol and a post trap of aqueous boric acid to catch any ammonia from the cell was also included. The gas chromatograph was calibrated in the range of interest to quantify hydrogen gas partial currents and Faradaic efficiencies (Figure S5).

Product Analysis

In general, the final combined solution was placed on a rotary evaporator under vacuum with a water bath at 40 °C. Once as dry as possible (should be a misty clear solid, potentially with bubbles, see Figure S3), 0.9 mL of 0.5 HCl in D₂O was added to each vial along with 0.1 mL of 0.1 M DMSO in the same solution (total 10 μmol of DMSO). The
solutions were sonicated at 45 °C for 30 min and thoroughly mixed (should be a slush by the end), then transferred to a 15 mL centrifuge tube and centrifuged at 6000 RPM for 10 minutes to separate the liquid from solid portions (Figure S3 shows examples at each step of the process). The liquid portion was analyzed via NMR using a Bruker Avance Neo NMR machine at 500 MHz with solvent suppression using the WET method as defined by the following $^1$H NMR parameters:

|        |       |                |                |                |
|--------|-------|----------------|----------------|
| TD     | 65536 | Size of fid    |                |
| NS     | 32    | Number of scans|                |
| D1     | 2 [sec]| Relaxation delay|               |
| Q1P    | 3.402 [ppm]| 1D Center frequency|          |
| SW     | 19.9868 [ppm]| 1D spectral width in ppm| |
| Q2P    | 39.500 [ppm]| 2D Center frequency|               |
| 1SW    | 19.9868 [ppm]| 2D spectral width in ppm|          |
| 1TD    | 65536 | Number of 2D increments|   |
| Q3P    | 2.000 [ppm]| F3 Center frequency|           |
| CNST13 | 1     | HMBC optimization|           |
| CNST18 | 1     | flip angle for variable pulse experiments| |
| D21    | 0     | 1D spin-echo delay|         |
| Lβ0    | 2     | Number of WET peaks|          |
| D0     | 0     | TOCSY spin-lock time (sec)|         |
| D8     | 0     | NOESY/NOESY mixing time (usec)|   |
| P13    | 0     | ROESY mixing time (usec)|       |
| Lβ4    | 0     | CPMG cycles (2ms per cycle)|    |
| CNST2  | 38    | HMOC and HSQC optimization|     |
| D40    | 0     | DQ/DY big delta (in seconds)|     |
| CNST10 | 1     | selective excitation bandwidth, Hz|    |
| CNST11 | 1     | selective excitation chemical shift, PPM|  |
| RG     | 16    | Receiver gain for QuickAcq|     |

If not enough solution was available after centrifuging, additional 0.5 M HCl in D$_2$O was added. NMR results were analyzed relative to the DMSO standard peak. Peak areas were quantified using calibration curves (Figure S3). In this solution, we found the peak for the benzylic hydrogens relative to DMSO (fixed at 2.6 ppm) are at 4.07 ppm, 4.15 ppm, and 4.99 ppm for the benzyl amine, dibenzyl amine, and 1,2-diphenylethendiamine products (note that the calibration curve used a 50/50 mixture of (1R,2R)-(+) and (1S,2S)-(−)-1,2-diphenylethendiamine and (1S,2S)-(−)-1,2-diphenylethendiamine which are not distinguishable in our NMR), respectively (Figure S3). To calculate partial currents, the average current from the electrochemical data was used in conjunction with the Faradaic efficiencies (FE) obtained from the NMR quantification and the total number of coulombs passed. Because dibenzyl amine necessarily goes through benzyl amine, all the first electron transfer toward dibenzyl amine is counted toward benzyl amine product whereas the second electron transfer is counted toward dibenzyl amine product when reporting partial FEs and currents. All data points presented in the main paper represent an average of at least two data points. Error bars on partial currents represent the error due to unsteadiness in the total current (specifically the standard deviation of the current during the experiment) unless otherwise stated.
NMR Data of Amine Products

Benzyl amine

\[
\text{\text{\rotatebox[origin=c]{0}{}}}_1^1\text{H NMR (500 MHz, D}_2\text{O): 4.07 (s, 2H), 6.8-7.9 (m, 5H)}
\]

Dibenzyl amine

\[
\text{\text{\rotatebox[origin=c]{0}{}}}_1^1\text{H NMR (500 MHz, D}_2\text{O): 4.15 (s, 4H), 6.8-7.9 (m, 10H)}
\]

1,2-diphenylethylenediamine

\[
\text{\text{\rotatebox[origin=c]{0}{}}}_1^1\text{H NMR (500 MHz, D}_2\text{O): 4.99 (s, 2H), 6.8-7.9 (m, 10H)}
\]

Data analysis

The majority of data analysis was done as described above with the exception of the descriptor optimization for Figure 3.

Volcano trend analysis

We propose the following method for optimizing our reactivity descriptor, noting that there remain many degrees of freedom in our optimization heuristic that only change our results to a minor degree. Essentially, the following heuristic enables quantification of a volcano-like trend, and can be easily verified visually (e.g., compare Figure 3d and Figure S8)

Heuristic: To find the optimal descriptor to create a volcano plot, first we must define a volcano. A detailed discussion about volcano plots is beyond the scope of this work, but a simple metric for quantitatively comparing volcanos would be two intersecting lines, one on the left going up the volcano and one on the right going down the volcano. For our purposes, these lines can be described by two parameters: a peak value, \( x_0 \), and a slope factor, \( m \) which is the ratio of the left slope to the right slope. To quantify how “good” a volcano descriptor \( x \) is given some reactivity data \( y \), we can first split our data into two halves: those where \( x < x_0 \) and those where \( x > x_0 \) . Then we transform the data as follows: \( y \rightarrow y' \), such that \( y' = \{ y_{i,x_i<x_0} \} \cup \{ m \times y_{i,x_i>x_0} \} \); and, \( x \rightarrow x' \), such that \( x' = \{ x_{i,x_i<x_0} \} \cup \{ 2 \times x_0 - x_{i,x_i>x_0} \} \). Essentially, this transformation flips the right half of the volcano to the left half and rescales it so that it has the same slope. At this point, we can perform linear regression on all of our points \( (x'_i, y'_i) \) and compare the fits via \( R^2 \) as a function of \( (x_0, m) \). There will be some value of \( (x_0, m)^{\text{opt}} \) for which \( R^2 \) is maximized. Likely, there is some uncertainty associated with this descriptor, and to account for it, we took an average of all \( z \) values that resulted in \( R^2 > 0.5 \) and used the standard deviation
of the mean of that set as an approximate error of the descriptor value. In practice, the choice in cutoff value for $R^2$ is arbitrary and does not affect the results.

This heuristic was followed at a grid of potential charge density cutoffs (specifically, 200 points in the range of 0.002 to 0.16 e/Bohr$^2$/Å), using the distance above the surface at which the charge density decays to that value as the descriptor. The optimal charge cutoff was determined to be 0.06 ± 0.003 e/Bohr$^2$/Å.

For the complimentary descriptor where the charge density was used at a fixed location above the surface, we first normalized the charge density as a function of position for each metal (Figure S7). This normalization is simply taking the vector of charge densities ($\rho_i$ for each metal $i$) at each $z$-point ($z_j$) and applying the following formula (Figure S7b):

$$\rho_i^{\text{norm}}(z_j) = \frac{\rho_i(z_j) - \text{mean}[\rho_i(z_j)]}{\text{std}[\rho_i(z_j)]}$$

(1)

Other normalization strategies, for example, using the median instead of the mean or the range instead of the standard deviation, do not alter the results. In our system, we found that the best fit occurred at $z = 0.95$ Å, with $R^2 = 0.69$. As mentioned above, this heuristic has many degrees of freedom, but it achieves its intended result: namely, a method for quantitatively converting from a series of charge density functions, $\rho_A(z)$, to a single charge density characteristic length or charge density value which can be used to compare metals. A comparison of non-optimal values for the cutoff charge density and a depiction of how this optimization produces values that track with the atomic radius, as expected, indicates the success of this heuristic (Figure S8).

**Bayesian Tafel analysis**

The Bayesian Tafel analysis was conducted as described in previous work. Specifically, the data were fit the following function:

$$\log_{10} i_{\text{fit}} = \log_{10} e \left( b + \alpha V_{\text{normalized}} - \log[i_{\text{lim}} + \exp(\alpha + V_{\text{normalized}})] \right)$$

Where the optimized parameters are $\alpha = 23.26$, $i_{\text{lim}} = 28.87$, and $b = 3.548$. $V_{\text{normalized}}$ represents the voltages normalized so that the lowest value is defined as 0. Note that the mean a posteriori (MAP) value for the Tafel slope is essentially the expected value of the distribution of possible Tafel slopes that are the output of the Bayesian analysis and shown in the inset of Figure 4a.

**Comparison to previous electrochemical works**

To further put this work in context of previous electrochemical studies of reductive amination, the following table provides information on all of the previous electrochemical reductive amination papers found by the authors. We do not expect this list is exhaustive, yet we believe it is comprehensive enough to reveal how our work builds on previous studies to develop electrochemical reductive amimation in a meaningful manner.
Table S2. Comparison of previous works on electrochemical reductive amination

<table>
<thead>
<tr>
<th>Paper</th>
<th>Reaction</th>
<th>Solvent&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Catalyst</th>
<th>Electrochemical Experiment&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Inner vs Outer sphere&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Root &amp; Smith&lt;sup&gt;4&lt;/sup&gt;</td>
<td>Secondary imine reduction w/ and w/o CO2</td>
<td>ACN or NH3</td>
<td>CV at Hg; CA at Pt + Hg</td>
<td>CV for kinetics; CA for conversion</td>
<td>Outer sphere</td>
</tr>
<tr>
<td>Zuman&lt;sup&gt;5&lt;/sup&gt;</td>
<td>Reduction of acetone and NH3</td>
<td>Aqueous w/ ammonium sulfate buffer</td>
<td>Hg</td>
<td>CV</td>
<td>Outer sphere</td>
</tr>
<tr>
<td>Zuman &amp; Exner&lt;sup&gt;6&lt;/sup&gt;</td>
<td>Oxime reduction</td>
<td>Water-ethanol mixtures</td>
<td>Hg</td>
<td>CV</td>
<td>Outer sphere</td>
</tr>
<tr>
<td>Scott &amp; Jura&lt;sup&gt;7&lt;/sup&gt;</td>
<td>Secondary imine reduction</td>
<td>DMF</td>
<td>Hg</td>
<td>CV</td>
<td>Outer sphere</td>
</tr>
<tr>
<td>Andrieux &amp; Saveant&lt;sup&gt;8&lt;/sup&gt;</td>
<td>Secondary imine reduction</td>
<td>ACN or DMF</td>
<td>Hg</td>
<td>LSV/CV</td>
<td>Outer sphere</td>
</tr>
<tr>
<td>Isse, Abdurahman, Vianello&lt;sup&gt;9&lt;/sup&gt;</td>
<td>Salicylideneaniline reduction</td>
<td>DMF</td>
<td>Hg</td>
<td>CV, CA</td>
<td>Outer sphere</td>
</tr>
<tr>
<td>Fry &amp; Reed&lt;sup&gt;10&lt;/sup&gt;</td>
<td>Secondary imine reduction</td>
<td>DMF</td>
<td>Hg</td>
<td>CV, CA</td>
<td>Outer sphere</td>
</tr>
<tr>
<td>Chiba, Okimoto, Nagai, Takata&lt;sup&gt;11&lt;/sup&gt;</td>
<td>Reduction of secondary imines, nitriles, nitros, and oximes</td>
<td>Methanol (w/ methoxide)</td>
<td>Raney Ni</td>
<td>CP</td>
<td>Inner sphere</td>
</tr>
<tr>
<td>Roylance &amp; Choi&lt;sup&gt;12&lt;/sup&gt;</td>
<td>Secondary imine (furfural + MeNH2) reduction</td>
<td>Aqueous methylamine buffer solution</td>
<td>Pt, Cu, Zn, Sn, Ag</td>
<td>CV, CA</td>
<td>Inner sphere</td>
</tr>
<tr>
<td>Zhang, Chen, Hao, Jiao, Ge, Fu, Lv&lt;sup&gt;13&lt;/sup&gt;</td>
<td>Nitriles (including acetonitrile) to amine</td>
<td>H2O</td>
<td>Cu &quot;nanoarrays&quot;</td>
<td>CV, CA, DFT</td>
<td>Inner sphere</td>
</tr>
<tr>
<td>Blanco, Dookkith, Modestino&lt;sup&gt;14&lt;/sup&gt;</td>
<td>Adiponitrile reduction</td>
<td>H2O/MeOH mixtures</td>
<td>Raney Ni</td>
<td>CP</td>
<td>Inner sphere</td>
</tr>
<tr>
<td><strong>This work</strong></td>
<td>Benzaldehyde + NH3 reduction</td>
<td>MeOH</td>
<td>GC, Pt, Ag, Cu, Au, Pd, Ni, Co, Fe, Rh, Zn</td>
<td>CA</td>
<td>Inner sphere</td>
</tr>
</tbody>
</table>

<sup>a</sup> ACN = acetonitrile, DMF = dimethylformamide
<sup>b</sup> CV = cyclic voltammetry, CA = chronoamperometry, CP = chronopotentiometry
<sup>c</sup> In general, anytime the electrode is mercury or glassy carbon, we can assume outer sphere.
As can be seen in Table S2, previous research has been focused on (1) outer sphere reactions; and (2) secondary imine or nitrile reduction reactions. To the best of our knowledge, no previous work is exhaustive in terms of investigating the influence of heterogeneous catalysts on this reaction of a prototypical primary amine or in characterizing the *inner sphere* mechanism of the reaction.

*Comparison of thermochemical and electrochemical rate constants*

Interpreting the rate constant of our system in the context of thermochemical work is important for understanding its utility and future potential. To do so, we need to extract a meaningful rate constant from our electrochemical data. First, we can take the partial current toward the primary amine product on Ag and calculate an initial rate of reaction. We find that the initial rate constant at the surface is, $k = 0.16 \, \mu\text{mol} \cdot \text{s}^{-1} \cdot \text{M}^{-1} \cdot \text{cm}^2$. This can be calculated based on the moles of primary amine produced when 2 C of current is passed (8 µmol) divided by the cell the reaction time, giving a rate of production of primary amine of 0.06 mmol/hr. This rate can be normalized by the electrode area and substrate concentration to get a rate constant. Because our system has a volume of 3.5 ml and an electrode surface area of 1 cm$^2$, this can be roughly “translated” to a bulk, volume rate constant of $k = 47 \times 10^{-6} \text{s}^{-1}$. Looking at three different papers on thermochemical reductive amination, we find that the bulk rate constant was $k = 16 \times 10^{-6} \text{s}^{-1}$, $k = 14 \times 10^{-6} \text{s}^{-1}$, and $k = 91 \times 10^{-6} \text{s}^{-1}$. Note that these thermochemical experiments were performed at high conversion (> 80%), so we would expect their average rate constant to be lower than their initial rate constant. Additionally, the translation between a surface rate constant (due to the nature of the heterogeneous electrochemical system) and bulk rate constant (due to the volumetric nature of the thermochemical systems) is extremely geometry dependent. Thus, without over-interpreting this analysis, we can only state that the electrochemical system is comparable to the thermochemical system in terms of initial reaction rate constant.

In terms of raw yield, when 2 C were passed, the system produced 8 µmol of primary amine with a conversion based on initial substrate of 4.4%. When 24 C were passed, the system produced 28 µmol of primary amine with a conversion of 16% (this low value is likely due the surface deactivation discussed in the main text).

*Synthesis routes for nitrogen-containing compounds in Figure 1*

In the main text, Figure 1 also shows schematic synthesis routes for various nitrogen-containing compounds. These routes provide a sense of the conditions, steps, and reactants involved in each process; these routes are not quantitative in terms of stoichiometry or exhaustive in terms of the breadth of industrially-practiced syntheses.
Not calculated but shown in Figure 1 is the synthesis of amino acids; Figure 1 depicts a qualitative Strecker synthesis of amino acids to demonstrate the potential role of cyanide. For the synthesis of hydrazine, the Raschig process is shown.¹⁸ Not shown are variations of the Rasching process (e.g., the Olin-Raschig process), processes using urea as a nitrogen source, the Bayer-Ketazine process, the peroxide process, or others; each of these processes have their own advantages and disadvantages, but often involve harsh conditions and multiple steps.¹⁸ The hydroxylamine synthesis shown in Figure 1 follows the Raschig process (distinct from the similarly eponymous process used to produce hydrazine).¹⁹ Alternative processes use hydrogenation of nitric oxide or nitrates. The synthesis of nitric acid shown follows the Ostwald process.²⁰ Note that the first step can utilize a range of pressures (ca. 2 – 12 bar) and temperatures (ca. 600°C – 950°C) depending on the exact reactor in order to optimize ammonia combustion. The urea synthesis shown relies on the Basaroff reactions, involving ammonia and carbon dioxide, and industrially often involves a complex stripping process to recycle gases.²¹ Slight differences in temperatures and pressures exist depending on the exact industrial process. Last, the cyanide synthesis shown is the Andussow process.²² Other alkanes besides methane (and even other carbon sources such as methanol) can be used as reactants. The Shawinigan process reacts ammonia and methane (or alkanes) at higher temperatures (> 1500°C) but without metal catalysts.

Supplementary Computational Methods

Equilibrium Potential Calculations
The calculation of the equilibrium potentials for Figure 1 in the main text used available thermodynamic data along with the expression $E^{eq} = -\frac{\Delta G}{nF}$, where $\Delta G$ is the Gibbs free energy of reaction at 298 K and 1 bar, $F$ is Faraday’s constant, and $n$ is the number of electrons passed during the reaction. Unless otherwise noted, all thermodynamic data is from NIST webbook for the molecule in the gas phase.²³

Table S3. Raw thermodynamic data
Enthalpies and entropies of formation for the given molecules in the gas phase at 298 K and 1 bar.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\Delta H^0$</th>
<th>$S^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>-45.9</td>
<td>192.8</td>
</tr>
<tr>
<td>H₂O</td>
<td>-241.8</td>
<td>188.8</td>
</tr>
<tr>
<td>H₂</td>
<td>0.0</td>
<td>130.7</td>
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<tr>
<td>O₂</td>
<td>0.0</td>
<td>205.2</td>
</tr>
<tr>
<td>N₂</td>
<td>0.0</td>
<td>191.6</td>
</tr>
<tr>
<td>N₂H₄</td>
<td>95.4</td>
<td>238.7</td>
</tr>
<tr>
<td>NH₂OH</td>
<td>-40.5ᵃ</td>
<td>234.5ᵃ</td>
</tr>
<tr>
<td>HNO₃</td>
<td>-134.3</td>
<td>266.4</td>
</tr>
<tr>
<td>Urea</td>
<td>-235.5</td>
<td>272.0ᵃ</td>
</tr>
<tr>
<td>HCN</td>
<td>135.1</td>
<td>201.8</td>
</tr>
<tr>
<td>CO₂</td>
<td>-393.5</td>
<td>213.8</td>
</tr>
<tr>
<td></td>
<td>Δ(H^\circ_{rxn})</td>
<td>Δ(S^\circ_{rxn})</td>
</tr>
<tr>
<td>-------------</td>
<td>------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>1/2 N(_2) + 3/2 H(_2)O → NH(_3) + 3/4 O(_2)</td>
<td>316.8</td>
<td>-32.4</td>
</tr>
<tr>
<td>NH(_3) → 1/2 N(_2)H(_4) + 1/2 H(_2)</td>
<td>93.6</td>
<td>-8.1</td>
</tr>
<tr>
<td>NH(_3) + H(_2)O → NH(_2)OH + H(_2)</td>
<td>247.3</td>
<td>-16.4</td>
</tr>
<tr>
<td>NH(_3) + 3H(_2)O → HNO(_3) + 4H(_2)</td>
<td>637.1</td>
<td>29.8</td>
</tr>
<tr>
<td>NH(_3) + 1/2 CO(_2) → 1/2 (NH(_2))(_2)CO + 1/4 O(_2) + 1/2 H(_2)</td>
<td>321.7</td>
<td>153.9</td>
</tr>
<tr>
<td>NH(_3) + CH(_4) → HCN + 3H(_2)</td>
<td>256.0</td>
<td>214.8</td>
</tr>
<tr>
<td>NH(_3) + (\begin{array}{c} CH_4 \end{array}) → (\begin{array}{c} \text{HCN} \end{array}) + (\begin{array}{c} 1/2 O_2 \end{array})</td>
<td>170.5</td>
<td>-66.5</td>
</tr>
</tbody>
</table>

**Table S4. Reaction thermodynamic data**

**DFT Calculations**

All DFT calculation were done with the Quantum Espresso\(^{25-27}\) electronic structure code using PAW type PBE functional\(^{28-30}\). Unless otherwise stated, a 60 Ry plane-wave cutoff and a 600 Ry density cutoff were used (see Table S5 for cutoffs and pseudopotential files used for each metal). All calculations used a Grimme-d3 van der Waals correction. A Monkhorst-Pack\(^{31}\) \(k\)-point grid of (16, 16, 16) for bulk and (8, 8, 4) for slab calculations and a 0.001 Ry Gaussian spreading for Brillouin-zone integration were used. Slabs were 4 layers with the bottom two layers frozen during atomic position relaxation. Spin-polarized calculations were used for ferromagnetic metals, namely Fe, Co, and Ni, with the magnetic moments allowed to converge during optimization. Lattice constants were determined by relaxing bulk metals (results given in Table S6). Because our system was in a methanol electrolyte, the environ module of Quantum Espresso was used to include implicit solvation in the slab calculations. Methanol is represented by a dielectric continuum with static permittivity of 33.0 and optical permittivity of 1.766.

The Environ input file is given as follows:

```environ
&ENVIRON
    verbose = 2
    environ_thr = 1.D-2
```

---

S13
environ_type = 'input'
env_static_permittivity = 33.00
env_optical_permittivity = 1.766
env_surface_tension = 0.0
env_pressure = 0.0
/
&BOUNDARY
   solvent_mode = 'electronic'
/
&ELECTROSTATIC
   solver = 'iterative'
auxiliary = 'full'
/
A typical quantum espresso input file looks as follows:

&SYSTEM
   ecutwfc = 60
ecutrho = 600
occupations = 'smearing'
degauss = 0.001
nspin = 1
tot_charge = 0.00000
ntyp = 1
nat = 4
ibrav = 0
vdw_corr = 'grimme-d3'
/
&ELECTRONS
   mixing_beta = 0.1
electron_maxstep = 350
/
&IONS
   ion_dynamics = 'bfgs'
/
ATOMIC_SPECIES
Pt  195.084  Pt.pbe-n-kjpaw_psl.1.0.0.UPF

K_POINTS automatic
8 8 4 0 0 0

CELL_PARAMETERS angstrom
2.78409513451269 0.000000000000000 0.0000000000000000 0.0000000000000000
1.39204756725634 2.41109711304064 0.0000000000000000
0.0000000000000000 0.0000000000000000 26.81961247492139
ATOMIC_POSITIONS angstrom
Pt    0.0000000000  0.0000000000  10.0000000000  0  0  0
Pt    1.3920475673  0.8036990377  12.2732041583  0  0  0
Pt    -0.0000000000  1.6073980754  14.5321429286
Pt    0.0000000000  0.0000000000  16.8293470733

DFT Output
Table S5. Quantum Espresso run details
Pseudopotential filenames represent pseudopotentials found on the Quantum Espresso website http://www.quantum-espresso.org/.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Pseudopotential Filename</th>
<th>ecutwfc</th>
<th>ecutrho</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
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<td>60</td>
<td>600</td>
</tr>
<tr>
<td>Pd</td>
<td>Pd.pbe-n-kjpaw_psl.1.0.0.UPF</td>
<td>60</td>
<td>600</td>
</tr>
<tr>
<td>Ag</td>
<td>Ag.pbe-n-kjpaw_psl.1.0.0.UPF</td>
<td>60</td>
<td>600</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu.pbe-dn-kjpaw_psl.1.0.0.UPF</td>
<td>60</td>
<td>600</td>
</tr>
<tr>
<td>Au</td>
<td>Au.pbe-n-kjpaw_psl.1.0.0.UPF</td>
<td>60</td>
<td>600</td>
</tr>
<tr>
<td>Zn</td>
<td>Zn.pbe-dnl-kjpaw_psl.1.0.0.UPF</td>
<td>60</td>
<td>600</td>
</tr>
<tr>
<td>Co</td>
<td>Co.pbe-spn-kjpaw_psl.0.3.1.UPF</td>
<td>80</td>
<td>600</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni.pbe-n-kjpaw_psl.0.1.UPF</td>
<td>80</td>
<td>600</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe.pbe-spn-kjpaw_psl.1.0.0.UPF</td>
<td>80</td>
<td>600</td>
</tr>
<tr>
<td>Rh</td>
<td>Rh.pbe-spn-kjpaw_psl.1.0.0.UPF</td>
<td>60</td>
<td>600</td>
</tr>
</tbody>
</table>

Table S6. Bulk properties of metals after optimization

<table>
<thead>
<tr>
<th>Metal</th>
<th>Lattice Structure</th>
<th>Exposed Surface</th>
<th>Lattice Constant a (bohr)</th>
<th>Lattice Ratio (a/c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>FCC</td>
<td>(111)</td>
<td>7.440</td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td>FCC</td>
<td>(111)</td>
<td>7.390</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>FCC</td>
<td>(111)</td>
<td>7.772</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>FCC</td>
<td>(111)</td>
<td>6.764</td>
<td></td>
</tr>
<tr>
<td>Au</td>
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<td>(111)</td>
<td>7.787</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>HCP</td>
<td>(0001)</td>
<td>4.950</td>
<td>1.827</td>
</tr>
<tr>
<td>Co</td>
<td>HCP</td>
<td>(0001)</td>
<td>4.629</td>
<td>1.619</td>
</tr>
<tr>
<td>Ni</td>
<td>FCC</td>
<td>(111)</td>
<td>6.589</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>BCC</td>
<td>(110)</td>
<td>5.286</td>
<td></td>
</tr>
<tr>
<td>Rh</td>
<td>FCC</td>
<td>(111)</td>
<td>7.174</td>
<td></td>
</tr>
</tbody>
</table>

Optimized Atomic Coordinates and Energy Output
Below are the cell parameters (three lattice vectors) used for each metal system, the optimized atomic coordinates, and the total energy of the system.
Platinum
CELL_PARAMETERS angstrom
2.78409513451269 0.00000000000000 0.00000000000000
1.39204756725634 2.41109711304064 0.00000000000000
0.00000000000000 0.00000000000000 26.81961247492139

ATOMIC_POSITIONS angstrom
Pt 0.0000000000 0.0000000000 10.0000000000 0 0 0
Pt 1.3920475673 0.8036990377 12.2732041583 0 0 0
Pt -0.0000000000 1.6073980754 14.5321429286
Pt 0.0000000000 0.0000000000 16.8293470733
!  total energy = -2989.24508188 Ry

Palladium
CELL_PARAMETERS angstrom
2.76532492138367 0.00000000000000 0.00000000000000
1.38266246069184 2.39484163163646 0.00000000000000
0.00000000000000 0.00000000000000 26.77363503039200

ATOMIC_POSITIONS angstrom
Pd 0.0000000000 0.0000000000 10.0000000000 0 0 0
Pd 1.3826624607 0.7982805439 12.2578783435 0 0 0
Pd 0.0000000000 1.5965610878 14.5046447491
Pd 0.0000000000 0.0000000000 16.7809725023
!  total energy = -1324.32426771 Ry

Silver
CELL_PARAMETERS angstrom
2.88895821104446 0.00000000000000 0.00000000000000
1.44447910552223 2.50191120123615 0.00000000000000
0.00000000000000 0.00000000000000 27.07647350528265

ATOMIC_POSITIONS angstrom
Ag 0.0000000000 0.0000000000 10.0000000000 0 0 0
Ag 1.4444791055 0.8339704004 12.2578783435 0 0 0
Ag 0.0000000000 1.6679408008 14.691167350
Ag 0.0000000000 0.0000000000 17.0928712376
!  total energy = -1421.26688322 Ry

Copper
CELL_PARAMETERS angstrom
2.53103585134358 0.00000000000000 0.00000000000000
1.26551792567179 2.19194134515271 0.00000000000000
0.00000000000000 0.00000000000000 26.19974635648258
ATOMIC_POSITIONS angstrom
Cu   0.0000000000  0.0000000000  10.0000000000  0 0 0
Cu   1.2655179257  0.7306471151  12.0665821188  0 0 0
Cu   0.0000000000  1.4612942301  14.1137988421  0 0 0
Cu   0.0000000000  0.0000000000  16.2034647402  0 0 0
! total energy = -852.40920942 Ry

Gold
CELL_PARAMETERS angstrom
2.91389140617846 0.00000000000000 0.00000000000000
1.45694570308923 2.52350398161971 0.00000000000000
0.00000000000000 0.00000000000000 27.13754711101819
ATOMIC_POSITIONS angstrom
Au   0.0000000000  0.0000000000 10.0000000000  0 0 0
Au   1.4569457031  0.8411679939 12.3791823703  0 0 0
Au   0.0000000000  1.6823359877 14.7404343264  0 0 0
Au   0.0000000000  0.0000000000 17.2437077528  0 0 0
! total energy = -3100.63482490 Ry

Zinc
CELL_PARAMETERS angstrom
2.61943033049830 0.00000000000000 0.00000000000000
1.30971516524915 2.26849320965500 0.00000000000000
0.00000000000000 0.00000000000000 27.17972591413821
ATOMIC_POSITIONS angstrom
Zn   0.0000000000  1.5123288064 10.0000000000  0 0 0
Zn   0.0000000000  0.0000000000 12.3932419714  0 0 0
Zn   0.0000000000  1.5123288064 14.6284036759  0 0 0
Zn   0.0000000000  0.0000000000 17.1149908146  0 0 0
! total energy = -974.94700577 Ry

Cobalt
CELL_PARAMETERS angstrom
2.44956982114361 0.00000000000000 0.00000000000000
1.22478491057180 2.1238969345407 0.00000000000000
0.00000000000000 0.00000000000000 25.9484516763605
ATOMIC_POSITIONS angstrom
Co   0.0000000000  1.4142597956 10.0000000000  0 0 0
Co   0.0000000000  0.0000000000 11.9828172255  0 0 0
Co   0.0000000000  1.4142597956 14.0552740234  0 0 0
Co   0.0000000000  0.0000000000 16.0108819410  0 0 0
! total energy = -1506.86091648 Ry
Nickel
CELL_PARAMETERS angstrom
2.46568249743879 0.00000000000000 0.00000000000000 1.23284124871939
2.13534368044865 0.00000000000000 0.00000000000000 26.03966398643632

ATOMIC_POSITIONS angstrom
Ni 0.0000000000 0.0000000000 10.0000000000 0 0 0
Ni 1.2328412487 0.7117812268 12.0132213288 0 0 0
Ni 0.0000000000 1.4235624536 14.0199115135
Ni 0.0000000000 0.0000000000 16.0332165766
! total energy = -742.80633759 Ry

Iron
CELL_PARAMETERS angstrom
2.79735853480897 0.00000000000000 0.00000000000000
1.39867926740449 1.97803118937349 0.00000000000000
0.00000000000000 0.00000000000000 25.93409356812046

ATOMIC_POSITIONS angstrom
Fe 0.0000000000 0.0000000000 10.0000000000 0 0 0
Fe 0.0000000000 0.0000000000 11.9780311894 0 0 0
Fe 0.0000000000 1.9780311894 13.9632575443
Fe 0.0000000000 1.5499333863 15.9310154912
! total energy = -1316.99822681 Ry

Rhodium
CELL_PARAMETERS angstrom
2.68456337345175 0.00000000000000 0.00000000000000
1.34228168672587 2.3249000007947846 0.00000000000000
0.00000000000000 0.00000000000000 26.57581044712146

ATOMIC_POSITIONS angstrom
Rh 0.0000000000 0.0000000000 10.0000000000 0 0 0
Rh 1.3422816867 0.7749666932 12.1919368157 0 0 0
Rh -0.0000000000 1.5499333863 14.3150935417
Rh -0.0000000000 -0.0000000000 16.5096209059
! total energy = -1880.66650571 Ry
**Figure S1.** Photos of cell before and after assembly. The PEEK cell consists of an aluminum current collector with Pt foil anode (a), an anode chamber (b), a cathode chamber with pseudo-reference (c), and an aluminum current collector (d). The completely assembled cell is then connected to the potentiostat (e).
Figure S2. Example Ferrocene/Ferrocenium redox calibration at 40 mV/s. At the start of each day’s experiments, a Ferrocene/Ferrocenium redox calibration was performed to calibrate the pseudo-reference. The redox potential is found by averaging the potential at the cathodic and anodic peaks. In practice, cyclic voltammetry scans at 20, 40, 60, 80, and 100 mV/s were performed and the redox potential for all five were averaged in MATLAB to calculate the final redox potential.
Figure S3. NMR calibration curves for known liquid amine products
Linear regression was performed by minimizing the square of the relative error, not the absolute error as is done in ordinary least squares. Note that the calibration curve used a 50/50 mixture of (1R,2R)-(+)\text{-}1,2\text{-}diphenylethylenediamine and (1S,2S)-(−)\text{-}1,2\text{-}diphenylethylene-diamine which are not distinguishable in our NMR.
Figure S4. NMR of system demonstrating full conversion of benzaldehyde to benzyl imine.
Shown are the NMR spectra without ammonia (a) and with ammonia (b) after ~20 hours. The peak associated with the benzylic H on benzaldehyde (~9.96 ppm) is no longer present after >12 hours in the presence of ammonia, and instead we see new peaks associated with cis and trans imines as well as trimers formed via an equilibrium reaction of three imines (8.5-8.65 ppm). Note that during the experiment we occasionally observed traces of benzyl alcohol.
Figure S5. Faradaic efficiency towards hydrogen gas on Ag
Calibration curve for gas chromatograph (a) and the Faradaic efficiency toward hydrogen
gas on Ag as a function of coulombs passed (b). The cell was run at a constant current
of 3.9 mA/cm$^2$, representing the average total current on Ag found in the 2 C experiments,
which is also within error of the average total current on Ag found in experiments where
more coulombs are passed. Reaction conditions are the same as in other experiments,
namely 0.1 M benzaldehyde and 1 bar of ammonia initially. 5 SCCM of Ar gas was
bubbled through the cell with a pre trap of methanol to keep the flow saturated with
methanol and a post trap of aqueous boric acid to catch any ammonia from the cell. Any
hydrogen evolution in this system will be less than 1 bar of hydrogen gas, and thus should
not result in any thermochemical reduction since larger pressures (>20 bar) are generally
needed to drive this reaction. Additionally, any thermochemical reaction of the hydrogen
gas is negligible because the FE appears to add to 100% for the case of Ag. Beyond Ag,
even for systems with large currents such as Pt, Rh, and Pd, the balance of the FE is
likely hydrogen gas due to these materials known ability to facilitate hydrogen evolution
in methanol-based electrolytes$^2$. Explicit quantification of hydrogen gas in these systems
is impossible at operating conditions due to the high currents exhibited at our potentials
and the speed of the experiments.
Figure S6. Partial current toward primary amine as a function of adsorption descriptors.

The partial current toward primary amine as a function of benzene adsorption energy (a) and hydrogen adsorption energy (b). The benzene adsorption energy were taken from DFT studies, although the data agrees with experimental results where available.\textsuperscript{33,34} Hydrogen adsorption energies were taken from DFT studies and represent the energy of the reaction $0.5H_2(g) + \ast \rightarrow H^*$.\textsuperscript{35} There is no clear trend, volcano-like or otherwise, as a function of the adsorption energies.

Figure S7. The charge density for all metals analyzed.

Charge density profiles as a function of position above the surface (a) and the normalized charge density as a function of position above the surface (b) as per equation (1).
Figure S8. Further investigation of DFT-calculated descriptors.

The partial current toward primary amine as a function of cutoff distance associated with a charge density of 0.01 e⁻/Bohr²/Å (a) and a demonstration of how as the density cutoff moves away from the critical value of 0.06 e⁻/Bohr²/Å, it no longer tracks with atomic radius (b). The partial current as a function of charge density at a fixed point above the surface (c) and how this descriptor also tracks well with atomic radius (d). The distance (c) was optimized as described in the ESI Data Analysis. The charge density cutoff of 0.01 e⁻/Bohr²/Å or 0.11 e⁻/Bohr²/Å clearly does not describe the system compared to the optimized value in the main paper of 0.06 e⁻/Bohr²/Å. Both a cutoff distance and the charge at a fixed distance are metrics of describing atomic radius (one is a characteristic length scale and the other is a characteristic charge density scale) and also describe the system well, indicating that the charge density distribution is the appropriate quantity to describe the system.
Figure S9. Raw data for Tafel slope analysis
The partial current toward various amine products (a) and the FE toward those products (b) at the potentials used in the Tafel analysis from the main text (Figure 4a).

Figure S10. Raw data for substrate dependence analysis
The partial current toward various amine products (a) and the FE toward those products (b) at the potentials used in the benzaldehyde substrate dependence analysis from the main text (Figure 4b).
Figure S11. Raw data for proton dependence analysis
The partial current toward various amine products (a) and the FE toward those products (b) at the potentials used in the trifluoroacetic acid (proton) dependence analysis from the main text (Figure 4c).

Figure S12. Raw data for coulomb dependence analysis
The partial current toward various amine products (a) and the FE toward those products (b) at the potentials used in the coulomb dependence analysis from the main text (Figure 4d).
Figure S13. Exploration of potential poisoning mechanisms

Partial current as a function of various tests to determine what is causing the decrease in FE and partial current as a function of number of coulombs passed (a). FE for same tests (b). On the left of each plot, standards for 2 C, 8 C, and 16 C passed are shown shaded, with dashed lines helping to guide the eye. When the system is doped with roughly 16 C equivalent of the three amine products, the partial current and FE remain generally at their regular levels. When the foil is replaced after 8 C and then an additional 8 C are passed with the same electrolyte, the current and FE decrease similarly to when 16 C are passed. When the same foil is used with fresh electrolyte after passing 8 C or 16 C in a previous experiment, the partial currents remain unaffected but the FE decreases significantly with increasing number of coulombs passed.

Supplementary references


