Electronic Supplementary Information

Cathode enabled high Faradaic efficiency: reduction of imines to

amines with H₂O as a H-source

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1. General Information

All reagents were purchased without further purification unless otherwise noted. Analytical thin-layer chromatography (TLC) was conducted with TLC silica gel GF254 under UV irradiation. Flash column chromatography was performed using silica gel 200-300 and columns were packed according to the dry or wet method. Nuclear Magnetic Resonance spectra were recorded on a Bruker Advance II 400 (400 MHz), Bruker Advance III 400 (400 MHz) or AVANCE III HD (600 MHz) NMR spectrometer and ¹H NMR reported in units of parts per million (ppm) relative to tetramethyl silane (δ 0 ppm) or CDCl₃ (δ 7.26 ppm). Multiplicities are given as: s (singlet), d (doublet), t (triplet), q (quartet), dt (doublets of triplet), td (triplet of doublets) or m (multiplet). ¹³C NMR spectra were recorded on a Bruker Advance II 400 (101 MHz), Bruker Advance III 400 (101 MHz) or AVANCE III HD (151 MHz) NMR spectrometer and reported in ppm relative to CDCl₃ (77.0 ppm). Coupling constants were reported as a J value in Hz. GC-MS data were recorded on SHIMADZU™ GCMS-QP2010. HR-MS analyses were performed on a Thermo Scientific Q Exactive Focus Orbitrap LC-MS/MS System. LSV determination was performed on CHI 760E (CH Instruments, Ins) with carbon fiber paper as working electrode, Ag/AgNO₃ or Ag/AgCl as reference electrode and a Mg sheet as counter electrode. The instrument for bulk electrolysis is dual display potentiostat (DJS-292B) (Shanghai xinrui instruments Co., Ltd). Imines (1a-1p) were synthesized by conventional methods and purified by recrystallization. Imine were prepared according to previous report^[1].

2. Experimental Procedures

2.1 Treatment of electrode materials

Pretreatment of carbon fiber paper (CP): cutting into pieces of 1.5 cm×1.0 cm and ultrasonicated with acetone for 10 minutes to remove organic molecules on the surface, then washed with water several times to remove acetone; Pretreatment of Ni foam (NF), Cu foam, Pt sheet, Al sheet, Zn sheet, Fe sheet, Co sheet, and Mo sheet: cutting into pieces of 1.5 cm×1.0 cm and sonicated with acetone, 3.0 M of HCl aqueous solution and deionized water several times respectively to remove the impurities (organic molecules and oxide layer) on the surface of the materials^[2].

2.2 The procedure for electrosynthesis in a two-electrode system



In an undivided flask equipped with a stir bar, CH₃CN (5 mL), H₂O (2 mL), LiClO₄ (63.8 mg, 0.6 mmol) and freshly substrate **1** (0.1 mmol) were added. The flask was equipped with Mg sheet (10 mm× 10 mm) as anode and carbon fiber paper (10 mm× 10 mm) as cathode, respectively. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA at room temperature for 5-8 h. After the reaction, extract with ethyl acetate and remove the organic phase by rotary evaporation. Then, the pure products were obtained by chromatography on silica gel by using petroleum ether and ethyl acetate as the eluent.

2.3 The procedure for electrosynthesis in a three-electrode system



In an undivided cell, equipped with carbon fiber paper as working electrode (10 mm× 10 mm), Mg sheet as the counter electrode (10 mm× 10 mm) and Ag/AgNO₃ (10 mM AgNO₃) as the reference electrode. Then, CH₃CN (5 mL), H₂O (2 mL),

LiClO₄ (63.8 mg, 0.6 mmol) and freshly **1a** (0.1 mmol) were added. A constant cathode potential was controlled using the chronoamperometry with a electrochemical workstation. The electrochemical reaction under magnetic stirring (500 rpm) without removing O₂. Linear sweep voltammetry (LSV), and chronoamperometry were performed using an electrochemical workstation. All experiments were carried out at room temperature without protection. After the electrochemical reaction finished, the electrolyte solution was extracted with ethyl acetate several times. The organic phasecontaining the imines products was subjected to GC-MS analysis. The yield (%) of the products, conversion (%) of the starting materials, and Faradaic efficiency were calculated according to the following equations (1) – (3):

Yield = (moles of target products)/ (initial moles of substrate) x 100% (1)

Conversion = (moles of reactant consumed)/ (initial moles of substrate) x 100% (2)

F.E. = (n x moles of target products)/ (total charge passed/F) x 100% (3)

2.4 Screening of optimal reaction conditions

N 1	a $Mg = CP$ $j = 8 \text{ mA/cm}^2$ $H_2O (2 \text{ mL}), \text{ MeCN (5 mL)}$ $LiClO_4 (0.6 \text{ mmol}), \text{ r.t., air}$	•	H H 2a
Entry	Variation from standard condition	Con.	Yield ^[b]
1	None	93%	91% ^c
2	EtOH	96%	85%
3	DMF	55%	18%
4	THF	85%	29%
5	acetone	83%	45%
6	Graphite rod as anode	99%	2%
7	Zn slice as anode	91%	64%
8	Ni slice as anode	99%	3%
9	12 mA, 4 h	86%	57%
10	4 mA, 8 h	92%	88%

 Table S1. Screening of optimal reaction conditions^[a].

^a 0.1 mmol of **1a** were dissolved in 7 mL of solvent.

^b Yields were determined by GC-MS using [1,1'-biphenyl]-4-carbonitrile as internal standard.

^c Isolated yield: 84%.

2.5 Potential-dependent conversion and yield of 2a over CP cathodes



Fig. S1. Potential-dependent conversion and yield of 2a over CP cathodes.

2.6 Time-dependent transformations of 1a to 2a



Fig. S2. Time-dependent transformations of 1a to 2a over CP at -1.7 V vs Ag/AgNO₃.

2.7 LSV of H₂O and imine 1p



Fig. S3. LSV of H_2O and imine 1p with CP cathode.

2.8 Amperometric i-t curve



Fig. S4. *j*-t curves of the electrochemical transformation of 1a to 2a over CP at -1.7 V vs $Ag/AgNO_3$.

2.9 the ratio value of deuterated and non-deuterated product.



Fig. S5. the ratio value of deuterated product 3a and non-deuterated product 2a.

2.10 Electrolysis Setup



Fig. S6. Electrolysis Setup

3. Characterization of Products

4-((p-tolylamino)methyl)benzonitrile (2a)^[3]



The pure product was obtained by flash chromatography on silica gel by using petroleum ether and ethyl acetate as the eluent (Petroleum ether: EtOAc = 5 : 1, Yellow solid, 18.6 mg, 84% yield).

¹**H NMR** (CDCl₃, 400 MHz): δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.50 (d, *J* = 8.4 Hz, 2H), 4.40 (s, 2H), 2.23 (s, 3H).

¹³C NMR (CDCl₃, 101 MHz): δ 145.6, 145.1, 132.4, 129.8, 127.7, 127.3, 118.9, 113.0, 110.8, 48.0, 20.3.

HRMS (ESI): calculated for $C_{15}H_{14}N_2^+$ [M + H]⁺: 223.1230; found: 223.1229.

N-(4-methylbenzyl)-4-methylthioaniline (2b)^[3]



The pure product was obtained by flash chromatography on silica gel by using petroleum ether and ethyl acetate as the eluent (Petroleum ether: EtOAc = 10 : 1, Yellow solid, 17.5 mg, 72% yield).

¹**H** NMR (CDCl₃, 400 MHz): δ 7.25 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.6 Hz, 2H), 7.16 (d, J = 7.8 Hz, 2H), 6.58 (d, J = 8.6 Hz, 2H), 4.27 (s, 2H), 2.41 (s, 3H), 2.35 (s, 3H).

¹³C NMR (CDCl₃, 101 MHz): δ 146.6, 137.0, 135.8, 131.4, 129.3, 127.5, 124.7, 113.7, 48.2, 21.1, 19.1.

HRMS (ESI): calculated for $C_{15}H_{17}NS^+$ [M + H]⁺: 224.1154; found: 224.1154.

4-(((4-methoxyphenyl)amino)methyl)benzonitrile (2c)



The pure product was obtained by flash chromatography on silica gel by using petroleum ether and ethyl acetate as the eluent (Petroleum ether: EtOAc = 5 : 1, Yellow oil, 19.1 mg, 80% yield).

¹**H NMR** (CDCl₃, 400 MHz): δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 8.9 Hz, 2H), 6.54 (d, *J* = 8.9 Hz, 2H), 4.38 (s, 2H), 3.73 (s, 3H).

¹³C NMR (CDCl₃, 101 MHz): δ 152.5, 145.6, 141.5, 132.4, 127.8, 118.9, 114.9, 114.2, 110.9, 55.7, 48.7.

HRMS (ESI): calculated for $C_{15}H14N_2O^+$ [M + H]⁺: 239.1179; found: 239.1178.

N-(4-methylbenzyl)-4-(trifluoromethyl)aniline (2d)^[4]



The pure product was obtained by flash chromatography on silica gel by using petroleum ether and ethyl acetate as the eluent (Petroleum ether: EtOAc = 10 : 1, White solid, 19.6 mg, 74% yield).

¹**H** NMR (CDCl₃, 400 MHz): δ 7.40 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 7.6 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 6.63 (d, J = 8.5 Hz, 2H), 4.33 (s, 2H), 2.37 (s, 3H). ¹³**C** NMR (CDCl₃, 101 MHz): δ 150.5, 137.2, 135.4, 129.4, 127.4, 126.6 (q, J = 4.1 Hz), 124.9 (q, J = 271.7 Hz), 118.9, 111.9 (q, J = 32.3 Hz), 47.6, 21.1.. HRMS (ESI): calculated for C₁₅H₁₄F₃N⁺ [M + H]⁺: 266.1151; found: 266.1151.

methyl 4-((p-tolylamino)methyl)benzoate (2e)



The pure product was obtained by flash chromatography on silica gel by using petroleum ether and ethyl acetate as the eluent (Petroleum ether: EtOAc = 10 : 1, White solid, 17.6 mg, 69% yield).

¹**H** NMR (CDCl₃, 400 MHz): δ 8.00 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 6.98 (d, J = 8.1 Hz, 2H), 6.53 (d, J = 8.4 Hz, 2H), 4.39 (s, 2H), 3.91 (s, 3H), 2.23 (s, 3H).

¹³C NMR (CDCl₃, 101 MHz): δ 166.9, 145.4, 145.1, 129.9, 129.8, 129.0, 127.1, 127.1, 113.1, 52.0, 48.3, 20.4.

HRMS (ESI): calculated for $C_{16}H_{17}NO_2^+$ [M + H]⁺: 256.1332; found: 256.1330.

3,4-dimethyl-N-(4-methylbenzyl)aniline (2f)



The pure product was obtained by flash chromatography on silica gel by using petroleum ether and ethyl acetate as the eluent (Petroleum ether: EtOAc = 20 : 1, Colorless oil, 17.3 mg, 77% yield).

¹**H** NMR (CDCl₃, 400 MHz): δ 7.27 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 7.8 Hz, 2H), 6.94 (d, J = 8.0 Hz, 1H), 6.49 (d, J = 2.6 Hz, 1H), 6.42 (dd, J = 8.1, 2.6 Hz, 1H), 4.26 (s, 2H), 2.35 (s, 3H), 2.20 (s, 3H), 2.16 (s, 3H).

¹³C NMR (CDCl₃, 101 MHz): δ 146.4, 137.3, 136.7, 136.7, 130.3, 129.3, 127.5, 125.5, 114.7, 110.3, 48.4, 21.1, 20.0, 18.7.

HRMS (ESI): calculated for $C_{16}H_{19}N^+$ [M + H]⁺: 226.1590; found: 226.1587.

N-benzyl-4-methylaniline (2g)



The pure product was obtained by flash chromatography on silica gel by using petroleum ether and ethyl acetate as the eluent (Petroleum ether: EtOAc = 20 : 1, Colorless oil, 16.2 mg, 82% yield).

¹**H NMR** (CDCl₃, 400 MHz): δ 7.27 (d, *J* = 10.5 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.15 (s, 1H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.47 (d, *J* = 8.1 Hz, 2H), 4.21 (s, 2H), 2.13 (s, 3H).

¹³C NMR (CDCl₃, 101 MHz): δ 145.7, 139.5, 129.7, 128.6, 127.5, 127.2, 126.9, 113.1, 48.7, 20.4.

HRMS (ESI): calculated for $C_{14}H_{15}N^+$ [M + H]⁺: 198.1277; found: 198.1279.

4-methyl-N-(4-methylbenzyl)aniline (2h)^[4]



The pure product was obtained by flash chromatography on silica gel by using petroleum ether and ethyl acetate as the eluent (Petroleum ether: EtOAc = 20 : 1, Colorless oil, 18.2 mg, 86% yield).

¹**H NMR** (CDCl₃, 400 MHz): δ 7.26 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 7.7 Hz, 2H), 6.98 (d, J = 8.2 Hz, 2H), 6.57 (d, J = 8.4 Hz, 2H), 4.26 (s, 2H), 2.34 (s, 3H), 2.23 (s, 3H).

¹³C NMR (CDCl₃, 101 MHz): δ 136.8, 136.3, 129.7, 129.3, 127.6, 120.8, 113.3, 48.6, 21.1, 20.4.

HRMS (ESI): calculated for $C_{15}H_{17}N^+$ [M + H]⁺: 212.1434; found: 212.1434.

N-(2,6-difluorobenzyl)-4-methylaniline (2i)



The pure product was obtained by flash chromatography on silica gel by using petroleum ether and ethyl acetate as the eluent (Petroleum ether: EtOAc = 10 : 1, Colorless oil, 17.9 mg, 77% yield).

¹**H NMR** (CDCl₃, 400 MHz): δ 7.24 – 7.16 (m, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.87 (t, *J* = 7.7 Hz, 2H), 6.66 (d, *J* = 8.2 Hz, 2H), 4.41 (s, 2H), 2.23 (s, 3H).

¹³**C** NMR (CDCl₃, 101 MHz): δ 161.8 (d, J = 252.5 Hz), 161.6 (d, J = 252.5 Hz), 144.9, 129.1 (d, J = 21.2 Hz), 127.4, 113.5, 111.3 (dd, $J_1 = 26.3$ Hz, $J_2 = 12.1$ Hz), 36.4, 20.4.

HRMS (ESI): calculated for $C_{14}H_{13}F_2N^+$ [M + H]⁺: 234.1089; found: 234.1088.

4-fluoro-N-(4-methylbenzyl)aniline (2j)



The pure product was obtained by flash chromatography on silica gel by using petroleum ether and ethyl acetate as the eluent (Petroleum ether: EtOAc = 10 : 1, Colorless oil, 16.7 mg, 73% yield).

¹**H NMR** (CDCl₃, 400 MHz): δ 7.28 (d, J = 3.0 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 6.90 (t, J = 8.7 Hz, 2H), 6.58 (dd, J = 9.0, 4.3 Hz, 2H), 4.26 (s, 2H), 2.37 (s, 3H). ¹³**C NMR** (CDCl₃, 101 MHz): δ 155.9 (d, J = 232.3 Hz), 144.4, 137.0, 136.1, 129.3, 127.5, 115.62 (d, J = 22.3 Hz), 113.67 (d, J = 7.4 Hz), 48.7, 21.1. **HRMS** (ESI): calculated for C₁₄H₁₄FN⁺ [M + H]⁺: 216.1183; found: 216.1182.

4-bromo-N-(4-methylbenzyl)aniline (2k)^[6]



The pure product was obtained by flash chromatography on silica gel by using petroleum ether and ethyl acetate as the eluent (Petroleum ether: EtOAc = 10 : 1, White solid, 19.9 mg, 72% yield).

¹**H NMR** (CDCl₃, 400 MHz): δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.53 (d, *J* = 8.4 Hz, 2H), 4.28 (s, 2H), 2.24 (s, 3H).

¹³C NMR (CDCl₃, 101 MHz): δ 145.4, 138.7, 131.6, 129.8, 129.0, 127.1, 120.8, 113.1, 48.0, 20.4.

HRMS (ESI): calculated for $C_{14}H_{14}BrN^+$ [M + H]⁺: 276.0382; found: 276.0382.

4-iodo-N-(4-methylbenzyl)aniline (21)^[5]



The pure product was obtained by flash chromatography on silica gel by using petroleum ether and ethyl acetate as the eluent (Petroleum ether: EtOAc = 10 : 1, White solid, 23.6 mg, 73% yield).

¹**H** NMR (CDCl₃, 400 MHz): δ 7.27 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.64 (d, *J* = 8.0 Hz, 2H), 4.29 (s, 2H), 2.35 (s, 3H).

¹³C NMR (CDCl₃, 101 MHz): δ 148.2, 136.9, 136.3, 129.3, 129.2, 127.5, 117.5, 112.8, 48.1, 21.1.

HRMS (ESI): calculated for $C_{14}H_{14}IN^+$ [M + H]⁺: 324.0244; found: 324.0242.

N-(4-fluorobenzyl)-4-methylaniline (2m)^[4]



The pure product was obtained by flash chromatography on silica gel by using petroleum ether and ethyl acetate as the eluent (Petroleum ether : EtOAc = 10 : 1, Colorless oil, 17.4 mg, 81% yield).

¹**H** NMR (CDCl₃, 400 MHz): δ 7.33 (dd, J = 8.4, 5.4 Hz, 2H), 7.03 (d, J = 8.6 Hz, 2H), 6.99 (d, J = 7.7 Hz, 2H), 6.56 (d, J = 8.2 Hz, 2H), 4.28 (s, 2H), 2.24 (s, 3H). ¹³**C** NMR (CDCl₃, 101 MHz): δ 162.0 (d, J = 242.4 Hz), 145.5, 129.8, 129.0 (d, J = 8.0 Hz), 127.0, 115.4 (d, J = 21.5 Hz), 113.1, 48.0, 20.4. HRMS (ESI): calculated for C₁₄H₁₄FN⁺ [M + H]⁺: 216.1183; found: 216.1184.

N-(4-chlorobenzyl)-4-methylaniline(2n)



The pure product was obtained by flash chromatography on silica gel by using petroleum ether and ethyl acetate as the eluent (Petroleum ether: EtOAc = 10 : 1, Colorless oil, 16.2 mg, 70% yield).

¹**H NMR** (CDCl₃, 400 MHz): δ 7.30 (s, 4H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.54 (d, *J* = 8.0 Hz, 2H), 4.29 (s, 2H), 2.25 (s, 3H).

¹³C NMR (CDCl₃, 101 MHz): δ 145.5, 138.2, 132.8, 129.8, 128.7, 128.7, 127.0, 113.0, 47.9, 20.4.

HRMS (ESI): calculated for $C_{14}H_{14}CIN^+$ [M + H]⁺: 232.0888; found: 232.0888.

N-(4-bromobenzyl)-4-methylaniline (20)



The pure product was obtained by flash chromatography on silica gel by using petroleum ether and ethyl acetate as the eluent (Petroleum ether: EtOAc = 10 : 1, White solid, 21.5 mg, 78% yield).

¹**H NMR** (CDCl₃, 400 MHz): δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.54 (d, *J* = 8.4 Hz, 2H), 4.28 (s, 2H), 2.24 (s, 3H).

¹³C NMR (CDCl₃, 101 MHz): δ 145.4, 138.7, 131.6, 129.8, 129.1, 127.1, 120.8, 113.1, 48.0, 20.4.

HRMS (ESI): calculated for $C_{14}H_{14}BrN^+$ [M + H]⁺: 276.0382; found: 276.0383.

4-methyl-*N*-(1-phenylethyl)aniline (2p)^[7]



The pure product was obtained by flash chromatography on silica gel by using petroleum ether and ethyl acetate as the eluent (Petroleum ether: EtOAc = 50 : 1, light yellow oil, 10.4 mg, 49% yield).

¹**H NMR** (CDCl₃, 600 MHz): δ 7.36 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.89 (d, *J* = 8.1 Hz, 2H), 6.43 (d, *J* = 8.4 Hz, 2H), 4.45 (q, *J* = 6.7 Hz, 1H), 3.90 (bs, 1H), 2.18 (s, 3H), 1.50 (d, *J* = 6.7 Hz, 3H).

¹³C NMR (CDCl₃, 151 MHz): δ 145.4, 145.0, 129.6, 128.6, 126.8, 126.3, 125.8, 113.4, 53.6, 25.0, 20.3.

4-((*p*-tolylamino-d)methyl-d)benzonitrile (3a)



The pure product was obtained by flash chromatography on silica gel by using petroleum ether and ethyl acetate as the eluent (Petroleum ether: EtOAc = 5 : 1, Yellow solid, 18.4 mg, 82% yield).

¹**H NMR** (CDCl₃, 400 MHz): δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.50 (d, *J* = 8.0 Hz, 2H), 4.39 (s, 1H), 2.23 (s, 3H).

¹³C NMR (CDCl₃, 101 MHz): δ 145.5, 145.0, 132.4, 129.8, 127.7, 127.4, 118.9, 113.0, 110.9, 47.8 (t, *J* = 20.8 Hz), 20.3.

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5. ¹H and ¹³C spectra of Product.

4-((p-tolylamino)methyl)benzonitrile (2a)





N-(4-methylbenzyl)-4- (methylthio)aniline (2b) (¹H NMR, CDCl₃, 400 MHz)



4-(((4-methoxyphenyl)amino)methyl)benzonitrile(2c) (¹H NMR, CDCl₃, 400 MHz)



N-(4-methylbenzyl)-4-(trifluoromethyl)aniline(2d) (¹H NMR, CDCl₃, 400 MHz)



methyl 4-((p-tolylamino)methyl)benzoate (2e) (¹H NMR, CDCl₃, 400 MHz)



3,4-dimethyl-N-(4-methylbenzyl)aniline (2f)



N-benzyl-4-methylaniline (2g)



4-methyl-N-(4-methylbenzyl)aniline (2h)



N-(2,6-difluorobenzyl)-4-methylaniline (2i)



4-fluoro-N-(4-methylbenzyl)aniline (2j)



4-bromo-N-(4-methylbenzyl)aniline (2k)





4-iodo-N-(4-methylbenzyl)aniline (2l)





N-(4-fluorobenzyl)-4-methylaniline (2m)



N-(4-chlorobenzyl)-4-methylaniline(2n)



N-(4-bromobenzyl)-4-methylaniline (20)





4-methyl-*N*-(1-phenylethyl)aniline (2p)

(13C NMR, CDCl₃, 151 MHz)



4-((p-tolylamino-d)methyl-d)benzonitrile (3a)

