Supporting Information

General information
All reagents and solvents were from commercial sources and used without further purification from freshly opened containers, NMR spectra were recorded at 400 and 500 MHz (¹H NMR), 101 and 126 MHz (¹³C NMR). Chemical shifts (δ) are reported in parts per million. Mass spectrometric measurements were performed by R. Jenkins/R. Hick/S. Waller at Cardiff University. Ions were generated by the atmospheric pressure Electrospray Ionization (ESI).

GC
The GC method was performed using a Perkin Elmer Clarus system (Clarus 680 GC, Clarus SQ8C Mass Spec), fitted with a Perkin Elmer Elite 1 30 m x 0.25 mm, 0.25 µm column. The results were processed using chromatogram software. The carrier flow was 1.0 mL min⁻¹ and split flow was 20 mL min⁻¹. The injection temperature was 100 °C; initial temperature 80 °C kept for 2 min, then 8 °C min⁻¹ to 280 °C, kept for 3 min. Compounds 1 and 2 were observed at 5.2 and 6.2 min; the cis- and trans-3 were observed at 7.9 and 8.2 min.

Electrochemical reactor:

Standalone reactor
Reactor with temperature control through the Vapourtec flow system
The ion electrochemical reactor from Vapourtec Ltd was used for the experiments.\textsuperscript{[3]} Electrode materials: Glassy Carbon, Graphite, 304 Stainless Steel (18% Cr, 8% Ni). The dimensions of the electrodes (5 x 5 cm\textsuperscript{2}) and the 0.5 mm spacer with a channel volume of 0.6 mL and an exposed electrode surface area of 2 x 12 cm\textsuperscript{2} is identical to the electrochemical reactor published previously.\textsuperscript{[4]}

General Procedure 1 (GP 1):
A solution of 1 (0.1 M, 60 mL) in MeOH containing Et\textsubscript{4}NBF\textsubscript{4} (0.05 M); (EtOH and PrOH: Bu\textsubscript{4}NBF\textsubscript{4}) was sonicated prior to the electrolysis to ensure complete dissolution. Two microreactors were connected and the aforementioned solution was pumped at 0.5 mL min\textsuperscript{-1} using a syringe pump or the Vapourtec E series, applying a constant current of 160 mA on each reactor. The first 5 mL were discarded, then the reaction mixture was collected for 110 min (55 mL). The alcohol was removed under reduced pressure, and the crude product was washed with water (50 mL) to remove the supporting electrolyte and extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 x 30 mL). The organic layers were combined, dried over anhydrous MgSO\textsubscript{4}, filtered, evaporated and dried under high vacuum. The residue was chromatographed through silica gel eluting with hexane / ethyl acetate.

General Procedure 2 (GP 2):
A solution of 1 (0.1 M, 60 mL) in MeOH containing Et\textsubscript{4}NBF\textsubscript{4} (0.05 M); (EtOH and PrOH: Bu\textsubscript{4}NBF\textsubscript{4}) was sonicated prior to the electrolysis to ensure complete dissolution. The aforementioned solution was pumped through one microreactor at 0.5 mL min\textsuperscript{-1} using a syringe pump or the Vapourtec E series, applying a constant current of 640 mA. The first 5 mL were discarded, then the reaction mixture was collected for 110 min (55 mL). MeOH was removed under reduced pressure, and the crude product was washed with
water (50 mL) to remove the supporting electrolyte and extracted with CH$_2$Cl$_2$ (3 x 30 mL). The organic layers were combined, dried over anhydrous MgSO$_4$, filtered, evaporated and dried under high vacuum. The residue was chromatographed through silica gel eluting with hexane / ethyl acetate.

Procedure 3 (Table 1, Entry 8):
The anolyte solution of 1 (0.1 M, 60 mL) in MeOH containing Et$_4$NBF$_4$ (0.05 M) and the catholyte solution, MeOH (60 mL) containing Et$_4$NBF$_4$ (0.05 M) were sonicated prior to the electrolysis to ensure complete dissolution. The aforementioned solutions were pumped through one microreactor divided by Nafion membrane (Nafion® N-324 membrane, 0.15 mm thick, Teflon® fabric reinforced Rf[OCF$_2$(CF$_3$)$_2$]$_n$OCF$_2$SO$_3$H) at 0.5 mL min$^{-1}$ each using syringe pump or the Vapourtec E series, applying a constant current of 160 mA. The first 5 mL were discarded, then the reaction mixture was collected for 110 min (55 mL). MeOH was removed under reduced pressure, and the crude product was washed with water (50 mL) to remove the supporting electrolyte and extracted with CH$_2$Cl$_2$ (3 x 30 mL). The organic layers were combined, dried over anhydrous MgSO$_4$, filtered, evaporated and dried under high vacuum. The residue was chromatographed through silica gel eluting with hexane / ethyl acetate.

Procedure 4 (batch reaction):
A solution of 1 (0.1 M, 60 mL) in MeOH containing Et$_4$NBF$_4$ (0.05 M) was sonicated prior to the electrolysis to ensure complete dissolution. The solution was electrolyzed (304 stainless steel cathode and graphite anode, both 1cm$^2$) stirred and electrolyzed for 160 min, applying a constant current of 10 mA. Then the reaction mixture was analyzed using GC to determine the conversion.

2-Methoxypyrrolidine-1-carbaldehyde (2):$^1$
Compound 2 was made following GP 1, using N-formylpyrrolidine 1 (545 mg, 5.5 mmol) to give the product as a colorless oil (629 mg, 89%), chromatography: hexane/ethyl acetate (1:1). NMR spectra show a mixture of rotamers (~ 5:1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.40_{\text{maj}}$ and 8.29$_{\text{min}}$ (s, 1H), 5.37$_{\text{min}}$ and 4.92$_{\text{maj}}$ (d, $J = 4.8$ Hz, 1H), 3.58 - 3.40 (m, 2H), 3.38$_{\text{min}}$ and 3.26$_{\text{maj}}$ (s, 3H), 2.13 - 1.79 (m, 4H) ppm; $^{13}$C NMR
(101 MHz, CDCl₃): δ = 162.6ₘₙ and 161.₄ₘₐ, 89.7ₘₐ and 85.₅ₘₚ, 56.₆ₘₚ and 54.₄ₘₐ, 45.₂ₘₚ and 42.₇ₘₐ, 31.₉ₘₚ and 31.₈ₘₐ, 22.₁ₘₙ and 21.₄ₘₚ ppm.

2,5-Dimethoxypyrrolidine-1-carbaldehyde (3):²
Compound 3 was made following GP 2, using N-formylpyrrolidine 1 (545 mg, 5.5 mmol) to give the product as a colorless oil (723 mg, 83%), chromatography: hexane/ethyl acetate (2:3). NMR spectra show a mixture of cis / trans stereoisomers. ¹H NMR (500 MHz, CDCl₃): δ = 8.49ₘₚ and 8.₄₉ₘₐ (s, 1H), 5.₄₀ₘₚ and 5.₃₀ₘₙ (d, J = 3.₁ Hz, 1H), 5.₀₀ₘₐ and 4.₉₇ₘₚ (d, J = 5.₄ Hz, 1H), 3.₄₁ₘₚ and 3.₃₉ₘₚ (s, 3H), 3.₃₀ₘₐ, 3.₂₉ₘₚ (s, 3H), 2.₁₅ – 1.₈₀ (m, 4H) ppm; ¹³C NMR (126 MHz, CDCl₃): δ = 162.₉, 162.₈, 90.₆, 89.₅, 86.₄, 86.₃, 5₇.₁, 5₆.₈, 5₄.₇, 5₄.₂, 3₀.₄, 3₀.₀, 2₈.₉, 2₈.₃ ppm; IR (neat): 2₉₈₇, 2₈₃₃, 1₆₈₁, 1₃₆₃, 1₀₇₆ cm⁻¹.

2-Ethoxypyrrolidine-1-carbaldehyde (4):
Compound 4 was made following GP 1, using N-formylpyrrolidine 1 (545 mg, 5.5 mmol) to give the product as a colorless oil (609 mg, 77%), chromatography: hexane/ethyl acetate (1:1). NMR spectra show a mixture of rotamers (~ 5:1). ¹H NMR (400 MHz, CDCl₃): δ = 8.₃₈ₘₐ (s, 1H), 8.₂₆ₘₚ (s, 1H), 5.₄₆ₘₚ (d, J = 3.₄ Hz, 1H), 5.₀₃ₘₐ (d, J = 4.₈ Hz, 1H), 3.₆₆ – 3.₂₅ (m, 4H), 2.₂₄ – 1.₆₈ (m, 4H), 1.₃₅ – 1.₀₆ (m, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ = 16₂.₈ₘₚ, 1₆₁.₇ₘₐ, 8₈.₃ₘₐ, 8₄.₁ₘₚ, 6₄.₅ₘₚ, 6₂.₅ₘₐ, 4₅.₂ₘₚ, 4₂.₇ₘₐ, 3₂.₂ₘₚ, 3₂.₂ₘₐ, 2₂.₂ₘₚ, 2₁.₅ₘₐ, 1₅.₄ₘₚ, 1₅.₁ₘₚ ppm; IR (neat): 2₉₈₇, 2₈₈₅, 1₆₆₆, 1₃₈₆, 1₀₆₆ cm⁻¹; HRMS (ESI): m/z calcd for C₇H₁₃NO₂⁺: 1₄₃.₀₉₄₆; found: 1₄₃.₀₉₅₄.

2,5-Diethoxypyrrolidine-1-carbaldehyde (5):²
Compound 5 was made following GP 2, using N-formylpyrrolidine 1 (545 mg, 5.5 mmol) to give the product as a colorless oil (527 mg, 51%), chromatography: hexane/ethyl acetate (1:1). ¹H NMR (500 MHz, CDCl₃): δ = 8.₄₈ₘₚ and 8.₃₈ₘₐ (s, 1H), 5.₆₅ – 5.₃₆ (m, 1H), 5.₀₈ (dd, J = ₁₃.₀, ₅.₅ Hz, 1H), 3.₇₅ – 3.₅₁ (m, 3H), 3.₄₆ – 3.₃₁ (m, 1H), 2.₂₁ – 1.₈₆ (m, 4H), 1.₂₇ – 1.₁₃ (m, 6H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ 1₆₂.₈, 8₉.₂, 8₄.₇, 6₄.₅, 6₂.₀, 3₀.₈, 3₀.₂, 1₅.₄, 1₅.₁ ppm.
2-Propoxypyrrolidine-1-carbaldehyde (6):
Compound 4 was made following GP 1, using N-formylpyrrolidine 1 (545 mg, 5.5 mmol) to give the product as a colorless oil (553 mg, 64%), chromatography: hexane/ethyl acetate (1:1). NMR spectra show a mixture of rotamers (~ 5:1). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 8.37\) \text{maj}, 8.25 \text{min} (s, 1H), 5.44 \text{min} and 5.00 \text{maj} (d, \(J = 4.7\) Hz, 1H), 3.61 – 3.18 (m, 4H), 2.28 – 1.69 (m, 4H), 1.69 – 1.34 (m, 2H), 0.88 (q, \(J = 7.9\) Hz, 3H) ppm; \(^1\)C NMR (126 MHz, CDCl\(_3\)): \(\delta = 162.42\) \text{min} and 161.34 \text{maj}, 88.37 \text{maj} and 84.22 \text{min}, 70.70 \text{maj} and 68.68 \text{maj}, 45.12 \text{min} and 42.62 \text{maj}, 32.11 \text{min} and 32.08 \text{maj}, 23.05 \text{min} and 22.78 \text{maj}, 22.19 \text{min} and 21.47 \text{maj}, 13.65 \text{min} and 10.66 \text{maj} ppm; IR (neat): 2962, 2877, 1668, 1386, 1074 cm\(^{-1}\); HRMS (ESI): \(m/z\) calcld for \(\text{C}_8\text{H}_{16}\text{NO}_2^+\): 158.1176; found: 158.1181.

2,5-Dipropoxypyrrolidine-1-carbaldehyde (7):
Compound 7 was made following GP 2, using N-formylpyrrolidine 1 (545 mg, 5.5 mmol) to give the product as a colorless oil (413 mg, 35%), chromatography: hexane/ethyl acetate (1:1). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 8.37\) (s, 1H), 5.46 (d, \(J = 2.7\) Hz, 1H), 5.08 (d, \(J = 5.4\) Hz, 1H), 3.58 – 3.48 (m, 2H), 3.44 (q, \(J = 7.4\) Hz, 1H), 3.27 (q, \(J = 7.4\) Hz, 1H), 2.15 – 1.91 (m, 4H), 1.65 – 1.49 (m, 4H), 0.94 – 0.82 (m, 6H) ppm. \(^1\)C NMR (126 MHz, CDCl\(_3\)): \(\delta = 162.8\), 89.3, 84.9, 70.7, 68.2, 30.8, 30.1, 23.0, 22.8, 10.74, 10.72 ppm; IR (neat): 2960, 2875, 1683, 1367, 1072 cm\(^{-1}\); HRMS (ESI): \(m/z\) calcld for \(\text{C}_{11}\text{H}_{21}\text{NO}_3^+\): 215.1521; found: 215.1521.

2-Butoxypyrrolidine-1-carbaldehyde (8):
Compound 8 was made following GP 1, using N-formylpyrrolidine 1 (545 mg, 5.5 mmol) to give the product as a colorless oil (457 mg, 48%), chromatography: hexane/ethyl acetate (1:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.38\) \text{maj} and 8.26 \text{min} (s, 1H), 5.43 \text{min} and 5.00 \text{maj} (d, \(J = 4.8\) Hz, 1H), 3.62 – 3.35 (m, 4H), 3.27 (dt, \(J = 8.8, 6.5\) Hz, 1H), 2.20 – 1.75 (m, 4H), 1.68 – 1.41 (m, 2H), 1.36 – 1.22 (m, 2H), 0.99 – 0.65 (m, 3H) ppm. \(^1\)C NMR (101 MHz, CDCl\(_3\)): \(\delta = 162.4\) \text{min}, 161.4 \text{maj}, 88.4 \text{maj}, 84.2 \text{min}, 68.8 \text{min}, 66.8 \text{maj}, 45.1 \text{min}, 42.6 \text{maj}, 32.11 \text{maj}, 31.9 \text{min}, 31.5 \text{maj}, 22.2 \text{min}, 21.5 \text{maj}, 19.4, 14.0 \text{min}, 13.9 \text{maj} ppm. IR (neat): 2956, 2872, 1670, 1384, 1076 cm\(^{-1}\); HRMS (ESI): \(m/z\) calcld for \(\text{C}_9\text{H}_{18}\text{NO}_2^+\): 172.1332; found: 172.1338.
2,5-Dibutoxypyrrolidine-1-carbaldehyde (9):

Compound 9 was made following GP 1, using N-formylpyrrolidine 1 (545 mg, 5.5 mmol) to give the product as a colorless oil (364 mg, 27%), chromatography; hexane/ethyl acetate (1:1). $^1$H NMR (400 MHz, CDCl₃): $\delta = 8.38$ (s, 1H), 5.47 (m, 1H), 5.08 (dd, $J = 5.5$, 2.5 Hz, 1H), 3.65 – 3.43 (m, 3H), 3.35 – 3.27 (m, 1H), 2.25 – 1.91 (m, 4H), 1.54 (dd, $J = 21.9$, 10.8, 6.6 Hz, 4H), 1.42 – 1.28 (m, 4H), 0.90 (dt, $J = 13.6$, 6.8 Hz, 6H) ppm. $^{13}$C NMR (101 MHz, CDCl₃): $\delta = 162.8$, 89.3, 84.8, 68.8, 66.3, 31.9, 31.6, 30.7, 30.1, 19.48, 19.45, 14.0, 13.9 ppm. IR (neat): 2962, 2877, 1668, 1386, 1074 cm⁻¹; HRMS (ESI): $m/z$ calcd for C₁₃H₂₆NO₃⁺: 244.1913; found: 244.1913.

2-(Pentyloxy)pyrrolidine-1-carbaldehyde (10):

Compound 10 was made following GP 1, using N-formylpyrrolidine 1 (545 mg, 5.5 mmol) to give the product as a colorless oil (431 mg, 42%), chromatography: hexane/ethyl acetate (1:1). $^1$H NMR (400 MHz, CDCl₃): $\delta = 8.38_{\text{maj}}$ and $8.26_{\text{min}}$ (s, 1H), 5.45$^{\text{min}}$ – 5.0$^{\text{maj}}$ (d, $J = 4.8$, 1H), 3.62 – 3.35 (m, 3H), 3.27 (dt, $J = 8.8$, 6.5 Hz, 1H), 2.20 – 1.75 (m, 4H), 1.60 – 1.46 (m, 3H), 1.34 – 1.20 (m, 4H), 0.91 – 0.83 (m, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl₃): $\delta = 162.4_{\text{min}}$, 161.4$^{\text{maj}}$, 88.4$^{\text{maj}}$, 84.2$^{\text{min}}$, 77.80, 69.1$^{\text{min}}$, 67.45$^{\text{maj}}$, 45.1$^{\text{min}}$, 42.6$^{\text{maj}}$, 32.14$^{\text{min}}$, 32.11$^{\text{maj}}$, 29.5$^{\text{min}}$, 29.2$^{\text{maj}}$, 28.4$^{\text{maj}}$, 22.6$^{\text{min}}$, 22.5$^{\text{maj}}$, 22.2$^{\text{min}}$, 21.5$^{\text{maj}}$, 14.15$^{\text{min}}$, 14.11$^{\text{maj}}$ ppm. IR (neat): 2954, 2860, 1670, 1384, 1076 cm⁻¹; HRMS (ESI): $m/z$ calcd for C₁₀H₂₀NO₂⁺: 186.1493; found: 186.1494.

2,5-Pip(pentyloxy)pyrrolidine-1-carbaldehyde (11):

Compound 11 was made following GP 1, using N-formylpyrrolidine 1 (545 mg, 5.5 mmol) to give the product as a colorless oil (342 mg, 22%), chromatography: hexane/ethyl acetate (1:1). $^1$H NMR (400 MHz, CDCl₃): $\delta = 8.37$ (s, 1H), 5.49 – 5.42 (m, 1H), 5.07 (dd, $J = 5.6$, 2.5 Hz, 1H), 3.65 – 3.40 (m, 3H), 3.34 – 3.24 (m, 1H), 2.15 – 1.94 (m, 4H), 1.54 (dd, $J = 21.1$, 14.0, 6.9 Hz, 4H), 1.37 – 1.21 (m, 8H), 0.92 – 0.81 (m, 6H) ppm. $^{13}$C NMR (101 MHz, CDCl₃): $\delta = 162.8$, 89.3, 84.8, 68.8, 66.3, 31.9, 31.6, 30.7, 30.1, 29.5, 29.2, 28.4, 22.6, 22.5, 14.13, 14.10 ppm. IR (neat): 2954, 2860, 1685, 1379, 1087 cm⁻¹; HRMS (ESI): $m/z$ calcd for C₁₅H₃₀N O₃⁺: 272.2222; found: 172.2226.
3-Methoxymorpholine-4-carbaldehyde (12):\textsuperscript{5}

Compound 12 was made following GP 1, using N-formylmorpholine (633 mg, 5.5 mmol) to give the product as a colorless oil (534 mg, 67\%), chromatography: hexane/ethyl acetate (1:1).

*trans*-Atropisomer (70\%): \textsuperscript{1}H (500 MHz, CDCl\textsubscript{3}): \(\delta = 8.19\) (s, 1H), 4.46 (s, 1H), 4.00 (dd, \(J = 11.6, 3.4\) Hz, 1H), 3.90–4.12 (m, 2H), 3.41–3.63 (m, 2H), 3.27 (s, 3H), 3.14 (td, \(J = 12.8, 3.9\) Hz, 1H) ppm. \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}): \(\delta = 161.2, 83.4, 70.0, 66.2, 54.6, 36.5\) ppm.

cis-Atropisomer (30\%): \textsuperscript{1}H (500 MHz, CDCl\textsubscript{3}): \(\delta = 8.18\) (s, 1H), 5.31 (m, 1H), 3.90–4.12 (m, 2H), 3.60–3.65 (m, 1H), 3.41–3.63 (m, 2H), 3.33 (s, 3H) ppm. \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}): \(\delta = 162.2, 77.0, 69.4, 67.0, 55.8, 41.6\) ppm.

IR (neat): 2943, 2885, 1664, 1415, 1064, 1033 cm\textsuperscript{-1}.

**GC:**

Table 1, entry 2

Table 1, entry 8
Table 1, entry 11

References:


NMR spectra:

2-Methoxypyrrolidine-1-carbaldehyde (2)
2,5-Dimethoxypyrrrolidine-1-carbaldehyde (3)
2-Ethoxypyrrolidine-1-carbaldehyde (4)
2,5-Diethoxypyrrolidine-1-carbaldehyde (5)
2-Propoxypyrrolidine-1-carbaldehyde (6)
2,5-Dipropoxypyrrolidine-1-carbaldehyde (7)
2-Butoxypyrrolidine-1-carbaldehyde (8)
2,5-Bibutoxypyrrolidine-1-carbaldehyde (9)
2-(Pentyloxy)pyrrolidine-1-carbaldehyde (10)
2,5-Bis(pentyloxy)pyrrolidine-1-carbaldehyde (11)
3-Methoxymorpholine-4-carbaldehyde (12)