Selected Supporting Data

Compound 6: ^{1}H NMR (400MHz, $CDCl_3$) δ 7.09 (app. t, *J* = 2.4 Hz, 1H), 4.22 (m, 2H), 3.97 (m, 2H), 3.74 (s, 3H), 2.47 (app. td, *J* = 6.4, 2.4 Hz, 2H), 2.18 (dd, *J* = 6.4, 6.4 Hz, 2H); ^{13}C NMR (100 MHz) δ 163.40, 149.30, 135.51, 117.92, 64.61, 52.05, 36.89, 27.73; exact mass calcd for $C_9H_{12}O_4$; 184.073559, observed [HRMS (EI)] 184.073522.

Compound 8a: reported as a mixture of 1:1, E/Z isomers; ^{1}H NMR (400MHz, $CDCl_3$) δ 9.68 (t, *J* = 1.6 Hz, 1H), 6.93 (dt, *J* = 16.4, 7.2 Hz, 1H), 6.44 (dt, *J* = 11.2, 7.6 Hz, 1H), 5.34-5.28 (m, 2H), 2.46-2.37 (m, 3H), 2.20 (app. q, *J* = 7.2 Hz, 1H), 1.60 (m, 2H), 1.45 (m, 2H); ^{13}C NMR (100 MHz) δ 201.78, 201.71, 155.07, 154.15, 117.21, 115.73, 99.89, 99.80, 43.15, 43.11, 32.76, 31.26, 27.30, 26.77, 21.20, 21.04; exact mass calcd for $C_8H_{12}NO$; 138.091889, observed [HRMS (CI/CH_4)] $(M+H)^+$ 138.092189.

Compound 8b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (t, *J* = 1.6 Hz, 1H), 6.93 (dt, *J* = 15.6, 6.8 Hz, 1H), 5.80 (dt, *J* = 15.6, 1.6 Hz, 1H), 3.70 (s, 3H), 2.25 (dt, *J* = 7.2, 1.6 Hz, 2H), 2.22 (ddd, *J* = 7.2, 7.2, 1.6 Hz, 2H), 1.64 (m, 2H), 1.48 (m, 2H); ^{13}C NMR (100 MHz) δ 202.06, 166.92, 148.59, 121.27, 51.36, 43.49, 31.80, 27.37, 21.39; exact mass calcd for $C_9H_{15}O_3$; 171.102120, observed [HRMS (CI/CH_4)] $(M+H)^+$ 171.102584.

Compound 9a: *trans* -hydroxy nitrile; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.29 (m, 1H), 2.62 (dd, *J* = 17.2, 4.4 Hz, 1H), 2.48 (dd, *J* = 17.2, 7.6 Hz, 1H), 2.16 (d, *J* = 5.2 Hz, 1H), 1.99 (m, 1H), 1.90 (m, 1H), 1.77 (m, 1H), 1.70 (m, 1H), 1.54 (m, 1H), 1.31-1.16 (m, 3H); ^{13}C NMR (100 MHz) δ 118.89, 72.99, 41.85, 35.83, 30.26, 25.05, 24.60, 20.59: *cis* -hydroxy nitrile; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.01 (m, 1H), 2.48 (dd, *J* = 16.8, 7.6, 1H), 2.32 (dd, *J* = 16.8, 7.6, 1H), 1.88 (m, 1H), 1.78 (m, 1H), 1.70 (m, 1H), 1.64-1.46 (m, 4H), 1.33 (m, 2H); ^{13}C NMR (100 MHz) δ 119.50, 67.71, 38.61, 32.83, 26.08, 24.51, 20.14, 19.59; exact mass calcd for $C_8H_{14}NO$; 140.107539, observed [HRMS (CI/CH_4)] $(M+H)^+$ 140.107161.

Compound 9b: *trans* -hydroxy ester; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.68 (s, 3H), 3.21 (m, 1H), 2.66 (dd, *J* = 15.2, 6.0 Hz, 1H), 2.19 (dd, *J* = 15.2, 6.4 Hz, 1H), 1.95 (m, 1H), 1.84 (d, *J* = 4.8 Hz, 1H) 1.80-1.71 (m, 3H), 1.66 (m, 1H), 1.26 (m, 3H), 1.02 (m, 1H); exact mass calcd for $C_9H_{17}O_3$; 173.117770, observed [HRMS (CI/CH_4)] $(M+H)^+$ 173.117990. The *cis* -hydroxy ester completely lactonizes over silica to give *cis* –lactone, **9c**.

Compound 9c: *cis* -lactone; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.52 (dd, *J* = 8.4, 4.4 Hz, 1H), 2.61 (dd, *J* = 16.8, 6.8 Hz, 1H), 2.39 (m, 1H), 2.35 (dd, *J* = 16.8, 2.8 Hz, 1H), 2.07 (m, 1H), 1.78-1.59 (m, 3H), 1.56-1.42 (m, 2H), 1.33-1.23 (m, 2H); exact mass calcd for $C_8H_{12}O_2$; 140.083730, observed [HRMS (EI)] 140.083213: *trans* –lactone (obtained from **9b** when the catholyte is treated with an aqueous acidic work up instead of a neutral water work-up); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (ddd, *J* = 11.2, 11.2, 3.6 Hz, 1H), 2.52 (dd, *J* = 16.4, 6.4 Hz, 1H), 2.23 (dd, *J* = 16.4, 13.2 Hz, 1H), 2.24 (m, 1H), 2.00-1.85 (m, 3H), 1.79 (m, 1H), 1.54 (app. dq, *J* = 12.4, 3.2 Hz, 1H), 1.47-1.23 (m, 3H); exact mass calcd for $C_8H_{13}O_2$; 141.091555, observed [HRMS (CI/CH_4)] $(M+H)^+$ 141.091710.

Compound 10: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.68 (m, 2H), 2.49-2.28 (m, 3H), 2.14 (m, 1H), 1.95 (m, 1H), 1.80-1.59 (m, 2H), 1.48 (m, 2H); ^{13}C NMR (100 MHz) δ 208.59, 118.50, 46.73, 41.51, 33.31, 27.45, 24.77, 17.75; exact mass calcd for $C_8H_{11}NO$; 137.084241, observed [HRMS (EI)] 137.084064.

Compound 11: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (m, 2H), 7.45 (m, 1H) 7.34 (m, 2H), 4,38 (m, 2H), 2.52 (m, 1H), 2.44 (m, 1H), 2.36-2.24 (m, 2H), 2.19 (m, 1H), 2.08 (m, 1H), 1.92 (m, 1H), 1.78-1.59 (m, 3H), 2.46 (m, 1H); ^{13}C NMR (100 MHz) δ 212.15, 166.45, 132.80, 130.22, 129.44, 128.26, 63.03, 47.38, 42.06, 34.13, 28.57, 27.93, 25.07.

Compound 15: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (m, 2H), 7.56 (m, 1H) 7.44 (m, 2H), 4,38 (m, 2H), 4.10 (m, 1H), 3.91 (m, 2H), 3.69 (s, 3H), 3.01 (app. dt, *J* = 10.8, 8.8 Hz, 1H), 3.01 (d, *J* = 8.8 Hz, 1H), 2.19 (m, 1H), 1.96 (m, 1H), 1.88-1.16 (14H); ^{13}C NMR (100 MHz) δ 173.84, 166.63, 132.82, 130.36, 129.50, 128.31, 117.06, 73.94, 65.19, 64.19, 63.78, 52.69, 51.98, 47.09 (broad), 39.30, 36.58, 32.16, 30.75, 27.50, 26.78, 23.61, 21.50: exact mass calcd for $C_{24}H_{32}O_7$; 432.214804, observed [HRMS (EI)] 432.215421.

Compound 17: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17-4.04 (m, 3H), 3.88 (dd, *J* = 12.4, 6.8 Hz, 1H), 3.23 (d, *J* = 10.4 Hz, 1H), 2.98 (app. dt, *J* = 10.4, 7.2 Hz, 1H), 2.78 (ddd, *J* = 16.8, 3.6, 1.2 Hz, 1H), 2.58 (dd, *J* = 16.8, 12.4 Hz, 1H), 2.45 (broad dd, *J* = 12.0, 2.8 Hz, 1H), 2.06 (m, 1H), 1.99-1.87 (m, 3H), 1.86-1.77 (m, 2H), 1.68 (m, 1H), 1.57-1.32 (m, 5H); ^{13}C NMR (100 MHz) δ 172.73, 118.78, 115.44, 85.25, 65.70, 65.55, 54.89, 45.81, 38.31, 35.72, 33.22, 25.94, 24.42, 22.99, 17.88, 16.65; exact mass calcd for $C_{16}H_{21}NO_4$; 291.147058, observed [HRMS (EI)] 291.146974. X-ray crystal structure data for **17**; one hundred milligrams of compound **17** was recrystalized from chloroform to provide colorless crystals of a monoclinic crystal system (0.50 x 0.040 x 0.20 mm), $C_{16}H_{21}NO_4$, M_r =291.34, space group P 21/c, a = 16.8836 (14) Å, b = 7.6779 (6) Å, c = 11.1378 (9) Å, V = 1443.3 (2) Å^3, Z =4, D_{calcd} = 1.341 Mg/m^3, T = 150 °K, F(000) = 624, μ(Mo Kα) = 0.096 mm^{-1}. Data were collected on a Bruker SMART CCD diffractometer with monochromatic Mo Kα radiation (λ = 0.71073 Å) by the ω/2θ at final convergence method in the range of $1.21 \leq \theta \leq 23.29$ °. $R_1[I > 2\sigma(I)] = 0.0325$, $\omega R_2 = 0.0894$ for 190 parameters, GOF = 1.161, $\Delta\rho_{max} = 0.189$, $\Delta\rho_{min} = -0.241$ e. Å^{-3}. The structure was solved using direct methods and refined by full matrix least-square on F^2 with all non-H atoms anisotropic and H atoms isotropic.

Compound 5: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.14 (m, 2H), 4.01 (m, 1H) 3.88 (m, 1H), 3.73 (dddd, *J* = 10.0, 6.4, 4.0, 2.4 Hz, 1H), 3.62 (m, 1H), 3.20 (d, *J* = 10.8 Hz, 1H), 2.89 (app. dt, *J* = 10.8, 8.0 Hz, 1H), 2.06-1.54 (10H), 1.5-1.38 (m, 2H), 1.36 (m, 3H); ^{13}C NMR (100 MHz) δ 174.30, 116.00, 87.50, 65.62, 65.23, 60.17, 55.30, 46.13, 42.90, 37.84, 32.64 (broad), 31.465, 27.36, 24.19, 23.69 (broad), 22.49: exact mass calcd for $C_{16}H_{24}O_5$; 296.162374, observed [HRMS (EI)] 296.163708.

Compound 18: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.15 (m, 2H), 4.01 (m, 1H) 3.88 (m, 1H), 3.36 (dddd, *J* = 10.0, 6.4, 4.0, 2.4 Hz, 1H), 3.16 (d, *J* = 10.8 Hz, 1H), 3.09 (ddd, *J* = 10.0, 6.0, 6.0 Hz, 1H), 2.86 (app. dt, *J* = 10.8, 8.0 Hz, 1H), 2.04-1.77 (m, 6H),

1.72-1.23 (m, 9H); ^{13}C NMR (100 MHz) δ 173.87, 116.02, 86.92, 65.64, 65.38, 55.23, 47.03, 46.13, 37.94, 32.82, 32.15, 26.46, 24.31, 23.68, 22.42, 5.24: exact mass calcd for $C_{16}H_{23}O_4I$; 406.064111, observed [HRMS (EI)] 406.062223.

Compound 4: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.61 (s, 1H), 4.08-3.90 (m, 4H) 2.42 (m, 1H), 2.35 (d, *J* = 8.8 Hz, 1H), 2.05-1.68 (m, 6H), 1.65-1.50 (m, 5H), 1.38-1.14 (m, 6H); ^{13}C NMR (100MHz) δ 119.75, 105.28, 80.28, 64.65, 63.27, 51.62, 49.84, 39.82, 36.17, 32.72, 32.32, 27.76, 25.87, 24.69, 23.77, 22.63: exact mass calcd for $C_{16}H_{24}O_4$; 280.167460, observed [HRMS (EI)] 280.168162. X-ray crystal structure data for **4**; fifteen milligrams of compound **4** was recrystalized from diethyl ether and hexane to provide colorless needles of a triclinic crystal system (0.52 x 0.040 x 0.040 mm), $C_{16}H_{24}O_4$, M_r =280.35, space group P-1, a = 5.505 (2) Å, b = 7.576 (2) Å, c = 17.429 (5) Å, V = 699.8 (4) Å^3, Z =2, D_{calcd} = 1.331 Mg/m^3, T = 150 °K, F(000) = 304, μ(Mo Kα) = 0.094 mm^{-1}. Data were collected on a Bruker SMART CCD diffractometer with monochromatic Mo Kα radiation (λ = 0.71073 Å) by the ω/2θ at final convergence method in the range of $1.18 \leq \theta \leq 24.99°$. $R_1[I > 2\sigma(I)] = 0.0444$, $\omega R_2 = 0.0929$ for 182 parameters, GOF = 0.892, $\Delta\rho_{max}$ = 0.199, $\Delta\rho_{min}$ = -0.246 e. Å^{-3}. The structure was solved using direct methods and refined by full matrix least-square on F^2 with all non-H atoms anisotropic and H atoms isotropic.