Supporting Information

Selective Electrosynthetic Hydrocarboxylation of α,β-Unsaturated Esters with Carbon Dioxide**

Ahmed M. Sheta, Anas Alkayal, Mohammad A. Mashaly, Samy B. Said, Saad S. Elmorsy, Andrei V. Malkov, and Benjamin R. Buckley*

anie_202105490_sm_misellaneous_information.pdf
2.0 PROCEDURE FOR PREPARING ACRYLATES VIA WITTIG AND HORNER–WADSWORTH–EMMONS REACTION

GENERAL PROCEDURE I: ................................................................. 4
GENERAL PROCEDURE II: ............................................................. 4
Methyl 3-phenyl-2-butenoate (1n) .................................................. 4
Methyl cyclobutylimideneacetate (1r) .............................................. 4
Methyl cyclopentylimideneacetate (1s) ............................................ 4
Methyl cyclohexylimideneacetate (1t) ............................................. 5
Methyl cycloheptylimideneacetate (1u) ......................................... 5
Methyl cyclooctylimideneacetate (1v) ............................................. 5
Methyl cyclododecylimideneacetate (1w) ........................................ 5

ESTRONE O-METHYL ETHER (1x') ...................................................... 5

(Z)-METHYL 2-[(85,95,135,145)-3-METHOXY-13-METHYL-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-ylidene]acetate (1x) .................................................. 6
tert-BUTYL 4-[2-METHOXY-2-OXOETHYLEN]Piperidine-1-carboxylate (1y) .................................................. 6
tert-BUTYL 3-[2-METHOXY-2-OXOETHYLENE]AZETIDINE-1-CARBOXYLATE (1z) ................................................ 6
(E,Z) TERT-BUTYL 3-[2-METHOXY-2-OXOETHYLENE]PYRROLIDINE-1-CARBOXYLATE (1AA) ................................................ 6
Ethyl 2-[(OXYETAN-3-YLIDENE)PROPANOATE (1AB) ................................................ 6
Methyl 2-[(3-OXETANYLIDENE)ACETATE (1AC) .................................. 7
Methyl 2-[(OXYDRO-3(2H)-FURANYLIDENE)ACETATE (1AD) ................................................ 7
Methyl 2-[(TETRAHYDRO-4H-PYRAN-4-YLIDENE)ACETATE (1AE) ................................................ 7
Methyl 3-METHYL-2-PENTENOATE (1AG) ......................................... 7

3.0 ELECTROCARBOXYLATION OF ACRYLATES USING A NON-SACRIFICIAL ELECTROCHEMICAL CELL ........8

GENERAL PROCEDURE III: ............................................................. 8
BUTANEDIOIC ACID 1-METHYL ESTER (2A) ....................................... 8
2-METHYL BUTANEDIOIC ACID 4-METHYL ESTER (2E) ....................... 8
2-METHYL BUTANEDIOIC ACID 1-METHYL ESTER (2F) ....................... 8
2-METHYL BUTANEDIOIC ACID (2G) .............................................. 8
BUTANEDIOIC ACID (2G') ............................................................... 8
2-METHYL BUTANEDIOIC ACID 1-EHYL ESTER (2H) .......................... 9
2-METHYL BUTANEDIOIC ACID 1-BENZYL ESTER (2I) ....................... 9
2-METHYL BUTANEDIOIC ACID 1-ALLYL ESTER (2J) ........................... 9
2-METHYL BUTANEDIOIC ACID 1-[(TERT-BUTYL) ESTER (2K) ............ 9
2-(METHOXYCARBONYLCYCLOHEXANE-1-CARBOXYLIC ACID (2I) ........ 9
2-PHENYL BUTANEDIOIC ACID 4-METHYL ESTER (2M) .................... 9
2-METHYL-2-PHENYL BUTANEDIOIC ACID 4-METHYL ESTER (2N) .......... 10
4-(2-(ISOETHYLOXY)ETHOXY)-3-METHYL-4-oxobutanoic acid (2P) ............ 10
2,2-DIMETHYL BUTANEDIOIC ACID 4-METHYL ESTER (2Q) ................. 10
METHYL 1-CARBOXYCLOBUTANEETACE (2R) .................................. 10
METHYL 1-CARBOXYCYCLOPENTANEETACE (2S) ................................ 10
METHYL 1-CARBOXYCYCLOHEXANEETACE (2T) ................................ 10
METHYL 1-CARBOXYCYCLOHEPTANEETACE (2U) ............................. 11
METHYL 1-CARBOXYCYCLOOCTANEETACE (2V) ............................... 11
METHYL 1-CARBOXYCYCLODECAETACE (2W) .................................. 11
(85,95,135,145)-3-METHOXY-17(2-METHOXY-2-OXOETHYL)-13-METHYL-7,8,9,11,12,13,14,15,16,17-DECAHYDRO-6H-cyclopenta[a]phenanthrene-17-CARBOXYLIC ACID (2X) ............. 11
1-(TERT-BUTOXYCARBONYL)-4-(2-METHOXY-2-OXOETHYL)Piperidine-4-CARBOXYLIC ACID (2Y) .................. 12
1-(TERT-BUTOXYCARBONYL)-3-(2-METHOXY-2-OXOETHYL)AZETIDINE-3-CARBOXYLIC ACID (2Z) .................. 12

S-1
1.0 General Experimental

**Reagents:** Commercially available materials (electrolytes, reducing agents, acrylates) were used without further purification. Substrates were purchased from commercial sources and used as received. Anhydrous $N,N$-dimethylformamide and toluene were purchased from Sigma-Aldrich and dried over 3Å molecular sieves prior to use. Tetraethylammonium iodide was also purchased from Sigma-Aldrich. Deuterated solvents were purchased from Fluorochem UK Ltd.

**Analytical Methods:** All infrared spectra were obtained using a Perkin-Elmer Spectrum 65 FT-IR spectrophotometer; thin film spectra were acquired using sodium chloride plates. All $^1$H and $^{13}$C NMR spectra were measured at 400 and 100 MHz using a Bruker Avance 400 MHz spectrometer, a Jeol ECS 400 MHz spectrometer or at 500 and 125 MHz on a Jeol ECZ 500 MHz spectrometer. The solvent used for NMR spectroscopy was CDCl$_3$ (unless stated otherwise) using TMS (tetramethylsilane) as the internal reference. Chemical shifts are given in parts per million (ppm) and J values are given in Hertz (Hz).

Analysis by GCMS utilised a Shimadzu QP2020, GC-2010 Plus, using a 15 m x 0.25 mm DB-5 column and an electron impact low resolution mass spectrometer, acids were converted to their corresponding methyl esters using TMSdiazomethane prior to sampling. Melting points were recorded using a Stuart Scientific melting point apparatus SMP3 and are uncorrected. All chromatographic manipulations used silica gel as the adsorbent. Reactions were monitored by GCMS or using thin layer chromatography (TLC) on aluminium backed plates with Merck Kiesel 60 F254 silica gel. TLC visualised by UV radiation at a wavelength of 254 nm. Purification by column chromatography used Apollo Scientific 60 40-63μm silica gel.

Headspace GC-MS analysis of CO$_2$ reduction was carried out on an Agilent 5977 GC-MS with a HP5-MS column 30 m long, 0.25 mm diameter, with 5% phenyl-methyl siloxane stationary phase, 0.25 μm thick. The programme was set with a 2-minute hold time at 40 °C followed by a ramp to 200 °C for 10 minutes. The headspace sample was introduced via a gas tight syringe.

Electrode electrochemical reactions were carried out using a 10mL reaction vial using a carbon anode and a carbon cathode supplied by IKA and the current was supplied from an IKA ElectraSyn 2.0
2.0 Procedure for preparing acrylates via Wittig and Horner–Wadsworth–Emmons reaction

\[
\begin{align*}
\text{O} & \quad \begin{array}{c}
R_1 \quad \text{Ph}_3\text{P} \quad \text{CO}_2\text{Me} \\
S_2
\end{array} \quad \xrightarrow{\text{Toluene, M.W., 10 min, 150 °C}} \quad \begin{array}{c}
R_1 \quad \text{CO}_2\text{Me} \\
S_1
\end{array} \\
R_2
\end{align*}
\]

**General Procedure I:** In a microwave vial (2-5 mL), Methyl (triphenylphosphoranylidene)acetate \(S_2\) (0.835 g, 2.5 mmol) and the aldehyde or ketone \(S_1\) were dissolved in toluene (3 mL). The reaction was run for 10 min at 150 °C. The reaction mixture was placed in a RBF (100 mL) and 5 g silica gel added. The solvent was removed under reduced pressure and the crude product was purified by column chromatography using hexane/AcOEt on silica gel affording acrylates \(1\).

\[
\begin{align*}
\text{O} & \quad \begin{array}{c}
R_1 \quad \text{Ph}_3\text{P} \quad \text{CO}_2\text{Me} \\
S_3
\end{array} \quad \xrightarrow{\text{NaH, THF, Reflux, 60 °C, overnight}} \quad \begin{array}{c}
R_1 \quad \text{CO}_2\text{Me} \\
S_1
\end{array} \\
R_2
\end{align*}
\]

**General Procedure II:** In 250 mL RBF, sodium hydride (0.240 g, 10 mmol) was suspended in THF (50 mL) and trimethyl phosphonoacetate \(S_3\) (1.62 mL, 10 mmol) was added dropwise. The reaction was then stirred under reflux for 1 hr at 60 °C then the corresponding ketone \(1\) (10 mmol) was dissolved in THF (10 mL) and added to the reaction carefully dropwise then the reaction was left under reflux overnight. After that, the reaction was cooled to rt, and 99% methanol (10 mL) of was added and around 10 g of silica gel. The solvent was removed under reduced pressure and the crude product was purified by column chromatography using hexane/AcOEt on silica gel affording acrylates \(1\).

**Methyl 3-phenyl-2-butenoate (1n).** Following the general procedure II using Acetophenone (1.16 mL, 10.0 mmol), affording \(1n\) (1.50 g, 85.2% yield). Colorless liquid.

\(^1\)H NMR (400 MHz, CDCl3) \(\delta\) 7.46 (m, 2H), 7.36 (m, 3H), 6.13 (s, 1H), 3.74 (s, 3H), 2.57 (s, 3H) ppm. \(^{13}\)C NMR (101 MHz, CDCl3) \(\delta\) 167.3, 155.9, 142.2, 129.1, 128.6, 126.3, 116.7, 51.1, 18.0 ppm.

**Methyl cyclobutylideneacetate (1r).** Following the general procedure I using Cyclobutanone (0.18 mL, 2.5 mmol), affording \(1r\) (0.25 g, 79.3% yield). Colorless liquid.

\(^1\)H NMR (400 MHz, CDCl3) \(\delta\) 5.54 (s, 1H), 3.62 (s, 3H), 3.07 (t, 2H), 2.78 (t, 2H), 2.04 (p, 2H) ppm. \(^{13}\)C NMR (101 MHz, CDCl3) \(\delta\) 167.9, 166.9, 111.9, 50.8, 33.7, 32.3, 17.6 ppm.

**Methyl cyclopentylideneacetate (1s).** Following the general procedure I using Cyclopentanone (0.22 mL, 2.5 mmol), affording \(1s\) (0.3 g, 85.7% yield). Colorless liquid.

\(^1\)H NMR (400 MHz, CDCl3) \(\delta\) 5.78 (s, 1H), 3.66 (s, 3H), 2.75 (t, 2H), 2.41 (t, 2H), 1.73 (p, 2H), 1.64 (p, 2H) ppm. \(^{13}\)C NMR (101 MHz, CDCl3) \(\delta\) 169.6, 167.4, 111.2, 50.8, 36.0, 32.7, 26.4, 25.5 ppm.
Methyl cyclohexylideneacetate (1t). Following the general procedure I using Cyclohexanone (0.26 mL, 2.5 mmol), affording 1t (0.36 g, 93.5% yield). Colorless liquid

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \delta 5.60 (s, 1H), 3.67 (s, 3H), 2.82 (t, 2H), 2.19 (t, 2H), 1.68-1.57 (m, 6H) ppm.} \]

\[ ^{13}C \text{ NMR (101 MHz, CDCl}_3 \delta 167.3, 163.9, 112.6, 50.8, 38.0, 29.9, 28.5, 27.8, 26.3 \text{ ppm.} \]

Methyl cycloheptylideneacetate (1u). Following the general procedure II using Cycloheptanone (1.17 mL, 10.0 mmol), affording 1u (1.35 g, 80.3% yield). Colorless liquid

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \delta 5.61 (s, 1H), 3.61 (s, 3H), 2.82 (t, 2H), 2.32 (t, 2H), 1.76-1.70 (m, 4H), 1.48-1.39 (m, 8H) ppm.} \]

\[ ^{13}C \text{ NMR (101 MHz, CDCl}_3 \delta 167.0, 115.1, 50.6, 39.0, 32.1, 29.8, 29.0, 28.0, 26.6 \text{ ppm.} \]

Methyl cyclooctylideneacetate (1v). Following the general procedure II using Cyclooctanone (1.32 mL, 10.0 mmol), affording 1v (1.40 g, 76.9% yield). Colorless liquid

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \delta 5.68 (s, 1H), 3.63 (s, 3H), 2.72 (t, 2H), 2.27 (t, 2H), 1.76-1.70 (m, 4H), 1.48-1.39 (m, 8H) ppm.} \]

\[ ^{13}C \text{ NMR (101 MHz, CDCl}_3 \delta 168.8, 166.7, 115.1, 50.6, 38.7, 30.7, 27.8, 27.6, 26.5, 25.6, 25.4 \text{ ppm.} \]

Methyl cyclododecylideneacetate (1w). Following the general procedure II using Cyclododecanone (1.82 g, 10.0 mmol), affording 1w (1.60 g, 67.2% yield). White solid m.p. 65 °C (No Lit. in Ref. 5).

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \delta 5.73 (s, 1H), 3.66 (s, 3H), 2.70 (t, 2H), 2.20 (t, 2H), 1.61-1.50 (m, 4H), 1.32-1.27 (m, 14H) ppm.} \]

\[ ^{13}C \text{ NMR (101 MHz, CDCl}_3 \delta 167.3, 163.6, 115.8, 50.8, 32.8, 29.9, 25.1, 24.9, 24.1, 24.0, 23.8, 23.5, 23.0, 22.1 \text{ ppm.} \]

\[ \text{IR (neat, cm}^{-1}) \text{ 2928, 2850, 1715, 1641, 1468, 1313, 1151.} \]

Estrone O-methyl ether (1x'). A solution of Estrone (2.70 g, 10 mmol) in dimethylformamide (50 mL) was treated with ground potassium hydroxide (0.67 g, 12 mmol) and iodomethane (0.75 mL, 12 mmol) in 20 mL DMF (dropwise over 5 min at 0 °C). The reaction was stirred at room temperature for 30 min and, after this time period, additional ground potassium hydroxide (0.67 g, 12 mmol) and iodomethane (0.75 mL, 12 mmol) in 20 mL DMF were added at 0 °C. The reaction was then left to stir for 3 h. The solution was poured onto ice and extracted with ethyl acetate (3x50 mL). The organic layers were washed with water, brine and dried by MgSO₄. The solvent was removed under reduced pressure to yield 1x' (2.80 g, 98.6%). White solid m.p 170 °C.

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \delta 7.19 (d, 1H), 6.70 (m, 2H), 3.77 (s, 3H), 2.89 (m, 2H), 2.52-1.92 (m, 7H), 1.65-1.37 (m, 6H), 0.89 (s, 3H) ppm.} \]

\[ ^{13}C \text{ NMR (101 MHz, CDCl}_3 \delta 221.0, 157.6, 137.8, 132.1, 126.4, 113.9, 111.6, 55.3, 50.4, 48.1, 44.0, 38.4, 35.9, 31.6, 29.7, 26.6, 26.0, 21.6, 13.9 \text{ ppm.} \]
(Z)-methyl 2-((8S,9S,13S,14S)-3-methoxy-13-methyl-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-ylidene)acetate (1x). Following the general procedure II using Estrone O-methyl ether (1x') (2.84 g, 10.0 mmol), affording 1x (2.0 g, 58.8% yield). White solid m.p. 150 °C.

1H NMR (400 MHz, CDCl3) δ 7.19 (d, 1H), 6.67 (m, 2H), 5.67 (s, 1H), 3.76 (s, 3H), 3.68 (s, 3H), 2.85 (m, 3H), 2.60 (m, 1H), 2.46 (m, 1H), 2.30 (m, 1H), 2.25 (m, 1H), 1.19 (m, 1H), 1.18 (m, 1H), 1.60-1.20 (m, 6H), 1.02 (s, 3H) ppm. 13C NMR (101 MHz, CDCl3) δ 171.9, 166.5, 157.5, 137.8, 132.7, 126.3, 113.8, 111.5, 111.1, 55.4, 55.2, 51.0, 46.2, 43.7, 38.3, 34.1, 33.9, 29.8, 27.7, 26.8, 23.5, 15.7 ppm. IR (neat, cm⁻¹) 2980, 2925, 2877, 1713, 1646, 1437, 1171. HRMS ESI, (C22H26NaO3) [M+Na]+ calculated 363.1931, found 363.1930.

tert-Butyl 4-(2-methoxy-2-oxoethylidene)piperidine-1-carboxylate (1y). Following the general procedure I using 1-Boc-4-piperidone (0.49 g, 2.5 mmol), affording 1y (0.51 g, 79.6% yield). White solid m.p. 61 °C.

1H NMR (400 MHz, CDCl3) δ 5.68 (s, 1H), 3.66 (s, 3H), 3.45 (p, 4H), 2.90 (t, 2H), 2.25 (t, 2H), 1.43 (s, 9H) ppm. 13C NMR (101 MHz, CDCl3) δ 166.8, 158.3, 154.6, 114.8, 79.9, 51.0, 36.5, 29.6, 28.4 ppm.

tert-Butyl 3-(2-methoxy-2-oxoethylidene)azetidine-1-carboxylate (1z). Following the general procedure I using 1-Boc-3-azetidinone (0.43 g, 2.5 mmol), affording 1z (0.45 g, 80.3% yield). White solid m.p. 45 °C.

1H NMR (400 MHz, CDCl3) δ 5.76 (s, 1H), 4.79 (dd, J = 6.4, 2.8 Hz, 2H), 4.57 (dd, J = 5.4, 3.3 Hz, 2H), 3.70 (s, 3H), 1.43 (s, 9H) ppm. 13C NMR (101 MHz, CDCl3) δ 165.7, 156.2, 153.1, 113.3, 80.1, 60.3, 57.8, 51.5, 28.4 ppm.

(E,Z) tert-Butyl 3-(2-methoxy-2-oxoethylidene)pyrrolidine-1-carboxylate (1aa). Following the general procedure I using 1-Boc-3-pyrrolidinone (0.46 g, 2.5 mmol), affording 1aa (0.5 g, 83.3% yield) E/Z ratio 1:1. Yellow liquid.

1H NMR (400 MHz, CDCl3) δ 5.80 (s, 1H), 4.40 (s, 1H), 4.10 (s, 1H), 3.69 (s, 3H), 3.54 (d, 2H), 3.10 (t, 1H), 2.72 (t, 1H), 1.45 (d, 9H) ppm. 13C NMR (101 MHz, CDCl3) δ 166.6, 160.9, 154.3, 112.2, 79.8, 51.7, 51.3, 51.2, 50.5, 28.5 ppm.

Ethyl 2-(oxetan-3-ylidene)propanoate (1ab). Following the general procedure I using 1-Oxetane (0.16 mL, 2.5 mmol) and Ethyl 2-(triphenylphosphoranylidene)propionate (0.9 g, 2.5 mmol), affording 1ab (0.25 g, 64.1% yield). Colorless liquid.

1H NMR (400 MHz, CDCl3) δ 5.33 (m, 2H), 5.19 (m, 2H), 4.09 (q, 2H), 1.61 (s, 3H), 1.20 (t, 3H) ppm. 13C NMR (101 MHz, CDCl3) δ 166.3, 151.1, 118.5, 80.8, 77.9, 60.5, 14.3, 12.7 ppm. IR (neat, cm⁻¹) 2981, 2927, 2857, 1728, 1710, 1447, 1295, 1195. HRMS ESI, (C8H12NaO3) [M+Na]+ calculated 179.0679, found 179.0679.

S-6
Methyl 2-(3-oxetanylidene)acetate (1ac). Following the general procedure I using 3-Oxetanone (0.16 mL, 2.5 mmol), affording 1ac (0.22 g, 68.7% yield). White solid m.p. 51 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 5.64 (s, 1H), 5.50 (dd, $J = 6.4$, 2.8 Hz, 2H), 5.30 (dd, $J = 5.6$, 2 Hz, 2H), 3.70 (s, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 165.7, 159.6, 110.8, 81.1, 78.5, 51.5 ppm.

Methyl 2-(dihydro-3(2H)-furanylideneacetate (1ad). Following the general procedure I using Tetrahydro-3-furanone (0.19 mL, 2.5 mmol), affording 1ad (0.28 g, 80.0% yield) E/Z ratio 2.5:1. Colorless liquid

$^1$H NMR (400 MHz, CDCl$_3$) δ 5.79 (s, 1H, E isomer), 5.74 (s, 1H, Z isomer), 4.64 (d, $J = 2$ Hz, 2H, E isomer), 4.31 (d, $J = 2$ Hz, 2H, Z isomer), 3.82 (m, 2H, Z isomer), 3.64 (s, 3H, E isomer), 3.63 (s, 3H, Z isomer), 2.96 (m, 2H, Z isomer), 2.65 (m, 2H, E isomer) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.7, 166.5, 163.2, 162.2, 111.2, 110.9, 110.5, 109.8, 72.0, 71.5, 68.9, 67.0, 51.2, 51.1, 34.4, 34.2, 32.6 ppm.

Methyl 2-(tetrahydro-4H-pyran-4-ylidene)acetate (1ae). Following the general procedure I using Tetrahydro-4H-pyran-4-one (0.23 mL, 2.5 mmol), affording 1ae (0.3 g, 76.9% yield). Colorless liquid

$^1$H NMR (400 MHz, CDCl$_3$) δ 5.63 (s, 1H), 3.70 (m, 4H), 3.63 (s, 3H), 2.95 (t, 2H), 2.28 (t, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.8, 157.6, 114.1, 69.0, 68.5, 51.0, 37.6, 31.1 ppm.

Methyl 3-methyl-2-pentenoate (1ag). Following the general procedure II using Butanone (0.89 mL, 10.0 mmol), affording 1ag (1.0 g, 78.1% yield) with E/Z ratio 1.7:1. Colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 5.56 (s, 1H, E isomer), 5.53 (s, 1H, Z isomer), 3.58 (s, 3H, E isomer), 3.57 (s, 3H, Z isomer), 2.53 (q, 2H, Z isomer), 2.07 (m, 5H, CH$_2$&CH$_3$ for E&Z isomers), 1.78 (s, 3H, Z isomer), 0.97 (t, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.2, 166.6, 162.3, 161.7, 114.9, 114.0, 50.6, 33.6, 26.4, 24.5, 18.6, 12.4, 11.8 ppm.
3.0 Electrocarboxylation of acrylates using a non-sacrificial electrochemical cell

![Diagram of the electrochemical cell](image)

**General Procedure III:** Substrate (1.0 mmol) was added to a solution of Et$_4$NI (128 mg, 0.5 mmol) and TEOA (149 mg, 1.0 mmol) in DMF (5 mL). The resulting mixture was flushed with CO$_2$ and kept under a positive pressure of CO$_2$. The mixture was electrolysed at a constant voltage of 10V in a single compartment cell containing carbon cathode and carbon anode with stirring for 4 h. The crude reaction mixture was acidified by addition of HCl/H$_2$O (1:1, 2 mL) and extracted with diethylether (3 x 5 mL). The combined organic phases were washed with brine, dried over MgSO$_4$ and filtered. The solvent was then removed under reduced pressure and the crude material was recrystallised by hexane.

**Butanedioic acid 1-methyl ester (2a).** Following the general procedure III using Methyl acrylate (86 mg, 1.0 mmol), affording 2a (100 mg, 75.7%). White solid m.p. 55°C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 3.69 (s, 3H), 2.69-2.60 (m, 4H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 177.3, 172.7, 52.0, 28.8, 28.7 ppm.

**2-Methyl butanedioic acid 4-methyl ester (2e).** Following the general procedure III using Methyl crotonate (100 mg, 1.0 mmol), affording 2e (115 mg, 78.7% yield). Colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 3.65 (s, 3H), 2.74 (m, 1H), 2.70 (dd, $J = 8, 16.8$ Hz, 1H), 2.40 (dd, $J = 6.4, 16.8$ Hz, 1H), 1.22 (d, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 181.2, 172.3, 51.9, 37.1, 35.7, 16.8 ppm.

**2-Methyl butanedioic acid 1-methyl ester (2f).** Following the general procedure III using Methyl methacrylate (100 mg, 1.0 mmol), affording 2f (110 mg, 75.3% yield). Colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 3.68 (s, 3H), 2.81 (m, 1H), 2.77 (dd, $J = 6.4, 13.6$ Hz, 1H), 2.43 (dd, $J = 4.8, 13.6$ Hz, 1H), 1.22 (d, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 177.7, 175.7, 52.1, 37.3, 35.5, 17.0 ppm.

**2-Methyl butanedioic acid (2g).** Following the general procedure III using Methacrylic acid (86 mg, 1.0 mmol), affording 2g (65 mg, 49.2% yield). White solid m.p. 110°C.

$^1$H NMR (400 MHz, D$_2$O) δ 2.75 (m, 1H), 2.55 (m, 1H), 2.42 (m, 1H), 1.06 (d, 3H) ppm. $^{13}$C NMR (101 MHz, D$_2$O) δ 180.5, 176.6, 37.3, 35.8, 16.2 ppm.

**Butanedioic acid (2g').** Following the general procedure III using Acrylic acid (72 mg, 1.0 mmol), affording 2g' (55 mg, 46.6% yield). White solid m.p. 180°C.
H NMR (400 MHz, D$_2$O) δ 2.57 (s, 4H) ppm. ¹³C NMR (101 MHz, D$_2$O) δ 177.1, 28.8 ppm.

2-Methyl butanedioic acid 1-ethyl ester (2h). Following the general procedure III using Ethyl methacrylate (114 mg, 1.0 mmol), affording 2h (115 mg, 71.8% yield). Colorless oil.

H NMR (400 MHz, CDCl$_3$) δ 4.12 (q, 2H), 2.86 (m, 1H), 2.74 (dd, J = 8.4, 17.2 Hz, 1H), 2.42 (dd, J = 6.0, 16.8 Hz, 1H), 1.23 (m, 6H) ppm. ¹³C NMR (101 MHz, CDCl$_3$) δ 177.6, 175.0, 135.9, 128.6, 128.2, 128.1, 166.6, 37.1, 35.6, 17.0 ppm.

2-Methyl butanedioic acid 1-benzyl ester (2i). Following the general procedure III using Benzyl methacrylate (176 mg, 1.0 mmol), affording 2i (150 mg, 67.5% yield). Colorless oil.

H NMR (400 MHz, CDCl$_3$) δ 7.36-7.29 (m, 5H), 5.13 (s, 2H), 2.94 (m, 1H), 2.80 (dd, J = 8.4, 16.8 Hz, 1H), 2.46 (dd, J = 6.0, 16.8 Hz, 1H), 1.25 (d, 3H) ppm. ¹³C NMR (101 MHz, CDCl$_3$) δ 176.5, 175.0, 135.9, 128.6, 128.2, 128.1, 66.6, 37.1, 35.7, 17.0 ppm.

2-Methyl butanedioic acid 1-allyl ester (2j). Following the general procedure III using Allyl methacrylate (126 mg, 1.0 mmol), affording 2j (115 mg, 66.8% yield). Colorless oil.

H NMR (400 MHz, CDCl$_3$) δ 5.92-5.84 (m, 1H), 5.32-5.20 (m, 2H), 4.57 (d, 2H), 2.90 (m, 1H), 2.78 (m, 1H), 2.65 (dd, J = 8.4, 16.2 Hz, 1H), 2.35 (dd, J = 5.6, 16.8 Hz, 1H), 1.39 (s, 9H), 1.15 (d, 3H) ppm. ¹³C NMR (101 MHz, CDCl$_3$) δ 178.1, 174.5, 80.8, 37.5, 36.5, 27.9, 17.0 ppm.

2-(methoxycarbonyl)cyclohexane-1-carboxylic acid (2i). Following the general procedure III using Methyl 1-cyclohexene-1-carboxylate (140 mg, 1.0 mmol), affording 2i (140 mg, 75.2% yield). Colorless oil.

H NMR (400 MHz, CDCl$_3$) δ 3.63 (s, 3H), 2.80 (m, 1H), 2.56 (m, 1H), 1.97 (m, 2H), 1.73 (m, 2H), 1.50-1.25 (m, 4H) ppm. ¹³C NMR (101 MHz, CDCl$_3$) δ 181.0, 179.9, 175.6, 174.2, 51.9, 51.7, 44.6, 44.5, 42.5, 42.3, 28.8, 26.2, 26.0, 25.2, 25.1, 23.8, 23.6 ppm.

2-Phenyl butanedioic acid 4-methyl ester (2m). Following the general procedure III using Methyl cinnamate (162 mg, 1.0 mmol), affording 2m (80 mg, 38.5% yield) purified by preparative TLC (40% EtOAc/Hexane). Colorless oil.

H NMR (500 MHz, CDCl$_3$) δ 7.34-7.26 (m, 5H), 4.11 (dd, J = 5.5, 10.0 Hz, 1H), 3.66 (s, 3H), 3.15 (dd, J = 10.5, 17.0 Hz, 1H), 2.67 (dd, J = 5.5, 12.0 Hz, 1H) ppm. ¹³C NMR (125 MHz, CDCl$_3$) δ 177.7, 171.9, 137.1, 129.0, 128.0, 127.9, 52.0, 47.0, 37.2 ppm.
2-Methyl-2-phenyl butanedioic acid 4-methyl ester (2n). Following the general procedure III using Methyl 3-phenyl-2-butenoate 1n (176 mg, 1.0 mmol), affording 2n (50 mg, 22.5% yield) purified by preparative TLC (40% EtOAc/Hexane). Colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.39-7.17 (m, 5H), 3.63 (s, 3H), 3.26 (d, $J = 16.4$ Hz, 1H), 2.83 (d, $J = 16.4$ Hz, 1H), 17.17 (s, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 180.5, 171.5, 141.8, 128.7, 127.5, 125.8, 51.8, 48.1, 43.2, 23.1 ppm.

IR (neat, cm$^{-1}$) 3583, 3061, 3027, 2991, 2953, 1739, 1706, 1438, 1296, 1171.

HRMS ESI, (C$_{12}$H$_{14}$NaO$_4$) $[\text{M+Na}]^+$ calculated 245.0784, found 245.0785.

4-(2-(isobutyryloxy)ethoxy)-3-methyl-4-oxobutanoic acid (2p). Following the general procedure III using Ethylene glycol dimethacrylate 1p (198 mg, 1.0 mmol), affording 2p (150 mg, 60.9% yield). Yellow liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 4.28 (m, 4H), 2.89 (m, 1H), 2.77 (m, 1H), 2.52 (m, 2H), 1.22 (d, 3H), 1.14 (d, 6H) ppm.

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 176.9, 174.8, 62.6, 61.9, 37.1, 35.5, 33.9, 18.9, 16.9 ppm.

IR (neat, cm$^{-1}$) 2976, 2937, 2882, 1738, 1713, 1278, 1159, 1057.

HRMS ESI, (C$_{11}$H$_{18}$NaO$_6$) $[\text{M+Na}]^+$ calculated 269.0996, found 269.0995.

2,2-Dimethyl butanedioic acid 4-methyl ester (2q). Following the general procedure III using Methyl 3,3-dimethylacrylate (114 mg, 1.0 mmol), affording 2q (130 mg, 81.2% yield). White solid m.p. 40 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 3.65 (s, 3H), 2.60 (s, 2H), 1.28 (s, 6H) ppm.

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 183.0, 171.7, 51.6, 43.8, 40.5, 25.2 ppm.

Methyl 1-carboxycyclobutaneacetate (2r). Following the general procedure III using Methyl cyclobutylideneacetate 1r (126 mg, 1.0 mmol), affording 2r (110 mg, 63.9% yield). Colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 10.81 (s, 1H), 3.62 (s, 3H), 2.83 (s, 2H), 2.55 (m, 2H), 2.02-1.93 (m, 4H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 182.2, 171.9, 51.7, 44.5, 41.1, 29.9, 15.8 ppm.

IR (neat, cm$^{-1}$) 3434, 1728, 1699, 1432, 1187.

HRMS ESI, (C$_{8}$H$_{12}$NaO$_4$) $[\text{M+Na}]^+$ calculated 195.0628, found 195.0630.

Methyl 1-carboxycyclopentaneacetate (2s). Following the general procedure III using Methyl cyclopentylideneacetate 1s (140 mg, 1.0 mmol), affording 2s (135 mg, 72.5% yield). White solid m.p. 60 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 3.65 (s, 3H), 2.69 (s, 2H), 2.21 (m, 2H), 1.75-1.57 (m, 6H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 182.5, 172.1, 51.7, 50.6, 42.4, 36.8, 25.4 ppm.

IR (neat, cm$^{-1}$) 3434, 2958, 1732, 1699, 1432, 1198. HRMS ESI, (C$_{9}$H$_{14}$NaO$_4$) $[\text{M+Na}]^+$ calculated 209.0628, found 209.0785.

Methyl 1-carboxycyclohexaneacetate (2t). Following the general procedure III using Methyl cyclohexylideneacetate 1t (154 mg, 1.0 mmol), affording 2t (162 mg, 81.0% yield). White solid m.p. 58 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 11.1 (s, 1H), 3.62 (s, 3H), 2.62 (s, 2H), 1.96 (m, 2H), 1.54-1.35 (m, 8H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 182.6, 171.5, 51.6,
Methyl 1-carboxycycloheptaneacetate (2u). Following the general procedure III using Methyl cycloheptylideneacetate 1u (168 mg, 1.0 mmol), affording 2u (145 mg, 67.7% yield). White solid m.p. 61 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 3.63 (s, 3H), 2.61 (s, 2H), 2.10 (m, 2H), 1.62-1.42 (m, 10H) ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 183.3, 171.7, 51.6, 47.5, 43.5, 35.4, 30.4, 23.4 ppm. IR (neat, cm\(^{-1}\)) 3413, 2980, 1720, 1704, 1640, 1420, 1150.

HRMS ESI, (C\(_{10}\)H\(_{16}\)NaO\(_4\)) [M+Na]\(^+\) calculated 223.0914, found 223.0941.

Methyl 1-carboxycyclooctaneacetate (2v). Following the general procedure III using Methyl cyclooctylideneacetate 1v (182 mg, 1.0 mmol), affording 2v (190 mg, 83.3% yield). White solid m.p. 93 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 3.63 (s, 3H), 2.61 (s, 2H), 2.04 (m, 2H), 1.56-1.48 (m, 12H) ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 182.6, 171.6, 51.6, 47.5, 42.0, 30.7, 28.3, 25.3, 22.9 ppm. IR (neat, cm\(^{-1}\)) 3440, 2999, 2987, 1745, 1713, 1476, 1170.

HRMS ESI, (C\(_{12}\)H\(_{22}\)NaO\(_4\)) [M+Na]\(^+\) calculated 251.1254, found 251.1254.

Methyl 1-carboxycyclododecanecacetate (2w). Following the general procedure III using Methyl cyclododecylideneacetate 1w (238 mg, 1.0 mmol), affording 2w (230 mg, 80.9% yield). White solid m.p. 120 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 3.64 (s, 3H), 2.60 (s, 2H), 1.66 (m, 4H), 1.32-1.22 (m, 18H) ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 181.8, 171.5, 51.6, 46.5, 41.1, 29.4, 26.2, 26.1, 22.3, 21.8, 18.9 ppm. IR (neat, cm\(^{-1}\)) 3435, 2932, 2862, 1739, 1701, 1471, 1198.

HRMS ESI, (C\(_{16}\)H\(_{28}\)NaO\(_4\)) [M+Na]\(^+\) calculated 307.1880, found 307.1880.

(8S,9S,13S,14S)-3-methoxy-17-(2-methoxy-2-oxoethyl)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-17-carboxylic acid (2x).

Following the general procedure III using (Z)-methyl 2-(((8S,9S,13S,14S)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-ylidene)acetate (1x). (340 mg, 1.0 mmol), affording 2x (250 mg, 64.7% yield) purified by preparative TLC (40% EtOAc/Hexane). White solid m.p. 220 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 10.65 (br, 1H), 7.11 (d, 1H), 6.64 (m, 2H), 3.76 (s, 3H), 3.65 (s, 3H), 3.01 (d, 1H), 2.83 (m, 2H), 2.74 (m, 1H), 2.42 (m, 1H), 2.21 (m, 2H), 1.90-1.30 (m, 10H), 0.82 (s, 3H) ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 180.8, 173.0, 157.3, 138.0, 132.4, 126.2, 113.8, 111.5, 57.7, 55.2, 51.7, 49.6, 47.1, 43.4, 39.1, 39.2, 34.5, 32.8, 29.8, 28.0, 26.4, 25.0. IR (neat, cm\(^{-1}\)) 2928, 2854, 1737, 1697, 1499, 1201, 1179, 1035. HRMS ESI, (C\(_{23}\)H\(_{30}\)NaO\(_5\)) [M+Na]\(^+\) calculated 409.1985, found 409.1985.
1-(tert-butoxycarbonyl)-4-(2-methoxy-2-oxoethyl)piperidine-4-carboxylic acid (2y). Following the general procedure III using tert-Butyl 4-(2-methoxy-2-oxoethylidene)piperidine-1-carboxylate 1y (255 mg, 1.0 mmol), affording 2y (210 mg, 69.7% yield). White solid m.p. 137 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.70 (m, 2H), 3.65 (s, 3H), 3.22 (m, 2H), 2.63 (s, 2H), 2.07 (m, 2H), 1.51 (m, 2H), 1.43 (s, 9H) ppm. \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 170.8, 154.8, 79.8, 51.8, 43.2, 42.8, 32.8, 28.5 ppm. IR (neat, cm\(^{-1}\)) 3435, 2983, 2902, 1729, 1464, 1206, 1018. HRMS ESI, (C\(_{14}\)H\(_{23}\)NNaO\(_5\)) \([\text{M+Na}]^+\) calculated 324.1418, found 324.1418.

1-(tert-butoxycarbonyl)-3-(2-methoxy-2-oxoethyl)azetidine-3-carboxylic acid (2z). Following the general procedure III using tert-Butyl 3-(2-methoxy-2-oxoethylidene)azetidine-1-carboxylate 1z (227 mg, 1.0 mmol), affording 2z (200 mg, 73.2% yield). White solid m.p. 122 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.26 (br, 2H), 3.76 (d, 2H), 3.63 (s, 3H), 2.94 (s, 2H), 1.39 (s, 3H), 1.28 (s, 9H) ppm. \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 177.6, 173.6, 77.0, 75.6, 61.1, 50.2, 42.7, 14.0, 154.8, 79.8, 51.8, 43.2, 42.8, 32.8, 28.3 ppm. IR (neat, cm\(^{-1}\)) 3447, 2979, 2894, 1735, 1698, 1695, 1436, 1156. HRMS ESI, (C\(_{12}\)H\(_{15}\)NNaO\(_6\)) \([\text{M+Na}]^+\) calculated 296.1105, found 296.1105.

1-(tert-butoxycarbonyl)-3-(2-methoxy-2-oxoethyl)pyrrolidine-3-carboxylic acid (2aa). Following the general procedure III using tert-Butyl 3-(2-methoxy-2-oxoethylidene)pyrrolidine-1-carboxylate 1aa (241 mg, 1.0 mmol), affording 2aa (208 mg, 72.4% yield). White solid m.p. 130 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.39 (m, 2H), 3.29 (m, 2H), 2.75 (m, 2H), 2.38 (m, 1H), 1.90 (m, 1H), 1.43 (s, 9H) ppm. \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 178.9, 171.4, 154.5, 79.9, 53.7, 52.0, 50.1, 44.3, 40.1, 34.2, 28.5 ppm. IR (neat, cm\(^{-1}\)) 3413, 2990, 2942, 1741, 1713, 1640, 1420, 1189. HRMS ESI, (C\(_{13}\)H\(_{21}\)NNaO\(_6\)) \([\text{M+Na}]^+\) calculated 310.1261, found 310.1260.

3-(2-ethoxy-2-methyl-2-oxoethyl)oxetane-3-carboxylic acid (2ab). Following the general procedure III using Ethyl 2-(oxetan-3-ylidene)propanoate 1ab (156 mg, 1.0 mmol), affording 2ab (130 mg, 64.3% yield). Yellow liquid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.08 (br, 1H), 5.01 (d, 1H), 4.89 (d, 1H), 4.74 (d, 1H), 4.62 (d, 1H), 4.11 (q, 2H), 3.13 (q, 1H), 1.33 (d, 3H), 1.21 (t, 3H) ppm. \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 177.6, 173.6, 77.0, 75.6, 61.1, 50.2, 42.7, 14.0, 11.9 ppm. IR (neat, cm\(^{-1}\)) 2983, 2902, 1729, 1464, 1206, 1018. HRMS ESI, (C\(_9\)H\(_{14}\)NaO\(_5\)) \([\text{M+Na}]^+\) calculated 225.0733, found 225.0734.

3-(2-methoxy-2-oxoethyl)oxetane-3-carboxylic acid (2ac) and 5-(2-methoxy-2-oxoethyl)1,3-dioxane-2-one-5-carboxylic acid (2ac'). Following the general procedure III using Methyl 2-oxetanylideneacetate 1ac (128 mg, 1.0 mmol), affording 2ac&2ac'.
(110 mg, 63.2% yield) with ratio 1:3 From 1H NMR and repeating the reaction but using LiBF₄ instead of Et₄NI the ratio was 1:1.3. Colourless liquid

1H NMR (400 MHz, CDCl₃) δ 4.83 (d, 2H), 4.50 (d, 2H), 3.63 (s, 3H), 2.91 (s, 2H) ppm. For 2ac δ 5.03 (d, 2H), 4.52 (d, 2H), 3.68 (s, 3H), 3.11 (s, 2H) ppm. 13C NMR (101 MHz, CDCl₃) δ 177.4, 171.5, 171.1, 77.9, 77.6, 52.1, 51.9, 45.5, 44.2, 39.4, 39.1 ppm. IR (neat, cm⁻¹) 3395, 2970, 1738, 1710, 1367, 1211. HRMS ESI, (C₇H₁₀NaO₅) [M+Na]⁺ calculated 197.0420, found 197.0421.

3-(2-methoxy-2-oxoethyl)tetrahydrofuran-3-carboxylic acid (2ad). Following the general procedure III using Methyl 2-(dihydro-3(2H)-furanyliden)acetate 1ad (142 mg, 1.0 mmol), affording 2ad (120 mg, 63.8% yield). Colourless liquid

1H NMR (400 MHz, CDCl₃) δ 4.16 (d, 1H), 3.91 (m, 2H), 3.71 (d, 1H), 3.65 (s, 3H), 2.77 (s, 2H), 2.48 (m, 1H), 1.87 (m, 1H) ppm. 13C NMR (101 MHz, CDCl₃) δ 179.8, 171.7, 75.8, 68.0, 51.9, 51.1, 40.4, 36.5 ppm. IR (neat, cm⁻¹) 3449, 2982, 1738, 1689, 1441, 1218. HRMS ESI, (C₉H₁₄NaO₅) [M+Na]⁺ calculated 211.0577, found 211.0578.

4-(2-methoxy-2-oxoethyl)tetrahydro-2H-pyran-4-carboxylic acid (2ae). Following the general procedure III using Methyl 2-(tetrahydro-4H-pyran-4-ylidene)acetate 1ae (156 mg, 1.0 mmol), affording 2ae (150 mg, 74.2% yield). White solid m.p. 59 °C.

1H NMR (400 MHz, CDCl₃) δ 3.76 (m, 2H), 3.67 (m, 5H), 2.67 (s, 2H), 2.10 (m, 2H), 1.63 (m, 2H) ppm. 13C NMR (101 MHz, CDCl₃) δ 180.4, 170.9, 64.5, 51.8, 43.4, 42.4, 33.6 ppm. IR (neat, cm⁻¹) 3434, 2995, 2982, 1731, 1691, 1443, 1098. HRMS ESI, (C₉H₁₄NaO₅) [M+Na]⁺ calculated 225.0733, found 225.0734.

2-Ethyl-2-methyl butanedioic acid 4-methyl ester (2ag). Following the general procedure III using Methyl 3-methyl-2-pentenoate (1ag) (128 mg, 1.0 mmol), affording 2ag (140 mg, 80.5% yield). White solid m.p. 55 °C.

1H NMR (400 MHz, CDCl₃) δ 10.37 (br, 1H), 3.62 (s, 3H), 2.74 (d, 1H), 2.39 (d, 1H), 2.16 (m, 2H), 1.21 (s, 3H), 0.85 (t, 3H) ppm. 13C NMR (101 MHz, CDCl₃) δ 182.7, 171.8, 51.6, 44.4, 42.0, 32.0, 20.9, 8.6 ppm.

Procedure for electrochemical flow reaction: In 50 mL Erlenmeyer flask, acrylate 1ag (1 g, 7.8 mmol) was added to a solution of Et₄NI (1 g, 3.9 mmol) and TEOA (1.16 g, 7.8 mmol) in DMF (25 mL). The resulting mixture was flushed with CO₂ and kept under a positive pressure of CO₂. The mixture was electrolysed at a constant voltage of 10V through a vapourtech ion electrochem reactor containing carbon cathode and carbon anode in closed cycle with speed of 0.5 mL/min for 4 h. The crude reaction mixture was acidified by addition of HCl/H₂O (1:1, 10 mL) and extracted with diethyl ether (3 x 15mL). The combined organic phases were washed with brine, dried over MgSO₄ and filtered. The solvent was then removed under reduced pressure and the crude material was recrystallised by hexane affording 2ag (1.1g, 80.8%).

Deuterium Labelling Studies

Following the general procedure III but using 10 eq of D₂O instead of TEOA and starting with Methyl 3,3-dimethylacrylate affording the deuterated product [D]2q.
"HO₂C CO₂Me

2aq"

"HO₂C CO₂Me

[D] 2aq"
4.0 Robustness Screen for the reaction:

\[
\begin{align*}
\text{MeO} & \quad \text{Et}_4\text{NI} \quad \text{TEOA} \quad \text{DMF} \quad 4 \text{ h, r.t.} \\
\text{MeO} & \quad \text{Et}_4\text{NI (0.5 equiv.),} \\
\text{Et}_4\text{NI} & \quad \text{TEOA (1.0 equiv.)} \\
\text{DMF} & \quad \text{(1.0 mmol) were added to a solution of Et}_4\text{NI (128 mg, 0.5 mmol) and TEOA (149 mg, 1.0 mmol) in DMF (5 mL).} \\
\text{The resulting mixture was flushed with CO}_2 \text{ and kept under a positive pressure of CO}_2. \\
\text{The mixture was electrolysed at a constant voltage of 10V in a single compartment cell containing carbon cathode and carbon anode with stirring for 4h.} \\
\text{The reaction mixture was diluted to 20 mL using chloroform and 178 mg (1.0 mmol) of Anthracene were added then analysed by GCMS.}
\end{align*}
\]

Procedure for screening

Methyl 3,3-dimethylacrylate 1q (1.0 mmol) and additive (1.0 mmol) were added to a solution of Et\(_4\)NI (128 mg, 0.5 mmol) and TEOA (149 mg, 1.0 mmol) in DMF (5 mL). The resulting mixture was flushed with CO\(_2\) and kept under a positive pressure of CO\(_2\). The mixture was electrolysed at a constant voltage of 10V in a single compartment cell containing carbon cathode and carbon anode with stirring for 4h. The reaction mixture was diluted to 20 mL using chloroform and 178 mg (1.0 mmol) of Anthracene were added then analysed by GCMS.

Procedure for gas chromatography batch calibration

Additives were individually analysed by gas chromatography to determine retention times. Calibration solutions with 16 compounds (1.0 mmol of each compound in 20 mL of chloroform) were subsequently prepared, ensuring compounds with similar retention times were separated. Standard gas chromatography calibration using anthracene as a standard was undertaken, and calibration lines produced for each additive.

Calibration for reaction yield

The calibration line for determination of the yield using gas chromatography analysis is given. Calibration was undertaken using anthracene as the standard.

Column: 15 m x 0.25 mm DB-5

Method: Initial temperature 60 °C, hold 1 min, final temperature 260 °C, hold 1.35 min.

Detection: MS detection.

Retention time: 2,2-Dimethyl butanedioic acid 4-methyl ester = 5.51 min.
Protocol for batch screening and analysis

Two calibration solutions containing 8 additives (1.0 mmol of each additive) and standard (1.0 mmol, anthracene) in chloroform (20 mL) are prepared, and analyzed.

Example GC method, compounds, retention times and chromatograms are provided:

Column: 15 m x 0.25 mm DB-5

Method: Initial temperature 60 °C, hold 1 min, final temperature 260 °C, hold 1.35 min.

Detection: MS detection.

Retention time of standard: Anthracene = 12.79 min.

|                     | Group A | Retention time (min) | Group B | Retention time (min) |
|---------------------|---------|----------------------|---------|----------------------|
| Compound            |         |                      | Compound|                      |
| Benzyl bromide      | 3.27    |                      | Thiol   | 2.30                 |
| Benzaldehyde        | 3.52    |                      | O-nBu   | 2.88                 |
| 1,6-Heptadiene      | 3.95    |                      | 4-Amino-phenyl | 3.61 |
| O-Methoxy-benzaldehyde | 4.71  |                      | Naphtalene | 3.64 |
| 7-Oh                  | 5.18    |                      | S-N     | 5.81                 |
| 9-Oh                  | 5.34    |                      | N-Bn    | 7.07                 |
The relative integrals of the additive to the standard can be used for a semi-quantitative determination of the amount of additive present in a reaction mixture.

The standard reaction is performed and the product isolated. Calibration of the product (1.0 mmol) against the standard (1.0 mmol) is undertaken.

The standard reaction is prepared 16 times containing one additive (1.0 mmol). After the given reaction time, the standard is introduced to each reaction (1.0 mmol), and analysis by the selected method undertaken.

The yield of the reaction and the amount of additive remaining as determined by comparison with the calibration is reported in the following table:

| Entry | Additive | Product Yield (%) | Additive remaining (%) | SM remaining (%) |
|-------|----------|-------------------|------------------------|-----------------|
| A0    | -        | 81.2              | -                      | 0               |
| A1    | \( \text{OH} \) | 64.8              | 91.8                   | 0               |
| A2    | \( \text{CN} \) | 63.9              | 81.4                   | 0               |
| A3    | \( \text{H} \) | 77.9              | 93.6                   | 0               |
| A4    | \( \text{H} \) | 78.7              | 79.4                   | 0               |
|   | Structure | δ (ppm) | J (Hz) | ppm |
|---|-----------|---------|--------|-----|
| A5 | ![Structure](image) | 70.1   | 55.5   | 0   |
| A6 | ![Structure](image) | 61.7   | 0      | 0   |
| A7 | ![Structure](image) | 69.6   | 95.5   | 0   |
| A8 | ![Structure](image) | 74.8   | 0      | 7.1 |
| A9 | ![Structure](image) | 74.7   | 59.8   | 0   |
| A10| ![Structure](image) | 78.1   | 9.5    | 0   |
| A11| ![Structure](image) | 16.1   | 0      | 25.3|
| A12| ![Structure](image) | 68.4   | 80.9   | 0   |
| A13| ![Structure](image) | 46.2   | 30.5   | 14.9|
| A14| ![Structure](image) | 45.4   | 35.4   | 5.9 |
| A15| ![Structure](image) | 61.6   | 79.7   | 6.9 |
| A16| ![Structure](image) | 63.8   | 11.6   | 0   |

**2-Methyl butanedioic acid 1-(1,2-dihydroxyprop-3-yl) ester (2ah).** Following the general procedure III using Oxiranylmethyl methacrylate 1ah (142 mg, 1.0 mmol), affording 2ah (110 mg, 57.8% yield). Colorless oil.  

**1H NMR** (500 MHz, CDCl₃) δ 5.20 (br, exchanges with D₂O, 2H), 4.27-4.07 (m, 3H), 3.59 (m, 2H), 2.91 (m, 1H), 2.73 (dd, J = 6.4, 16.8 Hz, 1H), 2.52 (dd, J = 6.0, 16.2 Hz, 1H), 1.24 (d, 3H ppm).  

**13C NMR** (125 MHz, CDCl₃) δ 176.7, 175.4, 69.6, 65.5, 45.5, 37.4, 35.7, 17.0 ppm.  

**IR** (neat, cm⁻¹) 3542, 3450, 2990, 2895, 1735, 1704, 1421, 1260, 1163.  

**HRMS** ESI, (C₈H₁₄NO₆)[M+Na]⁺ calculated 229.0683, found 229.0684.
5.0 Current Screening for the reaction:

![Chemical structure of 1q and 2q](image)

**Procedure for screening**

Methyl 3,3-dimethylacrylate \(1q\) (1.0 mmol) was added to a solution of \(\text{Et}_4\text{NI}\) (128 mg, 0.5 mmol) and \(\text{TEOA}\) (149 mg, 1.0 mmol) in \(\text{DMF}\) (5 mL). The resulting mixture was flushed with \(\text{CO}_2\) and kept under a positive pressure of \(\text{CO}_2\). The mixture was electrolysed at different interval current in a single compartment cell containing carbon cathode and carbon anode with stirring for 4 h. The reaction mixture was diluted to 20 mL using chloroform and 178 mg (1.0 mmol) of anthracene internal standard was added then analysed by GCMS.

| Current (mA) | Product GCMS Yield (%) | S.M Remaining (%) | Current Efficiency (%) |
|-------------|-------------------------|-------------------|-----------------------|
| 10          | 0                       | 100               | N/A                   |
| 30          | 31.8                    | 51.1              | 14                    |
| 60          | 68.9                    | 0                 | 15                    |
| 90          | 74                      | 0                 | 11                    |

6.0 Analysis of \(\text{CO}_2\) reduction by GC-MS Headspace analysis

**Reaction Using Dimethylacetamide (DMA):**

![Chemical structure of DMA reaction](image)

A solution of \(\text{LiBF}_4\) (47 mg, 0.5 mmol) and \(\text{TEOA}\) (149 mg, 1.0 mmol) in DMA (5 mL) was flushed with \(\text{CO}_2\) and kept under a positive pressure of \(\text{CO}_2\). The mixture was electrolysed at a constant voltage of 10 V in a single compartment cell containing carbon cathode and carbon anode with stirring for 2 h. Utilising the method of Sokoro *et al.*\textsuperscript{26} an aliquot (0.1 mL) was placed into a GC-MS vial and diluted to 1.0 mL with aq. \(\text{EtOH}\) (10% v/v), \(\text{c.H}_2\text{SO}_4\) (0.02 mL) was added and the vial top screwed into place. The vial was...
placed in an oven for 10 minutes at 60 °C along with a gas tight syringe. The vial was then allowed to cool for 5 minutes and 1.0 mL of the head space in the vial drawn into the syringe and immediately injected into the GC-MS.
Blank DMA GC-MS Spectra:
DMA (0.1 mL) was placed into a GC-MS vial and diluted to 1.0 mL with EtOH (10% v/v), c.H₂SO₄ (0.02 mL) was added and the vial top screwed into place. The vial was placed in an oven for 10 minutes at 60 °C along with a gas tight syringe. The vial was then allowed to cool for 5 minutes and 1.0 mL of the head space in the vial drawn into the syringe and immediately injected into the GC-MS.
Reaction Using Dimethylformamide (DMF):

\[ \text{CO}_2 \ (1 \text{ atm}) \]

\[ \xrightarrow{i) \text{C}(-) \text{V} \rightarrow \text{(+)} \text{C} \]

\[ \text{LiBF}_4 \ (0.5 \text{ equiv.}), \]

\[ \text{TEOA} \ (1.0 \text{ equiv.}) \]

\[ \text{DMF} \]

\[ 2 \text{ h, r.t.} \]

\[ \xrightarrow{\text{ii) 0.1 mL aliquot in}} \]

\[ 1 \text{ mL EtOH (10\% in H}_2\text{O)} \]

\[ 0.02 \text{ mL c.H}_2\text{SO}_4 \]

A solution of LiBF\(_4\) (47 mg, 0.5 mmol) and TEOA (149 mg, 1.0 mmol) in DMF (5 mL) was flushed with CO\(_2\) and kept under a positive pressure of CO\(_2\). The mixture was electrolysed at a constant voltage of 10V in a single compartment cell containing carbon cathode and carbon anode with stirring for 2h. An aliquot (0.1 mL) was placed into a GC-MS vial and diluted to 1.0 mL with aq. EtOH (10\% v/v), c.H\(_2\)SO\(_4\) (0.02 mL) was added and the vial top screwed into place. The vial was placed in an oven for 10 minutes at 60 °C along with a gas tight syringe. The vial was then allowed to cool for 5 minutes and 1.0 mL of the head space in the vial drawn into the syringe and immediately injected into the GC-MS.
**Blank DMF GC-MS Spectra**

DMF (0.1 mL) was placed into a GC-MS vial and diluted to 1.0 mL with EtOH (10% v/v), c.H₂SO₄ (0.02 mL) was added and the vial top screwed into place. The vial was placed in an oven for 10 minutes at 60 °C along with a gas tight syringe. The vial was then allowed to cool for 5 minutes and 1.0 mL of the head space in the vial drawn into the syringe and immediately injected into the GC-MS.
7.0 References:

1- G. Singh, M. L. Purkayastha, H. Ila, H. Junjappa, *J. Chem. Soc., Perkin Trans.* 1985, 7, 1289–1294.

2- K. F. Chin, X. Ye, Y. Li, R. Lee, A. M. Kablyda, D. Leow, X. Zhang, E. C. Xia Ang, C. Tan, *ACS Catalysis* 2020, 10, 2684–2691.

3- T. Kapferer, R. Brückner, *Eur. J. Org. Chem.* 2006, 9, 2119–2133.

4- A. Meden, D. Knez, M. Jukic, X. Brazzolotto, M. Grsic, A. Pislar, A. Zahirovic, J. Kos, F. Nachon, J. Svete, S. Gobec, U. Groselj, *Chem. Commun.* 2019, 55, 3765–3768.

5- G. Kang, D. Romo *ACS Catal.* 2021, 11, 1309-1315

6- Y. Wang, N. Wang, J. Zhao, M. Sun, H. You, F. Fang, Z. Liu, *ACS Cat.* 2020, 10, 6603–6612.

7- P. W. Smith, A. W. J. Cooper, R. Bell, I. J. M. Beresford, P. M. Gore, A. B. McElroy, J. M. Pritchard, V. Saez, N. R. Taylor, *J. Med. Chem.* 1995, 38, 3772–3779.

8- X. Yang, W. Kong, J. Gao, L. Cheng, N. Li, M. Li, H. Li, J. Fan, J. Gao, Q. Ouyang, J. Xie, *Chem. Commun.* 2019, 55, 12707–12710.

9- C. Xue, X. Chen, X. He, J. Roderick, R. L. Corbett, B. Ghavimi, R. Liu, M. B. Covington, M. Qian, M. D. Ribadeneira, K. Vaddi, J. Trzaskos, R. C. Newton, J.J.-W. Duan, C. P. Decicco, *Bioorg. Med. Chem. Lett.* 2004, 14, 4453–4459.

10- A. R. White, R. A. Kozlowski, S. Tsai, C. D. Vanderwal, *Angew. Chem.* 2017, 129, 10661–10665.

11- J. Duan, B. W. King, C. Decicco, T.P. Maduskuie Jr., M. E. Voss, *PCT Int. Appl.* 2001, WO 2001070734.

12- M. E. Kuehne, W. G. Bornmann, I. Marko, Y. Qin, K. L. LeBoulluec, D. A. Frasier, F. Xu, T. Mulamba, C. L. Ensinger, L. S. Borman, A. E. Huot, C. Exon, F. T. Bizzarro, J. B. Cheung, S. L. Bane, *Org. Biomol. Chem.* 2003, 1, 2120–2136.

13- S. G. Alcock, J. E. Baldwin, R. Bohlmann, L. M. Harwood, J. I. Seeman, *J. Org. Chem.* 1985, 50, 3526–3535.

14- J. Sedelmeier, S. V. Ley, I. R. Baxendale, M. Baumann, *Org. Lett.* 2010, 12, 3618–3621.

15- M. Ostermeier, B. Brunner, C. Korff, G. Helmchen, *Eur. J. Org. Chem.* 2003, 3453–3459.
16-K. Achiwa, P. A. Chaloner, D. Parker, *J. Organomet. Chem.* **1981**, *218*, 249–260.

17-L. Zetta, G. Gatti, *Tetrahedron* **1972**, *28*, 3773–3779.

18-S. Singh, M. Verma, K. N. Singh, *Synth. Commun.* **2004**, *34*, 4471–4475.

19-Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. *Org. Lett.* **2014**, *16*, 5960–5963.

20-D. B. Hansen, M. L. Starr, N. Tolstoy, M. A. Joullie, *Tetrahedron-Asymmetry* **2005**, *16*, 3623–3627.

21-Casimir, J. R.; Ettouati, L.; Paris, J. *Lett. Pept. Sci.* **1998**, *5*, 13–18.

22-Norman, M. H.; Rigdon, G. C.; Navas, F., III; Cooper, B. R. *J. Med. Chem.* **1994**, *37*, 2552–2563.

23-Hussain, S.A.M.T.; Ollis, W.D.; Smith, C. Stoddart, J.F. *J. Chem. Soc., Perkin I* **1974**, 1480–1483.

24-Smith, R. G. *PCT Int. Appl.* **1997**, WO 9741878.

25-Hajicek, J.; Holubek, J.; Trojanek, *J. Coll. Czech. Chem. Commun.* **1982**, *47*, 2749–2762.

26-A. Sokoro, D. Lehotay, J. Eichhorst, R. Treble, *J Anal Toxicol* **2007**, *31*, 342–346.
8.0 $^1$H and $^{13}$C NMR Spectra of the alkenes

![C NMR Spectra](image-url)
7.0 1H and 13C NMR Spectra of the alkenes

X : parts per Million : Proton

X : parts per Million : Carbon13

X : parts per Million : Proton

X : parts per Million : Carbon13
9.0 $^1$H and $^{13}$C NMR of the Carboxylic Acids

![NMR Spectra of Carboxylic Acids](image)

- HO$_2$C$_\text{CO}_2$Me
  - 2a

- HO$_2$C$_\text{CO}_2$H
  - 2a'

[X : parts per Million : Proton]
[X : parts per Million : Carbon13]
\[ \text{CH}_3\text{CO}_2\text{H} \]

2p

\[ \text{HO}_2\text{C} \]

2q

\[ \text{CO}_2\text{Me} \]
H and 13C NMR of the Carboxylic Acids

Abundance

X: parts per Million: Proton

Abundance

X: parts per Million: Carbon-13
