Supporting Information

Alkene reactions with superoxide radical anions in flow electrochemistry

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Table of Contents:

General Information

General:

All chemicals were purchased from Acros Organics, Alfa Aesar, Apollo Scientific Ltd, Fisher Scientific Ltd, Scientific Laboratory Supplies Ltd, Merck KGaA, Fluorochem Ltd, and Sigma-Aldrich. All purchased chemicals were used without further purification. Deuterated solvents for NMR analysis were purchased from Sigma-Aldrich. Room temperature (rt) stands for 20-25 °C. Thin layer chromatography (TLC) experiments were performed on aluminum plates coated with silica (TLC Silica gel 60 F_{254}) purchased from Merck, and visualised by UV light. Flash column chromatography was carried out on a Biotage® Isolera™ Four system using Biotage® Sfär Silica HC D 10 g cartridges.

NMR:

^{1}H NMR and ^{13}C NMR spectra were recorded at 298 K on a Bruker Fourier 300 MHz, Bruker DPX 400 MHz, or Bruker Avance 500 MHz instrument and were referenced relative to the residual solvent peaks ([1]H: $CDCl_3$, δ 7.26 ppm; [13]C: $CDCl_3$, δ 77.16 ppm). Chemical shifts are reported in ppm (δ). The spectra reported use the following abbreviations to express multiplicities: s = singlet, m = multiplet. The coupling constants (J) are expressed in Hertz (Hz).

HRMS:

High resolution mass spectra were obtained from Cardiff University on a Waters GC-TOF spectrometer. Ions were generated using electron ionisation (EI) techniques. All signals are reported with a mass-to-charge (*m/z*) ratio unit.

GC-FID:

Gas chromatography with flame ionisation detector (GC-FID) was performed on an Agilent 7890A GC system fitted with a Restek Rt-βDEXsm column (30 m × 0.25 mm ID) for optimisation, using benzonitrile as an internal standard.

GC-MS:

GC-MS spectra were recorded on a PerkinElmer Clarus 680 GC and a PerkinElmer Clarus SQ 8C MS fitted with a PerkinElmer Elite-1 100% dimethyl polysiloxane column (30 m × 0.25 mm ID).

Electrolysis:

Flow electrochemical experiments were performed using a stand-alone Vapourtec Ion Electrochemical Reactor, with an Aim-TTi EX354RD Dual Power Supply from Thurlby Thandar Instruments Ltd. Chemyx Fusion 100 Touch Syringe Pumps, a Vapourtec SF-10

Reagent Pump, a Vapourtec tuneable back pressure regulator (BPR), and an Omega FMA5500A series mass flow controller were used in the flow set-ups. Electrode materials employed were platinum (Pt) purchased from Goodfellow. The electrodes (5×5 cm^2) were separated by a 0.5 mm FEP spacer resulting in a reactor volume of 0.6 mL, with an exposed electrode surface area of 12 cm^2.

Melting points:

Melting points were measured using a Gallenkamp variable heater with samples in open capillary tubes and are uncorrected.

General Procedures

### General Flow Electrolysis Procedure:
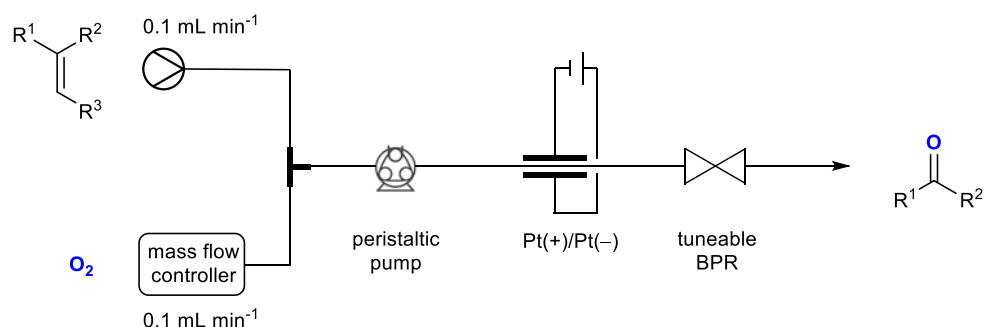
The electrolysis was performed in an undivided cell using a Vapourtec Ion Electrochemical Reactor[1] (FEP spacer = 0.5 mm, reactor volume = 0.6 mL), employing a platinum electrode as the anode and a platinum electrode as the cathode (active surface area = 12 cm^2 for each electrode). A solution of alkene (0.025 M, 1 equiv.) and ^{n}Bu$_4$NClO$_4$ (0.05 M, 2 equiv.) in isobutyronitrile was pumped with a flow rate of 0.1 mL min^{-1}, which combined at a T-piece with molecular oxygen flown through a mass flow controller at 0.1 mL min^{-1}.[2] The resulting biphasic system was pumped by use of a peristaltic pump[3] with a flow rate of 0.2 mL min^{-1} into the electrochemical reactor, and was electrolysed under pressurised conditions by use of a tuneable back pressure regulator at constant current conditions (16 mA, 2 F). The first one and a half reactor volumes were disposed to ensure a steady state of the system had been reached. After collection for a known period, the reaction mixture was treated with distilled water and the aqueous phase was extracted with dichloromethane (3 × 25 mL). The organic layers were combined, dried over MgSO$_4$, filtered, and the solvent was removed *in vacuo* to yield the crude product. The crude product was purified by flash column chromatography.

Optimisation Studies

Optimisation reactions:

Table S1: Set-up I optimisation.
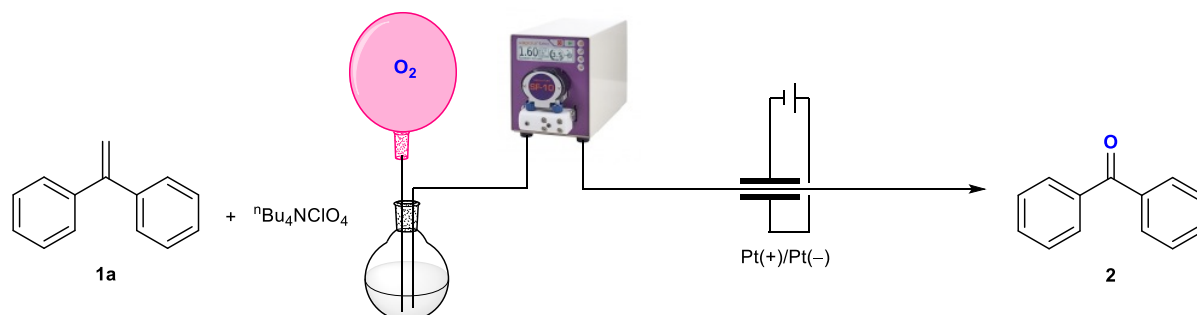
Entry	Flow rate (mL min^{-1})	Current (mA)	Charge (F)	Yield **2** (%)
1	0.1	24	3	-
2	0.1	32	4	2
3	0.1	40	5	2
4	0.05	12	3	5
5	0.05	16	4	6

a Standard reaction conditions: undivided flow cell, Pt anode (active surface area: 12 cm^2), Pt cathode, interelectrode distance: 0.5 mm, **1a** (0.05 M, 1 equiv.) and ^{n}Bu$_4$NClO$_4$ (0.05 M) in MeCN sat. with O$_2$. **b** Yield determined by GC-FID using benzonitrile as internal standard.

Table S2: Set-up II optimisation for flow rate.
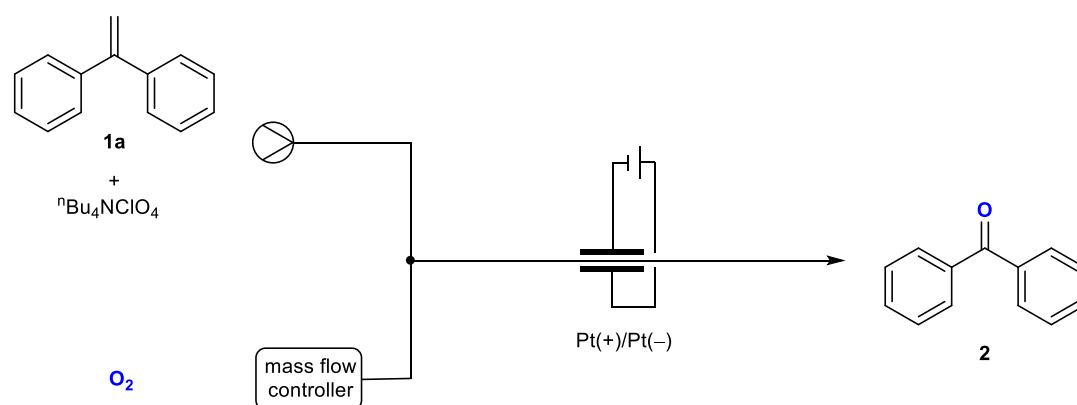
Entry	Flow rate (mL min^{-1})	Current (mA)	Charge (F)	Yield **2** (%)
1	0.2	32	2	9
2	**0.1**	**16**	**2**	**26**
3	0.05	8	2	30

Standard reaction conditions: undivided flow cell, Pt anode (active surface area: 12 cm^2),
Pt cathode, interelectrode distance: 0.5 mm, **1a** (0.05 M, 1 equiv.) and ^{n}Bu$_4$NClO$_4$ (0.05 M) in
MeCN sat. with O$_2$. **b** Yield determined by GC-FID using benzonitrile as internal standard.

**Table S3**: Set-up II optimisation for charge.
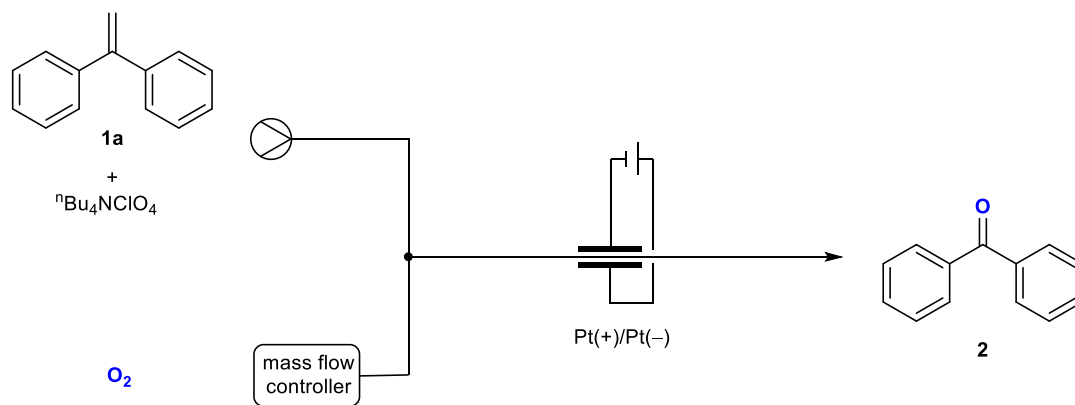
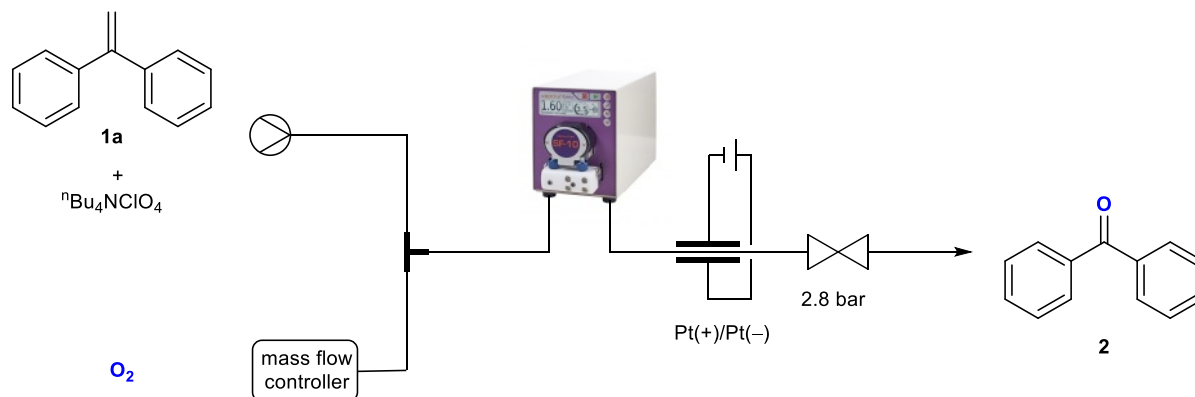| Entry	Flow rate (mL min^{-1})	Current (mA)	Charge (F)	Yield **2** (%)
1	0.1	32	4	5
2	0.1	24	3	14
3	**0.1**	**16**	**2**	**26**
4	0.1	8	1	13

a Standard reaction conditions: undivided flow cell, Pt anode (active surface area: 12 cm^2),
Pt cathode, interelectrode distance: 0.5 mm, **1a** (0.05 M, 1 equiv.) and ^{n}Bu$_4$NClO$_4$ (0.05 M) in
MeCN. **b** Yield determined by GC-FID using benzonitrile as internal standard.

Table S4: Set-up III optimisation.
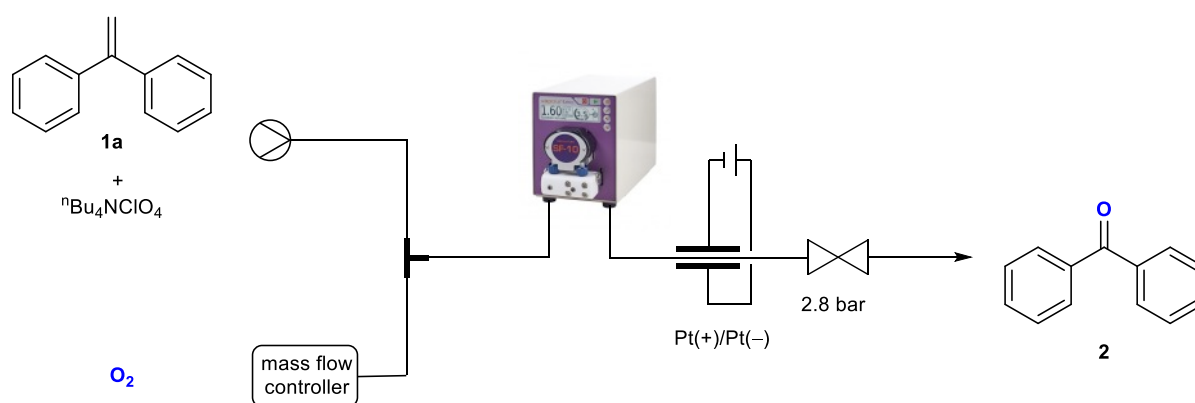
Entry	Flow rate (mL min^{-1})	Current (mA)	Charge (F)	Yield **2** (%)
1	0.1	16	2	25
2	0.1	24	3	21
3	**0.05**	**8**	**2**	**29**
4	0.05	12	3	27

a Standard reaction conditions: undivided flow cell, Pt anode (active surface area: 12 cm^2), Pt cathode, interelectrode distance: 0.5 mm, **1a** (0.05 M, 1 equiv.) and $^{n}Bu_4NClO_4$ (0.05 M) in MeCN. **b** Yield determined by GC-FID using benzonitrile as internal standard.


Table S5: Optimisation of anodic material.
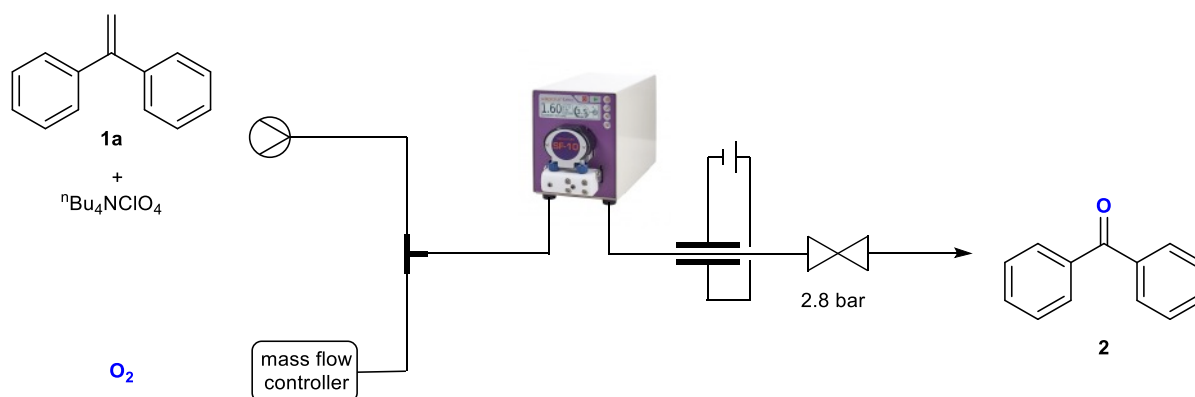
Entry	Anode	Flow rate (mL min^{-1})	Current (mA)	Charge (F)	Yield **2** (%)
1	Gr	0.1	16	2	17
2	Pt	0.1	16	2	25
3	Gr	0.05	8	2	21
4	Pt	0.05	8	2	29

Table S6: Optimisation of concentration.

Entry	[**1a**]$_0$ (M)	Flow rate (mL min^{-1})	Current (mA)	Charge (F)	Yield **2** (%)
1	0.025	0.1	12	3	25
2	0.05	0.1	24	3	21
3	0.025	0.05	6	3	33
4	0.05	0.05	12	3	27

a Standard reaction conditions: undivided flow cell, Pt anode (active surface area: 12 cm^2), Pt cathode, interelectrode distance: 0.5 mm, **1a** (x M, 1 equiv.) and ^{n}Bu$_4$NClO$_4$ (0.05 M) in MeCN. **b** Yield determined by GC-FID using benzonitrile as internal standard.

Table S7: Optimisation of cathodic material.
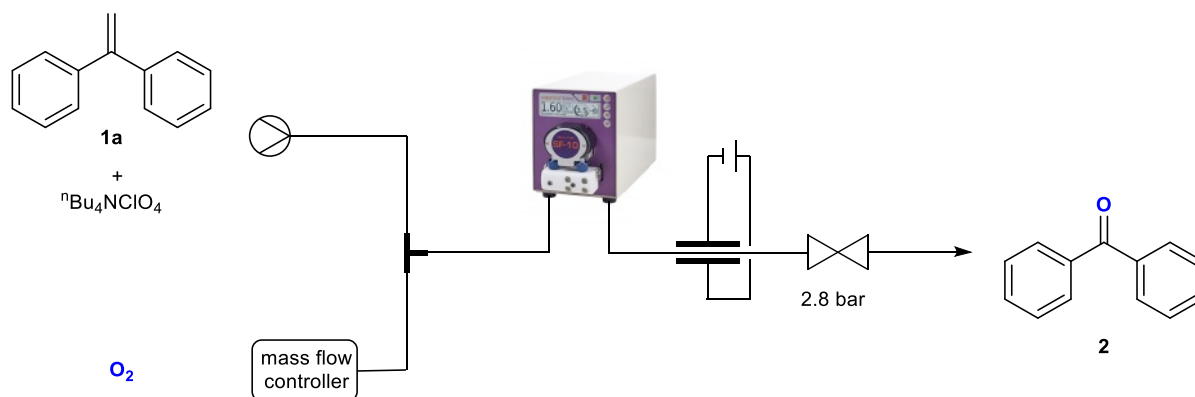
Entry	Cathode	Current (mA)	Charge (F)	Yield 2 (%)
1	Cu	16	2	26
2	Ni	16	2	25
3	Zn	16	2	26
4	SS	16	2	20
5	Pt	16	2	25

a Standard reaction conditions: undivided flow cell, Pt anode (active surface area: 12 cm^2), cathode, interelectrode distance: 0.5 mm, **1a** (0.05 M, 1 equiv.) and ^{n}Bu$_4$NClO$_4$ (0.05 M) in MeCN, combined flow rate: 0.1 mL min^{-1}. **b** Yield determined by GC-FID using benzonitrile as internal standard.

Table S8: Optimisation of solvent composition.
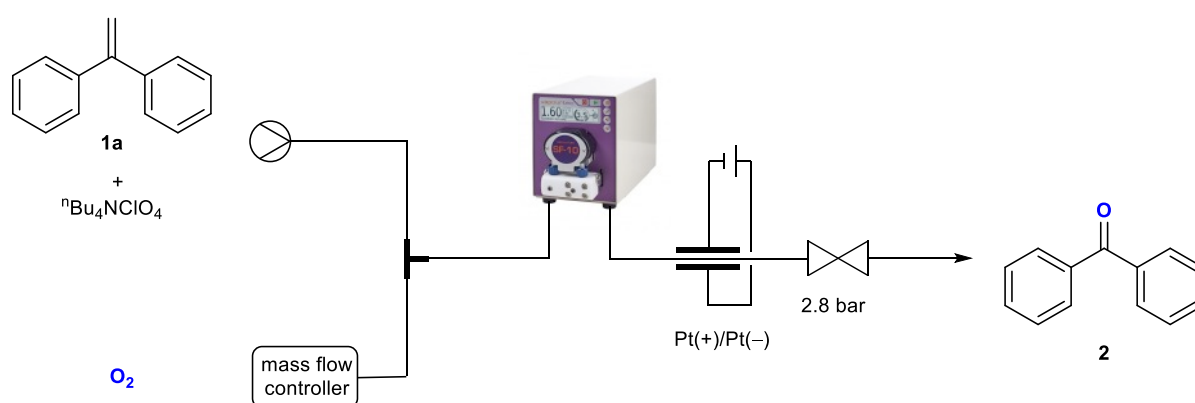
Entry	Solvent	Current (mA)	Charge (F)	Yield 2 (%)
1	THF	12	3	6
2	DCM	12	3	5
3	acetone	12	3	29
4	MeCN	12	3	25
5	**^{i}PrCN**	**12**	**3**	**36**

a Standard reaction conditions: undivided flow cell, Pt anode (active surface area: 12 cm^2), Pt cathode, interelectrode distance: 0.5 mm, **1a** (0.025 M, 1 equiv.) and ^{n}Bu$_4$NClO$_4$ (0.05 M) in solvent, combined flow rate: 0.1 mL min^{-1}. **b** Yield determined by GC-FID using benzonitrile as internal standard.

Table S9: Set-up IV optimisation for back pressure.
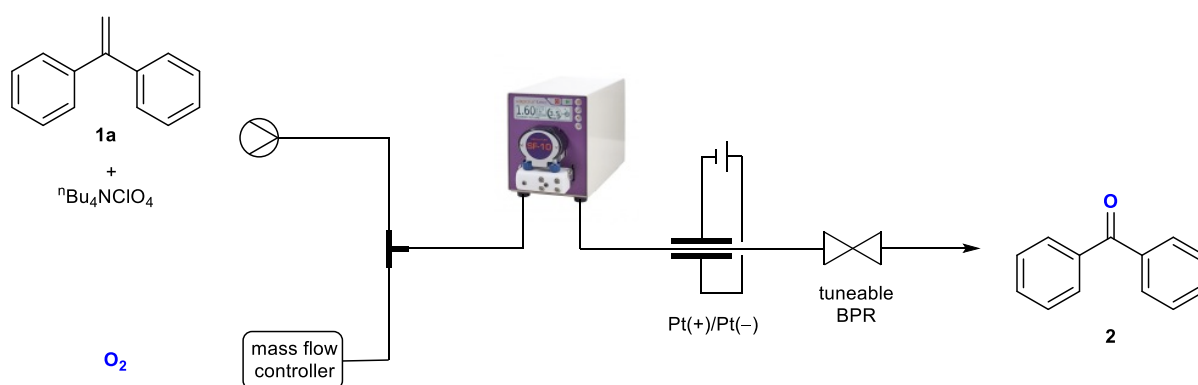
| Entry	Current (mA)	Charge (F)	Back pressure (bar)	Yield 2 (%)
1	16	2	0	41
2	**16**	**2**	**1.1**	**50**
3	16	2	2.2	51
4	16	2	2.8	53

a Standard reaction conditions: undivided flow cell, Pt anode (active surface area: 12 cm^2), Pt cathode, interelectrode distance: 0.5 mm, **1a** (0.025 M, 1 equiv.) and $^nBu_4NClO_4$ (0.05 M) in ^iPrCN, combined flow rate: 0.2 mL min^{-1}. **b** Yield determined by GC-FID using benzonitrile as internal standard.

Table S10: Set-up IV optimisation for charge.
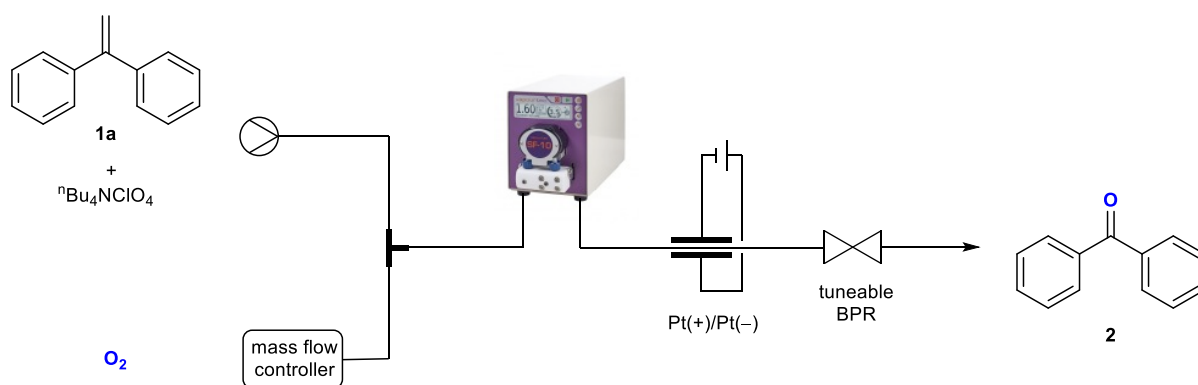
Entry	Current (mA)	Charge (F)	Back pressure (bar)	Yield 2 (%)
1	**16**	**2**	**1.1**	**51**
2	20	2.5	1.1	46
3	24	3	1.1	35

a Standard reaction conditions: undivided flow cell, Pt anode (active surface area: $12\ cm^2$), Pt cathode, interelectrode distance: 0.5 mm, **1a** (0.025 M, 1 equiv.) and $^{n}Bu_4NClO_4$ (0.05 M) in $^{i}PrCN$, combined flow rate: $0.2\ mL\ min^{-1}$. **b** Yield determined by GC-FID using benzonitrile as internal standard.

GC-MS study on side products

Crude GC-MS spectra of reaction performed in MeCN
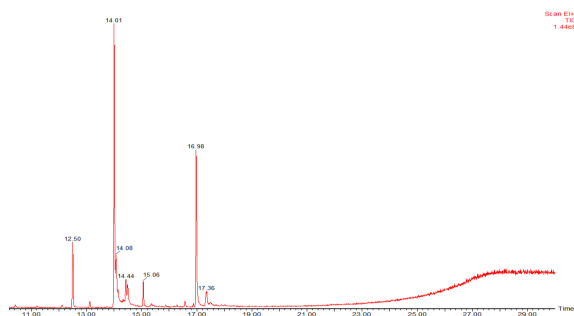
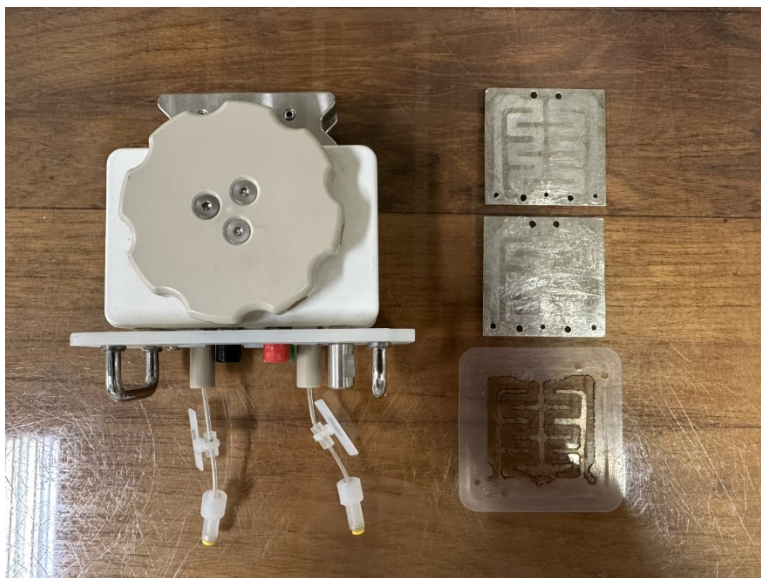Crude GC-MS spectra of reaction performed in ^{i}PrCN
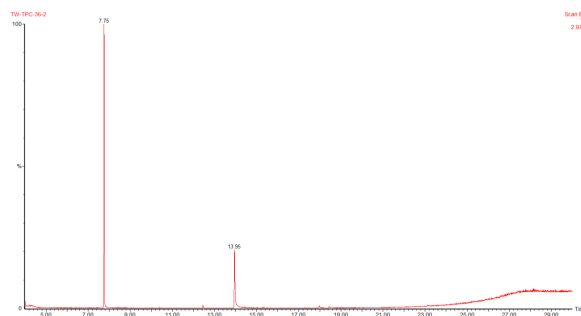
Electrochemical Flow Equipment

Figure S1: A closed Vapourtec Ion Electrochemical Flow Reactor (left), Pt electrode, Pt electrode and 0.5 mm FEP spacer (right).
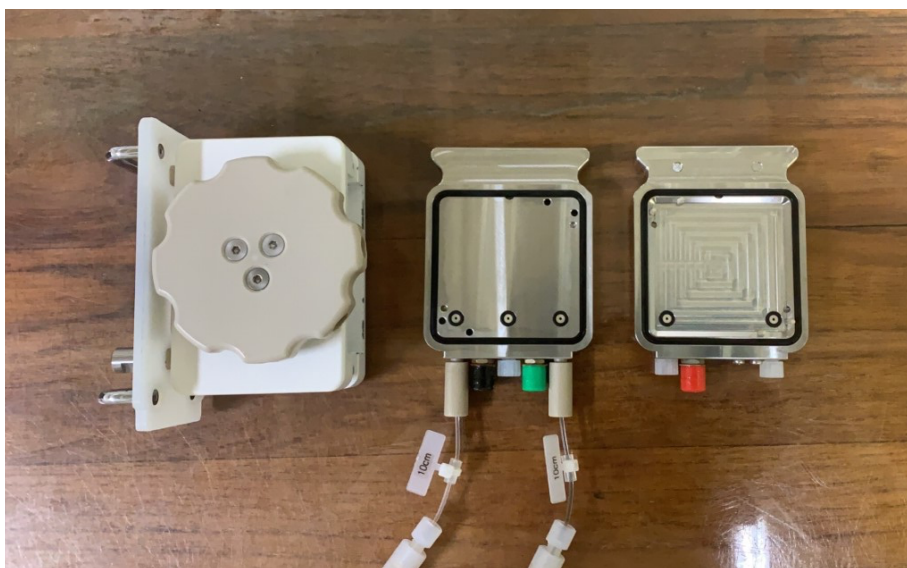
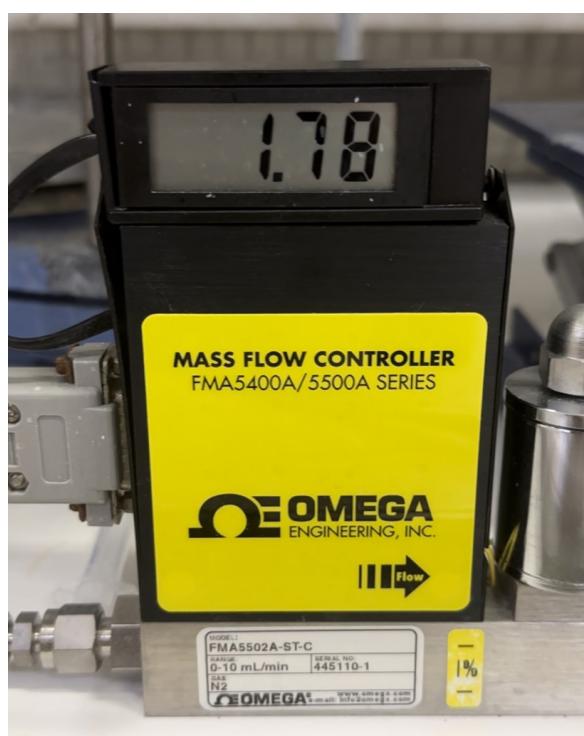**Figure S2**: An open Vapourtec Ion Electrochemical Flow reactor.

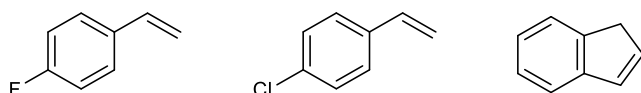
Figure S3: An Omega FMA5500A series mass flow controller.

Figure S4: Vapourtec SF-10 reagent pump.

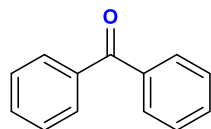**Figure S5**: Vapourtec tuneable back-pressure regulator.

Failed alkenes for oxidative cleavage

All starting material was consumed for all three substrates following the reaction, however only decomposition products were detected by ^1H NMR and ^{13}C NMR analysis.

Characterisation of the Products

Benzophenone (2)

Prepared according to the general procedure **A** from 1,1-diphenylethylene **1a** (68 mg, 0.375 mmol) over 2.5 h. The crude product was purified by flash column chromatography on silica gel (EtOAc:cyclohexane = 1:19) to give **2** as a colourless solid (30 mg, 0.17 mmol, 45%).

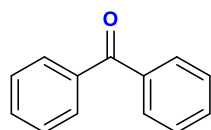**^{1}H NMR (500 MHz, CDCl$_3$)**: δ 7.82-7.80 (m, 4H), 7.61-7.57 (m, 2H), 7.50-7.47 (m, 4H).

^{13}C NMR (126 MHz, CDCl$_3$): δ 196.9, 137.7, 132.5, 130.2, 128.4.

HRMS (EI): *m/z* [M]$^+$ calcd for C$_{13}$H$_{10}$O 182.07262, found 182.0722.
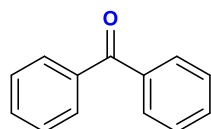
mp: 48–51 °C.

NMR data is identical to the literature data.[4]
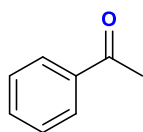

Benzophenone (2)

Prepared according to the general procedure **A** from 1,1-diphenyl-1-pentene **1b** (83 mg, 0.375 mmol) over 2.5 h. The crude product was purified by flash column chromatography on silica gel (EtOAc:cyclohexane = 1:19) to give **2** as a white solid (23 mg, 0.12 mmol, 33%).

Benzophenone (2)

Prepared according to the general procedure **A** from 1,1,2-triphenylethene **1c** (96 mg, 0.38 mmol) over 2.5 h. The crude product was purified by flash column chromatography on silica gel (EtOAc:cyclohexane = 1:19) to give **2** as a white solid (18 mg, 0.10 mmol, 27%).

Acetophenone (3)

Prepared according to the general procedure **A** from α-methylstyrene **1d** (59 mg, 0.50 mmol) over 3.33 h. The crude product was purified by column chromatography on silica gel (EtOAc:cyclohexane = 1:19) to give **3** as a clear oil (24 mg, 0.20 mmol, 39%).

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.97-7.95 (m, 2H), 7.58-7.54 (m, 1H), 7.48-7.44 (m, 2H), 2.60 (s, 3H).
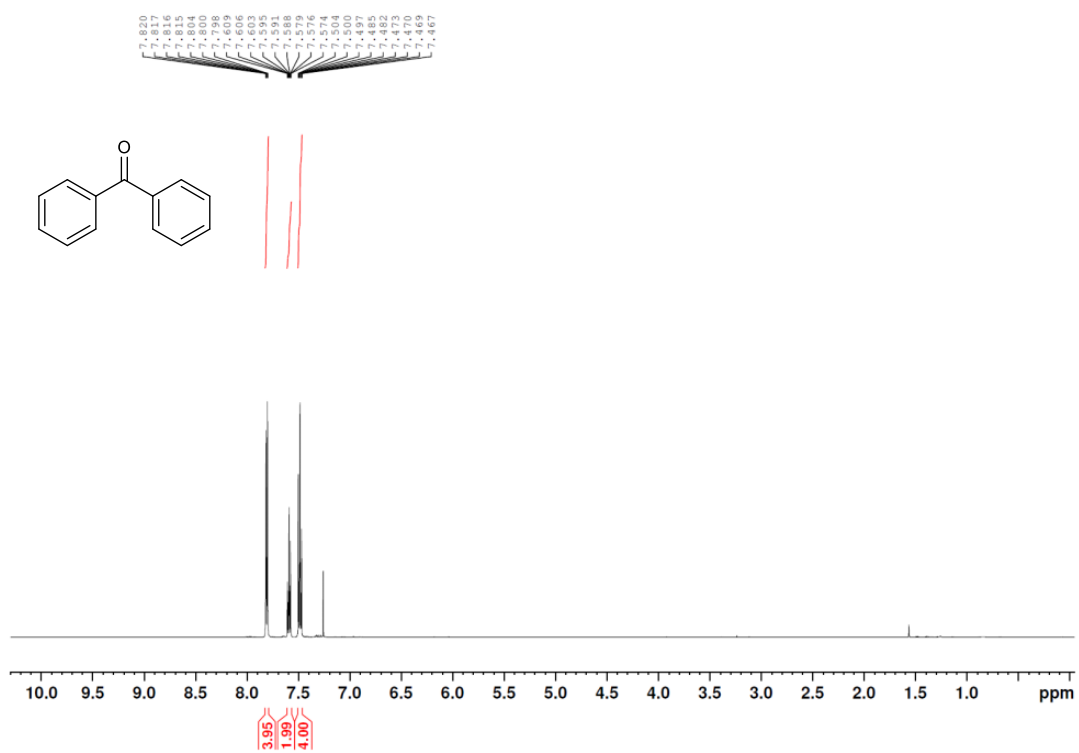
^{13}C NMR (126 MHz, CDCl$_3$): δ 198.3, 137.2, 133.2, 128.7, 128.4, 26.7.

HRMS (EI): *m/z* [M]$^+$ calcd for C$_8$H$_8$O 120.05697, found 120.0569.

NMR data is identical to the literature data.[4]
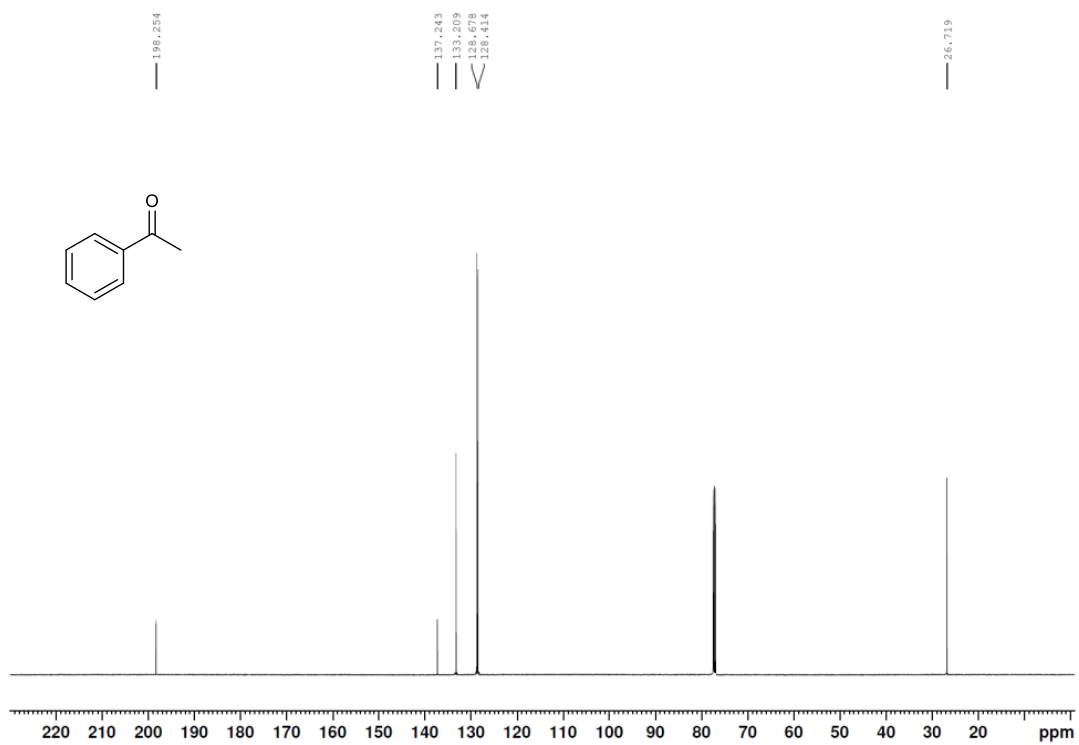
NMR Spectra

^{1}H NMR of benzophenone (2)

^{13}C NMR of benzophenone (2)

¹H NMR of acetophenone (3)

¹H NMR of acetophenone (3)

7.968
7.965
7.964
7.962
7.960
7.959
7.952
7.948
7.946
7.945
7.573
7.570
7.562
7.558
7.554
7.546
7.543
7.477
7.470
7.465
7.459
7.457
7.446
7.443
7.442
7.439

2.601

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

2.00 1.00 2.01 3.09
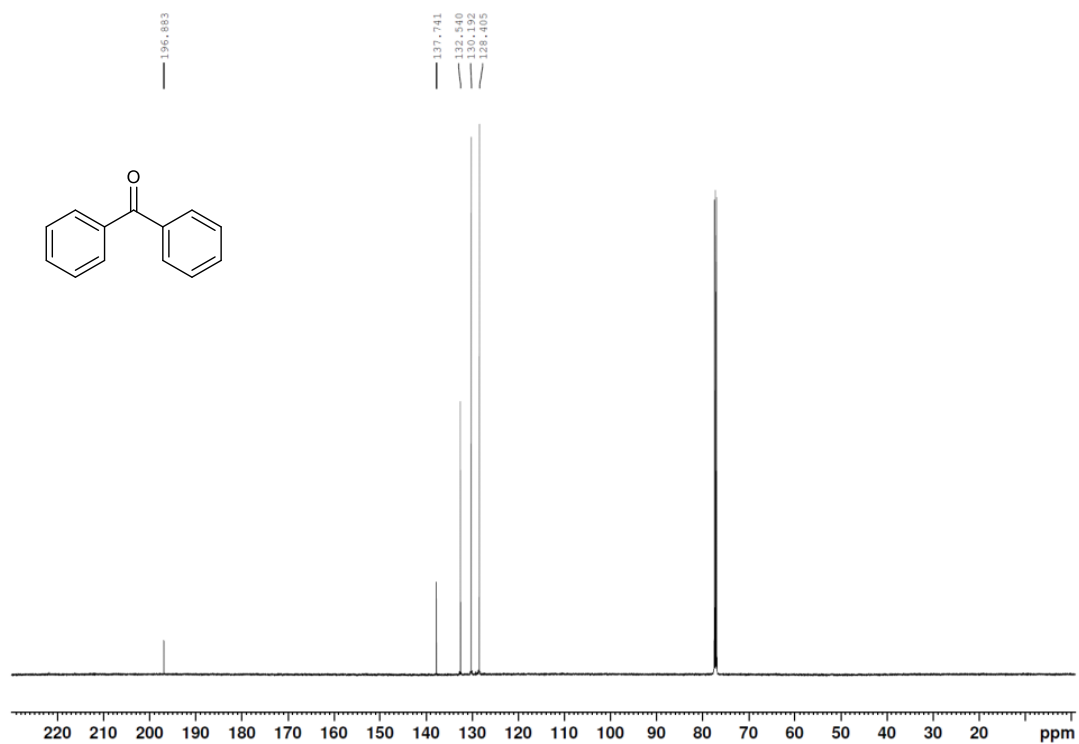
¹³C NMR of acetophenone (3)

¹³C NMR of acetophenone (3)

198.254

137.243
133.209
128.678
128.414

26.719

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm
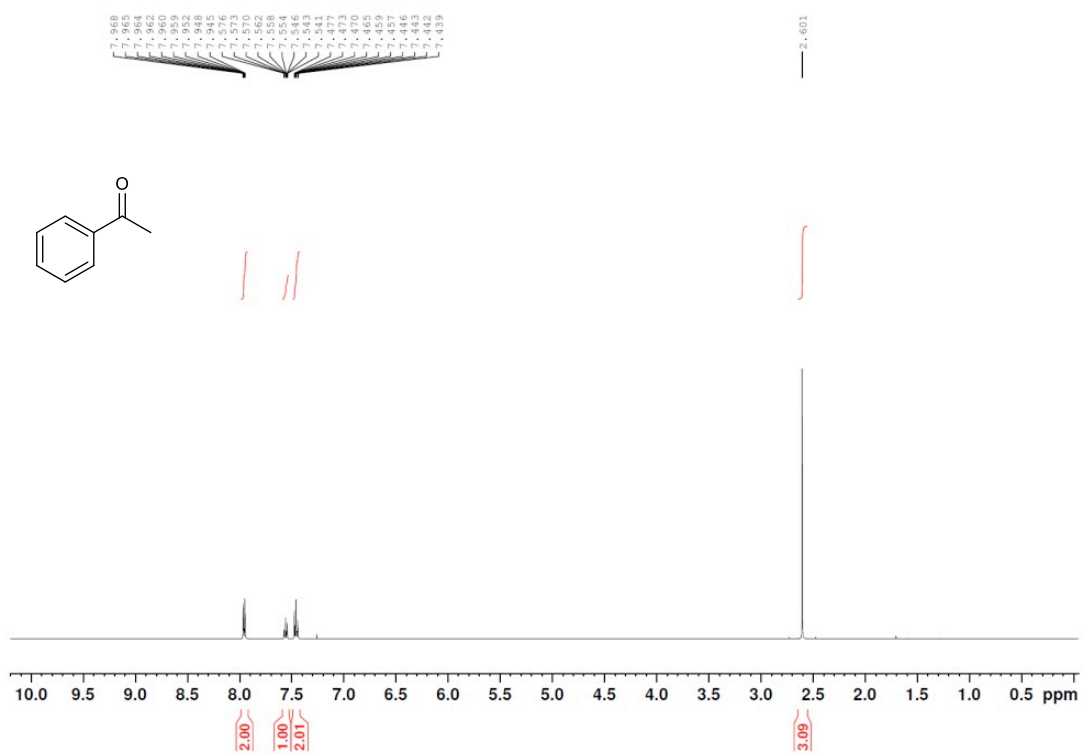
References

1. Ion stand-alone electrochemical reactor, https://www.vapourtec.com/products/flow-reactors/ion-stand-alone-electrochemical-reactor/ (accessed February 2023).

2. Gas Mass flowmeter and controllers, https://www.omega.co.uk/pptst/FMA5400A_5500A.html (accessed February 2023).

3. SF-10 reagent pump features, https://www.vapourtec.com/products/sf-10-pump-features/ (accessed February 2023).

4. Y. Imada, Y. Okada, K. Noguchi and K. Chiba, *Angew. Chem. Int. Ed.*, 2019, **58**, 125.