



Cite this: *Org. Biomol. Chem.*, 2017, **15**, 10010

Received 14th September 2017,
 Accepted 14th November 2017
 DOI: 10.1039/c7ob02300f
rsc.li/obc

Introduction

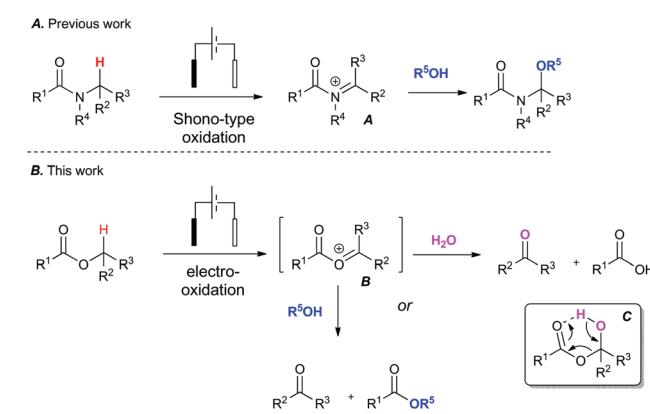
The controlled and chemo-selective oxidation of primary alcohols to aldehydes and secondary alcohols to the corresponding ketones are fundamental reactions in organic synthesis.¹ In turn, these aldehydes and ketones serve as precursors for a variety of complexity generating reactions.² However, the controlled oxidation of primary alcohols to aldehydes can be problematic due to over-oxidation to the carboxylic acid oxidation state.³ There are a range of versatile chemical oxidants available to the academic and industrial chemist that enable this transformation to be performed on demand.⁴ However, the majority of these oxidation reactions are stoichiometric in nature and therefore suffer from the generation of quantities of chemical waste.⁵

Recently, the field of electrosynthesis has undergone a renaissance⁶ and has found application in a variety of organic synthetic transformations, such as: C–H bond activation,⁷ total synthesis,⁸ and the Diels–Alder reaction⁹ amongst others.¹⁰ A fundamental advantage of the electrosynthesis approach is the replacement of the need to use stoichiometric oxidants and instead the oxidation reaction is performed on the electrode surface *via* quantum mechanical tunnelling¹¹ or through a mediator in solution.¹²

To address the challenge of identifying a cleaner oxidation, we explored the use of electrosynthesis to replace the need for both a chemical oxidant and mediator in these Redox trans-

formations. The simultaneous removal of oxidant and mediator would minimise chemical waste associated with the reaction. We have recently investigated the Shono-type oxidation of C–H bonds adjacent to a tertiary amide¹³ and our initial foray into this area began with attempting to expand the scope of the amide oxidation to esters (Fig. 1). It is known that the Shono electro-oxidation of amides proceeds through an *N*-acyl iminium species (**A**).¹⁴ It was therefore postulated that a transient *O*-acyloxonium species (**B**)¹⁵ could form under similar electro-oxidative conditions in esters bearing an α -methylene or methide group.

This unstable *O*-acyloxonium species (**B**) would in turn react further with adventitious water to form the aldehyde product and a carboxylic acid as a by-product *via* intermediate (**C**). Alternatively, an ester and aldehyde product could potentially form when conducted in an alcohol. To the best of our knowledge there are only limited reports of electro-oxidative cleavage of an ester group.¹⁶



^aDepartment of Chemical Engineering, University of São Paulo, Brazil

^bDivision of Chemistry and Environmental Science, Manchester Metropolitan University, M1 5GD, UK

^cSchool of Pharmacy, University of Birmingham, Edgbaston, B15 2TT, UK.

E-mail: a.m.jones.2@bham.ac.uk

† Electronic supplementary information (ESI) available: Copies of ¹H and ¹³C NMR spectra and cyclic voltammetry measurements (PDF). See DOI: 10.1039/c7ob02300f



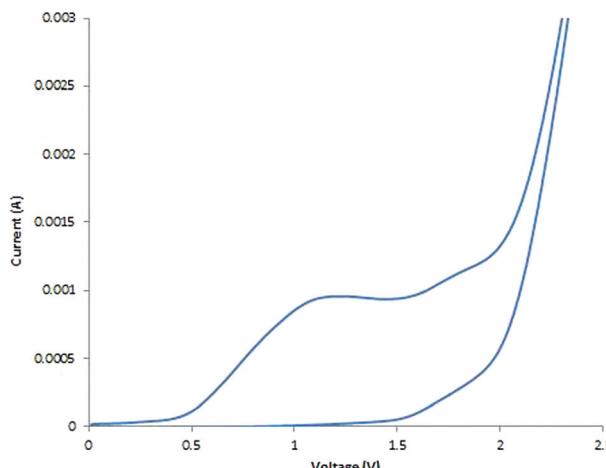


Fig. 2 Cyclic voltammetry measurement on substrate **1a** (5 mM) at a scan rate of 10 mV s⁻¹ in 9:1 acetonitrile : methanol and TBAP (0.5 M) using an RVC working electrode, RVC counter electrode and a Ag/AgCl reference electrode.

Results and discussion

To probe whether this methodological leap was indeed feasible, a collection of benzylic acetates were prepared including the parent benzyl acetate **1a**, a mild electron donating example **1b** and a mild electron withdrawing example **1c** (structures shown in Table 2). Cyclic voltammetry was recorded for **1a** (Fig. 2).

Using a sensitive measurement of 10 mV s⁻¹ scan rate it was observed in both electrolyte systems (LiClO_4 and Bu_4NClO_4)¹⁷ that oxidation waves for all three substrates were observed with +1.0 V (**1a**), +1.2 V (**1b**) and +0.9 V (**1c**) oxidation potentials (relative to Ag/AgCl) and a slightly improved peak current (I_p) measurement in Bu_4NClO_4 . On the basis of this positive oxidation result, screening of potential conditions to enable viable electro-oxidation of model benzylic acetate **1a** was attempted (Table 1).

In the first instance, potentiostatic conditions were screened with **1a** (entries 1–8) using both Bu_4NClO_4 and LiClO_4 as the electrolyte. The applied voltage was varied around the observed oxidation potential for **1a** (cyclic voltammetry measurement, +1.0 V) with up to an extra 300 mV applied to compensate for expected iR drop across the electrode surface.¹⁸ In all cases, the reaction was performed until $F \text{ mol}^{-1}$ equivalent to 4 electrons per mole of substrate was passed or starting material consumption was observed. Near the oxidation potential of **1a** trace conversion to the desired aldehyde **2a** was observed in both electrolyte systems (entries 3, 4 and 6, 7, respectively). However, at higher applied voltages degradation products were observed (entries 5 and 8, respectively), coupled with excessive time required for sufficient charge to be passed (24 h to 5 days), a controlled voltage approach was ruled out in this system early on. Switching to a galvanostatic approach, using the same electrolyte systems and

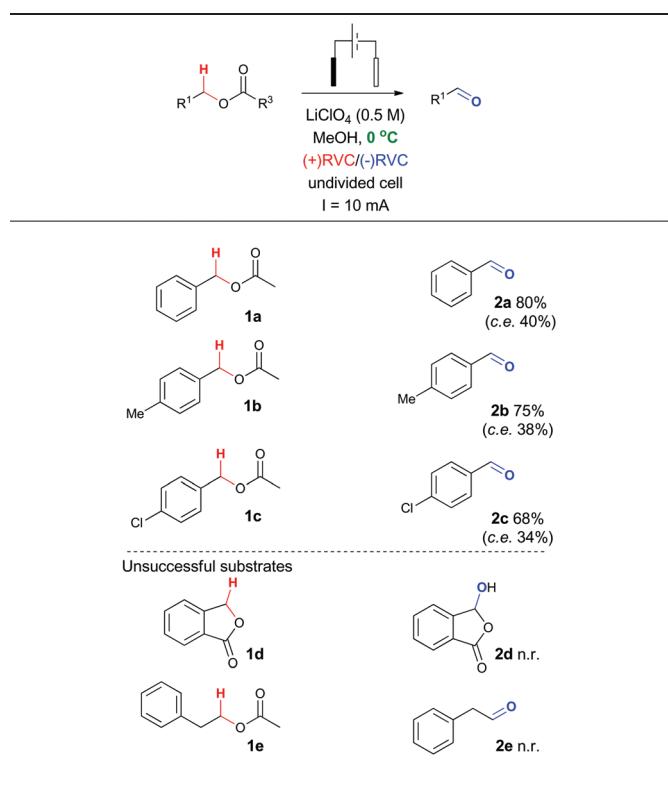
Table 1 Reaction condition optimisation for **1a** to **2a**

Entry	Electrolyte	Solvent	Voltage (mV)	Current (mA)	Conversion (%)
1	Bu_4NClO_4	MeCN/ MeOH	+900	—	0
2	Bu_4NClO_4	MeCN/ MeOH	+1000	—	0
3	Bu_4NClO_4	MeCN/ MeOH	+1100	—	<5
4	Bu_4NClO_4	MeCN/ MeOH	+1200	—	<5
5	Bu_4NClO_4	MeCN/ MeOH	+1300	—	Degradation
6	LiClO_4	MeCN/ MeOH	+1100	—	<10
7	LiClO_4	MeCN/ MeOH	+1200	—	<10
8	LiClO_4	MeCN/ MeOH	+1300	—	Degradation
9	Bu_4NClO_4	MeCN/ MeOH	—	20	27
10	Bu_4NClO_4	MeOH	—	20	34
11	Bu_4NClO_4	MeOH	—	10	49
12	LiClO_4	MeCN/ MeOH	—	20	25
13	LiClO_4	MeOH	—	20	57
14	LiClO_4	MeOH	—	10	84
15	LiClO_4	MeOH/ H_2O	—	10	38
16	LiClO_4	MeOH	—	—	0

reticulated vitreous carbon (RVC) electrodes produced more promising results (entries 9–15).

In particular, it was observed that a single solvent system gave higher yields than the previously optimized solvent system for the Shono oxidation,¹³ acetonitrile-methanol (entries 9 vs. 10 and 12 vs. 13, respectively). Lowering the current density across the electrode surface from an applied 20 mA to 10 mA, led to a doubling in reaction time (approx. 5–6 h) and a concomitant improvement in reaction yield in both electrolyte systems (entries 11 vs. 10 and 14 vs. 13, respectively). Lowering the current rate further led to modest improvements in conversion but unacceptable lengthening of the reaction time. It became clear that lithium perchlorate was superior to tetrabutylammonium perchlorate (entry 14 vs. 11) plus coupled with its ease of separation from the reaction products, was selected as the electrolyte. To probe whether additional water improved the reaction yield (entry 15) based on a postulated mechanism led to a reduced yield versus entry 14. Furthermore, passing no electrical current led to no reaction (entry 16). To test the hypothesis that C–H bond oxidation adjacent to an ester was possible, a collection of benzylic esters were prepared. Our initial results are detailed in Table 2. It was found using the optimised conditions, appreciable amounts of the desired aldehyde (**2a–2c**) were obtained from the benzylic acetates (**1a–1c**). To address, the mechanism issue identified in Fig. 1, a simple aqueous base wash removed the by-product. However, there were still limitations to this approach for example electro-oxidation of cyclic benzylic ester **1d** or homologated ester **1e**, did not



Table 2 Electro-oxidation of benzylic and homologated esters (n.r. = no reaction, c.e. = current efficiency)

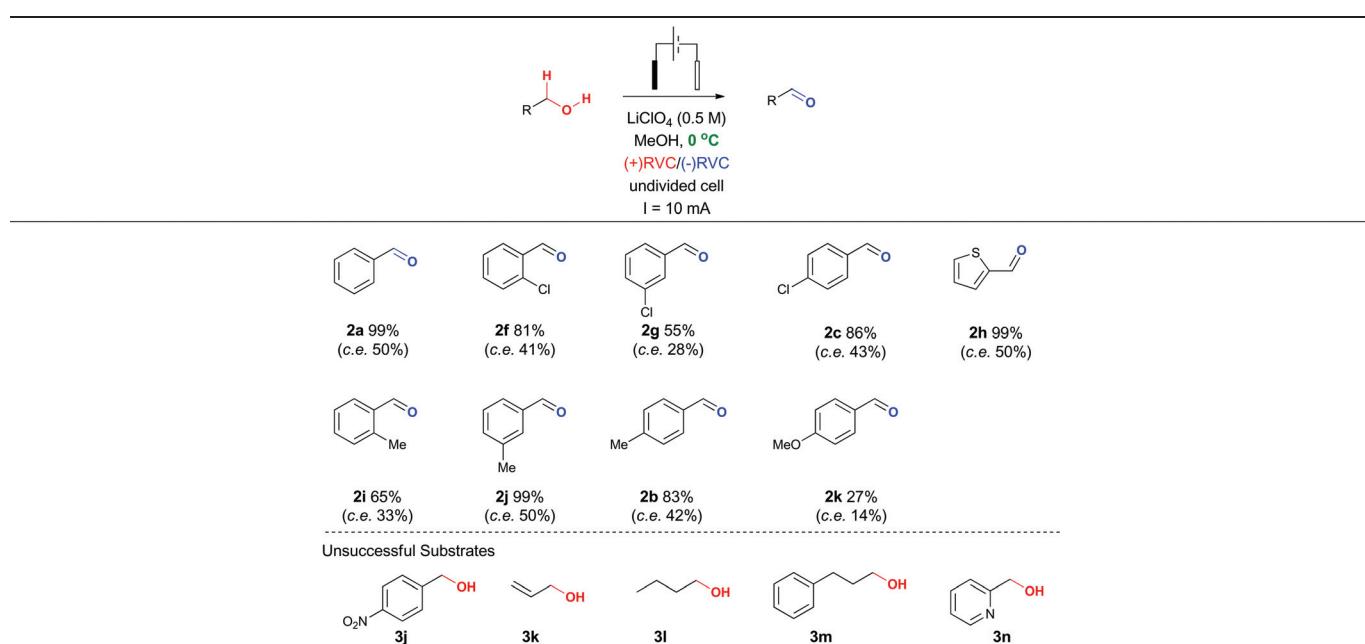
afford the aldehyde **2d** and **2e**, respectively. These limitations coupled with the use of an acyl ancillary group still did not meet our green chemistry standards due to the additional

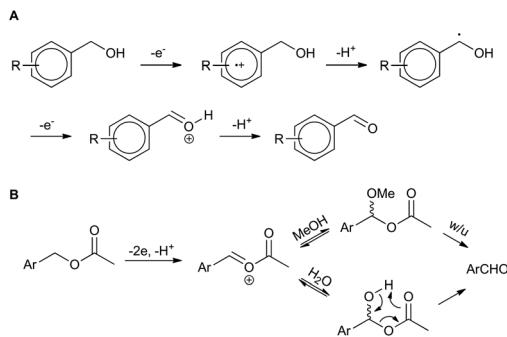
manipulation step required to prepare the acetate. We therefore considered whether a stabilising group on the heteroatom adjacent to the C–H bond was essential for successful electro-oxidation. Promisingly, cyclic voltammetry measurements on benzyl alcohol **3a** showed an oxidation wave at +1.2 V relative to Ag/AgCl.¹⁹ Using our previously optimised conditions for the ester electro-oxidation we explored the direct, mediator-free, oxidation on a range of commercially available alcohols (Table 3).

It was possible to cleanly convert benzyl alcohol (**3a**) to benzaldehyde (**2a**) under the mild conditions of lithium perchlorate in methanol in near quantitative yield and in improved yield compared to the chemical manipulation of forming the benzyl acetate (99% vs. 80%, respectively).²⁰ The scope of this reaction was further investigated *via* exploration of the effects of electron withdrawing and donating group around the ring system and steric effects around the reacting centre. The use of a chlorine atom as an electron withdrawing group in the *ortho*- (**2f**, 81%), *meta*- (**2g**, 55%) and *para*- (**2h**, 86%) positions was well tolerated. The use of a methyl group as a mild electron donating group in the *ortho*- (**2i**, 65%), *meta*- (**2j**, 99%) and *para*- (**2b**, 83%) positions also afforded good to excellent yields of the aldehyde.

Intriguingly, a strong electron donating group *para* to the reacting centre (from *para*-methoxy benzyl alcohol) resulted in a greatly reduced yield of aldehyde **2k** (27%). The relatively low yield of **2k** compared with other benzaldehydes is likely to be due to the *para*-methoxy group stabilizing the carbon-centred benzylic radical leading to further unproductive reaction pathways and oxidative decomposition of **2k**.

The result for a strongly electron withdrawing group in the 4-position of the substrate **3j** afforded only trace conversion to

Table 3 Results of direct alcohol electro-oxidation to aldehydes (c.e. = current efficiency)



Scheme 1 Proposed mechanisms for (a) benzyl alcohol and (b) benzyl acetate electro-oxidation (w/u = work-up).

the desired product as a result of the highly electron withdrawing nature of the *para*-nitro group. Based on the experimental results above and EPR literature²¹ of related systems a tentative mechanism can be proposed (Scheme 1A).

Electro-oxidation of the benzyl alcohol reveals a benzyl radical, subsequent oxidation of the hydroxyl group will deliver an aldehyde after deprotonation. Similarly, the benzylic acetate system could proceed *via* analogous initial steps to an *O*-acyloxonium species that could be trapped with water or methanol to deliver a hemiacetal or acetal species, respectively. In turn, the hemi-acetal or acetal intermediate would collapse upon work-up to deliver the aldehyde (Scheme 1B). We have shown that mild electron withdrawing and donating groups are tolerated in both systems but those that strongly donate or withdraw electrons were less compatible with direct electro-oxidation. Nitrogen containing heterocycle (**3n**) and non-benzylic substrates (**3k–3m**) gave trace conversion (<5%) to the aldehyde. However, changing the benzene ring to a thiophene was successful, affording aldehyde **2h** in quantitative yield, demonstrating the utility of the approach in other classes of heterocyclic systems.

Conclusion

The use of mediator-free, galvanostatic, direct electro-oxidation of benzylic alcohols and acetates shows scope on a range of substrates and offers an alternative and complementary approach to the preparation of valuable aldehydes. Mechanistic investigations to determine the sequence of electro-oxidation steps are now underway.

Experimental section

General methods

Reactions were carried out under nitrogen. Organic solutions were dried over MgSO_4 . Starting materials were purchased from commercial suppliers and were used without further purification. Solvents were dried over molecular sieves (3–4 Å). Flash silica chromatography was performed using Sigma-

Aldrich high-purity grade, pore size 60 Å, 200–400 mesh particle size silica gel. ^1H and ^{13}C NMR spectra were recorded on a JEOL ECS 400 NMR Spectrometer at 400 MHz or Bruker AVIII 300 or 400 MHz spectrometers. Chemical shifts (δ) are reported relative to TMS ($\delta = 0$) and/or referenced to the solvent in which they were measured. All chemical shifts (δ) are reported in parts per million, and coupling constants (J) are reported in Hertz. Low and High-resolution mass spectrometry analysis were obtained using an Agilent 6450 LC-MS/MS system. Infrared (IR) spectra were recorded on a ThermoScientific Nicolet Impact-380 ATR-FTIR spectrometer. Electrosynthesis and cyclic voltammetry were performed using a Metrohm Autolab PGSTAT100N with a 10 Amp Booster (Metrohm Autolab, UK) with an undivided electrochemical cell. Data was processed using Autolab Nova software (version 2.0). The electrode system for electrosynthesis consisted of two reticulated vitreous carbon (RVC) electrodes (supplier: ERG Aerospace; specifications: 45 pores per inch (PPI); 800 square foot per cubic foot; size $20 \times 11 \times 5$ mm) for galvanostatic reactions plus an additional *pseudo* Ag/AgCl reference electrode for potentiostatic reactions. Please see ref. 13 for further details and images of the reaction set-up.

General procedures and safety statements

Preparation of benzyl acetates.²² A round bottom flask equipped with a magnetic stirrer was charged with the appropriate benzyl alcohol (10.0 mmol) and acetic anhydride (15.0 mmol). The reaction mixture was refluxed (85 °C) for 15 h. Upon cooling to room temperature the reaction mixture was poured into water (50 mL). The aqueous phase was extracted with ethyl acetate (30 mL \times 3). The combined organic phase was washed with 1 M aq HCl (30 mL), saturated aq NaHCO_3 (30 mL), water (30 mL), brine (30 mL), and dried (MgSO_4). The solvent was evaporated under reduced pressure to afford the title compound without further purification.

Electrosynthetic oxidation reactions. A sealable electrochemical cell equipped with a magnetic stirrer was added anhydrous methanol (10 mL), lithium perchlorate (0.53 g [0.50 M]) and the alcohol (0.5 mmol [0.05 M]) or the benzyl acetate (0.5 mmol [0.05 M]) under study. Two reticulated vitreous carbon (RVC) electrodes were inserted into the solution at a distance of approximately 0.5 cm from each other and the vial sealed. The solution was cooled to 0 °C (ice-bath) and degassed with nitrogen. A fixed current (10 mA) was passed through the solution in an ice bath until the desired charge (Q) was transferred (on average $t = 5.5$ h). Upon completion of the reaction, the solvent was evaporated (at 35 °C), the residual oil was partitioned between water (10 mL) and ethyl acetate (5 mL \times 3). The combined organic extracts were dried (MgSO_4) and evaporated. Analytical quality sample of the aldehyde/ketone was obtained by column chromatography (SiO_2 ; cyclohexane–ethyl acetate) to afford the title compound.

Cyclic voltammetry studies. An undivided glass cell equipped with a rectangular reticulated vitreous carbon (RVC) anode (11 cm²) and rectangular RVC cathode (11 cm²), arranged opposite to one another at a distance of 3.0 mm with



a Ag/AgCl *pseudo* reference electrode placed 1.0 mm from the working electrode. To this reaction vessel was added the analyte under study (5.0 mM) in the relevant organic solvent(s) (total volume 6.0 mL) and electrolyte (*e.g.* tetrabutylammonium perchlorate (0.5 M)). Scan rate was varied using the Autolab Nova 2.0 software.

Caution: Perchlorates – May intensify fire. In combination with flammable solvents, all sources of ignition should be avoided. During the concentration stage of the work-up, low temperature rotary evaporation with a suitable shield should be employed. The aqueous layer (after extraction) was treated with excess sodium sulphite prior to disposal.

Caution: Passing an electrical current through flammable organic solvent – The potentiostat and wiring should be regularly inspected for faults and pass all relevant electrical tests prior to use.

Spectroscopic data

Benzyl acetate (1a).²³ The title compound was afforded as a clear oil (0.85 g, 56%) using general procedure A. ¹H NMR (400 MHz, CDCl₃) δ 7.42–7.29 (m, 5H), 5.12 (s, 2H), 2.11 (s, 3H) ppm; ¹³C NMR (100.1 MHz, CDCl₃) δ 171.0, 136.0, 128.7, 128.4, 128.3, 66.4, 21.1 ppm; *m/z* (ESI) = 151 [M + H]⁺. Spectroscopic data are in accordance with literature.

4-Methylbenzyl acetate (1b).²⁴ The title compound was afforded as a clear oil (0.78 g, 48%) using general procedure A. ¹H NMR (400 MHz, CDCl₃) δ 7.34–7.23 (m, 2H), 7.23–7.10 (m, 2H), 5.07 (s, 2H), 2.36 (s, 3H), 2.08 (s, 3H) ppm; ¹³C NMR (100.1 MHz, CDCl₃) δ 171.1, 138.2, 133.0, 129.3, 128.5, 66.4, 21.3, 21.2 ppm; *m/z* (ESI) = 165 [M + H]⁺. Spectroscopic data are in accordance with literature.

4-Chlorobenzyl acetate (1c).²⁵ The title compound was afforded as a clear oil (0.98 g, 53%) using general procedure A. ¹H NMR (400 MHz, CDCl₃) δ 7.34–7.30 (m, 2H), 7.30–7.25 (m, 2H), 5.05 (s, 2H), 2.08 (s, 3H) ppm; ¹³C NMR (100.1 MHz, CDCl₃) δ 170.9, 134.5, 134.2, 129.7, 128.8, 65.6, 21.1 ppm; *m/z* (ESI) = 185 [M³⁵Cl + H]⁺, 187 [M³⁷Cl + H]⁺. Spectroscopic data are in accordance with literature.

Phenylethyl acetate (1e).²⁶ The title compound was afforded as a clear oil (0.58 g, 36%) using general procedure A. ¹H NMR (400 MHz, CDCl₃) δ 7.34–7.19 (m, 5H), 4.27 (t, *J* = 7.0 Hz, 2H), 2.99–2.83 (t, *J* = 7.0 Hz, 2H), 2.03 (s, 3H) ppm; *m/z* (ESI) = 165 [M + H]⁺. Spectroscopic data are in accordance with literature.

Benzaldehyde (2a).²⁷ The title compound was afforded as a colourless oil (52 mg, 99%) using general procedure B (from benzyl alcohol, 3a). Alternatively, the title compound (42 mg, 80%) was prepared using general procedure B (from benzyl acetate, 1a). ¹H NMR (300 MHz, CD₃OD) δ 10.01 (s, 1H), 7.91–7.85 (m, 2H), 7.68–7.63 (m, 1H), 7.60–7.45 (m, 2H) ppm; ¹³C NMR (100.1 MHz, CD₃OD) δ 192.6, 136.4, 134.6, 129.9, 129.1 ppm; *m/z* (ESI) 106 [M]⁺. Spectroscopic data are in accordance with literature.

4-Methylbenzaldehyde (2b).²⁸ The title compound was afforded as a colourless oil (50 mg, 83%) using general procedure B (from 4-methylbenzyl alcohol, 3b). Alternatively, the title compound (90 mg, 75%) was prepared using general pro-

cedure B (from 4-methylbenzyl acetate, 1b). ¹H NMR (300 MHz, CD₃OD) δ 9.95 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H) ppm; ¹³C NMR (100.1 MHz, CD₃OD) δ 191.9, 145.5, 134.2, 129.8, 129.7, 21.7 ppm; *m/z* (ESI) 121 [M + H]⁺. Spectroscopic data are in accordance with literature.

4-Chlorobenzaldehyde (2c).²⁸ The title compound was afforded as a white powder (60 mg, 86%) using general procedure B (from 4-chlorobenzyl alcohol, 3c). Alternatively, the title compound (48 mg, 68%) was prepared using general procedure A (from 4-chlorobenzyl acetate, 1c). ¹H NMR (300 MHz, CDCl₃) δ 10.00 (s, 1H), 7.94–7.78 (m, 2H), 7.71–7.43 (m, 2H) ppm; ¹³C NMR (100.1 MHz, CDCl₃) δ 190.1, 140.7, 134.5, 130.1, 129.2 ppm; *m/z* (ESI) 139 [M – H]⁺. Spectroscopic data are in accordance with literature.

2-Chlorobenzaldehyde (2f).²⁸ The title compound was afforded as a colourless oil (57 mg, 81%) using general procedure B (from 2-chlorobenzyl alcohol, 3d). ¹H NMR (300 MHz, CDCl₃) δ 10.48 (s, 1H), 7.92–7.89 (m, 1H), 7.56–7.50 (m, 1H), 7.49–7.42 (m, 2H) ppm; ¹³C NMR (100.1 MHz, CDCl₃) δ ppm 190.0, 138.2, 135.2, 132.5, 130.7, 129.5, 127.4 ppm; *m/z* (ESI) 139 [M – H]⁺; Hi-Res LC-MS (ESI) *m/z* calcd for C₇H₅OCl [M – H]⁺ 138.9956, found 138.9961. Spectroscopic data are in accordance with literature.

3-Chlorobenzaldehyde (2g).²⁸ The title compound was afforded as a colourless oil (39 mg, 55%) using general procedure B (from 3-chlorobenzyl alcohol). ¹H NMR (300 MHz, CDCl₃) δ 9.97 (s, 1H) 7.89–7.83 (m, 1H) 7.79–7.73 (m, 1H) 7.51–7.45 (m, 2H) ppm; ¹³C NMR (100.1 MHz, CDCl₃) δ 190.8, 137.8, 135.4, 134.5, 130.5, 129.4, 127.8 ppm; *m/z* (ESI) 139 [M – H]⁺. Spectroscopic data are in accordance with literature.

Thiophene-2-carbaldehyde (2h).²⁹ The title compound was afforded as a pale yellow oil (55 mg, 99%) using general procedure B (from 2-thiophenemethanol). ¹H NMR (400 MHz, CDCl₃) δ 9.95 (d, *J* = 1.3 Hz, 1H), 7.78 (ddd, *J* = 5.0, 3.8, 1.2 Hz, 2H), 7.22 (dd, *J* = 5.0, 3.8 Hz, 1H) ppm; ¹³C NMR (100.1 MHz, CDCl₃) δ 183.0, 144.0, 136.3, 135.1, 128.3 ppm; *m/z* (ESI) 111 [M – H]⁺. Spectroscopic data are in accordance with literature.

2-Methylbenzaldehyde (2i).²⁷ The title compound was afforded as a colourless oil (39 mg, 65%) using general procedure B (from 2-methylbenzyl alcohol). ¹H NMR (300 MHz, CDCl₃) δ 10.29 (s, 1H), 7.82 (d, *J* = 7.3 Hz, 1H), 7.51–7.31 (m, 3H), 2.69 (s, 3H) ppm; ¹³C NMR (100.1 MHz, CDCl₃) δ 192.7, 140.2, 133.9, 133.5, 131.9, 131.5, 126.1, 20.1 ppm; *m/z* (ESI) 121 [M + H]⁺; Hi-Res LC-MS (ESI) *m/z* calcd for C₈H₈O [M + H]⁺ 121.0648, found 121.0644. Spectroscopic data are in accordance with literature.

3-Methylbenzaldehyde (2j).³⁰ The title compound was afforded as a clear oil (59 mg, 99%) using general procedure B (from 3-methylbenzyl alcohol). ¹H NMR (300 MHz, CDCl₃) δ 9.98 (s, 1H), 7.77–7.58 (m, 2H) 7.48–7.38 (m, 2H), 2.43 (s, 3H) ppm; ¹³C NMR (100.1 MHz, CDCl₃) δ 192.8, 138.4, 136.5, 135.4, 130.1, 129.0, 127.3, 21.5 ppm; *m/z* (ESI) 121 [M + H]⁺. Spectroscopic data are in accordance with literature.

4-Methoxybenzaldehyde (2k).²⁷ The title compound was afforded as a colourless oil (18 mg, 27%) using general pro-



cedure B (from 4-methoxybenzyl alcohol). ^1H NMR (300 MHz, CDCl_3) δ ppm 9.88 (s, 1H) 7.88–7.78 (m, 2H) 7.09–6.95 (m, 2H) 3.89 (s, 3H); ^{13}C NMR (100.1 MHz, CDCl_3) δ 190.4, 164.3, 131.5, 129.8, 113.9, 55.6 ppm; m/z (ESI) 135 [$\text{M} - \text{H}$] $^+$; Hi-Res LC-MS (ESI) m/z calcd for $\text{C}_8\text{H}_8\text{O}_2$ [$\text{M} - \text{H}$] $^+$; 135.0452, found 135.0454. Spectroscopic data are in accordance with literature.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

A. M. J. thanks the Royal Society of London (United Kingdom) for the award of a research grant (RG150135). The authors thank the analytical services at Manchester Metropolitan University and the Centre for Chemical and Materials Analysis in the School of Chemistry at the University of Birmingham for analytical support. The NMR instruments used in this research were obtained through Birmingham Science City: Innovative Uses for Advanced Materials in the Modern World (West Midlands Centre for Advanced Materials Project 2), with support from Advantage West Midlands (AWM) and part funded by the European Regional Development Fund (ERDF).

Notes and references

- (a) G. Tojo and M. I. Fernandez, *Oxidation of Alcohols to Aldehydes and Ketones: A Guide to Current Common Practice*, Springer, New York, 2006; (b) G. Franz and R. A. Sheldon, *Oxidation*, in *Ullmann's Encyclopaedia of Industrial Chemistry*, VCH-Verlag, Weinheim, 2000; (c) R. C. Larock, *Comprehensive Organic Transformations*, Wiley, New York, 2nd edn, 1999.
- (a) D. Lee, J. K. Sello and S. L. Schreiber, *Org. Lett.*, 2000, **2**, 709; (b) A. F. Abdel-Magid and S. J. Mehrman, *Org. Process Res. Dev.*, 2006, **10**, 971.
- M. Sankar, E. Nowicka, E. Carter, D. M. Murphy, D. W. Knight, D. Bethell and G. J. Hutchings, *Nat. Commun.*, 2014, **5**, 3332.
- (a) D. Könning, T. Olbrisch, F. D. Sypaseuth, C. C. Tzschucke and M. Christmann, *Chem. Commun.*, 2014, **50**, 5014; (b) J. E. Steves and S. S. Stahl, *J. Am. Chem. Soc.*, 2013, **135**, 15742; (c) S. B. Ley, J. Norman, W. P. Griffith and S. P. Marsden, *Synthesis*, 1994, 639.
- A. N. Campbell and S. S. Stahl, *Acc. Chem. Res.*, 2012, **45**, 851.
- (a) E. J. Horn, B. R. Rosen and P. S. Baran, *ACS Cent. Sci.*, 2016, **2**, 302; (b) E. J. Horn, B. R. Rosen, Y. Chen, J. Tang, K. Chen, M. D. Eastgate and P. S. Baran, *Nature*, 2016, **533**, 78; (c) M. Yan, Y. Kawamata and P. S. Baran, *Chem. Rev.*, 2017, **117**, 13230.
- (a) S. Liang, C.-C. Zeng, H.-Y. Tian, B.-G. Sun, X.-G. Luo and F. Z. Ren, *J. Org. Chem.*, 2016, **81**, 11565; (b) R. Hayashi, A. Shimizu, Y. Song, Y. Ashikari, T. Nokami and J.-I. Yoshida, *Chem. – Eur. J.*, 2016, **23**, 61; (c) Y. Kawamata, M. Yan, Z. Liu, D.-H. Bao, J. Chen, J. Starr and P. S. Baran, *J. Am. Chem. Soc.*, 2017, **139**, 7448; (d) A. G. O'Brien, A. Maruyama, Y. Inokuma, M. Fujita and P. S. Baran, *Angew. Chem., Int. Ed.*, 2014, **53**, 11868.
- B. R. Rosen, E. W. Werner, A. G. O'Brien and P. S. Baran, *J. Am. Chem. Soc.*, 2014, **136**, 5571.
- J. C. Moore, E. S. Davies, D. A. Walsh, P. Sharmaab and J. E. Moses, *Chem. Commun.*, 2014, **50**, 12523.
- P. Du, J. L. Brosmer and D. G. Peters, *Org. Lett.*, 2011, **13**, 4072.
- S. G. Christov, *Ber. Bunsenges. Phys. Chem.*, 1975, **79**, 357.
- (a) R. Ciriminna, M. Ghahremani, B. Karimi and M. Pagliaro, *ChemistryOpen*, 2017, **6**, 5; (b) A. Badalyan and S. S. Stahl, *Nature*, 2016, **535**, 406; (c) C.-B. Bai, N.-X. Wang, X.-W. Lan, Y.-J. Wang, Y. Xing, J.-L. Wen, X.-W. Gao and W. Zhang, *Sci. Rep.*, 2016, **6**, 20163.
- (a) A. M. Jones and C. E. Banks, *Beilstein J. Org. Chem.*, 2014, **10**, 3056; (b) P. Alfonso-Suárez, A. V. Koliopoulos, J. P. Smith, C. E. Banks and A. M. Jones, *Tetrahedron Lett.*, 2015, **56**, 6863.
- T. Shono, Y. Matsumura and K. Tsubata, *J. Am. Chem. Soc.*, 1981, **103**, 1172.
- A. K. Ghosh, S. S. Kulkarni, C.-X. Xu and K. Shurrush, *Tetrahedron: Asymmetry*, 2008, **19**, 1020.
- (a) E. Baciocchi, M. Mattioli, R. Romano and R. Ruzziconi, *J. Org. Chem.*, 1991, **56**, 7154; (b) C.-C. Zeng and J. Y. Becker, *J. Org. Chem.*, 2004, **69**, 1053; (c) E. A. Mayeda, L. L. Miller and J. F. Wolf, *J. Am. Chem. Soc.*, 1972, **94**, 6812; (d) H. Lund, *Acta Chem. Scand.*, 1957, **11**, 491.
- Scan rate sweeps for **1a–1c** can be found in the ESI.†
- W. Oelßner, F. Berthold and U. Guth, *Mater. Corros.*, 2006, **57**, 455.
- Cyclic voltammetry measurements of **3a** are in the accompanying ESI.†
- Exposure of **3a** to lithium perchlorate in methanol without passing an electric current did not afford any **2a** after 12 h.
- L. Meng, J. Su, Z. Zha, L. Zhang, Z. Zhang and Z. Wang, *Chem. – Eur. J.*, 2013, **19**, 5542.
- J. M. Álvarez-Calero, Z. D. Jorge and G. M. Massanet, *Org. Lett.*, 2016, **18**, 6344.
- B. Janza and A. Studer, *J. Org. Chem.*, 2005, **70**, 6991.
- T. Mino, Y. Hasegawa, M. Sakamoto and T. Fujita, *J. Organomet. Chem.*, 2007, **692**, 4389.
- J. W. J. Bosco and A. K. Saikia, *Chem. Commun.*, 2004, 1116.
- C. B. Rao, D. C. Rao, D. C. Babu and Y. Venkateswarlu, *Eur. J. Org. Chem.*, 2010, 2855.
- C. K. Lin and T.-J. Lu, *Tetrahedron*, 2010, **66**, 9688–9693.
- K. Moriyama, M. Takemura and H. Togo, *J. Org. Chem.*, 2014, **79**, 6094.
- S. Imai and H. Togo, *Tetrahedron*, 2016, **72**, 6948.
- A. Kamimura, H. Komatsu, T. Moriyama and Y. Nozaki, *Tetrahedron*, 2013, **69**, 5968.

