

# EcoMnOx, a Biosourced Catalyst for Selective Aerobic Oxidative Cleavage of Activated 1,2-Diols

Vincent Escande,\* Chun Ho Lam, Claude Grison, and Paul T. Anastas\*

## Supporting Information

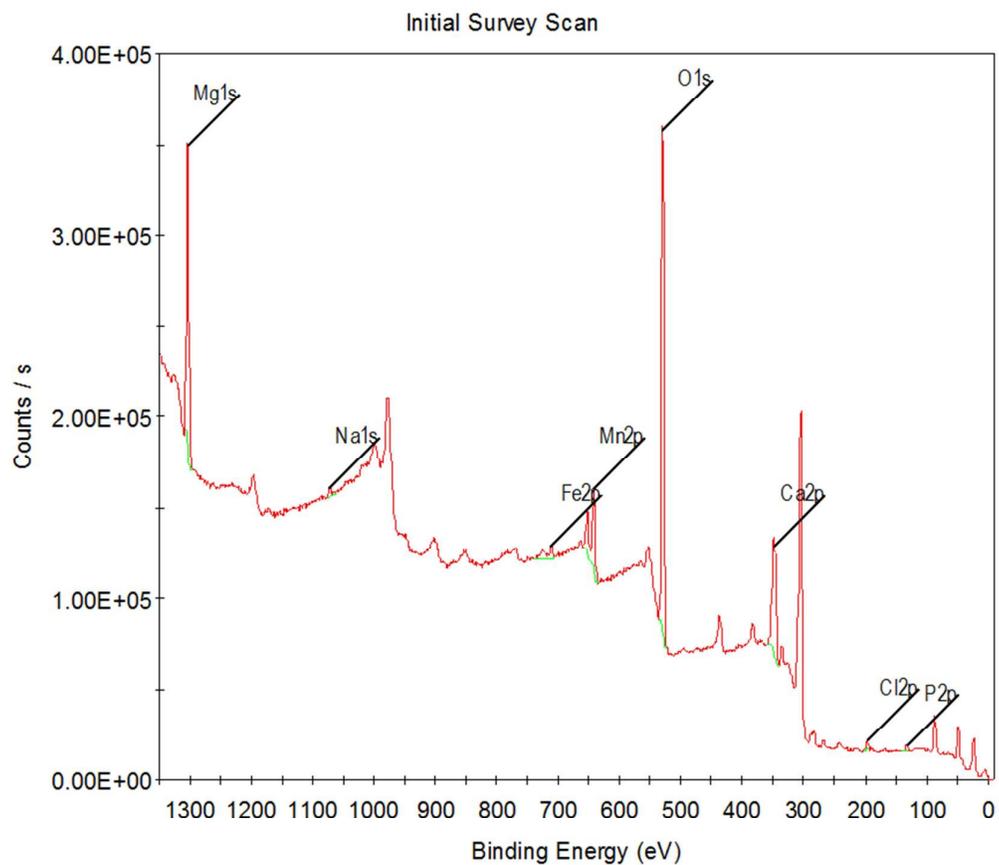
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## General methods

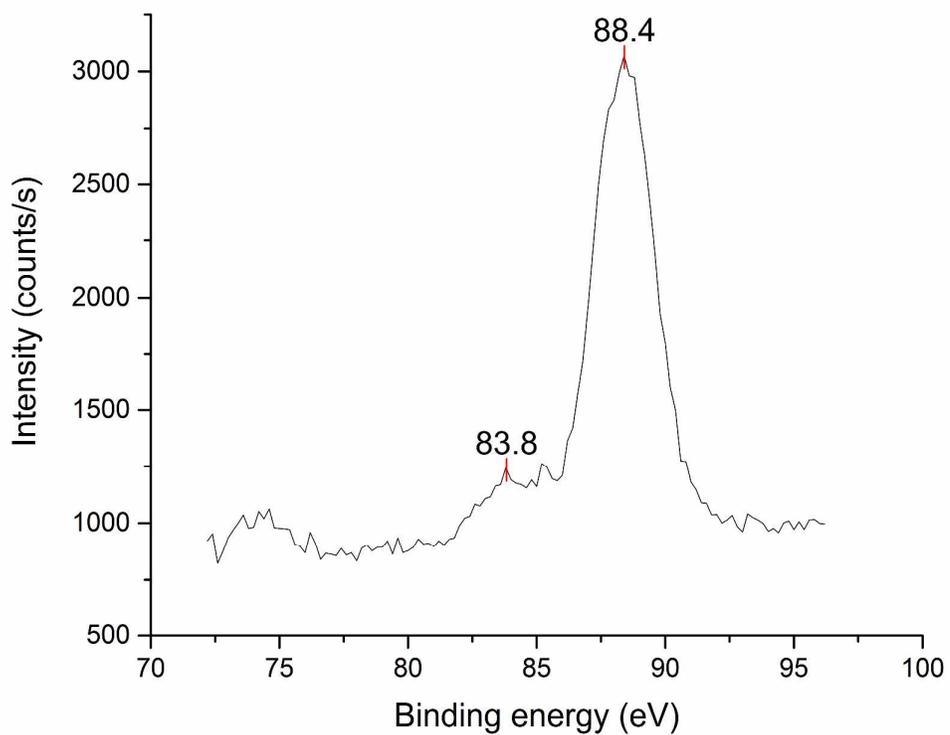
All common reagents and solvents were obtained from Sigma-Aldrich and Fisher Scientific, and were used without any further purification. Non-commercially available 1,2-diols were prepared by reduction of corresponding commercial diketones according to a known procedure.<sup>1</sup> Products were characterized by <sup>1</sup>H/<sup>13</sup>C NMR spectroscopy and by GC, by comparison of their retention times with those of pure standards, and analytical data were in accordance with those previously published. NMR characterization was performed with an Agilent DD2 400 MHz NMR spectrometer. GC were recorded on a Shimadzu GC-2010 Plus, equipped with an Agilent J&W GC column, DB-5, 60 m x 0.25 mm x 0.25 μm, using He as carrier gas, with a flame ionization detector (FID). All analyses were performed including dodecane as internal standard. FTIR spectra were recorded on a FTIR/Raman Thermo Nicolet 6700 spectrometer, in ATR mode. ICP-AES measurements were performed using the Perkin Elmer Optima 3000. Samples of 10 mg were digested and dissolved in 2% HNO<sub>3</sub> acid, and were quantified against external standards. SEM analyses were performed using the Hitachi SU-70 field emission microscope. Samples were pre-dried in vacuum overnight, and were examined with a 10kV beam power under ultra-high vacuum without surface treatment. Energy-dispersive X-ray spectroscopy analysis (EDX) was performed using a Zeiss EVO HD15 microscope coupled with an Oxford X-MaxN EDX detector. XRPD measurements were performed on a Rigaku SmartLab X-ray Diffractometer equipped with a Cu line-focus sealed tube and a NaI SC70 scintillation detector. Measurements were made with a 40 kV, 44 mA beam, with an incident slit of 2/3 deg and a length limiting slit of 5.00 mm, in the range 2θ from 10° to 90° locked couple scan type, a step size of 0.05° and a scan speed of 10.33 deg/min. XPS analysis was performed using a ThermoScientific ESCALAB 250 instrument. Spectra were collected using a monochromatic Al X-ray source. A low energy electron flood and top-side contact were used for charge neutralization. Survey spectra were collected using a pass energy of 150 eV. Multiplex composition scans were acquired with 20 eV pass energy. All dynamic light scattering (DLS) samples were suspended in methanol (1 mg/3 mL) and were sonicated for 5 minutes prior analysis. DLS was performed at an angle of 90 degrees (ALV-5000, ALV-GmbH) using an incident laser of wavelength 532 nm (coherent). 30 runs were recorded per sample, with a duration of 30 seconds per run. All DLS measurements were carried out at room temperature.

## XPS analysis



**Figure S1.** XPS survey spectrum of EcoMnOx.

XPS analysis shows the oxide nature of the polymetallic material.



**Figure S2.** XPS spectrum of Mn3s.

In spite of obscuration by the interfering Mg peak, Mn3s multiplet splitting (4.6 eV) is characteristic of  $\text{Mn}^{\text{IV}}$ .<sup>2</sup>

## ICP-AES analyses

**Table S1.** ICP-AES analysis of EcoMnOx catalysts prepared from different lots of *Grevillea exul* subsp. *rubiginosa*.

Type of catalyst	<i>G. exul</i> subsp. <i>rubiginosa</i>	Elements wt% ( $\pm$ sd)							
#batch number	Location of harvest (latitude and longitude)	Fe	Mn	Ni	Ca	Mg	Al	Na	K
EcoMn #1	« Col de Mourange » (-22.225415, 166.650282)	0.9 ( $\pm$ 0.008)	6.7 ( $\pm$ 0.04)	0.04 ( $\pm$ 0.0004)	10.4 ( $\pm$ 0.2)	5.3 ( $\pm$ 0.09)	0.2 ( $\pm$ 0.02)	2.0 ( $\pm$ 0.1)	4.3 ( $\pm$ 0.008)
EcoMnOx #1	« Col de Mourange » (-22.225415, 166.650282)	0.3 ( $\pm$ 0.006)	14.1 ( $\pm$ 0.4)	n.d. <sup>a</sup>	28.2 ( $\pm$ 0.2)	28.7 ( $\pm$ 0.3)	n.d. <sup>a</sup>	0.5 ( $\pm$ 0.09)	n.d. <sup>a</sup>
EcoMn #2	« Monts Kouanenoa » (-22.203329, 166.699232)	0.7 ( $\pm$ 0.003)	6.5 ( $\pm$ 0.04)	0.2 ( $\pm$ 0.0009)	7.9 ( $\pm$ 0.05)	5.4 ( $\pm$ 0.07)	0.3 ( $\pm$ 0.03)	0.8 ( $\pm$ 0.01)	3.8 ( $\pm$ 0.05)
EcoMnOx #2	« Monts Kouanenoa » (-22.203329, 166.699232)	1.3 ( $\pm$ 0.01)	10.0 ( $\pm$ 0.06)	0.07 ( $\pm$ 0.002)	18.7 ( $\pm$ 0.1)	29.5 ( $\pm$ 0.01)	0.6 ( $\pm$ 0.01)	n.d. <sup>a</sup>	n.d. <sup>a</sup>
EcoMn #3	« Rivière des Pirogues » (-22.187158, 166.721983)	0.3 ( $\pm$ 0.005)	2.7 ( $\pm$ 0.05)	0.02 ( $\pm$ 0.0004)	12.1 ( $\pm$ 0.4)	2.5 ( $\pm$ 0.02)	0.1 ( $\pm$ 0.01)	2.0 ( $\pm$ 0.03)	4.6 ( $\pm$ 0.07)
EcoMnOx #3	« Rivière des Pirogues » (-22.187158, 166.721983)	1.0 ( $\pm$ 0.005)	8.9 ( $\pm$ 0.05)	0.04 ( $\pm$ 0.0001)	22.5 ( $\pm$ 0.2)	8.3 ( $\pm$ 0.05)	0.5 ( $\pm$ 0.01)	n.d. <sup>a</sup>	n.d. <sup>a</sup>

<sup>a</sup>n.d.: not detected.

Comparison of several batches of EcoMn and their corresponding EcoMnOx, prepared from *Grevillea exul* subsp. *rubiginosa* harvested in different locations, shows some variation in elemental content, due to the natural origin of the biomass feedstock.

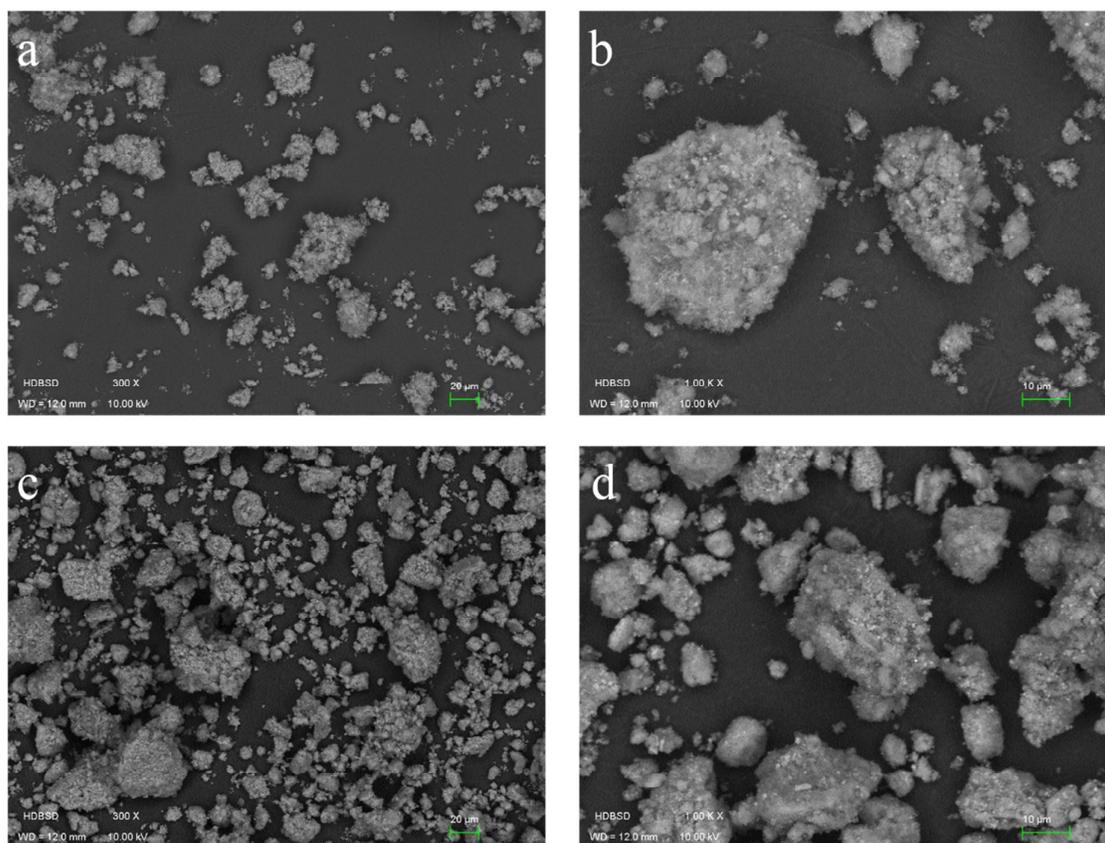
However, because the catalytic efficiency of EcoMnOx relies only on Mn content (other metal elements are spectator elements, as shown in Table 3), the different batches of EcoMnOx display the same performances when used in 10 mol% Mn for aerobic oxidative cleavage of *meso*-hydrobenzoin **1a**.

## Characterization of EcoMnOx after reaction

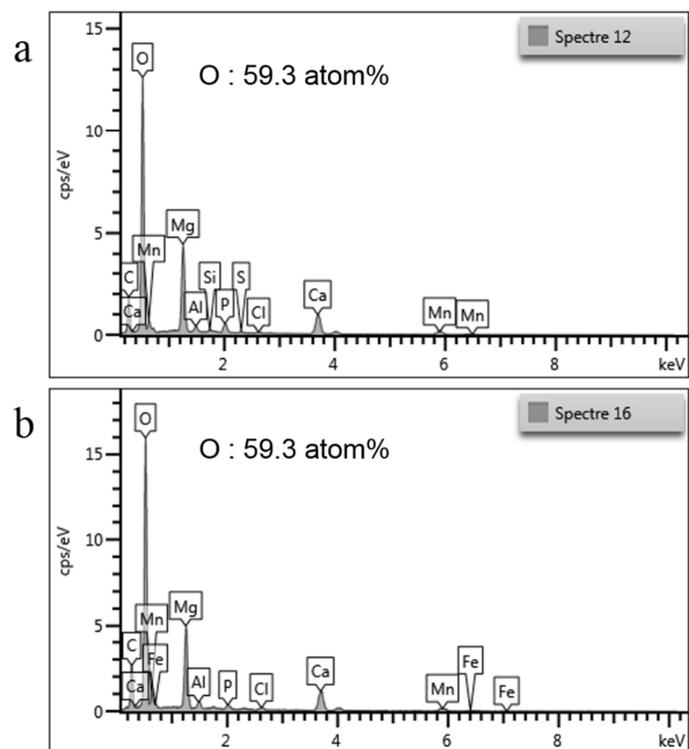
**Table S2.** ICP-AES analysis of EcoMnOx (EcoMnOx batch #3) before and after oxidative cleavage of *meso*-hydrobenzoin.

Type of catalyst	<i>G. exul</i> subsp. <i>rubiginosa</i>	Elements wt% ( $\pm$ sd)							
#batch number	Location of harvest (latitude and longitude)	Fe	Mn	Ni	Ca	Mg	Al	Na	K
EcoMnOx #3 (before reaction)	« Rivière des Pirogues » (-22.187158, 166.721983)	1.0 ( $\pm$ 0.005)	8.9 ( $\pm$ 0.05)	0.04 ( $\pm$ 0.0001)	22.5 ( $\pm$ 0.2)	8.3 ( $\pm$ 0.05)	0.5 ( $\pm$ 0.01)	n.d. <sup>a</sup>	n.d. <sup>a</sup>
EcoMnOx #3 (after reaction <sup>b</sup> )	« Rivière des Pirogues » (-22.187158, 166.721983)	1.2 ( $\pm$ 0.01)	8.8 ( $\pm$ 0.09)	0.05 ( $\pm$ 0.005)	24.2 ( $\pm$ 0.06)	8.2 ( $\pm$ 0.04)	0.5 ( $\pm$ 0.01)	n.d. <sup>a</sup>	n.d. <sup>a</sup>

<sup>a</sup>n.d.: not detected. <sup>b</sup>Catalyst recovered after centrifugation, rinsed with 2 x 4 mL of ethanol, and then dried in oven under air at 105 °C for 2 h.

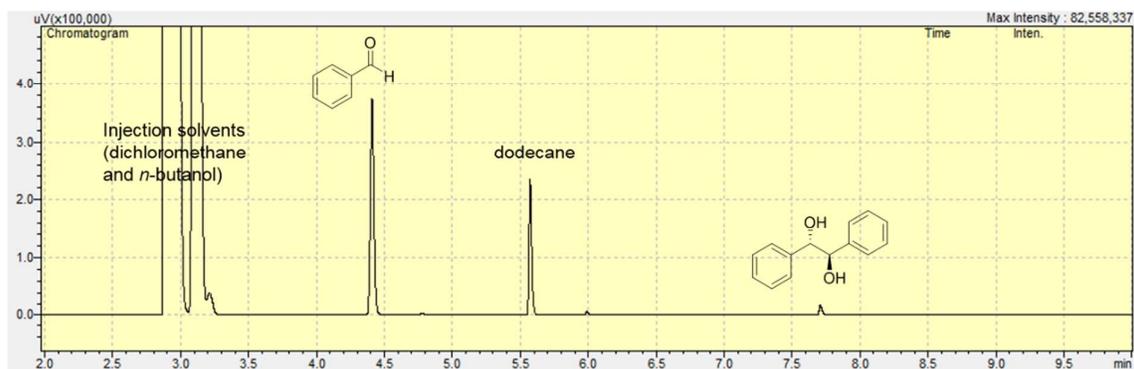


**Figure S3.** SEM images of EcoMnOx (EcoMnOx batch #3): a, b) before oxidative cleavage of *meso*-hydrobenzoin and c, d) after oxidative cleavage of *meso*-hydrobenzoin.

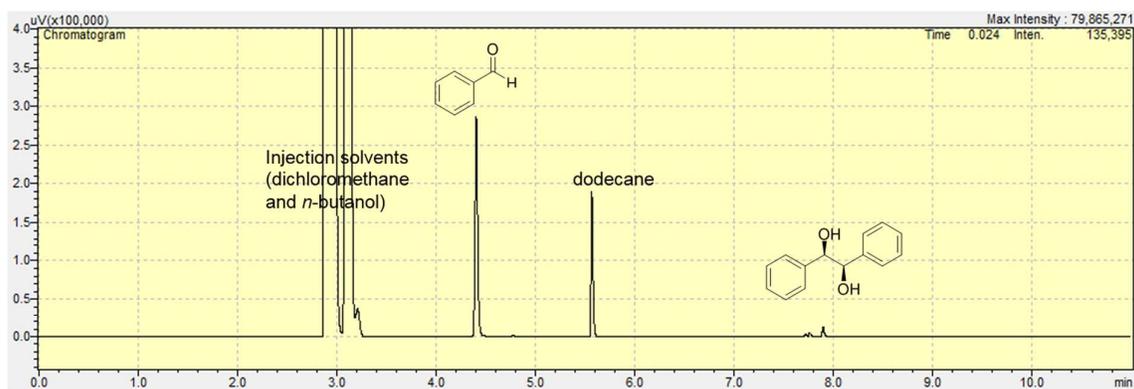


**Figure S4.** EDX spectra of EcoMnOx (EcoMnOx batch #3): a) before oxidative cleavage of *meso*-hydrobenzoin and b) after oxidative cleavage of *meso*-hydrobenzoin.

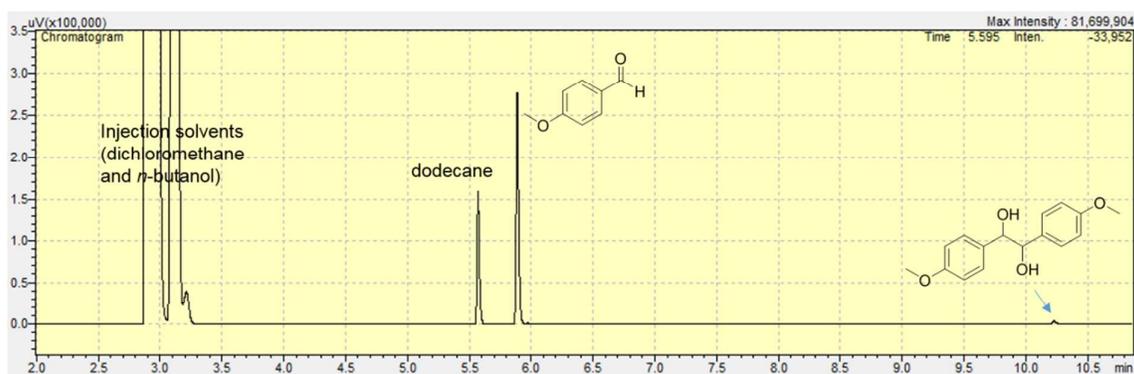
## GC chromatograms



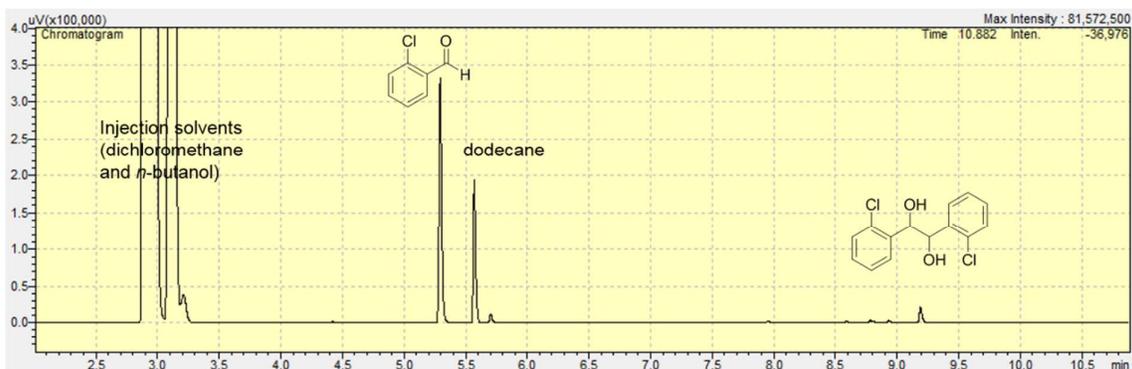
**Figure S5.** Oxidative cleavage of *meso*-hydrobenzoin **1a** analyzed after 1 h reaction.



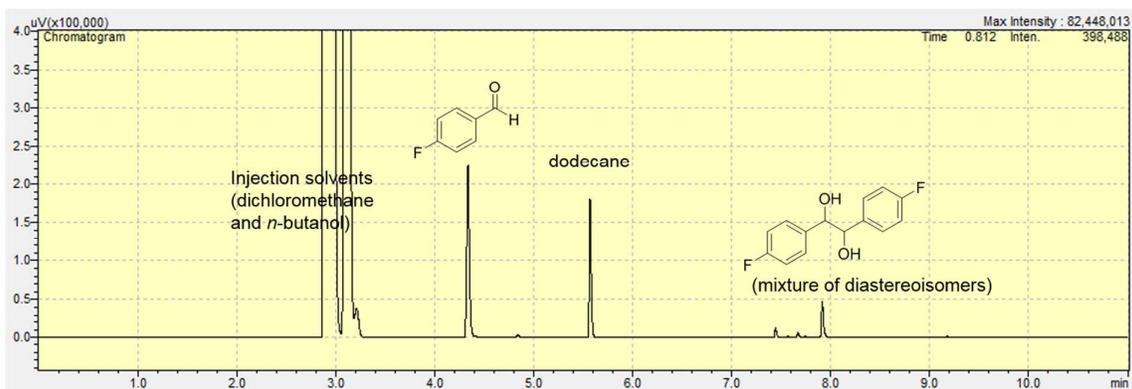
**Figure S6.** Oxidative cleavage of (*R,R*)-hydrobenzoin **1b** analyzed after 3 h reaction.



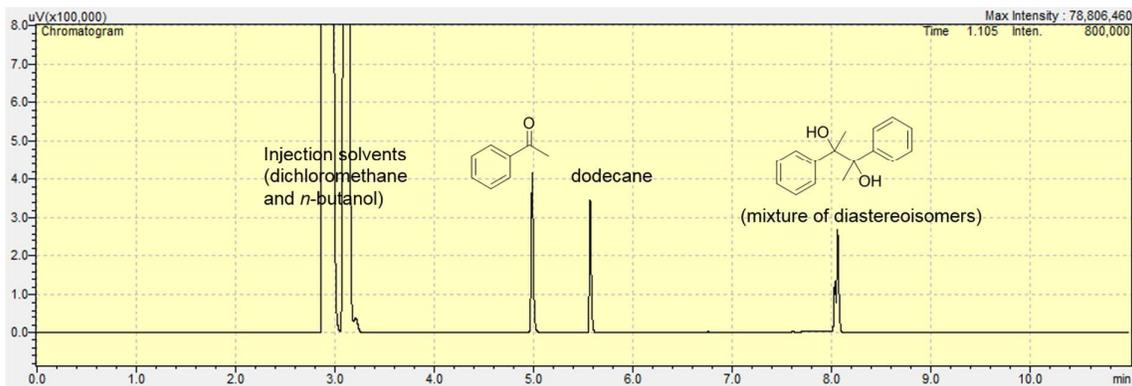
**Figure S7.** Oxidative cleavage of 4,4'-dimethoxyhydrobenzoin **1c** analyzed after 1 h reaction.



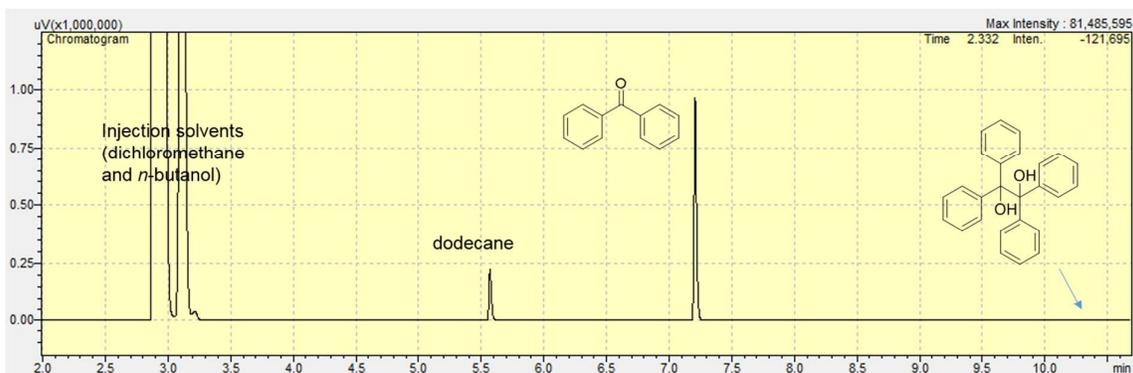
**Figure S8.** Oxidative cleavage of 2,2'-dichlorohydrobenzoin **1d** analyzed after 1 h reaction.



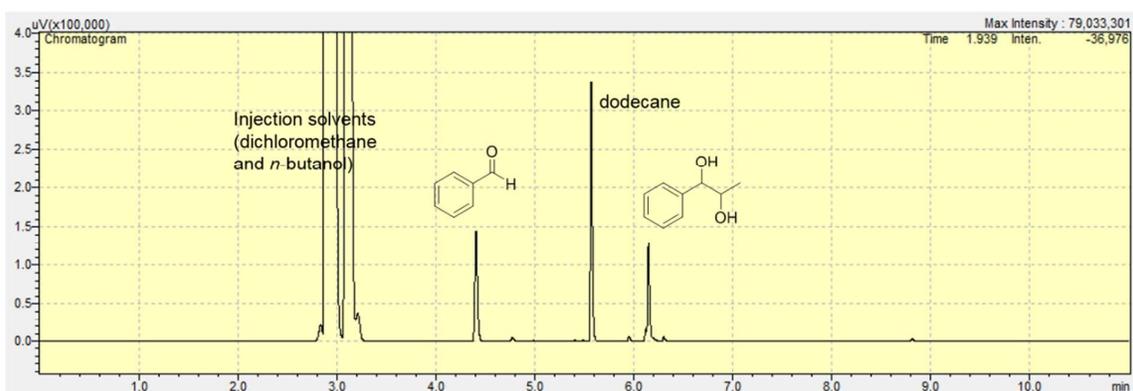
**Figure S9.** Oxidative cleavage of 4,4'-difluorohydrobenzoin **1e** analyzed after 1 h reaction.



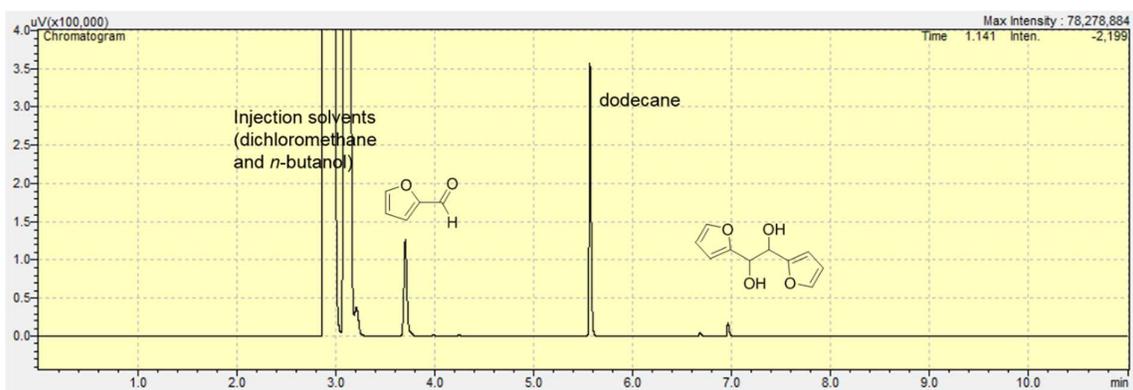
**Figure S10.** Oxidative cleavage of 2,3-diphenyl-2,3-butanediol **1f** analyzed after 24 h reaction.



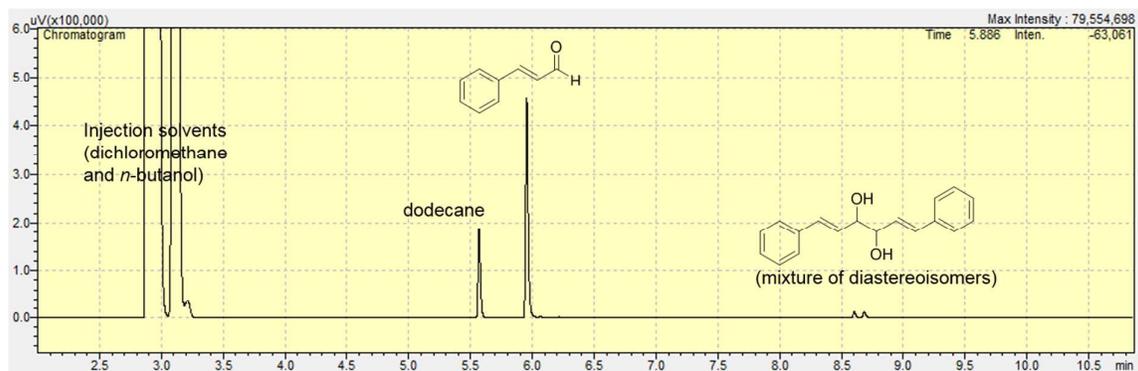
**Figure S11.** Oxidative cleavage of benzopinacol **1g** analyzed after 1 h reaction.



**Figure S12.** Oxidative cleavage of 1-phenyl-1,2-propanediol **1h** analyzed after 24 h reaction.



**Figure S13.** Oxidative cleavage of 1,2-di-2-furanyl-1,2-ethanediol **1j** analyzed after 24 h reaction.



**Figure S14.** Oxidative cleavage of 1,6-diphenyl-1,5-hexadiene-3,4-diol **1k** analyzed after 3 h.

## E-factor calculations

### Procedure for EcoMnOx-catalyzed *meso*-hydrobenzoin oxidative cleavage

A mixture of *meso*-hydrobenzoin (428.5 mg, 2.0 mmol), EcoMnOx (10 mol% Mn) and 1-butanol (1 mL) was added in a 7 mL flask, equipped with a O<sub>2</sub> balloon. The reaction was heated to 100 °C under magnetic stirring (400 rpm) for 1 h. After reaction, the catalyst was separated by filtration and washed with two 1 mL portions of 1-butanol. Evaporation of the combined 1-butanol fractions afforded pure benzaldehyde in 90% yield (382 mg, 3.6 mmol).

### Calculations

$$E = \frac{\sum_i m(\text{raw material}_i) - m_p}{m_p}$$

( $m_p$ : mass of product. Solvents are included assuming 90% recovery, catalysts are ignored if recovered and reused<sup>3</sup>)

$$E = \frac{0.429 + 0.243 - 0.382}{0.382} = 0.8$$

### References

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2. Junta, J. L.; Hochella, M. F., Manganese (II) oxidation at mineral surfaces: A microscopic and spectroscopic study. *Geochim. Cosmochim. Acta* **1994**, *58* (22), 4985-4999.
3. Sheldon, R. A., The E Factor: fifteen years on. *Green Chem.* **2007**, *9* (12), 1273-1283.