Electronic Supplementary Material (ESI) for ChemComm.

Modulating alkene reactivity from oxygenation to halogenation *via* electrochemical O_2 activation by Mn porphyrin

Nikolaos Kostopoulos,[a] Frédéric Banse,[b] Claire Fave,[a] Elodie Anxolabéhère-Mallart,[a,*]

[a] Université de Paris, Laboratoire d'Electrochimie Moléculaire UMR 7591, CNRS, F-75013 Paris, France.

[b] Université Paris-Saclay, CNRS, Institut de Chimie Moléculaire et des Matériaux d'Orsay, 91405, Orsay, France

1. General

1.1 Chemicals

All reagents and solvents were obtained commercially (Acros Organics and Sigma Aldrich). [Mn^{III}(TPP)Cl] (HPCL grade, ≥ 95%) was purchased from PorLab, tetrabutylammonium hexafluorophosphate ($TBAPF_6$, supporting electrolyte), tetrabutylammonium chloride (TBACl), N,N-Dimethylformamide (DMF, anhydrous, 99.8%), cyclooctene oxide, anisole, 1-Methylimidazole, and sodium hypochlorite solution (10 % w/w) were purchased from Sigma-Aldrich and used as received. CH_2Cl_2 was distilled over CaH_2 and purified by alumina before every experiment.

Cyclooctene was purified by alumina column before experiments. Its purity was reassured by GC/MS.

1.2 Cyclic voltammetry experiments

CV experiments were performed under argon or O_2 (air saturated) atmosphere. Dry O_2 atmosphere was achieved by purging the solution with compressed air via a glass tube filled with $CaCl_2$. Cyclic voltammograms were recorded on a Metrohm potentiostat (AUTOLAB PGSTAT302N model). For cyclic voltammetry, the counter electrode used was a Pt wire and the working electrode a glassy carbon disk (3 mm diameter) carefully polished before each voltammogram with a 1 µm diamond paste, sonicated in an ethanol bath and then washed with ethanol. The reference electrode used was an SCE (Saturated Calomel Electrode), isolated from the rest of the solution with a fritted glass bridge. The concentration of the supporting electrolyte was 0.1 M. Temperature regulation, when needed, was ensured by a Julabo circulation cryostat.

1.3 Preparative scale electrolysis

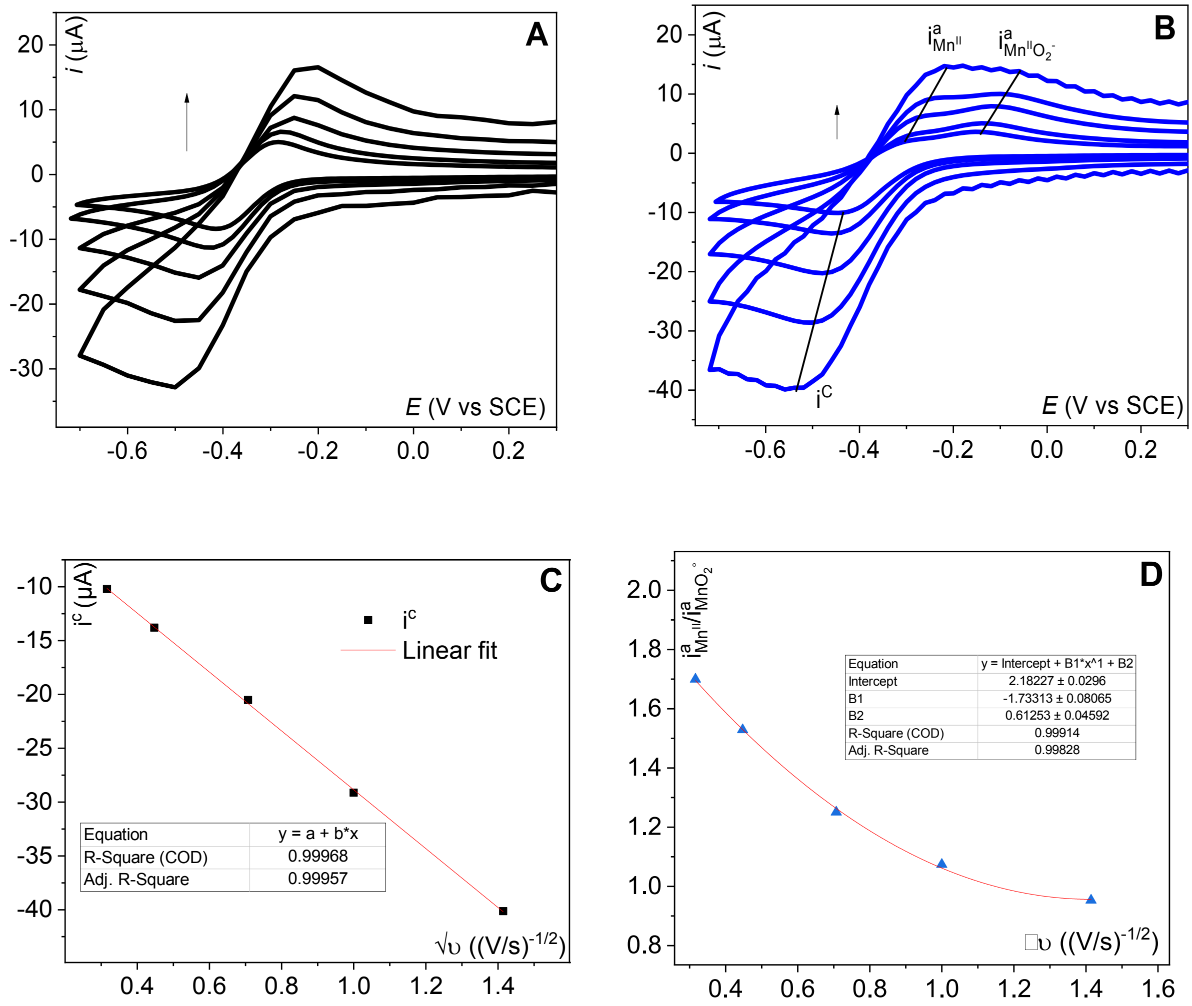
For controlled potential electrolysis, experiments were carried out in a cell using a glassy carbon plate as working electrode of a surface of 1.6 cm, and a SCE reference electrode closely positioned one from the other. The Pt grid counter electrode was separated from the cathodic compartment with a glass frit. During the electrolysis there was a continuous flow of dry air. Liquid samples where directly introduced from the electrolyzed solution in a GC/MS apparatus (shimadzu QP-2020).

1.4 UV-Vis Spectroelectrochemical experiments

Thin cell spectroelectrochemical data were obtained using a combination of three electrodes, a carbon paper as working electrode, a platinum grid as counter electrode as in preparative electrolysis and a carbon/Teflon reference electrode, in a thin cell (optical length = 0.1 cm otherwise noted) mounted on a UV/Vis Varian Cary 60 Spectrophotometer, equipped with a transparent dewar.[1] The former consists of a 0.2 cm quartz UV-Vis-NIR cell surmounted by a glass compartment. The entire solution was saturated with air (2.7 mM O_2 in CH_2Cl_2 and 1.2 mM in DMF [2]) and the dewar was cooled to 258 K by a Julabo circulation cryostat.

	1. Carbon paper electrode with holes that allow the light to pass 2. Platinum grid counter electrode in a frit. 3. Reference electrode carbon/Teflon[3] in a frit.

2. Cyclic voltammetry and UV-Vis spectroelectrochemistry



Equation	y = a + b*x
R-Square (COD)	0.99968
Adj. R-Square	0.99957

Equation	y = Intercept + B1*x^1 + B2
Intercept	2.18227 ± 0.0296
B1	-1.73313 ± 0.08065
B2	0.61253 ± 0.04592
R-Square (COD)	0.99914
Adj. R-Square	0.99828

Figure S1: CVs of 0.5 mM Mn^{III}(TPP)Cl on a 0.3 cm glassy carbon electrode, at 298 K, in 0.1 M TBAPF$_6$ / CH$_2$Cl$_2$ solution at various scan rate (0.1, 0.2, 0.5, 1 and 2 V/s). **A**) Under Ar. **B**) Under O$_2$. **C**) Variation of the cathodic peak current under O$_2$. **D**) Variation of the ratio between the two peaks of the anodic current under O$_2$.

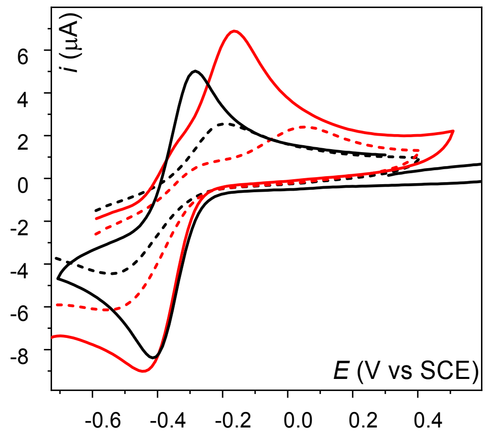


Figure S2: Variation of the temperature in CH_2Cl_2. CVs of 0.5 mM Mn^{III}(TPP)Cl on a 0.3 cm glassy carbon electrode in a 0.1 M $TBAPF_6$ / CH_2Cl_2 solution, under Ar at 298K (black trace), at 253 K (black dashed trace) and under O_2 at 298 K (red trace) and at 253 K (red dashed trace).

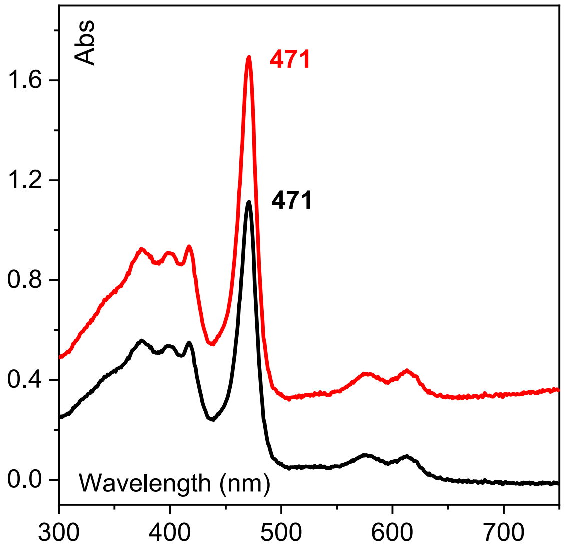


Figure S3: UV-vis spectrum of 0.1 mM Mn^{III}(TPP)Cl, at 298 K, in 0.2 M $TBAPF_6$/CH_2Cl_2. Under Ar (red trace) and under O_2 (black trace).

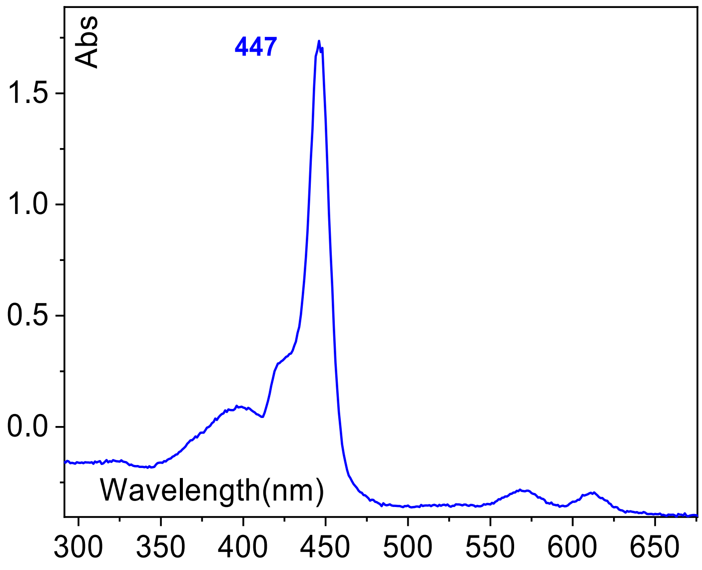


Figure S4: UV-vis spectrum of 0.1 mM Mn^{III}(TPP)Cl, at 253 K, in 0.2 M TBAPF$_6$/CH$_2$Cl$_2$ under O$_2$ and at E$_{app}$ = -0.45 V vs SCE.

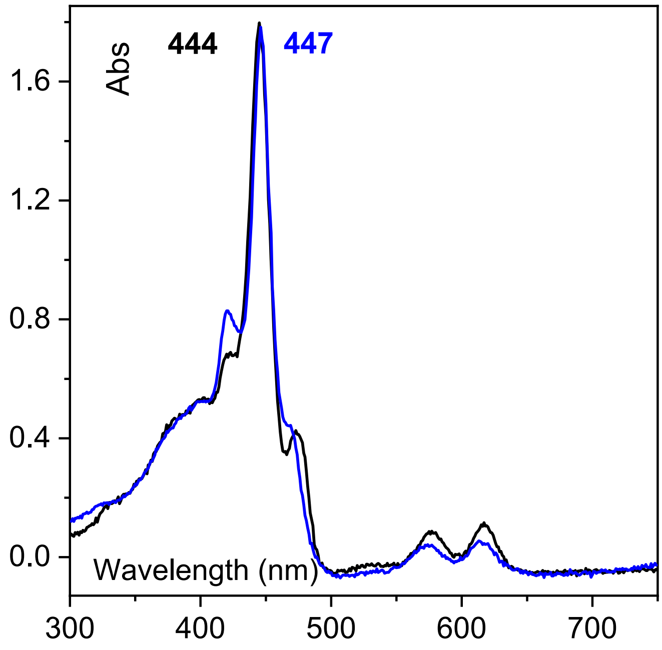


Figure S5: UV-vis spectrum of 0.1 mM Mn^{III}(TPP)Cl, at 298 K, in 0.2 M TBAPF$_6$/CH$_2$Cl$_2$ after 10 min at E$_{app}$ = -0.45 V vs SCE. Under Ar (black trace) and under O$_2$ (blue trace). The optical path for the experiment under Ar was 0.2 cm. The intensities are normalized and the baseline of the spectra is corrected.

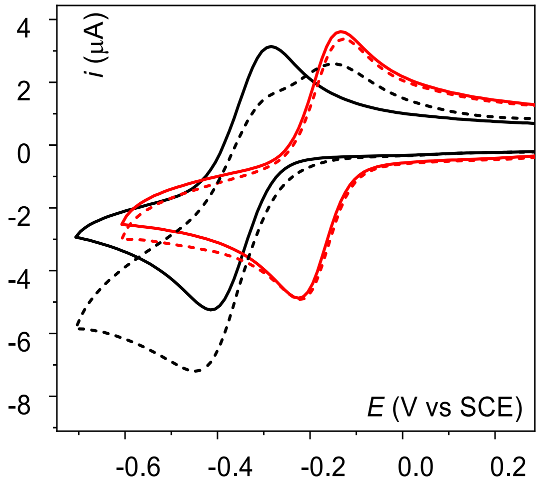


Figure S6: CVs of 0.5 mM Mn^{III}(TPP)Cl at 298 K on a 0.3 cm glassy carbon electrode under Ar in a 0.1 M $TBAPF_6$ /CH_2Cl_2 (black trace) or / DMF (red trace) and under O_2 in a 0.1 M $TBAPF_6$ /CH_2Cl_2 (dashed black trace) or / DMF (dashed red trace)

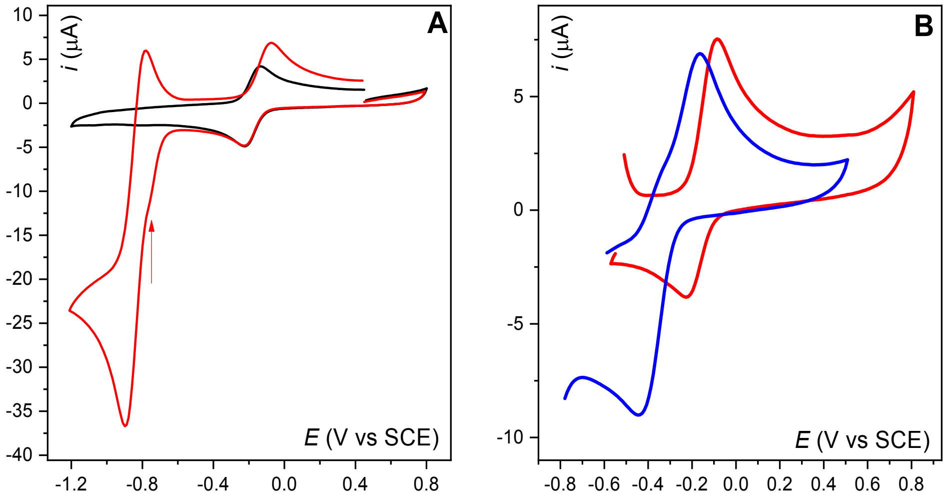


Figure S7: **A**) CVs of 0.5 mM Mn^{III}(TPP)Cl at 298 K on a 0.3 cm glassy carbon electrode in a 0.1 M $TBAPF_6$ /DMF under Ar (black trace) and under O_2 (red trace). **B**) CVs of 0.5 mM Mn^{III}(TPP)Cl at 298 K on a 0.3 cm glassy carbon electrode under O_2 in a 0.1 M $TBAPF_6$ / DMF (red trace) and in a 0.1 M $TBAPF_6$ /CH_2Cl_2 (blue trace). For the CVs: E_{app} = -0.85 V vs SCE during 15 s then CV recorded from – 0.6 V to 0.8 V vs SCE.

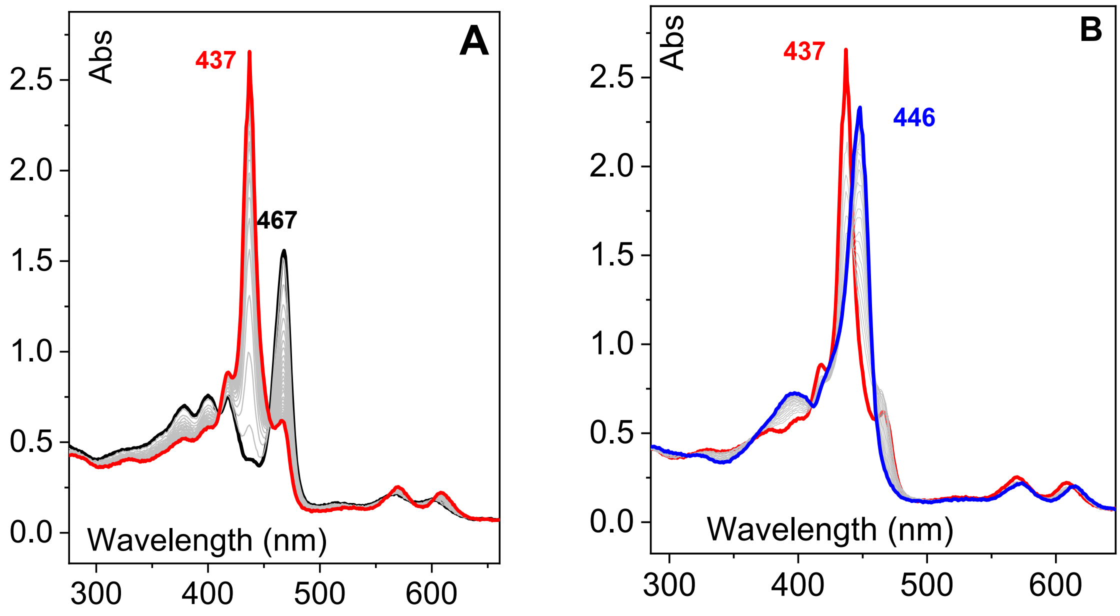


Figure S8: UV-vis spectrum of 0.1 mM Mn^{III}(TPP)Cl, at 253 K, in 0.2 M TBAPF$_6$ / DMF under O$_2$. **A**) Starting Mn^{III} complex (black trace) and after 10 min at -0.45 V (red trace). **B**) Evolution (from red trace to blue trace) after 10 min at -1.1 V vs SCE.

3. Reactivity – Preparative scale electrolysis

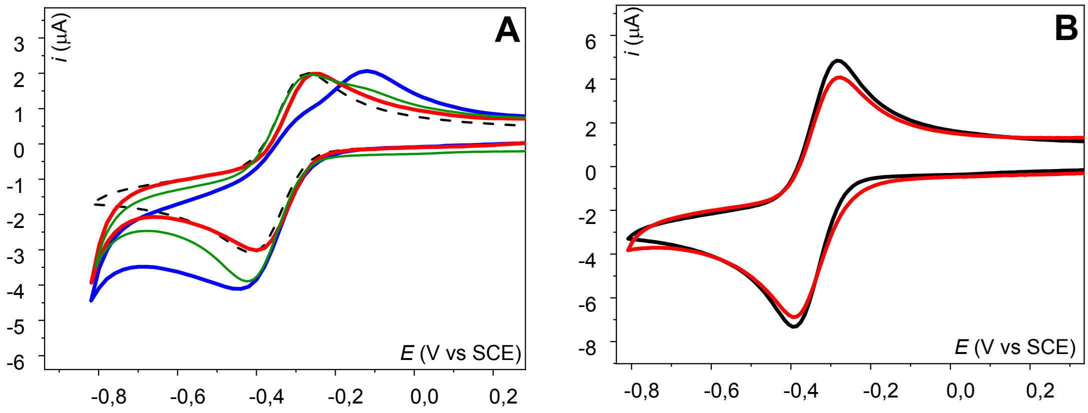


Figure S9: CVs of 0.5 mM Mn^{III}(TPP)Cl in 0.1 M $TBAPF_6$ /CH_2Cl_2 on a 0.3 cm glassy carbon electrode, at 298 K. **A:** Under Ar (black trace), under O_2 (blue trace), under O_2 with 20 mM of 1-MeIm (red trace) or with 5 mM of TBACl (green trace). **B:** Under Ar (black trace) and under Ar with 440 mM of anhydride (red trace).

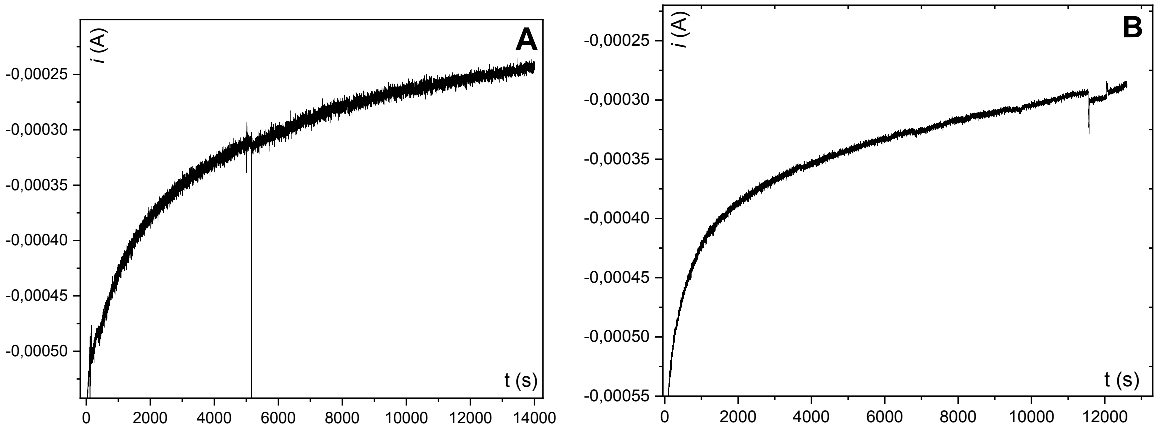


Figure S10: i(A) vs t(s) plot of preparative scale electrolysis at 298 K of a 0.5 mM solution of Mn^{III}(TPP)Cl in 0.1 M $TBAPF_6$/CH_2Cl_2 under O_2 in presence of 0.44 M of anhydride. **A)** and with 40 mM of 1-MeIm (faradaic efficiency for cyclooctene oxide 81%). **B)** and with 5 mM of TBACl with E_{app} = -0.45 V for 4 hours (faradaic efficiency for cyclooctene chloride 53%)

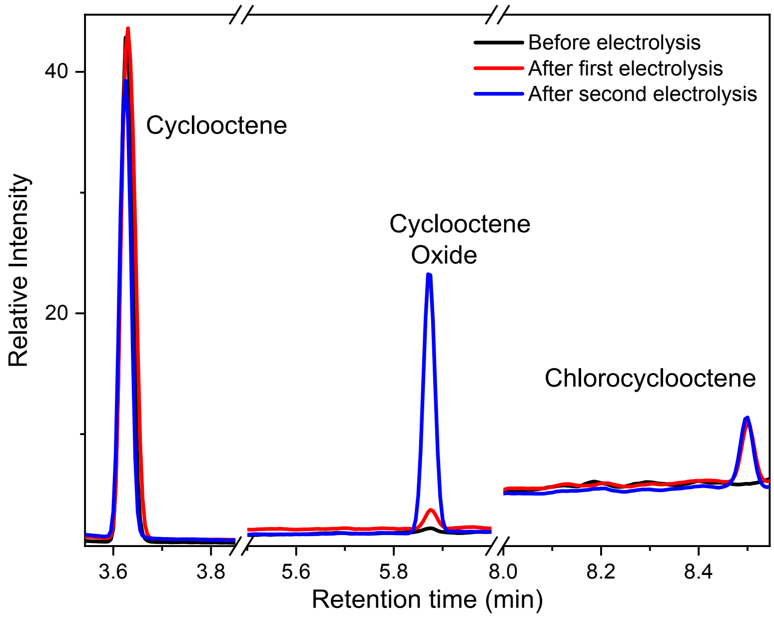


Figure S11: Preparative scale electrolysis of a 0.5 mM solution of $Mn^{III}(TPP)Cl$ in 0.1 M $TBAPF_6/CH_2Cl_2$ under O_2 in presence of 0.44 M of benzoic anhydride, 5 mM of TBACl and 10 mM of cyclooctene. E_{app} = -0.45 V for 4 hours. Chromatograms before electrolysis: black trace, after: red trace and after second electrolysis of the same solution for 12 hours after addition of 1-MeIm: blue trace. The experiment where both ligands are present from the beginning gave only the oxide (Table 2 of the main text, entry 2).

Quantification was achieved by calibration curve with internal standard (vide infra) for cyclooctene oxide. For chloro cyclooctene the same curve has been used.

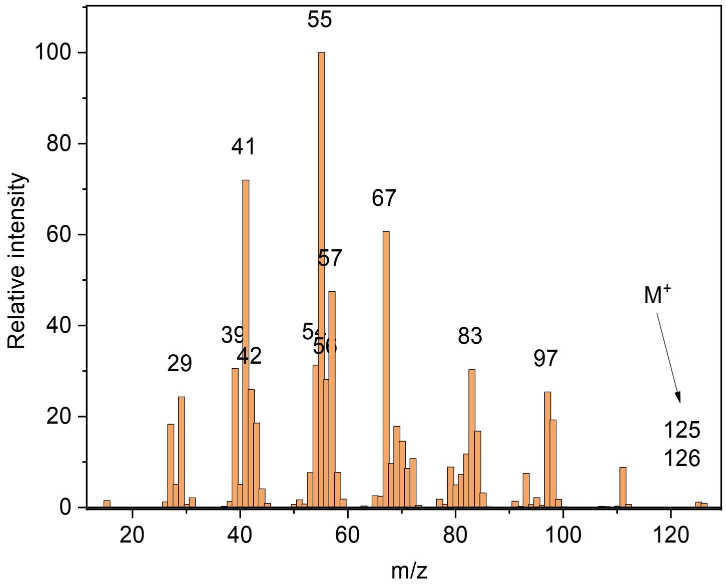


Figure S12: MS spectrum of the peak of the chromatogram of cyclooctene oxide, from an authentic sample.

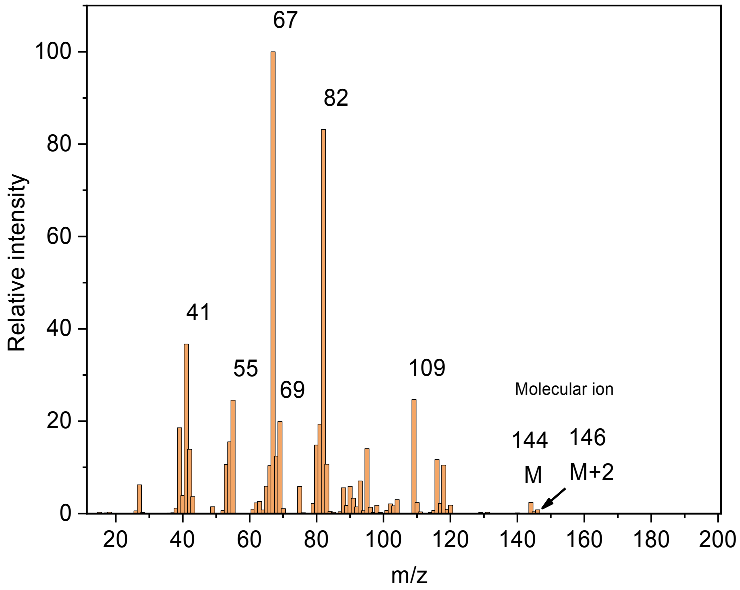
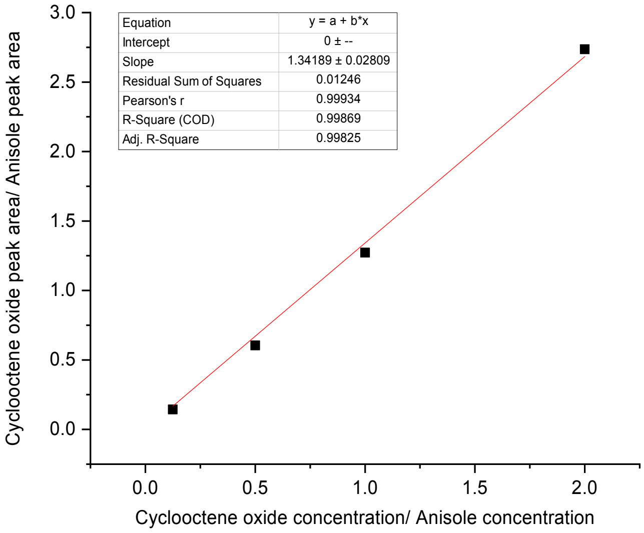


Figure S13: MS spectrum of the peak of the chromatogram attributed to the chloro-cyclooctene.



Equation	y = a + b*x
Intercept	0 ± --
Slope	1.34189 ± 0.02809
Residual Sum of Squares	0.01246
Pearson's r	0.99934
R-Square (COD)	0.99869
Adj. R-Square	0.99825

Figure S14: Calibration curve for cyclooctene oxide. The internal standard used was anisole. The concentration of the latter was 2 mM on every sample. The concentrations of cyclooctene were: 0.25 mM, 1 mM, 2 mM and 4 mM.

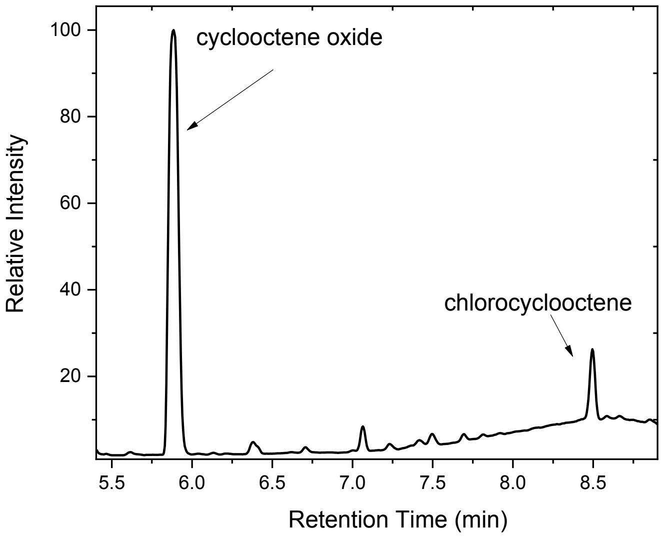


Figure S15: Chemical oxidation of cyclooctene using a modified literature procedure.[4] Stirring of two hours of the following biphasic system. Organic phase: 1 ml of Dichloromethane with 13 mM of MnTPPCl, 26 mM of TBACl as a surface factor, 0.2 M of cyclooctene. Aqueous phase: 2 ml of sodium hypochlorite solution 10 % w/w. Chromatogram obtained of the organic phase after removing the catalyst on a small silica column. Both oxidation and chlorination products are observed.

4. References

1. C. Gueutin and D. Lexa, *Electroanalysis,* 1996, **8**, 1029-1033.
2. T. Sato, Y. Hamada, M. Sumikawa, S. Araki and H. Yamamoto, *Industrial & Engineering Chemistry Research*, 2014, **53**, 19331-19337.
3. D. Weingarth, A. Foelske-Schmitz, A. Wokaun and R. Kotz, *ECS Transactions*, 2013, **50**, 111-117.
4. W. Liu and J. T. Groves, *J Am Chem Soc*, 2010, **132**, 12847-12849.