

Electronic Supporting Information

Biomimetic oxidation of cyclic and linear alkanes: high alcohol selectivity promoted by a novel manganese porphyrin catalyst

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The brominated free-base porphyrin $H_2[Br_{12}T4(-OMe)PP]$, Figure S1, was obtained according to the methodology described by Rebouças et al 2002 [1]. Then, the porphyrin was characterized by UV-Vis spectroscopy (Figure S2) and 1H NMR (Figure S4).

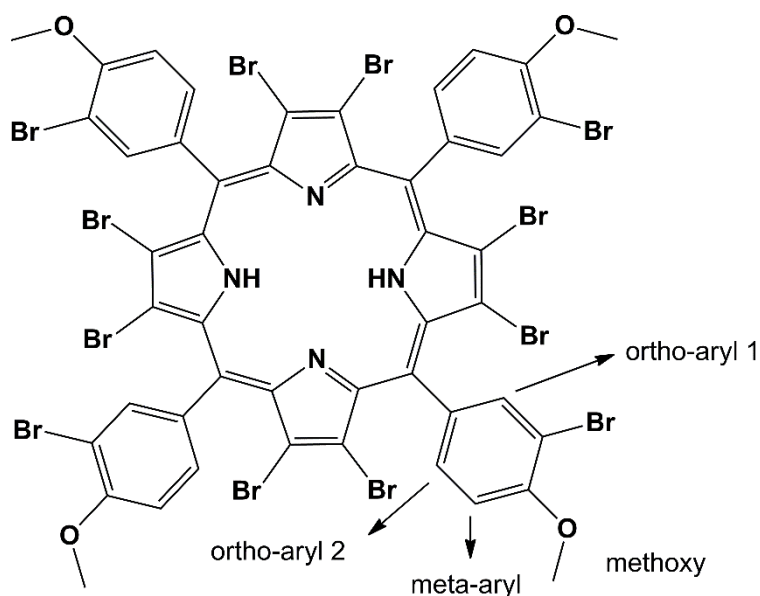


Figure S1. Structural representation of the brominated free-base porphyrin $H_2Br_{12}T4(-OMe)PP$ ($H_2Br_{12}Por$).

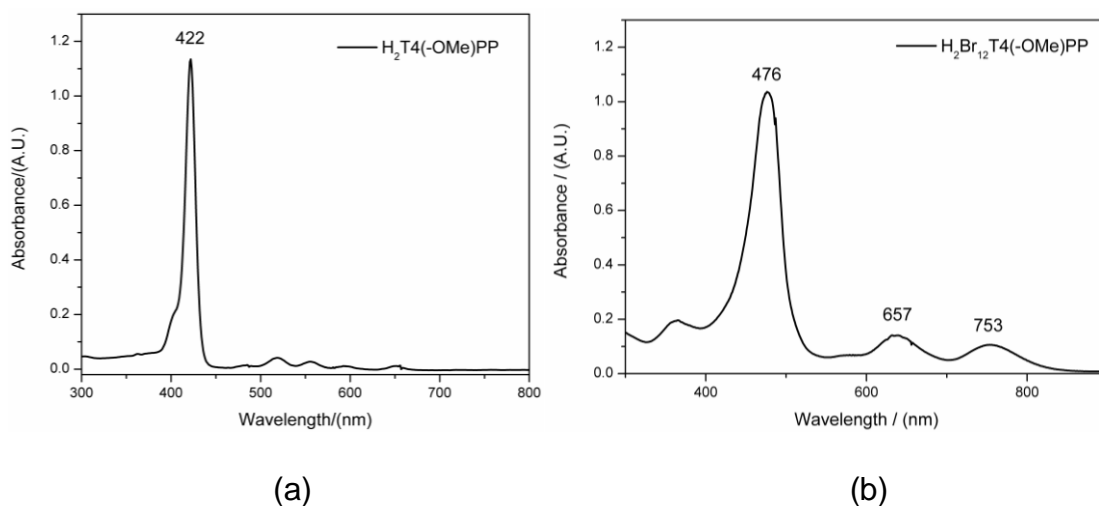


Figure S2. UV-vis spectrum of the (a) free-base porphyrin $H_2T4(-OMe)PP$ (H_2Por , $3.15 \times 10^{-6} \text{ mol L}^{-1}$) and (b) brominated free-base porphyrin $H_2Br_{12}T4(-OMe)PP$ ($H_2Br_{12}Por$) in CH_2Cl_2 .

The spectrum of the H₂Br₁₂T4(-OMe)PP Figure S2 (b) reveals a bathochromic shift of the Soret band as compared to the spectrum of the free-base porphyrin H₂T4(-OMe)PP Figure S2 (a). This usually occurs upon bromination of free-base porphyrins and has been reported in the literature [2, 3].

Analysis of the ¹H NMR spectra indicated that bromine atoms were introduced into one of the *ortho* positions relative to the methoxy (-OCH₃) substituents and into each of the β-pyrrole positions of the macrocycle.

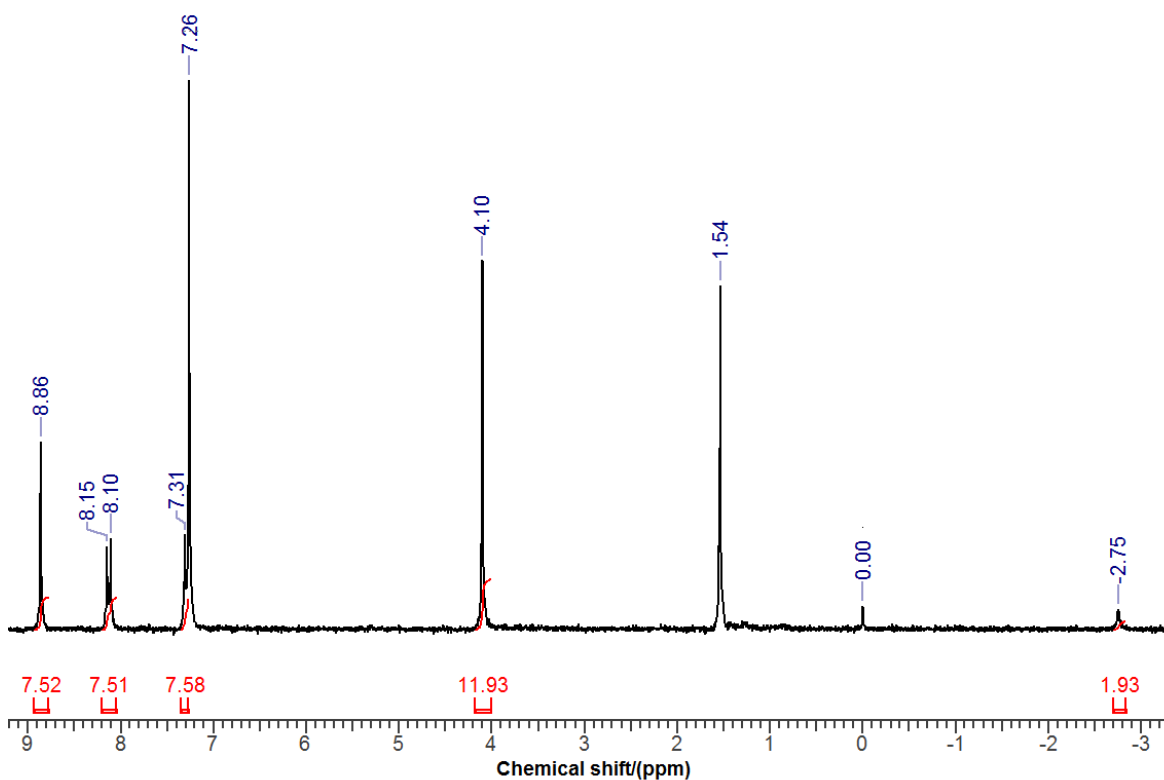


Figure S3. ¹H NMR spectrum of H₂T4(-OMe)PP (H₂Por) recorded at 400 MHz, in CDCl₃ at 25 °C. δ 8.86 (s, 8H, β-pyrrole) 8.15 (d, 4H, *ortho*-aryl), 8.07 (m, 8H, *meta*-aryl), 4.10 (s, 12H, methoxy) and -2.75 (s, 2H, pyrrole N-H).

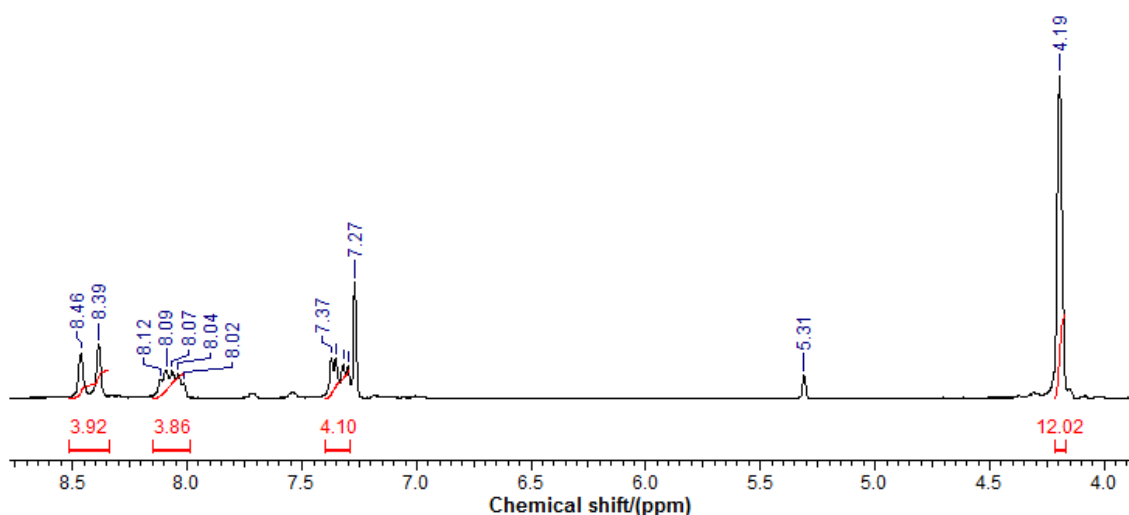


Figure S4. ^1H NMR spectrum of $\text{H}_2\text{Br}_{12}\text{T}_4(-\text{OMe})\text{PP}$ ($\text{H}_2\text{Br}_{12}\text{Por}$) recorded at 400 MHz, in CDCl_3 at 25 °C. δ 8.39 (d, 4H, *ortho*-aryl), 8.07 (m, 4H, *meta*-aryl), 7.35 (s, 4H, *ortho*-aryl), and 3.98 (s, 12H, methoxy).

The compounds studied here were characterized by infrared spectroscopy, Figure S5. The results confirmed the formation of the second- and third-generation metalloporphyrins.

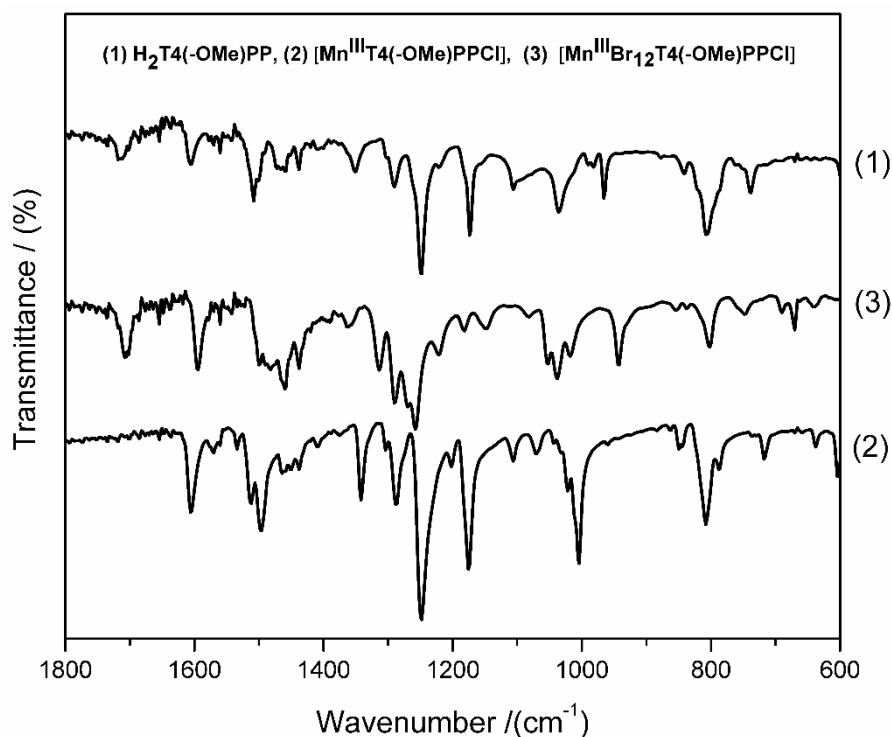


Figure S5. FTIR spectrum of $\text{H}_2\text{T}_4(-\text{OMe})\text{PP}$ (1), $[\text{Mn}^{\text{III}}\text{T}_4(-\text{OMe})\text{PPCl}]$ (2); and $[\text{Mn}^{\text{III}}\text{Br}_{12}\text{T}_4(-\text{OMe})\text{PPCl}]$ (3) in KBr pellets.

[Mn^{III}T4(-OMe)PPCI] FTIR in KBr (cm⁻¹): (1604) δ C=C; (1294) δ porphyrin skeleton; (1249) ν C-O-C; (1173) ν OCH₃; (1004) δ Mn-N.

[Mn^{III}Br₁₂T4(-OMe)PPCI] FTIR in KBr (cm⁻¹): (1594) δ C=C; (1289) δ porphyrin skeleton; (1272) ν C _{β} -Br; (1255) ν C-O-C; (1175) ν OCH₃; (1004) δ Mn-N.

The novel third-generation brominated manganese porphyrin (MnBr₁₂Por) was characterized by mass spectrometry (Figure S6).

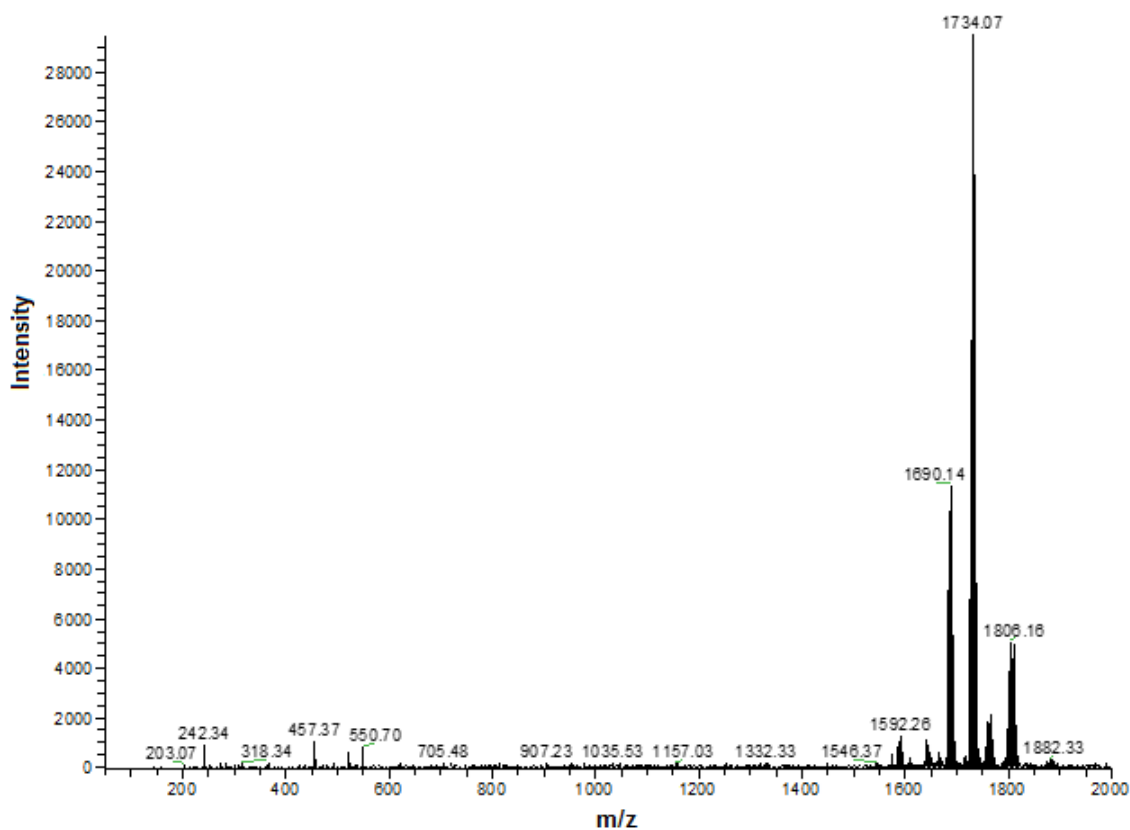


Figure S6. Mass spectrum of [Mn^{III}Br₁₂T4(-OMe)PPCI]. Analysis conducted in CH₃OH with the ESI-MS operating in the positive mode.

The peak at m/z 1734.07 is associated with the loss of chloride ion $[\text{Mn}^{\text{III}}\text{Br}_{12}\text{T4}(-\text{OMe})\text{PP}]^+$. The simulation of the spectrum using program ChemCalc (<http://www.chemcalc.org/>; Figure S7) is in agreement with the experimental spectrum. The peak at 1690.14 is associated with the loss of one bromine atom and protonation of macrocycle $[\text{Mn}^{\text{III}}\text{Br}_{11}\text{T4}(-\text{OMe})\text{PPCl} + \text{H}^+]$ which m/z corresponds to 1690.19. The peak at 1806.16 can be associated with $[\text{Mn}^{\text{III}}\text{Br}_{12}\text{T4}(-\text{OMe})\text{PPCl} + \text{HCl} + \text{H}^+]$, which m/z is equal 1806.08.

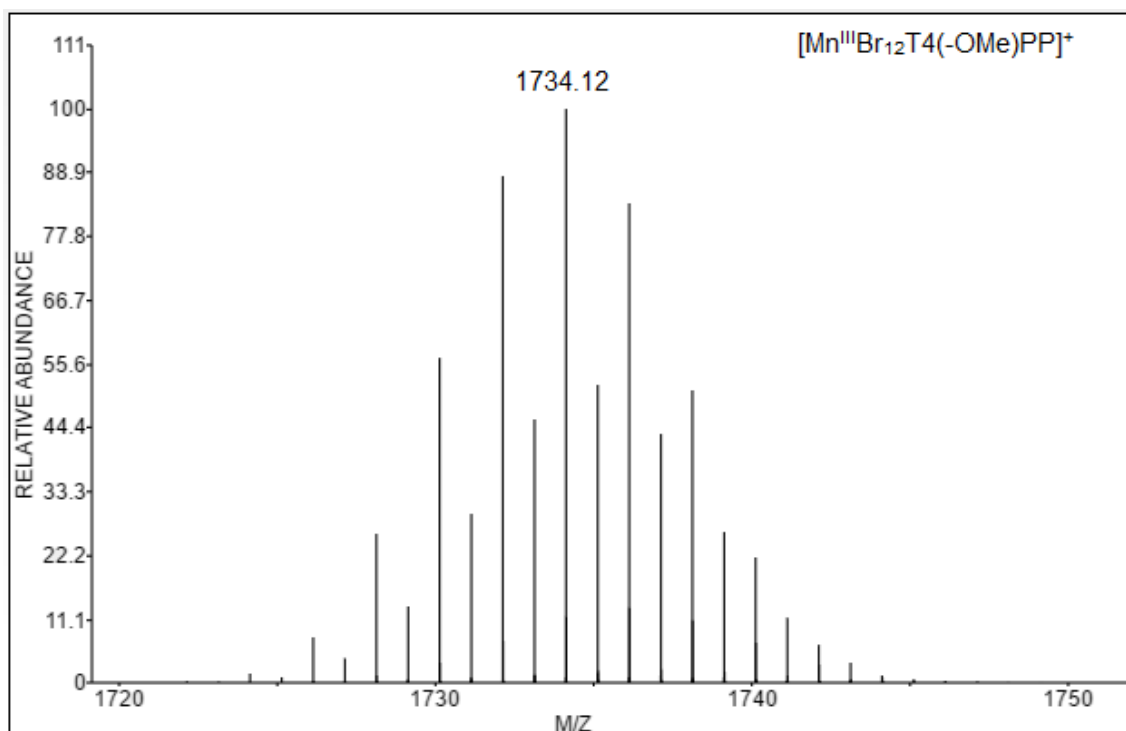


Figure S7. Simulated mass spectrum for the $[\text{Mn}^{\text{III}}\text{Br}_{12}\text{T4}(-\text{OMe})\text{PP}]^+$ ion, $\text{C}_{48}\text{H}_{24}\text{N}_4\text{O}_4\text{Br}_{12}\text{Mn}^+$.

Table S1. Product yields obtained during the oxidation of *n*-hexane by PhIO or PhI(OAc)₂ catalyzed by MnP in CH₂Cl₂ under aerobic condition. Yields based on the oxidant.

Entry	Catalyst	System	Product Yield (%)				TON	Bleaching ² (%)
			2-ol ^{1,3}	3-ol ^{1,3}	2-one ^{1,3}	3-one ^{1,3}		
27	MnPor	PhIO	2.8	3.7	2.5	3.4	1.2	61
28	MnBr ₁₂ Por	PhIO	4.7	5.4	4.1	4.3	1.8	55
29	MnPor	PhI(OAc) ₂	2.2	2.8	1.3	2.5	0.9	92
30	MnBr ₁₂ Por	PhI(OAc) ₂	2.9	3.3	2.5	2.9	1.1	68
31	MnPor		0	0	0	0	-	0
32	MnBr ₁₂ Por		0	0	0	0	-	0
33		PhIO	0	0	0	0	-	-
34		PhI(OAc) ₂	0	0	0	0	-	-
35	Mn(OAc) ₂	PhIO	0	0	0	0	-	-
36	Mn(OAc) ₂	PhI(OAc) ₂	0	0	0	0	-	-

Reaction conditions: [MnP or Mn(OAc)₂] = 5 × 10⁻⁴ mol L⁻¹, [PhIO or PhI(OAc)₂] = 5 × 10⁻³ mol L⁻¹, MnP/Oxidant/*n*-hexane/CH₂Cl₂ molar ratio = 1:10:3630:15550, 25 °C, magnetic stirring, 90 min of reaction.¹Yields based on the oxidant. 2-ol: 2-hexanol, 3-ol: 3-hexanol, 2-one: 2-hexanone and 3-one: 3-hexanone. ²The degree of catalyst destruction was calculated from the UV-Vis absorption spectra recorded at the end of the reaction. ³The maximum error is ± 0.5% with confidence level of 95%. ⁴TON = total moles products per mol catalyst.

Table S2. Product yields obtained during the oxidation of cyclohexane by PhIO or PhI(OAc)₂ catalyzed by MnP in CH₂Cl₂ under aerobic condition. Yields based on the oxidant.

Entry	Catalyst	System	Product Yield (/%)		TON	Select. ⁷ (/%)	Bleac. ² (/%)
			Cy-ol ^{1,3}	Cy-one ^{1,3}			
37		PhIO	0	0	-	-	-
38		PhI(OAc) ₂	0	0	-	-	-
39	MnP _{or}		0	0	-	-	0
40	MnBr ₁₂ Por		0	0	-	-	0
41	Mn(OAc) ₂	PhIO	0	0	-	-	-
42	Mn(OAc) ₂	PhI(OAc) ₂	0	0	-	-	-
43		PhIO ⁴	1.3	1.5	-	46	0
44		PhI(OAc) ₂ ⁴	0.6	1.2	-	33	0
45	MnBr ₁₂ Por ⁵	PhIO	1.2	2.0	1.6	38	100
46	MnBr ₁₂ Por ⁵	PhI(OAc) ₂	0.7	1.4	1.0	33	100
47	MnBr ₁₂ Por ⁶	PhIO	19.2	6.2	12.7	76	100
48	MnBr ₁₂ Por ⁶	PhI(OAc) ₂	9.6	4.2	6.9	70	100

Reaction conditions: MnP or Mn(OAc)₂/Oxidant/cyclohexane/CH₂Cl₂ molar ratio = 1:10:4650:15550, 25 °C, magnetic stirring, 90 min of reaction. ¹Yields based on the oxidant. ²The degree of catalyst destruction was calculated from the UV-Vis absorption spectra recorded at the end of the reaction. ³The maximum error is ± 0.5% with confidence level of 95%. ⁴Oxidant/cyclohexane/CH₂Cl₂ molar ratio = 50:4650:15550. ⁵MnP/Oxidant/cyclohexane/CH₂Cl₂ molar ratio = 1:50:50:23325. ⁶MnP/Oxidant/cyclohexane/CH₂Cl₂ molar ratio = 1:50:4650:15550. ⁷Selectivity for the alcohol was determined from the relation: Selectivity = 100 × [%Cy-ol / (%Cy-ol + %Cy-one)]. ⁸TON = total moles products per mol catalyst.

Table S3. Product yields obtained during the oxidation of adamantane by PhIO or PhI(OAc)₂ catalyzed by MnP in CH₂Cl₂ under aerobic condition. Yields based on the oxidant.

Entry	Catalyst	System	Product Yield (/%)		Bleac. ² (/%)
			1-Adol ¹	2-Adol ¹	
49	Mn(OAc) ₂	PhIO	0	0	-
50	Mn(OAc) ₂	PhI(OAc) ₂	0	0	-
51	MnP _{or}	-	0	0	0
52	MnBr ₁₂ Por	-	0	0	0

Reaction conditions: [MnP or Mn(OAc)₂] = 5 × 10⁻⁴ mol L⁻¹, [PhIO or PhI(OAc)₂] = 5 × 10⁻³ mol L⁻¹, MnP/Oxidant/adamantane/CH₂Cl₂ molar ratio = 1:10:100:23325, 25 °C, magnetic stirring, 90 min. of reaction. ¹Yields based on the oxidant. 1-adol: 1-adamantanol, 2-adol: 2-adamantanol. ²The degree of catalyst destruction was calculated from the UV-Vis absorption spectra recorded at the end of the reaction. ³TON = total moles products per mol catalyst.

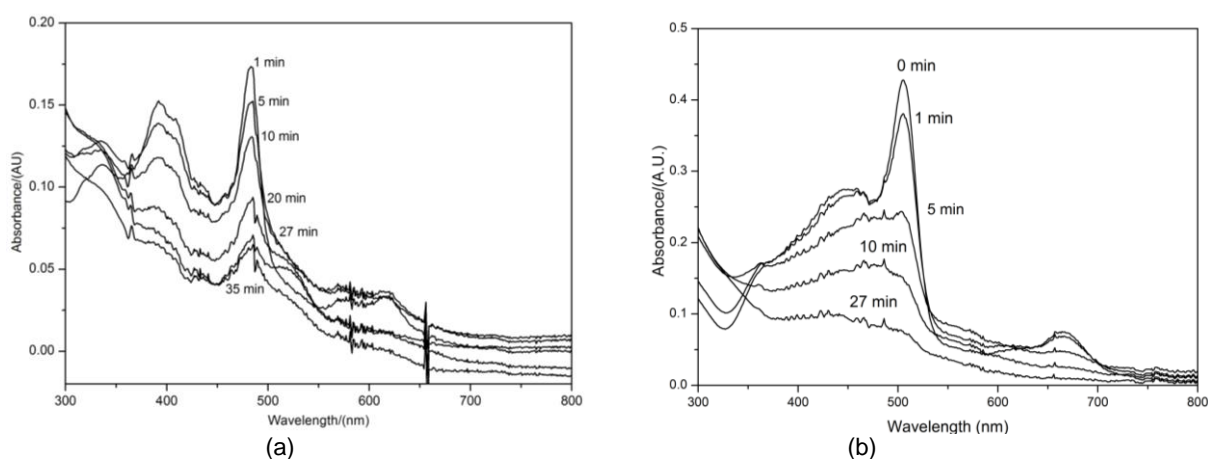


Figure S8. UV-vis transient spectra of (a) MnPor and (b) MnBr₁₂Por in presence of PhIO in CH₂Cl₂. Condition of reaction: molar ratio: MnP:PhIO 1:10.

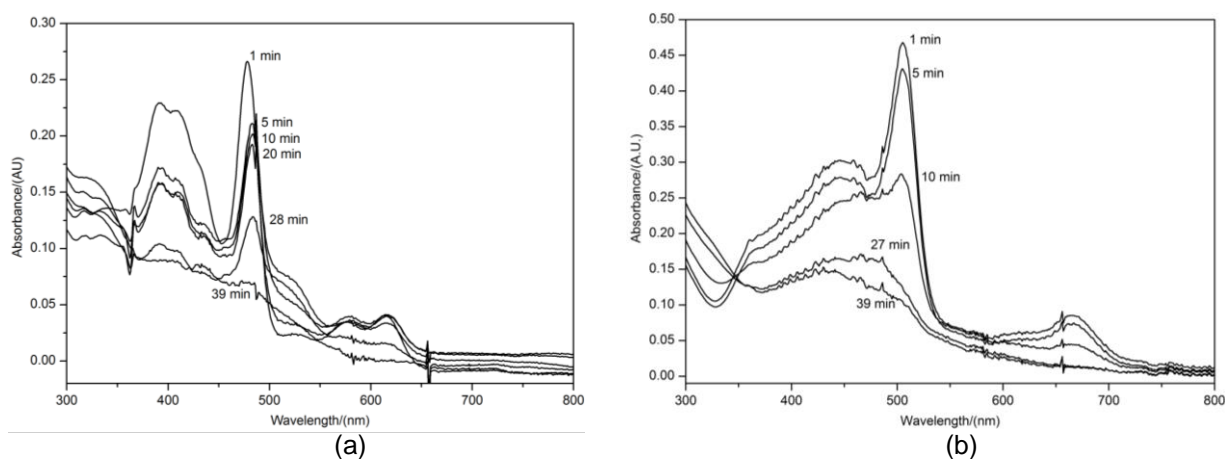


Figure S9. UV-vis transient spectra of (a) MnPor and (b) MnBr₁₂Por in presence of PhI(OAc)₂ in CH₂Cl₂. Condition of reaction: molar ratio: MnP:PhI(OAc)₂ 1:10.

References

- [1] J.S. Rebouças, M.E.M.D. de Carvalho, Y.M. Idemori, J. Porphyrins Phthalocyanines, 06 (2002) 50-57.
- [2] Y. Fang, P. Bhyrappa, Z. Ou, K.M. Kadish, Chem.-A Eur. J., 20 (2014) 524-532.
- [3] V.S. da Silva, L.I. Teixeira, E. do Nascimento, Y.M. Idemori, G. DeFreitas-Silva, Appl. Catal.A: Gen., 469 (2014) 124-131.