SUPPORTING INFORMATION

Selective oxidation of halophenols catalyzed by an artificial miniaturized peroxidase

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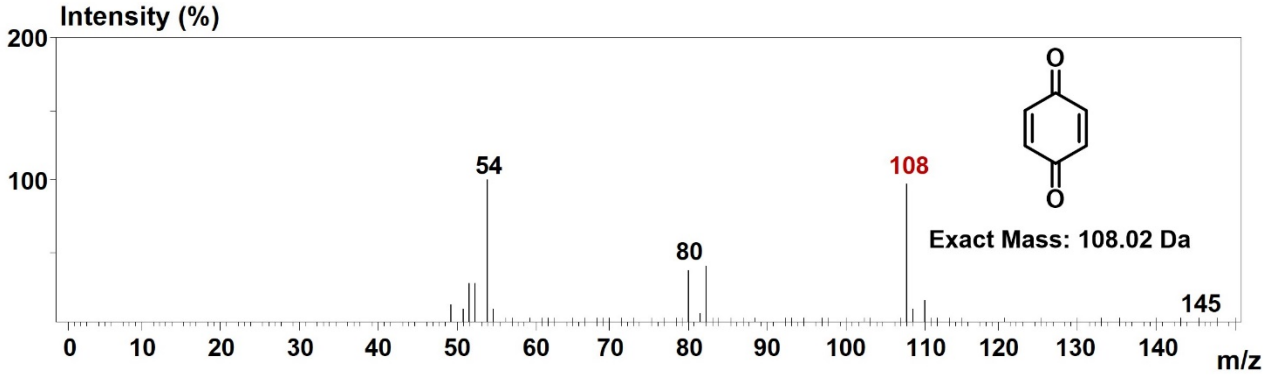


Figure S1. EI-MS analysis of the product obtained by the Fe-MC6*a-catalyzed 4FP oxidation in the presence of H_2O_2.

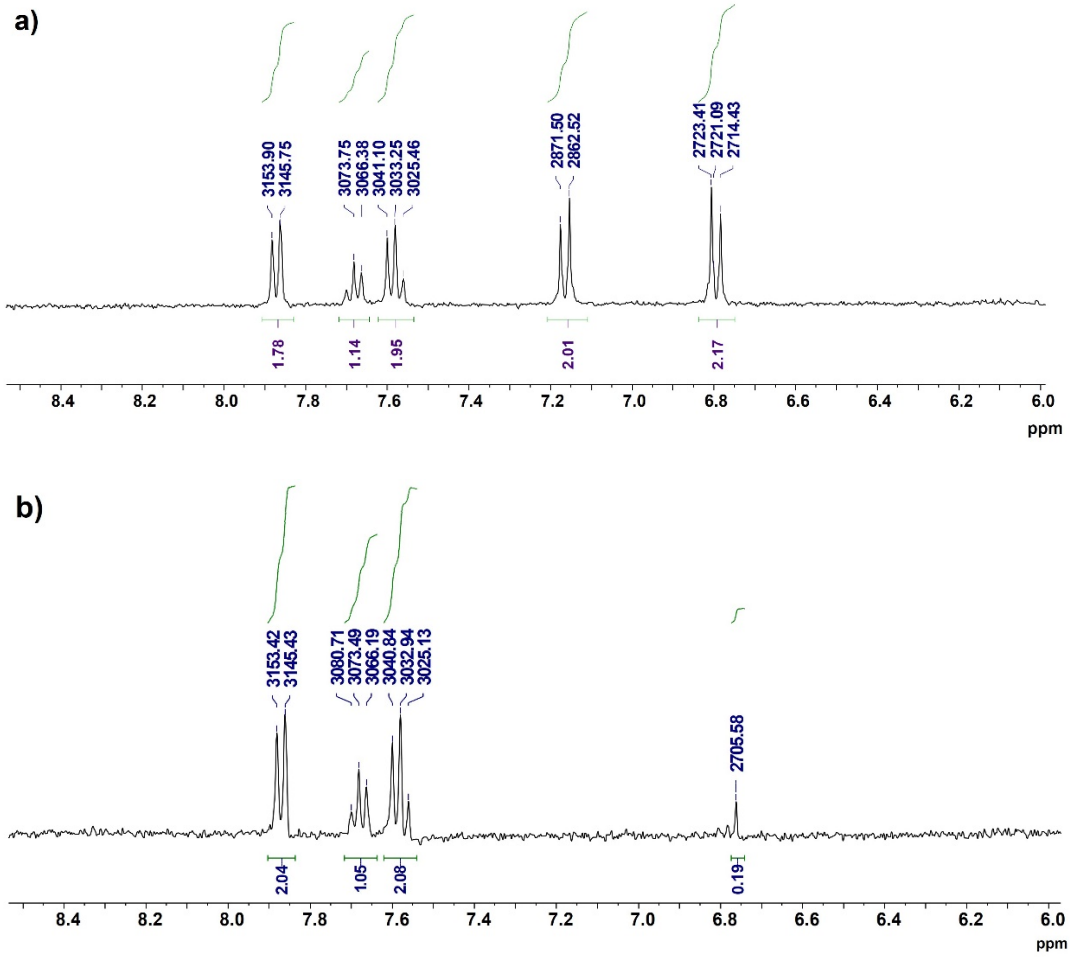


Figure S2. Close up views of the ^{1}H NMR spectra referred to the Fe-MC6*a-catalyzed 4-CP oxidation. Spectra were acquired at (a) t = 0 min and (b) t = 30 min from H_2O_2 addition. Reaction solvent was composed of phosphate buffer (50 mM), TFE and D_2O (40:50:10 v/v/v).

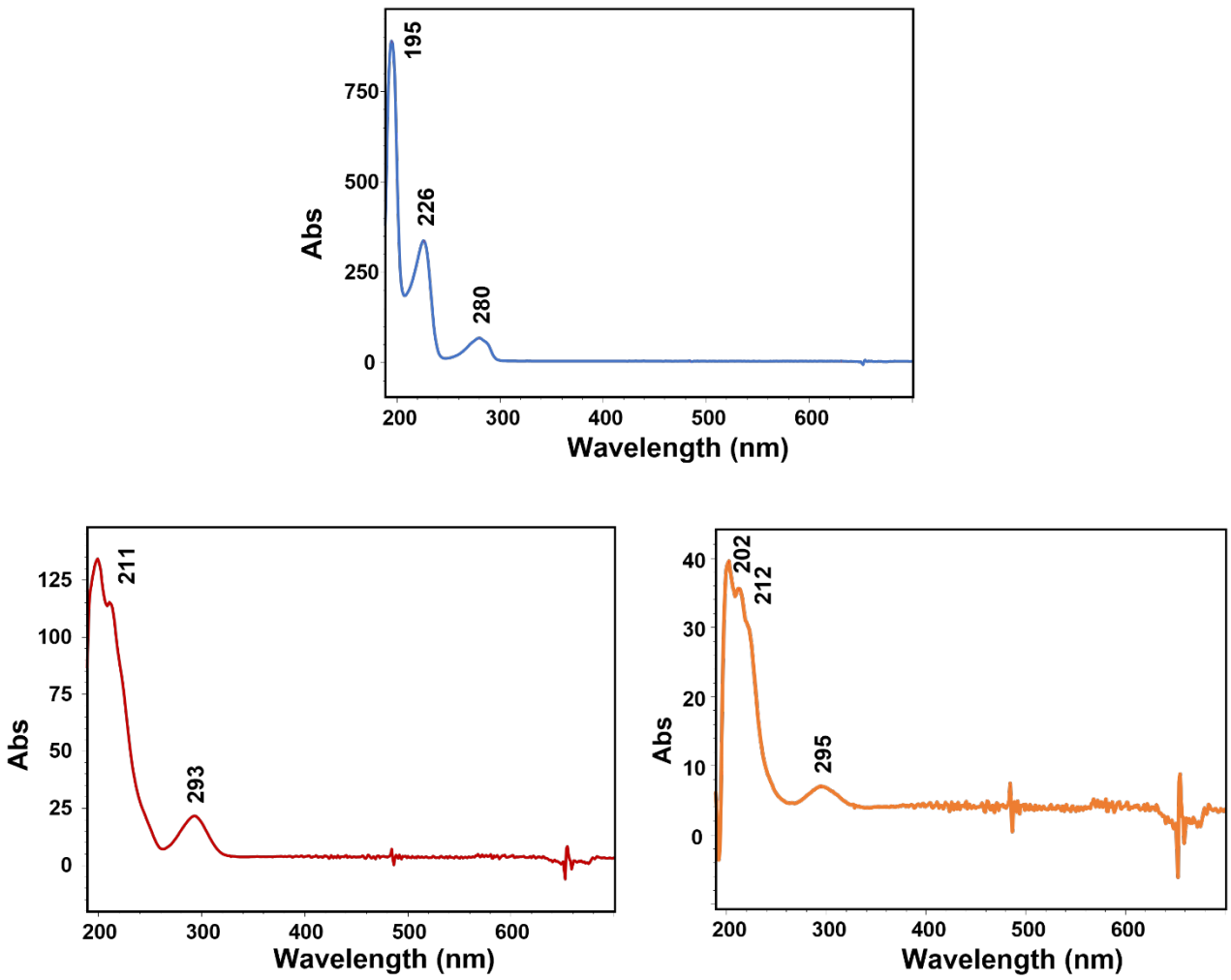


Figure S3. UV-Vis spectral profiles of the following products running in the UHPLC chromatogram (Figure 6): 4-CP (light blue curve, peak at Rt = 14.0 min), trimeric compound (dark red curve, peak at Rt = 21.8 min) and dimeric compound (orange curve, peak at Rt = 29.3 min).

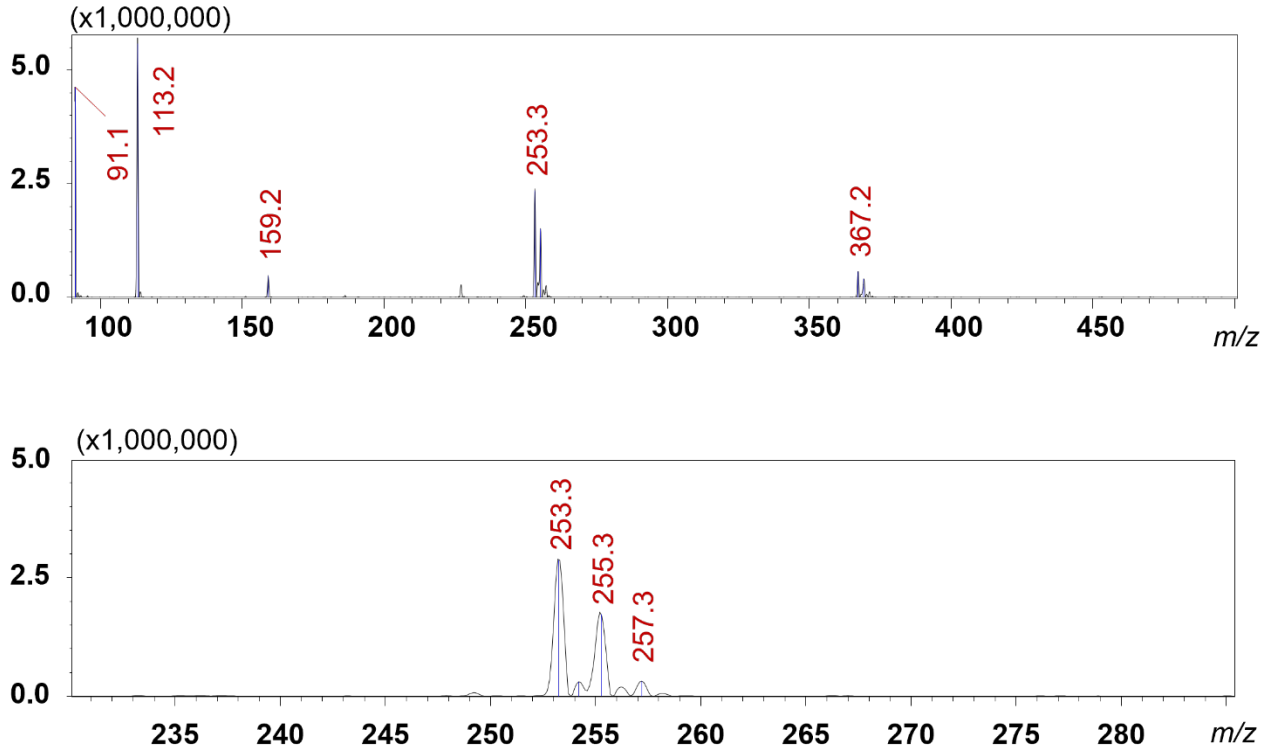


Figure S4. ESI-MS spectrum (negative ion mode, extracted from LC-MS analysis, peak at Rt = 29.3 min) of the dimeric compound obtained during 4-CP oxidation. The peak at m/z = 253.3 is referred to the molecular ion ($[M-H]^-$). In addition, peaks at m/z = 255 ($[M-H+2]^-$) and at m/z = 257.3 ($[M-H+4]^-$) are indicative of the presence of two chlorine atoms.

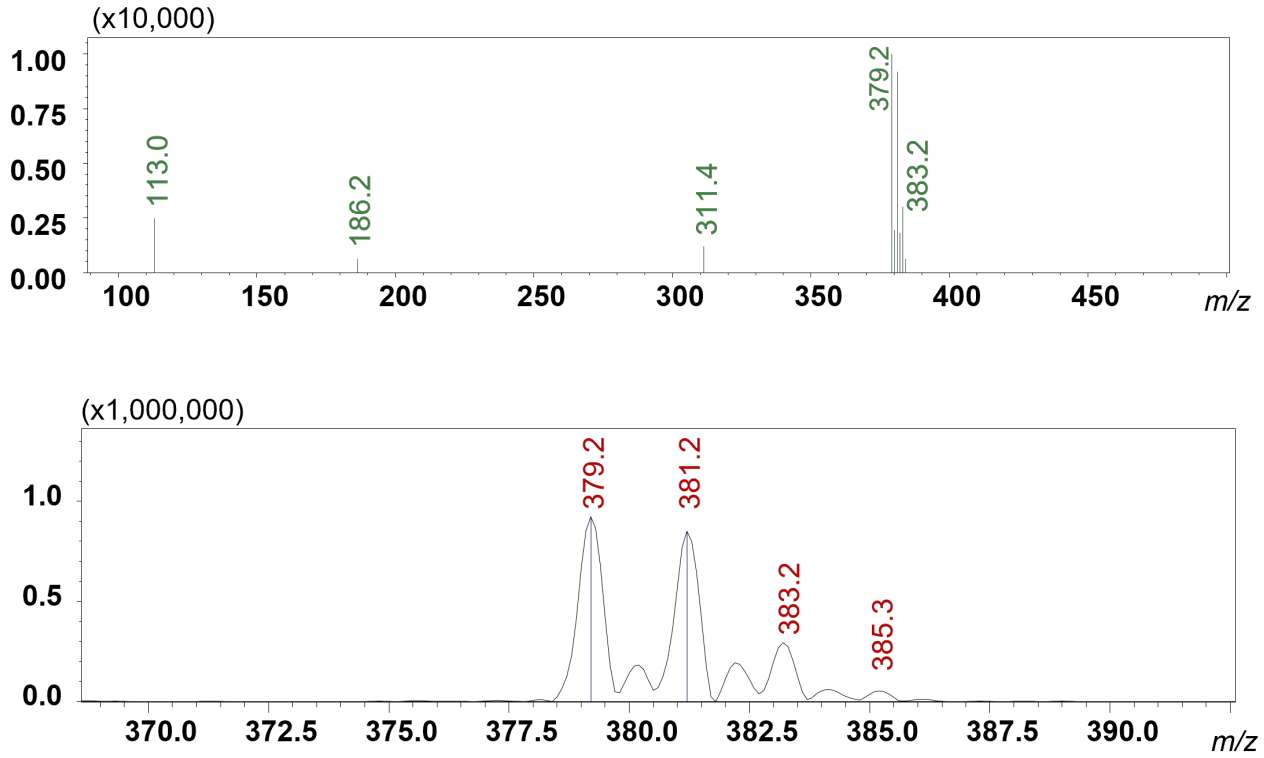


Figure S5. ESI-MS spectrum (negative ion mode, extracted from LC-MS analysis, peak at Rt = 21.8 min) of the trimeric compound obtained during 4-CP oxidation. The peak at m/z = 379.2 is referred to the molecular ion ($[M - H]^-$). In addition, peaks at m/z = 381.2 ($[M-H+2]^-$), m/z = 383.2 ($[M-H+4]^-$) and m/z = 385.3 ($[M-H+6]^-$) indicate the presence of three chlorine atoms.

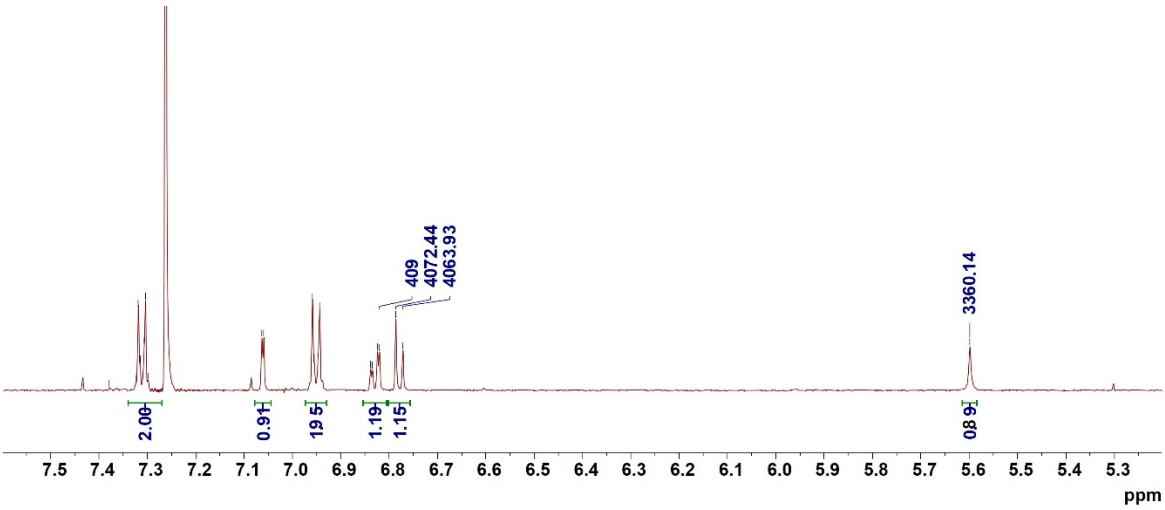


Figure S6. Close up view of the ^{1}H NMR spectrum of compound **1a** ($CDCl_3$, 600 MHz).

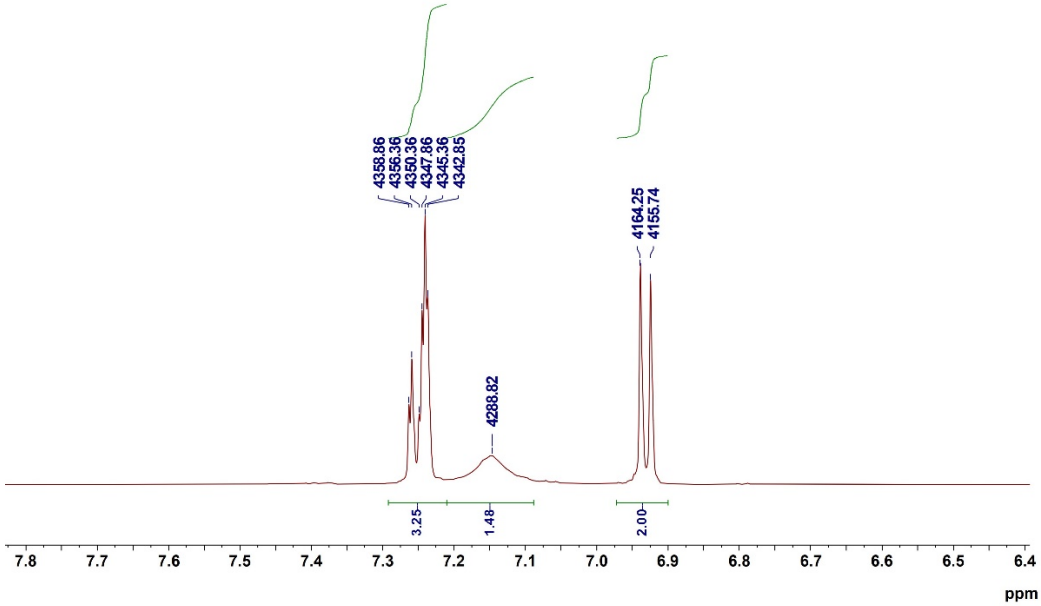


Figure S7. Close up view of the ^{1}H NMR spectrum of compound **1b** (ACN-d_3, 600 MHz).

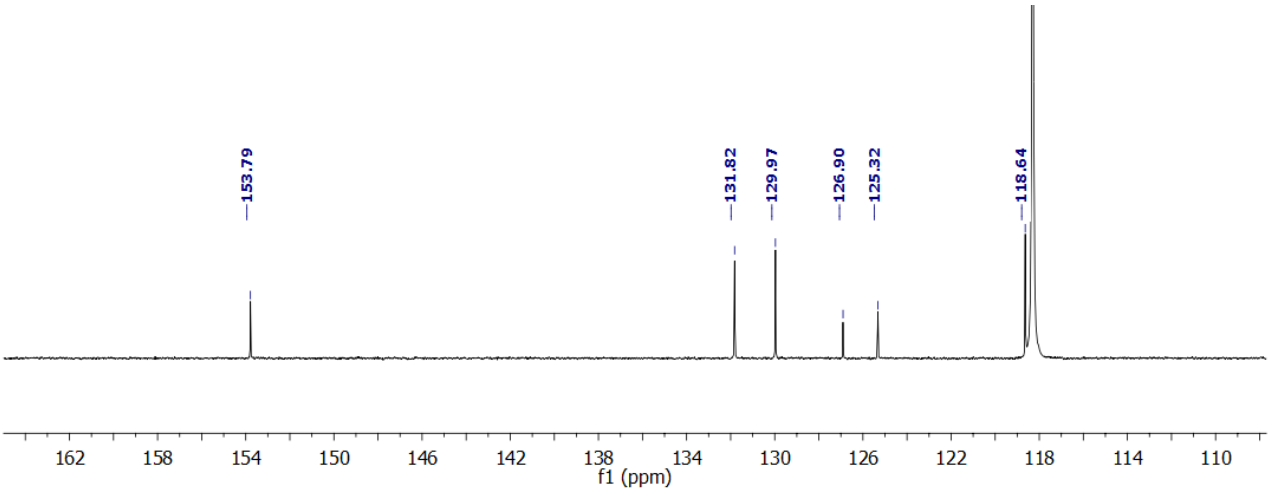


Figure S8. ^{13}C NMR spectrum of compound **1b** (ACN-d_3, 100 MHz).

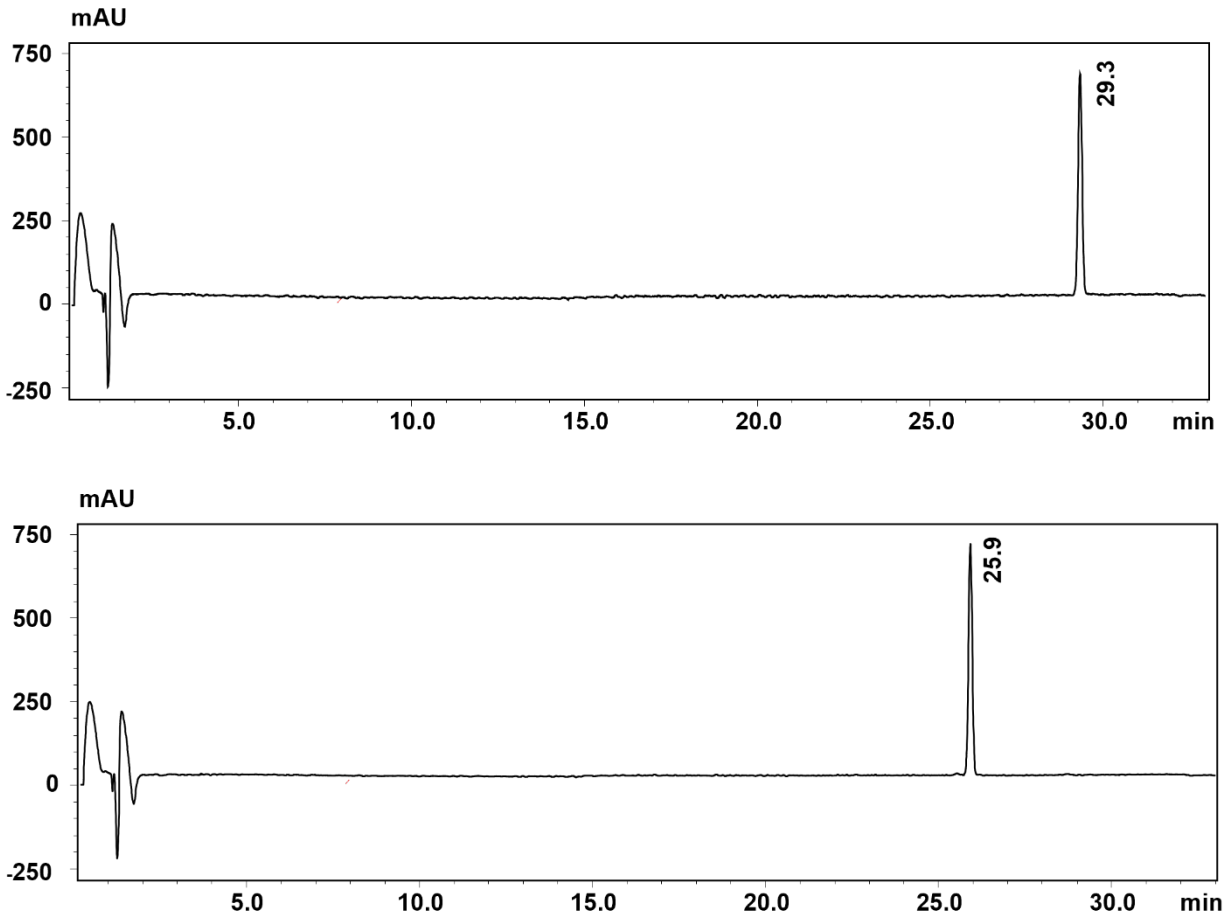


Figure S9. UHPLC runs of compounds **1a** (upper trace) and **1b** (lower trace).

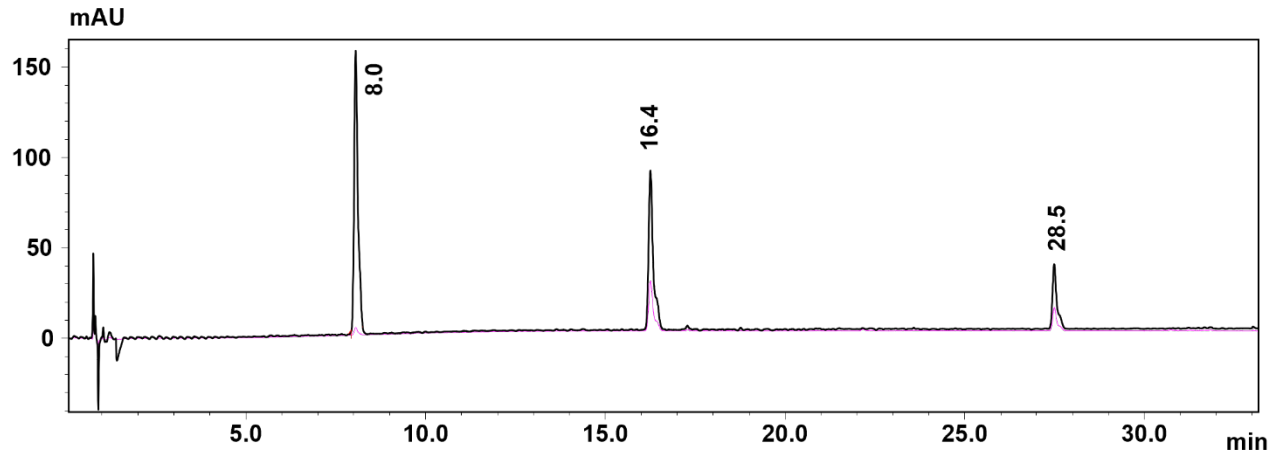


Figure S10. UHPLC traces (black line: λ = 220 nm, pink line: λ = 240 nm) of the Fe-MC6*a-catalyzed oxidation of 4-BP 30 min after H_2O_2 addition. The peak with Rt = 16.4 min corresponds to 4-BP; the peak with Rt = 8.0 min is MPS, used as internal standard. Reaction conditions: [Fe-MC6*a] = 6.25 x 10^{-6} M; [4-BP] = 2.5 mM; [H_2O_2] = 2.5 mM; phosphate buffer (50 mM) at pH 6.5 with 50% TFE (v/v).

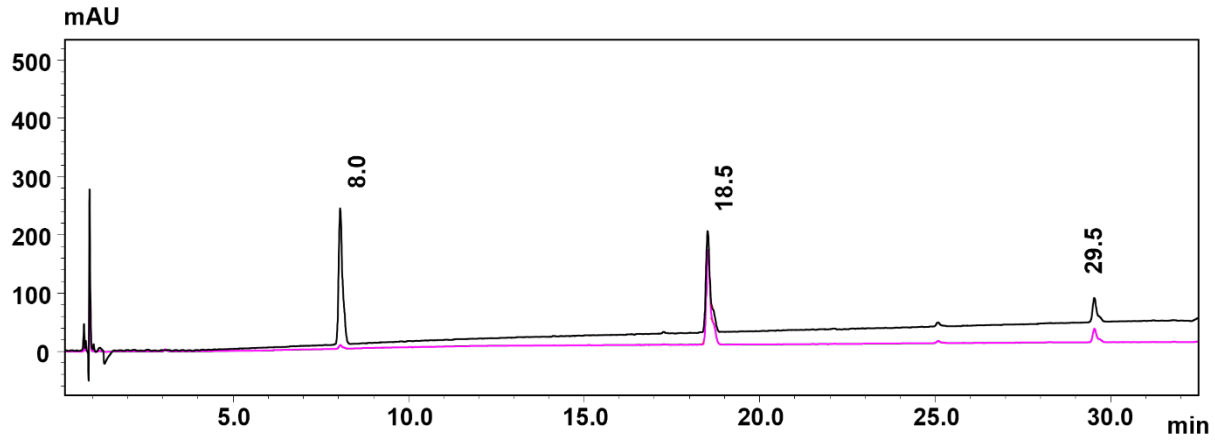


Figure S11. UHPLC traces (black line: λ = 220 nm, pink line: λ = 240 nm) of the Fe-MC6*a-catalyzed oxidation of 4-IP 30 min after H_2O_2 addition. The peak with Rt = 18.5 min corresponds to 4-iodophenol; the peak with Rt = 8.0 min is MPS, used as internal standard. The peak with Rt = 29.5 min corresponds to 4-IP dimer, as determined by LC-MS analysis. Reaction conditions: [Fe-MC6*a] = 6.25 x 10^{-6} M; [4-IP] = 2.5 mM; [H_2O_2] = 2.5 mM; phosphate buffer (50 mM) at pH 6.5 with 50% TFE (v/v).

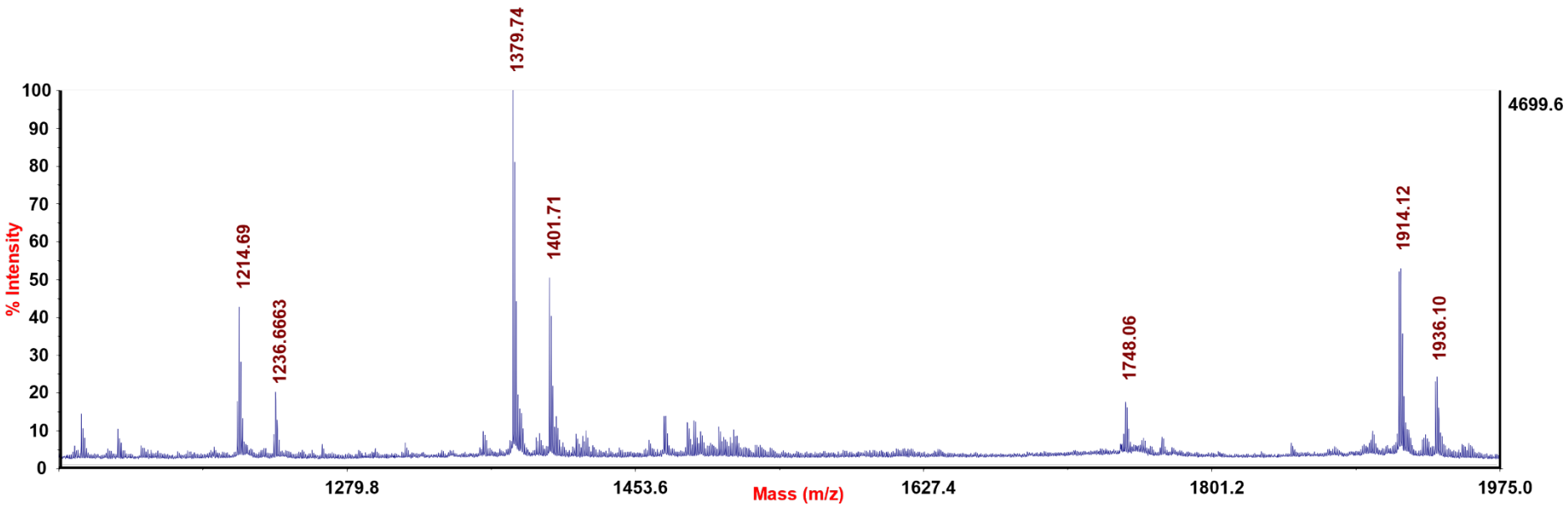
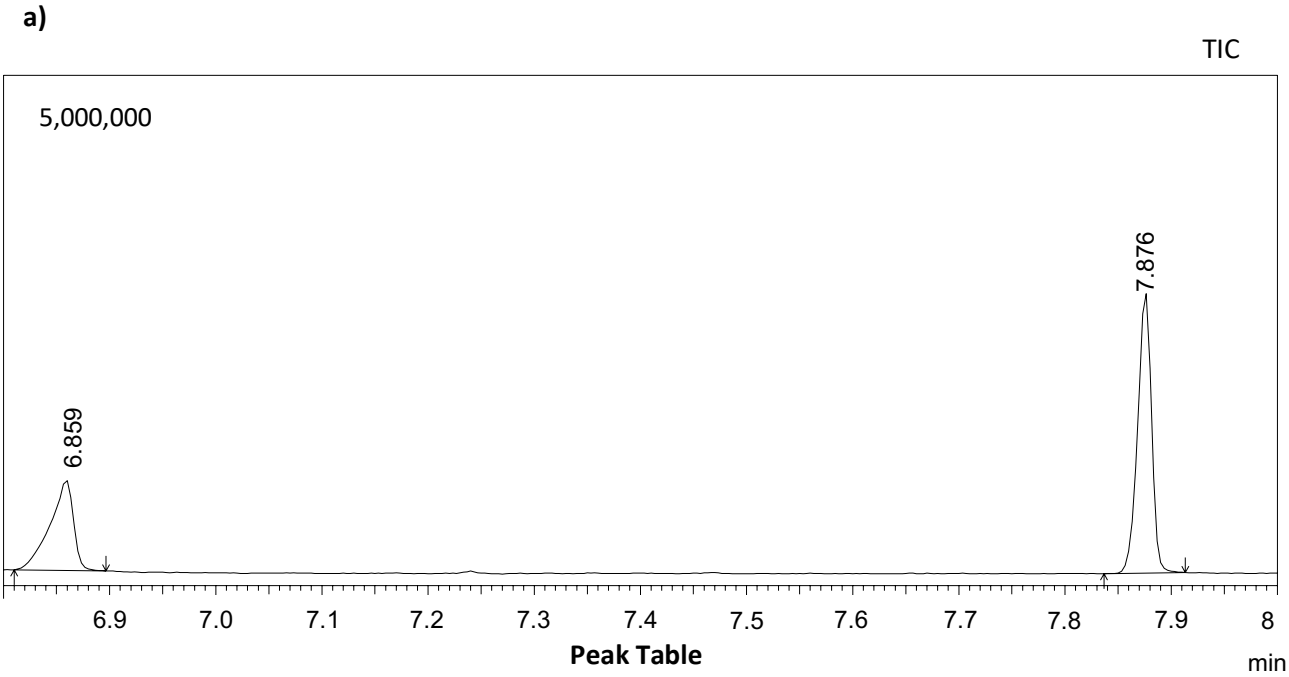
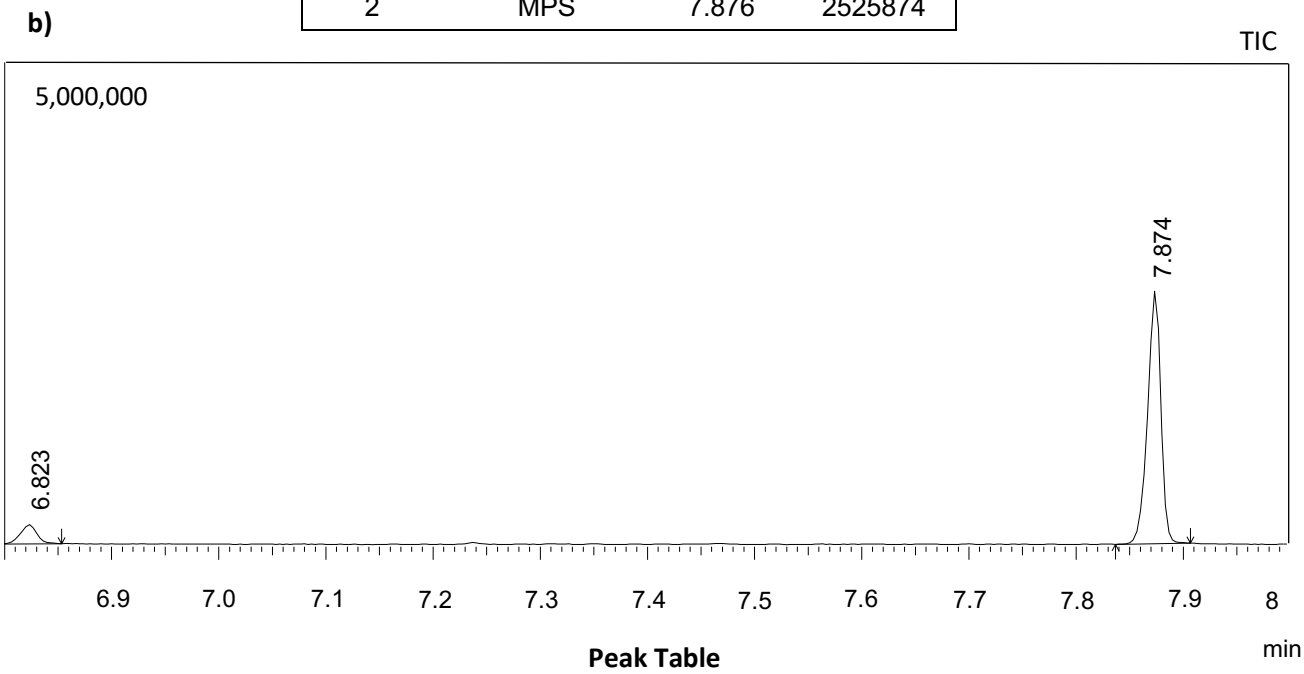


Figure S12. Close up view of the MALDI-MS spectrum of the insoluble material formed during the course of the Fe-MC6*a-catalyzed 4-CP oxidation.



Peak Table

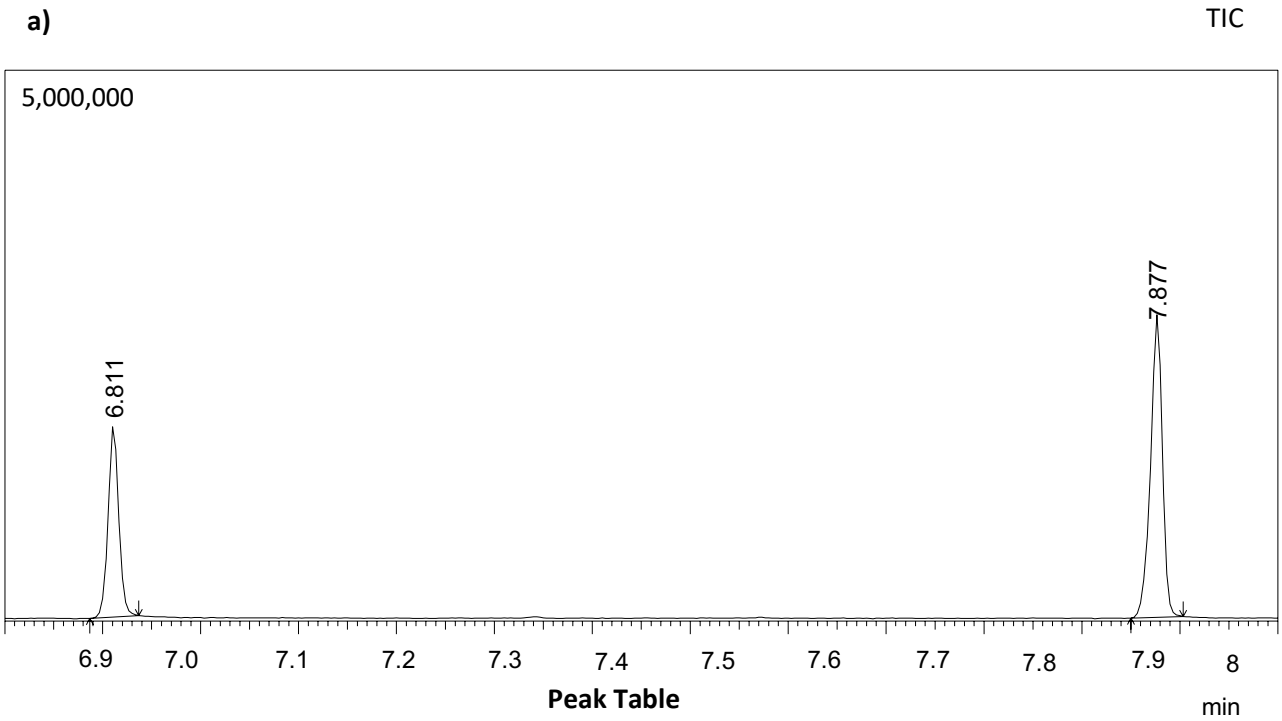
Peak #	Compound	Rt (min)	Area
1	4-CP	6.859	1382473
2	MPS	7.876	2525874



Peak Table

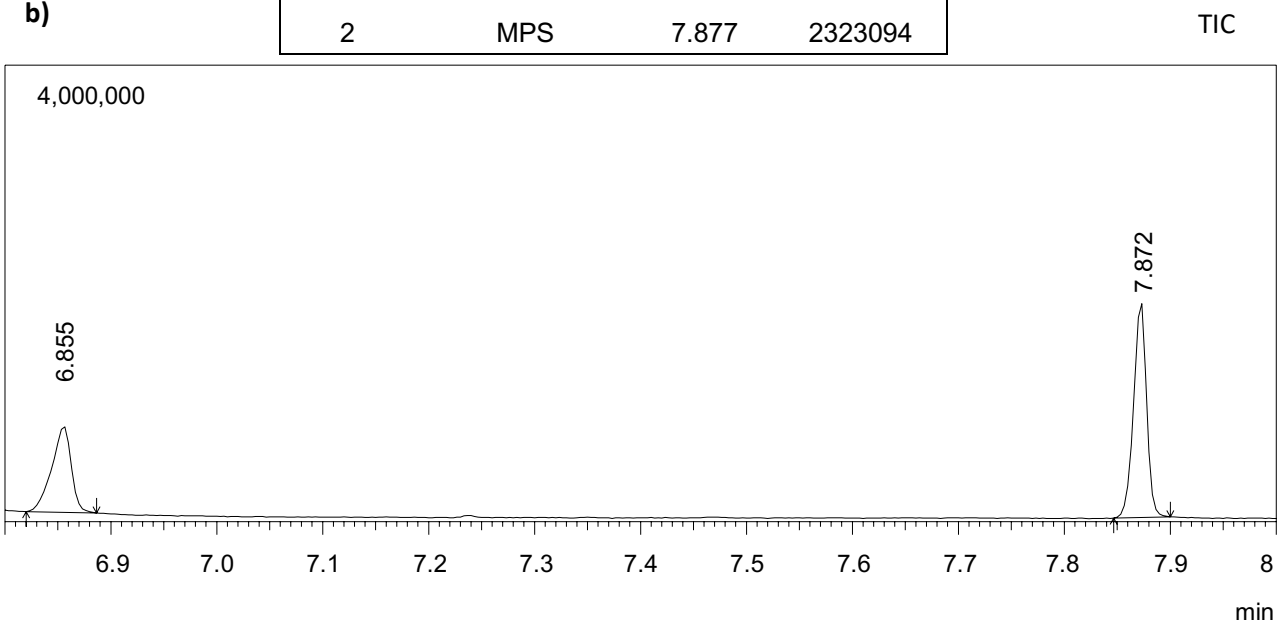
Peak #	Compound	Rt (min)	Area
1	4-CP	6.823	213410
2	MPS	7.874	2249164

Figure S13. GC-MS analysis of the FeMC6*a-catalyzed 4-CP oxidation (a) before and (b) 30 min after H_2O_2 addition. *Reaction conditions*: [Fe-MC6*a] = 1.0 x 10^{-3} mM; [4-CP] = 2.5 mM; [H_2O_2] = 2.5 mM; [MPS] = 2.5 mM; phosphate buffer (50 mM) at pH 6.5 with 50% TFE (v/v).



Peak Table

Peak #	Compound	Rt (min)	Area
1	4-CP	6.811	1327675
2	MPS	7.877	2323094



Peak Table

Peak #	Compound	Rt (min)	Area
1	4-CP	6.855	971181
2	MPS	7.872	1618738

Figure S14. GC-MS analysis of the FeMC6*a-catalyzed 4-CP oxidation (a) before and (b) 30 min after sequential H_2O_2 and DMPO additions. *Reaction conditions*: [Fe-MC6*a] = 1.0 x 10^{-3} mM; [4-CP] = 2.5 mM; [H_2O_2] = 2.5 mM; [MPS] = 2.5 mM; [DMPO] = 125 mM; phosphate buffer (50 mM) at pH 6.5 with 50% TFE (v/v).