

Supplementary Materials: A Comparative Study of the Catalytic Behaviour of Alkoxy-1,3,5-Triazapentadiene Copper(II) Complexes in Cyclohexane Oxidation

Oksana V. Nesterova, Maximilian N. Kopylovich and Dmytro S. Nesterov

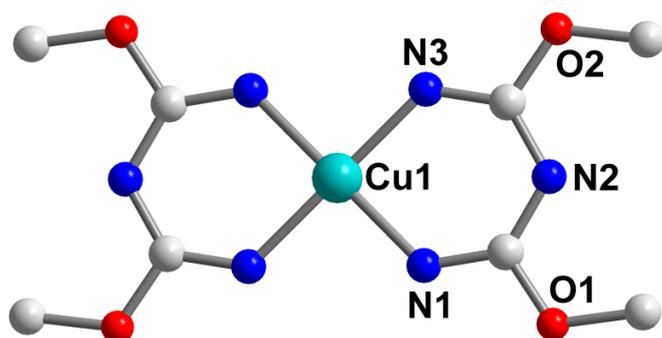


Figure S1. Ball-and-stick representation of **1** with atom numbering. H atoms are omitted for clarity.

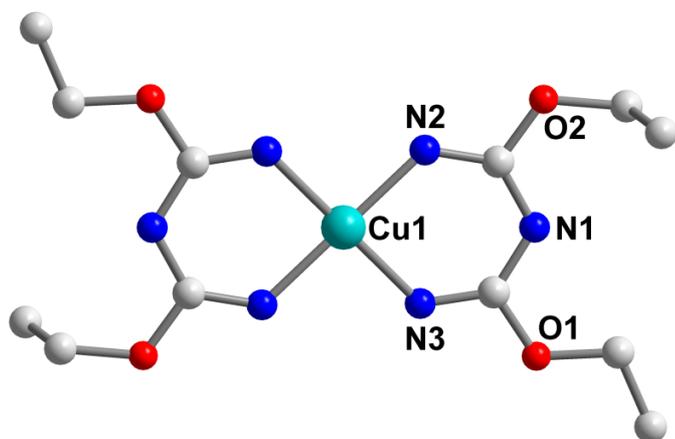


Figure S2. Ball-and-stick representation of **2** with atom numbering. H atoms are omitted for clarity.

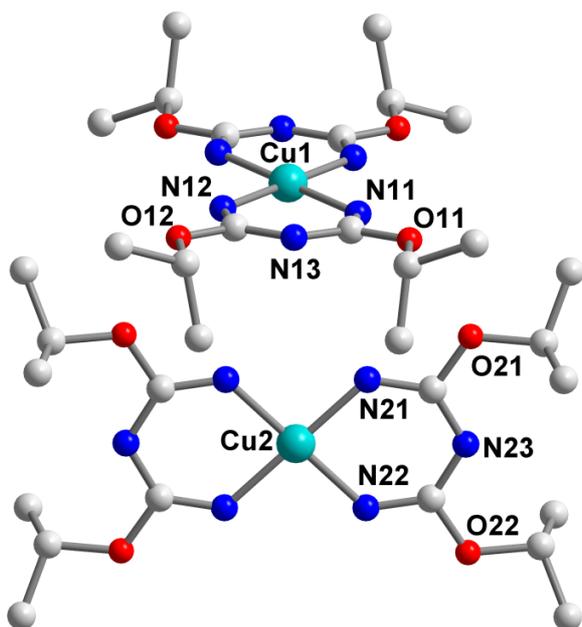


Figure S3. Ball-and-stick representation of **4** with atom numbering. H atoms are omitted for clarity.

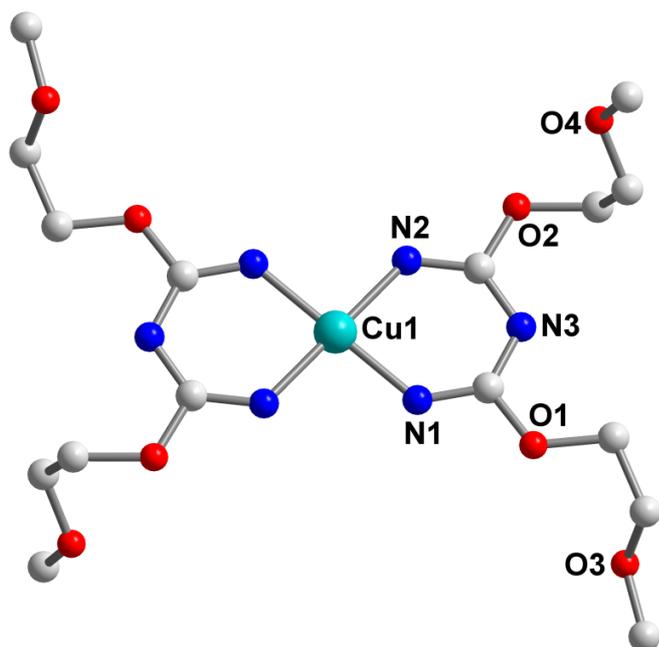


Figure S4. Ball-and-stick representation of **5** with atom numbering. H atoms are omitted for clarity.

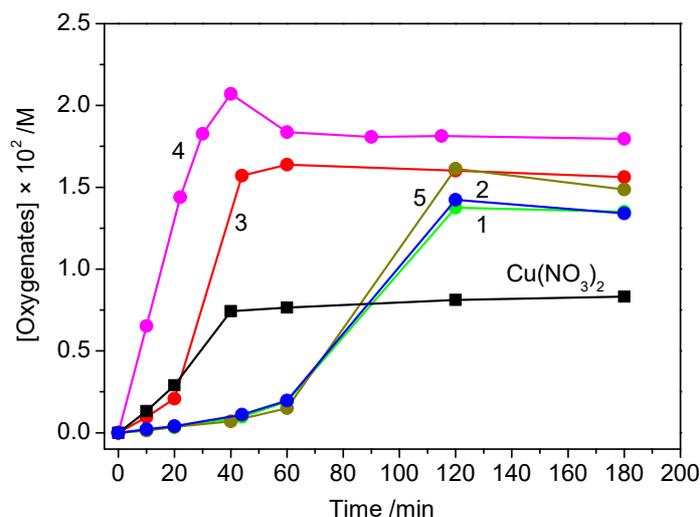


Figure S5. Accumulations of the reaction products (sum of cyclohexanol and cyclohexanone) in the oxidation of cyclohexane (0.2 M) with H₂O₂ (0.5 M) catalysed by **1–5** (1×10^{-3} M) and by Cu(NO₃)₂ (1×10^{-3} M) in the presence of pyridine (0.01 M) in acetonitrile at 50 °C.

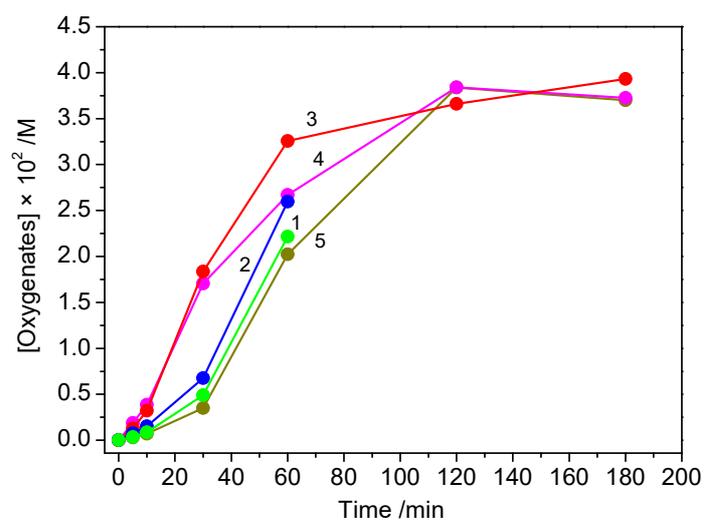


Figure S6. Accumulations of the reaction products (sum of cyclohexanol and cyclohexanone) in the oxidation of cyclohexane (0.2 M) with H₂O₂ (1 M) catalysed by **1–5** (1×10^{-3} M) in the presence of pyridine (0.01 M) in acetonitrile at 50 °C.

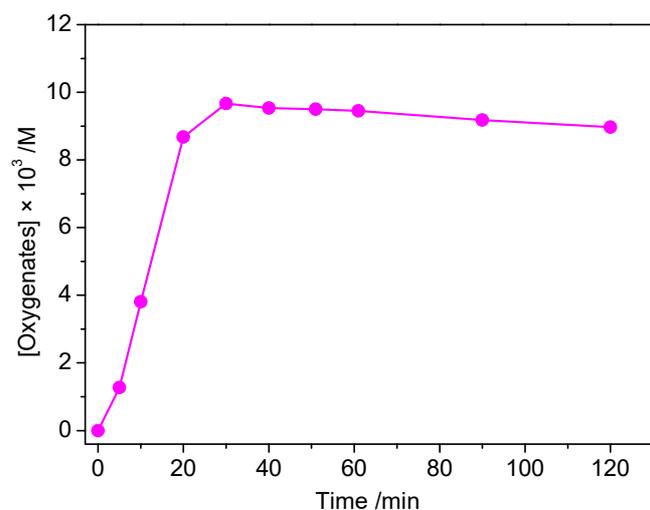


Figure S7. Accumulation of the reaction products (sum of cyclohexanol and cyclohexanone) in the oxidation of cyclohexane (0.2 M) with H_2O_2 (0.35 M) catalysed by **4** (1×10^{-3} M) in the presence of pyridine (0.01 M) in acetonitrile at 50 °C.

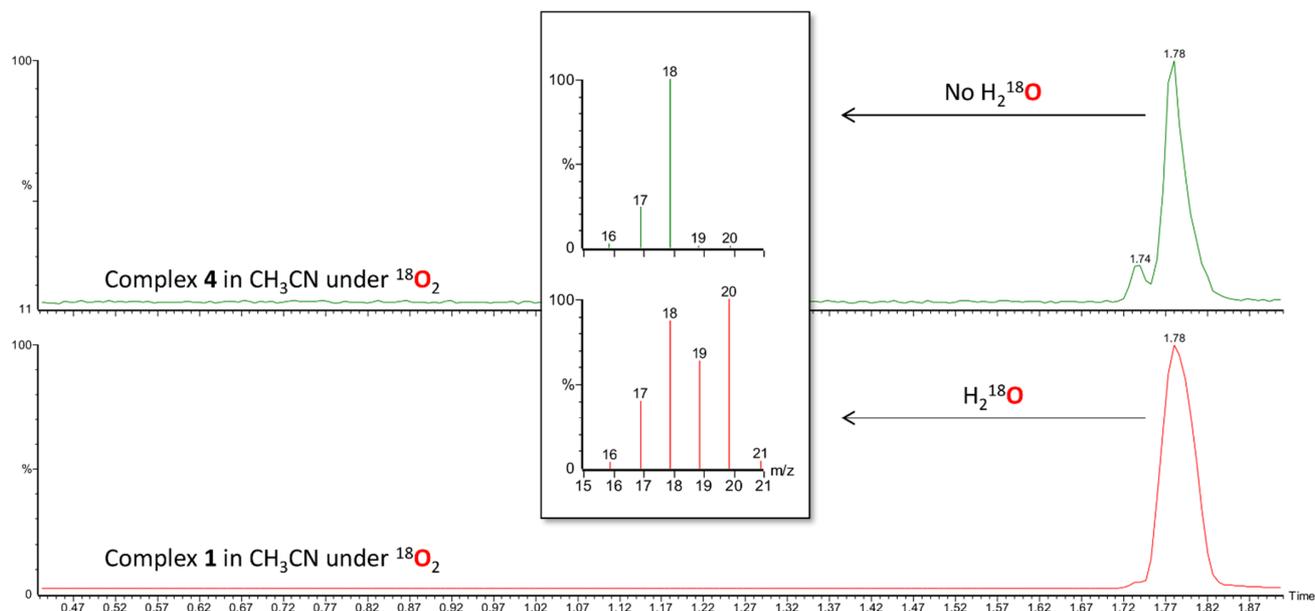


Figure S8. Fragments of the chromatograms of the acetonitrile solutions (2×10^{-3} M) of **1** (bottom) and **4** (top) after stirring for 24 h under $^{18}\text{O}_2$ atmosphere at room temperature, showing the peak at 1.78 min attributable to water. The inset shows the respective mass-spectra. The presence 19 and 20 m/z peaks in the case of the complex **1** account for H_2^{18}O water. The small peak at 1.74 min corresponds to air.

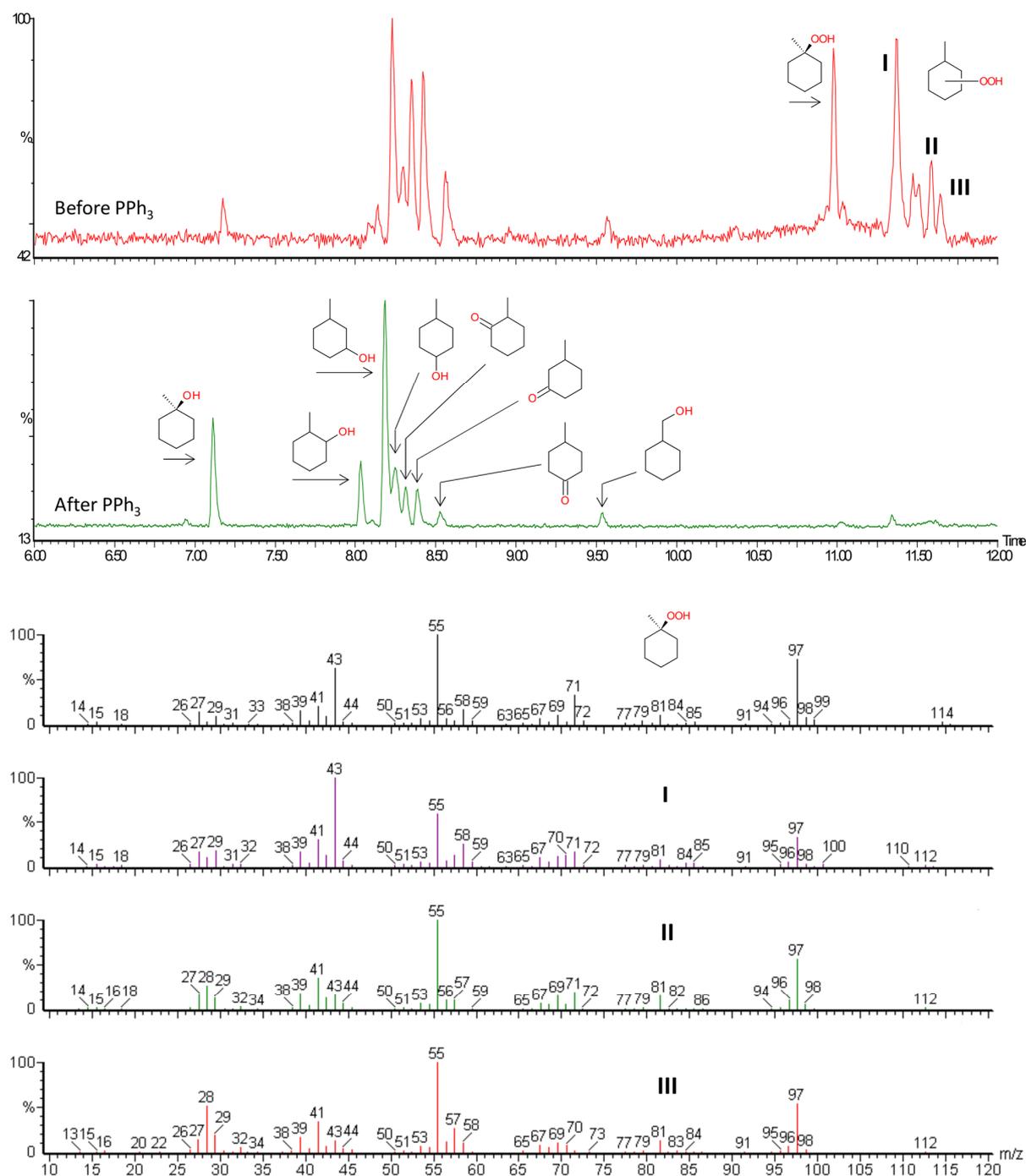


Figure S9. Top: fragments of the chromatograms recorded before and after addition of PPh₃ showing the reaction products in the oxidation of methylcyclohexane (0.2 M) with H₂O₂ (0.5 M) catalysed by **4** (1×10^{-3} M) in the presence of pyridine (0.01 M) in acetonitrile at 50 °C after 2 h. Bottom: EI-MS spectra of the peaks attributed to methylcyclohexyl hydroperoxides.

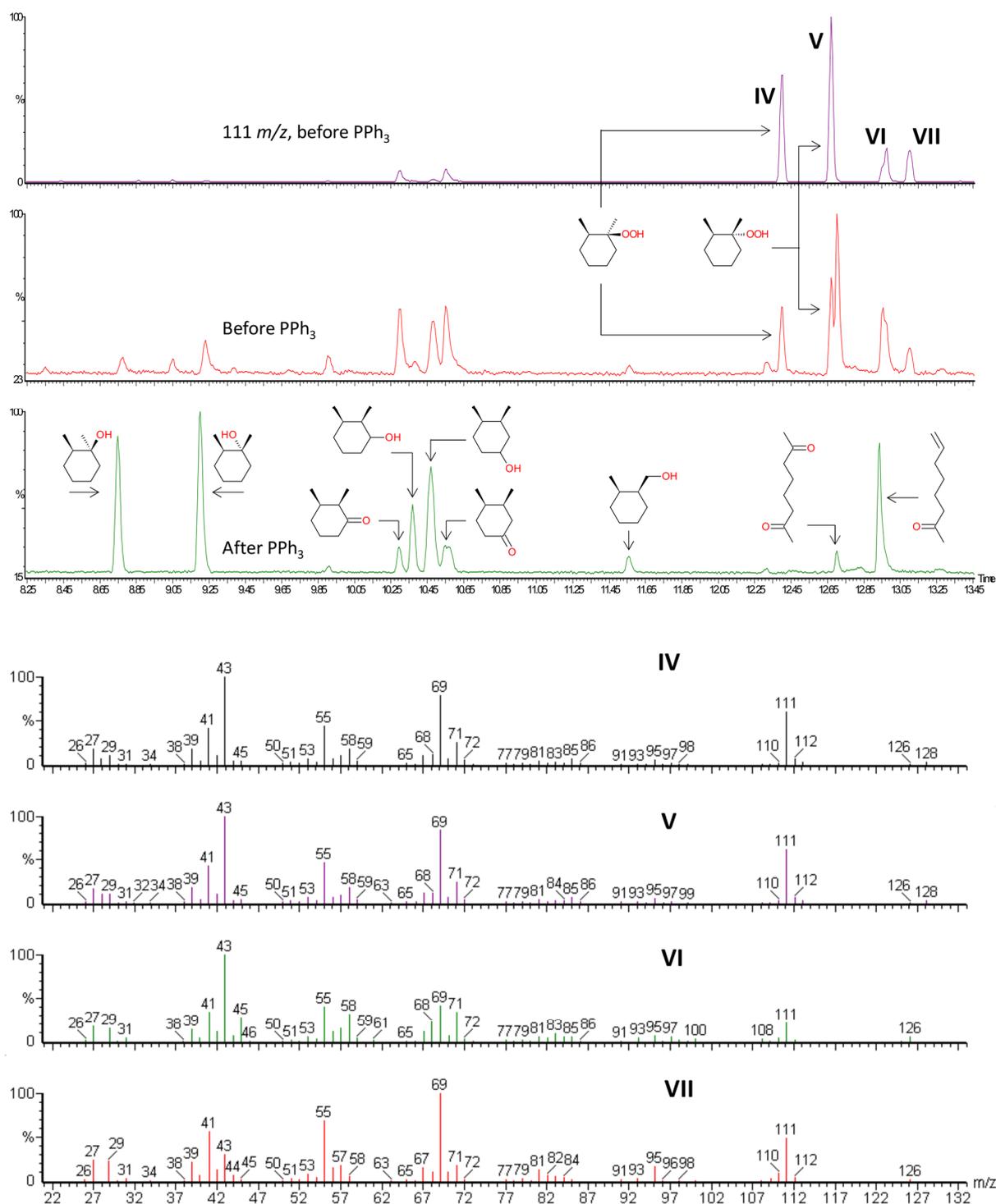


Figure S10. Top: fragments of the chromatograms recorded before and after addition of PPh₃ showing the reaction products in the oxidation of *cis*-1,2-dimethylcyclohexane (0.2 M) with H₂O₂ (0.5 M) catalysed by **4** (1×10^{-3} M) in the presence of pyridine (0.01 M) in acetonitrile at 50 °C after 2 h. Bottom: EI-MS spectra of the peaks attributed to *cis*-1,2-dimethylcyclohexyl hydroperoxides.

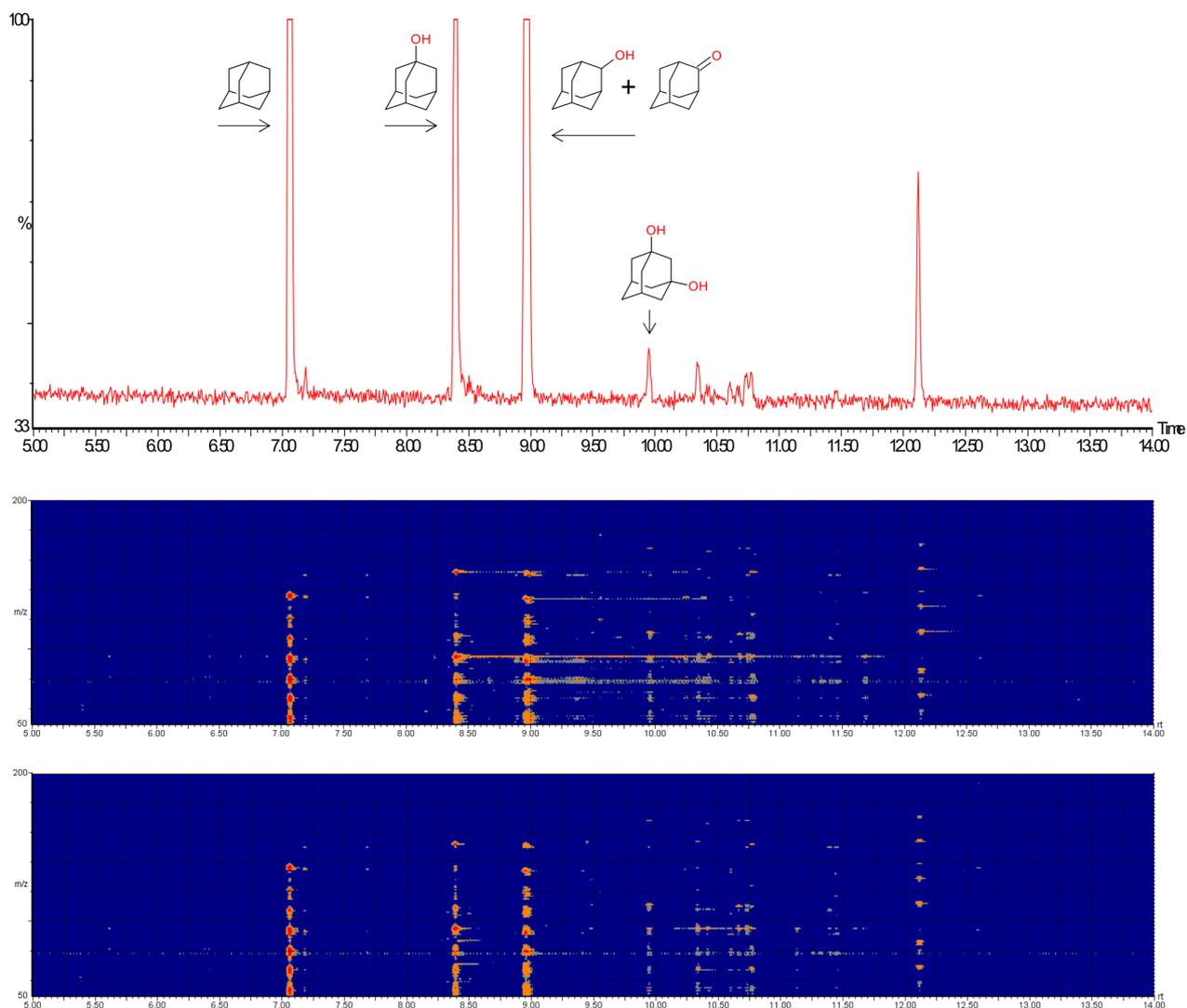


Figure S11 Top: fragment of the chromatograms recorded after addition of PPh₃ showing the reaction products in the oxidation of adamantane (0.2 M) with H₂O₂ (0.5 M) catalysed by **4** (1×10^{-3} M) in the presence of pyridine (0.01 M) in acetonitrile at 50 °C after 2 h. Middle and bottom: GCMS 2D maps of the chromatograms recorded before (middle) and after (bottom) addition of PPh₃, showing no difference in the by-products. The peak 12.2 min is believed to be a residue formed from the degradation of the complex **4**.