Electronic Supplementary Information

Stereoselective oxidation of alkanes with *m*-CPBA as an oxidant and cobalt complex with isoindole-based ligands as a catalyst

Oksana V. Nesterova,[a] Maximilian N. Kopylovich[a] and Dmytro S. Nesterov[a]*

[a] Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

E-mail: dmytro.nesterov@tecnico.ulisboa.pt

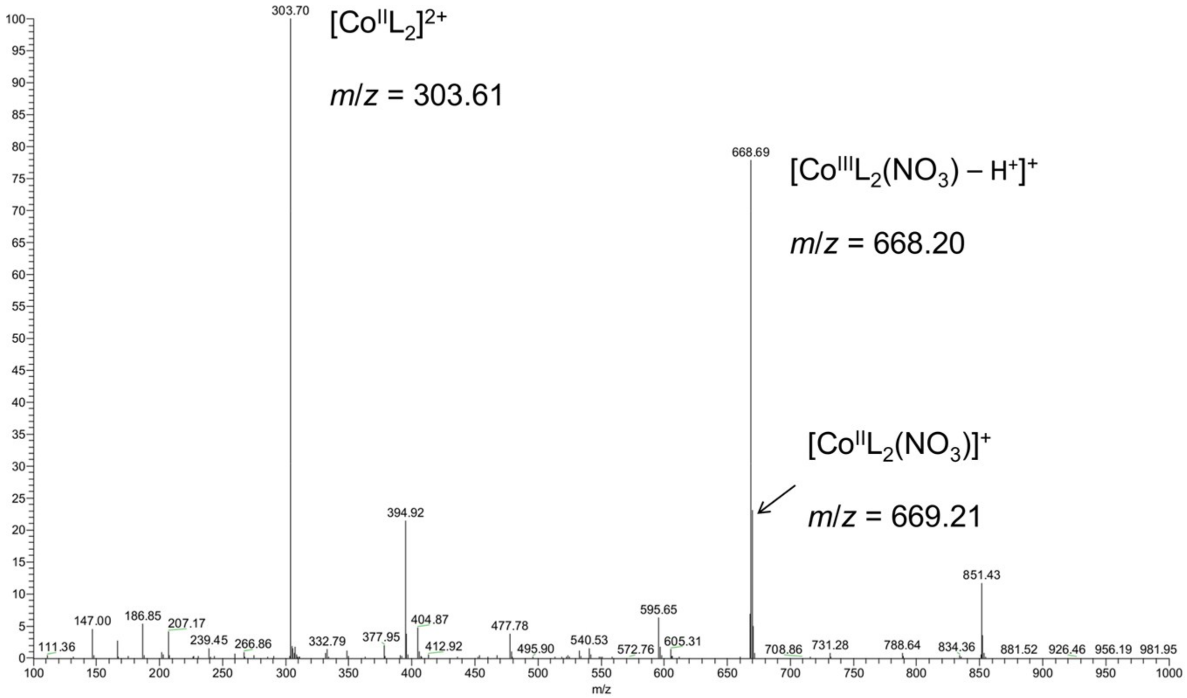

Fig. S1 ESI-MS (+) spectrum of acetonitrile solution of **1**.

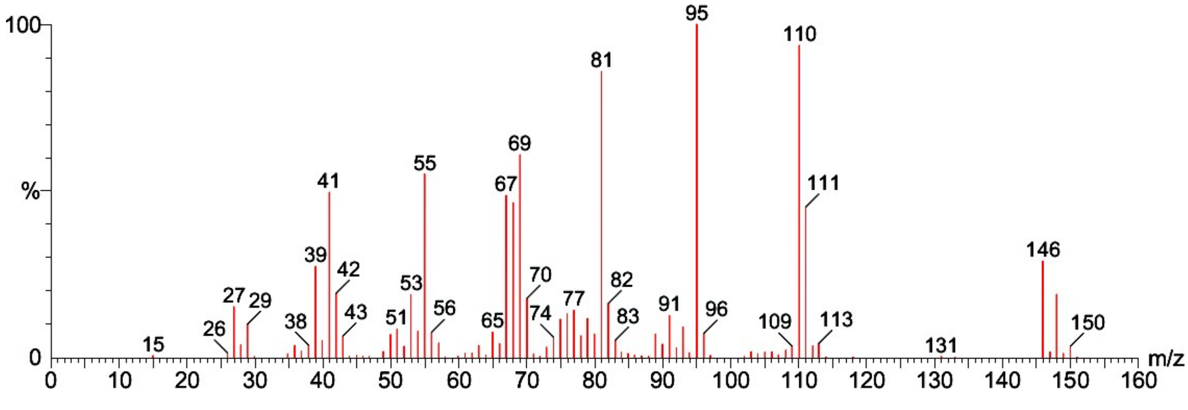

Fig. S2 EI mass spectrum of **I**.

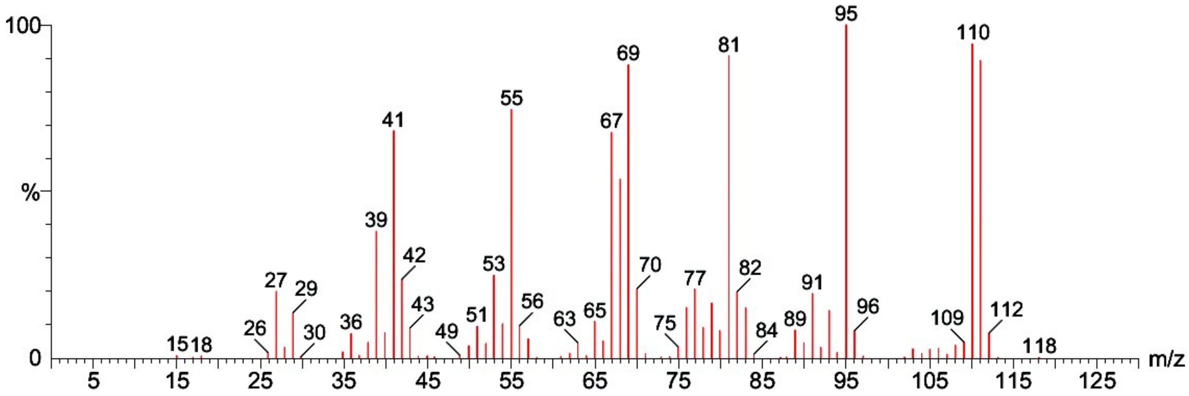

Fig. S3 EI mass spectrum of **II**.

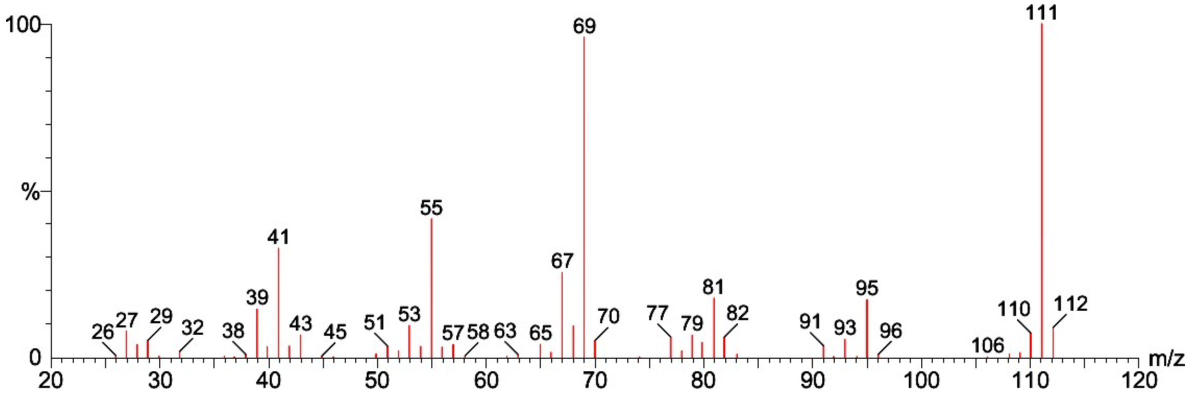

Fig. S4 EI mass spectrum of **V**.

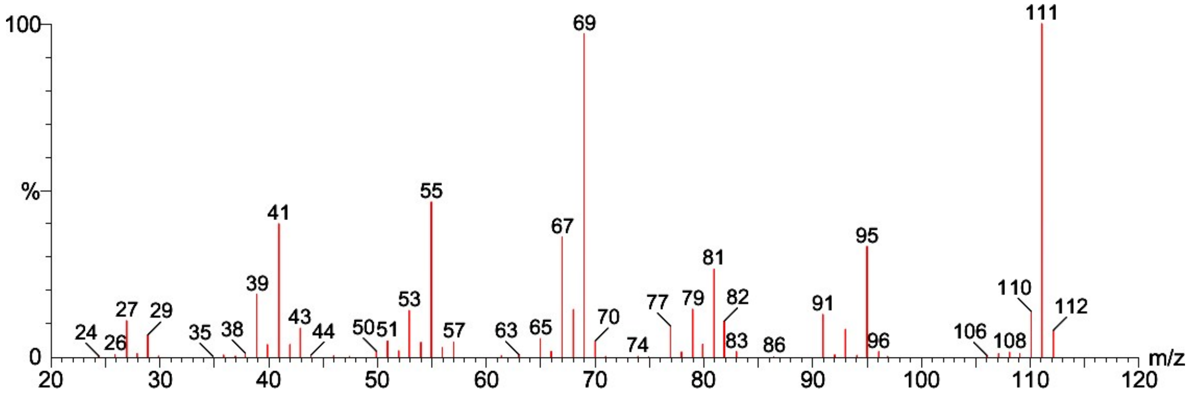

Fig. S5 EI mass spectrum of **VI**.

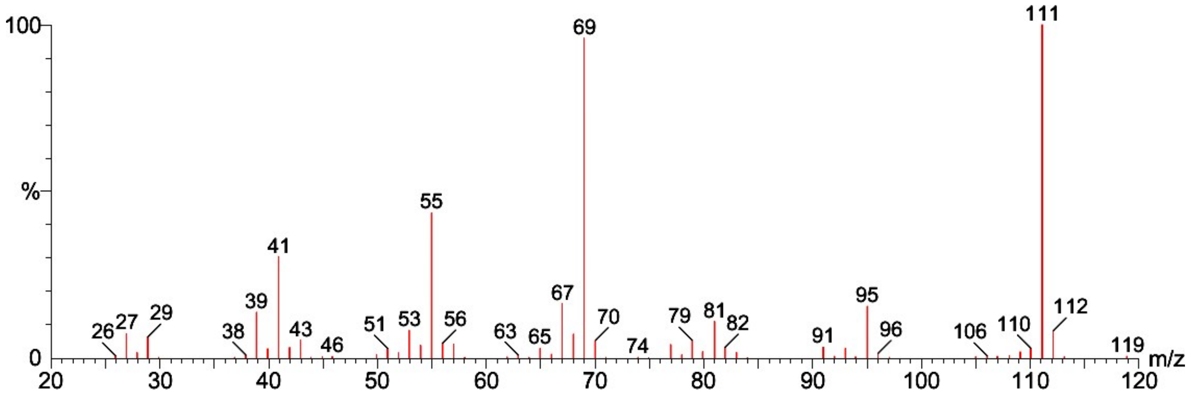

Fig. S6 EI mass spectrum of **VII**.

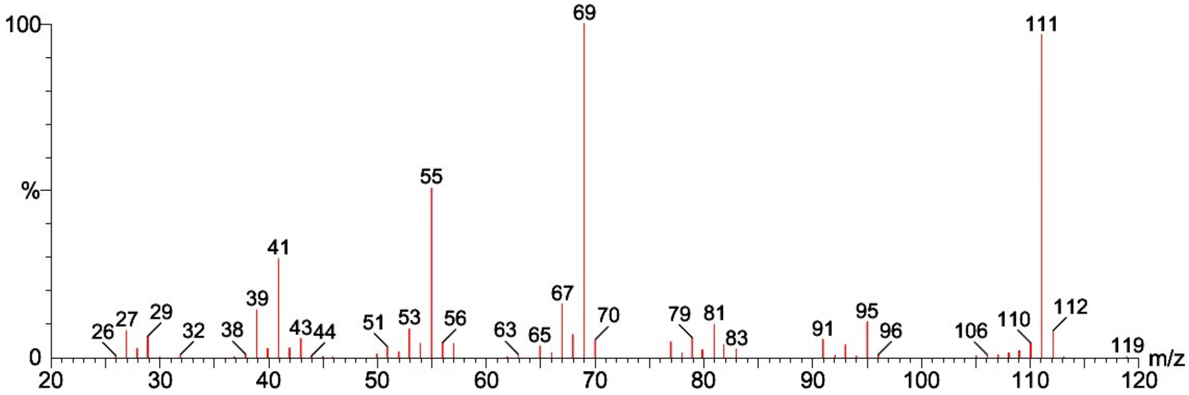

Fig. S7 EI mass spectrum of **VIII**.

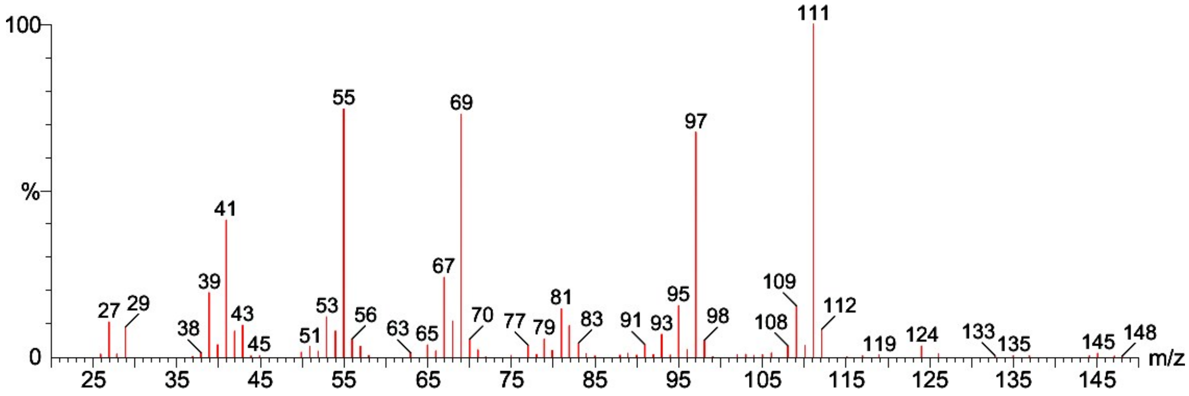

Fig. S8 EI mass spectrum of **IX**.

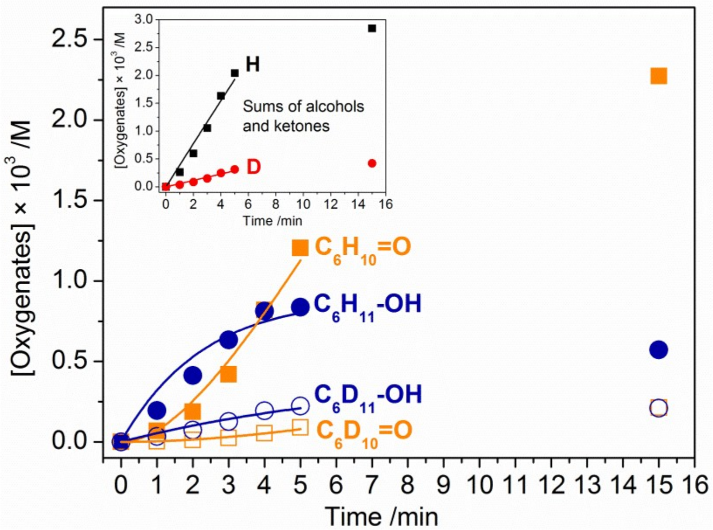

Fig. S9 Accumulations of oxidation products (alcohols and ketones, circles and squares, respectively) over time in the oxidation of equimolar mixture (0.05 M each) of normal (solid symbols) and deuterated (open symbols) cyclohexane with *m*-CPBA (0.027 M) catalysed by complex **1** (3.3×10^{-4} M) in CH_3CN at 40 °C. Inset shows accumulations of sums oxidation products (alcohol and ketone) of normal (black squares) and deuterated (red circles) cyclohexane. Solid lines are the respective fits (see main text).

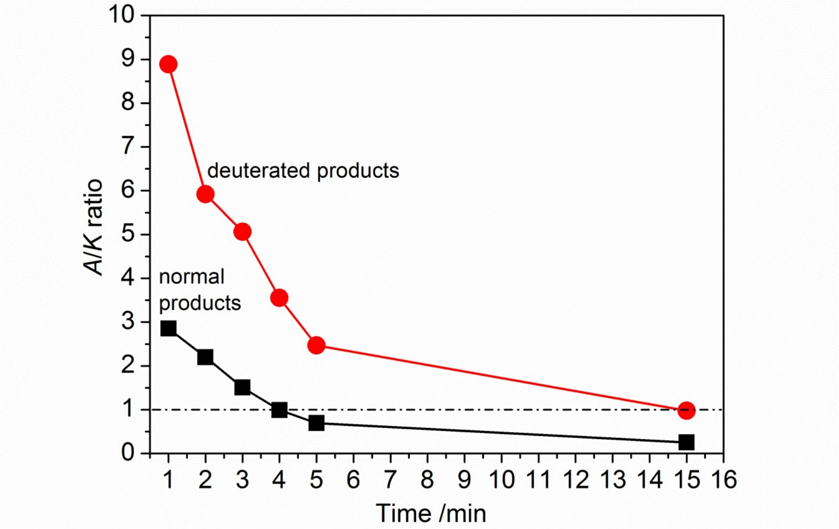

Fig. S10 Drop of the alcohol/ketone (A/K) ratio in the course of competitive oxidation of equimolar (0.05 M each) C_6H_{12}/C_6D_{12} mixture.

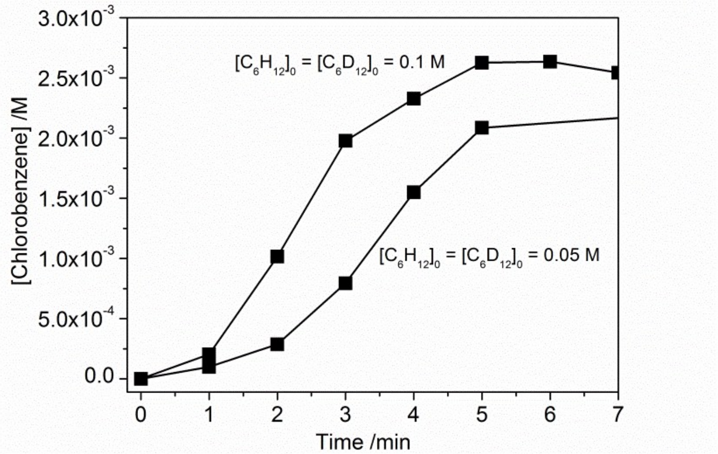

Fig. S11 Accumulations of chlorobenzene over time in the oxidation of equimolar mixture of normal and deuterated cyclohexane with *m*-CPBA (0.027 M) catalysed by complex **1** (3.3×10^{-4} M) in CH_3CN at 40 °C.

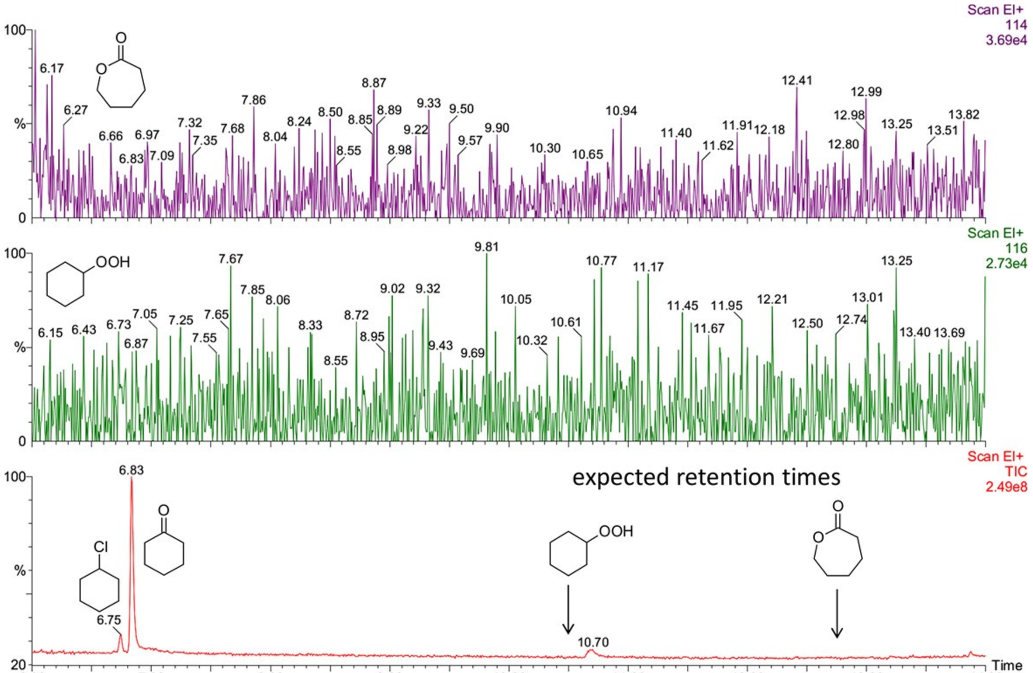

Fig. S12 Fragment of the chromatogram showing the main products (below) in the oxidation of normal cyclohexane (0.1 M) with *m*-CPBA (0.027 M) catalysed by complex **1** (3.3×10^{-4} M) in CH_3CN at 40 °C. The chromatogram was recorded after 20 min reaction time, prior addition of solid PPh_3 to the sample. Mass-spectra of normal chlorocyclohexane and deuterated one (the latter obtained in a similar test, but with oxidation of C_6D_{12}) are shown at Figs. S13. Chromatograms at top and in the middle show the intensities of 114 and 116 m/z signals, corresponding to the molecular ions of ε-caprolactone and cyclohexyl hydroperoxide, respectively. Mass-spectra of a normal and deuterated 10.70 min peak (not recognized) are shown at Fig. S14.

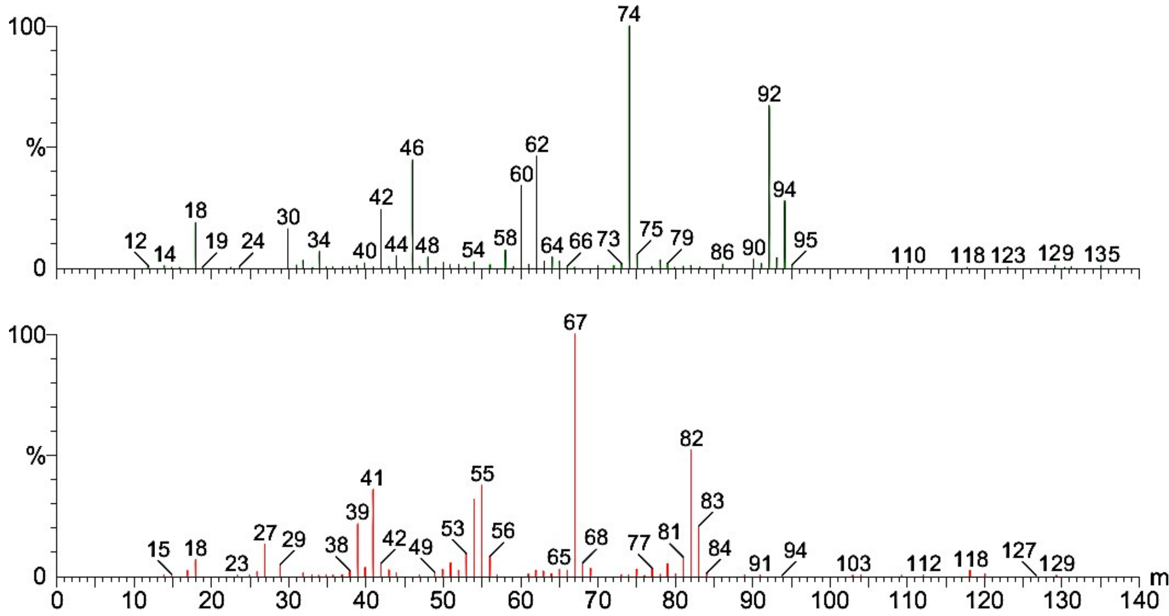

Fig. S13 EI mass-spectra of deuterated and normal chlorocyclohexanes (above and below, respectively).

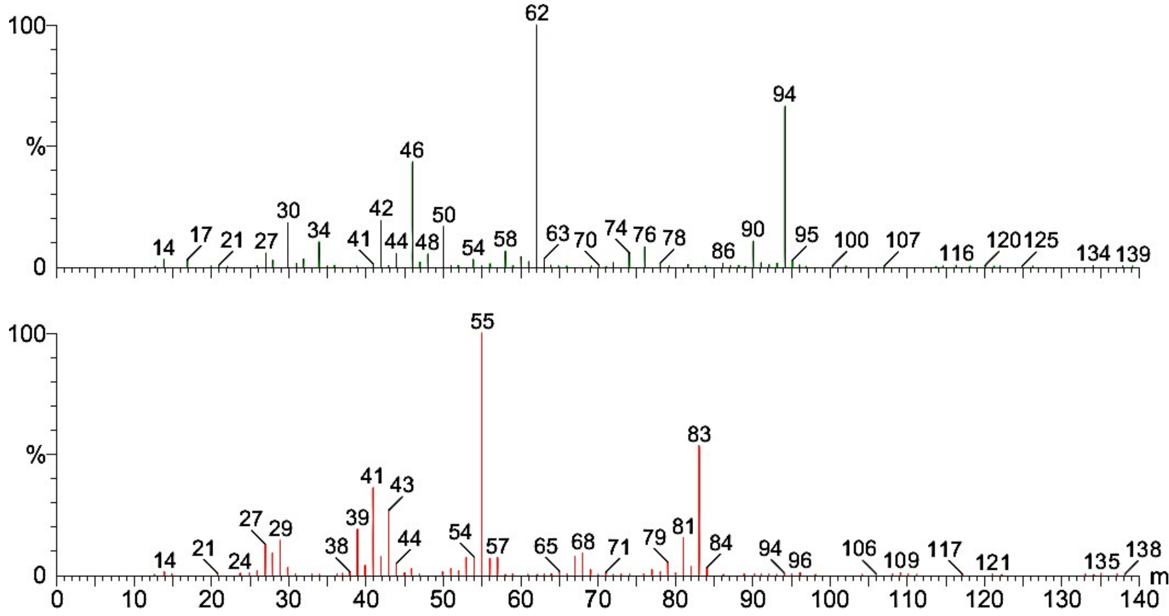

Fig. S14 EI mass-spectra of the peak at 10.70 min (Fig. S12) obtained in the course of oxidation of normal (below) and deuterated (above) cyclohexane. The mass-spectra were not assigned to any compound from the NIST database. The shift of +11 *m*/*z* between 94 and 83 *m*/*z* peaks points out that the respective compound contains at least 11 hydrogen atoms, suggesting that it could be some derivative of cyclohexane. Similar spectra were observed recently in the oxidation of cyclohexane with H_2O_2 catalysed by copper complexes (*New J. Chem.*, 2015, *39*, 187), also not recognised.

Cyclohexane oxidation fitting details

The analytical kinetic expression,[40] describing two-step irreversible reactions (rate constants k_1 and k_2)

$$k_1 \qquad A \rightarrow B$$

$$k_2 \qquad B \rightarrow C$$

where A is cyclohexane, B is cyclohexanol and C is cyclohexanone, has the following form

$$B(t) = \frac{A_0 k_1 (e^{-k_1 t} - e^{-k_2 t})}{k_2 - k_1}$$

$$C(t) = A_0 \left(1 - \frac{k_2 e^{-k_1 t}}{k_2 - k_1} - \frac{k_1 e^{-k_2 t}}{k_1 - k_2} \right)$$

where $B(t)$ and $C(t)$ are concentrations of cyclohexanol and cyclohexanone after reaction time t and A_0 is the initial concentration of cyclohexane.