

## Supplementary Information

### Identification of the cyclohexyl hydroperoxide

The presence of the hydroperoxide function was established with test strips sensitive to this function.

$\text{NaBH}_4$  reduction of the outflowing liquid was also carried out. A reducing solution was made by dissolving 15 mg of  $\text{NaBH}_4$  into 700  $\mu\text{l}$  of absolute ethanol, and 100  $\mu\text{l}$  of this solution was mixed with 100  $\mu\text{l}$  of the outflowing liquid containing the supposed cyclohexyl hydroperoxide. The comparison of the corresponding chromatographs showed a disappearance of the 8.03 min peak, while the cyclohexanol peak was increased (Fig. S1). This suggests the reduction of cyclohexyl hydroperoxide into cyclohexanol.

Synthesis of cyclohexyl hydroperoxide has eventually been performed by autoxidation of organoboranes<sup>1</sup>. The FID chromatogram of the reaction mixture (Fig. S2) showed several peaks, among which one at 8.03 min, matching with the retention time of the putative hydroperoxide, and the other having been ruled out by MS identification. The 8.03 min peak height was found to decrease with time, as expected for an unstable peroxide. We can therefore confirm the presence of cyclohexyl hydroperoxide amongst the oxidation products.

### References

- [1] H. C. Brown and M. M. Midland, *Tetrahedron*, 1987, **43**, 4059–4070.

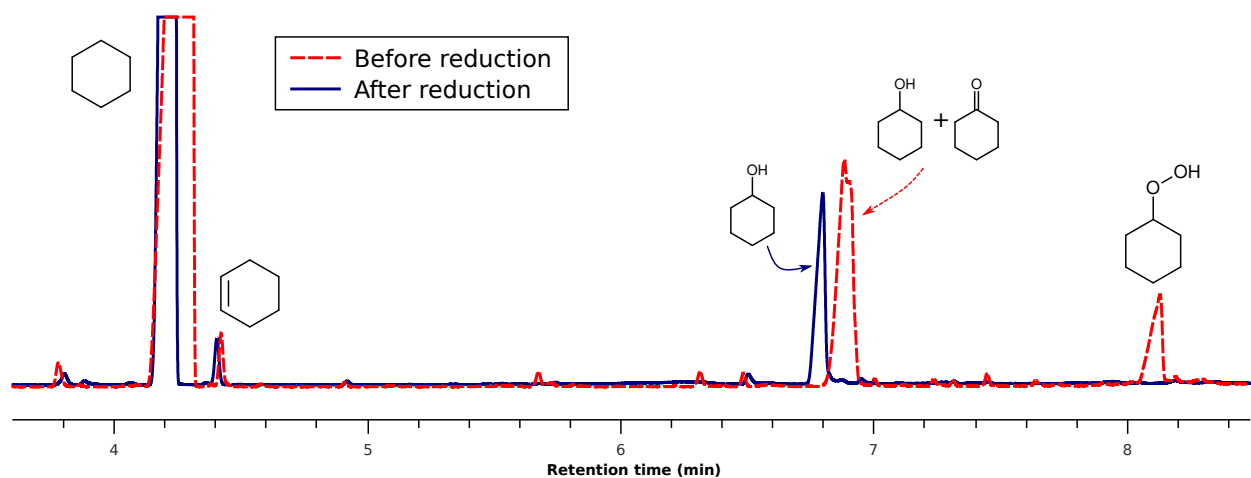


Figure S1: GC-FID chromatogram of the outflowing liquid after plasma reaction with  $O_2$  at 500 mW, before and after reduction by mixing with the  $NaBH_4$  solution. Both chromatographs were rescaled according to the area of the cyclohexane peak. After the reduction, the 8min peak has disappeared and the 7min double peak of cyclohexanol+cyclohexanone clearly changed its shape and looks more like a single peak. This is coherent with cyclohexyl hydroperoxide and cyclohexanone having turned into cyclohexanol.

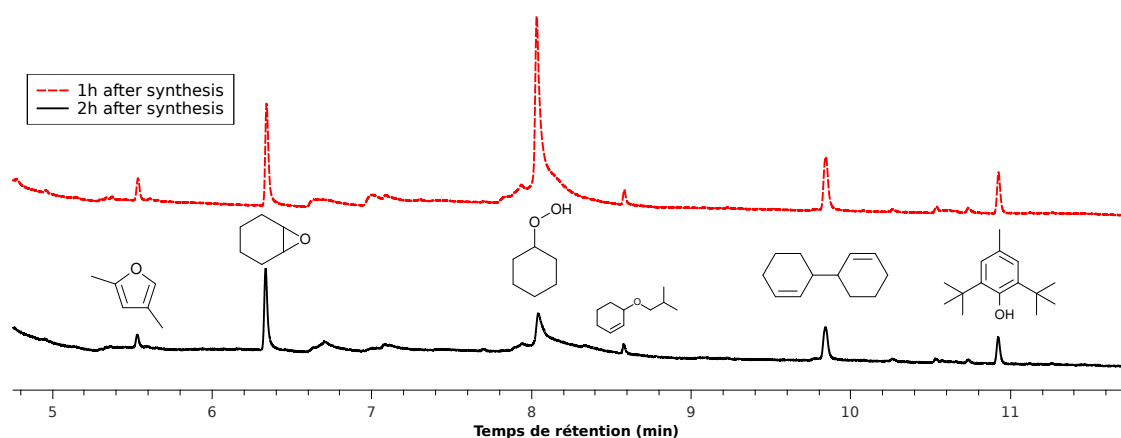


Figure S2: FID chromatogram of reacting mixture<sup>1</sup> used to synthesise cyclohexyl hydroperoxide.