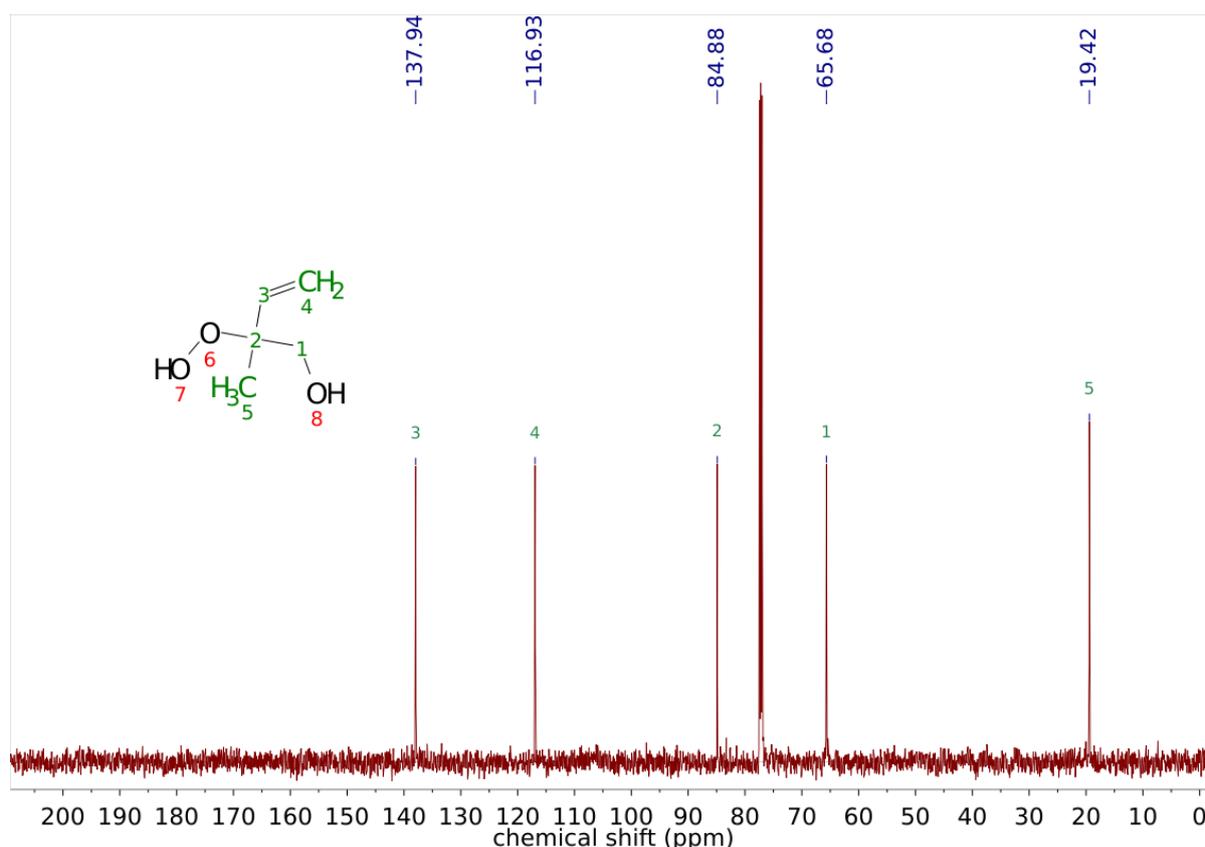


## Supplementary Materials

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### 1,2-ISOPOOH NMR spectra

In addition to the <sup>1</sup>H NMR spectrum of 1,2-ISOPOOH, the <sup>13</sup>C spectrum was recorded as shown in Figure S1, as well as common 2D spectra. The <sup>13</sup>C spectrum features 5 distinct signals other than the chloroform signal at 78 ppm matching the molecular structure of 1,2-ISOPOOH.



**Figure S1:** <sup>13</sup>C-NMR spectrum of 1,2-ISOPOOH in CDCl<sub>3</sub>.

Moreover, a correlated spectroscopy (COSY) experiment was performed with the resulting spectrum shown in Figure S2. A coupling of the olefinic protons 3 and 4 can be observed as well as a strong coupling of the geminal protons 1 and 1'. Additionally, a heteronuclear single quantum (HSQC) experiment as well as a heteronuclear multiple bond correlation (HMBC) experiment was performed of the same sample of 1,2-ISOPOOH with the spectra shown in Figure S3 and Figure S4, respectively. The resulting peak assignment is shown in Table S1.

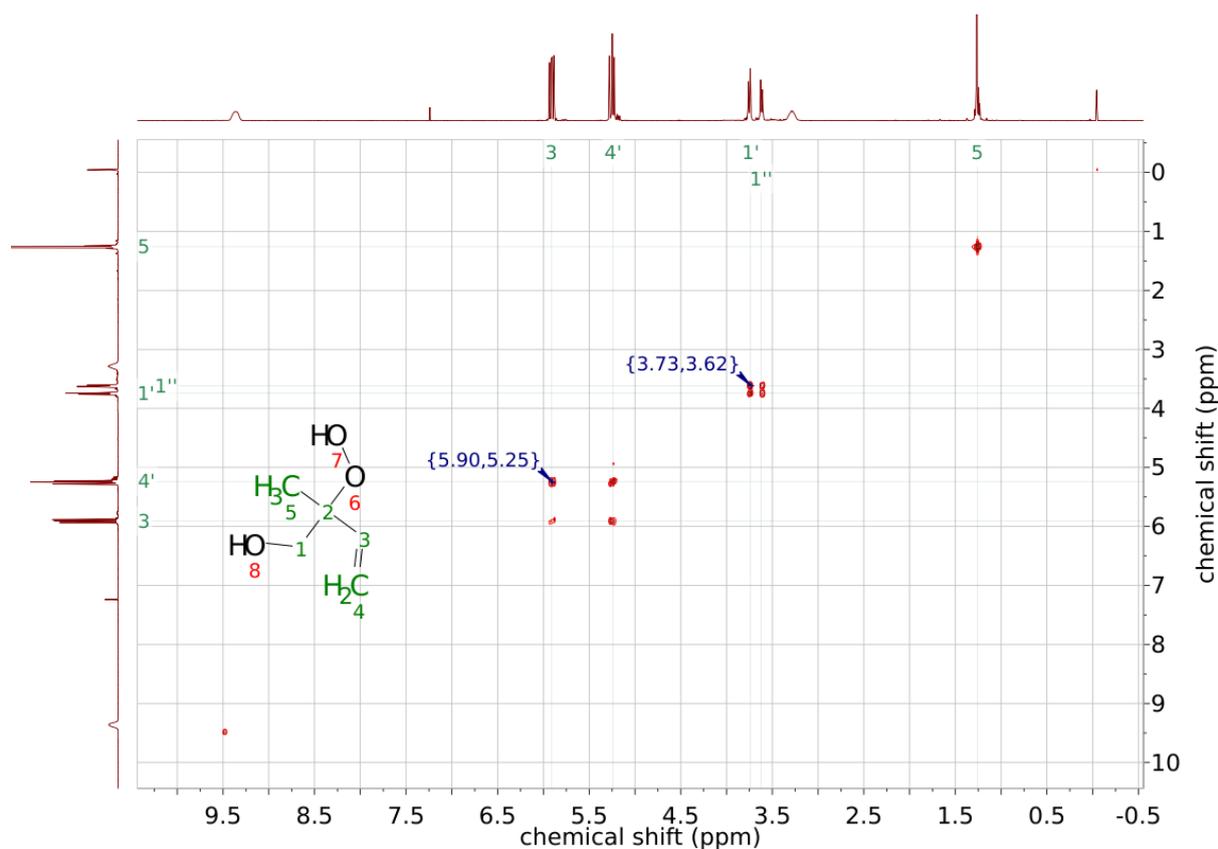


Figure S2: COSY spectrum of 1,2-ISOPOOH in CDCl<sub>3</sub> at 600 MHz.

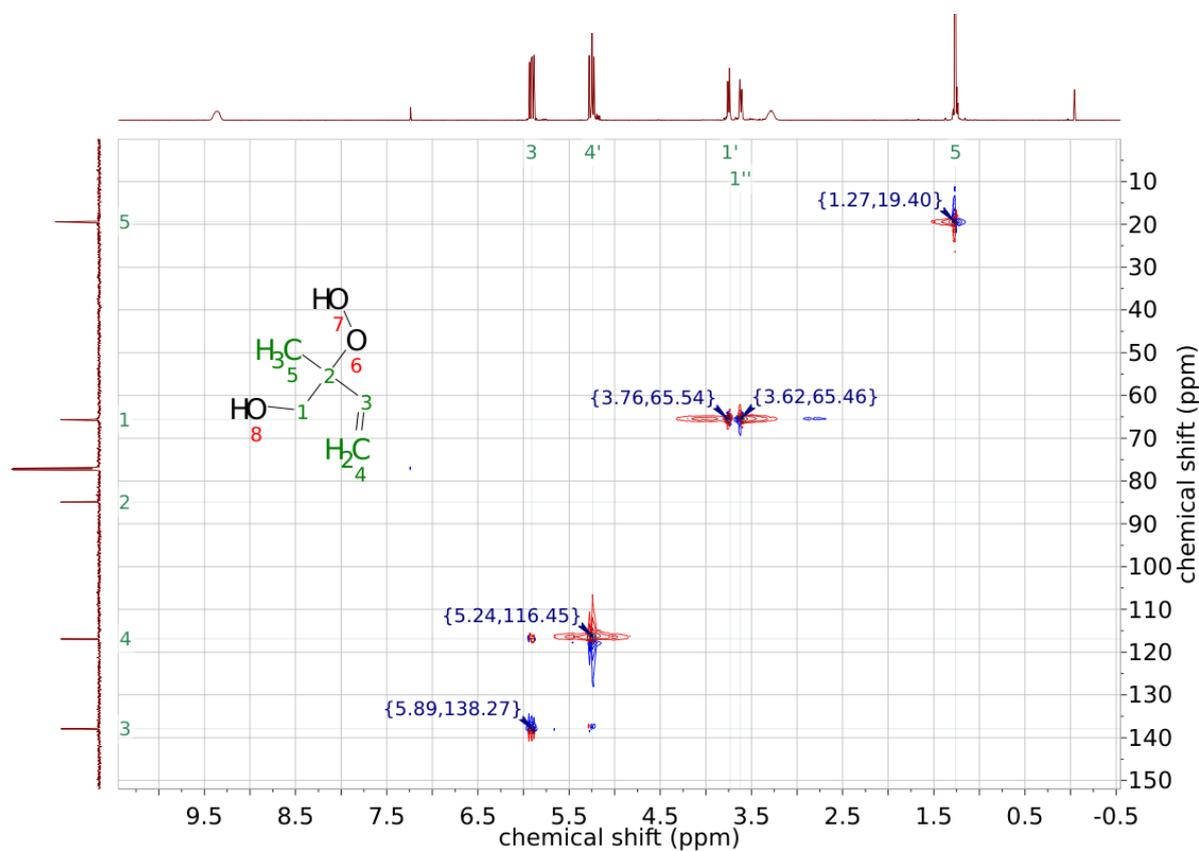


Figure S3: HSQC spectrum of 1,2-ISOPOOH in CDCl<sub>3</sub> at 600 MHz.

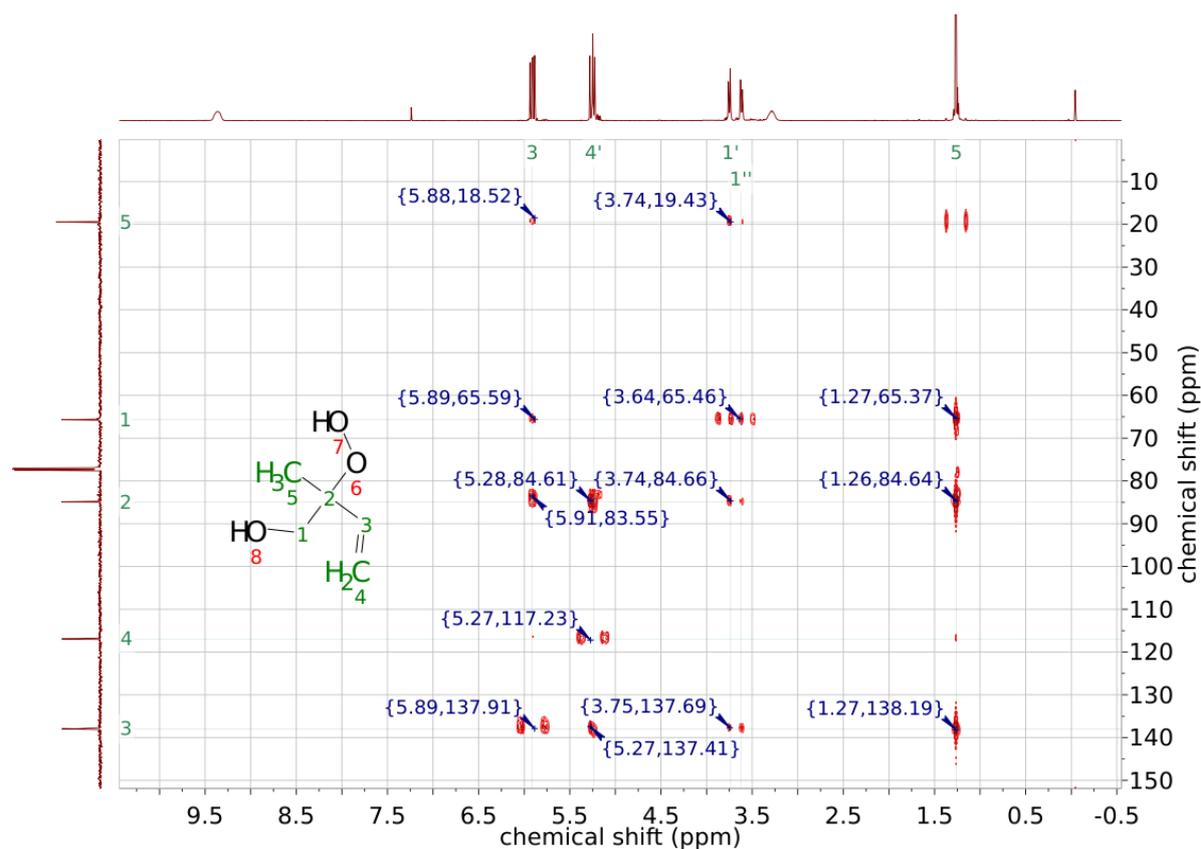
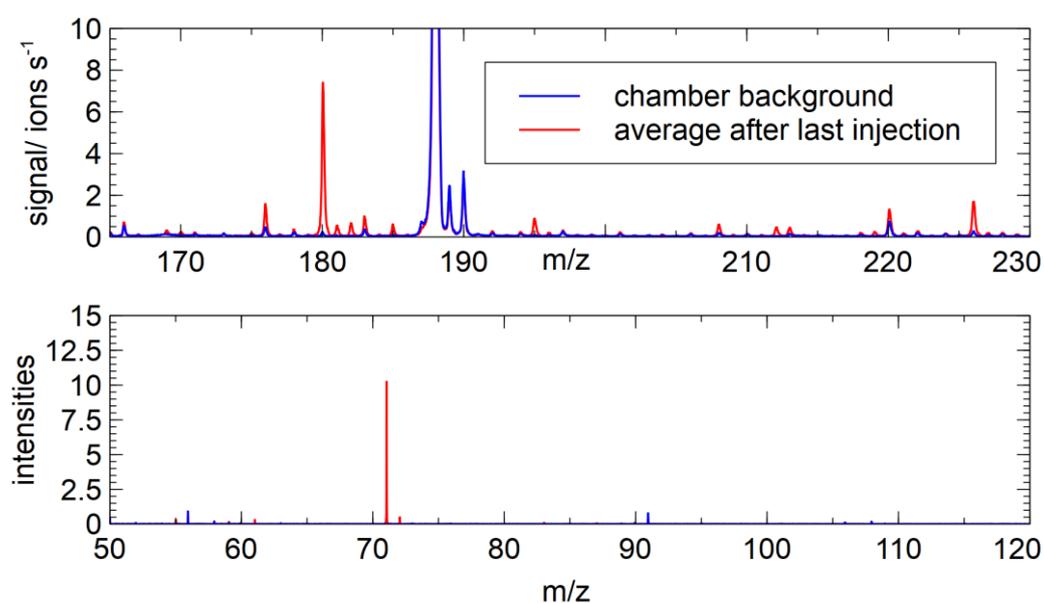


Figure S4: HMBC spectrum of 1,2-ISOPOOH in CDCl<sub>3</sub> at 600 MHz.

Table S1: Chemical shifts and coupling of NMR signals of 1,2-ISOPOOH.

Carbon atom number	Shift of carbon atom in <sup>13</sup> C-NMR/ ppm	Shift of hydrogen atom in <sup>1</sup> H-NMR	H-H coupling
1	65.68	1' 3.61 1'' 3.75	H1'-H1'' (12 Hz) H1''-H1' (12 Hz)
2	84.88		
3	137.94	5.91	H3-H4' (18 Hz); H3-H4'' (11.4 Hz)
4	116.93	4' 5.26 4'' 5.23	H4'-H4'' (1.2 Hz); H4'-H3 (18 Hz) H4''-H4' (1.2 Hz); H4''-H3 (11.4 Hz)
5	19.42	1.26	



**Figure S5:**  $\text{NO}_3^-$ -Cl-API-ToFMS spectrum (above) and PTR-ToFMS spectrum (below) of 1,2-ISOPOOH averaged over 5 minutes before the first and 10 minutes after the last injection.

#### 4,3-ISOPOOH NMR spectra

The  $^{13}\text{C}$  spectrum was recorded for 4,3-ISOPOOH and is shown in Figure S5, featuring similar chemical shifts for the carbon atoms compared to the spectrum of 1,2-ISOPOOH. The COSY spectrum is shown in Figure S6 with a vicinal coupling visible for the protons 1 and 2 as well as long-range coupling visible of the olefinic protons 4 with both the methyl group protons 5 and the methylene proton 2, also matching the molecular structure. The measured HSQC and HMBC spectra are shown in Figure S7 and Figure S8, respectively with the resulting peak assignments summarized in Table S2.

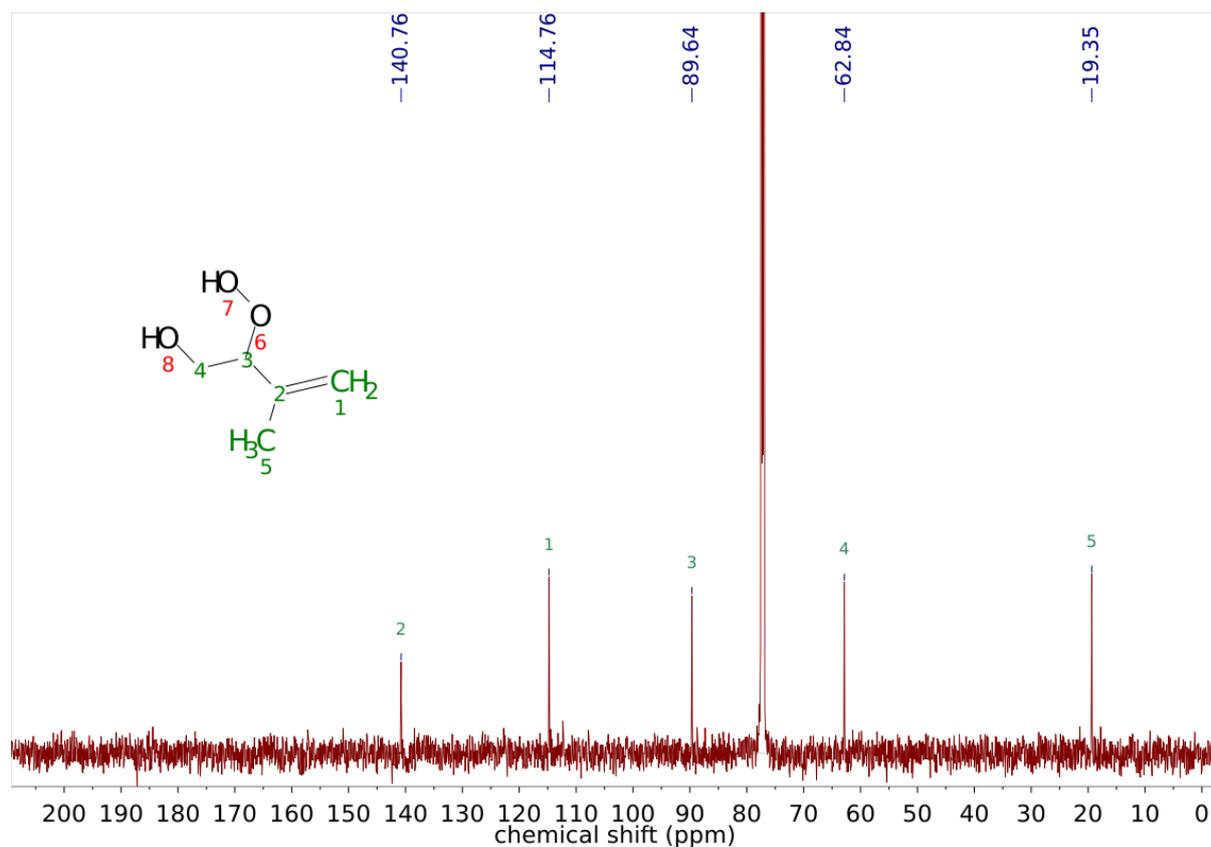


Figure S6:  $^{13}\text{C}$ -NMR spectrum of 4,3-ISOPOOH in  $\text{CDCl}_3$ .

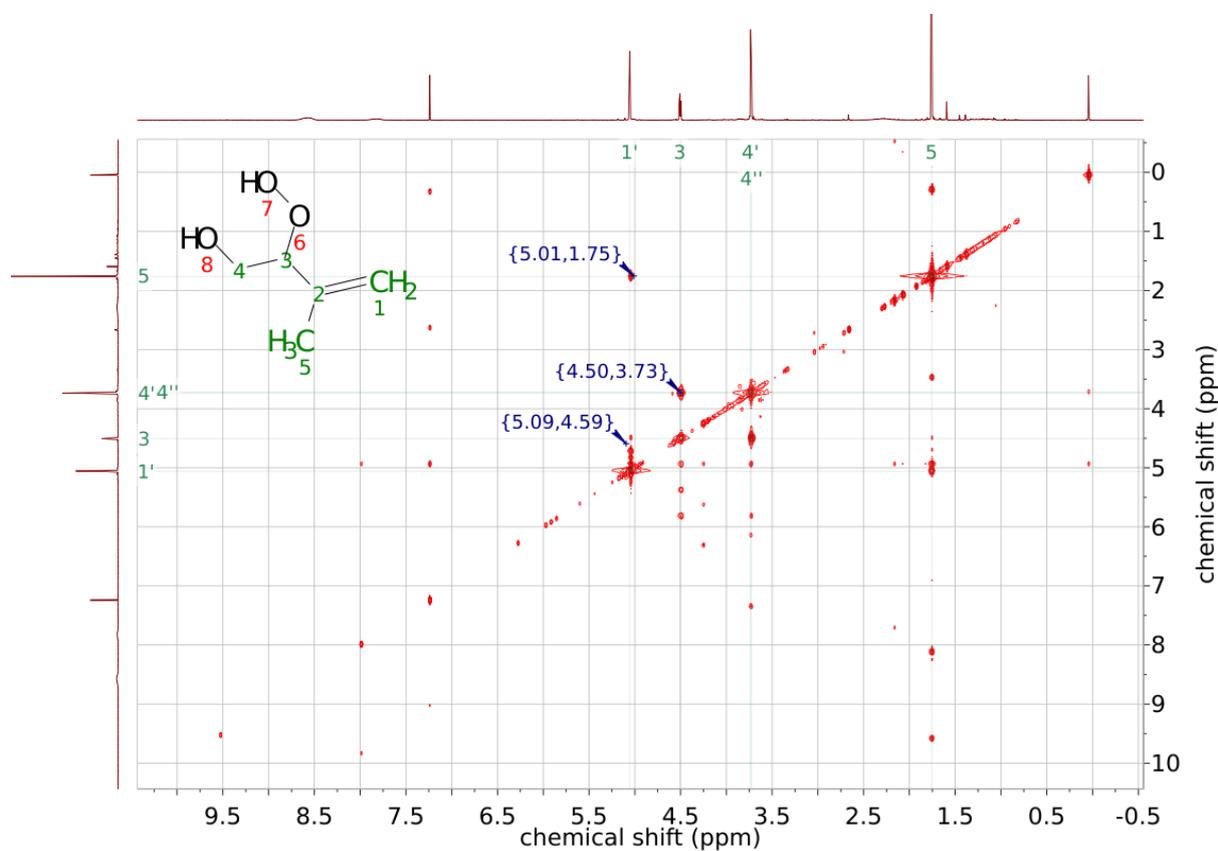


Figure S7: COSY spectrum of 4,3-ISOPOOH in  $\text{CDCl}_3$  at 600 MHz.

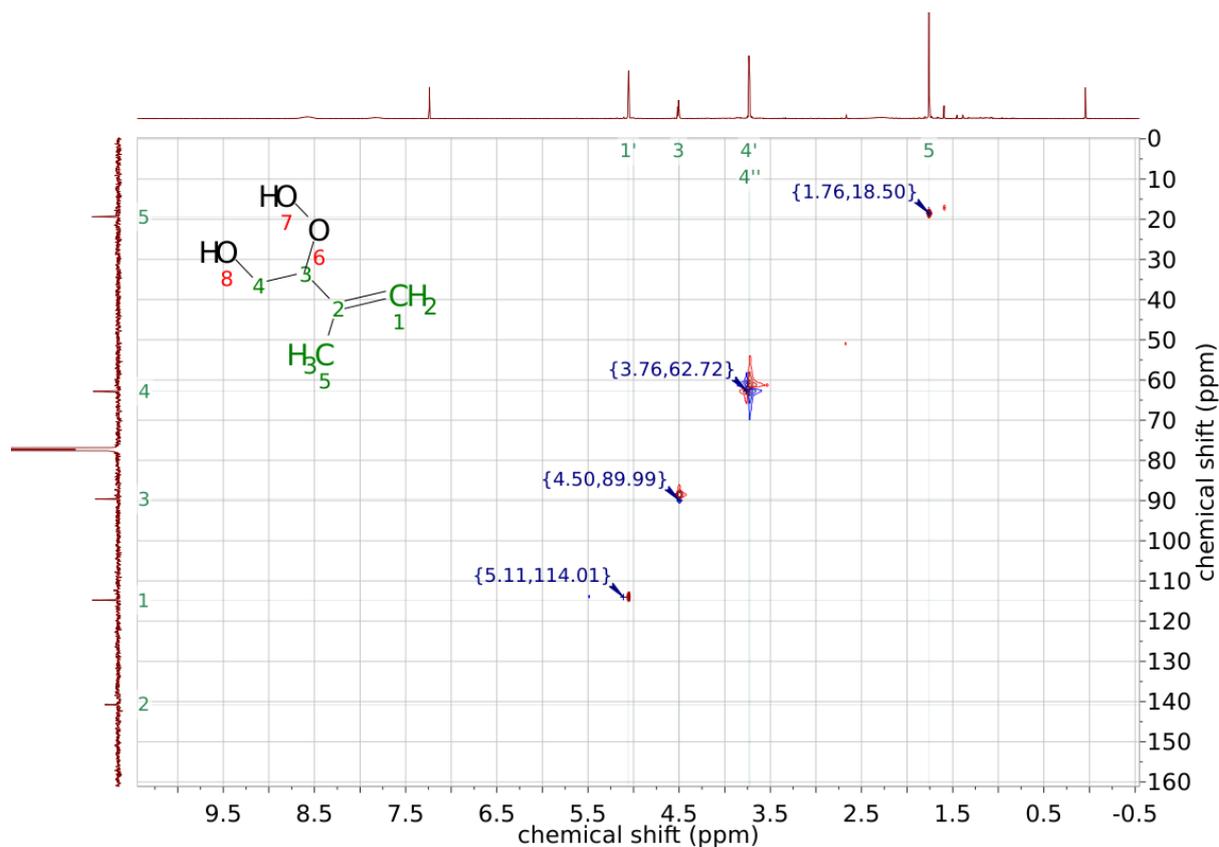


Figure S8: HSQC spectrum of 4,3-ISOPOOH in CDCl<sub>3</sub> at 600 MHz.

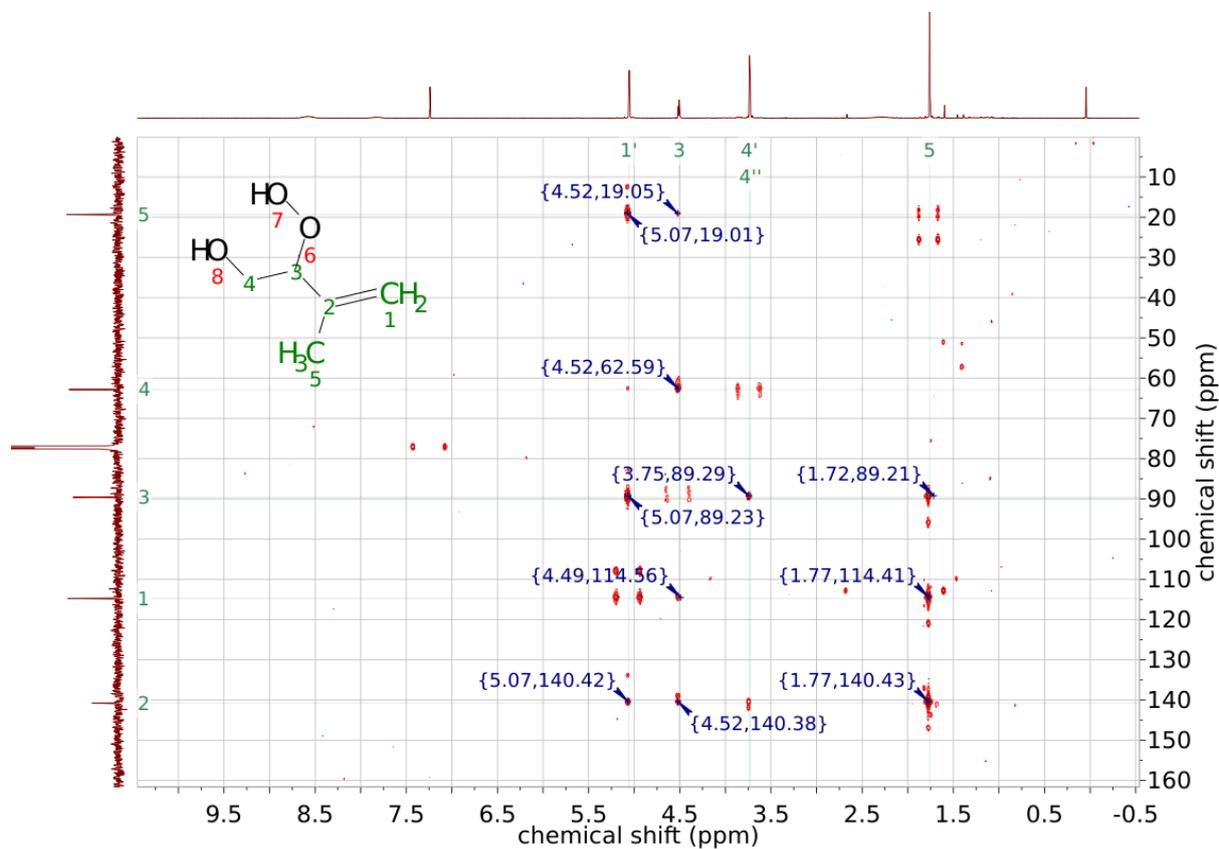


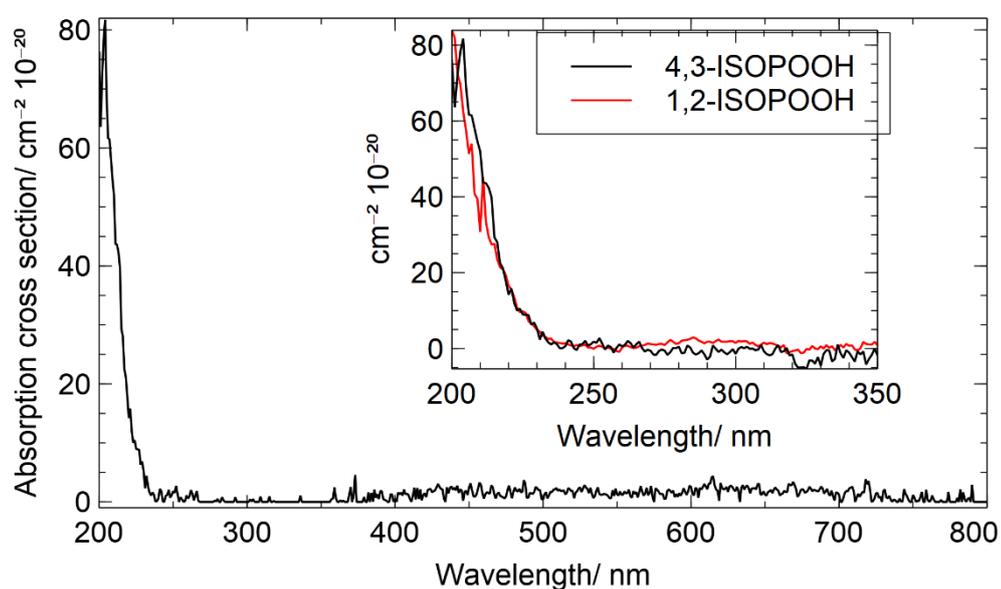
Figure S9: HMBC spectrum of 4,3-ISOPOOH in CDCl<sub>3</sub> at 600 MHz.

**Table S2:** Chemical shifts and coupling of NMR signals of 4,3-ISOPOOH.

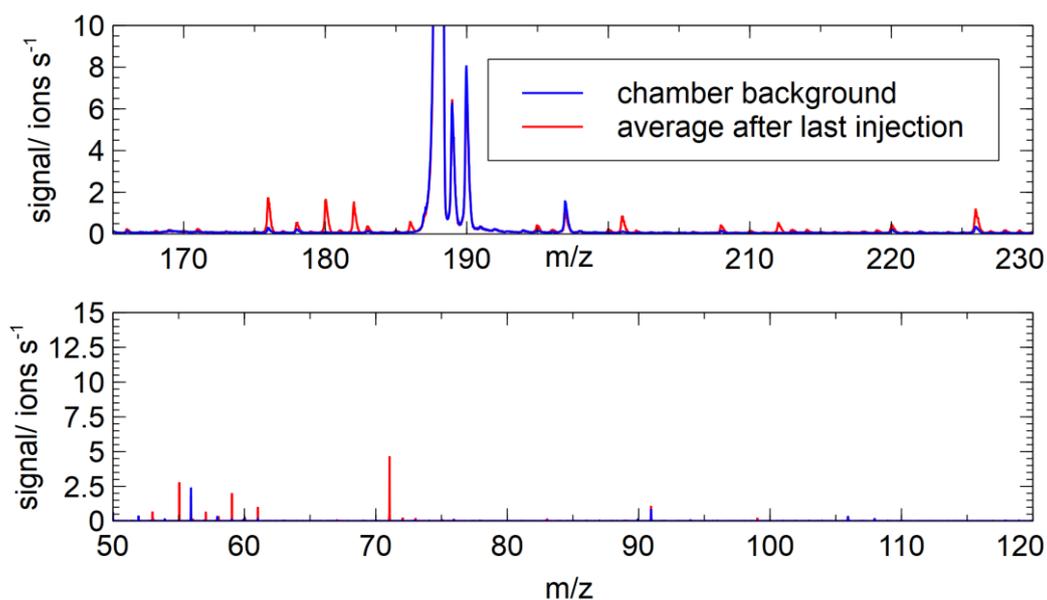
Carbon atom number	Shift of carbon atom in $^{13}\text{C}$ -NMR/ ppm	Shift of hydrogen atom in $^1\text{H}$ -NMR	H-H coupling
1	114.8	5.05	
2	140.8		
3	89.6	4.51	H3-H1, H3-H4
4	60.8	3.74	H4-H3
5	19.4	1.76	H5-H1

#### 4,3-ISOPOOH UV/VIS absorption spectrum

The UV/VIS spectrum of 4,3-ISOPOOH was recorded between 200 and 800 nm and the resulting absorption cross section is shown in Figure S9.



**Figure S10:** UV/VIS spectrum of 4,3-ISOPOOH, measured in a diluted gas stream at a mixing ratio of approximately  $3.16 \cdot 10^{13}$  molecule  $\text{cm}^3$ .



**Figure S11:**  $\text{NO}_3\text{-CI-APi-ToFMS}$  spectrum (above) and  $\text{PTR-ToFMS}$  spectrum (below) of 4,3-ISOPROOH averaged over 5 minutes before the first and 10 minutes after the last injection.

#### $\alpha$ -pinene hydroxy hydroperoxide NMR spectra

The  $^{13}\text{C}$  spectrum of the  $\alpha$ -pinene-derived hydroxy hydroperoxide was recorded in deuterated chloroform and is shown in Figure S10. Matching the assumed molecular structure as discussed in the main text, the spectrum shows ten individual signals. Two signals show chemical shifts indicating the restoration of a double bond and two signals appear with chemical shifts typical for hydroxy hydroperoxy moieties. The COSY spectrum is shown in Figure S11 and features mainly vicinal couplings along the six-membered ring. The coupling of the protons are summarized in Table 1. The corresponding HSQC spectrum is shown in Figure S12.

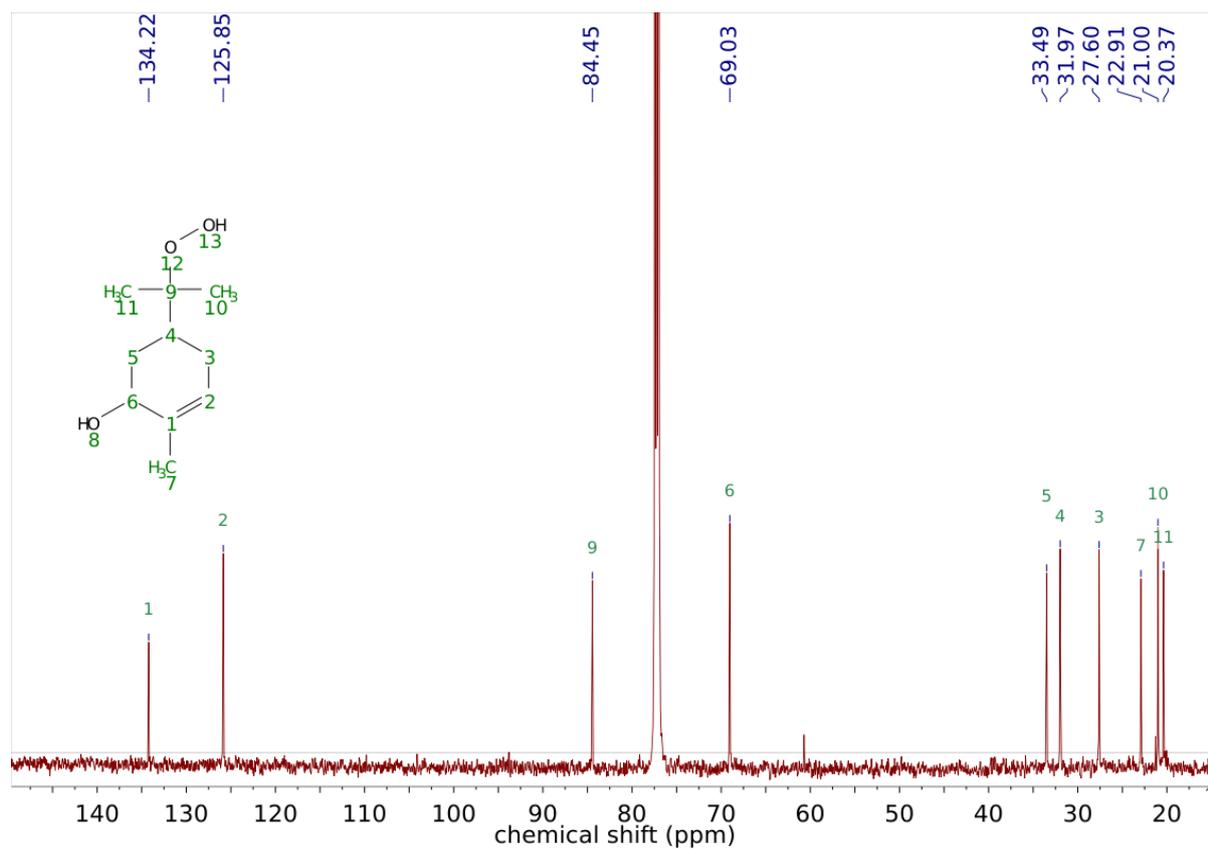


Figure S12:  $^{13}\text{C}$ -NMR spectrum of alpha pinene hydroxy hydroperoxide in  $\text{CDCl}_3$ .

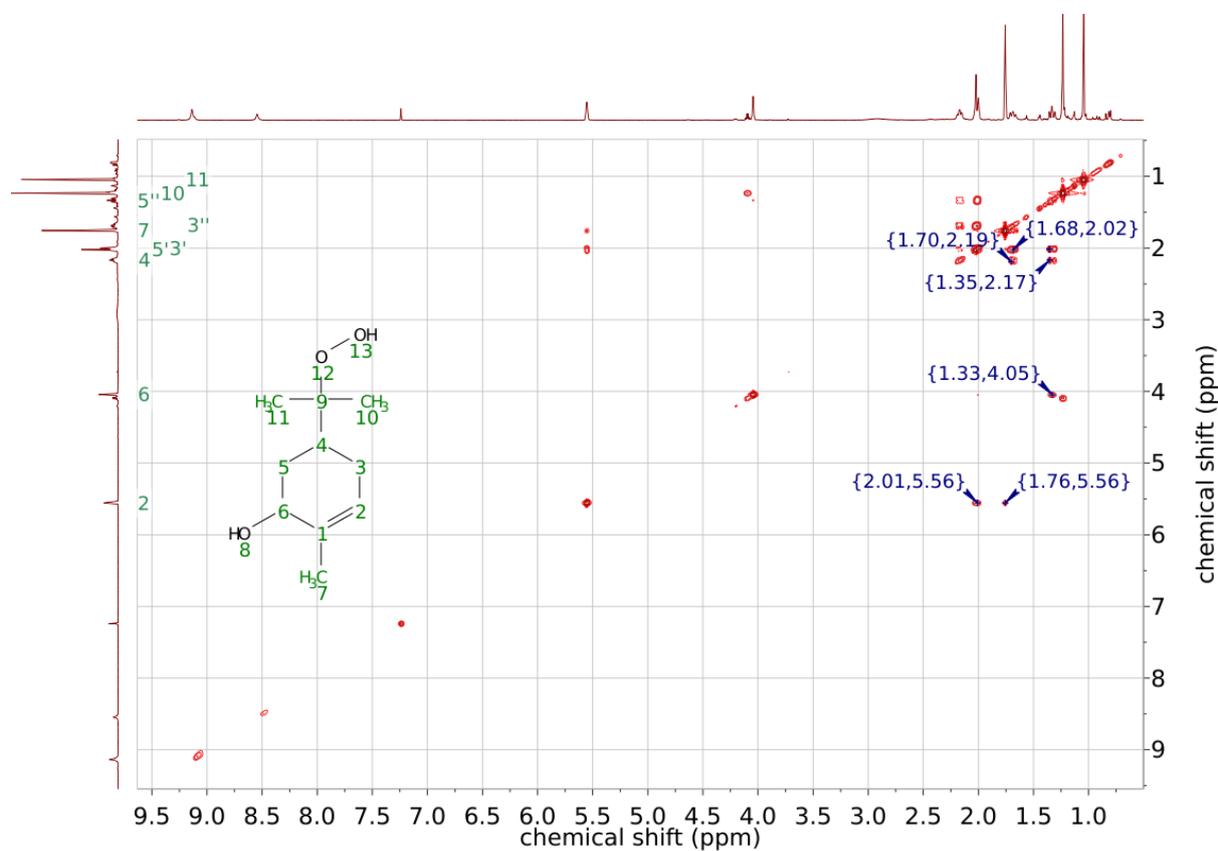


Figure S13: COSY spectrum of alpha pinene hydroxy hydroperoxide in  $\text{CDCl}_3$  at 600 MHz.

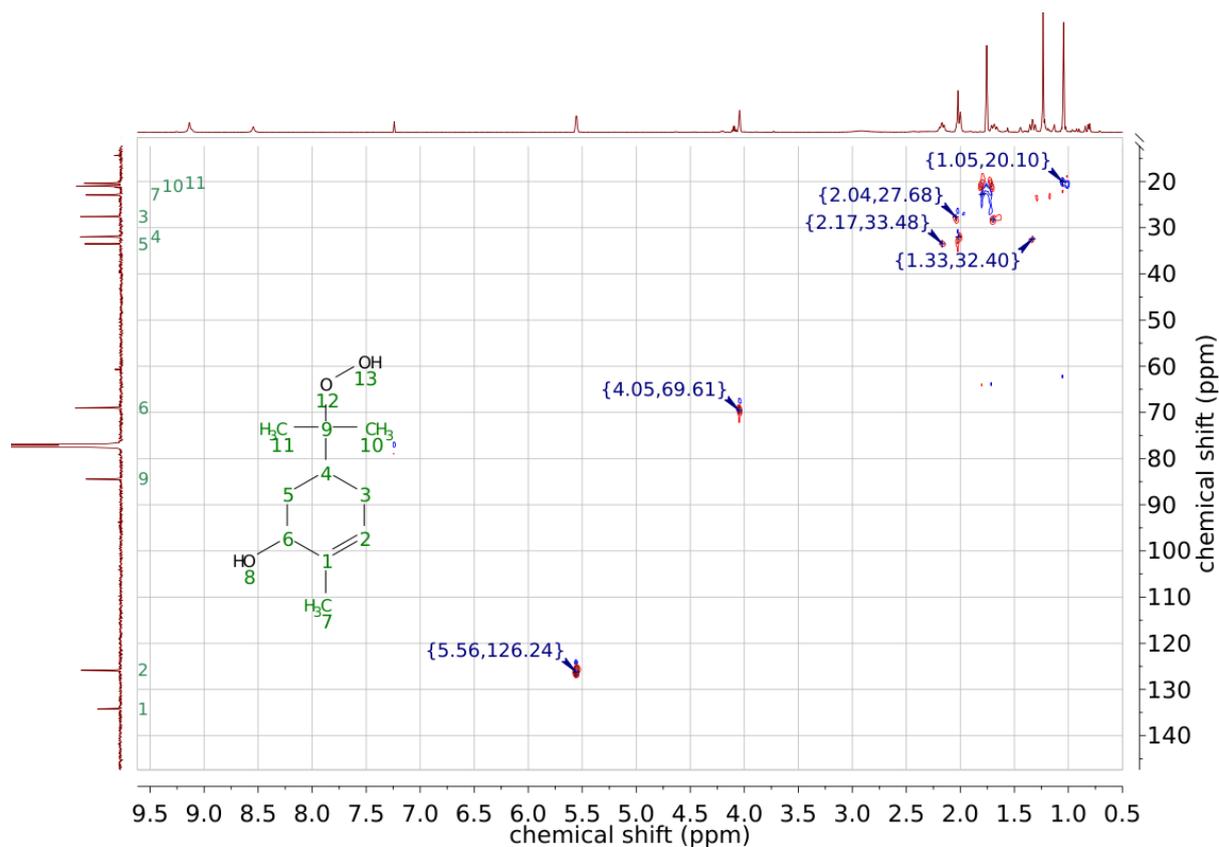


Figure S14: HSQC spectrum of alpha pinene hydroxy hydroperoxide in CDCl<sub>3</sub> at 600 MHz.

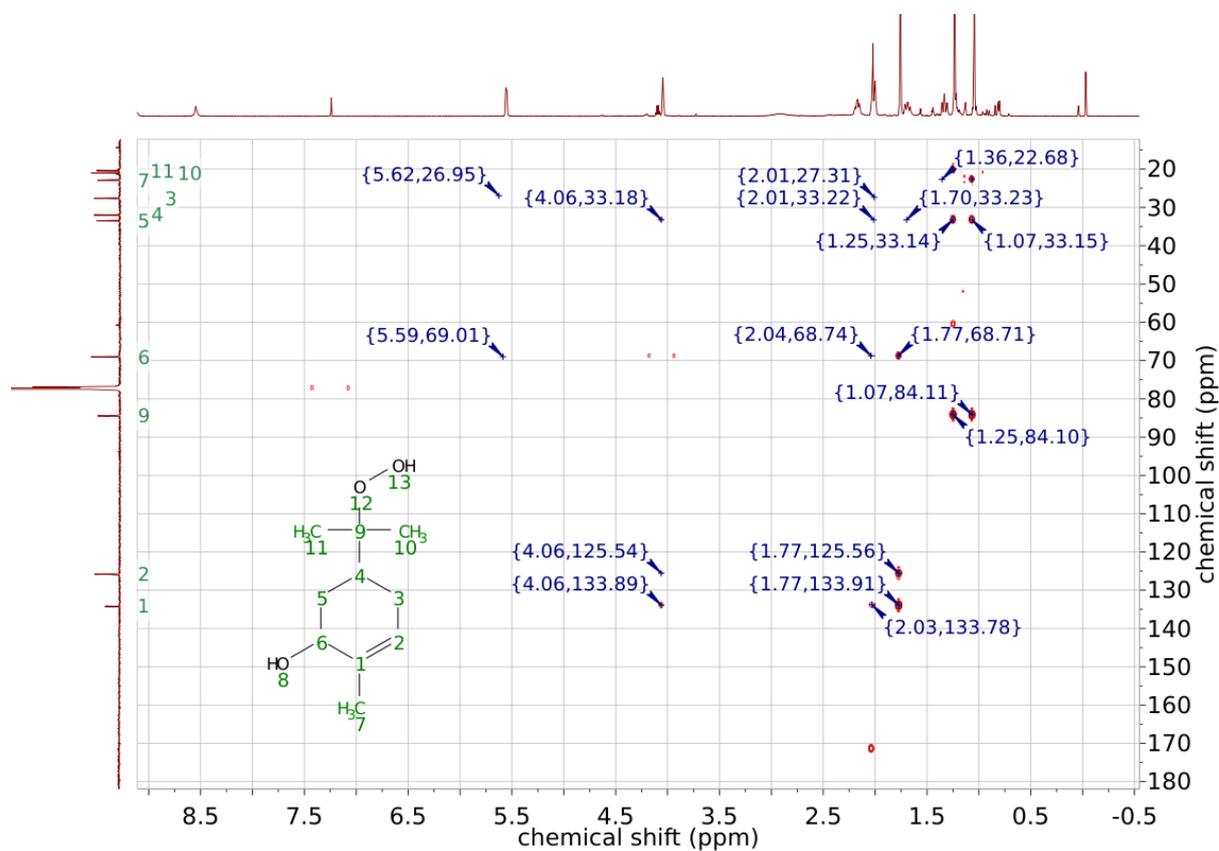
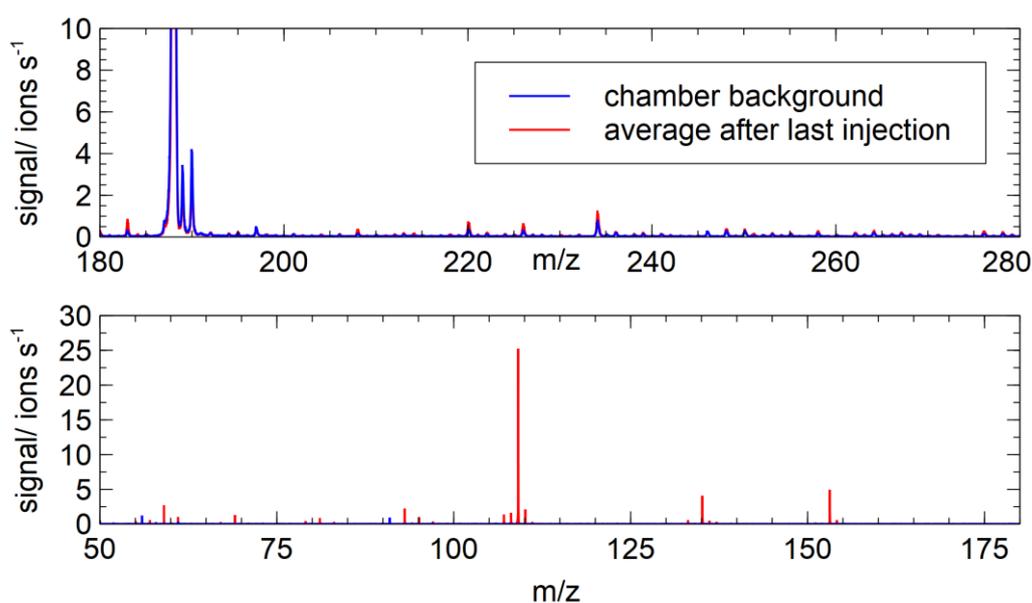


Figure S15: HMBC spectrum of  $\alpha$ -pinene hydroxy hydroperoxide in CDCl<sub>3</sub> at 600 MHz.



**Figure S16:**  $\text{NO}_3$ -CI-API-ToFMS spectrum (above) and PTR-ToFMS spectrum (below) of  $\alpha$ -pinene hydroxy hydroperoxide averaged over 5 minutes before the first and 10 minutes after the last injection.

#### CI-API-ToFMS tuning parameters

As the cluster stability and thus the sensitivity of the instrument for specific clusters is highly dependent on the instrument tuning, parameters used throughout the work are given in Table S3.

**Table S3:** TPS voltage settings for compact  $\text{NO}_3$ -CI-API-ToFMS.

TPS parameter	Value	TOF Parameter	Voltage Setting/ V
Nozzle	6.000 V	TOF Pulse	700.000
Q1 EP	6.052 V	TOF Ref	65.000
Q1 Front	9.038 V	TOF Extr 1	50.000
Q1 Back	9.000 V	TOF Extr 2	700.000
Lens Skimmer	9.000 V		
Skimmer	8.129 V	Drift	2000.000
		RG	244.300
Q2 Front	9.508 V	RB	700.000
Q2 Back	12.558 V	A	1850.000
Skimmer 2	14.000 V	MCP	2300.000
Reference (bias)	50.475 V	Ion Source	-118.000
Ion-Lens 2	104.701 V	Drift Tube	-118.000
Deflector Flange	42.865 V		
Deflector	38.969 V		
SSQ Freq.	2700000 Hz	BSQ Freq.	2400000 Hz
SSQ Amp.	200.000 V	BSQ Amp.	300.000 V