

Supplement of Atmos. Chem. Phys., 18, 10973–10983, 2018
<https://doi.org/10.5194/acp-18-10973-2018-supplement>
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Supplement of

Synthesis and characterisation of peroxydic acids as proxies for highly oxygenated molecules (HOMs) in secondary organic aerosol

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Pinic Acid NMR for structural assignment

All spectra for the assignment were obtained from a Bruker III HD Avance 500 MHz instrument with DUL 1H/13C cryoprobe (500.05 and 127.75 MHz, respectively) at a temperature of 298K.

5

Sample preparation

About 1.5 mg of pinic acid was dissolved in about 300 μ l 99.96%D acetonitrile and placed in a 3 mm NMR tube.

10 **NMR experimental**

All pulse sequences are the default (with the exception of the DEPT135) from the Topspin 3.2p17 software used to control the acquisition. The analysis required 1H, 13C, DEPT135, DFQCOSY, HSQC (with DEPT 135 editing) and HMBC spectra. All necessary shaped and decoupling pulses were calculated by the software, using defined 90 degree pulses.

15

1H

Pulse sequence used zg30 – PLW1=14W, P1=10.5 μ s, SW=20 ppm, TD=64 K, AQ=3.28 s, D1=1 s, NS=16.

13C

20 1024 scans (NS) were acquired using pulse sequence ‘zpgg30’, with waltz16 1H decoupling. 90 degree 13C pulse set to 21W (PLW1) for 9.5 μ s (P1). 209786 points (TD) were digitised over 3.02 s (AQ), relaxation delay set to 2 s (D1). Sweep width was 276 ppm (SW), with an irradiation frequency of 110 PPM (O1P).

DEPT135

25 Pulse sequence dept135sp – This is a minor modification of the DEPT sequence to optimise the spectral baseline and uses an adiabatic shape for 180 degree carbon pulses. Carbon pulse powers as 13C experiment above, SW=236.7 ppm, TD=65536, AQ=1.10 s, D1=2 s, O1=100 ppm, NS=64. Waltz16 decoupling.

30 ***DFQCOSY***

This is a double-quantum filtered experiment; using gradient selection; pulse sequence cosygpmf. Non-uniform sampling; using a Poisson-gap weighted schedule was used to acquire 37.5% of 512 increments, each with 2 scans (SWF2=13.37 ppm, TD=4k, AQ=0.31 s, D1=2 s). Proton pulse powers as above. Processed to 2k x2k points using a sine function (SSB=2.5)

HSQC

This experiment is configured to give -CH₂ groups an opposite phase to the -CH and -CH₃ groups, using the hsqcedetgppsp.3 pulse sequence. Acquired in phase sensitive mode using Echo/Antiecho-TPPI gradient selection, multiplicity edited during selection step with shaped adiabatic pulses. Non-uniform sampling; with a Poisson-gap weighted schedule was used to
5 acquire 25% of 1024 increments; each with 2 scans (SWF1=190 ppm, SWF2=12.99 ppm, TD=1816, AQ=0.14 s, D1=0.8 s). Carbon and proton pulse powers as above. Processed to 2048x2028 points using a qsrine function (SSB=2).

HMBC

This experiment is phase sensitive; uses Echo/Antiecho gradient selection, with a three-fold low-pass J-filter to suppress
10 one-bond correlations; pulse program 'hmbcetgpl3nd'. Acquired in phase sensitive mode using Echo/Antiecho-TPPI gradient selection, with a 3 step low pass j-filter to suppress 1 bond correlations. Long-range J-JCH parameters set to 10 Hz. Non-uniform sampling; with a Poisson-gap weighted schedule was used to acquire 37.5% of 768 increments; each with 2 scans (SWF1=250, SWF2=12.02 ppm, TD=4096, AQ=0.34 s, D1=2 s). Processed to 2048x2048 using a sine function (SSB=4 & 2 for F2 and F1), then converted to magnitude mode in F2. (Topspin command 'xf2m')

15

Results

With the data collected from the different NMR experiments, it was possible to determine the structure of the synthesised compound and confirm it as *cis*-pinic acid. A detailed list of the peak assignments is given in the main text.

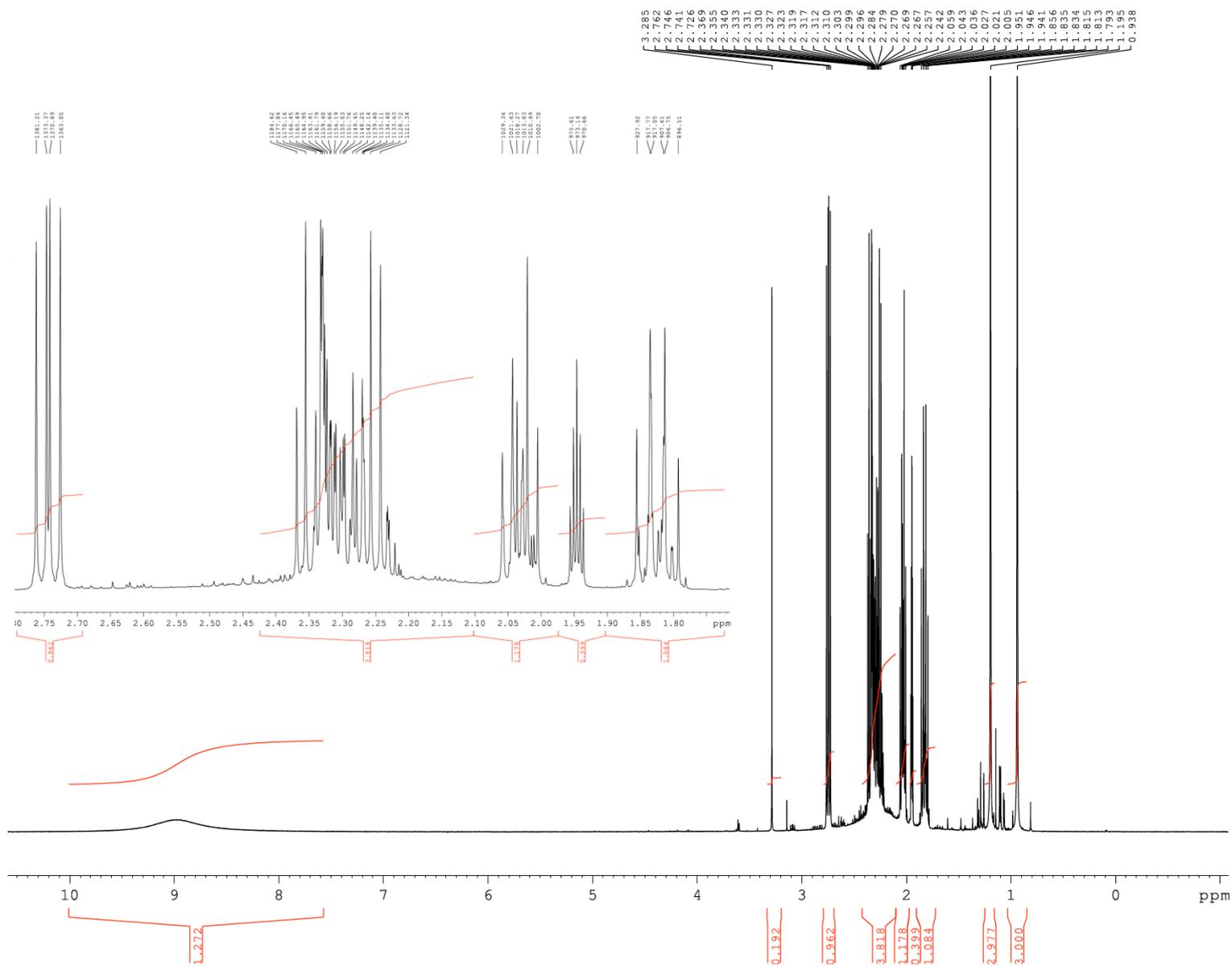


Figure S1: ^1H spectrum (CD_3CN , 500 MHz) of *cis*-pinic acid. The peak at $\delta=3.29$ belongs to residual methanol (used for cleaning).

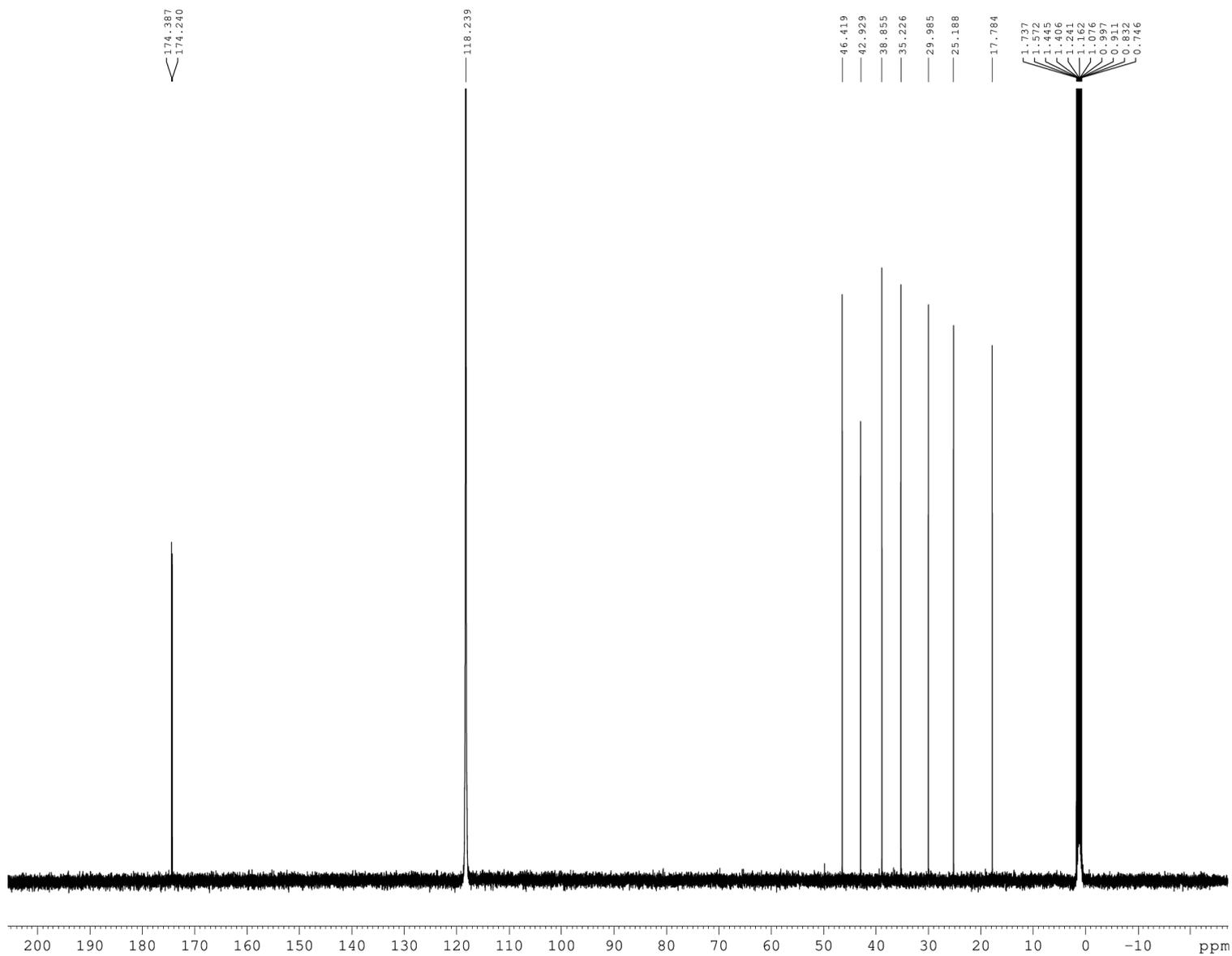


Figure S2: ^{13}C spectrum (CD_3CN , 500 MHz) of *cis*-pinic acid.

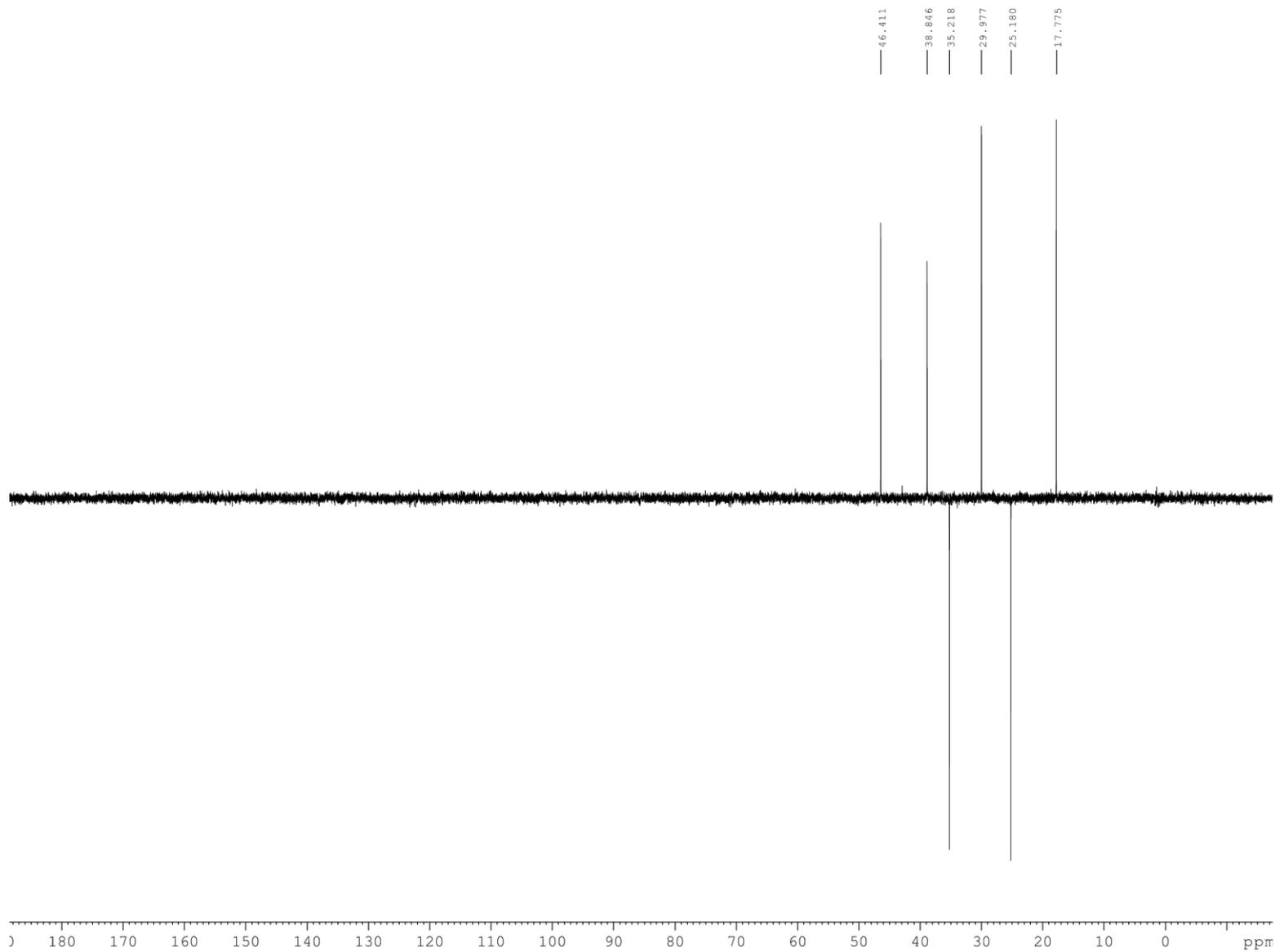


Figure S3: DEPT-135 spectrum of *cis*-pinic acid.

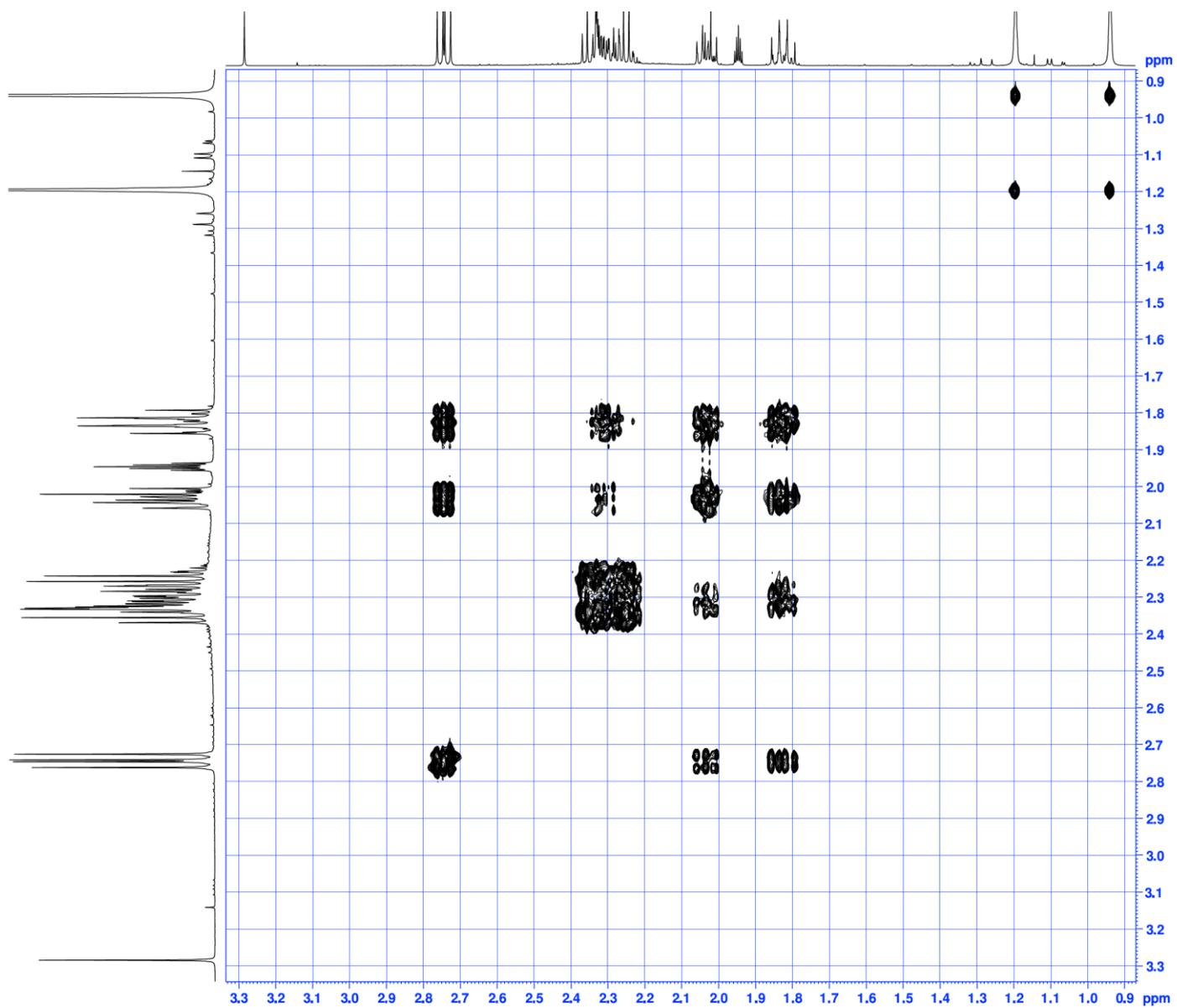


Figure S4: DFQCOSY spectrum of *cis*-pinic acid.

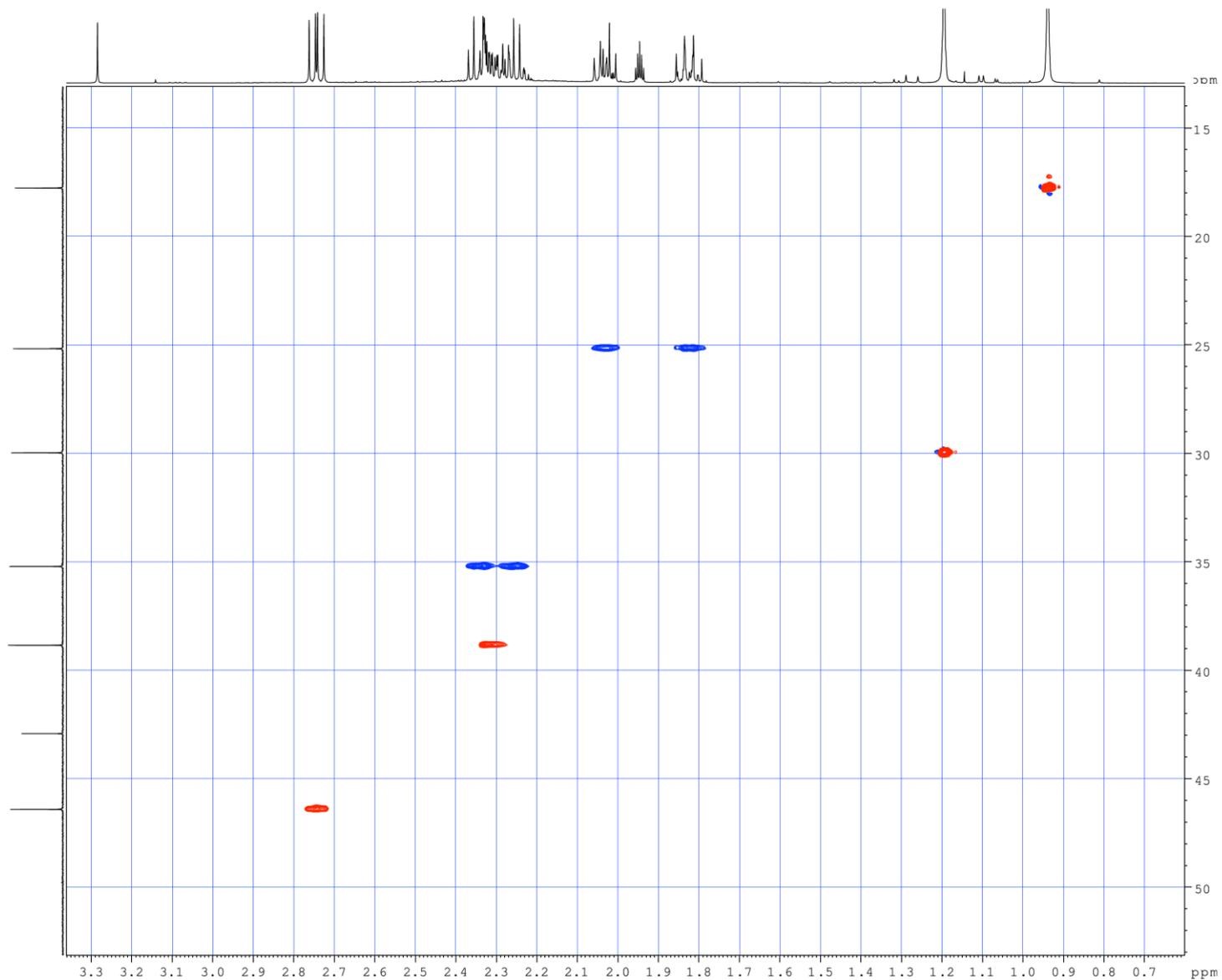


Figure S5: HSQC spectrum of *cis*-pinic acid. Even numbers of hydrogen are shown in blue, odd numbers in red.

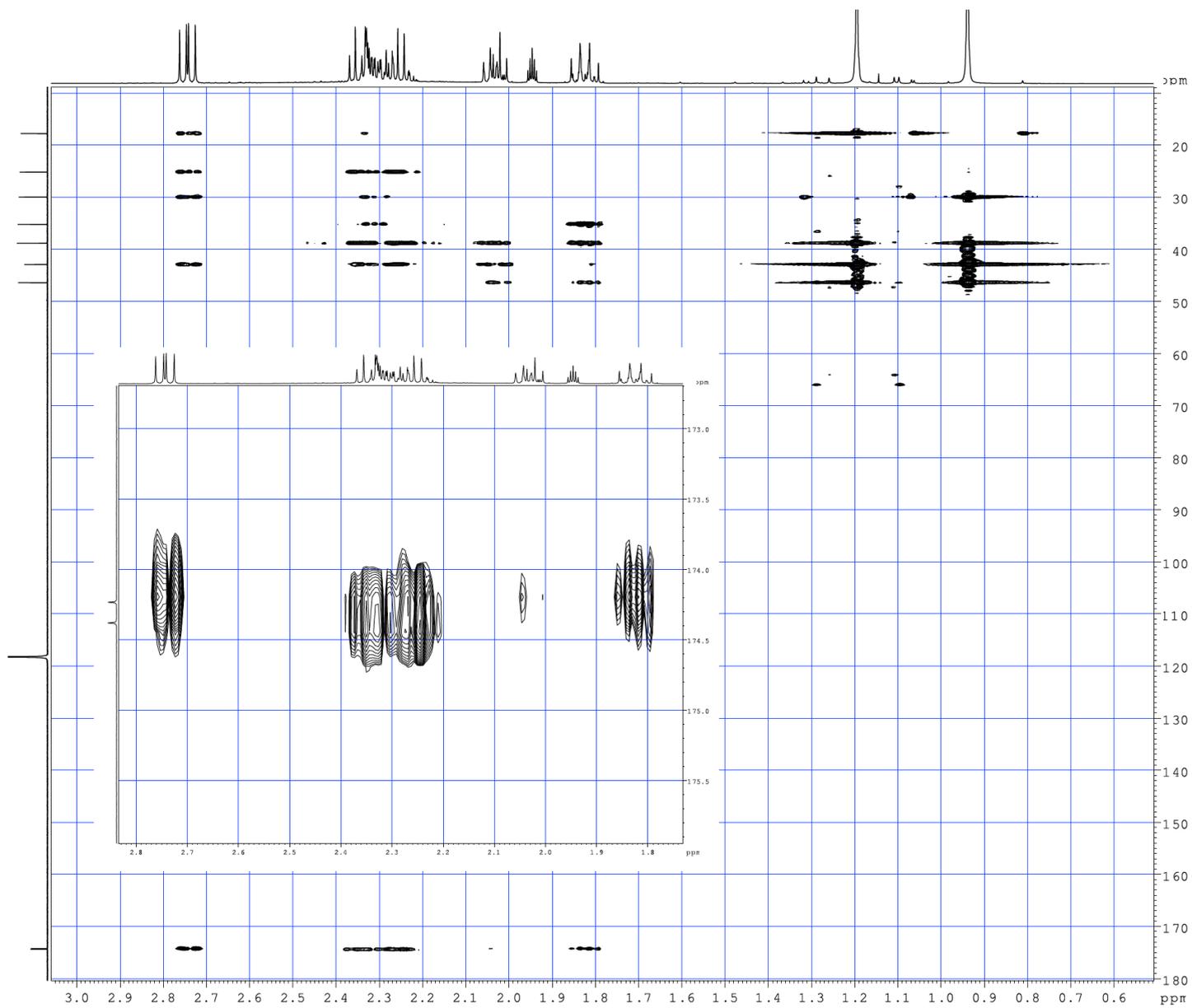


Figure S6: HMBC spectrum of *cis*-pinic acid. The inset shows an enlarged view of the correlations for the two carboxylic carbons.

NMR of the monoperoxyipinic acid and diperoxyipinic acid fraction

Sample preparation

Approximately 300 μ l of 99.96% CD₃CN was used to dilute the samples, which were placed into 3mm NMR tubes. Apart from the monoperoxyipinic acid and diperoxyipinic acid fraction, a pinic acid sample was also measured as a reference.

NMR experimental

All following spectra were obtained from a Bruker Avance 700 MHz instrument with 5 mm CPTXO 13C/15N-1H/D Z gradient cryoprobe. 1H and 13C frequencies 700.03 and 176.04 MHz, respectively, at a temperature of 298K.

All pulse sequences are from the Topspin 2.1pl4 software used to control the acquisition. All necessary shaped and decoupling pulses were calculated by the software, using defined 90 degree pulses.

1H Details

Pulse sequence used zg30 – PLW1=9.98W, P1=12 μ s, SW=13.95 ppm, TD=64 K, AQ=3.36 s, D1=1 s

HSQC details

Pulse sequence hsqcedetgmsp.3 as above. All pulses calibrated from defined 90 degrees pulses; 1H as above, 13C - P1=10 μ s, PL1W=51.24.

Pinic acid reference

1H – 128 scans

HSQC (hsqcedetgmsp.3) –F1SW=166.1 ppm, F2SW=10.0 ppm, TD=1958, AQ=0.14 s, 2 scans for 360 increments. Processed to 2048 x 2048 points with a qsine function (SSB=2)

Monoperoxyipinic acid fraction

1H – As 700 MHz pinic acid reference above. NS=1024.

HSQC (hsqcedetgmsp.3) –F1SW=166.1 ppm, F2SW=10.0 ppm, TD=1958, AQ=0.14 s, 64 scans for 172 increments. Processed to 2048 x 2048 points with a qsine function (SSB=2)

Diperoxyipinic acid fraction

¹H – As above. NS=1024

HSQC (hsqcedetgsp.3) - F1SW=166.1 ppm, F2SW=10.0 ppm, TD=1958, AQ=0.14 s, 8 scans for 360 increments. Processed to 2048 x 2048 points with a qsine function (SSB=2).

Monoperoxyipinic acid fraction results

The ¹H spectrum of the monoperoxyipinic acid fraction shows that the monoperoxy acid isomers are not stable under the present conditions, as the spectrum is dominated by pinic acid (Figure S7, Figure S8). However, both monoperoxyipinic acid isomers are present as well. This is most obvious for the H3 doublet of doublets, which is shifted downfield from 2.73 ppm for pinic acid to 2.75 ppm and 2.84 ppm for monoperoxyipinic acid isomer I and II, respectively (Figure S9). Comparing the H3 signal ~2.5 h after final fraction collection and ~18 h after fraction collection shows further decay of the monoperoxyipinic acids into pinic acid (Figure S9). The HSQC spectrum of the sample again demonstrates that the dominant compound is pinic acid (Figure S10).

The decay of the monoperoxyipinic acid isomers was confirmed by re-analysing the sample with LC-MS/MS, which shows the presence of pinic acid and both monoperoxyipinic acid isomers (Figure S11).

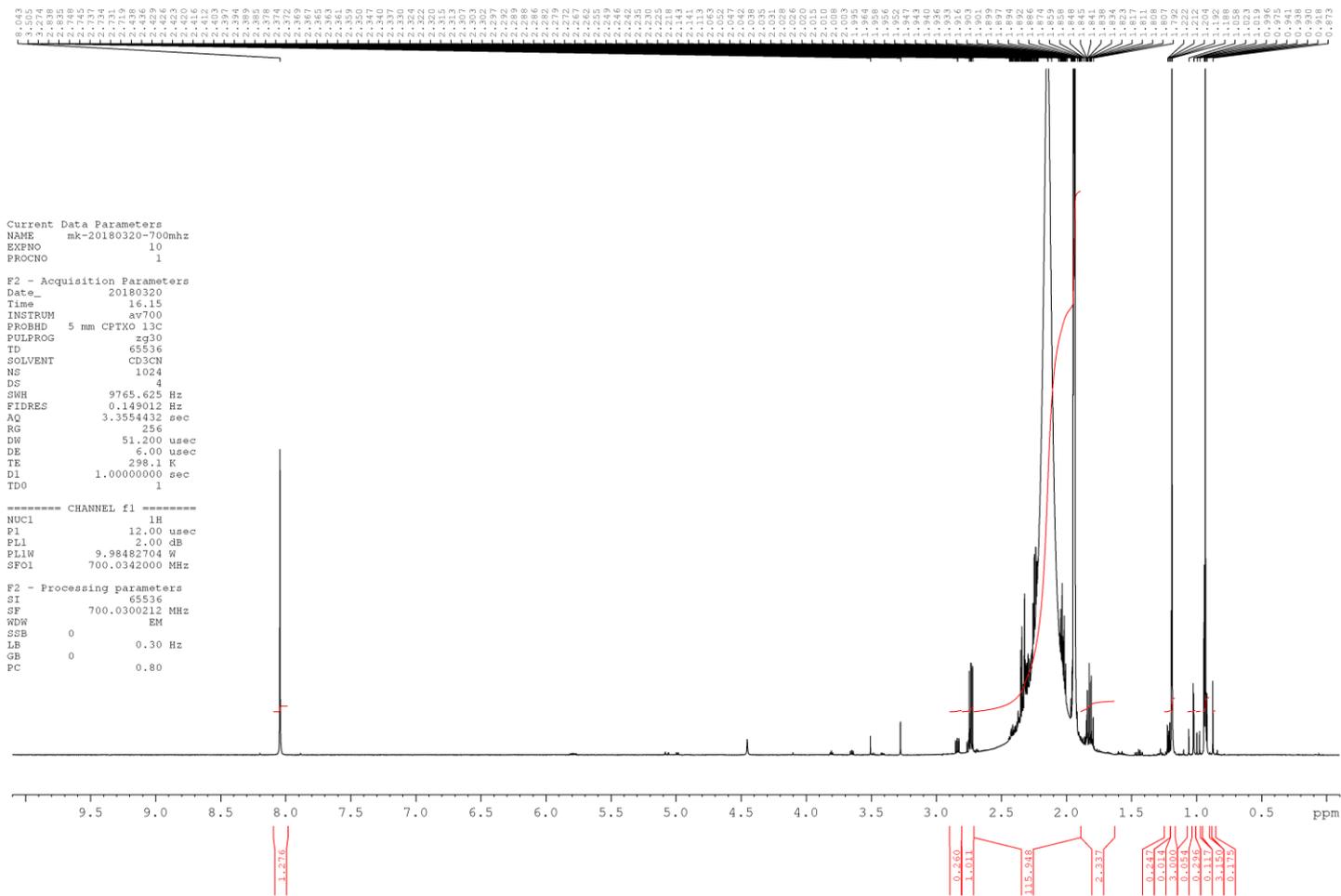


Figure S7: ^1H spectrum (CD_3CN , 700 MHz) of the monoperoxyipinic acid fraction, taken ~ 2.5 h after final fraction collection.

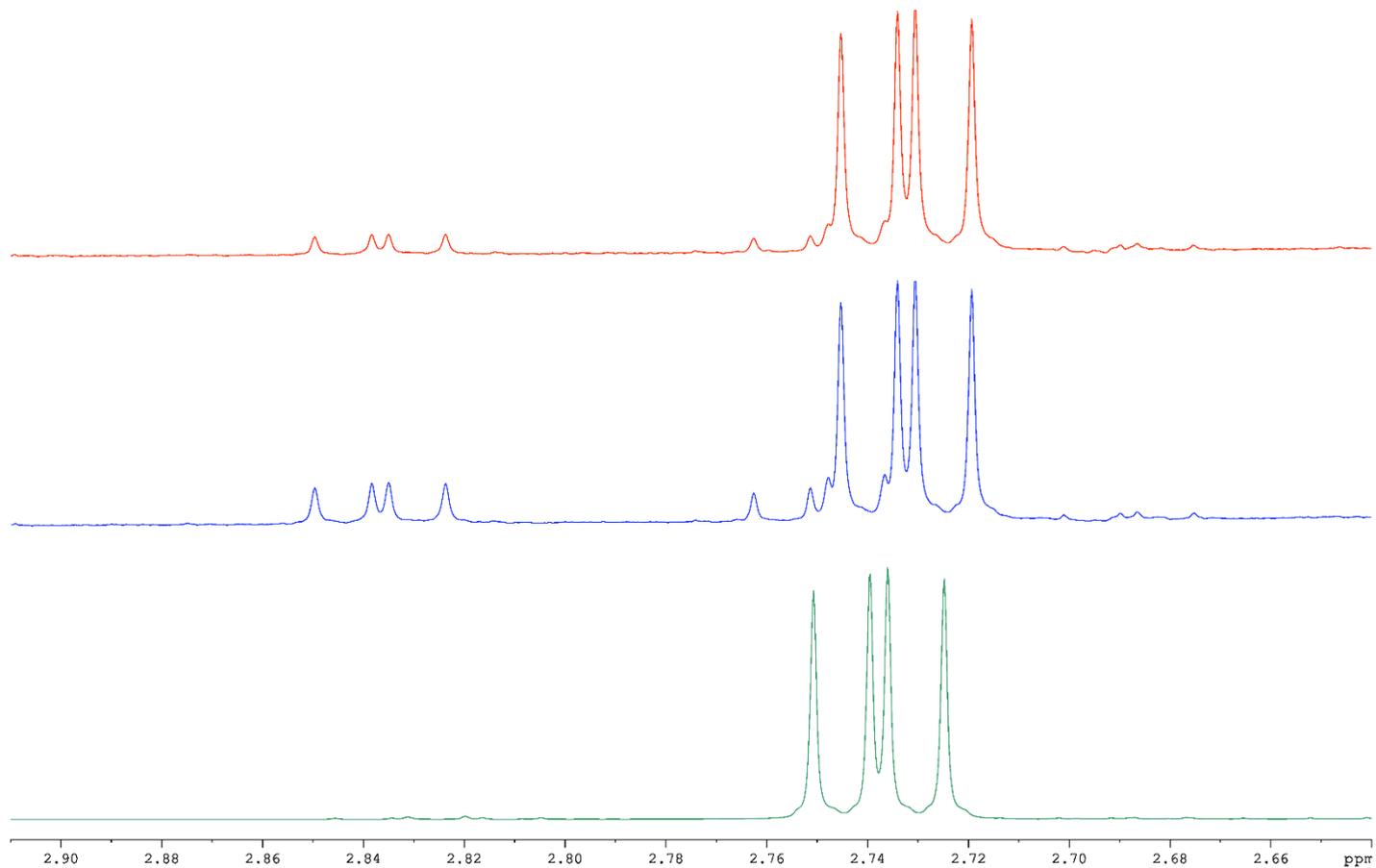


Figure S9: Signal of H3 for the monoperoxyipinic acid fraction ~2.5 h after final fraction collection (blue line, middle), ~18 h after final fraction collection (red line, top) and pinic acid reference (green line, bottom).

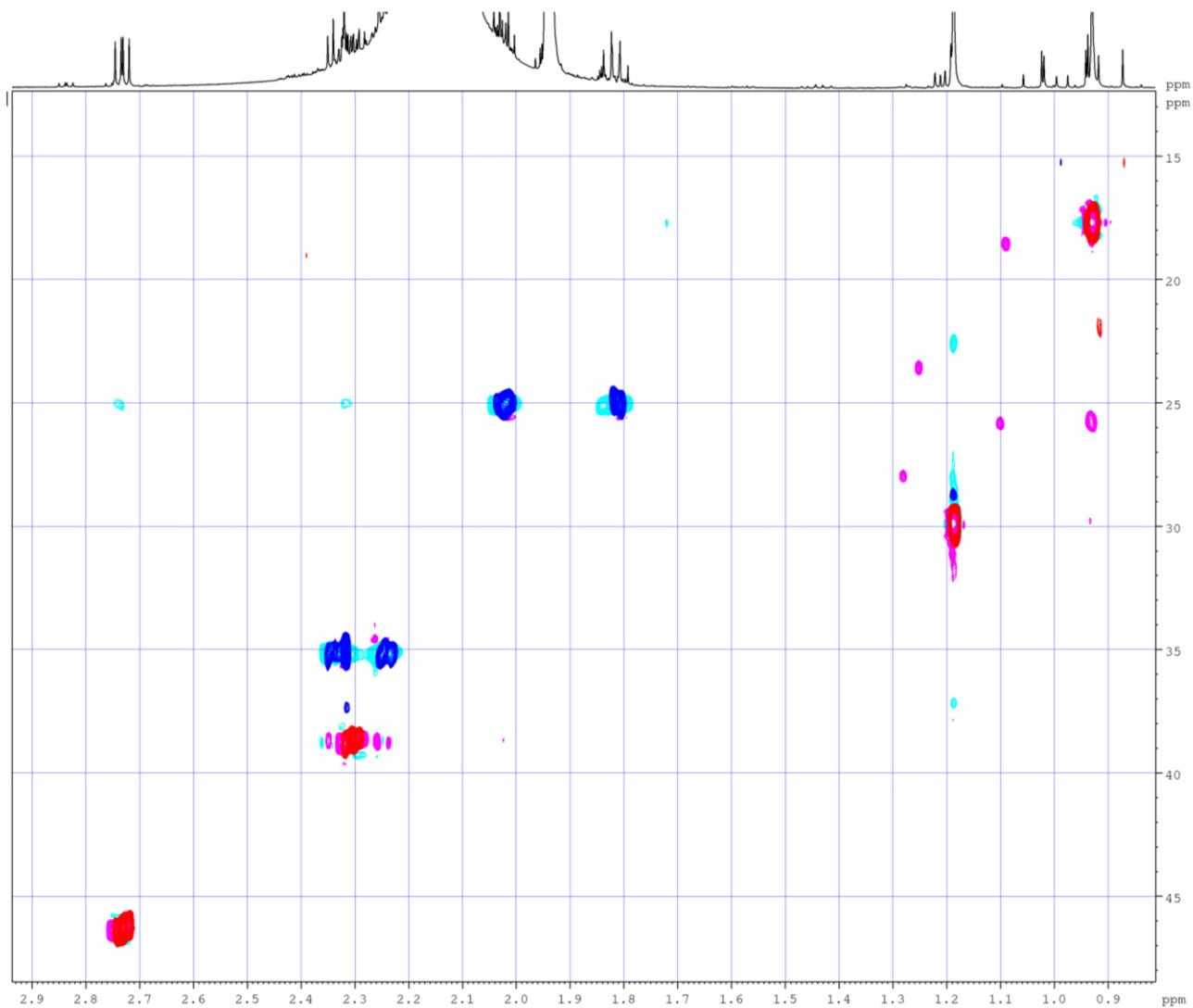


Figure S10: HSQC spectra of the monoperoxypinic acid fraction, taken ~19 h after final fraction collection (even numbers of hydrogen in blue, odd numbers in red) and the pinic acid reference (even numbers of hydrogen in cyan, odd numbers in magenta).

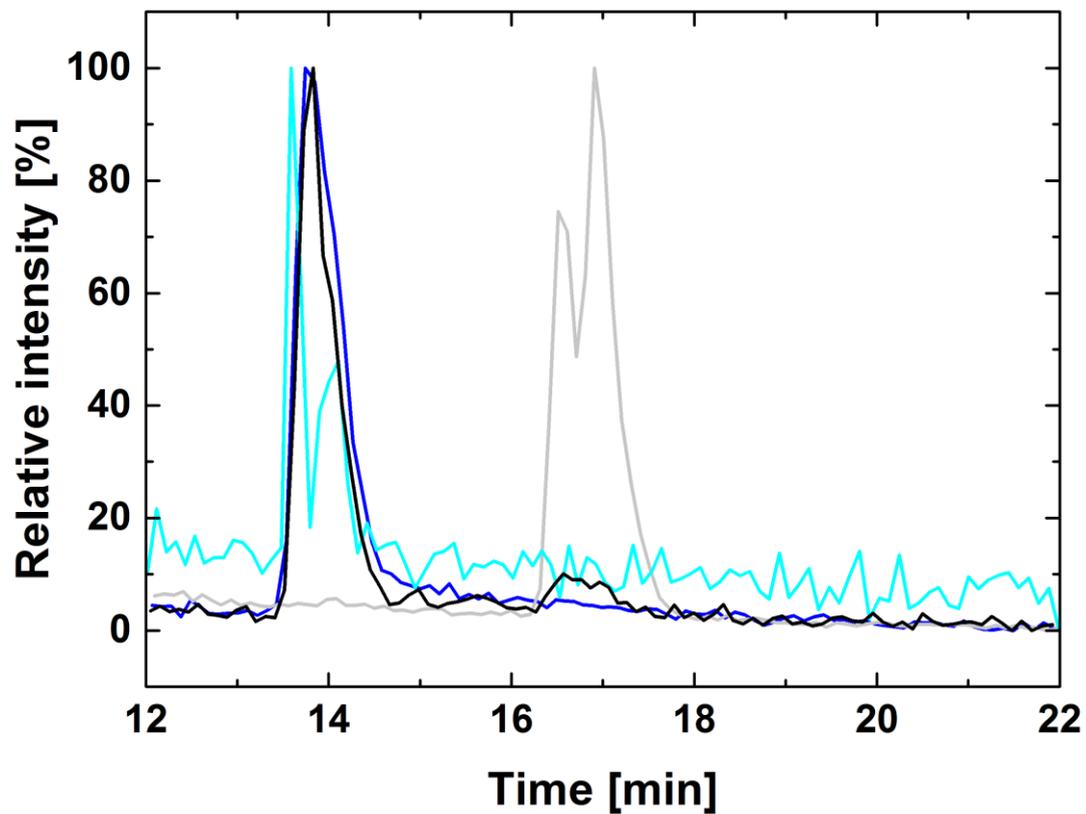


Figure S11: Chromatograms of the monoperoxyipinic acid fraction after NMR measurements. The black line shows the base peak chromatogram of the MS measurement, while the other three lines represent the base peak chromatograms of the MS/MS measurements at m/z 185.08 (pinic acid, blue line), m/z 201.08 (monoperoxyipinic acids, grey line) and m/z 217.07 (diperoxyipinic acid, cyan line). The chromatograms are normalised to the respective highest peak; absolute signals differ by more than two orders of magnitude.

Diperoxyypinic acid fraction results

The ^1H spectrum of the diperoxyypinic acid fraction shows that the diperoxy acid is not stable under the present conditions, since both monoperoxyypinic acid isomers and pinic acid are present as well. However, diperoxyypinic acid initially dominates the spectrum (Figure S12, Figure S13). In addition to the signals at 2.73 ppm, 2.75 ppm and 2.84 ppm, this sample shows a doublet of doublets at 2.85, which results from H3 of diperoxyypinic acid (Figure S14). Comparing the initial ^1H -NMR of the diperoxyypinic acid fraction with one taken after an additional 25 h, it can be seen that diperoxyypinic acid further decays into the monoperoxyypinic acids and then into pinic acid (Figure S14). These conclusions are supported by HSQC spectra taken at similar times (Figure S15, Figure S16)

The NMR results are supported by re-analysis of the sample with LC-MS/MS, which shows the presence of pinic acid, both monoperoxyypinic acid isomers and diperoxyypinic acid (Figure S17).

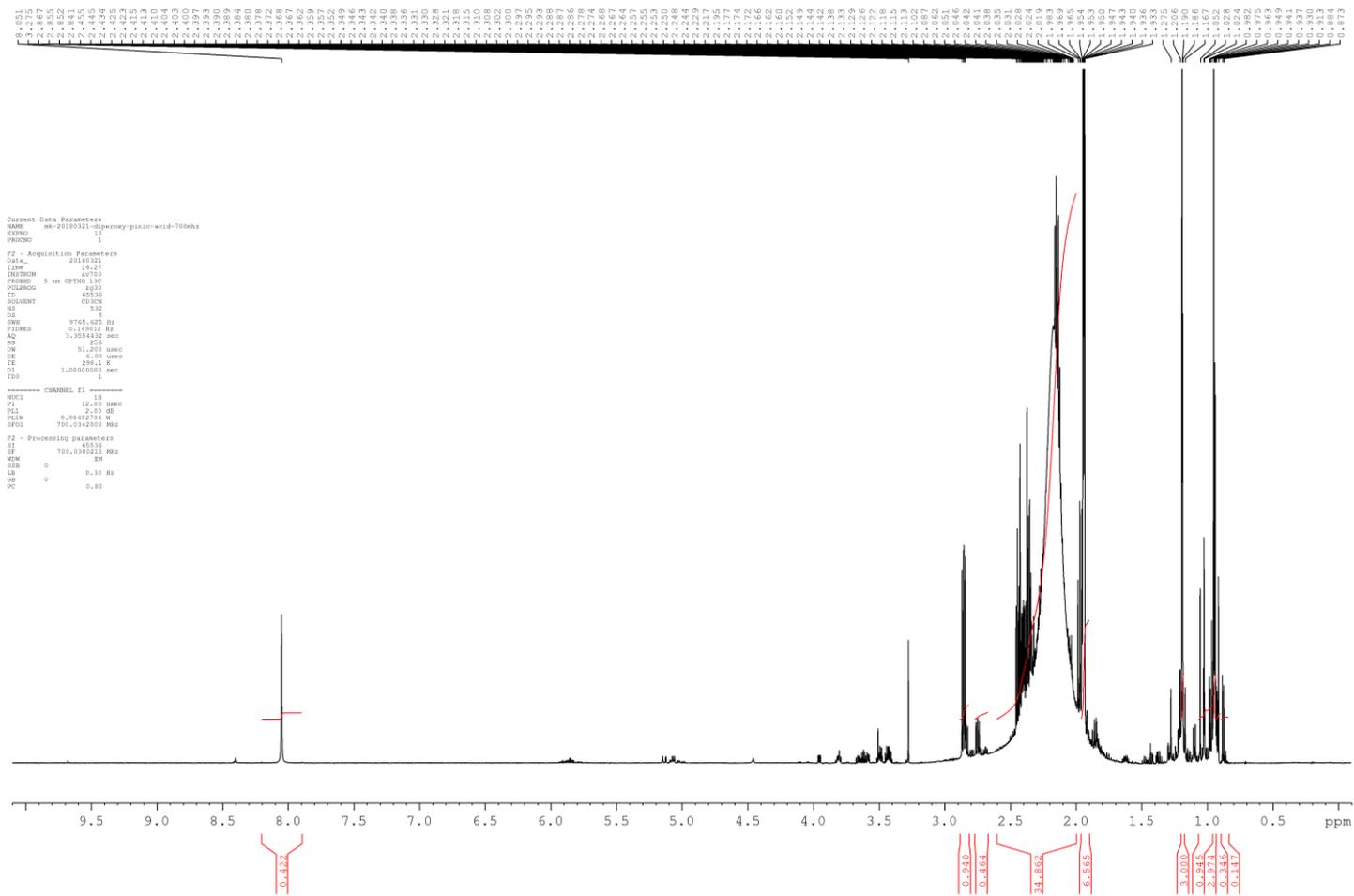


Figure S12: ^1H spectrum (CD_3CN , 700 MHz) of the diperoxy-pinic acid fraction, taken ~24.5 h after final fraction collection.

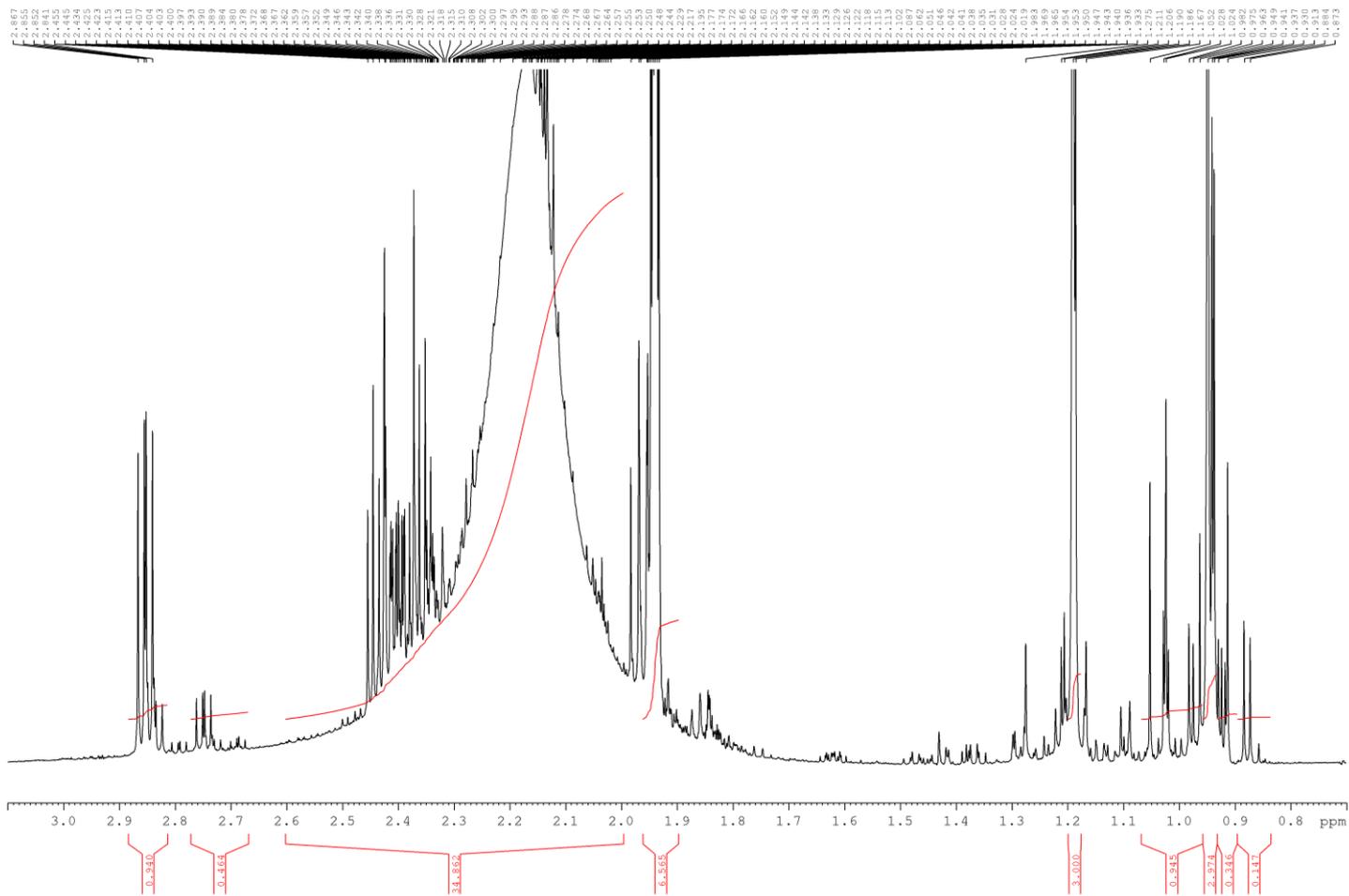


Figure S13: ^1H spectrum (CD_3CN , 700 MHz) of the diperoxy-pinic acid fraction, enlarged view of the 0.7-3.1 ppm region, ~24.5 h after final fraction collection.

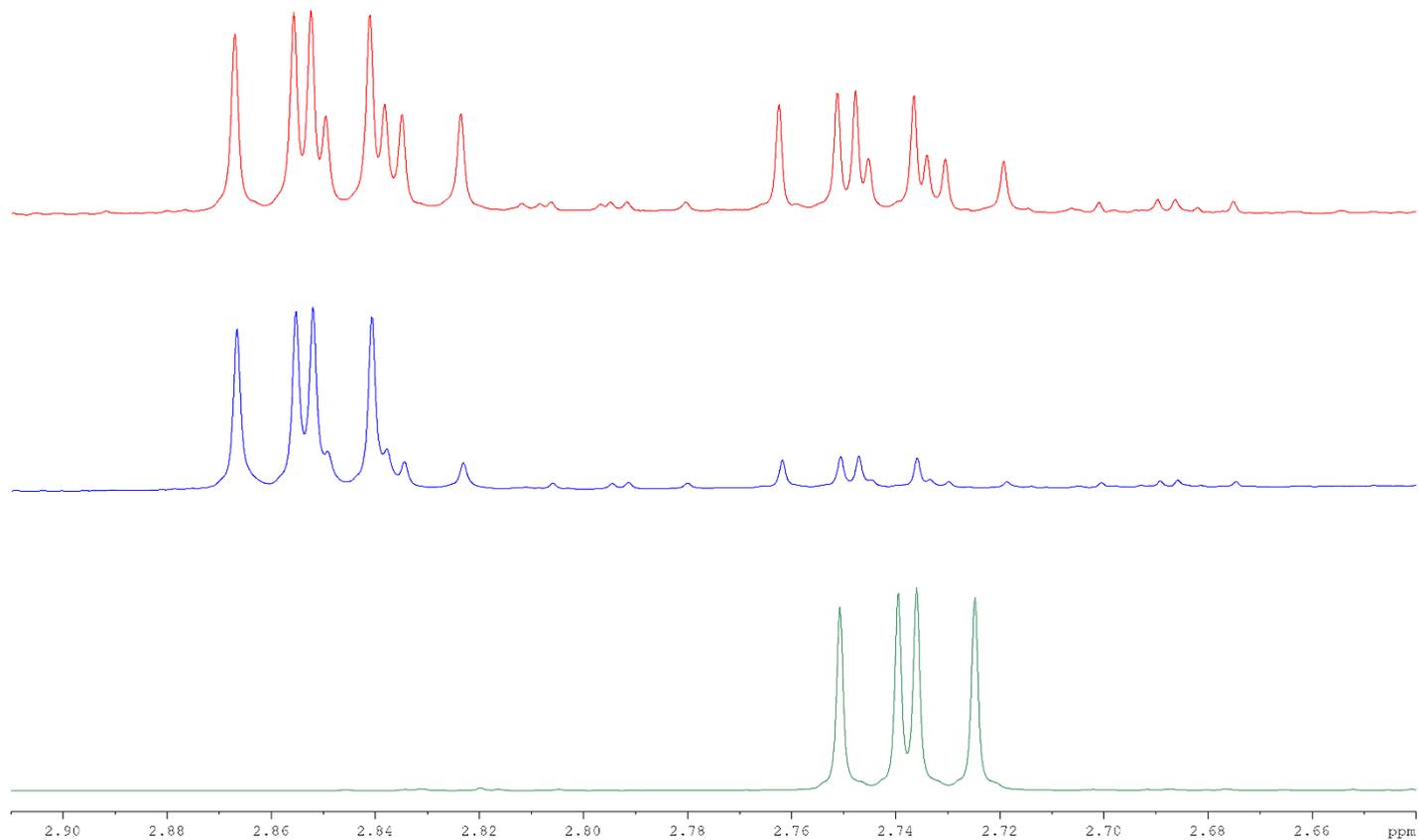


Figure S14: Signal of H3 for the diperoxyipinic acid fraction ~24.5 h after final fraction collection (blue line, middle), ~49.5 h after final fraction collection (red line, top) and pinic acid reference (green line, bottom).

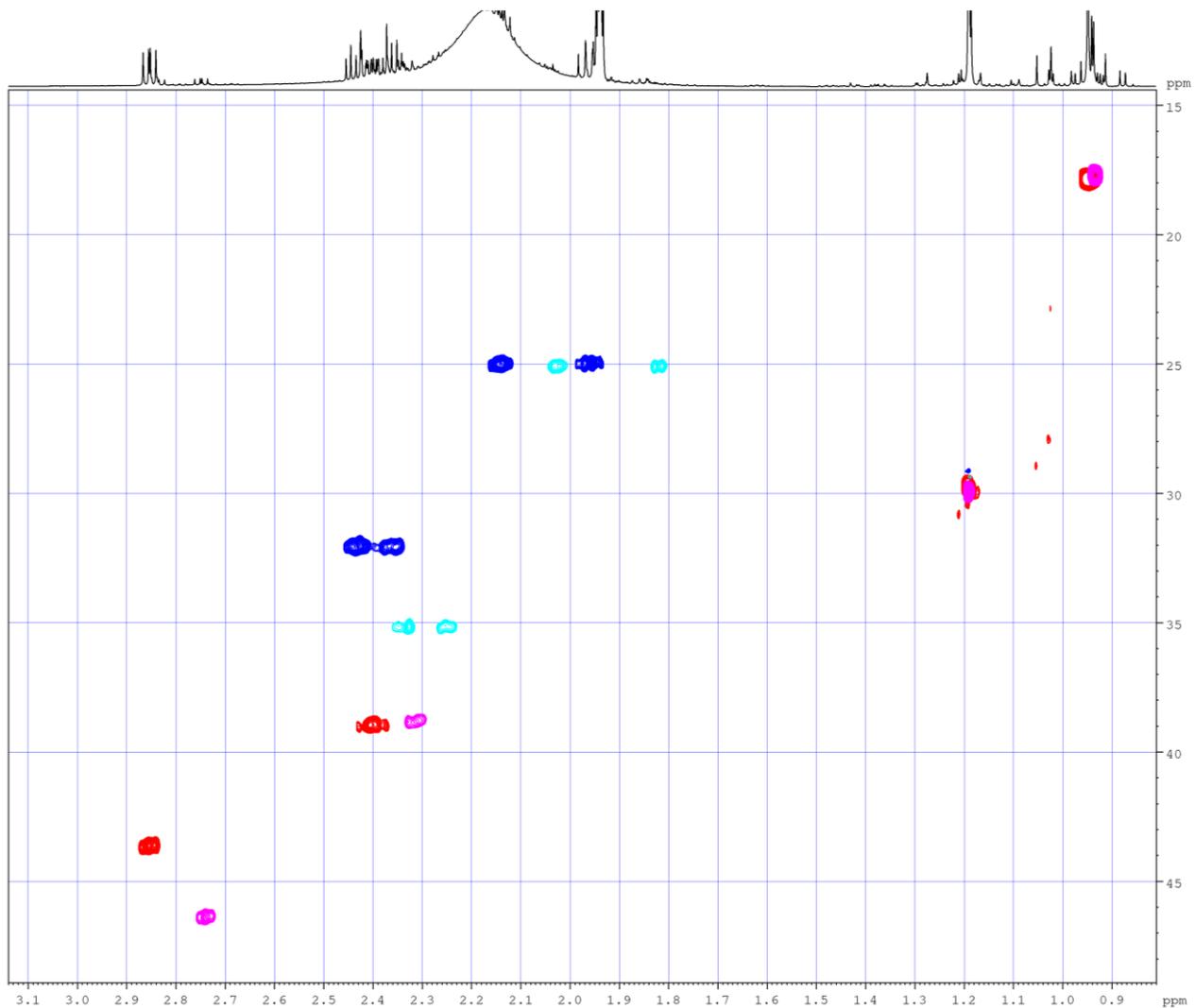


Figure S15: HSQC spectra of the diperoxylinic acid fraction, taken ~25 h after final fraction collection (even numbers of hydrogen in blue, odd numbers in red) and the pinic acid reference (even numbers of hydrogen in cyan, odd numbers in magenta).

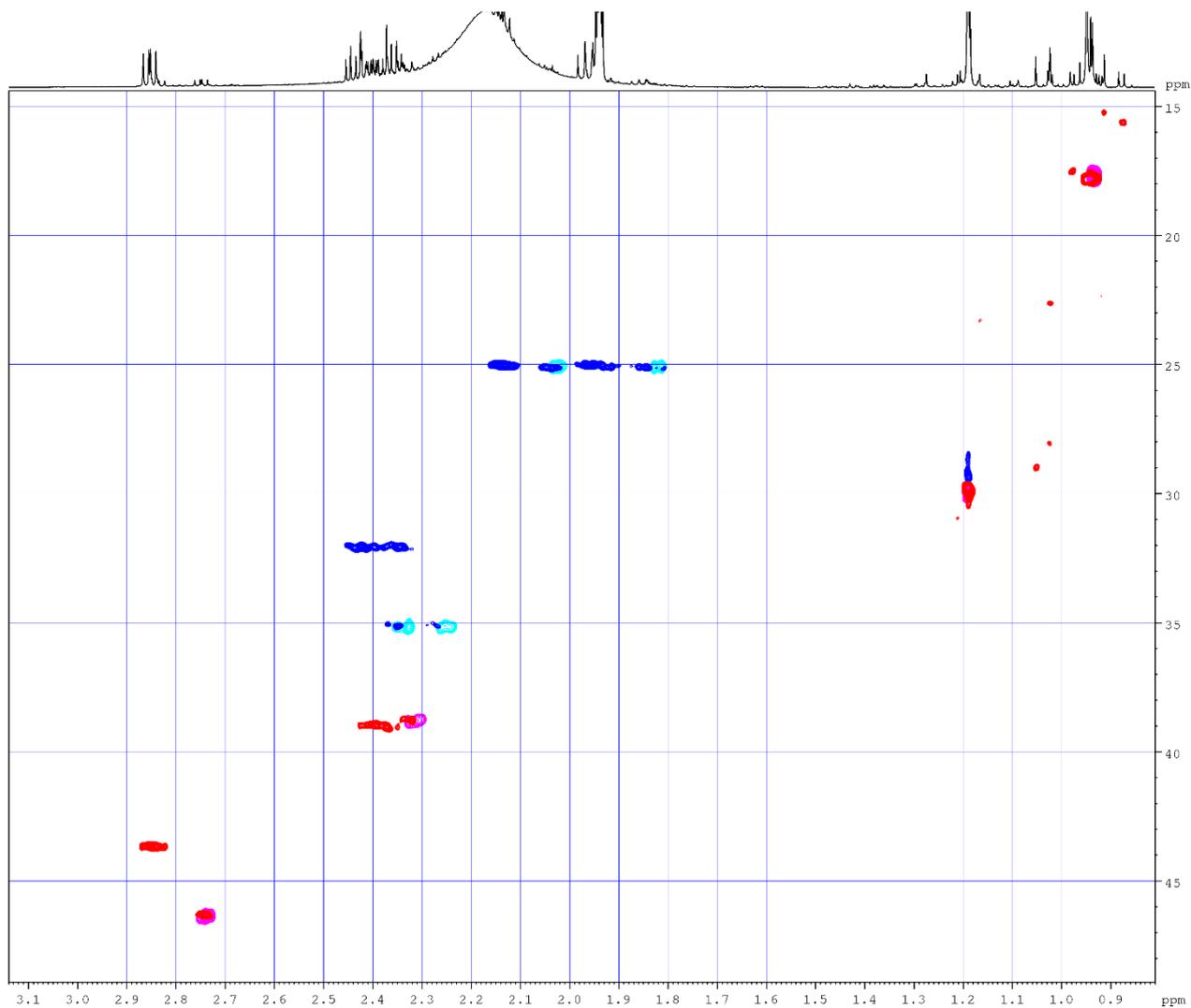


Figure S16: HSQC spectra of the diperoxyipinic acid fraction, taken ~45.5 h after final fraction collection (even numbers of hydrogen in blue, odd numbers in red) and the pinic acid reference (even numbers of hydrogen in cyan, odd numbers in magenta).

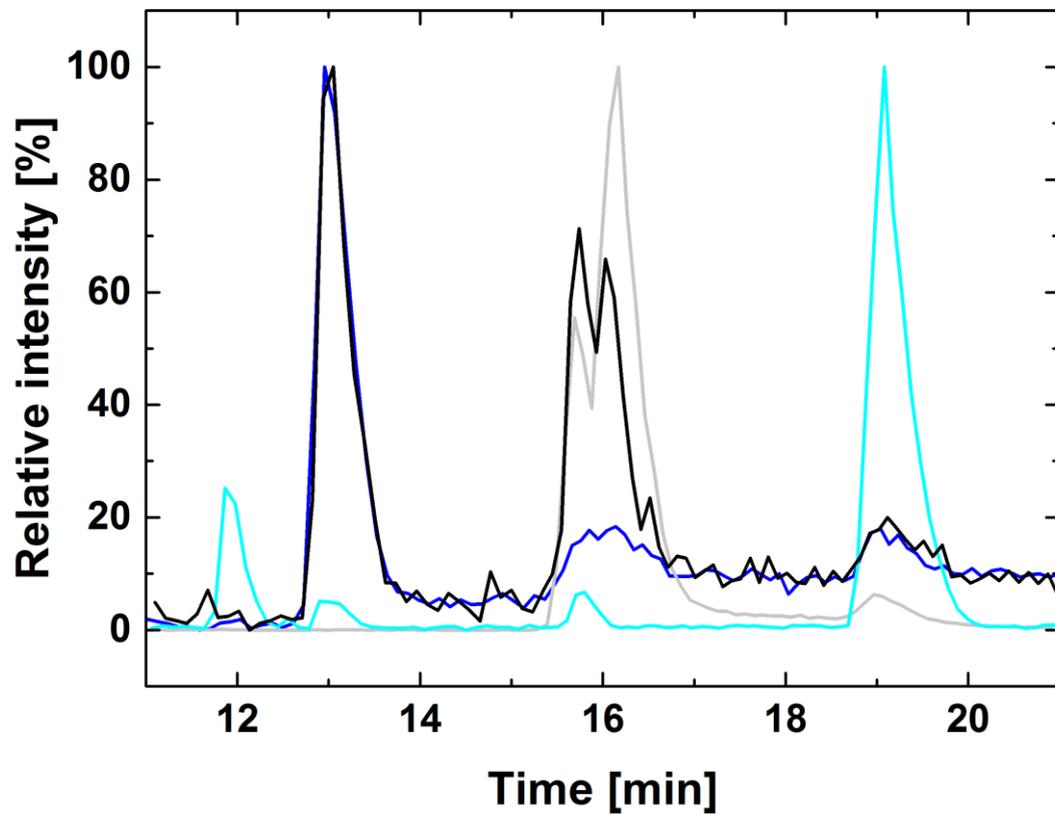


Figure S17: Chromatograms of the diperoxyipinic acid fraction after NMR measurements. The black line shows the base peak chromatogram of the MS measurement, while the other three lines represent the base peak chromatograms of the MS/MS measurements at m/z 185.08 (pinic acid, blue line), m/z 201.08 (monoperoxyipinic acids, grey line) and m/z 217.07 (diperoxyipinic acid, cyan line). The chromatograms are normalised to the respective highest peak; absolute signals differ by more than two orders of magnitude.

Mass spectrometry

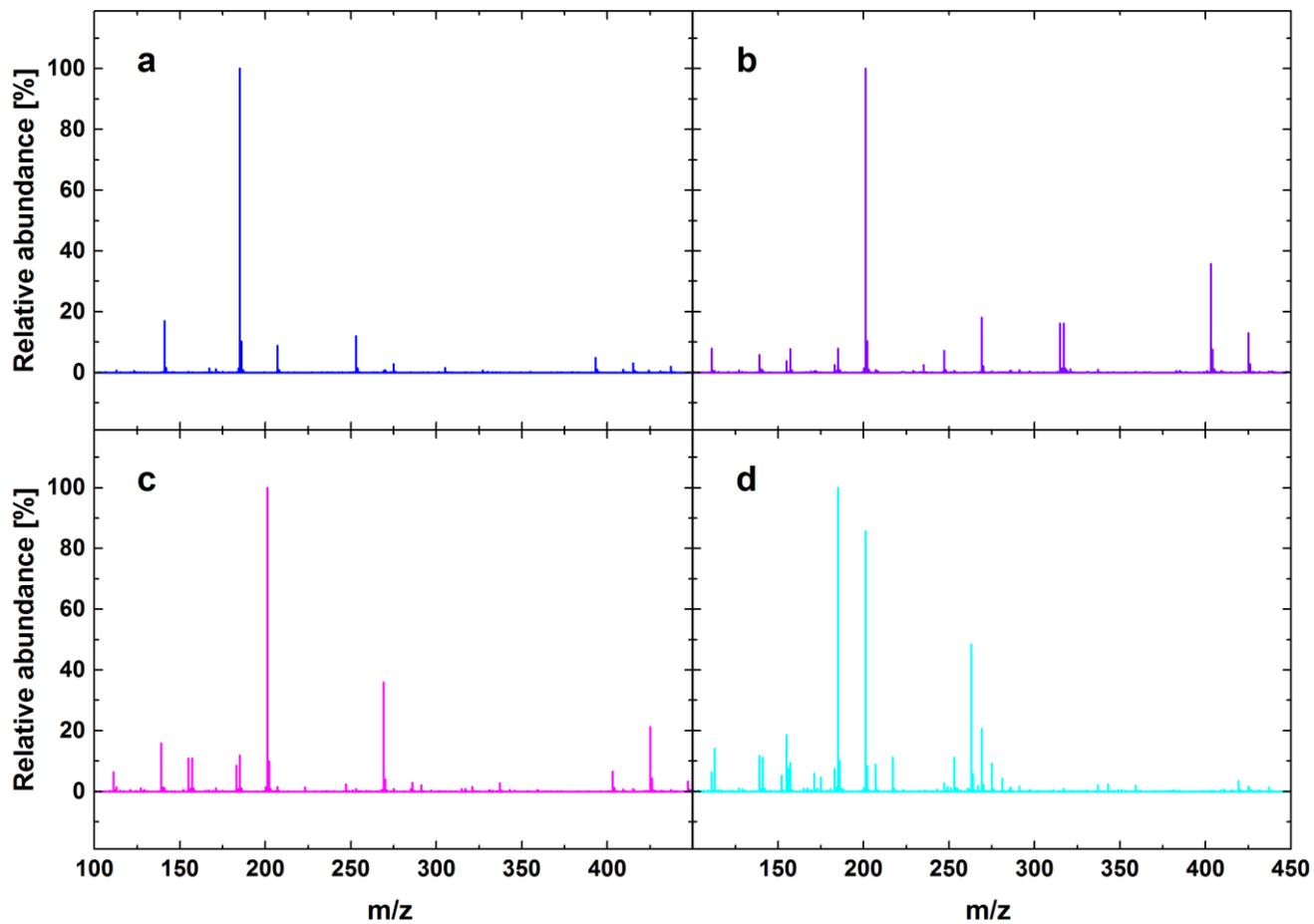


Figure S18: Mass spectra of pinic acid (a), monoperoxy-pinic acid isomer I (b), monoperoxy-pinic acid isomer II (c) and dipheroxy-pinic acid (d).

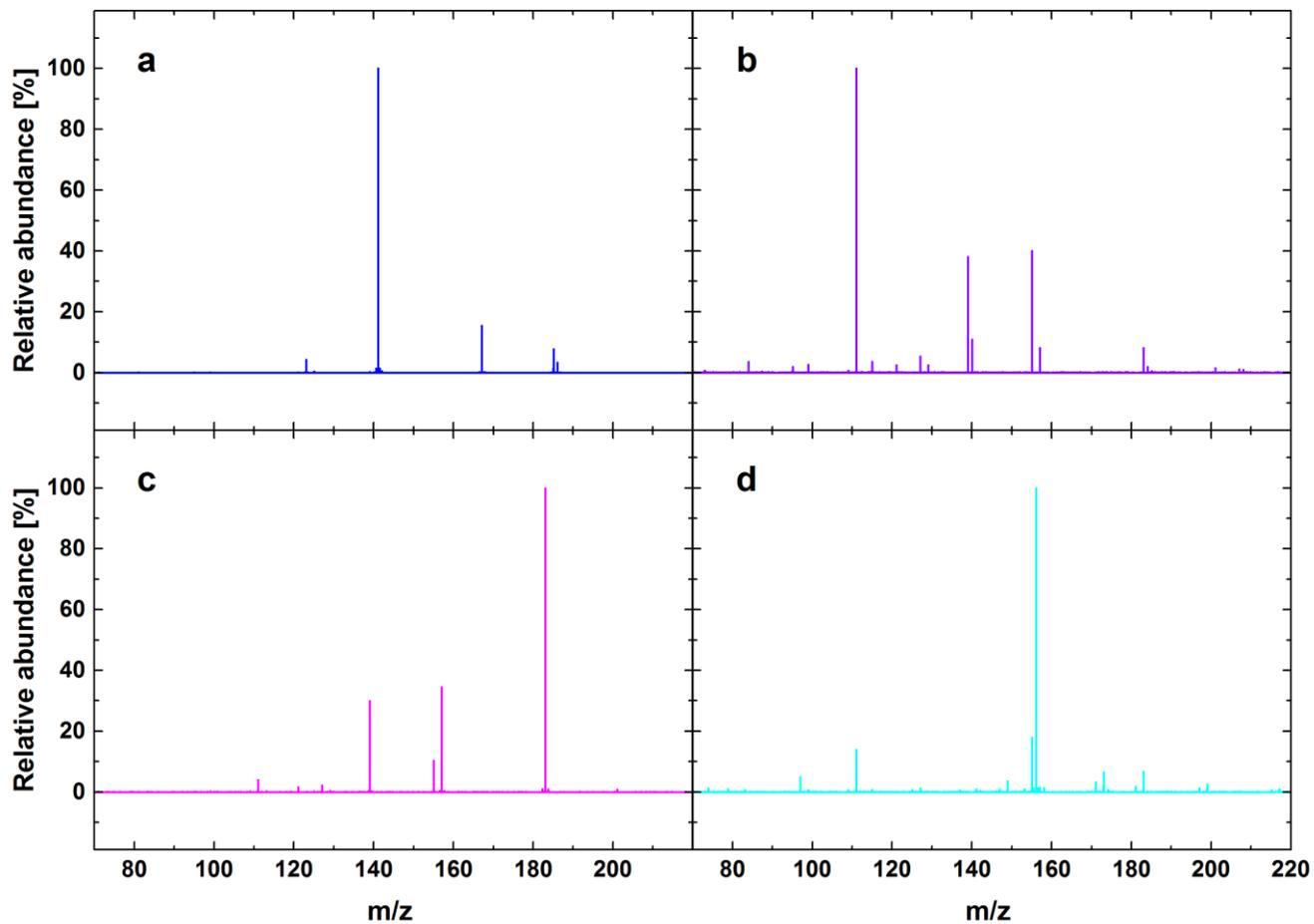


Figure S19: MS/MS spectra of the $[M - H]^-$ deprotonated molecule of pinic acid (a), monoperoxyipinic acid isomer II (c) and diperoxyipinic acid (d) as well as the MS³ spectrum of the deprotonated dimer adduct of monoperoxyipinic acid isomer I (b).

