

Supporting information for:

Hyphenated structural identification of additives in transmission fluids

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S1: Full MS chromatogram of sample vs. blank

In Figure S1, the MS chromatogram of the full sample in n-hexane is compared to a blank chromatogram of only n-hexane. The eluting masses in hexane are not overlapping with the fractions selected for SFC-NMR analysis.

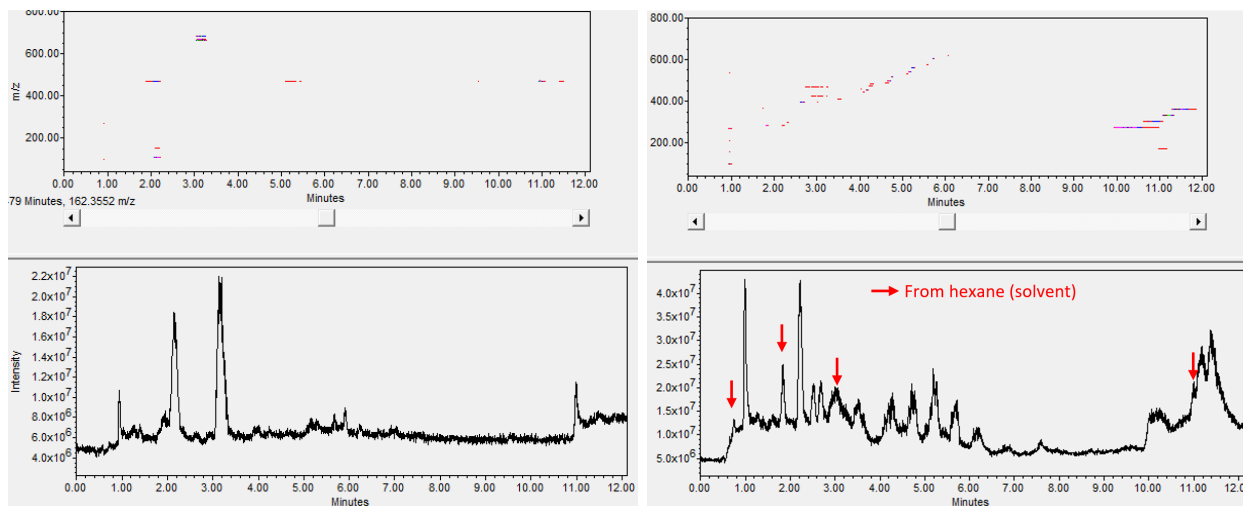


Figure S1: MS ESI+ chromatograms of the the full sample in n-hexane (right) compared to a blank n-hexane sample (left). The top of the image shows the eluting m/z over time and the bottom picture shows the total intensity (projection) over time.

S2: MS and UV spectra after SFC of three selected fractions

In Figure S2, the MS and UV spectra of the three selected fractions are shown. The main masses of 282, 338 and 394 are observed in each fraction respectively. Some other masses are observed as well, but at lower intensities. These could either be due to other compounds present, for example the mass of 282 is also present in fraction 2 with a main mass of 338, or they can originate from fragmentation during ionisation in the mass spectrometer.

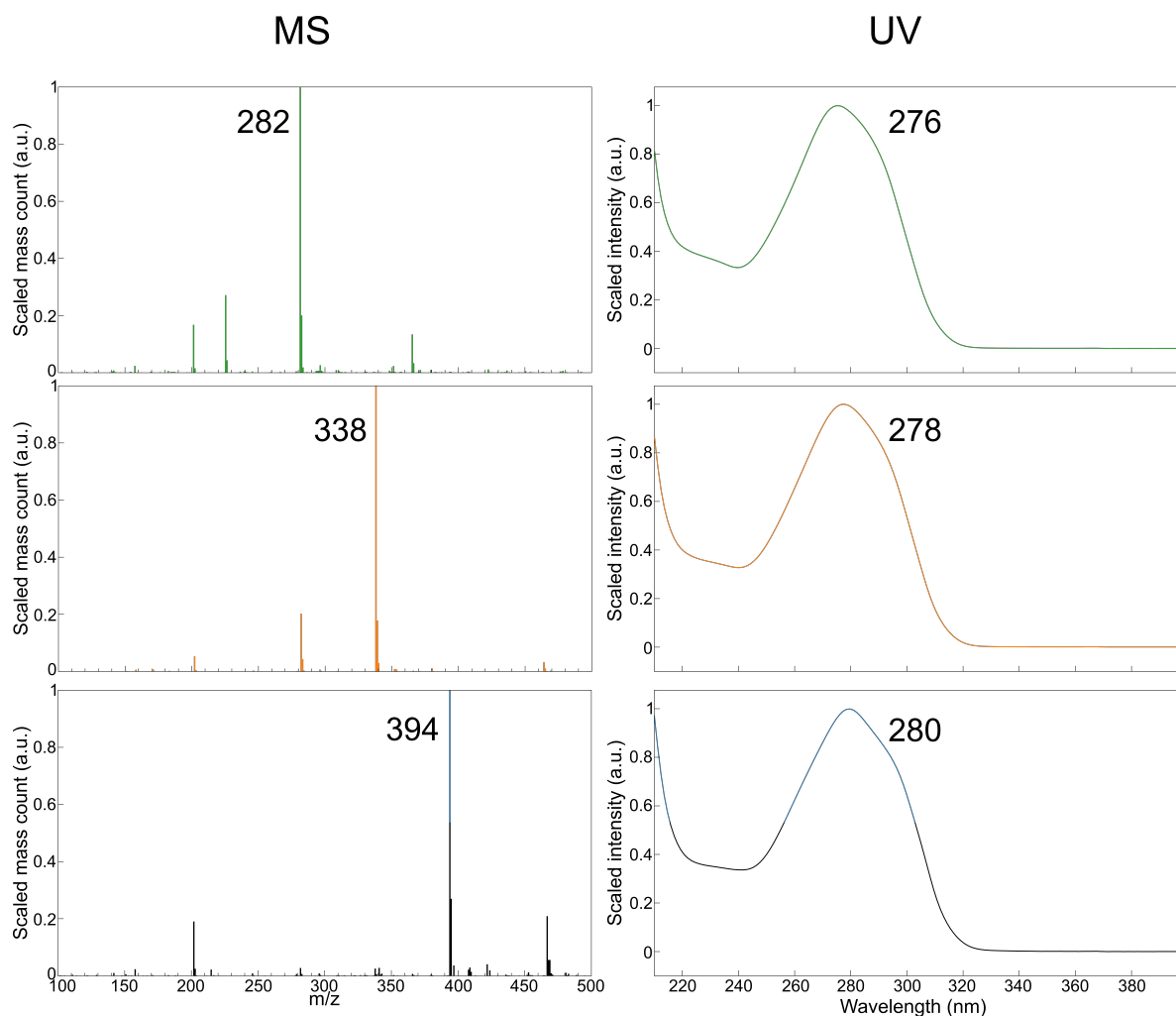


Figure S2: MS ESI+ (left column) and UV (right column) spectra of the three fractions recorded after SFC separation.

S3: SFC- ^1H NMR spectra of three selected fractions

In Figure S3, the full SFC- ^1H NMR spectra of the three selected fractions are shown. The water and chloroform peaks are due to the experimental set-up in which a plug of (partially) deuterated chloroform in a water flow is pushed through a tube containing the sample to collect it for NMR analysis. Traces of water and chloroform are therefore observed in the spectra. Methanol is used as a co-solvent in SFC and is therefore also observed in the spectrum. Most of these peaks do not overlap with the signals of interest.

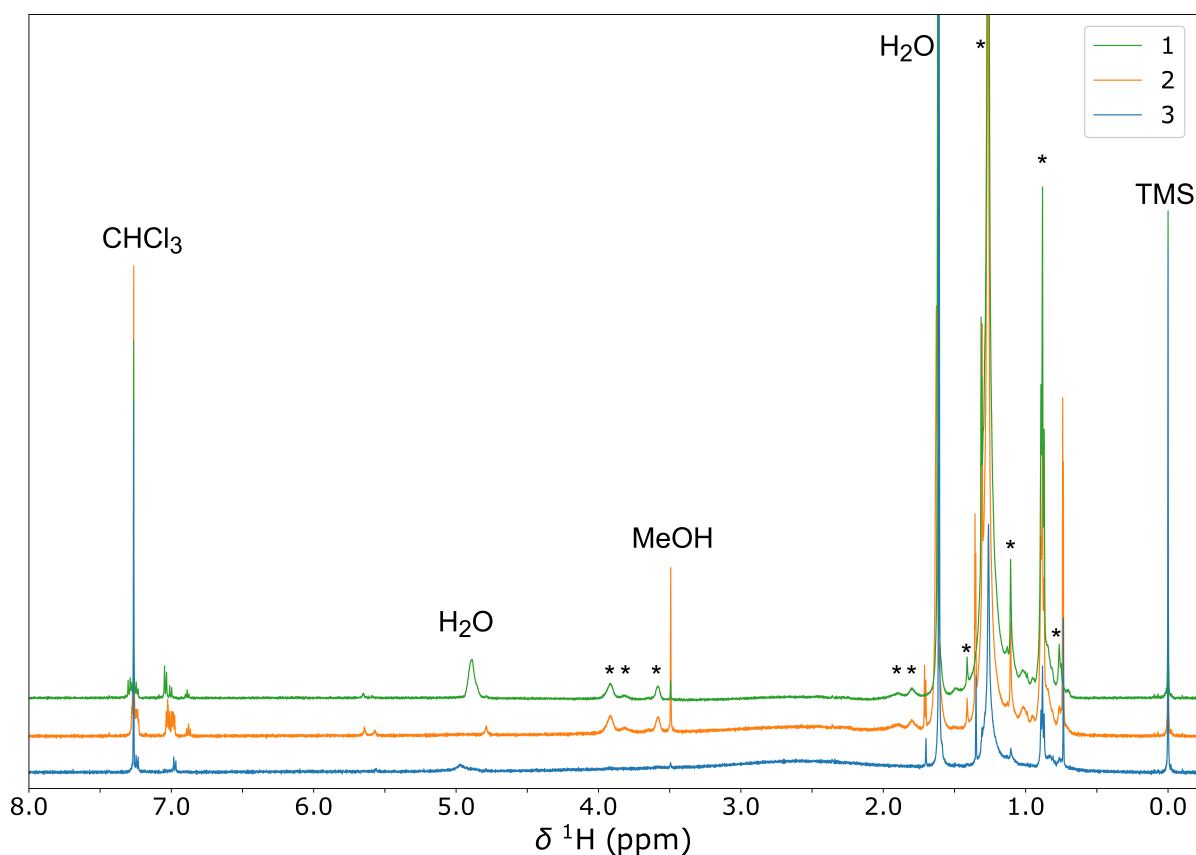


Figure S3: Full SFC- ^1H NMR of the three selected fractions. The *-symbols indicate peaks that do not originate from the compounds of interest, such as impurities.

S4: Predicted ^1H NMR spectra of proposed molecules

Below the spectral predictions for the proposed molecules in the main article are shown. The predictions were performed using the ACD/Labs software. In the predicted spectra, many multiplets and peak splittings due to J-coupling between neighbouring protons are observed. In experimental spectra, these couplings will not all be observed due to line broadening caused by for example field inhomogeneities. As an example, in the aromatic region in Figure S4a, two doublets will be observed in the experimental spectrum instead of the multiplets that are shown.

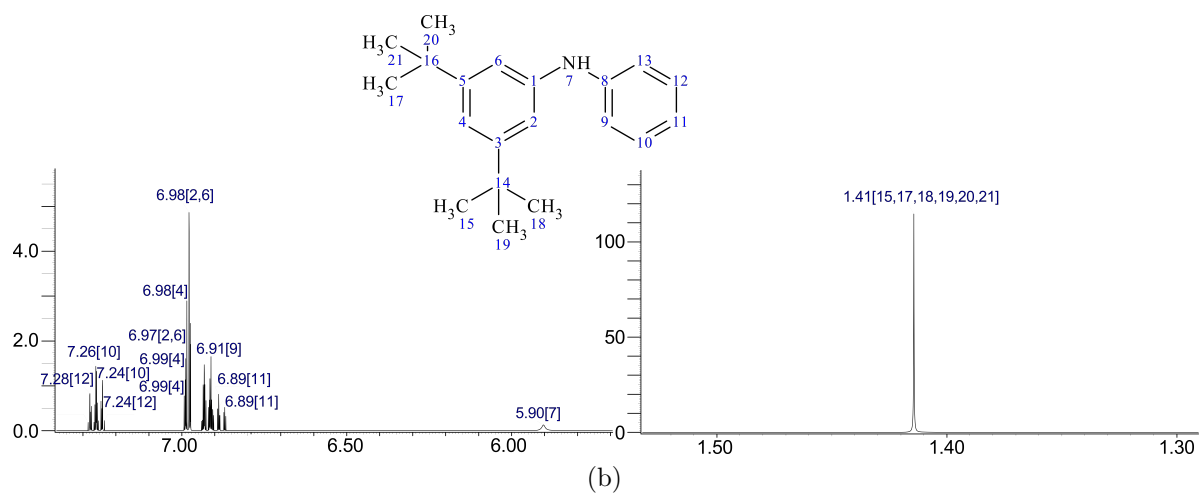
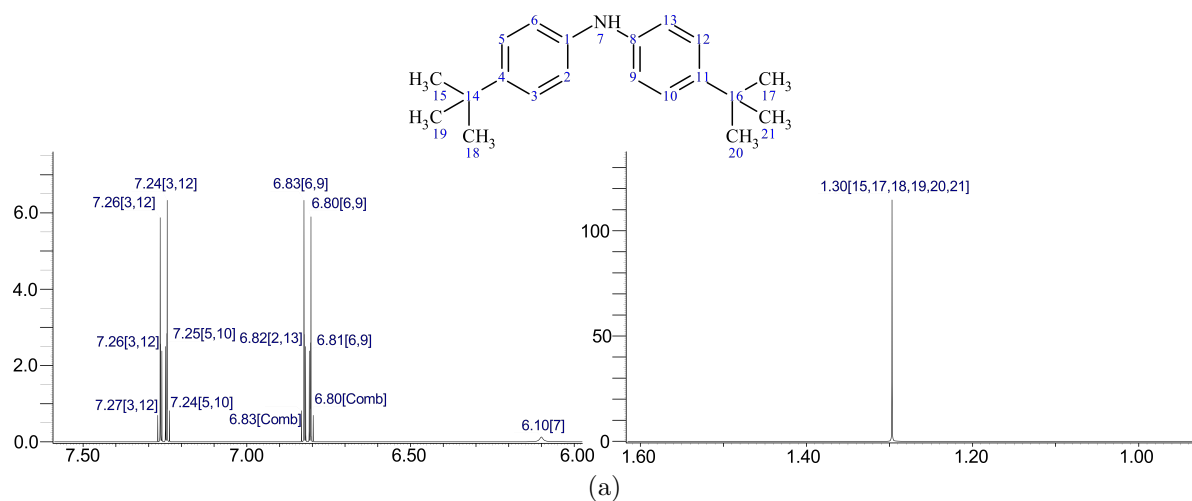


Figure S4: Predicted ^1H NMR spectra for the two proposed molecules in fraction 1. On the left the aromatic region is shown, on the right the alkyl region. Above each peak is its predicted chemical shift and in brackets the carbon atom to which the proton is attached from which the signal originates.

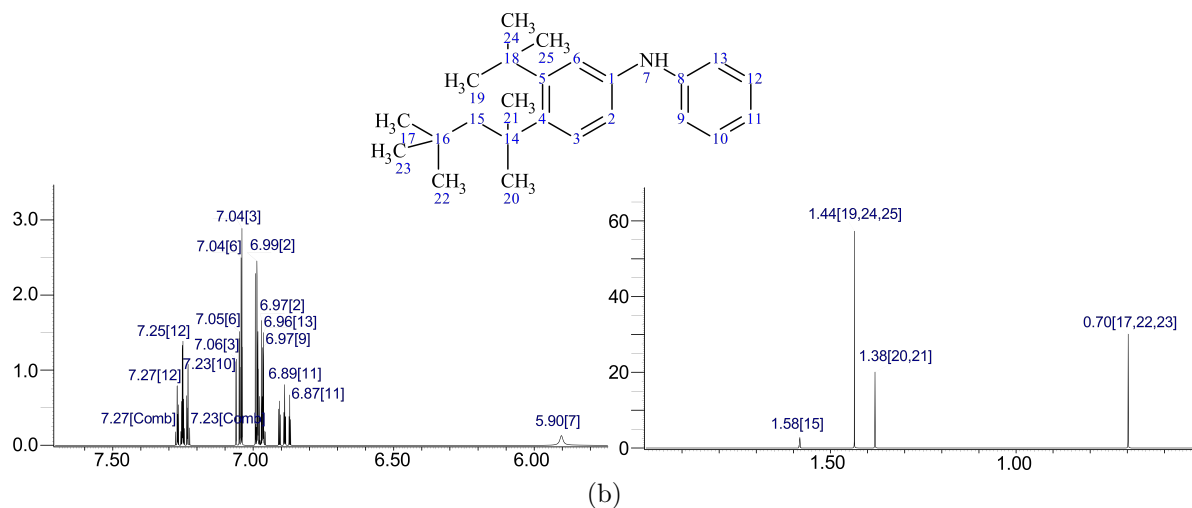
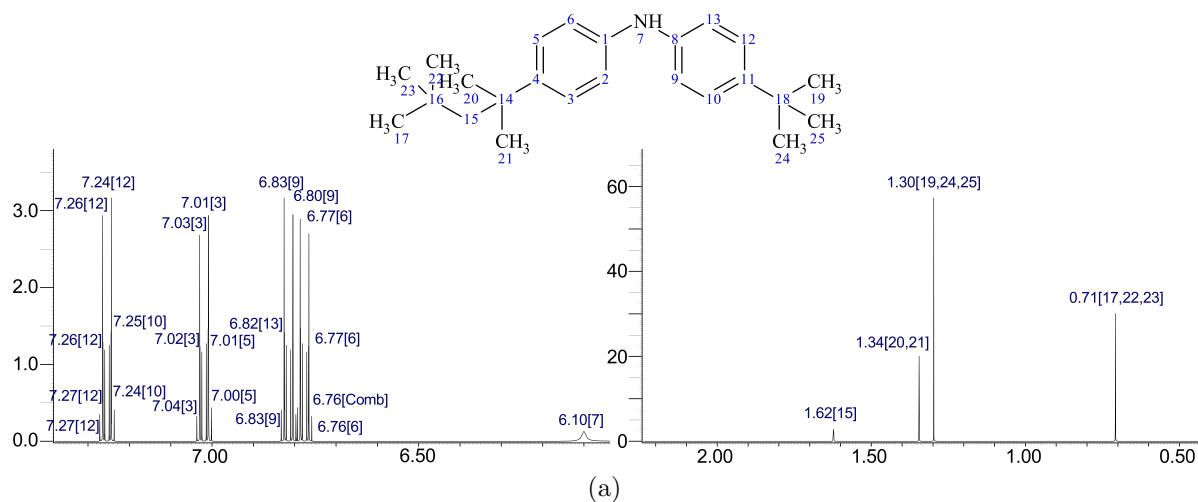


Figure S5: Predicted ^1H NMR spectra for the proposed molecules in fraction 2. On the left the aromatic region is shown, on the right the alkyl region. Above each peak is its predicted chemical shift and in brackets the carbon atom to which the proton is attached from which the signal originates.

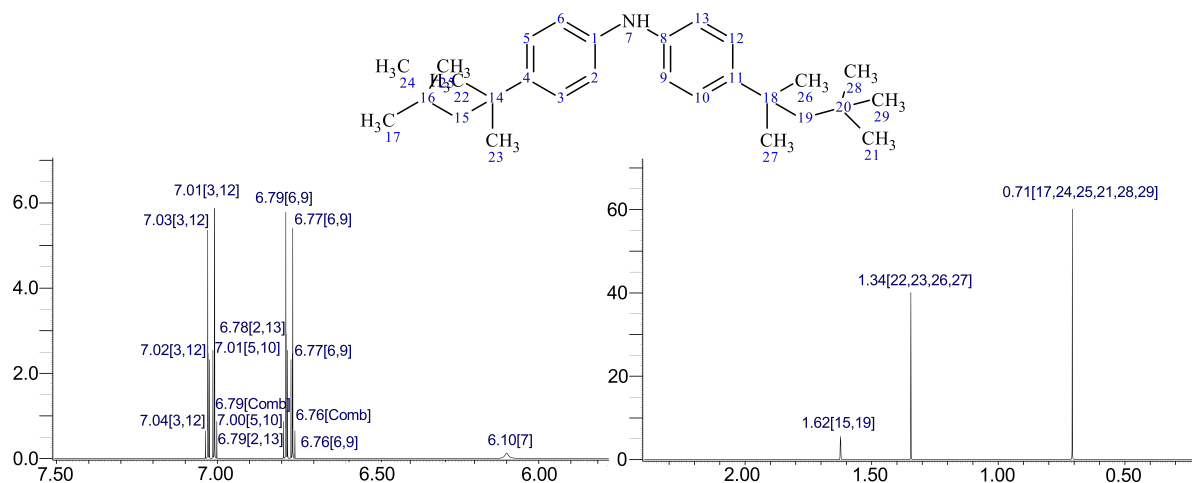


Figure S6: Predicted ^1H NMR spectra for the proposed molecule in fraction 3. On the left the aromatic region is shown, on the right the alkyl region. Above each peak is its predicted chemical shift and in brackets the carbon atom to which the proton is attached from which the signal originates.