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Supporting information

Chemoselective derivatisation and ultrahigh resolution mass spectrometry for the determination

of hydroxyl functional groups within complex bio-oils

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Contents

1.1 Description of standards	1
1.2 Chromatograms	3
	3
1.3 Reaction mechanisms	
1.4 Reactions	24
1.5 Mass spectra	26
1.6 Van Krevelen and DBE plots	28

1.1 Description of standards

Table S 1. Detailed list of standards

Name	CAS-No	Id	Vendor	Purity (%)	Structure
			Thermo		OH
2-methoxyphenol	90-05-1	Ph-1	Fisher	99	
2.4 dimothylphonol			Acros		OH
2,4-dimethylphenol	105-67-9	Ph-2	Organics	98	
o-cresol			Acros		OH
0-cresor	97-48-7	Ph-3	Organics	99	
			Sigma-		OH
4-ethylphenol	123-07-9	Ph-4	Aldrich	97	
bydroguinono			Sigma-		OH
hydroquinone	123-31-9	Ct-5	Aldrich	99	но
1-(2,5-					0
dihydroxyphenyl)propan-					OH
1-one	938-46-5	Ct-6	Abcr	97	HO

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	5-methylbenzene-1,3-			Sigma-		HO
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1207435-		4919-37-3		Abcr	98	
	Bio-oil	39-9	во			

1.2 Chromatograms

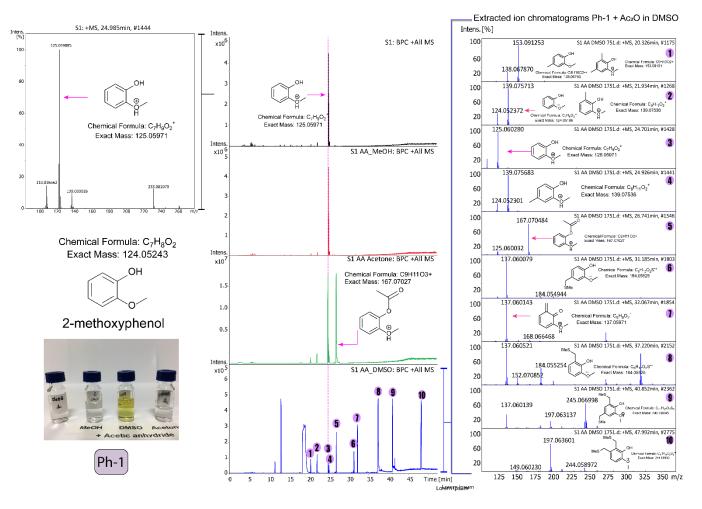


Fig. S1 Centre: chromatograms of Ph-1 without reaction (black), left: extracted MS of raw standard, right: MS at different RT for the reaction in DMSO-AC₂O. A photo of the samples is embedded on the left-bottom of the figure. Suggested structures have been embedded in the figure.

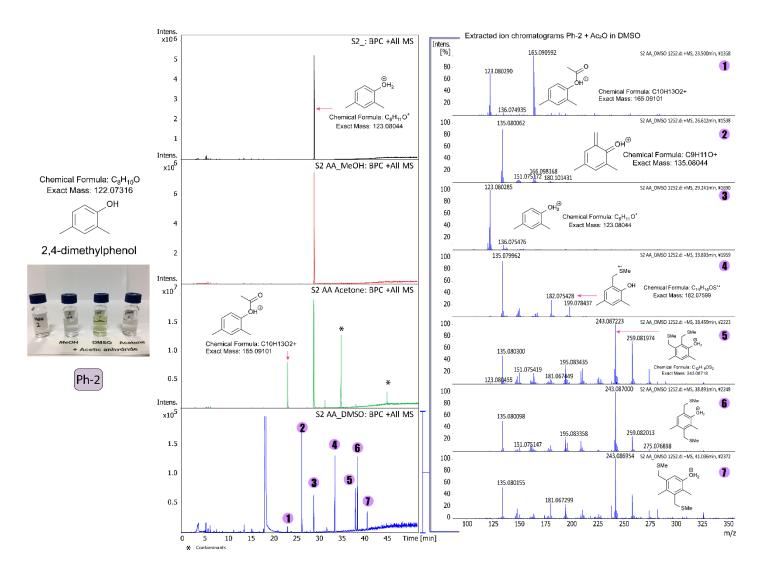


Fig. S2 Centre: chromatograms of Ph-2 without reaction (black), right: MS at different RT for the reaction in DMSO-AC₂O. A photo of the samples is embedded on the left-bottom of the figure. Suggested structures have been embedded in the figure.

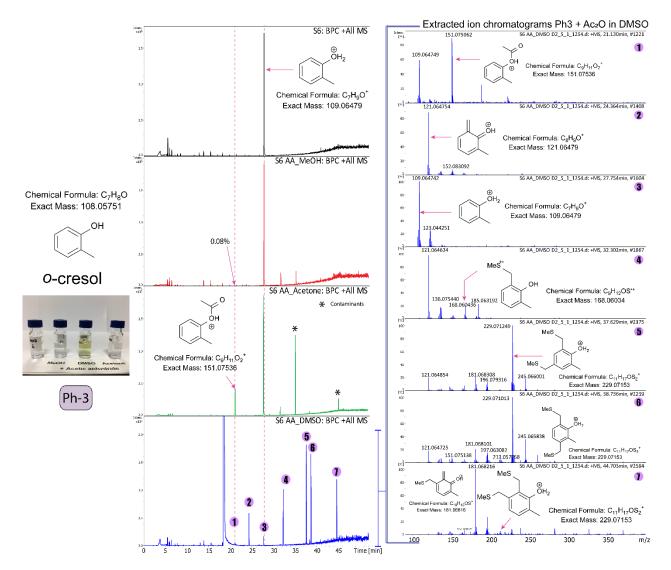


Fig. S3 Centre: chromatograms of Ph-3 without reaction (black), right: MS at different RT for the reaction in DMSO-AC₂O. A photo of the samples is embedded on the left-bottom of the figure. Suggested structures have been embedded in the figure.

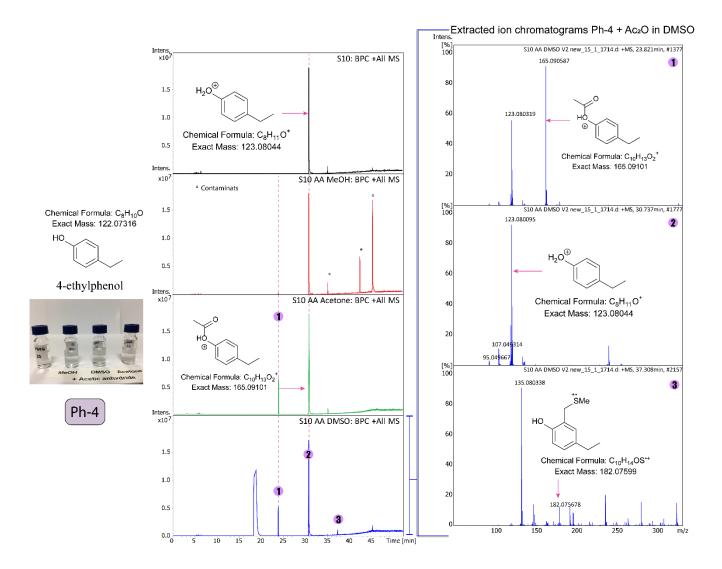


Fig. S4 Centre: chromatograms of Ph-4 without reaction (black), right: MS at different RT for the reaction in DMSO-AC₂O. A photo of the samples is embedded on the left-bottom of the figure. Suggested structures have been embedded in the figure.

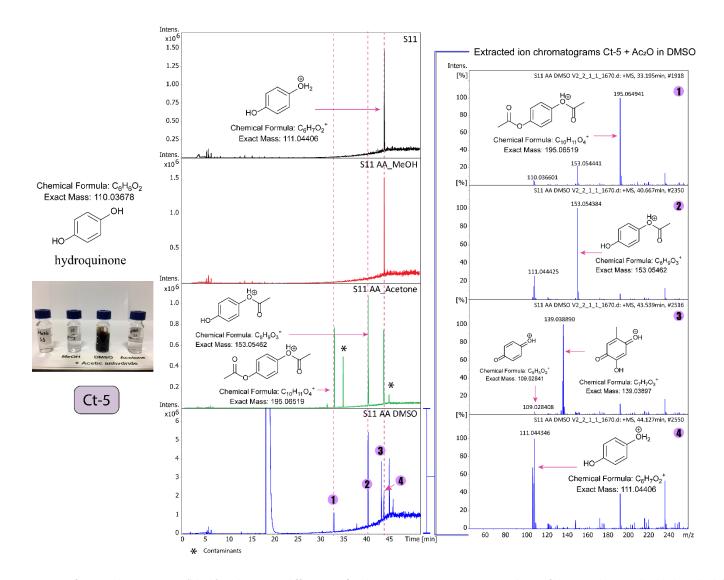


Fig. S5 Centre: chromatograms of Ct-5 without reaction (black), right: MS at different RT for the reaction in DMSO-AC₂O. A photo of the samples is embedded on the left-bottom of the figure. Suggested structures have been embedded in the figure.

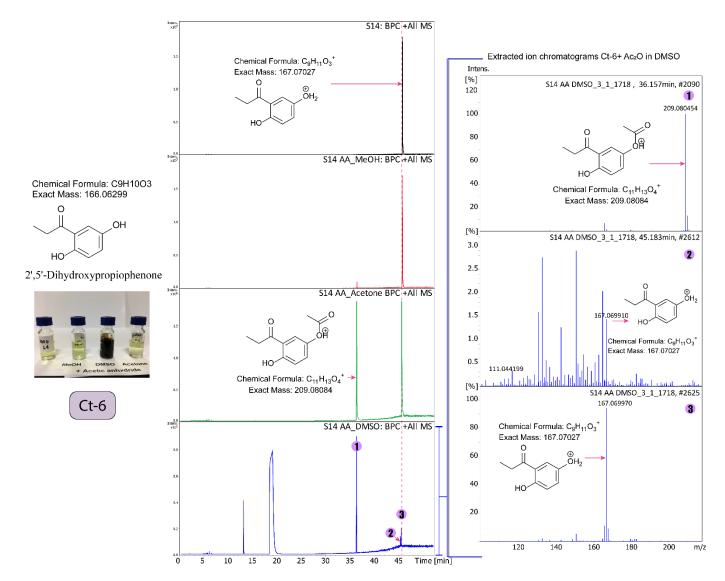


Fig. S6 Centre: chromatograms of Ct-6 without reaction (black), right: MS at different RT for the reaction in DMSO-AC₂O. A photo of the samples is embedded on the left-bottom of the figure. Suggested structures have been embedded in the figure.

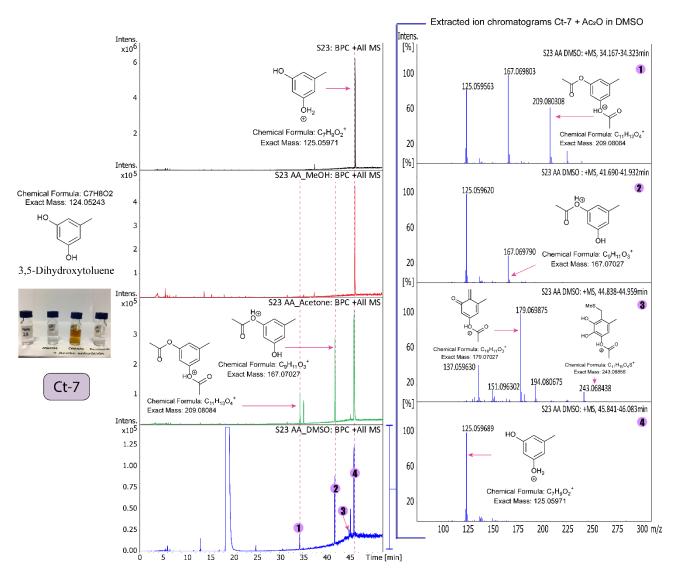


Fig. S7 Centre: chromatograms of Ct-7 without reaction (black), right: MS at different RT for the reaction in DMSO-AC₂O. A photo of the samples is embedded on the left-bottom of the figure. Suggested structures have been embedded in the figure.

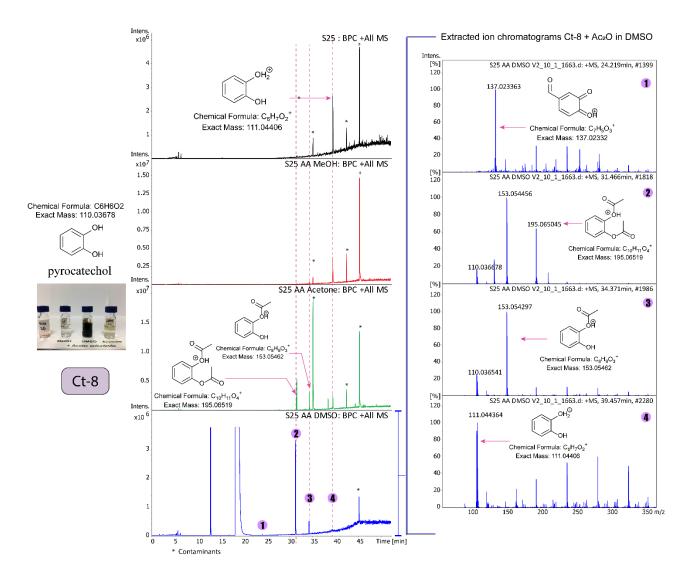


Fig. S8 Centre: chromatograms of Ct-8 without reaction (black), right: MS at different RT for the reaction in DMSO-AC₂O. A photo of the samples is embedded on the left-bottom of the figure. Suggested structures have been embedded in the figure.

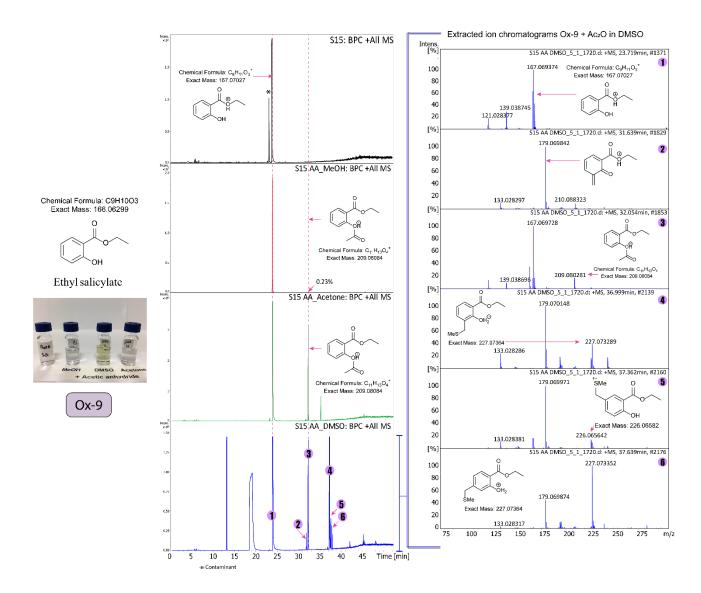


Fig. S9 Centre: chromatograms of Ox-9 without reaction (black), right: MS at different RT for the reaction in DMSO-AC₂O. A photo of the samples is embedded on the left-bottom of the figure. Suggested structures have been embedded in the figure.

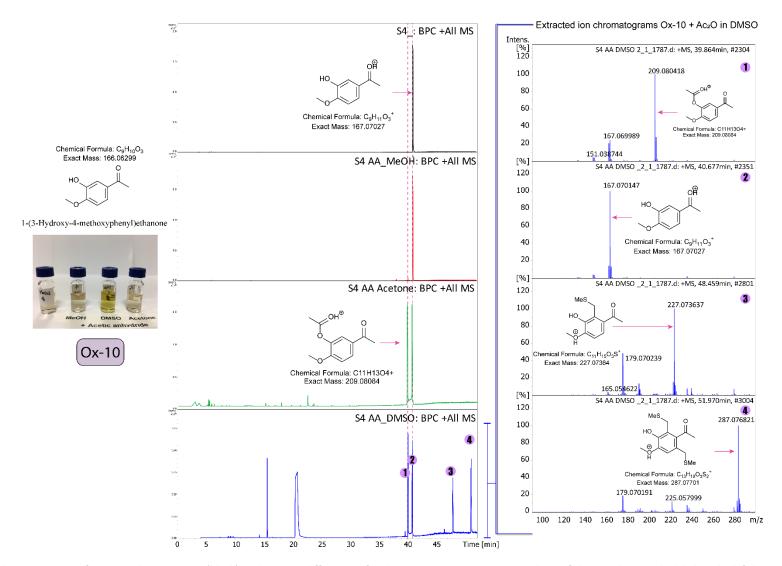


Fig. S10 Left: chromatograms of Ox-10 without reaction (black), right: MS at different RT for the reaction in DMSO-AC₂O. A photo of the samples is embedded on the left-bottom of the figure. Suggested structures have been embedded in the figure.

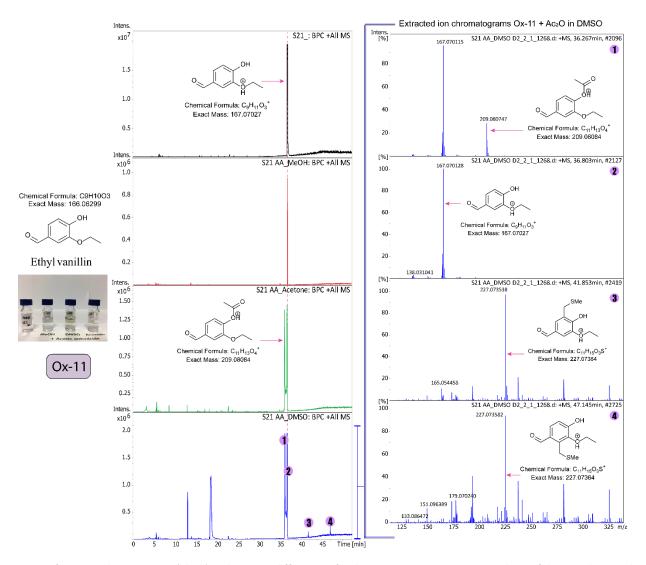


Fig. S11 Centre: chromatograms of Ox-11 without reaction (black), right: MS at different RT for the reaction in DMSO-AC₂O. A photo of the samples is embedded on the left-bottom of the figure. Suggested structures have been embedded in the figure.

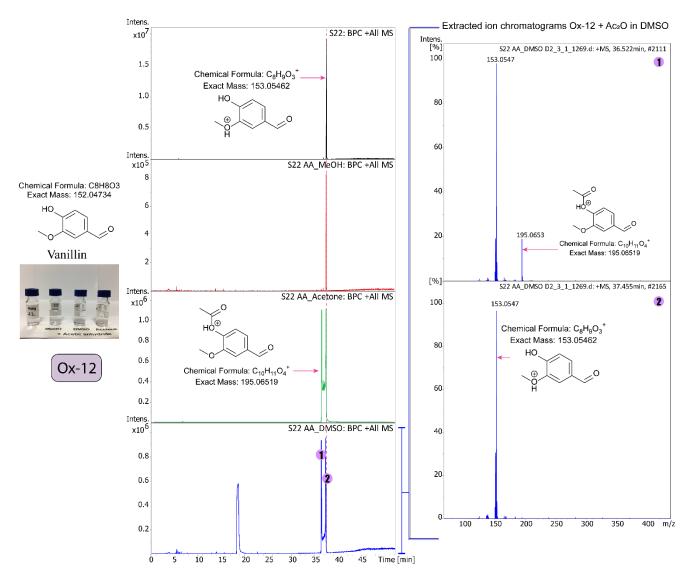


Fig. S12 Centre: chromatograms of Ox-12 without reaction (black), right: MS at different RT for the reaction in DMSO-AC₂O. A photo of the samples is embedded on the left-bottom of the figure. Suggested structures have been embedded in the figure.

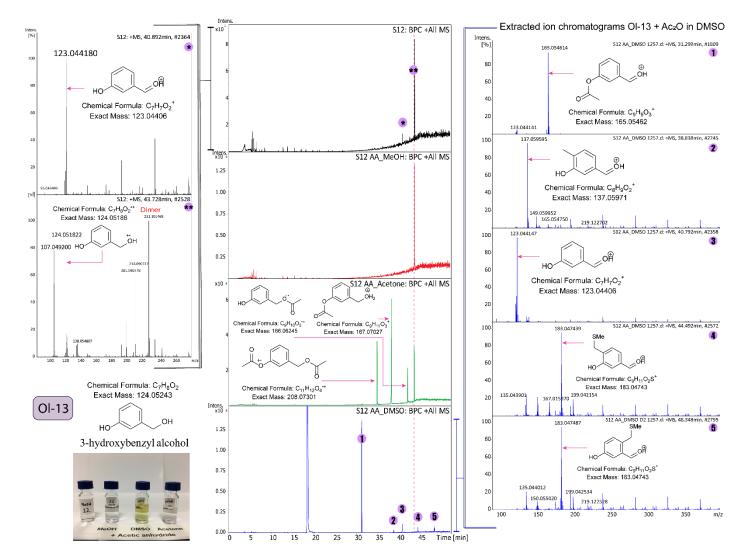


Fig. S13 Centre: chromatograms of Ol-13 without reaction (black), left: extracted MS of raw standard, right: MS at different RT for the reaction in DMSO-AC₂O. A photo of the samples is embedded on the left-bottom of the figure. Suggested structures have been embedded in the figure.

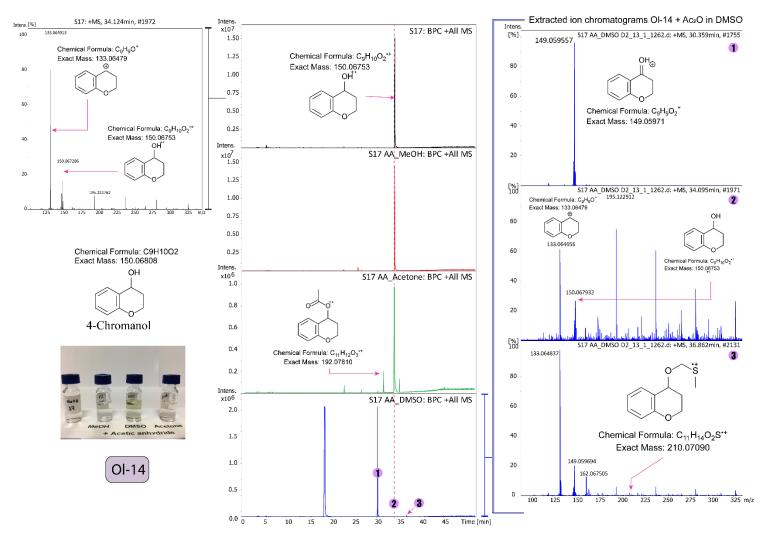


Fig. S14 Centre: chromatograms of Ol-14 without reaction (black), left: extracted MS of raw standard, right: MS at different RT for the reaction in DMSO-AC₂O. A photo of the samples is embedded on the left-bottom of the figure. Suggested structures have been embedded in the figure.

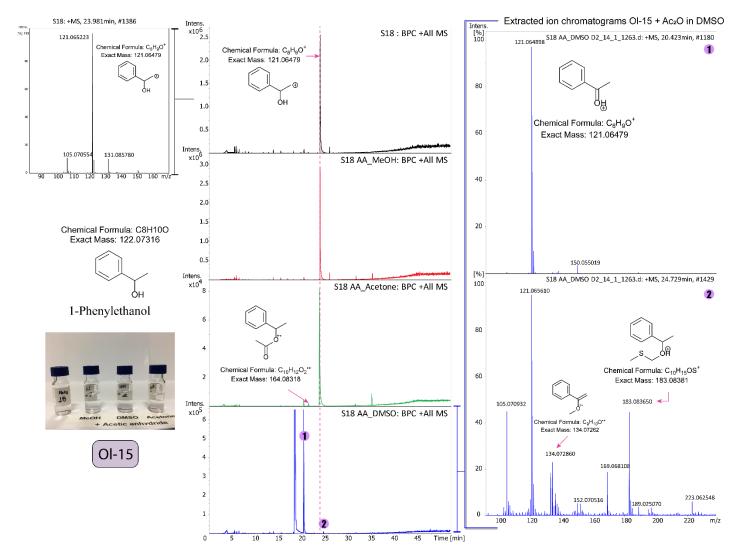


Fig. 15 Centre: chromatograms of Ol-15 without reaction (black), left: extracted MS of raw standard, right: MS at different RT for the reaction in DMSO-AC₂O. A photo of the samples is embedded on the left-bottom of the figure. Suggested structures have been embedded in the figure.

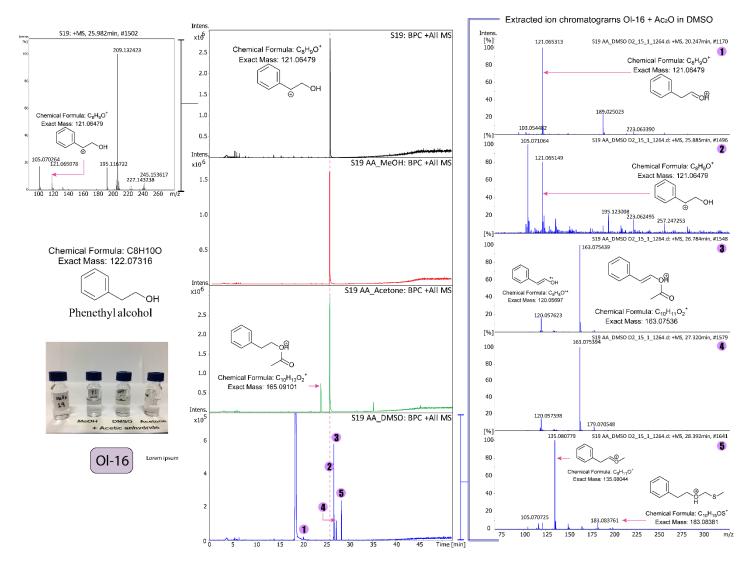


Fig. S16 Centre: chromatograms of Ol-16 without reaction (black), left: extracted MS of raw standard, right: MS at different RT for the reaction in DMSO-AC₂O. A photo of the samples is embedded on the left-bottom of the figure. Suggested structures have been embedded in the figure.

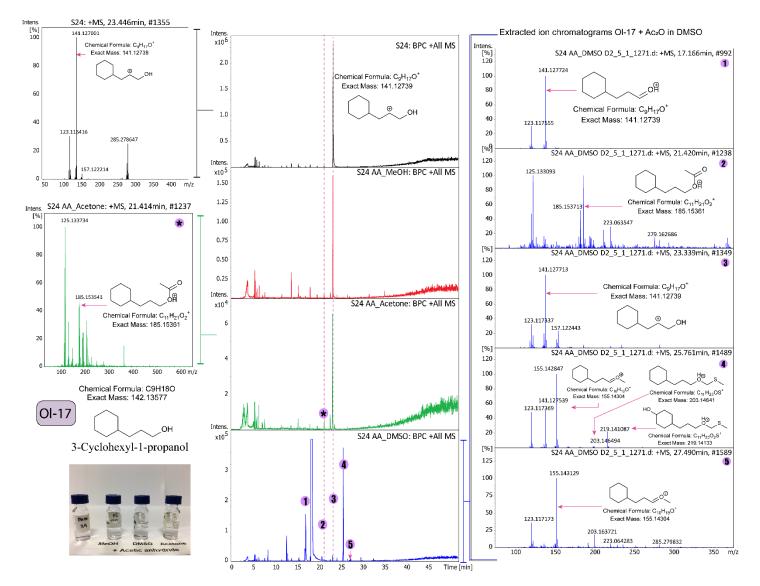


Fig. S17 Centre: chromatograms of Ol-17 without reaction (black), left: extracted MS of raw standard, right: MS at different RT for the reaction in DMSO-AC₂O. A photo of the samples is embedded on the left-bottom of the figure. Suggested structures have been embedded in the figure.

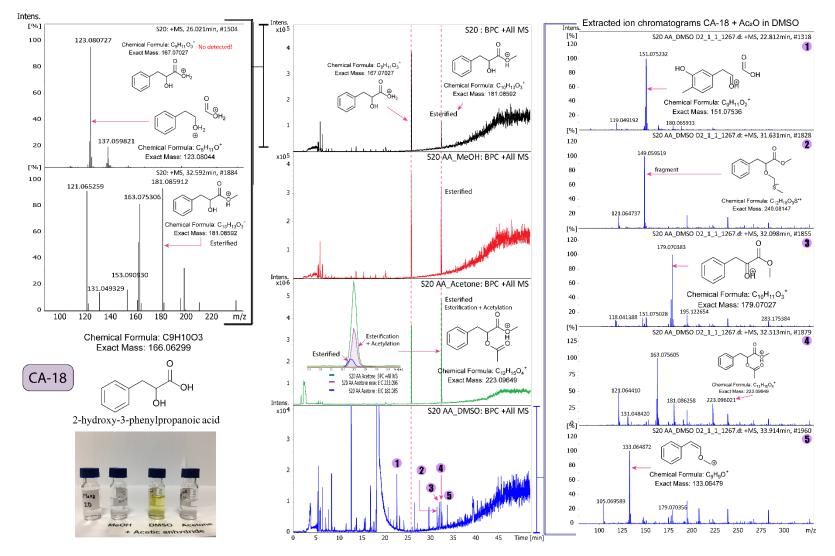


Fig. 18 Centre: chromatograms of CA-18 without reaction (black), left: extracted MS of raw standard, right: MS at different RT for the reaction in DMSO-AC₂O. A photo of the samples is embedded on the left-bottom of the figure. Suggested structures have been embedded in the figure.

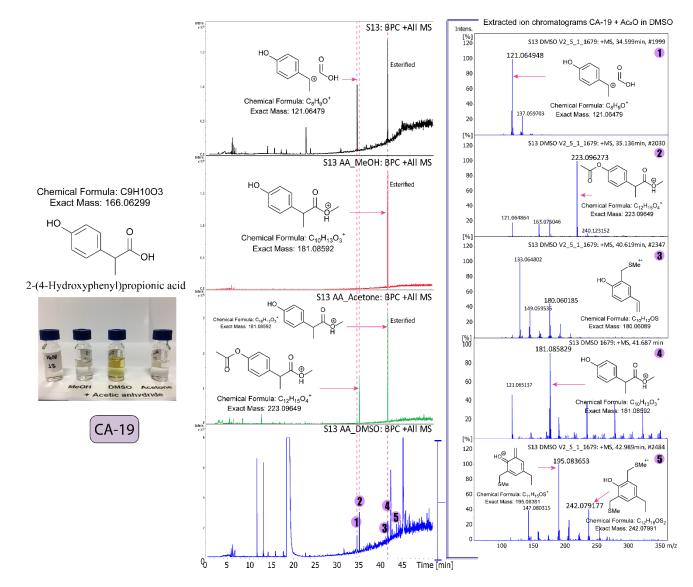


Fig. 19 Centre: chromatograms of CA-19 without reaction (black), right: MS at different RT for the reaction in DMSO-AC₂O. A photo of the samples is embedded on the left-bottom of the figure. Suggested structures have been embedded in the figure.

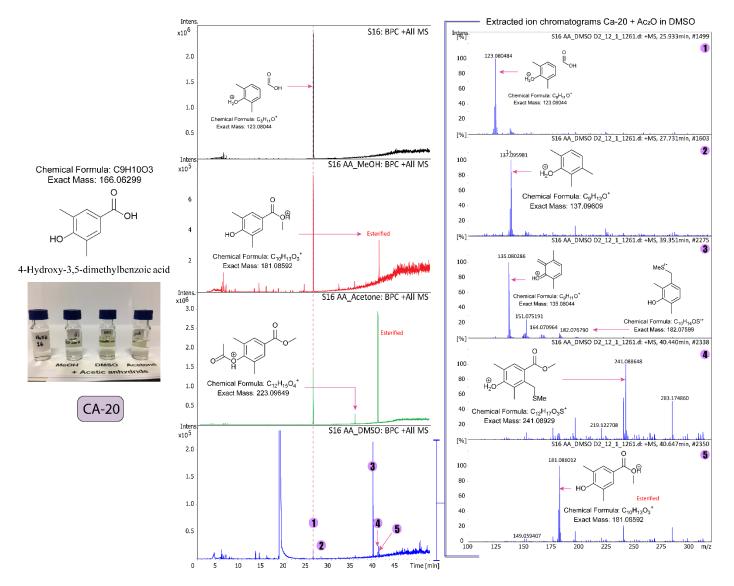


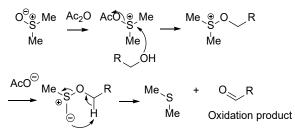
Fig. 20 Centre: chromatograms of CA-20 without reaction (black), right: MS at different RT for the reaction in DMSO-AC₂O. A photo of the samples is embedded on the left-bottom of the figure. Suggested structures have been embedded in the figure.

1.3 Reaction mechanisms

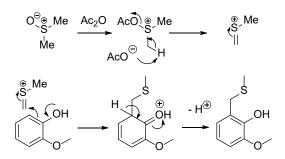
Mechanism of oxidation of alcohol to aldehyde:

The mechanism of the oxidation of alcohols to aldehydes by a combination of DMSO and acetic anhydride is a known reaction.¹ The mechanism for this reaction is illustrated below.

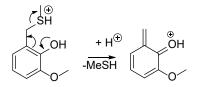
Mechanism of oxidation



The mechanism of formation of MTM derivatives of the phenols is shown below – this involves formation of a cationic intermediate followed by its reaction with the phenols:



Loss of SMe (possibly acid promoted) leads to a cation, which is also observed:



Aldehydes are formed from some alcohols in their reactions with DMSO/acetic anhydride, and these have the potential to undergo further reactions with organic molecules under the reaction conditions. These reactions would take place through an aldol condensation in which a new C-C bond is formed between the C of the C=O bond of the aldehyde and the alpha-C (relative to a C=O) of a ketone. This may be followed by elimination to an alkene. A phenol could also potentially react with an aldehyde under the reaction conditions to give an addition product. However, there was no evidence of products of this type in our study.

(1) J. D. Albright and L. Goldman, J. Am. Chem. Soc., 1967, 89, 2416–2423.

1.4 Reactions

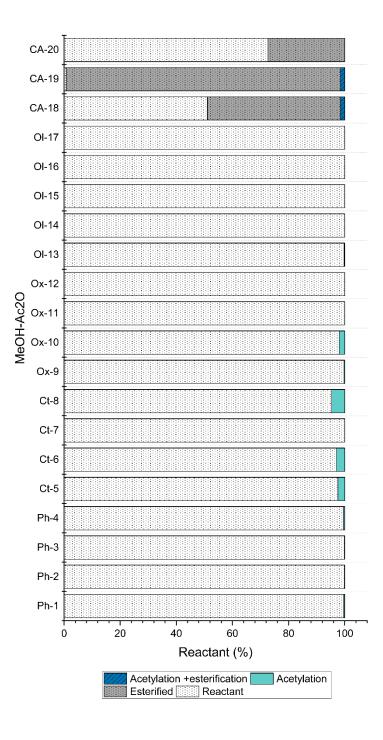


Fig. S21 Reaction products observed in MeOH-Ac₂O mixtures.

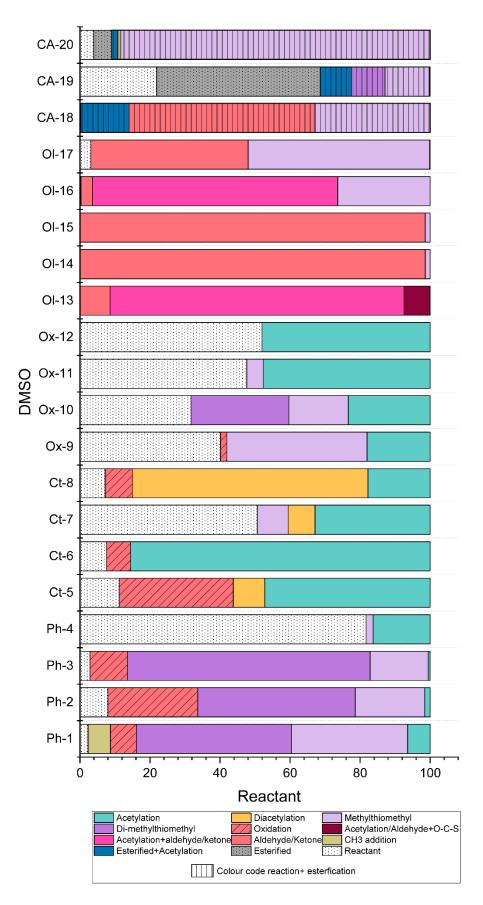


Fig. S22 Detailed reactions observed in DMSO-AC₂O mixtures.

1.5 Mass spectra

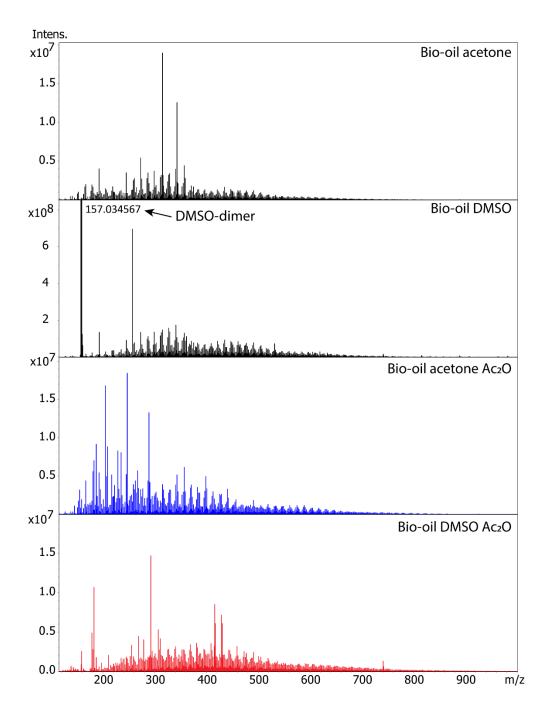


Fig. S23 Mass spectra of the bio-oil before and after derivatisation.

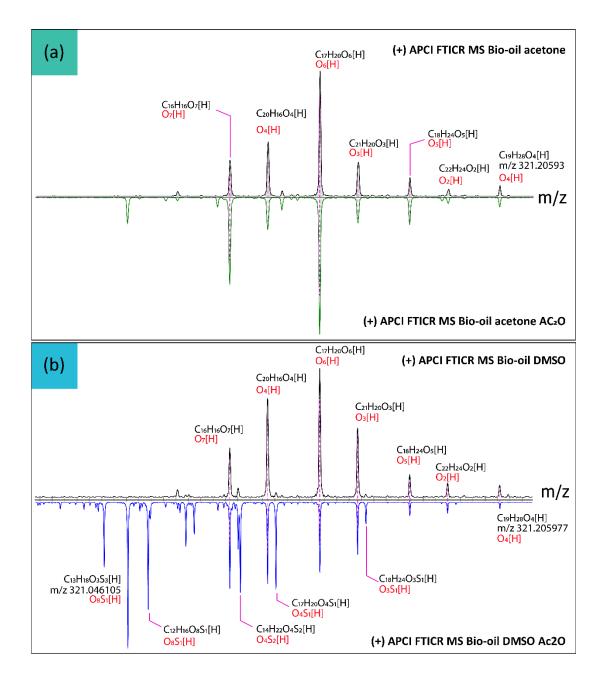
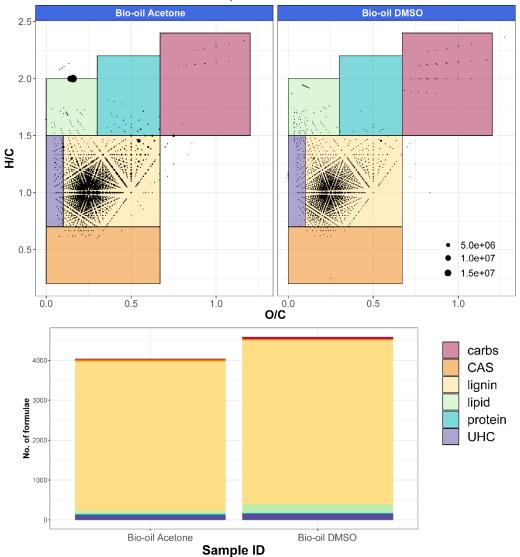


Fig. S24 Zoomed-in mass spectra at m/z 321. (a) bio-oil in acetone and (b) bio-oil in DMSO. Mixtures dopped with Ac_2O have been inverted in the y-axis.



1.6 Van Krevelen and DBE plots

Fig. S25 Van Krevelen diagram for the bio-oil samples blanks (acetic anhydride not added to the mixture). Bottom, relative contribution by category Carbs: carbohydrates, CAS: condensed aromatic ring structures and UHC: unsaturated hydrocarbons

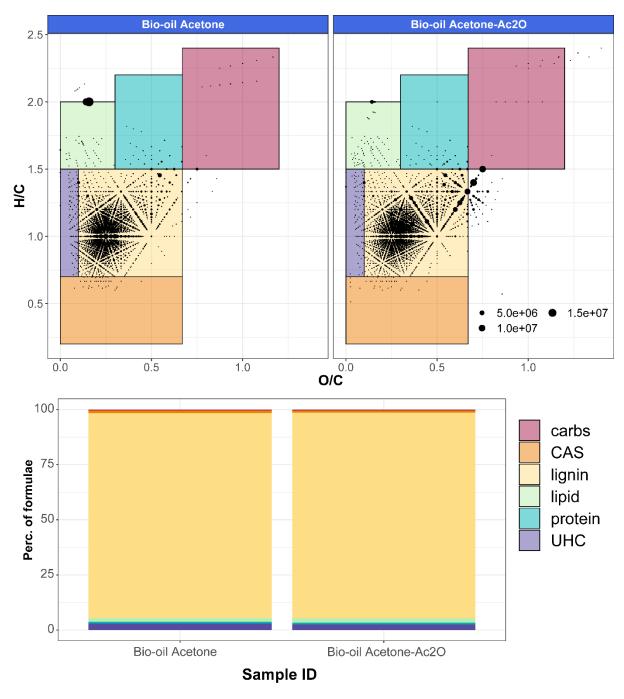


Fig. S26 Van Krevelen diagram for the bio-oil samples in acetone. Bottom, relative contribution by category Carbs: carbohydrates, CAS: condensed aromatic ring structures and UHC: unsaturated hydrocarbons.

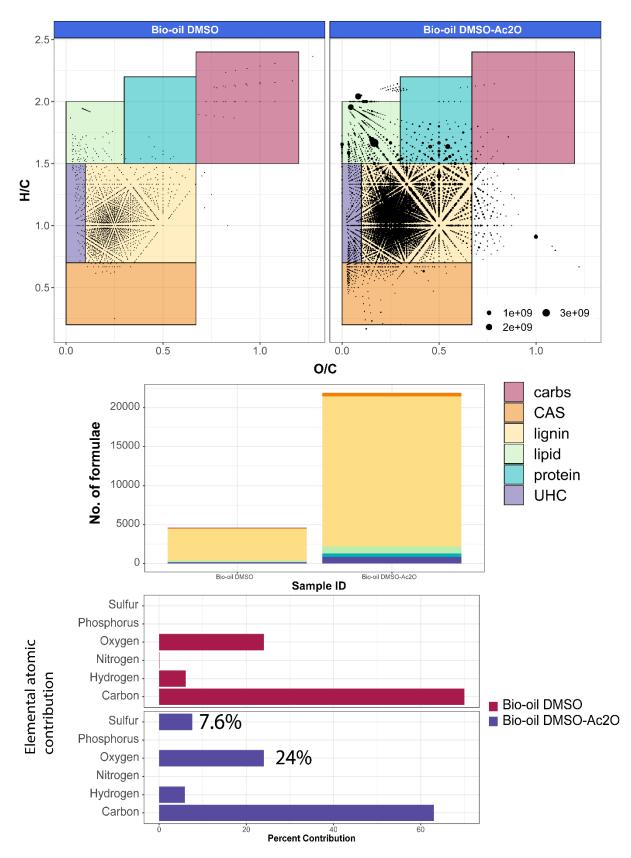


Fig. S27 Top: van Krevelen diagram for the bio-oil samples in DMSO. Centre, number of compositions by category; Carbs: carbohydrates, CAS: condensed aromatic ring structures and UHC: unsaturated hydrocarbons. Bottom: atomic contribution calculated using the detected molecular compositions.

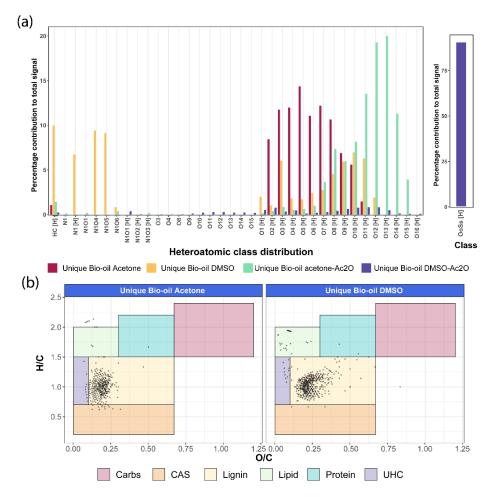


Fig. S28 (a) class distribution of unique elemental compositions weighted by relative contribution to the total intensity. (b) van Krevelen plot of the unique molecular compositions detected in the blanks. Coloured boxes are used to indicate compositions classified as carbohydrates (carbs), CAS: condensed aromatic ring structures, UHC: unsaturated hydrocarbons, lignin, lipids and proteins.

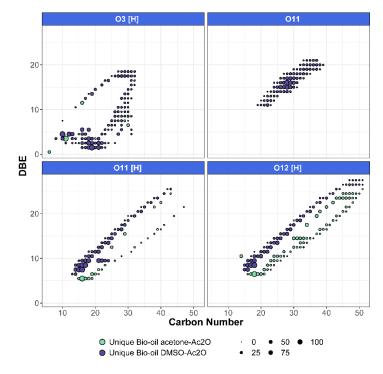


Fig. S29 Double bond equivalent plots of the unique compositions detected in Acetone-Ac₂O and DMSO-Ac₂O mixtures.

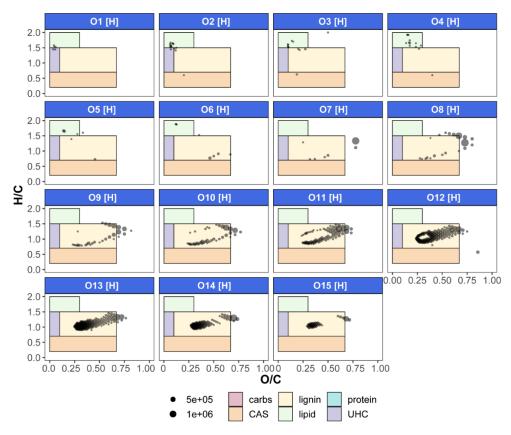


Fig. S30 Van Krevelen diagrams of even-electron ion species detected in the unique in Bio-oil acetone-Ac₂O.

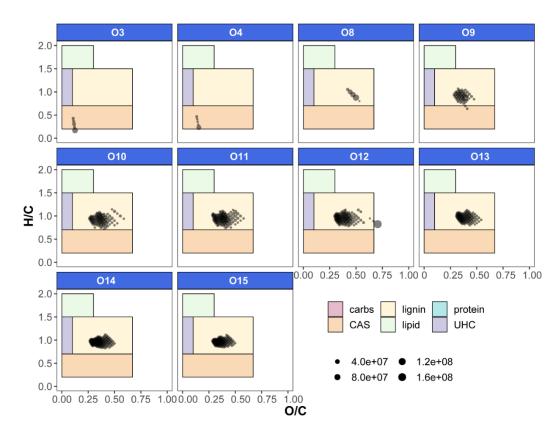


Fig. S31 Van Krevelen diagrams of odd-electron ion species detected in the unique in Bio-oil DMSO-Ac₂O.

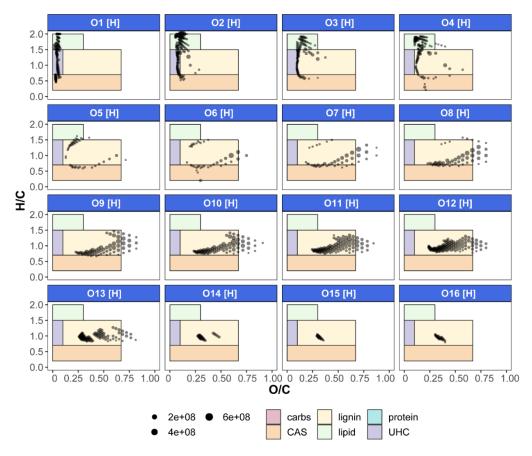


Fig. S32 Van Krevelen diagrams of even-electron ion species detected in the unique in Bio-oil DMSO-Ac₂O.

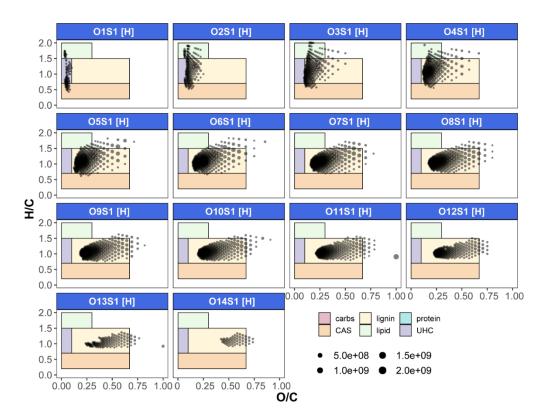


Fig. S33 Van Krevelen diagrams of $O_0S_1[H]$ species detected in the unique in Bio-oil DMSO-Ac₂O.

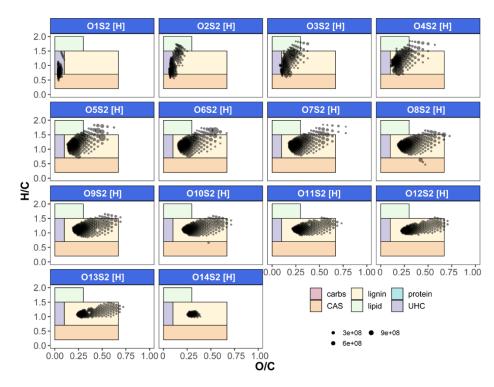


Fig. S34 Van Krevelen diagrams of $O_0S_2[H]$ species detected in the unique in Bio-oil DMSO-Ac₂O.

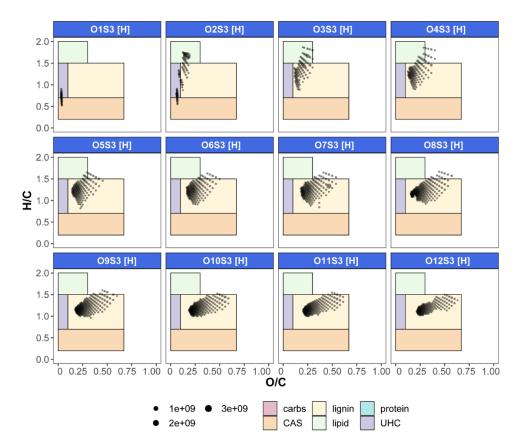


Fig. S35 Van Krevelen diagrams of $O_0S_3[H]$ species detected in the unique in Bio-oil DMSO-Ac₂O.