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Off-line LCxSFC-HRMS/MS method development for the non-target analysis of depolymerized lignin

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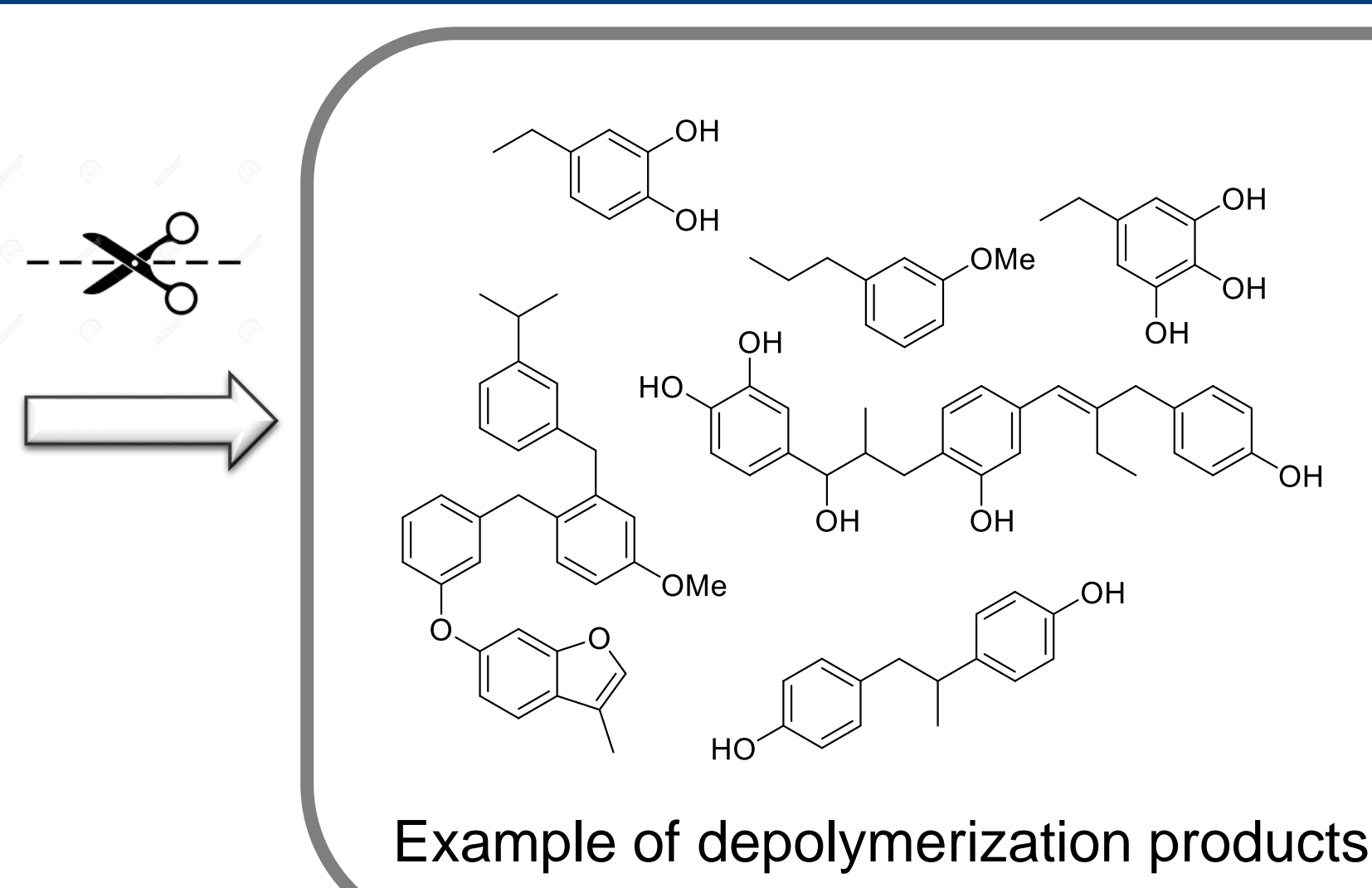
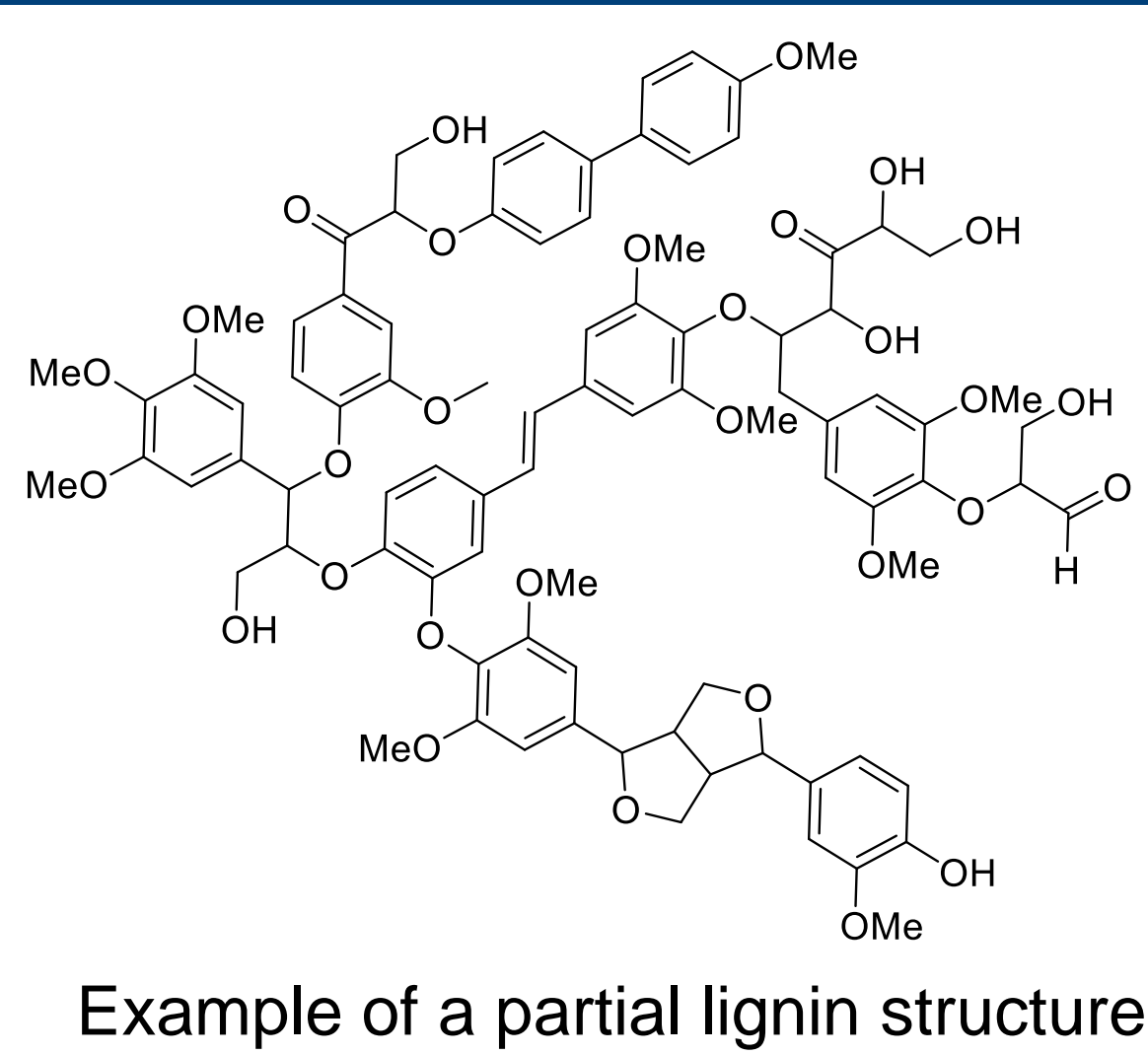
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Best Poster Award

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P-MDLC04

BACKGROUND: Bio-based Polymers from Lignin Oligomers (BIOPOLIOL project)

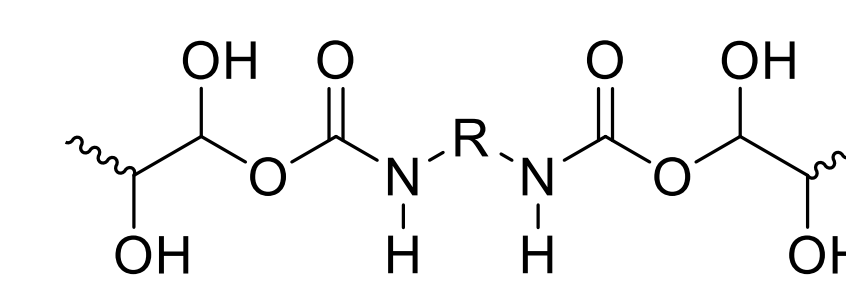


Research aim

For efficient lignin valorization, the depolymerization of lignin has to be **monitored**, which needs **powerful analysis methods**

However, depolymerized lignin is a **complex mixture**: structurally **similar neutral compounds, isomers, monomers and oligomers**

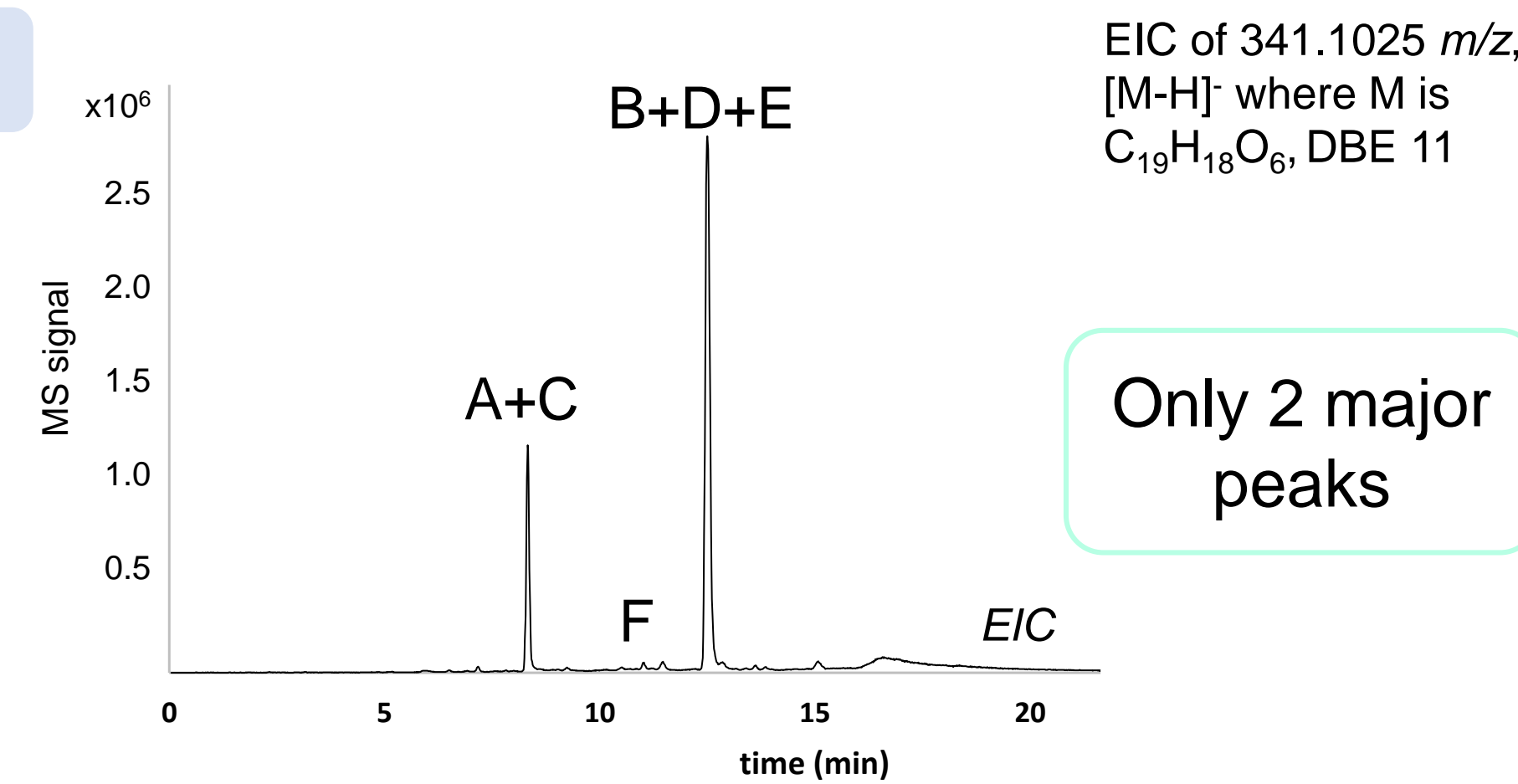
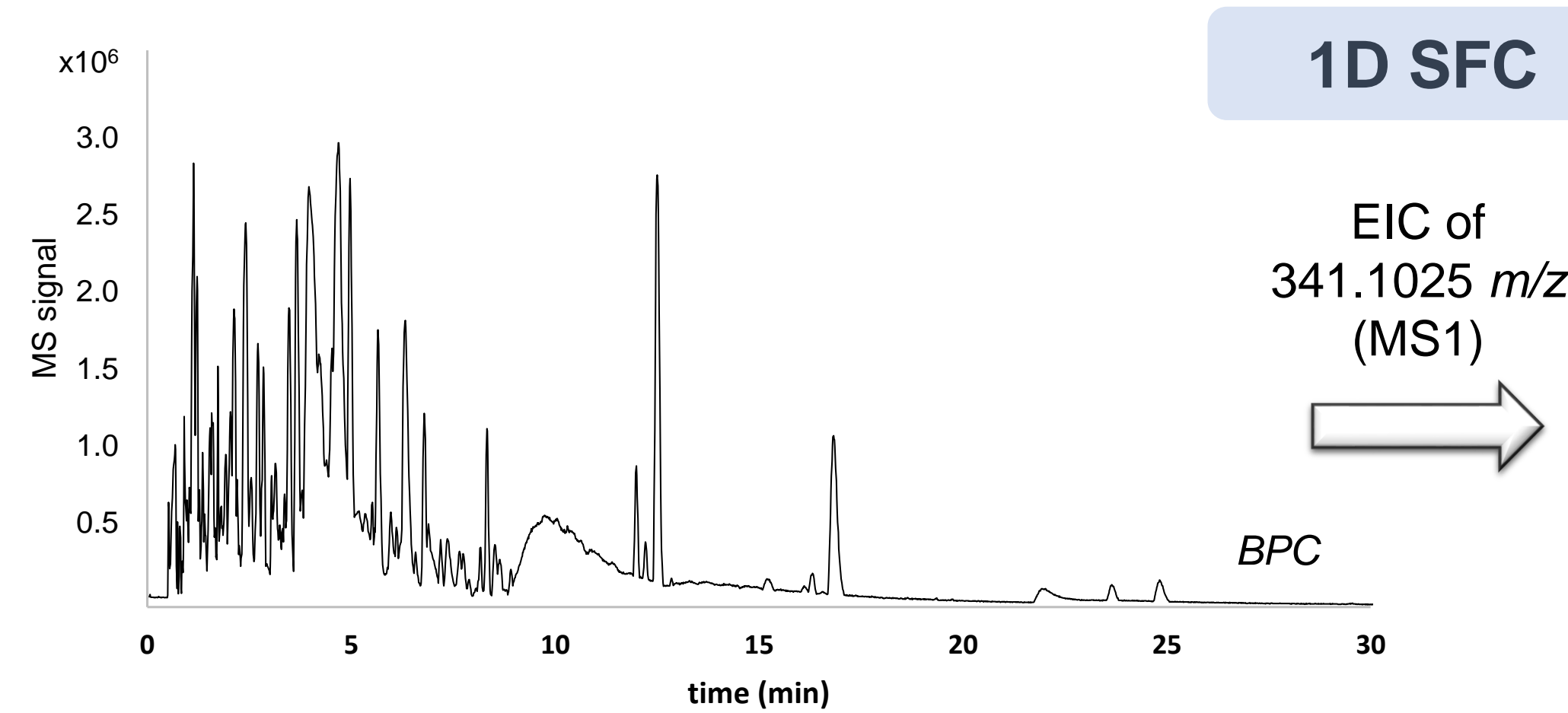
Synthesis of polyhydroxyurethanes (PHUs)



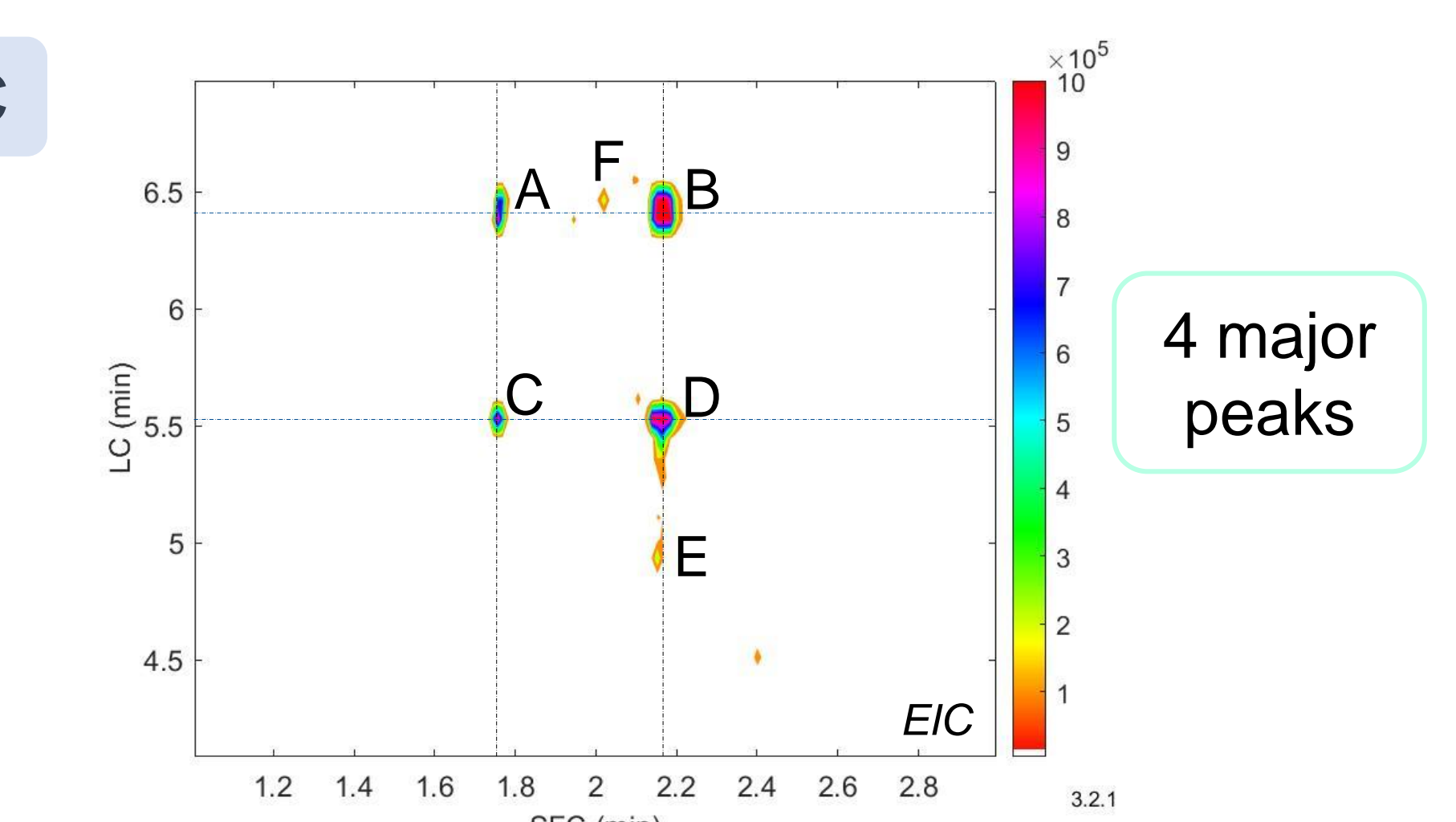
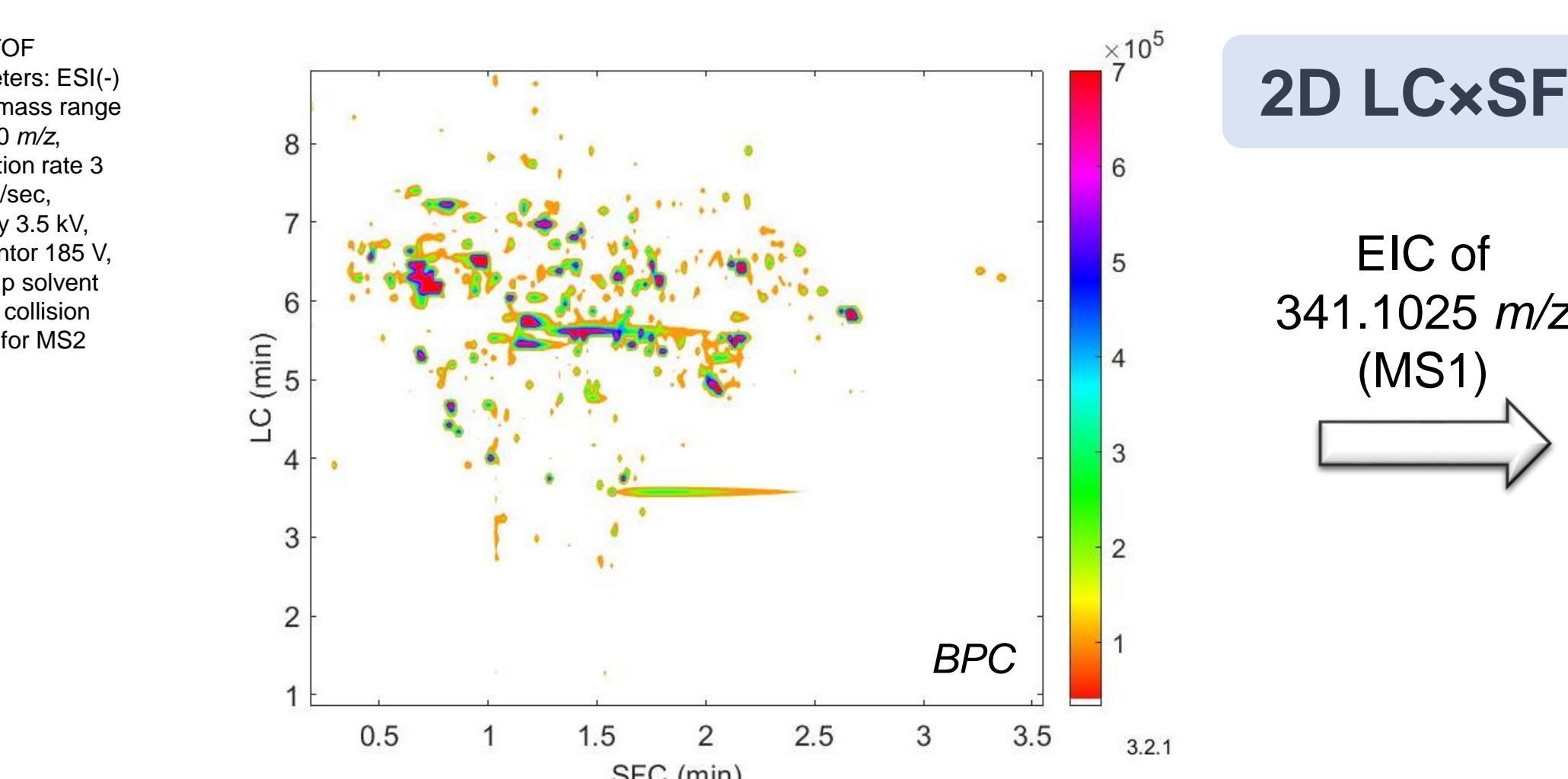
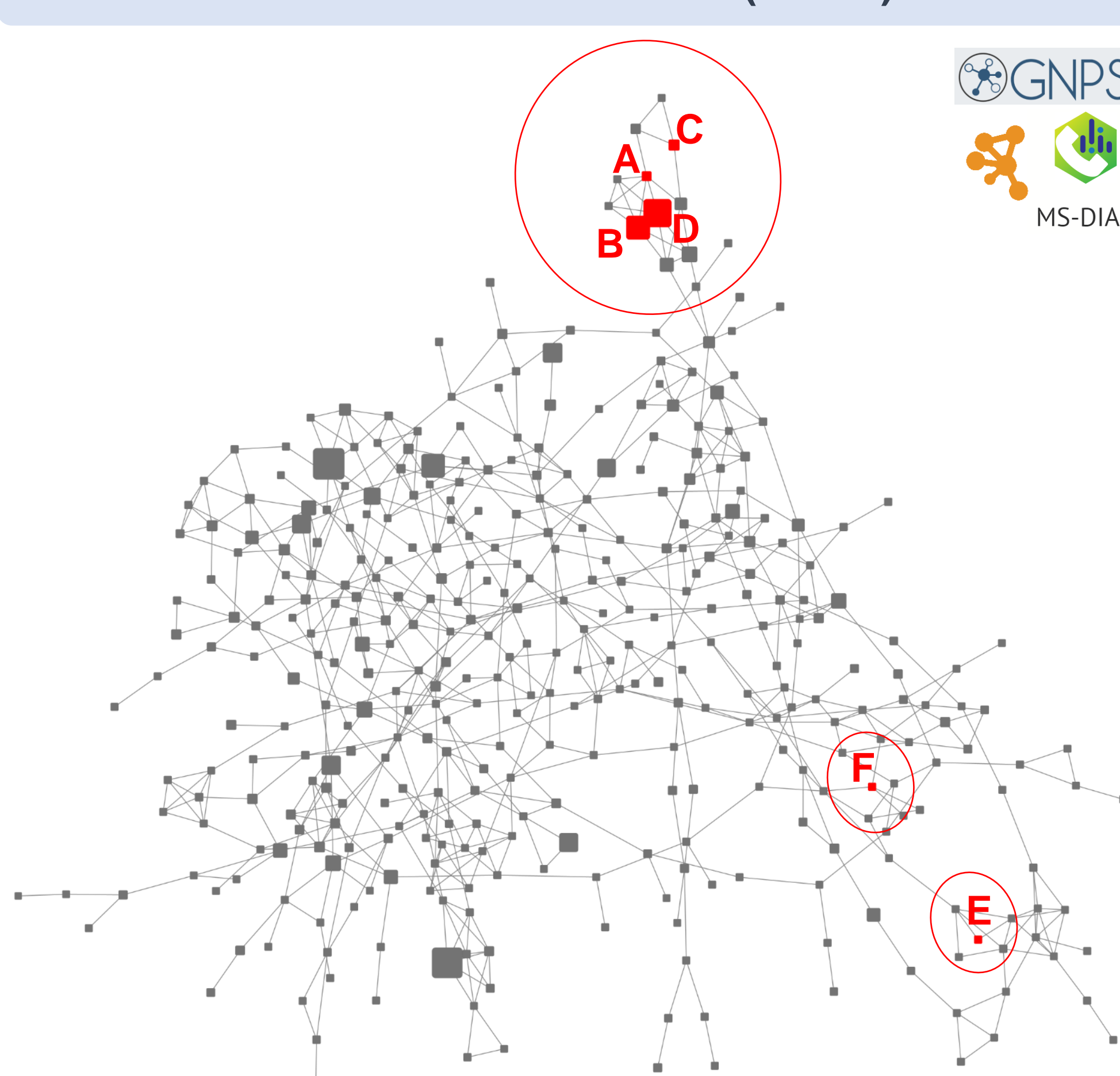
Example of a possible moiety

Promising **alternative of natural origin to polyurethane foams** (synthesis needs toxic isocyanates) used in construction

COMPARISON: SFC-HRMS vs. LCxSFC-HRMS

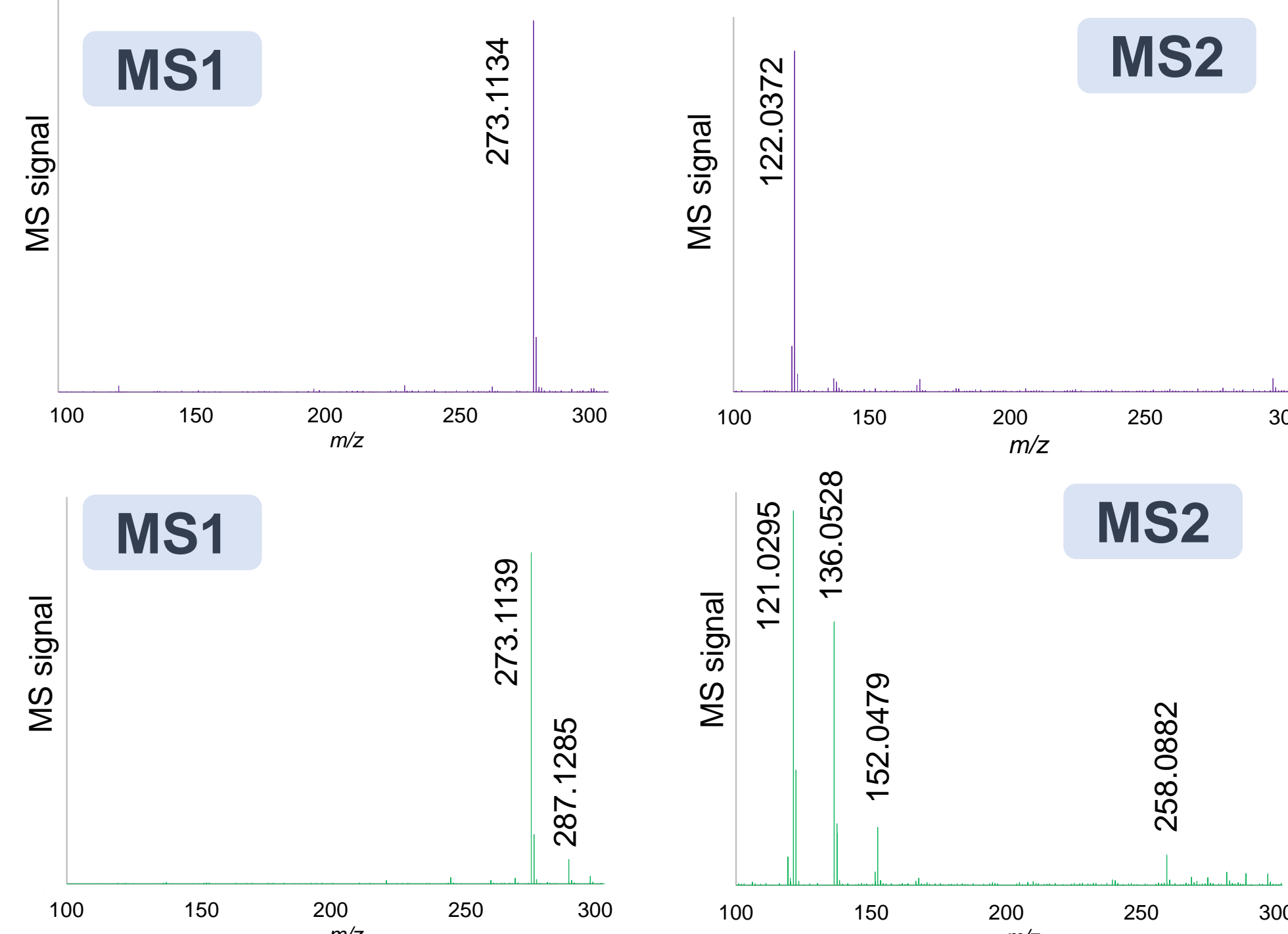
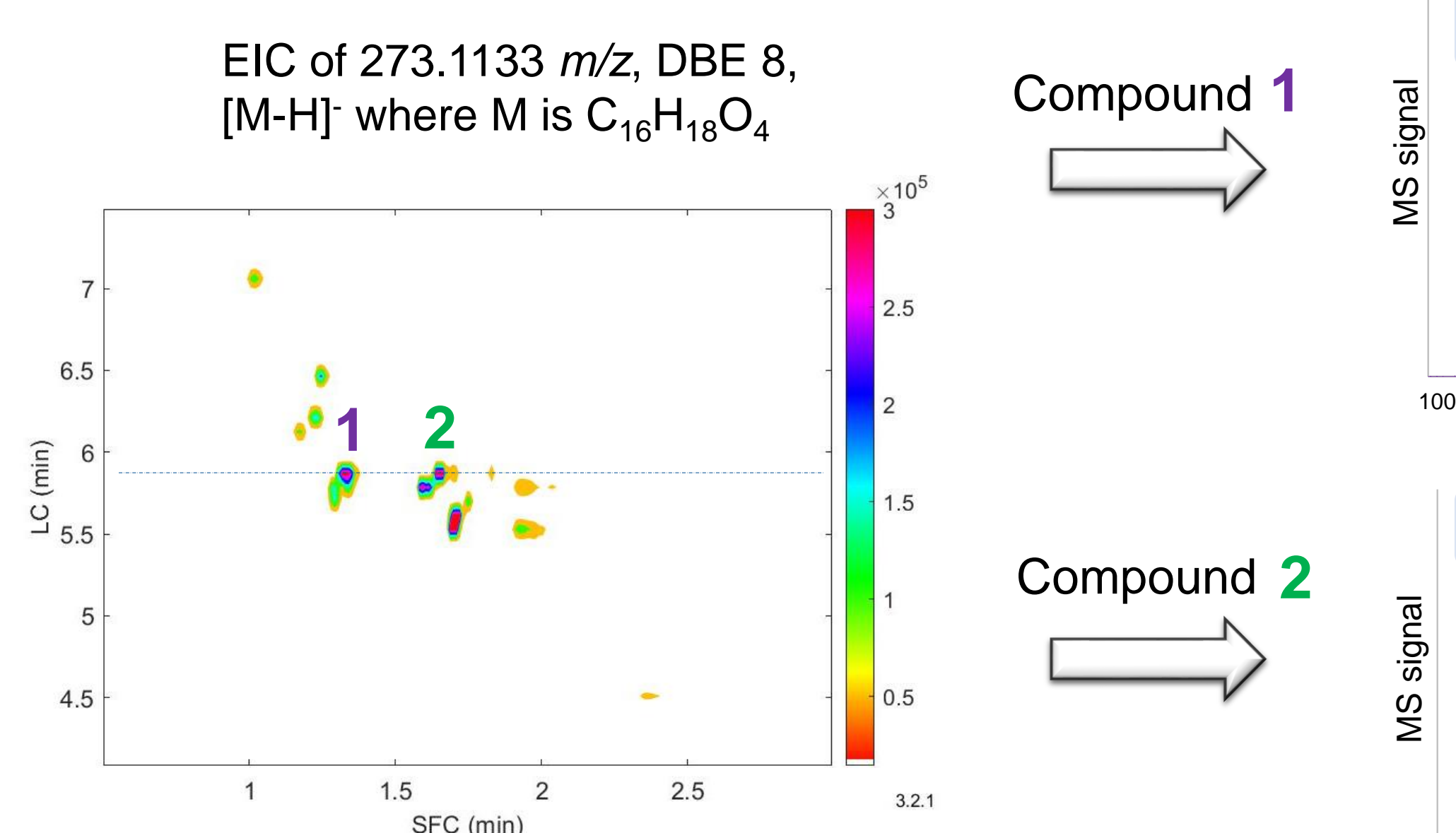


Feature-Based Molecular Network (FBMN) for LCxSFC



LCxSFC: Enables good separation of isomers

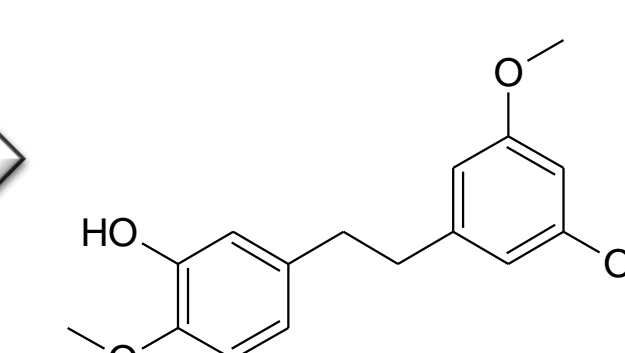
IDENTIFICATION: LCxSFC-HRMS/MS analysis of depolymerized lignin



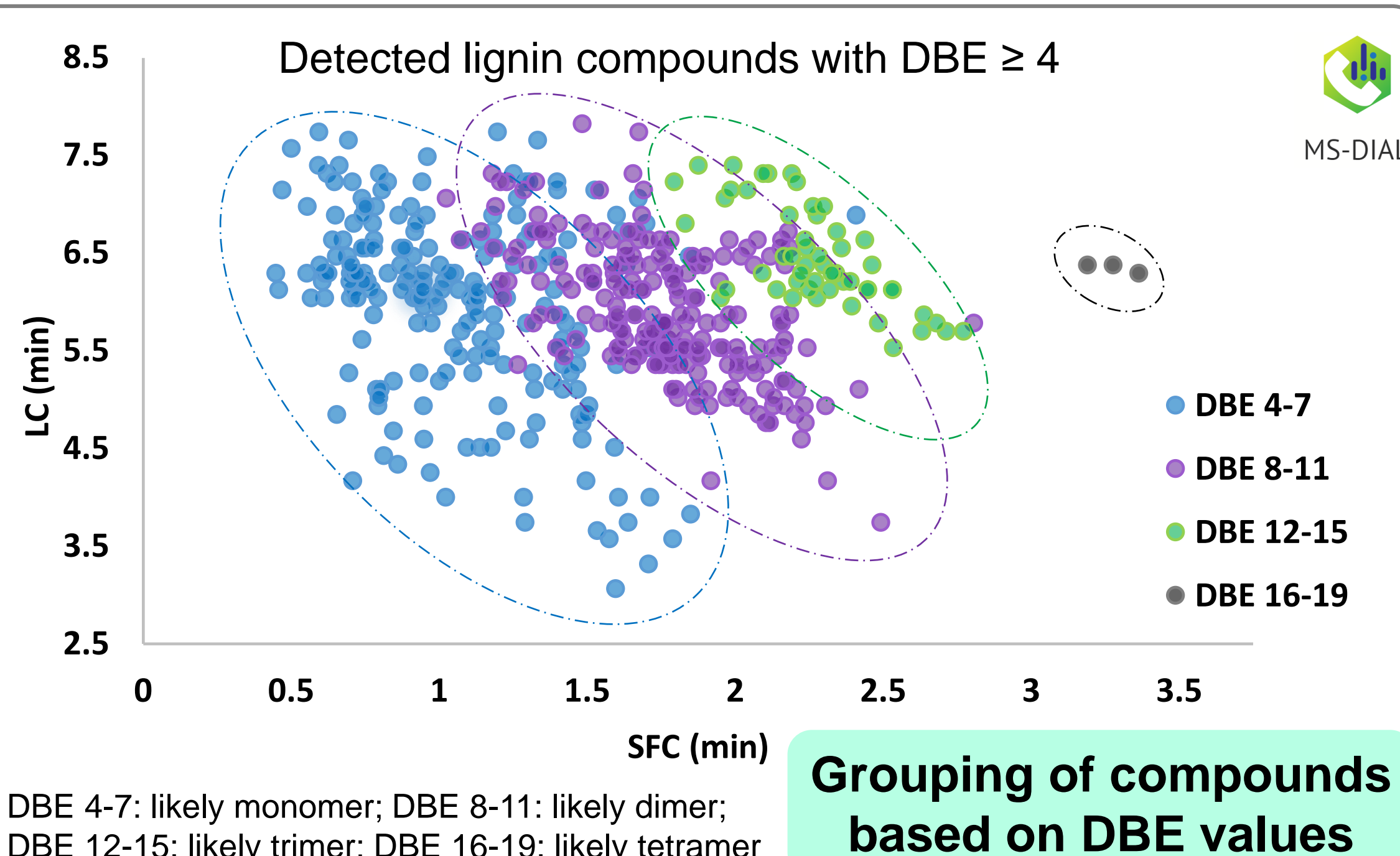
MS level	Detected m/z of [M-H] ⁻	Formula of M	DBE of M
MS1	273.1134	C ₁₆ H ₁₈ O ₄	8
MS2	122.0372	C ₇ H ₈ O ₂	4

MS level	Detected m/z of [M-H] ⁻	Formula of M	DBE of M
MS1	273.1139	C ₁₆ H ₁₈ O ₄	8
MS2	152.0479	C ₈ H ₉ O ₃	4.5
MS2	136.0528	C ₈ H ₉ O ₂	4.5
MS2	121.0295	C ₇ H ₆ O ₂	5

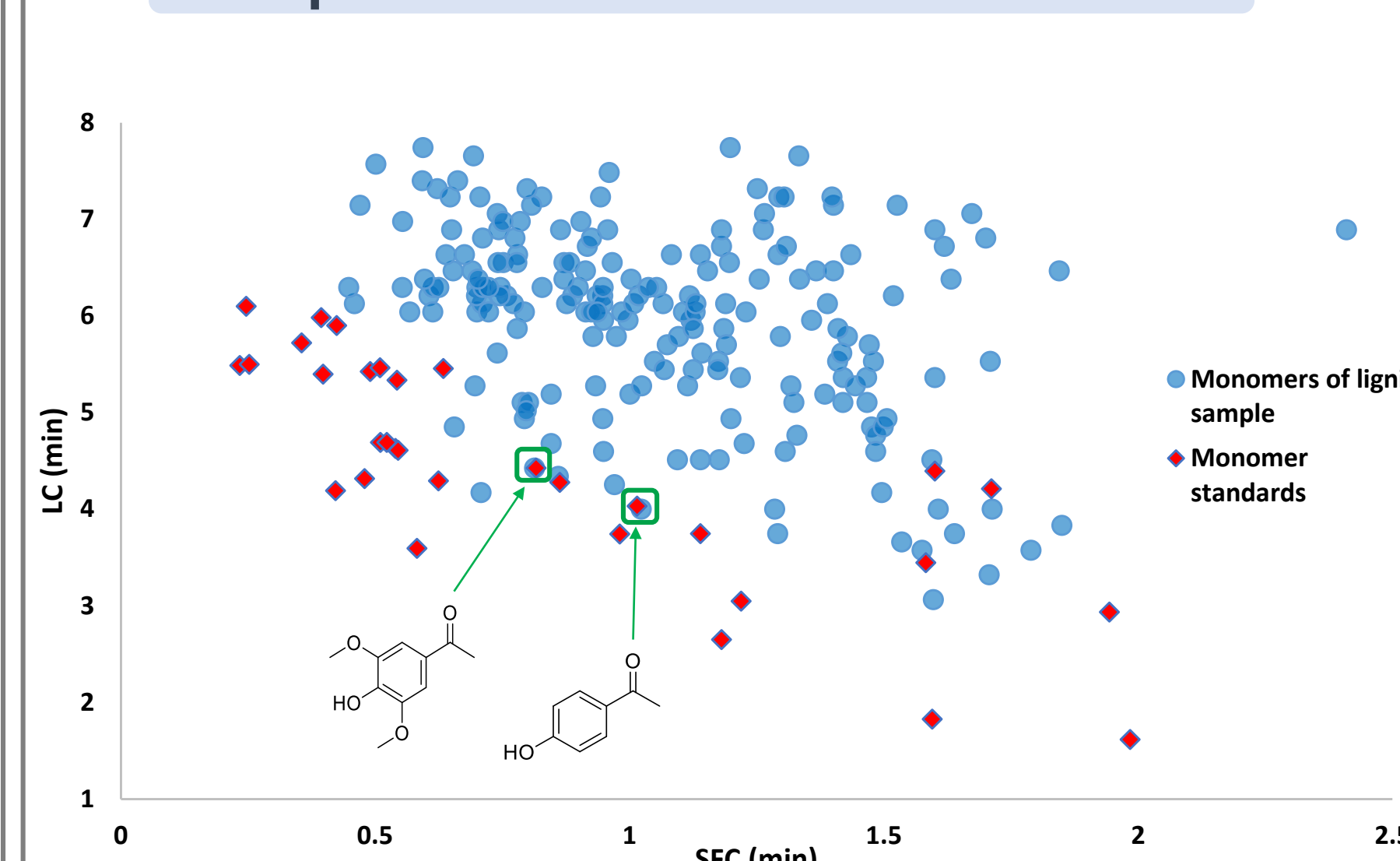
Positional isomers of:



Clean MS1 and MS2 spectra



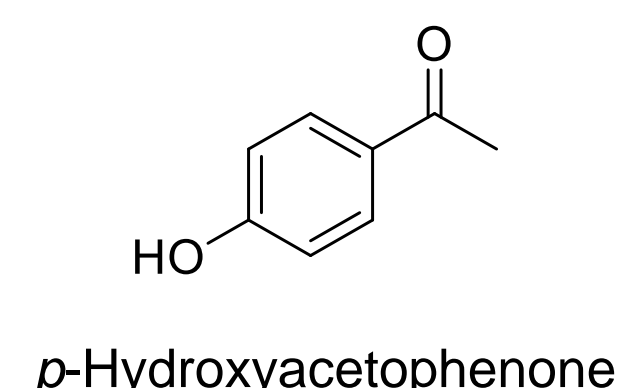
Comparison with monomer standards



Characteristics of one of the identified standards

t_R in LC	4.03 min
t_R in SFC	1.015 min
Exact mass of [M-H] ⁻	135.0453
Mass diff	0.93 ppm
Formula of M	C ₈ H ₈ O ₂
DBE of M	5

And confirmation with SIRIUS



Identification based on 4 criteria:

- 1) t_R in LC
- 2) t_R in SFC
- 3) exact mass
- 4) fragments

From 33 lignin monomer standards, detected only two: acetosyringone and p-hydroxyacetophenone

CONCLUSIONS

Off-line LCxSFC-HRMS/MS is an efficient method for the non-target analysis of depolymerized lignin:

- I. Good separation of isomers thanks to the orthogonal two dimensions
- II. Grouping of lignin compounds on the 2D plots based on their DBE value
- III. Clean and easily interpretable MS1/MS2 spectra can be obtained
- IV. Compound identification based on 4 criteria