Supporting Information

Two-step fractionation of a model technical lignin by combined organic solvent extraction and membrane ultrafiltration

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CONTENT

Panel A Panel B

Panel C

Figure S1: Apparatus used in the Fractionation process of a solution of Protobind 1000. (Panel A: Soxhlet extraction, Panel B: Details of solvent beakers, Panel C: Ultrafiltration apparatus; Photograph courtesy of Julien Troquet Copyright 2018).

	Ultrafiltration process data	Unit	Average values from 3 successive filtration trials	
			Step 1	**Step 2**
Membrane data	Membrane type		SARTORIUS STEDIM Hydrosart (305 144 29 01 E-SW)	SARTORIUS STEDIM Hydrosart (305 144 19 01 E-SW)
	Membrane material		Stabilized cellulose	Stabilized cellulose
	Membrane area	m^2	0.1	0.1
	Cut-off	kDa	5	2
	Clean water flow (CWF)	$L\ min^{-1}\ m^{-2}$	24	18
Process data*	Cross flow	$L\ min^{-1}$	1	0.5
	Feed pressure	bar	2.5	2.5
	TMP	bar	1.92	1.74
	Permeate flow	$mL\ min^{-1}$ $L\ min^{-1}\ m^{-2}$	0.2 0.002	2.2 0.022
	Time to process 500 mL	min	900	80

** Data obtained from 3 successive trials each realized with a starting volume of 1.5 L of the soluble extracted fraction (LF-S). The 3 trials have been runned with the same membranes which have been cleaned and tested (clean water flow measurement) between each trial.*

Table S2**:** Operational parameters for the membrane assisted ultrafiltration process.

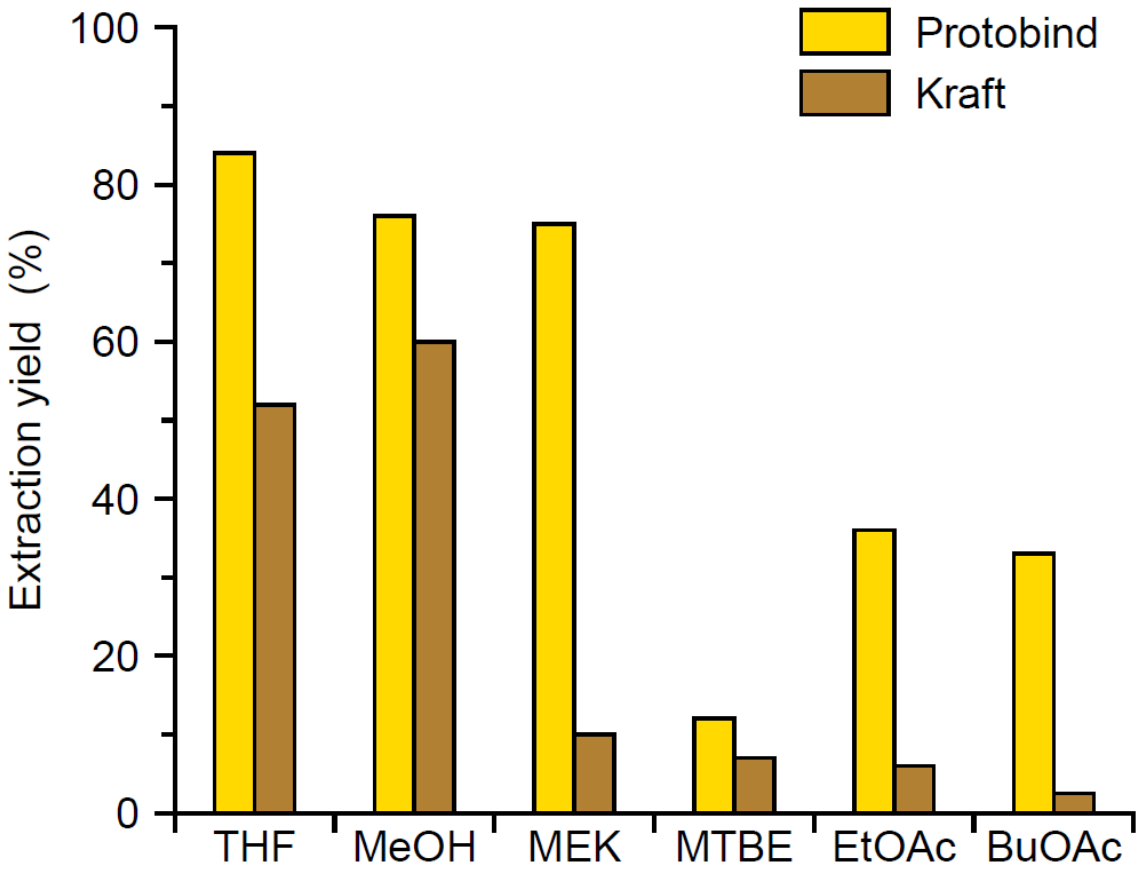


Figure S3: Comparison between the extraction yields (%w/w) of Protobind 1000 and Kraft Lignins in different solvents.

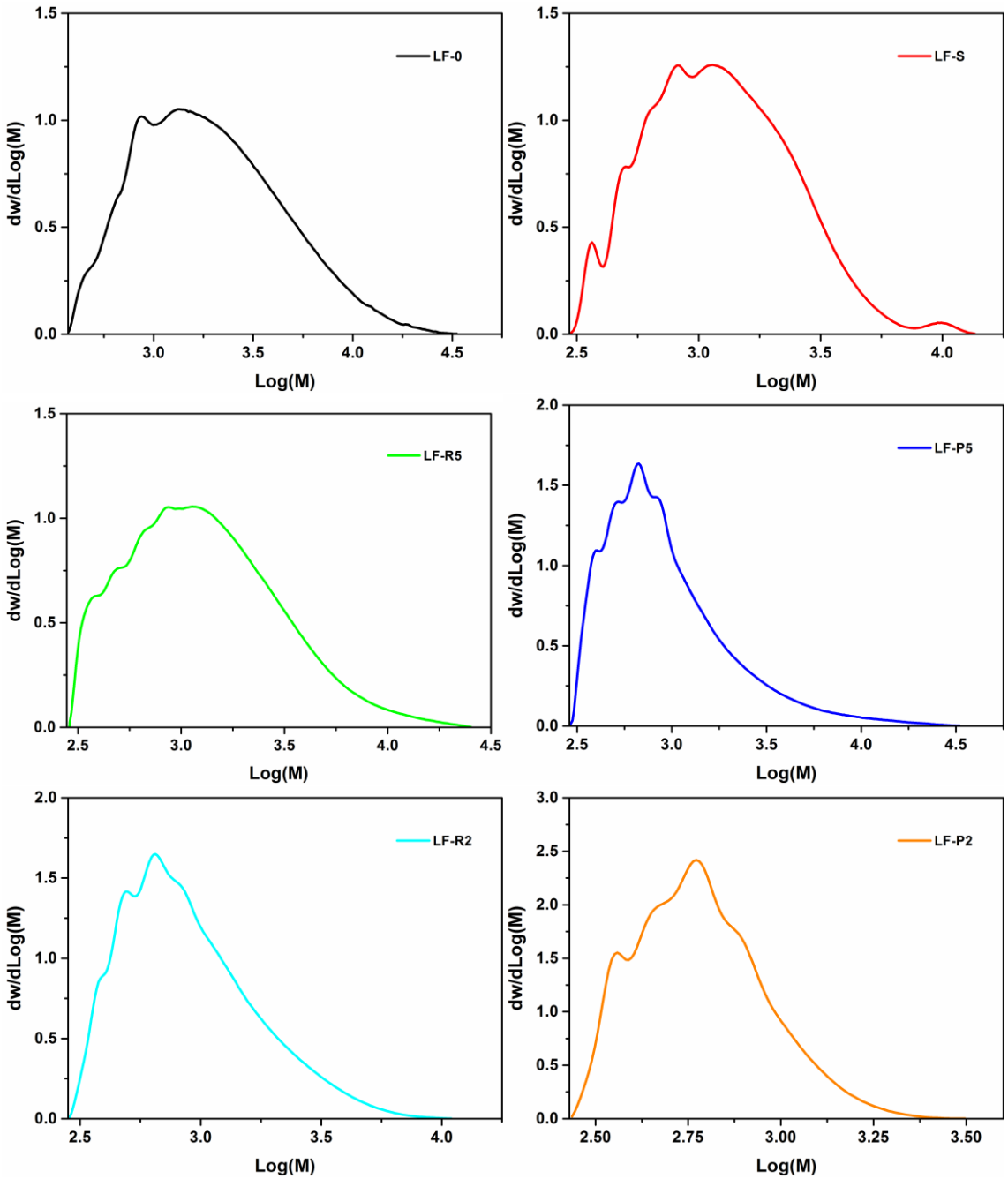


Figure S4: Molecular weight distributions of all extracted lignin fractions as obtained from GPC analysis (the parent material LF-0 is also reported as reference). Samples were acetylated prior to analysis.

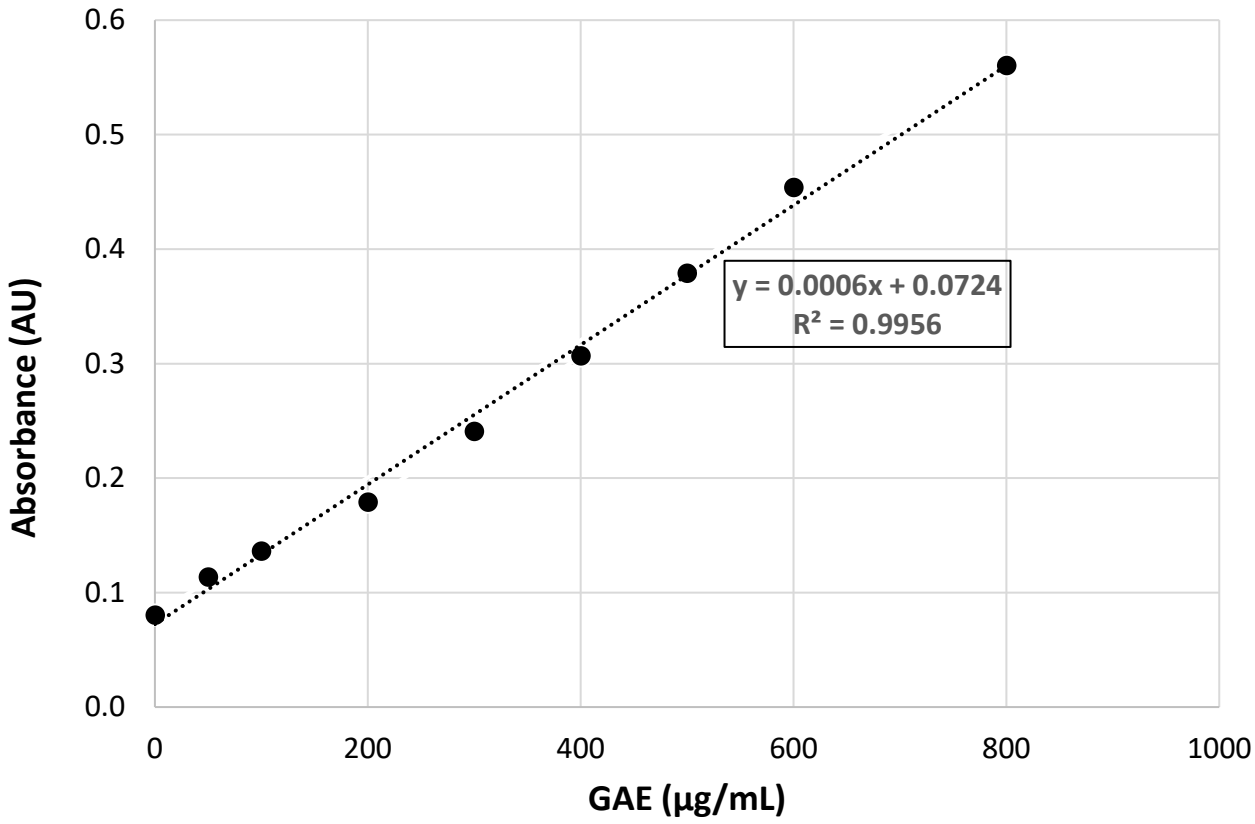


Figure S5: Calibration Curve of Folin-Ciocalteu phenol titration with gallic acid.

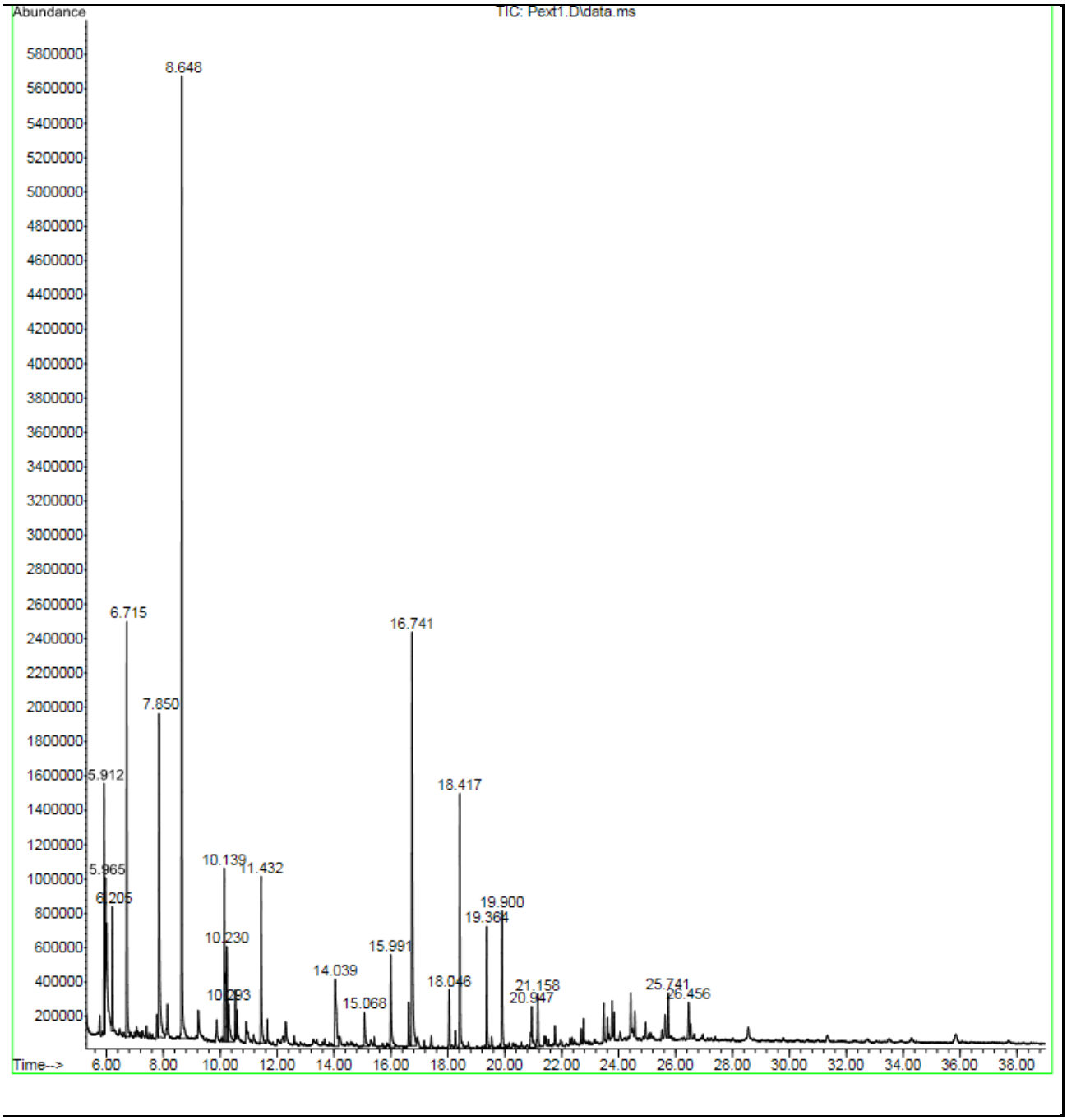


Figure S6: GC/MS chromatogram of LF-S.

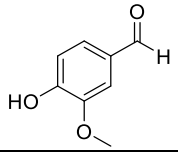
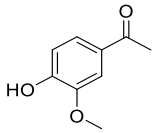
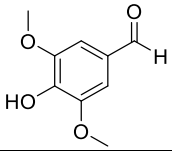
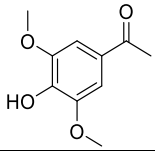
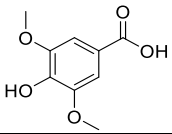
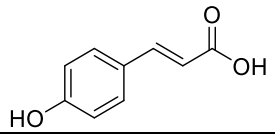
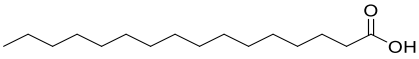
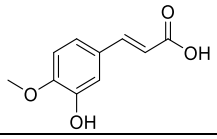
Retention time (min)	Molecule	Name	% in the analysis
14		**4-hydroxy-3-methoxybenzaldehyde**	3.4
15		**1-(4-hydroxy-3-methoxyphenyl)ethan-1-one**	1.3
15.9		**4-hydroxy-3,5-dimethoxybenzaldehyde**	3
16.74		**1-(4-hydroxy-3,5-dimethoxyphenyl)ethan-1-one**	11
18		**4-hydroxy-3,5-dimethoxybenzoic acid**	1.3
18.4		**(E)-3-(4-hydroxyphenyl)acrylic acid**	5.9
19.3		**hexadecanoic acid**	2.6
19.9		**(E)-3-(3-hydroxy-4-methoxyphenyl)acrylic acid**	3.38

Table S7: GC/MS Results of LF-S.

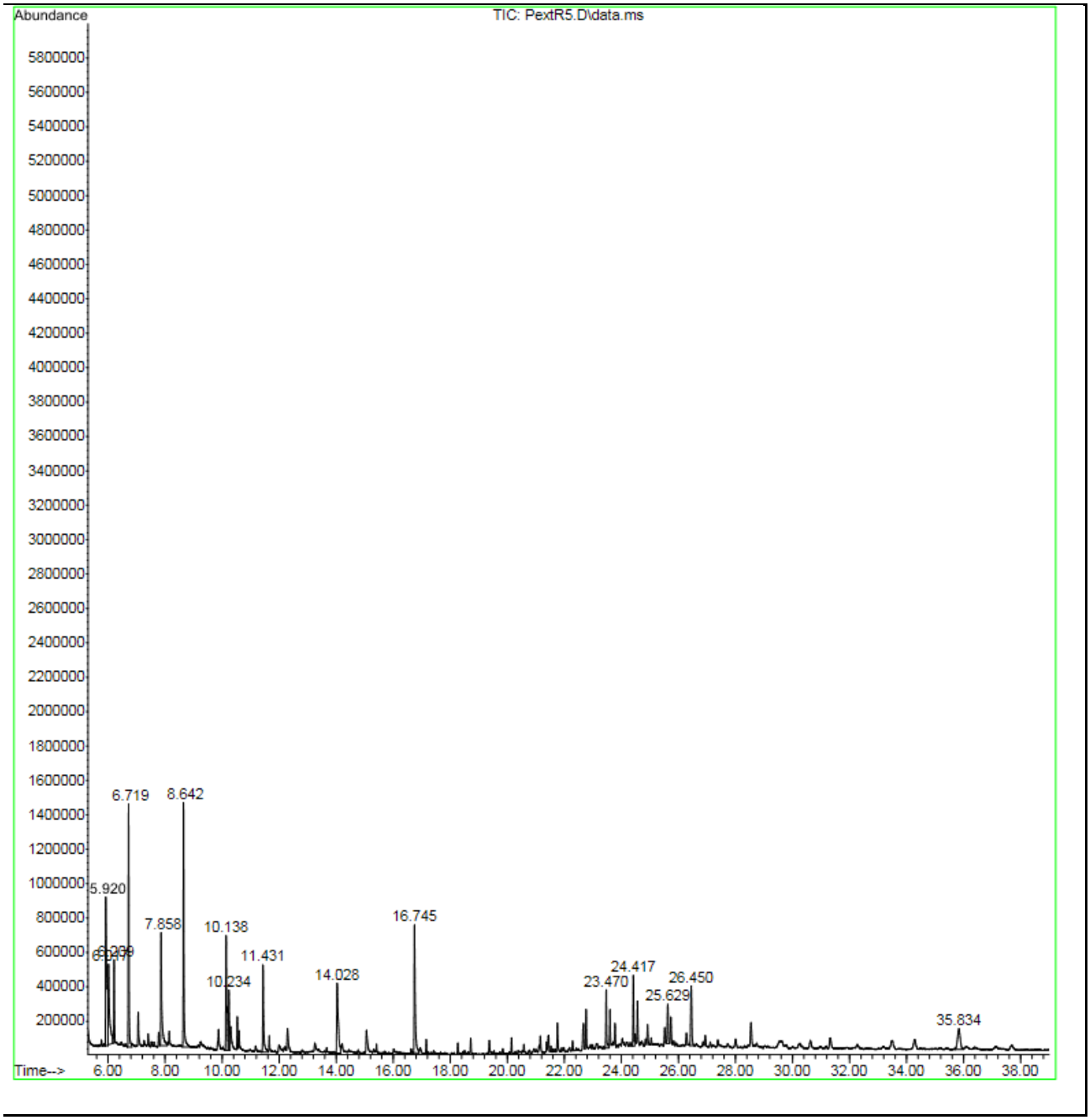


Figure S8: GC/MS chromatogram of LF-R5.

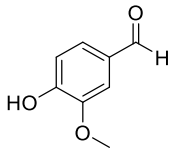
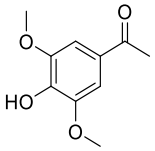
Retention time (min)	Molecule	Name	% in the analysis
14		**4-hydroxy-3-methoxybenzaldehyde**	14.9
16.7		**1-(4-hydroxy-3,5-dimethoxyphenyl)ethan-1-one**	18.1

Table S9: GC/MS Results of LF-R5.

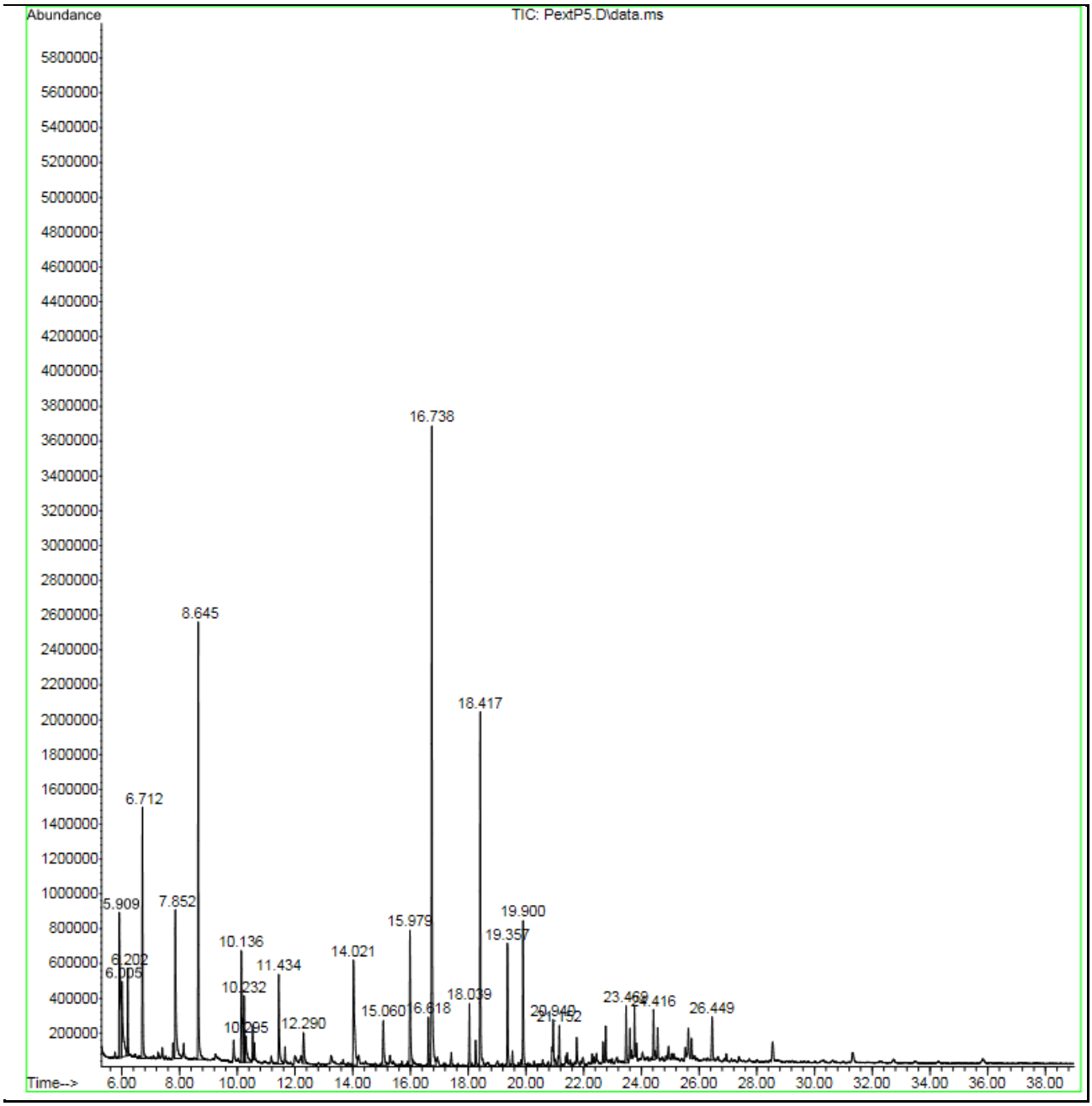


Figure S10: GC/MS chromatogram of LF-P5.

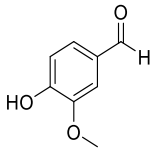
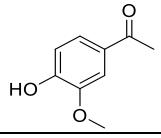
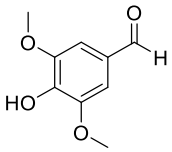
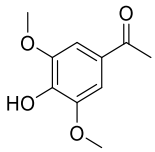
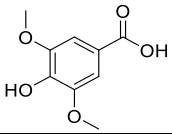
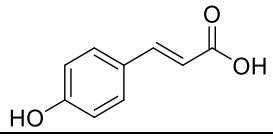
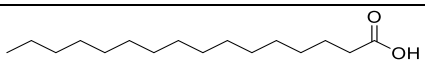
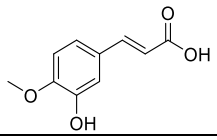
Retention time (min)	Molecule	Name	% in the analysis
14		**4-hydroxy-3-methoxybenzaldehyde**	4.9
15		**1-(4-hydroxy-3-methoxyphenyl)ethan-1-one**	1.9
15.9		**4-hydroxy-3,5-dimethoxybenzaldehyde**	4.3
16.74		**1-(4-hydroxy-3,5-dimethoxyphenyl)ethan-1-one**	17.5
18		**4-hydroxy-3,5-dimethoxybenzoic acid**	1.5
18.4		**(E)-3-(4-hydroxyphenyl)acrylic acid**	8.7
19.3		**hexadecanoic acid**	3.2
19.9		**(E)-3-(3-hydroxy-4-methoxyphenyl)acrylic acid**	3.6

Table S11: GC/MS Results of LF-P5.

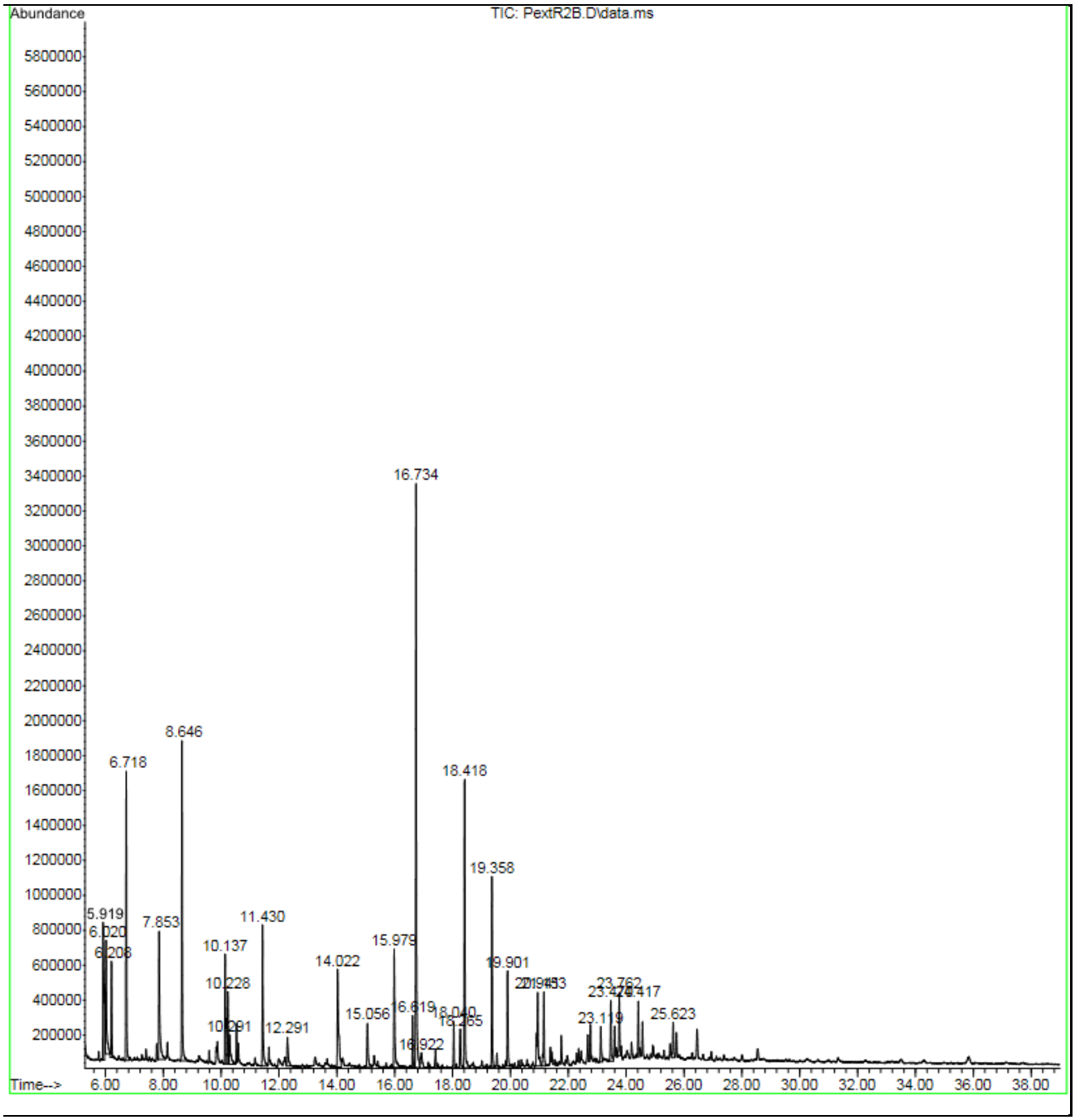


Figure S12: GC/MS chromatogram of LF-R2.

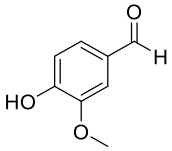
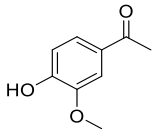
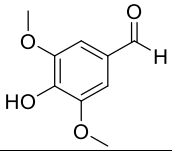
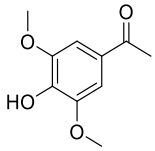
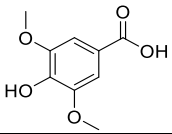
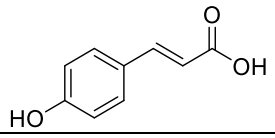
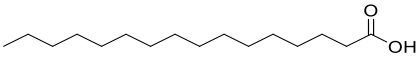
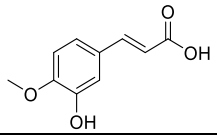
Retention time (min)	Molecule	Name	% in the analysis
14		**4-hydroxy-3-methoxybenzaldehyde**	6.3
15		**1-(4-hydroxy-3-methoxyphenyl)ethan-1-one**	2.7
15.9		**4-hydroxy-3,5-dimethoxybenzaldehyde**	5.7
16.74		**1-(4-hydroxy-3,5-dimethoxyphenyl)ethan-1-one**	22
18		**4-hydroxy-3,5-dimethoxybenzoic acid**	1.6
18.4		**(E)-3-(4-hydroxyphenyl)acrylic acid**	10.6
19.3		**hexadecanoic acid**	6.2
19.9		**(E)-3-(3-hydroxy-4-methoxyphenyl)acrylic acid**	3.4

Table S13: GC/MS Results of LF-R2.

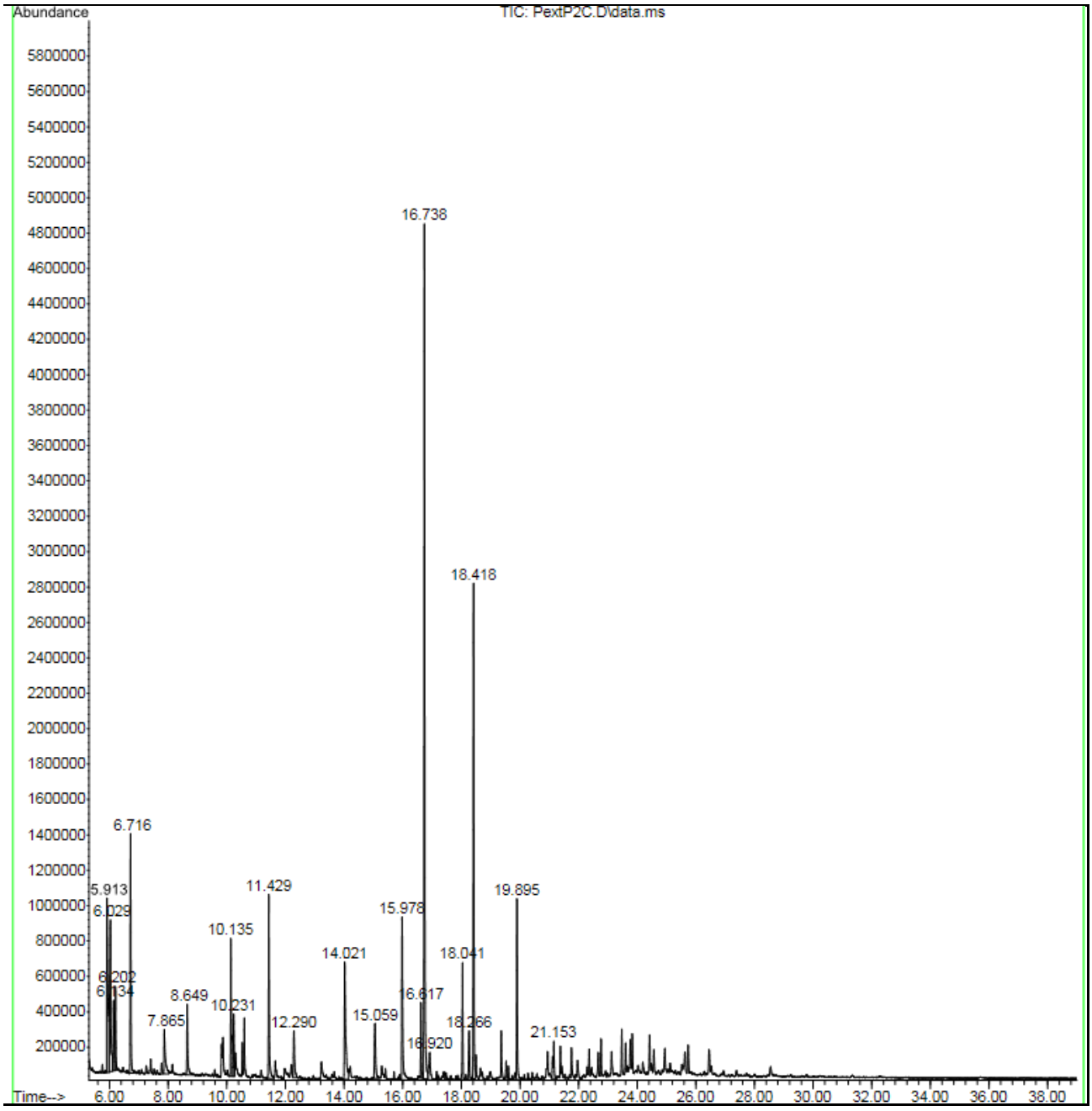


Figure S14: GC/MS chromatogram of LF-P2.

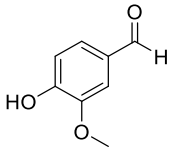
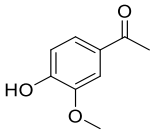
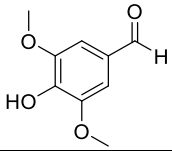
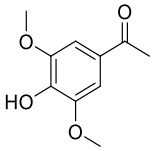
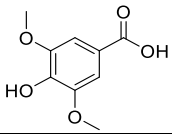
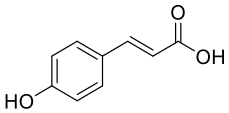
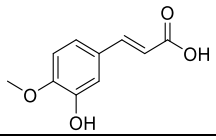
Retention time (min)	Molecule	Name	% in the analysis
14		**4-hydroxy-3-methoxybenzaldehyde**	6.9
15		**1-(4-hydroxy-3-methoxyphenyl)ethan-1-one**	3.2
15.9		**4-hydroxy-3,5-dimethoxybenzaldehyde**	7.3
16.74		**1-(4-hydroxy-3,5-dimethoxyphenyl)ethan-1-one**	30
18		**4-hydroxy-3,5-dimethoxybenzoic acid**	3.7
18.4		**(E)-3-(4-hydroxyphenyl)acrylic acid**	15.4
19.9		**(E)-3-(3-hydroxy-4-methoxyphenyl)acrylic acid**	6.4

Table S15: GC/MS Results of LF-P2.

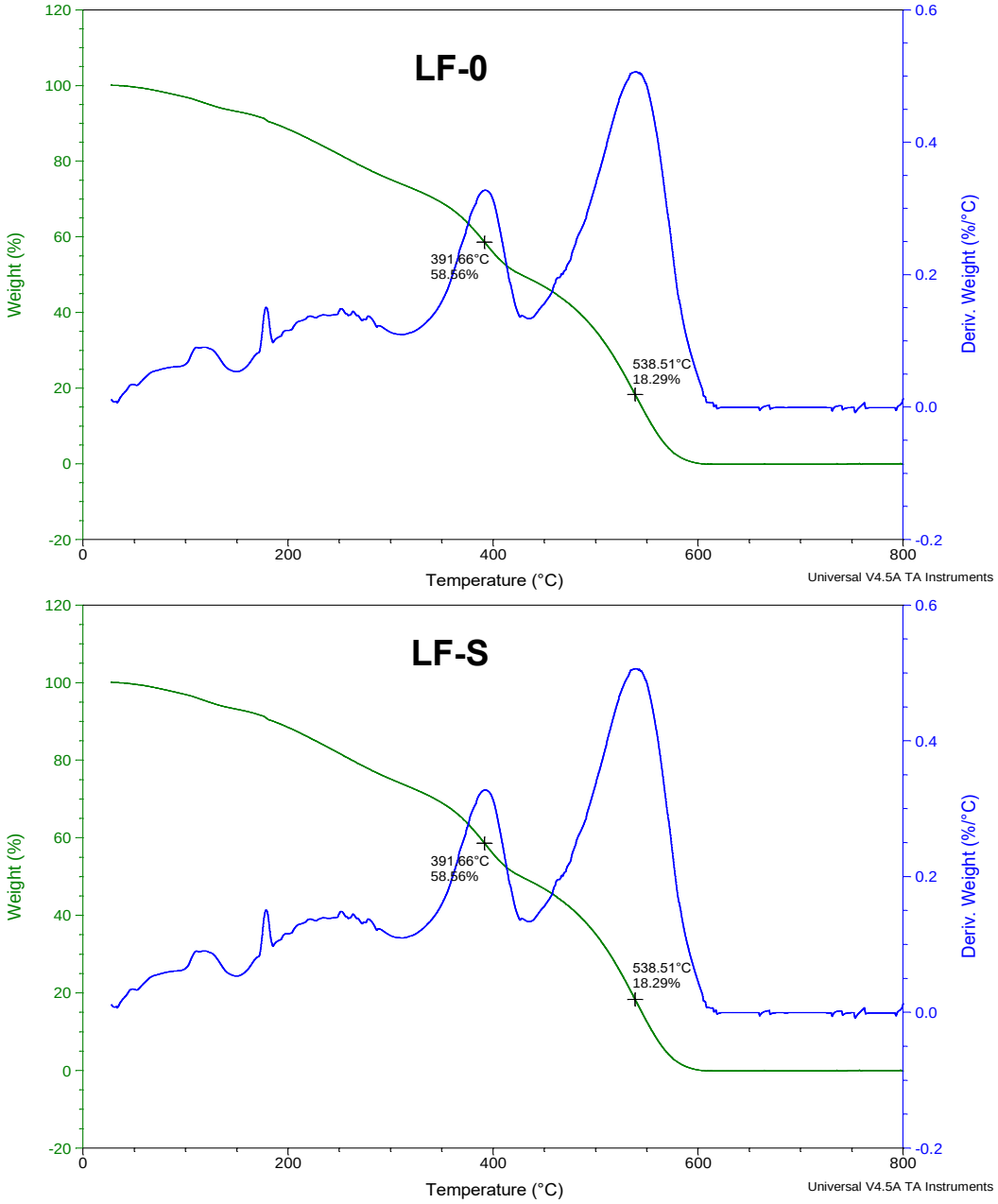


Figure S16: TGA curves of the lignin samples LF-0 (above) and LF-S (below) evaluated by Pyr-GC/MS. The weight loss is indicated by the green line (left green scale) The first derivation of the wieght loss is indicated by the blue line (right blue scale).

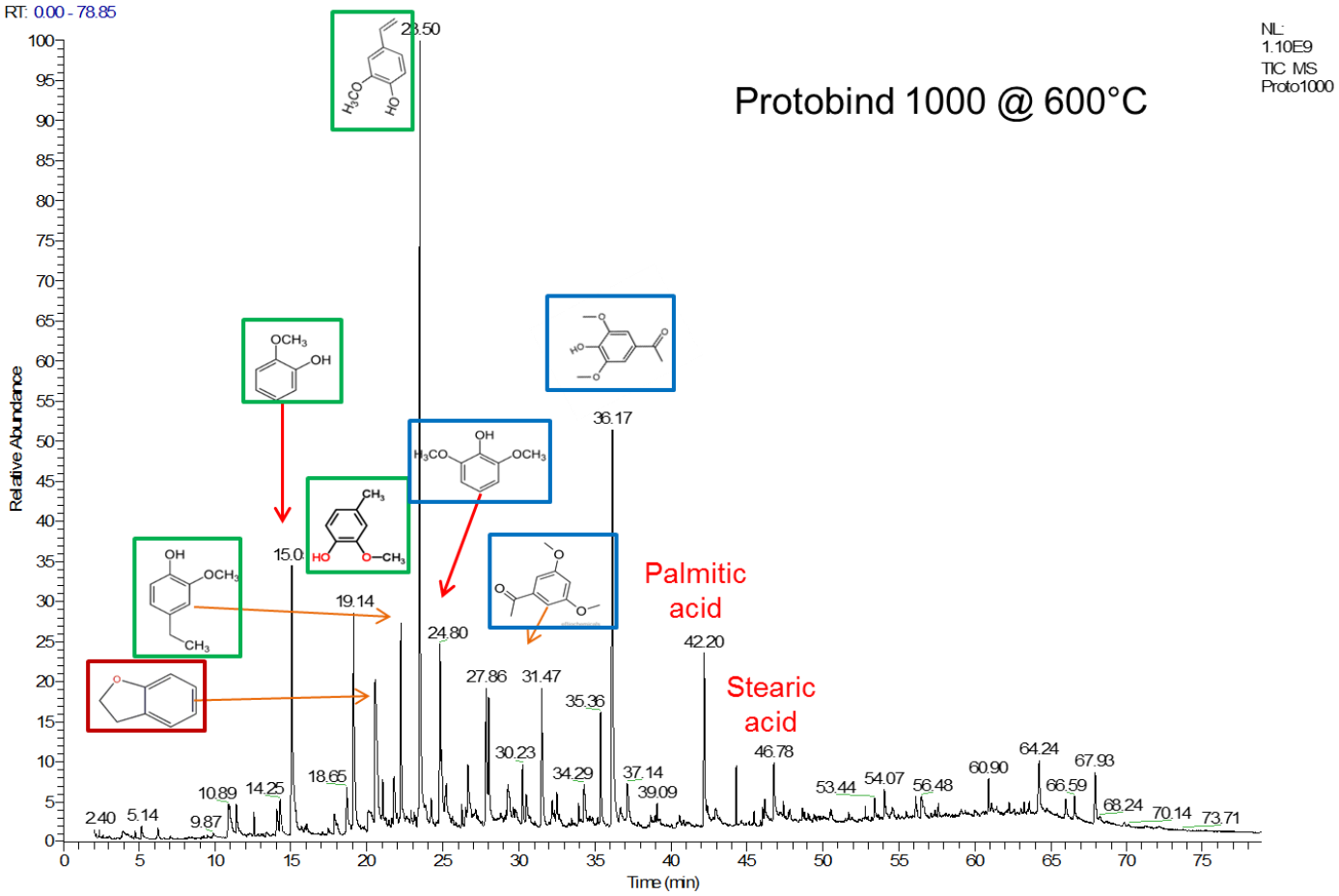


Figure S17: Identification of the main compounds identified in Pyr-GC/MS analysis of LF-0 at 600 °C.

Apex RT [min]	*CAS-Nr.*	*Name of Compound*	*Unit*
2.22	74-93-1	Methanthiol	
4.26	937-61-1	Benzylpropylether	C
5.95	98-01-1	Furfural	C
7.08	106-42-3	p-Xylene	C
10.63	20602-79-3	acryloylurea	C
11.54	108-95-2	Phenol	H
13.11	1461-27-4	m-Mentha-6,8-diene	
14.35	95-48-7	o-Cresol	H
15.2	106-44-5	p-Cresol	H
15.35	90-05-1	o-Methoxyphenol	G
18.57	123-07-9	p-Ethylphenol	H
18.72	18102-31-3	2-Methoxy-3-methylphenol	G
19.23	93-51-3	Creosol	G
20.04	120-80-9	Catechol	
20.51	496-16-2	Coumaran	
21.64	934-00-9	3-Methoxy-pyrocatechol	S
22.22	2785-89-9	p-Ethylguaiacol	G
23.25	488-17-5	3-Methylpyrocatechol	
23.52	7786-61-0	2-Methoxy-4-vinylphenol	G
24.07	3209-13-0	3-Methoxy-5-Methylphenol	
24.75	91-10-1	2,6-Dimethoxyphenol (Syringol)	S
24.88	97-53-0	Eugenol	G
25.01	2033-89-9	3,4-Dimethoxyphenol	S
25.2	2785-87-7	2-Methoxy-4-propylphenol	G
26.15	6380-23-0	3,4-Dimethoxystyrene	G
26.35	121-33-5	Vanillin	G
26.56	5932-68-3	trans-Isoeugenol	G
27.79	135-77-3	1,2,4-Trimethoxybenzene	S
27.95	5932-68-3	trans-Isoeugenol	G
29.05	6100-74-9	1-(3-Hydroxy-4-methoxyphenyl)ethanone (apocynin)	G
30.14	6443-69-2	3,4,5-Trimethoxytoluene	S
30.29	2503-46-0	Guaiacylacetone	G
32.4	6627-88-9	4-allyl-2,6-dimethoxyphenol	S
34.1	134-96-3	3,5-Dimethoxygallaldehyde	S
35.27	6627-88-9	4-allyl-2,6-dimethoxyphenol	S
36.11	2478-38-8	4'-Hydroxy-3',5'-Dimethoxyacetophenone	S
36.35	458-35-5	4-[(1E)-3-Hydroxy-1-propenyl]-2-methoxyphenol	
36.97	437-72-9	1-(2,6-Dihydroxy-4-methoxyphenyl)-1-butanone	

Table S18: Peak Identification of Protobind 1000 pyrolysed at 450 °C.