

Electronic Supplementary Information

Tuning the lignin oil OH-content with Ru and Pd catalysts during lignin hydrogenolysis on birch wood

S. Van den Bosch,^{a,1} W. Schutyser,^{a,1} S.-F. Koelewijn,^a T. Renders,^a C.M. Courtin,^b B.F. Sels^{*,a}

^a Center for Surface Chemistry and Catalysis, KU Leuven, Kasteelpark Arenberg 23, 3001 Heverlee, Belgium.
*E-mail: bert.sels@biw.kuleuven.be

^b Center for Food and Microbial Technology, KU Leuven, Kasteelpark Arenberg 22, 3001 Heverlee, Belgium.

¹ Authors contributed equally to this work.

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A. Experimental procedures

Chemicals and materials

All commercial chemicals were analytic reagents and were used without further purification. 5% Ru on carbon, 5% Pd on carbon, guaiacol (2-methoxyphenol, 98%), 4-*n*-propylguaiacol (>99%), syringol (2,6-dimethoxyphenol, 99%), 4-methylsyringol (>97%), methyl β -D-xylopyranoside (99%), 2-isopropylphenol (>98%) were purchased from Sigma Aldrich. 4-Ethylguaiacol (98%) was purchased from Acros organics. Methanol (>99%) and dichloromethane (>99%) were purchased from Fischer Chemical Ltd. 4-*n*-propanolguaiacol (3-(4-hydroxy-3-methoxyphenyl)-1-propanol, >98%) was purchased from TCI chemicals. Isoeugenol (2-methoxy-4-propenylphenol, >98%) was purchased from Alfa Aesar. Birch (*Betula pendula*) was obtained from a local sawmill (Ecobois, Ghent, Belgium).

Determination of the Klason lignin content

Product yields in lignin depolymerization literature are typically based on the amount of acid insoluble lignin, also called Klason lignin, in the lignocellulose sample. The determination of the Klason lignin content of birch, was based on a procedure from Lin & Dence.¹ The lignocellulose samples were sieved and the fraction of 0.25-0.50 mm was used for analysis. A Soxtec extraction was first executed to remove any extractives like fats, waxes, resins and terpenoids/steroids,² that can influence the Klason lignin determination. 10 g of oven dried substrate was therefore divided over 4 fritted glass extraction thimbles and extracted in a Soxtec 2055 Avanti with a 2:1 toluene:ethanol mixture. Prior to a 3 h standard extraction, a wet step was introduced for 15 min in which the samples were completely submerged in the toluene:ethanol solution to improve the speed of extraction and thus to reduce the total extraction time needed. After cooling, the samples were washed with ethanol and dried in an oven at 353 K for one night. Triplicate samples of extracted substrate (1 g) were transferred to 50 mL beakers after which 15 mL of a 72 wt% H₂SO₄-solution was added. The mixture was left at room temperature for 2 h while continuously stirred with a magnetic rod. Afterwards the content of each beaker was transferred to a round-bottom-flask which already contained 300 to 400 mL of water. The beakers were rinsed and additional water was added until a H₂SO₄ concentration of 3 wt% was reached. The diluted solution was boiled for 4 h under reflux conditions, to maintain a constant volume and acid concentration. After filtration of the hot solution, a brown lignin precipitate was retained. The precipitate was washed with hot water to remove any leftover acid and the obtained residue was dried in an oven at 353 K for one night. The reported Klason lignin content was determined relative to the oven dried substrate by averaging the measured weight of the residues and correcting for the amount of removed extractives.

Determination of the carbohydrate content and composition

The carbohydrate content and composition in birch sawdust as well as in the obtained carbohydrate pulps after hydrogenolysis were determined, using a standard total sugar determination procedure, adapted with hydrolysis conditions for cellulose-rich materials.³⁻⁵ Samples of 10 mg were pre-hydrolyzed in a 13 M H₂SO₄-solution (1 mL) at RT for 2 h and subsequently hydrolyzed in a diluted 2 M H₂SO₄-solution (6.5 mL) at 373 K for 2 h. The resulting monosaccharides were reduced to alditols and acetylated to increase their volatility for GC analysis. First, internal standard (1 mL of a 1 mg/mL β -D-allose solution of 1:1 benzoic acid:water) was added to 3 mL of the hydrolyzed sample. NH₃ 25% in water (1.5 mL) was added, as well as droplets of 2-octanol to avoid excessive foaming. Reduction was catalyzed with NaBH₄ (0.2 mL of a 200 mg NaBH₄/mL 2 M NH₃ solution) for 30 min at 313 K and the reaction was stopped by adding 0.4 mL acetic acid. At this point the procedure can be paused by placing the reaction tubes in a cold environment for 1 night. 1-methylimidazole (0.5 mL) was added to 0.5 mL of the reduced samples to catalyze the formation of alditol acetates after addition of acetic acid anhydride (5 mL). After 10 min, 1 mL of ethanol was added and 5 minutes later, the reaction was quenched by adding 10 mL of water. The reaction vials were placed in an ice bath and bromophenol blue (0.5 mL of a 0.4 g/L water solution) as well as KOH (2 x 5 mL of a 7.5 M solution) were added to color the aqueous phase blue. The yellow ethyl acetate phase, containing the acetylated monosaccharides, could then easily be separated with a Pasteur pipette and was dried with anhydrous Na₂SO₄ before transferring it into a vial. GC analysis was performed on a Supelco SP-2380 column with helium as carrier gas in a

Agilent 6890 series chromatograph equipped with an autosampler, splitter injection port (split ratio 1:20) and flame ionization detector (FID). Separation was executed at 498 K with injection and detection temperatures at 543 K. Calibration samples, containing known amounts of the expected monosaccharides were included in each analysis. To calculate the carbohydrate content in the analyzed samples, a correction factor was used to compensate for the addition of water during hydrolysis. Each substrate was analyzed in threefold and the average values were used in the calculation of the carbohydrate retention and the sugar polyol yields.

Lignin hydrogenolysis on birch sawdust

In a typical catalytic hydrogenolysis experiment, 2 g of extracted (same conditions as for Klason lignin determination) birch sawdust (*Betula pendula* from Ecobois, Ghent), 0.2 g Ru/C and 40 mL methanol were loaded into a 100 mL stainless steel batch reactor (Parr Instruments Co.). The reactor was sealed, flushed with N₂ and pressurized with 3 MPa H₂ at room temperature (RT). The mixture was stirred at 700 rpm and the temperature was increased to 523 K (~10 K.min⁻¹) at which the pressure reached ~12 MPa and the reaction was started. After reaction, the autoclave was cooled in water and depressurized at RT.

Lignin product analysis

To determine the degree of delignification, the raw filtered methanol product mixture was evaporated and a brown oil was obtained. This brown oil was subjected to threefold liquid-liquid extractions using dichloromethane (DCM) and water to separate the soluble lignin- and sugar-derived products. Finally the DCM-extracted phase was dried to obtain the 'lignin oil'. The weight of the lignin oil is then used to determine the degree of delignification (based on Klason lignin weight).

To analyze the lignin monomers after hydrogenolysis, a weighed amount of external standard (2-isopropylphenol) was added to the lignin oil after which the content was completely resolubilized in 10 mL methanol. A sample was then analyzed on a GC (Agilent 6890 series) equipped with a HP5-column and a flame ionization detector (FID). The following operating conditions were used: injection temperature of 573 K, column temperature program: 323 K (2 min), 15 K/min to 423 K, 10 K/min to 493 K and 20 K/min to 563 K (12 min), detection temperature of 573 K. Sensitivity factors of the products were obtained by calibration with commercial standards or obtained by ECN-based calculations⁶ due to lack of commercial standards. The product yield and the product selectivity were defined as followed:

$$Yield\ product\ A\ (C\%) = \frac{m_{product\ A} \times \frac{wt\%C_{product\ A}}{100}}{m_{lignocellulose\ substrate} \times \frac{wt\%Klason\ lignin}{100} \times \frac{wt\%C_{Klason\ lignin}}{100}} \times 100\%$$

$$wt\%C_{product\ A} = C_{product\ A} \times \frac{MW_c \left(= 12 \frac{g}{mol} \right)}{MW_{product\ A}} \times 100\%$$

$$wt\%C_{Klason\ lignin} = C_{lignin\ monomer,\ average} \times \frac{MW_c \left(= 12 \frac{g}{mol} \right)}{MW_{lignin\ monomer,\ average}} \times 100\%$$

$$\text{Selectivity product A (C\%)} = \frac{m_{\text{product A}} \times \frac{\text{wt\%} C_{\text{product A}}}{100}}{\sum_i m_{\text{product i}} \times \frac{\text{wt\%} C_{\text{product i}}}{100}} \times 100\%$$

In these definitions, $m_{\text{product A}}$ is the weight of product A, $\text{wt\%} C_{\text{product A}}$ is the weight percentage of carbon in product A, $m_{\text{lignocellulose substrate}}$ is the weight of the lignocellulose substrate, $\text{wt\%} C_{\text{Klason lignin}}$ is the weight percentage of Klason lignin in the lignocellulose substrate, $\text{wt\%} C_{\text{Klason lignin}}$ is the weight percentage of carbon in the Klason lignin, $C_{\text{product A}}$ is the number of C-atoms in 1 molecule of product A, $MW_{\text{product A}}$ is the molecular weight of product A, $C_{\text{lignin monomer, average}}$ is the average number of C-atoms in 1 lignin monomer and $MW_{\text{lignin monomer, average}}$ is the average MW of a lignin monomer. The $MW_{\text{lignin monomer, average}}$ and $C_{\text{lignin monomer, average}}$ were estimated, taking into account the relative distribution of the main building blocks in the lignin. The chemical structures of *p*-hydroxyphenyl-, guaiacyl- and syringyl-units in Klason lignin were herein represented by respectively *p*-coumaryl, coniferyl and sinapyl alcohol units with respective molecular weights of 150, 180 and 210 g/mol and respective $C_{\text{lignin monomer}}$ values of 9, 10 and 11. For birch with a S:G ratio of 74:26 (determined with 2D HSQC-NMR of the lignin oil)⁷, this resulted in a $MW_{\text{lignin monomer, average}}$ of 202.3 g/mol and a $C_{\text{lignin monomer, average}}$ of 10.74, corresponding to 63.7 wt% $C_{\text{Klason lignin}}$.

The dimer yield was analyzed in the same way as the monomer yield, yet a derivatization step was added to increase their volatility before GC analysis. Therefore, 0.2 mL of the resolubilized lignin oil with the internal standard 2-isopropylphenol, was dried under a N₂ flow and subsequently mixed with 0.5 mL of pyridine and 0.5 mL of *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide. The vial was sealed and put in an oven at 353 K for 30 min. After this the lignin products were quantified with GC analysis as described above.

Identification of the monomer and dimer signals was performed with GC-MS using an Agilent 6890 series GC equipped with a HP1-MS capillary column and an Agilent 5973 series Mass Spectroscopy detector. The following operating conditions were used: injection temperature of 523 K, column temperature program: 333 K (2 min), 10 K/min to 553 K (13 min), detection temperature of 563 K.

GC analysis of the gaseous phase was performed on an Interscience Trace GC equipped with HayeSep Q and RTX-1 columns and a FID and TCD detector.

To get more insight in the degree of lignin depolymerization, the distribution of the molar mass of the lignin products was investigated using gel permeation chromatography (GPC). Therefore a sample of the lignin oil was solubilized in THF (~2-5 mg/mL) and subsequently filtered with a 0.2 μm PTFE membrane to remove any particulate matter to prevent plugging of the columns. GPC analyses were performed at 40 °C on a Waters E2695 equipped with a M-Gel column 3 μm (mixed), using THF as the solvent (1 mL/min) and a UV detection at 280 nm with a Walters 2988 Photodiode array detector.

In addition with GC/MS and GPC analyses, the structural features of the lignin dimers and oligomers were analyzed with NMR. ¹H, ¹³C NMR, DEPT and HSQC spectra were acquired on a Bruker Avance 400 MHz. A sample of the lignin oil (100 mg) was dissolved in 0.7 mL of DMSO-*d*₆. The solvent peak was used as an internal reference (δ_C 39.5, δ_H 2.49 ppm). HSQC experiments had the following parameters: standard Bruker pulse sequence 'hsqcetgp' (double inept transfer, phase-sensitive), spectral width of 20 ppm in F2 (¹H dimension) by using 2048 data points for an acquisition time (AQ) of 128 ms, 219 ppm in F1 (¹³C dimension) by using 512 increments (AQ of 11.6 ms), 128 scans with a 1.5 s interscan delay (D1). The base level of the HSQC spectra was taken at 0.077% of the maximum intensity of the methoxy (-OCH₃) signal (δ_C 56.2, δ_H 3.74 ppm).

Theoretical maximum monomer yield

Lignin is a complex 3-dimensional irregular polymer with randomly cross-linked phenolic building blocks. To estimate the theoretical maximum monomer yield for a certain substrate, a simplified linear lignin polymer is imagined, in which each building block is linked to two other units, either by a C-C bond or an ether-bond. In a hydrogenolysis reaction, the ether bonds are cleaved to depolymerize the lignin structure. When a unit is now on both sides connected with an ether bond, the cleavage of the ether bonds will result in a monomer. Mathematically, the maximum amount of monomers coincides with the square of the fraction of ether bonds in the lignin structure.⁸⁻¹⁰ Reported values for the ether content of birch lignin typically range around 67-76%,^{11, 12} which implicates a theoretical maximum monomer yield, varying from 45% to 58% for birch. The here obtained monomer yields of around 50% are thus close to the theoretic maximum.

Determination of the OH-content in the lignin oil

The average number of OH-functionalities per phenolic moieties is an important parameter for potential applications in the polymer industry. To examine this, the lignin oil, was derivatized *via* acetylation of the OH-groups and subsequently analyzed by ¹H-NMR.¹³ Therefore, 200 mg of the lignin oil was dissolved in 4 mL pyridine to form a homogeneous solution. Then, 4 mL of acetic anhydride was added and stirred for 24 h at 313 K. The acetylated sample is purified by drop wise addition of the solution to ice-cold distilled water (150 mL) and subsequent extraction by dichloromethane (4 x 20 mL), followed by vacuum distillation of the extracted DCM solution (373 K, 50 mbar) for one hour. To completely remove pyridine impurities the sample is heated overnight in a vacuum oven (373 K, 4 mbar).

¹H-NMR spectra of the acetylated products were recorded on a Bruker Advance 300 MHz spectrometer in chloroform-*d*₁ at room temperature (128 scans). Pentafluorobenzaldehyde (PFB, 10.3 ppm) was added as an internal standard for quantification of the acetate groups coupled to both phenolic (2.3 ppm, s, 3H) and aliphatic (2.1 ppm, s, 3H) alcohol groups. By integrating both signals, the average amount of OH-functionalities per phenolic moieties can be determined.

B. Tables

Table S1 A more detailed phenolic monomer distribution of all reactions described in the article.^a

Entry	Catalyst	Mass Catalyst (g)	P H ₂ initial (bar)	4-ethylguaiacol	4- <i>n</i> -propylguaiacol	isoeugenol	4- <i>n</i> -propanolguaiacol	syringol	4-methylsyringol	4-ethylsyringol	4- <i>n</i> -propylsyringol	4-prop-1-enylsyringol	4- <i>n</i> -propanolsyringol	Total monomers	Selectivity PG+PS	Selectivity PohG+PohS
1	Ru/C	0.1	30	0.0	6.3	1.1	2.8	0.0	0.4	1.9	20.6	4.5	9.9	47.5	57	27
2 ^b	Ru/C	0.2	30	0.3	7.2	0.1	2.0	0.4	0.4	1.1	29.0	0.5	7.1	48.0	75	19
3 ^c	Ru/C	0.3	30	0.2	9.8	0.0	1.3	0.3	0.4	0.8	31.9	1.9	3.1	49.7	84	9
4	Ru/C	0.3	10	0.2	10.3	0.2	0.4	0.2	0.6	1.0	36.9	0.4	0.8	51.2	92	3
5	Ru/C	0.3	1 (N ₂)	0.5	8.2	0.6	0.0	0.0	1.1	1.1	26.4	1.3	0.6	39.7	87	1
6	Pd/C	0.1	30	0.3	0.3	0.3	9.0	0.4	0.3	2.5	1.3	0.0	33.2	47.7	3	89
7 ^d	Pd/C	0.2	30	0.2	0.4	0.0	9.7	0.4	0.3	1.6	1.4	0.0	35.2	49.3	4	91
8 ^e	Pd/C	0.3	30	0.1	0.3	0.0	9.8	0.3	0.3	1.8	1.4	0.0	34.6	48.5	3	91
9 ^f	Pd/C	0.3	10	0.3	0.4	0.1	8.7	0.4	0.3	3.7	2.0	0.0	31.8	47.8	5	85
10 ^g	Pd/C	0.3	1 (N ₂)	3.7	1.4	0.1	3.9	0.0	0.4	15.5	4.7	0.0	15.8	52.6	13	43

^a The reaction conditions are as follows: 2 g extracted birch sawdust (0.25-0.50 mm), 5% Ru/C or 5% Pd/C, 40 mL methanol, 3 h reaction time, 523 K.

Table S2 Comparing the adsorption of 4-*n*-propylguaiacol and 4-*n*-propanolguaiacol on Ru/C and Pd/C ^a

	Retention (%)	
	Ru/C	Pd/C
4- <i>n</i> -propylguaiacol	93.0 ± 1.6	97.0 ± 1.9
4- <i>n</i> -propanolguaiacol	96.6 ± 1.1	97.4 ± 2.1

^a 0.02 g 4-*n*-propylguaiacol, 0.02 g 4-*n*-propanolguaiacol and 0.02 g cyclohexanol (internal standard) were mixed in 2 mL methanol together with 0.01 g Ru/C or Pd/C. Samples were taken before adding the catalyst and after 1 h of mixing with the catalyst at 298 K. Retention is calculated as the amount of phenolics in solution after 1 h in presence of Ru/C or Pd/C, relative to the initial amount. No adsorption of cyclohexanol on the catalyst was assumed.

Table S3 Composition of the gas phase (vol%)^a

	With birch sawdust		Without birch sawdust	
	Ru/C	Pd/C	Ru/C	Pd/C
H ₂	92.7	94.2	63.6	94.1
N ₂	3.42	4.05	3.91	3.75
CH ₄	1.08 (0.08) ^b	0.22 (0.01)	28.3 (1.77)	0.27 (0.02)
CO	1.88 (0.13)	0.86 (0.05)	1.04 (0.07)	1.25 (0.08)
maximum loss of methanol into carbonaceous gasses (mol%) ^b	0.21	0.06	1.84	0.10

^a Reaction conditions: 2 g extracted birch sawdust (composition: 19.5 wt% Klason lignin, 41/21 wt% C6/C5 sugars), 0.2 g catalyst, 40 mL methanol, 523 K, 3 h and 3 MPa H₂ at RT (~12 MPa at 523 K). ^b Values in brackets relate the amount of gaseous compound to the initial amount of MeOH (mol%). Summation gives the maximum loss of MeOH to carbonaceous gasses.

C. Figures

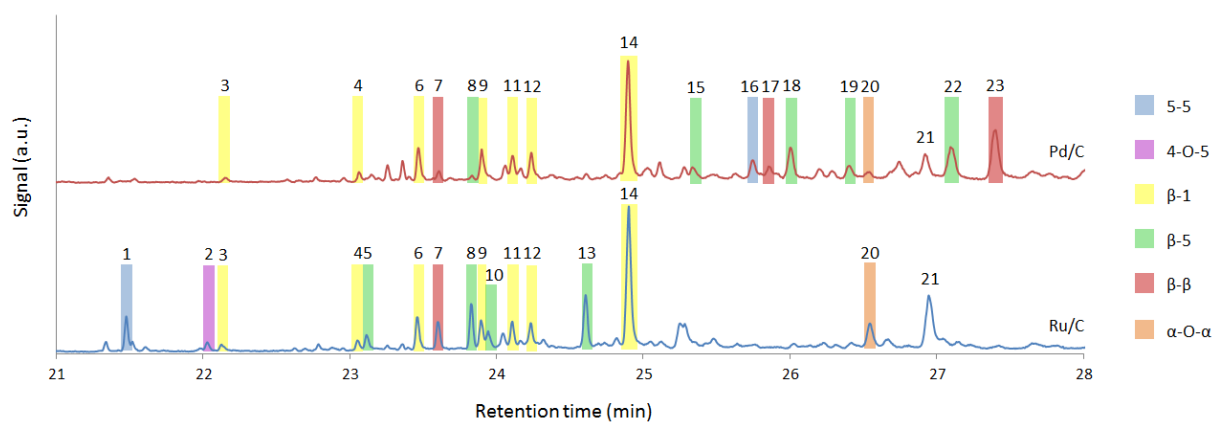
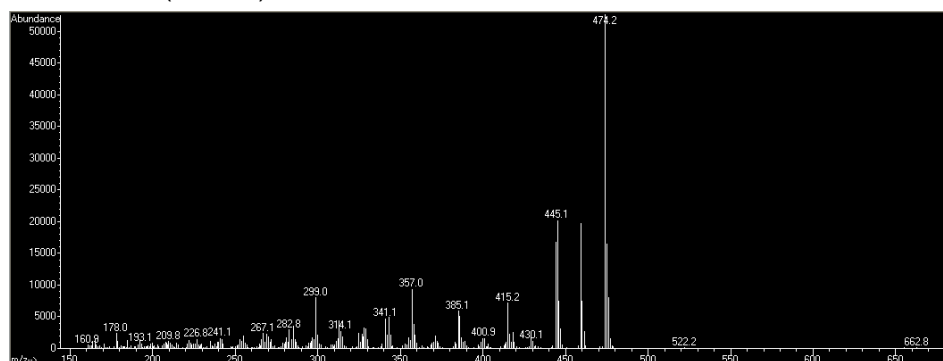
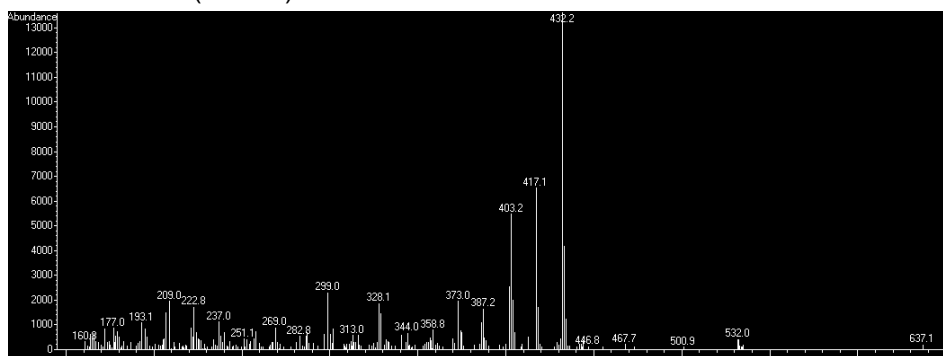


Fig. S1 GC-MS analyses to compare the lignin dimer product selectivities after the Ru/C and Pd/C catalyzed hydrogenolysis of birch wood. In support of this figure (also presented in the article as Fig. 1c), the corresponding mass spectrum for each peak are provided below, as well as the chemical structure of each identified dimer. The peak identification was confirmed by literature.¹⁴⁻¹⁸

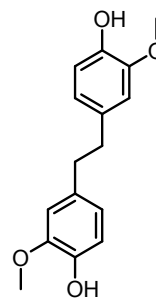
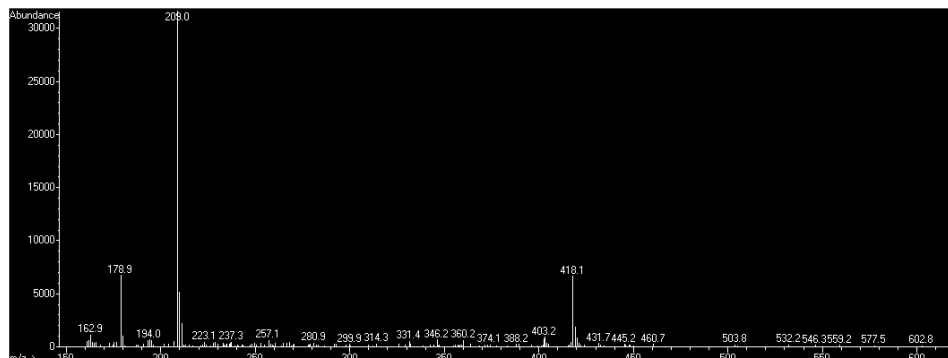
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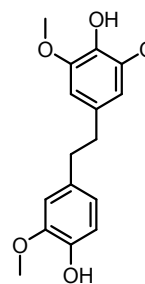
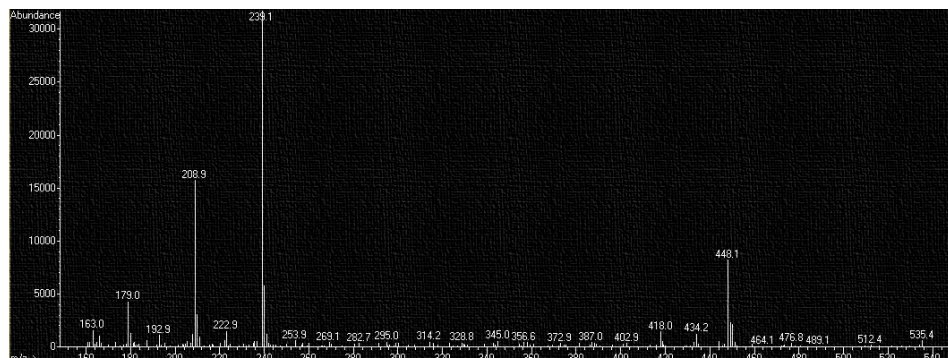
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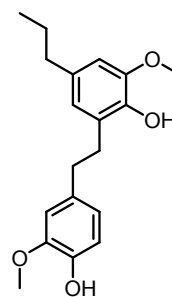
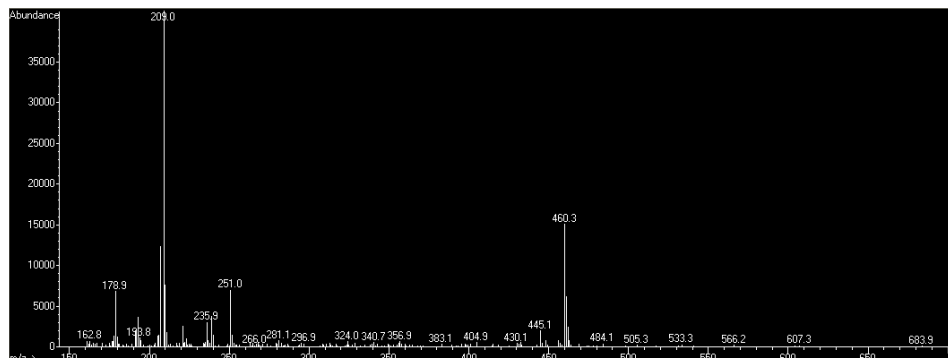
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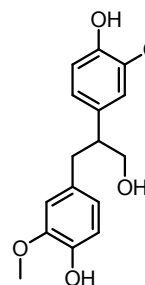
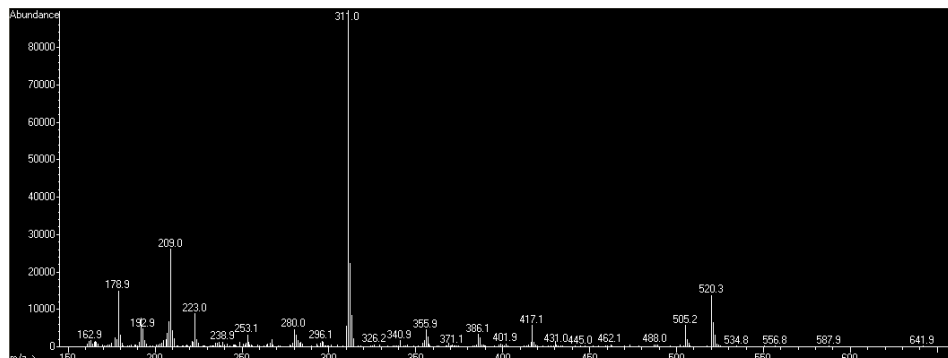
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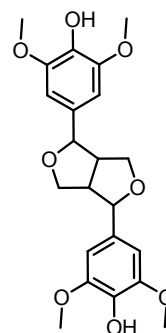
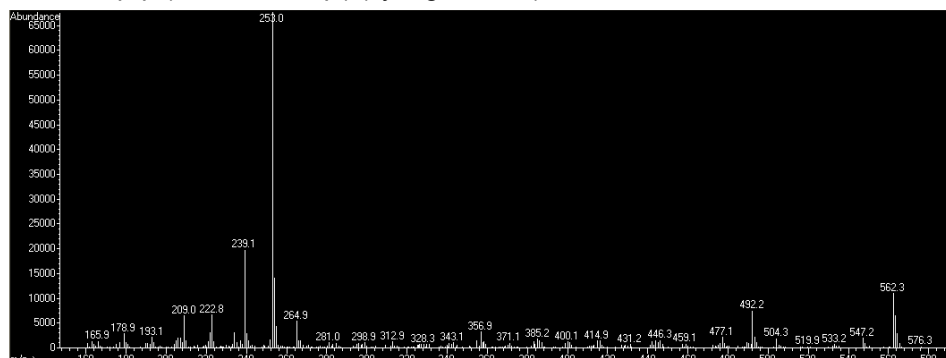
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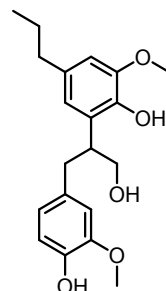
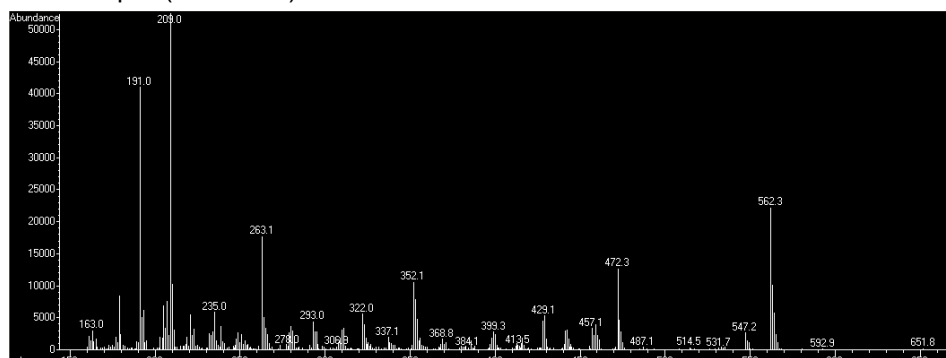
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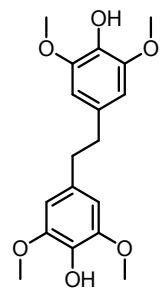
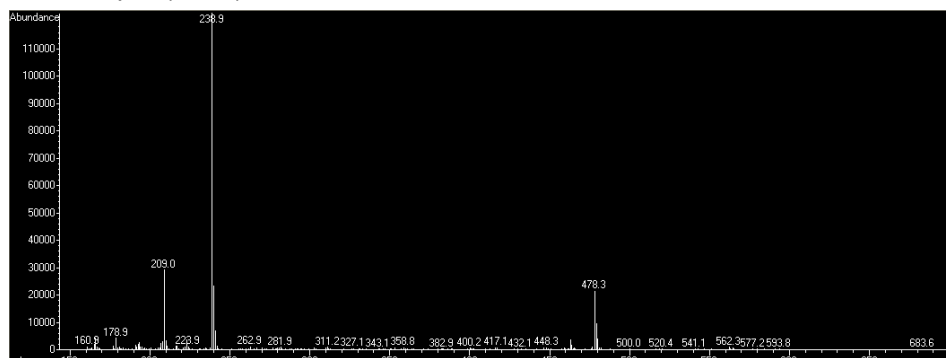
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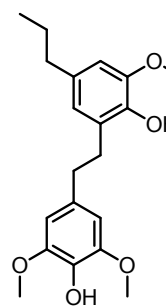
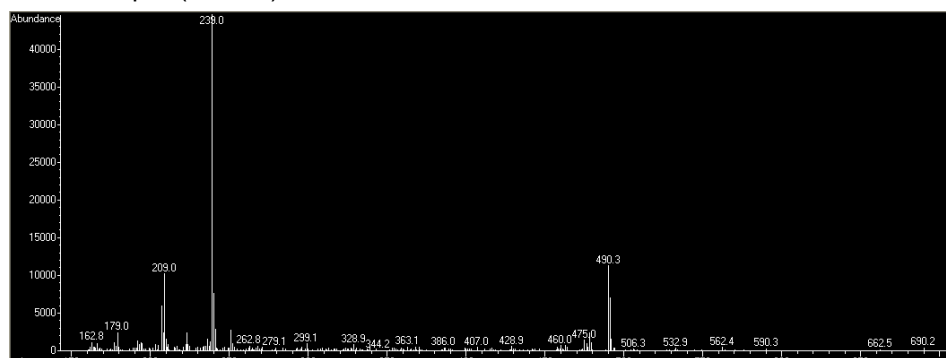
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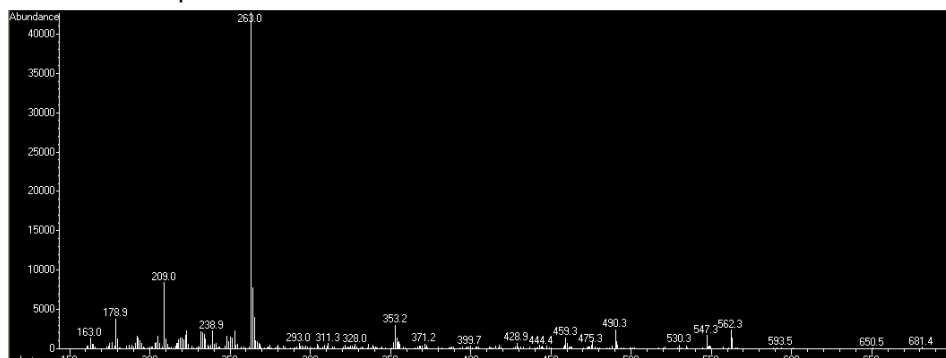
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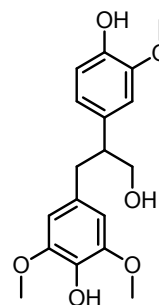
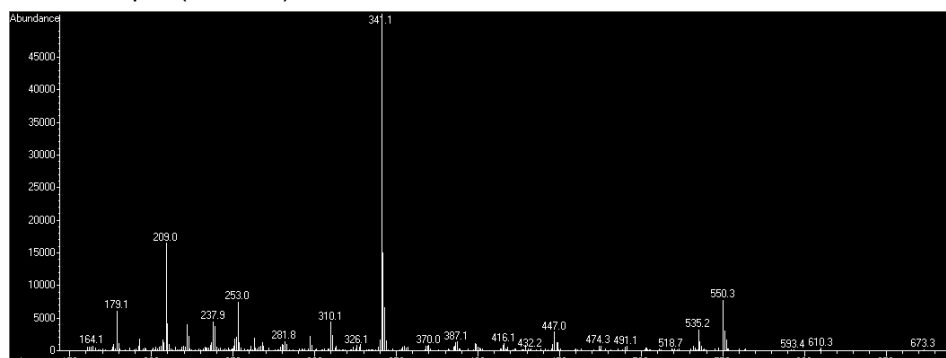
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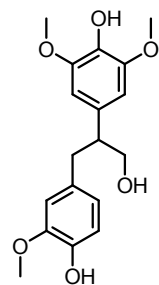
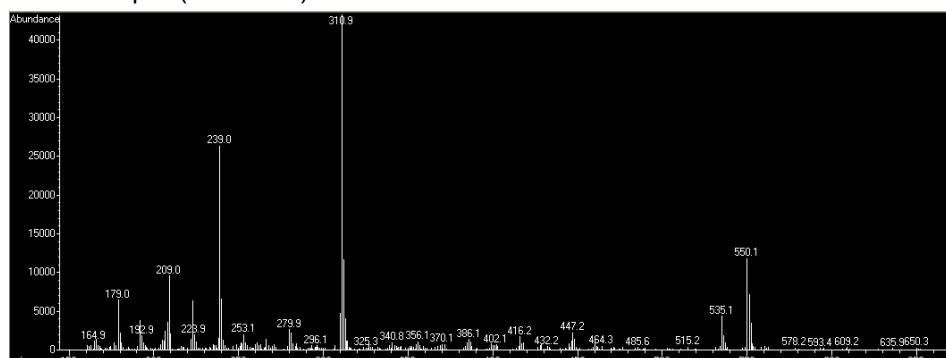
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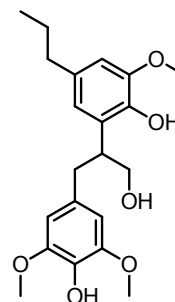
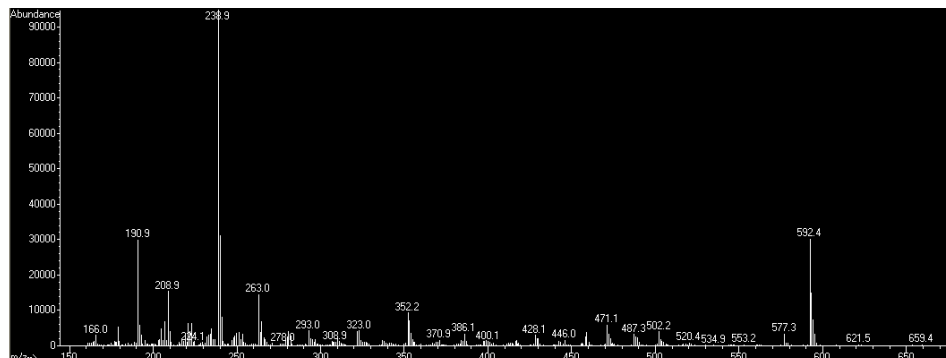
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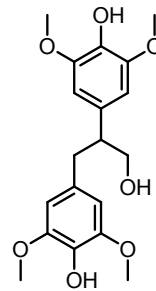
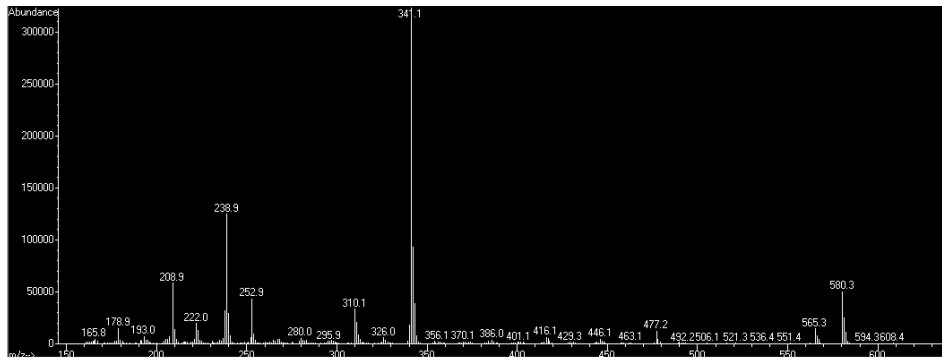
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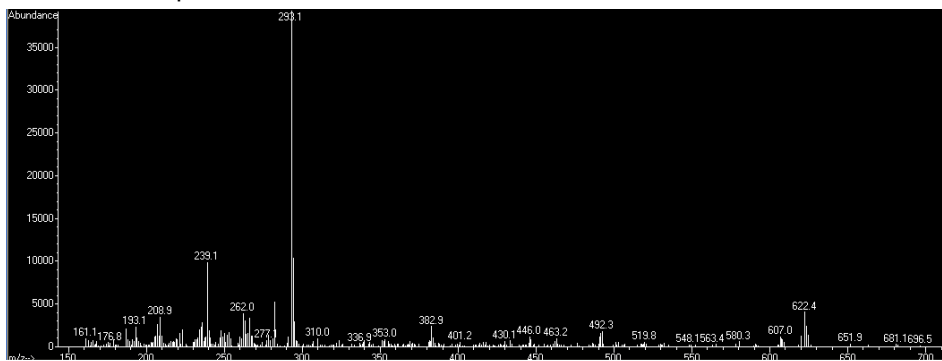
Dimer 13: β -5 (PohS-PG)



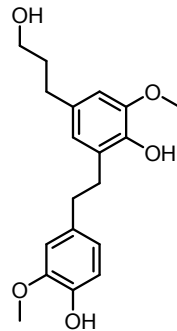
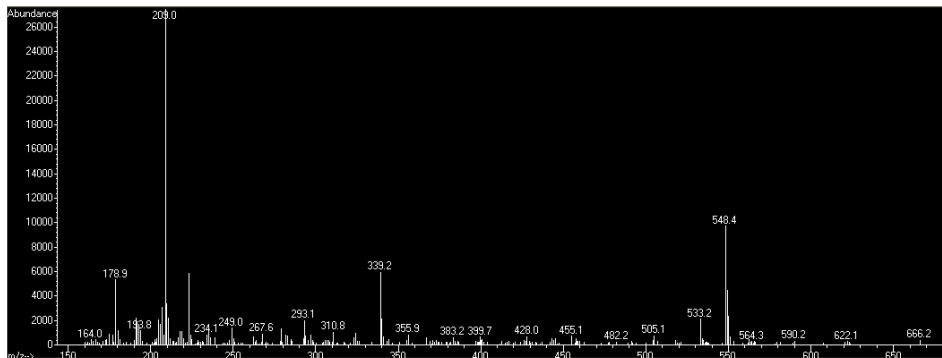
Dimer 14: β -1 (PohS-S)



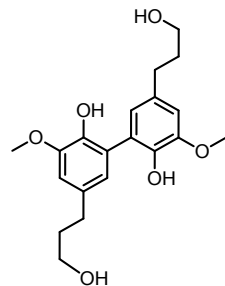
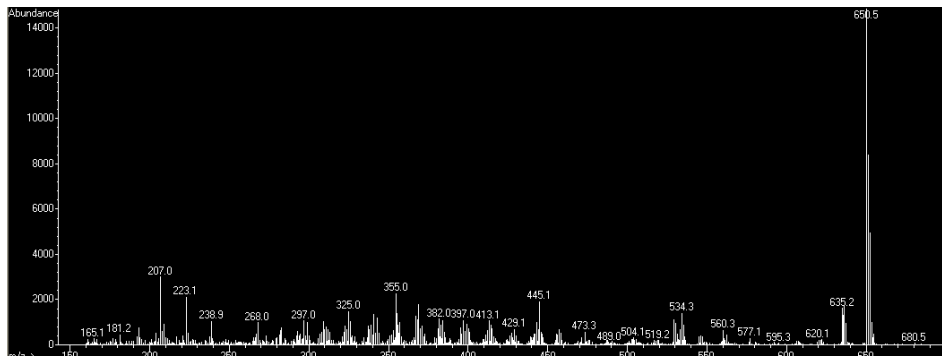
Unknown compound



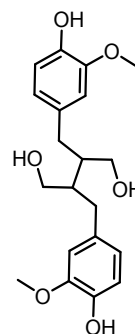
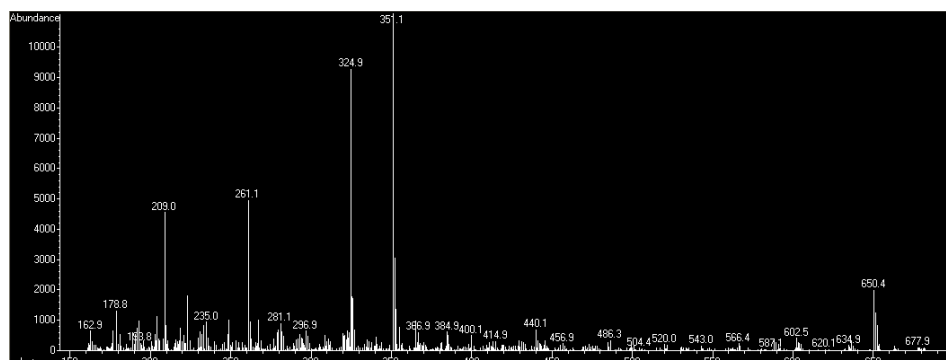
Dimer 15: β -5 (EG-PohG)



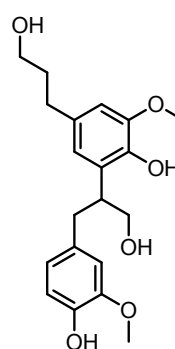
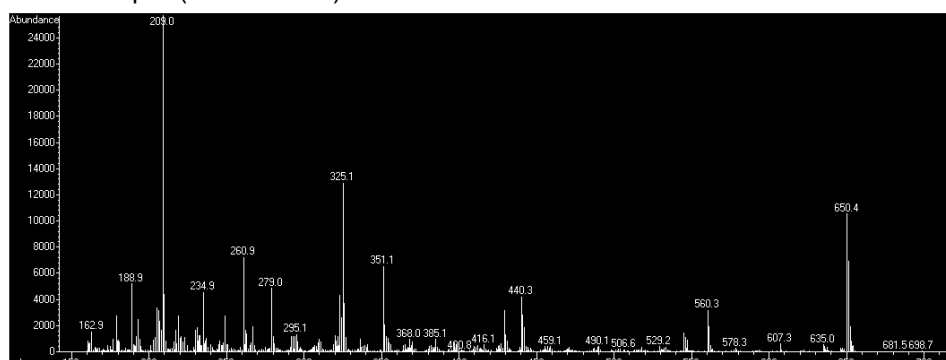
Dimer 16: 5-5 (PohG-PohG)



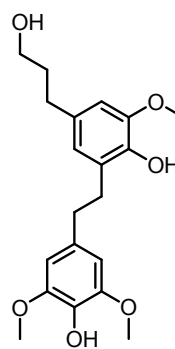
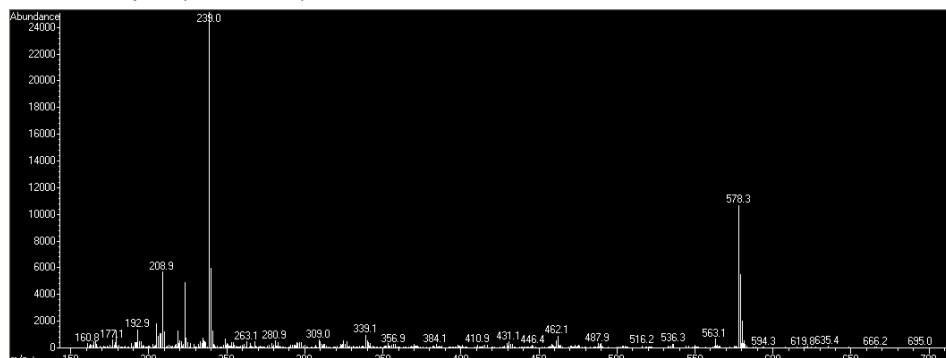
Dimer 17: β - β (PohG-PohG)



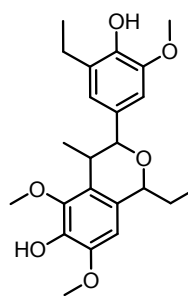
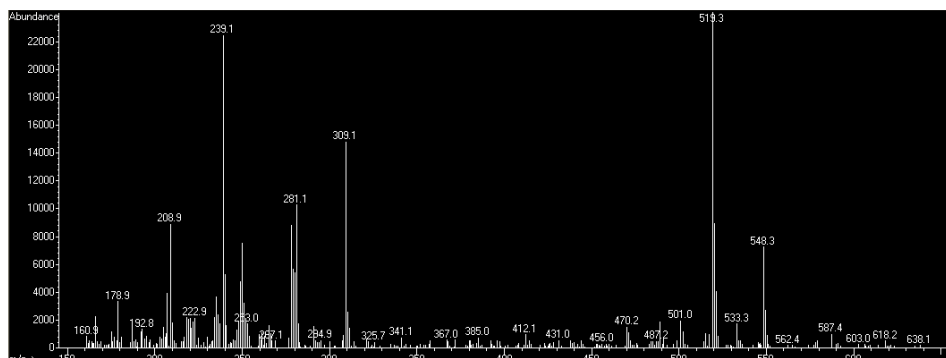
Dimer 18: β -5 (PohG-PohG)



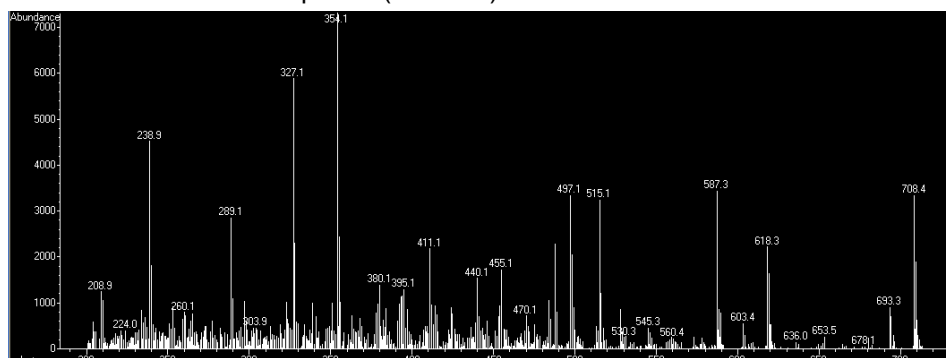
Dimer 19: β -5 (ES-PohG)



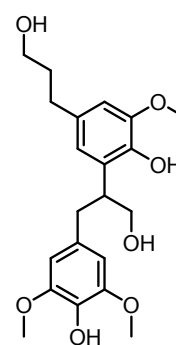
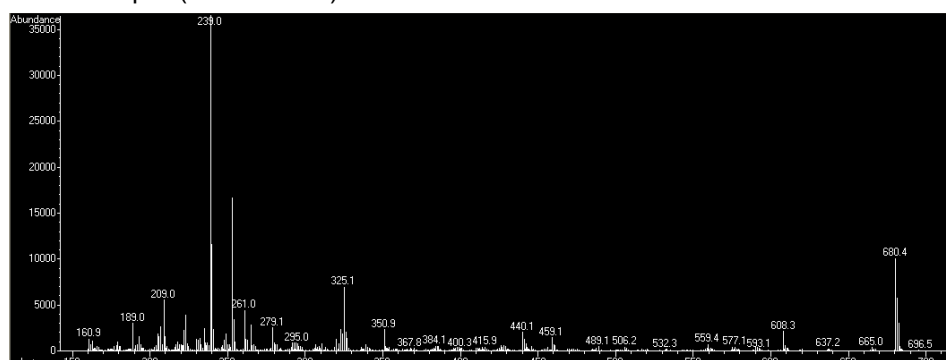
Dimer 20: Isochroman



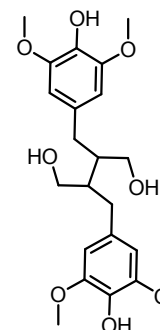
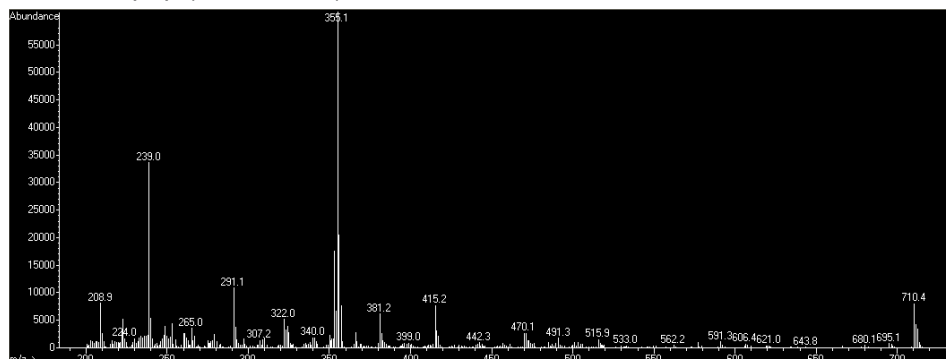
Dimer 21: Unknown compound (M^+ : 708)



Dimer 22: β -5 (PohS-PohG)



Dimer 23: β - β (PohS-PohS)



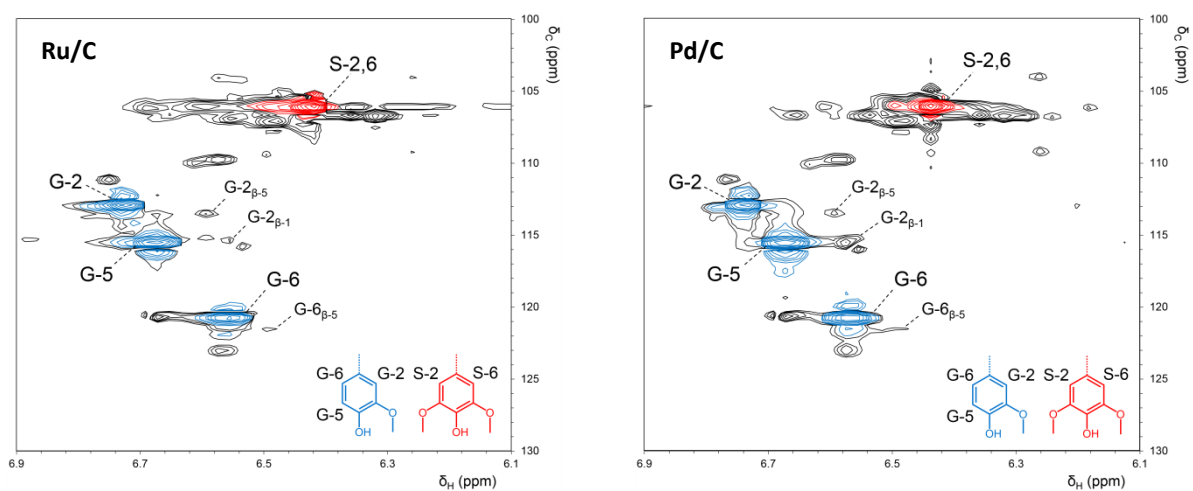


Fig. S2 Comparing the aromatic regions of the HSQC NMR spectra from the lignin oils obtained after birch hydrogenolysis with Ru/C (left) and Pd/C (right).

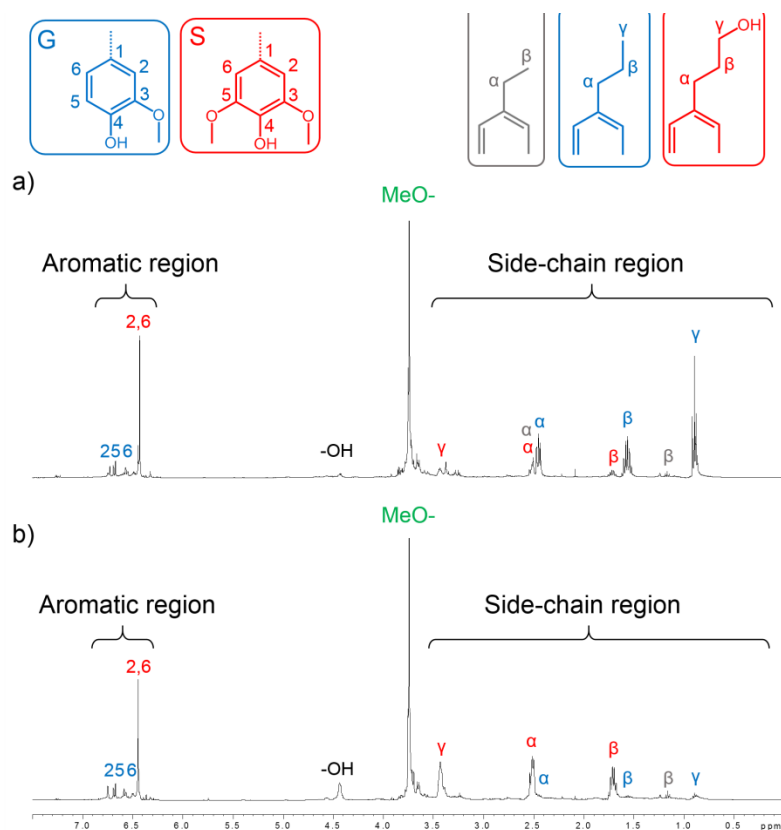


Fig. S3 Comparing the ^1H NMR spectra from the lignin oils obtained after birch hydrogenolysis with a) Ru/C and b) Pd/C.

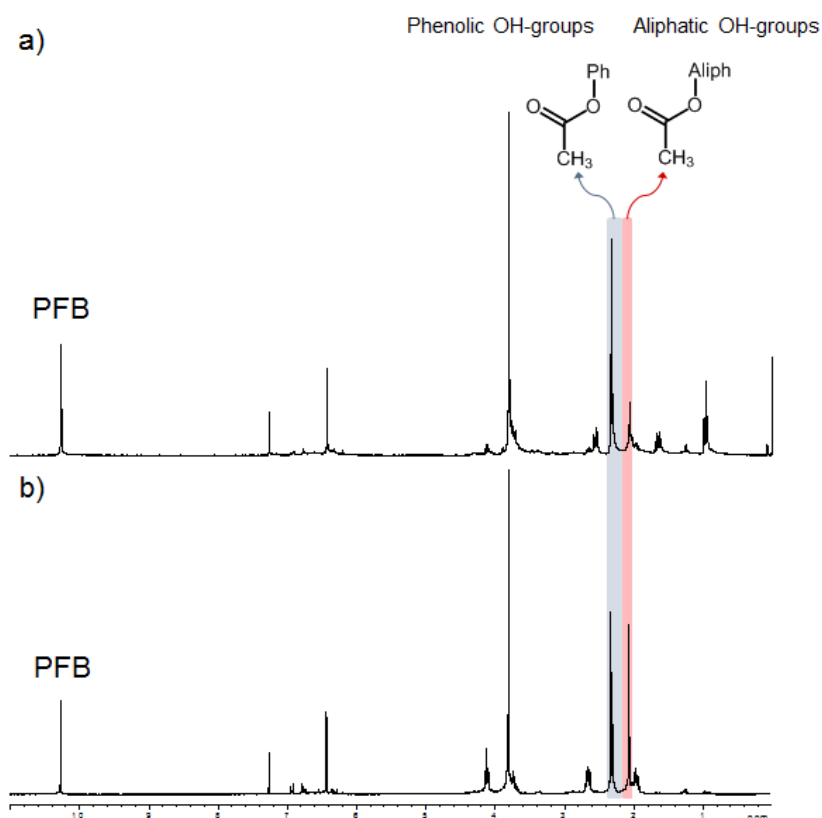


Fig. S4 Comparing the $^1\text{H-NMR}$ spectra of the acetylated lignin oil after reaction with a) Ru/C and b) Pd/C. Pentafluorobenzaldehyde (PFB, 10.3 ppm) was added as an internal standard for quantification of the acetate groups in each sample.

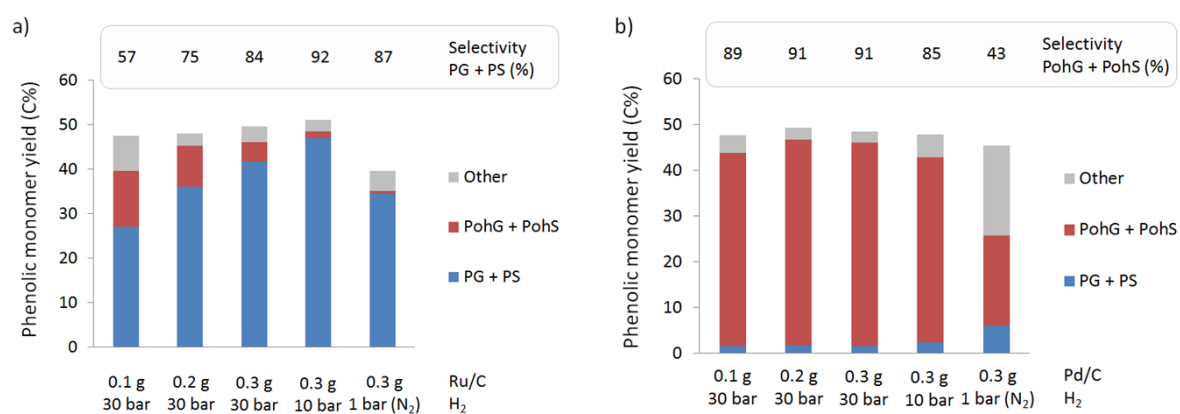


Fig. S5 Tuning the product selectivity. Both the catalyst to biomass ratio and the H_2 -pressure have a different influence on the selectivity of a) Ru/C and b) Pd/C. Reaction conditions: 2 g extracted birch sawdust, 40 mL methanol, 523 K, 3 h.

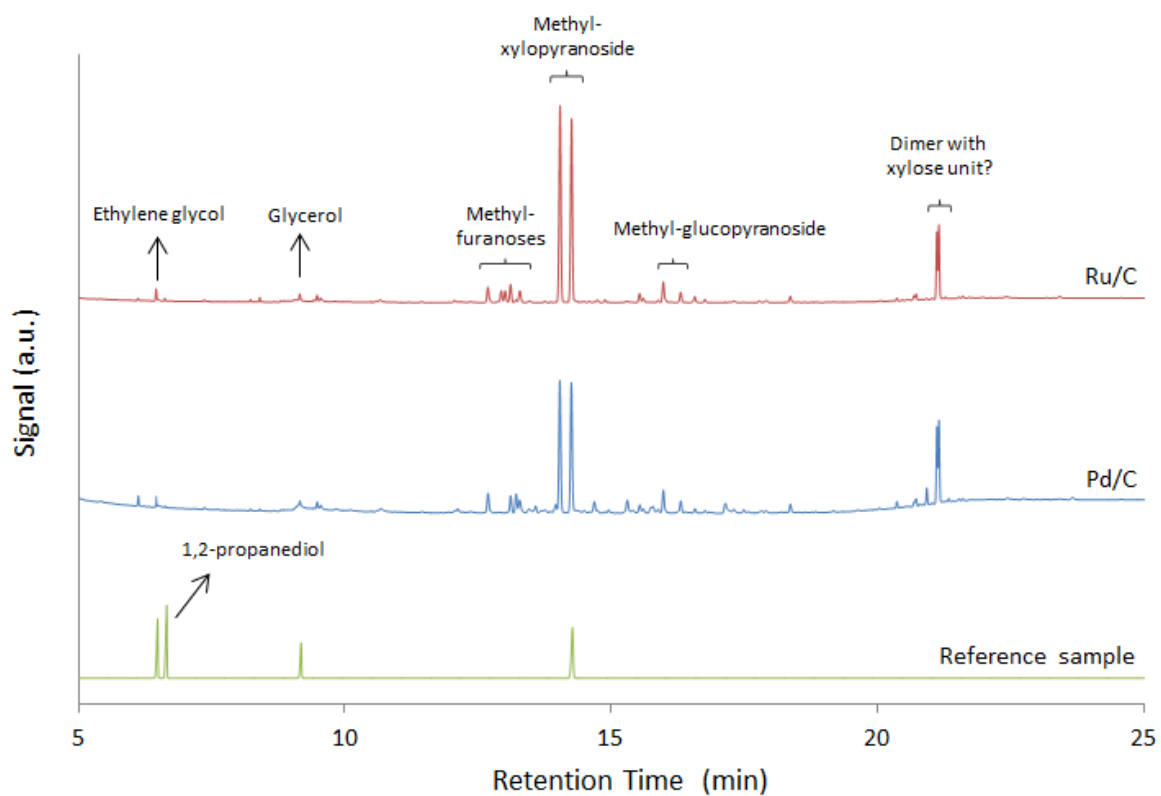


Fig. S6 Gas chromatogram of the solubilized sugar fraction after birch hydrogenolysis with Ru/C or Pd/C. The water soluble fraction was dried, derivatized via trimethylsilylation and analyzed via GC-MS. The gas chromatogram of a reference sample, containing ethylene glycol, 1,2-propanediol, glycerol and methyl β -D-xylopyranoside is also given.

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