Electronic Supplementary Information for

Lignin depolymerization to monophenolic compounds in a flow-through system

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1. General considerations

All chemicals were purchased from Sigma-Aldrich unless otherwise stated. Birch sawdust (mix of *Betula Pendula* and *Betula Pubescens*) was provided by Vanhälls Såg AB. The feedstock was air-dried (RT) and stored in closed containers until use, if necessary, milled with a cutting mill.

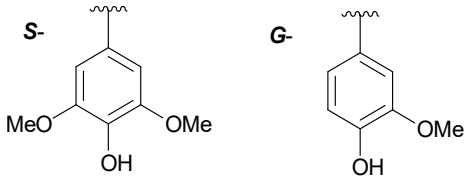
^{1}H NMR, ^{13}C NMR, and 2D NMR spectra were acquired on an Agilent 400-MR (400 MHz, 101 MHz respectively) spectrometer and a Bruker 600 MHz Avance III spectrometer equipped with a QCI-P cryoprobe. Chemical shifts are reported in parts per million (δ) relative to $CHCl_3$ (7.26 ppm for ^{1}H) as an internal standard.

Gas chromatography-mass spectrometry (GC-MS) spectra were recorded on an Agilent Technologies GC system 7820A and 7890A equipped with Mass Selective Detector (5975). The columns used for the experiments were fused silica capillary columns ZB-5HT and CP-SIL 8 CB Low Bleed, (30 m × 0.25 mm × 0.25 µm). Helium was used as a carrier gas. Mass selective detector with electron ionization (70 eV) was used for the analysis in a scan mode (m/z 50 to 500, ion max 2000000).

Size exclusion chromatography (SEC) was performed using a YL 9110 HPLC-GPC system (YL Instrument Co., Ltd., Dongan-gu, Anyang-si, Kyounggi-do, 431-836, The Republic of Korea) with three Styragel columns (HR 0.5, HR 1, and HR 3 7.8×300 mm each) connected in series (flow rate: 1 mL·min^{-1}; injection volume: 50 µL; THF), a UV detector (254 nm), and an auto-sampler. The system was calibrated using ReadyCal-Kit poly(styrene) (MP 266, 682, 1250, 2280, 3470, 4920, 9130, 15700, 21500, 28000, 44200, 66000 Da). Samples were dissolved in THF.

Absorption spectra were measured using a Shimadzu UV-1650PC spectrometer.

Syringol and guaiacol units are denoted with letters ***S*** and ***G***, respectively.



2. Scheme of the flow reactor

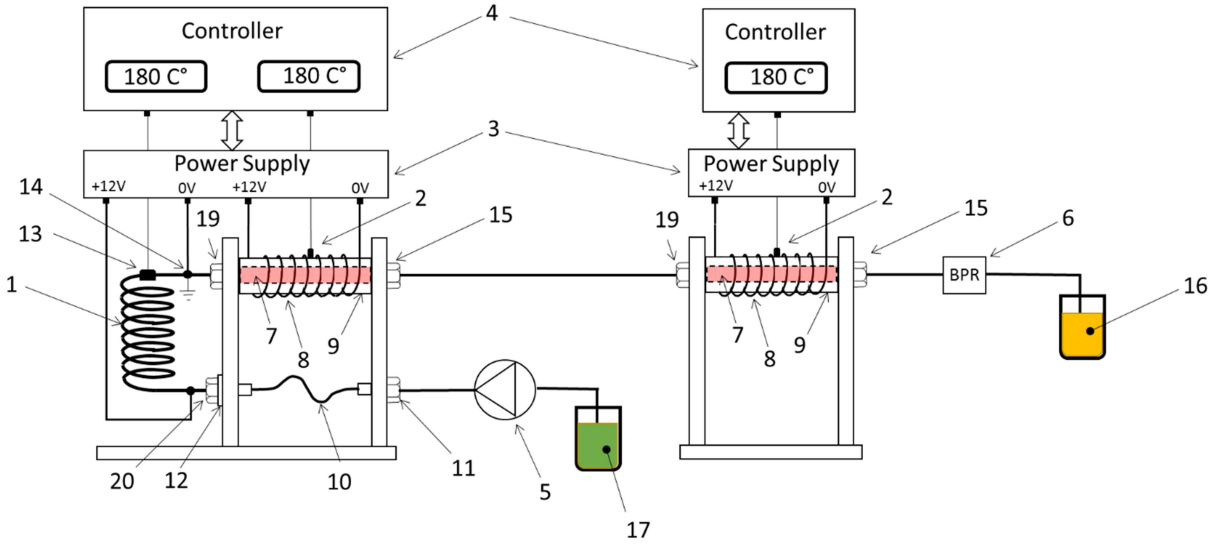


Fig S1. Schematic reactor representation.

The system has two separate flow reactors in series. First a pre-heater (1) to heat the reaction mixture (17) to a predetermined temperature before it enters into the cartridge flow reactor (7). The pre-heater consists of a coil reactor made of a stainless steel capillary. The volume of the pre-heater can easily be changed by varying the inner diameter and the length of the capillary. The volume and length of the pre-heater should be dimensioned in such a way that the desired outlet temperature is reached closed to the outlet of the pre-heater. If the flowrate, inner diameter of the capillary and thermal properties of the reaction mixture are known, the length of the pre-heater is easily calculated using known thermodynamic equations. Pre-heaters are available in different sizes and easily installed. The pre-heater is heated by resistive heating by passing a current through the capillary. The capillary in itself will be the heating element and the heat transfer to the liquid will be through convection. The temperature is controlled by having a thermocouple (13) close to the

outlet and connected to the controller and thereby regulating the temperature at the outlet to the desired value. The regulator is a PID type regulator with a switched solid state relay. The power supply (3) providing the power has its +12 volt connected to the inlet side of the coil and the 0 volt connected to the side that is attached to the cartridge heater. The +12 V side is galvanically isolated from the rest of the instrument by an isolator (12). The inlet of the system is connected to the pump (5) by a peace of PEEK tubing (10) to further galvanically isolate the inlet from the +12 V.

The cartridge heater is basically a small tunnel oven. The cartridge (7) is mounted in an aluminium oxide (Al_2O_3) tube (9) with two spring loaded end pieces (19, 20) as sealing elements. Outside the Al_2O_3 tube a heating coil (8) is arranged with good thermal contact with the Al_2O_3 tube. The generated heat is efficiently transferred to the cartridge through the Al_2O_3 tube, which has a very high heat transfer rate. The heating coil is connected to the power supply (3) and regulated through the same type of PID regulator as for the pre-heater. In this case the reactor (cartridge) is not in electrical contact with the power supply. The heat transfer will be through conduction and convection. The temperature sensor (2) is mounted close to the cartridge in the Al_2O_3 tube. The cartridge heater requires substantially less power as it only has to maintain a constant temperature of the preheated reaction mixture. The inlet (19) and outlet (15) end pieces of the cartridge heater has a spring loaded sealing mechanism to compensate for thermal movement of the components and secure a leak tight connection over the whole temperature and pressure range. The cartridge could easily be exchanged by unscrewing the front end piece (see Fig 4) and replace with a new cartridge.

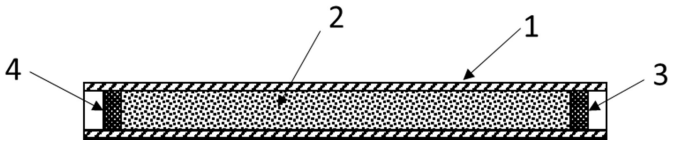


Fig S2. Scheme of the cartridge.

The cartridge (7; Fig S2) consists of a stainless steel tube (1) with an inner diameter of 4 mm and a total length of 35 mm. In both ends a stainless steel frit (3, 4) is inserted to hold the solid phase material (2) in place. The frit has a pore size of 5-10 µm. The cartridge can be packed with any solid material that could be used for chemical transformations. The cartridge is easily packed and sealed by using a packing device that inserts the both frits.

To maintain the necessary backpressure in the system a back pressure regulator (6) is mounted on the outlet (15) of the system. The back pressure regulator could generate a variable back pressure of 1–150 bar.

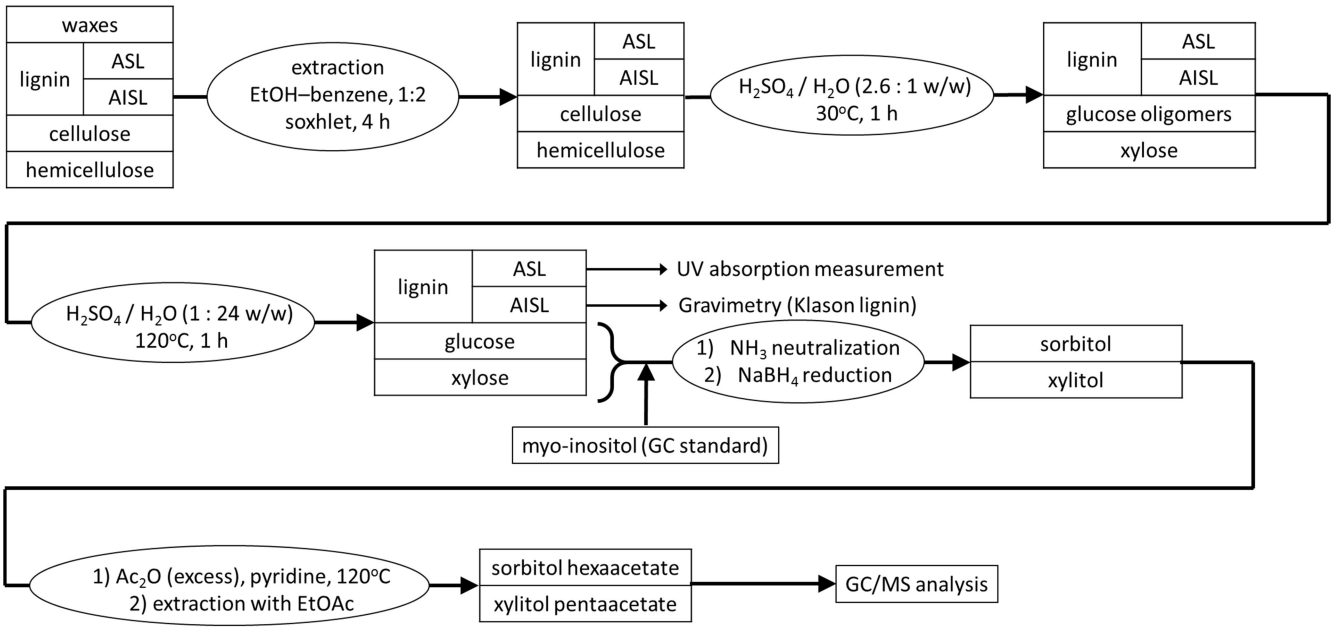
The system could be run without the pre heater. In this case a bypass capillary is mounted between connection 19 and 20 and the power supply +12V line disconnected. Another arrangement with a second cartridge heater is shown in the right part of Fig S1 where the outlet (15) of the first cartridge heater is connected directly to the inlet (19) of the second cartridge heater.

Technical specifications:
Pressure: 1–150 bar, adjustable with a back pressure regulator
Temperature: RT–250 °C
Flowrate: depending on desired residence time in the cartridge and pre-heater, typically 0.1–10 mL/min
Pre-heater volume: 0.1-5 ml, depending on inner diameter and length.
Cartridge volume: 0.35 ml

Fig S3. Photo of one assembled reactor.

Fig S4. Cartridge installation.

3. Analysis of wood meal composition



Scheme S1. Determination of the wood meal composition

3.1 Determination of extractives and ash content

Samples of sieved oven-dried wood meal (45 °C) were dewaxed using a Soxhlet extractor with an EtOH-benzene 1:2 mixture for 10 h, and then dried in vacuum at 40–50 °C for 5 h. The weight loss was recorded and the content of extractives in wood meal was determined as a ratio of a weight loss to the starting mass of wood meal. The ash content was determined gravimetrically by incinerating an oven-dried wood sample in a muffle furnace at about 500 °C for 2 h and weighing the residue (3.001 g of dry wood provided 44 mg ash, 1.5%).

3.1.1 Analysis of extractives. The solution obtained from the Soxhlet extractor was concentrated in vacuum and the oily residue was dissolved in $CDCl_3$ and subjected to NMR. Trace amounts of aromatic units were observed in the NMR analysis. A part of the solution (approximately 50 µL) was diluted with THF, treated with pyridine and BSTFA at 50 °C and subjected to GC-MS analysis.

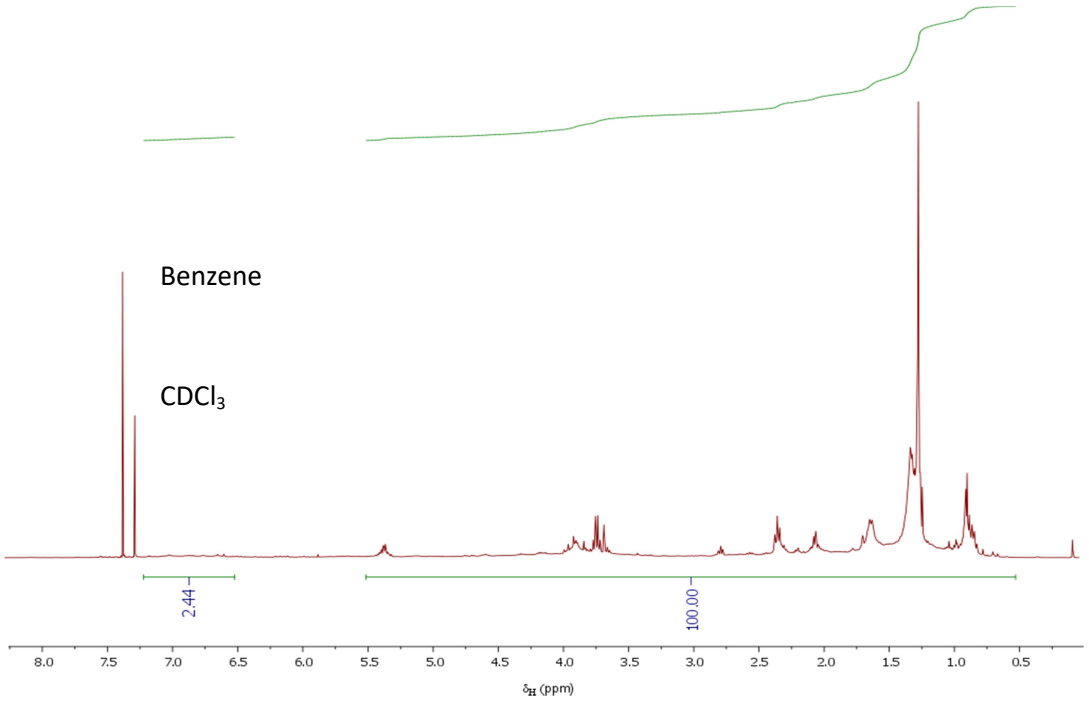


Fig S5. ^{1}H NMR spectrum of extractives.

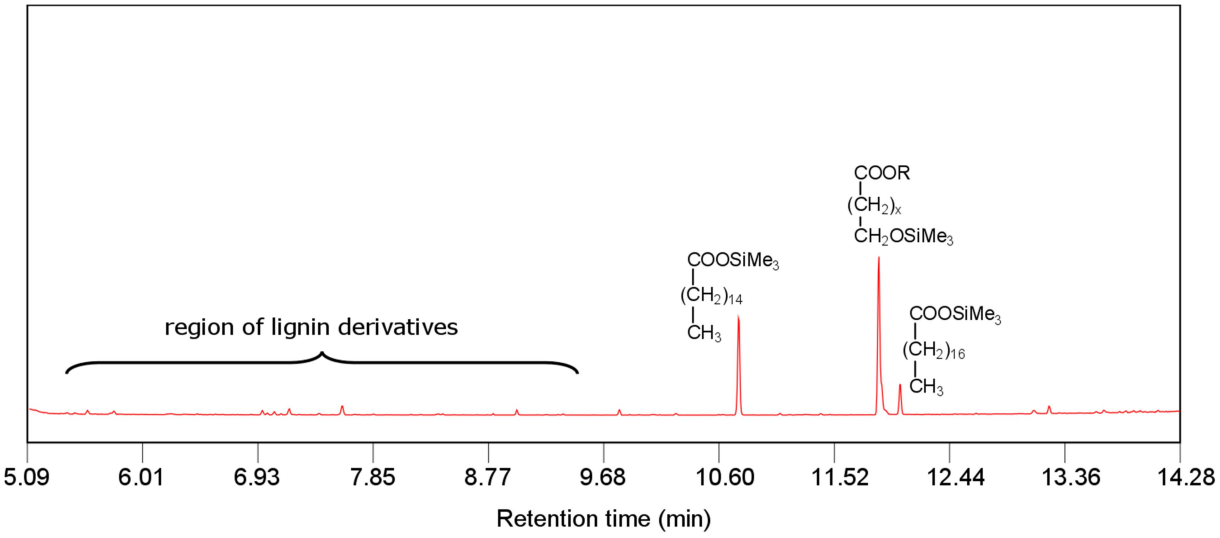


Fig S6. GC-MS spectrum of extractives.

3.2 Determination of carbohydrates and lignin content

Wood meal analysis of glucans, xylans, and lignin was performed according to a modified procedure of NREL/TP-510-4261.[1] Samples of sieved oven-dried wood meal (40 mg) were placed in pressure tubes together with 72% w/w aqueous sulfuric acid (0.4 mL). Each tube was capped, vortexed, and incubated at 30 °C for 1 h. Water (12 mL) was added and the tube was sealed (Mixture A). *D*-xylose (10 mg) and *D*-glucose (20 mg) were dissolved in 4% w/w aqueous sulfuric acid (12 mL). This solution (Mixture B) was placed in a pressure tube and treated in parallel with wood samples to estimate decomposition of carbohydrates during the analysis process. Each tube was incubated at 120 °C for 1 h. The tubes were cooled in an ice bath and *myo*-inositol (0.5 mL of 20 mg·mL^{-1} aqueous solution) as internal standard was added. The tubes were shaken for a few minutes.

3.2.1 Carbohydrates. Mixture A was filtered through a filter paper and 0.5 mL of filtrate was placed in another pressure tube and neutralized with NH_3 (0.2 mL, 30% water solution). $NaBH_4$ (0.1 mL, 0.1 g·mL^{-1} solution in 6% aqueous NH_3) was added to the neutralized filtrate and the resulting solution was kept at RT for at least 0.5 h. AcOH (0.2 mL), Ac_2O (5 mL), and pyridine (0.5 mL) were added to the solution, the tube was sealed, and incubated at 120 °C for 0.5 h. The tube was cooled in an ice bath and its contents were transferred to a separation funnel followed with EtOAc (10 mL) and water (10 mL). The funnel was shaken vigorously. After formation of two layers, the upper one was separated and subjected to GC-MS analysis. GC-MS analysis: injector was operated at 250 °C, and 1:10 split ratio was used. A temperature gradient program was used for the elution: from 100 to 300 °C (14 °C·min^{-1}). Retention times: xylitol pentaacetate 9.74 min, *myo*-inostiol hexaacetate 11.14 min, sorbitol hexaacetate 11.30 min. The content of cellulose and hemicellulose in wood was calculated from GC-MS data according to the following equations:

$$\frac{\%\text{hemicellulose}}{100} = \frac{I_A(\text{xylitol pentaacetate}) \cdot m_A(myo\text{-inostiol})}{I_A(myo\text{-inostiol hexaacetate}) \cdot m_A(\text{wood})} \cdot \frac{I_B(myo\text{-inostiol hexaacetate}) \cdot m_B(\text{xylose})}{I_B(\text{xylitol pentaacetate}) \cdot m_B(myo\text{-inostiol})}$$

$$\frac{\%\text{cellulose}}{100} = \frac{I_A(\text{sorbitol hexaacetate}) \cdot m_A(myo\text{-inostiol})}{I_A(myo\text{-inostiol hexaacetate}) \cdot m_A(\text{wood})} \cdot \frac{I_B(myo\text{-inostiol hexaacetate}) \cdot m_B(\text{glucose})}{I_B(\text{sorbitol hexaacetate}) \cdot m_B(myo\text{-inostiol})}$$

where indexes A and B correspond to chromatograms of treated wood hydrolyzates (Mixture A) and model mixtures of sugars (Mixture B), respectively.

3.2.2 Lignin. The total lignin content in wood meal was determined as a sum of acid insoluble lignin and acid-soluble lignin.

Acid insoluble lignin (AIL). The residue on the filter paper from filtering Mixture A was dried in air at 50 °C for 10 h and weighed. The content of acid insoluble lignin in wood was determined as the ratio of obtained mass to the mass of wood. Ash content was determined gravimetrically by incinerating the filter paper (ash-free) with the lignin sample in a muffle furnace at about 500 °C for 2 h and then weighing the resulting residue.

Acid-soluble lignin (ASL). The filtrate obtained from Mixture A was diluted 10 times and subjected to UV-spectrometry analysis. The absorbance was measured at 240 nm and the content of acid-soluble lignin (%ASL) in wood was estimated according to the equation:

$$\frac{\%\mathrm{ASL}}{100} = \frac{V_{\mathrm{filtrate}} \cdot \mathrm{Dilution}}{m(\mathrm{wood}) \cdot l} \cdot \frac{\mathrm{UVabs}(\lambda)}{\varepsilon(\lambda)}$$

where $\mathrm{UVabs}(\lambda)$ is absorbance at the certain wavelength, V_{filtrate} is the filtrate volume, $m(\mathrm{wood})$ is wood mass, l is the length of optical pathway (1 cm), and $\varepsilon(\lambda)$ is the molar extinction coefficient at the certain wavelength. The following value of extinction coefficient reported in the literature for the hardwood ASL was used: $\varepsilon(240\ \mathrm{nm}) = 12\ \mathrm{L} \cdot \mathrm{g}^{-1} \cdot \mathrm{cm}^{-1}$.[1]

3.3 Composition of the wood meal

Table S1. Composition of the wood meal in wt% on a dry basis.

Component	wt%
Extractives	3
Xylans	25
Glucans	38
Lignin (ASL+AIL)	23
Sum	89

3.4 Thioacidolysis

A wood sample (5 mg) was placed in a tube under argon atmosphere, followed by addition of 1 mL of the thioacidolysis reagent per mg of wood (10% v/v EtSH, 2.5% v/v $BF_3{\cdot}Et_2O$ in distilled 1,4-dioxane). The sealed tubes were placed in an oil bath (99 °C) for 4 h. The reaction was stopped by placing the tubes in an ice bath. Tetracosane was added to each tube as an internal standard for the GC-MS analysis (0.2 mL of 4 mg·mL^{-1} solution in DCM). The mixtures were basified with a saturated aqueous solution of $NaHCO_3$ to pH 3–5. Water (2 mL) and DCM (1 mL) were added to each tube. The tubes were shaken vigorously and the organic phase was separated with a Pasteur pipette and dried over Na_2SO_4. The obtained solutions were concentrated in vacuum. The residues were re-dissolved in DCM (1 mL), placed in GC-vials, derivatized by adding pyridine (0.2 mL), bis(trimethylsilyl)trifluoroacetamide (0.1 mL), and heated at 40 °C for 1 h prior to GC-MS analysis. GC-MS analysis: injector was operated at 300 °C, and 1:50 split ratio was used. The following temperature gradient program was used for the elution: from 50 to 100 °C (1.7 °C·min^{-1}), then to 320 °C in 13 min (17 °C·min^{-1}). Response factors for ***G*** and ***S*** unit derivatives were taken from the literature (0.47 and 0.53 correspondingly; TIC mode and tetracosane as an internal standard).[7] The average yield of lignin-derived monophenolic compounds of birch wood meal obtained from the thioacidolysis reaction was 45 wt%.

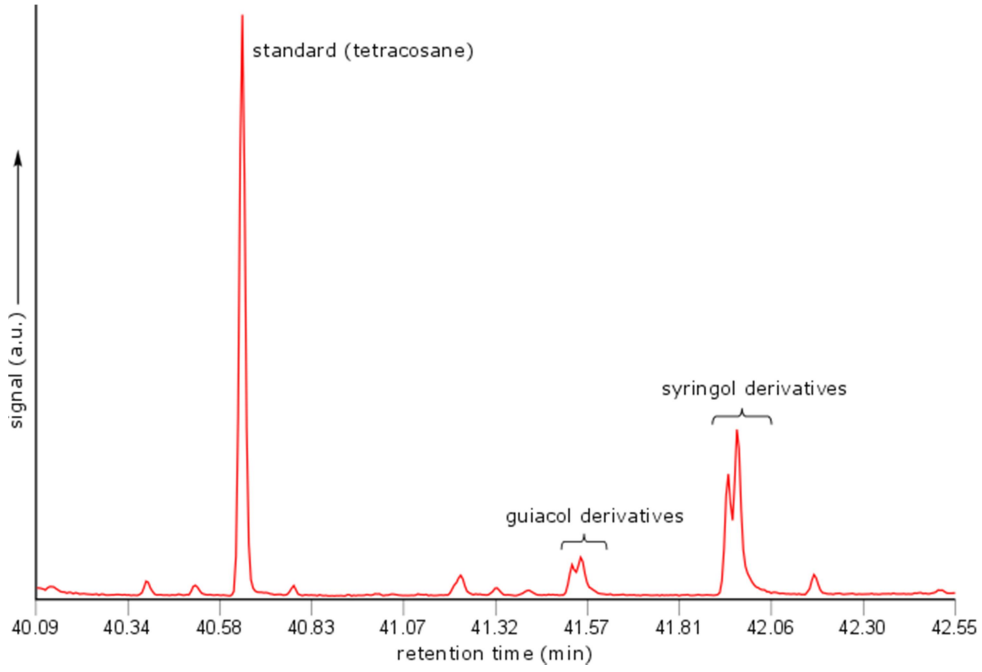


Fig S7. A part of typical gas chromatogram mass spectrometry detector trace for wood meal thioacidolysis products.

3.5 β-O-4' Bond content and theoretical yield of lignin-derived monophenolic compounds

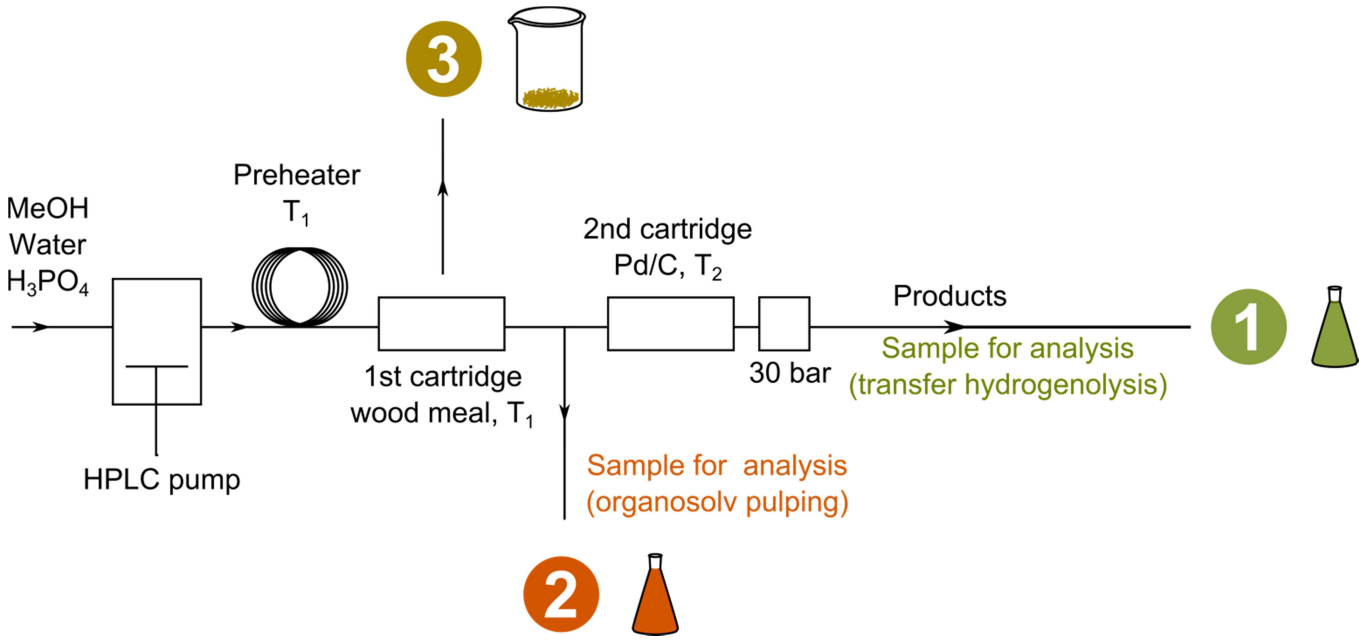
For simplifying the calculation, we assume that the lignin is a linear polymer of an infinite length. When a monomeric unit on both sides is connected with β-O-4' bonds, it will release a lignin-derived monophenolic compound after the thioacidolysis reaction. Mathematically, the maximum theoretical yield of lignin-derived monophenolic compounds will be equal to the square of the fraction of cleavable bonds in the polymer structure. If the yield of lignin-derived monophenolic compounds is known and we can assume that all β-O-4' bonds were cleaved, we can find the frequency of the β-O-4' bonding moiety. Using $k = 1$ in the formula for $p(k)$, one can obtain the theoretical yield of lignin-derived monophenolic compounds: $p(1) = \varphi_B^2$ (See section 9), where φ_B is the frequency of the β-O-4' moiety. As the average yield of lignin-derived monophenolic compounds for birch wood meal obtained from thioacidolysis reaction was 45 wt%, the β-O-4' bonds content is determined by:

$$\text{frequency of β-O-4' moiety (\%)} = \sqrt{\frac{45\%}{100\%}} \times 100\% = 67\%$$

A lignin polymer with 67% β-O-4' bonds should therefore have a theoretical maximum yield of lignin-derived monophenolic compounds of 45%.

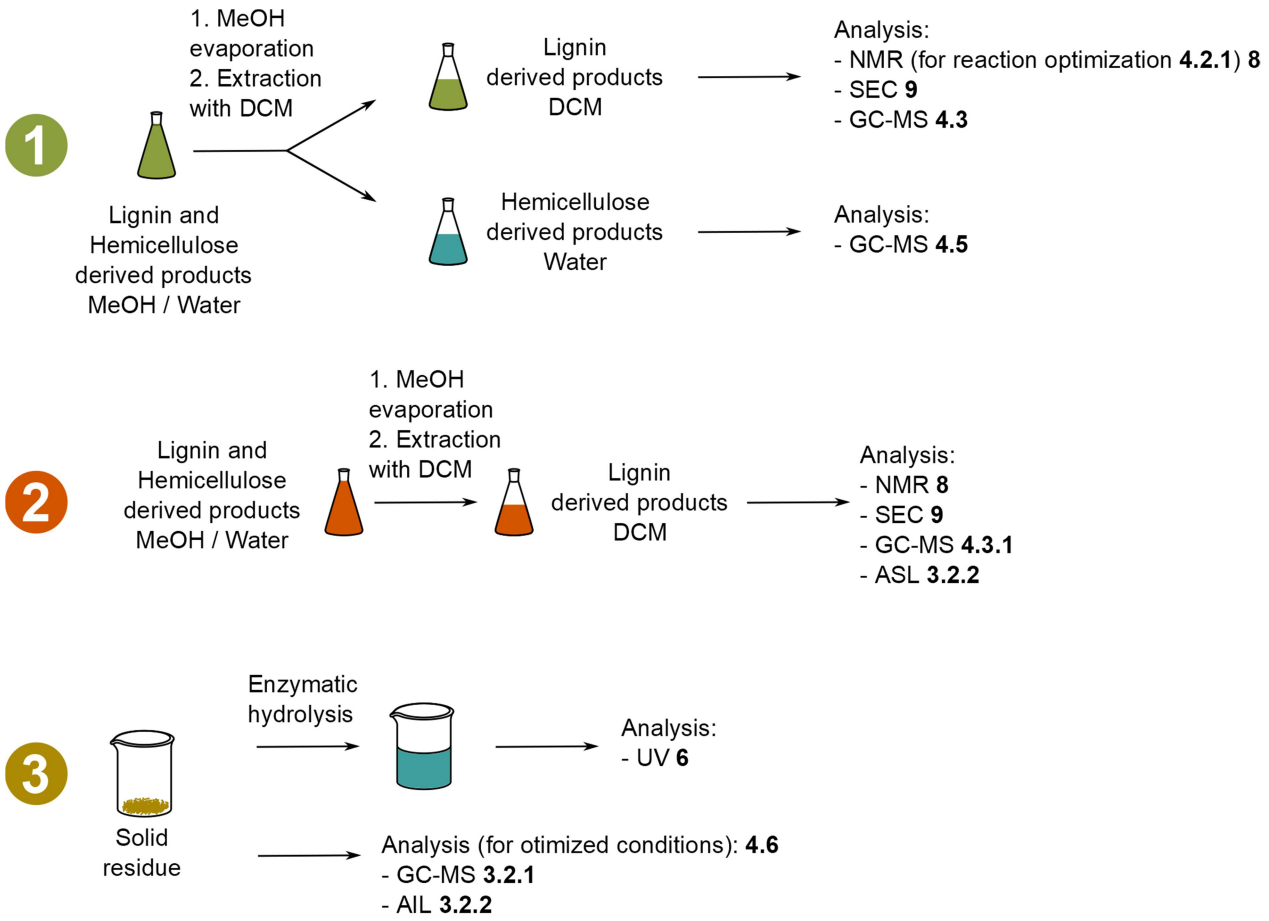
4. Flow reactions

4.1. General procedure



Scheme S2. Schematic representation of the experimental setup and main products obtained, where **1** is the liquid fraction obtained after organosolv pulping and Pd/C catalyzed transfer hydrogenation/hydrogenolysis; **2** is liquid fraction obtained after organosolv pulping solely; **3** is the solid wood meal residue after the pulping process. Back Pressure Regulator pressure for optimized reaction conditions.

Unless otherwise stated, untreated wood meal of birch was used in the experiments. A wood meal sample (125-150 mg) was loaded into the first cartridge, and Pd/C catalyst (125-150 mg, 5% Pd) was loaded into the second cartridge. In some experiments, wood meal was flushed with solvent or stored under solvent for a specified time or both (see 4.2.2). The whole system was then flushed with solvent, specified flow rate was adjusted, and the collection of solution coming out of the system was started. The second cartridge (Pd/C) was heated (20–40 °C·min^{-1}) to the specified temperature. After the desired temperature was reached, the first cartridge (wood meal) heating was turned on as well. The reaction mixture was collected for a specified period of time.



Scheme S3. Schematic representation of the analysis performed with each fraction. All analysis performed for the samples obtained at the optimized reaction conditions (Table S6, Entry 5). Optimization of the reaction conditions (4.2.2) is performed based on the ^{1}H NMR and SEC data.

4.2 Analysis of lignin fraction and optimization of reaction conditions

4.2.1 Estimation of the content of Lignin-derived monophenolic compounds by NMR spectroscopy. Methanol was removed from the reaction mixture under reduced pressure. When the sample was planned to be subjected to GC-MS analysis tetracosane (99% purity; 0.37 mg·mL^{-1} THF solution) was added to the residue as an internal standard. Then the mixture was extracted twice with DCM (total volume of solvent was 2 mL per mL of water). The organic phase was dried over Na_2SO_4 and concentrated in vacuum and water phase was preserved. The residue was dissolved in a standard solution of CH_3NO_2 (96% purity, spectrophotometric grade) in $CDCl_3$ (4 mg·mL^{-1}, 0.6 mL).

The less polar products were obtained in $CDCl_3$ and more polar products were obtained in water in the following analysis.

^{1}H NMR (400 MHz) was recorded to determine the content of ***G*** and ***S*** monophenolic units. The yield of reduced lignin-derived monophenolic compounds (% of total wood lignin) was estimated using ^{1}H NMR data, according to the following equation:

$$Monomer\ yield = \frac{m_{std} \cdot 0.96}{M_{std}} \cdot \frac{(M_S \cdot 1.5\ I_S + M_G \cdot 3.0\ I_G\ )}{I_{std}} \cdot \frac{1}{m(\text{wood}) \cdot \omega_L}$$

where m_{std} – mass of added CH_3NO_2; I_G – integral 6.75–6.83 ppm (guaiacol units, 1H); I_S – integral 6.36–6.42 ppm (syringol units, 2H); I_{std} – integral 4.28–4.31 ppm (methyl group in CH_3NO_2, 3H); M_G = 180 g·mol^{-1} – molar mass of coniferyl alcohol; M_S = 210 g·mol^{-1} – molar mass of sinapyl alcohol (syringol-derived monolignol); M_{std} = 61 g·mol^{-1} – molar mass of CH_3NO_2; $m(\text{wood})$ – mass of used wood; ω_L – total lignin content in wood.

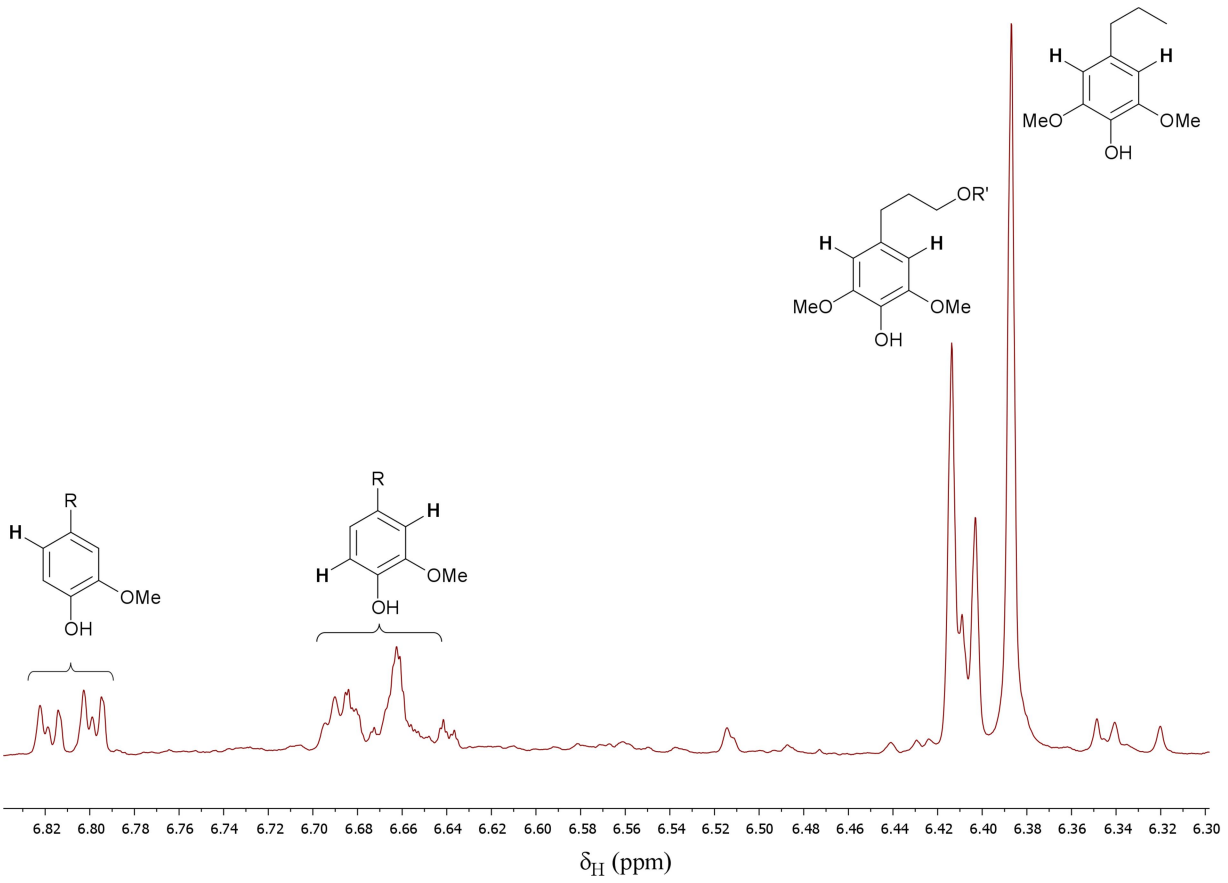


Fig S8. A part of typical ^{1}H NMR spectrum demonstrating the signals of syringol and guaiacol aromatic units chosen for quantification.

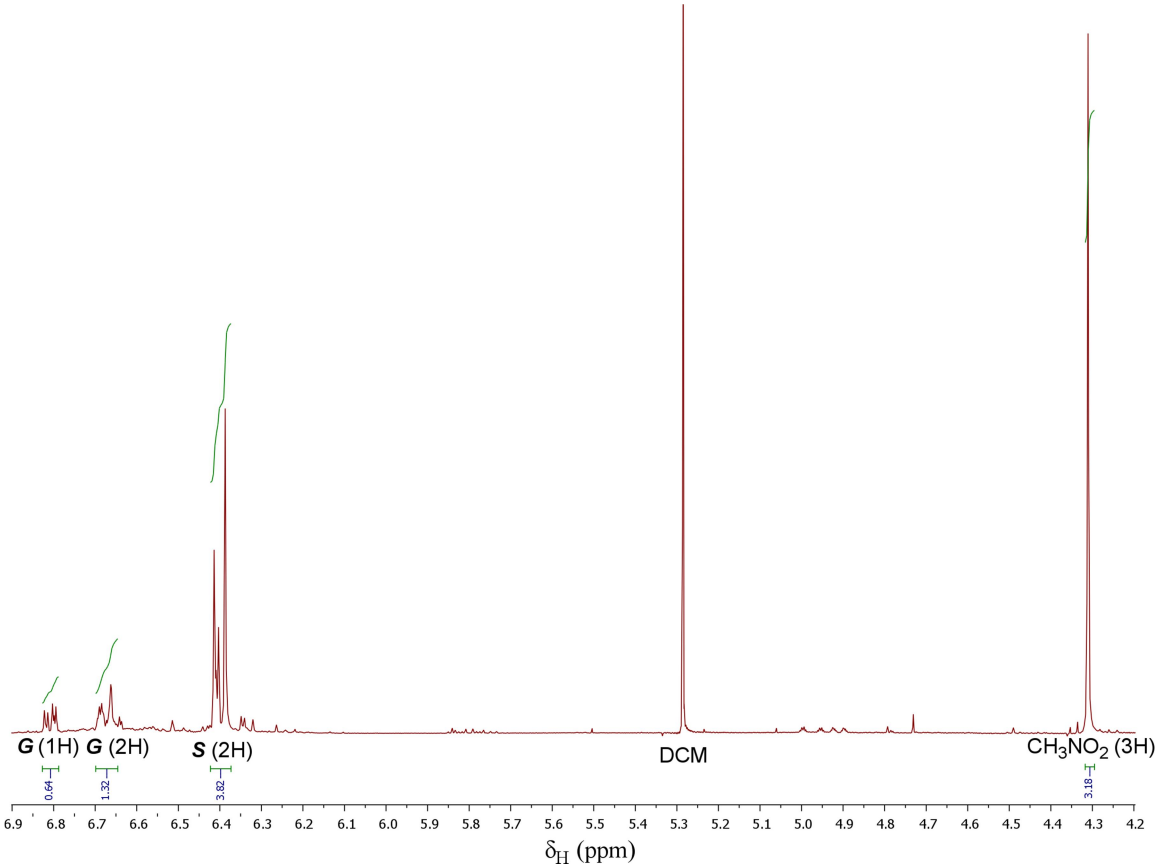


Fig S9. A part of typical ^{1}H NMR spectrum including the signal of the internal standard (CH_3NO_2).

4.2.2 Optimization of the reaction conditions. The reaction conditions were optimization was performed using ^{1}H NMR spectroscopy to determine lignin derived products (see section 4.2). When the conditions were determined as optimal, they were transferred to the next step of the optimization procedure–colored in gray in the following tables.

Table S1. Optimization step 1: variation of H_3PO_4 concentration. MeOH; preheater off; T_1 = 200 °C; T_2 = 180 °C; flow = 0.2 mL·min^{-1}; BPR = 30 bar; reaction time 3 h.

Entry	H_3PO_4 (g·L^{-1})	Guaiacol yield (µmol·g^{-1} wood)	Syringol yield (µmol·g^{-1}wood)	Total lignin-derived monophenolic compounds yield (wt% of total lignin)
1	0	1	4	0
2	0	0	7	1
3	0.9	17	39	5
4	1.9	16	63	7
5	2.8	20	81	9
6	5	14	43	5
7	10	21	46	6

Table S2. Optimization step 2: variation of water-methanol ratio. H_3PO_4 concentration 2.8 g·L^{-1}, preheater off; T_1 = 200 °C; T_2 = 180 °C; flow = 0.2 mL·min^{-1}; BPR = 30 bar reaction time 3 h.

Entry	Water (v%)	Guaiacol yield (µmol·g^{-1} wood)	Syringol yield (µmol·g^{-1}wood)	Total lignin-derived monophenolic compounds yield (wt% of total lignin)
1	10	33	79	10
2	20	38	107	13
3	30	21	125	14
4	50	6	113	11

Table S3. Optimization step 3: investigation the influence of the preheater. 2.8 g·L^{-1} H_3PO_4 in MeOH–H_2O 7:3 v/v; T_1 = 200 °C; T_2 = 180 °C; flow = 0.2 mL·min^{-1}; BPR = 30 bar reaction time 3 h.

Entry	Preheater	Guaiacol yield (µmol·g^{-1} wood)	Syringol yield (µmol·g^{-1} wood)	Total lignin-derived monophenolic compounds yield (wt% of total lignin)
1	Off	20	125	14
2	On	39	250	27

Table S4. Optimization step 4: variation of temperatures on cartridges. 2.8 g·L^{-1} H_3PO_4 in MeOH-H_2O 7:3 v/v; preheater on; flow = 0.2 mL·min^{-1}; BPR = 30 bar, for Entry 3 BPR = 50 bar; reaction time 3 h.

Entry	T_1 (°C)	T_2 (°C)	Guaiacol yield (µmol·g^{-1} wood)	Syringol yield (µmol·g^{-1} wood)	Total lignin-derived monophenolic compounds yield (wt% of total lignin)
1	180	180	17	167	17
2	200	180	39	250	27
3	220	180	81	180	24
4	200	200	24	214	22
5	200	160	63	188	22

Table S5. Optimization step 5: variation of flow rate and reaction time. 2.8 g·L^{-1} H_3PO_4 in MeOH-H_2O 7:3 v/v; preheater on; T_1 = 200 °C; T_2 = 180 °C; BPR = 30 bar.

Entry	Flow rate (mL·min^{-1})	*t* (h)	Guaiacol yield (µmol·g^{-1} wood)	Syringol yield (µmol·g^{-1} wood)	Total lignin-derived monophenolic compounds yield (wt% of total lignin)
1	0.5	1.2	44	131	16
2	0.5	3	60	172	21
3	0.3	2	60	244	28
4	0.3	3	68	271	31
5	0.2	3	39	250	27
6	0.1	3	~0	~0	~0
7	0.1	6	~0	~0	~0

Table S6. Optimization step 6: investigation of the wood meal pretreatment influence. 2.8 g·L^{-1} H_3PO_4 in MeOH-H_2O 7:3 v/v; preheater on; T_1 = 200 °C; T_2 = 180 °C; flow rate 0.3 mL·min^{-1}; BPR = 30 bar; reaction time 3 h

Entry	Pretreatment	Guaiacol yield (µmol·g^{-1} wood)	Syringol yield (µmol·g^{-1} wood)	Total lignin-derived monophenolic compounds yield (wt% of total lignin)
1	Dewaxed	34	164	18
2	Not dewaxed	68	271	31
3	Not dewaxed, flushed with solvent system before the reaction (RT, 0.3 mL·min^{-1}, 30 min)	92	269	33
4	Dewaxed, flushed with solvent system before the reaction (RT, 0.3 mL·min^{-1}, 30 min)	66	244	29
5	Not dewaxed, flushed with solvent system (RT, 0.3 mL·min^{-1}, 10 min) and left overnight before reaction	125	304	39

4.3 Determination of lignin-derived monophenolic compounds

The reaction mixtures obtained under the optimized reaction conditions (Table S6, Entry 5) were used in all following analysis and studies; also, the optimized reaction conditions were used to obtain the organosolv lignin fraction.

4.3.1 Lignin-derived monophenolic compounds obtained in transfer hydrogenolysis reaction; analysis by GC-MS. 0.1 mL of the solution in $CDCl_3$ (see section 4.2) was diluted with 1 mL THF. The reaction mixture was subjected to derivatization by silylation: pyridine (50 µL) and bis-(trimethylsilyl)trifluoroacetamide (80 µL) were added and the mixture was heated at 50 °C for 15 min. The obtained solution was subjected to GC-MS analysis. The following temperature gradient method was used: injector was operated at 250 °C, and 1:100 split ratio was used. The temperature gradient program was used for the elution: from 70 to 320 °C (20 °C·min^{-1}).

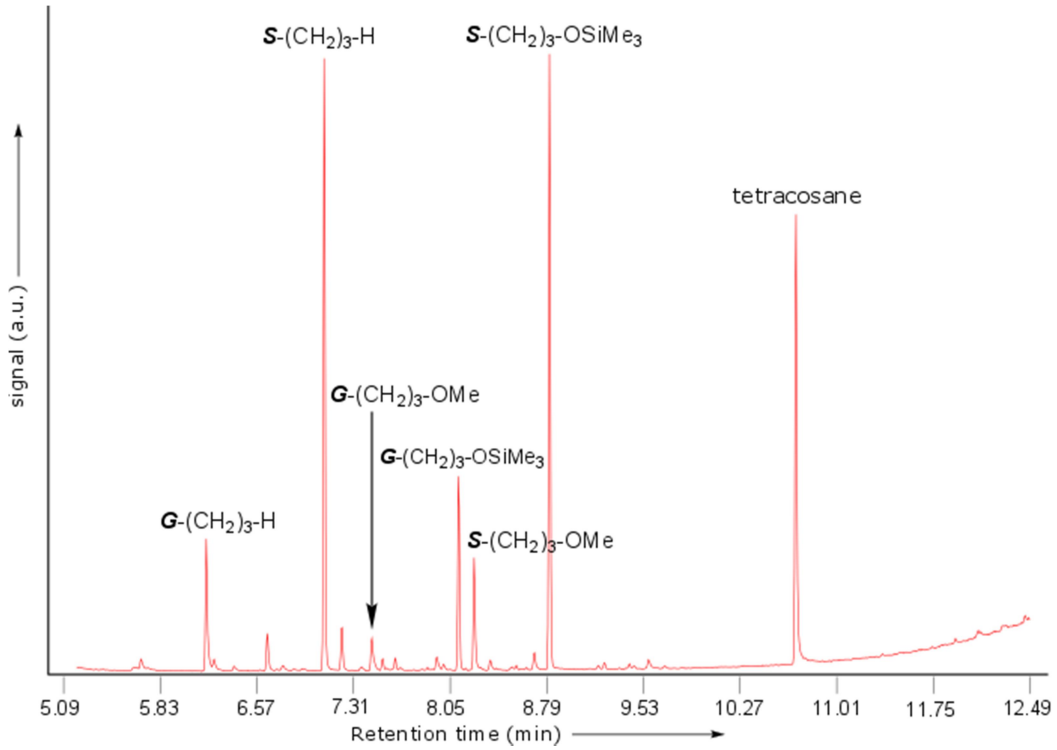


Fig S10. Typical gas chromatogram (MS trace) of monophenolic lignin products (with Pd/C cartridge in line; Reaction conditions: see Table S6, Entry 5) after derivatization.

From left to right:

G-$(CH_2)_3$-H is (2-methoxy-4-propylphenoxy)trimethylsilane;
S-$(CH_2)_3$-H is (2,6-dimethoxy-4-propylphenoxy)trimethylsilane;
G-$(CH_2)_3$-OMe is (2-methoxy-4-(3-methoxypropyl)phenoxy)trimethylsilane;
G-$(CH_2)_3$-$OSiMe_3$ is (3-(3-methoxy-4-((trimethylsilyl)oxy)phenyl)propoxy)trimethylsilane;
S-$(CH_2)_3$-OMe is (2,6-dimethoxy-4-(3-methoxypropyl)phenoxy)trimethylsilane;
S-$(CH_2)_3$-$OSiMe_3$ is (3-(3,5-dimethoxy-4-((trimethylsilyl)oxy)phenyl)propoxy)trimethylsilane.
Relative response factors of the lignin-derived monophenolic compound products were obtained by calibration with commercially available or synthesized standards (see section 9.1).

Table S7. Relative response factors of lignin-derived monophenolic compounds with tetracosane as internal standard; determined for derivatized compounds.

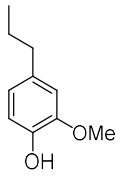
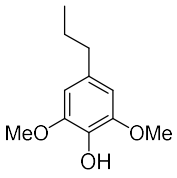
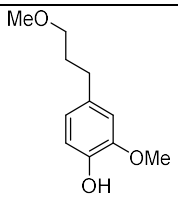
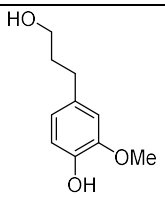
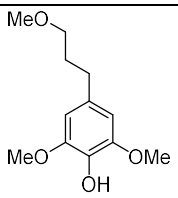
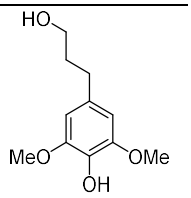
	S-	***G***-
-$(CH_2)_3$-H	0.96	0.92
-$(CH_2)_3$-$OSiMe_3$	0.90	0.73
-$(CH_2)_3$-OMe	0.97	–

4.3.2 Yield calculation of lignin-derived monophenolic compounds from the transfer hydrogenolysis reaction. The yield of six lignin-derived monophenolic compounds obtained at the optimized reaction conditions (Table S6, Entry 5) was determined according to the following formula:

$$\text{Monophenolic compounds yield} = \frac{m_{std} \cdot 0.99}{m(\text{wood}) \cdot \omega_L} \cdot \sum_i \left(a_i \frac{I_i}{I_{std}} + b_i \right)$$

where: m_{std} – mass of added tetracosane; I_i – integral of *i*-st product signal; ω_L –lignin content in wood (ASL + AIL), I_{std} – integral of tetracosane signal; a_i and b_i – parameters of calibration curve for *i*-st product (a_i is a relative response factor).

Table S8. Typical composition of the mixture of lignin-derived monophenolic compounds (with Pd/C cartridge in line; Reaction conditions: see Table S6, Entry 5), wt% of total wood lignin recalculated for non-derivatized lignin-derived monophenolic compounds.

Monophenolic compounds structural formula	 **5b**	 **5a**	 **4b**	 **3b**	 **4a**	 **3a**
wt%	1.9	8.7	1.8	4.2	6.4	14.0

The sum of the six monitored lignin-derived monophenolic compounds corresponds to a 37 wt% yield. The theoretical maximum yield of lignin-derived monophenolic compounds yield was estimated for birch wood meal (section 3.5) to 45%. Therefore, the yield of lignin-derived monophenolic compounds for the six analyzed lignin-derived monophenolic compounds could be calculated as following:

$$\frac{0.37}{0.45} * 100\% = 82\%$$

4.3.3 Concentration of lignin-derived monophenolic compounds obtained in the transfer hydrogenolysis reaction. After initial optimization, a typical concentration of the monophenolic products in the pulping liquor was:

$$c = \frac{(\text{wood mass}) \cdot (\text{total lignin content}) \cdot (\text{lignin} - \text{derived monophenolic compounds yield})}{(\text{flow rate}) \cdot (\text{reaction time})} = \frac{(125\ \text{mg}) \cdot (0.23) \cdot (0.37)}{(0.3\ \text{mL} \cdot \text{min}^{-1}) \cdot (180\ \text{min})}$$
$$= 0.2\ \text{mg} \cdot \text{mL}^{-1}$$

4.3.4 GC-MS analysis of the lignin-derived monophenolic compounds from organosolv pulping. Reaction conditions (Table S6, Entry 5), Pd/C catalysis step was omitted. 0.1 mL of the solution in $CDCl_3$ (see section 4.2) was diluted with 1 mL THF. The reaction mixture was subjected to silylation for derivatization: pyridine (50 µL) and bis-

(trimethylsilyl)trifluoroacetamide (80 µL) were added and the mixture was heated at 50 °C for 15 min. The obtained solution was subjected to GC-MS analysis. The following temperature gradient method was used: injector was operated at 250 °C, and 1:100 split ratio was used. The temperature gradient program was used for the elution: from 100 to 300 °C (14 °C·min^{-1}). The relative response factors of the lignin-derived monophenolic compound products were obtained by calibration with commercially available or synthesized standards (see section 9.1). Relative response factor of 2,6-dimethoxy-4-(3-methoxyprop-1-en-1-yl)phenol (**2a**) with tetracosane as internal standard, determined for derivatized version of the compounds, is 4.5. Relative response factors of compounds 4-(3-hydroxyprop-1-en-1-yl)-2,6-dimethoxyphenol (**1a**) and 2-methoxy-4-(3-methoxyprop-1-en-1-yl)phenol (**2b**) were assigned the same. In sum, the three monitored lignin-derived monophenolic compounds result in 21 wt% yield on average of three pulping experiment. The yield of 2,6-dimethoxy-4-(3-methoxyprop-1-en-1-yl)phenol (**2a**) was found to be 15wt%.

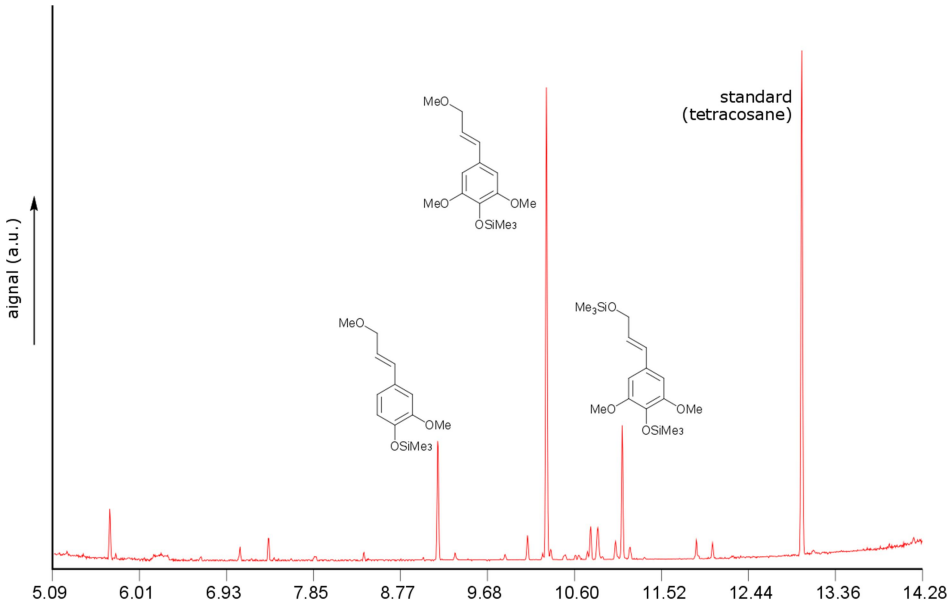


Fig S11. Typical gas chromatogram (MS trace) of monophenolic lignin products from the organosolv pulping process (no Pd/C catalysis, Reaction conditions: see Table S6, Entry 5) after silylation derivatization.

4.4 Studies of kinetics in wood delignification and coupled Pd/C catalysis

The kinetics of delignification in the absence of Pd catalyst was studied using UV spectrophotometry. Samples of fractions obtained at different times were diluted and the absorption at 240 nm corresponding to solubilized lignin compounds was measured. The lignin content was determined the same way as for ASL in the wood (see section 3.2.2). The kinetics for formation of reduced lignin-derived monophenolic compounds in the presence of Pd catalyst was studied using NMR spectroscopy, where yields were determining as described above. In both experiments, the optimized reaction conditions were used: solvent system MeOH-H_2O 7:3 with additive 85% aq. H_3PO_4 (2.8 g·L^{-1}); preheater temperature 200 °C; pulping temperature (1st cartridge, containing wood) 200 °C; hydrogenolysis temperature (2nd cartridge, containing Pd/C) 180 °C; solvent flow rate 0.3 mL·min^{-1}; reaction time 3 h. The two kinetic curves obtained were compared (Fig S12 and S13).

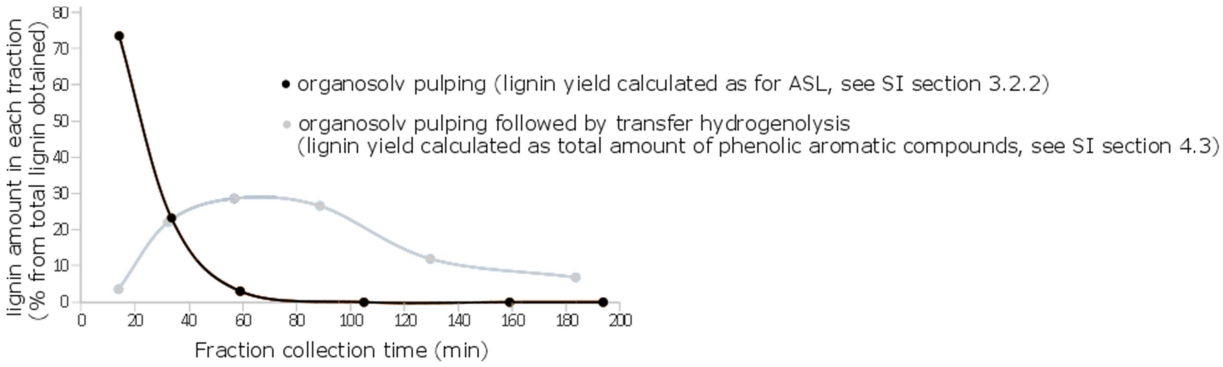


Fig S12. Lignin content in separate fractions obtained at different reaction times in Pd/C-involving and Pd/C-free flow processes (% from total lignin obtained). In case of Pd-free process, samples of organosolv lignin were collected directly after the mixture had passed the 1st cartridge; in case of Pd-catalyzed process, the samples were collected after the mixture had passed both cartridges.

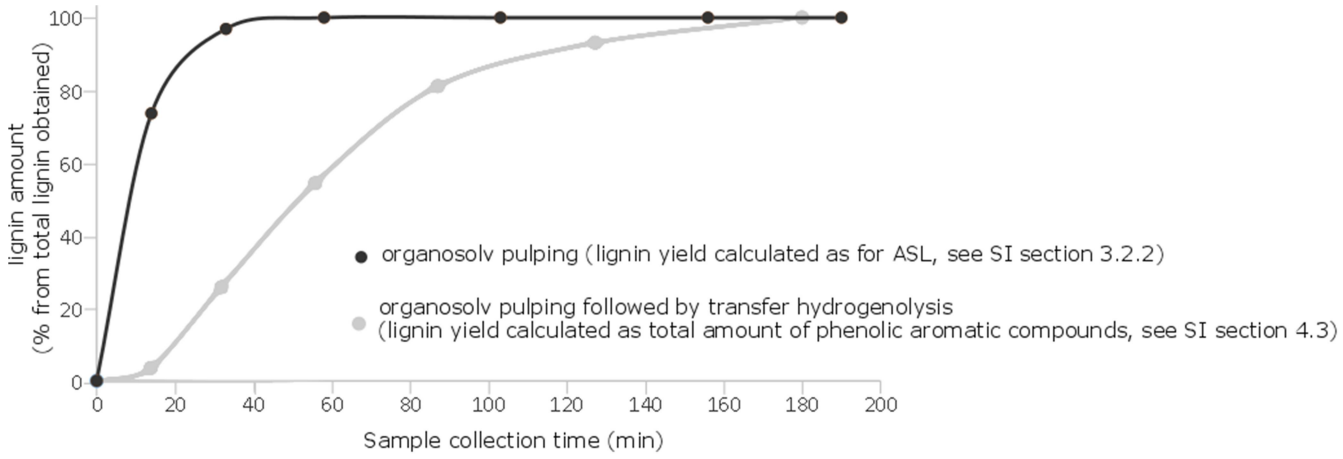


Fig S13. Dependence of lignin yield on time in Pd/C-involving and Pd/C-free flow processes (% from total lignin obtained). Calculated as sum of yields obtained in corresponding fractions (for instance, for the 4th point, sum of the first 4 fractions yields). In case of Pd-free process, samples were collected directly after the mixture had passed the 1st cartridge; in case of Pd-catalyzed process, the samples were collected after the mixture had passed both cartridges.

4.5 Determination of carbohydrate content.

The carbohydrate content of the extracted water phase (see sections 4.2) was determined by the following. 0.5 mL of water phase was placed in a pressure tube and neutralized with NH_3 (0.2 mL of 30% water solution). $NaBH_4$ (0.1 mL of 0.1 mg·mL^{-1} solution in 6% aqueous NH_3) was added to the neutralized filtrate and the resulting solution was kept at RT for at least 0.5 h. AcOH (0.2 mL), Ac_2O (5.0 mL), and pyridine (0.5 mL) were added to the solution, the tube was sealed and incubated at 120 °C for 0.5 h. Then the tube was cooled in the ice bath and its contents were transferred to a separation funnel together followed by addition of EtOAc (10 mL) and water (10 mL). The funnel was shaken vigorously. Immediately after the formation of two layers, the upper one was separated and subjected to GC-MS analysis. The content of carbohydrate derivatives was calculated using the approach shown in the section 3.2.1.

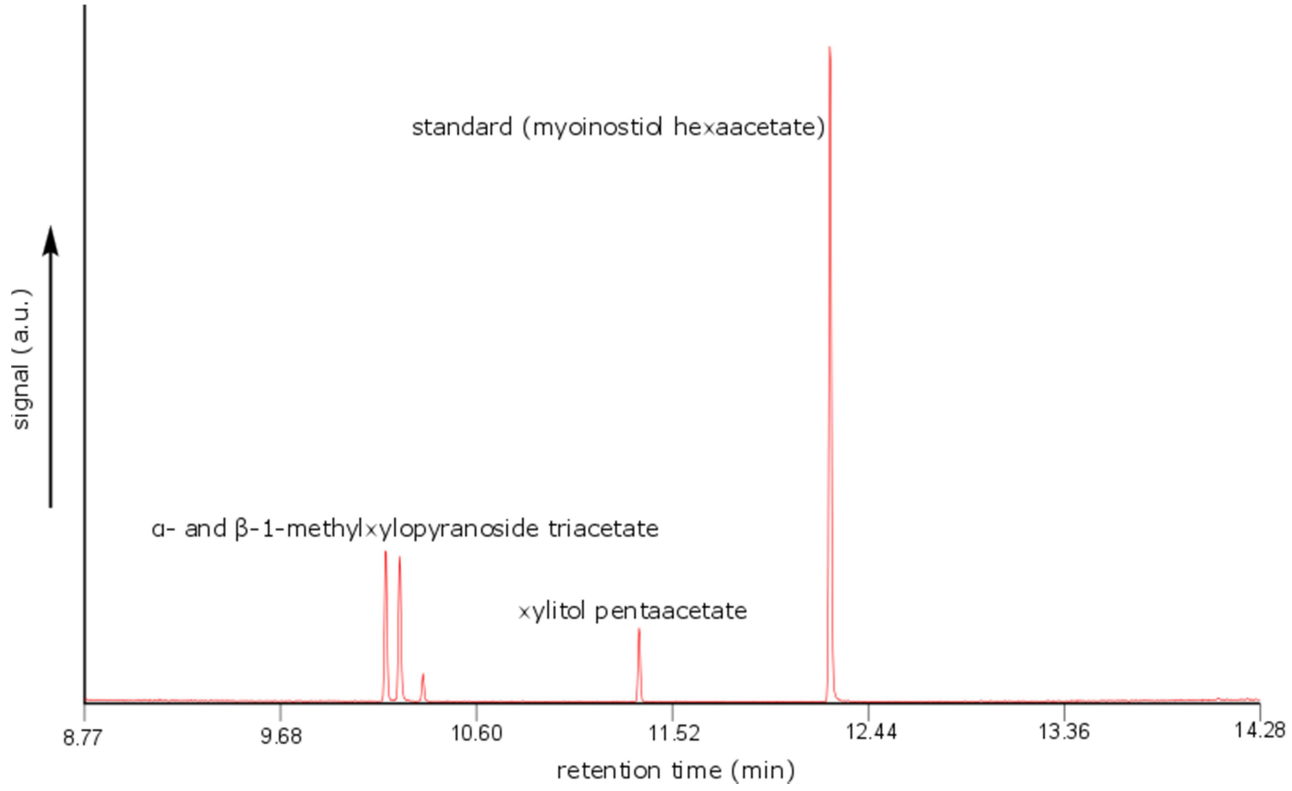


Fig S14. Gas chromatogram of hydrophilic compounds derivatives obtained from organosolv pulping followed by transfer hydrogenolysis reaction of birch wood meal. Reaction conditions: Table S6, Entry 5.

4.6. Determination of pulp composition

Wood pulp obtained in the flow process was analyzed for carbohydrates and lignin content in the same manner as initial wood (see section 3). Found: AIL –1.5 wt%; glucans – 35 wt%; xylans – 0 wt%.

4.7. Carbon balance

Carbon content in each biomass component depicted in Table 2 of the article was calculated according to the formula

$$v(C) = \frac{m \cdot n(C)}{M_w}$$

where m is mass of the certain biomass component (g), $n(C)$ is number of carbon atoms per assumed molecule of the component, and M_w is molecular weight (g·mol^{-1}):

Table S9. Values used in the carbon balance calculations.

	$n(C)$	M_w (g·mol^{-1})
Xylans	5	Xylose (in wood meal), 150 Methylxylopyranose (in liquid fraction), 164
Glucans	6	180
Lignin (wood meal)	9	204 (according to ratio S:G = 4:1 calculated from thioacidolysis GC data)
Lignin (in liquid fraction, as monophenolic compounds)	9	4-propylguaiacol, 166 4-propylsyringol, 196 4-(3-methoxypropyl)guaiacol, 196 4-(3-hydroxypropyl)guaiacol, 182 4-(3-methoxypropyl)syringol, 226 4-(3-hydroxypropyl)syringol, 212

5. Batch experiments

5.1 Determination of hydrogen donor origin

To determine if methanol or xylose is the main hydrogen source in the reactions, model batch experiments were performed. Isoeugenol was used as a model where the propenyl unit was monitored. Xylose (0.15 mmol), isoeugenol (0.15 mmol) and 5wt% Pd/C (0.01 mmol Pd) were mixed in a batch reactor with 4 mL of solvent (2.8 g·L^{-1} of 85% aq. H_3PO_4 in MeOH-H_2O 7 : 3 v/v) and heated 190–200 °C for 10 min.

Fig S15. Photo of reactors made of one stainless steel Swagelok unit (SS-1210-6) and two stainless steel plugs (SS-1210-P).

Table S10. Model experiments on hydrogenation of isoeugenol

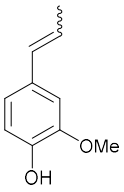
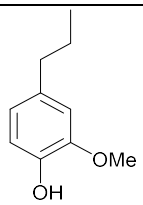
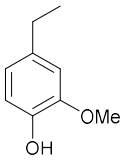
Entry	Xylose	Isoeugenol	Pd/C
1	✔	–	–
2	✔	–	✔
3	✔	✔	✔
4	–	✔	✔

The batch reactor was cooled with water, the residue was transferred to the test tube and centrifuged in order to get rid of the Pd/C. the solution was decanted, transferred into separation funnel, and diluted with 10 mL of water. Internal standard (*myo*-inositol; for GC analysis of carbohydrates) was added, and the mixture was extracted with 10 mL DCM. The water phase was analyzed for content of carbohydrates as described above (table S10). The organic phase was separated and subjected to GC-MS analysis. From these experiments it is clear that the hemicellulose is a more efficient hydrogen donor than methanol (Table S12).

Table S11. Xylose decomposition in model experiments

Entry	Xylose decomposition degree (%)
1	92
2	93
3	91

Table S12. Products of isoeugenol hydrogenation in model experiments (% of total phenolics)

Entry			
3	47	39	6
4	87	7	0

5.2 Pd-free batch depolymerization kinetics

Wood meal (125 mg) was placed a in batch reactor together with 4 mL of solvent system (2.8 $g \cdot L^{-1}$ of 85% aq. H_3PO_4 in MeOH-H_2O 7:3 v/v). Mixture was kept at r.t. for 1 hr and then placed in oil bath heated to 200 °C. After the specified time had passed, the batch reactor was rapidly cooled with ice. The mixture was filtered and the residue was washed with MeOH. To the filtrate, tetracosane (0.8 mL of 1 $mg \cdot mL^{-1}$ solution in THF) was added, followed by water (10 mL). Methanol was removed from the solution in vacuum, and remaining water was extracted with DCM (3x10 mL). The organic phase was dried with Na_2SO_4 and concentrated in vacuum then dissolved in $CDCl_3$ and CH_3NO_2 (70 mg of 15 $mg \cdot g^{-1}$ solution in $CDCl_3$) was added. The solution was subjected to NMR spectroscopy. Sample (0.2 mL) was diluted with THF (1 mL), treated with silylating reagent and subjected to GC-MS Injector that was operated at 250 °C, and 1:100 split ratio was used. The following temperature gradient program was used for the elution: from 100 to 300 °C (14 $°C \cdot min^{-1}$).

Table S13. GC yields (% from total lignin) of monophenolic compounds in Pd-free batch depolymerization reactions

t (min)	***S***-CH=CH-CH_2-OMe
5	0
15	13
30	15
180	0

6. Enzymatic hydrolysis

6.1. Calibration

A calibration curve for the photometric studies was obtained as following: 20 µL of standard solutions of glucose in water (1.01, 3.91, 7.10, 10.28, and 12.84 $mg \cdot mL^{-1}$ L) were added to glass tubes containing 3 mL of 6% solution of *o*-toluidine in glacial acetic acid. The obtained mixtures were heated to 10 min at 100 °C and their absorbance was measured at 630 nm

versus blank sample (20 µL H_2O + 3 mL of 6% solution of *o*-toluidine in glacial acetic acid, treated in the same way). Each measurement was duplicated.

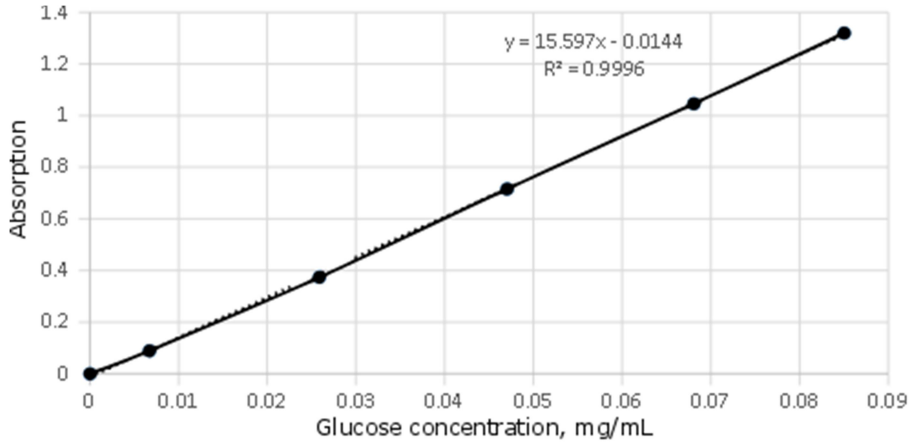


Fig S16. Calibration curve for photometric determination of glucose concentration.

6.2. Measurement of enzymatic activity

The activity of the cellulase blend used for hydrolysis of pulp was determined using procedure of Ghose and NREL LAP (NREL/TP-510-42628) in filter paper units (FPU) per gram of undiluted enzyme mixture. 1 FPU stands for enzyme activity where 2 mg (4%) of glucose are released from 50 mg of filter #1 paper in 1.5 mL of acetate buffer at 50 °C in 60 min. To three glass vials, filter №1 paper (50 mg), 0.05 M acetate buffer (total volume 1.5 mL) and enzyme (0.3 mg, as solution in the same buffer) were added. The vials were heated in heating blocks at 50 °C with gentle shaking (300 rpm) for 60 min. The vials were cooled with ice. 40 µL samples were taken and added to glass tubes containing 3 mL of 6% w/w solution of *o*-toluidine in glacial acetic acid. The obtained mixtures were heated to 10 min at 100 °C (oil bath) and their absorbance at 630 nm was measured towards a blank sample (40 µL H_2O + 3 mL of 6% solution of *o*-toluidine in glacial acetic acid, treated in the same way). The glucose concentration obtained from the absorption value was used to calculate the activity of enzyme in filter paper units (FPU) according to formula:

$$\text{Activity}\left(\frac{\text{FPU}}{g\ \text{enzyme}}\right) = \frac{c(\text{glucose in vials}) \cdot (\text{Vial volume}) \cdot (\text{Dilution of sample})}{m(\text{paper}) \cdot 0.04 \cdot m(\text{enzyme})}$$

Activity of used enzyme blend was calculated to be 430 FPU/g.

6.3. Enzymatic hydrolysis of pulp

The biomass containing cartridges used in the flow experiments were washed with water (10 min, 1 mL·min^{-1}) and then dissected. The obtained pulp was directly transferred into a vial together with 0.05 M acetate buffer (1.5 mL), sodium azide as antibiotic (10 µL of 7.5% aqueous solution), and enzyme (25 FPU per gram of pulp dry weight which was estimated by weighting dry pulp from previous experiments). The hydrolysis was carried out for 48 hours. Once in a while, samples (10 or 20 µL) were taken from reaction mixture and glucose concentration was determined using spectrophotometry as described above, and thus the kinetic curve of hydrolysis was built. Each measurement was duplicated. The yield of glucose was calculated towards overall cellulose content in pulp which was determined using common analytical procedure as described above.

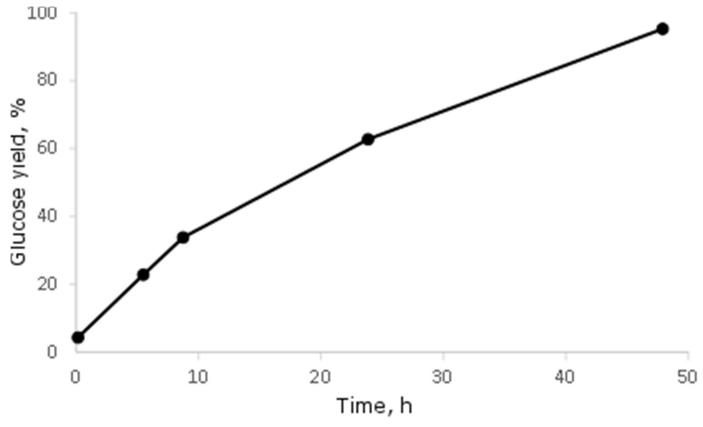


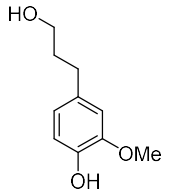
Fig S17. Enzymatic hydrolysis of cellulose

Table S14. Enzymatic hydrolysis of cellulose

t (h)	Glucose yield, %
0.17	4
5.5	23
8.8	34
23.9	63
47.9	95

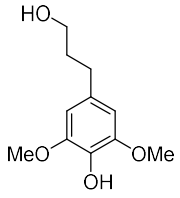
7. GC-MS

7.1. GC-MS calibration standards



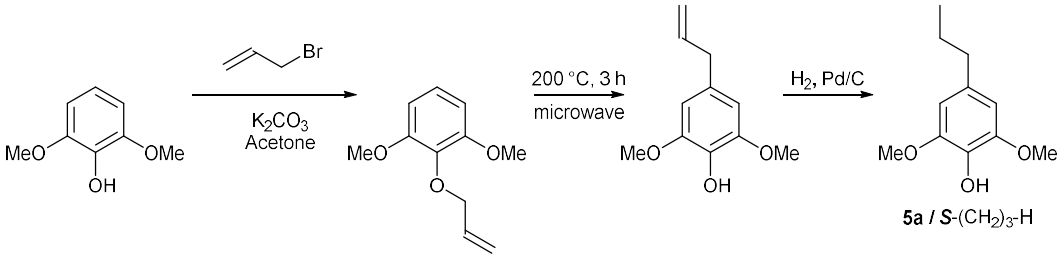
3b

4-(3-hydroxypropyl)-2-methoxyphenol (**3b** / ***G***-$(CH_2)_3$-OH) was purchased from Acros.



3a

4-(3-hydroxypropyl)-2,6-dimethoxyphenol (**3a** / ***S***-$(CH_2)_3$-OH) (98%) was purchased from Tokyo Chemical Industry Co., Ltd (Tokyo, Japan).



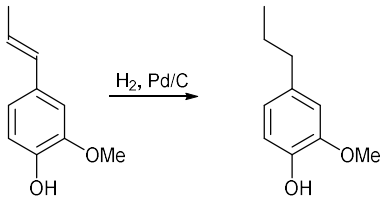
5a / ***S***-$(CH_2)_3$-H

2,6-dimethoxy-*O*-allylphenol: K_2CO_3 (12.5 g, 91 mmol) was suspended in acetone (100 mL). The flask was flushed with argon. Syringol (7.0 g, 45 mmol) was added, followed by allylbromide (4.3 mL, 6.0 g, 50 mmoL). The mixture was refluxed for 10 hours, filtered and concentrated. The residue was treated with EtOAc and aqueous 5% K_2CO_3, organic phase was washed with brine and dried over Na_2SO_4. The solvent was removed in vacuum and product was obtained as yellowish oil (8.1 g, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz): 3.84 (s, 6H), 4.52 (dt, 6.1 Hz, 1.3 Hz, 2H), 5.17 (dm, 10.3 Hz, 1H), 5.30 (dq, 17.2 Hz, 1.6 Hz, 1H), 6.06–6.17 (m, 1H), 6.57 (d, 8.4 Hz, 2H), 6.98 (t, 8.4 Hz, 1H). The NMR data is consistent with reported in literature [2].

2,6-dimethoxy-4-allylphenol: 2.0 g of 2,6-dimethoxy-*O*-allylphenol where heated in microwave at 200 °C for 3 h. The product was obtained as brownish liquid and used on next step without further purification. ^{1}H NMR ($CDCl_3$, 400 MHz): 3.31 (d, *J* = 6.6 Hz, 2H), 3.87 (s, 6H), 5.04 – 5.12 (m, 2H), 5.38 (brs, 1H), 5.89–6.01 (m, 1H), 6.41 (s, 2H). The NMR data is consistent with reported in literature [2].

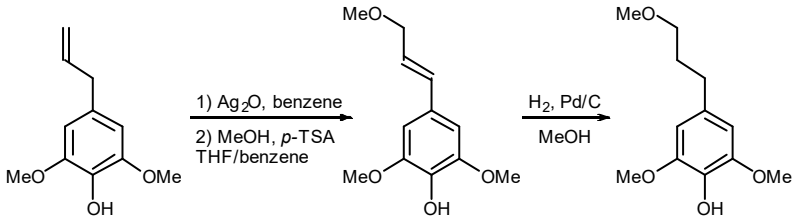
2,6-dimethoxy-4-propylphenol (**5a** / ***S***-$(CH_2)_3$-H). 2,6-dimethoxy-4-allylphenol (0.10 g) was placed in two-necked flask and dissolved in MeOH. 5% Pd/C (0.02 g, 0.01 mmol Pd) was added under flow of argon. The flask was flushed with hydrogen

and mixture was stirred under atmosphere of hydrogen for 2 hours. Then the mixture was filtered through celite and concentrated. The product was purified by column chromatography ($CHCl_3$, SiO_2). A colorless oil was obtained (0.09 g, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz): 0.94 (t, *J* = 7.2 Hz, 3H), 1.62 (m, 2H), 2.51 (t, *J* = 7.8 Hz, 2H), 3.88 (s, 6H), 6.40 (s, 2H). The NMR data is consistent with reported in literature [3].



5b / ***G***-$(CH_2)_3$-H

2-methoxy-4-propylphenol (**5b** / ***G***-$(CH_2)_3$-H)**:** Pd/C (5%) (0.13 g, 0.06 mmol Pd) was added to the stirred solution of isoeugenol (0.52 g, 3.2 mmol) in MeOH under argon atmosphere. The argon atmosphere was displaced with hydrogen. The reaction mixture was stirred for 2 h, filtered through celite and concentrated in vacuum. Column chromatography (SiO_2, $CHCl_3$) afforded product as colorless liquid (0.52 g, 99%). ^{1}H NMR ($CDCl_3$): 0.94 (s, *J* = 7.4 Hz, 3H), 1.61 (m, 2H), 2.52 (t, *J* = 7.4 Hz, 2H), 3.88 (s, 3H), 5.52 (brs, 1H), 6.67 (d, 1H), 6.68 (s, 1H), 6.83 (d, 1H). The NMR data is consistent with reported in literature [4].

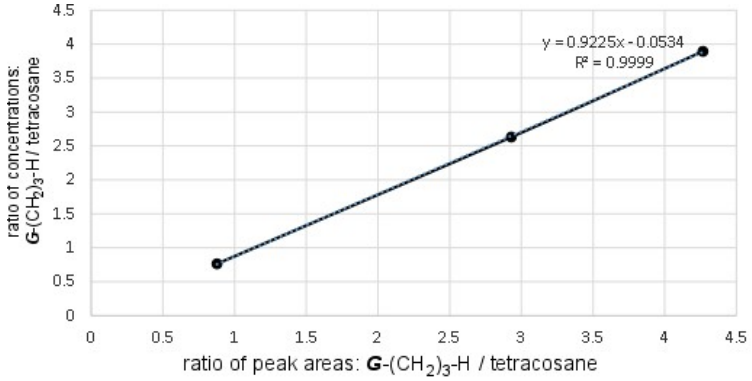


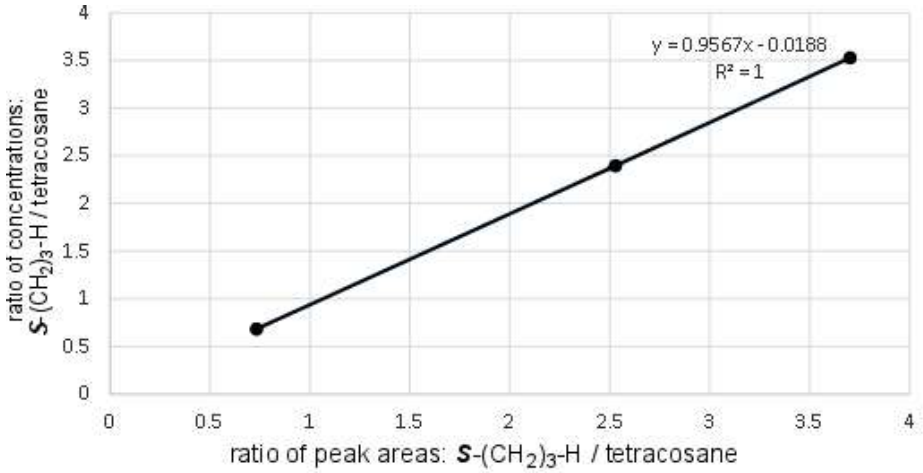
2a / ***S***-$(CH)_2CH_2OMe$ **4a** / ***S***-$(CH_2)_3$-OMe

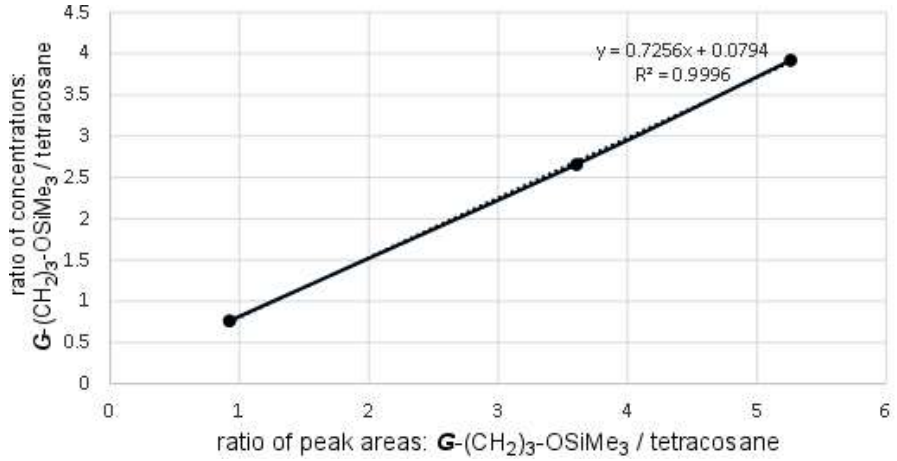
2,6-dimethoxy-4-(3-methoxyproyl)phenol (**4a** / ***S***-$(CH_2)_3$-OMe)**:** precursor of this compound (2,6-dimethoxy-4-(3-methoxypropenyl-1)phenol) was prepared according to published procedure [5]. Ag_2O (1.2 g) was added to stirred solution of 2,6-dimethoxy-4-allylphenol (0.50 g) in 40 mL of benzene. Vigorous stirring was continued for 10 minutes, followed by filtration through celite. To the filtrate, 10 mL of methanol and 3.9 mL of *p*TSA solution ($5.8\cdot10^{-3}$ M in benzene–THF 5:2) were added and the homogeneous solution was left overnight at room temperature. The solution was concentrated in vacuum and crude product was purified with coloumn chromatography (silica gel, pentane–EtOAc 2:1, R_f = 0.4). 50 mg of **2,6-dimethoxy-4-(3-methoxypropenyl-1)phenol** (**2a** / ***S***-$(CH)_2CH_2$-OMe) was dissolved in methanol (10 mL) under argon atmosphere. Pd/C (5%) (10 mg, $5\cdot10^{-3}$ mmol Pd) was added to the stirred solution and the argon atmosphere was displaced with hydrogen. The reaction mixture was stirred for 2 h, filtered through celite and concentrated in vacuum. Product (42 mg, 83%) was quantificated using ^{1}H NMR spectroscopy with CH_3NO_2 as internal standard. ^{1}H NMR ($CDCl_3$): 1.84 (m, 2H), 2.59 (t, *J* = 7.8 Hz, 2H), 3.33 (s, 3H), 3.36 (t, *J* = 6.4 Hz, 2H), 3.84 (s, 6H), 6.39 (s, 2H). The NMR data is consistent with reported in literature [6].

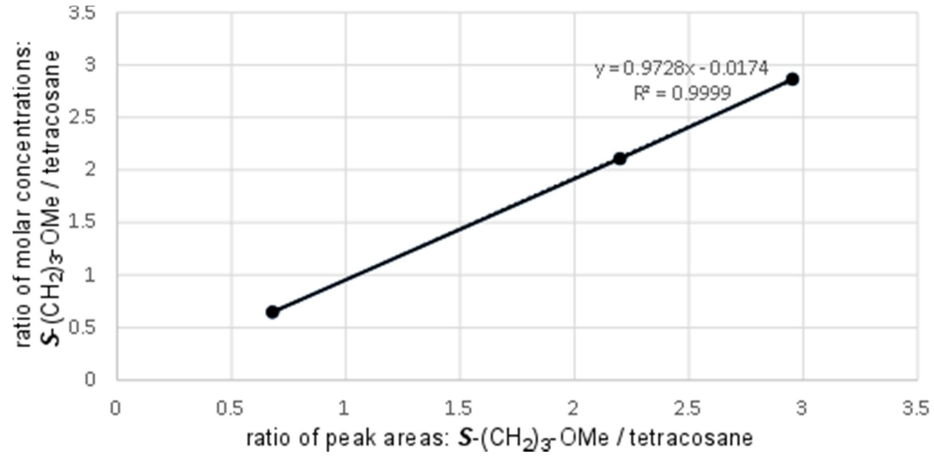
7.2. GC-MS calibration

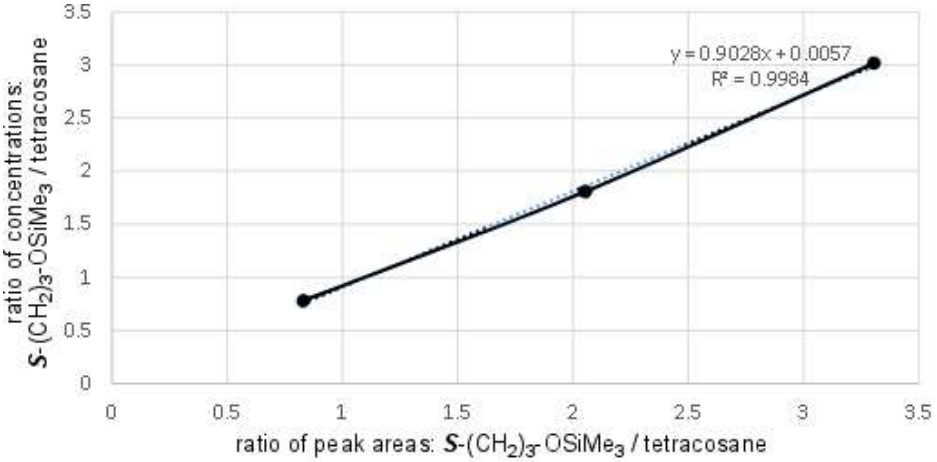
Calibration curves for GC determination of obtained products. Tetracosane (99%, Sigma-Aldrich) was used as internal standard. A calibration curve for G-OMe was not built since usual appearance of this product is less than 2% of overall amount of lignin-derived monophenolic compounds. Mass concentrations are used from here on.




y = 0.9567x - 0.0188
R² = 1
ratio of concentrations: S-(CH2)3-H / tetracosane
ratio of peak areas: S-(CH2)3-H / tetracosane


y = 0.7256x + 0.0794
R² = 0.9996
ratio of concentrations: G-(CH2)3-OSiMe3 / tetracosane
ratio of peak areas: G-(CH2)3-OSiMe3 / tetracosane


y = 0.9728x - 0.0174
R² = 0.9999
ratio of molar concentrations: S-(CH2)3-OMe / tetracosane
ratio of peak areas: S-(CH2)3-OMe / tetracosane


y = 0.9028x + 0.0057
R² = 0.9984
ratio of concentrations: S-(CH2)3-OSiMe3 / tetracosane
ratio of peak areas: S-(CH2)3-OSiMe3 / tetracosane

7.3. GC-MS of lignin derivatives

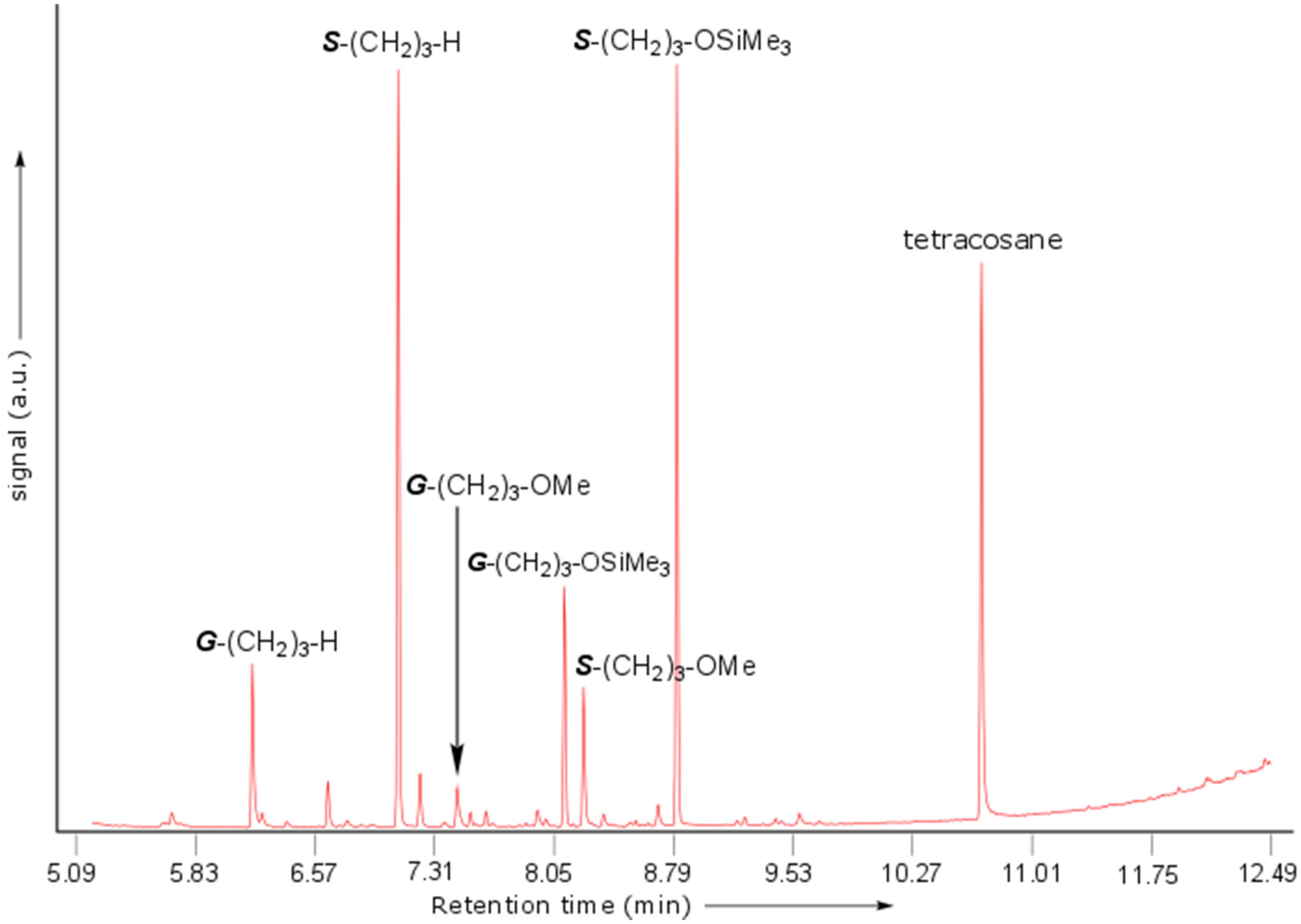


Fig S10. Typical gas chromatogram (MS trace) of monophenolic lignin products (with Pd/C cartridge in line; Reaction conditions: see Table S6, Entry 5) after silylation derivatization.

Table S15. Retention time and mass spectra of analysed monophenolic lignin products (with Pd/C cartridge in line; Reaction conditions: see Table S6, Entry 5) after silylation derivatization.

t_R, (min)	Monophenolic compounds	m/z (relative abundance)
6.11	***G***-$(CH_2)_3$-H	209 (100), 179 (85), 208 (57), 73 (51), 238 (M+, 43%), 28 (31), 149 (22), 223 (20), 210 (18), 45 (15), 180 (14), 59 (12), 32 (11), 75 (10), 239 (8), 44 (8), 77 (7), 89 (7), 163 (7), 91 (6).
7.01	***S***-$(CH_2)_3$-H	238 (100), 209 (88), 239 (74), 268 (M+, 59%), 73 (58), 253 (27), 210 (19), 240 (16), 179 (16), 151 (15), 45 (15), 59 (14), 269 (12), 166 (12), 75 (9), 28 (7), 195 (7), 91 (7), 136 (6), 89 (6).
7.39	***G***-$(CH_2)_3$-OMe	209 (100), 73 (99), 268 (M+, 85%), 180 (82), 179 (75), 206 (58), 45 (58), 75 (48), 44 (47), 238 (38), 210 (35), 205 (27), 253 (25), 149 (23), 59 (22), 207 (20), 269 (19), 77 (17), 181 (17), 91 (16).
8.06	***G***-$(CH_2)_3$-$OSiMe_3$	206 (100), 73 (60), 205 (50), 179 (33), 326 (M+, 25%), 207 (24), 28 (23), 180 (20), 209 (19), 75 (18), 59 (18), 236 (13), 45 (13), 210 (11), 89 (11), 149 (11), 221 (10), 311 (9), 32 (9), 192 (8).
8.18	***S***-$(CH_2)_3$-OMe	210 (100), 298 (M+, 84%), 73 (75), 209 (51), 28 (49), 240 (44), 239 (40), 45 (36), 268 (23), 283 (22), 179 (20), 75 (19), 211 (18), 59 (18), 299 (17), 32 (16), 193 (15), 223 (14), 44 (14), 225 (12), 151 (12).
8.76	***S***-$(CH_2)_3$-$OSiMe_3$	73 (100), 210 (72), 240 (64), 356 (M+, 61%), 209 (59), 236 (57), 235 (32), 59 (31), 75 (28), 239 (23), 341 (21), 45 (19), 179 (18), 357 (18), 89 (16), 205 (16), 163 (15), 237 (14), 211 (14), 225 (14), 193 (13).

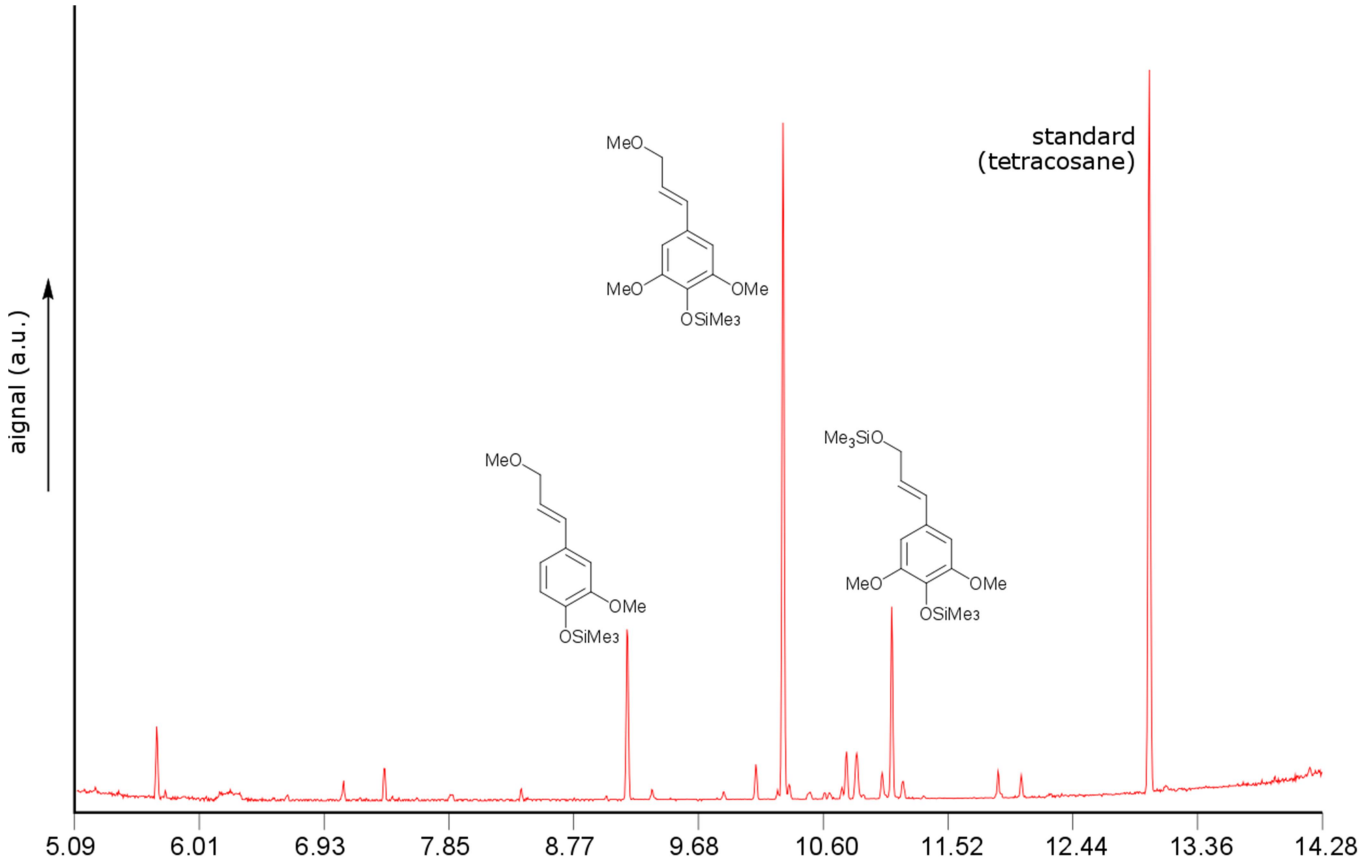


Fig S11. Typical gas chromatogram (MS trace) of monophenolic lignin products from organosolv pulping process (no Pd/C catalysis, Reaction conditions: see Table S6, Entry 5) after silylation derivatization.

Table S16. Retention times and mass spectra of monophenolic lignin products from organosolv pulping process (no Pd/C catalysis, Reaction conditions: see Table S6, Entry 5) after silylation derivatization.

t_R, (min)	Monophenolic compounds	m/z (relative abundance)
9.15	***G***-CH=CH-CH_2-OMe	266 (M+, 100%), 73 (67), 235 (65), 236 (53), 205 (50), 204 (46), 131 (33), 267 (21), 206 (21), 103 (19), 251 (19), 75 (15), 59 (15), 203 (14), 193 (13), 192 (12), 237 (11), 117 (11), 89 (11), 91 (10).
10.30	***S***-CH=CH-CH_2-OMe	296 (M+, 100%), 73 (47), 266 (47), 265 (39), 235 (36), 234 (32), 297 (21), 281 (21), 204 (19), 133 (19), 161 (16), 236 (14), 59 (12), 75 (12), 267 (10), 89 (10), 251 (9), 205 (9), 219 (8), 149 (8).
11.10	***S***-CH=CH-CH_2-$OSiMe_3$	73 (100), 354 (M+, 82%), 323 (37), 324 (31), 234 (26), 355 (24), 75 (20), 265 (18), 204 (17), 339 (15), 59 (12), 293 (12), 235 (10), 325 (10), 149 (10), 133 (9), 356 (9), 74 (9), 147 (8), 89 (8).

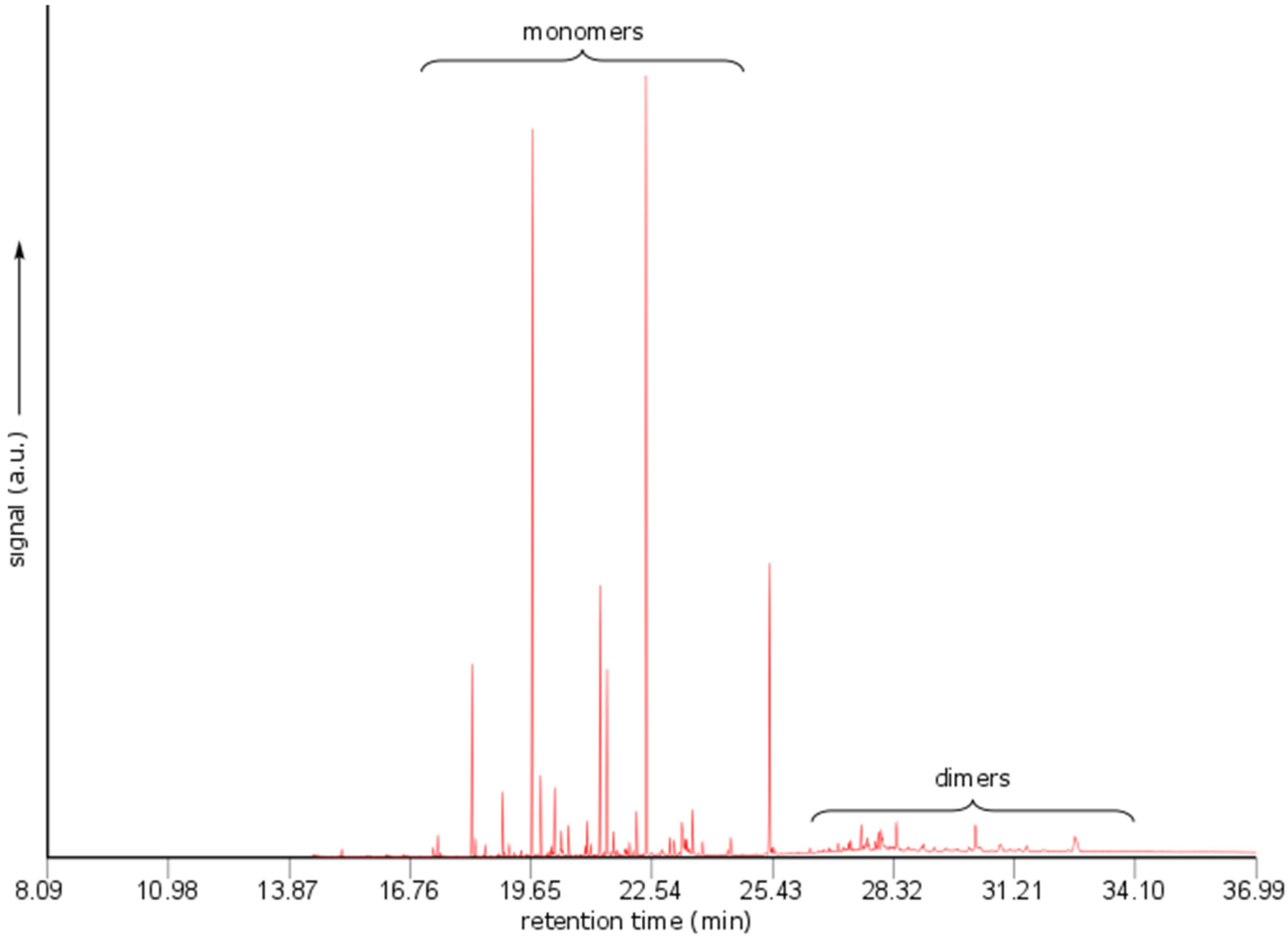


Fig S18 Gas chromatogram (Injector was operated at 250 °C, and 1:100 split ratio was used. The temperature gradient program was used for the elution: 60 °C (hold 2 min), from 60 to 280 °C (10 °C·min^{-1}), 280 °C (hold 13 min) of lignin products (with Pd/C cartridge in line; Reaction conditions: see Table S6, Entry 5) after silylation derivatization.

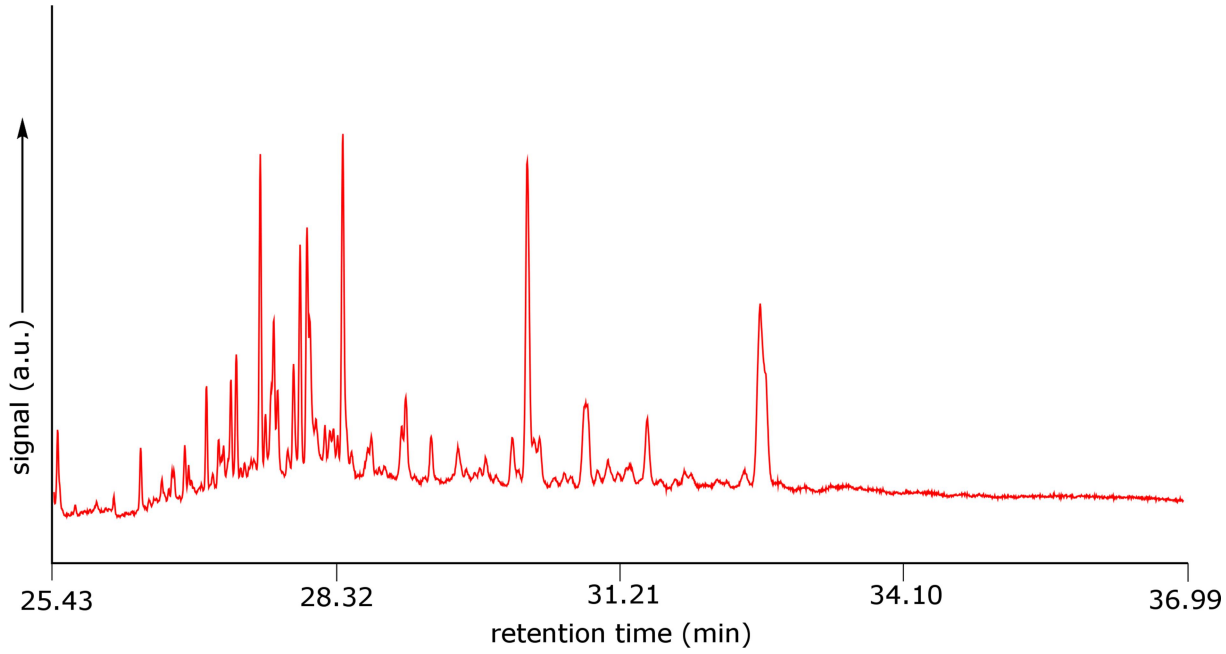
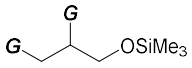
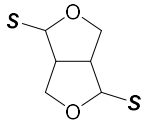
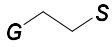
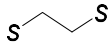
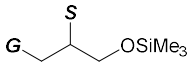
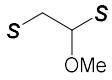
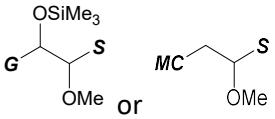
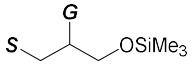
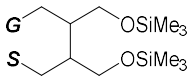
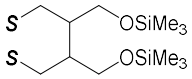


Fig S19. Area of dimers in the gas chromatogram Fig S18.

Table S17. Retention times and mass spectra of detected dimers

t_R, (min)	Monophenolic compounds	m/z (relative abundance)
24.20		311 (100), 73 (77), 209 (46), 207 (43), 312 (27), 281 (21), 75 (21), 179 (18), 208 (15), 520 (14), 223 (11), 313 (11), 149 (10), 253 (9), 210 (9), 192 (9), 193 (8), 239 (7), 282 (7), 167 (7), 74 (7), 269 (7).
24.53		253 (100), 73 (28), 207 (25), 239 (20), 254 (20), 281 (12), 75 (11), 327 (11), 209 (10), 223 (9), 492 (7), 255 (7), 208 (6), 240 (5), 193 (5), 282 (4), 191 (3), 179 (3), 328 (3), 269 (3), 167 (3), 133 (3).
24.58		73 (100), 209 (88), 239 (71), 207 (58), 191 (54), 75 (25), 281 (24), 210 (18), 179 (17), 263 (16), 240 (13), 193 (13), 208 (13), 253 (11), 352 (11), 192 (10), 74 (9), 472 (9), 353 (9), 221 (9), 149 (9), 147 (9).
24.90		239 (100), 73 (26), 240 (19), 209 (15), 478 (15), 207 (10), 241 (6), 479 (5), 75 (5), 281 (4), 327 (4), 223 (3), 210 (3), 179 (3), 463 (3), 253 (2), 208 (2), 74 (2), 193 (2), 480 (2), 254 (2), 255 (2).
24.97		341 (100), 73 (92), 207 (75), 209 (48), 281 (35), 75 (33), 239 (29), 342 (27), 253 (22), 490 (20), 475 (19), 208 (18), 179 (14), 343 (12), 193 (12), 282 (12), 445 (12), 210 (11), 191 (10), 147 (10), 238 (10), 167 (9).
25.08		269 (100), 270 (19), 73 (16), 207 (11), 239 (11), 271 (6), 327 (6), 281 (5), 224 (5), 209 (5), 75 (5), 253 (3), 208 (3), 223 (3), 240 (2), 222 (2), 193 (2), 341 (2), 89 (2), 282 (2), 297 (2), 328 (2).
25.42		269 (100), 296 (81), 297 (70), 207 (32), 73 (31), 239 (30), 270 (20), 298 (16), 209 (15), 281 (15), 223 (15), 75 (14), 266 (12), 236 (12), 520 (12), 224 (11), 167 (10), 267 (10), 195 (10), 253 (9), 193 (8), 208 (8).
25.98		341 (100), 73 (60), 239 (46), 342 (28), 209 (21), 207 (20), 253 (13), 343 (11), 269 (11), 240 (11), 75 (10), 281 (9), 238 (8), 310 (8), 327 (6), 222 (6), 297 (6), 296 (6), 311 (5), 210 (5), 208 (5), 340 (5).
28.40		73 (100), 327 (45), 354 (45), 239 (33), 207 (23), 289 (19), 103 (19), 328 (18), 355 (16), 75 (14), 147 (13), 209 (12), 515 (12), 281 (11), 497 (10), 74 (9), 240 (8), 488 (8), 253 (7), 349 (7), 329 (7), 356 (7).
31.44		239 (100), 73 (23), 240 (21), 207 (15), 354 (11), 209 (9), 265 (8), 241 (6), 281 (6), 193 (6), 356 (6), 75 (6), 355 (5), 103 (5), 210 (4), 341 (3), 208 (3), 313 (3), 253 (3), 236 (3), 266 (3), 133 (2).

8. NMR

8.1. HSQC $^{1}H–^{13}C$ spectra

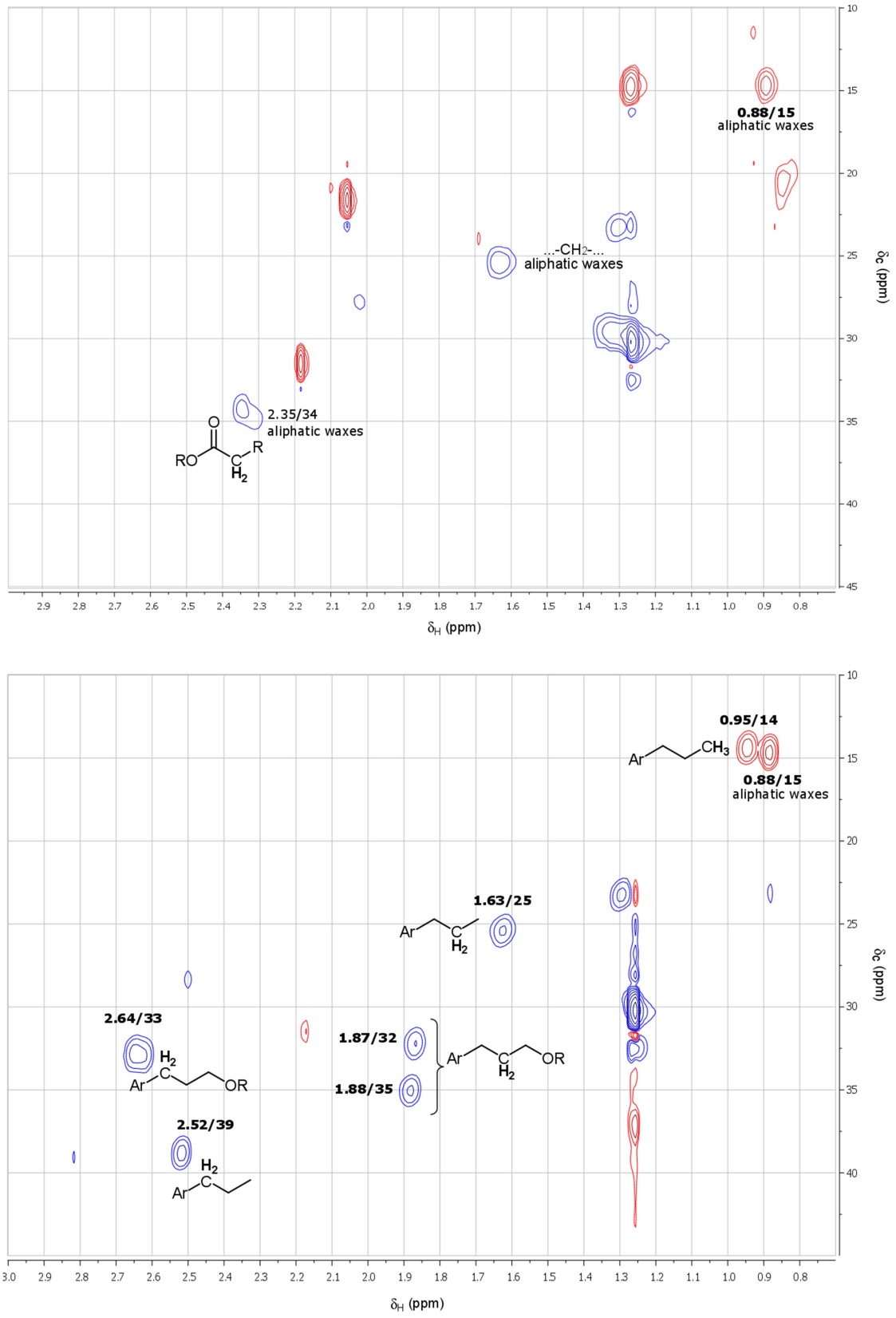
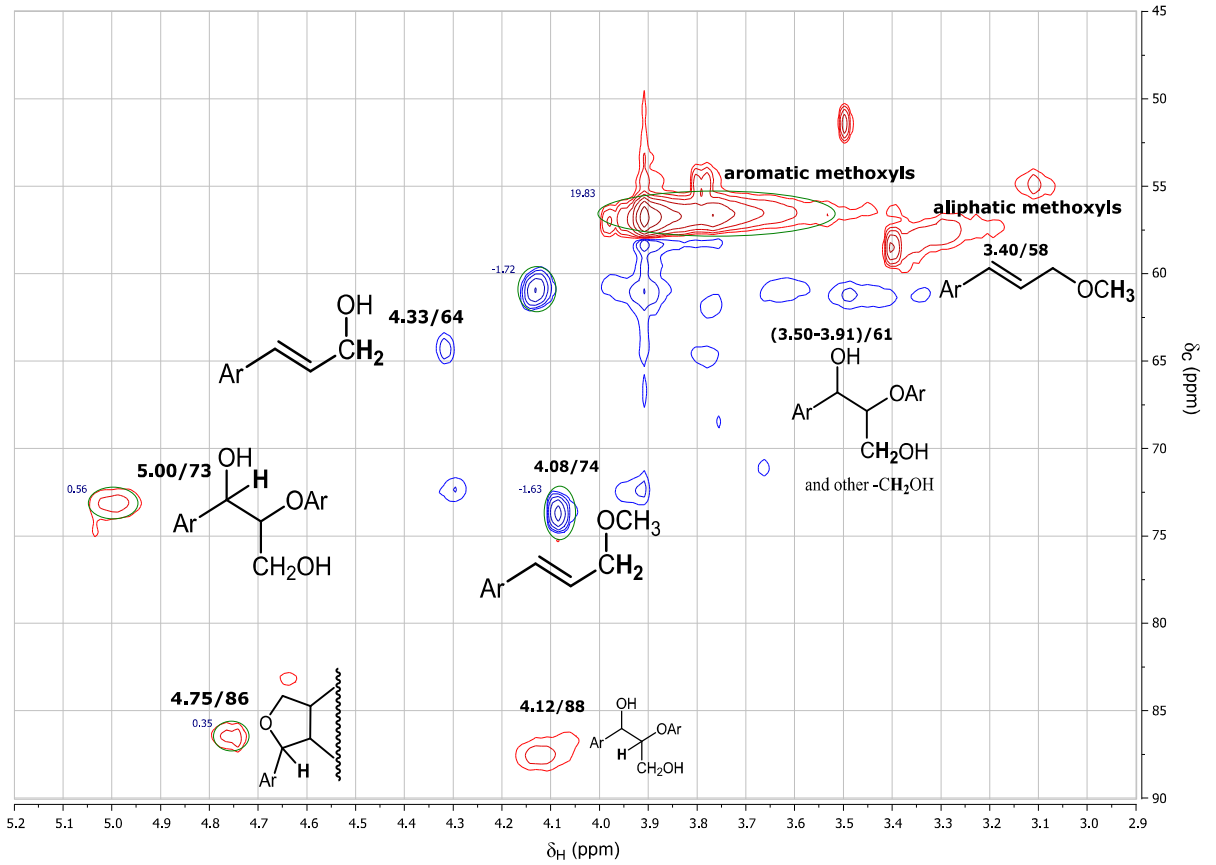


Fig S20. HSQC $^{1}H–^{13}C$ spectrum of organosolv lignin obtained in reaction without (up) and with (down) Pd/C catalysis applied, aliphatic region (^{1}H 0.7–3.0 ppm, ^{13}C 10–45 ppm).



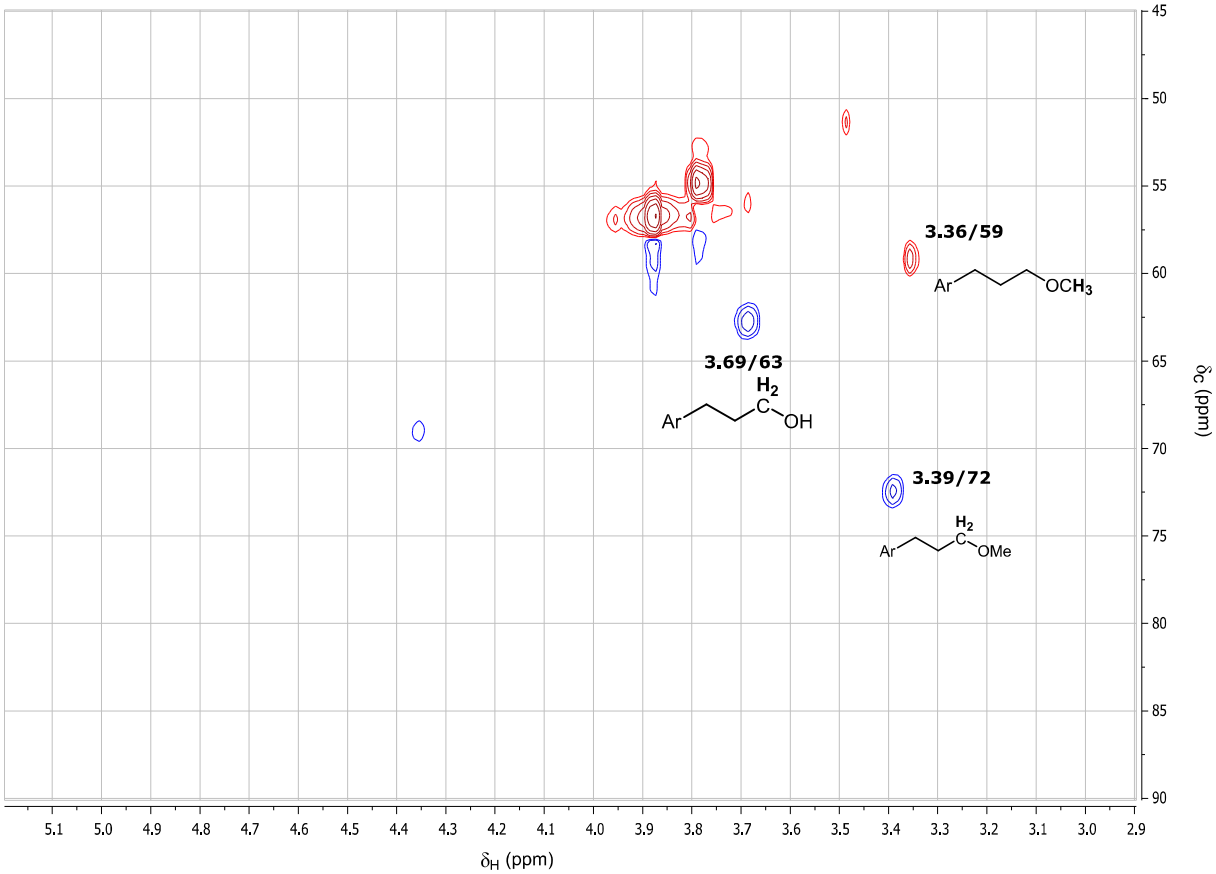


Fig S21. HSQC ^{1}H–^{13}C spectrum of organosolv lignin obtained in reaction without (up) and with (down) Pd/C catalysis applied, ether and alcohol region (^{1}H 2.9–5.2 ppm, ^{13}C 45–90 ppm).

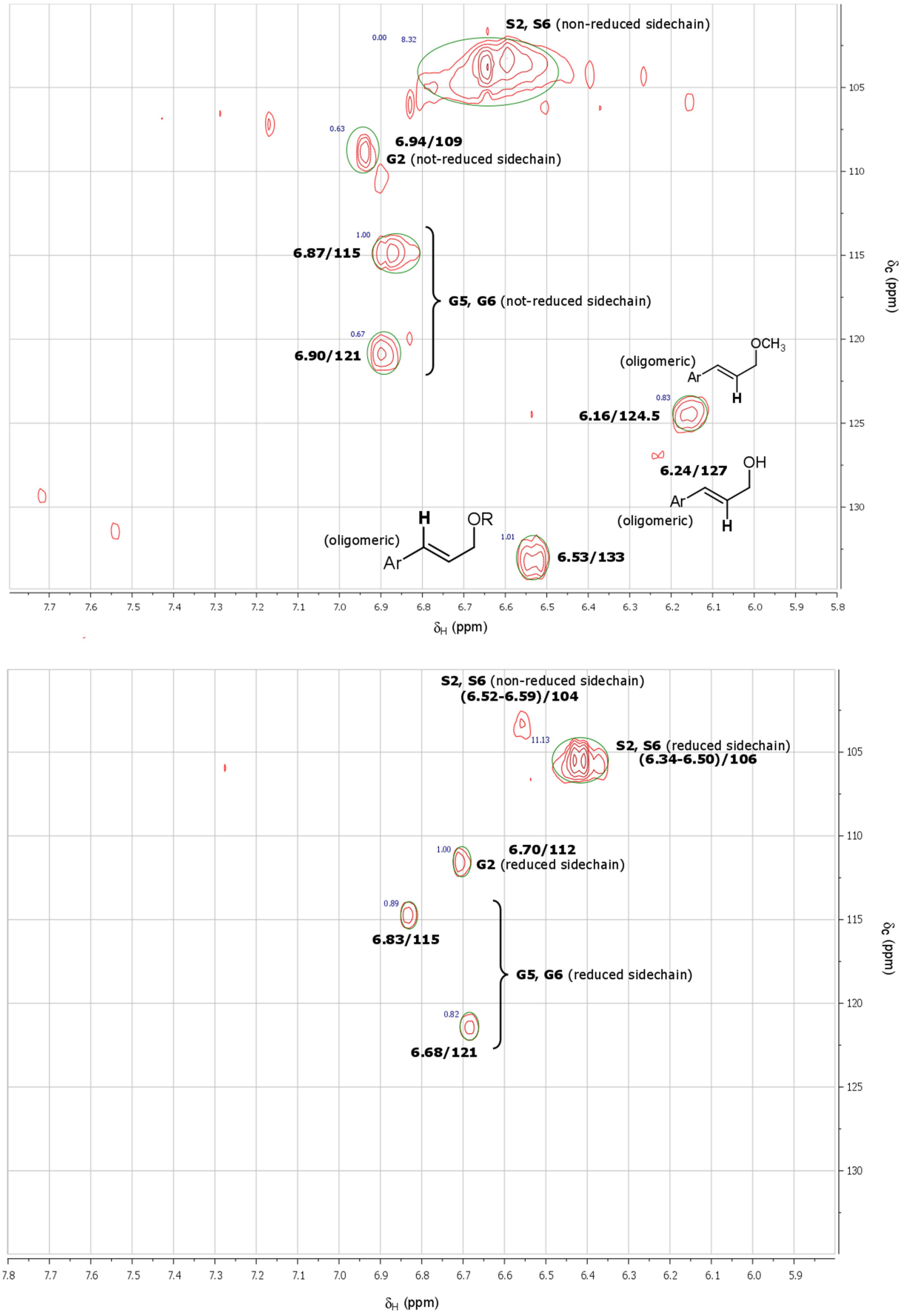


Fig S22. HSQC ^{1}H–^{13}C spectrum of organosolv lignin obtained in reaction without (up) and with (down) Pd/C catalysis applied, aromatic region (^{1}H 5.8–7.8 ppm, ^{13}C 100–135 ppm).

8.2. HMBC ^{1}H–^{13}C spectra

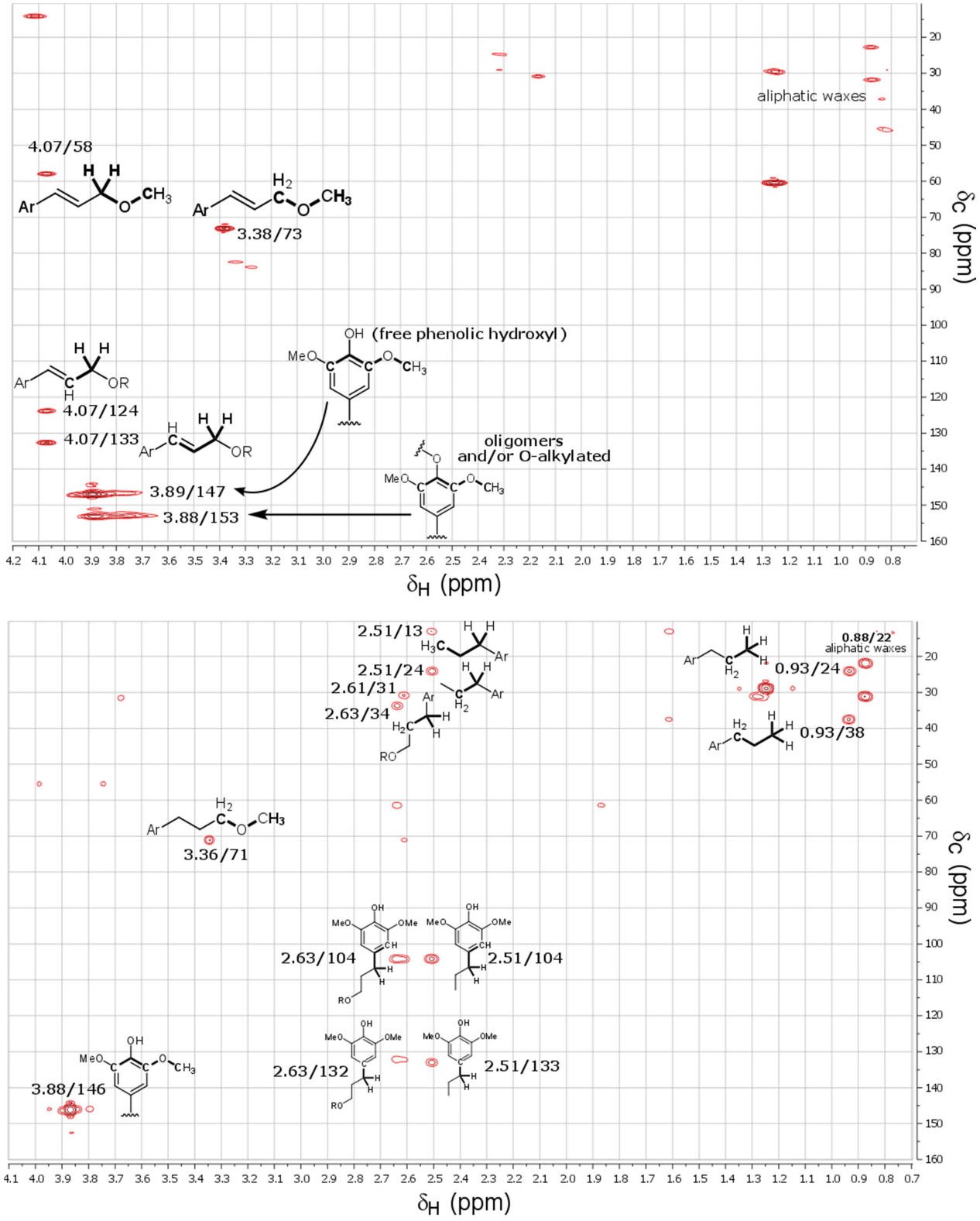


Fig S23. HMBC ^{1}H–^{13}C spectrum of organosolv lignin obtained in reaction without (up) and with (down) Pd/C catalysis applied, aliphatic and etheral regions (^{1}H 0.7–4.2 ppm, ^{13}C 10–160 ppm).

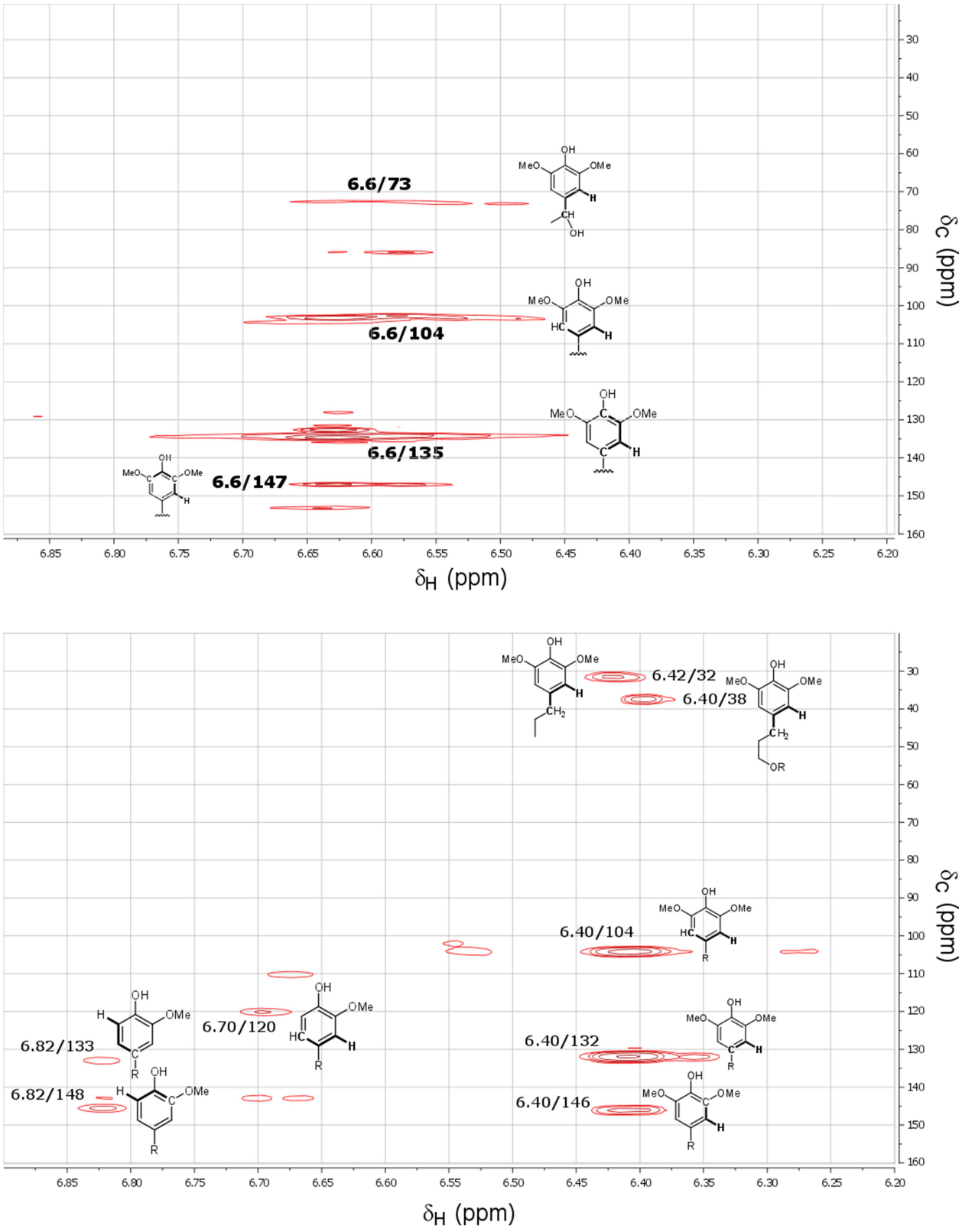


Fig S24. HMBC ^{1}H–^{13}C spectrum of organosolv lignin obtained in reaction without (up) and with (down) Pd/C catalysis applied, aromatic region (^{1}H 6.2–6.9 ppm, ^{13}C 20–160 ppm).

9. SEC

Lignin products were analysed by SEC. 0.1 mL of the solution (see section 4.2) in $CDCl_3$ was diluted with 1 mL THF and subjected to SEC analysis.

9.1. Theoretical distribution of lignin derived products

To theoretically estimate the distribution of lignin products, the following prediction was made. Because β-O-4' bond is more likely to undergo cleavage then all other types of bonds, an oligomer with *k* units is formed whenever the bond sequence B-A_{k-1}-B (B stands for β-O-4' bond and A stands for all other types) in the lignin structure is found. The probability to find β-O-4' bond is φ_B. After cleavage of the first β-O-4' bond, amount of bonds becomes *N – 1* and the probability to find A bond is $N\varphi_A/(N-1)$. After that, we have $N\varphi_A - 1$ β-O-4' bonds and *N – 2* bonds in total. For k-mer we have 2 B-bonds and *k – 1* A-bonds. Multiplying probabilities we obtain the following formulas:

$$k = 1 \qquad p(k) = \frac{\varphi_B(N\varphi_B - 1)}{N-1}$$

$$k > 1 \quad p(k) = \frac{\varphi_B \cdot N\varphi_A \cdot (N\varphi_A - 1) \cdot (N\varphi_A - 2) \cdots (N\varphi_A - k + 2) \cdot (N\varphi_B - 1)}{(N-1)(N-2)\cdots(N-k)}$$

Where *p* is the unnormalized probability to obtain an oligomer composed of *k* units. In case *N* >> 1:

$$p(k) = \varphi_B^2 \cdot \varphi_A^{k-1}$$

As the average thioacidolysis yield of lignin-derived monophenolic compounds was 45%, considering N >> 1 one can assume that $\varphi_B = \sqrt{0.45} = 0.67$.

9.2. Experimental data and plots

Table S18. SEC data on distribution of lignin products obtained at the first step (before Pd/C) and at the second step (after Pd/C) of the flow process

		Before Pd/C	After Pd/C
Fraction 1 (t_R 24.2–26.5 min)	Mn (g·mol^{-1})	210	242
	Mw (g·mol^{-1})	219	254
	PD = Mw/Mn	1.04	1.05
	Area (%)	50	54
Fraction 2 (t_R 22.5–24.2 min)	Mn (g·mol^{-1})	434	477
	Mw (g·mol^{-1})	440	486
	PD = Mw/Mn	1.01	1.02
	Area (%)	12	33
Fraction 3 (t_R 15.7–22.5 min)	Mn (g·mol^{-1})	1180	750
	Mw (g·mol^{-1})	1666	767
	PD = Mw/Mn	1.41	1.02
	Area (%)	39	15
Average (t_R 15.7–26.5 min)	Mn (g·mol^{-1})	357	329
	Mw (g·mol^{-1})	836	398
	PD = Mw/Mn	2.34	1.21

Expressions by which Mn (number average molecular weight), Mw (weight average molecular weight) and PD (polydispersity index) are defined (n_i stands for number of molecules of molecular weight M_i):

$$Mn = \frac{\sum M_i n_i}{\sum n_i}$$

$$Mw = \frac{\sum M_i^2 n_i}{\sum M_i n_i}$$

$$PD = \frac{M_w}{M_n}$$

Table S19. SEC data for standard lignin-derived monophenolic compounds

G-$(CH_2)_3$-H (t_R = 26.0 min)	Mn ($g \cdot mol^{-1}$)	171
	Mw ($g \cdot mol^{-1}$)	174
	PD = Mw/Mn	1.02
G-$(CH_2)_3$-OH (t_R = 24.9 min)	Mn ($g \cdot mol^{-1}$)	278
	Mw ($g \cdot mol^{-1}$)	280
	PD = Mw/Mn	1.01

Table S20. Kinetics of delignification (first step of the flow process): SEC data on distribution of lignin products released at different times

		t_1 = 14 min	t_2 = 32 min	t_3 = 56 min
Fraction 1 (t_R 24.2–26.5 min)	Mn ($g \cdot mol^{-1}$)	240	231	234
	Mw ($g \cdot mol^{-1}$)	248	237	247
	PD = Mw/Mn	1.03	1.02	1.06
	area (%)	43	34	15
Fraction 2 (t_R 22.5–24.2 min)	Mn ($g \cdot mol^{-1}$)	489	493	525
	Mw ($g \cdot mol^{-1}$)	496	500	536
	PD = Mw/Mn	1.02	1.01	1.02
	area (%)	18	13	20
Fraction 3 (t_R 15.7–22.5 min)	Mn ($g \cdot mol^{-1}$)	1195	1337	1356
	Mw ($g \cdot mol^{-1}$)	1571	2073	1937
	PD = Mw/Mn	1.31	1.55	1.43
	area (%)	39	53	65
Average (t_R 15.7–26.5 min)	Mn ($g \cdot mol^{-1}$)	413	470	649
	Mw ($g \cdot mol^{-1}$)	823	1220	1340
	PD = Mw/Mn	1.99	2.59	2.06

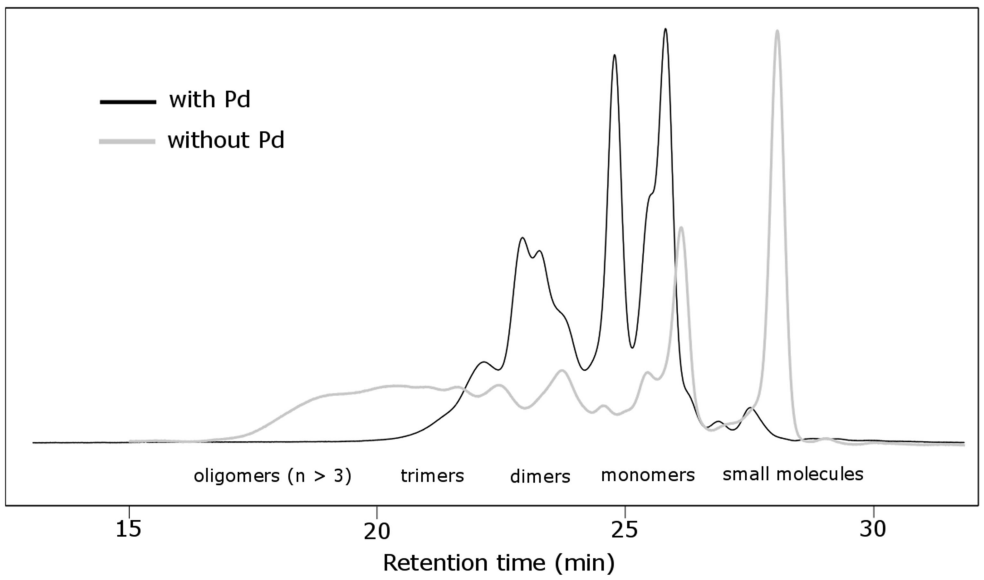


Figure S25. SEC of lignin obtained in reaction with and without Pd/C (dried briefly in rotary evaporator; small molecules such as solvents and organic acids are present)

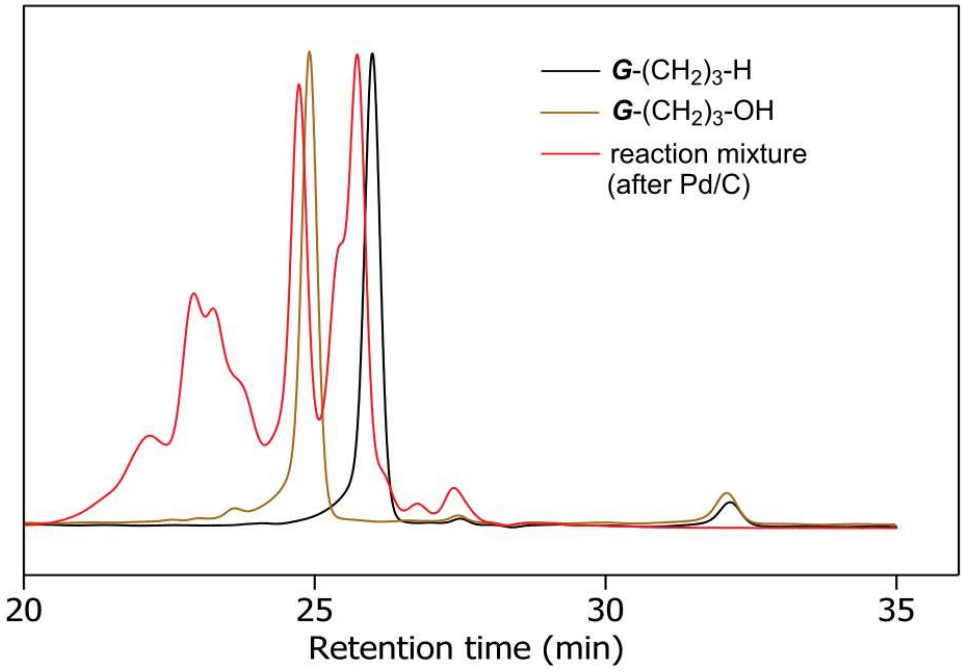


Figure S26. Comparison of SEC results for lignin obtained in the flow process with SEC results for standard lignin-derived monophenolic compounds.

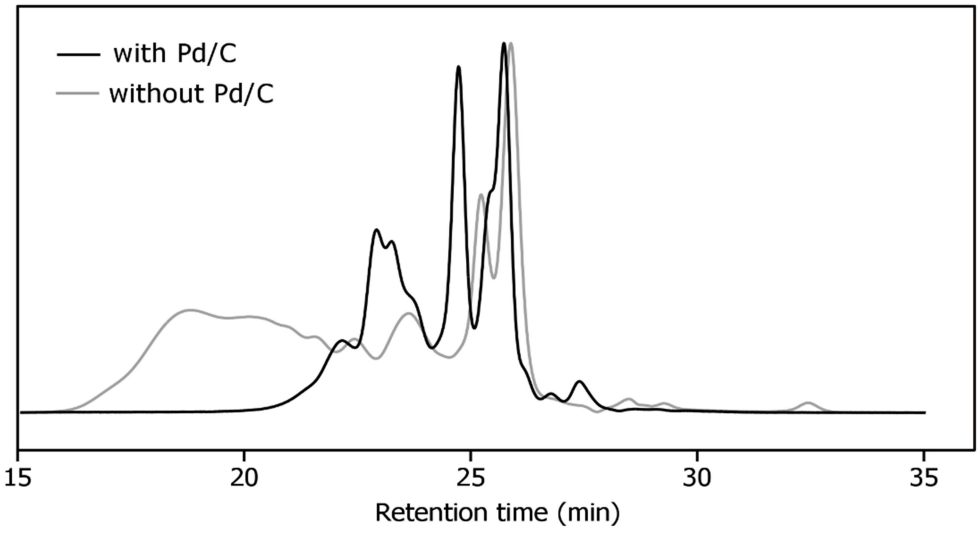


Figure S27. SEC of lignin obtained in reaction and without with Pd/C (dried in high vacuum; small molecules such as solvents and organic acids are **removed**)

10. Heat map

Temperatures in the parts of the flow machine which were not heated directly (cartridge outlets, connection tubes and backpressure regulator) were estimated using Seek Compact thermal camera.

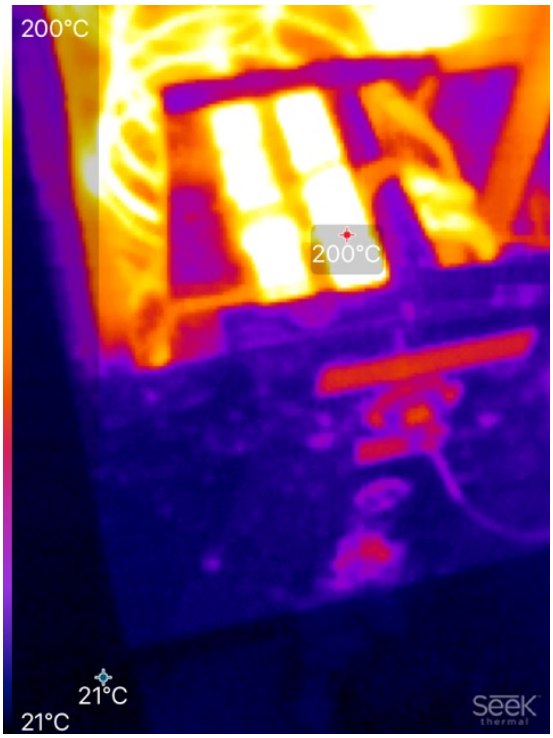


Fig S27. 1st cartridge

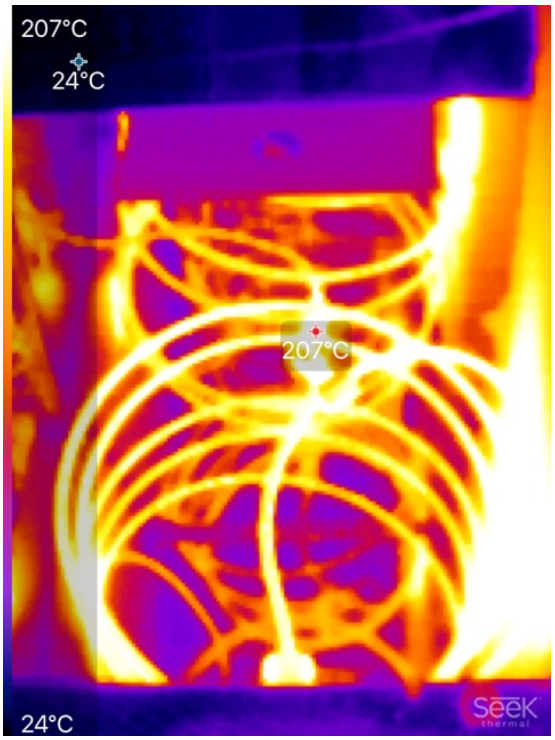


Fig S28. Preheater

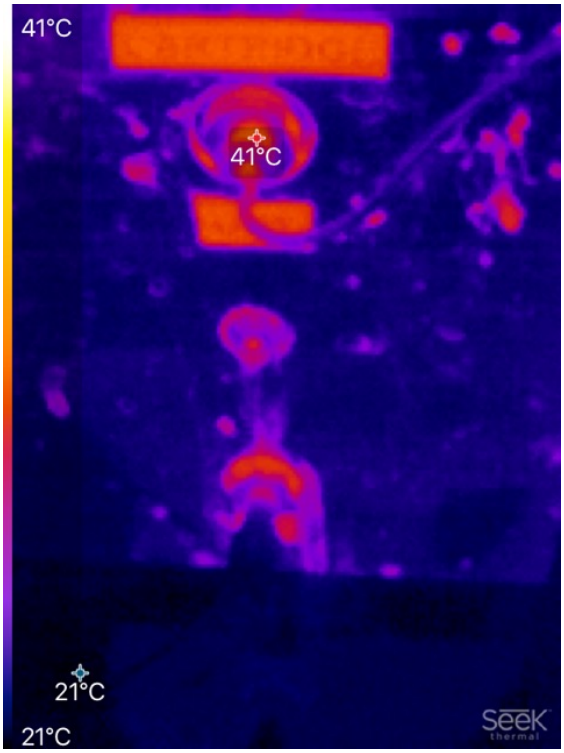


Fig S29. Outlet of the 1st cartridge and beginning of the tube which connects two cartridges.

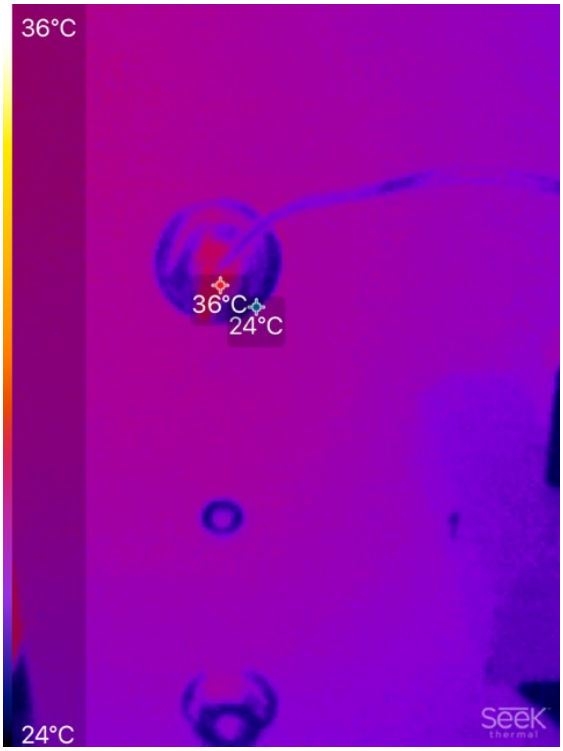


Fig S30. Outlet of the 2nd cartridge and beginning of the tube which connects the 2nd cartridge with the back pressure regulator.

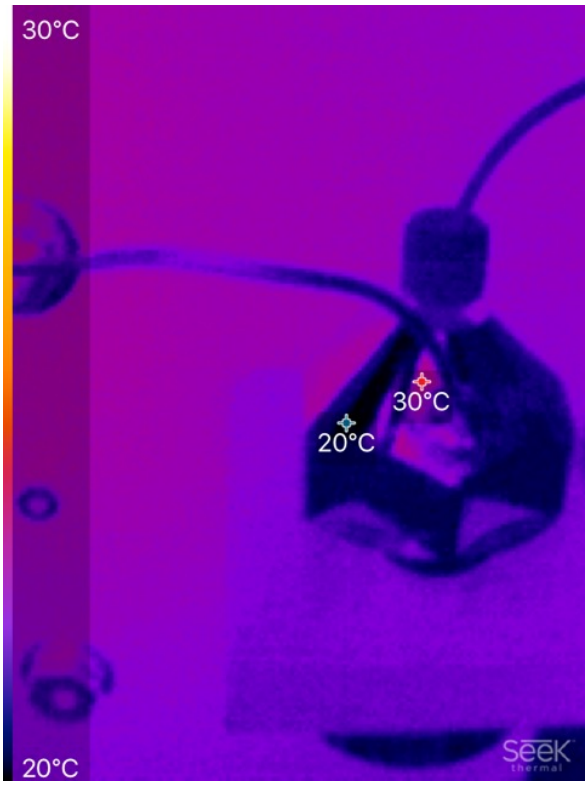


Fig S31. Back pressure regulator

11. Possible reaction mechanisms for lignin depolymerization

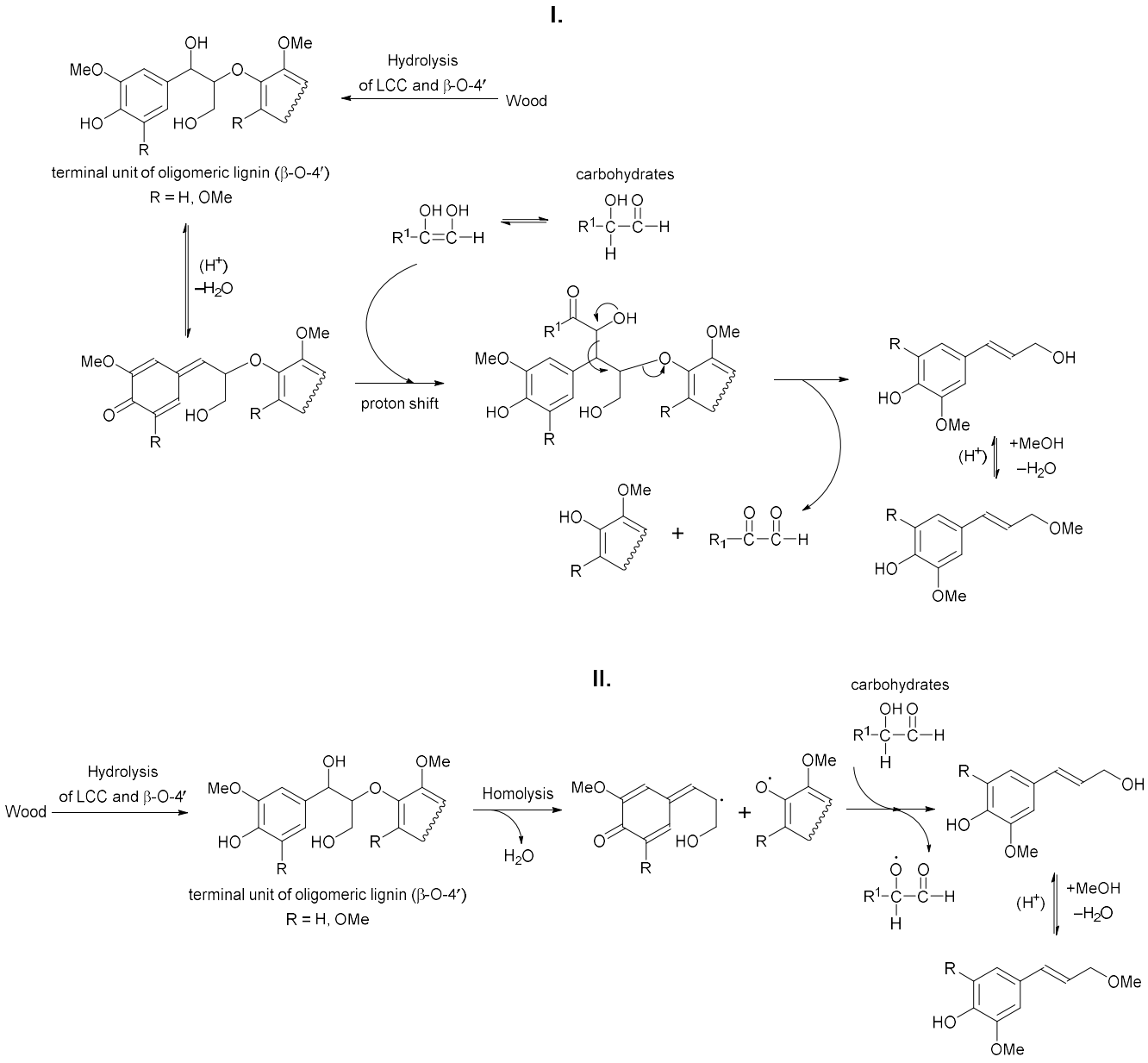


Figure S40. Proposed mechanism of reductive depolymerization of lignin results in allylic monolignol derivatives (the first step of the flow process, takes place in the first cartridge before interaction with Pd/C). Two possible pathways are depicted: **I** – ionic; **II** – radical. In the latter, methanol can act as radical scavenger (reducing agent) along with carbohydrates.

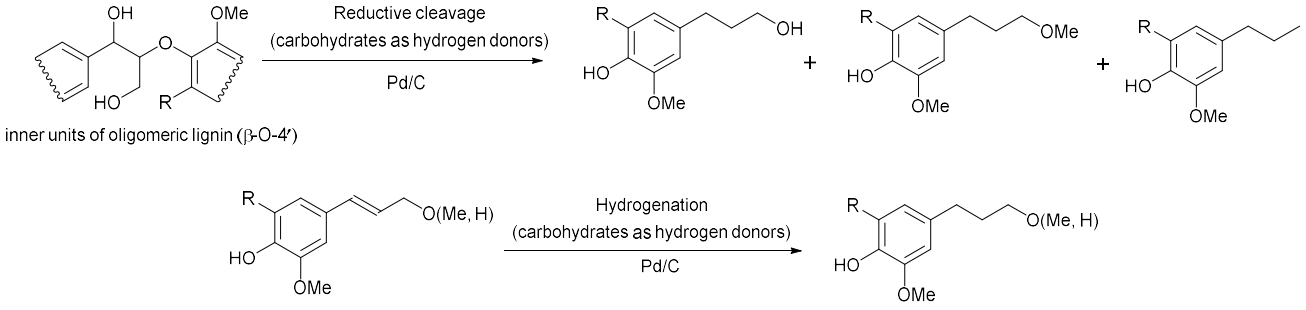


Figure S41. Reductive cleavage of β-O-4′ bonds (for mechanistic discussion, see [8], [9]) and hydrogenation of monolignols (the second step of the flow process, takes place in the second cartridge with Pd/C). Pd/C has previously been fully characterized [10]

12. Literature

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