

Supporting Information

Title

Controlling Lignin Solubility and Hydrogenolysis Selectivity by Acetal-mediated Functionalization

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Materials

Biological Materials

Birch wood (7A). The birch wood was procured from Dr. Michael Studer of the Bern University of Applied Sciences. The birch tree (*Betula pendula*, ca. 40 years old) was harvested in May of 2018 in Solothurn, Switzerland. The tree was debarked and the stem (trunk) was converted into wood chips then air-dried at 40 °C for 24 hours. These wood chips were then collected and transported to EPFL where they were sieved and sorted to remove residual bark and leaves. The wood chips were then milled using a 6 mm screen and then machine sieved with a 0.45 mm mesh to remove fines. Our internal serial number for this biomass feedstock is 7A.

Table 1. Composition of the Birch Wood Used for the Fractionation Procedures.^a

Ash	Hydration	Extractives ^b	Klason Lignin	Acid Soluble Lignin	Glucan	Xylan	Galactan	Arabinan	Mannan	Acetyl	Total
0.15%	6.09%	3.27%	17.94%	2.81%	32.16%	17.81%	2.01%	0.56%	0.26%	5.89%	88.95%

^a Fractions are presented as a wt/wt% of the raw biomass. The compositional analysis was determined according to the procedures outlined in *Talebi Amiri et. al.*¹ The data shown here is reproduced from that publication.

Table 2. Yield of Lignin Monomers from the Reductive Catalytic Fractionation of the Birch Wood on a Dry Basis.^a

Biomass	M1	M3	M5	M7	M15	M9	Total
Birch 7A	0.09%	1.74%	0.49%	8.04%	0.00%	0.30%	10.66%

^a Yields are presented as a wt/wt% of the total raw biomass on a dry basis and is corrected for any mass lost with respect to the monomers' initial structures in the native lignin polymer.

Chemicals

- 1,4-Dioxane ($\geq 99.5\%$ for Synthesis, Carl Roth AG – 4229)
- 2-Methyltetrahydrofuran ($\geq 99.5\%$, Sigma-Aldrich – 155810)
- Acetaldehyde ($\geq 99.5\%$, Roth – 3004.1)

- Benzaldehyde (≥99.5%, Roth – 4372.1)
- Chloroacetaldehyde (50 wt% in H₂O, Sigma-Aldrich – 317276)
- Chloral Hydrate (≥98.0%, Sigma-Aldrich – 23100)
- Decanaldehyde (95%, Acros Organics – 154971000)
- Deionized Water
- Dibutyl Ether (Merck EMD Millipore – 8.02892.2500)
- Dichloroacetaldehyde Hydrate
- Diethyl Ether (Pure, Stabilised with BHT, Carlo Erba – 528275)
- Dimethylsulfoxide-d₆
- Dodecanaldehyde (95%, ABCR – 116366)
- Ethanol (≥99.8% Analytical Reagent Grade, Ph. Eur., Fisher Chemical – E/0650DF/15)
- Ethyl Acetate (Thommen-Furler AG – 142-VL54K)
- Glycoaldehyde Dimer (Mixture of Stereoisomers, Sigma-Aldrich – G6805)
- Glyoxylic Acid Monohydrate (97%, Fluorochem – 143700)
- Hexanes (Fraction, Thommen-Furler AG – 272-VL54K)
- Hydrochloric Acid (37 wt%, Analytical Reagent Grade, Fisher Chemical – H/1200/PB15)
- Isobutyraldehyde (≥99%, Sigma-Aldrich – 240788)
- Isopropanol (99%, Thommen-Furler AG – 172-VL54TE)
- Isooctane (≥99.5%, Sigma-Aldrich – 32291)
- Methanol (≥99%, Thommen-Furler AG – 203-VL54K)
- *m*-Hydroxybenzaldehyde (≥97%, Roth – 4493.1)
- *n*-Decane (≥99%, Sigma-Aldrich – D901)
- Octanaldehyde (99%, Sigma-Aldrich – O5608)
- *p*-(Trifluoromethyl)benzaldehyde (98%, Apollo Scientific – PC7502)
- *p*-Anisaldehyde (≥97.5%, FCC, FG, Sigma-Aldrich – W267007)
- *p*-Chlorobenzaldehyde (97%, Sigma-Aldrich – 112216)
- *p*-Formylbenzoic Acid (99%, Fluorochem – 078635)
- *p*-Hydroxybenzaldehyde (99%, Roth – 3870.2)
- Pivaldehyde (96%, Sigma-Aldrich – T71501)
- Propionaldehyde (97%, Sigma-Aldrich – 538124)
- *p*-Tolualdehyde (97%, Sigma-Aldrich – T35602)
- Ruthenium on Carbon (5%, Strem Chemicals – 44-4050)
- Salicylaldehyde (≥99%, Roth – 4662.1)
- Sodium Hydroxide (Pastilles, Reactolab SA – 99792)
- Sodium Lignosulfonate (≥93%, Roth – 8999.1)
- Syringaldehyde (95%, Fluorochem – 132400)
- Tetrahydrofuran (ACS Reagent Grade, Stabilised with BHT, Honeywell – 10315843)
- Toluene (ACS Reagent Grade, VWR – 28676.297)
- Vanillin (≥99%, Roth – 7887.1)

Gases

- Hydrogen (≥99.999%, Alphagaz™ 1 Hydrogen; Air Liquide (Carbagas) – P0231L50R2A001)
- Nitrogen (≥99.999%, Alphagaz™ 1 Nitrogen; Air Liquide (Carbagas) – P0271L50S2A001)
- Synthetic Air (≥99.999%, 20% ± 2% O₂, Balance N₂; Air Liquide (Carbagas) – I4520L50R2A001)

Reagent Preparation

n-Decane Gas Chromatography Standard

n-Decane (400 mg, 2.81 mmol) was massed into a 10 mL volumetric flask and diluted with 1,4-dioxane to 10 mL. The solution can be stored at 23 °C for up to 6 months after which it must be tested for peroxides due to the 1,4-dioxane. If no peroxides have formed, it can be stored for an additional 6 months after which it must be tested again.

Equipment

Glassware, Reactors, and Consumables

- 2 Dram Vials with Septum Caps
- Bubbler, 40 mL (VWR – 89063-988)
- Clamping Lid (Plexiglas for 200 mm Diameter Test Sieves; Fritsch – 31.2020.00)
- Dimroth Reflux Condenser (29/32 joint, 160 mm height, Duran; VWR – 210-1681)
- Erlenmeyer Flask, 500 mL (VWR – 214-1133)
- Filter Flask, 250 mL (Duran – 21 204 36 5)
- Gas Chromatography Caps (Infochroma AG – G004-HP-CR-SKFK10)
- Gas Chromatography Vials (Infochroma AG – G004-HP-H)
- Glass Filter Funnel (Porosity Grade 3), 50 mL (Duran – 25 852 0X3)
- Graduated Cylinder, 50 mL (Duran – 21 390 17 06)

- Hypodermic Needles, 21G x 38 mm (BD – 305167)
- Membrane Filtration Apparatus, 250 mL (Duran – 25 710 54 51)
- Neoprene Vacuum Adapters (VWR – KART420)
- NMR Tubes (400 MHz, 5mm x 177.8 mm, 0.43 mm wall; Wilmad – WG-1228-7)
- Nylon Membrane Filters (0.8 µm pore size, 47 mm diameter; Whatman – 7402-004)
- Oil Bath, 1 L (Heidolph – 504-93000-00)
- Pipette Tips, 20-200 µL (Tipone – S1111-0706)
- PTFE Coated Stir-bars (Oval, 20 mm length x 10 mm diameter; Bar, 30 mm length x 10 mm diameter)
- Reagent Bottle with GL 45 Polypropylene Cap, 100 mL (Simax – 1632414321100)
- Reagent Bottle with GL 45 Polypropylene Cap, 500 mL (Simax – 1632414321500)
- Reducing Adapter 45/40 male, 29/32 female (Roth AG – KN64.1)
- Round-Bottom Flask, 29/32, 100 mL (Duran – 24 170 27)
- Round-Bottom Flask, 29/32, 250 mL (Duran – 24 170 37)
- Round-Bottom Flask, 29/32, 500 mL (Duran – 24 170 46)
- Sieve Pan (Stainless Steel for 200 mm Diameter Test Sieves; Height: 50 mm; Fritsch – 31.1000.03)
- Soxhlet Extractor, 29/32 male, 45/40 female, 100 mL (Carl Roth AG – Y353.1)
- Soxhlet Extractor Socks
- Spatulas
- Syringes, 1 mL (Braun – 9166106V)
- Syringes, 5 mL (Codan – 62.5607)
- Syringes, 10 mL (Codan – 62.6612)
- Syringe Filter (Macherey-Nagel, Chromafil Xtra H-PTFE 20/25 – 729245)
- Test Sieve (Diameter: 200 mm; Height: 32 mm; Mesh Size: 0.450 mm; VWR – 510-0642)
- Vacuum Desiccator with Socket Valve (Plate Diameter: 235 mm; Diameter: 320 mm; Height: 349 mm; VWR – Type; 250 – 7571-434; Orange Indicating Silica Gel Dessicant)
- Variable Volume Single-Channel Pipette, 20-200 µL (VWR – 613-5263)
- Volumetric Flask, 10 mL (Duran – 24 671 10 54)

Instruments

- Anti-Static Device (Haug Static Line Discharge Power Supply EN SL 230V/50-60 Hz – 51.7780.220W; PRX U-Electrode Anti-Static Frame – 03.8591.006)
- Automated Column Machine (Biotage Isolera Prime, One Channel, Single Collection Bed, 200-400 nm Detector – ISO-PSV)
- Cutting Mill (Retsch – SM 200)
- Agilent Technologies Gas Chromatography System 7890B with Autosampler 7963 and a Flame Ionization Detector (GC-FID) equipped with an Agilent Technologies HP-5 Column (Length: 30 m, Diameter: 0.320 mm, Film: 0.25 µm)
- Agilent Technologies Gas Chromatography System 7890B with Autosampler 7963 and Mass Spectrometer Detector (MSD) 5977A (GC-MS) equipped with an Agilent Technologies HP-5MS UI Column (Length: 30 m, Diameter: 0.320 mm, Film: 0.25 µm)
- High Pressure Reactor for Hydrogenolysis consisting of a Parr Reactor (Rated to 200 bar at 350 °C; 50 mL; Hastelloy C-276, Moveable Head with Thermowell, 200 bar Pressure Gauge with Gauge Adapter and Valve, Rupture Disk Assembly, and Double Valve Assembly with Dip Tube; 200 Bar Rupture Disk, PTFE Flat Gasket; ASME Certified; Part Number – 4792-50mL-T-HC-VGR-DVD-3000-ASME), Hot Plate Stirrer (Heidolph – 505-30000-00-4), Thermocouple (K-Type; Parr Instrument Company – D002E4), Temperature Control Box (230 VAC; Omega – CN7823), and Ceramic Band Heater (500W, 230 VAC; Equilabo – FOURMICRO2550K)
- Hot Plate Stirrer with Temperature Regulator (Heidolph – 505-30081-00-4)
- Microbalance (Ohaus – AX324)
- Nuclear Magnetic Resonance (Bruker Avance III 400 MHz spectrometer with BBFO-plus probe)
- Rotary Evaporator (Heidolph Hei-VAP Advantage Rotary Evaporator – 562-01310-00-1; Buchi V-300 Vacuum Pump with I-300 Interface – 11V300220)
- Shaking Incubator (New Brunswick Scientific – Innova 26, 2.5 cm (1 in) orbit diameter)
- Sonicator (VWR – USC 300 TH – 142-0084)
- UV-Vis Scanning Spectrophotometer (VWR – UV-3100PC – 10037-438)
- Vibratory Sieve Shaker (Fritsch Analysette)

Instrument Methods

Gas Chromatography – No Hydrodeoxygenation Products

Injection Volume	1 µL
Septum Purge Flow	3 mL·min ⁻¹
Split Ratio	50:1
Split Flow Rate	161.18 mL·min ⁻¹
Injection Temperature	300 °C
Column Temperature	40 °C for 3 min, ramp at 30 °C·min ⁻¹ to 100 °C (2 minutes), ramp at 40 °C·min ⁻¹ to 300 °C (5 minutes), hold at 300 °C (5 min)
Carrier Gas	He at 3.2236 mL·min ⁻¹ and 13.302 PSI
FID Detection Temperature	300 °C
FID Gases	H ₂ at 30 mL·min ⁻¹ , synthesis air at 400 mL·min ⁻¹ , and N ₂ at 25 mL·min ⁻¹

Gas Chromatography – With Hydrodeoxygenation Products

Injection Volume	1 μL
Septum Purge Flow	3 $\text{mL}\cdot\text{min}^{-1}$
Split Ratio	10:1
Split Flow Rate	32.236 $\text{mL}\cdot\text{min}^{-1}$
Injection Temperature	300 $^{\circ}\text{C}$
Column Temperature	40 $^{\circ}\text{C}$ initial temperature, ramp at 15 $^{\circ}\text{C}\cdot\text{min}^{-1}$ to 225 $^{\circ}\text{C}$ (12 minutes, 20 seconds), hold at 225 $^{\circ}\text{C}$ (5 min)
Carrier Gas	He at 3.2236 $\text{mL}\cdot\text{min}^{-1}$ and 13.302 PSI
FID Detection Temperature	300 $^{\circ}\text{C}$
FID Gases	H_2 at 30 $\text{mL}\cdot\text{min}^{-1}$, synthesis air at 400 $\text{mL}\cdot\text{min}^{-1}$, and N_2 at 25 $\text{mL}\cdot\text{min}^{-1}$

Methods

Lignin Extraction Procedure

The procedure outline below was modified from our previous publication on the fractionation of lignocellulose using an optimized aldehyde assisted fractionation (AAF) procedure.¹

General Reaction Conditions

Biomass (5.0000 g) was massed into a tared, 100 mL reagent bottle. The aldehyde (66 mmol, 6.6 equiv.), 1,4-dioxane (25 mL), hydrochloric acid (37 wt/wt%, 0.83 mL, 10 mmol, 1.0 equiv.), and a PTFE coated stir bar were then added to the flask. The reagent bottle was sealed with a GL 45 cap and heated with stirring to 85 $^{\circ}\text{C}$ for 3 to 5 hours (depends on the aldehyde, see below).

Optional Modifications: 2-methyltetrahydrofuran can be substituted for 1,4-dioxane. For aldehydes without hydrogens alpha to the carbonyl (e.g., benzaldehyde or glyoxylic acid), the loading of aldehyde can be reduced to 16.5 mmol (1.65 equiv.) per 5 grams of biomass. The reduction in aldehyde loading is made possible by the fact that aldehydes without hydrogens alpha to the carbonyl cannot undergo aldol reactions. Aldol reactions are observed when aldehydes with hydrogens alpha to the carbonyl are used for the fractionation (e.g., acetaldehyde, propionaldehyde).

Aldehydes That Require a Three-Hour Reaction Time

- Acetaldehyde
- Benzaldehyde
- Chloral Hydrate
- Decanaldehyde
- Dichloroacetaldehyde Hydrate
- Dodecanaldehyde
- Glycolaldehyde Dimer
- Glyoxylic Acid Mono Hydrate
- Isobutyraldehyde
- *m*-Hydroxybenzaldehyde
- Octanaldehyde
- *p*-(Trifluoromethyl)benzaldehyde
- *p*-Anisaldehyde
- *p*-Chlorobenzaldehyde
- *p*-Formylbenzoic Acid
- *p*-Hydroxybenzaldehyde
- Pivaldehyde
- Propionaldehyde
- *p*-Tolualdehyde
- Salicylaldehyde
- Syringaldehyde
- Vanillin

Aldehydes That Require a Five-Hour Reaction Time

- Chloroacetaldehyde

Note

We have observed that good lignin yields correlate with the qualitative observation of the biomass deconstruction over the course of the reaction. Large residual plant particles indicate that the biomass is not fully fractionated and therefore lignin yields will be low. Once the plant particles deconstruct into a powder, forming a slurry in the reaction solution, the fractionation is typically complete. Full deconstruction of the biomass typically requires ~ 3 hours at 85 $^{\circ}\text{C}$, but some aldehydes require longer. The reaction is not too sensitive to additional treatment time (e.g., an additional 30 minutes of treatment time does not substantially impact the yields), therefore it is more important to completely deconstruct the biomass. The reaction time is also dependent upon the particle size with smaller particles requiring less time than larger particles.²

Work-up

The reaction was cooled to room temperature (~23-30 °C) and filtered through a ground glass frit (porosity grade 3) washing with dioxane (25 mL) to remove the cellulose-rich solids. The filtrate was then transferred to a 29/32, 250 mL round-bottom flask and concentrated on a rotovap with a bath temperature of 45 °C and an ultimate pressure of 10 mbar. The lignin was then precipitated according to the procedures outlined in the next section.

General Purification Procedure

The different aldehyde-stabilised lignins and aldehyde-stabilised sugars have different solubilities, complicating the development of a general purification strategy. In addition, the lignins have both a Klason component and acid-soluble component, which can present different solubilities. To maximize the possible yield that one could obtain from the hydrogenolysis, the lignins were initially precipitated in a non-polar solvent (*e.g.*, pentane, hexanes, heptane, or dibutyl ether). If the residual aldehyde and aldehyde stabilised xylose are soluble in water (*e.g.*, glyoxylic acid and glyoxylic acid stabilised xylose), it can be substituted for the non-polar solvents in the precipitation. The lignins were then collected by filtration through a nylon membrane filter (0.8 µm) and washed with the precipitation solvent. The lignins were then transferred into a tared 29/32, 100 mL, round-bottom flasks and dried *in vacuo* to yield the lignins as powders.

After a sample of the lignin had been set aside for hydrogenolysis (see conditions below), the lignins were further purified by Soxhlet extraction. Briefly, the lignins were transferred using the extraction solvent (diethyl ether or ethyl acetate) into a Soxhlet extractor sock, which was placed into a 100 mL Soxhlet extractor. A 500 mL round bottom flask with PTFE coated stir-bar was filled with the extraction solvent (250 mL, diethyl ether or ethyl acetate) and then fitted with the Soxhlet extractor. The Soxhlet extractor and round bottom flask were then clamped in place and fitted with a reducing adapter, Dimroth reflux condenser, and an oil bubbler. The round bottom flask was then heated to reflux, and the material was extracted until the solvent drained clear. This step removes residual sugars, unreacted aldehyde, and highly soluble lignin species from the stabilised lignins for determination of their solubility parameters. After completion, the apparatus was dismantled. The Soxhlet extractor sock was placed into a vacuum desiccator to remove any residual extraction solvent. The next day, the lignin was transferred into a tared 100 mL round bottom flask with a quantitative transfer being insured by washing with dioxane. The solvent was removed *in vacuo* first on a rotovap and then using a Schlenk line. The flask was re-tared, and the mass was recorded.

Note

The lignins that we isolated have different and often unexpected colours. We do not know the exact cause of the colours, but we do know that they are feedstock, acid, and aldehyde dependent. Furthermore, redissolution of the lignin in solvents other than 1,4-dioxane or treatment of the lignin with acids or bases can change the colour of the lignin.

Acetaldehyde Stabilised Lignin Extraction

Reaction Conditions: The general procedure was followed using birch wood (5.0447 g), acetaldehyde (3.8 mL, 68 mmol), hydrochloric acid (0.85 mL, 10 mmol), and dioxane (25 mL).

Precipitation: The concentrated crude reaction mixture was diluted with dioxane (10 mL) and then added dropwise using a glass pipette to a 500 mL reagent bottle containing hexanes (250 mL) that was being stirred by a bar-type PTFE coated stir-bar at 250 RPM. Filtration and drying yielded a pink powder (1.5865 g, 31.4 wt/wt%). A sample of which was subjected to hydrogenolysis (0.2301 g).

Soxhlet Extraction: The residual precipitated lignin was extracted using diethyl ether to yield the lignin as a pink powder (0.7578 g, 17.6 wt/wt% corrected for the hydrogenolysis sample).

Propionaldehyde Stabilised Lignin Extraction

Reaction Conditions: The general procedure was followed using birch wood (5.0737 g), propionaldehyde (4.8 mL, 67 mmol), hydrochloric acid (0.85 mL, 10 mmol), and dioxane (25 mL).

Precipitation: The concentrated crude reaction mixture was diluted with dioxane (10 mL) and then added dropwise using a glass pipette to a 500 mL reagent bottle containing hexanes (250 mL) that was being stirred by a bar-type PTFE coated stir-bar at 250 RPM. Filtration and drying yielded a pink powder (1.6644 g, 32.8 wt/wt%). A sample of which was subjected to hydrogenolysis (0.2653 g).

Soxhlet Extraction: The residual precipitated lignin was extracted using diethyl ether yielding the lignin as a pink powder (0.7216 g, 16.9 wt/wt% corrected for the hydrogenolysis sample).

Propionaldehyde Stabilised Lignin Extraction Using 2-Methyltetrahydrofuran as the Extraction Solvent

Reaction Conditions: The general procedure was followed using birch wood (2.03 g), propionaldehyde (2.0 mL, 28 mmol), hydrochloric acid (0.38 mL, 4.5 mmol), and 2-methyltetrahydrofuran (10 mL).

Precipitation: The concentrated crude reaction mixture was diluted with ethyl acetate (5 mL) and then added dropwise using a glass pipette to a 250 mL reagent bottle containing hexanes (100 mL) that was being stirred by a bar-type PTFE coated stir-bar at 250 RPM. Filtration and drying yielded a pink powder (0.4327 g, 21.315 wt/wt%). A sample of which was subjected to hydrogenolysis (0.2034 g).

Trituration: The residual precipitated lignin was extracted using diethyl ether (25 mL x 3) yielding the lignin as a pink powder (0.3764 g, 18.5 wt/wt% corrected for the hydrogenolysis sample).

Isobutyraldehyde Stabilised Lignin Extraction

Reaction Conditions: The general procedure was followed using birch wood (5.0334 g), isobutyraldehyde (6 mL, 66 mmol), hydrochloric acid (0.85 mL, 10 mmol), and dioxane (25 mL).

Precipitation: The concentrated crude reaction mixture was diluted with dioxane (10 mL) and then added dropwise using a glass pipette to a 500 mL reagent bottle containing hexanes (250 mL) that was being stirred by a bar-type PTFE coated stir-bar at 250 RPM. Filtration and drying yielded a pink powder (1.5709 g, 31.2 wt/wt%). A sample of which was subjected to hydrogenolysis (0.2084 g).

Soxhlet Extraction: The residual precipitated lignin was extracted using diethyl ether yielding the lignin as a pink powder (0.5819 g, 13.3 wt/wt% corrected for the hydrogenolysis sample).

Pivaldehyde Stabilised Lignin Extraction

Reaction Conditions: The general procedure was followed using birch wood (5.0227 g), pivaldehyde (7.2 mL, 66 mmol), hydrochloric acid (0.85 mL, 10 mmol), and dioxane (25 mL).

Precipitation: The concentrated crude reaction mixture was added dropwise using a glass pipette to a reagent bottle containing hexanes (250 mL) that was being stirred by a bar-type PTFE coated stir-bar at 250 RPM. A quantitative transfer was affected using ethyl acetate. Filtration and drying yielded a purple powder (1.3703 g, 27.3 wt/wt%). A sample of which was subjected to hydrogenolysis (0.2087 g).

Trituration: As opposed to Soxhlet extraction, the lignin was instead triturated by sonicating it with dibutyl ether (50 mL). Filtration and drying yielded a brown powder (1.0073 g, 23.7 wt/wt% after correcting for the hydrogenolysis sample).

Octanaldehyde Stabilised Lignin Extraction

Reaction Conditions: The general procedure was followed using birch wood (5.0361 g), octanaldehyde (10.5 mL, 67 mmol), hydrochloric acid (0.85 mL, 10 mmol), and dioxane (25 mL).

Precipitation: The concentrated crude reaction mixture was added dropwise using a glass pipette to a reagent bottle containing hexanes (250 mL) that was being stirred by a bar-type PTFE coated stir-bar at 250 RPM. A quantitative transfer was affected using ethyl acetate. Filtration and drying yielded a brown powder (1.4479 g, 28.8 wt/wt%). A sample of which was subjected to hydrogenolysis (0.2113 g).

Trituration: The residual precipitated lignin was triturated with dibutyl ether (50 mL). Filtration and drying yielded a purplish-brown powder (0.9860 g, 22.9 wt/wt% after correcting for the hydrogenolysis sample).

Decanaldehyde Stabilised Lignin Extraction

Reaction Conditions: The general procedure was followed using birch wood (5.0075 g), decanaldehyde (12.5 mL, 66 mmol), hydrochloric acid (0.85 mL, 10 mmol), and dioxane (25 mL).

Precipitation: The concentrated crude reaction mixture was added dropwise using a glass pipette to a reagent bottle containing hexanes (250 mL) that was being stirred by a bar-type PTFE coated stir-bar at 250 RPM. A quantitative transfer was affected using ethyl acetate. Filtration and drying yielded a brown powder (1.3176 g, 26.3 wt/wt%). A sample of which was subjected to hydrogenolysis (0.2247 g).

Soxhlet Extraction: The lignin was not extracted.

Dodecanaldehyde Stabilised Lignin Extraction

Reaction Conditions: The general procedure was followed using birch wood (5.0569 g), dodecanaldehyde (12.2386 g, 66.3976 mmol), hydrochloric acid (0.85 mL, 10 mmol), and dioxane (25 mL).

Precipitation: The concentrated crude reaction mixture was added dropwise using a glass pipette to a reagent bottle containing hexanes (250 mL) that was being stirred by a bar-type PTFE coated stir-bar at 250 RPM. A quantitative transfer was affected using hexanes. The bottle was then placed in the refrigerator overnight to facilitate precipitation of the lignin. The next day, filtration and drying yielded a brown powder (1.1607 g, 23.0 wt/wt%). A sample of which was subjected to hydrogenolysis (0.2372 g).

Soxhlet Extraction: The lignin was not extracted.

Chloroacetaldehyde Stabilised Lignin Extraction

Reaction Conditions: The general procedure was followed using birch wood (5.0439 g), chloroacetaldehyde solution (50 wt/wt% in water, 8.5 mL, 67 mmol), hydrochloric acid (0.85 mL, 10 mmol), and dioxane (25 mL).

Precipitation: The concentrated crude reaction mixture was diluted with dioxane (10 mL) and added dropwise using a glass pipette to a 500 mL round-bottom flask containing dibutyl ether (250 mL) that was being stirred by an oval-type PTFE coated stir-bar at 250 RPM. Filtration and drying yielded a pink powder (1.7008 g, 33.7 wt/wt%). A sample of which was subjected to hydrogenolysis (0.2522 g).

Soxhlet Extraction: The residual precipitated lignin was extracted using diethyl ether to yield the lignin as a pink powder (0.8662 g, 20.2 wt/wt% corrected for the hydrogenolysis sample).

Dichloroacetaldehyde Stabilised Lignin Extraction

Reaction Conditions: The general procedure was followed using birch wood (5.0248 g), dichloroacetaldehyde hydrate (7.7660 g, 59.310 mmol), hydrochloric acid (0.85 mL, 10 mmol), and dioxane (25 mL).

Precipitation: The concentrated crude reaction mixture was diluted with dioxane (10 mL) and added dropwise using a glass pipette to a 500 mL round-bottom flask containing dibutyl ether (250 mL) that was being stirred by an oval-type PTFE coated stir-bar at 250 RPM. Filtration and drying yielded a dark brown powder (1.9296 g, 38.4 wt/wt%). A sample of which was subjected to hydrogenolysis (0.2150 g).

Soxhlet Extraction: The residual precipitated lignin was extracted using diethyl ether to yield the lignin as a dark brown powder (1.0421 g, 23.3 wt/wt% corrected for the hydrogenolysis sample).

Chloral Stabilised Lignin Extraction

Reaction Conditions: The general procedure was followed using birch wood (5.0026 g), chloral monohydrate (11.0047 g, 66.5379 mmol), hydrochloric acid (0.85 mL, 10 mmol), and dioxane (25 mL).

Precipitation: The concentrated crude reaction mixture was diluted with dioxane (10 mL) and added dropwise using a glass pipette to a 500 mL round-bottom flask containing dibutyl ether (250 mL) that was being stirred by an oval-type PTFE coated stir-bar at 250 RPM. Filtration and drying yielded a brown powder (1.3290 g, 26.6 wt/wt%). A sample of which was subjected to hydrogenolysis (0.2792 g).

Soxhlet Extraction: The residual precipitated lignin was extracted using diethyl ether to yield the lignin as a brown powder (0.4644 g, 11.8 wt/wt% corrected for the hydrogenolysis sample).

Glycolaldehyde Stabilised Lignin Extraction

Reaction Conditions: The general procedure was followed using birch wood (5.0114 g), glycolaldehyde dimer (3.9703 g, 33.058 mmol), hydrochloric acid (0.85 mL, 10 mmol), and dioxane (25 mL).

Precipitation: The concentrated crude reaction mixture was diluted with dioxane (10 mL) and added dropwise using a glass pipette to a 500 mL round-bottom flask containing dibutyl ether (250 mL) that was being stirred by an oval-type PTFE coated stir-bar at 250 RPM. Filtration and drying yielded a brown powder (3.9739 g, 79.3 wt/wt%). A sample of which was subjected to hydrogenolysis (0.2499 g).

Soxhlet Extraction: The residual precipitated lignin was extracted using ethyl acetate to yield the lignin as a brown powder (1.4492 g, 30.9 wt/wt% corrected for the hydrogenolysis sample).

Glyoxylic Acid Stabilised Lignin Extraction

Reaction Conditions: The general procedure was followed using birch wood (5.0469 g), glyoxylic acid monohydrate (6.0942 g, 66 mmol), hydrochloric acid (0.85 mL, 10 mmol), and dioxane (25 mL).

Precipitation: Into the concentrated lignin solution was added de-ionized water (100 mL) followed by an oval-type PTFE coated stir-bar. The mixture was stirred at 500 RPM for 30 minutes to break the large agglomerations. The stir-bar was then removed. Filtration and drying yielded a beige powder (1.0731 g, 21.3 wt%). A sample of which was subjected to hydrogenolysis (203.2 mg).

Soxhlet Extraction: The lignin was not extracted.

4-Formylbenzoic Acid Stabilised Lignin Extraction

Reaction Conditions: The general procedure was followed using birch wood (5.0755 g), 4-formylbenzoic acid (9.9178 g, 66.061 mmol), hydrochloric acid (0.85 mL, 10 mmol), and dioxane (25 mL).

Precipitation: The concentrated crude reaction mixture was diluted with dioxane (10 mL) and added dropwise using a glass pipette to a 500 mL round-bottom flask containing dibutyl ether (250 mL) that was being stirred by an oval-type PTFE coated stir-bar at 250 RPM. Filtration and drying yielded a purplish-brown powder (7.4325 g, 146.4 wt/wt%). A sample of which was subjected to hydrogenolysis (206.6 mg).

Soxhlet Extraction: The residual precipitated lignin was extracted using diethyl ether to yield the lignin as a purplish-brown powder (0.7646 g, 15.6 wt/wt% corrected for the hydrogenolysis sample).

4-Chlorobenzaldehyde Stabilised Lignin Extraction

Reaction Conditions: The general procedure was followed using birch wood (5.0661 g), *p*-chlorobenzaldehyde (9.2794 g, 66.014 mmol), hydrochloric acid (0.85 mL, 10 mmol), and dioxane (25 mL).

Precipitation: The concentrated crude reaction mixture was diluted with dioxane (10 mL) and added dropwise using a glass pipette to a 500 mL round-bottom flask containing dibutyl ether (250 mL) that was being stirred by an oval-type PTFE coated stir-bar at 250 RPM. Filtration and drying yielded a purple powder (1.4018 g, 27.7 wt/wt%). A sample of which was subjected to hydrogenolysis (0.2011 g).

Soxhlet Extraction: The residual precipitated lignin was extracted using diethyl ether to yield the lignin as a purple powder (0.6437 g, 14.8 wt/wt% corrected for the hydrogenolysis sample).

Benzaldehyde Stabilised Lignin Extraction

Reaction Conditions: The general procedure was followed using birch wood (5.0691 g), benzaldehyde (6.8 mL, 67 mmol), hydrochloric acid (0.85 mL, 10 mmol), and dioxane (25 mL).

Precipitation: The concentrated crude reaction mixture was diluted with dioxane (10 mL) and added dropwise using a glass pipette to a 500 mL round-bottom flask containing dibutyl ether (250 mL) that was being stirred by an oval-type PTFE coated stir-bar at 250 RPM. Filtration and drying yielded a pink powder (1.2832 g, 25.3 wt/wt%). A sample of which was subjected to hydrogenolysis (0.2259 g).

Soxhlet Extraction: The residual precipitated lignin was extracted using diethyl ether to yield the lignin as a pink powder (0.7000 g, 16.8 wt/wt% corrected for the hydrogenolysis sample).

4-Tolualdehyde Stabilised Lignin Extraction

Reaction Conditions: The general procedure was followed using birch wood (5.0293 g), *p*-tolualdehyde (8.0 mL, 68 mmol), hydrochloric acid (0.85 mL, 10 mmol), and dioxane (25 mL).

Precipitation: The concentrated crude reaction mixture was diluted with dioxane (10 mL) and added dropwise using a glass pipette to a 500 mL round-bottom flask containing dibutyl ether (250 mL) that was being stirred by an oval-type PTFE coated stir-bar at 250 RPM. Filtration and drying yielded a purple powder (1.5429 g, 30.7 wt/wt%). A sample of which was subjected to hydrogenolysis (0.2275 g).

Soxhlet Extraction: The residual precipitated lignin was extracted using diethyl ether to yield the lignin as a purplish-brown powder (1.0137 g, 23.6 wt/wt% corrected for the hydrogenolysis sample).

4-(Trifluoromethyl)benzaldehyde Stabilised Lignin Extraction

Reaction Conditions: The general procedure was followed using birch wood (5.0794 g), *p*-(trifluoromethyl)benzaldehyde (9.0 mL, 66 mmol), hydrochloric acid (0.85 mL, 10 mmol), and dioxane (25 mL).

Precipitation: The concentrated crude reaction mixture was diluted with dioxane (10 mL) and added dropwise using a glass pipette to a 500 mL round-bottom flask containing dibutyl ether (250 mL) that was being stirred by an oval-type PTFE coated stir-bar at 250 RPM. Filtration and drying yielded a purple powder (1.3719 g, 27.0 wt/wt%). A sample of which was subjected to hydrogenolysis (0.2210 g).

Soxhlet Extraction: The residual precipitated lignin was extracted using diethyl ether to yield the lignin as a purple powder (0.6279 g, 14.7 wt/wt% corrected for the hydrogenolysis sample).

4-Anisaldehyde Stabilised Lignin Extraction

Reaction Conditions: The general procedure was followed using birch wood (5.0424 g), *p*-anisaldehyde (8.0 mL, 66 mmol), hydrochloric acid (0.85 mL, 10 mmol), and dioxane (25 mL).

Precipitation: The concentrated crude reaction mixture was diluted with dioxane (10 mL) and added dropwise using a glass pipette to a 500 mL round-bottom flask containing dibutyl ether (250 mL) that was being stirred by an oval-type PTFE coated stir-bar at 250 RPM. Filtration and drying yielded a dark brown powder (1.7877 g, 35.5 wt/wt%). A sample of which was subjected to hydrogenolysis (0.2185 g).

Soxhlet Extraction: The residual precipitated lignin was extracted using diethyl ether to yield the lignin as a dark brown powder (0.9491 g, 21.4 wt/wt% corrected for the hydrogenolysis sample).

4-Hydroxybenzaldehyde Stabilised Lignin Extraction

Reaction Conditions: The general procedure was followed using birch wood (5.0515 g), *p*-hydroxybenzaldehyde (8.0571 g, 65.975 mmol), hydrochloric acid (0.85 mL, 10 mmol), and dioxane (25 mL).

Precipitation: The concentrated crude reaction mixture was diluted with dioxane (10 mL) and added dropwise using a glass pipette to a 500 mL round-bottom flask containing dibutyl ether (250 mL) that was being stirred by an oval-type PTFE coated stir-bar at 250 RPM. Filtration and drying yielded a brown powder (1.6236 g, 32.1 wt/wt%). A sample of which was subjected to hydrogenolysis (0.2460 g).

Soxhlet Extraction: The residual precipitated lignin was extracted using diethyl ether to yield the lignin as a dark brown powder (0.8358 g, 19.5 wt/wt% corrected for the hydrogenolysis sample).

3-Hydroxybenzaldehyde Stabilised Lignin Extraction

Reaction Conditions: The general procedure was followed using birch wood (5.0022 g), *m*-hydroxybenzaldehyde (8.0573 g, 65.977 mmol), hydrochloric acid (0.85 mL, 10 mmol), and dioxane (25 mL).

Precipitation: The concentrated crude reaction mixture was diluted with dioxane (10 mL) and added dropwise using a glass pipette to a 500 mL round-bottom flask containing dibutyl ether (250 mL) that was being stirred by an oval-type PTFE coated stir-bar at 250 RPM. Filtration and drying yielded a brown powder (1.7702 g, 35.4 wt/wt%). A sample of which was subjected to hydrogenolysis (0.2514 g).

Soxhlet Extraction: The residual precipitated lignin was extracted using diethyl ether to yield the lignin as a brown powder (0.8378 g, 19.5 wt/wt% corrected for the hydrogenolysis sample).

Salicylaldehyde Stabilised Lignin Extraction

Reaction Conditions: The general procedure was followed using birch wood (5.0353 g), salicylaldehyde (7.0 mL, 66 mmol), hydrochloric acid (0.85 mL, 10 mmol), and dioxane (25 mL).

Precipitation: The concentrated crude reaction mixture was diluted with dioxane (10 mL) and added dropwise using a glass pipette to a 500 mL round-bottom flask containing dibutyl ether (250 mL) that was being stirred by an oval-type PTFE coated stir-bar at 250 RPM. Filtration and drying yielded a dark brown powder (1.3134 g, 26.1 wt/wt%). A sample of which was subjected to hydrogenolysis (0.2521 g).

Soxhlet Extraction: The residual precipitated lignin was extracted using diethyl ether to yield the lignin as a dark brown powder (0.6601 g, 16.2 wt/wt% corrected for the hydrogenolysis sample).

Vanillin Stabilised Lignin Extraction

Reaction Conditions: The general procedure was followed using birch wood (5.0430 g), vanillin (10.1061 g, 66.4220 mmol), hydrochloric acid (0.85 mL, 10 mmol), and dioxane (25 mL).

Precipitation: The concentrated crude reaction mixture was diluted with dioxane (10 mL) and added dropwise using a glass pipette to a 500 mL round-bottom flask containing dibutyl ether (250 mL) that was being stirred by an oval-type PTFE coated stir-bar at 250 RPM. Filtration and drying yielded a dark brown powder (2.1594 g, 42.8 wt/wt%). A sample of which was subjected to hydrogenolysis (0.2010 g).

Soxhlet Extraction: The residual precipitated lignin was extracted using diethyl ether to yield the lignin as a dark brown powder (0.9699 g, 21.2 wt/wt% corrected for the hydrogenolysis sample).

Syringaldehyde Stabilised Lignin Extraction

Reaction Conditions: The general procedure was followed using birch wood (5.0693 g), syringaldehyde (12.0132 g, 65.9450 mmol), hydrochloric acid (0.85 mL, 10 mmol), and dioxane (25 mL).

Precipitation: The concentrated crude reaction mixture was diluted with dioxane (10 mL) and added dropwise using a glass pipette to a 500 mL round-bottom flask containing dibutyl ether (250 mL) that was being stirred by an oval-type PTFE coated stir-bar at 250 RPM. Filtration and drying yielded a brownish white powder. Due to an excess of residual syringaldehyde that was spread inhomogeneously throughout the precipitated lignin, the reaction could not be sampled for a hydrogenolysis sample.

Soxhlet Extraction: The precipitated lignin was extracted using diethyl ether to yield the lignin as a dark brown powder (1.2506 g, 24.7 wt/wt%)

Preparation of Sodium Carboxylate Lignin Salts

General Reaction Conditions

Lignin stabilised with an aldehyde containing a carboxylic acid (0.5000 g) was massed into a 20 mL vial. A PTFE coated stir-bar was added to the vial followed by deionized water (3 mL). With stirring, 2 N NaOH solution (2 mL) was then added and the solution was stirred until the lignin fully dissolved. Testing with a strip of pH paper was performed to ensure a pH \geq 10. Separately ethanol (50 mL) was added to a 250 mL Erlenmeyer flask with a PTFE coated stir-bar. The ethanol solution was stirred, and the lignin solution was added dropwise, precipitating the lignin salt. A quantitative transfer was affected with deionized water. The resulting lignin precipitate was collected by filtration on a 0.8 μ m nylon membrane filter. The lignin was air dried then transferred to a 100 mL round bottom flask and dried *in vacuo*.

Lignin Hydrogenolysis

Organic Solvent

Aldehyde-stabilised lignin (200 mg), and ruthenium on carbon (5 wt/wt%, 100 mg), were added to a 50-mL Parr reactor (see *Equipment* section) followed by a bar-type PTFE coated stir-bar and solvent (20 mL, THF unless otherwise noted). The reactor was sealed and then back filled with hydrogen gas (40 bar) three times. The reactor was then heated to 250 °C for 3 h with stirring. The reactor was then cooled to room temperature (~23-30 °C) and depressurized. The *n*-decane standard (200 μ L) was then added to the reaction solution using an autopipette. The solution was stirred using a spatula and then 1 mL was removed using a 1-mL syringe, filtered into a gas chromatography vial using a syringe filter, and injected onto the GC using the method described in the *Equipment* section. The appropriate peaks were integrated to determine the yield of the reaction as described in the *Equations* section.

Water

Aldehyde-stabilised lignin (200 mg), and ruthenium on carbon (5 wt/wt%, 100 mg), were added to a 50-mL Parr reactor (see *Equipment* section) followed by a bar-type PTFE coated stir-bar and de-ionized water (20 mL). The reactor was sealed and then back filled with hydrogen gas (40 bar) three times. The reactor was then heated to 250 °C for 3 h with stirring. The reactor was then cooled to room temperature (~23-30 °C) and depressurized. The reaction solution was then transferred to a 100 mL volumetric flask and diluted with THF to a volume of just under 100 mL. The *n*-decane standard (200 μ L) was then added to the reaction solution using an autopipette. The solution was then diluted to 100 mL with THF

and the sealed flask was shaken to ensure homogeneity. Using a 1-mL syringe, a 1 mL aliquot was removed, filtered into a gas chromatography vial using a syringe filter, and injected onto a GC using the method described in the *Equipment* section. The appropriate peaks were integrated to determine the yield of the reaction as outlined in the *Equations* section.

Note

The GC-FID will often contain the reduced form the stabilising aldehydes. Care should be taken to integrate the appropriate peaks as indicated in the Tables S6-8. Lignins stabilised by vanillin or syringaldehyde will produce 4-methylguaiacol and 4-methylsyringol during the hydrogenolysis. These monomers are minor products of the hydrogenolysis of the other acetal-stabilised lignins in THF (~1% of all monomers) and were not observed during the reductive catalytic fractionation of the feedstock biomass. Consequently, their contributions can be safely ignored in the calculation of the lignin monomer yields for the vanillin and syringaldehyde stabilised lignins.

Hydrogenolysis of Aldehyde-Stabilised Lignin Solutions

The raw biomass (1.0000 g) was massed into a tared, 20 mL vial. The aldehyde (13.5 mmol, 6.6 equiv.), 1,4-dioxane (5 mL), hydrochloric acid (37 wt/wt%, 0.17 mL, 2 mmol, 1.0 equiv.), and a PTFE coated stir bar were then added to the vial. The vial was sealed and heated with stirring to 85 °C. After 3 or 5 hours (depending on the aldehyde, see above), the reaction was cooled to room temperature (~23-30 °C) and filtered through a ground glass frit (porosity grade 3) washing with dioxane (~5-10 mL) to remove the cellulose-rich solids. The filtrate was then transferred to a 29/32, 100 mL round-bottom flask and concentrated on a rotovap with a bath temperature of 45 °C and an ultimate pressure of 10 mbar. The aldehyde-stabilised lignin solution was diluted with THF (20 mL) and transferred into a 50-mL Parr reactor. Ruthenium on carbon (5 wt/wt%, 100 mg) and a bar-type, PTFE-coated stir-bar (20 mm length x 10 mm diameter) were added. The reactor was then sealed and back filled with hydrogen gas (40 bar) three times. The reactor was then filled with H₂ gas (40 bar) and heated to 250 °C with stirring for 15 hours. The timer was started as soon as the reactor began heating. After 15 hours, the Parr reactor was cooled to room temperature (~25-30 °C) and depressurized. Once the reactor was opened, *n*-decane stock solution (200 µL) was added to the reaction solution and the solution was stirred with a spatula. To the reaction solution was then added the *n*-decane standard (200 µL) using an autopipette. Using a 1 mL syringe, a sample of the reaction solution was withdrawn from the Parr reactor and filtered through a syringe filter (0.2 µm) to remove the catalyst and other insoluble material into a gas chromatography vial. The vial was capped and injected into the gas chromatography instrument using the method described under *Instrument Methods: Gas Chromatography*. The appropriate peaks were integrated and processed using the relative response factors listed in **Table S6-S8** and **Equations 1-4** described under *Equations: Gas Chromatography Yield Determination* to determine the yield of the reaction.

Aldehyde-Stabilised Lignin Solutions That Were Hydrogenolysed

Syringaldehyde

Note

The GC-FID will often contain the reduced form the stabilising aldehydes. Care should be taken to integrate the appropriate peaks as indicated in the Tables S6-8. Lignins stabilised by vanillin or syringaldehyde will produce 4-methylguaiacol and 4-methylsyringol during the hydrogenolysis. These monomers are minor products of the hydrogenolysis of the other acetal-stabilised lignins in THF (~1% of all monomers) and were not observed during the reductive catalytic fractionation of the feedstock biomass. Consequently, their contributions can be safely ignored in the calculation of the lignin monomer yields for the vanillin and syringaldehyde stabilised lignins.

Reductive Catalytic Fractionation (RCF)

The raw biomass (1.0000 g), ruthenium on carbon (5 wt/wt%, 200 mg), and methanol (20 mL) were added into a 50 mL Parr reactor with bar-type, PTFE-coated stir-bar (20 mm length x 10 mm diameter). The Parr reactor was sealed and then backfilled with H₂ gas by filling it with 40 bar of H₂ and slowly releasing the pressure. The back-fill was repeated for a total of 3 times. The reactor was then filled with 40 bar of H₂ gas and heated to 250 °C with stirring for 15 hours. The timer was started as soon as the reactor began heating. After 15 hours, the Parr reactor was cooled to room temperature (~25-30 °C) and depressurized. The *n*-decane standard (200 µL) was added to the reaction solution using an autopipette and the solution was stirred with a spatula. Using a 1 mL syringe, a sample of the reaction solution was withdrawn from the Parr reactor and filtered through a syringe filter (0.2 µm) to remove the catalyst and other insoluble material into a gas chromatography vial. The vial was capped and injected into the gas chromatography instrument using the method described under *Instrument Methods: Gas Chromatography*. The appropriate peaks were integrated and processed using the relative response factors listed in **Table S6-S8** and **Equations 1-4** described under *Equations: Gas Chromatography Yield Determination* to determine the yield of the reaction.

Determination of the Lignin Solubility

For each solvent and each acetal-stabilised lignin, three 2-dram vials with septum caps were prepared. Each vial was labelled, had a hypodermic needle inserted through the septum cap, and then tared. Acetal-stabilised lignin (125 mg) was massed into a separate vial and the solvent (900 mg) being evaluated was added. After sufficient time had passed to dissolve the lignin (with limited sonication if necessary), the residual solids were allowed to settle, and the lignin solution was drawn into a 1 mL syringe. The syringe was then fitted with a 0.2 µm syringe filter and the solution was dispensed into the tared vials (~0.3 mL into each vial). The vials were then re-tared, placed in a vacuum oven at 45 °C and 20 mbar, and dried *in vacuo* overnight. The next day after the bulk of the solvent had evaporated, a stronger vacuum pump was used to further dry the samples (<1 mbar) for 4 hours at 45 °C. The vials were then re-tared to determine the solubility of the lignin in the solvent based on the dry mass of lignin in vials versus the initial mass of lignin solution that they contained (**Equation 5**). The solubilities were determined based on the average of three samples.

Hansen Solubility Parameters

Hansen solubility parameters (HSP) were determined using the HSPiP Software (available at <https://www.hansen-solubility.com/>). To determine the parameters, lignin was deemed to be soluble in a solvent if a concentration of at least 5 wt/wt% could be achieved. The lone exception to this is the pivaldehyde stabilised lignin, which was deemed to have similar solubility parameters to octanaldehyde stabilised lignin due to its solubility in toluene (3.5 wt/wt%). Solvents that reacted with the lignin were excluded from the calculation.

NMR Assignments

The NMR structures were assigned by comparing the obtained spectra with previously reported and assigned spectra and MestreNova Mnova (version 14.1.2) NMR predictions of fragments of the proposed lignin structures.

Equations

Gas Chromatography Yield Determination

Use **Equations 1-4** to calculate the yield of each monomer based on its integrated area and Relative Response Factor (RRF). The RRFs of the monomers and *n*-decane can be found in **Table S1**. The molecular weights provided in **Tables S6-S8** are the reconstituted or so-called “native” molecular weights of the lignin monomers as they would appear in the lignin polymer.³ Abbreviations: mass (m), moles (n), molecular weight (MW), area of peak (A), monomer *i* (M_i)

$$n_{decane} = \frac{m_{decane \text{ in sample}}}{MW_{decane}} \quad (1)$$

$$n_{M_i} = \frac{A_{M_i}}{A_{decane}} \cdot \frac{RRF_{decane}}{RRF_{M_i}} \cdot n_{decane} \quad (2)$$

$$m_{M_i} = n_{M_i} \cdot MW_{M_i} \quad (3)$$

$$Yield_{M_i} = \frac{m_{M_i}}{m_{hydrogenolysis \ sample}} \cdot \frac{m_{isolated \ lignin}}{m_{biomass}} \cdot 100\% \quad (4)$$

Lignin Solubility Determination

Use **Equation 5** to calculate the solubility of the acetal-stabilised lignin in a solvent according to the procedure outlined in *Methods: Determination of the Lignin Solubility*. Abbreviations:

$$S_{Lignin} = \frac{m_{vial \ with \ dry \ lignin} - m_{vial}}{m_{vial \ with \ lignin \ solution} - m_{vial}} \cdot 100\% \quad (5)$$

Estimated β -O-4 Content Based on Lignin Monomer Yield

Use **Equations 6 and 7** to estimate the β -O-4 content of the isolated lignin based on the total yield of lignin monomers ($Yield_{total \ monomers}$). The yield of monomers in this case can be either on a dry or wet biomass basis if it is consistent with the dry or wet biomass basis of the Acid Soluble Lignin (ASL) and Klason Lignin (KL) content.

$$Yield_{total \ monomers} = \sum_{i=1}^{\infty} Yield_{M_i} \quad (6)$$

$$\beta-O-4 \ Content = \sqrt{\frac{Yield_{total \ monomers}}{KL + ASL}} \quad (7)$$

Total yield of Lignin Monomers (mol)

Use **Equation 8** to calculate the total yield of monomers on a mol basis based on the yield of lignin monomers ($Yield_{M_i}$).

$$Yield_{mol \ monomers} = \sum_{i=1}^{\infty} \frac{Yield_{M_i}}{MW_{M_i}} \cdot m_{biomass} \quad (8)$$

Aldehyde Contribution to Lignin Yield

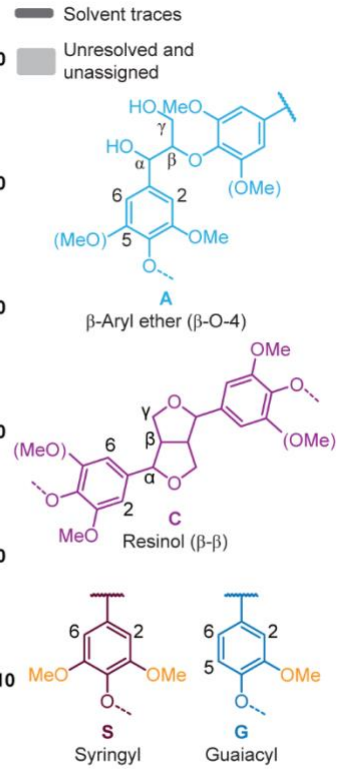
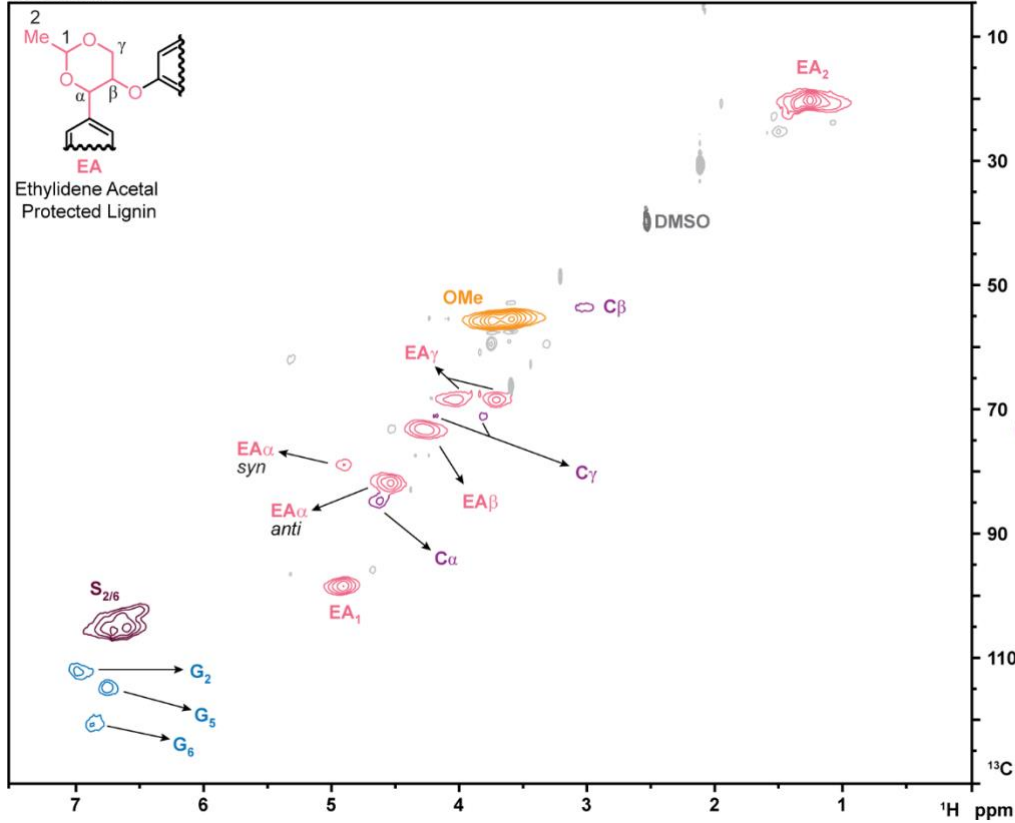
Use **Equation 9** to estimate the contribution of the mass of the stabilising aldehyde to the lignin yield from the biomass fractionation. If the lignin is extracted to remove residual sugars and aldehyde, acid soluble lignin is often also removed. To determine the corrected contribution of the stabilising aldehyde to the mass of the extracted lignin ($m_{aldehyde \ EL}$), a sample of the extracted lignin needs to be hydrogenolyzed. After the yield of monomers is calculated from the hydrogenolysis of the extracted lignin ($Yield_{total \ monomers \ EL}$), **Equation 10** can be used to calculate the corrected contribution of the stabilising aldehyde to the mass of the extracted lignin.

$$m_{aldehyde} = \left(MW_{aldehyde} - 18.0153 \frac{g}{mol} \right) \cdot \left(\frac{\beta-O-4 \ Content}{\frac{Yield_{total \ monomers}}{KL + ASL}} \right) \cdot Yield_{mol \ monomers} \quad (9)$$

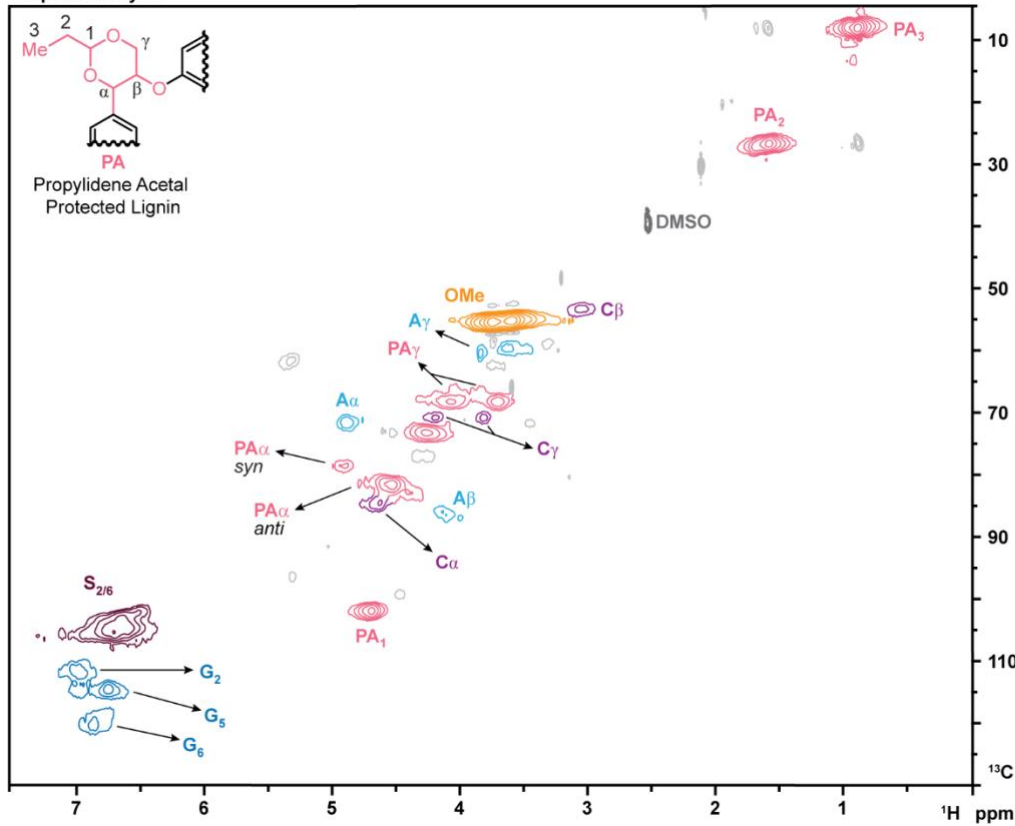
$$m_{aldehyde \ EL} = (m_{aldehyde}) \cdot \left(\frac{Yield_{total \ monomers \ EL}}{Yield_{total \ monomers}} \right) \quad (10)$$

NMR Spectra

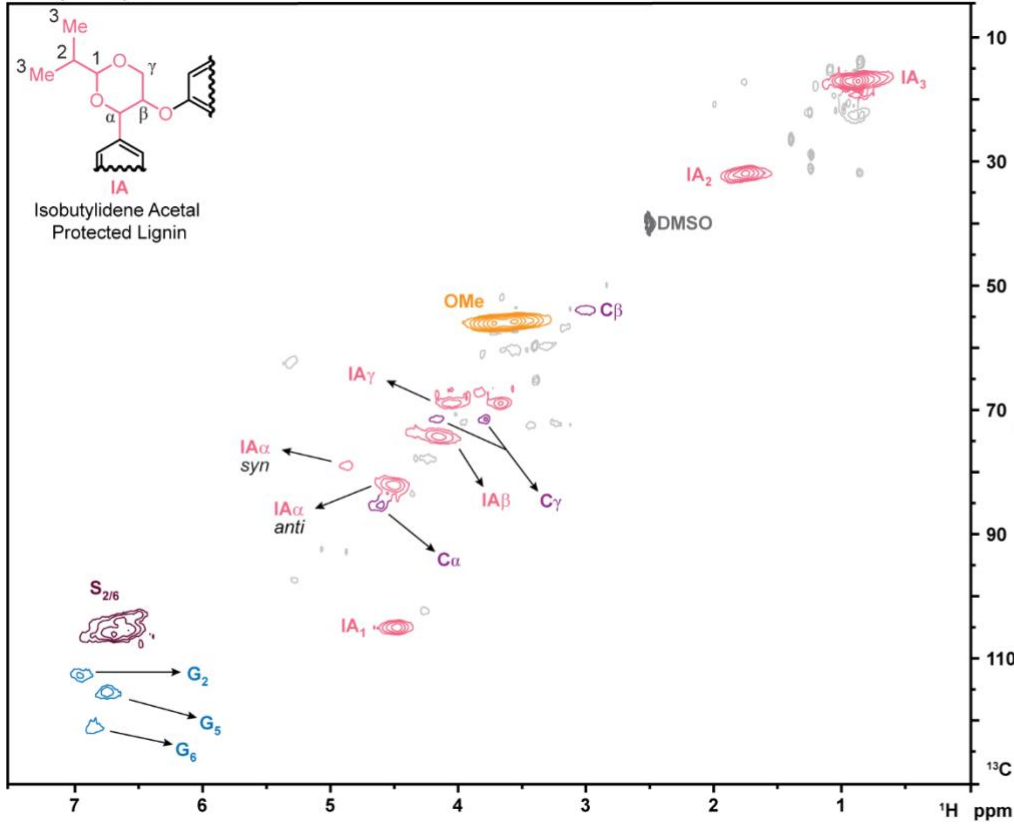
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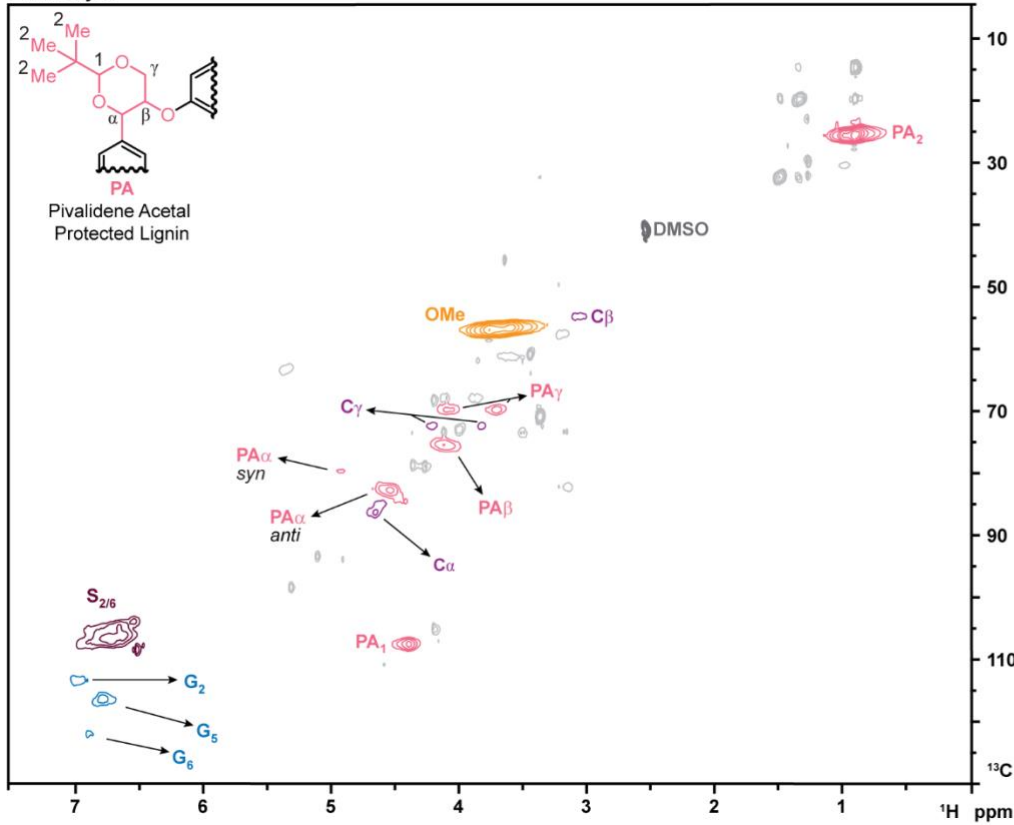
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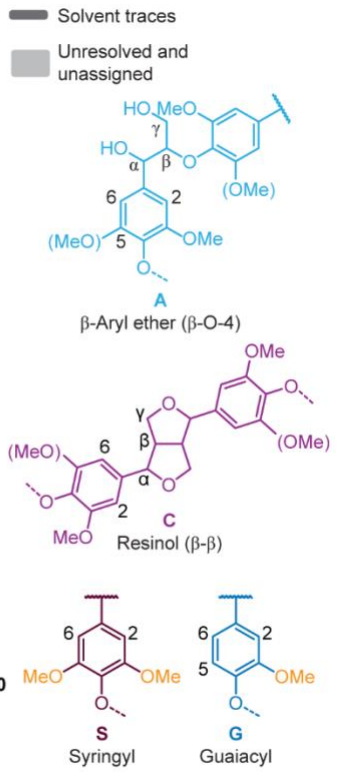
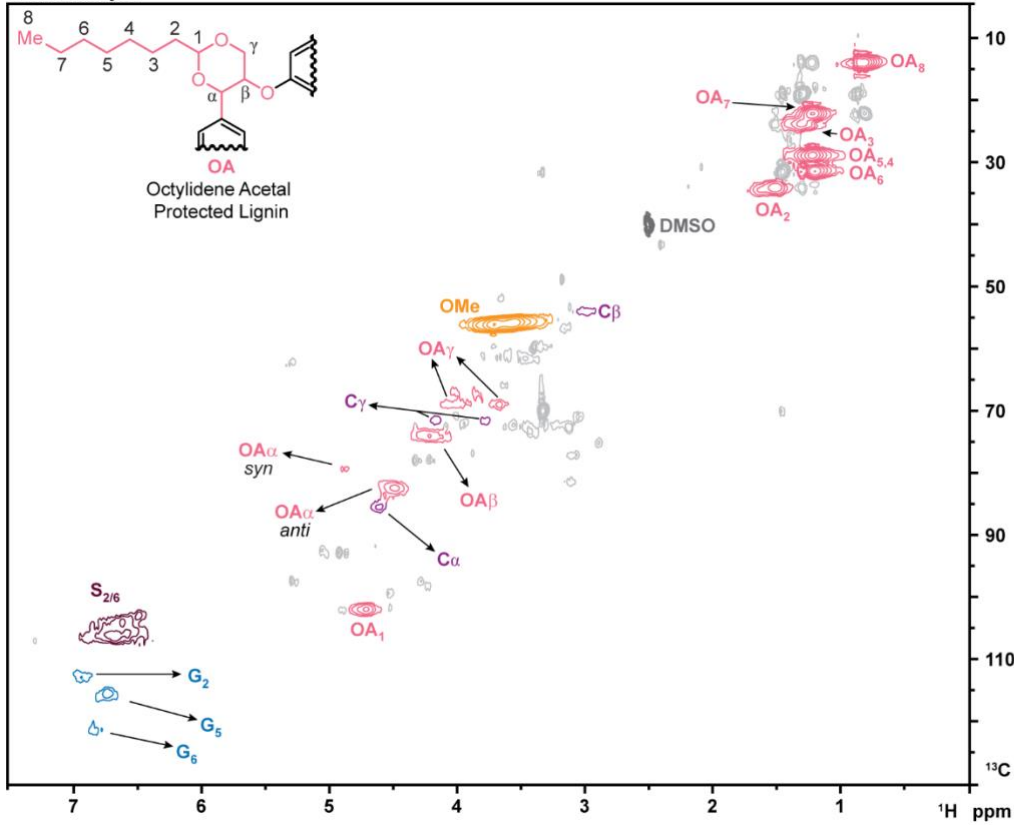
Isobutyraldehyde



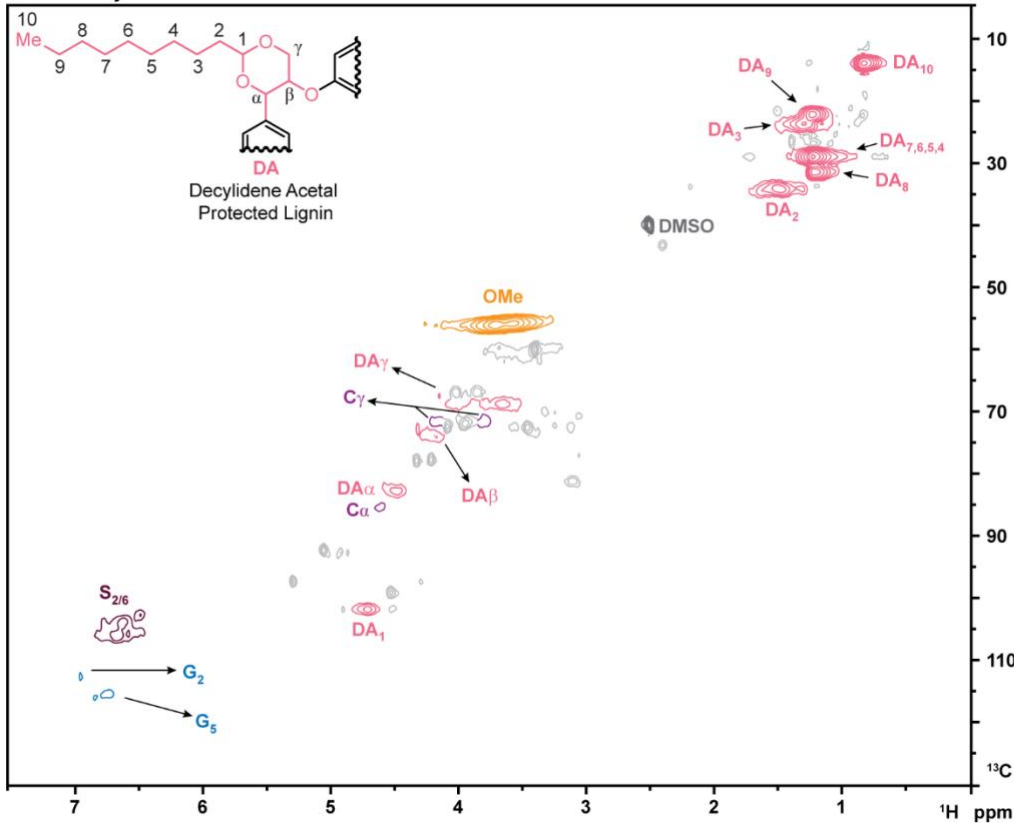
Pivaldehyde



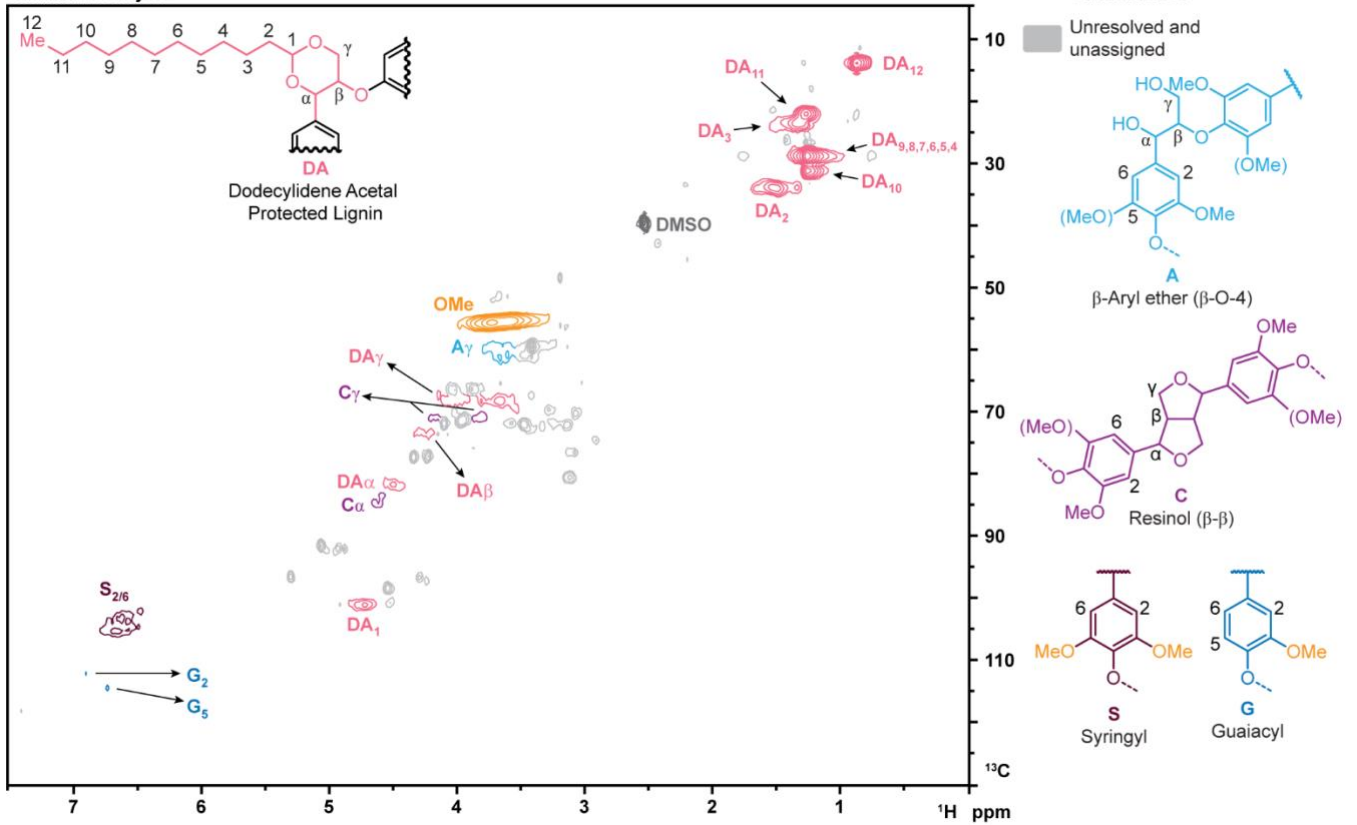
Octanaldehyde



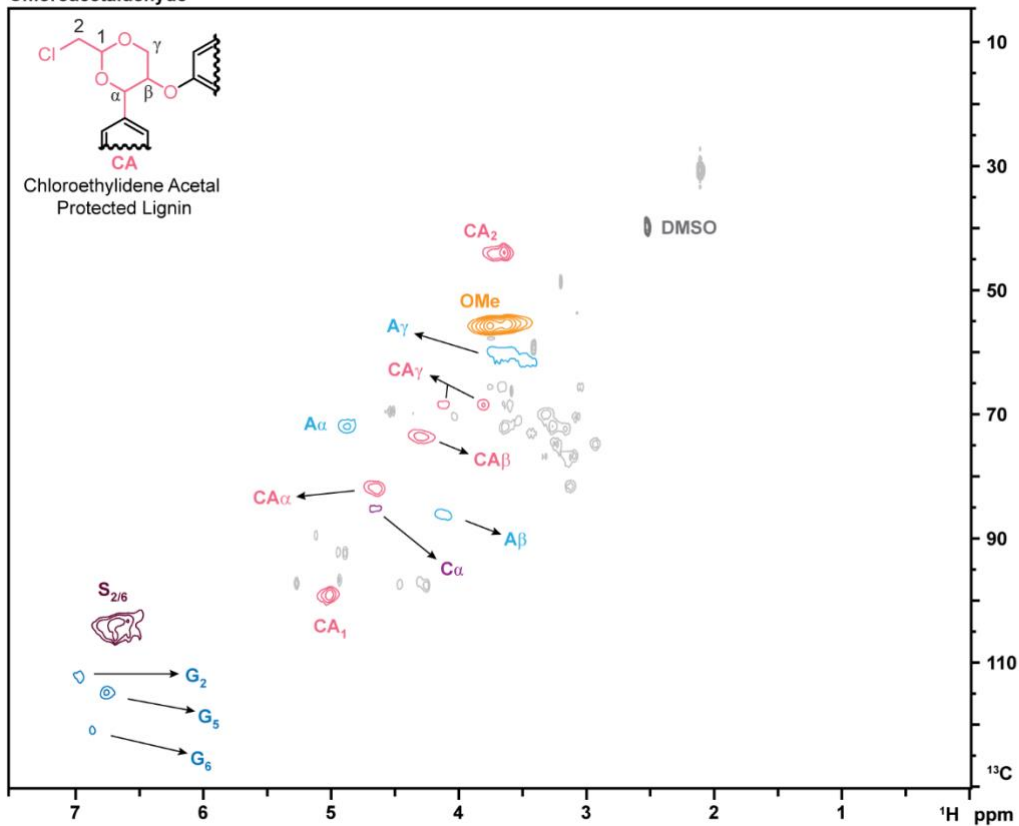
Decanaldehyde



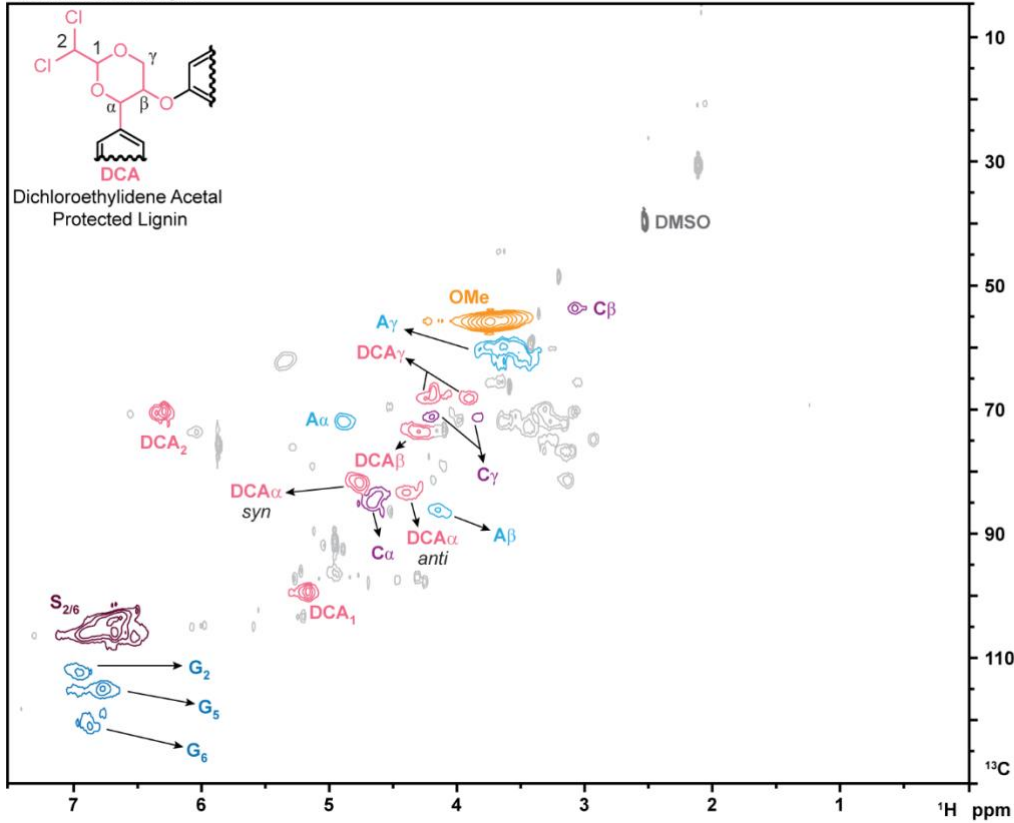
Dodecanaldehyde



Chloroacetaldehyde

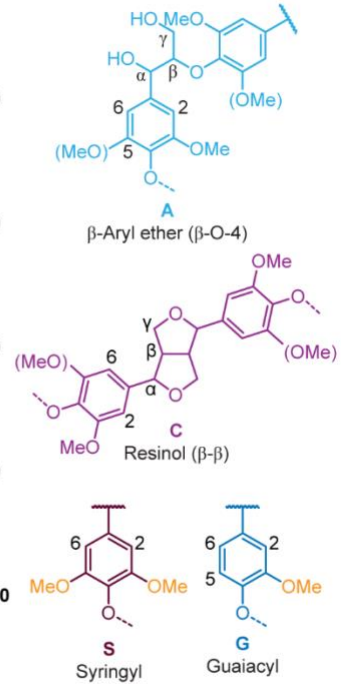


Dichloroacetaldehyde

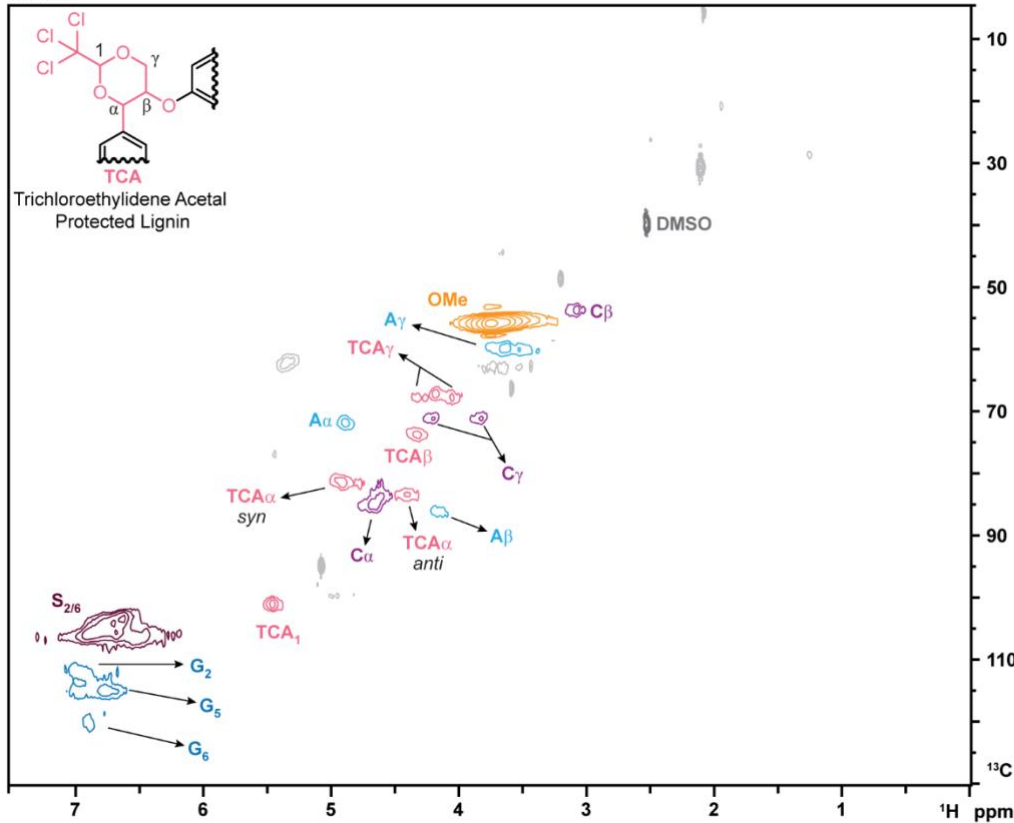


— Solvent traces

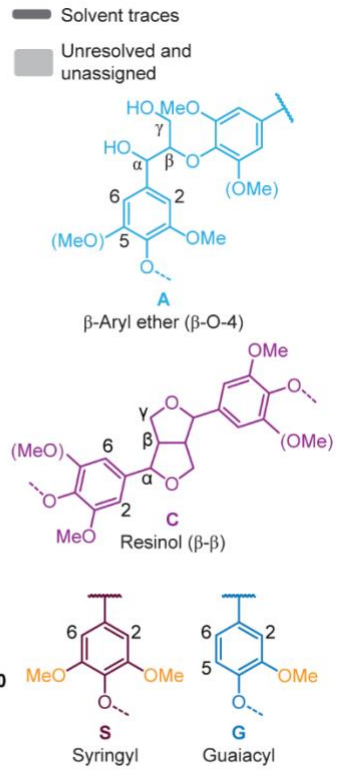
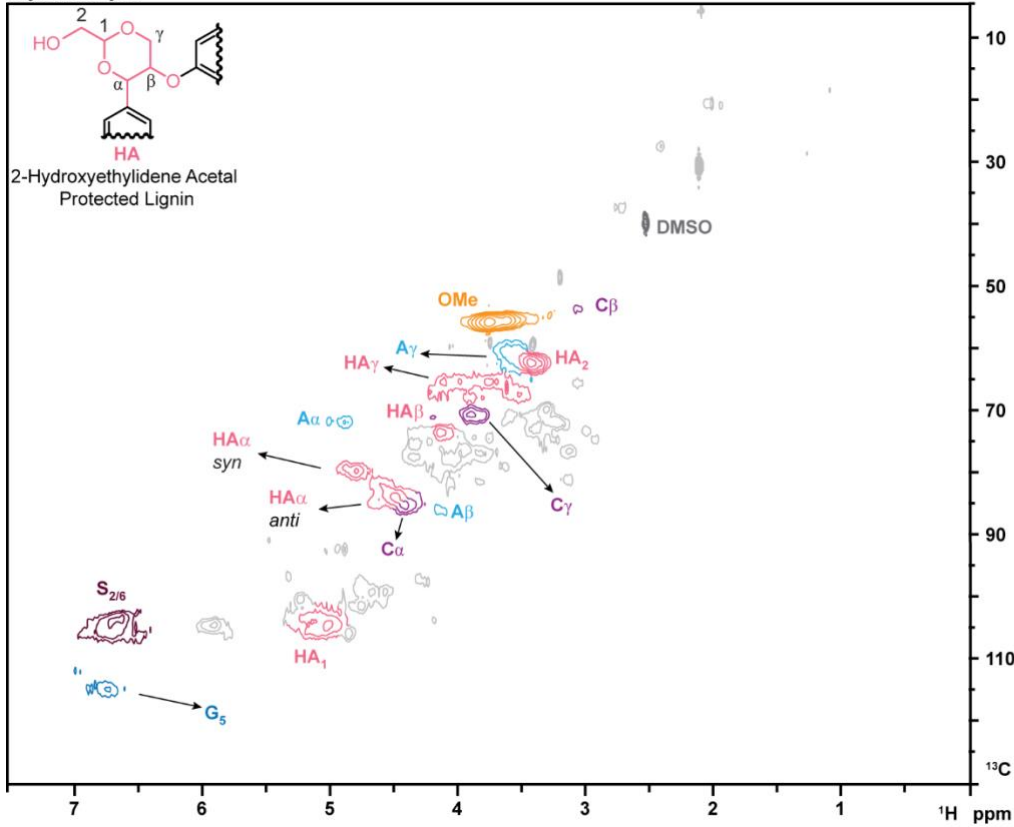
■ Unresolved and unassigned



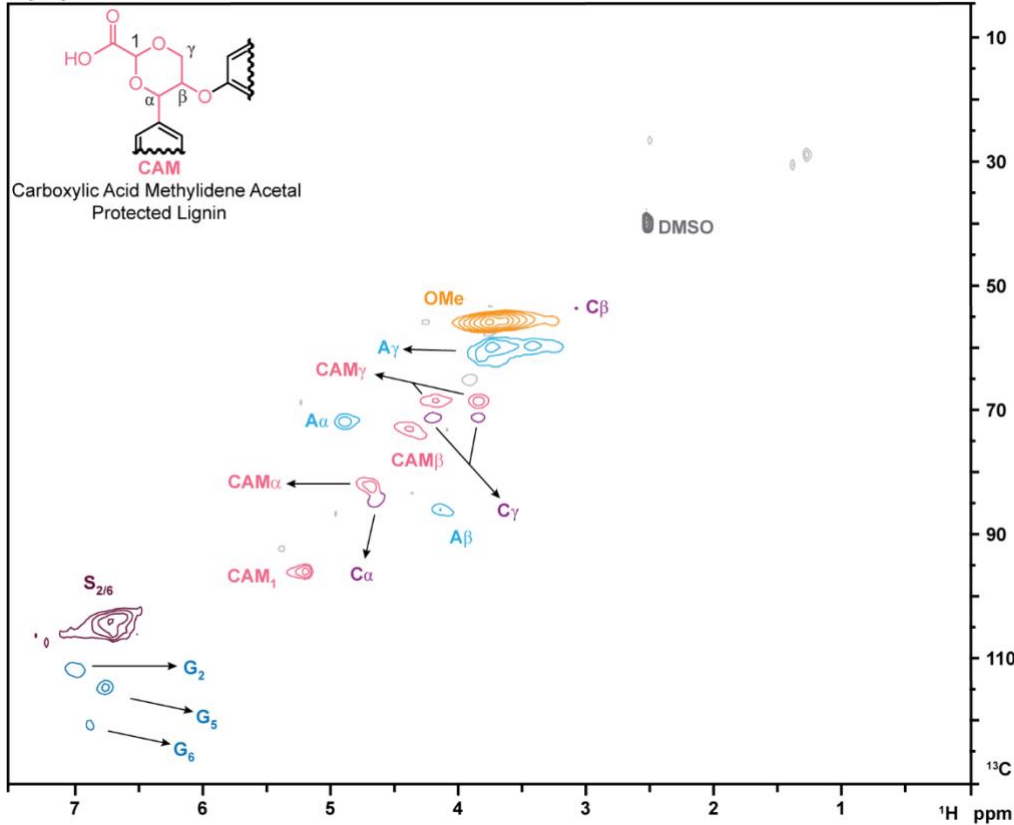
Chloral



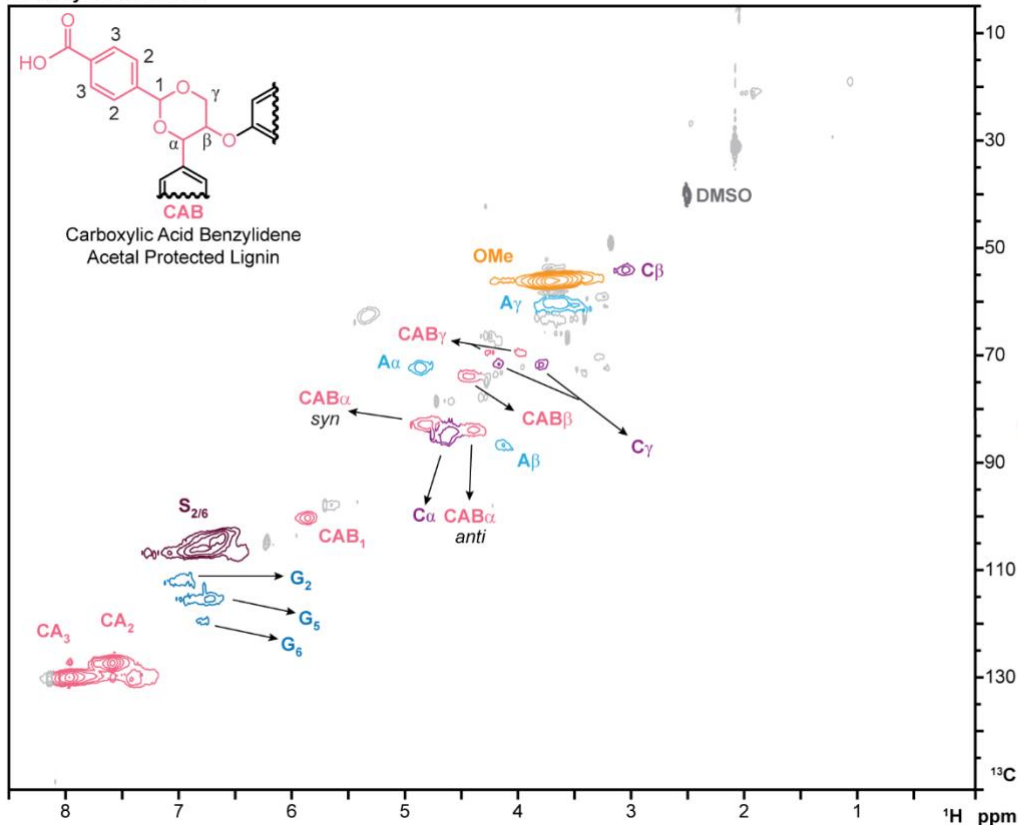
Glycoaldehyde



Glyoxylic Acid

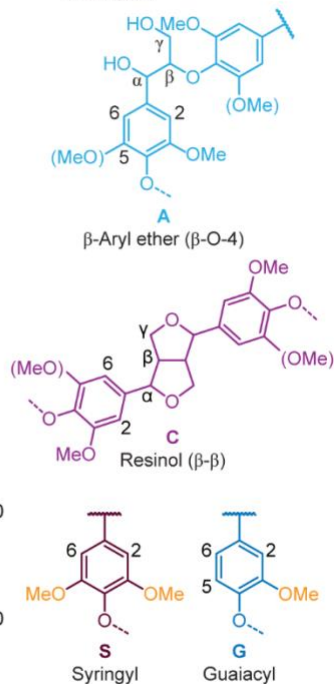


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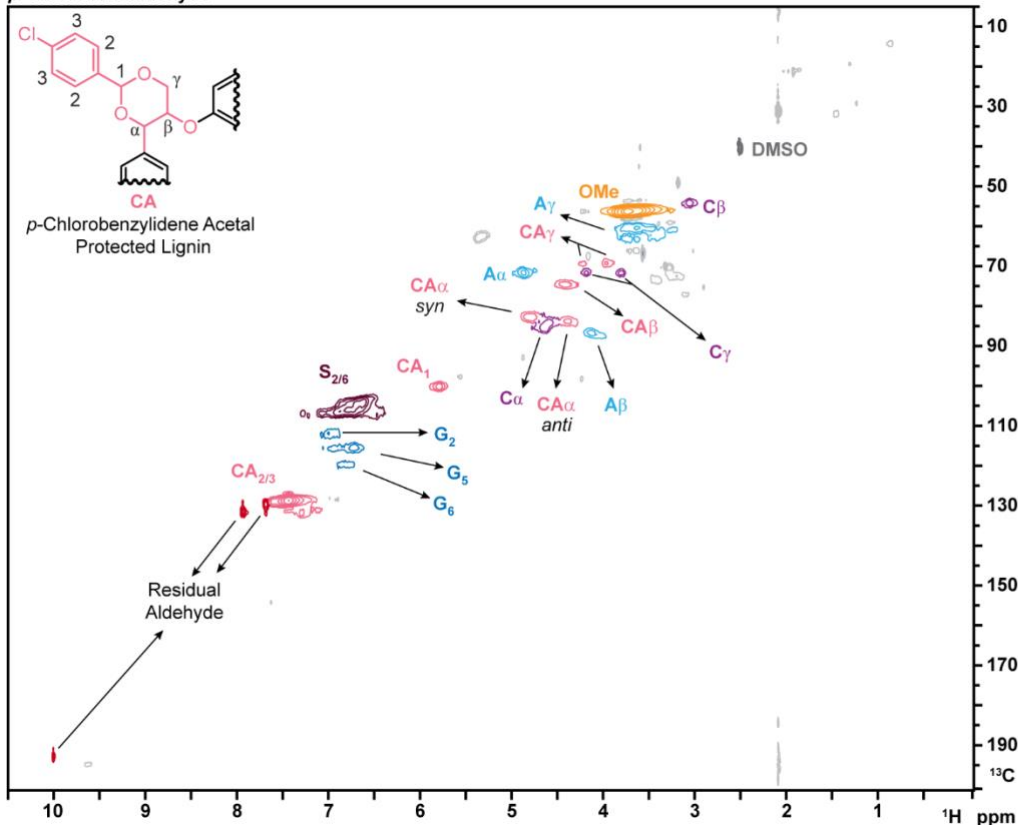


— Solvent traces

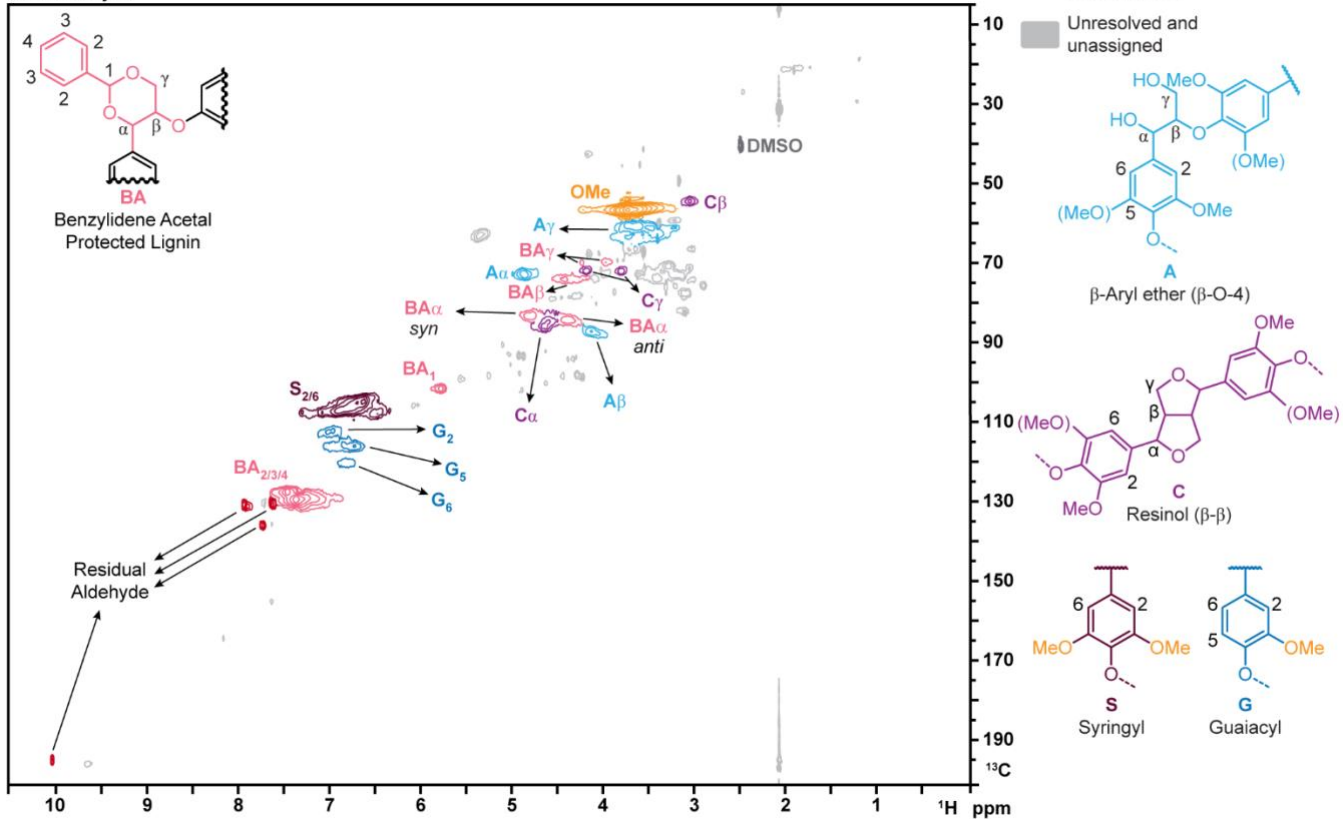
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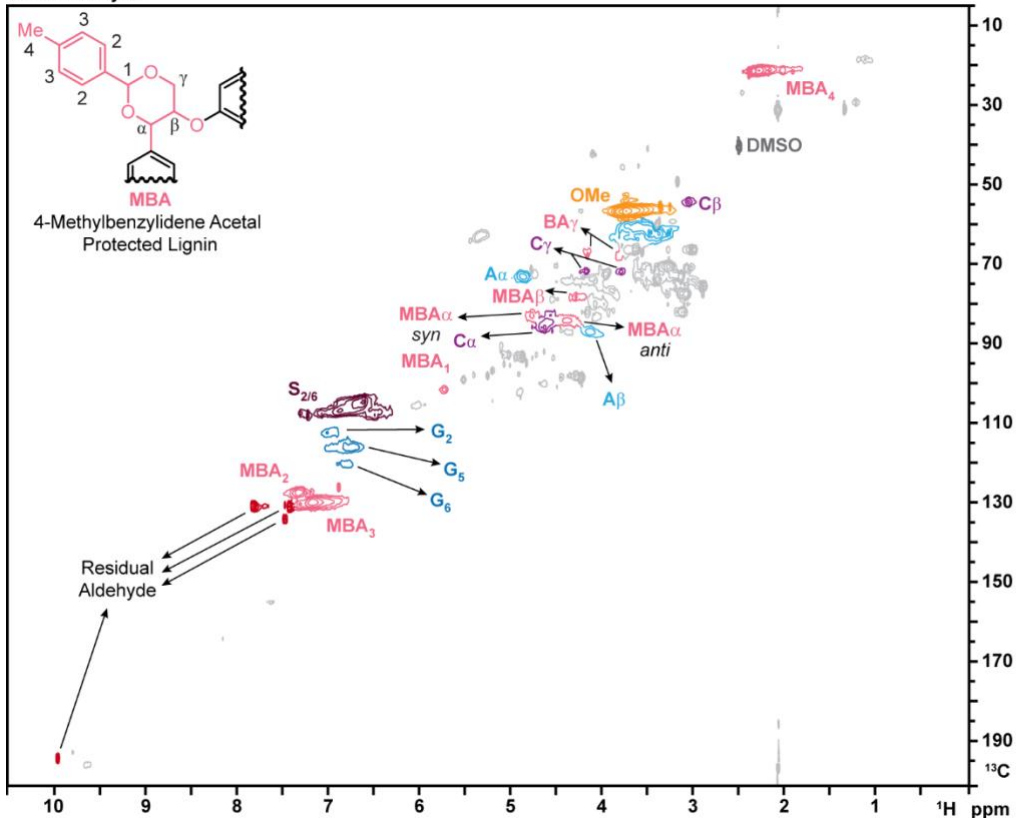
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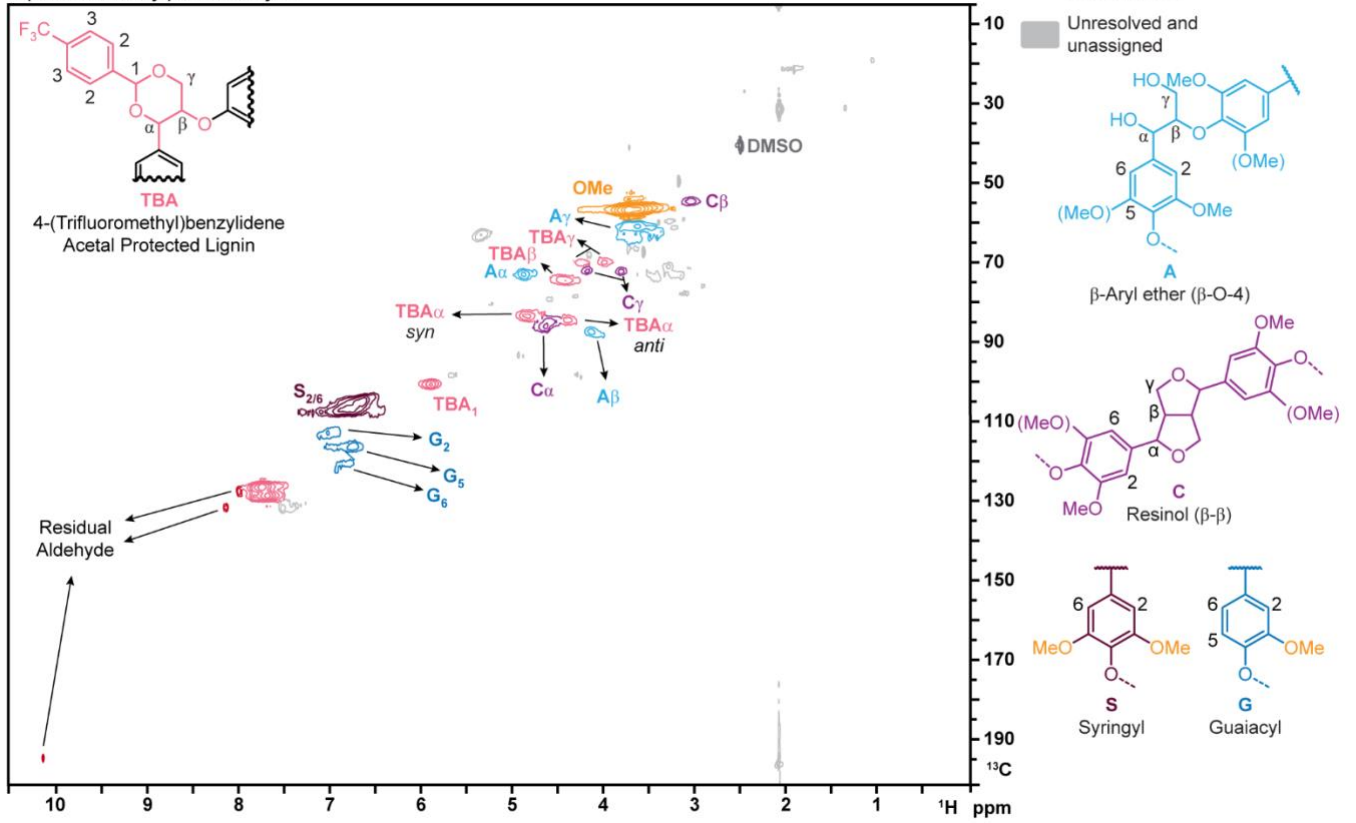
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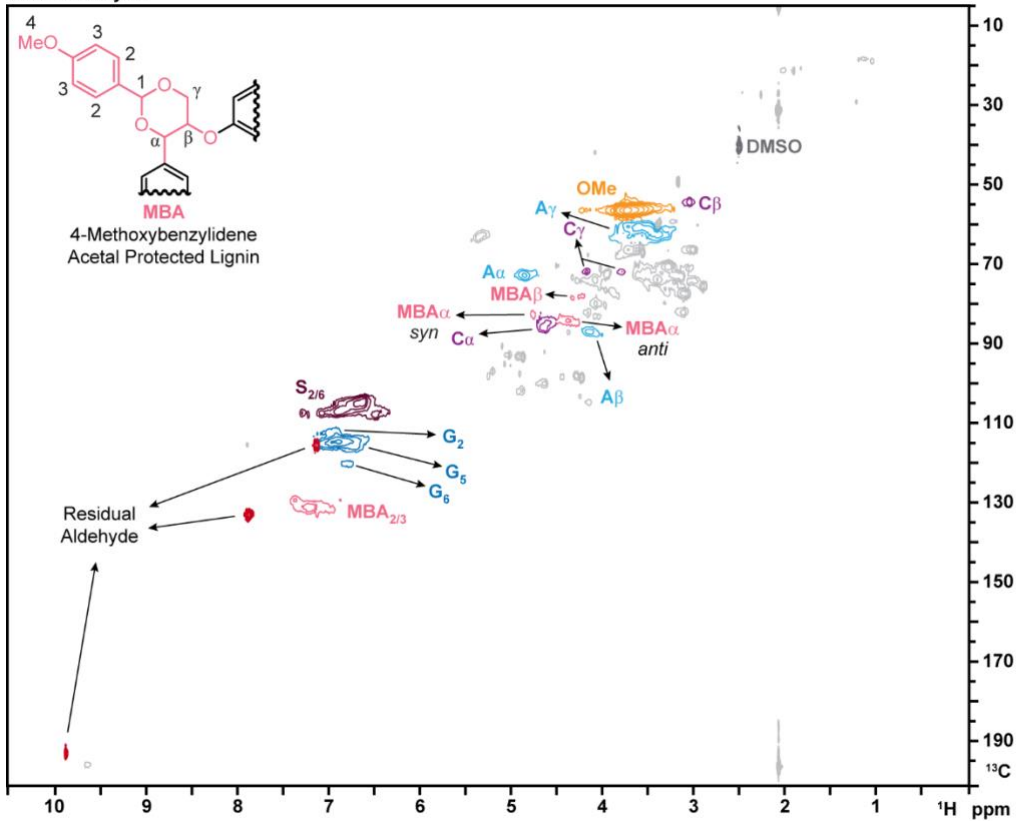
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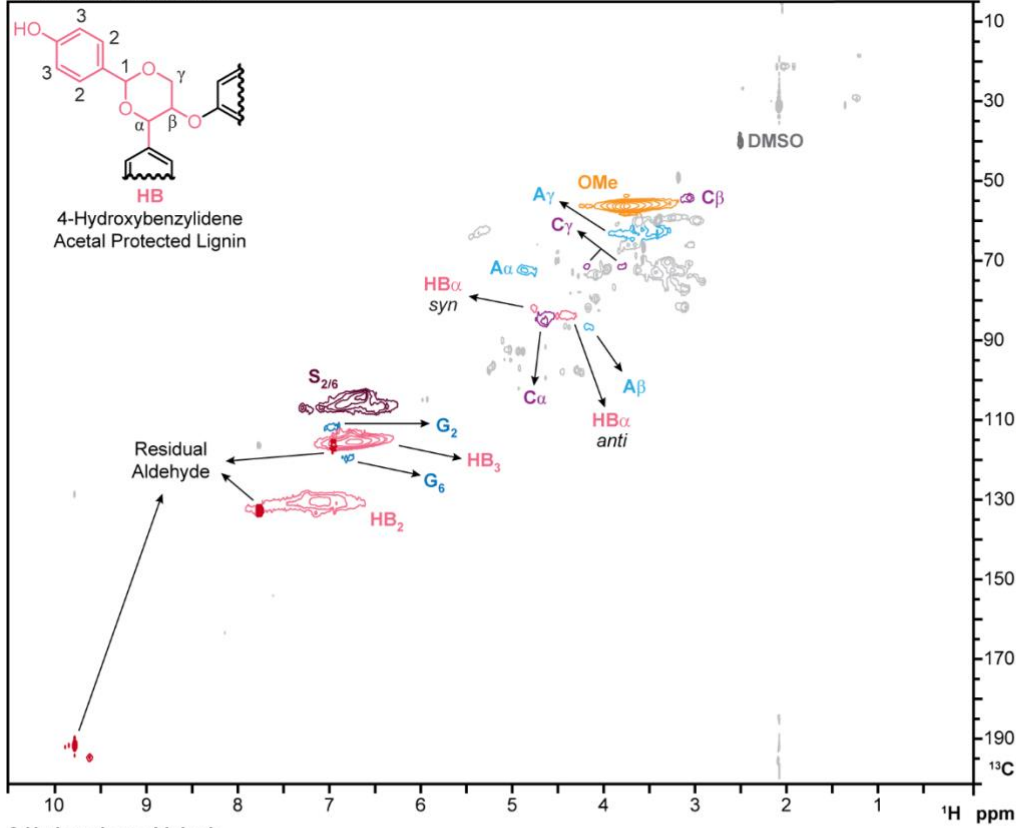
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4-Anisaldehyde

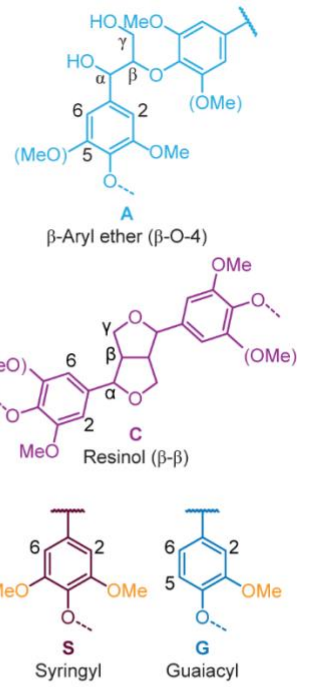


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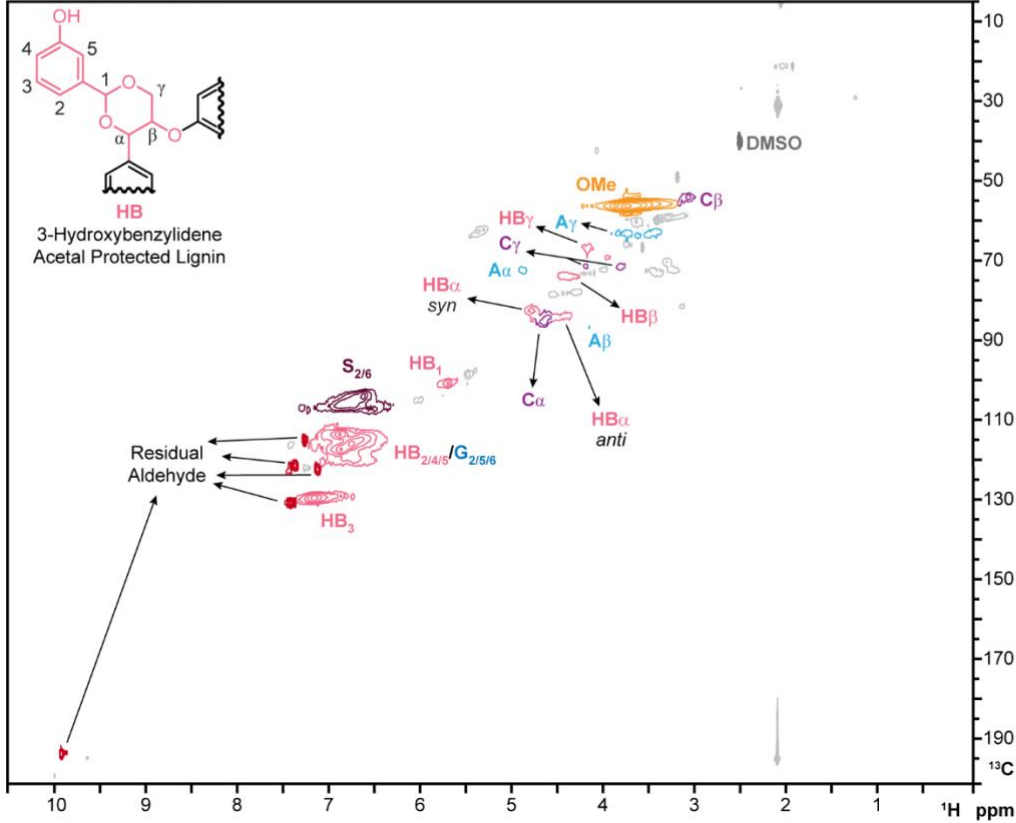


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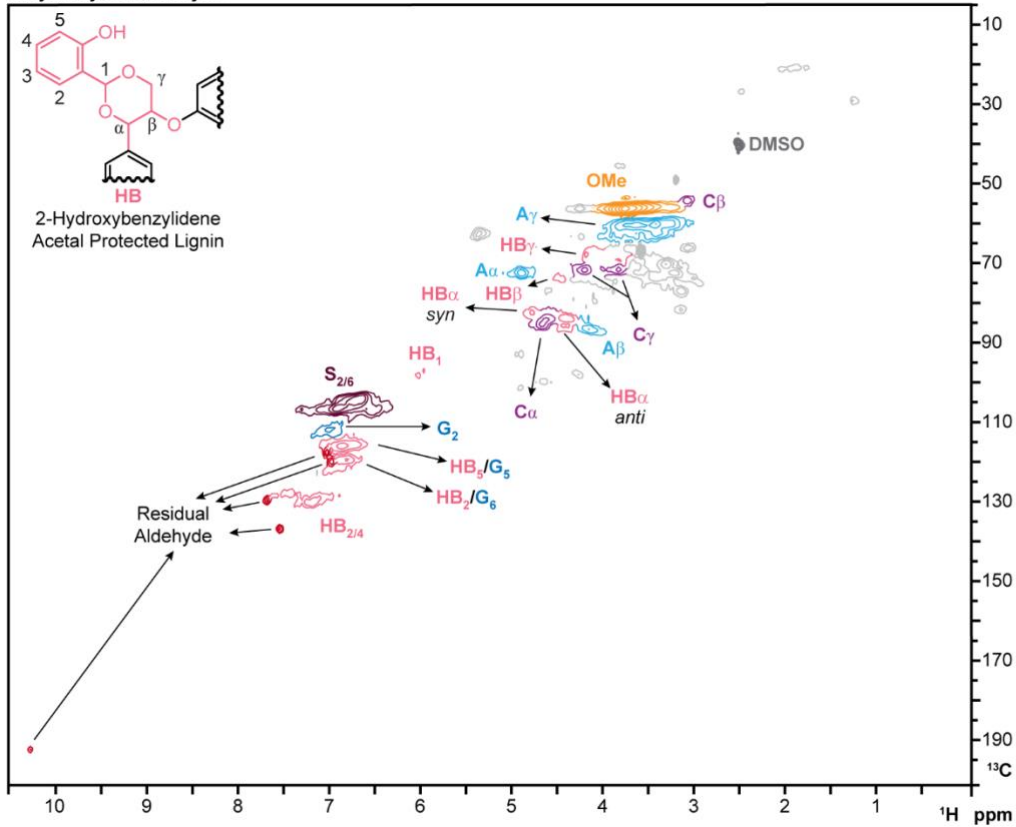
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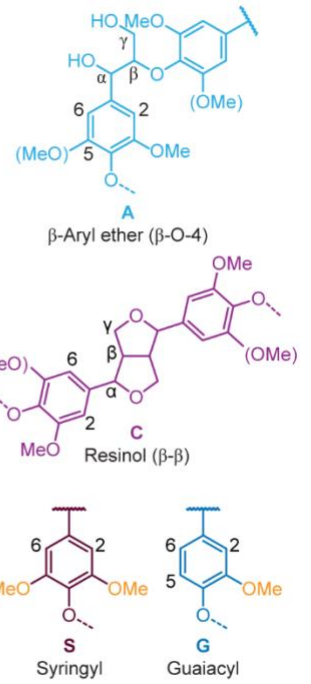


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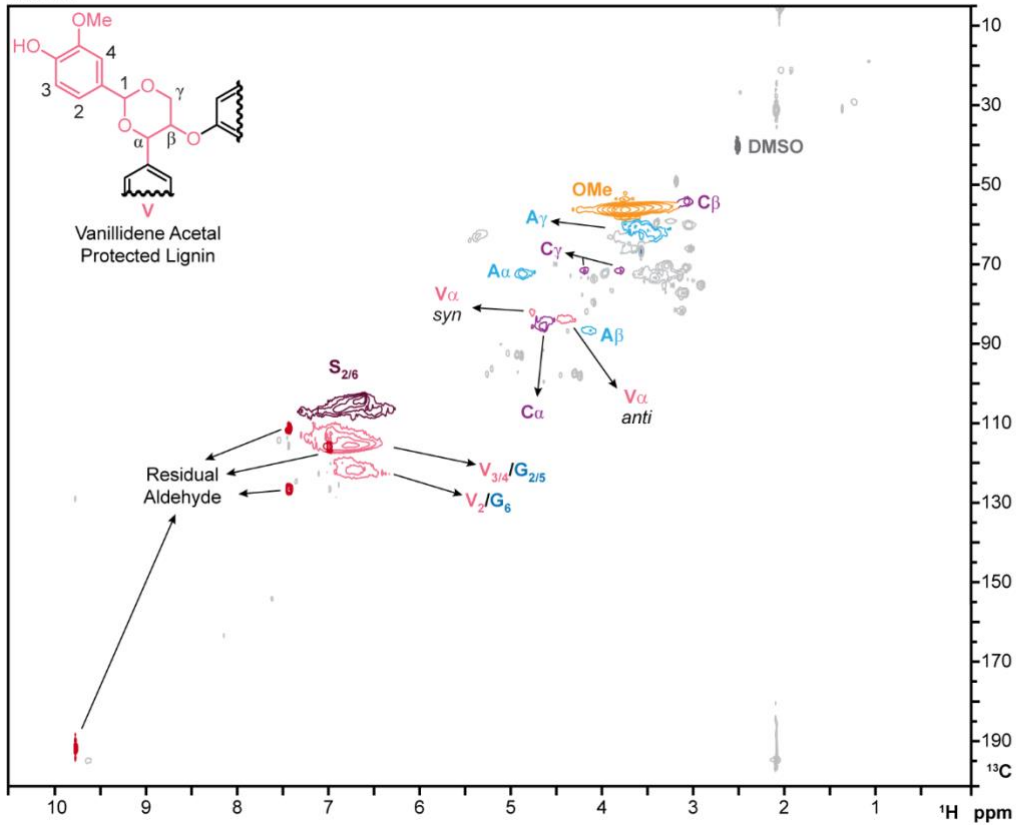


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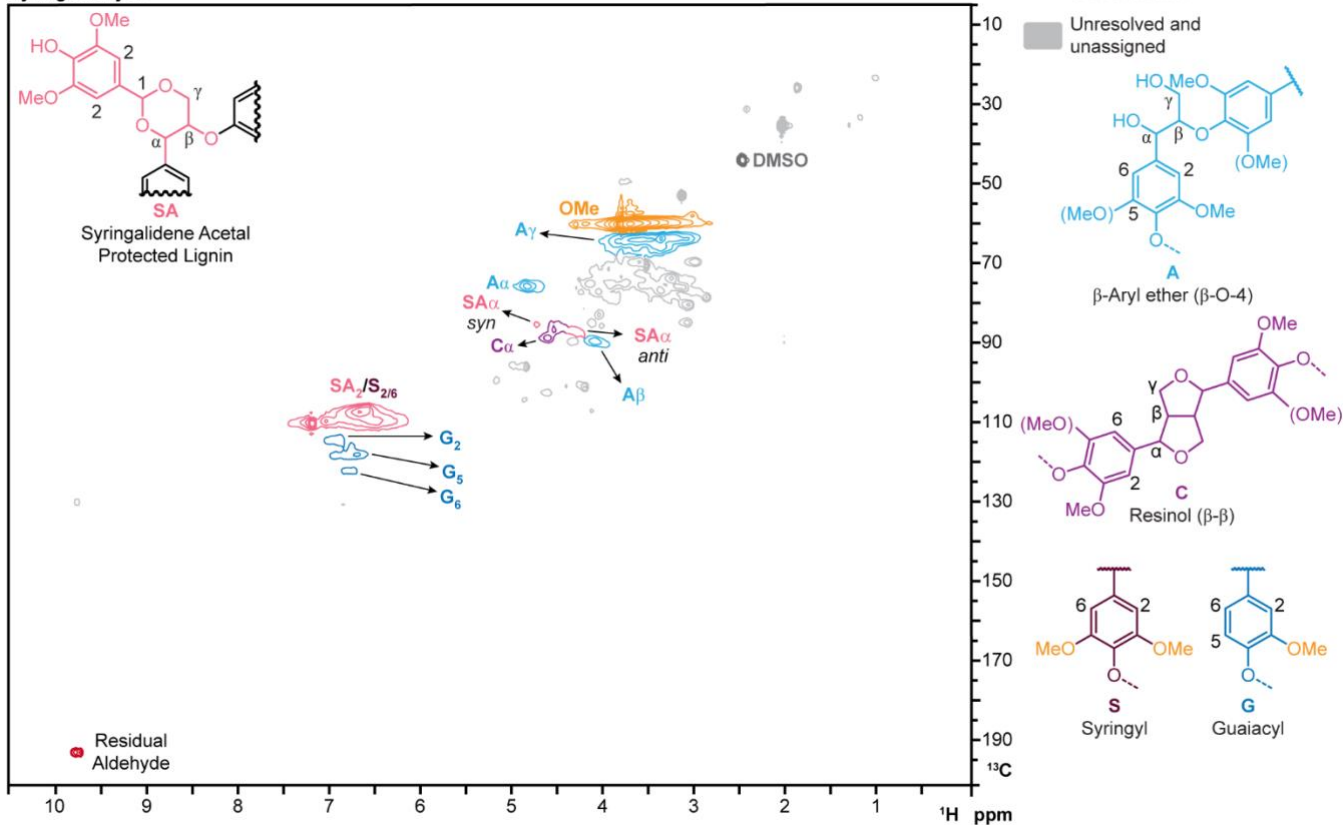
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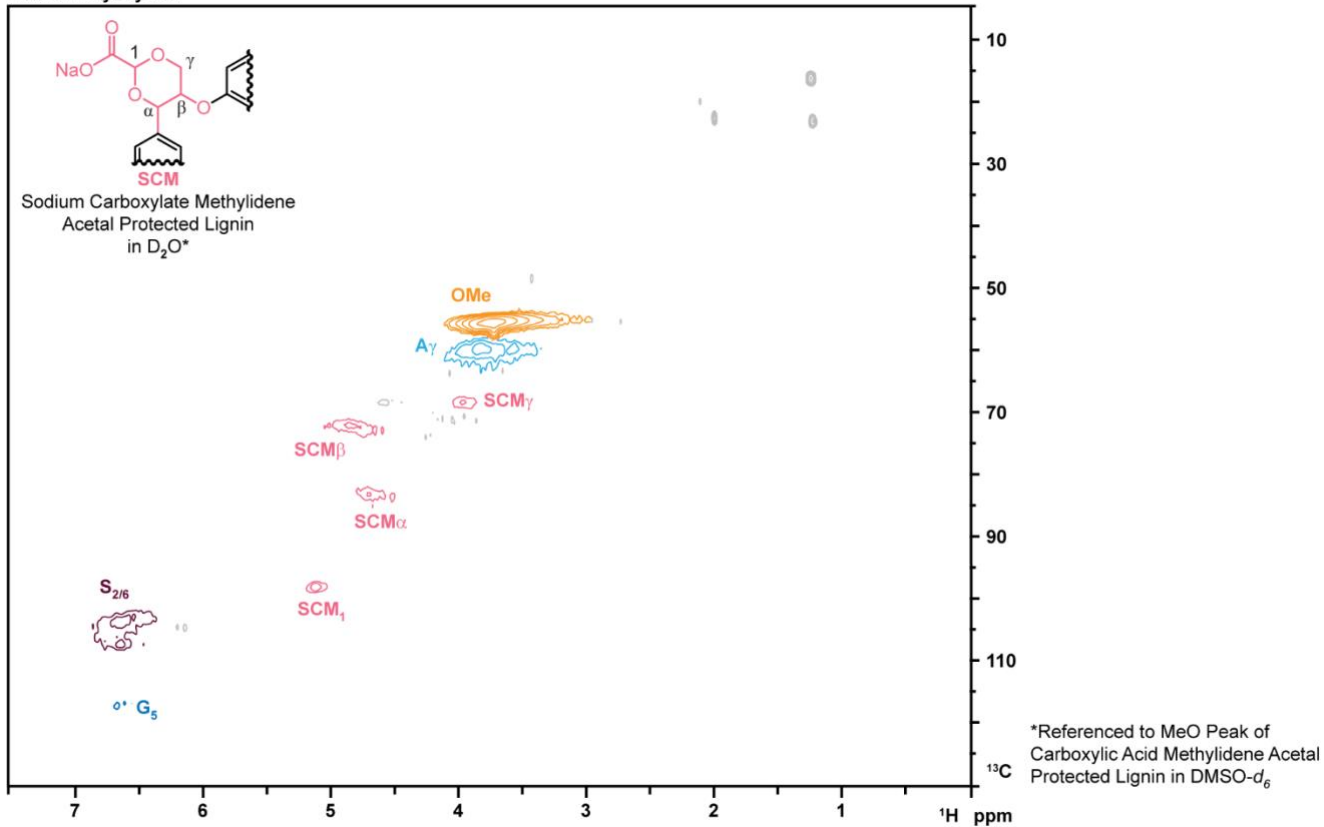
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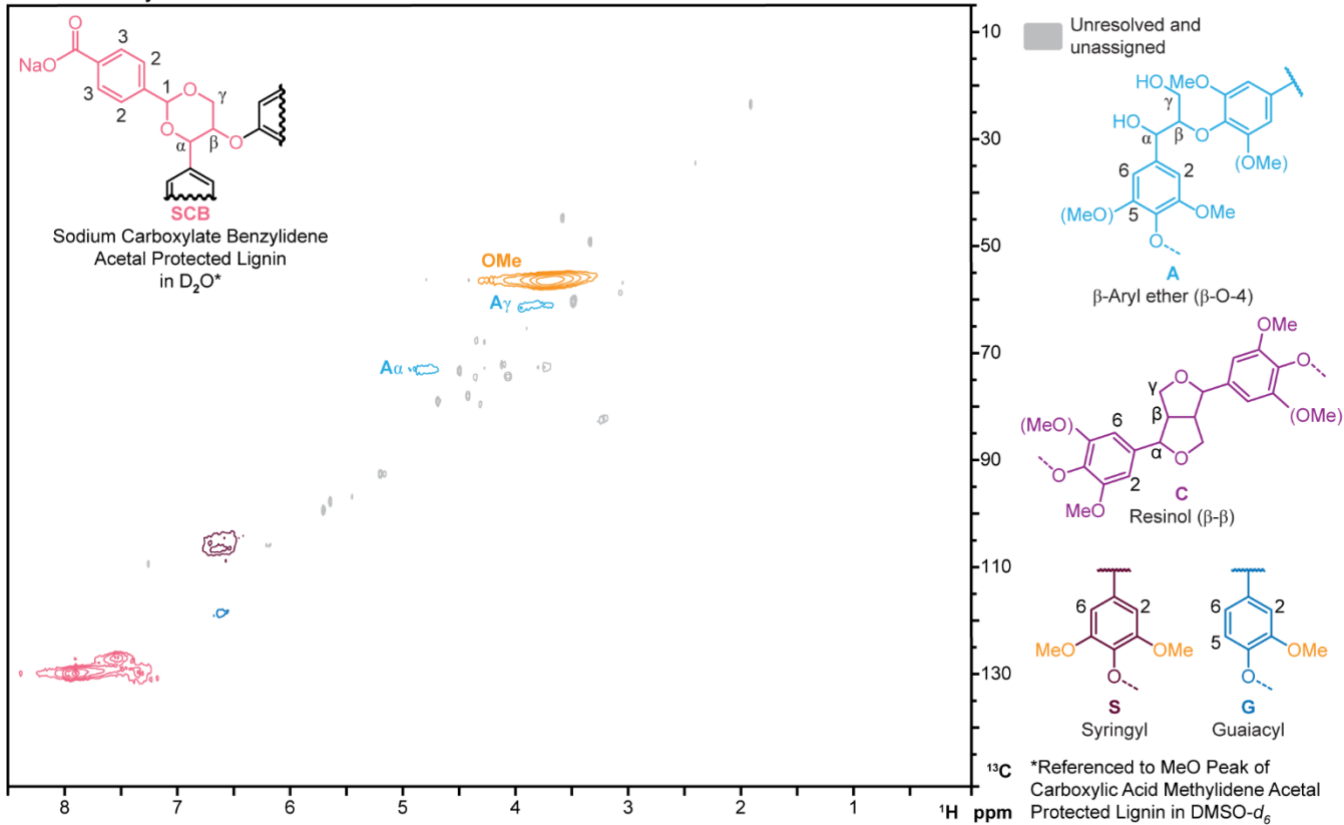
Syringaldehyde



Sodium Glyoxylate



Sodium 4-Formylbenzoate



Figures


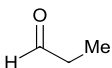
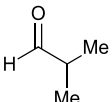
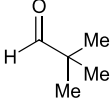
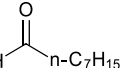
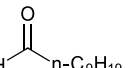
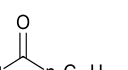
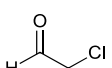
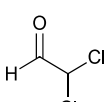
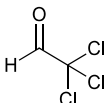
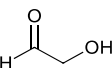
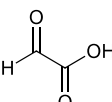
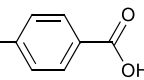
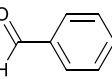
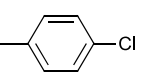
Stabilising Group	Toluene	Et ₂ O	Me-THF	THF	EtOAc	1,4-Dioxane	EtOAc: MeOH (50:50)	<i>i</i> PrOH	EtOH	MeOH	Water	HSP ^a
	Insoluble	Insoluble	≥10.0%	≥10.0%	5.1%	≥10.0%	8.1%	0.2%	1.5%	1.7%	Insoluble	δ _d = 17.99 δ _p = 9.10 δ _n = 9.60 R = 7.4
	Insoluble	Insoluble	≥10.0%	≥10.0%	9.8%	≥10.0%	8.5%	0.6%	2.1%	2.1%	Insoluble	δ _d = 17.99 δ _p = 9.10 δ _n = 9.60 R = 7.4
	Insoluble	Insoluble	≥10.0%	≥10.0%	≥10.0%	≥10.0%	≥10.0%	0.4%	1.3%	2.3%	Insoluble	δ _d = 17.99 δ _p = 9.10 δ _n = 9.60 R = 7.4
	3.5%	2.0%	≥10.0%	≥10.0%	≥10.0%	≥10.0%	≥10.0%	2.2%	2.2%	2.1%	Insoluble	δ _d = 18.18 δ _p = 8.84 δ _n = 6.27 R = 8.6
	9.9%	1.9%	≥10.0%	≥10.0%	9.9%	≥10.0%	9.0%	1.0%	1.5%	1.9%	Insoluble	δ _d = 18.18 δ _p = 8.84 δ _n = 6.27 R = 8.6
	9.7%	9.8%	≥10.0%	≥10.0%	≥10.0%	≥10.0%	9.7%	2.6%	2.8%	1.9%	Insoluble	δ _d = 17.52 δ _p = 8.91 δ _n = 6.23 R = 8.7
	≥10.0%	≥10.0%	≥10.0%	≥10.0%	9.4%	≥10.0%	≥10.0%	2.2%	4.0%	2.0%	Insoluble	δ _d = 17.52 δ _p = 8.91 δ _n = 6.23 R = 8.7
	Insoluble	Insoluble	≥10.0%	≥10.0%	8.3%	≥10.0%	≥10.0%	0.4%	2.3%	3.9%	Insoluble	δ _d = 17.99 δ _p = 9.10 δ _n = 9.60 R = 7.4
	Insoluble	Insoluble	≥10.0%	≥10.0%	8.3%	≥10.0%	≥10.0%	1.0%	2.8%	3.4%	Insoluble	δ _d = 17.99 δ _p = 9.10 δ _n = 9.60 R = 7.4
	Insoluble	Insoluble	9.2%	9.7%	5.8%	≥10.0%	≥10.0%	4.0%	5.5%	6.6%	Insoluble	δ _d = 15.61 δ _p = 8.85 δ _n = 13.13 R = 10.0
	Insoluble	Insoluble	Insoluble	6.3%	Insoluble	≥10.0%	5.4%	Insoluble	0.7%	3.0%	1.6%	δ _d = 19.02 δ _p = 8.80 δ _n = 9.99 R = 7.7
	Insoluble	Insoluble	2.3%	≥10.0%	1.3%	≥10.0%	Lignin Reacts ^b	0.4%	Lignin Reacts ^b	Lignin Reacts ^b	Insoluble	δ _d = 17.09 δ _p = 3.65 δ _n = 8.50 R = 2.2
	Insoluble	Insoluble	≥10.0%	≥10.0%	2.7%	≥10.0%	Lignin Reacts ^b	1.8%	5.0%	Lignin Reacts ^b	0.1%	δ _d = 22.02 δ _p = 14.74 δ _n = 11.26 R = 15.8
	Insoluble	Insoluble	≥10.0%	≥10.0%	4.6%	≥10.0%	≥10.0%	1.0%	Insoluble	1.9%	Insoluble	δ _d = 17.99 δ _p = 9.10 δ _n = 9.60 R = 7.4
	Insoluble	Insoluble	≥10.0%	≥10.0%	3.7%	≥10.0%	8.1%	0.8%	Insoluble	0.8%	Insoluble	δ _d = 17.99 δ _p = 9.10 δ _n = 9.60 R = 7.4

Fig. S1. Tabulated Solubility Data for All of the Aldehyde Stabilised Lignins. Birch wood was fractionated using the aldehydes identified on the left-hand-side of the table and the aldehyde-stabilised lignins were isolated as bench-stable solids. These aldehyde-stabilised lignins were dissolved in various solvents or solvent-mixtures at room temperature (~23-30 °C) and passed through syringe filters into tared vials. The vials were dried overnight in a vacuum oven at 45 °C and 20 mbar and re-tared to determine the quantity of lignin in the solvent. Concentrations exceeding 10.0 wt/wt% were often observed, but highly concentrated solutions became viscous, almost gel-like. Consequently, the maximum concentration targeted was 10 wt/wt%. Each reported number represents the average of three measurements and is reported as a wt/wt%. None of the lignins were soluble in hexanes. ^aHansen Solubility Parameters (HSP). ^bEsterification of these lignins with these solvents was observed by HSQC NMR.

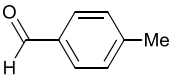
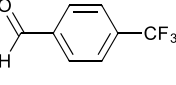
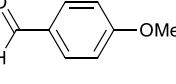
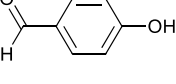
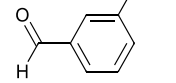
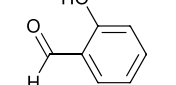
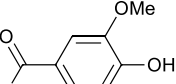
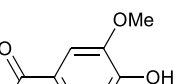
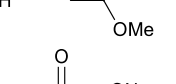
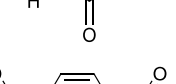
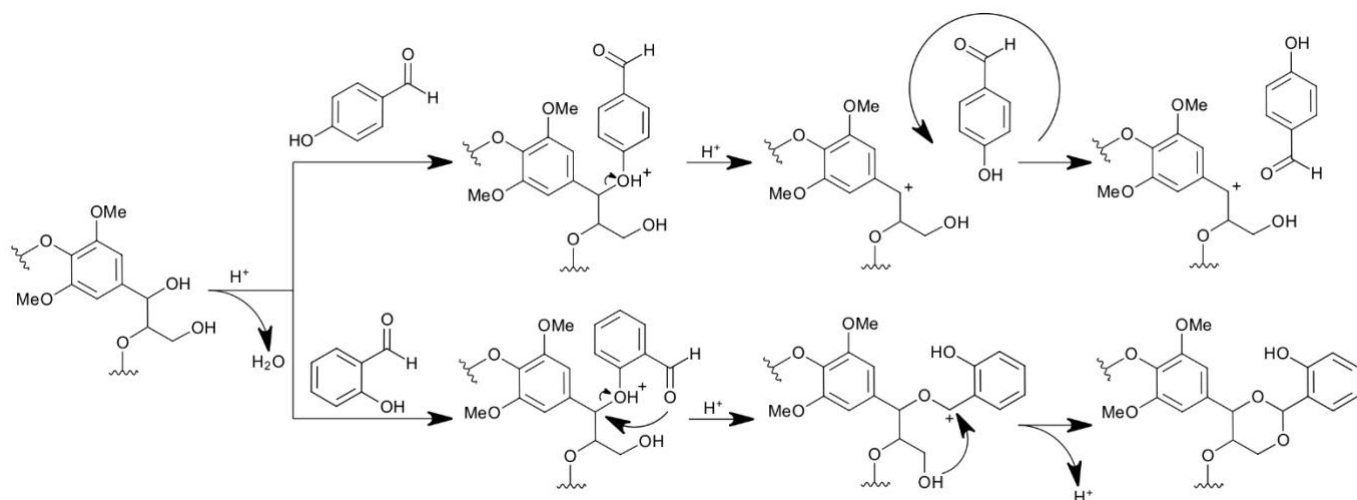
Stabilising Group	Toluene	Et ₂ O	Me-THF	THF	EtOAc	1,4-Dioxane	EtOAc: MeOH (50:50)	iPrOH	EtOH	MeOH	Water	HSP ^a
	Insoluble	Insoluble	≥10.0%	≥10.0%	5.3%	≥10.0%	≥10.0%	0.6%	1.3%	5.4%	Insoluble	δ _d = 17.94 δ _p = 9.09 δ _h = 9.81 R = 7.4
	Insoluble	Insoluble	≥10.0%	≥10.0%	≥10.0%	≥10.0%	≥10.0%	0.9%	0.2%	2.7%	Insoluble	δ _d = 17.94 δ _p = 9.09 δ _h = 9.81 R = 7.4
	Insoluble	Insoluble	≥10.0%	≥10.0%	3.7%	≥10.0%	≥10.0%	0.6%	0.3%	4.2%	Insoluble	δ _d = 17.94 δ _p = 9.09 δ _h = 9.81 R = 7.4
	Insoluble	Insoluble	≥10.0%	≥10.0%	6.9%	≥10.0%	≥10.0%	3.0%	7.0%	9.3%	Insoluble	δ _d = 15.79 δ _p = 8.70 δ _h = 13.24 R = 10.0
	Insoluble	Insoluble	≥10.0%	≥10.0%	7.0%	≥10.0%	≥10.0%	0.6%	3.0%	6.2%	Insoluble	δ _d = 17.94 δ _p = 9.09 δ _h = 9.81 R = 7.4
	Insoluble	Insoluble	≥10.0%	≥10.0%	4.4%	≥10.0%	≥10.0%	1.0%	1.0%	3.9%	Insoluble	δ _d = 17.94 δ _p = 9.09 δ _h = 9.81 R = 7.4
	Insoluble	Insoluble	≥10.0%	≥10.0%	6.6%	≥10.0%	≥10.0%	1.5%	4.7%	8.3%	Insoluble	δ _d = 15.79 δ _p = 8.70 δ _h = 13.24 R = 10.0
	Insoluble	Insoluble	≥10.0%	≥10.0%	3.5%	≥10.0%	7.7%	1.5%	0.4%	4.3%	Insoluble	δ _d = 17.94 δ _p = 9.09 δ _h = 9.81 R = 7.4
	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	1.2%	≥10.0%	δ _d = 15.14 δ _p = 13.85 δ _h = 32.32 R = 10.3
	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	5.3%	≥10.0%	δ _d = 15.14 δ _p = 13.85 δ _h = 32.32 R = 10.3

Fig. S2. Tabulated Solubility Data for All of the Aldehyde Stabilised Lignins Continued. Birch wood was fractionated using the aldehydes identified on the left-hand-side of the table and the aldehyde-stabilised lignins were isolated as bench-stable solids. These aldehyde-stabilised lignins were dissolved in various solvents or solvent-mixtures at room temperature (~23-30 °C) and passed through syringe filters into tared vials. The vials were dried overnight in a vacuum oven at 45 °C and 20 mbar and re-tared to determine the quantity of lignin in the solvent. Concentrations exceeding 10.0 wt/wt% were often observed, but highly concentrated solutions became viscous, almost gel-like. Consequently, the maximum concentration targeted was 10 wt/wt%. Each reported number represents the average of three measurements and is reported as a wt/wt%. None of the lignins were soluble in hexanes. ^aHansen Solubility Parameters (HSP).

Schemes



Scheme S1. The Elimination of the Phenolic Benzylic Ethers of p-Hydroxybenzaldehyde and Salicylaldehyde. (Top) The aldehyde of the p-hydroxybenzaldehyde cannot participate in the elimination of the phenolic benzylic ether due to its orientation and distance from the ether bond. After the elimination occurs, the 4-hydroxybenzaldehyde must rotate 180° before it can react with the benzylic carbocation during which the carbocation can react with other nucleophiles. (Bottom) The orientation of the aldehyde of salicylaldehyde enables it to participate in the elimination of the benzylic ether, intercepting the formation of the benzylic carbocation through a cyclic six-membered transition state.

Tables

Table S3. Yield of Lignin Monomers from the Hydrogenolysis of the Isolated Acetal-stabilised Lignins.^a

Aldehyde	M1	M3	M5	M7	M15	M9	Total
Acetaldehyde	0.40%	0.98%	2.91%	6.10%	0.00%	0.00%	10.39%
Propionaldehyde	0.31%	0.80%	2.44%	5.32%	0.00%	1.22%	10.10%
Propionaldehyde ^b	0.43%	0.43%	3.41%	2.24%	0.00%	1.17%	7.67%
Isobutyraldehyde	0.35%	0.65%	4.35%	4.45%	0.00%	0.29%	10.08%
Pivaldehyde	0.36%	0.55%	2.91%	2.97%	0.00%	2.15%	8.93%
Octanaldehyde	0.13%	0.94%	0.91%	5.23%	0.00%	1.81%	9.02%
Decanaldehyde	0.26%	0.72%	2.27%	3.78%	0.00%	0.50%	7.53%
Dodecanaldehyde	0.31%	0.34%	2.14%	1.44%	0.00%	0.62%	4.85%
Chloroacetaldehyde	0.20%	1.03%	1.74%	5.98%	0.00%	0.00%	8.94%
Dichloroacetaldehyde	0.00%	1.01%	0.31%	6.91%	0.00%	0.11%	8.35%
Chloral	0.01%	0.36%	0.27%	2.72%	0.00%	0.14%	3.51%
Glycolaldehyde	0.29%	0.49%	3.19%	2.51%	0.00%	0.43%	6.91%
Glyoxylic Acid	0.25%	0.63%	1.46%	2.69%	0.00%	0.22%	5.24%
<i>p</i> -Formylbenzoic Acid	0.00%	0.00%	5.63%	1.08%	0.00%	0.00%	6.72%
Benzaldehyde	0.15%	0.60%	1.48%	4.68%	0.00%	0.00%	6.90%
<i>p</i> -Chlorobenzaldehyde	0.31%	0.65%	1.06%	4.97%	0.00%	0.67%	7.67%
<i>p</i> -Tolualdehyde	0.26%	0.59%	1.87%	3.74%	0.00%	0.41%	6.88%
<i>p</i> -(Trifluoromethyl)benzaldehyde	0.23%	0.58%	2.20%	4.12%	0.00%	0.73%	7.86%
<i>p</i> -Anisaldehyde	0.09%	0.46%	1.20%	3.66%	0.00%	0.35%	5.77%
Salicylaldehyde	0.07%	0.37%	0.83%	2.84%	0.00%	0.52%	4.63%
<i>m</i> -Hydroxybenzaldehyde	0.00%	0.28%	0.95%	1.92%	0.00%	0.32%	3.46%
<i>p</i> -Hydroxybenzaldehyde	0.00%	0.16%	0.87%	1.21%	0.00%	0.25%	2.48%
Vanillin	0.08%	0.24%	1.56%	1.41%	0.00%	0.00%	3.28%
Syringaldehyde	0.10%	0.32%	0.28%	2.98%	0.00%	0.00%	3.69%

^a Yields are presented as a wt/wt% of the total raw biomass on a dry basis and is corrected for any mass lost with respect to the monomers' initial structures in the native lignin polymer. ^b Fractionation performed using 2-methyltetrahydrofuran as the solvent, substituting 1,4-dioxane.

Table S4. Yield of Lignin Monomers from the Hydrogenolysis of Select Isolated Acetal-stabilised Lignins in Various Solvents.^a

Aldehyde	Octanaldehyde				Acetaldehyde				Sodium Glyoxylate			
	Isooctane	Toluene	THF	Water	Isooctane	Toluene	THF	Water	Isooctane	Toluene	THF	Water
M24	0.03%	0.00%	0.01%	0.00%	0.07%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
M25	0.03%	0.00%	0.02%	0.69%	0.00%	0.00%	0.01%	0.66%	0.02%	0.00%	0.00%	0.24%
M27	0.00%	0.00%	0.02%	0.20%	0.03%	0.00%	0.01%	0.04%	0.00%	0.00%	0.30%	0.34%
M26	0.03%	0.00%	0.01%	1.33%	0.00%	0.00%	0.25%	0.56%	0.00%	0.00%	0.00%	0.01%
M28	0.05%	0.00%	0.00%	0.02%	0.02%	0.00%	0.00%	0.00%	0.00%	0.00%	0.33%	0.48%
M29	0.08%	0.00%	0.03%	0.00%	0.02%	0.00%	0.00%	0.00%	0.00%	0.00%	1.20%	2.45%
M11	0.00%	0.02%	0.00%	0.02%	0.01%	0.01%	0.01%	0.00%	0.00%	0.00%	0.00%	0.02%
M30	0.10%	0.00%	0.02%	0.11%	0.02%	0.00%	0.00%	0.02%	0.00%	0.00%	0.35%	0.51%
M12	0.00%	0.08%	0.00%	0.04%	0.06%	0.01%	0.01%	0.00%	0.00%	0.03%	0.00%	0.10%
M1	0.13%	0.46%	0.25%	0.00%	0.09%	0.33%	0.35%	0.00%	0.00%	0.15%	0.00%	0.00%
M13	0.00%	0.02%	0.00%	0.06%	0.01%	0.01%	0.04%	0.00%	0.00%	0.00%	0.00%	0.00%
M3	0.25%	0.53%	0.62%	0.11%	0.15%	0.56%	0.65%	0.00%	0.00%	0.03%	0.00%	0.00%
M14	0.28%	0.19%	0.11%	0.05%	0.25%	0.11%	0.10%	0.00%	0.00%	0.29%	0.00%	0.00%
M5	0.63%	2.71%	3.14%	0.50%	0.43%	2.33%	2.41%	0.00%	0.00%	0.90%	0.00%	0.00%
M7	1.59%	2.64%	2.94%	0.97%	0.76%	3.28%	3.18%	0.00%	0.00%	0.27%	0.00%	0.00%
M9	0.00%	1.20%	0.31%	0.00%	0.02%	0.77%	1.05%	0.00%	0.00%	0.00%	0.00%	0.00%
Total	3.20%	7.86%	7.84%	4.11%	1.93%	7.41%	8.11%	1.28%	0.02%	1.66%	2.17%	4.15%

^a Yields are presented as a wt/wt% of the total raw biomass on a dry basis and is corrected for any mass lost with respect to the monomers' initial structures in the native lignin polymer.

Table S5. Yield of Lignin Monomers from the Hydrogenolysis of Technical Lignins in Various Solvents. ^a

Source	Kraft Lignin				Sodium Lignosulfonate			
	Isooctane	Toluene	THF	Water	Isooctane	Toluene	THF	Water
M24	0.00%	0.00%	0.00%	0.00%	0.02%	0.00%	0.00%	0.00%
M25	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.04%
M27	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
M26	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
M28	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
M29	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
M11	0.05%	0.09%	0.00%	0.10%	0.07%	0.17%	0.23%	0.14%
M30	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
M12	0.04%	0.09%	0.02%	0.05%	0.00%	0.02%	0.05%	0.05%
M1	0.13%	0.14%	0.10%	0.12%	0.02%	0.08%	0.14%	0.12%
M13	0.00%	0.00%	0.02%	0.01%	0.02%	0.00%	0.01%	0.02%
M3	0.21%	0.15%	0.28%	0.27%	0.00%	0.04%	0.18%	0.28%
M14	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
M5	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
M7	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
M9	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
Total	0.47%	0.46%	0.41%	0.55%	0.12%	0.31%	0.60%	0.66%

^a Yields are presented as a wt/wt% of the total estimated raw biomass on a dry basis and is corrected for any mass lost with respect to the monomers' initial structures in the native lignin polymer. The total raw biomass was estimated from the Klason Lignin content of the birch wood used in this paper.

Table S6. Relative Response Factors for the Gas Chromatography Method that Does Not Quantify the Hydrodeoxygenation Monomers.

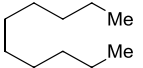
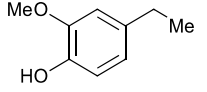
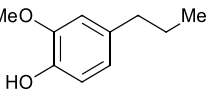
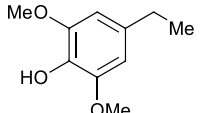
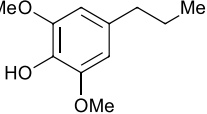
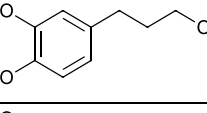
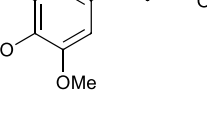
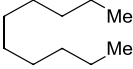
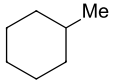
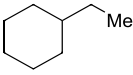
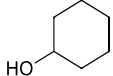
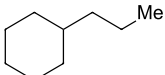
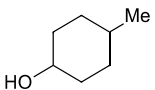
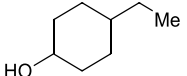
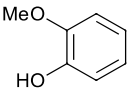
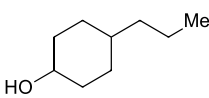
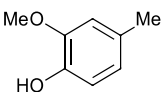
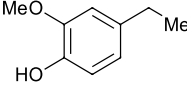
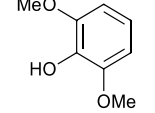
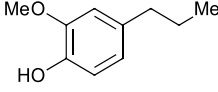
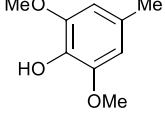
Monomer Number	Monomer Structure	Molecular Weight (g·mol ⁻¹)	Native Molecular Weight (g·mol ⁻¹)	Solvent	Relative Response Factor (RRF)	Elution Time (min)
<i>n</i> -decane		142.29	142.29	Isooctane	10	5.401
				Toluene	10	5.401
				Tetrahydrofuran	10	5.401
				Methanol	10	5.401
M1		152.19	196.20	Isooctane	7.61	6.850
				Toluene	7.59	6.854
				Tetrahydrofuran	7.65	6.854
				Methanol	8.19	6.878
M3		166.22	196.20	Isooctane	8.69	7.170
				Toluene	8.69	7.178
				Tetrahydrofuran	8.76	7.178
				Methanol	9.02	7.184
M5		182.22	226.23	Isooctane	6.99	7.695
				Toluene	7.16	7.715
				Tetrahydrofuran	6.90	7.714
				Methanol	7.06	7.735
M7		196.25	226.23	Isooctane	7.56	7.936
				Toluene	7.66	7.942
				Tetrahydrofuran	7.49	7.948
				Methanol	7.78	7.950
M15		182.22	196.20	Isooctane	N/A	N/A
				Toluene	6.08	8.156
				Tetrahydrofuran	6.65	8.125
				Methanol	6.95	8.135
M9		212.24	226.23	Isooctane	N/A	N/A
				Toluene	6.09	8.705
				Tetrahydrofuran	6.40	8.701
				Methanol	6.65	8.701

Table S7. Relative Response Factors for the Gas Chromatography Method that Quantifies the Hydrodeoxygenation Monomers.

Monomer Number	Monomer Structure	Molecular Weight (g·mol ⁻¹)	Native Molecular Weight (g·mol ⁻¹)	Solvent	Relative Response Factor (RRF)	Elution Time (min)
<i>n</i> -decane		142.29	142.29	Isooctane	10	3.83
				Toluene	10	3.83
				THF	10	3.83
				Methanol	10	3.83
M24		98.19	221.37 ^a	Isooctane	7.02	1.794
				Toluene	N/A	N/A
				THF	6.77	1.746
				Methanol	7.02	1.714
M25		112.21	221.37 ^a	Isooctane	8.13	2.408
				Toluene	8.12	2.408
				THF	7.40	2.408
				Methanol	7.11	2.392
M27		100.16	221.37 ^a	Isooctane	5.44	2.823
				Toluene	5.36	2.823
				THF	5.51	2.823
				Methanol	5.87	2.831
M26		126.24	221.37 ^a	Isooctane	9.17	3.206
				Toluene	9.18	3.206
				THF	9.00	3.206
				Methanol	9.07	3.198
M28		114.19	221.37 ^a	Isooctane	6.36	3.363
				Toluene	6.19	3.363
				THF	6.38	3.363
				Methanol	6.55	3.368
M29		128.21	221.37 ^a	Isooctane	7.23	4.395 & 4.430
				Toluene	7.07	4.395 & 4.430
				THF	7.25	4.395 & 4.430
				Methanol	7.56	4.397 & 4.430
M11		124.14	196.20	Isooctane	5.56	4.747
				Toluene	5.61	4.747
				THF	5.51	4.747
				Methanol	5.21	4.746
M30		142.24	221.37 ^a	Isooctane	7.84	5.331 & 5.359
				Toluene	7.68	5.331 & 5.359
				THF	7.46	5.331 & 5.359
				Methanol	8.00	5.331 & 5.358
M12		138.16	196.20	Isooctane	6.36	5.733
				Toluene	6.40	5.733
				THF	6.40	5.733
				Methanol	6.01	5.727
M1		152.19	196.20	Isooctane	7.34	6.523
				Toluene	7.53	6.523
				THF	7.05	6.523
				Methanol	6.87	6.517
M13		154.16	226.23	Isooctane	5.41	7.162
				Toluene	5.53	7.162
				THF	5.22	7.162
				Methanol	5.52	7.159
M3		166.22	196.20	Isooctane	8.29	7.293
				Toluene	8.71	7.293
				THF	7.92	7.293
				Methanol	7.75	7.290
M14		168.19	226.23	Isooctane	6.30	7.968
				Toluene	6.18	7.968
				THF	6.18	7.968
				Methanol	6.44	7.961

^aWeighted average of the reconstructed guaiacyl and syringyl species based on the monomer distribution from the reductive catalytic fractionation of the birch wood (Table S2).

Table S8. Relative Response Factors for the Gas Chromatography Method that Quantifies the Hydrodeoxygenation Monomers Continued.

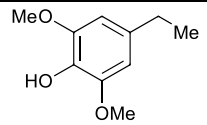
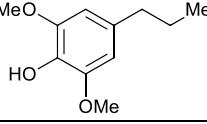
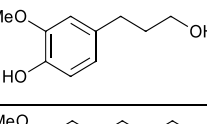
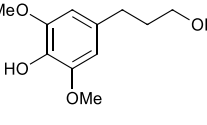
Monomer Number	Monomer Structure	Molecular Weight (g·mol ⁻¹)	Native Molecular Weight (g·mol ⁻¹)	Solvent	Relative Response Factor (RRF)	Elution Time (min)
M5		182.22	226.23	Isooctane	7.13	8.565
				Toluene	6.94	8.562
				THF	6.74	8.562
				Methanol	6.66	8.563
M7		196.25	226.23	Isooctane	7.59	9.207
				Toluene	7.64	9.207
				THF	7.23	9.206
				Methanol	7.94	9.204
M15		182.21	196.20	Isooctane	N/A	N/A
				Toluene	6.45	9.531
				THF	5.37	9.536
				Methanol	5.31	9.528
M9		212.24	226.23	Isooctane	N/A	N/A
				Toluene	4.95	11.234
				THF	4.45	11.242
				Methanol	4.67	11.237

Table S9. Estimated β -O-4 content and Lignin Yield Corrected for Aldehyde Protection Based on the Yield of Lignin Monomers.

Aldehyde	Yield of Monomers, Klason and ASL Basis (wt/wt%) ^a	Estimated β -O-4 Content	Mass Extracted Lignin (g) ^b	Yield of Monomers (mmol) ^c	Aldehyde Contribution to Extracted Lignin Mass (g) ^d	Corrected Extracted Lignin Mass (g) ^b	Corrected Lignin Yield (wt/wt%)
Direct Hydrogenolysis	48.24%	69.46%	-	0.4582	0.0000	-	-
Acetaldehyde	47.02%	68.57%	0.8864	2.2200	0.0708	0.8155	16.17%
Propionaldehyde	45.70%	67.60%	0.8584	2.1626	0.0908	0.7677	15.13%
Isobutyraldehyde	45.64%	67.56%	0.6709	2.1389	0.1198	0.5511	10.95%
Pivaldehyde	40.43%	63.59%	1.1883	1.8917	0.1407	1.0476	20.86%
Octanaldehyde	40.83%	63.90%	1.1545	1.9203	0.2274	0.9271	18.41%
Decanaldehyde	34.09%	58.39%	1.3176	1.5968	0.3317	0.9859	19.69%
Dodecanaldehyde	21.94%	46.84%	1.1607	1.0386	0.3227	0.8380	16.57%
Chloroacetaldehyde	40.46%	63.61%	1.0170	1.9108	0.1266	0.8904	17.65%
Dichloroacetaldehyde	37.80%	61.48%	1.1728	1.7743	0.1887	0.9841	19.58%
Chloral	15.90%	39.88%	0.5879	0.7416	0.1648	0.4231	8.46%
Glycolaldehyde	31.27%	55.92%	1.5464	1.4623	0.0777	1.4688	29.31%
Glyoxylic Acid	23.73%	48.71%	1.0731	1.1266	0.1160	0.9571	18.96%
<i>p</i> -Formylbenzoic Acid	30.40%	55.13%	0.7924	1.4150	0.2322	0.5602	11.04%
Benzaldehyde	31.25%	55.90%	0.8496	1.4770	0.1606	0.6890	13.59%
<i>p</i> -Chlorobenzaldehyde	34.69%	58.90%	0.7515	1.6430	0.2343	0.5172	10.21%
<i>p</i> -Tolualdehyde	31.15%	55.82%	1.1890	1.4644	0.1843	1.0047	19.98%
<i>p</i> -(Trifluoromethyl) benzaldehyde	35.57%	59.64%	0.7485	1.6832	0.3010	0.4475	8.81%
<i>p</i> -Anisaldehyde	26.09%	51.08%	1.0813	1.2244	0.1942	0.8870	17.59%
Salicylaldehyde	20.95%	45.78%	0.8169	0.9819	0.1535	0.6634	13.17%
<i>m</i> -hydroxybenzaldehyde	15.67%	39.59%	0.9765	0.7279	0.1316	0.8449	16.89%
<i>p</i> -hydroxybenzaldehyde	11.24%	33.53%	0.9851	0.5260	0.1123	0.8728	17.28%
Vanillin	14.83%	38.50%	1.0694	0.6958	0.1659	0.9035	17.92%
Syringaldehyde	16.68%	40.84%	1.2506	0.7892	0.2165	1.0341	20.40%

^aThe total lignin content of the biomass is combination of the Acid Soluble Lignin (ASL) and Klason Lignin (20.75 wt/wt%). ASL is stabilised by aldehydes and is isolated with the rest of the lignin during the first precipitation, which is why it needs to be included for this calculation. ^bCorrected for the hydrogenolysis sample and based on 5 g of birch wood. ^cBased on 5 g of birch wood except for the direct hydrogenolysis sample which was based on 1 g of birch wood. ^dThe yield of lignin monomers produced from the extracted lignin is less than the unextracted lignin as more soluble lignin fragments are washed away with the residual sugars and aldehyde. To correct for this, we used the yield from the hydrogenolysis of the extracted acetaldehyde stabilised lignin estimate the reduced contribution of the aldehyde modification to the extracted lignins. Due to the way that they were isolated, the contributions of the aldehydes to the yields of the decanaldehyde, dodecanaldehyde, and glyoxylic acid stabilised lignins were not reduced.

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- 2 J. Behaghel De Bueren, F. Héroguel, C. Wegmann, G. R. Dick, R. Buser and J. S. Luterbacher, *ACS Sustain. Chem. Eng.*, 2020, **8**, 16737–16745.
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Author Contributions

GRD and JSL conceived of the project and designed the research. GRD and AOK performed the experiments and analyses and curated the data. GRD and JSL drafted, reviewed, and edited the publication.