SUPPORTING INFORMATION FOR

Convergent Reductive Depolymerization of Wood Lignin to Isolated Phenol Derivatives by Metal-Free Catalytic Hydrosilylation

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Experimental details

1. General considerations

All reactions and manipulations were performed at 20 °C in a recirculating mBraun LabMaster DP inert atmosphere (Ar) drybox and vacuum Schlenk lines. Glassware was dried overnight at 60 °C before use. $^1$H and $^{13}$C NMR spectra were obtained using a Bruker DPX 200 MHz spectrometer. Chemical shifts for $^1$H and $^{13}$C{$^1$H} NMR spectra were referenced to solvent impurities. HSQC (heteronuclear single quantum coherence) analyses were performed on a Bruker Avance 400 MHz spectrometer. Unless otherwise noted, reagents were purchased from commercial suppliers and dried over 4 Å molecular sieves prior to use. 4 Å molecular sieves (Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use. The reagents used for lignin extractions were: acetic acid (≥ 99.85 %), formic acid (≥ 96.0 %), ethanol (≥ 99.8 %), methanol (99.8 %), acetone (99.5 %) and HCl (37 %). Dichloromethane (and $d_2$-CH$_2$Cl$_2$) was dried over CaH$_2$ and distilled before use. Elemental analyses and HR-MS were performed at the CNRS facility in Gif-Sur-Yvette (France). Mass spectrometer data were collected on a Shimadzu GCMS-QP2010 Ultra gas chromatograph mass spectrometer equipped with a Supelco SLB™-ms fused silica capillary column (30 m x 0.25 mm x 0.25 µm). Gas chromatography analyses were executed on a Shimadzu GC-2010 Plus gas chromatograph equipped with a Carboxen™ 1006 PLOT silica capillary column (30 m x 0.53 mm). Compound 1 was synthesized according to the procedure described in the literature.$^6$ Et$_3$SiD was obtained using procedure described in reference 7. In all cases, sawdust extracted from wood was used as the vegetable matter and was dried overnight at 60 °C before use. In all cases sawdust pieces had a length less than 2 cm and a thickness of less than 0.1 cm.
2. Supplementary equations:

1.1. Equation S1: Depolymerization of compound 1 using TMDS

When 7 equiv. of TMDS are added only the disilylated propylcatechol derivative was detected by $^1$H NMR and $^{13}$C NMR analysis. When adding a stoichiometric quantity of TMDS (3.5 equiv.) a mixture of silylated primary alcohol, the silylated alkane and the substrate was obtained.

N.B: The use of PMHS is followed by the formation of a gel which increases the viscosity of the solution and renders the reaction difficult to achieve. Heating the solution (100°C for 16 h) and increasing the amount of catalyst had no visible influence on the reaction. Increasing (doubling) the volume of solvent (dichloromethane) did not prevent the formation of the gel. On the other hand, carrying out the reaction in benzene limits its formation, but only the dehydrogenation of alcohols is carried out.

1.2. Equation S2: Reduction of compound [3,3-D$_2$]-1 using Et$_3$SiH

The results of this labeling study suggest that there is probably no semi-pinacol rearrangement in the hydrosylilation of [3,3-D$_2$]-1.
1.3. **Equation S3: Depolymerization of industrial pine lignin using TMDS**

\[
\text{Industrial pine Formacell lignin} + 1880 \text{ wt\% TMDS} \xrightarrow{\text{Bi(C6F5)3 (30 wt\%)}} \text{C}_6\text{D}_6, \text{RT, 3 h}} \xrightarrow{-X_3\text{SiOSiX}_3} X_3\text{SiO}_3\text{SiX}_3 \approx 9 \text{ wt\%}
\]

The hydrosilylation reaction using TMDS in CD₂Cl₂ is very fast and a gel is formed immediately. The reaction is slower in benzene or in toluene, but necessitates a large excess of TMDS to occur. The major product formed was the disilylated propylcatechol. The yield (~9 wt%) was difficult to determine since multiple silylated species of the propyl catechol were formed and these products were very difficult to purify using silica gel chromatography.

3. **Description of lignin extraction methods**

3.1. **Extraction of lignin from wood sawdust using a Formacell process**

Lignin derived from wood was extracted using the Formacell process described by Delmas et al.³ This process was originally optimized for triticale straw extraction and the same conditions were used for the extraction of lignin from wood. The extraction was carried out in a 500 mL round-bottom flask equipped with a magnetic stir bar and a reflux condenser. A total of 15 g of sawdust was used for each test, applying a ratio of liquor to solid of L/S: 10.0/0.83. The cooking liquor is a mixture of formic acid/acetic acid/water in a 30/50/20 % volume ratio. The suspension was heated at 107 °C for 3 h (boiling point of water/formic acid azeotrope). After cooling the system to room temperature, the suspension was filtered under reduced pressure through a porosity 3 frit and the solid was washed twice with 25 mL of a mixture of the previous formic acid/acetic acid/water mixture. The solvents were then evaporated under reduced pressure from the dark colored solution (in most cases brown).
containing lignin and the hemicellulose derivatives. Addition of distilled water (25 mL) to the solid residue led to the solubilization of the hemicellulose part and precipitation of lignin. The suspension was filtered through a porosity 4 frit and the solid was further washed with water until the washings were colorless. Finally, lignin was dried overnight under primary vacuum. The soluble sugars in the water phase were recovered after removal of water under vacuum. The yields in lignin and hemicellulose derivatives are highly dependent on the wood species. The obtained yields are summarized in **Table S1**.

**Table S1:** The yields for the extracted lignin and for hemicellulose derived compounds are determined with respect to the initial loading of sawdust.

<table>
<thead>
<tr>
<th>Usual name</th>
<th>Binomial Name</th>
<th>Origin</th>
<th>Softwood v/s Hardwood</th>
<th>% wt of extracted lignin (%)</th>
<th>color of extracted lignin</th>
<th>% wt of the hemicellulose part (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nordmann fir</td>
<td><em>Abies nordmanniana</em></td>
<td>France</td>
<td>SW</td>
<td>20</td>
<td>Violine</td>
<td>13</td>
</tr>
<tr>
<td>Green plum</td>
<td><em>Prunus cerasifera</em></td>
<td>Lebanon</td>
<td>HW</td>
<td>18</td>
<td>Brown</td>
<td>27</td>
</tr>
<tr>
<td>Black poplar</td>
<td><em>Populus nigra</em></td>
<td>Russia</td>
<td>HW</td>
<td>17</td>
<td>Brown</td>
<td>28</td>
</tr>
<tr>
<td>Common beech</td>
<td><em>Fagus sylvatica</em></td>
<td>Romania</td>
<td>HW</td>
<td>14</td>
<td>Violine</td>
<td>22</td>
</tr>
<tr>
<td>Silver birch</td>
<td><em>Betula pendula</em></td>
<td>France</td>
<td>HW</td>
<td>13</td>
<td>Brown</td>
<td>28</td>
</tr>
<tr>
<td>Evergreen oak</td>
<td><em>Quercus ilex</em></td>
<td>France</td>
<td>HW</td>
<td>12</td>
<td>Violine</td>
<td>32</td>
</tr>
<tr>
<td>Date palm</td>
<td><em>Phoenix dactylifera</em></td>
<td>Lebanon</td>
<td>HW</td>
<td>10</td>
<td>Auburn</td>
<td>35</td>
</tr>
<tr>
<td>Hybrid plane</td>
<td><em>Platanus × acerifolia</em></td>
<td>France</td>
<td>HW</td>
<td>10</td>
<td>Beige</td>
<td>20</td>
</tr>
<tr>
<td>River Red gum</td>
<td><em>Eucalyptus camaldulensis</em></td>
<td>Lebanon</td>
<td>HW</td>
<td>9</td>
<td>Beige</td>
<td>11</td>
</tr>
<tr>
<td>Industrial pine</td>
<td><em>(industrial pine)</em></td>
<td>France</td>
<td>SW</td>
<td>8</td>
<td>Violine</td>
<td>7</td>
</tr>
<tr>
<td>Parasol pine</td>
<td><em>Pinus pinea</em></td>
<td>France</td>
<td>SW</td>
<td>8</td>
<td>Beige</td>
<td>7</td>
</tr>
<tr>
<td>Pacific redcedar</td>
<td><em>Thuja plicata</em></td>
<td>USA</td>
<td>SW</td>
<td>7</td>
<td>Brown</td>
<td>13</td>
</tr>
<tr>
<td>African ebony</td>
<td><em>Diospyros crassiflora</em></td>
<td>Madagascar</td>
<td>HW</td>
<td>7</td>
<td>Brown</td>
<td>17</td>
</tr>
<tr>
<td>Norway spruce</td>
<td><em>Picea abies</em></td>
<td>Russia</td>
<td>SW</td>
<td>6</td>
<td>Beige</td>
<td>20</td>
</tr>
</tbody>
</table>
3.2. Extraction of lignin from industrial pine sawdust using ethanol (EOL)

Lignin was extracted with ethanol using the procedure described by Bauer et al.\(^1\) In a 500 mL round-bottom flask equipped with a magnetic stir bar and a reflux condenser, 15 g of industrial pine sawdust was heated at reflux for 4 h in a mixture of ethanol/water (liquid to liquid ratio: ethanol / water 95:5 v:v) containing 0.2 M HCl. The liquid to solid ratio was L/S: 10.0/1.8 and the reaction was carried out at ambient pressure. After cooling the system to room temperature, lignin was isolated using the same procedure described for the Formacell process (described in section 3.1). Finally, lignin was obtained as a gray powder in 3.0 wt% yield with respect to the initial loading of sawdust.

3.3. Extraction of lignin from industrial pine sawdust using methanol

Lignin was extracted with methanol using a modified version of the procedure described by Anastas et al.\(^2\) In a 500 mL round-bottom flask equipped with a magnetic stir bar and a reflux condenser, 136 mL methanol and 15 g of wood sawdust were combined (liquid to solid ratio of 10.0/1.4). The mixture was stirred under reflux for 12 h and then cooled to room temperature. The solid was removed by filtration through a porosity 3 frit and was washed with methanol (2 x 25 mL). The solvents were then evaporated under reduced pressure and 25 mL of water were added to the solid residue leading to the precipitation of lignin. The suspension was filtered under reduced pressure through a porosity 4 frit and the solid was washed with water until the washings were colorless. Finally, lignin was dried under reduced pressure to yield 2.0 wt% of lignin with respect to the initial loading of sawdust.
3.4. Extraction of lignin from industrial pine sawdust using acetone

Lignin was extracted with acetone using the procedure described by Bauer et al.\(^1\) In a 500 mL round-bottom flask equipped with a magnetic stir bar and a reflux condenser, lignin originating from industrial pine sawdust was extracted by refluxing for 4 h a suspension of sawdust (liquid to solid ratio of 10.0/1.8) in 95 % acetone (liquid to liquid ratio: acetone/water 95:5 v:v) at ambient pressure and in the presence of 0.2 M HCl. After cooling the system to room temperature, lignin was isolated using the procedure described for the Formacell process. Lignin was obtained as a light brown powder in 2.0 wt% yield with respect to the initial loading of sawdust.

4. Elemental analyses of extracted lignin

Table S2: elemental analyses of extracted lignin samples and proposed chemical formulas

<table>
<thead>
<tr>
<th>Species</th>
<th>Extraction method</th>
<th>C(%)</th>
<th>H(%)</th>
<th>O(%)</th>
<th>S(%)</th>
<th>H/C</th>
<th>O/C</th>
<th>Proposed chemical formula (in C10)</th>
<th>Proposed chemical formula (in C11)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial pine (wood chips)</td>
<td>without extraction</td>
<td>50.30</td>
<td>5.96</td>
<td>43.00</td>
<td>0.00</td>
<td>1.4</td>
<td>0.6</td>
<td>C10.00H14.22O6.41</td>
<td>C11.00H15.64O7.05</td>
</tr>
<tr>
<td>Industrial pine</td>
<td>Formacell</td>
<td>62.45</td>
<td>5.86</td>
<td>31.69</td>
<td>0.00</td>
<td>1.1</td>
<td>0.4</td>
<td>C10.00H11.26O3.81</td>
<td>C11.00H12.39O4.18</td>
</tr>
<tr>
<td>Parasol pine</td>
<td>Formacell</td>
<td>61.97</td>
<td>5.94</td>
<td>32.09</td>
<td>0.00</td>
<td>1.2</td>
<td>0.4</td>
<td>C10.00H11.50O3.88</td>
<td>C11.00H12.65O4.27</td>
</tr>
<tr>
<td>Norway spruce</td>
<td>Formacell</td>
<td>61.47</td>
<td>5.67</td>
<td>32.86</td>
<td>0.00</td>
<td>1.1</td>
<td>0.4</td>
<td>C10.00H11.07O4.01</td>
<td>C11.00H12.18O4.41</td>
</tr>
<tr>
<td>Hybrid plane</td>
<td>Formacell</td>
<td>59.42</td>
<td>5.69</td>
<td>34.89</td>
<td>0.00</td>
<td>1.1</td>
<td>0.4</td>
<td>C10.00H11.49O4.40</td>
<td>C11.00H12.64O4.84</td>
</tr>
<tr>
<td>Parasol pine</td>
<td>ethanol/HCl</td>
<td>65.72</td>
<td>7.19</td>
<td>27.09</td>
<td>0.00</td>
<td>1.3</td>
<td>0.3</td>
<td>C10.00H13.13O3.09</td>
<td>C11.00H14.44O3.40</td>
</tr>
<tr>
<td>Evergreen oak</td>
<td>Formacell</td>
<td>58.31</td>
<td>5.62</td>
<td>35.66</td>
<td>0.00</td>
<td>1.2</td>
<td>0.5</td>
<td>C10.00H11.56O4.59</td>
<td>C11.00H12.72O5.05</td>
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<tr>
<td>Kraft lignin</td>
<td>Kraft</td>
<td>47.51</td>
<td>5.16</td>
<td>36.01</td>
<td>0.00</td>
<td>1.3</td>
<td>0.6</td>
<td>C10.00H13.03S0.685</td>
<td>C11.00H14.34O6.25S0.32</td>
</tr>
<tr>
<td>Kraft lignin then Formacell</td>
<td>Kraft then Formacell</td>
<td>59.06</td>
<td>5.14</td>
<td>30.42</td>
<td>2.89</td>
<td>1.0</td>
<td>0.4</td>
<td>C10.00H10.44O3.86S0.18</td>
<td>C11.00H11.49O4.25S0.20</td>
</tr>
</tbody>
</table>
**Discussion**: In all the samples the nitrogen content was lower than 0.3%. Elemental analyses of lignin provide the general chemical formulas of the polymeric materials. Generally, gymnosperms are exclusively made of G residues linked by β-O-4 linkages, the general theoretical formula of the lignin polymer would be \([C_{10}H_{12}O_4]_n\) (Mw=196.20 g/mol). In the case of angiosperms exclusively made of S residues linked by β-O-4 linkages the general formula of the lignin polymer would be \([C_{11}H_{14}O_5]_n\) (Mw=226.23 g/mol). In the case of the Formacell extracted lignins one can see that the deduced chemical formulas are very close to theoretical polymeric formulas. Given that both experimental formulas are close to theoretical results and in order to determine an order of magnitude of the quantity of mono-aromatics in the lignin starting material, an approximation of the mole number of aromatic entities could be calculated by dividing the lignin initial weight by the molar mass of the theoretical polymer.
5. Typical procedures for the catalytic hydrosilylation of lignin

5.1. Obtaining pure 3G from convergent reductive depolymerization of lignin

The procedure is detailed for the conversion of lignin (extracted with the Formacell process from industrial pine) to 3G, using Et₃SiH as the reductant. Nevertheless, *Picea abies*, *Pinus pinea* and *Cedrus libani* could be used to obtain the same product with yields ranging from 18 to 25 wt% and with similar purities.

A 50 mL round bottom flask equipped with a magnetic stir bar was charged with 400 mg (approximatively 2.0 mmol) of lignin, previously extracted from wood (using the Formacell process), and CH₂Cl₂ (2 mL). On the other hand, a mixture of Et₃SiH (1220.8 mg, 10.5 mmol, 305.2 wt%) and B(C₆F₅)₃ (100.0 mg, 0.2 mmol, 25 wt%) in CH₂Cl₂ (2 mL) was added slowly (30 min), at RT. Methane formation was detected by GC chromatography. After 1h, the entire solid was dissolved and the solution turned from transparent to brown. Stirring was continued for 19 h at RT and the reaction was monitored by GC-MS. The solvent was then evaporated under reduced pressure and the crude residue was purified by flash chromatography (using pentane/CH₂Cl₂ (8:2) mixture as the eluent). After solvent removal under reduced pressure, 3G was obtained as a pale yellow oil (108.0 mg, 0.3 mmol, 27 wt%) that could be further purified by distillation (boiling point: 86°C under 6 mbars) or by another column chromatography to give pure 3G as a colorless oil (76.0 mg, 0.2 mmol, 19 wt%). The purity of the compound was evaluated by elemental analysis. **Anal. Calcd.** for C₂₁H₄₀O₂Si₂ (mol. wt. 380.72): C, 66.25; H, 10.59. **Found:** C, 65.73; H, 10.79.
5.2. Obtaining pure 4S from convergent reductive depolymerization of lignin

The procedure is detailed for the conversion of lignin (extracted with the Formacell process from *Hybrid plane*) to 4S, using Et₃SiH as the reductant. Yet, *evergreen oak*, *silver birch*, *common beech*, and *black poplar* could be used to obtain the same product with yields ranging from 50 to 126 wt% and with similar purities.

A 50 mL round-bottom flask equipped with a magnetic stir bar was charged with 400 mg of lignin, previously extracted from wood (using the Formacell process), and CH₂Cl₂ (2 mL). On the other hand, a mixture of Et₃SiH (1017.6 mg, 8.8 mmol, 254.4 wt%) and B(C₆F₅)₃ (80.0 mg, 0.16 mmol, 20 wt%) in CH₂Cl₂ (2 mL) was added slowly (30 min), at RT. After 1h of the reaction the entire solid was dissolved and the solution turned from transparent to brown. Stirring was continued for 2 h at RT and the reaction was monitored by GC-MS. The solvent was then evaporated under reduced pressure and the crude residue was purified by flash chromatography (using pentane/CH₂Cl₂ (7:3) mixture as the eluent). After solvent removal under reduced pressure, 4S was obtained as a pale yellow oil (504.0 mg, 0.8 mmol, 126 wt%) that could be further purified by undertaking another column chromatography (using pentane and CH₂Cl₂ gradient starting from (100 % pentane to 7:3 pentane/CH₂Cl₂) to give pure 4S as a colorless oil (360.0 mg, 0.6 mmol, 90 wt%). Anal. Calcd. for C₃₃H₆₈O₄Si₄ (mol. wt. 640.24): C, 61.81; H, 10.69. Found: C, 60.90; H, 10.82.
6. Typical procedure for the hydrolysis of silylated aromatic compounds

The procedure for the hydrolysis of silylated aromatic compounds was detailed for compound 3G. To a solution of 3G (380.7 mg; 1.0 mmol, 1 equiv.) in 4 mL of THF under argon n-Bu₄NF 3H₂O (315.5 mg; 2.1 mmol, 2.1 equiv.) was added slowly, and the solution was stirred for 1 h at ambient temperature. The volatiles were then removed under vacuum and 4 mL of dichloromethane were added. Afterwards, the solution was column chromatographed on silica gel using a gradient mixture of dichloromethane and ethyl acetate as eluent (gradient starting from (100 % dichloromethane to 3:7 dichloromethane/ ethyl acetate) to give 3G’ (141.5 mg; 0.9 mmol; 84 %) as a colorless oil.

Table S3: Hydrolysis results of silylated monoaromatic products:

<table>
<thead>
<tr>
<th>Product</th>
<th>TBAF quantity (equiv.)</th>
<th>Physical appearance</th>
<th>Isolated yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3G’</td>
<td>2.1</td>
<td>Colorless oil</td>
<td>84</td>
</tr>
<tr>
<td>4G’</td>
<td>3.1</td>
<td>Colorless oil</td>
<td>86</td>
</tr>
<tr>
<td>3S’</td>
<td>3.1</td>
<td>White powder or colorless crystals.</td>
<td>94</td>
</tr>
<tr>
<td>4S’</td>
<td>4.1</td>
<td>White gum</td>
<td>82</td>
</tr>
<tr>
<td>3H’</td>
<td>1.1</td>
<td>Colorless oil</td>
<td>77</td>
</tr>
<tr>
<td>4H’</td>
<td>2.1</td>
<td>White powder</td>
<td>92</td>
</tr>
</tbody>
</table>
7. Synthesis of [3,3-D$_2$]-1

[3,3-D$_2$]-1 was prepared using the same procedure employed for the synthesis of 1 using LiAlD$_4$ (69.3 mg, 1.65 mmol, 2.5 equiv.) and ethyl 3-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propanoate (250 mg, 0.66 mmol, 1 equiv.). After solvent removal under reduced pressure (200 mg, 0.59 mmol, 89 %), the erythro isomer of [3,3-D$_2$]-1 was obtained as a white solid.

![Chemical structure](image)

$^1$H NMR (200 MHz, CDCl$_3$, Me$_4$Si) $\delta$ (ppm) = 7.19-6.67 (m, 7H, 1-2-3-6-13-14-17), 4.98 (d, $J$ = 4.6 Hz, 1H, 11), 4.15 (d, $J$ = 4.6 Hz, 1H, 8), 3.90-3.84 (m, 1H, 9), 3.93-3.78 (m, 9H, 7-10-12), 2.56 (br.s, 2H, OH).

$^{13}$C NMR (50 MHz, CDCl$_3$, Me$_4$Si): $\delta$ (ppm) = 151.7, 149.1, 148.5, 146.9, 132.5, 124.4, 121.8, 121.1, 118.5, 112.2, 111.0, 109.2, 87.5, 72.7, 56.0.
8. Synthesis of molecular standards

8.1. Synthesis of 3G

A suspension of 2-methoxy-4-propylphenol (2.5 g, 15.0 mmol, 1.0 equiv.) in CH$_2$Cl$_2$ (40 mL) was stirred under argon. A mixture of Et$_3$SiH (4.0 g, 34.5 mmol, 2.3 equiv.) and B(C$_6$F$_5$)$_3$ (77.0 mg, 0.15 mmol, 1 mol %) in CH$_2$Cl$_2$ (50 mL) was added slowly at RT, and stirring was continued for 2 h. The solvent was then evaporated under reduced pressure and the crude residue was purified by flash chromatography (using a pentane/CH$_2$Cl$_2$ (8:2) mixture as the eluent). After solvent removal under reduced pressure, 3G was obtained as a colorless oil (5.5 g, 14.4 mmol, 96 %).

$^1$H NMR (200 MHz, CDCl$_3$, Me$_4$Si) δ (ppm) = 6.71 (1 H, d, $^3$J = 8.1 Hz, Ar-H), 6.63 (1 H, s, Ar-H), 6.58 (1 H, d, $^3$J = 8.1 Hz, Ar-H), 2.45 (2 H, t, $^3$J = 7.8 Hz, Ar-CH$_2$), 1.57 (2 H, sext, $^3$J = 7.8 Hz, CH$_2$-CH$_3$), 0.98 (18 H, t, $^3$J = 7.9 Hz, CH$_2$CH$_2$Si), 0.90 (3 H, t, $^3$J = 7.8 Hz, CH$_3$CH$_2$-CH$_2$), 0.74 (12 H, q, $^3$J = 7.9 Hz, CH$_3$CH$_2$Si).

$^{13}$C NMR (50 MHz, CDCl$_3$, Me$_4$Si): δ (ppm) = 146.5, 144.7, 136.0, 121.3, 120.9, 120.2, 37.4, 24.7, 13.9, 6.9, 5.3, 5.2.

MS: IE (m/z): 380 (9); 351 (4); 207 (8); 117 (4); 116 (11); 115 (100); 88 (7); 87 (74); 59 (45); 58 (4).

HR-MS (APPI): calcd (M+) (C$_{21}$H$_{40}$O$_2$Si$_2$), m/z 380.2566; found (M+), m/z 380.2559.
**Anal. Calcd.** for C$_{21}$H$_{40}$O$_2$Si$_2$ (mol. wt. 380.72): C, 66.25; H, 10.59. **Found:** C, 66.18; H, 10.46.

**Boiling point:** 86°C under 6 mbars.

### 8.2. Synthesis of 4G

![Chemical structure of 4G](image.png)

To a solution of 3-(3,4-dimethoxyphenyl)propanoic acid (4.0 g, 16.7 mmol, 1.0 equiv) in anhydrous Et$_2$O (130 mL), LiAlH$_4$ (1.9 g, 50.0 mmol, 3.0 equiv) was added carefully at RT, under an argon atmosphere. After 3 h, the reaction was quenched prudently with water. The mixture was then stirred for 30 min at ambient temperature. The suspension was filtered through celite, extracted with (3 x 50 mL) Et$_2$O, washed with brine and dried over Na$_2$SO$_4$ to give (1.1 g, 5.6 mmol, 34 %) of 3-(3,4-dimethoxyphenyl)propan-1-ol as a colorless oil. **NMR** $^1$H and $^{13}$C data were consistent with those described in the literature for this compound.$^4$

**Compound 4G** was prepared using the same procedure described for compound 3G starting from 3-(3,4-dimethoxyphenyl)propan-1-ol (1.0 g, 5.1 mmol, 1.0 equiv), Et$_3$SiH (1.8 g, 15.8 mmol, 3.1 equiv) and B(C$_6$F$_3$)$_3$ (26.09 mg, 0.05 mmol, 1.0 mol %) in CH$_2$Cl$_2$ (30 mL). After solvent removal under reduced pressure the crude residue was purified by flash chromatography (using a 7:3 pentane/CH$_2$Cl$_2$ mixture as the eluent). After solvent removal under reduced pressure **4G** was obtained as a colorless oil (2 g, 3.9 mmol, 78 %).
**1H NMR** (200 MHz, CDCl$_3$, Me$_4$Si) $\delta$ (ppm) = 6.79 – 6.50 (3 H, m, Ar-H), 3.60 (2 H, t, $^3J = 6.6$ Hz, CH$_2$-O), 2.54 (2 H, t, $^3J = 7.6$ Hz, Ar-CH$_2$), 1.79 (2 H, quint, $^3J = 7.0$ Hz, Ar-CH$_2$-CH$_2$), 1.05 – 0.88 (27 H, m, CH$_2$CH$_2$Si), 0.84 – 0.48 (18 H, m, CH$_3$CH$_2$Si).

**13C NMR** (50 MHz, CDCl$_3$, Me$_4$Si): $\delta$ (ppm) =146.5, 144.8, 135.4, 121.3, 120.9, 120.3, 62.3, 34.7, 31.5, 6.9, 6.8, 5.2, 5.2, 4.6.

**MS**: IE (m/z): 511 (8), 337 (9), 235 (11), 207 (24), 116 (6), 115 (57), 89 (28), 88 (10), 87 (100), 86 (6), 59 (38), 32 (16).

**Anal. Calcd.** for C$_{27}$H$_{54}$O$_3$Si$_3$ (mol. wt. 510.98): C, 63.47; H, 10.65. **Found:** C, 62.96; H, 10.82.

### 8.3. Synthesis of 3S

A suspension of 4S (5.5 g, 8.6 mmol, 1.0 equiv.) in CH$_2$Cl$_2$ (25 mL) was stirred under argon. A mixture of Et$_3$SiH (2.0 g, 17.2 mmol, 2.0 equiv.) and B(C$_6$F$_5$)$_3$ (87.9 mg, 0.02 mmol, 1.0 mol %) in CH$_2$Cl$_2$ (50 mL) was added slowly at RT, and stirring was continued for 16 h. The solvent was then evaporated under reduced pressure and the crude residue was purified by flash chromatography (using pentane/CH$_2$Cl$_2$ (8:2) mixture as the eluent). After solvent removal under reduced pressure 3S was obtained as a colorless oil (3.3 g, 6.5 mmol, 75 %).
**H NMR** (200 MHz, CDCl$_3$, Me$_4$Si) $\delta$ (ppm) = 6.27 (2 H, s, Ar-H), 2.39 (2 H, t, $^3J = 7.5$ Hz, Ar-CH$_2$), 1.69 - 1.45 (2 H, m, CH$_2$-CH$_3$), 1.1 - 0.84 (27 H, m, CH$_3$CH$_2$Si), 0.90 – 0.81 (3 H, m, CH$_2$CH$_2$-CH$_2$), 0.83 – 0.65 (18 H, m, CH$_3$CH$_2$Si).

**C NMR** (50 MHz, CDCl$_3$, Me$_4$Si): $\delta$ (ppm) = 147.8, 146.5, 134.5, 113.6, 37.7, 24.6, 13.7, 7.0, 6.8, 5.4, 5.2.

**MS:** IE (m/z): 510 (8); 339 (4); 338 (10); 337 (31); 116 (7); 115 (60); 88 (10); 87 (100); 86 (4); 59 (49).

**Anal. Calcd.** for C$_{27}$H$_{54}$O$_3$Si$_3$ (mol. wt. 510.98): C, 63.47; H, 10.65. **Found:** C, 63.51; H, 10.73.

Boiling point: 155°C under 7 mbars.

### 8.4. Synthesis of 4S

A suspension of 3-(3,4,5-trimethoxyphenyl)propanoic acid (4.0 g, 17.0 mmol, 1 equiv.) in Et$_2$O (125 mL) was stirred at 0 °C under argon, and LiAlH$_4$ (1.94 g, 51.0 mmol, 3.0 equiv.) was added slowly under argon over 20 min. When gas evolution ended, the mixture was warmed to RT and stirred for 3 h. After cooling to 0 °C, the mixture was quenched by adding distilled water (25 mL). The mixture was then stirred for 30 min at ambient temperature. The suspension was filtered through celite, extracted twice with Et$_2$O (3 x 50 mL). After evaporation of the solvent, the crude residue was purified by flash chromatography (using a 5:5 pentane/AcOEt mixture as the eluent). After solvent removal under reduced pressure 3-
(3,4,5-trimethoxyphenyl)propan-1-ol was obtained as a pale yellow oil (3.0 g, 78%). NMR
$^1$H and $^{13}$C data were consistent with those described in the literature for this compound.$^5$

Compound 4S was prepared using the same procedure described for compound 3G starting from 3-(3,4,5-trimethoxyphenyl)propan-1-ol (2.5 g, 11.0 mmol, 1.0 equiv), Et$_3$SiH (5.3 g, 45.3 mmol, 3.1 equiv) and B(C$_6$F$_5$)$_3$ (112.6 mg, 0.2 mmol, 2.0 mol %) in CH$_2$Cl$_2$ (70 mL). After solvent removal under reduced pressure the crude residue was purified by flash chromatography (using a 7:3 pentane/CH$_2$Cl$_2$ mixture as the eluent). After solvent removal under reduced pressure 4S was obtained as a colorless oil (6.2 g, 9.7 mmol, 89%).

$^1$H NMR (200 MHz, CDCl$_3$, Me$_4$Si) δ (ppm) = 6.28 (2 H, s, Ar-H), 3.59 (2 H, t, $^3$J = 6.7 Hz, CH$_2$-O), 2.48 (2 H, t, $^3$J = 7.5 Hz, Ar-CH$_2$), 1.78 (2 H, quint, $^3$J = 7.3 Hz, Ar-CH$_2$-CH$_2$), 1.13 – 0.85 (36 H, m, CH$_3$CH$_2$Si), 0.84 – 0.49 (24 H, m, CH$_3$CH$_2$Si).

$^{13}$C NMR (50 MHz, CDCl$_3$, Me$_4$Si): δ (ppm) =147.9, 136.6, 134.0, 113.6, 62.3, 34.6, 31.7, 6.9, 6.8, 5.4, 5.2, 4.5.

MS: IE (m/z): 642 (5), 640 (5), 641 (9), 467 (8), 365 (7), 337 (6), 116 (4), 115 (36), 89 (19), 88 (9), 87 (100), 59 (32).

8.5. **Synthesis of 3H**

Compound 3H was prepared using the same procedure described for compound 3G starting from 4-propylphenol (3.0 g, 22.0 mmol, 1.0 equiv), Et₃SiH (5.1 g, 44.1 mmol, 2.0 equiv) and B(C₆F₅)₃ (112.6 mg, 0.2 mmol, 1.0 mol %) in CH₂Cl₂ (50 mL). After solvent removal under reduced pressure the crude residue was purified by flash chromatography (using a 8:2 pentane/CH₂Cl₂ mixture as the eluent). After solvent removal under reduced pressure 3H was obtained as a colorless oil (5.3 g, 21.2 mmol, 96%).

**¹H NMR** (200 MHz, CDCl₃, Me₄Si) δ (ppm) = 7.03 (2 H, d, ³J = 7.7 Hz, Ar-H), 6.77 (2 H, ³J = 7.7 Hz, Ar-H), 2.52 (2 H, t, ³J = 7.3 Hz, Ar-CH₂), 1.61 (2 H, sext, ³J = 7.4 Hz, CH₂-CH₃), 1.09 – 0.86 (9 H, m, CH₃CH₂Si), 0.97 – 0.85 (3 H, m, CH₃CH₂-CH₂), 0.83 – 0.64 (6 H, m, CH₃CH₂Si).

**¹³C NMR** (50 MHz, CDCl₃, Me₄Si): δ (ppm) = 153.5, 135.5, 129.4, 119.7, 37.4, 24.9, 13.9, 6.8, 5.1.

**MS**: IE (m/z): 250 (37), 222 (21), 221 (100), 193 (51), 165 (26), 163 (13), 151 (16), 135 (13), 91 (32), 87 (21), 82 (17), 59 (29), 43 (23).

**Anal. Calcd.** for C₁₅H₂₆OSi (mol. wt. 250.46): C, 71.93; H, 10.46. **Found**: C, 71.53; H, 10.47.

Boiling point: 183°C under 1 atm.
8.6. Synthesis of 4H

Compound 4H was prepared using the same procedure described for compound 3G starting from 4-(3-hydroxypropyl)phenol (2.0 g, 13.1 mmol, 1.0 equiv), Et₃SiH (3.5 g, 30.2 mmol, 2.3 equiv) and B(C₆F₅)₃ (67.3 mg, 0.1 mmol, 1.0 mol %) in CH₂Cl₂ (30 mL). After solvent removal under reduced pressure the crude residue was purified by flash chromatography (using a 7:3 pentane/CH₂Cl₂ mixture as the eluent). After solvent removal under reduced pressure 4H was obtained as a colorless oil (4.3 g, 11.3 mmol, 86%).

¹H NMR (200 MHz, CDCl₃, Me₄Si) δ (ppm) = 7.03 (2H, d, ³J = 8.7 Hz, Ar-H), 6.76 (2H, d, ³J = 8.5 Hz, Ar-H), 3.61 (2H, t, ²J = 6.8 Hz, CH₂-O), 2.60 (2H, t, ³J = 7.8 Hz, Ar-CH₂); 1.87 (2H, quint, ³J = 7.5 Hz, Ar-CH₂-CH₂); 1.08 – 0.89 (18 H, m, CH₃CH₂Si), 0.81 – 0.50 (12 H, m, CH₃CH₂Si).

¹³C NMR (50 MHz, CDCl₃, Me₄Si): δ (ppm) = 153.6, 134.9, 129.4, 119.8, 62.3, 34.7; 31.4, 7.0, 6.8, 5.1, 4.6.

MS: IE (m/z): 380 (6), 352 (11), 351 (26), 248 (53), 219 (57), 161 (18), 147 (21), 133 (21), 119 (10), 91 (18), 89 (100), 87 (55), 75 (16), 59 (45).

9. Characterization of hydrolyzed products

9.1. Compound 3G'

\[ \text{H NMR (200 MHz, CDCl}_3, \text{ Me}_4\text{Si)} \delta (\text{ppm}) = 6.89 - 6.54 (3H, m, Ar-H), 5.34 \ (2H, \text{ br.s, OH}), 2.47 \ (2H, t, ^3J = 7.7 \text{ Hz, Ar-CH}_2), 1.58 \ (2H, \text{ sext, } ^3J = 7.5 \text{ Hz, Ar-CH}_2-\text{CH}_2), 0.92 \ (3 \text{ H, t, } ^3J = 7.3 \text{ Hz, CH}_3\text{CH}_2). \\
\text{C NMR (50 MHz, CDCl}_3, \text{ Me}_4\text{Si): } \delta (\text{ppm}) = 143.4, 141.3, 136.2, 121.0, 115.7, 115.3; \ 37.4, 24.8, 13.9. \]

9.2. Compound 4G'

\[ \text{H NMR (200 MHz, D}_2\text{O, Me}_4\text{Si)} \delta (\text{ppm}) = 6.88 - 6.57 (3H, m, Ar-H), 4.79 \ (3H, \text{ br.s, OH}), 3.54 \ (2H, t, ^3J = 6.6 \text{ Hz, CH}_2-\text{O}), 2.50 \ (2H, t, ^3J = 7.6 \text{ Hz, Ar-CH}_2), 1.75 \ (2 \text{ H, quint, } ^3J = 6.9 \text{ Hz, Ar-CH}_2-\text{CH}_2). \\
\text{C NMR (50 MHz, D}_2\text{O, Me}_4\text{Si): } \delta (\text{ppm}) = 143.9, 141.8, 135.3, 120.6, 116.2, 61.1, 33.3, 30.6. \]
9.3. **Compound 3S’**

![Compound 3S’](image)

$^1$H NMR (200 MHz, CDCl$_3$, Me$_4$Si) δ (ppm) = 6.31 (2H, s, Ar-H), 5.35 (3H, br.s, OH), 2.40 (2H, t, $^3$J = 7.6 Hz, Ar-CH$_2$), 1.55 (2H, sext, $^3$J = 7.3 Hz, Ar-CH$_2$-CH$_2$), 0.90 (3 H, t, $^3$J = 7.3 Hz, CH$_3$CH$_2$).

$^{13}$C NMR (50 MHz, CDCl$_3$, Me$_4$Si): δ (ppm) = 143.9, 135.6, 129.5, 108.3, 37.6, 24.6, 13.9.

9.4. **Compound 4S’**

![Compound 4S’](image)

$^1$H NMR (200 MHz, D$_2$O, Me$_4$Si) δ (ppm) = 6.36 (2H, s, Ar-H), 4.79 (4H, br.s, OH), 3.54 (2H, t, $^3$J = 6.7 Hz, CH$_2$-O), 2.45 (2H, t, $^3$J = 7.5 Hz, Ar-CH$_2$), 1.73 (2 H, quint, $^3$J = 7.1 Hz, Ar-CH$_2$-CH$_2$).

$^{13}$C NMR (50 MHz, D$_2$O, Me$_4$Si): δ (ppm) = 145.4, 135.1, 130.0, 108.1, 61.1, 33.2, 30.8.

9.5. **Compound 3H’**

![Compound 3H’](image)
$^1$H NMR (200 MHz, CDCl$_3$, Me$_4$Si) δ (ppm) = 7.04 (2H, d, $^3J$ = 8.3 Hz, Ar-H), 6.75 (2H, d, $^3J$ = 8.4 Hz, Ar-H), 2.65 (1H, br.s, OH), 2.52 (2H, t, $^3J$ = 7.6 Hz, Ar-CH$_2$); 1.60 (2H, sext, $^3J$ = 7.4 Hz, Ar-CH$_2$-CH$_2$), 0.92 (3 H, t, $^3J$ = 7.3 Hz, CH$_3$CH$_2$).

$^{13}$C NMR (50 MHz, CDCl$_3$, Me$_4$Si): δ (ppm) = 153.3, 135.2, 129.7, 115.2, 37.2; 24.9, 13.9.

9.6. Compound 4H'

\[
\text{HO} \quad \text{HO}
\]

$^1$H NMR (200 MHz, CDCl$_3$, Me$_4$Si) δ (ppm) = 7.06 (2H, d, $^3J$ = 8.2 Hz, Ar-H), 6.75 (2H, d, $^3J$ = 8.3 Hz, Ar-H), 3.68 (2H, t, $^3J$ = 6.3 Hz, CH$_2$-O), 3.52 (1H, br.s, OH), 2.64 (2H, t, $^3J$ = 7.6 Hz, Ar-CH$_2$), 2.14 (1H, br.s, OH), 1.86 (2H, quint, $^3J$ = 7.1 Hz, Ar-CH$_2$-CH$_2$).

$^{13}$C NMR (50 MHz, CDCl$_3$, Me$_4$Si): δ (ppm) = 153.9, 133.9, 129.6, 115.4, 62.5, 34.5; 31.3.
10. Characterization of deuterium labeled products

10.1. Characterization of [2,3-D$_2$]-4G

[2,3-D$_2$]-4G was obtained upon reduction of compound 1 (16.7 mg, 0.050 mmol, 1 equiv.) with 7 equiv. Et$_3$SiD (41.0 mg, 0.35 mmol) and 2 mol% B(C$_6$F$_5$)$_3$ (0.5 mg; 0.001 mmol) in 300 µL CD$_2$Cl$_2$, following the procedure detailed in reference 6 for the reductive hydrosilylation of lignin models.

$^1$H NMR (200 MHz, CD$_2$Cl$_2$, Me$_4$Si) δ (ppm) = 7.03-6.62 (m, 3H, Ar-H), 3.60 (d, $^3$$J_{H-H}$ = 6.1 Hz, 2H, CH$_2$-O), 2.52 (d, $^3$$J_{H-H}$ = 8.2 Hz, 1H, Ph-CHD), 1.76 (m, 1H, CH$_2$-CHD), 1.10-0.89 (m, 27 H, CH$_3$), 0.88-0.69 (m, 18 H, Si-CH$_2$).

$^{13}$C NMR (50 MHz, CD$_2$Cl$_2$, Me$_4$Si): δ (ppm) = 147.4, 145.1, 135.9, 121.7, 121.2, 120.6, 62.4, 34.7 (t, $J_{C-D}$=19.6 Hz), 31.3 (t, $J_{C-D}$=19.6 Hz), 6.8, 5.5, 5.2, 4.5.

MS: IE (m/z): 512 (7); 339 (9); 237 (11); 208 (19); 207 (5); 117 (5); 116 (7); 115 (61); 90 (14); 89 (19); 88 (13); 87 (100); 60 (5); 59 (42); 32 (16).
10.2. Characterization of [1,2,3-D₃]-3G

[1,2,3-D₃]-3G was obtained upon reduction of compound 1 (16.7 mg, 0.050 mmol, 1 equiv.) with 8 equiv. Et₃SiD (46.9 mg, 0.4 mmol), using 2 mol% B(C₆F₅)₃ (0.5 mg; 0.001 mmol) in 300 μL CD₂Cl₂, following the procedure detailed in reference 6 for the reductive hydrosilylation of lignin models.

\[ \text{1H NMR (200 MHz, CD}_2\text{Cl}_2, \text{Me}_4\text{Si)} \delta (ppm) 7.02 – 6.51 (3 H, m, Ar-H), 2.46 (1 H, d, } ^3J_{H-H} = 8.2 \text{ Hz, Ar-CHD), 1.55 (1 H, t, } ^3J_{H-H} = 8.3 \text{ Hz, CHD-CH}_2\text{D), 1.09 - 0.90 (18 H, m, CH}_3\text{CH}_2\text{Si), 0.96 – 0.82 (2 H, m, -CH}_2\text{D), 0.70 – 0.49 (12 H, m, CH}_3\text{CH}_2\text{Si).} \]

\[ \text{13C NMR (50 MHz, CD}_2\text{Cl}_2, \text{Me}_4\text{Si): } \delta (ppm) \text{=147.4, 145.1, 136.5, 121.7, 121.3, 120.6, 37.3 (t, } J_{C-D} = 19.5 \text{ Hz), 24.7 (t, } J_{C-D} = 19.4 \text{ Hz), 13.6 (t, } J_{C-D} = 19.2 \text{ Hz), 7.0, 5.7, 5.6.} \]

\[ \text{MS: IE (m/z): 383 (7); 208 (9); 207 (3); 150 (4); 117 (4); 116 (12); 115 (100); 89 (3); 87 (85); 86 (4); 85 (3) ; 60 (4); 59 (52); 58 (5); 57 (4); 45 (4); 31 (4).} \]

10.3. Characterization of [1,1-D₂]-4G

[1,1-D₂]-4G was obtained upon reduction of compound [3,3-D₂]-1 (16.8 mg, 0.050 mmol, 1 equiv.) with 7 equiv. Et₃SiH (40.7 mg, 0.35 mmol), using 2 mol% B(C₆F₅)₃ (0.5 mg; 0.001 mmol) in 300 μL CD₂Cl₂, following the detailed procedure detailed in reference 6 for the reductive hydrosilylation of lignin models.
$^1$H NMR (200 MHz, CD$_2$Cl$_2$, Me$_4$Si) δ (ppm) = 6.92-6.56 (m, 3H, Ar-H), 2.89 (t, $^3$J$_{H-H}$ = 5.9 Hz, 2H, Ph-CH$_2$), 1.76 (t, $^3$J$_{H-H}$ = 5.9 Hz, 2H, CH$_2$CD$_2$), 1.10-0.89 (m, 27 H, CH$_3$), 0.88-0.69 (m, 18 H, Si-CH$_2$).

$^{13}$C NMR (50 MHz, CD$_2$Cl$_2$, Me$_4$Si): δ (ppm) = 147.5, 145.1, 136.0, 121.7, 121.2, 120.7, 62.8-61.9 (m), 34.8, 31.7, 7.0, 5.5, 5.2, 4.5.

MS: IE (m/z): 512 (8); 380 (5); 340 (7); 339 (20); 237 (17); 208 (6); 207 (19); 116 (9); 115 (69); 88 (10); 87 (100); 59 (44); 91 (29).

### 10.4. Characterization of [3,3-D$_2$]-3G

[3,3-D$_2$]-3G was obtained upon reduction of compound [3,3-D$_2$]-1 (16.8 mg, 0.050 mmol, 1 equiv.) with 8 equiv. Et$_3$SiH (46.5 mg, 0.4 mmol), using 2 mol% B(C$_6$F$_5$)$_3$ (0.5 mg; 0.001 mmol) in 300 µL CD$_2$Cl$_2$, following the detailed procedure detailed in reference 6 for the reductive hydrosilylation of lignin models.
\textbf{\textsuperscript{1}H NMR} (200 MHz, CD\textsubscript{2}Cl\textsubscript{2}, Me\textsubscript{4}Si) \( \delta \) (ppm) = 6.90-6.53 (m, 3H, Ar-H), 2.47 (t, \( ^3J_{H,H} = 7.5 \) Hz, 2H, Ph-CH\textsubscript{2}), 1.60 (t, \( ^3J_{H,H} = 7.5 \) Hz, 2H, CH\textsubscript{2}CD\textsubscript{2}), 1.10-0.88 (m, 18 H, CH\textsubscript{3}), 0.80-0.62 (m, 12 H, Si-CH\textsubscript{2}).

\textbf{\textsuperscript{13}C NMR} (50 MHz, CD\textsubscript{2}Cl\textsubscript{2}, Me\textsubscript{4}Si): \( \delta \) (ppm) = 147.4, 145.1, 136.5, 121.7, 121.3, 120.6, 37.8, 25.1, 14.5-12.9 (m), 7.1, 6.9, 5.6, 5.6.

\textbf{MS}: IE (m/z): 383 (7); 382 (19); 353 (6); 207 (6); 117 (5); 116 (12); 115 (100); 88 (7); 87 (67); 60 (3); 59 (36); 58 (3).
11. Size Exclusion Chromatography (SEC)

Number average molecular weights ($M_n$), weight average molecular weight ($M_w$), and molecular weight distribution ($M_w/M_n$) were determined using a GPC 220 system from PolymerLabs (Agilent Technologies) in THF at 35°C with a flow rate of 1 mL.min$^{-1}$. A series of two 7.5 mm diameter × 300 mm Polymer Labs 5 μm particle diameter mixed-E PLgel columns were connected in line to the GPC system. Samples were detected at 280 nm using a UV detector (Varian). The system was calibrated using poly(ethylene glycol) standards (PolymerLabs) in the range of molecular weights 43580-106 g.mol$^{-1}$.

Molecular weight analysis by Size Exclusion Chromatography (SEC) has been performed from samples dissolved in THF (5 mg/mL) followed by filtration. The depolymerization residue of parasol pine lignin was analyzed after the removal of the catalyst by column chromatography using 100 % ethyl acetate as the eluent. The two samples of lignin extracted with the Kraft process could not be properly analyzed owing to their insolubility in THF. The weak peaks obtained from these two samples look also very broad suggesting a large molecular weight distribution. The other samples obtained either by the Formacell or the EOL process, lead to “hydrophobic” or “functionalized” lignins that can be easily dissolved in organic solvent.

Table S4: Summary of the SEC analysis results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Extraction method</th>
<th>$M_n$ (g.mol$^{-1}$)</th>
<th>$M_w$ (g.mol$^{-1}$)</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial pine</td>
<td>Formacell</td>
<td>1099</td>
<td>1829</td>
<td>1.66</td>
</tr>
<tr>
<td>Parasol pine</td>
<td>Formacell</td>
<td>952</td>
<td>1709</td>
<td>1.79</td>
</tr>
<tr>
<td>Parasol pine</td>
<td>Ethanol/HCl</td>
<td>669</td>
<td>1167</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>Process</td>
<td>Elution Time (s)</td>
<td>Relative Abundance (%)</td>
<td>Solubility Pb</td>
</tr>
<tr>
<td>------------------------</td>
<td>-----------------</td>
<td>------------------</td>
<td>------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>Evergreen oak</td>
<td>Formacell</td>
<td>952</td>
<td>1657</td>
<td>1.74</td>
</tr>
<tr>
<td>Evergreen oak</td>
<td>Ethanol/HCl</td>
<td>802</td>
<td>1088</td>
<td>1.35</td>
</tr>
<tr>
<td>Kraft lignin Aldrich</td>
<td>Re-extraction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>of the lignin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>by the Formacell process</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Solubility Pb</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>/</td>
</tr>
<tr>
<td>Kraft lignin Aldrich</td>
<td>Kraft</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Solubility Pb</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>/</td>
</tr>
<tr>
<td>Depolymerization</td>
<td>Formacell</td>
<td>268</td>
<td>273</td>
<td>1.01</td>
</tr>
<tr>
<td>residue of Parasol</td>
<td></td>
<td>902</td>
<td>1037</td>
<td>1.15</td>
</tr>
<tr>
<td>pine</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure S1.** SEC chromatograms of lignin samples. A and C: parasol pine extracted with the Formacell process and ethanol respectively; B and D: evergreen oak extracted with the Formacell process and ethanol respectively.
11.1. **Determination of the average degree of polymerization**

**Table S5:** The average degree of polymerization was obtained from the ratio of the number average molecular weight ($M_n$), versus the average molar mass of the main residue in lignin.

<table>
<thead>
<tr>
<th>Species</th>
<th>extraction method</th>
<th>Major residue</th>
<th>$M_n$ (g/mol)</th>
<th>Average DP</th>
<th>$\tau(N)$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial pine</td>
<td>Formacell</td>
<td>G (Mr=196.2 g/mol)</td>
<td>1099</td>
<td>N=6</td>
<td></td>
</tr>
<tr>
<td>Parasol pine</td>
<td>Formacell</td>
<td>G (Mr=196.2 g/mol)</td>
<td>952</td>
<td>N=5</td>
<td>46</td>
</tr>
<tr>
<td>Evergreen oak</td>
<td>Formacell</td>
<td>S (Mr=226.23 g/mol)</td>
<td>835</td>
<td>N=4</td>
<td></td>
</tr>
</tbody>
</table>
12. Theoretical yield and efficiency calculations

12.1. Theoretical yield calculation

To evaluate the maximum theoretical yields of monomeric aromatic products recoverable from the reductive depolymerization of lignin, the following assumptions were made:

- **Lignin is assimilated to a linear polymer formed from a single monolignol** (100% of the same residue). This approximation is especially valid for gymnosperm species which mainly feature G residues. Because organosolv lignin samples exhibit a low degree of polymerization (4 to 6), the probability of having a ramified structure is low.

- **Lignin is assimilated to a polymer formed by monomers bonded together by two types of bonds**: (A) cleavable bonds (such as the β-O-4 and α-O-4 linkages) and (B) non-cleavable bonds (such as the β-5 and 4-O-5 linkages).

- **The percentage of cleavable bonds was set to A = 60%**, corresponding to the average percentages of β-O-4 and α-O-4 linkages present in lignin.

- **Lignin is considered as a mono-disperse polymer**, with all the polymer chains having the same degree of polymerization. This approximation may be valid for lignin samples extracted by an organosolv process, as they show low molecular weight distributions (*i.e.* 1.5 in Formacell lignin).

![Diagram of lignin polymer](image)

**Figure S2.** A representation of the theoretical model of lignin polymer with $N=4$.

The theoretical average number of mono-aromatic products, that can be obtained by cleavage of the A linkages in a lignin sample having a polymerization degree of $N$, is noted $\tau(N)$. For
an infinite lignin chain \((N=\infty)\), a mono-aromatic product is formed for each series of two consecutive A linkages. \(\tau(N=\infty)\) is thus the probability to find two successive A linkages in a chain featuring 60 % A bonds and 40 % B bonds.

Hence, \(\tau(N = \infty) = 0.6^2 \times 100 \% = 36 \%\)

For a finite lignin chain with \(N\) monolignols, 2 aromatic units are located in the chain-ends while \(N-2\) aromatic units are surrounded with A or B linkages (Figure S2). 60 % of the chain-ends can thus yield a mono-aromatic product, while 36 % of the remaining \(N-2\) monolignols can produce mono-aromatics.

Hence, \(\tau(N) = \frac{(N-2) \times 0.6^2 + 2 \times 0.6}{N} \times 100 \%\)

Using the average molar mass obtained from the SEC analyses one can calculate the average degree of polymerization (DP) by dividing the average molar weight \(M_n\) by the average molar mass of the main residue in lignin DP= \(\frac{M_n}{196.2}\) for gymnosperms and DP= \(\frac{M_n}{226.23}\) for angiosperms. With reference to the \(\tau(N)\) curve, one can deduce the value of \(\tau(N)\) for each type of lignin. Since the values of \(\tau(N)\) is quite similar for \(N=5\pm1\) an average value of \(\tau(N)=5\) was taken regardless of the lignin source.

Using the molecular weights of the theoretical general formulas of lignin polymers (196.2 g/mol for gymnosperms and 226.2 g/mol for angiosperms) and considering that lignin accounts for 25 wt% of wood weight, the maximum theoretical yield of mono-aromatic product/wood weight \(T\) (wt%) would be:

For the synthesis of \(3G\) from gymnosperms:

\[
T(3G) = \frac{0.46 \times 0.25 \times 380.71}{196.2} \times 100 = 22.3 \text{ wt\% /wood weight}
\]

For the synthesis of \(4G\) from gymnosperms:

\[
T(4G) = \frac{0.46 \times 0.25 \times 510.98}{196.2} \times 100 = 30.0 \text{ wt\% /wood weight}
\]
For the synthesis of $3S$ from angiosperms:

$$T(3S) = \frac{0.46 \times 0.25 \times 510.97}{226.23} \times 100 = 26.0 \text{ wt\%}/\text{wood weight}$$

For the synthesis of $4S$ from angiosperms:

$$T(4S) = \frac{0.46 \times 0.25 \times 641.23}{226.23} \times 100 = 32.6 \text{ wt\%}/\text{wood weight}$$

For the synthesis of $3G'$ from gymnosperms:

$$T(3G') = \frac{0.46 \times 0.25 \times 152.19}{196.2} \times 100 = 8.9 \text{ wt\%}/\text{wood weight}$$

For the synthesis of $4G'$ from gymnosperms:

$$T(4G') = \frac{0.46 \times 0.25 \times 168.19}{196.2} \times 100 = 9.9 \text{ wt\%}/\text{wood weight}$$

For the synthesis of $3S'$ from angiosperms:

$$T(3S') = \frac{0.46 \times 0.25 \times 168.19}{226.23} \times 100 = 8.5 \text{ wt\%}/\text{wood weight}$$

For the synthesis of $4S'$ from angiosperms:

$$T(4S') = \frac{0.46 \times 0.25 \times 184.19}{226.23} \times 100 = 9.4 \text{ wt\%}/\text{wood weight}$$

12.2. Efficiency calculation

- The extraction efficiency ($E(\text{ex})$) is the ratio between the experimental weight of extracted lignin ($M_{\text{exp}}$) and the theoretical content of lignin in wood evaluated to 25 wt\% ($M_{\text{theo}}$). Thus: $E(\text{ex}) = \frac{M_{\text{exp}}}{M_{\text{theo}}} \times 100$

- The depolymerization step efficiency ($E(\text{depol})$) is the ratio between the experimental weight of the mono-aromatic product ($P_{\text{exp}}$) and the calculated theoretical weight of mono-aromatic product ($P_{\text{theo}}$) (see above). Thus: $E(\text{depol}) = \frac{P_{\text{exp}}}{P_{\text{theo}}} \times 100$
- The purification efficiency \( E(\text{pur}) \) is the ratio between the experimental weight of purified product \( Q_{\text{exp}} \) and the theoretical weight of the product after purification \( Q_{\text{theo}} \). In this case one can consider that the theoretical yield of the purification step is 100 %. Thus: 
\[
E(\text{pur}) = \frac{Q_{\text{exp}}}{Q_{\text{theo}}} \times 100
\]

- The Global efficiency \( E(\text{tot}) \) is the ratio between the experimental weight of purified hydrolysed product \( S_{\text{exp}} \) and the theoretical weight of purified hydrolysed product \( S_{\text{theo}} \) (calculated above). Thus: 
\[
E(\text{tot}) = \frac{S_{\text{exp}}}{S_{\text{theo}}} \times 100
\]
Table S6: Results summary and global efficiency calculation

<table>
<thead>
<tr>
<th>Species</th>
<th>Experimental (wt%)</th>
<th>Theoretical (wt%)</th>
<th>Efficiency (%)</th>
<th>Product</th>
<th>Experimental (wt%)</th>
<th>Theoretical (wt%)</th>
<th>Efficiency (%)</th>
<th>Product</th>
<th>Experimental (wt%)</th>
<th>Theoretical (wt%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial Pine</td>
<td>8</td>
<td>25</td>
<td>32</td>
<td>4G</td>
<td>52</td>
<td>120</td>
<td>43</td>
<td>4G</td>
<td>36*</td>
<td>52</td>
<td>70</td>
</tr>
<tr>
<td>hybrid plane</td>
<td>10</td>
<td>25</td>
<td>40</td>
<td>4S</td>
<td>111</td>
<td>130</td>
<td>85</td>
<td>4S</td>
<td>90</td>
<td>111</td>
<td>81</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>Product</th>
<th>wt% of the hydrolysed product/lignin</th>
<th>wt% of the hydrolysed product/wood</th>
<th>wt% of the silylated product/wood</th>
<th>Global Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial Pine</td>
<td>4G*</td>
<td>10*</td>
<td>12</td>
<td>4G*</td>
<td>0.8*</td>
</tr>
<tr>
<td>hybrid plane</td>
<td>4S*</td>
<td>24</td>
<td>26</td>
<td>4S*</td>
<td>2.4</td>
</tr>
</tbody>
</table>

a Weight percentage of lignin extracted by the Formacell process calculated relatively to the wood initial weight (%wt). b Weight percentage of the silylated products calculated relatively to the lignin initial weight (%wt). c Weight percentage of the hydrolysed products calculated relatively to the lignin initial weight) (%wt). d Weight percentage of the hydrolysed product calculated relatively to the initial wood weight (%wt). e Theoretical weight percentage of the hydrolysed product calculated relatively to the initial wood weight (%wt) and considering that lignin constitutes 25 %wt of the total wood weight.* Estimated yield by considering 70% yield of purification.
13. DEPT 135 superposition spectra

13.1. Formation of 3G

Figure S3. (A) DEPT 135 of industrial pine lignin extracted with the Formacell process. (B) DEPT 135 of the reaction medium after 20 h (using the reaction conditions given in Eq(5)). (C) DEPT 135 of the oil obtained after purification by column chromatography. (D) DEPT 135 of 3G synthesized using petrochemical raw materials.
13.2. Formation of 4G

Figure S4. (A) DEPT 135 of industrial pine lignin extracted with the Formacell process. (B) DEPT 135 of the reaction medium after 3 h (using the reaction conditions given in Eq(7)). of (C) DEPT 135 of the oil obtained after purification by column chromatography. (D) DEPT 135 of 4G synthesized using petrochemical raw materials.
13.3. Formation of 3S

Figure S3. (A) DEPT 135 of hybrid plane lignin extracted with the Formacell process. (B) DEPT 135 of the reaction medium after 20 h (using the reaction conditions given in Eq(8)). (C) DEPT 135 of the oil obtained after purification by column chromatography. (D) DEPT 135 of 3S synthesized using petrochemical raw materials.
13.4. Formation of 4S

Figure S4. (A) DEPT 135 of hybrid plane lignin extracted with the Formacell process. (B) DEPT 135 of the reaction medium after 3 h (using the reaction conditions given in Eq(9)). (C) DEPT 135 of the oil obtained after purification by column chromatography. (D) DEPT 135 of 4S synthesized using petrochemical raw materials.
14. GC-MS chromatograms

All depolymerization samples were prepared according to the procedures of depolymerization described above to obtain 3G, 4G, 3S or 4S as the major product. The reactions were carried out using 40 mg of lignin, all previously extracted with the Formacell process. After completion of the reaction (depending on the desired product), CH₂Cl₂ was added to the solutions to obtain a total volume of 1.5 mL. The solutions were directly analyzed by GC-MS and without further purification. The spectrum part with retention time greater than 20 min was omitted since it does not contain any product signal.

We used the following GC conditions in analyzing all the samples: **Injector temp.**: 250 °C; **Carrier gas**: helium; **Pressure**: 120.0 kPa; **Linear velocity**: 51.9 cm/sec.; **Oven temp.**: 50 °C (hold 1 min.) to 200 °C at 40 °C/min, then to 280°C at 15 °C/min then 280°C (hold 20 min). **Detector**: MS (EI); **Interface temp.**: 250 °C; **Detector voltage**: 0.8 kV
14.1. Formation of 3G

Figure S5. (A) GC-MS chromatogram of the depolymerization residue of industrial pine lignin extracted with the Formacell process. (B) GC-MS chromatogram of the depolymerization residue of parasol pine lignin extracted with the Formacell process. (C) GC-MS chromatogram of the depolymerization residue of Norway spruce lignin extracted with the Formacell process. (D) GC-MS chromatogram of the depolymerization residue of Lebanon cedar lignin extracted with the Formacell process. (E) GC-MS chromatogram of 3G synthesized using petrochemical raw materials.
**Table S7:** Summary of the results obtained during the depolymerization of gymnosperm organosolv lignin into compound 3G.

<table>
<thead>
<tr>
<th>Species</th>
<th>Extraction method</th>
<th>Compound 3G (%wt)</th>
<th>Compound 4G (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nordmann fir&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Formacell</td>
<td>3</td>
<td>------</td>
</tr>
<tr>
<td>Norway spruce&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Formacell</td>
<td>21</td>
<td>------</td>
</tr>
<tr>
<td>Industrial pine&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Formacell</td>
<td>25</td>
<td>------</td>
</tr>
<tr>
<td>Parasol pine&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Formacell</td>
<td>24</td>
<td>------</td>
</tr>
<tr>
<td>Lebanon Cedar&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Formacell</td>
<td>18</td>
<td>------</td>
</tr>
<tr>
<td>Pacific redcedar&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Formacell</td>
<td>8</td>
<td>------</td>
</tr>
<tr>
<td>Industrial pine&lt;sup&gt;a&lt;/sup&gt;</td>
<td>EOL</td>
<td>18</td>
<td>------</td>
</tr>
<tr>
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<td>AOL</td>
<td>4</td>
<td>------</td>
</tr>
</tbody>
</table>

<sup>a</sup> Detection of other unidentified volatile products. <sup>b</sup> No other major volatile products were detected. ---- Not detected.
14.2. Formation of 4G

Figure S6. (A) GC-MS chromatogram of the depolymerization residue of industrial pine lignin extracted with the Formacell process. (B) GC-MS chromatogram of the depolymerization residue of parasol pine lignin extracted with the Formacell process. (C) GC-MS chromatogram of the depolymerization residue of Norway spruce lignin extracted with the Formacell process. (D) GC-MS chromatogram of the depolymerization residue of Lebanon cedar lignin extracted with the Formacell process. (E) GC-MS chromatogram of 4G synthesized using petrochemical raw materials.
**Table S8:** Summary of the results obtained during the depolymerization of gymnosperm Formacell lignin into compound 4G.

Formacell lignin into compound 4G.

<table>
<thead>
<tr>
<th>Species</th>
<th>Extraction method</th>
<th>Compound 3G (%wt)</th>
<th>Compound 4G (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial pine</td>
<td>Formacell</td>
<td>2</td>
<td>52</td>
</tr>
<tr>
<td>Parasol pine</td>
<td>Formacell</td>
<td>1</td>
<td>50</td>
</tr>
<tr>
<td>Norway spruce</td>
<td>Formacell</td>
<td>2</td>
<td>34</td>
</tr>
<tr>
<td>Lebanon Cedar</td>
<td>Formacell</td>
<td>--------</td>
<td>42</td>
</tr>
</tbody>
</table>

---- Not detected.
14.3. Formation of 3S

Figure S7. (A) GC-MS chromatogram of the depolymerization residue of evergreen oak lignin extracted with the Formacell process. (B) GC-MS chromatogram of the depolymerization residue of silver birch lignin extracted with the Formacell process. (C) GC-MS chromatogram of the depolymerization residue of common beech lignin extracted with the Formacell process. (D) GC-MS chromatogram of the depolymerization residue of hybrid plane lignin extracted with the Formacell process. (E) GC-MS chromatogram of the depolymerization residue of black poplar lignin extracted with the Formacell process. (F) GC-MS chromatogram of 3S synthesized using petrochemical raw materials.
**Table S9:** Summary of the results obtained during the depolymerization of angiosperm organosolv lignin into compound 3S.

<table>
<thead>
<tr>
<th>Species</th>
<th>Extraction method</th>
<th>Compound 4G (%wt)</th>
<th>Compound 3G (%wt)</th>
<th>Compound 4S (%wt)</th>
<th>Compound 3S (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green plum&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Formacell</td>
<td>10</td>
<td>1</td>
<td>98</td>
<td>6</td>
</tr>
<tr>
<td>Black poplar&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Formacell</td>
<td>-------</td>
<td>15</td>
<td>-------</td>
<td>34</td>
</tr>
<tr>
<td>Common beech&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Formacell</td>
<td>-------</td>
<td>8</td>
<td>-------</td>
<td>32</td>
</tr>
<tr>
<td>Silver birch&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Formacell</td>
<td>-------</td>
<td>8</td>
<td>-------</td>
<td>23</td>
</tr>
<tr>
<td>Evergreen oak&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Formacell</td>
<td>-------</td>
<td>6</td>
<td>-------</td>
<td>45</td>
</tr>
<tr>
<td>Date palm&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Formacell</td>
<td>10</td>
<td>-------</td>
<td>-------</td>
<td>78</td>
</tr>
<tr>
<td>Hybrid plane&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Formacell</td>
<td>-------</td>
<td>9</td>
<td>-------</td>
<td>51</td>
</tr>
<tr>
<td>River Red gum&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Formacell</td>
<td>-------</td>
<td>6</td>
<td>-------</td>
<td>23</td>
</tr>
<tr>
<td>Evergreen oak&lt;sup&gt;a&lt;/sup&gt;</td>
<td>EOL</td>
<td>-------</td>
<td>10</td>
<td>-------</td>
<td>35</td>
</tr>
</tbody>
</table>
a Detection of other unidentified volatile products. b No other major volatile products were detected. ---- Not detected. The best results were mainly obtained with evergreen oak, silver birch, common beech and hybrid plane.
14.4. Formation of 4S

Figure S8. (A) GC-MS chromatogram of the depolymerization residue of evergreen oak lignin extracted with the Formacell process. (B) GC-MS chromatogram of the depolymerization residue of silver birch lignin extracted with the Formacell process. (C) GC-MS chromatogram of the depolymerization residue of common beech lignin extracted with the Formacell process. (D) GC-MS chromatogram of the depolymerization residue of hybrid plane lignin extracted with the Formacell process. (E) GC-MS chromatogram of the depolymerization residue of black poplar lignin extracted with the Formacell process. (F) GC-MS chromatogram of 4S synthesized using petrochemical raw materials.

Table S10: Summary of the results obtained during the depolymerization of angiosperm organosolv lignin into compound 4S.

<table>
<thead>
<tr>
<th>Species</th>
<th>Extraction method</th>
<th>Compound 4G (%wt)</th>
<th>Compound 3G (%wt)</th>
<th>Compound 4S (%wt)</th>
<th>Compound 3S (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evergreen oak$^b$</td>
<td>AVIDEL</td>
<td>12</td>
<td>------</td>
<td>111</td>
<td>7</td>
</tr>
<tr>
<td>Silver birch$^b$</td>
<td>AVIDEL</td>
<td>16</td>
<td>------</td>
<td>86</td>
<td>4</td>
</tr>
<tr>
<td>Common beech&lt;sup&gt;b&lt;/sup&gt;</td>
<td>AVIDEL</td>
<td>8</td>
<td>------</td>
<td>54</td>
<td>------</td>
</tr>
<tr>
<td>-------------------------</td>
<td>--------</td>
<td>----</td>
<td>--------</td>
<td>------</td>
<td>--------</td>
</tr>
<tr>
<td>Hybrid plane&lt;sup&gt;b&lt;/sup&gt;</td>
<td>AVIDEL</td>
<td>16</td>
<td>------</td>
<td>126</td>
<td>5</td>
</tr>
<tr>
<td>Black poplar&lt;sup&gt;b&lt;/sup&gt;</td>
<td>AVIDEL</td>
<td>14</td>
<td>2</td>
<td>50</td>
<td>3</td>
</tr>
</tbody>
</table>

<sup>b</sup> No other major volatile products were detected. ---- Not detected.
15. 2D NMR spectroscopy

HSQC analyses were performed on a Bruker Avance 400 MHz spectrometer. The central DMSO solvent peak was used as internal reference (δC 39.5, δH 2.49 ppm). The $^{13}$C–$^1$H correlation experiment was an HSQC which was done using Bruker standard pulse sequence ‘hsqcetgpsi2’ (phase-sensitive gradient-edited-2D HSQC). HSQC experiments were carried out at 25°C using the following parameters: acquired from -12 ppm to 1 ppm in F2 (1H), 170 to 0 ppm in F1 (13C) with 256 increments of 100 scans with a 1.5 s interscan delay and the d24 delay was set to 0.86 ms. The total acquisition time was 12 hours. Data analysis was performed using MestReNova software (version 6.0.2-5475).
Figure S9. Partial 2D HSQC NMR spectra of *Pinus pinea* lignin extracted with the Formacell process (in 4:1 DMSO-\textit{d}_6/pyridine-\textit{d}_5). This spectrum clearly indicates the presence of β-O-4 linkage in the Formacell lignin and the absence of Syringyl (S) residues.
The HSQC correlations were in agreement with those described in the literature for organosolv lignin.\textsuperscript{8}
Figure S10. Partial 2D HSQC NMR spectra of the depolymerization residue of *Pinus pinea* lignin extracted with the Formacell process (in CD$_2$Cl$_2$). The same experimental conditions
used for the depolymerization of industrial pine lignin to form compound \( \text{3G} \) were employed starting with 40 mg of lignin. This spectrum clearly indicates the absence of \( \beta\text{-O-4} \) linkage in the depolymerization residue and the formation of compound \( \text{3G} \).
**Figure S11.** Partial 2D HSQC NMR spectra of evergreen oak lignin extracted with the Formacell process (in 4:1 DMSO-$d_6$/pyridine-$d_5$). This spectrum clearly indicates the presence of β-O-4 linkage in the Formacell lignin and the presence of both Syringyl (S) and guaiacyl (G) residues. The HSQC correlations were in agreement with those described in the literature for organosolv lignin.$^8$
Figure S12. Partial 2D HSQC NMR spectra of the depolymerization residue of evergreen oak lignin extracted with the Formacell process (in CD$_2$Cl$_2$). The same experimental
conditions used for the depolymerization of hybrid plane lignin to form compound 3S were employed starting with 40 mg of lignin. This spectrum clearly indicates the depolymerization of β-O-4 linkages in the depolymerization residue and the formation of compounds 3G and 3S.

16. Crystallography

The data were collected at 150(2) K on a Nonius Kappa-CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystals were introduced into glass capillaries with a protective coating of Paratone-N oil (Hampton Research). The unit cell parameters were determined from ten frames, then refined on all data. The data (combinations of φ- and ω-scans with a minimum redundancy of 4 for 90% of the reflections) were processed with HKL2000. No absorption correction was done. The structures were solved by direct methods with SHELXS-97, expanded by subsequent difference Fourier synthesis and refined by full-matrix least-squares on F² with SHELXL-97. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to oxygen atoms were found on difference Fourier maps, and those bound to carbon atoms were introduced at calculated positions; all were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom (1.5 for CH₃, with optimized geometry). The structural plots were drawn with ORTEP-3 and VESTA.

Crystal data for 3S*: C₉H₁₂O₃, M = 168.19, monoclinic, space group P2₁/c, a = 9.0223(6), b = 35.5424(15), c = 9.3818(6) Å, β = 118.650(3)°, V = 2640.2(3) Å³, Z = 12. Refinement of 328 parameters on 4985 independent reflections out of 66403 measured reflections (R_{int} = 0.036) led to R₁ = 0.045, wR₂ = 0.129, S = 1.049, Δρ_{min} = -0.31, Δρ_{max} = 0.37 e Å⁻³.
Crystal data for 4H*: C₉H₁₂O₂, \( M = 152.19 \), orthorhombic, space group Pca2₁, \( a = 18.8855(12) \), \( b = 7.9784(6) \), \( c = 11.2136(6) \) Å, \( V = 1689.62(19) \) Å³, \( Z = 8 \). Refinement of 199 parameters on 1682 independent reflections out of 39599 measured reflections (\( R_{\text{int}} = 0.027 \)) led to \( R_1 = 0.033 \), \( wR_2 = 0.082 \), \( S = 1.079 \), \( \Delta \rho_{\text{min}} = -0.16 \), \( \Delta \rho_{\text{max}} = 0.09 \) e Å⁻³.

**Figure S13.** View of the packing of hydrogen bonded sheets in 3S’. Hydrogen atoms are excluded for clarity.

**Figure S14.** View of the two crystallographically independent molecules in the crystal structure of 4H’. Displacement ellipsoids are drawn at the 50% probability level.
17. Calibration curves

17.1. Calibration curve of 3G

\[ y = 1 \times 10^7 x - 4934.6 \]
\[ R^2 = 0.999 \]

17.2. Calibration curve of 4G

\[ y = 2 \times 10^7 x + 8912.3 \]
\[ R^2 = 0.999 \]
17.3. Calibration curve of 3S

\[ y = -6E+07x^2 + 2E+07x - 5317,2 \]
\[ R^2 = 0,999 \]

17.4. Calibration curve of 4S

\[ y = 8E+07x^2 + 1E+07x + 23514 \]
\[ R^2 = 0.998 \]
17.5. Calibration curve of 4H

![Graph of calibration curve for 4H]

\[ y = 1E+07x + 13085 \]

\[ R^2 = 0.996 \]

17.6. Calibration curve of 3H

![Graph of calibration curve for 3H]

\[ y = 1E+07x + 10082 \]

\[ R^2 = 0.999 \]
18. NMR spectra

$^1$H NMR of 3G in CDCl$_3$
$^{13}$C NMR of $3G$ in CDCl$_3$
$^1$H NMR of 3S in CDCl$_3$
$^{13}$C NMR of 3S in CDCl$_3$
$^1$H NMR of 3H in CDCl$_3$
$^{13}$C NMR of 3H in CDCl$_3$
$^1$H NMR of 4G in CDCl$_3$
$^{13}$C NMR of 4G in CDCl$_3$
$^1$H NMR of 4S in CDCl$_3$
$^{13}$C NMR of 4S in CDCl$_3$
$^1$H NMR of $4\text{H}$ in CDCl$_3$
$^{13}$C NMR of 4H in CDCl$_3$
H NMR of [3,3-D_2]-1 in CDCl_3
$^{13}$C NMR of $[3,3$-$D_2]$-1 in CDCl$_3$
$^{13}$C NMR of 2 + [1,2,3-D$_3$] 3G in CD$_2$Cl$_2$
$^1$H NMR of 3S' in CDCl$_3$
$^{13}$C NMR of 3G' in CDCl$_3$
$^{13}$C NMR of 4G$^*$ in D$_2$O
References: