Electronic Supplementary Information

Efficient reductive depolymerization of hardwood and softwood lignins with Brookhart’s iridium(III) catalyst and hydrosilanes

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I) General considerations

Syntheses and manipulations of the compounds were conducted under ultra-high purity argon atmosphere with rigorous exclusion of air and water, using Schlenk-vessel and vacuum-line techniques and/or glove boxes. Glassware was dried overnight at 75 °C before use. The $^1$H, and $^{13}$C{$^1$H} NMR spectra were recorded on a Bruker DPX 200 MHz instrument and referenced internally using the residual protio solvent resonances relative to tetramethylsilane ($\delta$ 0). Unless otherwise noted, reagents were purchased from commercial suppliers and the liquids dried over 4 Å molecular sieves prior to use. Molecular sieves (Aldrich) were activated by drying under dynamic vacuum at 250 °C for 48 h. The reagents used for lignin extractions were: acetic acid ($\geq$ 99.85 %), formic acid ($\geq$ 96.0 %), ethanol ($\geq$ 99.8 %), methanol (99.8 %), acetone (99.5 %) and HCl (37%). Dichloromethane (and $d_2$-CH$_2$Cl$_2$) and chlorobenzene (and $d_5$-C$_6$H$_5$Cl) were dried over CaH$_2$ and distilled before use. Deuterated solvents were obtained from Eurisotop and the non-deuterated organic solvents from Carlo Erba. The hydrosilanes and siloxanes (Et$_2$SiH$_2$, Ph$_3$SiH, Ph$_2$SiH$_2$, (EtO)$_3$SiH, PMHS and TMDS) were purchased from Aldrich, stored in the gloves box and used without further purification. Mass spectrometer data were collected on a Shimadzu GCMS-QP2010 Ultra gas chromatograph mass spectrometer equipped with a Supelco SLBTM-ms fused silica capillary column (30 m x 0.25 mm x 0.25 μm). B(C$_6$F$_5$)$_3$ was supplied from Aldrich, degassed and stored under argon in the gloves box. Brookhart’s catalyst was synthesized from reported procedure but protonation to form the cationic species [(‘BuPOCOP)IrH(THF)][B(C$_6$F$_5$)$_4$] (‘BuPOCOP = 1,3{‘Bu$_2$PO}$_2$(C$_5$H$_3$); [1][B(C$_6$F$_5$)$_4$], M = 1351 g/Mol) was carried out in THF instead of acetone.$^1$ Compounds 5a and 5b were prepared according to the method of Ellman et al.$^2$ Compounds 7 and 9 were synthesized following literature.$^3$ Softwood and hardwood lignin samples were extracted from wood sawdust following Formacell process described by
Delmas et al.\textsuperscript{1} In all cases, wood sawdust were used as starting materials and dried overnight under vacuum 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.

Methane was observed \textit{in situ} in \textsuperscript{1}H NMR but not quantified.

Methane: \textbf{\textsuperscript{1}H NMR} (200 MHz, C\textsubscript{6}D\textsubscript{5}Cl) \(\delta_{\text{H}}(\text{ppm}) = 0.15\) (s)

Siloxane was observed \textit{in situ} in \textsuperscript{13}C NMR but not quantified. (\textsuperscript{1}H NMR observation is not possible because Et\textsubscript{3}Si signals of the silylated ether ROSiEt\textsubscript{3} and the hydrosilane Et\textsubscript{3}SiH are overlapping)

Et\textsubscript{3}SiOSiEt\textsubscript{3}: \textbf{\textsuperscript{13}C NMR} (200 MHz, C\textsubscript{6}D\textsubscript{5}Cl) \(\delta_{\text{C}}(\text{ppm}) = 6.8, 6.5\).
II) Typical procedures for the catalytic hydrosilylation of lignin model molecules

II.a) Hydrosilylation of (benzyloxy)benzene (2)

**Equation 1**

![Equation 1](image)

In an NMR tube equipped with a J. Young valve, Et₃SiH (19.1 µL, 0.12 mmol, 1.2 equiv.) and mesitylene (13.9 µL, 0.10 mmol, 1.0 equiv., used as an internal standard) were added to a mixture of 2 (18.2 mg, 0.10 mmol, 1.0 equiv.) and [1][B(C₆F₅)₄] (2.7 mg, 0.002 mmol, 2.0 mol%) in C₆D₅Cl (0.3 mL). The clear orange solution was stirred at RT for 16 h during which no change of color was observed. The reaction was monitored by ¹H NMR and the spectra showed the formation of the ortho-isomer (2-benzylphenoxy)triethylsilane 4 as the major product (ratio ortho/para: 9/1) together with triethyl(phenoxy)silane 3a (<5%) and toluene (<5%).

Characterization of triethyl(phenoxy)silane (3a)

¹H NMR (C₆D₅Cl, 298 K) δH(ppm): 7.22 (dd, 2H, J = 8.0 Hz and 7.8 Hz, H₂); 6.93 (t, 1H, J = 8 Hz, H₁); 6.85 (d, 2H, J = 7.8 Hz, H₃), 0.99 (t, 9H, J = 8 Hz, CH₃-CH₂-Si); 0.74 (m, 6H, CH₂-Si); ¹³C NMR (C₆D₅Cl, 298 K) δC(ppm): 155.6, 129.5, 121.3, 120.0, 6.4, 4.9. SM-EI (m/z): 209 (8), 208 (46), 180 (25), 179 (100), 152 (24), 151 (98), 149 (10), 123 (64), 121 (46), 79 (12), 77 (28).
Characterization of (2-benzylphenoxy)triethylsilane (o-4)

^1H NMR (C₆D₅Cl, 298 K) δ_H(ppm) = 7.38–6.89 (m, 9H, ArH), 4.26 (s, 2H, CH₂), 1.17 (t, 9H, J = 8 Hz, CH₂-Si), 0.96–0.71 (m, 6H, CH₂-Si); ^13C NMR (C₆D₅Cl, 298 K) δ_C(ppm) = 153.7, 140.2, 131.0, 129.6, 129.0, 128.5, 127.4, 125.9, 121.3, 118.4, 36.7, 6.74, 5.40.

NB: The products o-4 and p-4 can easily be identified in ^13C NMR by the distinct chemical shift of the methylene groups: δ_C[-CH₂ (o-4)] = 36.7 and δ_C[-CH₂ (p-4)] = 41.3.

The mixture of the ortho and the para isomer of the (benzylphenoxy)triethylsilane 4 could not be separated by classical flash chromatography on silica gel. Consequently, the isomers of 4 have been synthetized independently:

In a 10 mL round bottom flask equipped with a magnetic stirring bar under inert atmosphere, Et₃SiH (176 µL, 127.9 mg, 1.1 mmol, 1.1 eq.) was added to 2-(benzyl)phenol or 4-(benzyl)phenol (184 mg, 1 mmol, 1 eq.) and [1][B(C₆F₅)₄] (5.0 mg, 4 µmol, 0.03 mol%) in C₆H₅Cl (2 ml). The mixture was stirred at room temperature until the end of the gas release (1h). The solvent was then evaporated off under vacuum and the crude solid residue purified by flash chromatography on silica gel (using a pentane/AcOEt (95:5) mixture as eluent). Evaporation of the solvents of the collected fractions afforded pure p-4 or o-4 in 94% and 92% yield respectively.
Characterization of (4-benzylphenoxy)triethylsilane (p-4)

Colorless oil, 281 mg, 94% yield

\[ \text{H NMR (CD}_2\text{Cl}_2, 298 \text{ K}) \delta \text{H (ppm)}: \delta 7.34 - 7.19 \text{ (m, 5H)}, 7.07 \text{ (d; 2H, } J = 8.3 \text{ Hz)}, 6.80 \text{ (d; 2H, } J = 8.3 \text{ Hz)}, 3.92 \text{ (s; 2H)}, 1.02 \text{ (t, 9H, } J = 7.7 \text{ Hz, CH}_2-\text{Si}), 0.74 \text{ (m, 6H, CH}_2-\text{Si).} \]

\[ \text{13C NMR (CD}_2\text{Cl}_2, 298 \text{ K}) \delta \text{C (ppm)} = 154.28, 142.21, 134.44, 130.12, 129.15, 128.78, 126.32, 120.19, 41.44, 6.81, 5.28. \]

HRMS (ESI) \text{m/z } [M + H]^+ \text{ calcd. for C}_{19}\text{H}_{27}\text{OSi}^+ 299.1826; \text{ found : 299.1834.}

\[ [M + Na]^+ \text{ calcd. for C}_{19}\text{H}_{26}\text{OSiNa}^+ 321.1645; \text{ found : 321.1644.} \]

Characterization of (2-benzylphenoxy)triethylsilane (o-4)

Limpid brown oil, 275 mg, 92 % yield

\[ \text{H NMR (CD}_2\text{Cl}_2, 298 \text{ K}) \delta \text{H (ppm)} = 7.35 - 7.21 \text{ (m, 5H)}, 7.18 - 7.11 \text{ (m, 2H)}, 6.96 - 4.87 \text{ (m; 2H)}, 4.02 \text{ (s; 2H)}, 1.03 \text{ (t, } J = 7.6 \text{ Hz, 9H)}, 0.93 - 0.70 \text{ (m, 6H).} \]

\[ \text{13C NMR (CD}_2\text{Cl}_2, 298 \text{ K}) \delta \text{C (ppm)} = 154.1, 141.8, 132.2, 131.1, 129.3, 128.6, 127.7, 126.2, 121.4, 118.7, 36.7, 6.9, 5.7. \]

HRMS (ESI) \text{m/z } [M + H]^+ \text{ calcd. for C}_{19}\text{H}_{25}\text{OSi}^+ 299.1826; \text{ found : 299.1834.}

\[ [M + Na]^+ \text{ calcd. for C}_{19}\text{H}_{24}\text{OSiNa}^+ 321.1645; \text{ found : 321.1644.} \]
II.b) Hydrosilylation of 2-phenoxy-1-phenylethan-1-ol (5a)

Equation 4

In an NMR tube equipped with a J. Young valve, Et₃SiH (47.8 µL, 0.3 mmol, 3.0 equiv.) and mesitylene (13.9 µL, 0.10 mmol, 1.0 equiv., used as an internal standard) were added to a mixture of 5a (21.4 mg, 0.10 mmol, 1.0 equiv.) and [1][B(C₆F₅)₄] (2.7 mg, 0.002 mmol, 2.0 mol%) in C₆D₅Cl (0.3 mL). The clear orange solution was stirred until complete dissolution of the starting materials and the end of the gas release. The tube was then heated at 70°C for 16 h without any change of color. The reaction was monitored by ¹H NMR and the spectra showed only the formation of triethyl(phenoxy)silane 3a (92%) and triethyl(phenylethoxy)silane 6 (92%).

The ¹H NMR yields of compounds 3a and 6 were confirmed with GC-MS analyses.

Characterization of triethyl(phenylethoxy)silane (6)

¹H NMR (C₆D₅Cl, 298 K) δ_H(ppm): 7.32–7.15 (m, 5H); 3.83 (t; 2H, J = 7.5 Hz, H₁); 2.85 (t, 2H, J = 7.5 Hz, H₂), 0.97 (t, 9H, J = 8 Hz, CH₃); 0.58 (m, 6H, CH₂-Si); ¹³C NMR (C₆D₅Cl, 298 K) δ_c(ppm): 140.1, 129.9, 128.9, 126.8, 64.1, 39.9, 7.3, 5.1. SM-EI (m/z): 208 (19), 207 (100), 179 (7), 161 (12), 117 (10), 115 (7), 105 (23), 103 (12), 87 (11), 75 (21), 59 (10), 47 (6).
II.c) Hydrosilylation of 2-(2-methoxyphenoxy)-1-phenylethan-1-ol (5b)

**Equation 5**

In an NMR tube equipped with a J. Young valve, Et₃SiH (63.8 µL, 0.4 mmol, 4.0 equiv.) and mesitylene (13.9 µL, 0.10 mmol, 1.0 equiv., used as an internal standard) were added to a mixture of 5b (24.4 mg, 0.10 mmol, 1.0 equiv.) and [1][B(C₆F₅)₄] (2.7 mg, 0.002 mmol, 2.0 mol%) in C₆D₅Cl (0.3 mL). The clear orange solution was stirred until complete dissolution of the reagents and the end of the gas release. The tube was then heated at 70°C for 16 h without any change of color. The reaction was monitored by ¹H NMR and the spectrum showed the quantitative formation of 1,2-bis((triethylsilyl)oxy)benzene 3b and triethyl(phenylethoxy)silane 6. The ¹H NMR yields of compounds 3b and 6 were confirmed with GC-MS analyses.

**Characterization of 1,2-bis((triethylsilyl)oxy)benzene (3b)**

¹H NMR (C₆D₅Cl, 298 K)  δH(ppm) : 6.85–6.77 (m, 4H); 1.05–0.89 (m, 18H, CH₃–CH₂–Si); 0.85–0.69 (m, 12H, CH₂–Si); ¹³C NMR (C₆D₅Cl, 298 K)  δC(ppm) : 147.8, 121.9, 121.0, 7.1, 5.4. SM IE (m/z) : 339 (8), 338 (12), 309 (23), 116 (12), 115 (100), 87 (56), 77 (1), 59 (25).
II.d) Reaction of hydrosilylation of 2-phenoxy-1-phenylpropane-1,3-diol (7)

Equation 6

\[
\begin{align*}
\text{Et}_3\text{SiH (6 equiv.)} & \quad \text{[1][B(C_6F_5)_4] (2 mol\%)} \\
\text{C}_6\text{D}_5\text{Cl}, 70^\circ\text{C}, 16\text{h} & \quad \text{Et}_3\text{SiOH} & \quad \text{Et}_3\text{Si(OH)}\text{SiEt}_3 \\
\quad & \quad \text{3a} \quad 99\% & \quad \text{8} \quad 83\%
\end{align*}
\]

In an NMR tube equipped with a J. Young valve, Et\(_3\)SiH (95.7 µL, 0.6 mmol, 6.0 equiv.) and mesitylene (13.9 µL, 0.10 mmol, 1.0 equiv., used as an internal standard) were added to a mixture of 7 (24.4 mg, 0.10 mmol, 1.0 equiv.) and [1][B(C\(_6\)F\(_5\))\(_4\)] (2.7 mg, 0.002 mmol, 2.0 mol%) in C\(_6\)D\(_5\)Cl (0.3 mL). The clear orange solution was stirred until complete dissolution of the starting materials and the end of the gas release. The tube was then heated at 70°C for 16 h without any change of color. The reaction was monitored by \(^1\)H NMR and the spectra showed the quantitative formation of triethyl(phenoxysilane 3a and of 2-methylhydroxy-1-phenylethanol 8 (83%) with traces of triethyl(3-phenylpropoxy)silane. The yield of 3a was quantitative according to GC/MS analysis.

Characterisation of 2-methylhydroxy-1-phenylethanol (8)

\(^1\)H NMR (C\(_6\)D\(_5\)Cl, 298 K) \(\delta_{\text{H(ppm)}}\) : 7.13–6.99 (m, 5H), 4.21 (d, 4H, \(^3J = 6.0\) Hz, H\(_1\)), 3.16 (q, 1H, \(^3J = 6.0\) Hz, H\(_2\)), 1.19–1.13 (m, 18H, CH\(_3\)-CH\(_2\)-Si), 0.84–0.72 (m, 12H, CH\(_2\)-Si); \(^{13}\)C NMR (C\(_6\)D\(_5\)Cl, 298 K) \(\delta_{\text{C(ppm)}}\) : 148.8, 128.6, 128.1, 126.5, 63.6, 51.1, 6.9, 4.5.
II.e) Hydrosilylation of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy) propane-1,3-diol (9)

Equation 7

In an NMR tube equipped with a J. Young valve, Et₃SiH (127.6 µL, 0.8 mmol, 8.0 equiv.) and mesitylene (13.9 µL, 0.10 mmol, 1.0 equiv., used as an internal standard) were added to a mixture of 9 (33.4 mg, 0.10 mmol, 1.0 equiv.) and [1][B(C₆F₅)₄] (2.7 mg, 0.002 mmol, 2.0 mol%) in C₆D₅Cl (0.3 mL). The clear orange solution was stirred until complete dissolution of the starting materials and the end of the gas release. The tube was heated at 70°C for 16 h without any change of color. The reaction was monitored by ¹H NMR and the spectra showed the quantitative formation of 1,2-bis((triethylsilyl)oxy)benzene 3b and 10G (87%). The ¹H NMR yields of compounds 3b and 10G were confirmed with GC-MS analysis.

Characterization of compound 10G

¹H NMR (C₆D₅Cl, 298 K) δ_H(ppm) : 7.13–6.99 (m, 3H); 3.83 (t, 2H, 𝑗 = 7.6 Hz, H₁); 2.84 (t, 2H, 𝑗 = 7.6 Hz, H₃), 2.03 (q, 2H, 𝑗 = 7.6 Hz, H₂), 1.23–1.16 (m, 27H, CH₃-CH₂-Si); 0.82–0.70 (m, 18H, CH₂-Si);

¹³C NMR (C₆D₅Cl, 298 K) δ_C(ppm) : 147.7, 145.2, 136.5, 121.7, 121.3, 120.7, 62.0, 35.0, 31.7, 6.9, 6.8, 5.2, 5.2, 4.8. SM IE (m/z): 511 (8), 510 (18) 337 (19), 235 (24), 207 (36), 116 (10), 115 (84), 89 (31), 88 (10), 87 (100), 86 (5), 59 (34), 32 (16).
III) Typical procedure for the hydrolysis of silylated aromatic compounds

The procedure for the hydrolysis of silylated aromatic compounds 10G and 10S are identical and the reaction is exemplified with compound 10G, as followed:

Under inert atmosphere (Argon), $^n$Bu$_4$NF·3H$_2$O (1.08 g; 3.4 mmol, 3.4 equiv.) was added slowly to a solution of 10G (511.0 mg; 1.0 mmol, 1 equiv.) in 4 mL of THF. The colorless solution was stirred at room temperature. After for 2 h, the solvent was evaporated off under vacuum and the solid residue was chromatographed on a silica gel column by using a mixture of pentane and ethyl acetate as eluent (2:8 pentane/acetate). Compound 10G' was obtained pure as a colorless oil (141.3 mg; 0.9 mmol; 84%).

**Equation 8**

![Equation 8](image)

**Characterization of compound 10G’**

$^1$H NMR (D$_2$O, 298 K) $\delta_{H}(ppm)$ = 6.88-6.57 (3H, m, Ar-H), 4.79 (3H, br.s, OH), 3.54 (2H, t, $^3J = 6.6$ Hz, CH$_2$-O), 2.50 (2H, t, $^3J = 7.6$ Hz, Ar-CH$_2$), 1.75 (2 H, quint, $^3J = 6.9$ Hz, Ar-CH$_2$-CH$_2$).

$^{13}$C NMR (D$_2$O, 298 K) $\delta_c(ppm) =$ 143.9, 141.8, 135.3, 120.6, 116.2, 61.1, 33.3, 30.6
From 10S (640.0 mg; 1.0 mmol, 1 equiv.) with $^n\text{Bu}_4\text{NF} \cdot 3\text{H}_2\text{O}$ (1.4 mg; 4.4 mmol, 4.4 equiv.)

Characterization of compound (10S')

1H NMR (D$_2$O, 298 K) $\delta_{\text{H}}$(ppm) = 6.36 (2H, s, Ar-H), 4.79 (4H, br.s, OH), 3.54 (2H, t, $^3J$ = 6.7 Hz, CH$_2$-O), 2.45 (2H, t, $^3J$ = 7.5 Hz, Ar-CH$_2$), 1.73 (2 H, quint, $^3J$ = 7.1 Hz, Ar-CH$_2$-CH$_2$).

13C NMR (D$_2$O, 298 K) $\delta_{\text{C}}$(ppm) = 145.4, 135.1, 130.0, 108.1, 61.1, 33.2, 30.8
IV) Supplementary equations

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IV.a) Attempts of reduction of 5a at room temperature

\[
\text{Equation 10}
\]

\[
\begin{align*}
\text{Et}_3\text{SiH} \text{ (2 equiv.)} & \quad \text{[1][B(C_6F_5)_4]} \text{ (2 mol\%)} \\
\text{C}_6\text{D}_5\text{Cl, RT, 16h} & \quad \text{-H}_2
\end{align*}
\]

In an NMR tube equipped with a J. Young valve, Et$_3$SiH (34.4 µL, 0.2 mmol, 2.0 equiv.) and mesitylene (13.9 µL, 0.10 mmol, 1.0 equiv., used as an internal standard) were added to a mixture of 5a (21.4 mg, 0.10 mmol, 1.0 equiv.) and [1][B(C$_6$F$_5$)$_4$] (2.7 mg, 0.002 mmol, 2.0 mol%) in C$_6$D$_5$Cl (0.3 mL). The clear orange solution was stirred for 16 h at RT without any change of color. The reaction was monitored by $^1$H NMR and $^{13}$C NMR and the spectra showed only the quantitative formation of the silylated derivative of 5a.

In order to further reduce compound 5a, as in equation 2, heating for hours at 70°C is required. This is consistent with the findings of Brookhart et al. for bulky substrates.$^5$

Characterisation of triethyl(2-phenoxy-1-phenylethoxy)silane

\begin{align*}
\text{$^1$H NMR (C}_6\text{D}_5\text{Cl, 298 K) } & \delta_{\text{H (ppm)}}: 7.52–7.29 \text{ (m, 5H), 7.08–6.84} \\
\text{(m, 5H), 5.14 (t, 1H, J = 5.8 Hz, H1), 3.96 (m, 2H, H2), 1.08–1.01} \text{ (m,} \\
\text{9H, CH}_2{-}\text{CH}_2{-}\text{Si); 0.73–0.56} \text{ (m, 6H, CH}_2{-}\text{Si); $^{13}$C NMR (C}_6\text{D}_5\text{Cl, 298 K) } & \delta_{\text{C (ppm)}}: 159.2, \\
\text{142.4, 129.5, 128.3, 127.8, 126.3, 120.7, 114.5, 74.0} \text{ (C}_2, \\
\text{73.7} \text{ (C}_1), 6.9, 5.0.
\end{align*}
Labelling experiments on 5a with Et₃SiD

**Equation 11**

IV.b) Labelling experiments on 5a with Et₃SiD

In an NMR tube equipped with a J. Young valve, Et₃SiD (29.2 mg, 0.25 mmol, 2.5 equiv.) and mesitylene (13.9 µL, 0.10 mmol, 1.0 equiv., used as an internal standard) were added to a mixture of 5a (21.4 mg, 0.10 mmol, 1.0 equiv.) and [1][B(C₆F₅)₄] (2.7 mg, 0.002 mmol, 2.0 mol%) in C₆D₅Cl (0.3 mL). The clear orange solution was stirred for 16 h without any change of color. The reaction was monitored by ¹H NMR and ¹³C NMR and the spectra showed only the quantitative formation of the labelled derivative 6-D₁.

**Characterisation of triethyl(2-phenyloxy-1-phenylethoxy)silane (6-D₁)**

**¹H NMR** (C₆D₅Cl, 298 K) δH(ppm) : 7.32–7.15 (m, 5H); 3.83 (broad t; 1H, ²J = 6.6 Hz, HD); 2.85 (broad d, 2H, ³J = 6.6 Hz, H), 0.97 (t, 9H, ³J = 8 Hz, CH₃-CH₂-Si); 0.58 (m, 6H, CH₂-Si); **¹³C NMR** (C₆D₅Cl, 298 K) δC(ppm) : 140.1, 129.9, 128.9, 126.8, 64.3, 39.9, 7.3, 5.1.
IV.c) Catalytic reduction of 10S into 11S and 11S' with Et₃SiH

**Equation 12**

In an NMR tube equipped with a J. Young valve, Et₃SiH (16 µL, 0.1 mmol, 2 equiv.) was added to a mixture of 10S (32 mg, 0.05 mmol, 1.0 equiv.) and [1][B(C₆F₅)₄] (2.7 mg, 0.002 mmol, 4.0 mol%) in C₆D₅Cl (0.3 mL). The clear orange solution was stirred 5 days at 90°C without any change of color. Reduction to the propylcatechol derivatives 11S' and 11S was effective but the reaction incomplete. As observed by Brookhart et al., elimination of Et₃SiOH on the pendant chain produced the corresponding alkene that can be further reduced into 11S by the neutral [(tBuPOCOP)IrH₂] dihydride complex formed *in situ.* NMR and GC-MS spectra confirmed the formation of compounds 11S (tr = 11.916 minutes) and 11S' (tr = 11.007 minutes). However, purification of 11S' and 11S compounds by flash chromatography on a column was difficult due to their similar chemical properties.

**Scheme 1: GC-MS chromatogram of the reduction of 10S with Et₃SiH**

11S': SM IE (m/z): 508 (21), 365, 364 (25), 363 (42), 336 (18), 335 (29), 116 (7), 115 (54), 88 (10), 87 (100), 59 (43).

11S: SM IE (m/z): 510 (8), 339 (27), 338 (35), 337 (32), 116 (10), 115 (82), 88 (9); 87 (100), 59 (36).
IV.d) Reduction of model 5b with a variety of hydrosilanes

**Equation 13**

\[
\text{Compound 5b was treated under the conditions of equation 4 with a variety of hydrosilanes (Et}_2\text{SiH}_2, \text{Ph}_3\text{SiH, Ph}_2\text{SiH}_2, (\text{EtO})_3\text{SiH, PMHS and TMDS). The n values and the number of equiv. silane correspond to 4 Si-H per molecule of 5b. Its hydrosilylation was observed by NMR spectroscopy which spectra showed the formation of an intricate mixture of silylated products impeding the determination of the yields.}
\]

**Scheme 2: GC-MS chromatogram of the hydrosilylation of 5b with TMDS**
V) Typical procedures for the catalytic hydrosilylation of lignins

V.a) Typical procedures for the catalytic hydrosilylation of softwood lignins

The procedure is detailed for the conversion of industrial pine lignin (extracted with the Formacell process) into 10G by using Et₃SiH as reductant. Norway spruce, Lebanese cedar and Pacific red cedar similarly afforded compound 10G in yields ranging from 11 to 120 wt%. In the same manner, hardwood lignin of the evergreen oak, hybrid plane, common beech and black poplar essences gave the two compounds 10G and 10S in yields varying from 20 to 42 wt% and 61 to 130 wt%, respectively.

In a 50 mL round bottom flask equipped with a magnetic stirring bar under inert atmosphere, Et₃SiH (600 mg, 5.2 mmol, 300 wt% from lignin) was added to 200 mg of lignin (~0.2 mmol lignin (Mn ~ 980 g/mole, N_{aromatic} = 5), ~1.0 mmol of aromatic units) and [1][B(C₆F₅)₄] (40.0 mg, 0.03 mmol, 20 wt% from lignin) in C₆H₅Cl (2 ml). The mixture was stirred at room temperature until complete dissolution of the starting materials and the end of the gas release. After 20 min, the solid has completely disappeared and the initial red-orange solution turned brown. The clear solution was then stirred at 70 °C for 24-48 h. The solvent was then evaporated off under vacuum and the crude solid residue purified by flash chromatography on silica gel (using pentane/CH₂Cl₂ (8:2) mixture as the eluent). All the by-products and in particular the potential diaromatic molecules were retained in the column. Evaporation of the solvent (ca 500 ml) of the collected fractions afforded pure 10G as a colorless oil (100 wt%, 202 mg).

Yields are given in weight percent (wt%) which correspond to the weight of silylated monolignols derivatives over the weight in lignin (wt of 10S or 10G)/(wt of lignin). (See Section VII.a)
V.b) Optimization of the conditions for the industrial pine lignin

**Equation 14**

\[
\text{Industrial pine lignin (softwood)} \xrightarrow{\text{[1][B(C_6F_5)_4], Et_3SiH}} \text{Et}_3\text{SiO} \text{SiEt}_3
\]

**Table 1:** Attempts at optimizing the depolymerization of industrial pine lignin. The tests have been led on 40 mg (≈ 0.2 mmol in aromatic units) of industrial pine lignin.

<table>
<thead>
<tr>
<th>Entry</th>
<th>[1][B(C_6F_5)_4] (wt%)</th>
<th>Et_3SiH (wt%)</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>10G (wt%) (GC Yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1*a</td>
<td>50</td>
<td>273</td>
<td>70</td>
<td>16</td>
<td>65</td>
</tr>
<tr>
<td>2*a</td>
<td>25</td>
<td>273</td>
<td>90</td>
<td>24</td>
<td>99</td>
</tr>
<tr>
<td>3*a</td>
<td>25</td>
<td>300</td>
<td>70</td>
<td>24</td>
<td>120</td>
</tr>
<tr>
<td>4*a</td>
<td>20</td>
<td>273</td>
<td>70</td>
<td>24</td>
<td>110</td>
</tr>
<tr>
<td>5*a</td>
<td>20</td>
<td>273</td>
<td>70</td>
<td>36</td>
<td>120</td>
</tr>
<tr>
<td>6*a</td>
<td>10</td>
<td>300</td>
<td>70</td>
<td>48</td>
<td>120</td>
</tr>
<tr>
<td>7*a</td>
<td>5</td>
<td>400</td>
<td>70</td>
<td>72</td>
<td>-</td>
</tr>
</tbody>
</table>

*aDetection of other unidentified volatile products

**Scheme 3:** GC-MS chromatograms of the depolymerization residues of industrial pine lignin

The optimal conditions for the depolymerization of industrial pine lignin were: 10 wt% of [1][B(C_6F_5)_4], 273 wt% of Et_3SiH, 70 °C, 48 h, solvent = C_6H_5Cl

The peak at 12 mn is not attributed.
V.c) Depolymerization of softwood lignins

**Equation 15**

\[
\text{Softwood lignin} \xrightarrow{300 \text{ wt\% Et}_3\text{SiH}} \text{Et}_3\text{SiO} \begin{array}{c} \text{Et}_3\text{SiO} \end{array} \text{Et}_3 \\
\text{C}_9\text{D}_5\text{Cl}, 70^\circ\text{C}, 30\text{h} \quad -\text{H}_2, -\text{CH}_4 \quad -\text{Et}_3\text{SiOSiEt}_3 \\
\text{10G}
\]

**Table 2: Results Summary of softwood lignin depolymerization**

<table>
<thead>
<tr>
<th>Softwood lignin</th>
<th>Et\textsubscript{3}SiH (wt%)</th>
<th>10G (wt%)</th>
<th>Yield\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial pine</td>
<td>300</td>
<td>120\textsuperscript{a}</td>
<td>46 %</td>
</tr>
<tr>
<td>Norway spruce</td>
<td>300</td>
<td>81\textsuperscript{b}</td>
<td>31 %</td>
</tr>
<tr>
<td>Lebanese cedar</td>
<td>300</td>
<td>69\textsuperscript{a}</td>
<td>27 %</td>
</tr>
<tr>
<td>Pacific red cedar</td>
<td>300</td>
<td>11\textsuperscript{b}</td>
<td>4 %</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Detection of other unidentified volatile products. \textsuperscript{b} No other major volatile products were detected. \textsuperscript{c} Molar yield is calculated with respect to 10G (see section VII.b).  

**Scheme 4: GC-MS chromatograms of the crude depolymerization residues of softwood lignins obtained from Eq. 15**
V.d) Optimization of the depolymerization conditions for black poplar lignin

**Equation 16**

![Depolymerization reaction with Et₃SiH](image)

**Table 3:** Attempts at optimization for depolymerization of black poplar lignin (40 mg ≈ 0.2 mmol).

<table>
<thead>
<tr>
<th>Entry</th>
<th>[1][B(C₆F₅)₄] (wt%)</th>
<th>Et₃SiH (wt%)</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>10G (wt%)</th>
<th>10S (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1ᵃ</td>
<td>50</td>
<td>273</td>
<td>25</td>
<td>72</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2ᵇ</td>
<td>50</td>
<td>273</td>
<td>70</td>
<td>16</td>
<td>36</td>
<td>55</td>
</tr>
<tr>
<td>3ᵇ</td>
<td>25</td>
<td>273</td>
<td>70</td>
<td>16</td>
<td>13</td>
<td>9</td>
</tr>
<tr>
<td>4ᵇ</td>
<td>25</td>
<td>300</td>
<td>90</td>
<td>24</td>
<td>30</td>
<td>26</td>
</tr>
<tr>
<td>5ᵇ</td>
<td>20</td>
<td>300</td>
<td>70</td>
<td>48</td>
<td>24</td>
<td>17</td>
</tr>
<tr>
<td>6ᵇ</td>
<td>20</td>
<td>300</td>
<td>70</td>
<td>36</td>
<td>22</td>
<td>61</td>
</tr>
<tr>
<td>7ᵃ</td>
<td>10</td>
<td>300</td>
<td>70</td>
<td>48</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Detection of other unidentified volatile products. ᵇNo other major volatile products were detected.

**Scheme 5:** GC-MS chromatograms of the depolymerization residues of black poplar lignin

Optimized conditions for the depolymerization of black poplar lignin: 20 wt% of [1][B(C₆F₅)₄], 300 wt% of Et₃SiH, 70°C, 48 h, solvent = C₆H₅Cl. The peak at 10 mn is not attributed.
V.e) Depolymerization of hardwood lignins

Equation 17

![Equation 17 image]

Table 4: Results Summary of hardwood lignin depolymerization

<table>
<thead>
<tr>
<th>Hardwood Lignin</th>
<th>$\text{Et}_3\text{SiH}$ (wt%)</th>
<th>Time (h)</th>
<th>$10G$ (wt%)</th>
<th>$10S$ (wt%)</th>
<th>Yield $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evergreen Oak $^b$</td>
<td>364</td>
<td>36</td>
<td>32</td>
<td>130</td>
<td>58 %</td>
</tr>
<tr>
<td>Hydrid Plane $^a$</td>
<td>364</td>
<td>48</td>
<td>36</td>
<td>94</td>
<td>47 %</td>
</tr>
<tr>
<td>Common Beech $^a$</td>
<td>364</td>
<td>48</td>
<td>42</td>
<td>83</td>
<td>46 %</td>
</tr>
<tr>
<td>Black Poplar $^b$</td>
<td>364</td>
<td>36</td>
<td>20</td>
<td>80</td>
<td>36 %</td>
</tr>
</tbody>
</table>

$^a$ Detection of other unidentified volatile products. $^b$ No other major volatile products were detected. $^c$ Calculation of the yield is based on the 10G and 10S yields (see assumptions in section VII.b)

Scheme 6: GC-MS chromatogram of the depolymerization of hardwood lignin

![Scheme 6 image]
VI) Characterizations of softwood and hardwood lignins.

Elemental analysis and SEC analyses of lignin have been previously reported in the following publication: E. Feghali, G. Carrot, P. Thuery, C. Genre, T. Cantat, *Energy Environ. Sci.*, 2015, 8, 2734.7a

VI.a) Elemental analyses

Table 5: Elemental analyses of extracted lignin samples and proposed chemical formulas

<table>
<thead>
<tr>
<th>Species</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</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>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>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>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>Evergreen oak</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>
</tr>
</tbody>
</table>

With the approximation that softwood lignins are exclusively composed of G residues, the general theoretical formula of the lignin polymer would be \([C_{10}H_{12}O_4]_n\) (Mw = 196.20 g/mol). (G residues represent about 90% of the of the total residues)8

With the approximation that hardwood lignins are exclusively composed of S residues, the general formula of the lignin polymer would be \([C_{11}H_{14}O_5]_n\) (Mw = 226.23 g/mol).
VI.b) Size Exclusion Chromatography (SEC)

**Table 6: 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>Evergreen oak</td>
<td>Formacell</td>
<td>952</td>
<td>1657</td>
<td>1.74</td>
</tr>
</tbody>
</table>

According to the SEC analyses, formation of reduced monomers is not observed. (Cf reference 7a)
VI.c) 2D NMR spectroscopy

HSQC NMR spectra were recorded on a Bruker Avance 600 MHz spectrometer. The central DMSO solvent peak was used as internal reference (δ_C 39.5, δ_H 2.49 ppm). The ¹³C–¹H correlation experiment was an HSQC sequence started with the Bruker standard pulse sequence ‘hsqcetgpis2’ (phase-sensitive gradient-edited-2D HSQC). HSQC experiments were performed at 10°C using the following parameters: acquired from 12 to -1 ppm in F2 (1H), 200 to 0 ppm in F1 (13C). The semi quantitative (Relative Quantitative Method) 2D-HSQC spectra were performed in accordance with the original reference as reported before.⁹ Data analysis was performed using MestReNova software (version 6.0.2-5475) and TopSpin 3.5. The 2D HSQC NMR correlations were in agreement with those described in the literature for organosolv lignin.¹⁰

**NB:** The abundances of different linkages were estimated from the C₆–H₆ correlations in the following region spectra (side chain region): 2.5-6 ppm in F2 (¹H) and 40-100 ppm in F1 (¹³C). In the aromatic region, C₅–H₂, C₆–H₆ correlations from G, and S lignin units were used to estimate their relative abundances in hardwood lignin as previously described.⁹a
VI.c.1) 2D NMR HSQC spectra of lignins

**Figure 1:** Partial 2D HSQC NMR spectra of Norway spruce lignin extracted with the Formacell process (in 4:1 DMSO-d$_6$/pyridine-d$_5$).
Figure 2: Partial 2D HSQC NMR spectra of pacific red cedar lignin extracted with the Formacell process (in 4:1 DMSO-d$_6$/pyridine-d$_5$).
Figure 3: Partial 2D HSQC NMR spectra of Lebanese cedar lignin extracted with the Formacell process (in 4:1 DMSO-d$_6$/pyridine-d$_5$).
Figure 4: Partial 2D HSQC NMR spectra of industrial pine lignin extracted with the Formacell process (in 4:1 DMSO-d$_6$/pyridine-d$_5$).
Figure 5: Partial 2D HSQC NMR spectra of common beech lignin extracted with the Formacell process (in 4:1 DMSO-d_6/pyridine-d_5).

Common beech lignin
Figure 6: Partial 2D HSQC NMR spectra of black poplar lignin extracted with the Formacell process (in 4:1 DMSO-d$_6$/pyridine-d$_5$).
Figure 7: Partial 2D HSQC NMR spectra of evergreen oak extracted with the Formacell process (in 4:1 DMSO-d$_6$/pyridine-d$_5$)
Figure 8: Partial 2D HSQC NMR spectra of hybrid plane extracted with the Formacell process (in 4:1 DMSO-d$_6$/pyridine-d$_5$).
VI.c.2) 2D NMR HSQC of lignins: examples

**Figure 9:** Quantitative integration of partial 2D HSQC NMR spectra of Pacific red cedar lignin extracted with the Formacell process (in 4:1 DMSO-d$_6$/pyridine-d$_5$).
Figure 10: Quantitative integration of partial 2D HSQC NMR spectra of black poplar lignin extracted with the Formacell process (in 4:1 DMSO-d$_6$/pyridine-d$_5$).
Figure 11: Quantitative integration of partial 2D HSQC NMR spectra of hybrid plane lignin extracted with the Formacell process (in 4:1 DMSO-d<sub>6</sub>/pyridine-d<sub>5</sub>).
Figure 12: Integration of partial 2D HSQC NMR spectra of evergreen oak lignin extracted with the Formacell process (in 4:1 DMSO-d$_6$/pyridine-d$_5$).
Figure 13: Quantitative integration of partial 2D HSQC NMR spectra of:

A) Evergreen oak lignin extracted with the Formacell process (in 4:1 DMSO-d$_6$/pyridine-d$_5$).
B) Crude of the depolymerization reaction of evergreen oak lignin in C$_6$H$_5$Cl/C$_6$D$_6$.
VI.c.3) Summary of 2D HSQC NMR informations

The abundances of different linkages were estimated from the integration of $C_{\alpha}-H_{\alpha}$ correlations in the side chain region: 2.5-6 ppm in F2 ($^1$H) and 40-100 ppm in F1 ($^{13}$C). In the aromatic region, $C_2-H_2$, $C_6-H_6$ correlations from G, and S lignin units were used to estimate their relative abundances in hardwood lignin as previously described.\textsuperscript{9a} $\beta$-O-4 linkages which will be used further have been estimated with two classical approaches:

Approach 1: The integration of $C_{\alpha}-H_{\alpha}$ correlation of each linkage was calibrated with respect to the integration of the $C_2-H_2$ and $C_6-H_6$ correlations of the G and S aromatic units. The linkages are expressed per 100 aromatics.

\textbf{Approach 1:} The integration of $C_{\alpha}-H_{\alpha}$ correlation of each linkage was calibrated with respect to the integration of the $C_2-H_2$ and $C_6-H_6$ correlations of the G and S aromatic units. The linkages are expressed per 100 aromatics. (see figures 9-12)

\textbf{Approach 2:} The amount of each lignin linkage is estimated relatively to the total amount of interunit linkages (in the side chain region). The sum of the integrations of $C_{\alpha}-H_{\alpha}$ correlations of each linkage (A, B, C and D) is arbitrarily calibrated to 100, \textit{e.g.} $A + B + C + D = 100$.

For example, $A\% = \frac{A}{A+B+C+D}$
Table 7: Summary of the 2D HSQC NMR results of the content of main linkages in lignins expressed per 100 aromatics (and expressed as Percentage of Total Side Chains.)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Softwood lignins</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Industrial Pine</td>
<td>35.1 (63 %)</td>
<td>13.7 (25 %)</td>
<td>6.9 (12 %)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Norway Spruce</td>
<td>30.2 (46 %)</td>
<td>19.7 (30 %)</td>
<td>15.7 (24 %)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lebanese Cedar</td>
<td>38.9 (59 %)</td>
<td>20.6 (31 %)</td>
<td>6.7 (10 %)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pacific Red Cedar</td>
<td>21.1 (20 %)</td>
<td>43.2 (41 %)</td>
<td>39.6 (39 %)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Hardwood lignins</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Evergreen Oak</td>
<td>48.10 (70 %)</td>
<td>8.11 (12 %)</td>
<td>8.4 (12 %)</td>
<td>4.3 (6 %)</td>
<td>75/25</td>
</tr>
<tr>
<td>Black Poplar</td>
<td>47.2 (76 %)</td>
<td>3.70 (6 %)</td>
<td>5.9 (10 %)</td>
<td>4.8 (8 %)</td>
<td>69/31</td>
</tr>
<tr>
<td>Hybrid Plane</td>
<td>42.5 (65 %)</td>
<td>6.4 (10 %)</td>
<td>11.1 (17 %)</td>
<td>5.6 (8 %)</td>
<td>68/32</td>
</tr>
<tr>
<td>Common Beech</td>
<td>43.7 (65 %)</td>
<td>6.0 (9.0 %)</td>
<td>12.2 (18 %)</td>
<td>5.23 (8 %)</td>
<td>63/37</td>
</tr>
</tbody>
</table>

*a In parentheses: percentage based on the total side chains linkages observed in HSQC (A + B + C + D = 100)
VII) Definition of the yield, theoretical yield and efficiency in the depolymerization of lignin

VII.a) Experimental yield

For a product X, the experimental yield $R(X)_{\text{exp}}$ (in wt%) is defined as the mass of isolated silylated product over the initial mass of lignin:

$$R(X)_{\text{exp}} = \frac{m(\text{silylated compound})}{m(\text{lignin})} \times 100$$

VII.b) Experimental molar yield

For a product X, the experimental molar yield $R_{\text{mol}}(X)_{\text{exp}}$ is expressed as the molar number of isolated silylated product over the molar number of the aromatics units in lignin:

$$R_{\text{mol}}(X)_{\text{exp}} = \frac{n(\text{silylated compound})}{n(\text{monomer in lignin})} \times 100$$

For example, if we consider that industrial pine lignin (IPL) is only composed of the G residues ($\text{Mw}(G) = 196.2 \ \text{g.mol}^{-1}$). For 100 mg of IPL, thus the molar number of monoaromatic units in lignin is:

$$n(\text{IPLmonomer}) = 100.10^{-3}/196.2 = 0.51 \ \text{mmol}.$$

We recover 120 mg of $10G$, ($\text{Mw}(10G) = 510.98)$:

$$n(10G) = 120.10^{-3}/510.98 = 0.23 \ \text{mmol}.$$
R_{\text{mol(X)exp}} = \frac{n (10G)}{n(\text{IPLmonomer})} \times 100 = \frac{0.23}{0.51} \times 100 = 46 \%

VII.c) Theoretical yield

Calculation of the theoretical yield in monomeric aromatics and the efficiency of wood lignin depolymerization have been previously reported by our group. The calculation is based on a fine description of the considered lignin. Size exclusion chromatography, 2D NMR and elemental analysis were performed to characterize industrial pine and evergreen oak lignins. We have previously presented these characterizations. Here, we proposed a revised and more precise method for the calculation of the efficiency in hardwood lignin by considering the yields in both G and S aromatics.

**NB:** In the following sections, the percentage P of cleavable linkages in lignin (i.e. aryl-O-alkyl bonds) is approximated to the percentage of $\beta$-O-4 linkages determined by HSQC NMR.

The percentage of $\beta$-O-4 linkages estimated by the approach 1 (see VI.c.3) does not fit with the model for the calculation of the theoretical yield. We thus only considered the result from the approach 2 (See summary and discussions S55-56).
VII.c.1) Theoretical yield for softwood lignins

This statistical reasoning on the theoretical yield in monomeric aromatics products as well as determination of the efficiency are based on a fine description of the softwood lignin preparation\(^7\text{a}\) and lie on some assumptions:

- We have shown that the degree of polymerization of lignin is very low when obtained by the Formacell organosolv process; a softwood lignin is thus considered as a linear polymer containing a unique oxidized G residue ((MeO)\(_2\)PhC(O)CH\(_2\)CH\(_2\)OH) (DP (degree of polymerization) = 5±1, \(M_w(G) = 196.2\) g/mol).\(^7\text{a}\)

- The percentages of cleavable linkages in softwood lignins strongly depend on the wood sources. However, softwood lignins classically contain 40-60\% of cleavable linkages (aryl-O-alkyl bonds).\(^8-13\) In the following demonstration, the percentage of C-O cleavable linkages, \(\text{eg} P = 60\%\), was that determined for industrial pine lignin from 2D NMR studies (see VI.c.2. 2D NMR spectra).

Considering that a lignin sample has a polymerization degree \(N = 2\) (or contains 2 mono aromatic units), the maximum theoretical yield in monoaromatic, \(\text{eg} \tau(N=2)\) \((S\text{ for softwood})\), is \(\tau(N=2)_S = 0.6\). In a longer polymer, the condition for having mono-aromatic derivatives requires to have two consecutive cleavable linkages on an aromatic unit.

Thus, for an infinite chain \(N = \infty\), \(\tau(N = \infty)_S = 0.6^2 \times 100 = 36\%\). (36\% corresponding to the asymptote of the curve \(\tau(N)_S = f(N)\).

For a finite lignin polymer involving \(N\) monolignols, 2 aromatic units are located in the chain-ends while (\(N-2\)) aromatic units are surrounded with either cleavable or non-cleavable linkages. 60\% of the chain-ends can thus yield a mono-aromatic product, while 36\% of the remaining (\(N-2\)) monolignols can afford mono-aromatics. The maximum theoretical yield in mono aromatic compounds can be expressed as below for softwood lignin:
\[ \tau(N)_S = \frac{(N-2) \times 0.6^2 + 2 \times 0.6}{N} \times 100 \]

Considering that softwood lignin involves a single mono-aromatic unit, the degree of polymerization (DP) of each lignin source has been evaluated (\( DP = \frac{M_n}{M_w} \), where \( M_n \) = molar mass of the polymer and \( M_w \) = molar mass of the constituting monolignol). As mentioned above, the DP for a lignin polymer is \( DP = 5 \). Since the values of \( \tau(N) \) are quite similar (\( \tau(N) = 0.44 \) to 0.48) for \( N \) varying between 4 to 6, an average value of \( \tau(N) = 5 \) was taken regardless of the softwood lignin source.

\[ \tau(4) = 48 \% \quad \tau(5) = 46 \% \quad \tau(6) = 44 \% \]

\( < \tau(5 \pm 1) > = 46 \% \)

Using the molar mass of the theoretical general formulas of lignin oligomers\(^7\) \(((196.2)_N g/mol)\) for softwood, the maximum theoretical yield \( R(X) \) (in wt\%) of a mono-aromatic product \( X \) versus the initial mass of lignin would be:

\[
R(X) = \frac{m \text{ (theor in silylated compound)}}{m \text{ (lignin)}} \times 100 = \frac{\tau(N)_S \times M_w(X)}{M_w \text{ (monolignol)}} \times 100
\]

For the synthesis of 10G from industrial pine:

\[
R(10G) = \frac{0.46 \times 510.98}{196.2} \times 100 = 119.8 \text{ wt\% / wood lignin weight}
\]

The wt\% maximum theoretical yields \( R(10G) \) have been calculated for all the lignin samples of this study by taking into account their respective percentages of cleavable linkages P
determined by HSQC NMR (P is approximated to the percentage of β-O-4 linkages in lignin).

The results are summarized up in table 8.

Table 8: Calculation of the wt% maximum theoretical yield R(X) for the softwood lignins with β-O-4 expressed as percentage per 100 aromatics.

<table>
<thead>
<tr>
<th>Lignin</th>
<th>P (% of cleavable linkages) β-O-4 per 100 aromatics</th>
<th>τ(5) (N = 5)</th>
<th>Theoretical yield R(10G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial Pine</td>
<td>35 (60 %)(^a)</td>
<td>21 % (46 %)(^b)</td>
<td>55 wt% (120 wt%)</td>
</tr>
<tr>
<td>Norway Spruce</td>
<td>30 (50 %)(^a)</td>
<td>17 % (35 %)</td>
<td>45 wt% (91 wt%)</td>
</tr>
<tr>
<td>Lebanese Cedar</td>
<td>39 (60 %)(^a)</td>
<td>25 % (46 %)</td>
<td>64 wt% (120 wt%)</td>
</tr>
<tr>
<td>Pacific Red Cedar</td>
<td>20 (20 %)(^a)</td>
<td>10 % (10 %)</td>
<td>27 wt% (27 wt%)</td>
</tr>
</tbody>
</table>

\(^a\)The values within parentheses represent the percentage of linkage based on the total linkages (β-O-4′ + β-β′ + β-5′ + β-1′ = 100) 

\(^b\)The values in parentheses represent the calculation of the theoretical yield based on the relative percentage of β-O-4 in lignin (β-O-4′ + β-β′ + β-5′ + β-1′ = 100)
This statistical reasoning on the theoretical yield in monomeric aromatics products as well as determination of the efficiency are based on a fine description (SEC, elementary analyses and HSQC NMR data) of the hardwood lignin preparation and lie on the following assumptions:

- The degree of lignin polymerization is known to be very low when obtained by the Formacell organosolv process (Cf. section VI.a and VI.b); hardwood lignin is thus considered as a linear polymer containing both G and S ((MeO)₃PhC(O)CH₂CH₂OH) units (DP = 4, $M_w(S) = 226.2$ g/mol, $M_w(G) = 196.2$ g/mol).

- The S/G ratio varies from each essence of hardwood lignin. Classically, the S/G ratio is between 1/1 to 4/1. In this study, the mean S/G ratio in hardwood lignins is approximated to 7/3 based on HSQC NMR integration (the S/G ratio are in the range 65/35 to 75/25).

- Hardwood lignins contain 60-62% of β-O-4 and 3-11% of α-O-4 linkages. The percentages of cleavable bonds in hardwood lignins strongly depend on the wood sources. In the following demonstration, the percentage of C-O cleavable linkages, eg P = 70%, was determined for lignin from 2D HSQC NMR studies (see VI.c.2. 2D NMR spectra)

Considering that a lignin sample has a polymerization degree $N = 2$, the maximum theoretical yield $\tau(N)_H$ (H for hardwood) is $\tau(N = 2)_H = 70\%$. In a longer polymer, the condition for having mono-aromatic derivatives requires to have two consecutives cleavable linkages on an aromatic unit.

Thus, for an infinite chain $N = \infty$, $\tau(N = \infty)_H = 0.7^2 \times 100 \% = 49 \%$. (49 % corresponding to the asymptote of the curve $\tau(N)_H = f(N)_H$.)
For a finite lignin polymer involving with N monolignols, 2 aromatic units are located in the chain-ends while (N–2) aromatic units are surrounded with either cleavable or non-cleavable linkages. 70 % of the chain-ends can thus yield a mono-aromatic product, while P² = (0.7)² = 49 % of the remaining (N–2) monolignols can afford mono-aromatics. The theoretical yield τ(N)H in mono aromatic compounds can be expressed as below for a hardwood lignin:

\[ \tau(N)_H = \frac{(N - 2) \times 0.7^2 + 2 \times 0.7}{N} \times 100 \]

Considering that lignin involves 30 % of mono-aromatic units G and 70 % of mono-aromatic units S, the degree of polymerization (DP) of each lignin source has been evaluated:

\[ DP = \frac{M_n}{0.3 \times M_w(\text{monolignol } G) + 0.7 \times M_w(\text{monolignol } S)} \]

where \( M_n \) = mean molecular weight of the polymer (determined by SEC measurement) and \( M_w = \) molar mass of the considered monolignol. As mentioned above, the DP for a hardwood Formacell lignin polymer is DP = 4.7

\[ \tau(4)_H = 60 \% \]

Using the molar mass of the theoretical general formulas of lignin oligomers\(^7\) (theoretical general formulas: \( (G_{0.3}-S_{0.7})_N \), \( M_w = N \times [0.3 \times 196.2 + 0.7 \times 226.2] \) g/mol) the wt% maximum theoretical yield \( R(X) \) in a mono-aromatic product X/lignin weight would be:

\[ R(X) = \frac{m(\text{theor in silylated compound } X)}{m(\text{lignin})} = \frac{\tau(N)_H \times y \times M_w(X)}{0.3 \times M_w(\text{monolignol } G) + 0.7 \times M_w(\text{monolignol } S)} \times 100 \]

where \( y \) is the rate (in %) of the considered monoaromatic unit in lignin.
For the synthesis of $10\text{G}$ and $10\text{S}$ from hardwood:

$$R(10\text{G}) = \frac{0.6 \times 0.3 \times 510.98}{(0.3 \times 196.2) + (0.7 \times 226.2)} \times 100 = 42.3 \text{ wt% / wood lignin weight}$$

$$R(10\text{S}) = \frac{0.6 \times 0.7 \times 640.23}{(0.3 \times 196.2) + (0.7 \times 226.2)} \times 100 = 123.8 \text{ wt% / wood lignin weight}$$

**Table 9:** Calculation of the wt% maximum theoretical yield $R(X)$ for the hardwood lignins with $\beta$-O-4 expressed as percentage per 100 aromatics.

<table>
<thead>
<tr>
<th>Lignin</th>
<th>P (% of cleavable linkages)</th>
<th>$\tau(4)$ (N = 4)</th>
<th>Theoretical yield $R(10\text{G})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evergreen Oak</td>
<td>48.1 $^a$ (70 %)$^b$</td>
<td>36 % $^a$ (60 %)$^b$</td>
<td>25 / 74 wt% $^a$ (42 / 124 wt%)$^b$</td>
</tr>
<tr>
<td>Black Poplar</td>
<td>47.2 (70 %)</td>
<td>34 % (60 %)</td>
<td>24 / 70 wt% (42 / 124 wt%)</td>
</tr>
<tr>
<td>Hybrid Plane</td>
<td>42.5 (70 %)</td>
<td>30 % (60 %)</td>
<td>21 / 61 wt% (42 / 124 wt%)</td>
</tr>
<tr>
<td>Common Beech</td>
<td>43.7 (70 %)</td>
<td>32 % (60 %)</td>
<td>23 / 66 wt% (42 / 124 wt%)</td>
</tr>
</tbody>
</table>

$^a$ Values obtained from approach 1; $^b$ The values in parentheses obtained from approach 2 (see VI.c.3)
VII.d) Efficiency of lignin depolymerization

The efficiency of lignin depolymerization (E) is defined as being the ratio of the experimental mass yield \( (R(X)_{\text{exp}} = \frac{\text{wt of product } X}{\text{wt of lignin}}) \) of a mono-aromatic product X over the theoretic mass yield \( R(X)_{\text{theo}} \) in mono-aromatic X.

\[
E = \frac{R(X)_{\text{exp}}}{R(X)_{\text{theo}}} \times 100
\]

In the case of hardwood, the efficiency is the sum of the efficiencies of \textbf{10G} and \textbf{10S} weighted by their occurrences in native lignin which are 0.3 and 0.7, respectively:

\[
E = 0.3 \times \frac{R(10G)_{\text{exp}}}{R(10G)_{\text{theo}}} + 0.7 \times \frac{R(10S)_{\text{exp}}}{R(10S)_{\text{theo}}}
\]

The above formula is obtained as followed:

\[n = \text{molar number (mol)}\]

\[n(\text{lignol}) \times \tau(N)_H = \text{theoretical number of lignol (maximum available)}\]

\[n(\text{lignol}) = \frac{m(\text{lignin})}{\text{average } M_w \text{ (monolignol)}}\]

\[M_w(x) = \text{molar weight (g.mol}^{-1}\text{) of compound X}\]

\[G \text{ and } S = \text{monolignol units}\]

\[m(X) = \text{weight in compound X(g)}\]

The molar efficiency is:

\[
E = \frac{n(10G)_{\text{exp}} + n(10S)_{\text{exp}}}{n(\text{lignol}) \times \tau(N)}
\]

\[
E = \frac{m(10G)_{\text{exp}}/M_w(10G)}{\tau(N) \times m(\text{lignin})/M_w(\text{lignol})} + \frac{m(10S)_{\text{exp}}/M_w(10S)}{\tau(N) \times m(\text{lignin})/M_w(\text{lignol})}
\]
\[ E = \frac{m(10G)\exp \times Mw(\text{lignol})}{\tau(N) \times m(\text{lignin}) \times Mw(10G)} + \frac{m(10S)\exp \times Mw(\text{lignol})}{\tau(N) \times m(\text{lignin}) \times Mw(10S)} \]

As we know:

\[ R(10G)\exp = \frac{m(10G)\exp}{m(\text{lignin})} \quad \text{and} \quad R(10S)\exp = \frac{m(10S)\exp}{m(\text{lignin})} \]

So, the efficiency can be expressed,

\[ E = R(10G)\exp \times \frac{Mw(\text{lignin})}{\tau(N) \times Mw(10G)} + R(10S)\exp \times \frac{Mw(\text{lignin})}{\tau(N) \times Mw(10S)} \]

\[ E = R(10G)\exp \times \frac{0.3 \times Mw(G) + 0.7 \times Mw(S)}{\tau(N) \times M(10G)} + R(10S)\exp \times \frac{0.3 \times Mw(G) + 0.7 \times Mw(S)}{\tau(N) \times M(10S)} \]

And we know:

\[ R(10G) = \frac{\tau(N) \times 0.3 \times M(10G)}{0.3 \times Mw(G) + 0.7 \times Mw(S)} \quad \text{and} \quad R(10S) = \frac{\tau(N) \times 0.7 \times M(10S)}{0.3 \times Mw(G) + 0.7 \times Mw(S)} \]

\[ \frac{0.3 \times Mw(G) + 0.7 \times Mw(S)}{\tau(N) \times M(10G)} = \frac{0.3}{R(10G)} \quad \text{and} \quad \frac{0.3 \times Mw(G) + 0.7 \times Mw(S)}{\tau(N) \times M(10S)} = \frac{0.7}{R(10S)} \]

Then, the formula is:

\[ E = 0.3 \times \frac{R(10G)\exp}{R(10G)\text{theo}} + 0.7 \times \frac{R(10S)\exp}{R(10S)\text{theo}} \]
Table 10: Experimental results and efficiency calculations for depolymerization of lignins

<table>
<thead>
<tr>
<th>Species</th>
<th>Product</th>
<th>wt% of silylated product/lignin weight</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>R(10G) Experimental (wt%)</td>
<td>R(10G) Theoretical (wt%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>R(10G)</td>
<td>R(10G)</td>
</tr>
<tr>
<td><strong>Softwood</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Industrial pine</td>
<td>10G</td>
<td>120</td>
<td>55 (120)(^a)</td>
<td></td>
</tr>
<tr>
<td>Norway spruce</td>
<td>10G</td>
<td>81</td>
<td>45 (91)</td>
<td></td>
</tr>
<tr>
<td>Lebanese cedar</td>
<td>10G</td>
<td>69</td>
<td>64 (120)</td>
<td></td>
</tr>
<tr>
<td>Pacific cedar</td>
<td>10G</td>
<td>11</td>
<td>27 (27)</td>
<td></td>
</tr>
<tr>
<td><strong>Hardwood</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Evergreen oak</td>
<td>10G / 10S</td>
<td>32 / 130</td>
<td>25 / 74 (42 / 124)(^b)</td>
<td></td>
</tr>
<tr>
<td>Hydrid plane</td>
<td>10G / 10S</td>
<td>36 / 94</td>
<td>24 / 70 (42 / 124)</td>
<td></td>
</tr>
<tr>
<td>Common beech</td>
<td>10G / 10S</td>
<td>42 / 83</td>
<td>21 / 61 (42 / 124)</td>
<td></td>
</tr>
<tr>
<td>Black poplar</td>
<td>10G / 10S</td>
<td>20 / 80</td>
<td>23 / 66 (42 / 124)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)The values in parentheses represent calculations based on the relative percentage of \(\beta\)-O-4 in lignin (\(\beta\)-O-4′ + \(\beta\)-\(\beta\)′ + \(\beta\)-5′ + \(\beta\)-1′ = 100)

\(^b\)
VII.e) Global efficiency extraction of lignin monomers from wood

Considering that the maximum theoretical yield of extracted lignin by the Formacell process is 25 wt% of the initial weight of wood \(^7\) (Weight of lignin on the initial weight of wood (%wt)), thus the efficiency of the extraction of industrial pine lignin is \(8/25 = 32\%\). (8 wt% of lignin have been extracted from the wood see Table 11).

Considering that the yields of purification and hydrolysis of compounds \(\text{10G}\) are respectively 70 % and 84 %, then the global efficiency is evaluated to 18.8%.

The same approach is applied for evergreen oak lignin.

<table>
<thead>
<tr>
<th>Species</th>
<th>Product</th>
<th>wt% lignin extracted by the Formacell process/wood weight</th>
<th>wt% of silylated product/lignin weight</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Experimental (wt%)</td>
<td>Theoretical (wt%)</td>
</tr>
<tr>
<td>Industrial pine</td>
<td>10G</td>
<td>8</td>
<td>25</td>
</tr>
<tr>
<td>Evergreen Oak</td>
<td>10G/10S</td>
<td>10</td>
<td>25</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>Product</th>
<th>wt% of silylated product after purification/lignin weight</th>
<th>wt% hydrolyzed product/lignin weight</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Experimental (wt%)</td>
<td>Theoretical (wt%)</td>
</tr>
<tr>
<td>Industrial Pine</td>
<td>10G</td>
<td>96</td>
<td>120</td>
</tr>
<tr>
<td>Evergreen oak</td>
<td>10G/10S</td>
<td>112</td>
<td>130</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>Product</th>
<th>Global Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial Pine</td>
<td>10G</td>
<td>21.5 ((0.84 \times 0.8 \times 1 \times 0.32))</td>
</tr>
<tr>
<td>Evergreen Oak</td>
<td>10G/10S</td>
<td>31.0 ((0.94 \times 0.86 \times 0.96 \times 0.40))</td>
</tr>
</tbody>
</table>
VII.f) Discussions

VII.f.1) Efficiencies based on β-O-4 content per 100 aromatics

Table 12: Calculations of Efficiencies based on β-O-4 linkages per 100 aromatics

<table>
<thead>
<tr>
<th>Column</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin source</td>
<td>β-O-4’ content (per 100 aromatics)</td>
<td>Yield 10G/10S (%)</td>
<td>Theoretical yield (%)</td>
<td>Eff(b) Based on β-O-4 content in lignin per 100 aromatics</td>
</tr>
<tr>
<td>Industrial Pine</td>
<td>35.1</td>
<td>46 %</td>
<td>21 %</td>
<td>&gt; 100 %</td>
</tr>
<tr>
<td>Norway Spruce</td>
<td>20.2</td>
<td>31 %</td>
<td>17 %</td>
<td>&gt; 100 %</td>
</tr>
<tr>
<td>Lebanese Cedar</td>
<td>38.9</td>
<td>27 %</td>
<td>25 %</td>
<td>&gt; 100 %</td>
</tr>
<tr>
<td>Pacific Red Cedar</td>
<td>21</td>
<td>4 %</td>
<td>10 %</td>
<td>42 %</td>
</tr>
<tr>
<td>Evergreen Oak</td>
<td>48.1</td>
<td>58 %</td>
<td>36 %</td>
<td>&gt; 100 %</td>
</tr>
<tr>
<td>Hybrid Plane</td>
<td>42.5</td>
<td>47 %</td>
<td>30 %</td>
<td>&gt; 100 %</td>
</tr>
<tr>
<td>Common Beech</td>
<td>43.7</td>
<td>46 %</td>
<td>32 %</td>
<td>&gt; 100 %</td>
</tr>
<tr>
<td>Black Poplar</td>
<td>47.2</td>
<td>36 %</td>
<td>34 %</td>
<td>&gt; 100 %</td>
</tr>
</tbody>
</table>

The proportion of β-O-4 in lignin was first estimated with respect to the quantity of aromatics moieties. In agreement with the literature, hardwood lignin contains a higher proportion of β-O-4 linkages (42.5 to 48.1 per 100 aromatics) than softwood lignin (20.2 to 35.1 per 100 aromatics). Such values led to low theoretical maximum yield (10-36 %, Table 12, column 3) and consequently outliers of efficiencies (>100 %, Table 12, Column 4). These outliers could be caused by the underestimation of cleavable interunit linkages of lignin because β-O-4 linkages are the sole linkages observable. The uncertainty of the integration of HSQC NMR spectra could also contribute to these excessive values because of the different T2 relaxation rate and the $^1J_{CH}$ spin coupling of the distinct nucleus (e.g. the aromatic C-H and aliphatic C-H bond).
VII.f.2) Efficiencies based on the relative proportion of β-O-4 linkages

Table 13: Calculations of Efficiencies based on the relative proportion of β-O-4 linkages

<table>
<thead>
<tr>
<th>Lignin source</th>
<th>β-O-4’ content</th>
<th>Yield ( \frac{10G}{10S} ) (%)</th>
<th>Theoretical yield (%)</th>
<th>Eff(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial Pine</td>
<td>63 %</td>
<td>46 %</td>
<td>46 %</td>
<td>100 %</td>
</tr>
<tr>
<td>Norway Spruce</td>
<td>46 %</td>
<td>31 %</td>
<td>35 %</td>
<td>89 %</td>
</tr>
<tr>
<td>Lebanese Cedar</td>
<td>59 %</td>
<td>27 %</td>
<td>46 %</td>
<td>58 %</td>
</tr>
<tr>
<td>Pacific Red Cedar</td>
<td>20 %</td>
<td>4 %</td>
<td>10 %</td>
<td>42 %</td>
</tr>
<tr>
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<td>36 %</td>
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In this study, we focused on the main linkages present in lignins. As spirodienone and dibenzodioxocin linkages are not observed or not sufficiently resolved in the 2D HSQC NMR spectra, we only considered β-O-4, resinol and phenylcoumaran structures which represent 70-90% of the linkages in lignin. The undetected linkages in HSQC NMR are those of non-cleavable linkages (C-C bonds: 4-O-5’, 5-5, etc.) and also of cleavable linkages (C-O bonds: α-O-4, dibenzodioxocin, …). As all of the undetected linkages are minor in lignin, the percentage of cleavable linkages in lignin (i.e. aryl-O-alkyl bonds) is approximated to the percentage of β-O-4 linkages determined by semi quantitative HSQC NMR method.

These calculations do not take into account of the carbohydrates content in lignin neither the carbohydrates-lignin complexes (LCC). Yet, LCC should affect the efficiencies since the yield of monoaromatic products is over-estimated. Interestingly, correlations between a decrease in efficiencies and the lignin-carbohydrates complexes (LCC) have been observed. For instance, HSQC NMR experiments reveal higher contents of carbohydrates in hybrid plane lignin than in evergreen oak lignin. This results in lower efficiencies for the former lignin depolymerization than those of the latter.
VIII) Hydrosilylating depolymerization of lignin: comparison of the two catalysts B(C_6F_5)_3 and [1][B(C_6F_5)_4]

VIII.a) Comparison between B(C_6F_5)_3 and [1][B(C_6F_5)_4] on lignin models

Scheme 7: Comparison between B(C_6F_5)_3 and [1][B(C_6F_5)_4] on lignin models
VIII.b) Comparison between B(C₆F₅)₃ and [I][B(C₆F₅)₄] on wood lignins

Comparison of yield and efficiency between B(C₆F₅)₃ and [I][B(C₆F₅)₄]

Table 14: Comparison of yield and efficiency between B(C₆F₅)₃ and [I][B(C₆F₅)₄]

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<td>Black poplar</td>
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* Values obtained from data reported in reference 7a
Calculation of TONs and TOFs of B(C₆F₅)₃ and [1][B(C₆F₅)₄]

The catalytic activity and properties of B(C₆F₅)₃ and [1][B(C₆F₅)₄] are compared for evaluating their respective optimal conditions in the depolymerization of lignin with hydrosilanes. B(C₆F₅)₃ performs best in the presence of Et₃SiH in CH₂Cl₂ at room temperature while [1][B(C₆F₅)₄] depolymerizes lignin at higher temperature (70°C) with Et₃SiH in C₆H₅Cl. This allows an evaluation of the TONs and TOFs and a quantification of the robustness and efficiency of the catalytic systems. In fact, a strict comparison would need operating systems within similar conditions. We have thus considered the two catalysts within the same conditions of depolymerization for industrial pine lignin (catalytic loading, temperature, solvent, etc.).

In our study, catalytic loadings, turn over numbers (TONs), and turn-over frequencies (TOFs) were calculated as described below:

Catalytic loadings were evaluated by considering the exact number of aromatic units in the lignin sample to provide the most realistic TONs and TOFs. It has been previously reported that lignin is an aromatic oligomers involving:7a

- For industrial pine lignin (softwood) : an average number of 5 aromatic units with a mean molecular weight of 1099 g/mol⁻¹.
- For evergreen oak lignin (hardwood) : an average number of 4 aromatic units with a mean molecular weight of 835 g/mol⁻¹.

Catalytic loadings were evaluated considering the number of aromatic units in lignin while TONs and TOFs require a calculation based on the products i.e. the aromatic groups extracted from the depolymerization of lignin.

For industrial pine lignin, considering its average molecular weight (Mₐ = 1099 g.mol⁻¹) and its polymerization degree of 5, the catalytic loading in [1][B(C₆F₅)₄] corresponds to 1.6 mol% with respect to the molar quantity of aromatic units.
For example: For 110 mg of softwood lignin (0.1 mmol), 0.5 mmol of G aromatic units (Mw = 196.2 g.mol⁻¹) can be theoretically extracted. So 10 wt% of [1][B(C₆F₅)₄] corresponds with ca 1.6 mol% (M_w = 1351 g.mol⁻¹). With the same method, we can deduce that 15 wt% of B(C₆F₅)₃ (M_w = 511.98 g.mol⁻¹) corresponds with ca 6.4 mol% ((0.110 x 0.15)/(511.98 x 5)).

For industrial pine lignin, for which a depolymerization efficiency of 100 % is obtained, the yield of depolymerization is maximum, and for 110 mg (0.1 mmol) lignin (theoretical molar yield τ(5) = 46 %) is equal to 0.46 x 0.1 x 5 = 0.23 mmol in G lignol derivative. This later values (0.23 mmol) with a catalyst charge in [1][B(C₆F₅)₄] (10 wt%, 0.00814 mmol) gives a TON of 28.4. With catalyst B(C₆F₅)₃ (15wt%, 0.0323mmol) which led to an efficiency of 43%, 0.11 mmol (0.46 x 0.43 x 0.5) of G units is obtained giving a TON of 3.1.

\[
\text{TON([1][B(C₆F₅)₄])} = \frac{0.23}{0.0081} = 28.4
\]
\[
\text{TON(B(C₆F₅)₃)} = \frac{0.1}{0.0323} = 3.1
\]

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Comparison of the catalytic activity of B(C₆F₅)₃ and [1][B(C₆F₅)₄] within similar conditions

For a proper comparison of the stabilities and activities of the two B(C₆F₅)₃/hydrosilane and [1][B(C₆F₅)₄]/hydrosilane systems, we carried out catalytic experiments under the optimal conditions, e.g. 70°C in chlorobenzene (scheme 8).

In an NMR tube equipped with a J. Young valve under inert atmosphere, Et₃SiH (120 mg, 1.1 mmol, 300 wt% from lignin) was added to 40 mg of lignin (~0.04 mmol lignin (Mₙ= 980 g/mole, N_aranomic = 5), ~0.2 mmol of aromatic units) and [1][B(C₆F₅)₄] (4.0 mg, 2.9 µmol, 10 wt%) in C₆H₅Cl (3 ml). The mixture was stirred at room temperature until complete dissolution of the starting materials and the end of the gas release. After 20 min, all the solid were dissolved and the initial red-orange solution turned brown. The clear solution was then heated at 70°C for 48 h with stirring. Yields in mono aromatic(s) were determined by GC-MS analysis.

**Scheme 8:** Comparison between B(C₆F₅)₃ and [1][B(C₆F₅)₄] in similar conditions
IX) NMR Spectra

**Figure 14:** $^1$H NMR spectra of the triethyl(phenoxyl)silane 3a in CD$_2$Cl$_2$
Figure 15: $^{13}$C NMR spectra of the triethyl(phenoxyl)silane 3a in CD$_2$Cl$_2$
Figure 16: $^1$H NMR spectra of the 1,2-bis((triethylsilyl)oxy)benzene 3b in CD$_2$Cl$_2$
Figure 18: $^{13}$C NMR spectra of the 1,2-bis((triethysilyl)oxy)benzene 3b in CD$_2$Cl$_2$
Figure 19. $^1$H NMR spectra of the (4-benzylphenoxy)triethyilsilane $p$-4 in CD$_2$Cl$_2$
Figure 20: $^{13}$C NMR spectra of the (4-benzylphenoxy)triethylsilane $p$-4 in CD$_2$Cl$_2$
Figure 21: $^1$H NMR spectra of the (2-benzylphenoxy)triethylsilane $o$-4 in CD$_2$Cl$_2$
Figure 22: $^{13}$C NMR spectra of the (2-benzylphenoxy)triethylsilane o-4 in CD$_2$Cl$_2$
Fragmentation:

$m/z = 133 : \text{Et}_3\text{SiOH}^+$

$m/z = 115 : \text{Et}_3\text{Si}^+$

$m/z = 338 : \text{contaminant} = \text{erucamide}$
Figure 23: $^1$H NMR spectra of the triethyl(phenylethoxy)silane 6 in CD$_2$Cl$_2$
Figure 24: $^{13}$C NMR spectra of the triethyl(phenylethoxy)silane 6 in CD$_2$Cl$_2$
Figure 25: $^1$H NMR spectra of the compound 10G in CD$_2$Cl$_2$
Figure 26: $^{13}$C NMR spectra of the compound 10G in CD$_2$Cl$_2$
Figure 27: $^1$H NMR spectra of the compound 10S in CD$_2$Cl$_2$
Figure 28: $^{13}$C NMR spectra of the compound 10S in CD$_2$Cl$_2$
Figure 29: $^1$H NMR spectra of the compound 11S in CD$_2$Cl$_2$
Figure 30: $^{13}$C NMR spectra of the compound 11S in CD$_2$Cl$_2$
X) Mechanistic investigations from DFT calculations

The M06-2X functional was used to optimize the equilibrium molecular structure of the model compounds (obtained by replacing SiEt₃ groups with SiMe₃). The 6-31+G* basis set was used for carbon, hydrogen, oxygen and silicon. All geometries were fully optimized without any symmetry constrains. Harmonic vibrational analyses were performed to characterize the structures as minima or transition states. Free energies were calculated within the harmonic approximation for vibrational frequencies. All calculations were fully optimized with solvents effects (PCM = chlorobenzene). All calculations were carried out using the Gaussian09 suite of codes and NBO6.

Computed pathways

**Scheme 9:** Computed pathways for the conversion of 5a⁺ and 5a''⁺ to 6a⁺ and 6a''⁺
**Scheme 10:** Computed pathways for the conversion of MeO-5a\(^+\) and MeO-5a\(^{++}\) to MeO-6a\(^+\), MeO-6a\(^{++}\)
Computed structures

![Chemical Structure Image]

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Sum of electronic and thermal Free Energies= -1509.244688 Hartree

Lowest Frequencies: 460.5262 cm⁻¹
28.3989 cm⁻¹
36.7053 cm⁻¹
Sum of electronic and zero-point Energies = \(-1509.217110\) Hartree

Sum of electronic and thermal Energies = \(-1509.189523\) Hartree

Sum of electronic and thermal Enthalpies = \(-1509.188579\) Hartree

Sum of electronic and thermal Free Energies = \(-1509.273454\) Hartree

Lowest Frequency: 31.669 cm\(^{-1}\)
Sum of electronic and zero-point Energies= -615.797271 Hartree
Sum of electronic and thermal Energies= -615.784742 Hartree
Sum of electronic and thermal Enthalpies= -615.783798 Hartree
Sum of electronic and thermal Free Energies= -615.840179 Hartree

Lowest Frequency: 2.8862 cm⁻¹
-1.722276000000  1.964897000000 -0.532654000000
H  -2.467549000000  1.823866000000 0.258118000000
H   -1.769576000000  3.010718000000 -0.858670000000
H  -2.007511000000  1.335769000000 -1.383376000000
C  0.502156000000  2.705732000000 1.465858000000
H  -0.202261000000  2.643412000000 2.302725000000
H  1.499976000000  2.457137000000 1.843678000000
H  0.520547000000  3.743985000000 1.115412000000
C  1.222998000000  1.633519000000 -1.338686000000
H  2.235413000000  1.374750000000 -1.008184000000
H  0.945296000000  0.946962000000 -2.147783000000
H  1.253164000000  2.645676000000 -1.759122000000
O  0.000000000000  0.000000000000 0.717165000000

Si  0.000000000000  1.544470000000  0.085816000000
Si -1.544470000000  0.085816000000  0.000000000000
C  -0.520547000000  3.743985000000  1.115412000000
C  -2.007511000000  1.335769000000 -1.383376000000
C  -0.202261000000  2.643412000000  2.302725000000
C  1.499976000000  2.457137000000  1.843678000000
C  0.520547000000  3.743985000000  1.115412000000
C  1.222998000000  1.633519000000 -1.338686000000
C  2.235413000000  1.374750000000 -1.008184000000
C  0.945296000000  0.946962000000 -2.147783000000
C  1.253164000000  2.645676000000 -1.759122000000
H  0.520547000000  3.743985000000  1.115412000000
H  1.222998000000  1.633519000000 -1.338686000000
H  2.235413000000  1.374750000000 -1.008184000000
H  0.945296000000  0.946962000000 -2.147783000000
H  1.253164000000  2.645676000000 -1.759122000000
H  0.000000000000  0.000000000000  0.717165000000

Sum of electronic and zero-point Energies= -615.797271 Hartree
Sum of electronic and thermal Energies= -615.784742 Hartree
Sum of electronic and thermal Enthalpies= -615.783798 Hartree
Sum of electronic and thermal Free Energies= -615.840179 Hartree

Lowest Frequency: 32.4296 cm⁻¹
\[
\begin{align*}
&\text{Sum of electronic and zero-point Energies} = -1509.19603 \text{ Hartree} \\
&\text{Sum of electronic and thermal Energies} = -1509.167726 \text{ Hartree} \\
&\text{Sum of electronic and thermal Enthalpies} = -1509.166782 \text{ Hartree} \\
&\text{Sum of electronic and thermal Free Energies} = -1509.253686 \text{ Hartree} \\
&\text{Lowest Frequencies: } -148.4961 \text{ cm}^{-1} \\
&\quad 27.0383 \text{ cm}^{-1} \\
&\quad 37.3375 \text{ cm}^{-1}
\end{align*}
\]
Sum of electronic and zero-point Energies= -1738.108854 Hartree
Sum of electronic and thermal Energies= -1738.074783 Hartree
Sum of electronic and thermal Enthalpies= -1738.073839 Hartree
Sum of electronic and thermal Free Energies= -1738.176013 Hartree

Lowest Frequency: 9.6318 cm⁻¹
Sum of electronic and zero-point Energies= -1738.082123 Hartree
Sum of electronic and thermal Energies= -1738.047476 Hartree
Sum of electronic and thermal Enthalpies= -1738.046532 Hartree
Sum of electronic and thermal Free Energies= -1738.149804 Hartree

Lowest Frequency: 510.9628 cm⁻¹
13.7989 cm⁻¹
25.5911 cm⁻¹
Sum of electronic and zero-point Energies= -1738.108662 Hartree
Sum of electronic and thermal Energies= -1738.075993 Hartree
Sum of electronic and thermal Enthalpies= -1738.075049 Hartree
Sum of electronic and thermal Free Energies= -1738.170594 Hartree

Lowest Frequency: 27.2052 cm⁻¹
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<th></th>
<th>X</th>
<th>Y</th>
<th>Z</th>
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<td>0.374776</td>
<td>-1.112461</td>
<td>1.061563</td>
<td>0.034689</td>
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<td>C</td>
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<td>-0.119600</td>
<td>1.249955</td>
<td>1.750321</td>
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<tr>
<td>C</td>
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<td>0.448014</td>
<td>1.299387</td>
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<tr>
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<td>0.697091</td>
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<td>-2.303193</td>
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<td>-2.030621</td>
<td>0.650856</td>
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Sum of electronic and zero-point Energies = -844.703174 Hartree
Sum of electronic and thermal Energies = -844.685258 Hartree
Sum of electronic and thermal Enthalpies = -844.684313 Hartree
Sum of electronic and thermal Free Energies = -844.751570 Hartree

Lowest Frequency: 22.4212 cm$^{-1}$
Sum of electronic and zero-point Energies= -1738.094177 Hartree
Sum of electronic and thermal Energies= -1738.059842 Hartree
Sum of electronic and thermal Enthalpies= -1738.060786 Hartree
Sum of electronic and thermal Free Energies= -1738.157916 Hartree
Lowest Frequencies: -271.7288 cm\(^{-1}\)
26.2879 cm\(^{-1}\)
32.7071 cm\(^{-1}\)
XI) GC-MS calibration curves

GC conditions for the analysis of 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); Ion source temp.: 200 °C; Interface temp.: 250 °C; Detector voltage: 0.8 kV

XI.a) Calibration curve of compound 3a

\[ Y = 16477 \times 241.39x \]
\[ R^{2} = 0.99 \]
XI.b) Calibration curve of compound 3b

XI.c) Calibration curve of compound 6
XI.d) Calibration curve of compound 10G

y = 19 315 298,79x
R² = 1,00

XI.e) Calibration curve of compound 10S

y = 77 585 940,03x² + 11 474 305,36x
R² = 1,00
XI.f) Calibration curve of compound 11G

\[ y = 14184.588.48x \]
\[ R^2 = 1.00 \]

XI.g) Calibration curve of compound 11S

\[ y = 16378.669.70x \]
\[ R^2 = 0.97 \]


XII) References