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PAPER

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

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The first examples of reductive depolymerization of lignin are reported under metal-free conditions. Using hydrosilanes as reductants and $B(C_6F_5)_3$ as a Lewis acidic catalyst, wood lignin is efficiently converted to a narrow distribution of phenol derivatives, at room temperature. A three-step methodology based on the selection of the wood species and the lignin extraction method, followed by a convergent reductive depolymerization enables the production of four structurally defined aromatic compounds. The phenol products were successfully isolated in 7 to 24 wt% yield from lignin and 0.5 to 2.4 wt% yield from wood. The strategy is found robust and is applied to 15 different wood plants, including gymnosperm and angiosperm species. The efficiency of this novel methodology has been evaluated based on spectroscopic characterization of the lignin preparations and isolated yields of mono-aromatic products.

Broader context

Lignin represents the most abundant source of renewable aromatics. Yet, although the paper industry alone produces about 1.1 million tons of lignin each year, only <3 % integrate a value chain after transformation. Vanillin remains the main aromatic product derived from lignin with a low 0.3 wt% yield from wood. These limitations primarily derive from the complex and heterogeneous structure of lignin, which varies with the wood species, and the polymeric structure of lignin which relies on inert C–C and ether C–O bonds. Depolymerization methods applied so far in lignin conversion suffer from harsh reaction conditions and yield complex mixtures of products, from which isolation of pure products is an issue. To circumvent this issue, a novel catalytic reductive depolymerization strategy was developed to isolate for the first time four different aromatic products from lignin. This methodology reveals the importance of combining the selection of the plant species with the lignin extraction method and the depolymerisation method to control the nature, the purity and the yield of the final product.

Introduction

The production of organic chemical commodities relies heavily on fossil resources as more than 95 % of all organic chemicals currently derive from petrochemistry. The development of innovative synthetic methods utilizing renewable carbon feedstocks is thus attractive to improve the sustainability of this industrial sector.[1-7] In this context, CO_2 is the subject of increased attention, and novel catalytic transformations have been unveiled over the last decade to take advantage of this carbon waste for the formation of formic acid, methanol and chemicals.[8-12] Nonetheless, it is already foreseeable that the scope of products available from CO_2 will be mostly limited to

C_1-chemicals, complex compounds such as aromatics being more conveniently isolated from biomass waste, as an alternative carbon feedstock. Indeed, lignocellulose represents the main renewable source of aromatics and the depolymerization of lignin has been identified as a prominent challenge to produce bulk and fine chemicals in a sustainable manner.[13-17] Lignin is a complex polymer biosynthesized from propenyl-phenol derivatives, namely *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Fig. 1). The oxidative radical polymerization of these three monolignols is responsible for the highly heterogenous structure of lignin, which is characterized by a variety of stable C–O ether linkages and C–C bonds between propenyl-phenol units.[18, 19] In most plants, the β-O-4 linkage is predominant and this alkyl-aryl ether linkage results from the addition of the phenol group of one monolignol to the C_β–atom on the propyl chain of a second monolignol. While the α-O-4 or 4-O-5 linkages also bear ether functionalities, the β-β', 5-5' and β-1 linkages connect two monolignols *via* a C–C bond.[20-22] The isolation of

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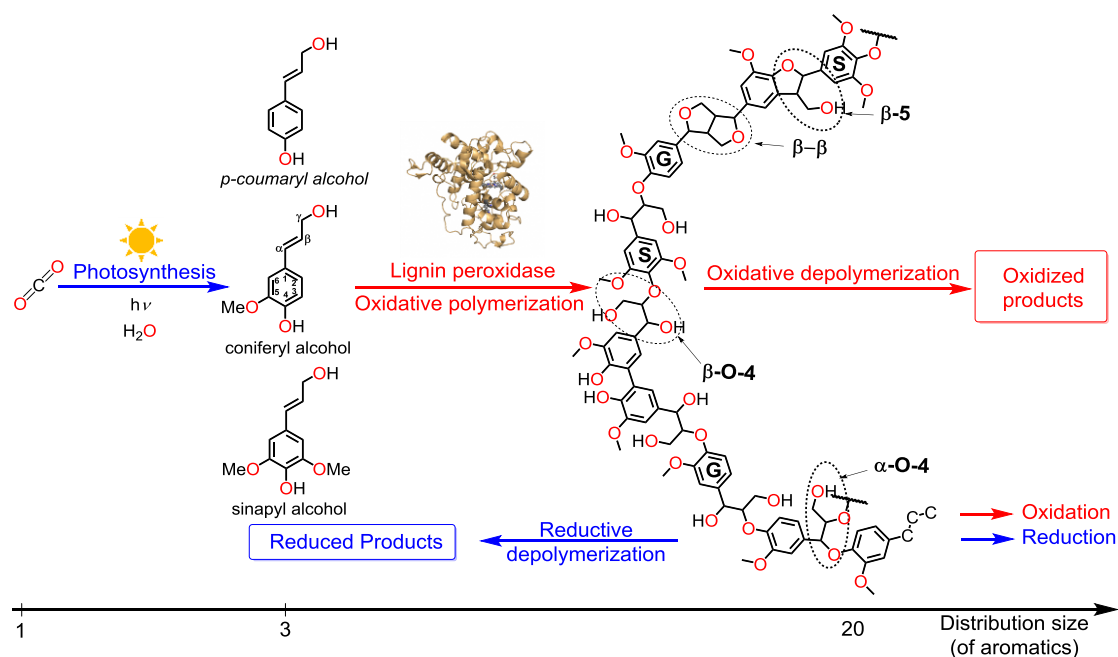   *Fax: (+33) 1.6908.6640; E–mail: thibault.cantat@cea.fr*

Fig. 1 Schematic representation of the distribution size of aromatic rings in monolignols, wood lignin and depolymerization products.

aromatic products from lignin is thus limited by the large distribution of aromatic rings, whose substitution patterns vary largely because of the low selectivity of lignin peroxidase polymerization and the presence of H, G and S residues (Fig. 1). In addition, efficient depolymerization methods must cleave strong C–O and/or C–C bonds and tolerate the large variability of lignin samples deriving from different types of plants.[23-25]

The depolymerization of lignin under oxidative conditions has been the focus of extensive efforts and recent successes have demonstrated the potential of this approach.[15, 26, 27] Markedly, Stahl and coworkers have developed an efficient oxidation method, under aerobic conditions, and the resulting oxidized lignin structure was depolymerized to low-molecular-mass aromatics in >60 wt%, using formic acid.[28] Nevertheless, the oxidation strategies applied so far in lignin conversion lack chemoselectivity and yield complex mixtures with a wide distribution of aromatics, from which isolation of well-defined chemicals is an issue (Fig. 1).

In contrast, we hypothesized that reduction chemistry could promote the depolymerization of lignin while converging the products to a narrow distribution, from which aromatics can be easily isolated in a pure form. By replacing C–O bonds with C–H bonds, deoxygenation reactions are indeed expected to cleave ether groups to low-molecular-mass products with a distribution size close to that of the monolignols (1-3) (Fig. 1). This approach yet suffers from the lack of efficient catalysts able to reduce ether linkages.[17, 29, 30] Interestingly, Westwood and coworkers explored the reduction of oxidized lignin models with stoichiometric amounts of zinc metal and the methodology, applied to organosolv lignin from birch sawdust, led to an isolable phenol product in 5 wt%/lignin wt.[31] In parallel, Wang, Xu and coworkers demonstrated that propylsyringol could be isolated from birch

lignin, using a catalyst based on nickel on activated charcoal (Ni/C) and alcohols as reductants, under harsh conditions (200 °C).[32] Homogeneous catalysts, able to access the reactive sites in lignin, are thus attractive to promote the reductive depolymerization of lignin, under mild conditions and with enhanced chemoselectivity.[33, 34] While the reductive cleavage of lignin model compounds was developed using ruthenium[35-39] and nickel-based[40-42] catalysts, few examples of lignin depolymerization are known, mostly because of catalyst deactivation by the impurities present in the lignin matrix or by coordination to lignin.[37, 43]

Herein, we disclose the first examples of the reductive depolymerization of lignin, extracted from softwood and hardwood, under metal-free conditions. Using hydrosilanes as reductants, propylphenol derivatives were successfully isolated in good 0.5 to 2.4 wt% yield from 15 different wood species (7 to 24 wt% from lignin), at room temperature.

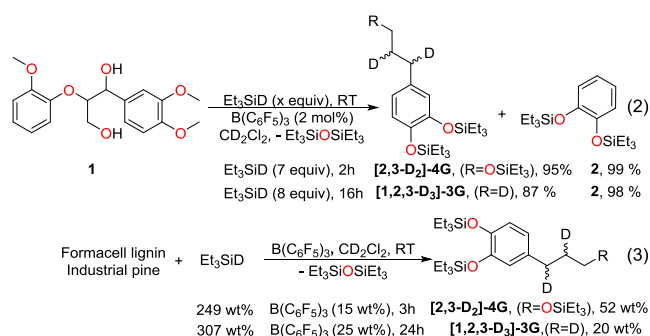## Results and discussion

Hydrosilanes are mild reductants and their slightly polar Si–H bond can be activated at low temperature with molecular organometallic or organic catalysts to reduce C–O bonds.[44-46] For instance, $B(C_6F_5)_3$ is a potent Lewis acid, able to promote the reduction of a variety of
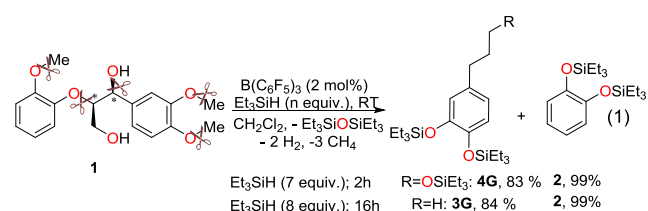
Scheme 1 Reductive cleavage of β-O-4 model **1** with Et_3SiH and catalyst $B(C_6F_5)_3$.

carbonyl derivatives, including ketones, esters, amides and recently carbonates under mild conditions.[45, 47-52, 53-55] Importantly, it can also serve as catalyst in the hydrosilylation of alcohols and alkyl-ethers and we have recently shown that $B(C_6F_5)_3$ is able to cleave the β-O-4 and α-O-4 linkages in simple lignin models, to yield 4-propylphenol derivatives.[56] The reaction is chemoselective and diaryl-ethers and C–C bonds are left untouched under these conditions. For example, treatment of **1**, a model of β-O-4 linkage with a guaiacyl residue, with 8 equiv. Et_3SiH leads to the formation of two catechol derivatives **2** and **3G**, in the presence of 2 mol% $B(C_6F_5)_3$ after 16 h at RT (Scheme 1). Interestingly, the primary silylether **4G** can be obtained in >80 % yield with a default of hydrosilane (7 equiv. Et_3SiH) after 2 h at RT. The production of **2**, **3G** and **4G** results from the reductive cleavage of the O–H and C_{alkyl}–O bonds in **1**, promoted by the $B(C_6F_5)_3$/Et_3SiH system. Unlike simpler lignin models,[56] no semi-pinacol rearrangement is observed with the guaiacyl residue and this fact was confirmed by the formation of D-labelled **[1,2-D_2]-4G** and **[1,2,3-D_2]-3G** from the reaction between **1** and Et_3SiD (Eq. 2 in Scheme 2 and SI).

Fig. 2 Room temperature depolymerization of black poplar lignin with $B(C_6F_5)_3$/Et_3SiH (Eq(4)). GC-MS chromatograms of the depolymerization residue of Formacell lignin from black poplar (A), and standards **3G** (B), **3S** (C), **4G** (D) and **4S** (E) synthesized from petrochemical raw materials.

Scheme 2 Reductive cleavage of β-O-4 model **1** with Et_3SiD and catalyst $B(C_6F_5)_3$ (Eq. 2). Reductive depolymerization of Formacell lignin from industrial pine lignin with Et_3SiD and catalyst $B(C_6F_5)_3$ (Eq. 3).

These results suggest that the depolymerization of lignin could be undertaken under hydrosilylation conditions *via* reductive cleavage of the β-O-4 and α-O-4 linkages. To test this hypothesis, hardwood lignin was first extracted from chunks of black poplar using an organosolv process Formacell (*vide infra*)[57, 58], so as to eliminate the cellulose and hemicellulose parts of the wood cells. The resulting lignin preparation was then reacted with 276 wt% Et_3SiH in CH_2Cl_2 at room temperature (RT), in the presence of 25 wt% $B(C_6F_5)_3$ (Eq. 4 in Fig. 2). Based on simple estimations, these conditions correspond to a catalytic loading of 10 mol% with 5 equiv. Et_3SiH with respect to the molar quantity of aromatic units in the lignin preparation (see SI). Within 3 h, the lignin material was completely dissolved in the reaction medium to afford a brown solution which was analysed by GC/MS. As depicted in Fig. 2, a small distribution of low-molecular-mass products is obtained from the depolymerization of lignin. Formation of the siloxane by-product $Et_3SiOSiEt_3$ confirms the successful deoxygenation of the starting lignin material. The chromatogram also shows the formation of 4 different mono-aromatic products in 9–34 wt%/lignin wt. Two of these products correspond to compounds **3G** and **4G** obtained from
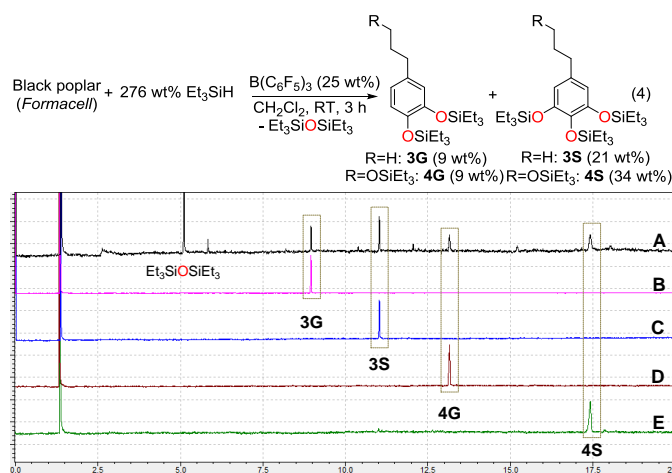
the hydrosilylation of model **1**. Hardwood lignin generally features guaiacyl (G) and sinapyl (S) residues because its biosynthesis relies on coniferyl and sinapyl alcohols, with ratios varying with the plant type.[18, 19] As such, the sinapyl derivatives **3S** and **4S** are also expected to form upon reductive depolymerization of black poplar lignin. Authentic samples of **3S** and **4S** were synthesized from petrochemical raw materials (see SI), thereby validating the formation of **3S** and **4S** in the reduction of lignin (Fig. 2). Whereas previous reductive depolymerization methods rely on the use of metal catalysts working at elevated temperature (>150 °C) or stoichiometric amounts of low valent metals as reductants, the formation of **3G**, **3S**, **4G** and **4S** represents the first example of reductive depolymerization of lignin under metal-free conditions. It likely results from the reductive cleavage of the β-O-4 and α-O-4 linkages, thereby supporting the possible transposition of the hydrosilylation of model **1** to the successful depolymerization of hardwood lignin. Interestingly, formation of silylethers **4G** and **4S** indicates that the partial reduction of the β-O-4 and α-O-4 linkages can be promoted in lignin, to preserve functional chemical groups. Quantitatively, 19 wt% of lignin is converted to the mono-aromatics **3G**, **3S**, **4G** and **4S** while the remaining 81 wt% presumably afford poly-aromatic compounds, because the β-β', 5-5', β-1 and β-5 linkages can be modified, yet not cleaved with the $B(C_6F_5)_3$/Et_3SiH system. These figures roughly represent a 25 % molar yield to mono-aromatics. Notably, no
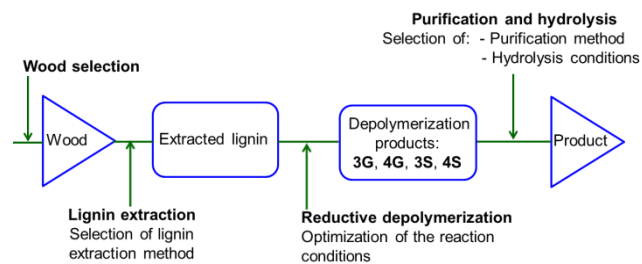

Fig. 3 Convergent reductive depolymerization strategy enabling the formation of pure mono-aromatic products from wood.

product derived from the reduction of the H residue was detected.

As hypothesized, the reductive depolymerization of lignin carried out in Eq. 4 affords a small distribution of 4 mono-aromatic products. The selective formation of **3G**, **3S**, **4G** and **4S** was next sought after to avoid problematic separation procedures. As depicted in Fig. 3, different parameters govern the products composition. First, the wood species imposes the H/G/S ratio in the lignin matrix and four types have been unveiled based on the classification of lignin (based on a chemical approach), namely G, GS, HGS and HG.[59] Previous studies have established that, while gymnosperm plants primarily feature guaiacyl (G) residues, angiosperm species present a higher component of sinapyl (S) units. Additionally, the wood species could be advantageously selected so as to maximize the amount of lignin present in the lignocellulose matrix and the occurrence of reactive β-O-4 and α-O-4 linkages (which averages 50 to 60 % in wood lignin). Secondly, the extraction method utilized to separate lignin from cellulose and hemicellulose strongly influences the chemical properties of the lignin starting material, such as its solubility in different solvents, its degree of polymerization (DP) and the nature of the linkages. Changing the chemical properties of the lignin material strongly alter its behavior regarding to the depolymerization method. Finally, as derived from the reaction chemistry of the lignin models, the depolymerization step itself controls the reduction of lignin and longer reaction times in the presence of an excess of hydrosilane should favor the formation of reduced 4-propylphenol derivatives **3G** and **3S** over **4G** and **4S**. Based on an integration of these different parameters, the selective formation of **3G** was first explored (Fig. 4).
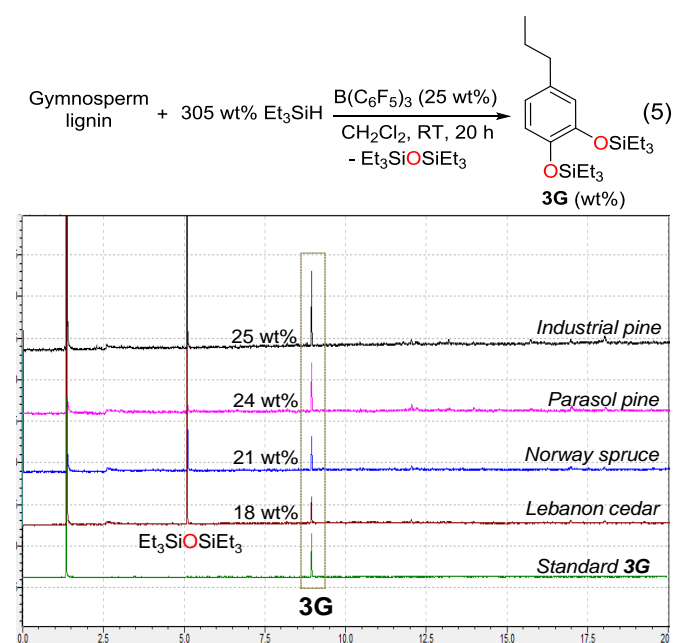
$$\text{Gymnosperm lignin} + 305\ wt\%\ Et_3SiH \xrightarrow[\substack{CH_2Cl_2,\ RT,\ 20\ h \\ -\ Et_3SiOSiEt_3}]{B(C_6F_5)_3\ (25\ wt\%)} \quad \mathbf{3G}\ (wt\%) \quad (5)$$

Fig. 4 Room temperature depolymerization of gymnosperm lignin with B(C₆F₅)₃/Et₃SiH to **3G** (Eq. 5). GC-MS chromatograms of the depolymerization residue of Formacell lignin from industrial pine, parasol pine, Norway spruce, Lebanon cedar and standard **3G** synthesized from petrochemical raw materials.
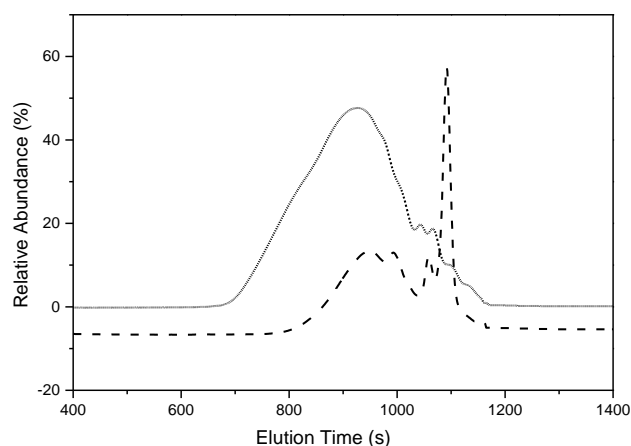
Fig. 5 SEC chromatograms of parasol pine lignin extracted with Formacell process (dot line); the crude mixture after reductive depolymerization with 305 wt% Et₃SiH and 25 wt% B(C₆F₅)₃ (20 h at RT, in CH₂Cl₂) (dash line). According to fig. 5, number-average molecular weight M_n is decreasing from 952 g.mol^{-1} to 268 g.mol^{-1} after depolymerisation.

Because softwood lignin extracted from gymnosperm species features a prominent portion of G residues[60, 61], synthesis of **3G** was attempted with Nordmann fir, Norway spruce, parasol pine, Lebanon cedar and Pacific red cedar. Several pretreatment methods have been developed to separate lignin, hemicellulose and cellulose in wood. The sulfite and Kraft processes target the production of high quality cellulose for the pulp and paper industry and the resulting Kraft lignin[62] and lignosulfonates[63] are generated as by-products. Valorization of these lignin preparations is thus attractive. Nevertheless, because lignin is obtained under harsh and/or acidic conditions, the resulting polymeric structure is significantly altered from native lignin and features an increased proportion of C–C based linkages.[64] As a result, using Kraft or sulfite lignin, only negligible amounts of **3G** were obtained in the presence of 305 wt% Et₃SiH and 25 wt% B(C₆F₅)₃.[65] In contrast, extraction methods utilizing organic solvents (organosolv treatment) operate under milder conditions and they are known to preserve the native structure of lignin by reducing C–C coupling reactions. Using Formacell lignin[57, 58] extracted from Norway spruce (*Picea abies*) with formic acid, acetic acid and water, **3G** is formed in 21 wt% yield after 20 h at RT in the presence of 305 wt% Et₃SiH and 25 wt% B(C₆F₅)₃. Similarly, other wood species tested under these conditions afforded **3G** in 18-25 wt% yield (Fig. 4). Size Exclusion Chromatography (SEC) confirmed that organosolv lignin only contains a small proportion of low-molecular-mass fragments (Fig. 5). Notably, the efficiency of the reductive depolymerization is demonstrated by SEC analysis of the crude solution after hydrosilylation of lignin, which shows the conversion of longer chain fragments to di- and tri-aromatics, together with the formation of a narrow distribution of mono-aromatic products. Additionally, two dimensional HSQC NMR spectroscopy revealed that the β-O-4 linkages (only G residues) present in the lignin preparation are quantitatively cleaved upon depolymerization, leading to the formation of **3G** (see SI). Interestingly, no re-polymerization was observed, likely because the mild reaction

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conditions (RT, P = 1 atm) prevent C-C coupling reactions of the lignin residues.

Additionally, deuterated **[1,2,3-D$_3$]-3G** is obtained when Et$_3$SiD is used in place of Et$_3$SiH in the depolymerization of industrial pine lignin, showing that the mechanism responsible for the reductive cleavage of the β-O-4 model **1** can be confidently transposed to lignin (Eq. 3 in Scheme 2).[56] The extraction method has a notable influence on the productivity and the selectivity. While **3G** is obtained in 25 wt% yield from industrial pine sawdust treated with a Formacell method, the corresponding yield drops to 18, 12 and 4 wt% when ethanol (EOL), methanol (MOL) or acetone (AOL) organosolv lignin is used, and other unidentified volatiles were detected as side-products. Interestingly, when Kraft lignin is re-extracted using the Formacell process, the resulting lignin preparation is not depolymerized with the B(C$_6$F$_5$)$_3$/Et$_3$SiH system, confirming that the Kraft process strongly modifies the structure of lignin. The depolymerization of Formacell lignin with PMHS (polymethylhydrosiloxane) and TMDS (tetramethyldisiloxane) hydrosilanes led to formation of a gel in CH$_2$Cl$_2$. Nevertheless, a disilylated propylcatechol product (analogous to **3G**) is successfully formed with TMDS when benzene is used as a solvent, albeit with a modest~ 9 wt% yield (compared to 25 wt% with Et$_3$SiH) (see SI).

As depicted in Fig. 4, **3G** is the main low-molecular-mass product obtained upon depolymerization of softwood lignin under the applied conditions and **4G**, **3S** and **4S** were not detected. Facilitated by the convergence, the purification of the crude mixture by flash chromatography enables the isolation of **3G** as a pure product in 19 wt%/lignin wt. A boiling point of 230 °C was measured for **3G** (at 760 Torr) and **3G** could also be recovered by distillation. From a practical viewpoint, this method has the advantage of utilizing less solvent for a larger scale synthesis of **3G**. Hydrolysis of **3G** with [*n*-Bu$_4$N$^+$, F$^-$] in THF affords the valuable 4-propylbenzene-1,2-diol (**3G'**) in 84 % yield from **3G** and 3 to 10 wt% yield from lignin, depending on the wood source and the nature of the pre-treatment (Scheme 3 and Table S3). In comparison, Westwood *et al.* were able to isolate 3-hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)propan-1-one in 5 wt% by depolymerization of oxidized lignin, using a stoichiometric quantity of zinc(0) metal.[31] **3G'** is a common skeleton in a wide range of useful chemicals and it is indeed a starting material for the synthesis of Quinone methides, which are currently studied for their anti-oxidant and cytotoxic properties.[66] Moreover, **3G'** has been utilized as an intermediate for the formation of benzodioxole derivatives, used as perfume ingredients,[67] as well as the synthesis of liquid crystals[68] and fuels.[69]
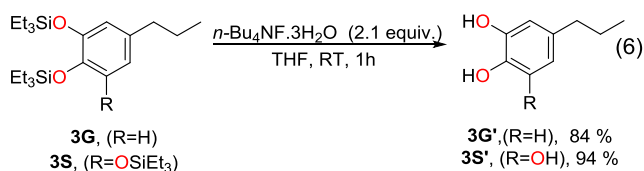
Scheme 3 Hydrolysis reaction of **3G** and **3S** to **3G'** and **3S'** respectively using [*n*-Bu$_4$N$^+$,F$^-$] in THF (Eq(6)).
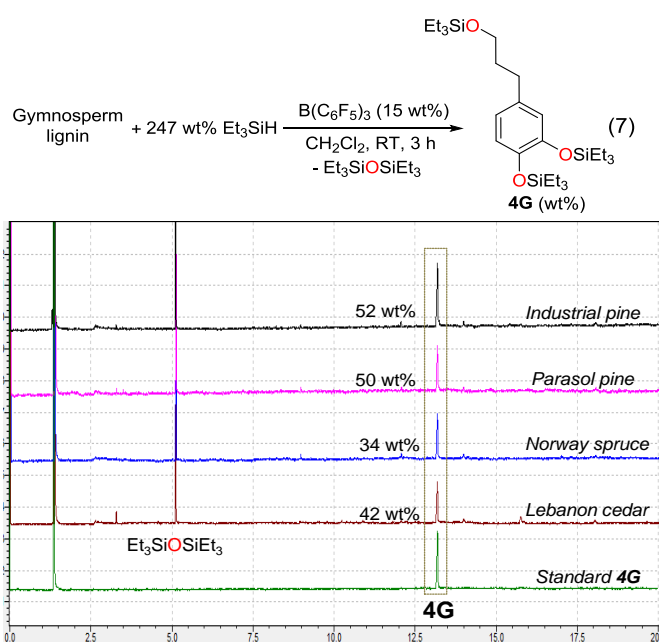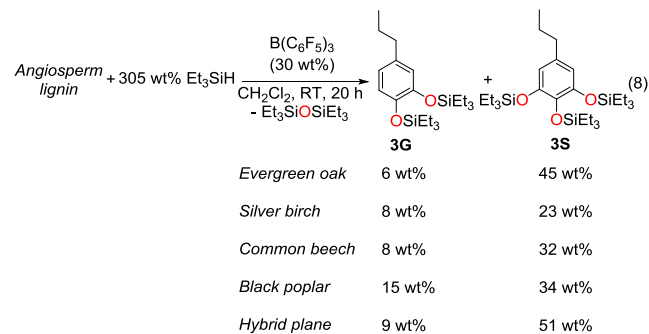
Fig. 6 Room temperature depolymerization of gymnosperm lignin with B(C$_6$F$_5$)$_3$/Et$_3$SiH to 4G (Eq. 7). GC-MS chromatograms of the depolymerization residue of Formacell lignin from industrial pine, parasol pine, Norway spruce, Lebanon cedar and standard 4G synthesized from petrochemical raw materials.

production of **3G** (and **3G'**) from lignin results from the ability of the B(C$_6$F$_5$)$_3$/Et$_3$SiH system to (i) cleave the β-O-4 and α-O-4 linkages and (ii) converge the resulting mono-aromatics by reductive deoxygenation of their propyl-chain. Importantly, the loss of chemical functionalities associated with reductive deoxygenation has been identified as a drawback in the depolymerization of lignin with reductants.[32, 70, 71] Nonetheless, the formation of **4G** suggests that this issue could be tackled with the present hydrosilylation approach, which is able to balance the reactivity of the different C–O bonds in lignin. Based on the reactivity of lignin models with the hydrosilane-B(C$_6$F$_5$)$_3$ system, the depolymerization of Formacell pine lignin was carried out with 247 wt% Et$_3$SiH and 15 wt% B(C$_6$F$_5$)$_3$. After 3 h at RT, GC/MS analysis of the crude mixture revealed the selective formation of **4G** as the only mono-aromatic product, in 52 wt% yield (Fig. 6).

Replacing industrial pine with parasol pine, Lebanon cedar or Norway spruce, **4G** was obtained in 50, 42 and 34 wt% yield, respectively. As expected, **4G** is an intermediate in the formation of

	3G	3S
Evergreen oak	6 wt%	45 wt%
Silver birch	8 wt%	23 wt%
Common beech	8 wt%	32 wt%
Black poplar	15 wt%	34 wt%
Hybrid plane	9 wt%	51 wt%

Scheme 4 Room temperature depolymerization of Formacell lignin (from angiosperm wood) to **3S**, with B(C$_6$F$_5$)$_3$/Et$_3$SiH.
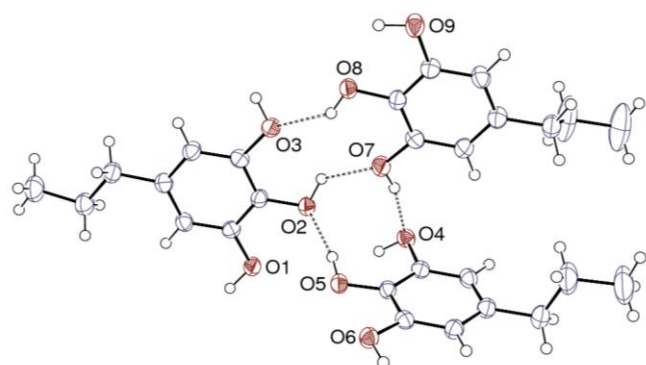
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Fig. 7 View of the three crystallographically independent molecules in the crystal structure of **3S'**, with part of the hydrogen bonding network. Displacement ellipsoids are drawn at the 50% probability level.

3G and monitoring the reduction of lignin with 305 wt% Et$_3$SiH and 25 wt% B(C$_6$F$_5$)$_3$ over time reveals the formation of **4G** and its subsequent reduction to **3G**. These results show that the chemoselectivity of the B(C$_6$F$_5$)$_3$/Et$_3$SiH system enables the convergent formation of **4G** while maintaining a reactive functional group. Notably, hydrolysis of **4G** affords **4G'** in 84% yield. **4G'** formally results from the hydroxylation of a terminal C–H bond on the propyl chain of **3G'** and, hence, offers extended reactivity patterns for future utilization.

3S and **4S** are sinapyl analogues of **3G** and **4G**, respectively. Their selective formation was thus investigated using the convergent reductive depolymerization method described for **3G** and **4G**. Angiosperm species are of the GS and HGS types and can thus contain a large portion of sinapyl residues. For example, common beech (*Fagus sylvatica*) and blue gum (*Eucalyptus globulus*) present >75 % S residues and about 20 % and 5 % G and H residues, respectively.[72, 73] Formacell lignin extracted from black poplar, common beech, silver birch, evergreen oak, date palm, hybrid plane and river red gum were subjected to depolymerization with the hydrosilane-B(C$_6$F$_5$)$_3$ system. Addition of 305 wt% Et$_3$SiH and 30 wt% B(C$_6$F$_5$)$_3$ to a CH$_2$Cl$_2$ suspension of lignin from evergreen oak resulted in the complete dissolution of the solid materials after 20 h at RT and GC/MS analysis of the solution confirms the formation of **3S** as the major low-molecular-mass product in 45 wt% yield. **3G** is also formed as a side product under these conditions, reflecting the natural coexistence of S and G residues in native lignocellulose. HSQC analysis of a sample of Formacell lignin derived from
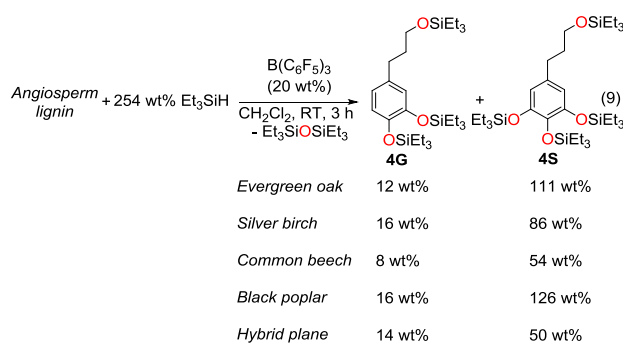
Scheme 5 Room temperature depolymerization of Formacell lignin (from angiosperm wood) to **4S**, with B(C$_6$F$_5$)$_3$/Et$_3$SiH.

evergreen oak indeed revealed the presence of S and G residues linked mainly through β-O-4 linkage. As expected, the absence of β-O-4 signals and the presence of signals for **3G** and **3S** were observed after depolymerization (see SI). Depending on the wood species, **3S** was successfully obtained in 23 to 51 wt% yield and the best results were obtained with evergreen oak and hybrid plane wood, which afforded selectively **3S** in 45 wt% and 51 wt% yield respectively with relatively low amounts of **3G** (Scheme 4). Hydrolysis of **3S** (bp=300±10 °C at 760 Torr) affords **3S'** in 87 % yield. **3S'** is a crystalline material and its structure was determined by single-crystal X-ray diffraction (Fig. 7). All the hydroxyl groups are involved in intermolecular hydrogen bonding, which gives rise to the formation of sheets parallel to the (0 1 0) plane. While the hydroxyl groups are located inside the sheets, the alkyl chains protrude outside, thus defining hydrophobic inter-layer spaces (see Fig. S13 in the SI). The crystallinity of **3S** can be advantageously utilized to separate **3S** from the oily **3G** product, without the need for an expensive chromatographic method. In fact, **3S** can be isolated in 94 % yield by recrystallization from a hot CHCl$_3$ solution of **3S'**/**3G'** (3:1).

Importantly, the more functionalized **4S** product can also be isolated, by controlling the experimental conditions of the hydrosilylative depolymerization of hardwood lignin. As shown in Scheme 5, Formacell lignin affords **4S** in 50 to 126 wt% yield, after 3 h at RT, in the presence of a limited quantity of hydrosilanes (254 wt% Et$_3$SiH) and a low catalyst loading of 20 wt%. Hydrolysis of **4S** could be carried out using [*n*-Bu$_4$N$^+$,F$^-$] in THF, to afford **4S'** in 82 % yield (see SI).

Table 1: Catalytic conversion of angiosperm and gymnosperm lignin to **3G**, **4G**, **3S** and **4S**. Isolated yields are given in brackets.

Species	Et$_3$SiH (wt%)	B(C$_6$F$_5$)$_3$ (wt%)	Reaction time (h)	Isolated product	Yield (wt%/lignin wt)
Gymnosperm wood lignin from: Industrial pine; *Norway spruce; Lebanon cedar; Pinus pinea*	247	15	3	**4G**	34 – 52
	305	25	20	**3G**	18 – 25 (19)
Angiosperm wood lignin from: *Evergreen oak; silver birch, common beech, black poplar* and *hybrid plane*	254	20	3	**4S**	50-126 (90)
	305	30	20	**3S**	23-51

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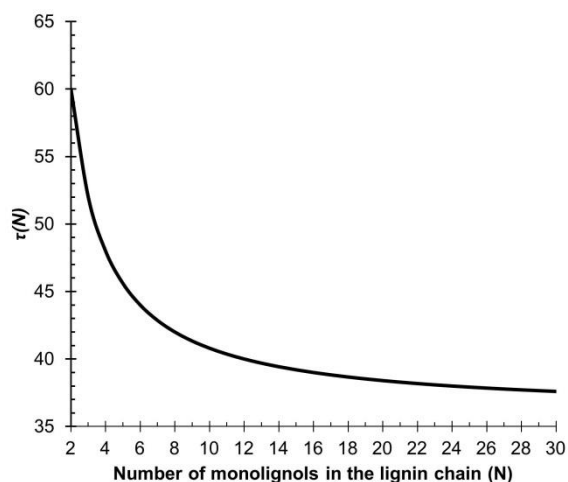
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Fig. 9 Variation of the maximum molar yield of mono-aromatics $\tau(N)$ as a function of the polymer chain length (N), for the reductive depolymerization of lignin by cleavage of β-O-4 and α-O-4 linkages.

Overall, isolation of compounds **3G**, **4G**, **3S** and **4S** was performed on a large range of 15 different wood species and the respective yields and depolymerization conditions are summarized in Table 1. The hydrolyzed products can be isolated in high yield, so that **3G'**, **4G'**, **3S'** and **4S'** are formed selectively in 9–12 wt% from the pre-treated lignin material and 0.5 to 2.4 wt% from wood. In comparison, vanillin is today the only industrial mono-aromatic chemical obtained from lignin and it is produced since 1993 by the Norwegian company Borregaard by oxidation of lignosulfonate using a copper catalyst. Starting from 1 ton of wood an average of 3 kg of vanillin is obtained with a global efficiency of 0.3 wt%.[13, 74] In order to address the efficiency of the present integrated depolymerization strategy, we calculated the maximum theoretical yield for the formation of **3G'**, **4G'**, **3S'** and **4S'**. Three successive steps are involved in the production of these compounds, namely (i) the extraction of lignin from wood sawdust or wood chunks using an organosolv process, (ii) the reductive depolymerization of the lignin preparation and (iii) the isolation, hydrolysis and purification of the end-product (Fig. 3). As depicted in Fig. 6, the amount of lignin extracted using a Formacell process varies with the wood species from 7 to 20 wt% yield and the efficiency of this step is in general greater for angiosperm species. This is likely due to the larger content of α-O-4 linkages in hardwood, these linkages being more easily cleavable by the lignin extraction method.[75] Since the lignin content in the selected wood samples averages 20–30 wt%, the efficiency of the organosolv process is close to 40 %.

Evaluation of the efficiency of the depolymerization step requires a finer description of the lignin preparation. Indeed, the theoretical yield for the formation of **3G** (for example) depends on the proportion of β-O-4 and α-O-4 linkages, cleavable with the hydrosilane-B(C₆F₅)₃ system, and the degree of polymerization in the lignin starting material. While hardwood contains about 60 % β-O-4 and 6-8 % α-O-4 linkages, the proportions of cleavable ether linkages is somewhat lower in softwood lignin (46 % β-O-4 and 6-8 % α-O-4). Assuming that lignin is a linear polymer containing about P=60 % β-O-4 and α-O-4 linkages (cleavable linkages), an infinite lignin chain will afford a maximum of P²=36 % mono-aromatics. The successful formation of a C9 unit indeed necessitates that two consecutive cleavable linkages are located in the polymer chain. Because the depolymerization step is unreactive towards aryl-ethers and C–C bonds, phenol units linked through 4-O-5, β-β', 5-5' and β-1 bonds yield dimers or heavier poly-aromatics. For a finite lignin chain featuring N monolignols, the theoretical yield $\tau(N)$ follows the expression (see SI):

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

As depicted in Fig. 9, $\tau(N)$ decreases rapidly from 60 % (N=2) to its 36 % asymptote with increasing N values, as the number of chain-ends decreases with longer chains. Size exclusion chromatography (SEC) was thus utilized to estimate the degree of polymerization (DP) of Formacell lignin in the studied samples (see SI and Fig. 5). Lignin samples extracted with the Formacell or ethanol method from parasol pine or evergreen oak are partially soluble in THF and from SEC, number-average molecular weights (M_n) of lignin were calculated ranging from 669 to 1099 g.mol⁻¹, with a polydispersity (M_w/M_n) between 1.35 and 1.8 (Fig. 5 and SI). This result suggests a

Table 2 Efficiency calculations for the isolation of **3G'**, **3S'**, **4G'**, **4S'** from industrial pine and *hybrid plane*.

Species	Formacell lignin from wood[a] (wt%/wood wt)	Silylated mono-aromatic product[b] (wt%/lignin wt)	Isolated silylated mono-aromatic product (wt%/lignin wt)	Isolated mono-aromatic product[c] (wt%/lignin wt)	Isolated mono-aromatic product[d] (wt%/wood wt)	Theoritical yield[e] (wt%/wood wt)	Global efficiency[f] (%)
Industrial Pine	8 (32)	**4G** 52 (43)	**4G** 36*(70)	**4G'** 10* (84)	**4G'** 0.8*	9.9	8.1*
	8 (32)	**3G** 25 (28)	**3G** 19 (76)	**3G'** 7 (86)	**3G'** 0.5	8.9	5.6
hybrid plane	10 (40)	**4S** 111 (85)	**4S** 90 (81)	**4S'** 24 (94)	**4S'** 2.4	9.4	25.5
	10 (40)	**3S** 45 (43)	**3S** 32*(70)	**3S'** 9* (82)	**3S'** 0.9*	8.5	10.6*

[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 initial lignin 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 (70 % efficiency). Values in brackets correspond to the calculated efficiency of the step.

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relative narrow molecular weight distribution with a DP of 5±1. Accordingly, a maximum of $\tau(5)$=46 % phenol units can be extracted by hydrosilylative depolymerization of lignin, while 9–35 mol% yields were measured experimentally for the conversion of lignin to **3G**, **4G**, **3S** and **4S**. This calculation in fact shows that the depolymerization step with the hydrosilane-B(C_6F_5)$_3$ system is rather efficient, with an efficiency of 28 to 85 % depending on the wood source and the targeted product. Finally, isolation and purification of **3G'**, **4G'**, **3S'** and **4S'** products from their silylated analogues was achieved experimentally with >82 % yield and efficiency (see SI). Overall, pure **3G'**, **4G'**, **3S'** and **4S'** were isolated in 0.7 to 3.0 wt% yield from wood over three steps. Theoretically, the maximum yield for the extraction of these products is 9±1 wt%, revealing that the present three steps procedure exhibits an efficiency of 6–26 % (Table 2). Unsurprisingly, the isolation and purification step presents the best efficiency as it involves classical and robust separation techniques, at the molecular level. These results finally show that the depolymerization methodology described herein is able to selectively yield mono-aromatic products by reductive cleavage of the β-O-4 and α-O-4 linkages, at room temperature under metal-free conditions. Nevertheless, the application of this strategy to the large scale transformation of lignin might suffer from practical limitations, which derive from the cost of the boron catalyst and the use of stoichiometric amounts of hydrosilanes. The search for cost efficient reduction catalysts and the use of renewable sources of hydrides, such as molecular hydrogen or formic acid, will guide future efforts devoted to improving the sustainability and efficiency of the method. Additionally, replacement of CH_2Cl_2 with a greener solvent is desirable. In this respect, the compatibility of benzene with the hydrosilane-B(C_6F_5)$_3$ system (see SI) indicates that aromatic solvents are attractive alternative in this technology.

Conclusions

In summary, we have reported herein the first examples of reductive depolymerization of lignin under metal-free conditions. The reaction is carried out under mild conditions, i.e. ambient pressure and temperature, thereby preventing a problematic re-polymerization of the products *via* C–C bond formation. Labelling studies show that the depolymerization of lignin follows the mechanism unveiled for the hydrosilylation of lignin models and relies on the selective reductive cleavage of the β-O-4 and α-O-4 linkages in the lignin chain. The versatility of the approach is demonstrated by the successful depolymerization of different lignin preparations, derived from 15 gymnosperms and angiosperms species. For the first time, several different aromatic products can thus be isolated selectively from wood, by tuning the catalytic conditions and selecting the wood source and lignin extraction method. The methodology indeed yields a narrow distribution of low molecular mass products containing essentially one or two mono-aromatic products (together with longer oligomers), which are easily separable using chromatography, distillation and/or crystallization. The resulting phenol derivatives, e. g. 5-(3-hydroxypropyl)benzene-1,2,3-triol and 4-propylbenzene-1,2-diol, were isolated in 7 to 24 wt% yield from lignin and 0.5 to 2.4 wt% yield from wood. The global efficiency of the process ranges 5 to

25 %; and current efforts are devoted to increase this performance by optimizing the extraction method of lignin designing novel catalysts with enhanced activity. In this respect, other benign processes causing minimal disruption to the lignin structure will be considered,[76] such as the steam explosion and ammonia freeze explosion (AFEX) processes.[77, 78] Additionally, genetically modified species containing exclusively one type of residue (H, G or S) linked through β-O-4 and α-O-4 linkages could significantly increase the yield and facilitate the purification of the final phenolic product.

Materials and Methods

Extraction of lignin from wood sawdust using a Formacell process

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 the water/formic acid azeotrope). After cooling the mixture 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 volatiles were then removed 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 depend on the wood species. The obtained yields are summarized in the SI (Table S1).

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 Et$_3$SiH 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 CH_2Cl_2 (2 mL). On the other hand, a mixture of Et$_3$SiH (1220.8 mg, 10.5 mmol, 305.2 wt%) and B(C_6F_5)$_3$ (100.0 mg, 0.2 mmol, 25 wt%) in CH_2Cl_2 (2 mL) was added slowly (over 30 min), at RT. Methane formation was detected by GC chromatography. After 1h, the entire solid was dissolved and the solution turned from colorless 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 a pentane/CH_2Cl_2 (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 assessed by elemental analysis. **Anal. Calcd.** for $C_{21}H_{40}O_2Si_2$ (mol. wt. 380.72): C, 66.25; H, 10.59. **Found:** C, 65.73; H, 10.79.

Typical procedure for the hydrolysis of silylated phenolic compounds

The procedure for the hydrolysis of silylated phenolic compounds is detailed for compound **3G**. To a solution of **3G** (380.7 mg; 1.0 mmol, 1 equiv.) in 4 mL THF *n*-Bu$_4$NF 3H$_2$O (315.5 mg; 2.1 mmol, 2.1 equiv.) was added slowly, under argon, and the solution was stirred for 1 h at room temperature. The volatiles were then removed under vacuum and 4 mL 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/ethylacetate) to afford **3G'** (141.5 mg; 0.9 mmol; 84 %) as a colorless oil.

Acknowledgements

Notes

Supporting Information

Details of experimental procedures: lignin extraction methods and characterization, procedures for the catalytic depolymerization of lignin, procedure for the hydrolysis of silylated aromatic compounds, synthesis of standards, characterization of new compounds as well as deuterium labeled products, HSQC analyses, GC-MS chromatograms, DEPT 135 spectra, SEC chromatograms, GC-MS calibration plots, theoretical yields and global efficiency calculations, tables of crystal data, atomic positions and displacement parameters, anisotropic displacement parameters, and bond lengths and bond angles in CIF format. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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

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