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Electronic Supplementary Information

Application of mild autohydrolysis to facilitate the dissolution of wood chips in direct-dissolution solvents

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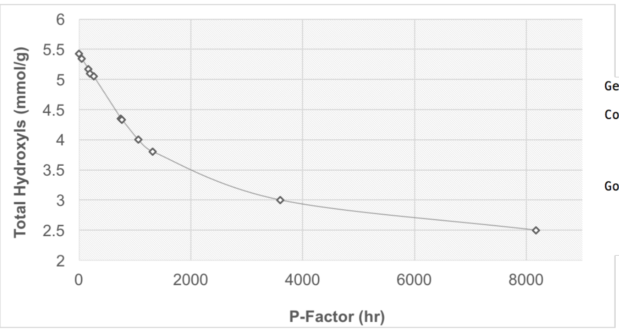
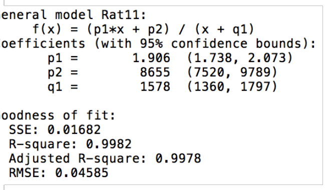
S1. Available Hydroxyls in Lignin

The available hydroxyls in lignin were extrapolated from literature values.[1] These literature values were obtained by autohydrolysis of birch sawdust followed by extraction and ^{31}P NMR analysis of the milled wood lignin. The extrapolated values represent decreases in lignin OH values as P-Factors increase, due to lignin condensation under the harsh autohydrolysis. conditions. The literature values in this report are for untreated birch sawdust (P-Factor 0 hr) and the additional P-Factors of 200 and 750 hr. The remainder of the values were extrapolated to an estimated value of 2.5 mmol/g for 'fully condensed' lignin at the highest P-Factor of 8170 hr. This is an estimated value for fully condensed lignin. To the best of our knowledge there are no exact values in the literature for 'fully condensed' lignin and not likely to be. These are the best estimates we can provide and are expected to provide little error in the final calculations of theoretical hydroxyls due to the minimal contribution by lignin to the total OH in wood samples, compared to the polysaccharide fractions.





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General model Rat11:
     f(x) = (p1*x + p2) / (x + q1)
Coefficients (with 95% confidence bounds):
       p1 =       1.906  (1.738, 2.073)
       p2 =        8655  (7520, 9789)
       q1 =        1578  (1360, 1797)

Goodness of fit:
  SSE: 0.01682
  R-square: 0.9982
  Adjusted R-square: 0.9978
  RMSE: 0.04585
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P-Factor (hr)	OH value (mmol/g)
0	5.43
50	5.34
170	5.17
200	5.1
260	5.05
750	4.35
770	4.33
1060	4
1320	3.8
3600	3
8170	2.5

The extrapolated values in Figure S1 can be fitted with the following equation:

$$TOH = \frac{(1.906 \times PF)\ + 8655}{PF + 1578}$$

where PF is the P-Factor (hr) and TOH is the total OH values for lignins extracted from autohydrolysed birch (mmol/g).

S2. *Theoretical OH Values*

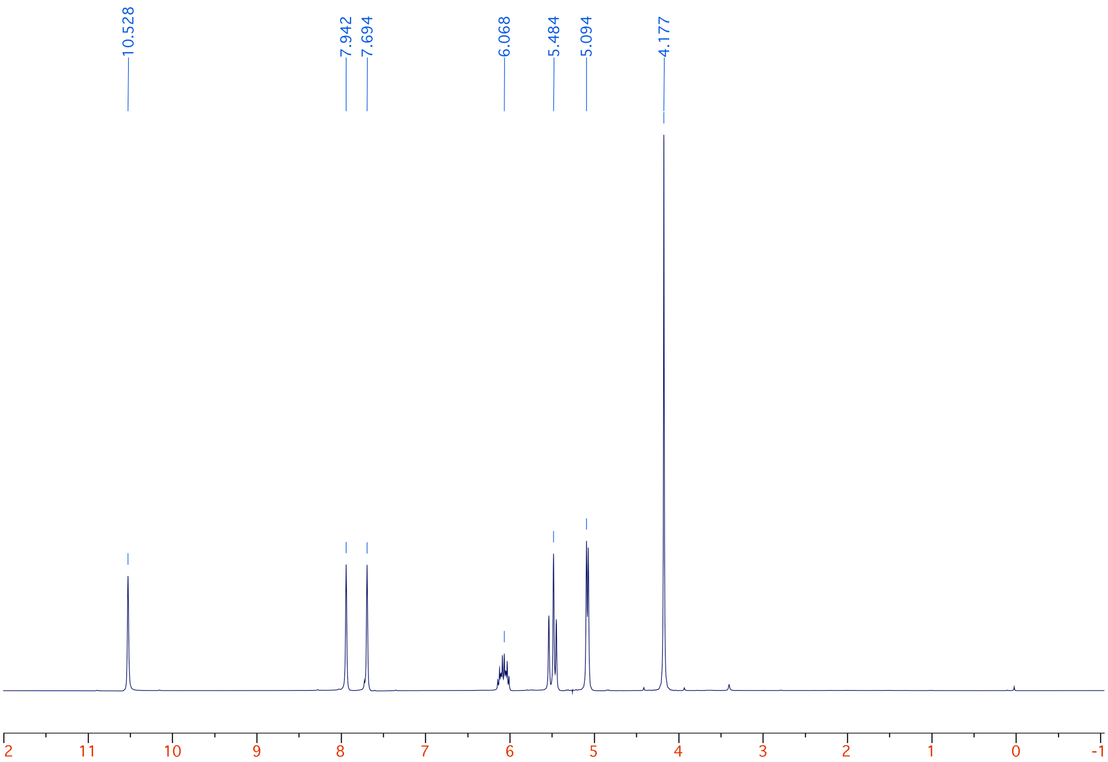
	$\%_{(X)}$ (%)[a]						XOH (mmol/g)[b]				$OH_{(X)}$ (mmol/g)[c]				Totals (mmol/g)	
P-Factor	$\%_{(Cell)}$	$\%_{(Xyl)}$	KL[d]	ASL[e]	$\%_{(Lig)}$	$\%_{(Ac)}$	CellOH[f]	XylOH[g]	LigOH[h]	AcOH[i]	$OH_{(Cell)}$	$OH_{(Xyl)}$	$OH_{(Lig)}$	$OH_{(Ac)}$	$\mathbf{OH_{(Th)}}$	$\mathbf{OH_{(Exp)}}$
0	42.3	27.3	21.7	4.4	26.1	3.7	18.5	14.2	5.4	23.3	7.8	3.9	1.4	0.9	12.3	1.5
51	42.1	27.7	22.5	3.9	26.4	3.7	18.5	14.2	5.3	23.3	7.8	3.9	1.4	0.9	12.3	5.3
167	45.7	24.5	23.0	2.9	25.9	3.7	18.5	14.2	5.2	23.3	8.4	3.5	1.3	0.9	12.4	11.9
262	45.5	23.8	24.5	2.8	27.3	2.2	18.5	14.2	5.0	23.3	8.4	3.4	1.4	0.5	12.6	11.5
766	49.9	18.8	25.9	2.6	28.5	0.8	18.5	14.2	4.3	23.3	9.2	2.7	1.2	0.2	12.9	13.4
1057	51.7	14.6	27.6	2.2	29.8	0.5	18.5	14.2	4.0	23.3	9.6	2.1	1.2	0.1	12.7	11.9
1322	55.6	9.0	30.5	2.5	33.0	0.8	18.5	14.2	3.8	23.3	10.3	1.3	1.3	0.2	12.6	12.6
3600	59.8	2.1	34.5	2.2	36.8	0.4	18.5	14.2	3.0	23.3	11.1	0.3	1.1	0.1	12.4	12.8
8166	62.1	0.3	34.4	2.2	36.6	0.2	18.5	14.2	2.5	23.3	11.5	0.0	0.9	0.0	12.4	12.8

[a] $\%_{(X)}$ is the percentage of each biomass component in the samples and the data was provided by Borrega *et al.*,[2] [b] XOH is the OH value (mmol/g) for each species, [c] $OH_{(X)}$ are the total contributions for each species, [d] Klason lignin, [e] acid-soluble lignin, [f] three hydroxyls in cellulose divided by the molar mass of the anhydroglucose unit (AGU, 162 g/mol), [g] as determined by King *et al.*,[3] [h] according to the data presented in S1 (ESI), [i] one hydroxyl consumed (acetylated) divided by the molar mass of the acetyl functionality (Ac, 43 g/mol).

S3. Synthesis of [amim]Cl[4]

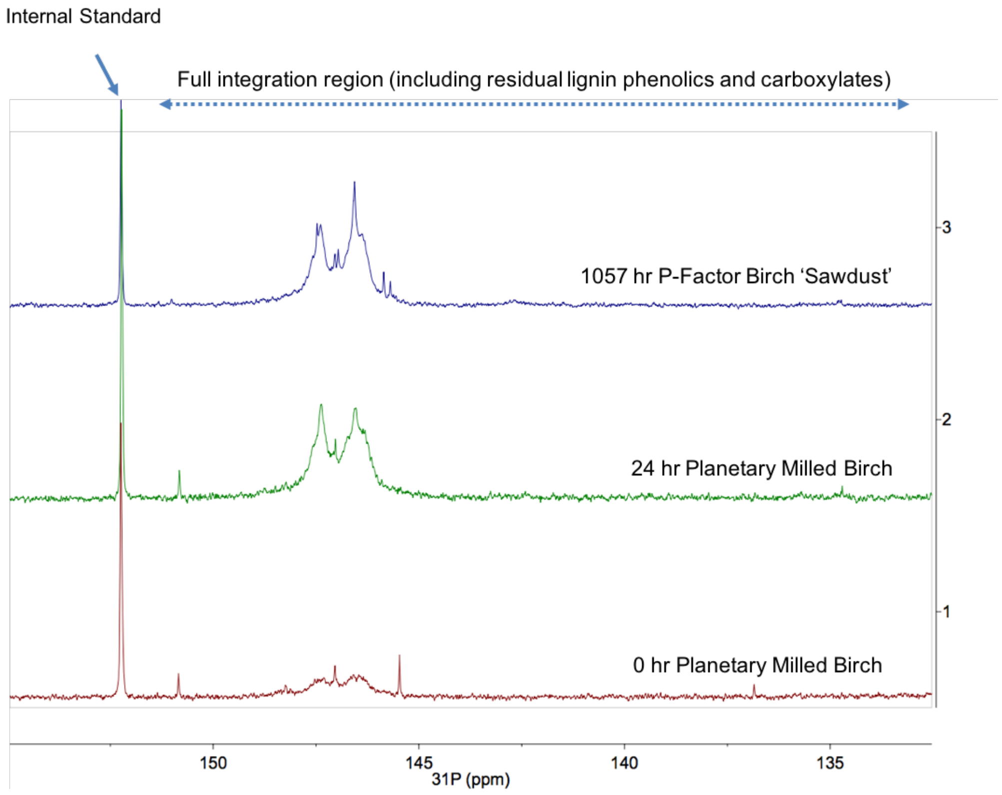
1-Methylimidazole (125 ml, 1.57 mol) was added slowly (over 1 h) to neat allyl chloride (160 ml, 1.97 mol) at room temperature, with stirring under argon. The mixture was then refluxed at 55 °C for 18 h under argon. Excess allyl chloride was removed by rotary evaporation, in a fume-hood. The mixture was then rotary evaporated at 70 °C under high vacuum (vacuum pump) for 6 h, to yield a clear orange liquid (15.80 g, 100%). It is critical to avoid the introduction of moisture into the mixture before all traces of allyl chloride are removed. ^{1}H NMR (300 MHz; $CDCl_3$): δ 10.53 (1H, s), 7.94 (1H, s), 7.69 (1H, s), 6.07 (1H, ddt, *J* = 16.9, 10.3, 6.5 Hz), 5.48 (2H, m), 5.09 (2H, d, *J* = 6.4 Hz), 4.18 (3H, s). Water content was determined to be less than 0.4 % w/w by Karl-Fischer titration. The mixture was stored in a tightly sealed bottle to avoid moisture uptake.

^{1}H NMR Spectra:



S4. ^{31}P NMR Analysis Procedure[4]

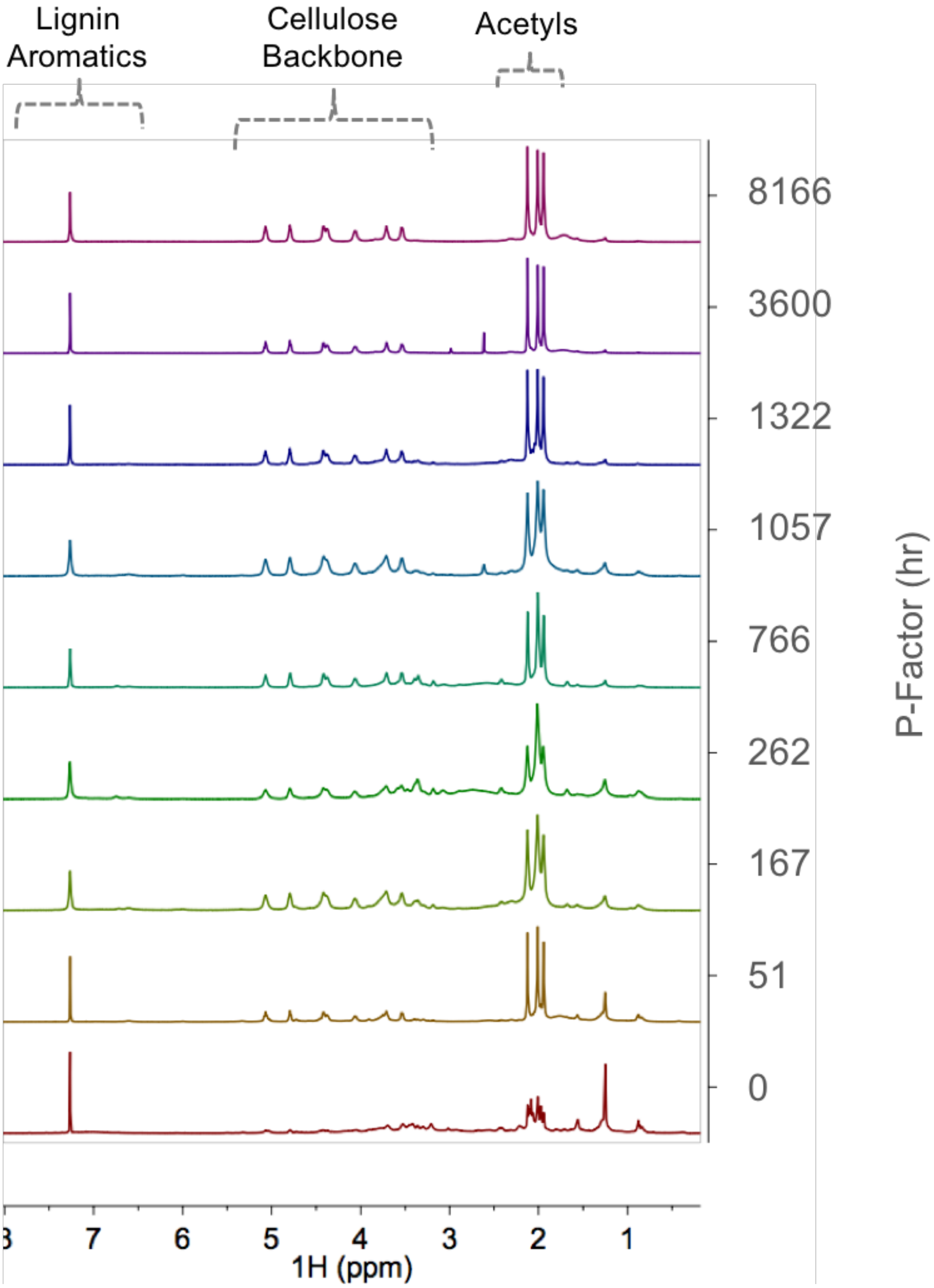
Wood samples were phosphitylated and analysed using the following procedure: Ionic liquid (~0.40 ml, 475 mg) was added, by syringe, to pulverized wood (25 mg) in in a 8 ml sample vial The mixture was manually mixed with a needle, until homogeneous, flushed with argon and sealed. The sample was heated at 90 °C until clear (or a maximum time of 18 hr was reached). Pyridine (150 µl, 1.88 mmol) was added in one portion and the sample vortexed, at 2500 rpm, using an Janke & Kunkel Vibrofix VF1 Electronic orbital shaker, until visibly homogeneous (~20 s). The sample was allowed to cool to room temperature, whereby 2-Cl-TMDP (200 µl, 1.26 mmol) was added in one portion and vortexed until visibly homogeneous (~30 s), as a cream paste. A stock solution of Cr(acac)$_3$/CDCl$_3$ (0.04 M, 500 µl) was added in 4*125 µl portions with vortexing (~30 s) between each addition. *e*-HNDI solution (121.5 mM in 3:2 pyridine:CDCl$_3$, 125 µl) was added in one portion and the solution vortexed (~30 s). Further Cr(acac)$_3$/CDCl$_3$ (0.04 M, 3.5 ml) was added in a 500 µl and 3*1 ml portions, with vortexing (~30 s) between each addition. ^{31}P NMR spectra (243 MHz) were recorded with 700 µl samples, in a 5 mm o.d. NMR tube. Spectral width was 20000 Hz. The transmitter offset was centered on 150 ppm. The pulse flip angle was 80 °. The pre-relaxation delay was 5 s and acquisition time was 1 s. The samples were measured using a Varian Inova 600 MHz spectrometer equipped with a direct detection probe for broadband nuclei such as ^{31}P. CDCl$_3$ was used as locking solvent, and standard transients of 700 were collected. The experiment temperature was maintained at 27 °C for all experiments. The anhydride peak, derived from reaction of 2-Cl-TMDP with water, was used as the calibration peak at 132.2 ppm. The 'total hydroxyl' integration region was 133 - 151.5 ppm. This includes both the phenolic and carboxylic acid region, although, in practise this has little contribution to the integral compared to the aliphatic signals. Sample Spectra:



S5. Full NMR Spectra for Acetylated Woods in $CDCl_3$

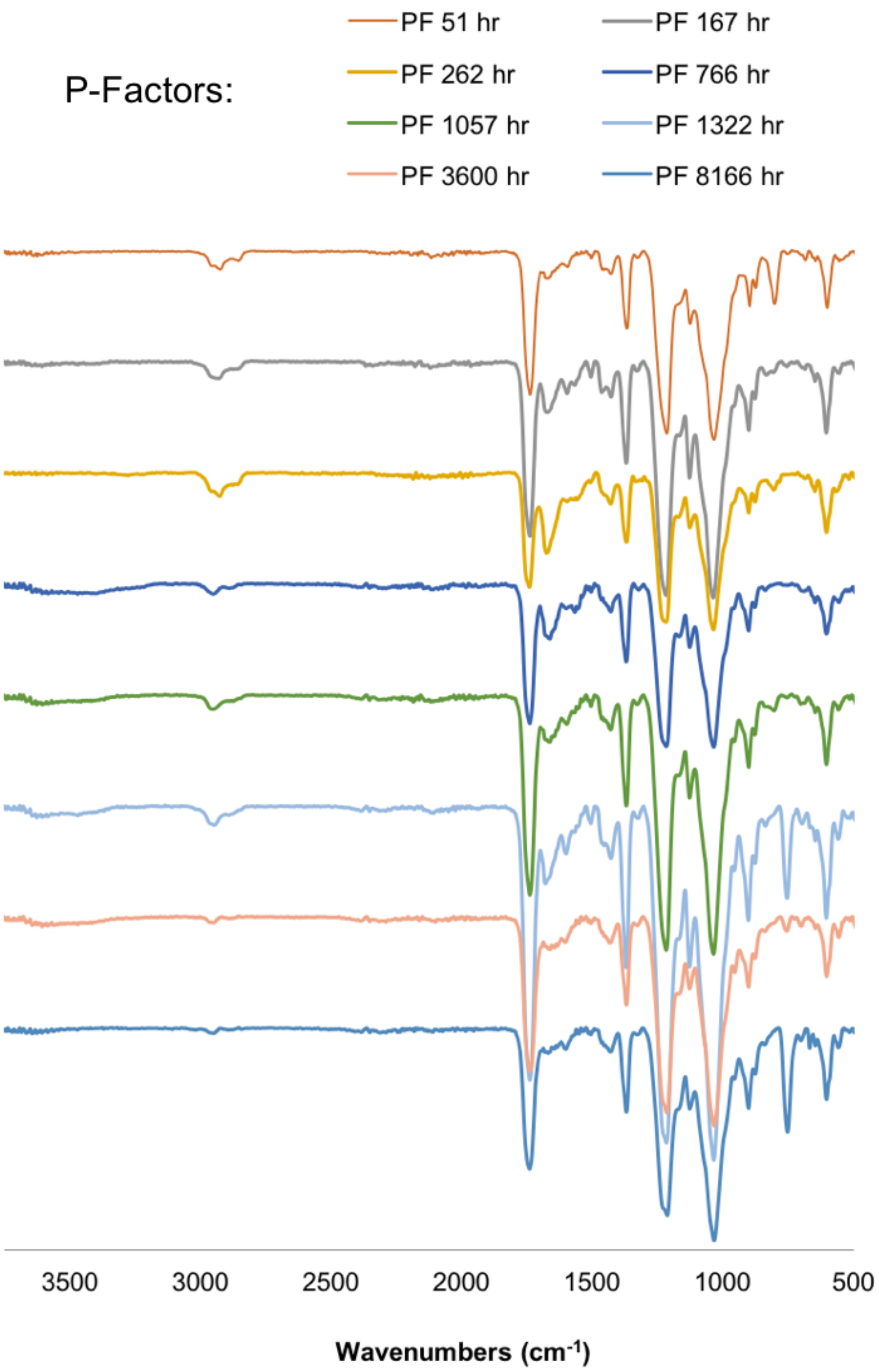
Samples were acetylated in [DBNH][OAc] with isopropenyl acetate, according to the main text. ^1H NMR spectra (600 MHz) were recorded with 700 μl samples, in a 5 mm o.d. NMR tube at 27 °C. DEPT-edited-HSQC were also run under similar conditions using the standard DEPT-edited gHSQC pulse sequence.

Full ^1H Spectra for the autohydrolysed wood samples:



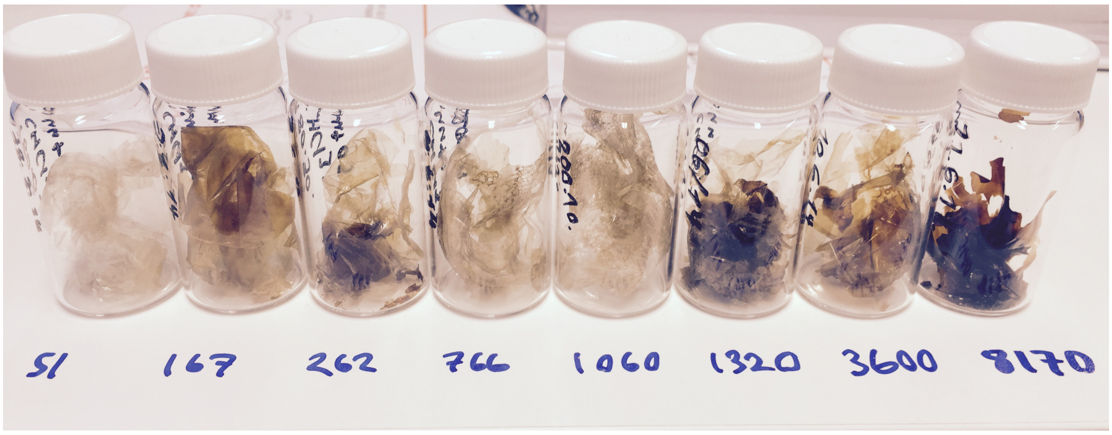
S6. ATR-IR Analysis of Acetylated Wood Samples

After acetylation and drying all samples were analysed by ATR-IR and exhibit significant carbonyl stretches, common with highly acetylated wood and cellulose samples:



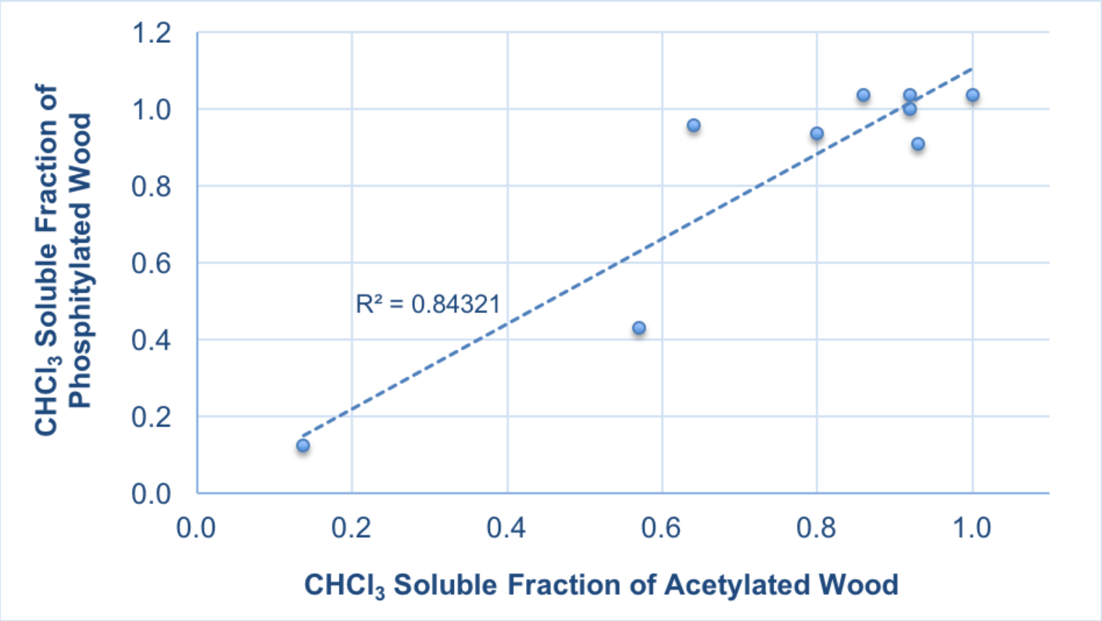
S7. Acetylated Wood Films

After regeneration of the acetylated wood samples and extraction with chloroform, the samples were rotary evaporated. All were film-forming after evaporation:



S8. Correlation Between the ^{31}P NMR Acetylation Analyses

The ^{31}P NMR results that are plotted are the experimental available hydroxyls divided by the theoretical hydroxyls, i.e. the fraction of the theoretical hydroxyls that are soluble. These are termed as the chloroform ($CHCl_3$) soluble fraction of phosphitylated wood as the analytical procedure is essentially measuring the chloroform soluble fraction after phosphitylation. The acetylation results are plotted as the chloroform soluble yield divided by the experimental WPG yield, i.e. the fraction of the recovered acetylated material that is soluble in chloroform:

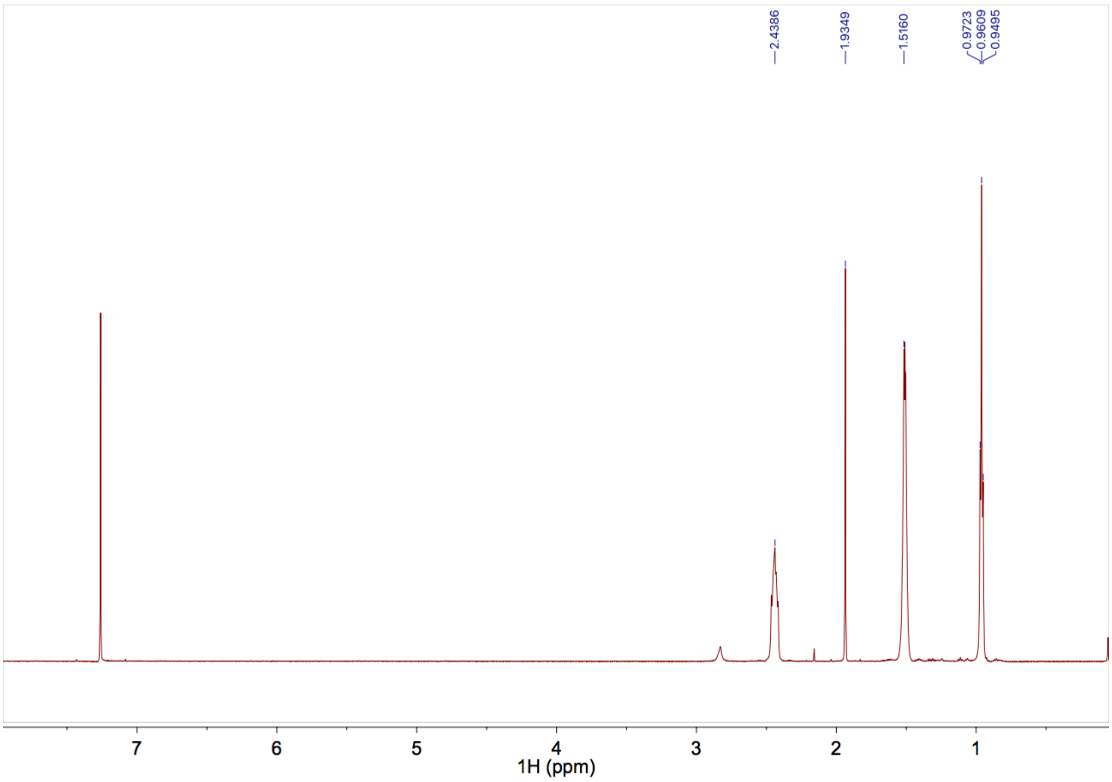


S9. *Synthesis of [P$_{4444}$][OAc]*[5]

[P$_{4444}$]Cl (CYPHOS 443W, 80% w/w in H_2O) was dried on a high-vacuum rotary evaporator (3 hr, 70 ºC). Silver acetate (7.71 g, 0.0466 mol) was weighed into a conical flask and isopropanol (300 ml) was added. [P$_{4444}$]Cl (13.73 g, 0.0466 mol) was added to the reaction mixture. The flask was purged with argon, covered with tinfoil to prevent decomposition of AgCl and the mixture was left to stir at room temperature for 16 hr. The precipitate was filtered through celite and the filtrate evaporated on a rotary evaporator. The crude products were allowed to sit for a further day open to the atmosphere and light. The mixture was then dissolved in methanol (300 ml) and again filtered through celite and evaporated down. The mixture was then dried in a high-vacuum rotary evaporator (70 ºC, 6 hr) and the product was recovered as a pale-yellow crystalline material (13.03 g, 96.3% yield).

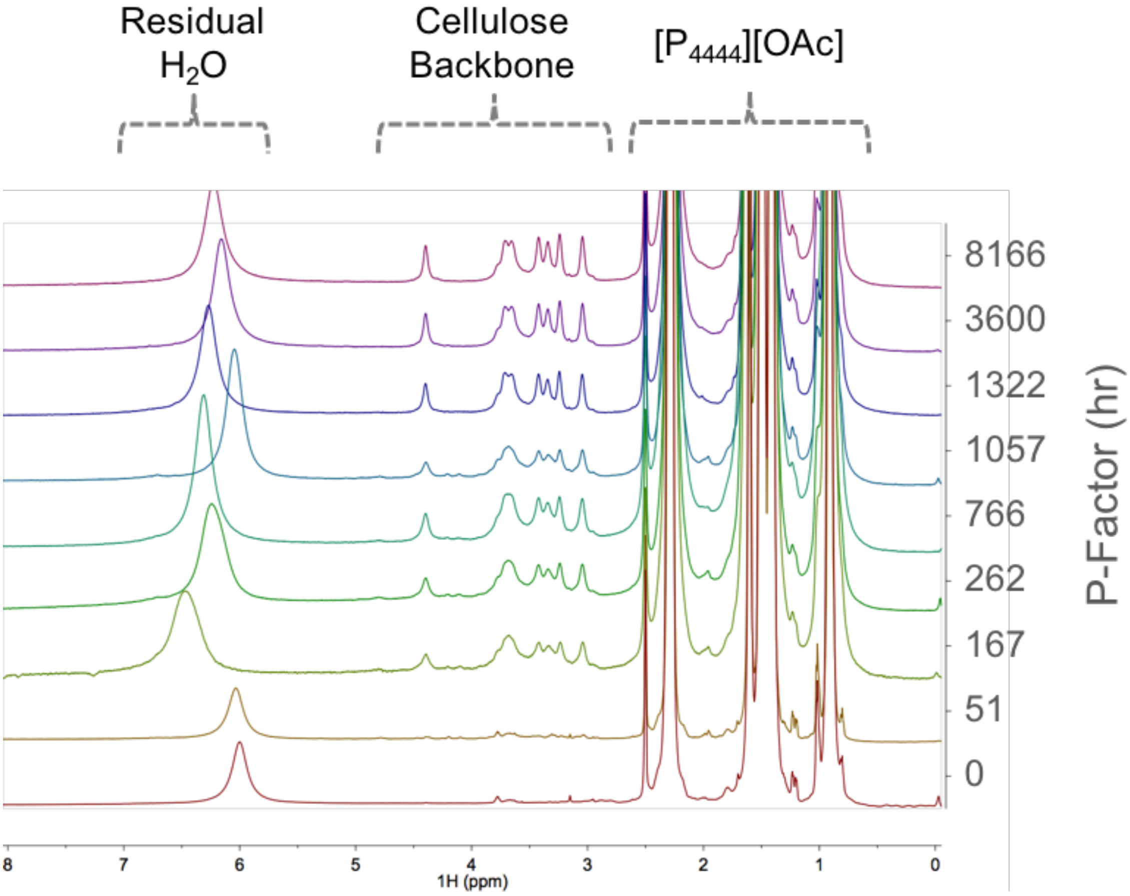
^{1}H NMR (600 MHz, $CDCl_3$) δ 0.96 (12H, t, J=6.84 Hz, $P(CH_2)_3CH_3$), 1.52 (16H, m, $PCH_2(CH_2)_2CH_3$), 1.94 (3H, s, CO_2CH_3), 2.44 (8H, m, $PCH_2(CH_2)_2CH_3$).

^{1}H NMR Spectrum for [P$_{4444}$][OAc]:



S10. Full NMR Spectra for Unacetylated Woods in $[P_{4444}][OAc]$:DMSO-d6

Samples were dissolved according to the main text. ^{1}H NMR spectra were collected using standard ^{1}H parameters, at 65 °C in a 5 mm o.d. NMR tube:



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