

Supplementary Information for:

‘Lignin and extractives first’ conversion of lignocellulosic residual streams using UV light from LEDs

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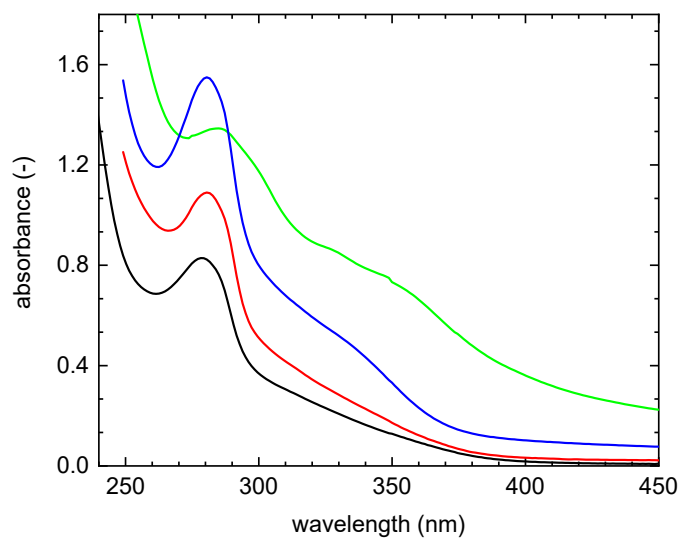


Figure S1. Representative UV-vis absorption spectra of softwood sawdust, extracted with water (black), methanol (red), water:NaOH pH 12 (green) and acetonitrile (blue).

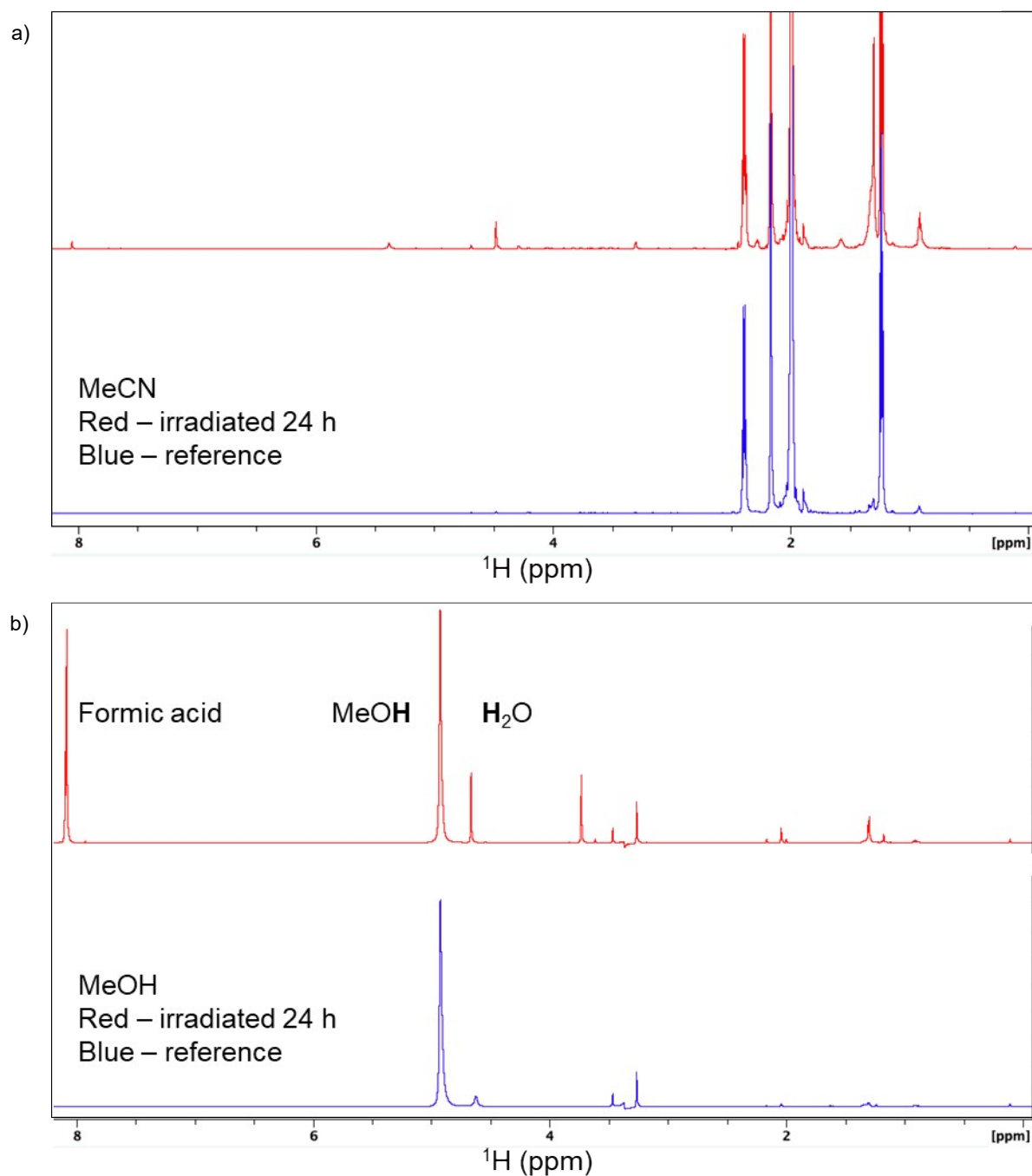


Figure S2. ^1H NMR spectra of (a) acetonitrile and (b) methanol. Reference samples of the pure solvent are presented in blue and the solvent irradiated for 24 h are presented in red. Irradiation of methanol results in the formation of formic acid and water whilst acetonitrile is more stable towards UV-irradiation.

ELEMENT	MeOH (mg/kg)	MeCN (mg/kg)
Al	<0.5	<0.5
As	<0.002	<0.002
Ca	<2	<2
Cd	<0.0002	<0.0002
Co	<0.0005	<0.0005
Cr	<0.005	<0.005
Cu	0.026	0.021
Fe	<0.02	0.0924
Hg	<0.0005	<0.0005
K	8.04	<0.2
Mn	0.542	0.0481
Mo	<0.002	<0.002
Na	0.999	<0.2
Ni	<0.005	0.0131
P	<0.5	1.63
Pb	<0.001	<0.001
S	<1	<1
Si	<5	<5
Ti	<0.2	<0.2
V	<0.0005	<0.0005
Zn	<0.05	<0.05

Figure S3. ICP analysis of control samples extracted in methanol and acetonitrile. Results indicate a low concentration of metal ions. Numbers in red indicate the detection limit i.e. these ions could not be quantified.

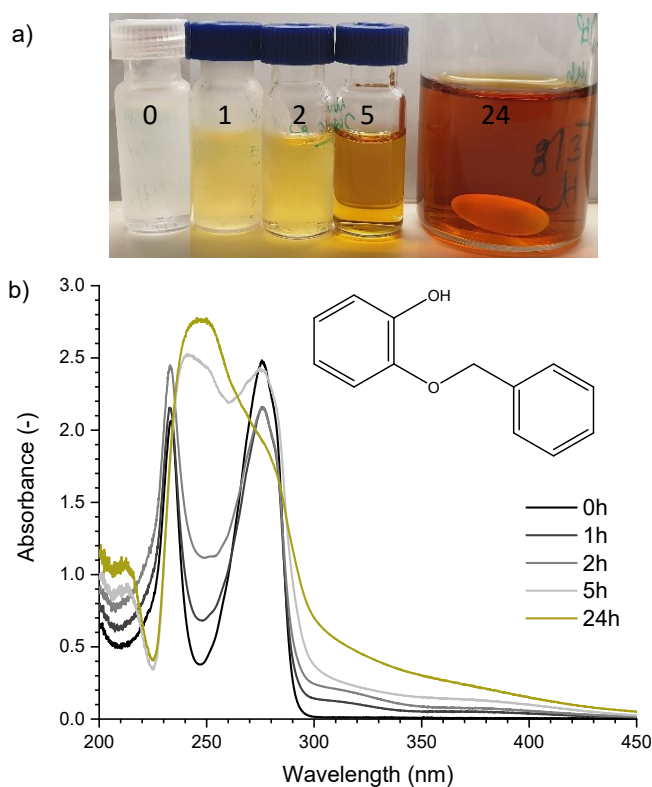


Figure S4. (a) Observed colour change with time for 2-benzyloxyphenol (2BP) in acetonitrile upon irradiation. (b) Representative UV-vis absorption spectra of 2BP in acetonitrile, irradiated with $\lambda \sim 265$ nm from 0 to 24 h. Inset in (b) shows chemical structure of 2BP.

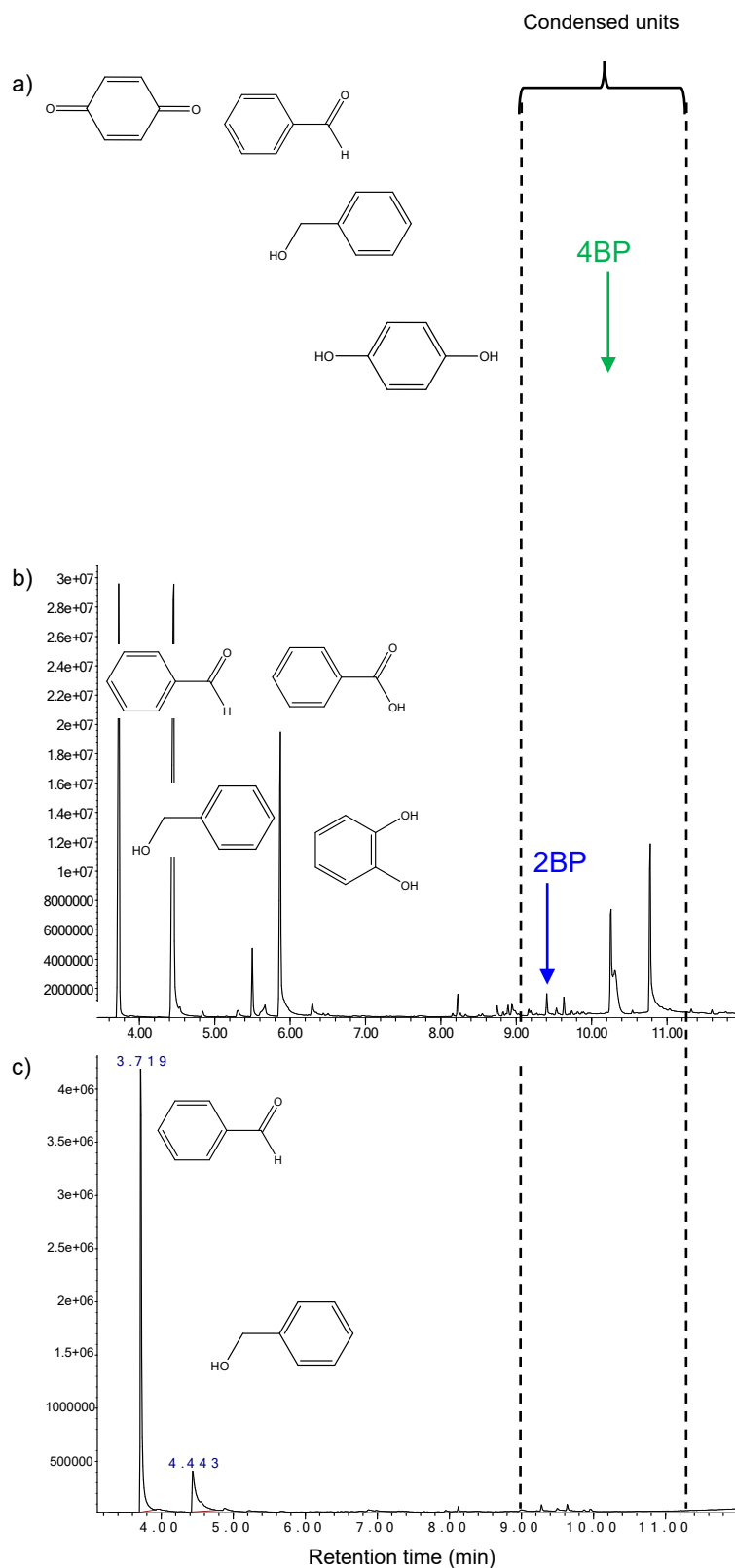


Figure S5. GC-MS chromatograms for (a) 4-benzyloxyphenol (4BP) and (b) 2-benzyloxyphenol (2BP) 10 g L^{-1} in acetonitrile, irradiated for 24 h. Starting compound 4BP is found at 10.27 min (green arrow) and 2BP is found at retention time 9.4 min (blue arrow) (c) 2BP 1 g L^{-1} in acetonitrile irradiated for 24 h. Inset molecules in each graph show the formed products, identified using the NIST library.

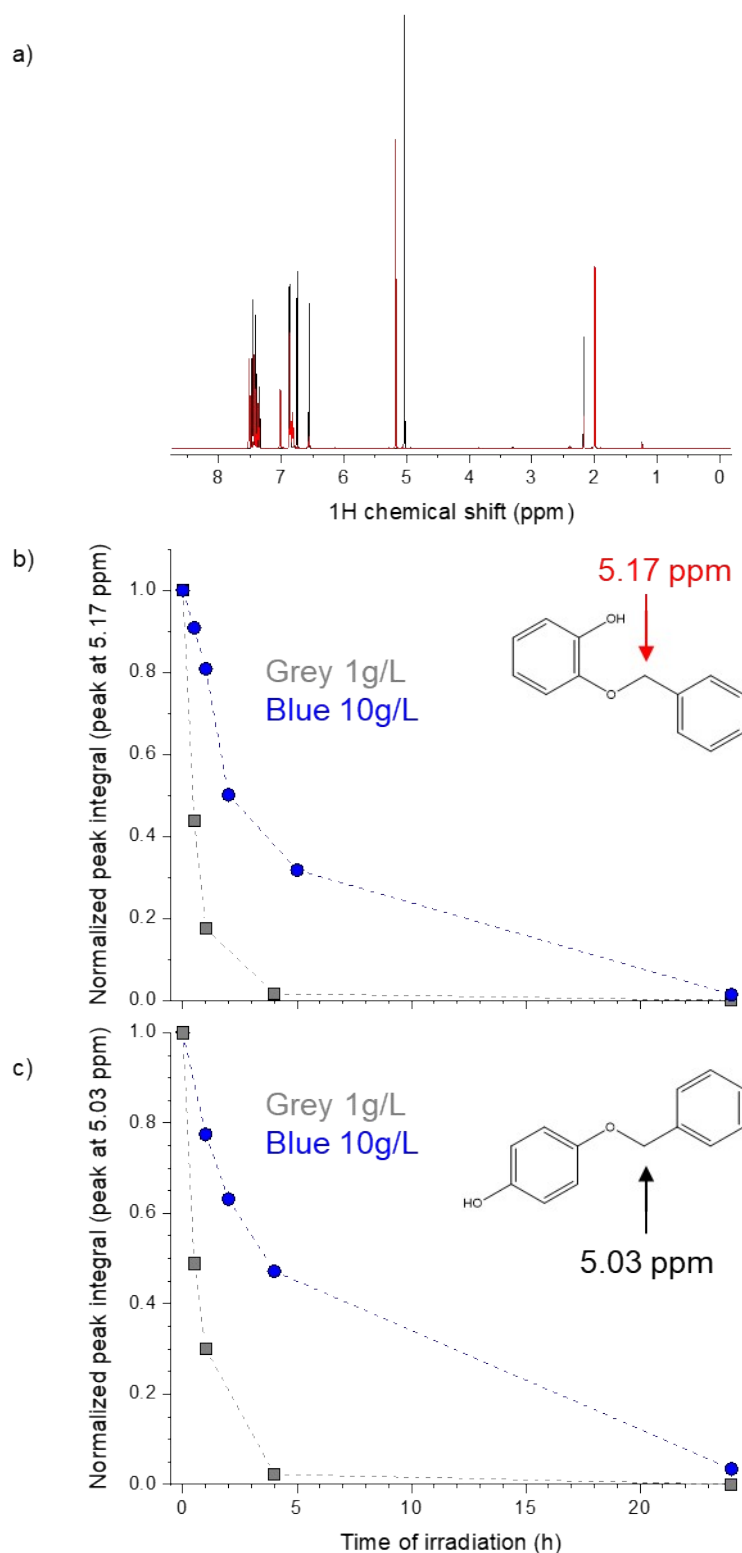


Figure S6. (a) NMR spectra of 2BP (red) and 4BP (black). Normalised ^1H NMR peak integral at (b) 5.17 ppm (2BP) and (c) 5.03 ppm (4BP)—plotted against time of irradiation—maximum peak integral for the control sample was normalised to 1. Rate of conversion for the starting molecule 2BP the first hour of irradiation was estimated to 0.8 g h^{-1} at 1 g L^{-1} and 1.8 g h^{-1} at 10 g L^{-1} , for 4BP the rate of conversion was estimated to 0.7 g h^{-1} at 1 g L^{-1} and 2.3 g h^{-1} at 10 g L^{-1} .

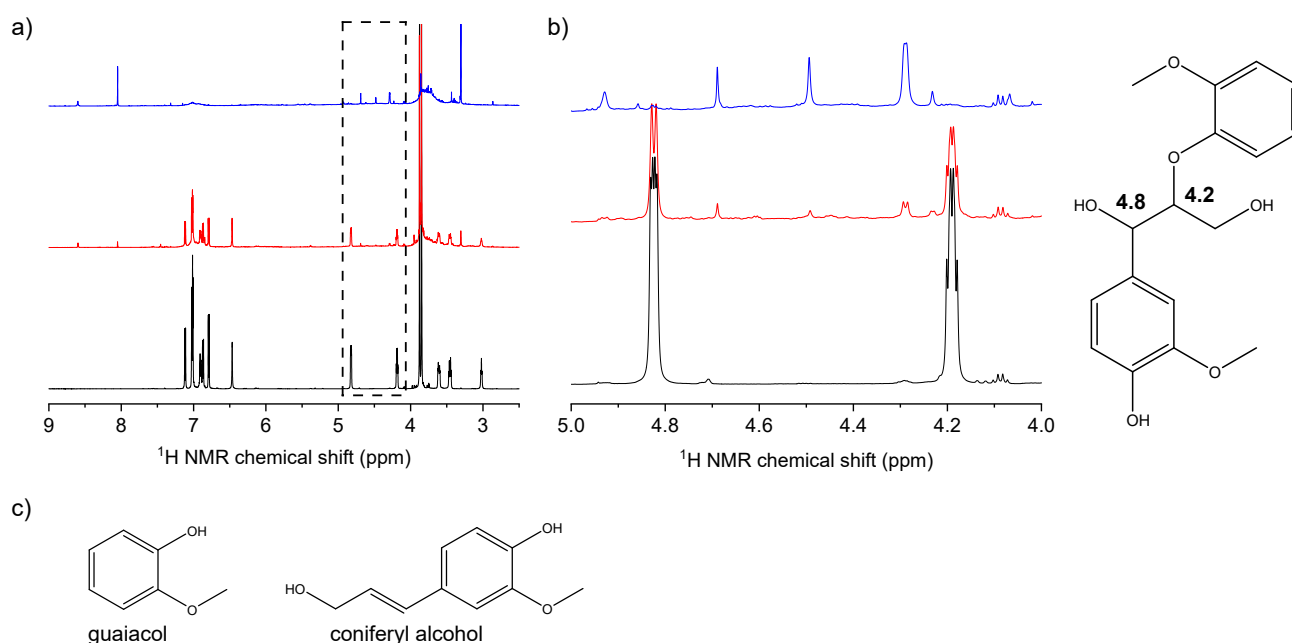


Figure S7. (a) ¹H NMR spectra of guaiacylglycerol-β-guaiacyl ether at 0h (black), 4h of irradiation (red) and 24h of irradiation (blue) using UV-LED's, $\lambda \sim 265\text{nm}$. Area marked by the dashed region is plotted in (b) showing the chemical shifts in the inset chemical structure of guaiacylglycerol-β-guaiacyl ether. The decrease of shifts at 4.2 and 4.8 ppm is indicative of the breakage of the β-O-4 bond. This was confirmed using GC-MS where guaiacol and coniferyl alcohol was found as major products upon irradiation, chemical structures presented in (c).

Experimental 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (guaiacylglycerol-β-guaiacyl ether) synthesis and irradiation

Guaiacylglycerol-β-guaiacyl ether was synthesized according to protocol in Shiming L. et al., *Acta Chem. Scand.*, 1995, 49, 623-624. Irradiation of guaiacylglycerol-β-guaiacyl ether was performed in MeCN and followed the same experimental procedure as described in the manuscript for 2BP and 4BP.

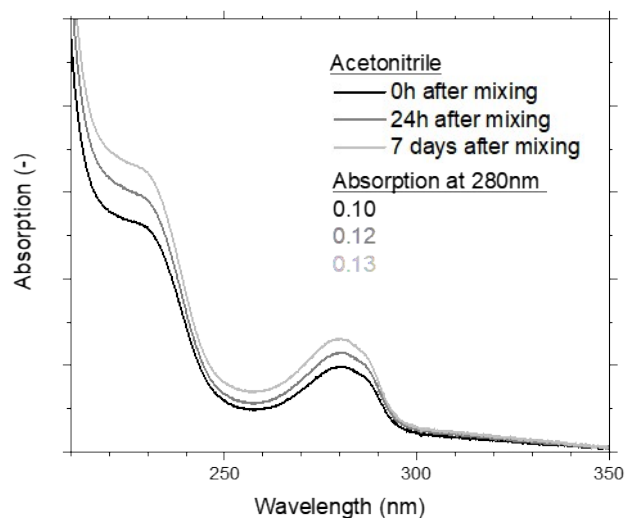


Figure S8. Representative UV-vis absorption spectra of softwood extracted in acetonitrile at 24 h (dark grey) and 7 days (light grey) after mixing. Spectra indicate that acetonitrile continues to slowly extract the softwood even after mixing. However, the increase in the concentration of UV absorbing extractives is insignificant after seven days.

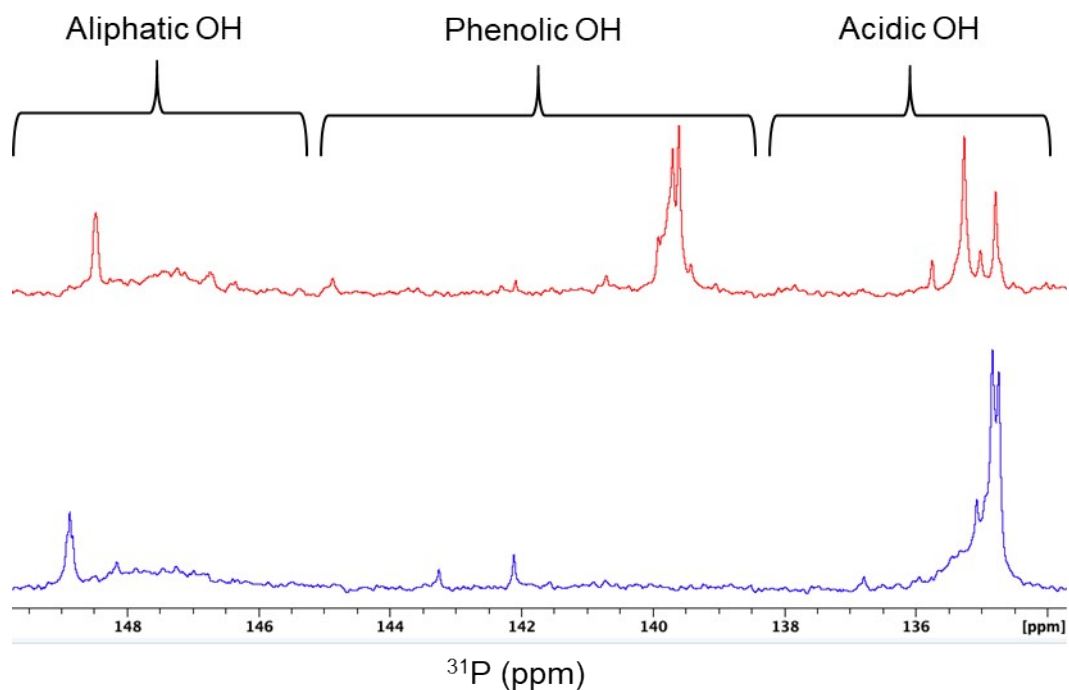


Figure S9. ^{31}P NMR of softwood lignin and extractives. Non-irradiated sample (red) and irradiated (blue), the phenolic hydroxyl groups indicating guaiacyl units (139-140 ppm) are absent after irradiation.