

Supplemental Information:

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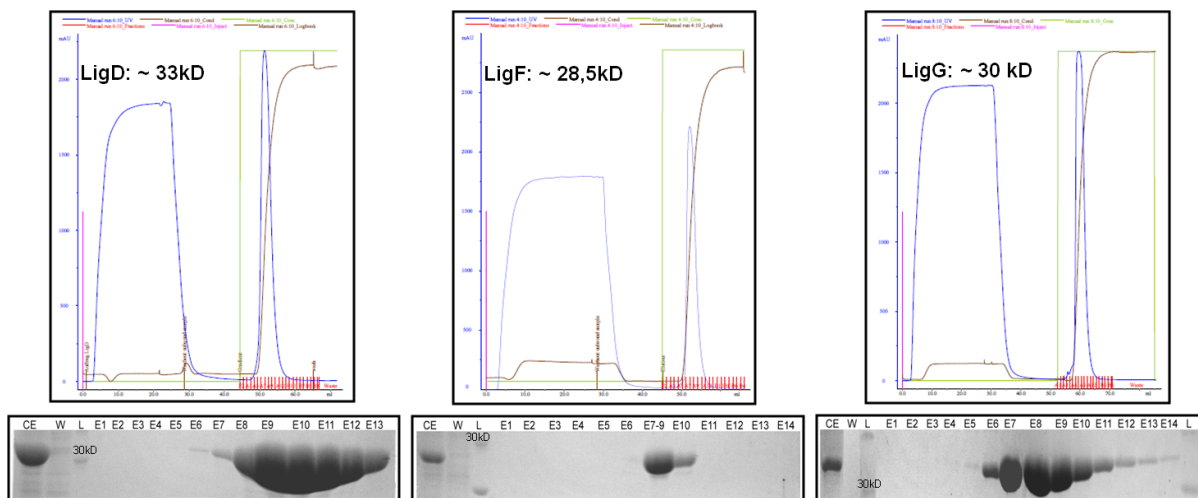
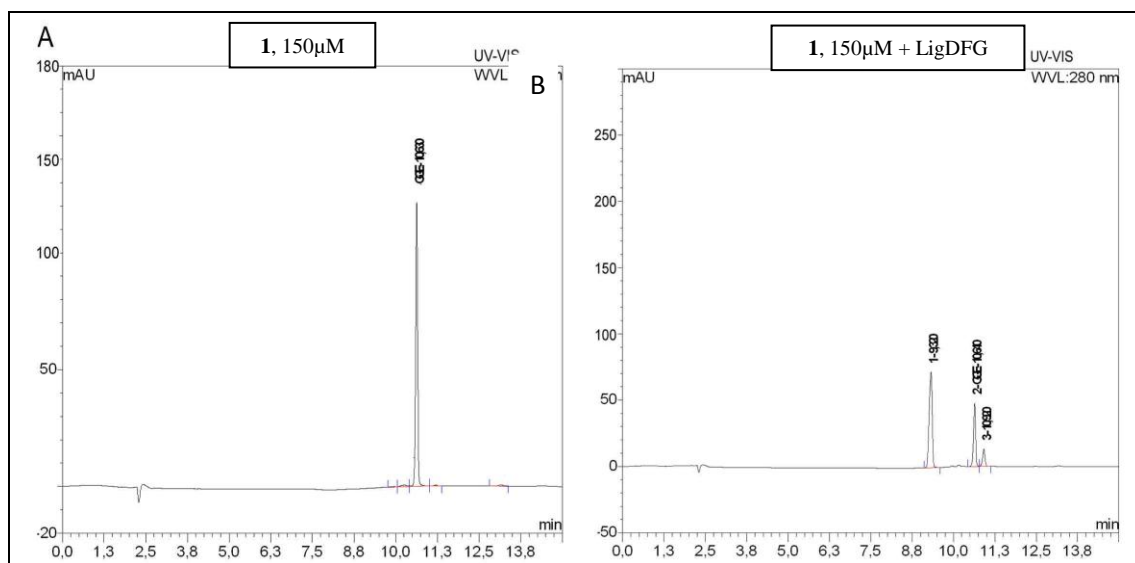


Figure S1: Aekta-purification of LigDFG with purity test by SDS-Page



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Figure S2. Detection of the cleavage products of the model substance **1** via HPLC. **1** in the non-enzyme control (**A**) is cleaved into **3** and **5** in the LigDFG samples (**B**).

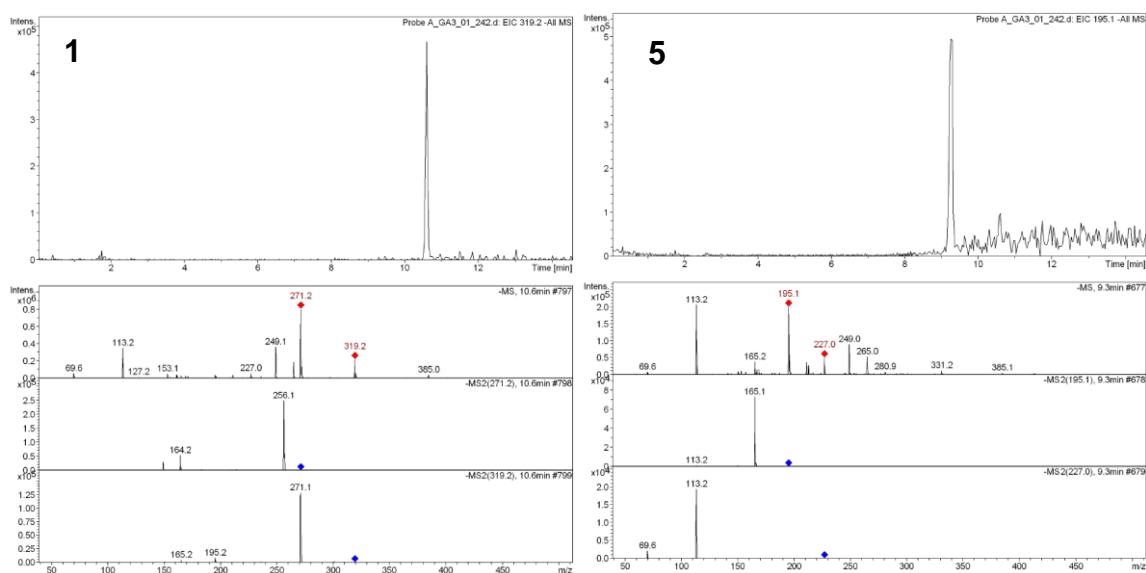


Figure S3. Detection of the substrate **1** and cleavage product **5** in LigDFG probes with LC-MS.

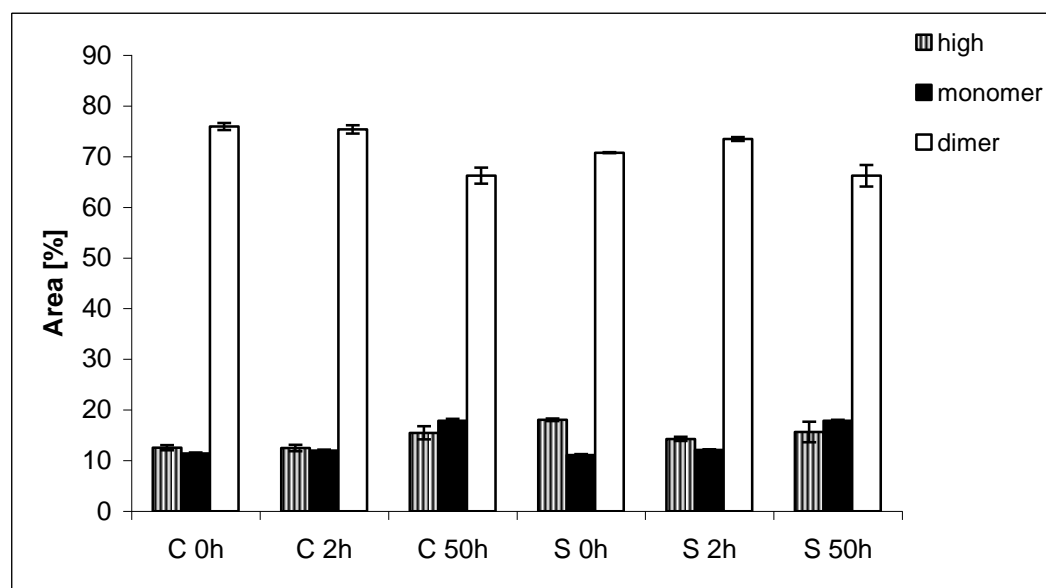
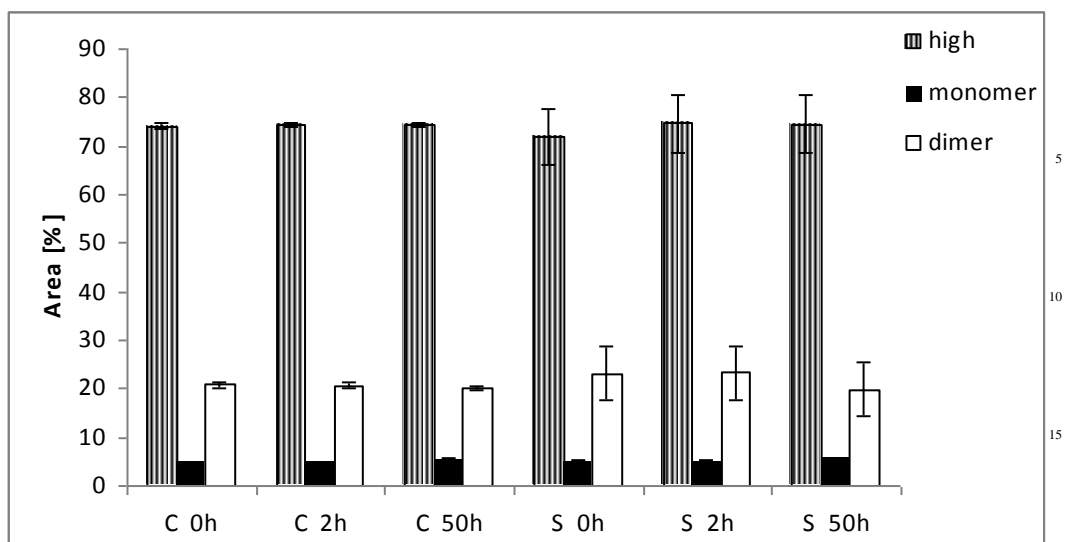


Figure S4. GPC analysis of bagasse lignin with (S) and without (C) LigDFG. Both probes had a concentration of 10 mM NAD⁺ and glutathione. Area % of the monomer (~ 150 MW), dimer (~ 300 MW) and high molecular weight fractions (~ 800-1,000,000 MW) are depicted at 0 h, 2 h and 50 h.

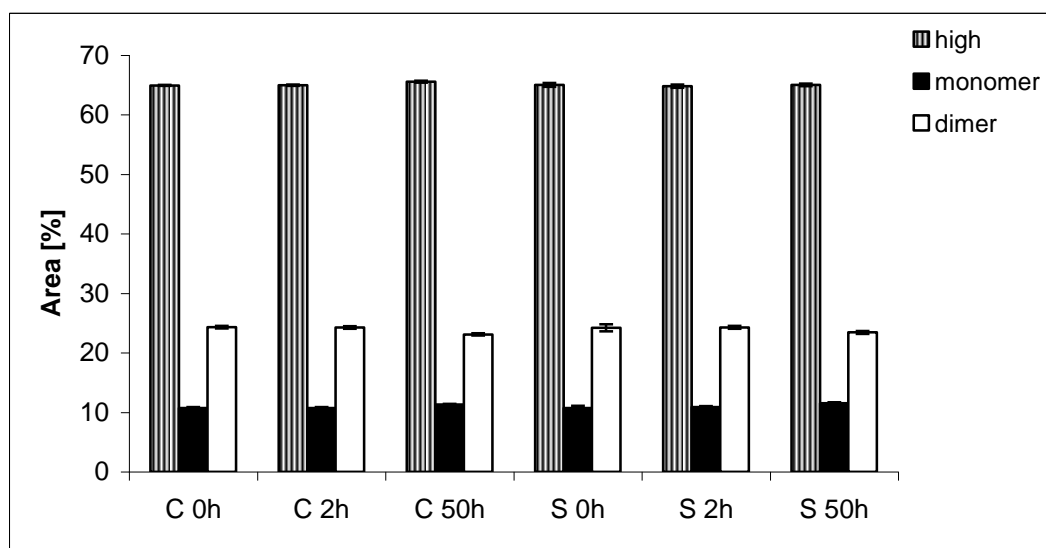
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20 **Figure S5.** GPC analysis of alkali softwood lignin with (S) and without (C) LigDFG. Both probes had a concentration of 10 mM NAD⁺ and glutathione. Area % of the monomer (~ 150 MW), dimer (~ 300 MW) and high molecular weight fractions (~ 800-1,000,000 MW) are depicted at 0 h, 2 h, 50 h.



25 **Figure S6.** GPC analysis of alkali hardwood lignin with (S) and without (C) LigDFG. Both probes had a concentration of 10 mM NAD⁺ and glutathione. Area % of the monomer (~ 150 MW), dimer (~ 300 MW) and high molecular weight fractions (~ 800-1,000,000 MW) are depicted at 0 h, 2 h and 50 h.