Supporting Information for

Title

The Importance of Ester Cleavage in the Butylamine Pretreatment of Hybrid Poplar

Authors

Joseph M. Palasz[1], Anagha Krishnamoorthy[1], Raynald A. Giovine[2], Xueli Chen[1], Venkataramana Pidatala[1,3], Emine A. Turumtay[1,3], Tyrell S. A. Lewis[4], Edward E. K. Baidoo[1,3], Chang Dou[4], Hemant Choudhary[3,5], Ning Sun[4], Blake A. Simmons[1,3*]

Affiliations

1 Biological Systems and Engineering Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

2 Pines Magnetic Resonance Center (PMRC) – Core Facility, College of Chemistry, University of California, Berkeley, CA 94720, USA

3 Joint BioEnergy Institute, Emeryville, CA 94608, USA

4 Advanced Biofuels and Bioproducts Process Development Unit, Lawrence Berkeley National Laboratory, Emeryville, CA 94608, USA

5 Department of Bioresource and Environmental Security, Sandia National Laboratories, Livermore, CA 94550, USA

*** Corresponding author;** Blake A. Simmons

e-mail address: basimmons@lbl.gov

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Supplemental Tables

Table S1: Sugar Yield data for varying water content pretreatments of hybrid poplar

Butylamine: Water Ratio	**Glucose Yield (%)**	**Glucose Yield (STDEV)**	**Xylose Yield (%)**	**Xylose Yield (STDEV)**	**Solvent Removal (%)**
No Pretreatment	26.9	0.13	21.27	0.19	NA
1:0	90.76	1.50	71.09	6.07	96.42
1:1	90.04	2.52	63.30	5.74	98.04
1:2	88.76	2.12	72.02	0.71	97.28
1:4	89.68	2.21	70.55	3.51	97.31
1:8	89.16	2.72	75.27	5.15	97.47
1:16	84.44	1.70	71.06	1.89	97.11

Table S2: Sugar Yield data for controlled atmospheric composition pretreatment of hybrid poplar using 75 mL Parr reactors.

Controlled Atmosphere Runs (75 mL Parr Scale)					
Atmospheric Composition	**Glucose Yield (%)**	**Glucose Yield (STDEV)**	**Xylose Yield (%)**	**Xylose Yield (STDEV)**	**Solvent Removal (%)**
N2	94.51	4.10	76.97	3.79	NA*
O2	97.86	0.51	77.50	0.86	NA*
CO2	96.51	2.26	74.93	1.12	NA*

*Solid was lost during transfer and drying preventing full mass balance

Supplemental Figures

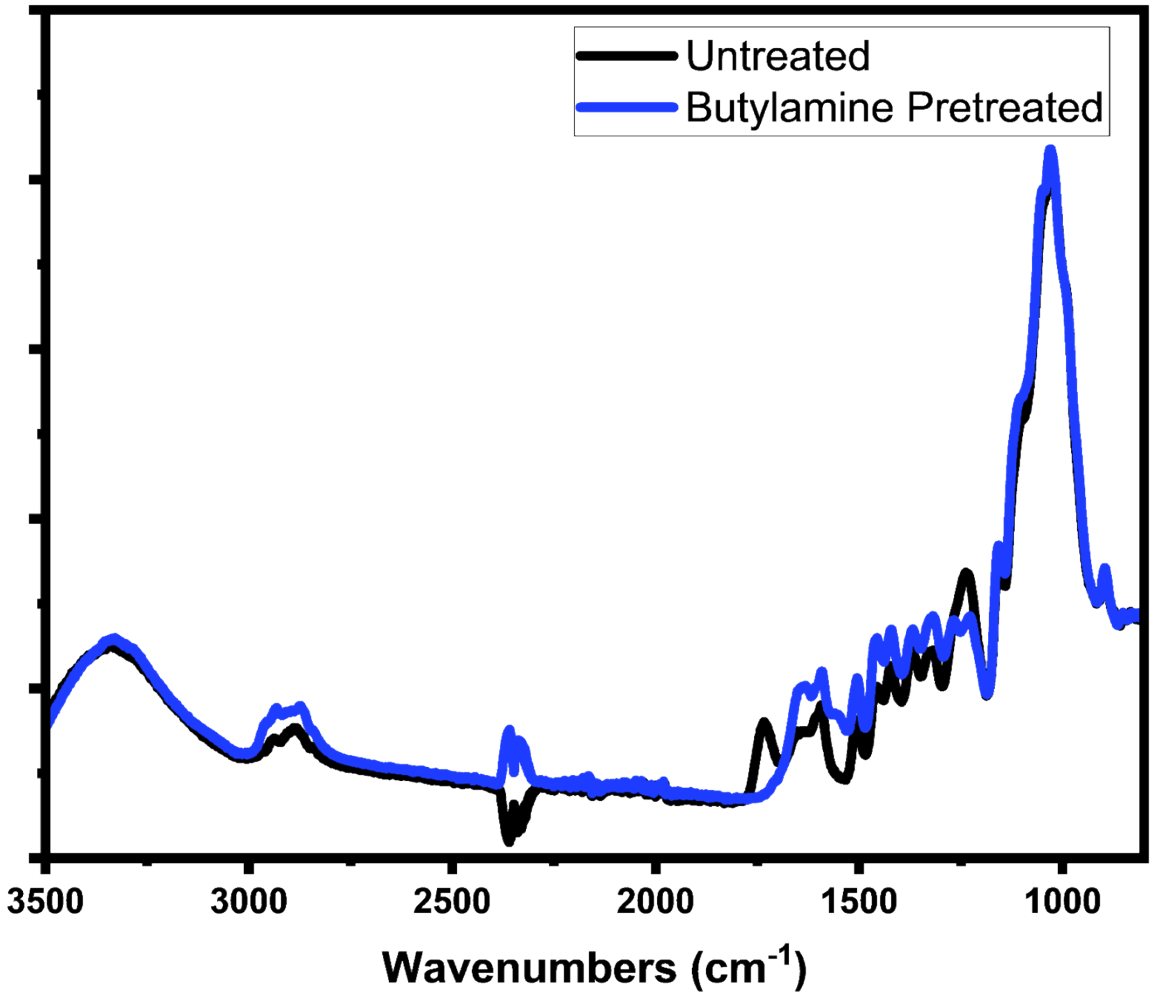

Figure S1: Full ATR-FTIR spectra of untreated (black) and butylamine pretreated (blue) hybrid poplar.

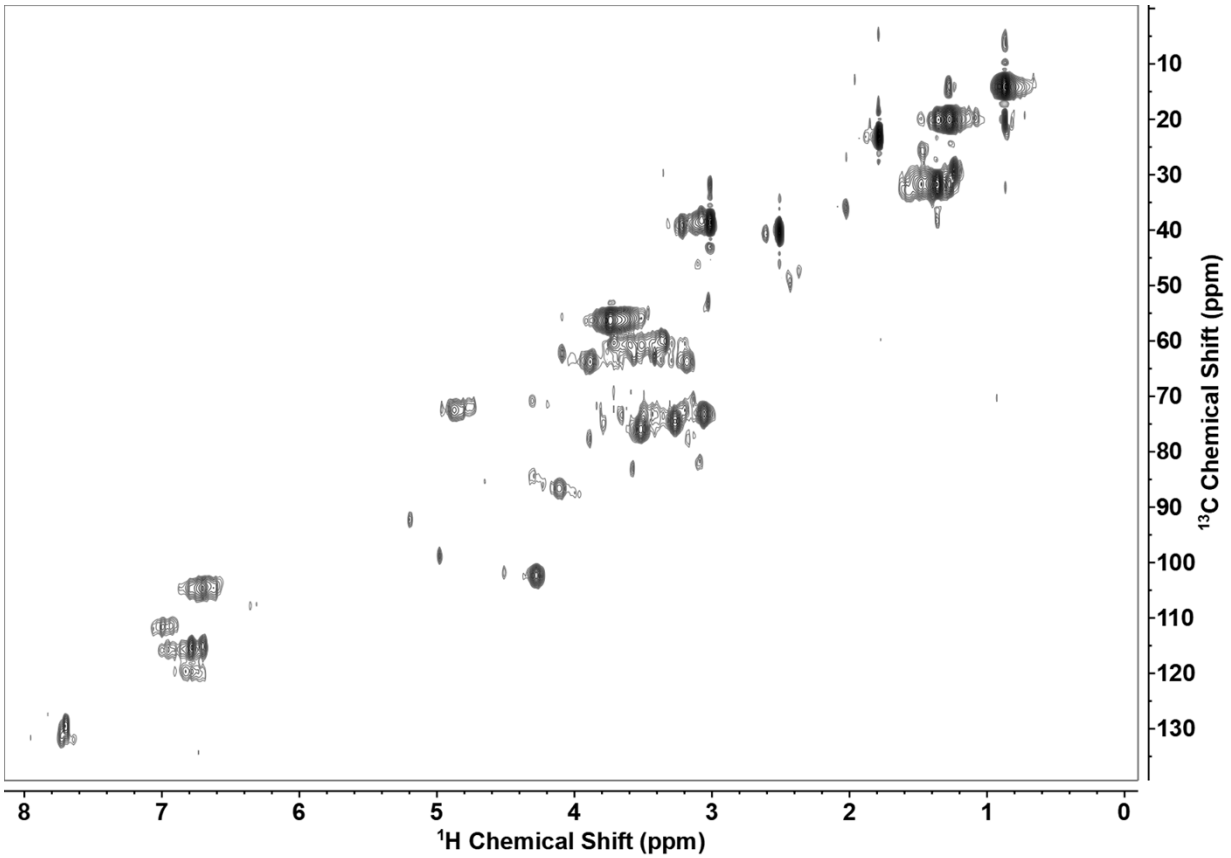

Figure S2: HSQC spectra of the DMSO-d6 extract from a pretreated and dried hybrid poplar sample.

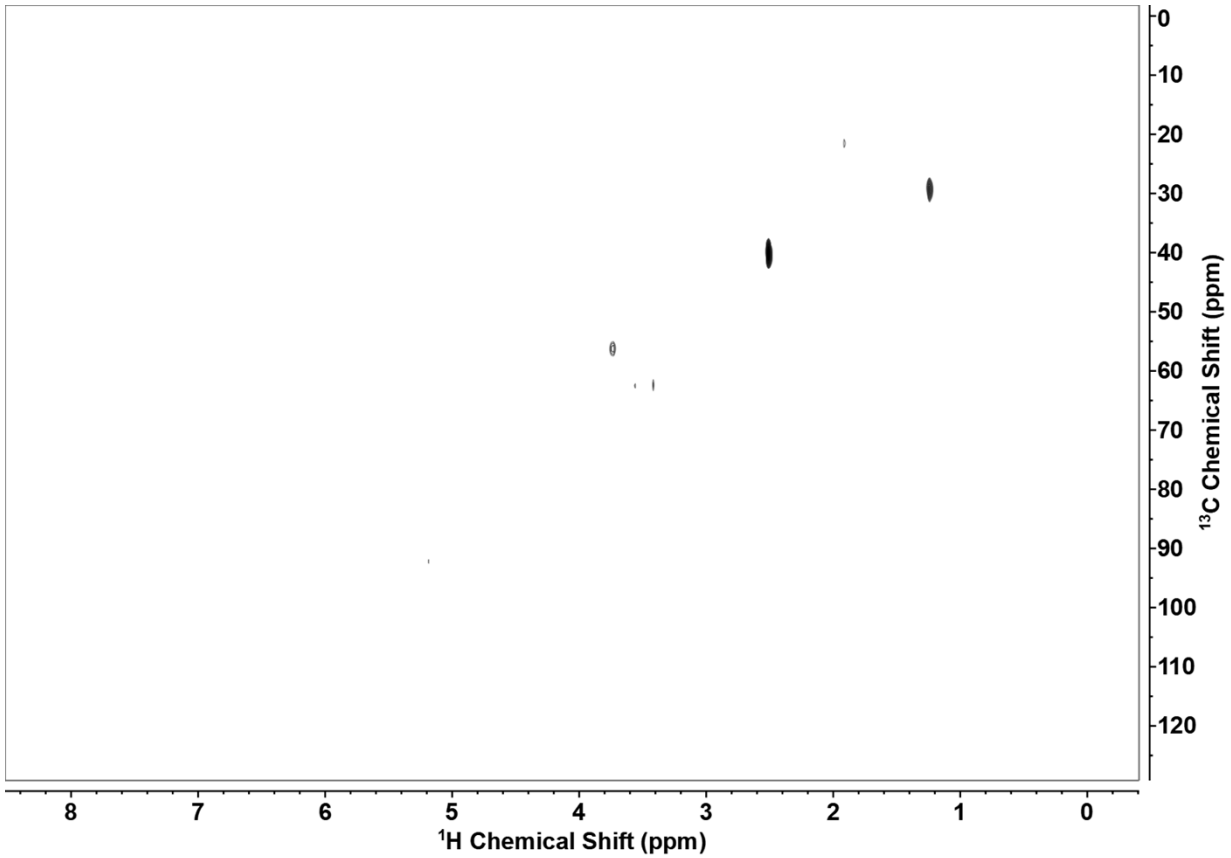

Figure S3: HSQC spectra of the DMSO-d6 extract from an untreated dried hybrid poplar sample.

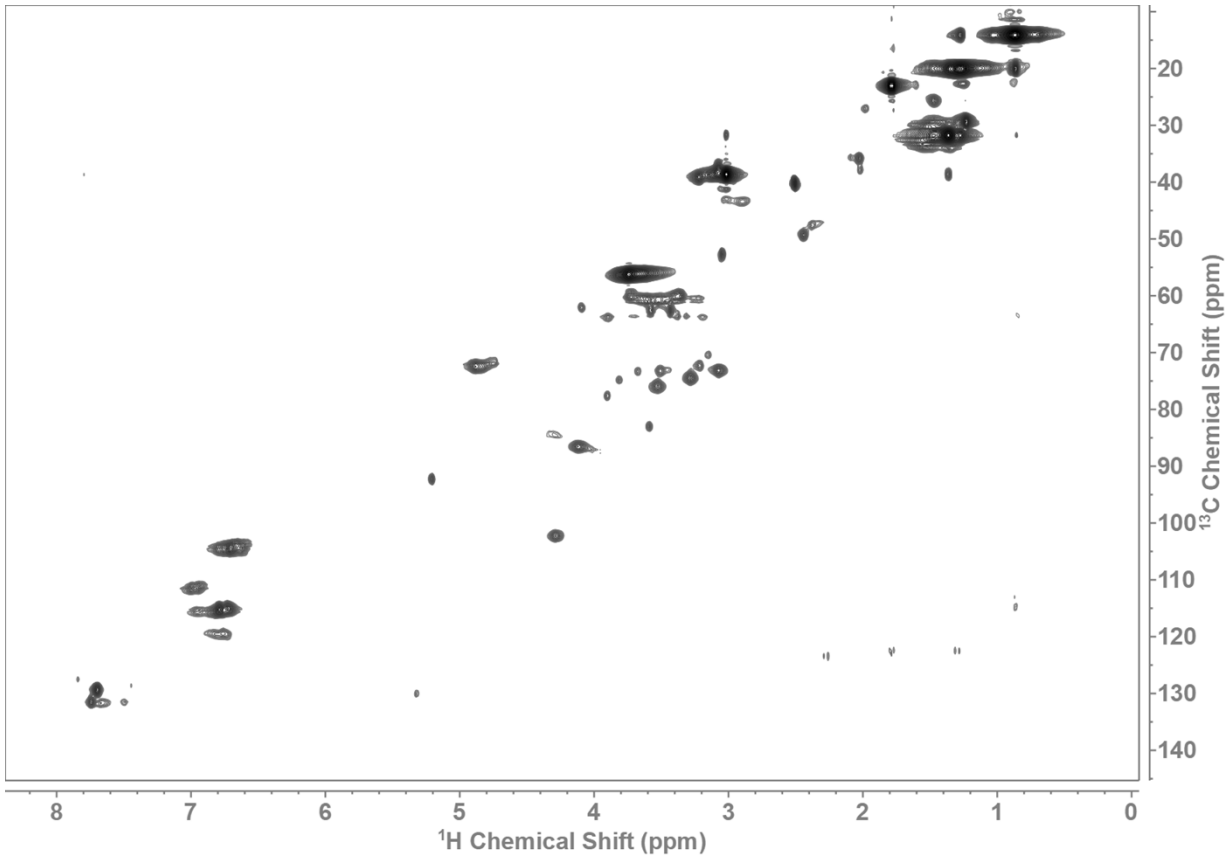

Figure S4: HSQC of the butylamine filtrate from a hybrid poplar pretreatment dissolved in DMSO-d6

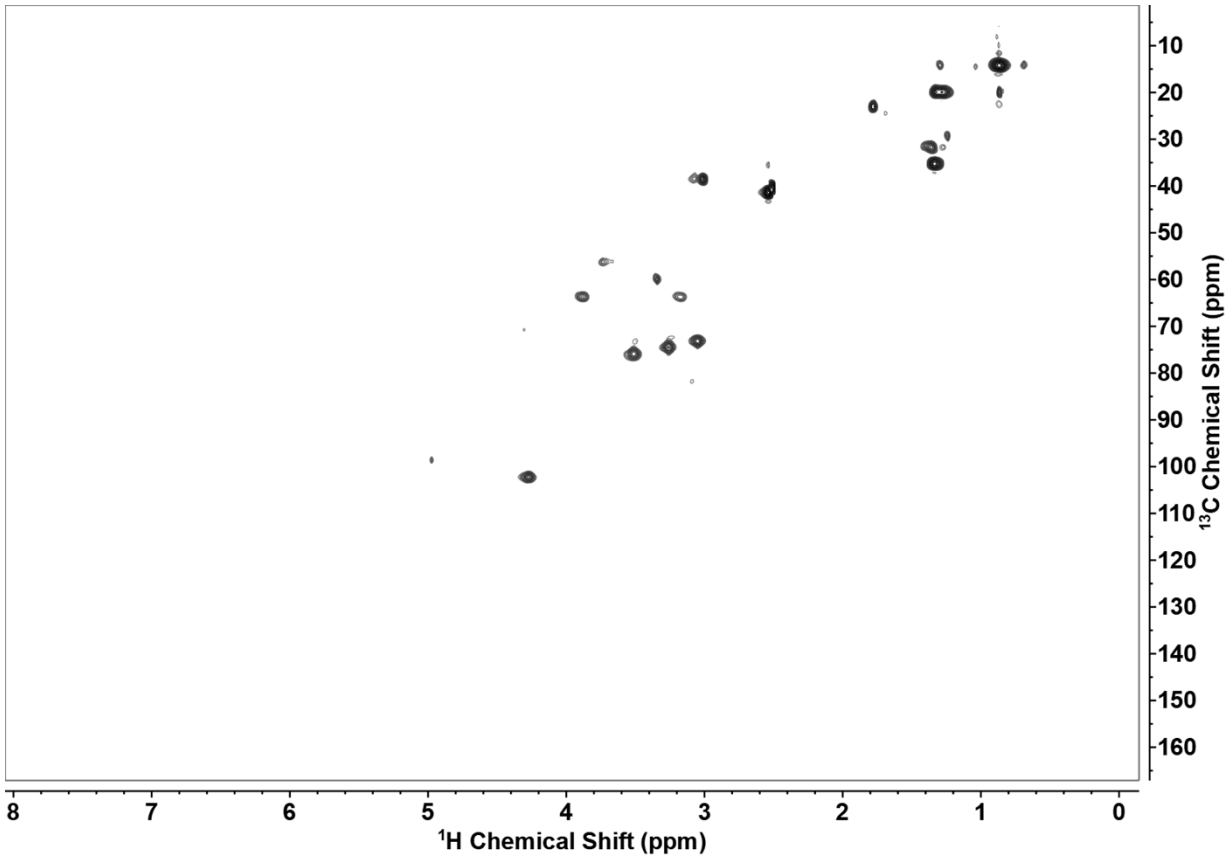

Figure S5: HSQC of the residual solid after the butylamine filtrate was washed off after a hybrid poplar pretreatment. Residual solid extracted into DMSO-d6.

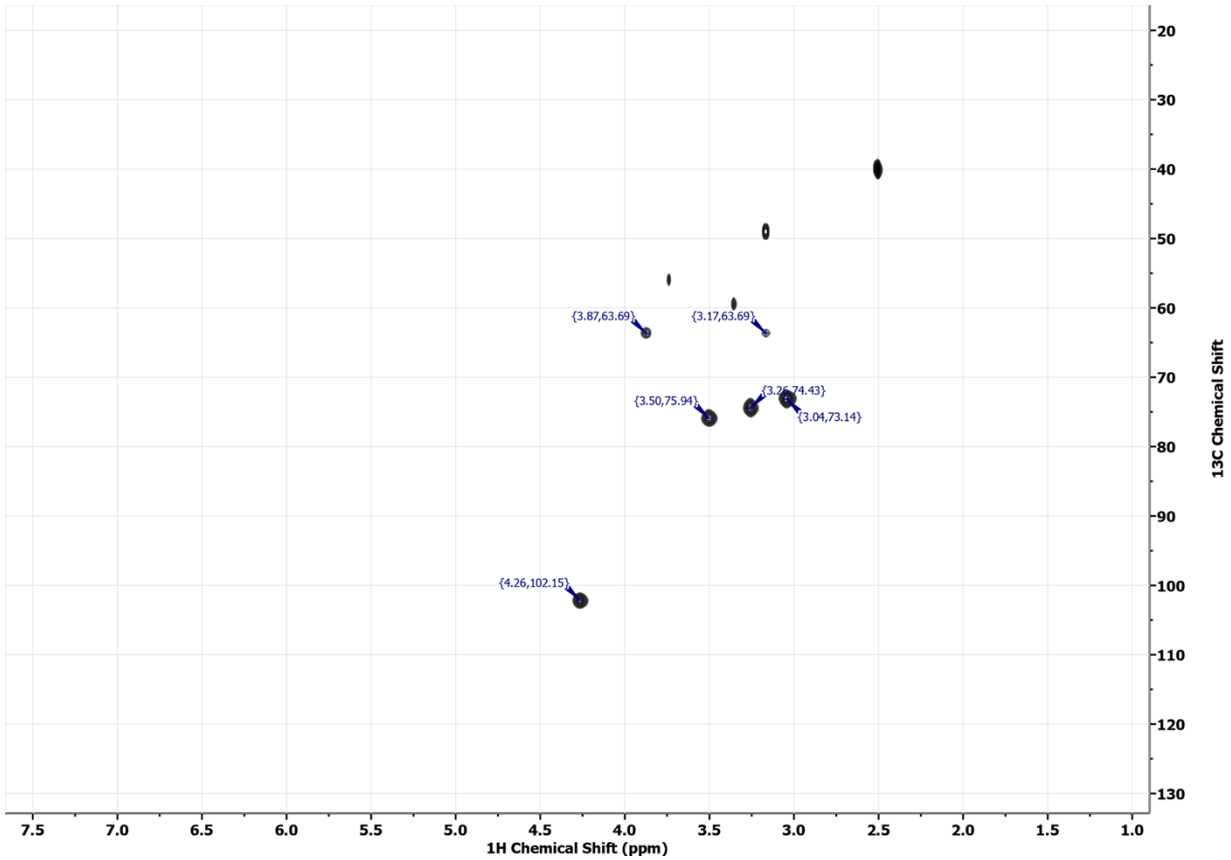

Figure S6: Reference HSQC of xylan isolated from beechwood dissolved in DMSO-d6.

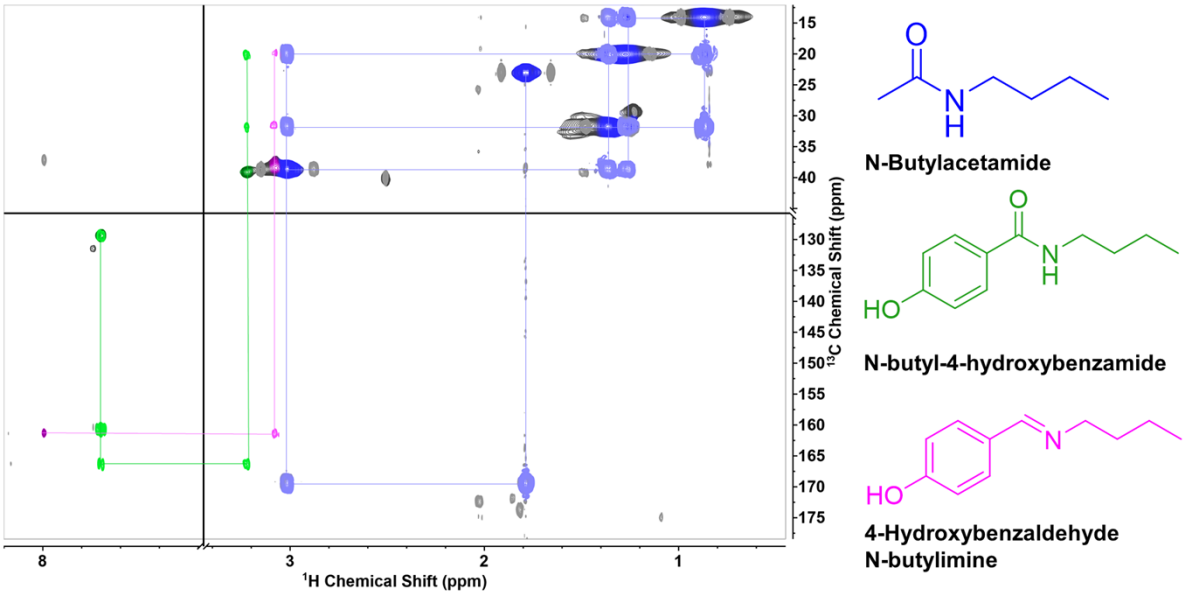

Figure S7: Overlaid HSQC (Dark traces) and HMBC (Pale traces) spectra of the butylamine filtrate from the pretreatment of hybrid poplar, concentrated in-vacuo and dissolved in DMSO-D6. Peaks assigned to N-butylacetamide (Blue), N-Butylformamide (Magenta) and N-butyl-4-hydroxybenzamide (Green) are color coded and labelled with vertical and horizontal lines to better show the connectivity network.

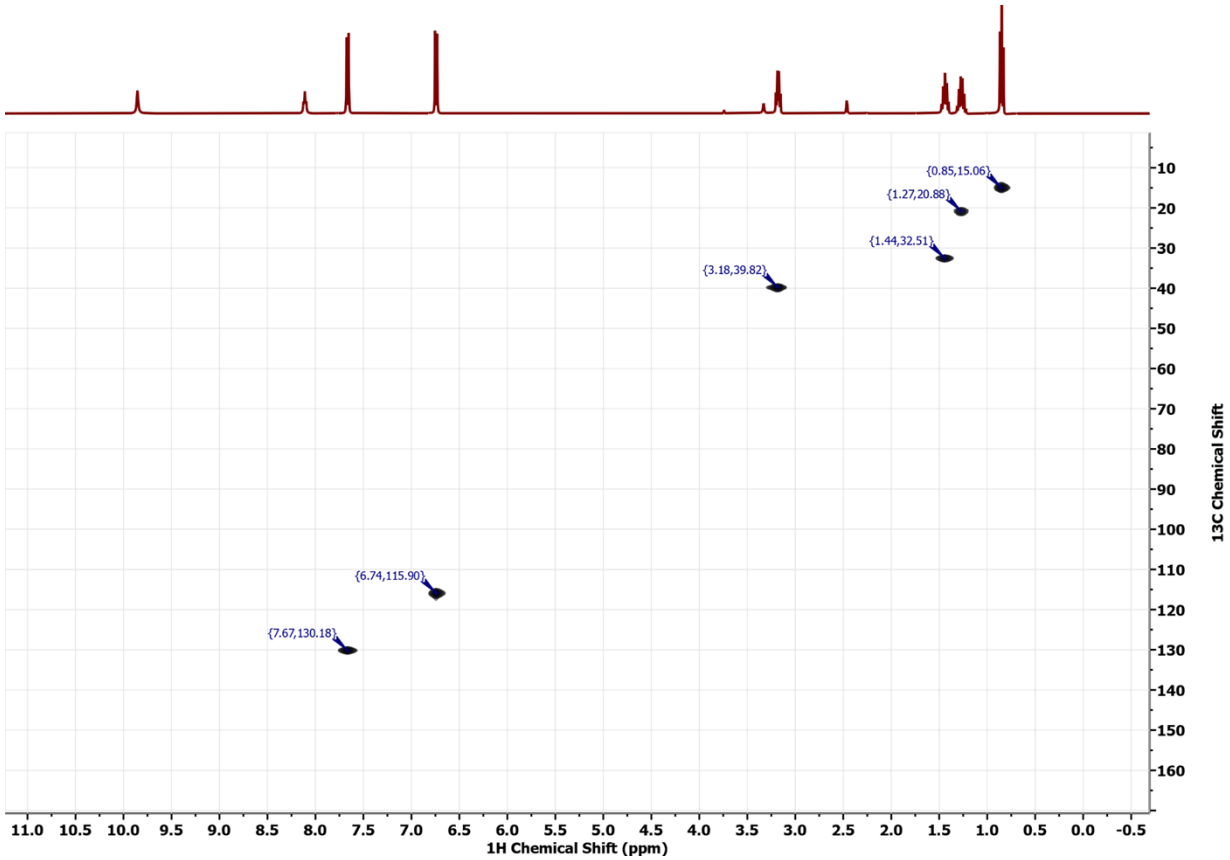

Figure S8: Reference ^{1}H and HSQC NMR spectra of N-butyl-4-hydroxybenzamide (4HBAmide) dissolved in DMSO-d6.

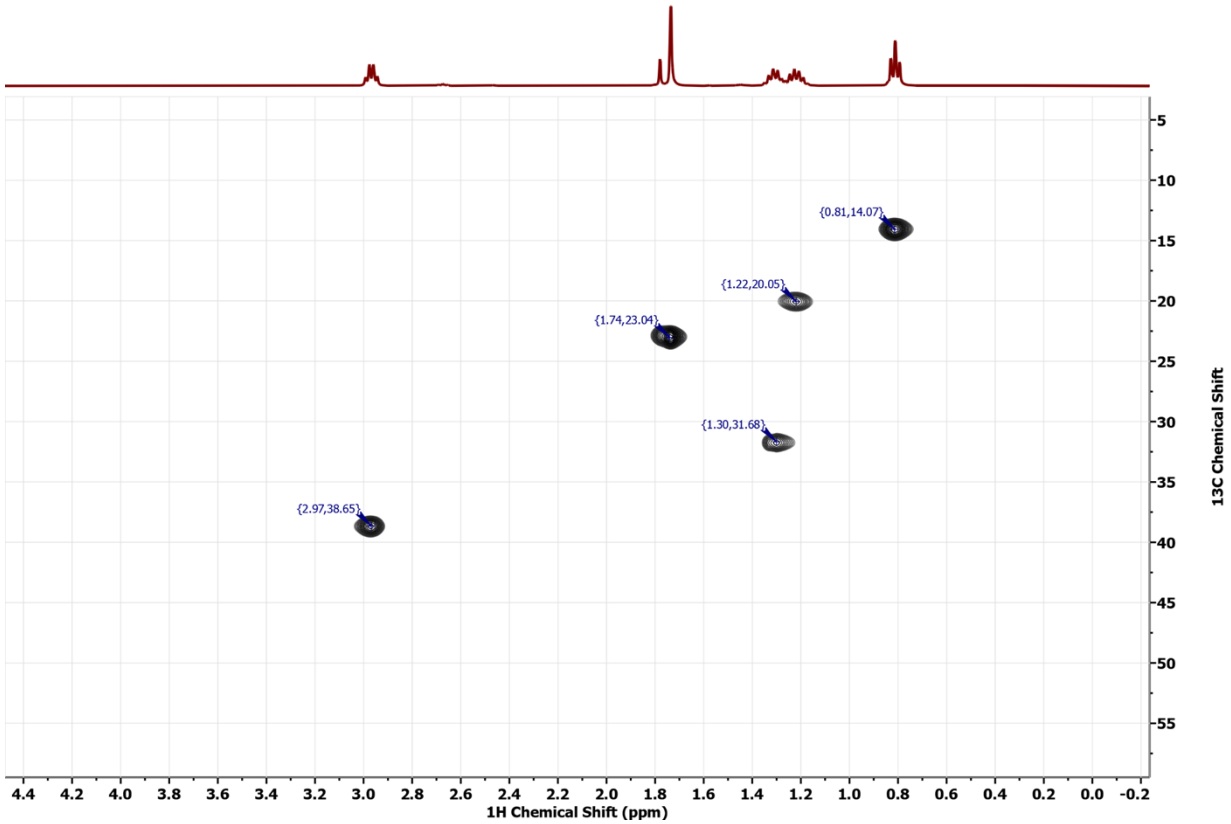

Figure S9: Reference [1]H and HSQC NMR spectra of N-butylacetamide dissolved in DMSO-d6

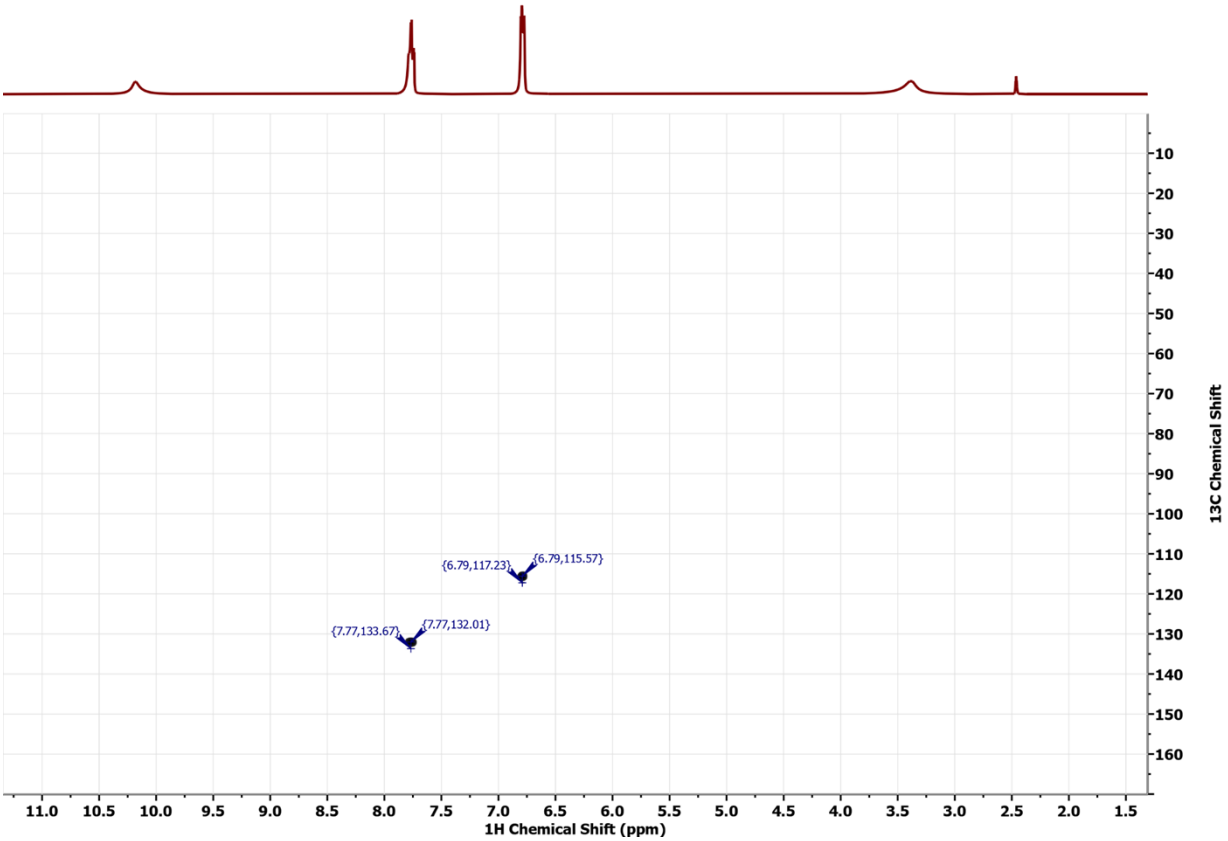

Figure S10: Reference ^{1}H and HSQC NMR spectra of 4-hydroxybenzoic acid dissolved in DMSO-d6

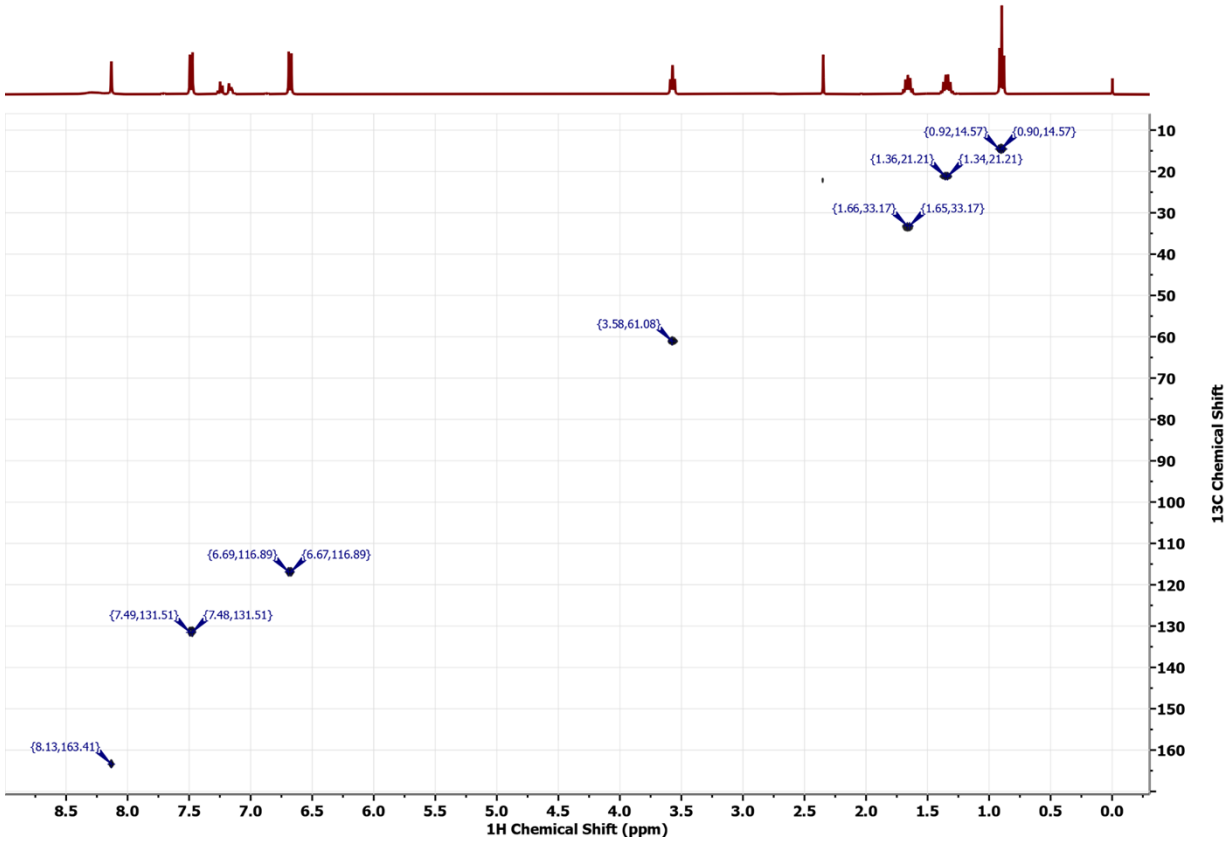

Figure S11: Reference ^{1}H and HSQC NMR spectra of 4-((butylimino)methyl)phenol taken in DMSO-d6.

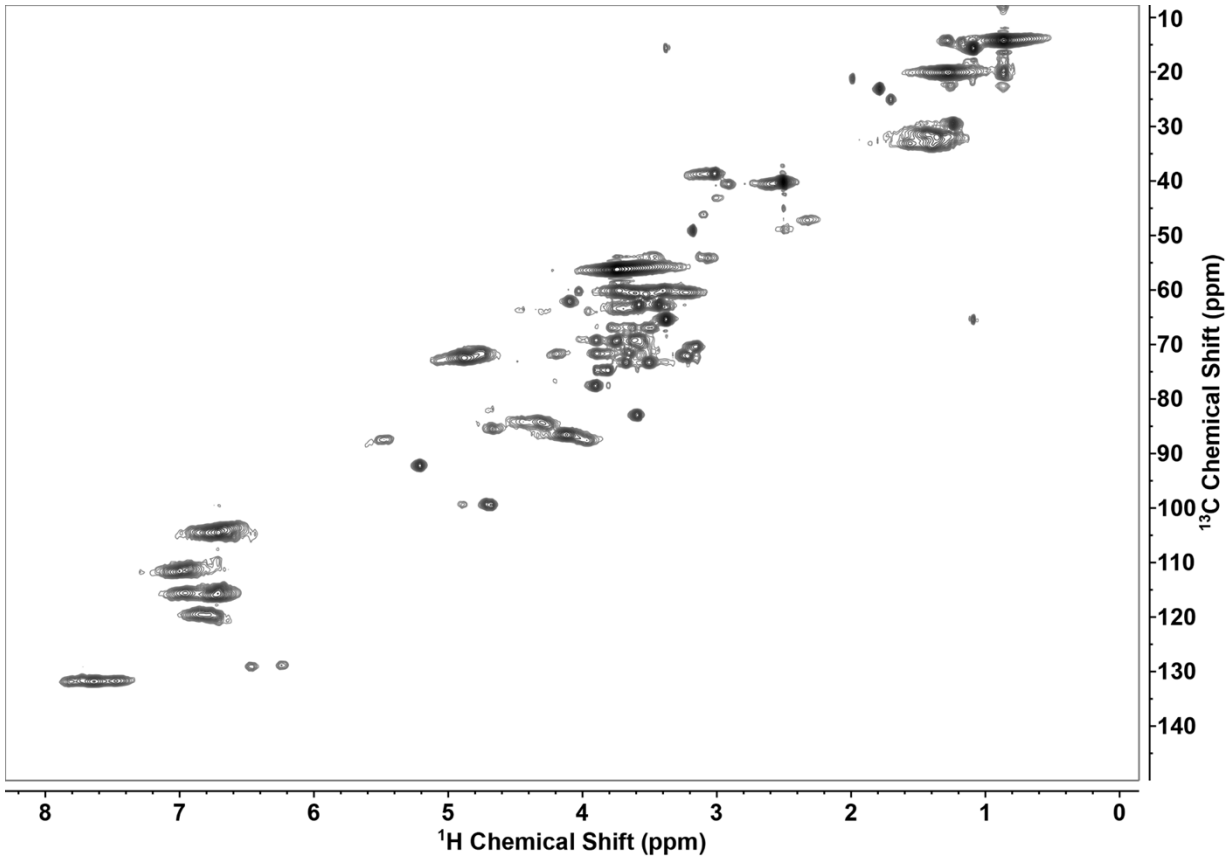

Figure S12: Full HSQC Spectrum of the methanol-extracted, ether-precipitated lignin fraction from pretreated biomass, taken in DMSO-d6.

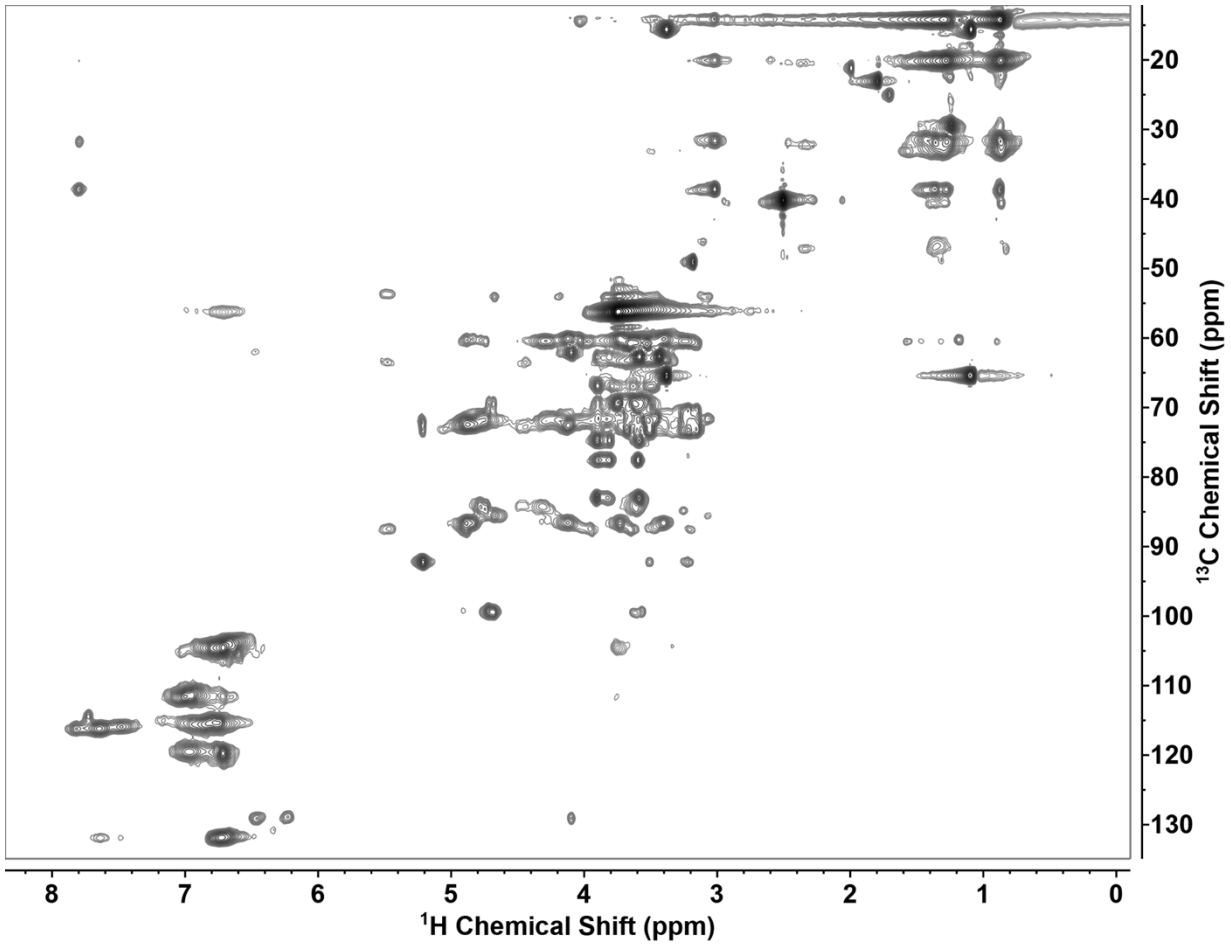

Figure S13: Full TOSCY:HSQC Spectrum of the methanol-extracted, ether-precipitated lignin fraction from pretreated biomass, dissolved in DMSO-d6.

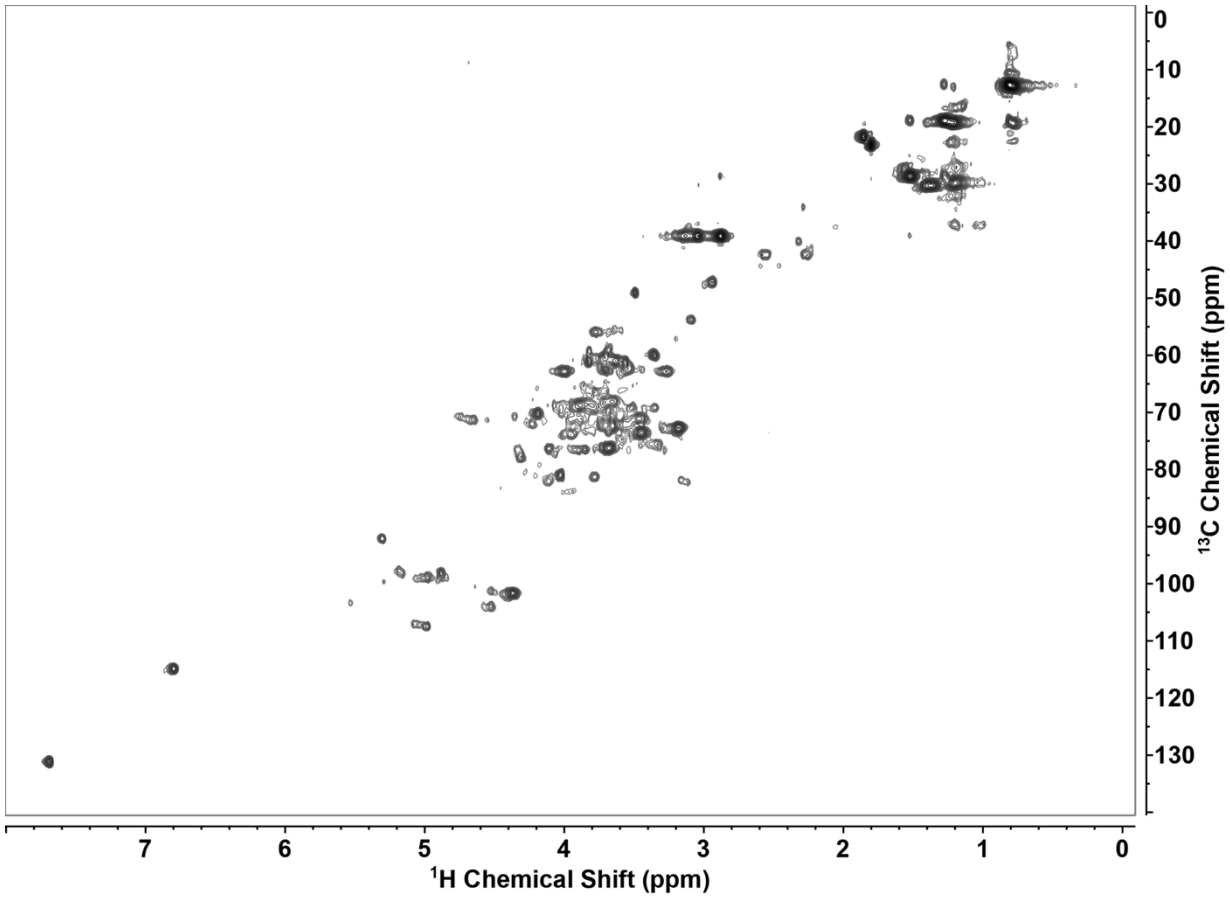

Figure S14: Full HSQC spectra of the sequentially methanol-extracted, aqueous-extracted filtrate of pretreated biomass dissolved in D_2O showing the hemicellulose rich fraction.

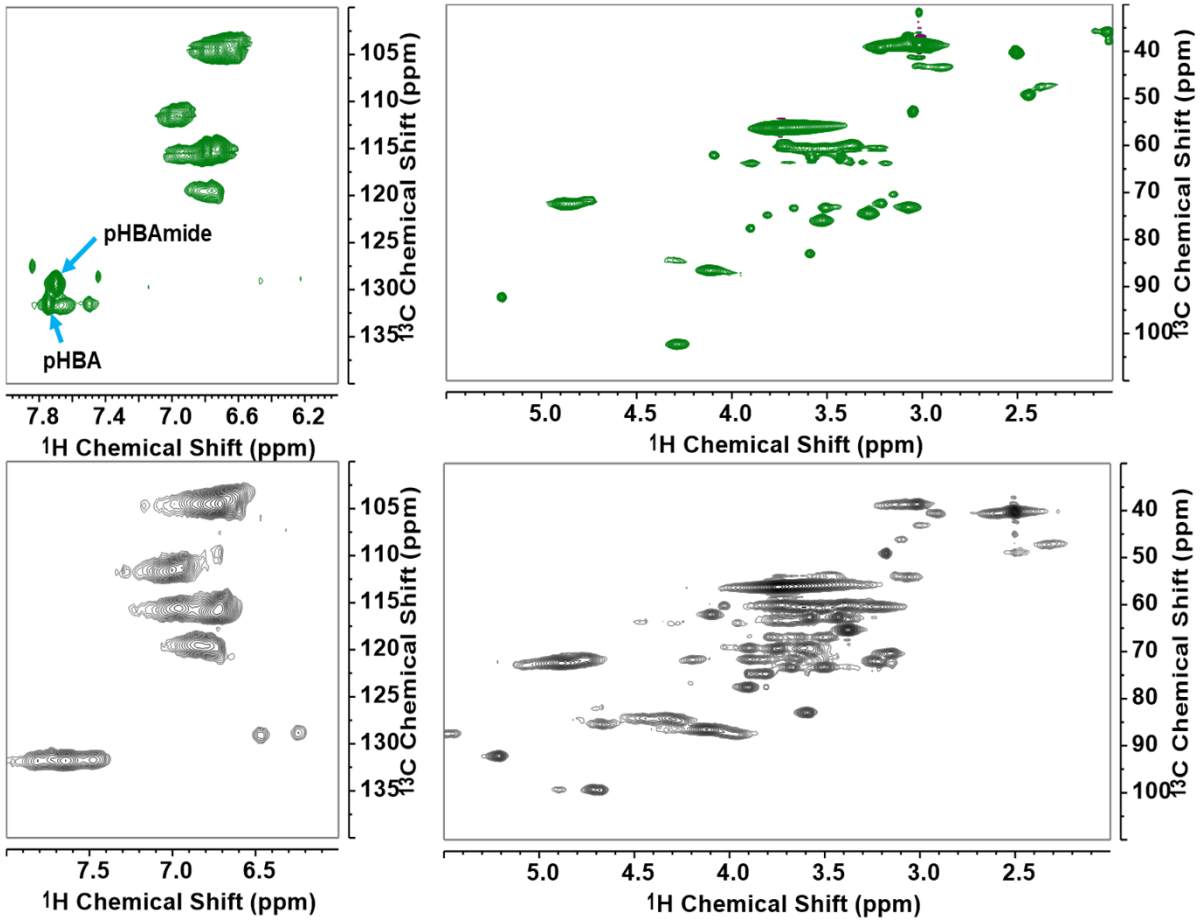

Figure S15: Comparison of the HSQC spectra of the DMSO-D6 extract of pretreated biomass (top, green) and the methanol-extracted, ether precipitated lignin fraction (bottom, grey) in the aromatic (left) and aliphatic (right) regions demonstrating the loss of the identified small molecule and xylan components of the extract in the lignin isolation protocol.

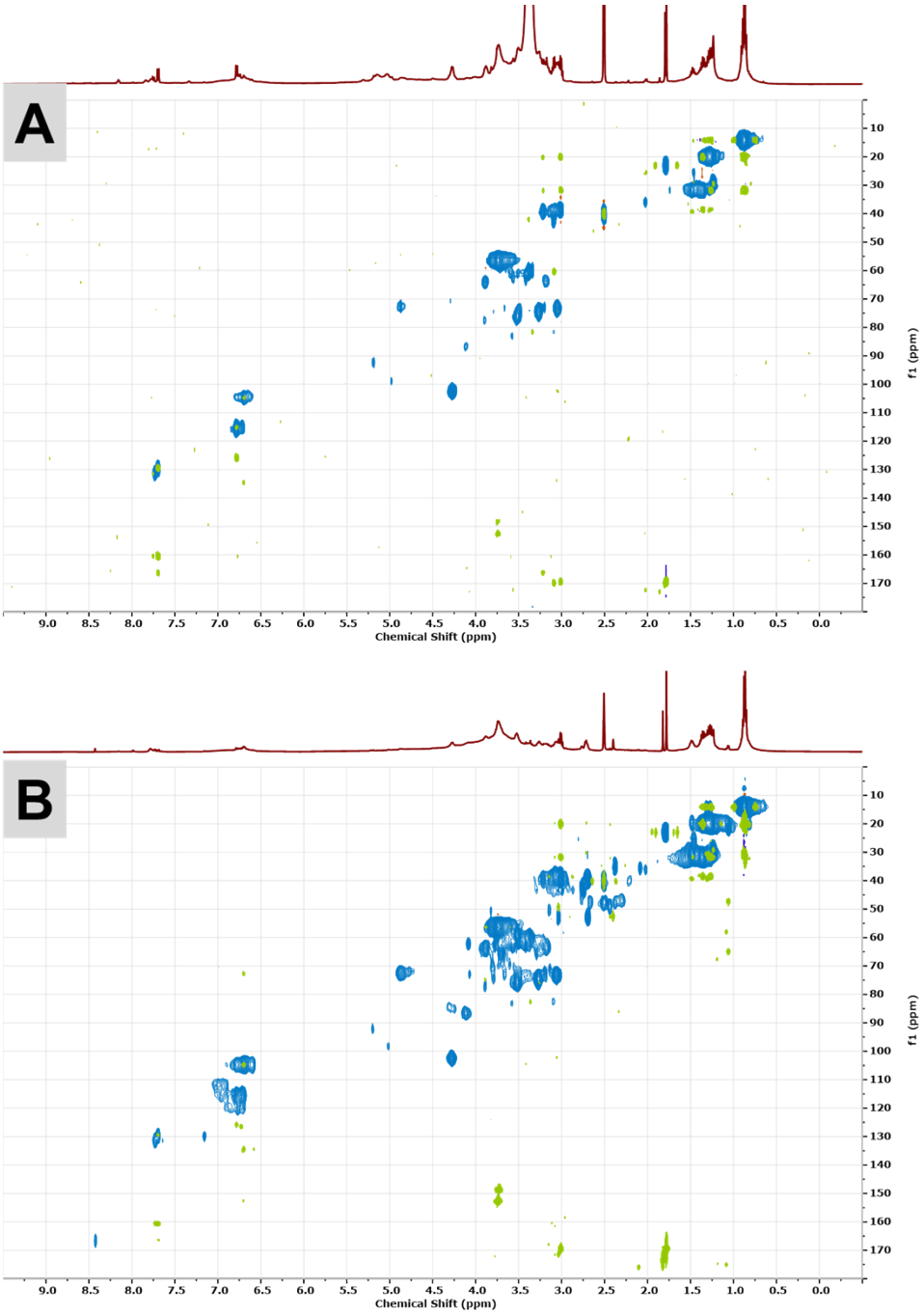

Figure S16: 1D 1H NMR Spectrum (red trace) and overlaid HSQC (blue) and HMBC (green) spectra of DMSO-d6 extracts prepared from hybrid poplar pretreated with neat butylamine (A, top) and a 50 wt% solution of butylamine in water (B, bottom)

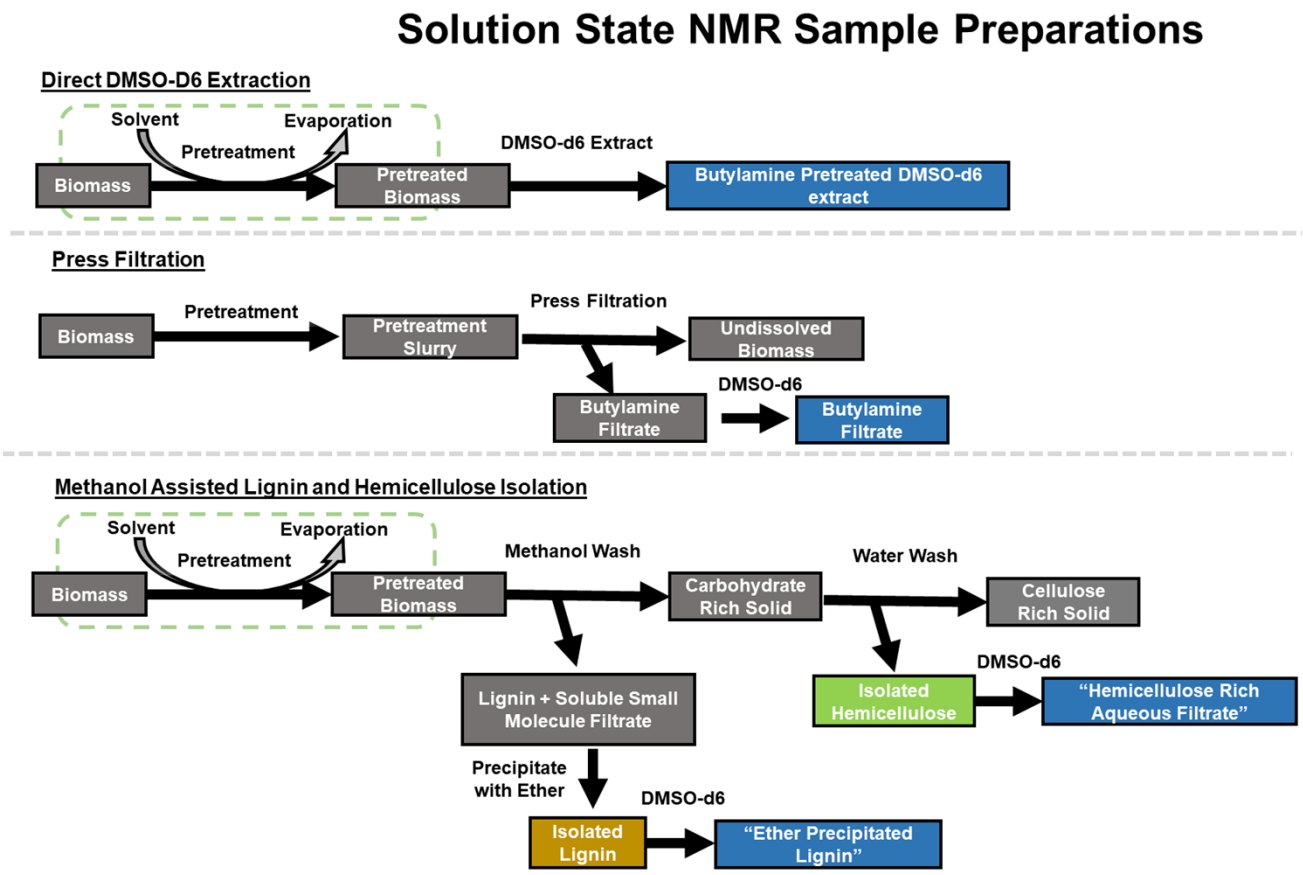

Figure S17: Schematic representation of the isolation schemes used to prepare the various solution state NMR samples within this manuscript. Blue boxes indicate the samples characterized and named in the main text.