Supporting Information

EXPERIMENTAL PROCEDURES

Sample Preparation. The compound cellulose in the form of microcrystalline powder extracted from cotton linters was obtained from Sigma-Aldrich (St. Louis, USA). Lignin (kraft lignin) was obtained from Sunila Mill (Kotka, Finland). European spruce wood (*Picea abies*) and maple (*Acer sp.*) were obtained from commercial suppliers of musical instrument tonewood. These were unprocessed and air-dried wood normally stored under ambient air. To examine the effect of heat treatment on wood structure in air, spruce slices of thickness from 0.5 to 1 mm were treated at 80 °C for 15 min, followed by a heat treatment at 220 °C for a pre-determined period, viz., 1, 2, and 4 hours. Wood samples were manually cut with scalpels and reduced to small particles around 0.1-0.5 mm in diameter for packing into NMR rotors (Figure S9). Mechanical grinding was avoided to prevent heat-induced modifications in wood.

Solid-state NMR. The ^{1}H-detected ^{1}H/^{13}C heteronuclear correlation (HETCOR) spectra were acquired at 9.4 T (^{13}C and ^{1}H Larmor frequencies of 100.6 and 400.1 MHz, respectively) and 18.8 T (201.2 and 800.2 MHz) on Bruker Avance III spectrometers equipped with homebuilt 0.51-mm probes. The rotor of approximately 200 nL in volume was fully packed with sample for each measurement. Wood samples (~0.2 mg) were finely cut using scalpels. The wood spectra were acquired at a spinning frequency of 140 or 150 kHz. The durations of ^{1}H and ^{13}C $\pi/2$ pulses were set to 1 and 5 μs, respectively. The initial cross-polarization (CP) contact time was set to 2 ms, whereas the second contact time was 600 μs. During the CP period, the ^{13}C nutation frequency was set to 50 kHz and that of ^{1}H was linearly ramped from 195 to 205 kHz to fulfill the Hartmann-Hahn matching condition for zero-quantum process.[1] Water suppression by the MISSISSIPPI method was applied,[2] in which the four pulses with alternating X and Y phases were applied on resonance at 4.7 ppm, each with a duration of 25 ms and an rf field of 37.5 kHz, to saturate the proton signals. A total of 160 increments were acquired at steps of 23.66 μs. The recycle delay was about 1 s to enhance the sensitivity. The number of transients accumulated for each t_1 increment was 320. Quadrature detection in the indirect dimension was achieved by the States-TPPI method. All the HETCOR spectra were processed with an exponential window function (line broadening 100 Hz) in the F_2 dimension and a squared sine bell shifted by $\pi/3$ in the F_1 dimension. The Radon transformation is realized in TopSpin 4.0.8 with the built-in command *ptilt1* to tilt the spectra along columns. The corresponding tilt angles are calculated by $\arctan[\Delta\delta(^{13}C)/\Delta\delta(^{1}H)]$, where ΔCS is the spectral shift in ppm. The spectral deconvolutions of the ^{1}H projection spectra were carried out using the software of DMFit 2019.[3] Each peak was fitted with 80% Gaussian and 20% Lorentzian components.

The ^{13}C{^{1}H} CPMAS NMR spectra were acquired at ^{13}C and ^{1}H frequencies of 150.9 MHz and 600.1 MHz, respectively, on a Bruker Avance III NMR spectrometer (14.1 T) equipped with a commercial 4-mm probe with spinning at 12.5 kHz. During the CP contact, the ^{1}H nutation frequency was linearly ramped from 35 kHz to 50 kHz, and that of ^{13}C was optimized for the Hartmann-Hahn matching condition. Proton decoupling of 75 kHz was applied during the acquisition period. The recycle delay was set to 2.0 s.

Thermogravimetric Analysis. This was conducted using a Mettler TGA/DSC 1 instrument (Columbus, OH). Before analysis, finely cut wood samples were equilibrated for 48 h at room temperature (~23 °C) in a sealed chamber with saturated potassium carbonate solution (relative humidity 43%). The sample was then moved into a second chamber for 72 h with saturated sodium bromide solution (relative humidity 58%). It took around 5 min to transfer ~5 mg of wood from the chamber to an aluminum crucible with a pierced lid and placed inside the TGA instrument at 34 °C. The sample was preheated to 84 °C for 10 min for drying and then heated at 220 °C for 1–4 h of thermal treatment.

FIGURES

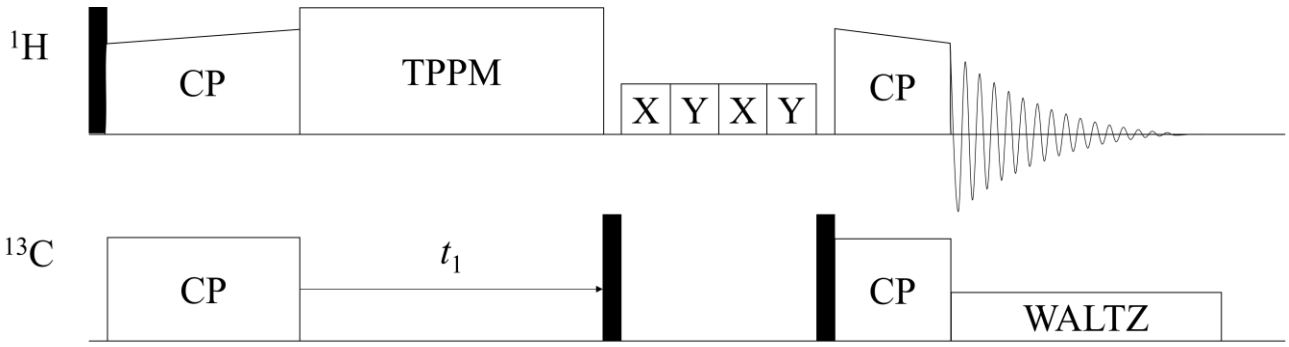

Figure S1. Pulse sequence employed for the acquisition of the HETCOR spectra. The filled rectangles denote $\pi/2$ pulses. The first contact time was set to 2 ms. Because we intended to enhance the ^{1}H signals corresponding to one-bond transfer, the contact time during the second CP period was limited to 600 μs.

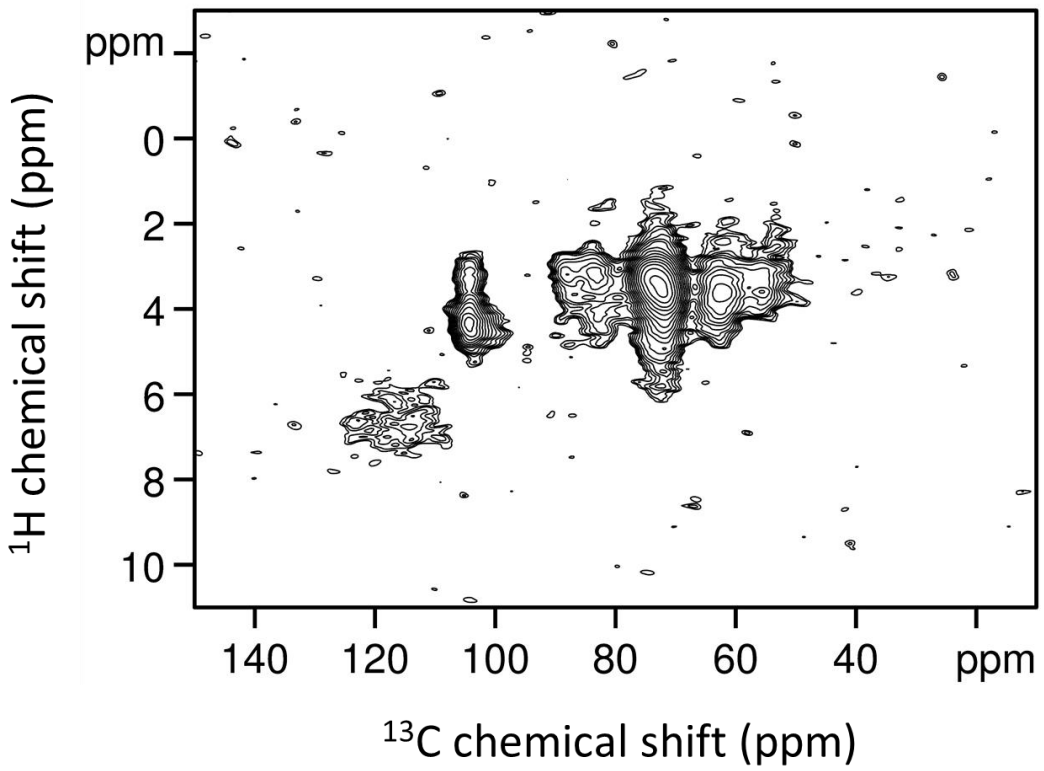

Figure S2. Full spectrum of spruce acquired at 140 kHz and 18.8 T. Other processing parameters are identical to the spectrum shown in Figure 1c.

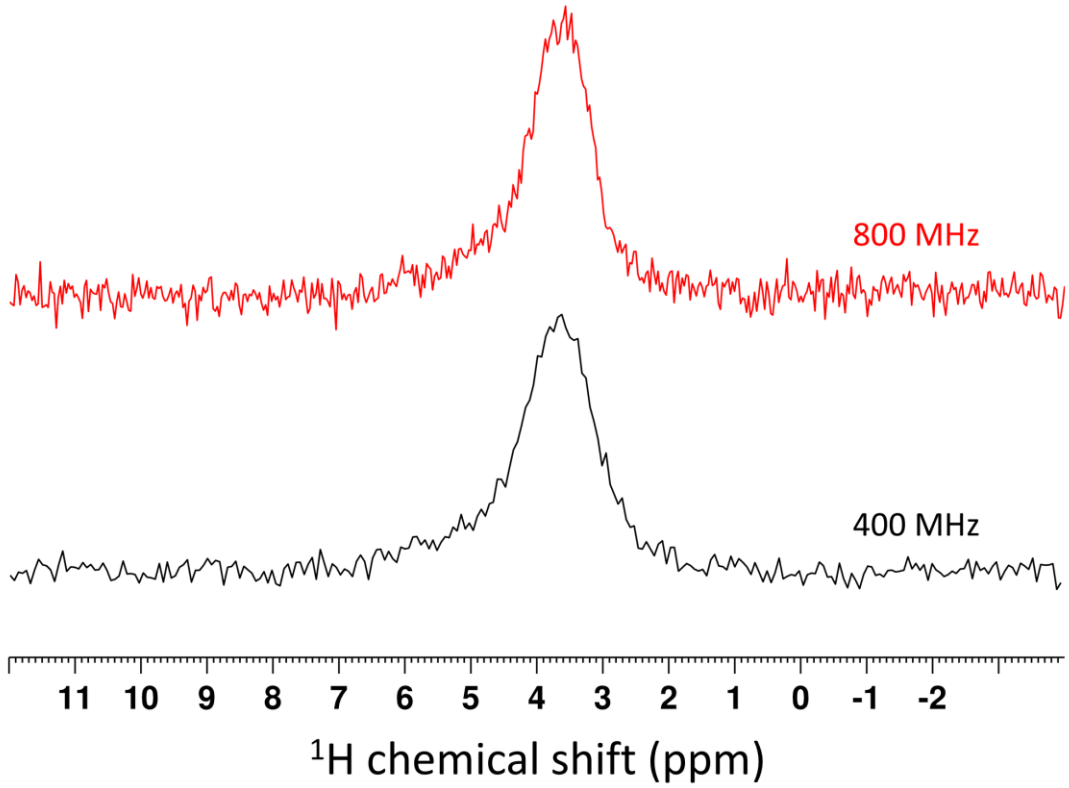

Figure S3. ^{1}H projections of the $^{1}H\{^{13}C\}$ CP-HETCOR spectra of spruce acquired at 9.4 and 18.8 T. The peaks were correlated to the ^{13}C signal at peaks 73 ppm. The similar line widths in ppm indicated that the signals were largely inhomogeneously broadened.

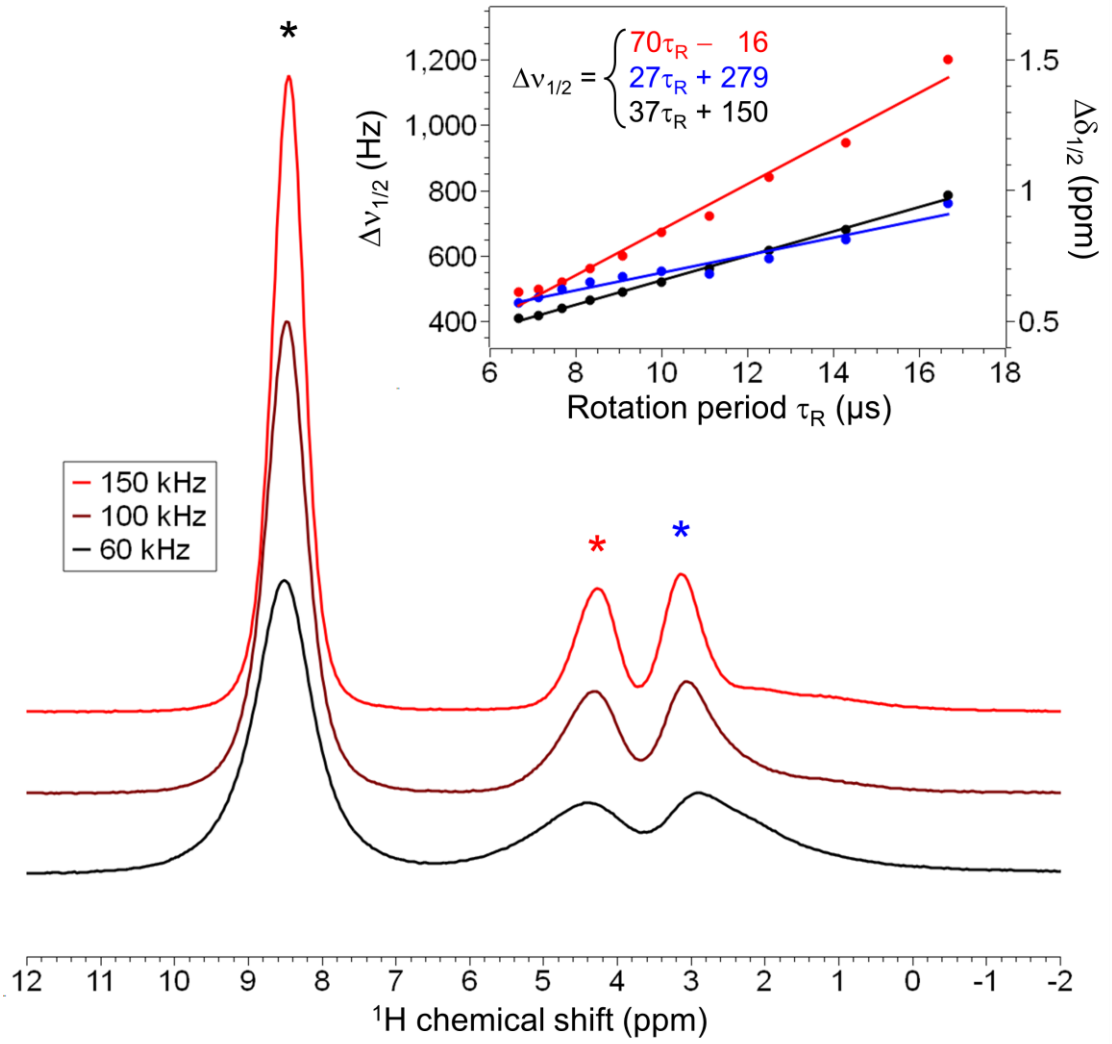

Figure S4. ^{1}H MAS spectra of glycine at a spinning frequency from 60–150 kHz. Extrapolation of the correlation lines to the y-axis gave an estimate of the upper bound of the residual homogeneous line width at half maximum ($\Delta\nu_{1/2}$ or $\Delta\delta_{1/2}$).

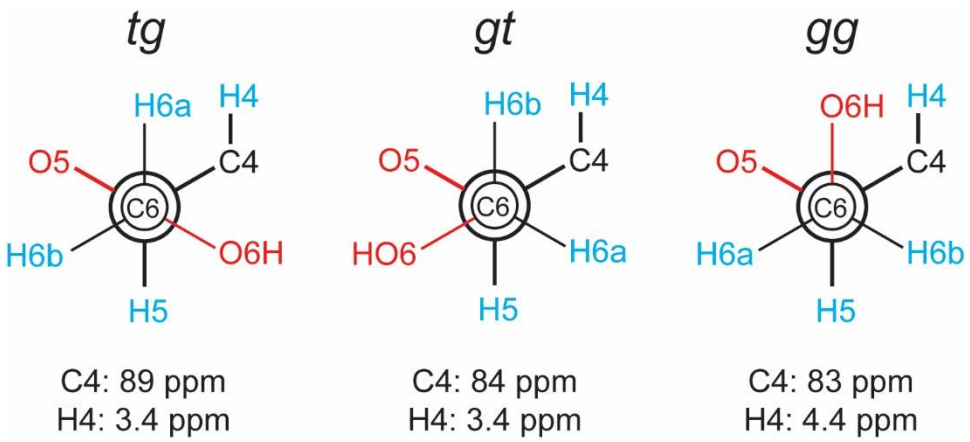

Figure S5. Rotation around the C5-C6 bond of cellulose results in three conformations: trans-gauche (tg), gauche-trans (gt), and gauche-gauche (gg). The values of C4-H4 chemical shifts in spruce wood are listed.

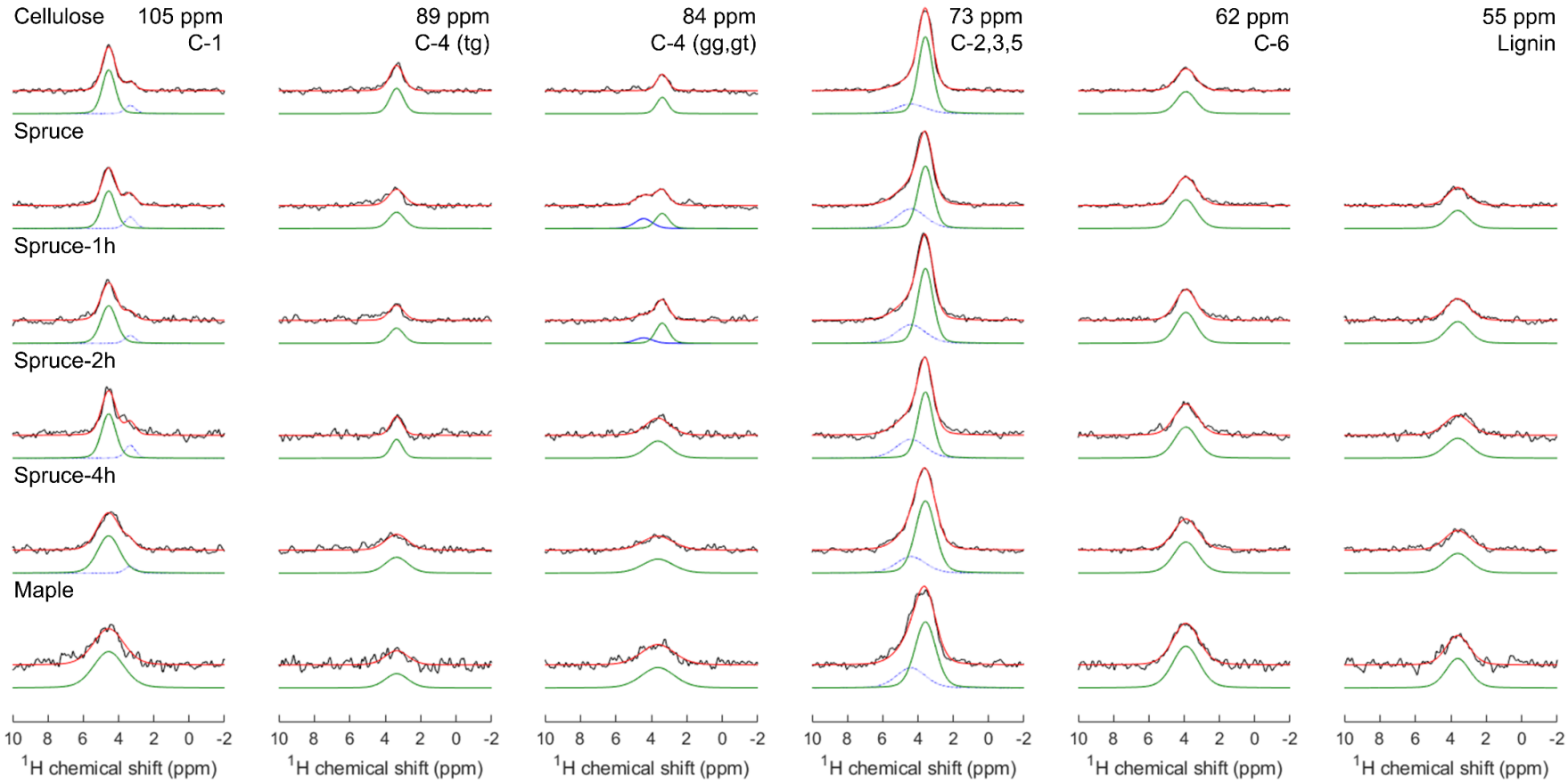

Figure S6. Deconvolution of the ^{1}H projections of the ^{1}H{^{13}C} CP-HETCOR spectra. For each column of the ^{1}H spectra, the chemical shift of the correlated ^{13}C signal and its assignment were indicated. The red lines are the sum of the spectral components obtained by spectral deconvolution. The assigned and unassigned components were indicated by solid and dotted lines, respectively. The chemical shift of the spectral component in green was globally optimized among all spectra in each column. That is, the green components have the same chemical shift for all the spectra in the same column but their line widths at half maximum could be different. For the blue component, both the chemical shifts and line widths were globally fitted among all spectra in each column, where only the signal intensities were varied individually. See Tables S1–2 for a summary of the NMR parameters and a more detailed assignment.

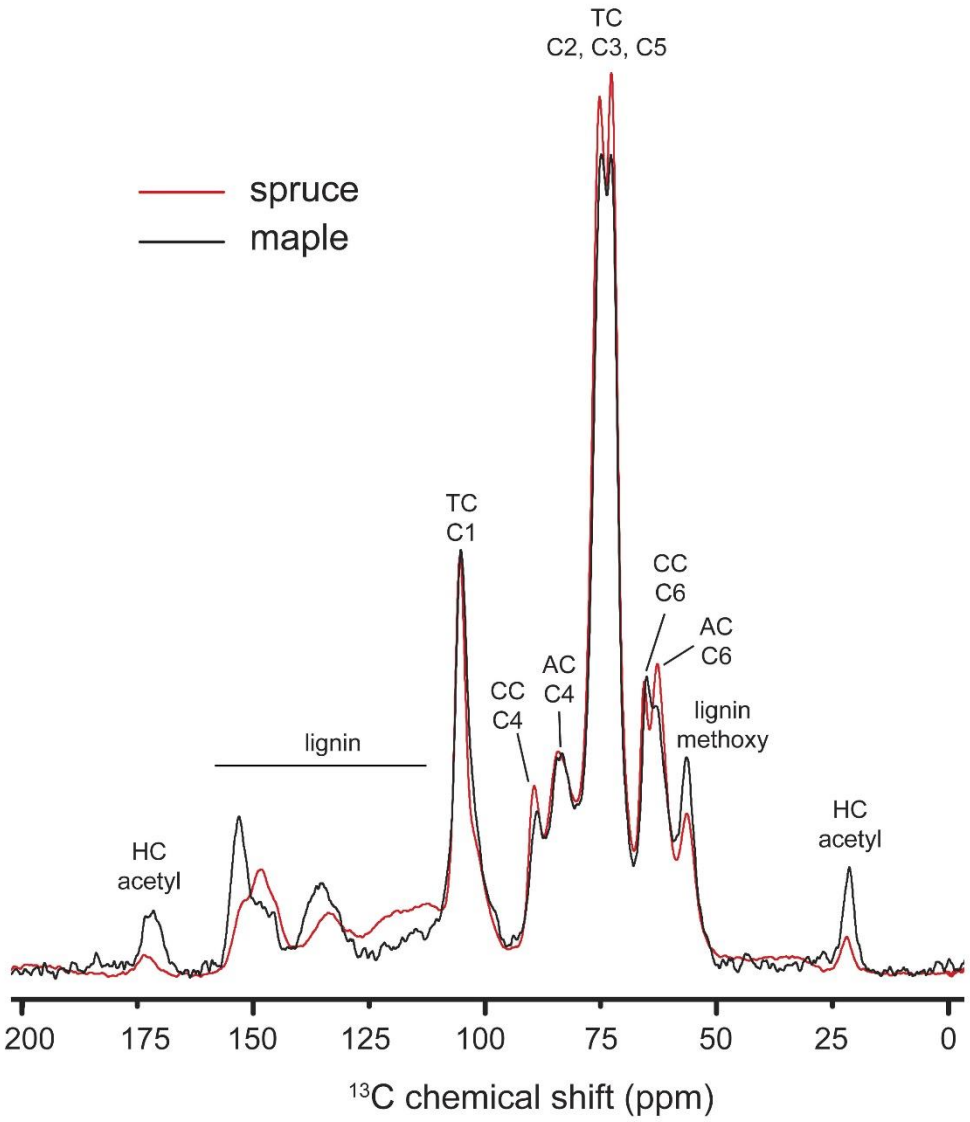

Figure S7. $^{13}C\{^{1}H\}$ CPMAS spectra of untreated spruce and maple. The spectra were normalized with respect to the C-1 peak at 105 ppm. The assignment of the signals at 84 and 89 ppm to C4 of AC and CC, respectively, is what commonly accepted in the literature (see the main text). Spruce has a higher 89 ppm/84 ppm ratio, suggesting a higher degree of cellulose crystallinity. The cellulose C-1 signal is centered around 105 ppm (crystalline plus amorphous cellulose), so it is labeled as total cellulose (TC). The hemicellulose (amorphous) C1 signal is a broader and much weaker peak centered around 102 ppm. The cellulose C6 signal is split into 62 ppm (amorphous cellulose, AC) and 65 ppm (crystalline cellulose, CC).

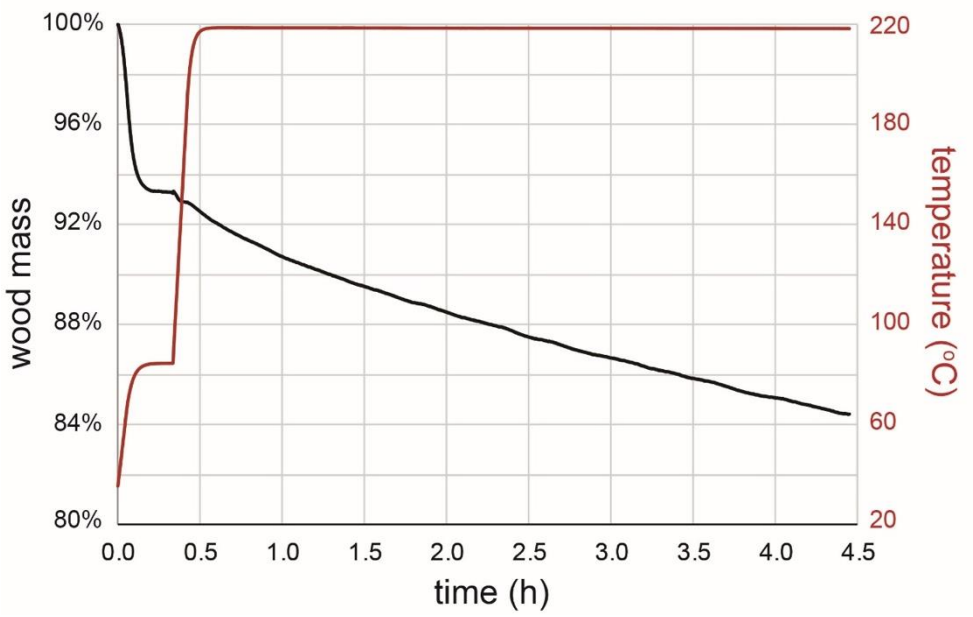

Figure S8. Thermogravimetric analysis of spruce wood undergoing thermal treatment. The initial mass loss represents moisture reduction during preheating stage at 84 °C. Subsequent mass loss during heating at 220 °C represents HC decomposition.

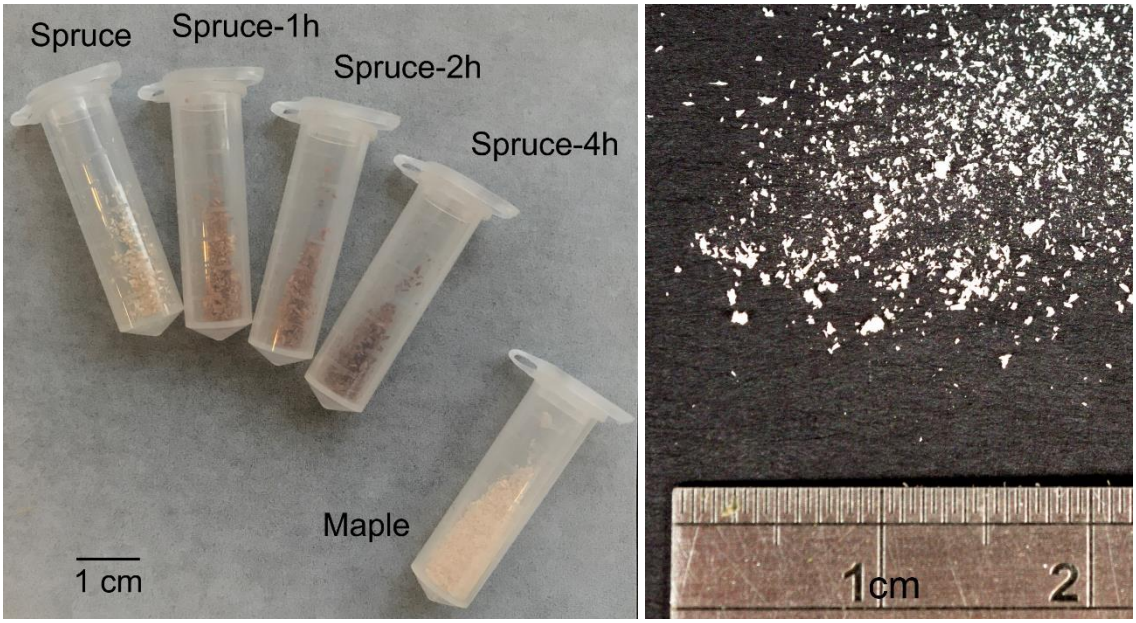

Figure S9. Wood samples studied in this work. The samples were hand cut into small particles without any directionality. The samples were carefully loaded into the rotors without further grinding to avoid excessive heat generation. Spruce particles shown on the right are 0.1–0.5 mm in diameter.

Table S1. ^{1}H chemical shifts (δ) and full widths at half maximum ($\Delta\nu_{1/2}$) extracted from the $^{1}H\{^{13}C\}$ HETCOR spectra of the cellulose, spruce, and maple samples.[a]

Assignment		Cellulose		Spruce		Maple		^{13}C chemical shift[b] (ppm)
		δ (ppm)	$\Delta\nu_{1/2}$ (ppm)	δ (ppm)	$\Delta\nu_{1/2}$ (ppm)	δ (ppm)	$\Delta\nu_{1/2}$ (ppm)	
-OC**H**$_3$, lignin		-	-	3.6	1.4	3.6	1.6	55
-C**H**$_2$OH, C-6		3.9	1.3	3.9	1.4	3.9	1.8	62
-(C**H**OH)-, C-2,3 -(C**H**O-)-, C-5		3.6	1.0	3.6	1.0	3.6	1.4	73
-(C**H**O-)-, C-4	gg	--	--	4.4	1.2	3.6	2.2	84
	gt	3.4	0.8	3.4	0.9			
	tg	3.4	0.9	3.4	1.1	3.4	1.5	89
-C**H**(O-)$_2$, C-1		4.6	0.9	4.6	0.9	4.6	2.0	105

[a] The uncertainties in ^{1}H chemical shifts were 0.1 ppm. [b] The ^{13}C signals to which the ^{1}H signals are correlated.

Table S2. ^{1}H chemical shifts (δ) and full widths at half maximum ($\Delta\nu_{1/2}$) extracted from the $^{1}H\{^{13}C\}$ HETCOR spectra of the spruce samples with different thermal treatment periods (1, 2, and 4 h).

Assignment		1 h		2 h		4 h		^{13}C chemical shift (ppm)
		δ (ppm)	$\Delta\nu_{1/2}$ (ppm)	δ (ppm)	$\Delta\nu_{1/2}$ (ppm)	δ (ppm)	$\Delta\nu_{1/2}$ (ppm)	
-OC**H**$_3$, lignin		3.6	1.5	3.6	1.7	3.6	1.7	55
-C**H**$_2$OH, C-6		3.9	1.4	3.9	1.6	3.9	1.6	62
-(C**H**OH)-, C-2,3 -(C**H**O-)-, C-5		3.6	1.0	3.6	1.0	3.6	1.3	73
-(C**H**O-)-, C-4	gg	4.4	1.2	3.6	1.6	3.6	2.0	84
	gt	3.4	0.9					
	tg	3.4	1.0	3.4	0.8	3.4	1.5	89
-C**H**(O-)$_2$, C-1		4.6	1.1	4.6	1.0	4.6	1.5	105

References

1 B. Meier, *Chem. Phys. Lett.*, 1992, **188**, 201–207.

2 D. H. Zhou and C. M. Rienstra, *J. Magn. Reson.*, 2008, **192**, 167–172.

3 D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calve, B. Alonso, J. O. Durand, B. Bujoli, Z. H. Gan and G. Hoatson, *Magn Reson Chem*, 2002, **40**, 70–76.