SUPPLEMENTARY MATERIAL

Insights into the borohydride reduction of dialdehyde cellulose: The dilemma of competing reduction and β-elimination reactions

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Table of contents

1) Characterization of the Softwood Kraft Pulp

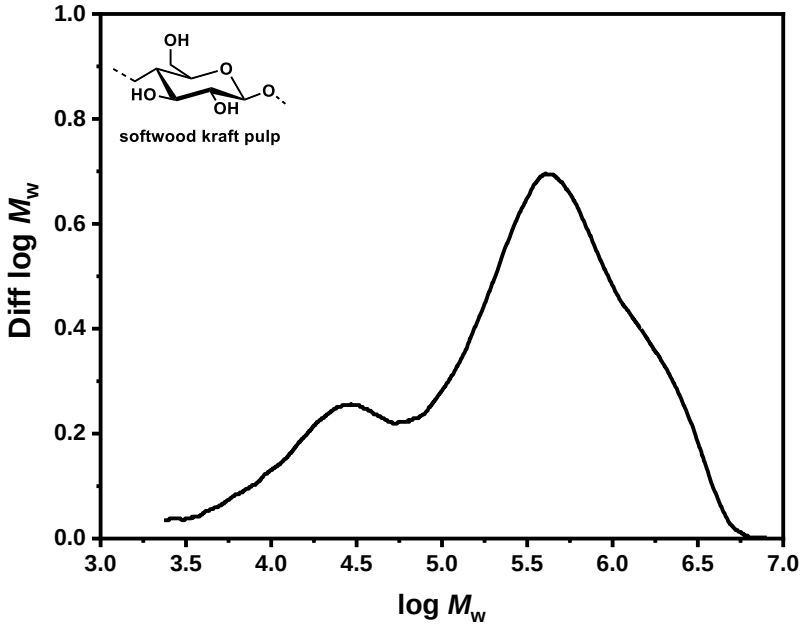

Figure S1. Molecular weight distribution of untreated softwood kraft pulp.

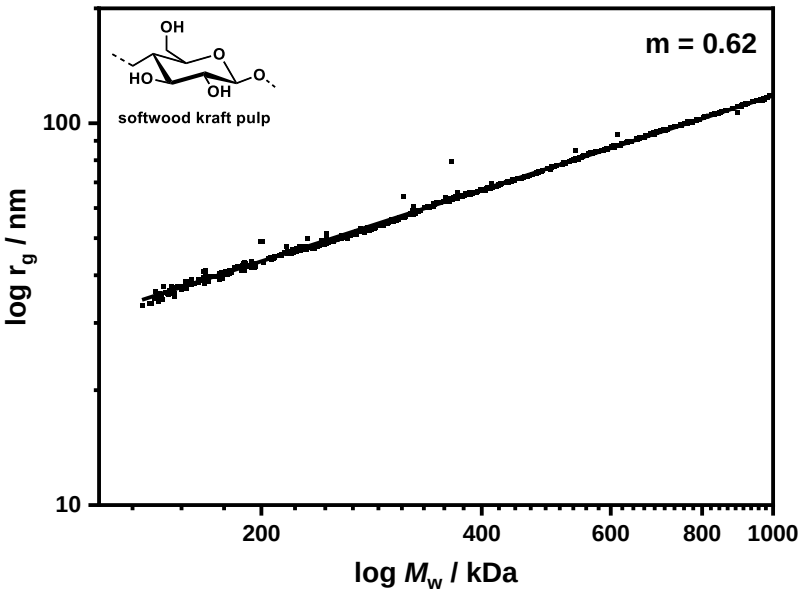

Figure S2. Conformation plot of untreated softwood kraft pulp. The slope of the linear regression of the light scattering data is 0.62.

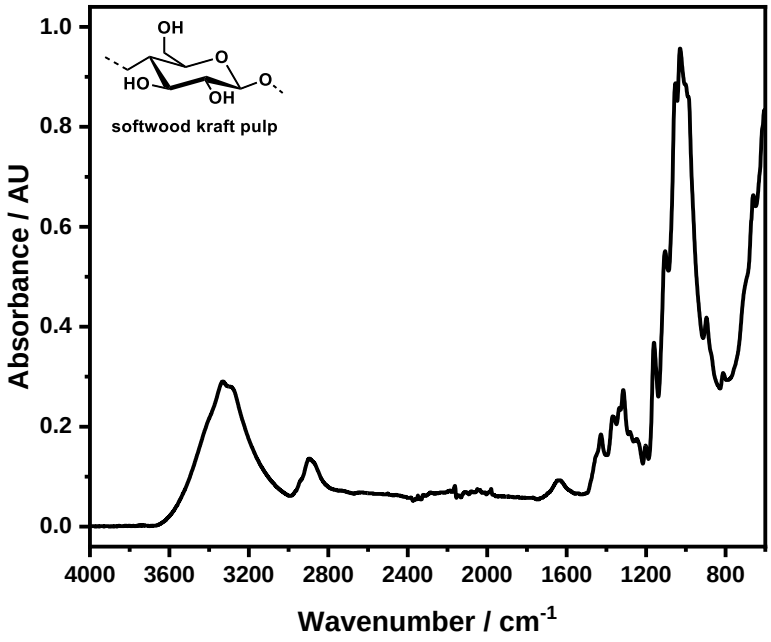

Figure S3. Normalized Fourier-transform infrared spectra of untreated softwood kraft pulp.

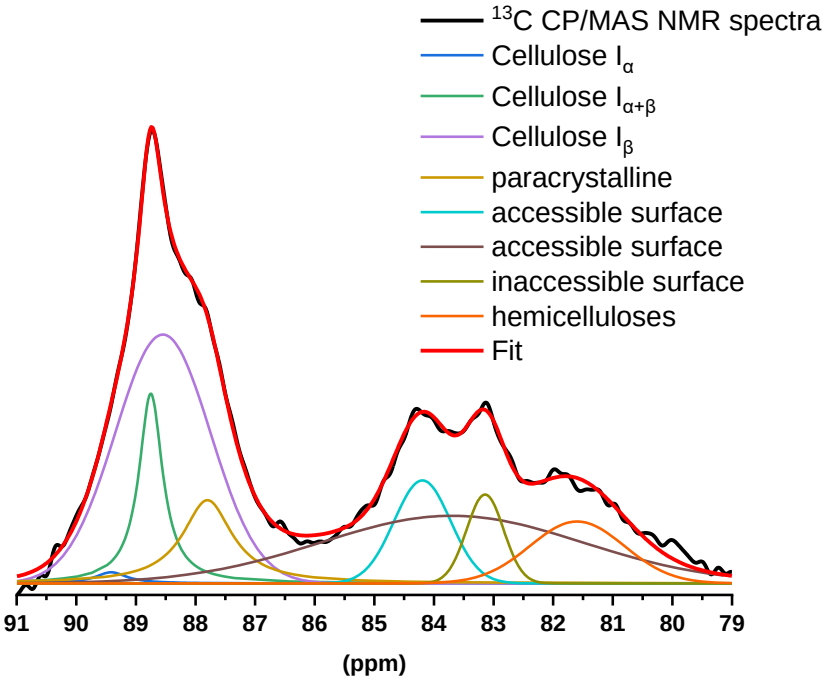

Figure S4. C4 resonance in ^{13}C CP/MAS NMR spectrum of untreated softwood kraft pulp deconvoluted according to Jusner et al.[1]

Table S1. Contributors to the C4 resonance in ^{13}C CP/MAS NMR spectrum of untreated softwood kraft pulp.

	(ppm)	Width (ppm)	Integral [91-79ppm] (%)
Cellulose I_α	89.42	0.64	0.72
Cellulose $I_{\alpha+\beta}$	88.75	0.48	9.47
Cellulose I_β	87.80	1.01	8.49
Paracrystalline	88.55	1.88	34.35
Accessible surface I	84.19	1.12	8.45
Inaccessible surface	83.70	5.17	25.29
Accessible surface II	83.14	0.73	4.77
Hemicelluloses	81.60	1.86	8.46
Sum			**100.00**

Table S2. Amounts of carbohydrates expressed as µg/mg determined by methanolysis and gas chromatography according to Sundberg et al.[2]

	Ara	Xyl	Man	Gal	Glc
Softwood kraft pulp	7.72	32.31	16.30	2.50	27.73

2) Cellulose solution state NMR data

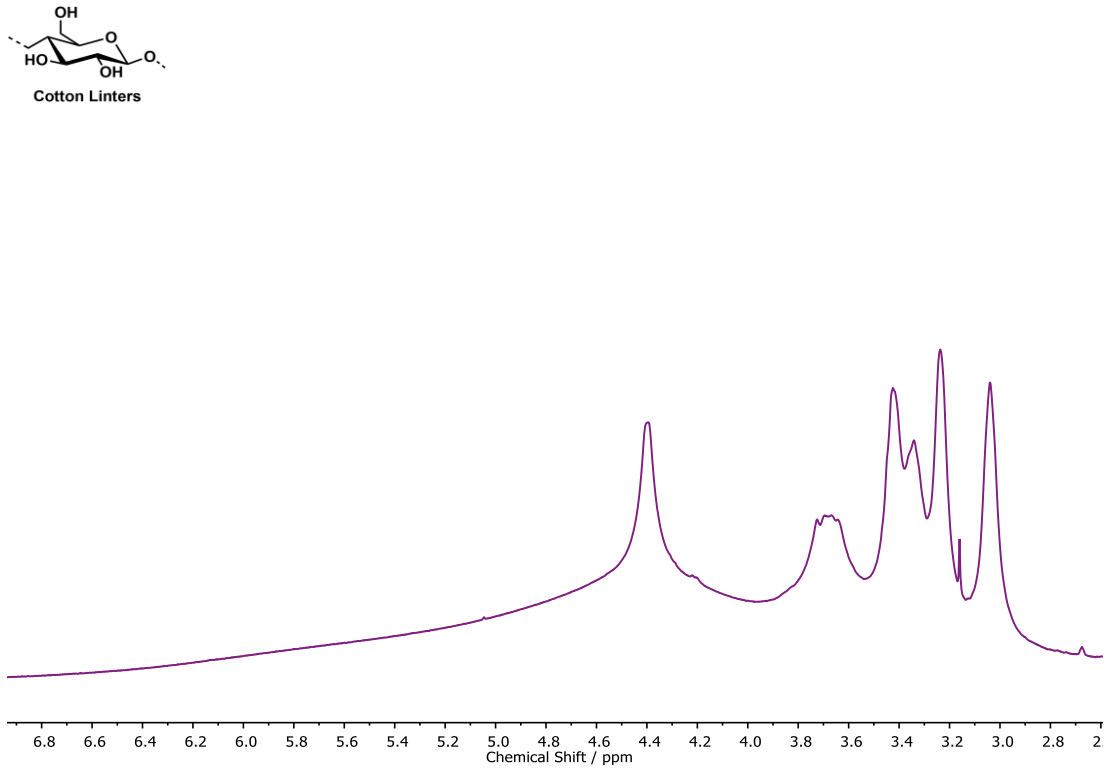

Figure S5. Quantitative ^{1}H NMR spectrum ([P_{4444}][OAc] : DMSO-d_6,1:4 wt%; 400 MHz; 65°C) of cotton linters (2.5 wt%); enlarged into the polysaccharide spectral window.

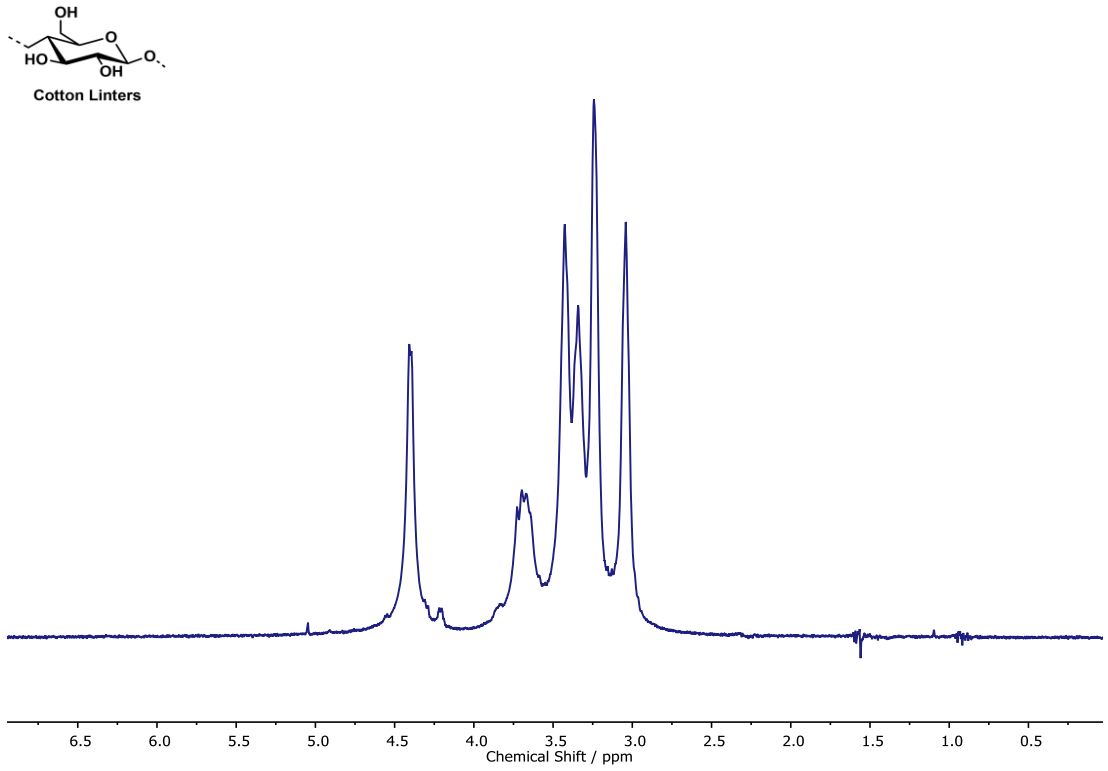

Figure S6. Diffusion edited ^{1}H NMR spectrum ([P_{4444}][OAc] : DMSO-d_6, 1:4 wt%; 400 MHz; 65°C) of cotton linters (2.5 wt%).

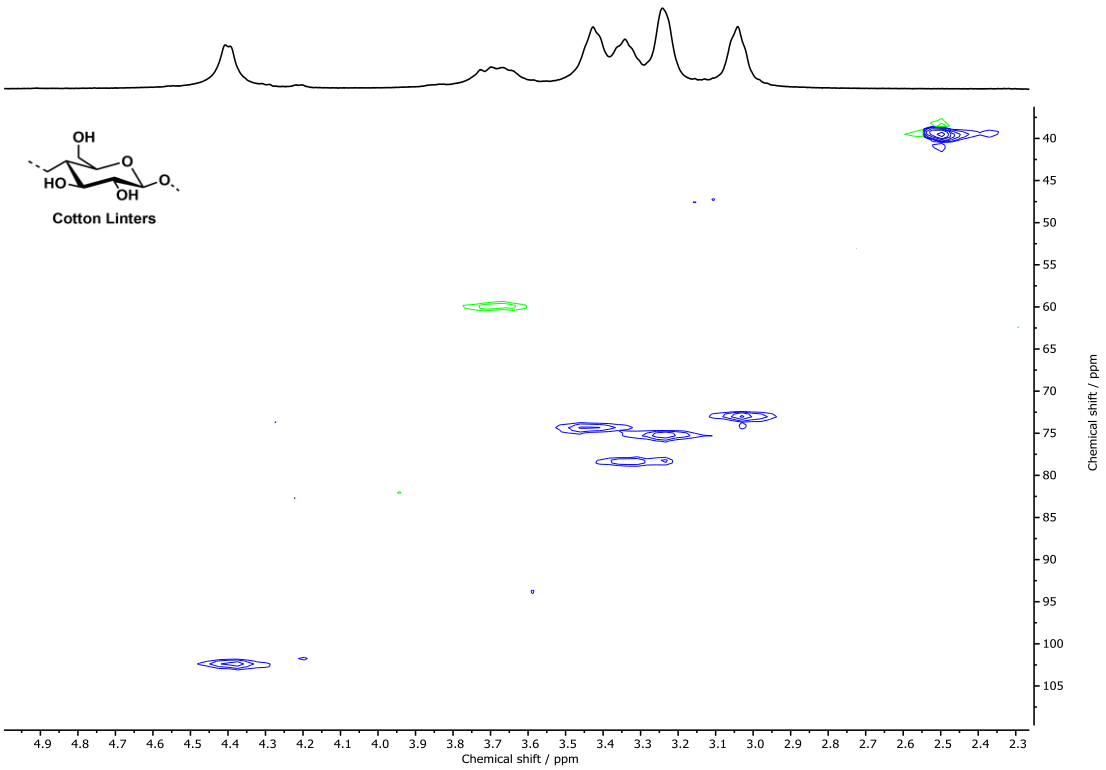

Figure S7. Multiplicity-edited HSQC spectrum ([P_{4444}][OAc] : DMSO-d_6, 1:4 wt%; 400 MHz; 65°C) of cotton linters. CH_2 resonances are shown in green, CH/CH_3 signals are shown in blue. Diffusion edited ^{1}H trace shown on top. Only the zoom into the polysaccharide region is shown.

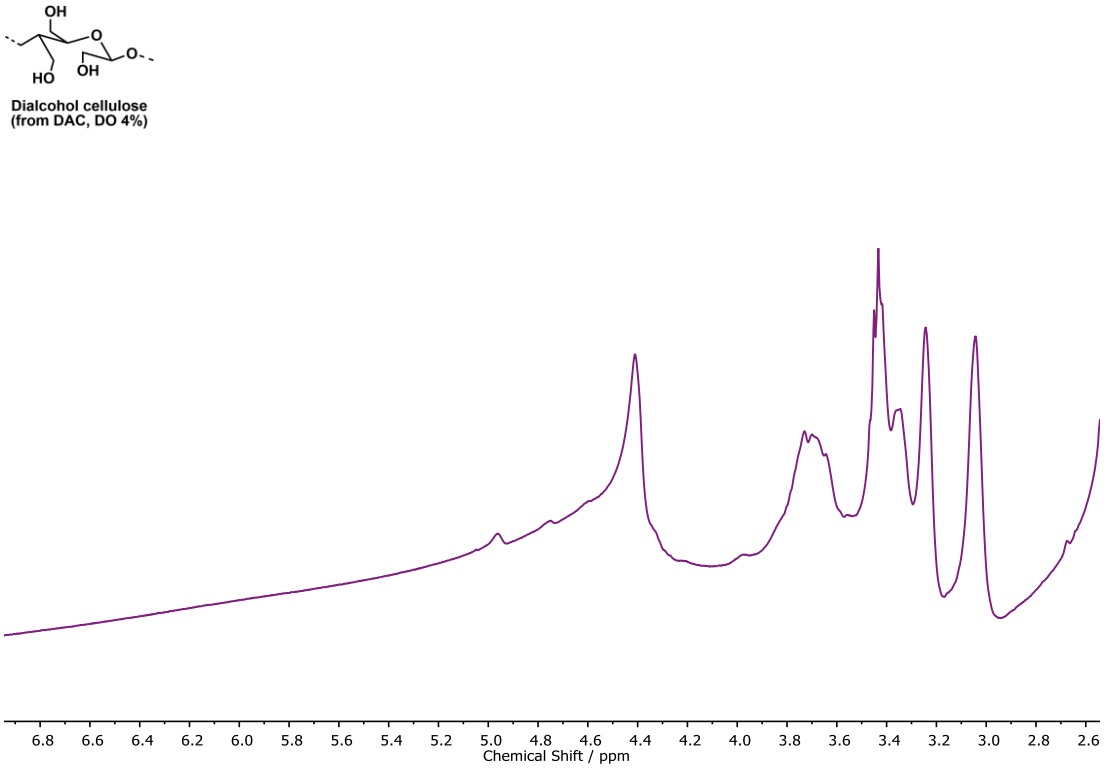

Figure S8. Quantitative ^{1}H NMR spectrum ([P_{4444}][OAc] : DMSO-d_6, 1:4 wt%; 400 MHz; 65°C) of dialcohol cellulose obtained from DAC (DO = 4%; starting material = cotton linters; 2.5 wt%), enlarged into the polysaccharide spectral window.

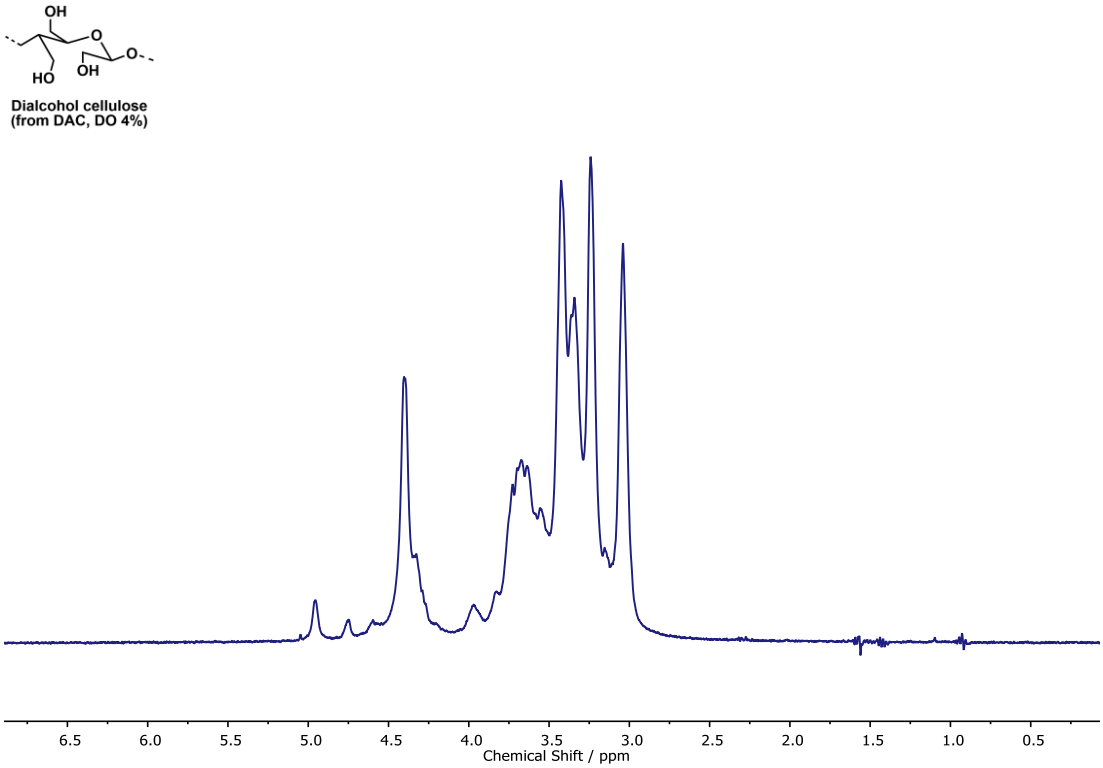

Figure S9. Diffusion edited ^{1}H NMR spectrum ([P$_{4444}$][OAc] : DMSO-*d*$_6$, 1:4 wt%; 400 MHz; 65°C) of dialcohol cellulose obtained from DAC (DO = 4%; starting material = cotton linters; 2.5 wt%).

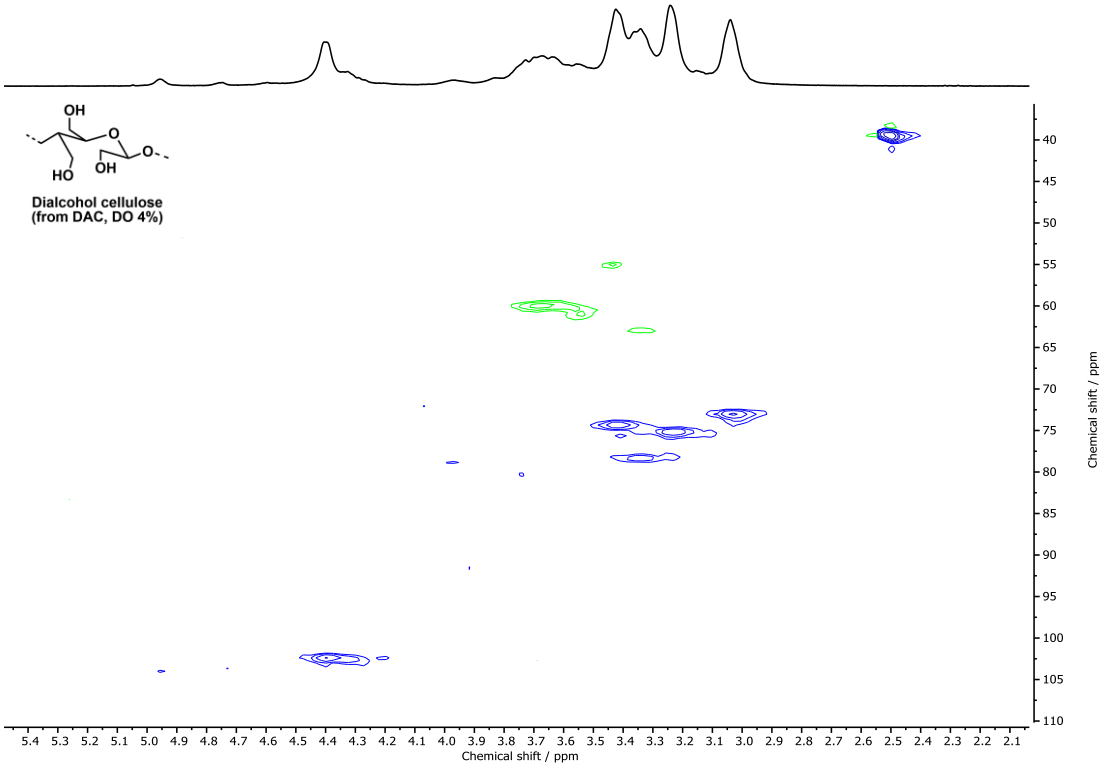

Figure S10. Multiplicity-edited HSQC spectrum ([P$_{4444}$][OAc] : DMSO-*d*$_6$, 1:4 wt%; 400 MHz; 65°C) of dialcohol cellulose obtained from DAC (DO = 4%; starting material = cotton linters; 2.5 wt%). CH_2 resonances are shown in green, CH/CH_3 signals are shown in blue. Diffusion edited ^{1}H trace shown on top. Only the zoom into the polysaccharide region is shown.

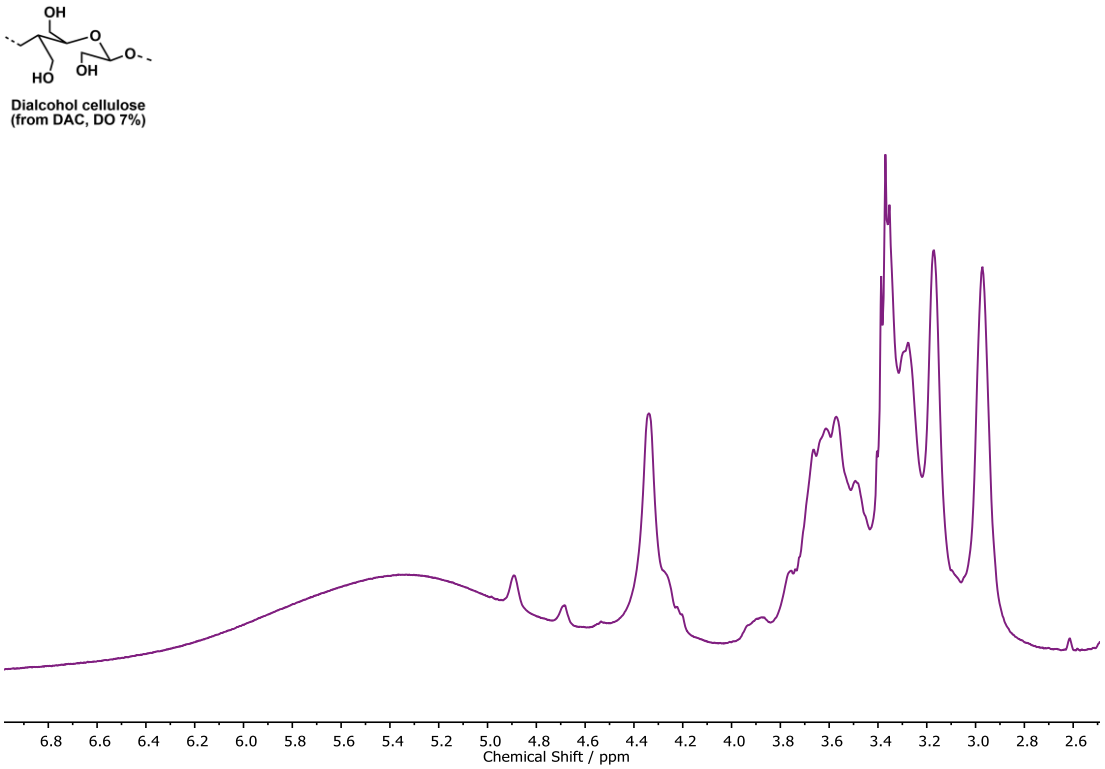

Figure S11. Quantitative ^{1}H NMR spectrum ([P_{4444}][OAc] : DMSO-d_6, 1:4 wt%; 400 MHz; 65°C) of dialcohol cellulose obtained from DAC (DO = 7%; starting material = cotton linters; 2.5 wt%), enlarged into the polysaccharide spectral window.

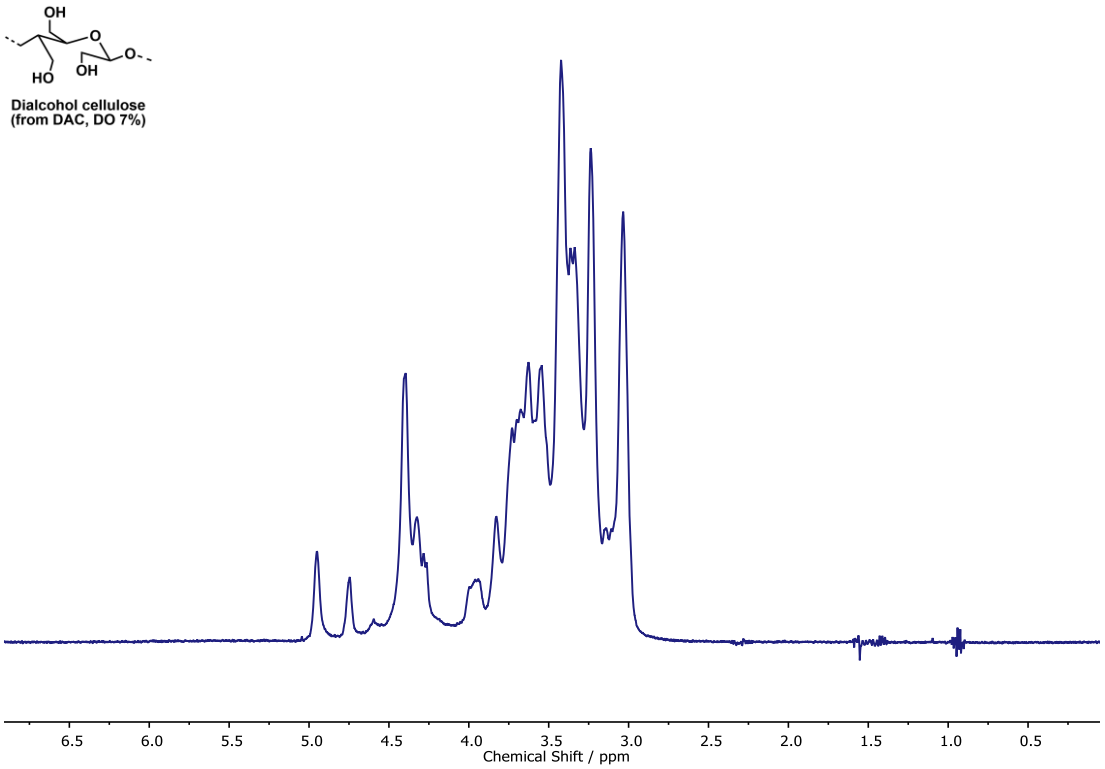

Figure S12. Diffusion edited ^{1}H NMR spectrum ([P_{4444}][OAc] : DMSO-d_6, 1:4 wt%; 400 MHz; 65°C) of dialcohol cellulose obtained from DAC (DO = 7%; starting material = cotton linters; 2.5 wt%).

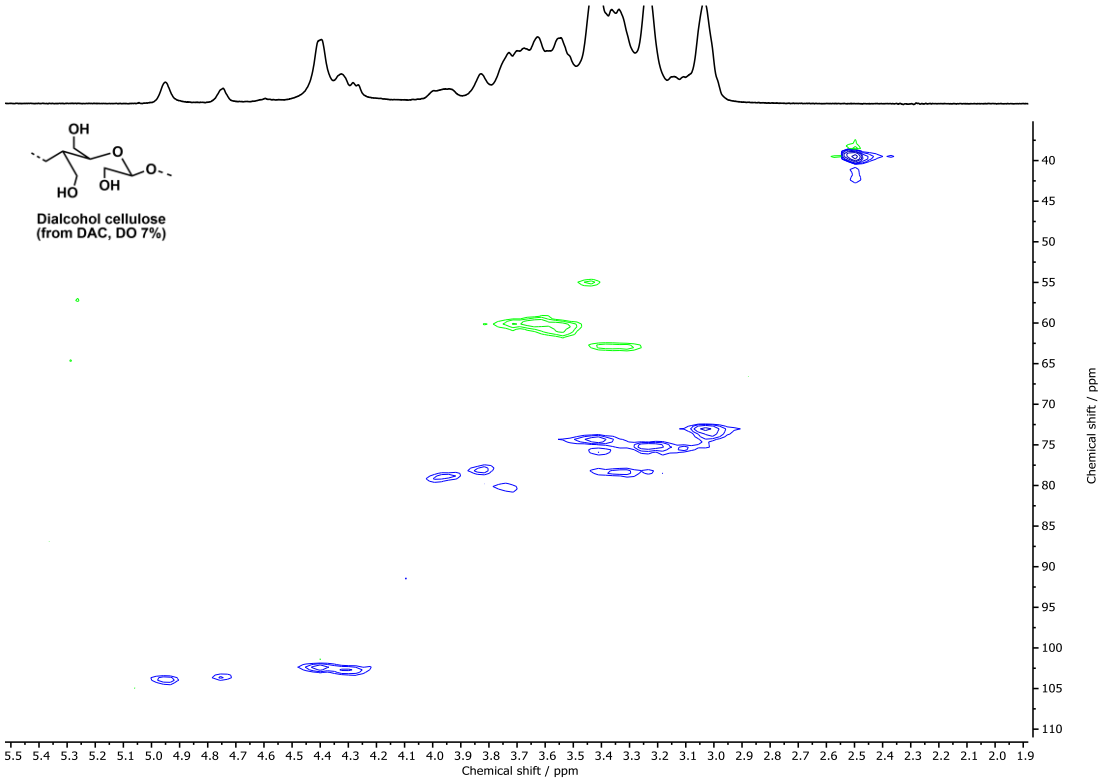

Figure S13. Multiplicity-edited HSQC spectrum ([P_{4444}][OAc] : DMSO-d_6, 1:4 wt%; 400 MHz; 65°C) of dialcohol cellulose obtained from DAC (DO = 7%; starting material = cotton linters; 2.5 wt%). CH_2 resonances are shown in green, CH/CH_3 signals are shown in blue. Diffusion edited ^1H trace shown on top. Only the zoom into the polysaccharide region is shown.

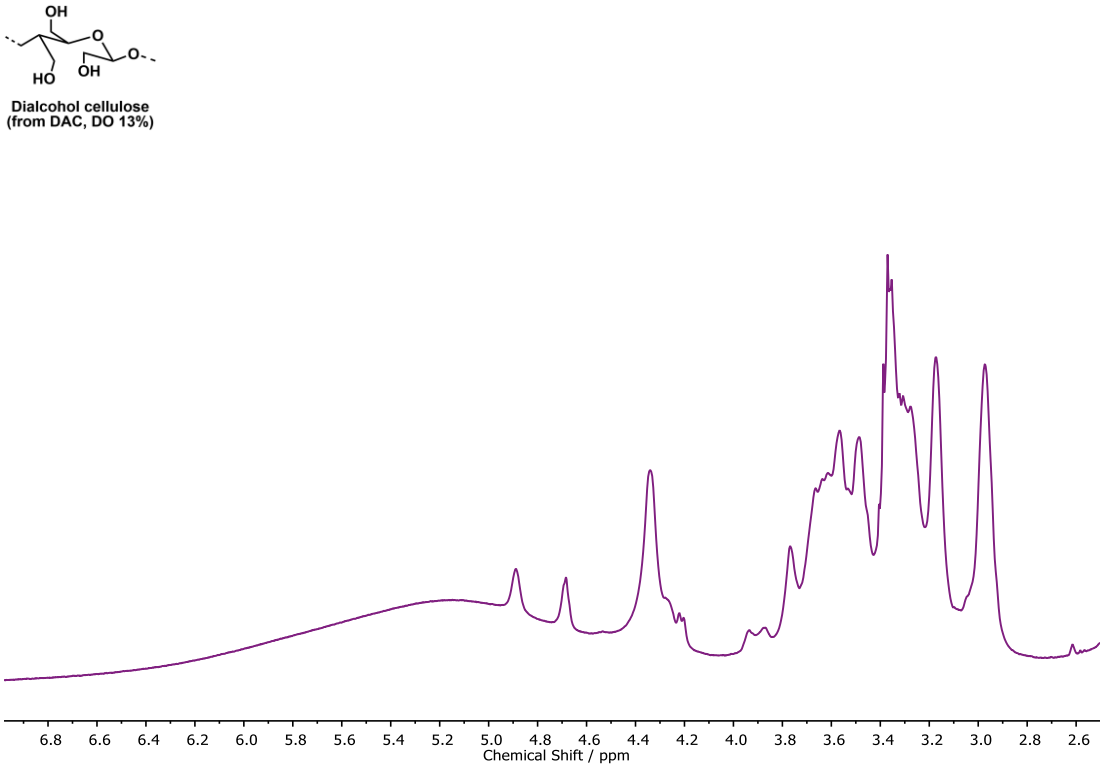

Figure S14. Quantitative ^1H NMR spectrum ([P_{4444}][OAc] : DMSO-d_6, 1:4 wt%; 400 MHz; 65°C) of dialcohol cellulose obtained from DAC (DO = 13%; starting material = cotton linters; 2.5 wt%), enlarged into the polysaccharide spectral window.

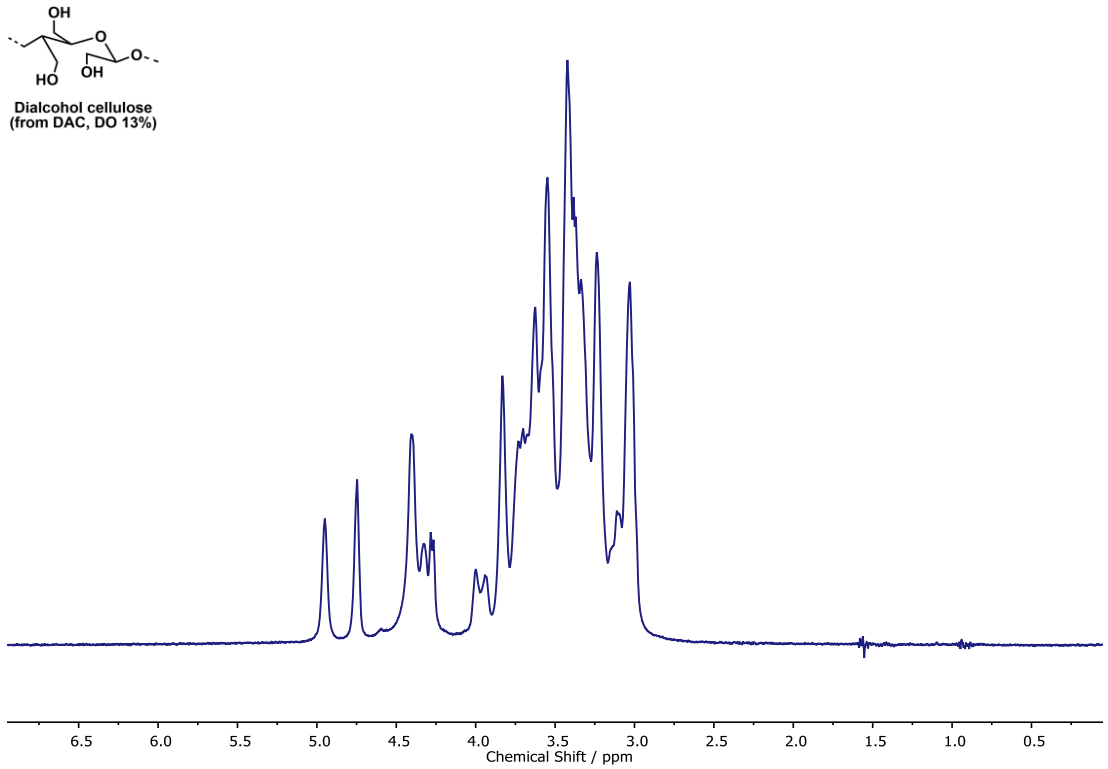

Figure S15. Diffusion edited ^{1}H NMR spectrum ([P_{4444}][OAc] : DMSO-d_6, 1:4 wt%; 400 MHz; 65°C) of dialcohol cellulose obtained from DAC (DO = 13%; starting material = cotton linters; 2.5 wt%).

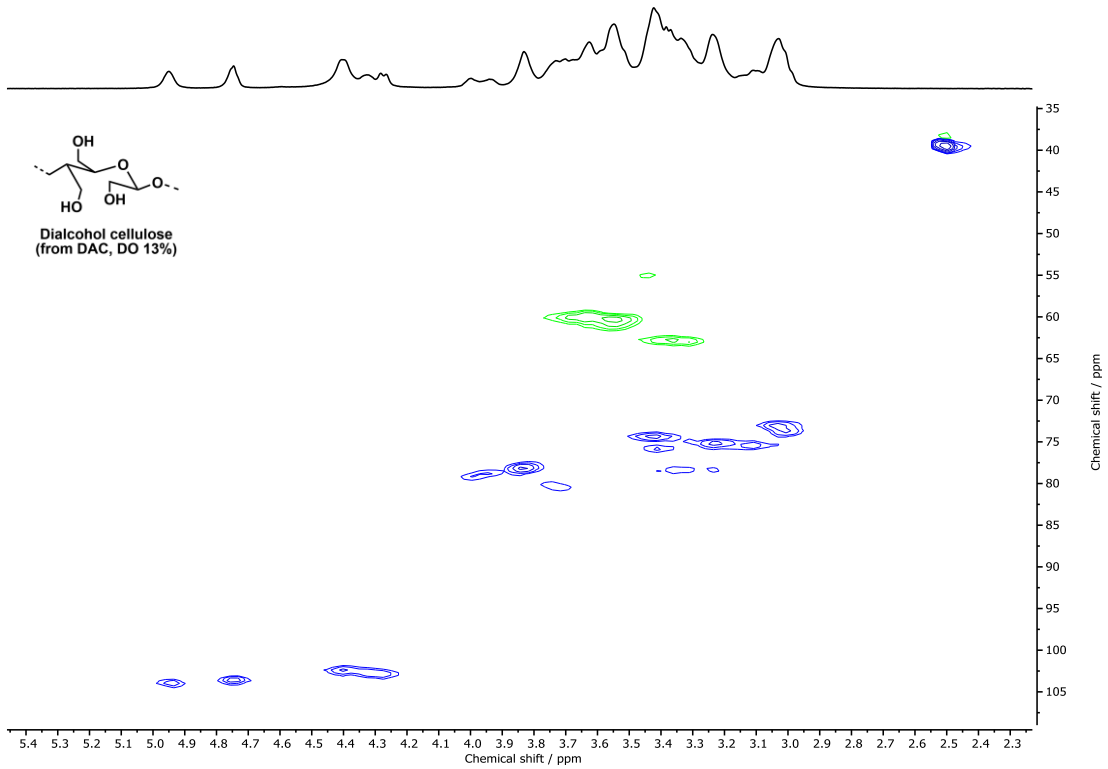

Figure S16. Multiplicity-edited HSQC spectrum ([P_{4444}][OAc] : DMSO-d_6, 1:4 wt%; 400 MHz; 65°C) of dialcohol cellulose obtained from DAC (DO = 13%; starting material = cotton linters; 2.5 wt%). CH_2 resonances are shown in green, CH/CH_3 signals are shown in blue. Diffusion edited ^{1}H trace shown on top. Only the zoom into the polysaccharide region is shown.

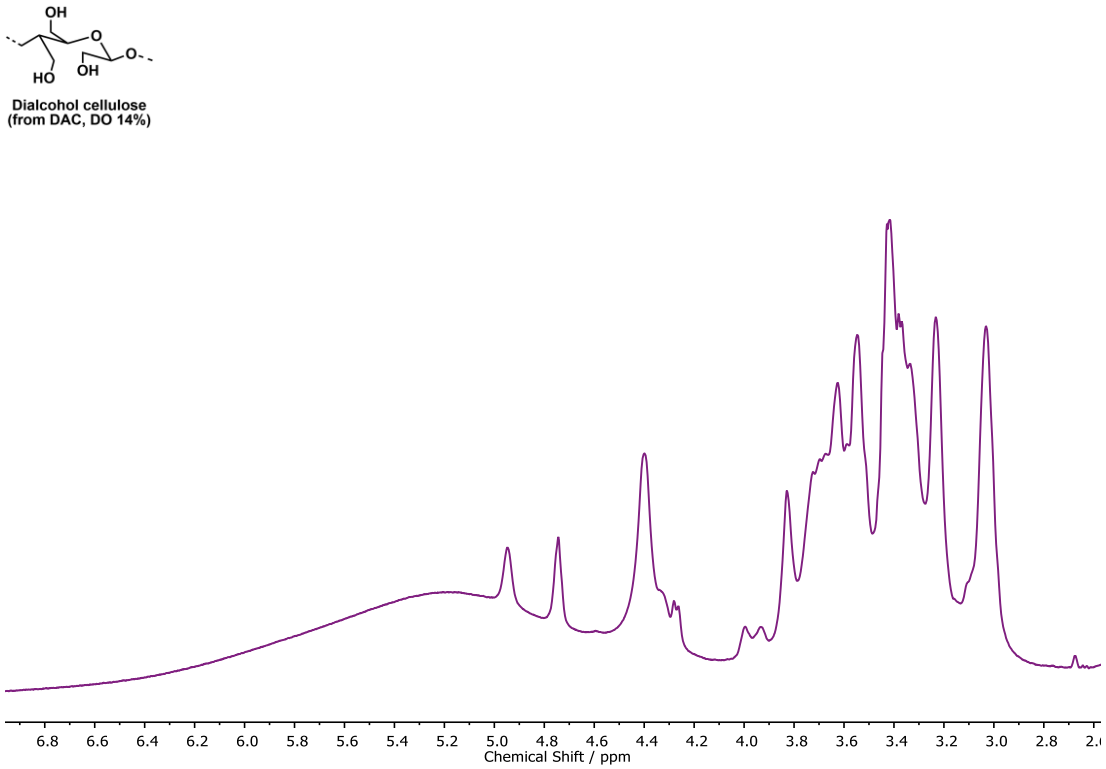

Figure S17. Quantitative ^{1}H NMR spectrum ([P_{4444}][OAc] : DMSO-d_6, 1:4 wt%; 400 MHz; 65°C) of dialcohol cellulose obtained from DAC (DO = 14%; starting material = cotton linters; 2.5 wt%), enlarged into the polysaccharide spectral window.

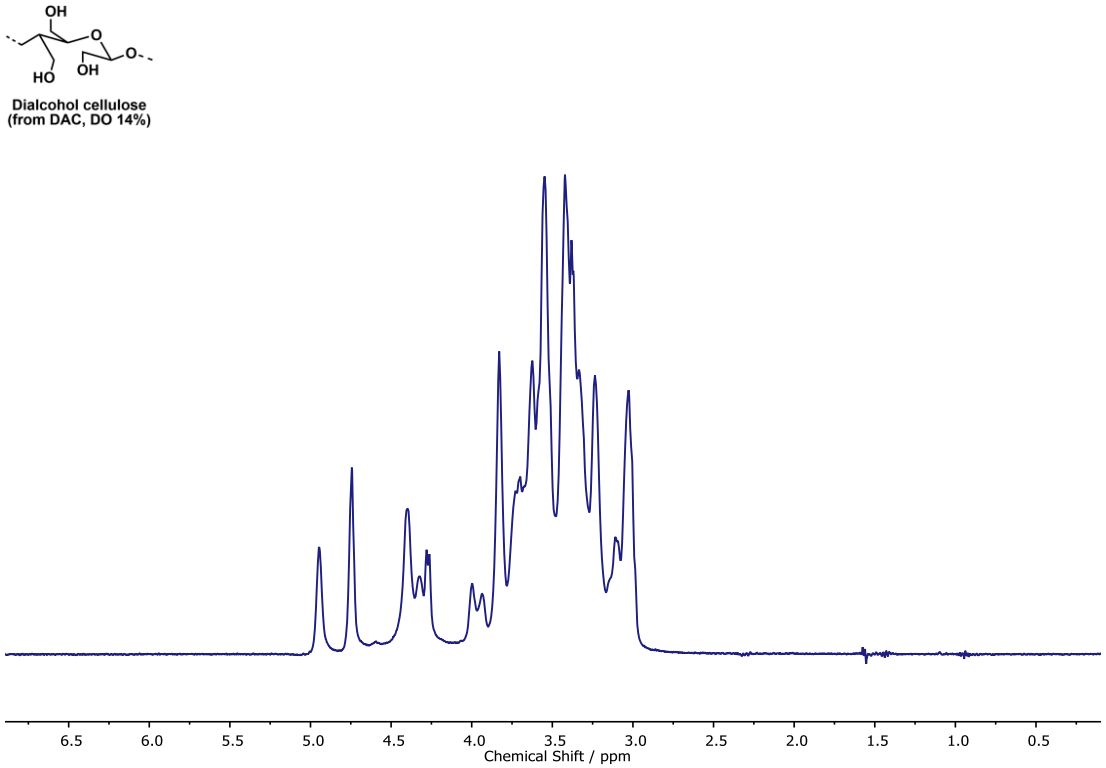

Figure S18. Diffusion edited ^{1}H NMR spectrum ([P_{4444}][OAc] : DMSO-d_6, 1:4 wt%; 400 MHz; 65°C) of dialcohol cellulose obtained from DAC (DO = 14%; starting material = cotton linters; 2.5 wt%).

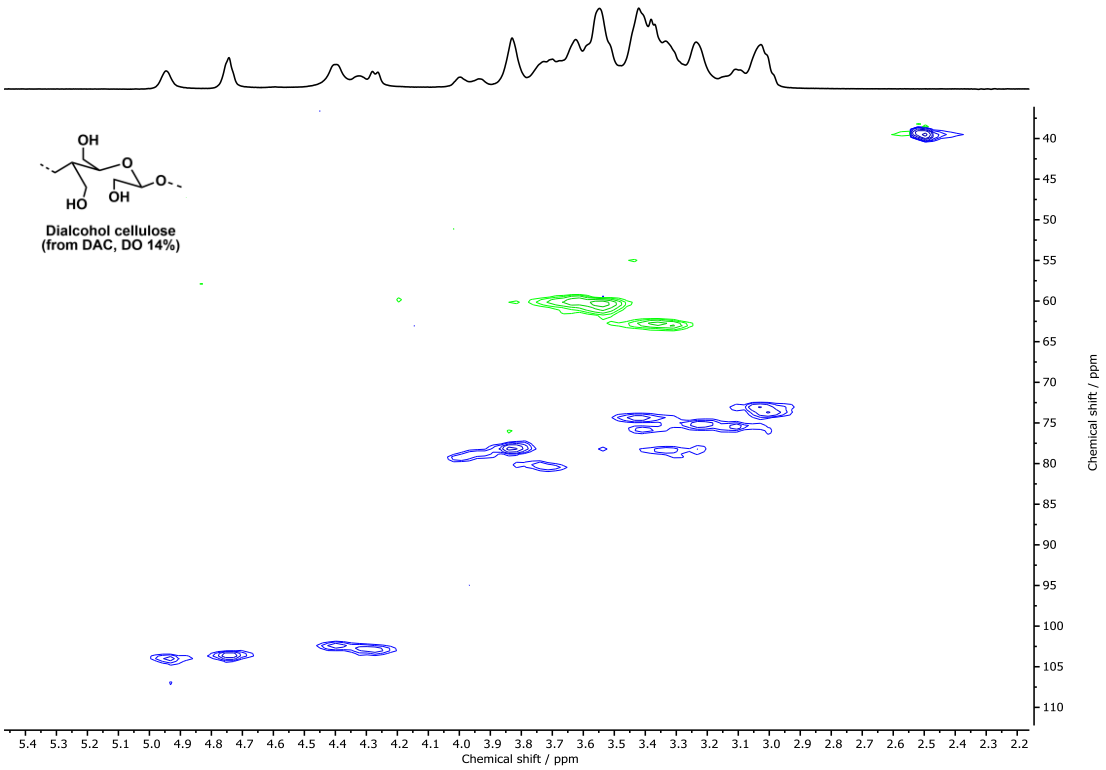

Figure S19. Multiplicity-edited HSQC spectrum ([P_{4444}][OAc] : DMSO-d_6, 1:4 wt%; 400 MHz; 65°C) of dialcohol cellulose obtained from DAC (DO = 14%; starting material = cotton linters; 2.5 wt%). CH_2 resonances are shown in green, CH/CH_3 signals are shown in blue. Diffusion edited ^1H trace shown on top. Only the zoom into the polysaccharide region is shown.

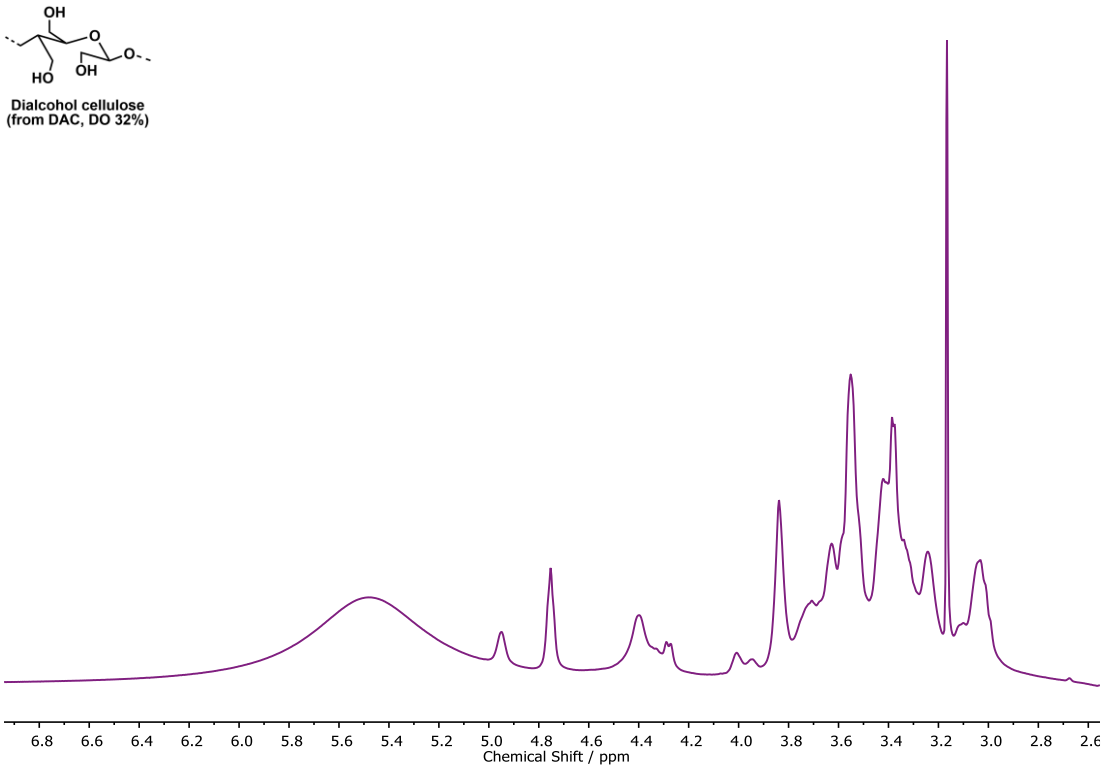

Figure S20. Quantitative ^1H NMR spectrum ([P_{4444}][OAc] : DMSO-d_6, 1:4 wt%); 400 MHz; 65°C) of dialcohol cellulose obtained from DAC (DO = 32%; starting material = cotton linters; 5 wt%), enlarged into the polysaccharide spectral window.

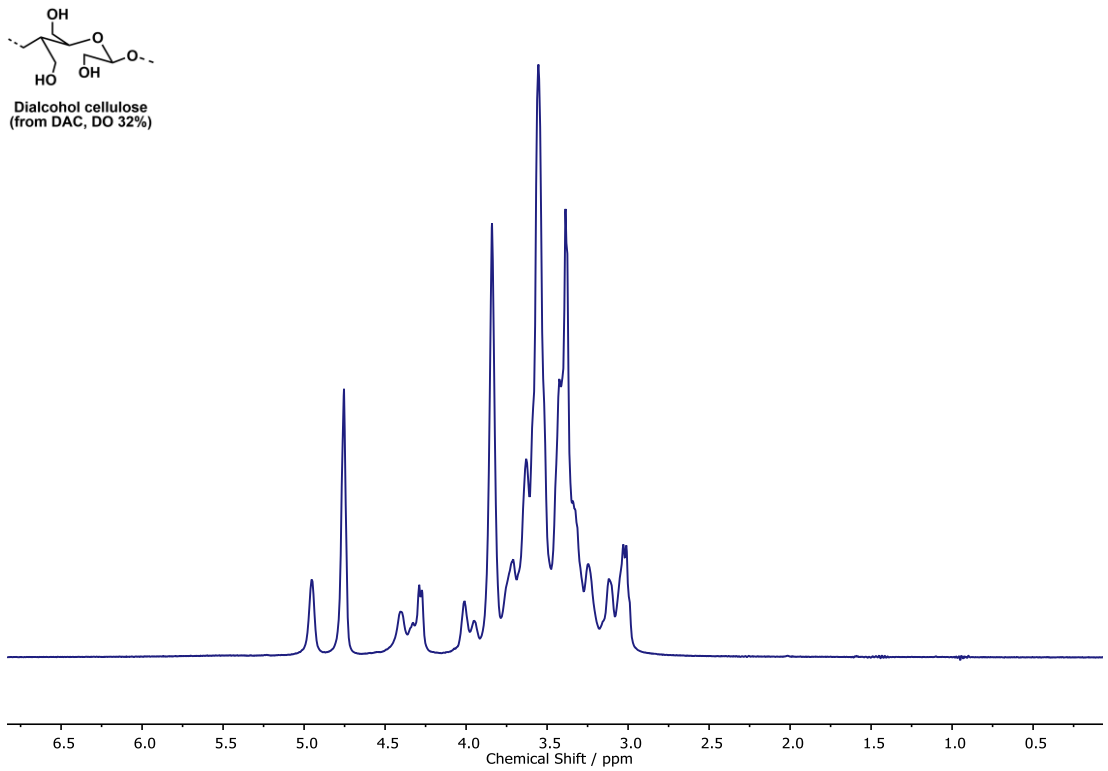

Figure S21. Diffusion edited ^{1}H NMR spectrum ([P_{4444}][OAc] : DMSO-d_6, 1:4 wt%; 400 MHz; 65°C) of dialcohol cellulose obtained from DAC (DO = 32%; starting material = cotton linters; 5 wt%).

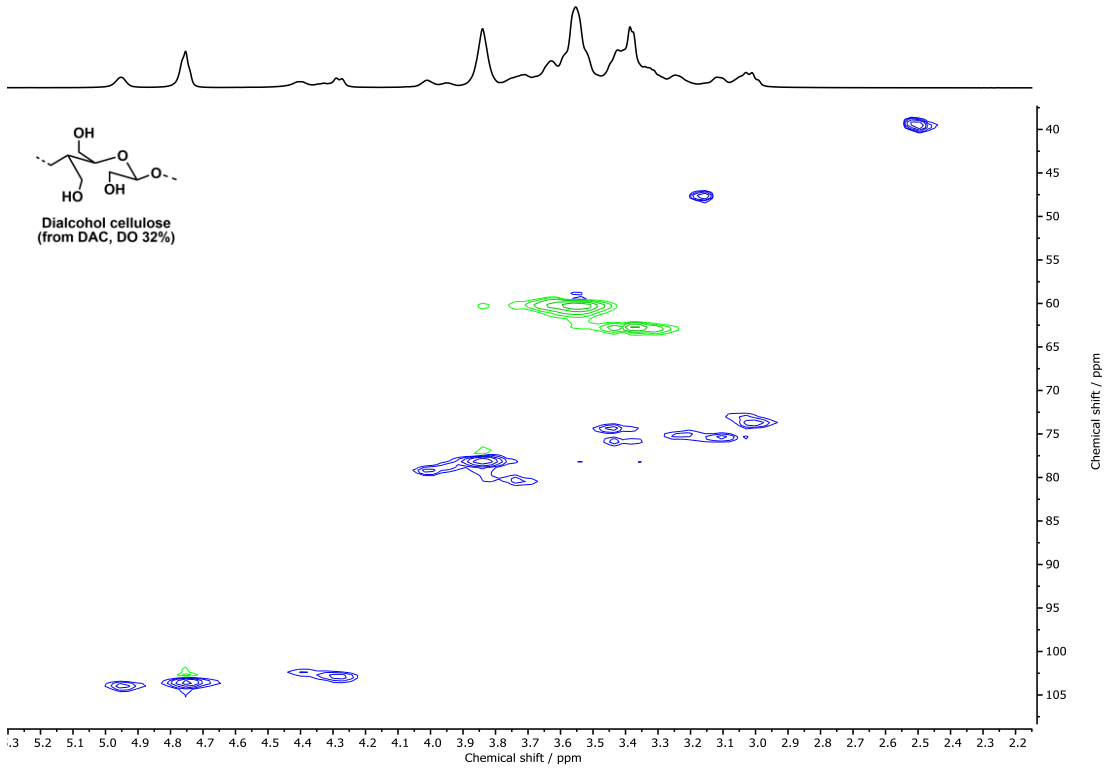

Figure S22. Multiplicity-edited HSQC spectrum ([P_{4444}][OAc] : DMSO-d_6, 1:4 wt%; 400 MHz; 65°C) of dialcohol cellulose obtained from DAC (DO = 32%; starting material = cotton linters; 5 wt%). CH_2 resonances are shown in green, CH/CH_3 signals are shown in blue. Diffusion edited ^{1}H trace shown on top. Only the zoom into the polysaccharide region is shown. Peak at ^{1}H = 3.16 ppm / ^{13}C = 47.6 ppm due to slight methanol impurities stemming from the precipitation.

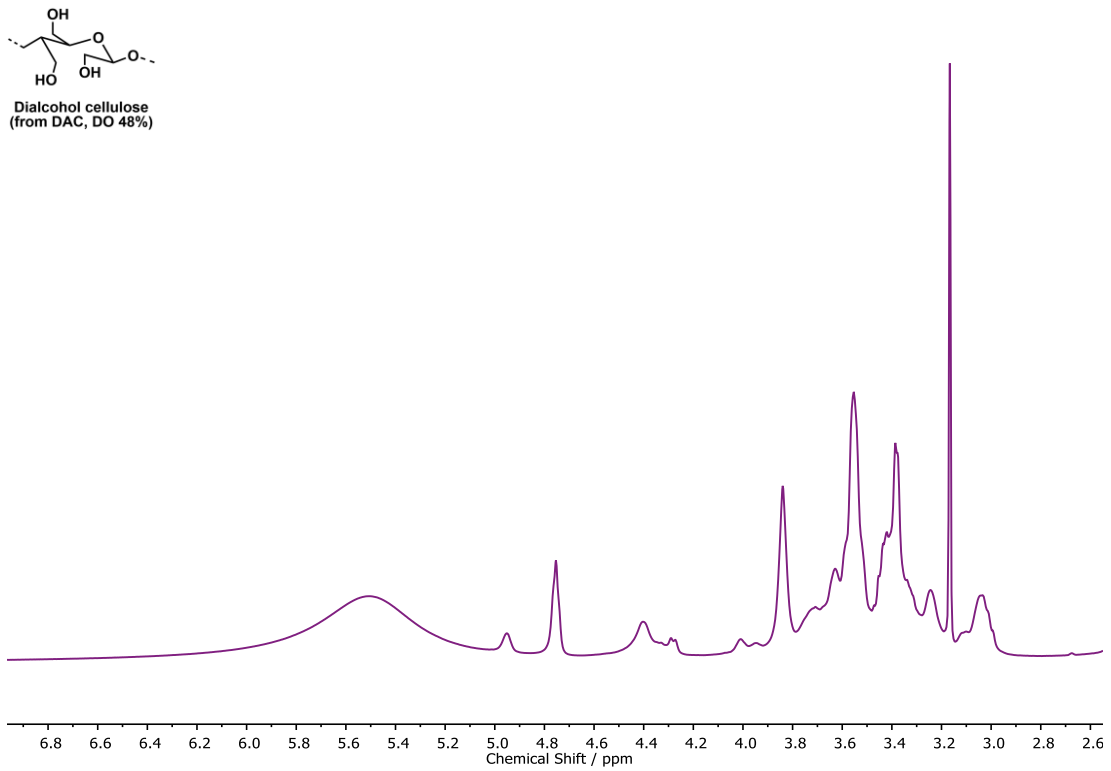

Figure S23. Quantitative ^{1}H NMR spectrum ([P_{4444}][OAc] : DMSO-d_6, 1:4 wt%; 400 MHz; 65°C) of dialcohol cellulose obtained from DAC (DO = 48%; starting material = cotton linters; 5 wt%), enlarged into the polysaccharide spectral window.

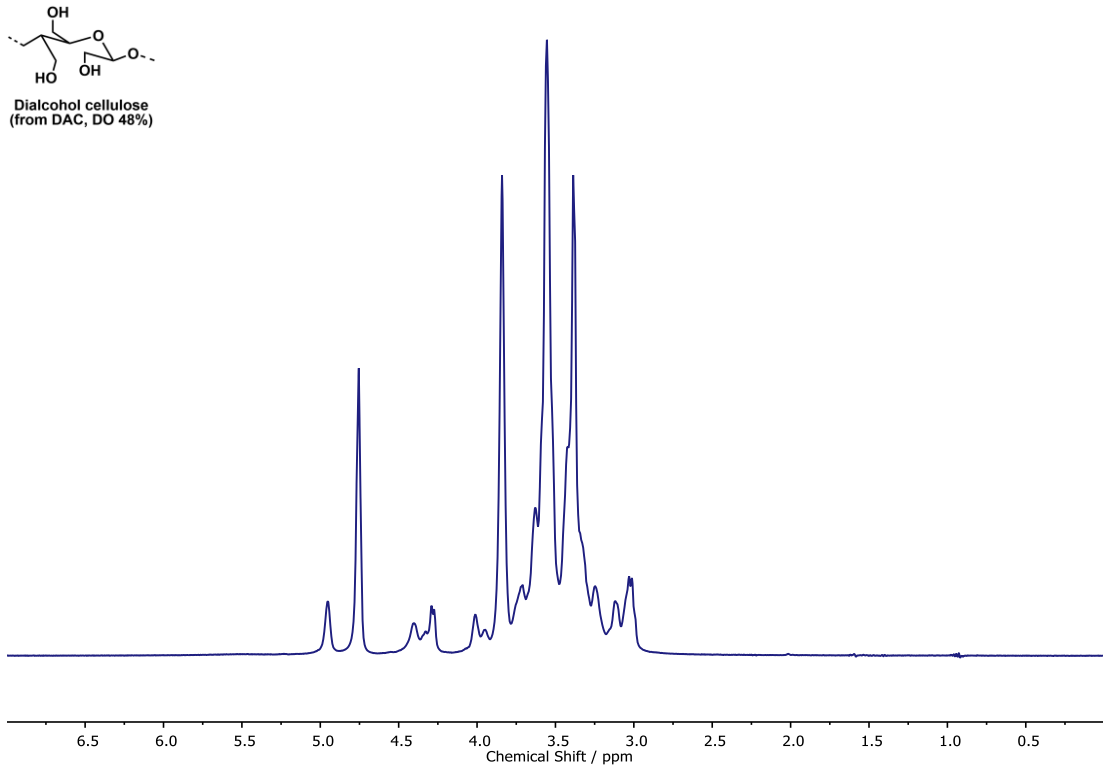

Figure S24. Diffusion edited ^{1}H NMR spectrum ([P_{4444}][OAc] : DMSO-d_6, 1:4 wt%; 400 MHz; 65°C) of dialcohol cellulose obtained from DAC (DO = 48%; starting material = cotton linters; 5 wt%).

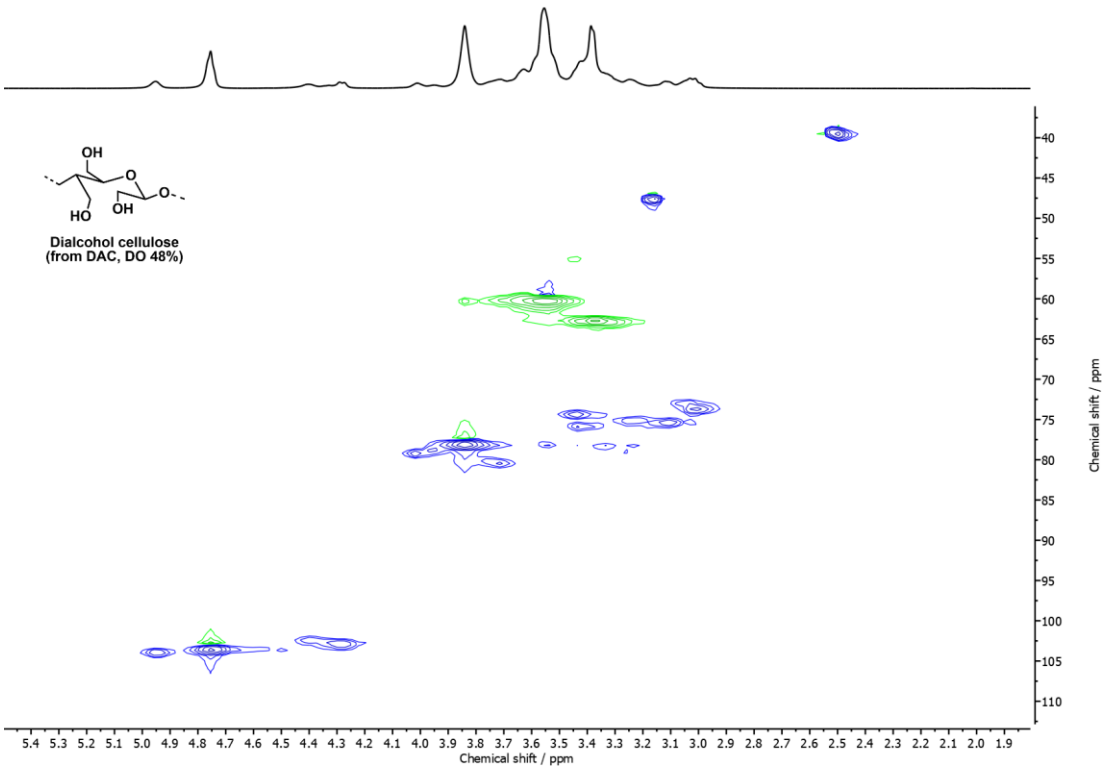

Figure S25. Multiplicity-edited HSQC spectrum ([P_{4444}][OAc] : DMSO-d_6, 1:4 wt%; 400 MHz; 65°C) of dialcohol cellulose obtained from DAC (DO = 48%; starting material = cotton linters; 5 wt%). CH_2 resonances are shown in green, CH/CH_3 signals are shown in blue. Diffusion edited ^1H trace shown on top. Only the zoom into the polysaccharide region is shown. Peak at ^1H = 3.16 ppm / ^{13}C = 47.6 ppm due to slight methanol impurities stemming from the precipitation.

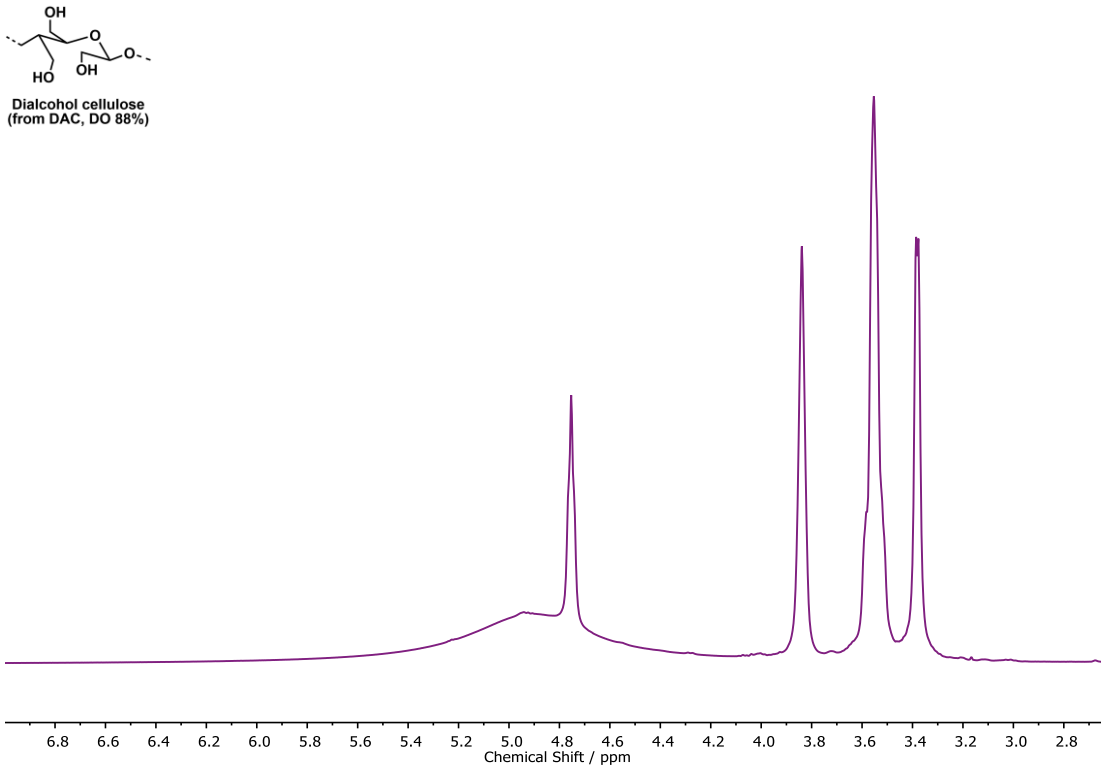

Figure S26. Quantitative ^1H NMR spectrum ([P_{4444}][OAc] : DMSO-d_6, 1:4 wt%; 400 MHz; 65°C) of dialcohol cellulose obtained from DAC (DO = 88%; starting material = cotton linters; 5 wt%), enlarged into the polysaccharide spectral window.

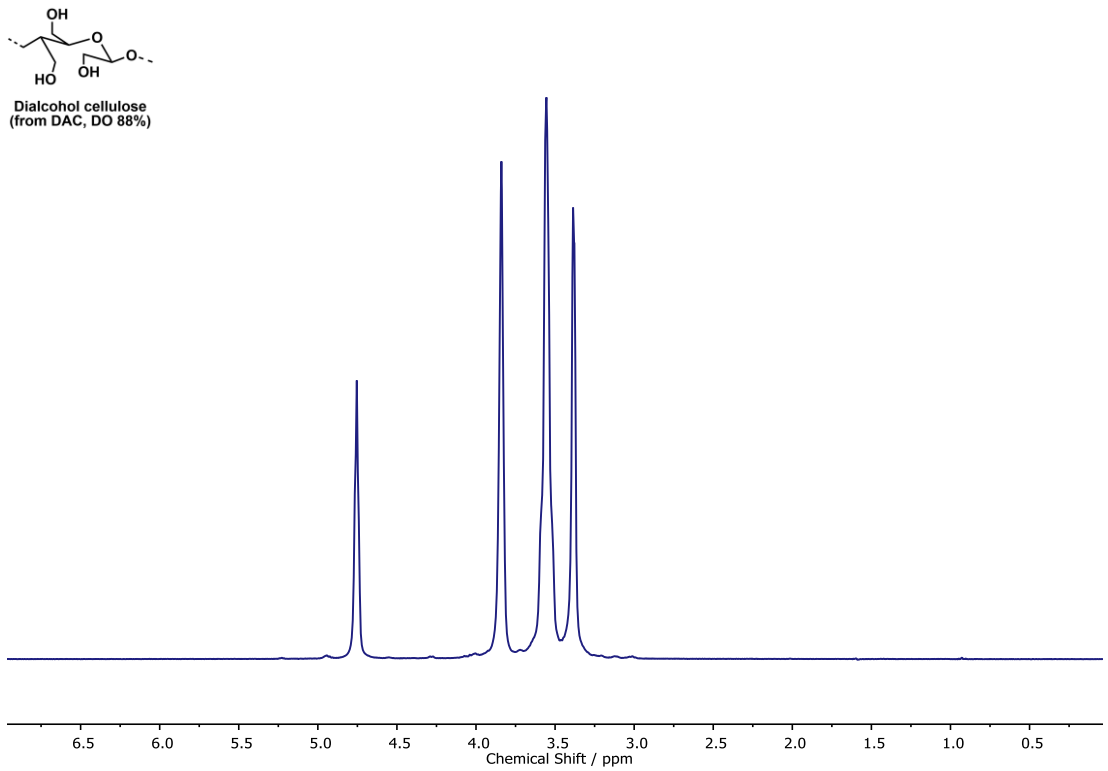

Figure S27. Diffusion edited ^{1}H NMR spectrum ([P_{4444}][OAc] : DMSO-d_6; 1:4 wt%; 400 MHz; 65°C) of dialcohol cellulose obtained from DAC (DO = 88%; starting material = cotton linters; 5 wt%).

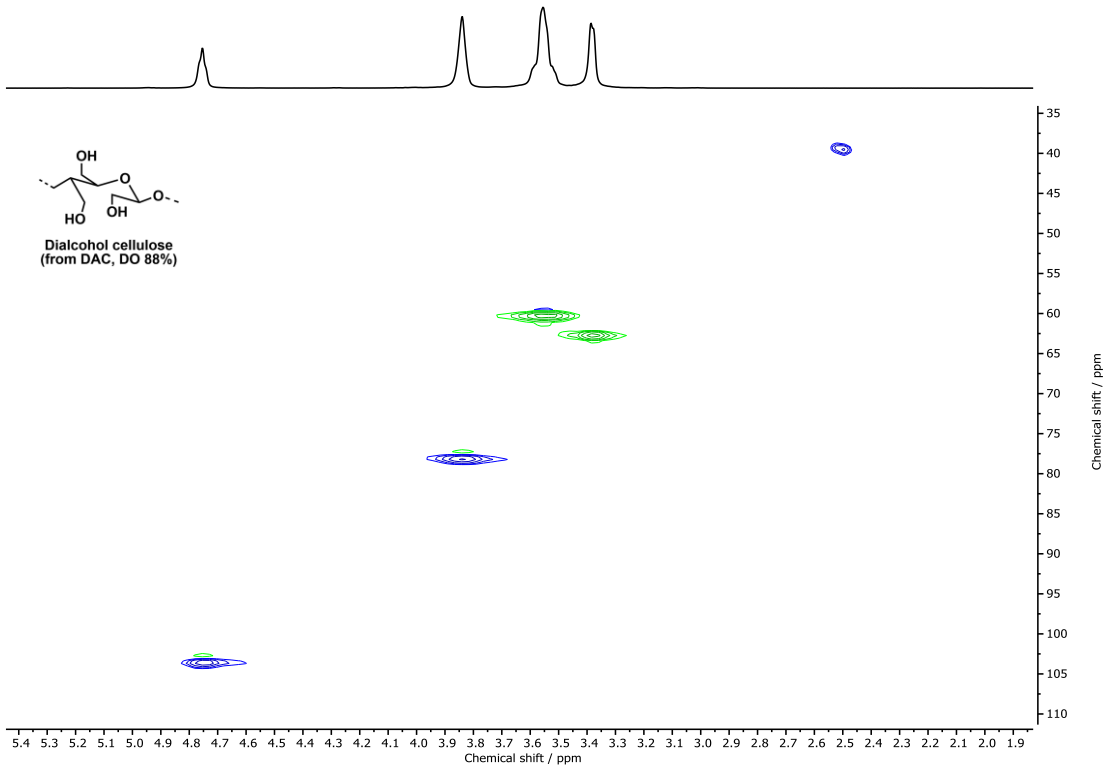

Figure S28. Multiplicity-edited HSQC spectrum ([P_{4444}][OAc] : DMSO-d_6, 1:4 wt%; 400 MHz; 65°C) of dialcohol cellulose obtained from DAC (DO = 88%; starting material = cotton linters; 5 wt%). CH_2 resonances are shown in green, CH/CH_3 signals are shown in blue. Diffusion edited ^{1}H trace shown on top. Only the zoom into the polysaccharide region is shown.

3) Peak Deconvolution of the C1-H moieties

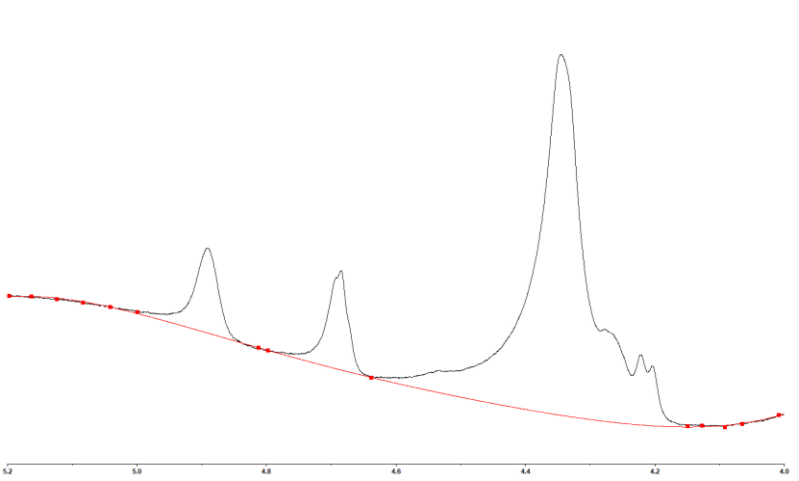

Figure S29. Baseline correction to consider the prominent water peak in the quantitative ^{1}H NMR spectra which partially overlaps with the C1-H signals.

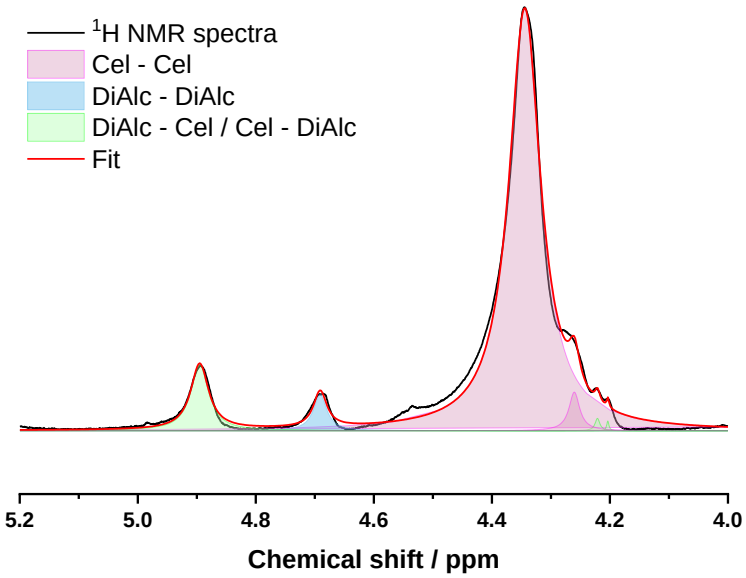

Figure S30. Peak deconvolution of the C1-H moieties of dialcohol cellulose obtained from DAC (DO = 7%; starting material = cotton linters).

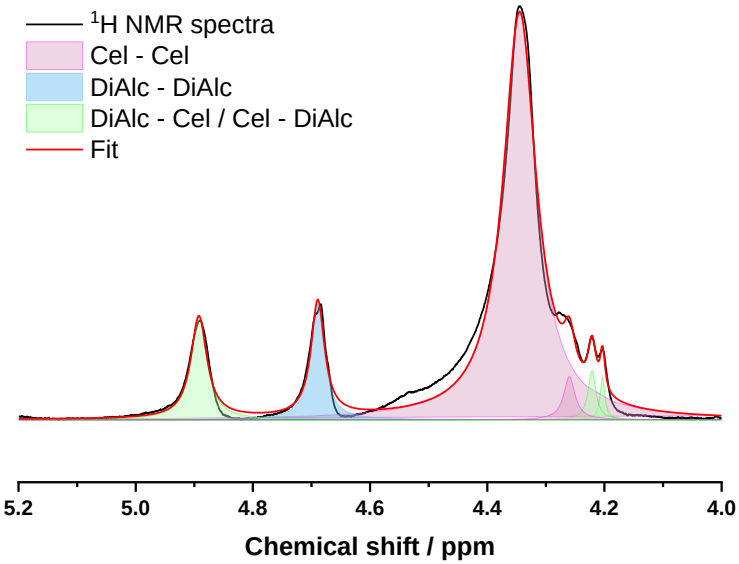

Figure S31. Peak deconvolution of the C1-H moieties of dialcohol cellulose obtained from DAC (DO = 13%; starting material = cotton linters).

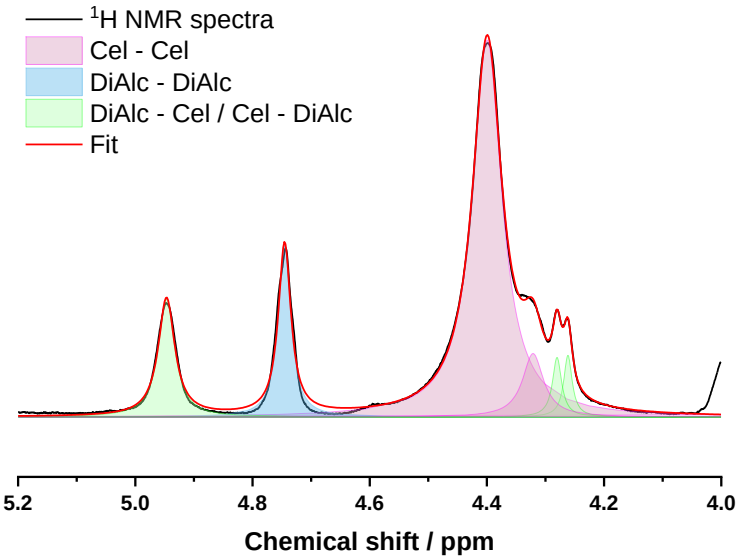

Figure S32. Peak deconvolution of the C1-H moieties of dialcohol cellulose obtained from DAC (DO = 14%; starting material = cotton linters).

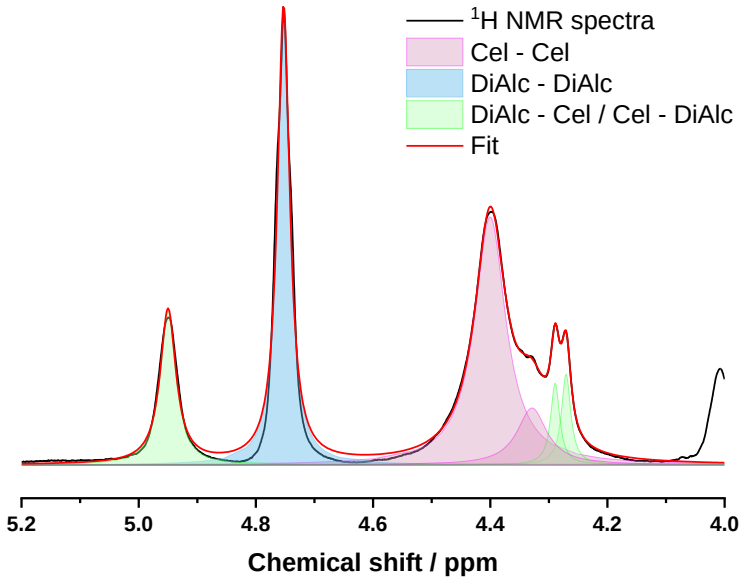

Figure S33. Peak deconvolution of the C1-H moieties of dialcohol cellulose obtained from DAC (DO = 32%; starting material = cotton linters).

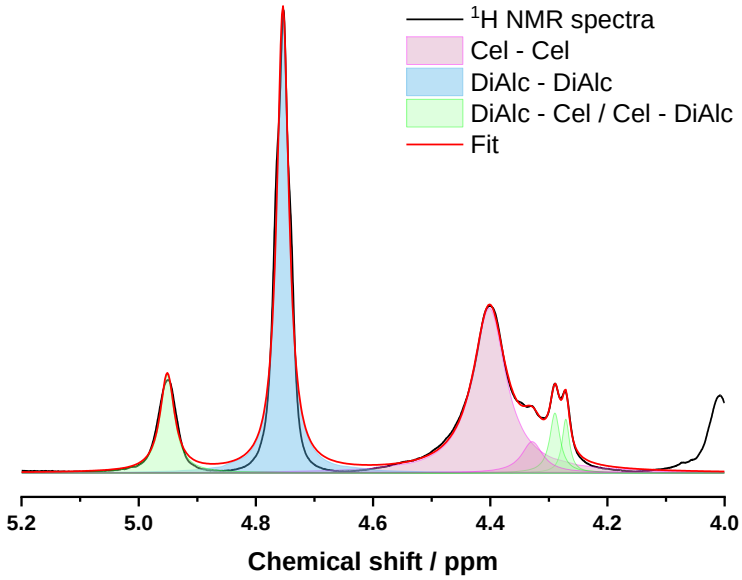

Figure S34. Peak deconvolution of the C1-H moieties of dialcohol cellulose obtained from DAC (DO = 48%; starting material = cotton linters).

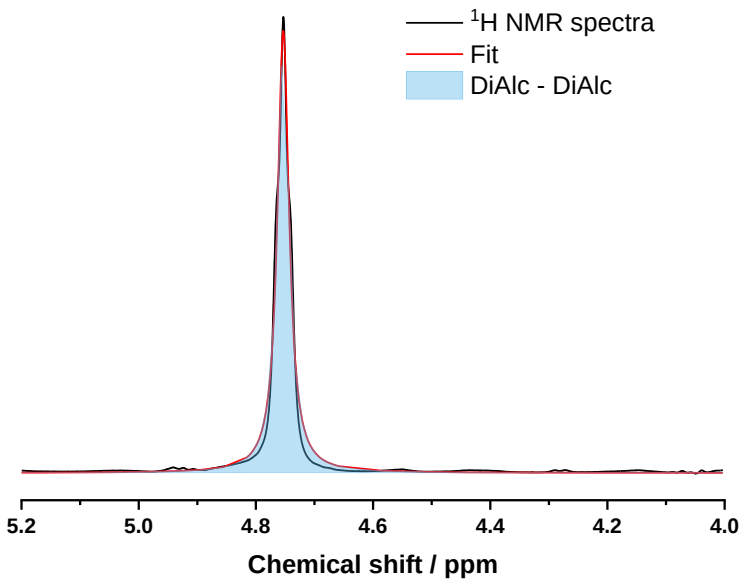

Figure S35. Peak deconvolution of the C1-H moieties of dialcohol cellulose obtained from DAC (DO = 88%; starting material = cotton linters).

4) GPC/MALLS-RI data

4.1) Cotton linters and its derived dialcohol celluloses from NMR study

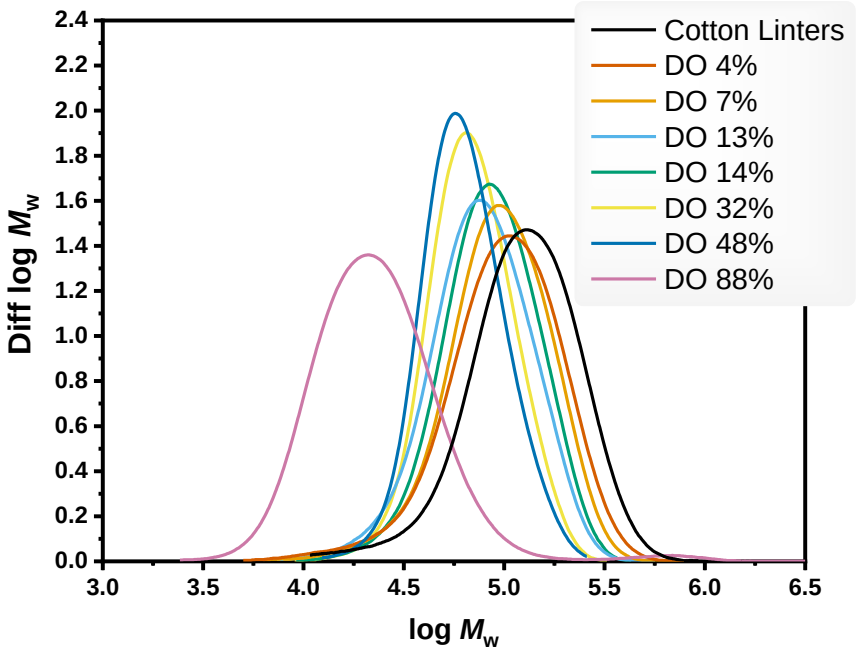

Figure S36. Molecular weight distributions of dialcohol celluloses with varying degree of oxidation obtained from partially oxidized cotton linters used for NMR study.

4.2) Influence of the degree of oxidation on the GPC data during sodium borohydride reduction

Table S3. GPC-MALLS statistical moments for the dialcohol celluloses obtained from partially oxidized softwood kraft pulp with varying degrees of oxidation.

Entry	Degree of oxidation (DO) [a] / %	M_n / kDa	M_w / kDa	M_z / kDa	$Đ$	Yield [b] / %
1	softwood kraft pulp	55	614	1651	11.09	no
2	8	62	482	1474	7.81	90
3	11	45	160	445	3.59	93
4	14	39	147	440	3.74	-
5	18	29	62	125	2.14	81
6	20	29	66	132	2.25	-
7	21	25	46	73	1.88	-
8	28	23	37	54	1.62	64
9	30	21	35	57	1.63	62
10	35	32	58	115	1.80	67
11	47	20	32	53	1.56	71
12	50	34	48	65	1.41	-
13	56	28	41	55	1.45	60
14	65	33	46	63	1.40	57
15	69	47	63	93	1.36	-
16	74	24	36	55	1.55	61

[a] Degree of oxidation of the dialdehyde cellulose used for sodium borohydride reduction. [b] Yields were not determined for all dialcohol celluloses but only for reproduced experiments which were freeze-dried after isolation.

4.3) Influence of the degree of oxidation on the GPC data during beta-elimination

Table S4. GPC-MALLS statistical moments for the dialdehyde celluloses treated at pH 10 without adding sodium borohydride obtained from partially oxidized softwood kraft pulp with varying degrees of oxidation.

Entry	Degree of oxidation (DO) [a] / %	M_n / kDa	M_w / kDa	M_z / kDa	$Đ$
1	softwood kraft pulp	55	614	1651	11.09
2	8	26	57	107	2.21
3	12	20	41	112	2.07
4	18	16	30	46	1.92
5	26	15	24	35	1.57
6	30	17	25	35	1.45
7	39	15	23	31	1.46
8	60	14	20	26	1.43

[a] Degree of oxidation of the dialdehyde cellulose used for sodium borohydride reduction.

4.4) GPC data from kinetic study

Table S5. GPC-MALLS statistical moments for the dialcohol celluloses isolated in the kinetic study

Entry	Reaction duration	M_n / kDa	M_w / kDa	M_z / kDa	$Đ$
1	6 min	26	34	42	1.31
2	30 min	26	33	41	1.27
3	60 min	25	32	41	1.32
4	2 hours, 22 minutes	25	32	39	1.26
5	24 hours	23	30	39	1.32

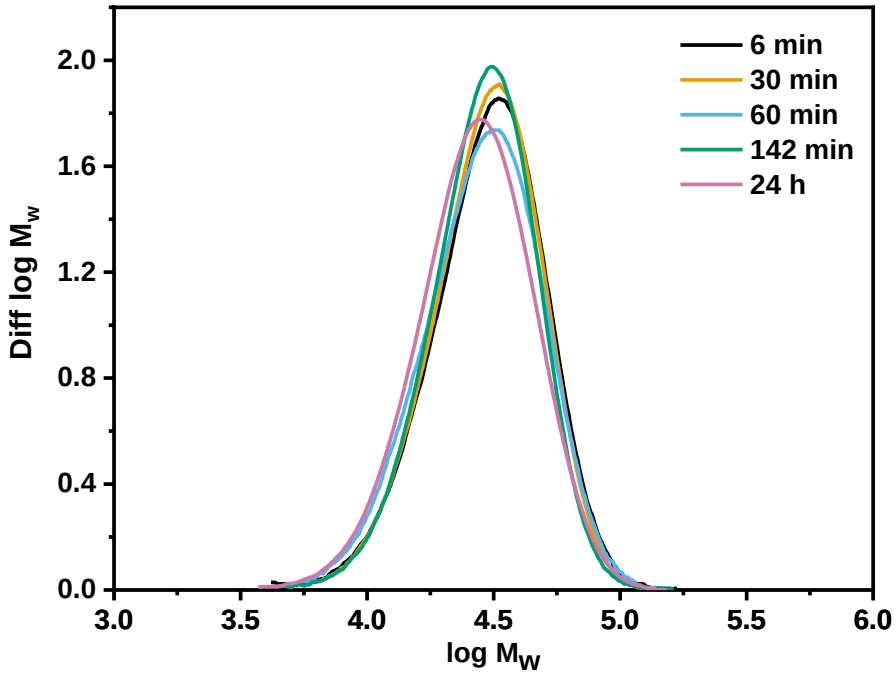

Figure S37. Molecular weight distributions of dialcohol celluloses obtained from periodate oxidation of softwood kraft pulp to dialdehyde cellulose followed by sodium borohydride reduction for varying reaction times.

4.5) Influence of the pH on the molecular weight distributions during sodium borohydride reduction

Table S6. GPC-MALLS Statistical Moments and Remaining Aldehyde Content for the Dialcohol Celluloses Obtained from 10%-oxidized Softwood Kraft Pulp by Borohydride Reduction at Varying pH.

Entry	pH		M_n / kDa	M_w / kDa	M_z / kDa	$Đ$	Aldehyde content[a] / µmol/g
	at the beginning	*at the end*					
1	7.9	8.0	73	249	601	3.41	477
2	8.4	8.4	64	179	406	2.80	344
3	9.0	9.0	46	126	298	2.73	267
4	9.5	9.6	32	70	136	2.18	66
5	9.7	9.9	40	89	168	2.21	54
6	9.8	9.9	24	47	82	2.00	49

[a] Aldehyde content was determined by fluorescence measurement after labeling with Carbazole-9-carbonyloxyamine (CCOA).

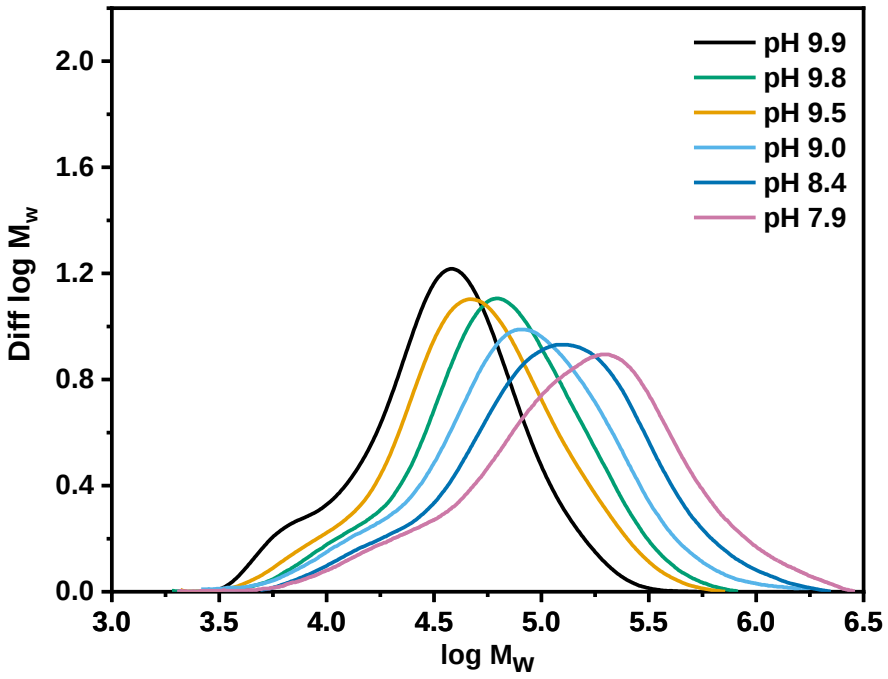

Figure S38. Molecular weight distributions of dialcohol celluloses from periodate oxidation of softwood kraft pulp to dialdehyde cellulose (DO 10%) followed by sodium borohydride reduction at varying pH.

Table S7. GPC-MALLS statistical moments for the dialcohol celluloses obtained from 18%-oxidized softwood kraft pulp by sodium borohydride reduction at varying pH.

Entry	pH		M_n / kDa	M_w / kDa	M_z / kDa	$Đ$
	at the beginning	*at the end*				
1	8.2	8.2	57	124	239	2.20
2	8.6	8.6	33	62	100	1.90
3	9.4	9.4	45	81	131	1.83
4	9.6	9.7	25	41	61	1.67
5	9.8	9.9	17	28	40	1.65
6	9.8	10.0	30	49	71	1.62

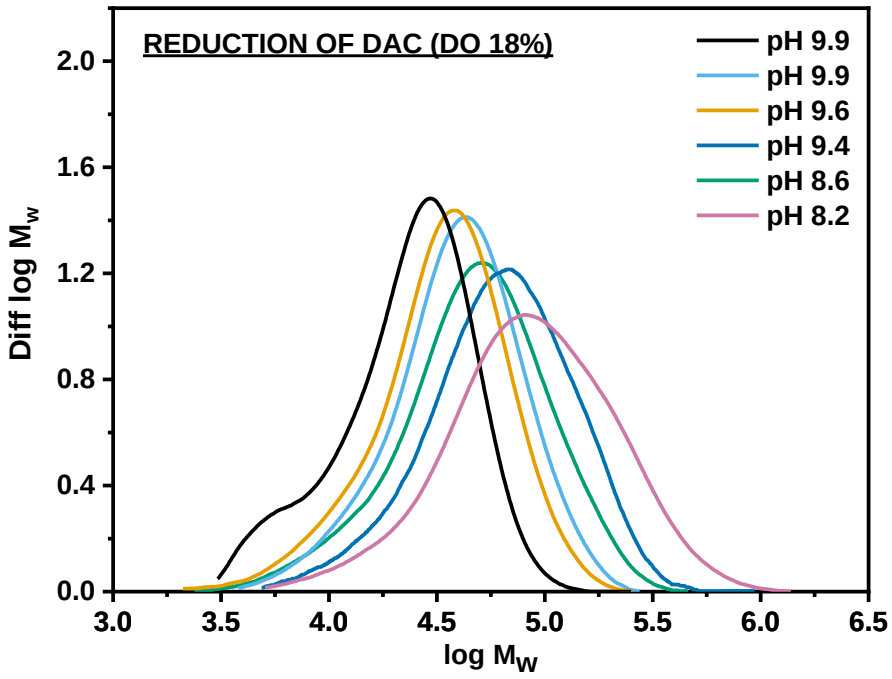

Figure S39. Molecular weight distributions of dialcohol celluloses from periodate oxidation of softwood kraft pulp to dialdehyde cellulose (DO 18%) followed by sodium borohydride reduction at varying pH.

Table S8. GPC-MALLS statistical moments for the dialcohol celluloses obtained from 26%-oxidized softwood kraft pulp by sodium borohydride reduction at varying pH.

Entry	pH		M_n / kDa	M_w / kDa	M_z / kDa	$Đ$
	at the beginning	*at the end*				
1	8.4	8.4	41	67	101	1.65
2	8.7	8.7	32	51	73	1.61
3	9.5	9.7	32	43	54	1.32
4	9.5	9.8	18	30	42	1.61
5	9.8	10.0	16	26	35	1.56
6	10.0	10.2	26	37	49	1.42

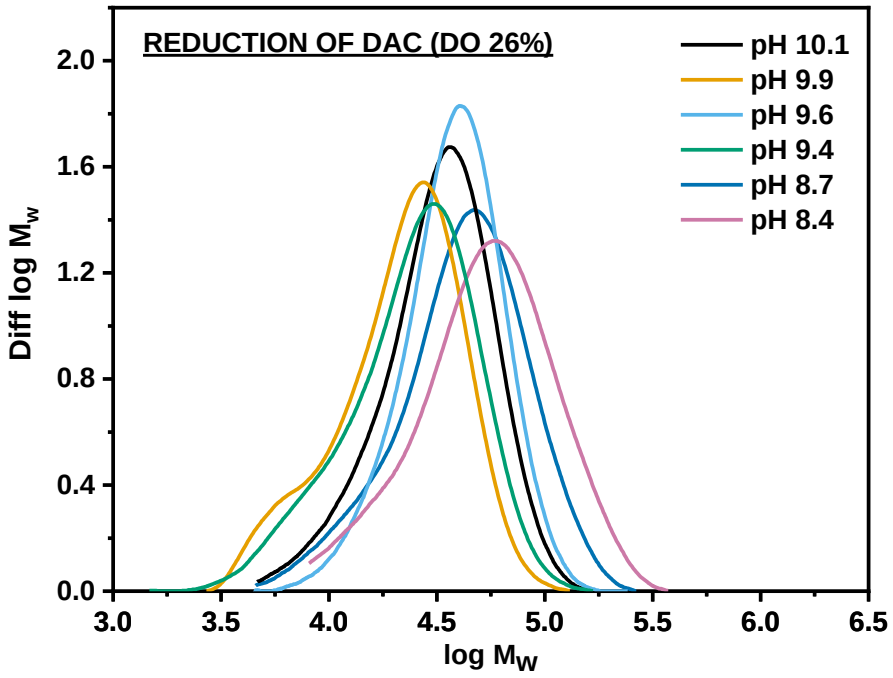

Figure S40. Molecular weight distributions of dialcohol celluloses from periodate oxidation of softwood kraft pulp to dialdehyde cellulose (DO 26%) followed by sodium borohydride reduction at varying pH.

References

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