(Supporting Information)

Fully bio-based cellulose ester synthesis from natural aldehydes via aerobic oxidation

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Materials

Cellulose (Avicel®PH-101, particle size < 50 μm), anhydrous dimethyl sulfoxide (DMSO) and Emim chloride (EmimCl) and benzaldehyde (**1**) were obtained from Sigma-Aldrich Co. LLC. (St. Louis, MO, USA). The number-average degree of polymerization of Avicel was calculated to be 105.[1] 2-Hydroxypyridine, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC), 4-dimethylaminopyridine (DMAP), anhydrous *N,N*-dimethylacetamide (DMA), anhydrous *N,N*-dimethylformamide (DMF), acetic acid, cuminaldehyde (**2**), anisaldehyde (**3**), vanillin (**4**), syringaldehyde (**5**), veratraldehyde (**6**), 3,4,5-trimethoxybenzaldehyde (**7**), furfural (**8**) and *trans*-cinnamaldehyde (**9**) were purchased from Tokyo Chemical Industry (TCI, Tokyo, Japan). Emim acetate (EmimOAc) was available from Nippon Nyukazai Co., Ltd. (Tokyo, Japan). Citronellal (**10**) was obtained from Kanto Chemical Co., Inc. (Tokyo, Japan). Emim 2-pyridinolate (EmimOPy) was synthesized according to conventional protocols.[2] Other chemicals were obtained from commercial sources and were used as-received unless otherwise stated.

Instruments

^{1}H and ^{13}C NMR spectra were recorded using JNM-ECA 400 and 600 spectrometers (JEOL Ltd., Tokyo, Japan) in deuterated solvents, and the chemical shifts (δ, ppm) were referenced to either the residual solvent peak or tetramethylsilane [TMS, δ = 0 (ppm)] as the internal standard. Fourier transform-infrared (FT-IR) spectra were recorded using a Thermo Fisher Scientific Nicolet IS10 (Thermo Fisher Scientific Inc., Tokyo, Japan) spectrometer equipped with an attenuated total reflection (ATR) unit. The size exclusion chromatography (SEC) measurements were performed with a Shimadzu (Kyoto, Japan) Prominence gel permeation chromatography system (DGU-20A degassing unit, LC-20AD pump, SIL-20A HT auto sampler, CTP-20A column oven, and RID-20A refractive index detector). All SEC measurements were carried out at 40 °C using TSK gel α-M (Tosoh Co., Tokyo, Japan), and DMF was used as an eluent at a flow rate of 1.0 mL/min. The molecular weight calibration curves were obtained with polystyrene standards (Tosoh).

Experimental procedures

General procedure for the oxidative esterification of cellulose via aerobic oxidation

Cellulose (120 mg, [OH] = 2.22 mmol) in IL (2.22 mmol) was dried for 3 h *in vacuo* at 80 °C. After the drying process was completed, DMSO (3.15 mL) was added and the mixture was stirred under air. After 1 h, aldehyde (2.22 mmol) was added and the reaction mixture was stirred for 24 h at 60 °C. The resulting solution was poured into a large amount of MeOH. The polymer was purified by reprecipitation (from an acetone solution to water) to give a white fibrous solid.

Per-acetylation of resulting polymer using acetic acid

Obtained cellulose esters (50.0 mg), acetic acid (97.3 μL, 1.85 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodimide (355 mg, 1.85 mmol) and 4-dimethylaminopyridine (226 mg, 1.85 mmol) were added in DMA (3.0 mL) and the mixture was stirred at room temperature. After 24 h, the resulting solution was poured into a large amount of MeOH. The polymer was purified by reprecipitation (from acetone solution to water) to give acetylated products.

Evaluation of the degree of substitution values of the cellulose esters

The degree of substitution (DS) in cellulose esters was determined using ^{1}H NMR measurements conducted in DMSO-d_6 or acetone-d_6 depending on the solubility of the product and overlap between the target and solvent peaks. The DS estimation was done after acetylation processing to enhance their solubility in organic solvent.

Generally, the DS values derived from desired substituent (DS_{main}) were calculated using the following equation (1):

$$DS_{main} = (I_{main}/X)/(I_{AGU}/7) \qquad (1)$$

The DS_{main} values of cellulose benzoate (Table 2, entry 1), 4-isopropylbenzoate (entry 2), 4-methoxybenzoate (entry 3), 3,4-dimethoxybenzoate (entry 6), 3,4,5-trimethoxybenzoate (entry 7), 3-phenylpropionate (entry 9), and dimethyloctenoate (entry 10) were calculated from the integrals of the corresponding peaks (I_{main}) at around 8.3−7.0 ppm (X = 5), 8.3−6.8 ppm (X = 4), 8.3−6.5 ppm (X = 4), 8.0−6.5 ppm (X = 3), 8.0−6.5 ppm (X = 2), 7.4−6.8 ppm (X = 5), 1.7−1.5 ppm (X = 6), respectively, and the anhydroglucose unit (AGU) peaks (I_{AGU})

at around 5.5−3.0 ppm in the ^{1}H NMR spectra of corresponding per-acetylated products. In the cases of cellulose 4-methoxybenzoate (Table 2, entry 3), 3,4-dimethoxybenzoate (entry 6), 3,4,5-trimethoxybenzoate (entry 7), and dimethyloctenoate (entry 10), the peaks of their methoxy and alkene groups at around 4.0−3.0 ppm and 6.0−5.0 ppm, respectively, overlapped with the AGU signals at around 5.5−3.0 ppm. Thus, I_{AGU} value was corrected by subtracting the value corresponding to I_{main}.

In Figure S2a, because I_{AGU} value could not be calculated due to the overlapping among the proton peaks of cellulose backbone and water in DMSO-d_6, the DS values derived from undesired acetyl group (DS_{side}) were calculated using the following equation (2):

$$DS_{side} = DS_{main}(I_{side}/3)/(I_{main}/5) \qquad (2)$$

The DS_{side} value of cellulose benzoate acetate was calculated from the integrals of the corresponding proton peaks on aromatic ring (I_{main}) at around 8.3−7.0 ppm, acetyl proton peaks (I_{side}) at around 2.2−1.8 ppm in the ^{1}H NMR spectra of obtained products, and corresponding DS_{main} value of per-acetylated product shown in Figure S2b. The DS_{side} value of cellulose benzoate acetate in Table 1 is similarly calculated.

Supporting data

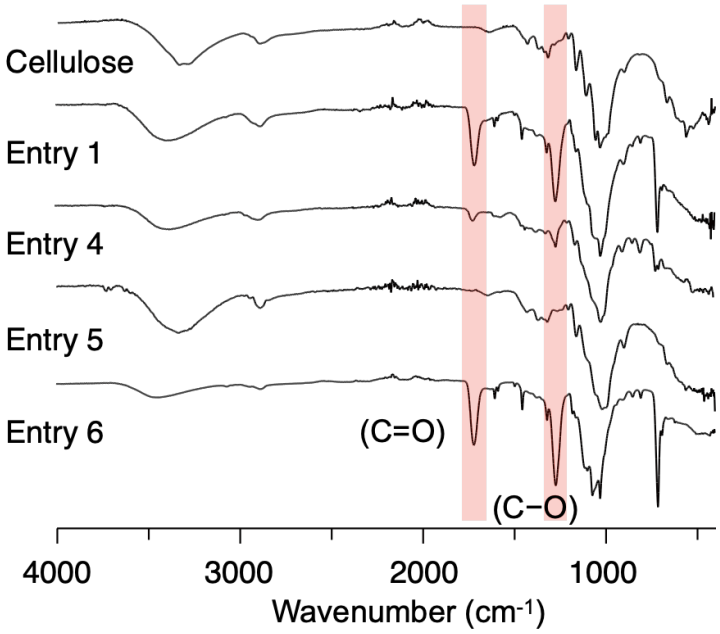

Figure S1. ATR-mode FT-IR of resulting cellulose derivatives in Table 1.

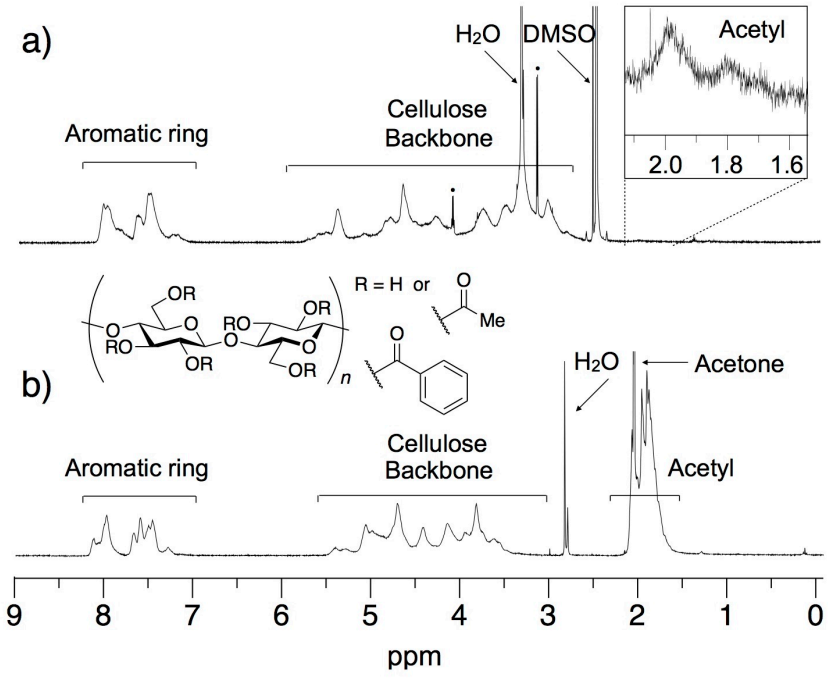

Figure S2. ^{1}H NMR spectra of the cellulose ester product shown in Table 1 (entry 1) in DMSO-d_6 (a) and the cellulose ester product after per-acetylation in acetone-d_6 (b) measured at room temperature.

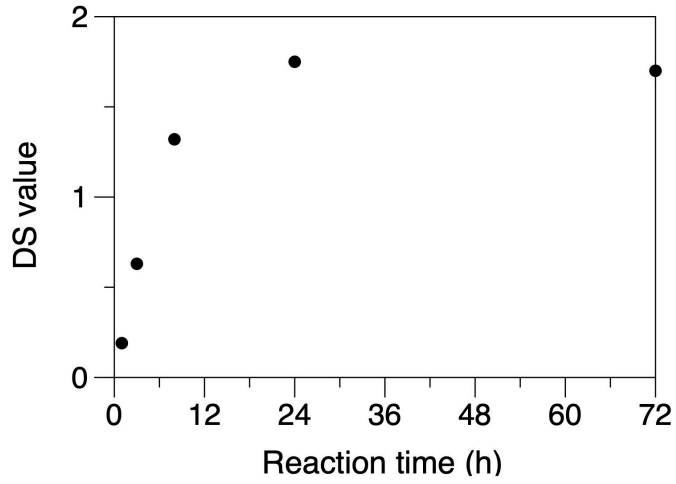

Figure S3. Time-dependent change of DS value of cellulose benzoate (Reaction condition: Table 1, entry 6).

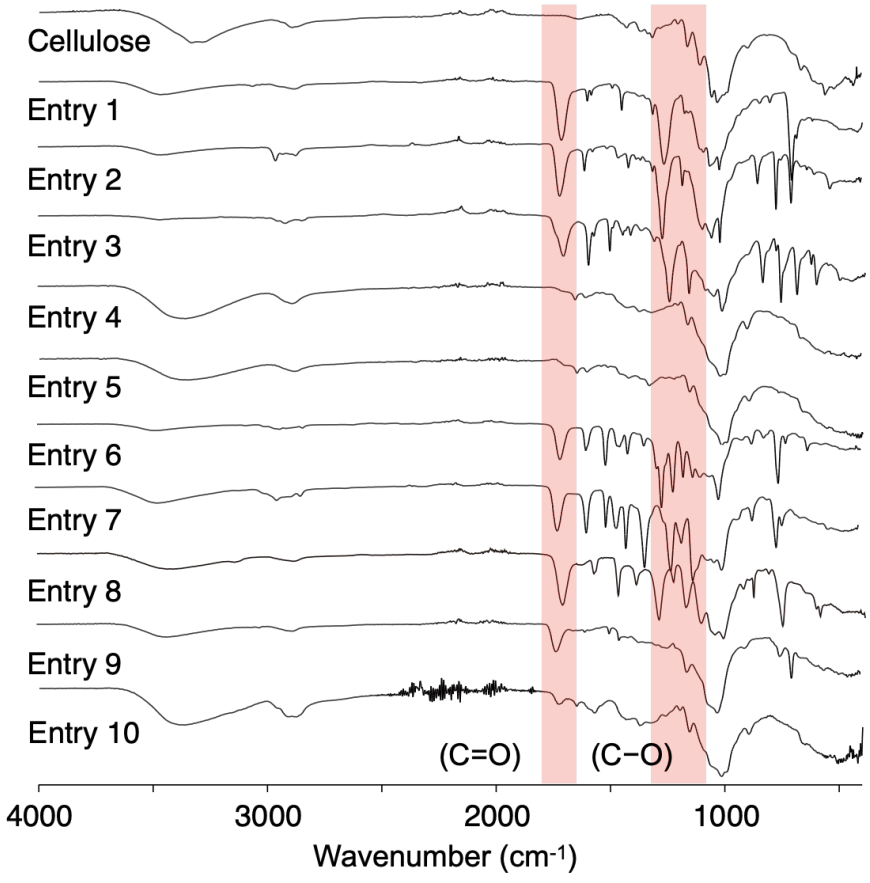

Figure S4. ATR-mode FT-IR of resulting cellulose derivatives in Table 2.

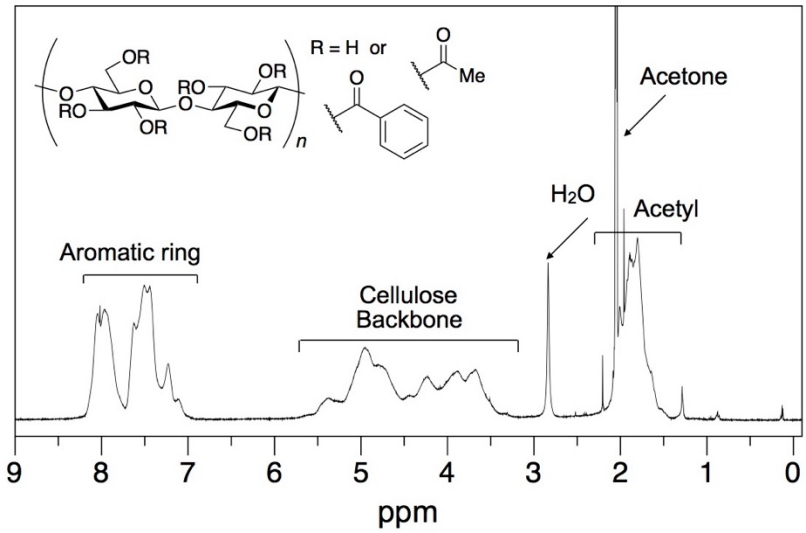

Figure S5. ^{1}H NMR spectra of per-acetylated cellulose ester derived from **1** in Table 2, measured in acetone-d_6 at rt.

Cellulose benzoate (DS = 1.38) [Table 2, entry 1]: (before acetylation) 118 mg. (after acetylation) ^{1}H NMR (600 MHz, acetone-d_6, rt): δ 8.3–7.0 (br, Ar), 5.5–3.0 (br, cellulose backbone), 2.1–1.5 (br, Ac).

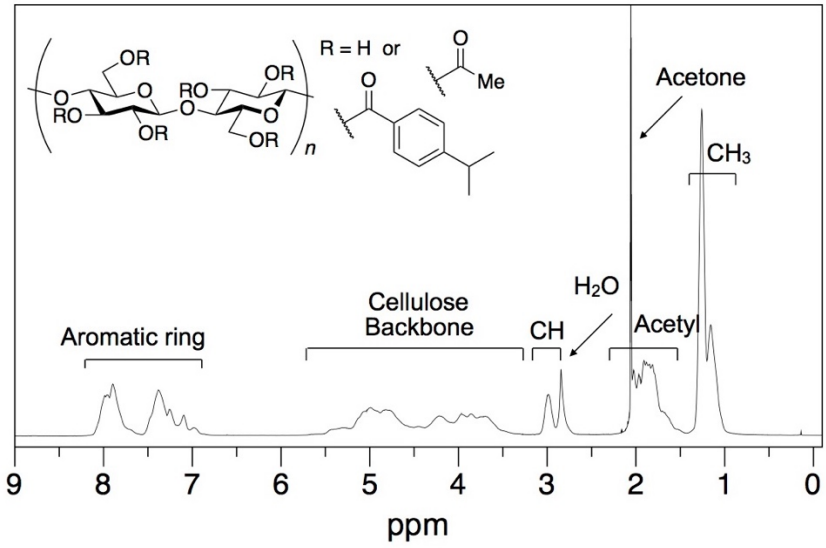

Figure S6. ^{1}H NMR spectra of per-acetylated cellulose ester derived from **2** in Table 2, measured in acetone-d_6 at rt.

Cellulose 4-isopropylbenzoate (DS = 1.33) [Table 2, entry 2]: (before acetylation) 105 mg. (after acetylation) ^{1}H NMR (600 MHz, acetone-d_6, rt): δ 8.3–6.8 (br, Ar), 5.5–3.0 (br, cellulose backbone), 2.1–1.5 (br, Ac), 1.3–0.9 (br, CH_3).

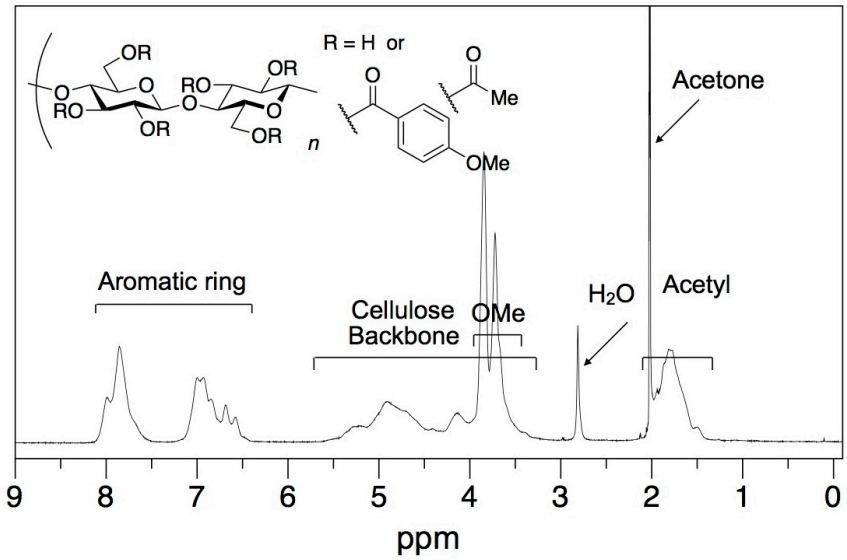

Figure S7. ^{1}H NMR spectra of per-acetylated cellulose ester derived from **3** in Table 2, measured in acetone-d_6 at rt.

Cellulose 4-methoxybenzoate (DS = 1.69) [Table 2, entry 3]: (before acetylation) 149 mg. (after acetylation) ^{1}H NMR (600 MHz, acetone-d_6, rt): δ 8.3–6.5 (br, Ar), 5.5–3.2 (br, cellulose backbone, OMe), 2.1–1.4 (br, Ac).

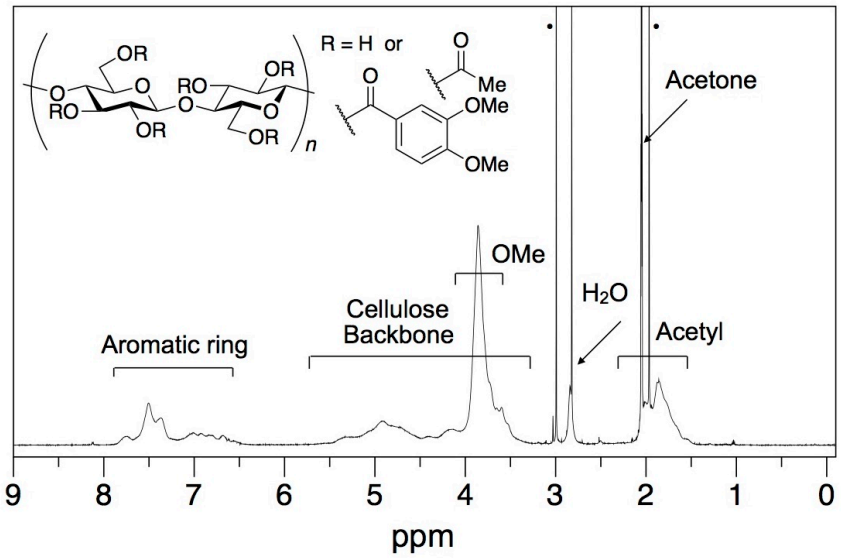

Figure S8. ^{1}H NMR spectra of per-acetylated cellulose ester derived from **6** in Table 2, measured in acetone-d_6 at rt.

Cellulose 3,4-dimethoxybenzoate (DS = 1.48) [Table 2, entry 6]: (before acetylation) 190 mg. (after acetylation) ^{1}H NMR (600 MHz, acetone-d_6, rt): δ 8.0–6.5 (br, Ar), 5.5–3.1 (br, cellulose backbone, OMe), 2.1–1.5 (br, Ac).

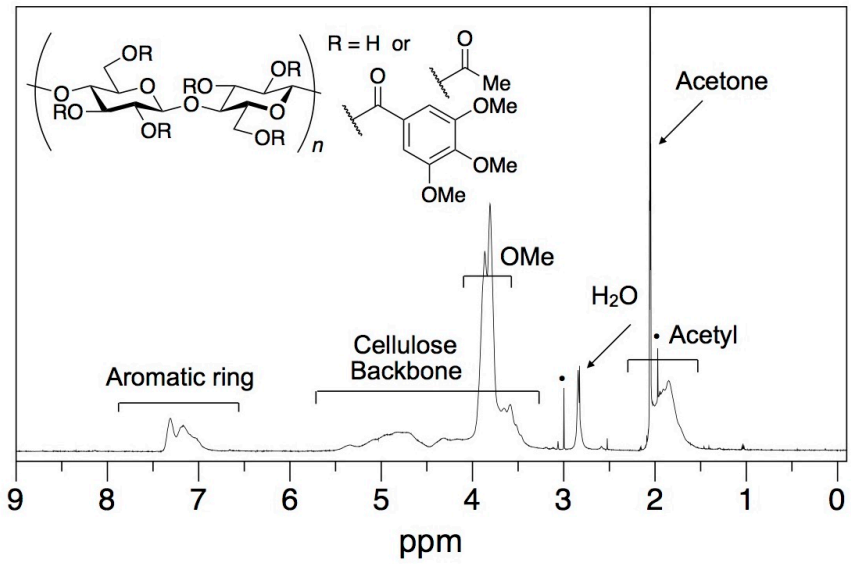

Figure S9. ^{1}H NMR spectra of per-acetylated cellulose ester derived from **7** in Table 2, measured in acetone-d_6 at rt.

Cellulose 3,4,5-trimethoxybenzoate (DS = 1.22) [Table 2, entry 7]: (before acetylation) 200 mg. (after acetylation) ^{1}H NMR (600 MHz, acetone-d_6, rt): δ 7.4–6.8 (br, Ar), 5.5–3.3 (br, cellulose backbone, OMe), 2.1–1.5 (br, Ac).

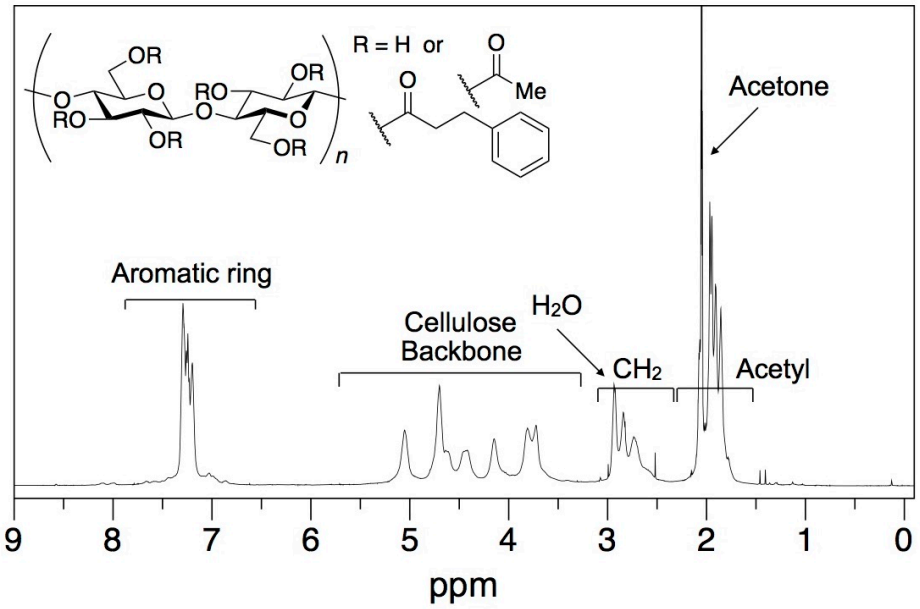

Figure S10. ^{1}H NMR spectra of per-acetylated cellulose ester derived from **9** in Table 2, measured in acetone-d_6 at rt.

Cellulose 3-phenylpropanoate (DS = 0.79) [Table 2, entry 9]: (before acetylation) 120 mg. (after acetylation) ^{1}H NMR (600 MHz, acetone-d_6, rt): δ 7.8–6.8 (br, Ar), 5.5–3.3 (br, cellulose backbone), 3.0–2.5 (br, CH_2), 2.1–1.5 (br, Ac).

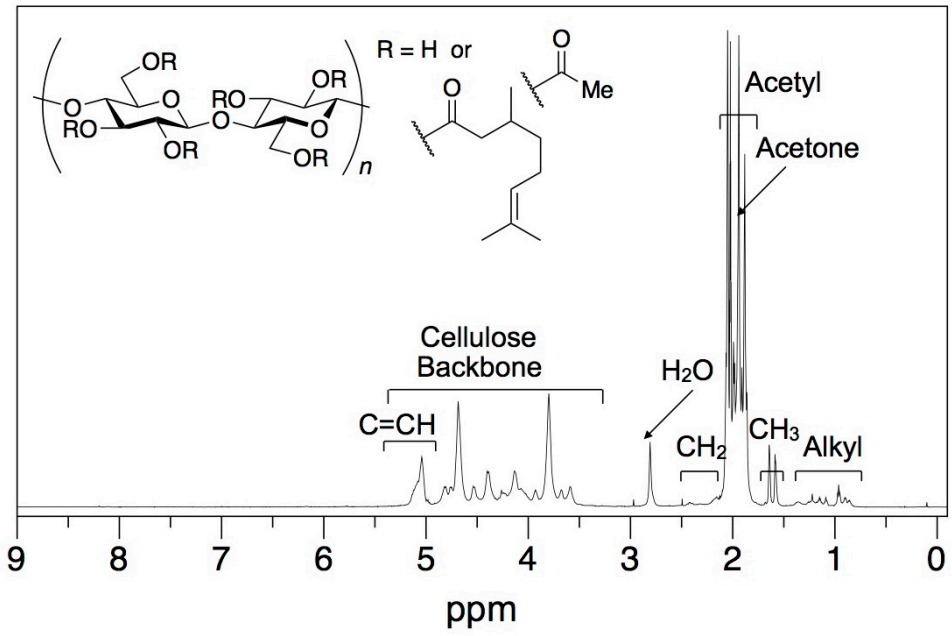

Figure S11. ^{1}H NMR spectra of per-acetylated cellulose ester derived from **10** in Table 2, measured in acetone-d_6 at rt.

Cellulose 3,7-dimethyloct-6-enoate (DS = 0.10) [Table 2, entry 10]: (before acetylation) 65.2 mg. (after acetylation) ^{1}H NMR (600 MHz, acetone-d_6, rt): δ 8.3–7.0 (br, Ar), 5.5–3.0 (br, cellulose backbone, C=CH), 2.5–2.2 (br, $COCH_2$), 2.2–1.8 (br, Ac), 1.7–1.5 (br, $C=C(CH_3)_2$), 1.5–0.8 (br, alkyl).

Table S1. SEC Results of highly substituted (DS > 1.0) cellulose esters (Table 2).

	M_n (10^{-4})[a]	M_w/M_n [a]
entry 1	4.6	2.3
entry 2	—[b]	—[b]
entry 3	3.7	1.8
entry 6	4.1	3.2
entry 7	4.6	2.7

[a]Determined by SEC (eluent: DMF, PSt standards). [b]Microscopic aggregates formation is expected to interfere with accurate molecular weight analysis.

Table S2. Solubility test (*ca.* 1.0 mg/mL) of resulting cellulose esters (before acetylation) in Table 2 at room temperature.

	$CHCl_3$	THF	Acetone	DMF	DMSO	MeOH	H_2O
entry 1	X	X	X	○	○	X	X
entry 2	X	○	X	○	○	X	X
entry 3	X	X	X	○	○	X	X
entry 6	X	X	X	○	○	X	X
entry 7	X	X	X	○	○	X	X
entry 9	X	X	X	○	○	X	X
entry 10	X	X	X	X	X	X	X

○: Soluble, X: Insoluble (lower than *ca.* 1.0 mg/mL).

Reference

1. R. Kakuchi, R. Ito, S. Nomura, H. Abroshan, K. Ninomiya, T. Ikai, K. Maeda, H. J. Kim and K. Takahashi, *RSC Adv.*, 2017, **7**, 9423-9430.
2. S. B. W. Kusuma, D. Hirose, A. Yoshizawa, L. Szabó, D. Ina, N. Wada and K. Takahashi, *ACS Sustain. Chem. Eng.*, 2021, **9**, 8450-8457.