Highly regioselective surface acetylation of cellulose and shaped cellulose constructs in the gas-phase

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1. Materials and methods

Different celluloses were used in our reactivity studies; FD-CNCs (freeze-dried softwood CNCs, derived from sulphuric acid digestion of southern pine dissolving pulp, FPL/UMaine PDC), Enocell bleached hardwood pre-hydrolysis kraft pulp (P-H Kraft pulp, 6.8 % hemicellulose), beech bleached sulphite pulp (Sulphite pulp, 3.8 % hemicellulose), CNC aerogel as well as regenerated fibres air-gap spun from [DBNH][OAc] (Sixta et al. 2015) using the IONCELL technology (IONCELL Fibres). Tetrabutylphosphonium acetate ([P\textsubscript{4444}][OAc]) was prepared to high purity, according to the literature procedures (King et al. 2018; Koso et al., 2020). All the reagents and solvents were high purity (≥98%) and were used as obtained from the commercial suppliers, without further purification. Acetic anhydride (AA) 98% was used as acetylating agent. Products were characterized by Attenuated Total Reflection Infra-Red spectroscopy (ATR-IR) and liquid-state NMR spectroscopy on a Bruker NEO Avance (600 MHz \textsuperscript{1}H-frequency) spectrometer. Wide-angle X-ray scattering (WAXS) measurements were performed on a PANalytical X’Pert Pro MPD system, with Bragg-Brentano (reflectance) geometry. The diffracted intensity of Cu(K\textalpha) radiation (\lambda = 1.54 Å, under a condition of 45 kV and 40 mA) was measured in a 2\theta range between 5° and 50°; The samples for WAXS were prepared by pressing 50 mg of sample in a KBr-IR press, before calibrating on a glass slide. FE-SEM/STEM (Hitachi S4800) was used for crystallinity characterization of selected samples.

1.1 Preparation of the [P\textsubscript{4444}][OAc]:DMSO-d\textsubscript{6} Electrolyte for NMR Analysis

Tri-n-butylphosphine (35 ml, 28.7 g, 142 mmol) and n-butyl chloride (30 ml, 26.7 g, 288 mmol) were added sequentially and in one portion to a Teflon-lined 125 ml Parr acid digestion vessel. The vessel was sealed and its contents reacted at 120 °C for 24 h under magnetic stirring. Note: a sealed vessel is necessary as trialkylphosphines of the like rapidly oxidize in the presence of air. Moreover, tributylphosphine is pyrophoric in air. After letting the vessel cool to room temperature, the crude and still mostly liquid product mixture was transferred to a round-bottomed flask (during this stage, rapid crystallization may occur). Excess n-butyl chloride (bp 78 °C) was evaporated off using a rotary evaporator. Finally, the product was dried using a high-vacuum rotary evaporator at 80 °C for 5 h, yielding a white crystalline mass (40.3 g, 137 mmol, 98% of theory); mp = 60-65 °C (from the melt) \textsuperscript{1}H NMR (600 MHz, DMSO-d\textsubscript{6}) \delta 2.24 – 2.16 (m, 8H), 1.51 – 1.36 (m, 16H), 0.92 (t, J = 7.2 Hz, 12H).

Dry [P\textsubscript{4444}]Cl (5.00 g, 16.96 mmol) and potassium acetate (1.67 g, 17.0 mmol) were added to isopropyl alcohol (50 ml, HPLC grade). These were mixed and refluxed with stirring for 20 h. After letting the mixture cool to room temperature and then cooling at -20 °C for 18 h, precipitated potassium chloride was filtered off over Celite 545 and the filtrate evaporated in a rotary evaporator. Chloroform (50 ml) was added and the mixture was again cooled to -20 °C for 18 h, to precipitate further salts, followed by filtration through Celite 545. Finally, the solvent was evaporated and the product dried in a high vacuum rotary evaporator at 90 °C for 6 h to give a pale-yellow crystalline mass (5.20 g, 16.32 mmol, 96% of theory); mp = 46 °C (from the melt); \textsuperscript{1}H NMR (600 MHz, DMSO-d\textsubscript{6}) \delta 2.27 – 2.17 (m, 8H), 1.62 (s, 3H), 1.51 – 1.36 (m, 16H), 0.91 (t, J= 7.2 Hz, 12H). The electrolyte was prepared by weighing dry [P\textsubscript{4444}][OAc] into DMSO-d\textsubscript{6} in a 1:4 w/w proportion. This was stored in a sealed vessel to avoid water uptake. The sample was analyzed by NMR to assess purity (Fig. S1).
1.2. Typical gas-solid phase acetylation of the cellulosic material

100 mg (0.617 mmol) of cellulose was placed into an opened 4 ml vial and sealed in a 100 ml Schott bottle (Figure S2), containing 0.58 ml (0.63 g; 6.17 mmol) of acetic anhydride. The reaction chamber was left to stand at the specified temperature for a fixed time. After cooling, the vial with the cellulosic material was removed. The acetylated cellulose was then washed with EtOH (2-3 × 3.5 ml) and centrifuged, followed by freeze-drying, for analysis. The acetylated CNC aerogel sample was dried only using vacuum at RT, allowing for complete removal of acetic anhydride or acetic acid.
1.3. Typical liquid-solid phase acetylation of the FD-CNCs

100 mg (0.617 mmol) of FD-CNCs were placed in the vial and 0.58 ml (0.63 g; 6.17 mmol) of acetic anhydride was added. If required, catalyst (1.85 mmol, 3 eq. to the amount of AGU) was then added. The vessel was sealed and left to stand at ambient temperature (unless stated otherwise) for stated amount of time. The vial contents then washed with EtOH (4-6 x 3.5 ml), centrifuged and freeze-dried for analysis.

1.4. Crystallinity index and periodic plane size determination

The crystallinity index (CI) was determined as described in the previous article supporting information (del Cerro et al. 2020). WAXS diffractograms were fitted with contributions representing background (glass support), amorphous component and main crystalline diffraction plane peaks. “Fityk” 1.3.1 peak-fitting software (Wojdyr 2010) was used to process the data through semi-automatic fitting; fitting of functions corresponding to the glass and amorphous backgrounds, as well as set of pseudoVoigt functions.

Fig. S3 Fitting of the WAXS diffractogram for the commercial FD-CNC (freeze-dried cellulose nanocrystals) sample in Fityk. Data & functions: raw data (green), fitted data (yellow), amorphous function (cyan), background (magenta), crystalline functions (red) and residual baseline error (green at the bottom of the figure).
**Fig. S4** Fitting of the WAXS diffractogram for the beech BH-S-P (bleached hardwood sulphite pulp) sample in Fityk. Data & functions: raw data (green), fitted data (yellow), amorphous function (cyan), background (magenta), crystalline functions (red) and residual baseline error (green at the bottom of the figure).

**Fig. S5** Fitting of the WAXS diffractogram for the Enocell P-H Kraft (bleached hardwood pre-hydrolysis kraft pulp) sample in Fityk. Data & functions: raw data (green), fitted data (yellow), amorphous function (cyan), background (magenta), crystalline functions (red) and residual baseline error (green at the bottom of the figure).
Fig. S6 Fitting of the WAXS diffractogram for the freeze-dried Enocell Kraft pulp (bleached hardwood pre-hydrolysis kraft pulp) sample in Fityk. Data & functions: raw data (green), fitted data (yellow), amorphous function (cyan), background (magenta), crystalline functions (red) and residual baseline error (green at the bottom of the figure).

Fig. S7 Fitting of the WAXS diffractogram for the commercial FD-CNC (freeze-dried cellulose nanocrystals) sample, acetylated in system “gas-solid” for 6 days at ambient temperature, in Fityk. Data & functions: raw data (green), fitted data (yellow), amorphous function (cyan), background (magenta), crystalline functions (red) and residual baseline error (green at the bottom of the figure).
Fig. S8 Fitting of the WAXS diffractogram for the commercial FD-CNC (freeze-dried cellulose nanocrystals) sample, acetylated in system “gas-solid” for 15 days at ambient temperature, in Fityk. Data & functions: raw data (green), fitted data (yellow), amorphous function (cyan), background (magenta), crystalline functions (red) and residual baseline error (green at the bottom of the figure).

Fig. S9 Fitting of the WAXS diffractogram for the commercial FD-CNC (freeze-dried cellulose nanocrystals) sample, acetylated in system “gas-solid” for 32 days at ambient temperature, in Fityk. Data & functions: raw data (green), fitted data (yellow), amorphous function (cyan), background (magenta), crystalline functions (red) and residual baseline error (green at the bottom of the figure).
**Fig. S10** Fitting of the WAXS diffractogram for the commercial FD-CNC (freeze-dried cellulose nanocrystals) sample, acetylated in system “gas-solid” for 6 days at 80 °C, in Fityk. Data & functions: raw data (green), fitted data (yellow), amorphous function (cyan), background (magenta), crystalline functions (red) and residual baseline error (green at the bottom of the figure).

**Fig. S11** Fitting of the WAXS diffractogram for the beech sulphite pulp (bleached hardwood sulphite pulp) sample, acetylated in system “gas-solid” for 6 days at ambient temperature, in Fityk. Data & functions: raw data (green), fitted data (yellow), amorphous function (cyan), background (magenta), crystalline functions (red) and residual baseline error (green at the bottom of the figure).
**Fig. S12** Fitting of the WAXS diffractogram for the Enocell P-H kraft pulp (bleached hardwood pre-hydrolysis kraft pulp) sample, acetylated in system “gas-solid” for 6 days at ambient temperature, in Fityk. Data & functions: raw data (green), fitted data (yellow), amorphous function (cyan), background (magenta), crystalline functions (red) and residual baseline error (green at the bottom of the figure).

**Fig. S13** Fitting of the WAXS diffractogram for the Enocell P-H kraft (bleached hardwood pre-hydrolysis kraft pulp) sample, acetylated in system “gas-solid” for 6 days at ambient temperature, in Fityk. Data & functions: raw data (green), fitted data (yellow), amorphous function (cyan), background (magenta), crystalline functions (red) and residual baseline error (green at the bottom of the figure).
Fig. S14 Fitting of the WAXS diffractogram for the commercial FD-CNC (freeze-dried cellulose nanocrystals) sample, acetylated in system “liquid-solid” for 6 days at ambient temperature, in Fityk. Data & functions: raw data (green), fitted data (yellow), amorphous function (cyan), background (magenta), crystalline functions (red) and residual baseline error (green at the bottom of the figure).

Fig. S15 Fitting of the WAXS diffractogram for the commercial FD-CNC (freeze-dried cellulose nanocrystals) sample, acetylated in system “liquid-solid” for 6 days at 80 °C, in Fityk. Data & functions: raw data (green), fitted data (yellow), amorphous function (cyan), background (magenta), crystalline functions (red) and residual baseline error (green at the bottom of the figure).
Fig. S16 Fitting of the WAXS diffractogram for the commercial FD-CNC (freeze-dried cellulose nanocrystals) sample, acetylated in system “liquid-solid” with DABCO for 6 days at ambient temperature, in Fityk. Data & functions: raw data (green), fitted data (yellow), amorphous function (cyan), background (magenta), crystalline functions (red) and residual baseline error (green at the bottom of the figure).

Fig. S17 Fitting of the WAXS diffractogram for the commercial FD-CNC (freeze-dried cellulose nanocrystals) sample, acetylated in system “liquid-solid” with DABCO for 6 days at 80 °C, in Fityk. Data & functions: raw data (green), fitted data (yellow), amorphous function (cyan), background (magenta), CTA functions (red), cellulose I\(_{\beta}\) 200 function (white) and residual baseline error (green at the bottom of the figure).
**Fig. S18** Fitting of the WAXS diffractogram for the commercial FD-CNC (freeze-dried cellulose nanocrystals) sample, acetylated in system “liquid-solid” with pyridine for 6 days at ambient temperature, in Fityk. Data & functions: raw data (green), fitted data (yellow), amorphous function (cyan), background (magenta), crystalline functions (red) and residual baseline error (green at the bottom of the figure).

**Fig. S19** Fitting of the WAXS diffractogram for the commercial FD-CNC (freeze-dried cellulose nanocrystals) sample, acetylated in system “liquid-solid” with pyridine for 6 days at 80 °C, in Fityk. Data & functions: raw data (green), fitted data (yellow), amorphous function (cyan), background (magenta), crystalline functions (red) and residual baseline error (green at the bottom of the figure).
Fig. S20 WAXS diffractogram for the commercial spray-dried CNCs (SD-CNC) sample.

Fig. S21 Fitting of the WAXS diffractogram for the commercial SD-CNC (spray-dried cellulose nanocrystals) sample, acetylated in system “gas-solid” for 6 days at ambient temperature, in Fityk. Data & functions: raw data (green), fitted data (yellow), amorphous function (cyan), background (magenta), crystalline functions (red) and residual baseline error (green at the bottom of the figure).
Fig. S22 WAXS diffractogram for the IONCELL fibre sample.

Fig. S23 WAXS diffractogram for the IONCELL fibre sample, acetylated in system “gas-solid” for 6 days at 80 °C.
Rough periodic plane sizes were calculated using the Scherrer equation [Eq.(1)]:

\[
L = \frac{K\lambda}{\beta \cos\theta}
\]  

(1)

which is commonly used for determining the dimension (L, nm) of cellulose crystallites, where \(\beta\) is the full width half maximum (FWHM) for particular periodic plane, \(K\) (the Scherrer constant) is 0.94 for spherical crystallites with cubic symmetry. \(\lambda\) is the X-ray wavelength (1.54178 Å in our case for Cu K\(\alpha\)) and \(\theta\) is \(2\theta/2\) (in radians). The FWHM values were determined from the Gaussian functions, in Fityk. The results are given in the main text. The crystallite sizes for the (200) plane for each sample were calculated (Table S1).

**Table S1.** Crystallite sizes calculated for the samples, using the FWHM values for the (200) planes.

| Sample                  | (200) FWHM (°) | (200) Crystallite size (nm) | Cl (%) |
|-------------------------|----------------|-----------------------------|--------|
| FD-CNC                  | 1.88           | 4.50                        | 57     |
| FD-CNC-GS-6D RT         | 1.88           | 4.50                        | 68     |
| FD-CNC-GS-15D RT        | 1.84           | 4.60                        | 73     |
| FD-CNC-GS-32D RT        | 1.84           | 4.60                        | 68     |
| FD-CNC-GS-6D 80 °C      | 1.87           | 4.53                        | 63     |
| FD-CNC-LS-6D RT         | 1.82           | 4.65                        | 77     |
| FD-CNC-LS-6D 80 °C      | 1.86           | 4.55                        | 65     |
| FD-CNC-LS-6D DABCO, RT  | 1.73           | 4.89                        | 72     |
| FD-CNC-LS-6D DABCO, 80 °C | -             | -                           | -      |
| FD-CNC-LS-6D Py, RT     | 1.87           | 4.53                        | 69     |
| FD-CNC-LS-6D Py, 80 °C  | 2.16           | 3.93                        | 42     |
2. Crystallite Models

For estimation of the bulk DS values for full surface coverage (6-OH acetylation only), there are 4 important elementary fibrillar cross-section models to consider, based on diffraction, molecular dynamics and NMR experiments (Figure S24) (Wang et al., 2015; Oehme et al., 2015; Paajanen et al., 2019; Fernandes et al., 2011). These are the 18-chain hexagonal (DS = 0.33), 24-chain rhomboid (DS = 0.33), 24-chain hexagonal (DS = 0.25) and 36-chain hexagonal (DS = 0.22). It is assumed that the woody microfibril consists of most probably 18 or 24 individual cellulose chains, with the softwood model the 24-chain rhomboid model (Fernandes et al., 2011). Based on these models and different chain assemblies (Figures S24 A-D) the maximum degree of substitution of the C6-OH is estimated to ranging from 0.22 to 0.33. An approximate maximum of 0.33 can is assumed.

Figure S24: Superstructure of the cellulose microfibril based on different chain models.

3. NMR supplementary data

3.1. NMR sample preparation
To prepare the samples for NMR analysis, typically 50 mg of dried sample is added to a sealable sample vial and made up to 1 g, by addition of stock [P4444][OAc]:DMSO-d6 (20:80 wt%) electrolyte solution (King et al. 2018; Koso et al. 2020). The samples were magnetically stirred at RT until they were visibly clear. This typically
takes less than 1 hr period and even a few minutes for some samples. If the samples did not go clear during that time, the temperature was increased to 65 °C. All further NMR experiments were recorded on a Bruker AVANCE NEO 600 MHz spectrometer equipped with a 5 mm SmartProbe™.

3.2. Diffusion-edited ¹H experiments
The diffusion-edited ¹H experiment used a 1D bipolar-pulse pair with stimulated echo (BPPSTE) (Wu et al. 1995) diffusion-ordered spectroscopy (DOSY) pulse sequence (Bruker pulse program ‘ledbpgp2s1d’), with 3 s relaxation delay (d1), 0.5 s acquisition time (aq), 16 dummy scans (ds) and 512 transient scans (ns), a sweep-width (sw) of 20 ppm with the transmitter offset on 6.1 ppm (o1p), a diffusion time (d20) of 200 ms, a gradient recovery delay (d16) of 0.2 ms, an eddy current delay (d21) of 5 ms, a diffusion gradient pulse duration (p30) of 2.5 ms and a z-gradient strength (gpz6) of 90% at 50 G/cm (probe z-gradient strength). These conditions are specific to the Bruker AVANCE NEO 600 MHz - SmartProbe™ system.

3.3. Multiplicity-Edited HSQC Experiments
The HSQC experiments on cellulose samples used either a multiplicity-edited phase sensitive HSQC sequence with echo/antiecho-TPPI gradient selection (Bruker pulse program ‘hsqcedetgp’) (Willker et al. 1993) or a sensitivity improved multiplicity-edited phase sensitive HSQC sequence with echo/antiecho-TPPI gradient selection and adiabatic pulses (Bruker pulse program ‘hsqcedetgpsisp2.2’), for increased sensitivity (Willker et al. 1993; Palmer III et al. 1991; Kay et al. 1992; Schleucher et al. 1994). Typical parameters are as follows: spectral widths (sw) were 13.03 and 165 ppm, with transmitter offsets (o1p) of 6.18 and 75 ppm, for ¹H and ¹³C dimensions, respectively. The time-domain size (td1) in the indirectly detected ¹³C-dimension (f1) was 512 or 1024, corresponding to 256 increments, or 512 t₁-increments for the real spectrum. There were 16 dummy scans (ds), typically 8 (or multiples of 8) scans (ns), an acquisition time (aq) of 0.065 s for f2 and a relaxation delay of 1.5 s. Window functions were typically sine squared (90°) in f1 and f2.

3.4. DS determination from ¹H NMR spectral data
As all the samples were completely solubilised in [P₄₄₄₄][OAc]:DMSO-d₆ electrolyte, it was possible to determine the bulk degree of acetylation on the cellulosic backbone directly from the ¹H NMR spectra by peak fitting and calculation according to the equation [Eq. (2)]

\[
DS = \frac{I_A/3}{I_C/7}
\]  

(2)

Here, \(I_A\) is the acetate signal peak area (~1.8 – 2.2 ppm) and \(I_C\) is the cellulose backbone combined signal peak area (~2.8 – 5.5 ppm). “3” and “7” are the total number of protons for abovementioned fragments of acetate and cellulose, respectively. As we do not use the diffusion-edited ¹H NMR for DS estimations, but rather quantitative ¹H NMR, correction coefficient (del Cerro et al. 2020) is not applicable.

All the spectra were recorded with a 10 s relaxation delay (30° pulse) and 16 or 32 transients were collected. The spectra were calibrated and phased in Bruker TopSpin (4.0.5). MNova (10.0.2) was used to convert the spectral data into .xy format, for Fityk processing. An aggressive spline baseline correction was performed before peak fitting the corresponding H1-H6 and acetate peak regions. Examples of spline baseline correction and peak fitting are shown in Figures S25-27.
Fig. S25 Example of the spline baseline correction for the FD-CNCs sample, acetylated in system “gas-solid” for 6 days at ambient temperature, in *Fityk*.

Fig. S26 Example of the Gaussian deconvolution of the AGU (cellulose) peaks for the FD-CNCs sample, acetylated in system “gas-solid” for 6 days at ambient temperature, in *Fityk*.
3.5. Regioselectivity determination from $^1$H NMR spectral data

6 vs 2 vs 3-OH acetylation regioselectivity could be determined through peak-fitting of the acetate region (~2 ppm) from the quantitative $^1$H spectra. Application of spline baseline correction (see above) and then application of Gaussian guesses and automatic fitting usually gives nice defined peak volumes corresponding to the different acetate signals. Some manual fitting of the parameters may be required, e.g. to prevent the automatic fitting of too large Gaussians which may encompass the whole acetate region.

The signals for the high DS cellulose acetate (DS 2.4) are very characteristic and the 3 main peaks of cellulose triacetate (CTA) clearly visible, with a little variation in peak positioning corresponding to AGUs with mono and diacetate (Figure S27a). The regioselectivity is defined as the percentage of 6-OAc (mono acetate) vs the sums of the 2-OAc, 3-OAc and 6-OAc (CTA). This can be calculated from the sums of the Gaussian peak volumes fitted for each region; the peaks for each region are assigned by having peak centers (ppm) laying within defined regions, as illustrated for the solid-liquid acetylated samples at 80 °C (Figure S27b-c).

![Fig. S27 Example of peak-fitting using Fityk, and the appropriate peak regions, for determination of 6-OH acetylation regioselectivity and DS determination.](image-url)
Table S2. Bulk degree of acetylation for gas-phase reactions on the different substrates.

| Starting material | Conditions                    | Catalyst | Degree of substitution (DS)\(^1\) | Product allomorph |
|------------------|-------------------------------|----------|-----------------------------------|------------------|
| FD-CNCs\(^2\)    | gas-solid, rt, 1 day         | –        | 0.007                             | –                |
| FD-CNCs          | gas-solid, rt, 2 days        | –        | 0.010                             | –                |
| FD-CNCs          | gas-solid, rt, 6 days        | –        | 0.029                             | Cellulose I 68   |
| FD-CNCs          | gas-solid, rt, 15 days       | –        | 0.116                             | Cellulose I 73   |
| FD-CNCs          | gas-solid, rt, 32 days       | –        | 0.290                             | Cellulose I 68   |
| FD-CNCs          | gas-solid, 80 °C, 1 day      | –        | 0.120                             | –                |
| FD-CNCs          | gas-solid, 80 °C, 2 days     | –        | 0.226                             | –                |
| FD-CNCs          | gas-solid, 80 °C, 6 days     | –        | 0.405                             | Cellulose I 63   |
| SD-CNCs\(^3\)    | gas-solid, rt, 6 days        | –        |                                   | Cellulose I 75   |
| BH-S-P\(^4\)     | gas-solid, rt, 6 days        | –        | 0.020                             | Cellulose I 59   |
| BH-PHK-P\(^5\)   | gas-solid, rt, 6 days        | –        | 0.007                             | Cellulose I 80   |
| ND-BH-PHK-P\(^6\)| gas-solid, rt, 6 days        | –        | 0.005                             | Cellulose I 60   |
| CNC-AG\(^7\)     | gas-solid, rt, 6 days        | –        | 0.136                             | Cellulose I –    |
| BC-AG\(^8\)      | gas-solid, rt, 6 days        | –        |                                   | Cellulose I –    |
| IONCELL-F\(^9\)  | gas-solid, 80 °C, 6 days     | –        | 0.141                             | Cellulose II –   |
Table S3. Bulk degree of acetylation for liquid-phase reactions of FD-CNCs without and with the presence of catalyst.

| Starting material | Conditions                     | Catalyst | DS (NMR) | Product allomorph Cl, % |
|-------------------|-------------------------------|----------|----------|------------------------|
| FD-CNCs           | liq-solid, rt, 1 day          | –        | 0.012    | –                      |
| FD-CNCs           | liq-solid, rt, 2 day          | –        | 0.019    | –                      |
| FD-CNCs           | liq-solid, rt, 6 day          | –        | 0.021    | Cellulose I 77          |
| FD-CNCs           | liq-solid, 80 °C, 1 day       | –        | 0.076    | –                      |
| FD-CNCs           | liq-solid, 80 °C, 2 days      | –        | 0.154    | –                      |
| FD-CNCs           | liq-solid, 80 °C, 6 days      | –        | 0.426    | Cellulose I 65          |
| FD-CNCs           | liq-solid, rt, 1 day          | DABCO    | 0.013    | –                      |
| FD-CNCs           | liq-solid, rt, 2 day          | DABCO    | 0.021    | –                      |
| FD-CNCs           | liq-solid, rt, 6 day          | DABCO    | 0.042    | Cellulose I 72          |
| FD-CNCs           | liq-solid, 80 °C, 1 day       | DABCO    | 0.470    | –                      |
| FD-CNCs           | liq-solid, 80 °C, 2 days      | DABCO    | –        | –                      |
| FD-CNCs           | liq-solid, 80 °C, 6 days      | DABCO    | –        | Cellulose I 5 + CTA     |
| FD-CNCs           | liq-solid, rt, 1 day          | Pyridine | 0.037    | –                      |
| FD-CNCs           | liq-solid, rt, 2 day          | Pyridine | 0.043    | –                      |
| FD-CNCs           | liq-solid, rt, 6 day          | Pyridine | 0.063    | Cellulose I 69          |
| FD-CNCs           | liq-solid, 80 °C, 1 day       | Pyridine | 0.314    | –                      |
| FD-CNCs           | liq-solid, 80 °C, 2 days      | Pyridine | 0.594    | –                      |
| FD-CNCs           | liq-solid, 80 °C, 6 days      | Pyridine | 2.025    | Cellulose I 42          |
3.6. The NMR data

Fig. S28 Expanded diffusion-edited $^1$H NMR spectra for FD-CNC samples, acetylated in system “gas-solid” at ambient temperature for 1, 2, 6, 15 and 32 days.
**Fig. S29** Expanded diffusion-edited $^1$H NMR spectra for FD-CNC samples, acetylated in system “gas-solid” at 80 °C for 1, 2 and 6 days.

**Fig. S30** Expanded diffusion-edited $^1$H NMR spectra for FD-CNC samples, acetylated in system “liquid-solid” at ambient temperature for 1, 2 and 6 days.
**Fig. S31** Expanded diffusion-edited $^1$H NMR spectra for FD-CNC samples, acetylated in system "liquid-solid" at 80 °C for 1, 2 and 6 days.

**Fig. S32** Expanded diffusion-edited $^1$H NMR spectra for FD-CNC samples, acetylated in system "liquid-solid" in the presence of DABCO at ambient temperature for 1, 2 and 6 days.
Fig. S33 Expanded diffusion-edited $^1$H NMR spectra for FD-CNC samples, acetylated in system “liquid-solid” in the presence of DABCO at 80 °C for 1 day.

Fig. S34 Expanded diffusion-edited $^1$H NMR spectra for FD-CNC samples, acetylated in system “liquid-solid” in the presence of pyridine at ambient temperature for 1, 2 and 6 days.
Fig. S35 Expanded diffusion-edited $^1$H NMR spectra for FD-CNC samples, acetylated in system “liquid-solid” in the presence of pyridine at 80 °C for 1, 2 and 6 days.
**Fig. S36** Expanded diffusion-edited \(^1\text{H}\) NMR spectra for beech BH-S-P (bleached hardwood sulphite pulp), acetylated in system “gas-solid” at ambient temperature for 6 days.

![NMR spectra for beech BH-S-P](image)

**Fig. S37** Expanded diffusion-edited \(^1\text{H}\) NMR spectra for Enocell BH-PHK-P (bleached hardwood pre-hydrolysis kraft pulp), acetylated in system “gas-solid” at ambient temperature for 6 days.

![NMR spectra for Enocell BH-PHK-P](image)
**Fig. S38** Expanded diffusion-edited $^1$H NMR spectra for never-dried Enocell ND-BH-PHK-P (bleached hardwood pre-hydrolysis kraft pulp), acetylated in system “gas-solid” at ambient temperature for 6 days.

![6 days](image1)

**Fig. S39** Expanded diffusion-edited $^1$H NMR spectra for cellulose nanocrystal aerogel, acetylated in system “gas-solid” at ambient temperature for 6 days.

![6 days](image2)

**Fig. S40** Expanded diffusion-edited $^1$H NMR spectra for Ioncell-F, acetylated in system “gas-solid” at 80 °C for 6 days.

![6 days](image3)
HSQC spectrum of the gem-6 AGU region for 32 d acetylated FD CNCs, showing approximate 1:1 ratio of gem-6-OH and gem-6-OAc peaks.
4. AFM

Fig. S42 AFM images of unsubstituted commercial FD-CNCs.
Fig. S43 Further AFM images of commercial FD-CNCs, acetylated in the system “gas-solid” for 32 days at ambient temperature, with determined sizes.
5. ATR-IR

**Figure S44** ATR-IR spectrum of commercial SD-CNC (spray-dried cellulose nanocrystals) sample, acetylated in system “gas-solid” for 6 days at ambient temperature.
6. XPS

Spectra were recorded on a Kratos Axis Supra X-ray Photoelectron Spectrometer employing a monochromated Al Kα (hv = 1486.7 eV, 8 mA) X-ray source, hybrid (magnetic/electrostatic) optics with a slot aperture, hemispherical analyser, multichannel plate and delay line detector (DLD) with a take-off angle of 90°. The analyser was operated in fixed analyser transmission (FAT) mode with survey scans taken with a pass energy of 160 eV and high-resolution scans with a pass energy of 20 eV. The resulting spectra were processed using CasaXPS software. Binding energy was referenced to aliphatic carbon at 285.0 eV. High resolution spectra were fitted using the “LA(α,m)” lineshape for symmetric peaks corresponding to a numerical convolution of Lorentzian functions (with exponent α) with a Gaussian (width m). Details of this line shape function is available in the CasaXPS documentation online.

Empirical relative sensitivity factors supplied by Kratos Analytical (Manchester, UK) were used for quantification. Use of these relative sensitivity factors does not account for any attenuation due to overlayers or other surface contamination and assumes a uniform depth distribution of elements within the information depth of the sample. Matrix effects are also discounted. Quoted standard deviations result from averages of three measurements per sample.

Figure S45 XPS wide scan spectra of FD-CNCs and SD-CNCs.
Figure S46 Peak fitting XPS of commercial FD-CNCs.

Figure S47 Peak fitting XPS of SD-CNCs.
7. Computational Experimental

The transition states (TS) for acetylation of 2,3 and 6-OH acetylation were located through relaxed potential energy surface (rPES) scans for low energy acetate orientations (corresponding dihedral angles between AGU and acetate) in positions 6, 3 and 2 on a cellulose I\textsubscript{\beta} surface fragment. This was followed by rPES bond-length scans for the low energy acetate conformers, for the acetylation-deacetylation reaction coordinates. Transition states searches (OptTS) with final analytical frequency calculations (Freq) were then performed from the rough rPES transition states. The Gibbs energies of the transition states only were compared, against the lowest transition state energy. Full reaction profiling was not performed as there is a significant contribution from basis set superposition error (BSSE) using the current basis set (def2-SVP). Rather, the BSSE for the transition states was assumed to be approximately the same, allowing for direct comparison of the transition state energies. This is not possible with starting, intermediate and ending reaction geometries which have fully separated species, in some cases, leading to much less basis-set overlap.

The ORCA 4 package (Neese 2018) was used with the B86 GGA functional (Becke 1988; Perdew 1986), def2-SVP basis set, Grimme’s D3 dispersion correction (Grimme 2010) with Becke-Johnson dampening (Grimme 2011) and the resolution-of-identity (RI) approximation (Eichkorn et al. 1995; Eichkorn et al. 1997).

The initial cellulose Ib fibril (hexagonal 36 chain) with a polymer length of 4 glucose units was generated using the ‘Cellulose-Builder’ (Gomes et al. 2012) web interface (http://cces-sw.iqm.unicamp.br/cces/admin/cellulose/view). This was then edited in Avogadro 1.2 (Hanwell et al. 2012) to remove all polymer chains except for a (110) surface section of 3 stacked polymer chains with a length of 4 AGUs each (Figure S48).

Figure S48. Initial cellulose Ib surface fragment used for the calculations.

Hydroxyl groups were added to the reducing ends, as these are missing in the Cellulose-Builder outputs. For the rPES scans, an acetate was added to the relevant OH (2, 3 or 6) of a central AGU. A rPES scans for dihedral angles corresponding to acetate group rotation were completed at the RI-BP86/def2-SVP-D3(BJ) level throughout the full 360°; except in the case of 3-OAc where the calculations failed at certain dihedral ranges, due to steric interactions giving highly distorted geometries (Figure 3, main text); constraints were used on all atoms except the 6-OAc, all oxygens, all 1,2,3,4-hydrogens attached to OHs and the 6-CH\textsubscript{2} positions attached to 6-OH and 6-OAc (Figure S49).
This prevented movement of the AGUs away from the geometry found in the typical cellulose I\(\beta\) crystalline structure but allowed for enough freedom for formation and breakage of H-bonds, necessary for the stabilization of the conformers. The dihedral rPES scans and final TS geometries are shown in Figure 3 (main text). The final TS geometries (and expanded images) are given below:

**6-OAc Transition State**

Coordinates from ORCA-job orca

| C   | 7.90039044001538 | -10.66124842721790 | 11.07556328989531 |
H  9.53873997677899  -10.52504000030139  21.56899000503710
C  8.20077998251938  -11.82003001442338  20.46482997151800
H  7.13354996738559  -12.07778998663908  20.4734499767095
C  8.60495004988675  -11.40791003364017  19.05466993982260
H  9.69103002389142  -11.26863002944452  18.98624007462662
C  7.86335000032003  -10.11610996404179  18.6797999536280
H  6.78663001739414  -10.32400002947797  18.63136997818432
C  8.13014999195363  -9.03503995491921  19.73850999953626
H  9.18043000909983  -8.73337005425397  19.69224999262288
C  7.23909000036556  -7.8088299921960  19.49319001184784
H  6.2249500208369  -8.1316299881809  19.23497000057534
H  7.16302999917037  -7.2195899861084  20.41329000104045
O  9.01260997614376  -12.91971999803672  20.83562999284228
O  8.2078037426305  -12.48098996035162  18.21102963851546
O  8.29851998259715  -9.58359995155728  17.44526993593621
O  7.80041999561665  -9.48611000783672  21.03708000420225
O  7.71627995740204  -6.99788995296340  18.42143000919124
H  8.78562000569233  -13.20970999224260  21.74784000076451
H  8.41467957383932  -12.24200005086210  17.28413048693296
H  8.56192998051233  -6.58096997644965  18.68055003868315
C  11.28071991760698  -6.32069998315102  18.57163999580129
H  12.33450002629571  -6.04202000301353  18.69685996934184
C  11.19260010253408  -7.50669014427604  17.60410991755325
H  10.1850796844965  -7.92877002466351  17.61190004582075
C  11.57188996315714  -7.08620991648934  16.18976996406782
H  12.65947993361299  -6.98118979224412  16.11484003524121
C  10.86413000835283  -5.78111006807822  15.7969700318059
H  9.79490992193274  -5.98382995097812  15.66605999398747
C  11.02639844726038  -4.69825429599384  16.87548942585076
H  12.10022679146881  -4.41374248199549  16.9920654307445
C  10.20489999646851  -3.45874999936606  16.5766899824293
| Atom | X-Coord | Y-Coord | Z-Coord |
|------|---------|---------|---------|
| C    | 11.243  | -4.524  | 22.789  |
| H    | 12.263  | -4.139  | 22.704  |
| C    | 11.397  | -6.235  | 20.961  |
| H    | 12.459  | -6.046  | 20.717  |
| C    | 11.362  | -7.318  | 22.051  |
| H    | 10.325  | -7.617  | 22.244  |
| C    | 12.190  | -8.567  | 21.699  |
| H    | 10.752  | -6.751  | 19.796  |
| O    | 10.414  | -3.524  | 23.374  |
| O    | 10.991  | -3.831  | 20.546  |
| H    | 10.950  | -2.759  | 22.767  |
| C    | 8.071   | -10.005 | 26.610  |
| C    | 8.286   | -8.845  | 25.639  |
| H    | 9.357   | -8.617  | 25.555  |
| C    | 7.756   | -9.250  | 24.274  |
| H    | 6.669   | -9.387  | 24.312  |
| C    | 8.453   | -10.551 | 23.832  |
| H    | 9.522   | -10.344 | 23.677  |
| C    | 8.294   | -11.636 | 24.911  |
| H    | 7.243   | -11.952 | 24.968  |
| C    | 9.142   | -12.916 | 24.581  |
| H    | 10.149  | -12.619 | 24.274  |
| H    | 9.233   | -13.503 | 25.504  |
|   |   |   |   |
|---|---|---|---|
| H | 9.57407999772235 | -9.79384000029849 | 27.85544000014093 |
| H | 15.7783299966683 | -0.87643999850444 | 27.50703000129943 |
| H | 10.1626999940069 | -6.0304999943917 | 23.94661000800429 |
| O | 11.8612199978555 | -5.39605999854121 | 24.9486099930295 |
| H | 11.40628999797057 | -4.62450000174380 | 25.34156999849899 |
| H | 7.42001004327828 | -8.82184008703825 | 6.80452013021436 |
| H | 10.85076930797601 | -5.87426390425053 | 3.53540664327763 |
| H | 13.2374609266498 | -1.57472211776881 | 6.07130667473890 |
| H | 13.6554778915125 | 1.06663194943027 | 7.03696955949250 |
| H | 13.87248478467456 | 1.30417073974413 | 17.30761072354009 |
| H | 13.78832656345432 | 1.51111536150297 | 25.02743656926699 |
| H | 13.32346506104373 | 1.57004194253939 | 14.78202912512313 |
| C | 12.95249507851196 | -10.65925913300467 | 14.32273468426927 |
| O | 14.08845891709015 | -9.43398191753144 | 12.50668881007315 |
| H | 12.72137940385980 | -9.81409026287713 | 15.00331560864595 |
| H | 13.8525328967729 | -11.20308616674428 | 14.66927234493131 |
| H | 12.07944082077780 | -11.3352072655847 | 14.31967055765638 |
| H | 11.67403828463259 | -14.26999497585592 | 11.77435251828867 |
| O | 10.75321761309695 | -11.62661809993189 | 12.15432552600566 |
| H | 11.05268038364970 | -10.34033271115861 | 12.40480198522904 |
| C | 11.75087319073501 | -13.47018193398041 | 11.00842487200555 |
| C | 11.83627452429667 | -12.14190820223752 | 11.71624911410498 |
| O | 12.98779998814378 | -11.59542840803211 | 11.85221140093042 |
| H | 12.64913872044643 | -13.65537018897817 | 10.39267432131320 |
| H | 10.81697528077324 | -13.49191956862691 | 10.41328796914033 |
### 2-OAc Transition State

| Atom | X-Coordinate | Y-Coordinate | Z-Coordinate |
|------|--------------|--------------|--------------|
| C    | 19.23        | 3.72         | 3.17         |
| H    | 20.31        | 3.78         | 3.37         |
| C    | 18.93        | 2.58         | 2.18         |
| H    | 17.85        | 2.39         | 2.16         |
| C    | 19.35        | 2.94         | 0.76         |
| H    | 20.41        | 2.96         | 0.64         |
| C    | 18.82        | 4.31         | 0.36         |
| H    | 17.74        | 4.21         | 0.22         |
| C    | 19.13        | 5.36         | 1.44         |
| H    | 20.20        | 5.58         | 1.44         |
| C    | 18.35        | 6.66         | 1.16         |
| H    | 17.33        | 6.41         | 0.84         |
| O    | 19.64        | 1.41         | 2.08         |
| O    | 18.80        | 1.98         | -0.14        |
| O    | 19.47        | 4.69         | -0.85        |
| O    | 18.70        | 4.94         | 2.73         |

Coordinates from ORCA-job orca
C   18.72707999694824    4.43236999751861    8.35973000031514
H   17.64540999980255    4.36083000195087    8.53470000137554
C   19.02503000740728    5.56449999635816    7.37387999506191
H   20.10250999707601    5.73760999735576    7.32359000198034
C   18.52409000435665    5.19349002531805    5.98447999394776
H   17.42866000332275    5.13586999460389    5.97016000160700
C   19.14031994284214    3.84880010390598    5.56906999605307
H   20.22678000144774    3.97462996850737    5.45950001027509
C   18.84933999320663    2.78410000833628    6.64008999019006
H   17.77499000546702    2.5523899939172    6.64634000127766
C   19.60649999658118    1.43949999596668    6.34167999830383
H   20.65787000150615    1.6553100020965    6.13630000381765
H   19.56469000370823    0.81881000223237    7.24640000225898
O   18.33934000114392    6.73253000084783    7.79544999896849
O   18.96650000198886    6.2309799957003    5.1154099828668
O   18.57596010196386    3.36819978181448    4.3615499415563
O   19.27623000091118    3.19836999645962    7.92136000266177
O   19.0823899979153    0.75078000286888    5.21244000062556
H   18.6142999757627    6.96159000182124    8.712899988726
H   18.6780199969126    6.01368000248915    4.2043399796131
H   18.1591899802505    0.48762000098382    5.3850699918689
C   25.58818000231038    12.58769000065524    8.36217000251989
H   24.50991000151104    12.5216299985992    8.54426000157725
C   25.89373000227245    13.7019900015561    7.36127000114707
H   26.9779000088958    13.86237000154719    7.3179099857166
C   25.37533000116727    13.32638000180804    5.98205000039395
H   24.27991000195995    13.26883000130182    5.9736500007550
C   26.00359000094805    11.99295000049817    5.565899999059
H   27.08825000146300    12.12484999748554    5.4634599813067
C   25.71243999803584    10.93284000225080    6.6414899875826
H   24.64188999862366    10.70944000244450    6.6481399914224
C  26.45407999678581      9.58024999728507      6.33103000225404
H  27.49154000060270      9.78959999793947      6.05461999826757
H  26.47020000001119      8.98360000169475      7.25158000116216
O  25.24459999793444      14.87008000026835      7.84695000181365
O  25.77692998827242      14.40288000014607      5.14120000014941
O  25.46753000118271      11.49851000010557      4.35828999737571
O  26.14330000177752      11.35855000076064      7.92054999838996
O  25.85472998610259      8.86964003194416      5.25518000120277
H  25.57142000239413     14.17742000233958      4.20780000194680
H  25.03370002147988      8.43017996728127      5.55296999848412
C  19.25738999758513      3.71559000197169     13.54451000111131
H  20.33536999904882      3.78280000039601      6.73081000158451
C  18.96504000062412      4.29336999866608     12.5603999870863
H  17.76004000062412      4.1695399976053      10.65474000103906
C  19.13531999748787      5.36256000183708      11.82841000027351
H  20.05800000170484      5.58671000015128     11.83615000002963
C  18.34930000148927      6.64921000167701     11.53609000178887
H  17.32957000088092      6.39987999973014     11.22616999832162
H  18.26985000119621      7.24687000100108      12.45040000117517
O  19.67430000133778      1.42928000065597      12.97380998813049
H  19.03980999901474      1.91275999994611     10.31068999913673
H  19.380950000251916      4.7921099879705      9.54753000241619
O  18.707190000262538      4.94298999981083      13.10871000053278
O  18.93953000195953      7.41805000180710      10.4895399992650
H  19.3801199869281       1.16101000068799      13.87340000194244
H  19.3109199780897       2.13156000111162      9.39544999736345
H  19.79890000004483      7.77352000040327      10.79156000034788
C  22.53143001534444      7.834560999850154     10.82295000970384
| Atom | X-coordinate | Y-coordinate | Z-coordinate |
|------|--------------|--------------|--------------|
| H    | 23.5949      | 8.0363       | 11.0021      |
| C    | 22.4068      | 6.6534       | 9.8534       |
| H    | 21.3722      | 6.3059       | 9.8096       |
| C    | 22.8881      | 7.0384       | 8.4601       |
| H    | 23.9829      | 7.0635       | 8.4414       |
| C    | 22.9863      | 8.3962       | 8.0298       |
| H    | 21.2256      | 8.2647       | 7.8441       |
| C    | 24.7559      | 9.4450       | 9.1293       |
| H    | 23.5419      | 9.6543       | 9.2801       |
| C    | 21.7714      | 10.7575      | 8.7720       |
| H    | 20.7322      | 10.5592      | 8.4893       |
| H    | 21.7555      | 11.4085      | 9.6515       |
| O    | 23.1139      | 5.5484       | 10.4328      |
| O    | 22.4459      | 6.0127       | 7.5591       |
| O    | 22.9217      | 8.8804       | 6.8570       |
| O    | 21.8807      | 9.0000       | 10.3387      |
| O    | 22.4600      | 11.4396      | 7.7163       |
| H    | 22.7852      | 6.2607       | 6.6663       |
| H    | 22.1438      | 12.3640      | 7.6909       |
| C    | 26.1206      | 11.8615      | 13.5448      |
| H    | 27.2022      | 11.9331      | 13.7213      |
| C    | 25.8228      | 10.7308      | 12.5596      |
| H    | 24.7452      | 10.5577      | 12.5112      |
| C    | 26.3239      | 11.1034      | 11.1715      |
| H    | 27.4191      | 11.1632      | 11.1593      |
| C    | 25.7031      | 12.4785      | 10.7598      |
| H    | 24.6172      | 12.3205      | 10.6520      |
| C    | 25.9971      | 13.5107      | 11.8328      |
| H    | 27.0720      | 13.7406      | 11.8383      |
| C    | 25.2117      | 14.7946      | 11.5313      |
| H    | 24.1911      | 14.5540      | 11.2100      |
| Element | X-Coordinate | Y-Coordinate | Z-Coordinate |
|---------|--------------|--------------|--------------|
| C       | 18.51430000229648 | 5.19685000049180 | 16.3389999886826 |
| H       | 17.41944000197142  | 5.13961999871724  | 16.3217199759615 |
| C       | 19.13619000176511  | 3.8467999995291   | 15.93549000008599 |
| H       | 20.2236799996443   | 3.97440999792679  | 15.83557999904928 |
| C       | 18.84339999876769  | 2.78068999823363  | 17.00614000258270 |
| H       | 17.77027000220299   | 2.54287999924667  | 17.00843000107501 |
| C       | 19.6115799815429    | 1.44123000212192  | 16.72077000090681 |
| H       | 20.65160000143518   | 1.66207000243070  | 16.46630000053552 |
| H       | 19.61201999841990   | 0.85412999853639  | 17.64823000081861 |
| O       | 18.34277000131977   | 6.75532000158708  | 18.1493299779806 |
| O       | 18.96212000078157   | 6.22998000011571  | 15.46888000080201 |
| O       | 18.59356999903284   | 3.3585999825483   | 14.7286899918992 |
| O       | 19.25943000241982   | 3.21812000266687  | 18.28401000006450 |
| O       | 19.0552099769413    | 0.71098999790616  | 15.63415000177536 |
| H       | 18.53363000136143   | 6.88083999929573  | 19.10059000195006 |
| H       | 18.6922999836101    | 6.0040999964146   | 14.55373000156957 |
| H       | 18.14190000053659   | 0.44334999922005  | 15.84717000122091 |
| C       | 25.5085899868857    | 12.58265000054037 | 18.7009999975039 |
| C       | 25.86082000072240   | 13.7100499874743  | 17.7295599739442 |
| H       | 26.94982000080736   | 13.84960999914413 | 17.70298999918230 |
| C       | 25.36857000042682   | 13.33357000134361 | 16.34137999982458 |
| H       | 24.2734599857566    | 13.27450999894247 | 16.325280000022124 |
| C       | 26.00181000196853   | 11.99580000143312 | 15.93517000134394 |
| H       | 27.08733000044955   | 12.12649000225240 | 15.83735999770524 |
| C       | 25.70805000145083   | 10.936380000181662| 17.00640999957996 |
| H       | 24.63535999968209   | 10.71759000227352 | 17.00907999987015 |
| C       | 26.42991999931780   | 9.57505000086416  | 16.69945000145157 |
| H       | 27.44933000014816   | 9.76745000178430  | 16.35453000046922 |
| H       | 26.49432999905926   | 9.01855000258082  | 17.64276999800790 |
| O       | 25.22639999748568   | 14.90145000088868 | 18.1704499994215 |
| O       | 25.77983000050419   | 14.40858000069101 | 15.50287000011446 |
3-OAc Transition State

Coordinates from ORCA-job orca

\[
\begin{align*}
\text{C} & : 19.233430, 3.715518, 3.166919 \\
\text{H} & : 20.306100, 3.778842, 3.366231 \\
\text{C} & : 18.929280, 2.581030, 2.180440 \\
\text{H} & : 17.852290, 2.390400, 2.163560 \\
\text{C} & : 19.351890, 2.942800, 0.762940 \\
\text{H} & : 20.409240, 2.964650, 0.639660 \\
\text{C} & : 18.815750, 4.309810, 0.362780
\end{align*}
\]
| Atom | X-Cartesian Coordinate | Y-Cartesian Coordinate | Z-Cartesian Coordinate |
|------|------------------------|------------------------|------------------------|
| O    | 22.484640              | 11.486930              | -2.618750              |
| H    | 22.932421              | 5.341312               | 0.752083               |
| H    | 22.695736              | 5.243014               | -2.565779              |
| H    | 22.716940              | 10.857070              | -3.332130              |
| C    | 26.119950              | 11.865130              | 3.168930               |
| H    | 27.201660              | 11.934190              | 3.344840               |
| C    | 25.822140              | 10.734840              | 2.181630               |
| H    | 24.745030              | 10.558820              | 2.131960               |
| C    | 26.326640              | 11.108740              | 0.791570               |
| H    | 27.422200              | 11.160700              | 0.780850               |
| C    | 25.717900              | 12.455030              | 0.375450               |
| H    | 24.635570              | 12.325990              | 0.238790               |
| C    | 26.001060              | 13.518130              | 1.449920               |
| H    | 25.209070              | 14.797840              | 1.150200               |
| H    | 24.188160              | 14.549630              | 0.837470               |
| H    | 25.116270              | 15.397630              | 2.061260               |
| O    | 26.495670              | 9.545300               | 2.569270               |
| O    | 25.904350              | 10.131790              | -0.161260              |
| O    | 26.292770              | 12.953340              | -0.827800              |
| O    | 25.579820              | 13.095540              | 2.738000               |
| O    | 25.865370              | 15.589120              | 0.165860               |
| H    | 26.239770              | 9.301830               | 3.489500               |
| H    | 26.268280              | 9.271850               | 0.125910               |
| C    | 22.306880              | 8.499910               | 5.658490               |
| H    | 21.245520              | 8.282720               | 5.828691               |
| C    | 22.437020              | 9.662200               | 4.669950               |
| H    | 23.475260              | 9.997970               | 4.622460               |
| C    | 21.958010              | 9.274320               | 3.271080               |
| H    | 20.863530              | 9.240170               | 3.251260               |
| C    | 22.549110              | 7.926250               | 2.846190               |
H     23.622810  8.039920  2.658230
C     22.353370  6.917920  3.995820
H     21.287510  6.698190  4.130950
C     23.101134  5.606065  3.645474
O     21.605660 10.717060  5.128580
O     22.407330 10.305890  2.395910
O     21.926670  7.439260  1.655580
O     22.968841  7.349650  5.179280
H     21.941510 10.997530  6.007440
H     22.019190 10.160170  1.508520
C     18.727080  4.432370  8.359730
H     17.645410  4.360830  8.534700
C     19.025030  5.564500  7.373880
H     20.102510  5.737610  7.323590
C     18.524090  5.193490  5.984480
H     17.428660  5.135870  5.970160
C     19.140320  3.848803  5.569071
H     20.226781  3.974629  5.459500
C     18.849340  2.784100  6.640090
H     17.774990  2.552390  6.646340
C     19.606500  1.439500  6.341680
H     20.657870  1.655310  6.136300
H     19.564690  0.818810  7.246400
O     18.339340  6.732530  7.795450
O     18.966500  6.230980  5.115410
O     18.575960  3.368200  4.361550
O     19.276230  3.198370  7.921360
O     19.082390  0.750780  5.212440
H     18.614300  6.961590  8.712900
H     18.678020  6.013680  4.204340
H     18.159190  0.487620  5.385070
C      25.588180     12.587689      8.362170
H      24.509910     12.521631      8.544260
C      25.893730     13.701990      7.361270
H      26.977900     13.862370      7.317910
C      25.375330     13.326380      5.982050
H      24.279910     13.268830      5.973650
C      26.003590     11.992950      5.566590
H      27.088250     12.124850      5.463460
C      25.712440     10.932840      6.641490
H      24.641890     10.709440      6.648140
C      26.454080      9.580250      6.331029
H      27.491540      9.789600      6.054620
H      26.470200      8.983600      7.251580
O      25.244600     14.870080      7.846950
O      25.776930     14.402880      5.141200
O      25.467530     11.498510      4.358290
O      26.143300     11.358550      7.920550
O      25.854732      8.869640      5.255186
H      25.571420     14.177420      4.207800
H      25.033697      8.430180      5.552964
C      19.257390      3.715590     13.544510
H      20.335370      3.782800     13.730810
C      18.965040      2.583370     12.560400
C      19.470220      2.958130     11.172560
H      20.565650      3.017610     11.160180
C      18.845150      4.298690     10.758500
H      17.760050      4.169540     10.654740
C      19.135320      5.362560     11.828420
H      20.205800      5.586710     11.836150
C      18.349930      6.649210     11.536090
H      17.329570      6.399880     11.226170
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| H       | 24.745200 | 10.557750 | 12.511200 |
| C       | 26.323990 | 11.103420 | 11.171530 |
| H       | 27.419130 | 11.163260 | 11.159370 |
| C       | 25.703150 | 12.447860 | 10.759820 |
| H       | 24.617270 | 12.320510 | 10.652010 |
| C       | 25.997120 | 13.510760 | 11.832900 |
| H       | 27.072060 | 13.740620 | 11.838370 |
| C       | 25.211740 | 14.794650 | 11.531350 |
| H       | 24.191160 | 15.554080 | 11.210030 |
| H       | 25.114860 | 15.390660 | 12.444260 |
| O       | 26.497620 | 9.558410  | 12.989330 |
| O       | 25.881280 | 10.063400 | 10.303350 |
| O       | 26.243110 | 12.947380 | 9.550020  |
| O       | 25.572170 | 13.090170 | 13.116090 |
| O       | 25.869340 | 15.624360 | 10.584650 |
| H       | 26.183640 | 9.316500  | 13.891510 |
| H       | 26.178210 | 10.273820 | 9.393980  |
| C       | 22.223840 | 8.459100  | 15.975860 |
| C       | 22.408060 | 9.648940  | 15.030870 |
| H       | 23.456690 | 9.958280  | 14.999130 |
| C       | 21.946700 | 9.265950  | 13.631610 |
| H       | 20.852940 | 9.239650  | 13.606410 |
| C       | 22.539980 | 7.910980  | 13.204230 |
| H       | 23.615520 | 8.032860  | 13.026230 |
| C       | 22.360870 | 6.850090  | 14.302770 |
| H       | 21.296510 | 6.628700  | 14.442700 |
| C       | 23.092688 | 5.535839  | 13.997929 |
| H       | 24.137682 | 5.754153  | 13.679722 |
| H       | 23.135212 | 4.965562  | 14.951727 |
| O       | 21.641114 | 10.721016 | 15.578327 |
| O       | 22.378390 | 10.314060 | 12.763560 |
C  26.001810  11.995800  15.935170
H  27.087330  12.126490  15.837360
C  25.708050  10.936380  17.006410
H  24.635360  10.717590  17.009080
C  26.429920   9.575050  16.699450
H  27.449330   9.767450  16.354530
H  26.494330   9.018550  17.642770
O  25.226400  14.901450  18.170450
O  25.779830  14.408580  15.502870
O  25.467450  11.495190  14.728860
O  26.131420  11.375480  18.277540
O  25.764650   8.829230  15.686660
H  25.586430  14.182220  14.568210
H  24.937010   8.446040  16.043010
H  24.422920  12.476150  18.832290
O  25.982660  12.846630  20.005370
H  17.567310   4.325620  18.826830
O  19.144630   4.739330  19.985590
H  20.100550   4.539880  20.009910
H  26.948770  12.979930  19.972920
H  21.162560   8.231400  16.132680
O  22.849060   8.745290  17.220400
H  22.432040   9.549830  17.588520
H  19.108930   5.564360 -1.125210
H  22.980580   8.237230  -4.216660
H  26.145790  12.298890  -1.537680
H  26.061170  15.008940  -0.598630
H  25.761690  15.259160   9.680350
H  25.294110  15.547100  17.438510
H  25.323450  15.564000   7.162200
O  22.613644   4.874209  2.525769
| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| H    | 23.111131 | 4.974890 | 4.551202 |
| H    | 24.155711 | 5.861773 | 3.418652 |
| H    | 21.755638 | 4.471505 | 2.758554 |
| H    | 17.859641 | 2.437548 | 12.514046 |
| H    | 22.850389 | 5.317054 | 11.263951 |
| C    | 22.732016 | 4.207671 | 7.952921 |
| O    | 22.137254 | 3.860711 | 8.910966 |
| C    | 22.810803 | 3.623671 | 6.590817 |
| H    | 22.961682 | 2.533212 | 6.704688 |
| H    | 23.627890 | 4.045131 | 5.988641 |
| H    | 21.847833 | 3.799690 | 6.078483 |
| O    | 24.900141 | 5.849891 | 6.703924 |
| H    | 27.385709 | 5.306534 | 6.881983 |
| H    | 23.629773 | 5.947853 | 6.909769 |
| H    | 27.106927 | 5.731697 | 8.603834 |
| C    | 26.856679 | 5.003490 | 7.803904 |
| C    | 25.361975 | 5.037149 | 7.588420 |
| H    | 27.181790 | 4.003397 | 8.143503 |
| O    | 24.635012 | 4.286886 | 8.311933 |

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