

SUPPLEMENTARY INFORMATION

Thin multifunctional coatings for textiles based on the layer-by-layer application of polyaromatic hybrid nanoparticles

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1. Analysis of the starting materials

1.1 The ^1H , ^{13}C and HSQC NMR spectra of the starting materials

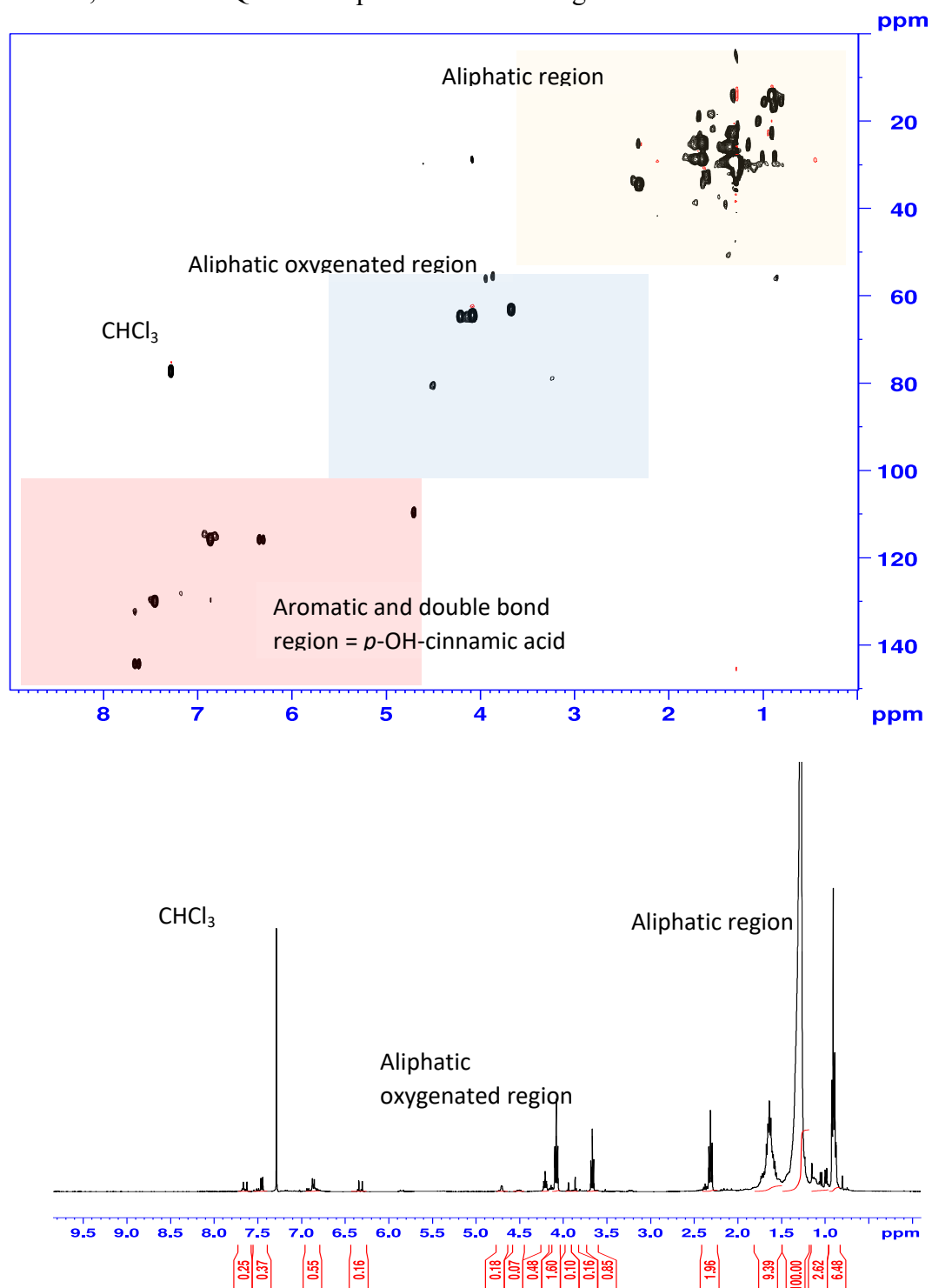


Figure S1. HSQC NMR and ^1H NMR spectra of the Carnuba wax showing that the mixture contains both aliphatic and aromatic functionalities. The aromatic signals indicate the presence of mostly *p*-OH cinnamic acid groups.

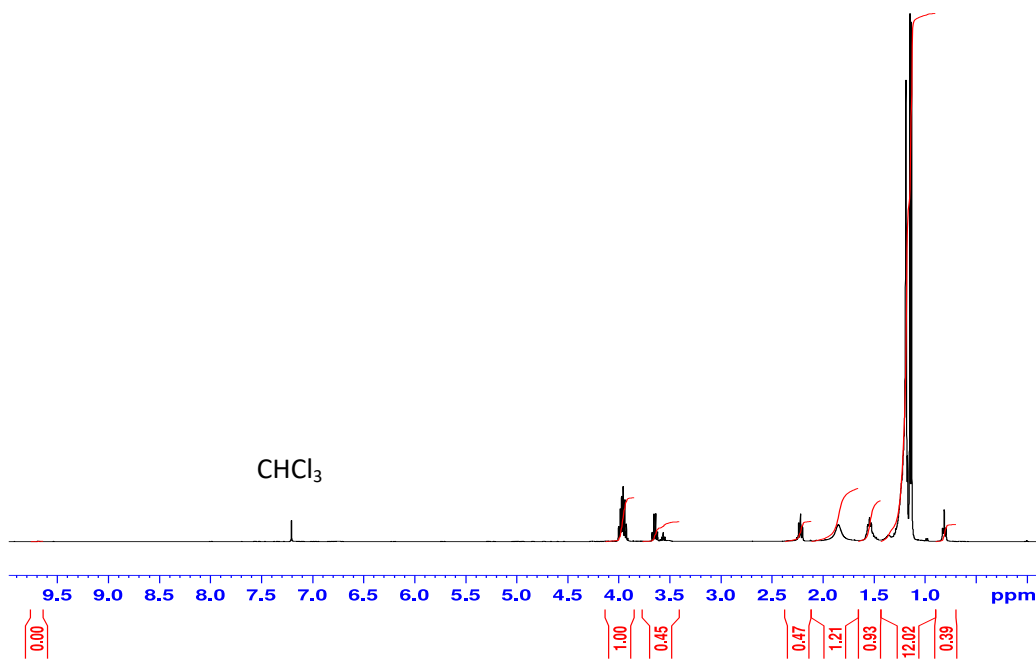
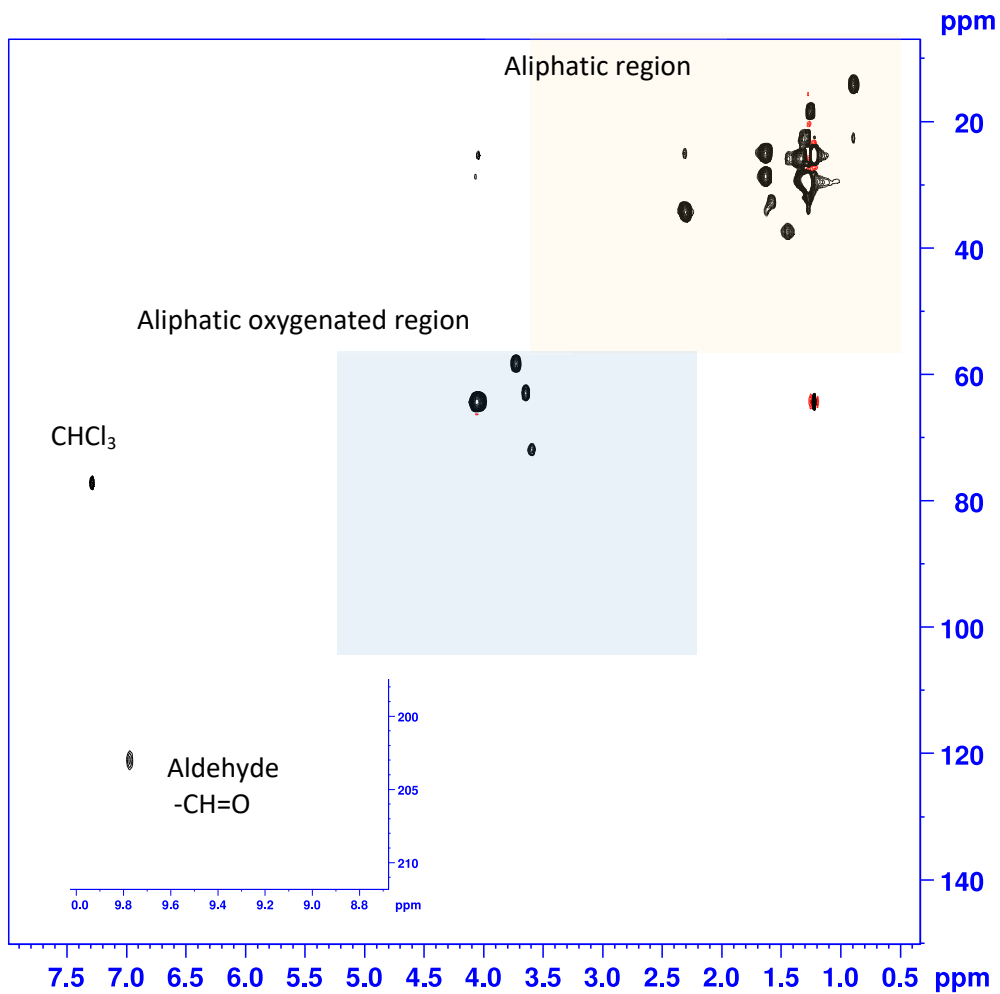


Figure S2. HSQC NMR and ^1H NMR spectra of Spruce needle wax. The spectra shows that the mixture consists of aliphatic hydrocarbons with some aldehyde groups and structures with

oxygen bonds, connected possibly as alcohols, esters or ether bonds. The mixture does not contain aromatic structures.

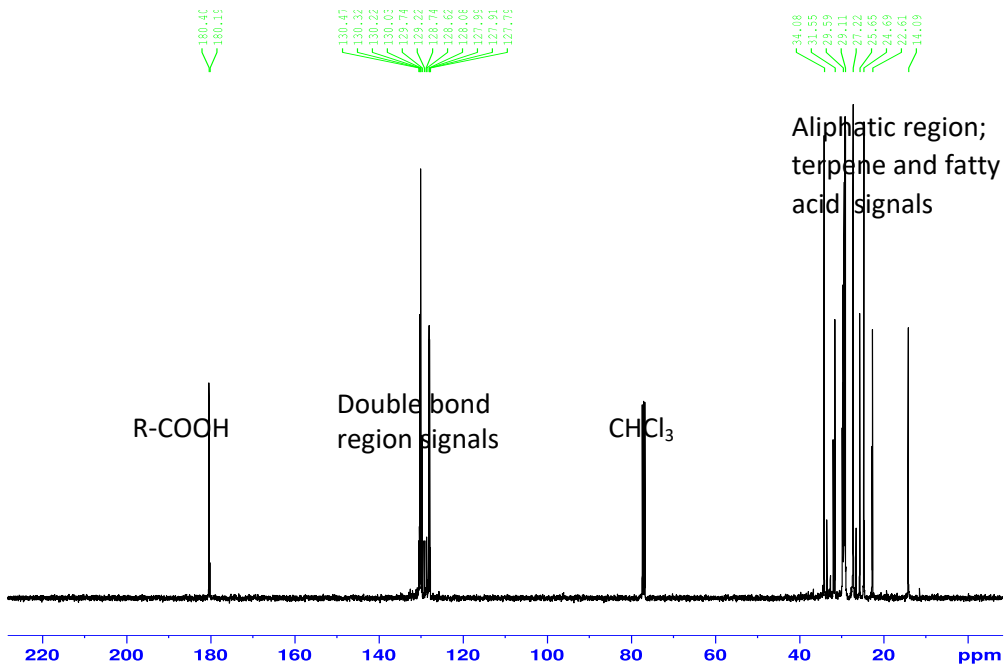
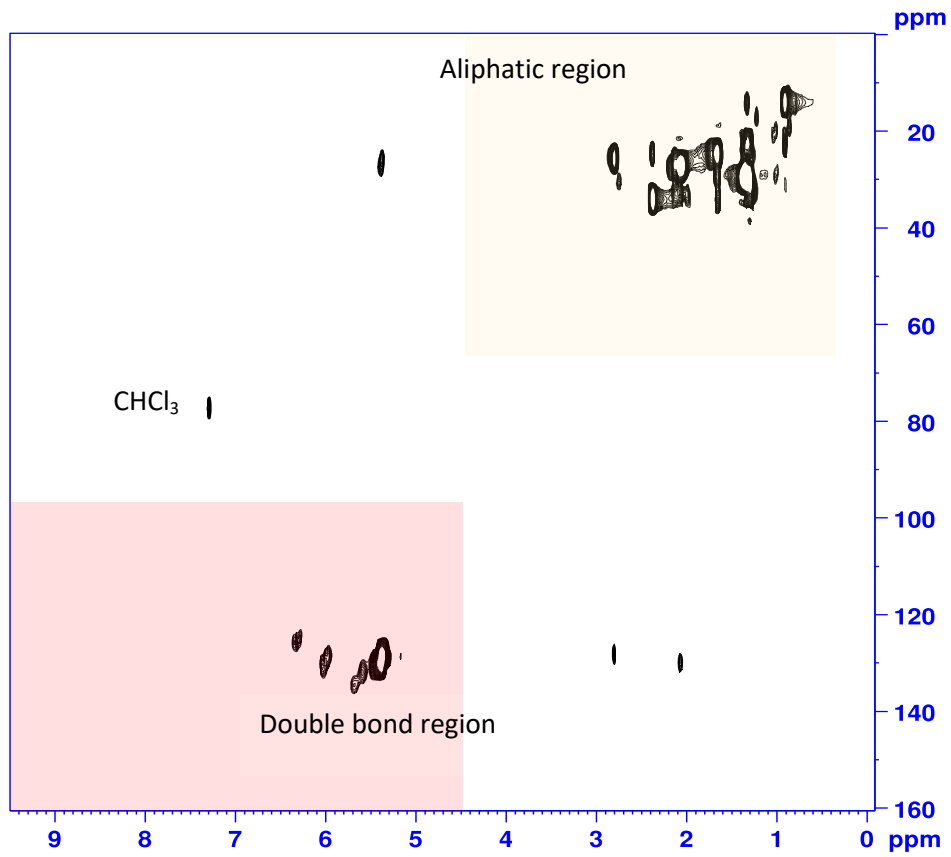


Figure S3. HSQC and ^{13}C NMR spectra of TOFA 98 shows the presence of hydrocarbons at 1-3 ppm/15-40 ppm with multiple of double bonds at 5-7 ppm/125-135 ppm. The carboxylic acid carbonyl peak signals are at 179-181 ppm.

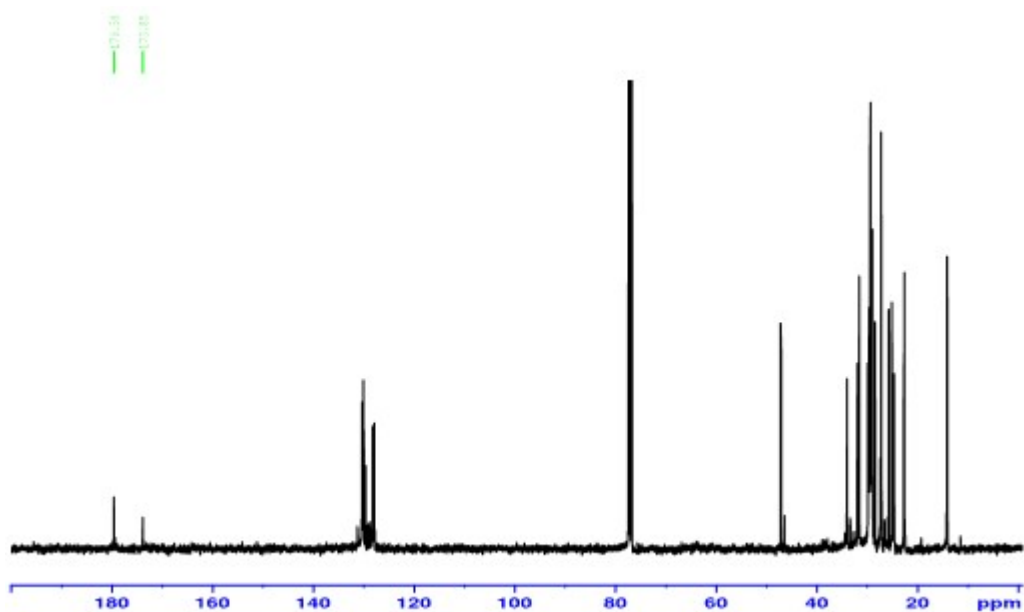


Figure S4. ^{13}C NMR spectrum of the TOFA-chloride. The carbonyl signals of TOFA-Cl are at 173-174 ppm.

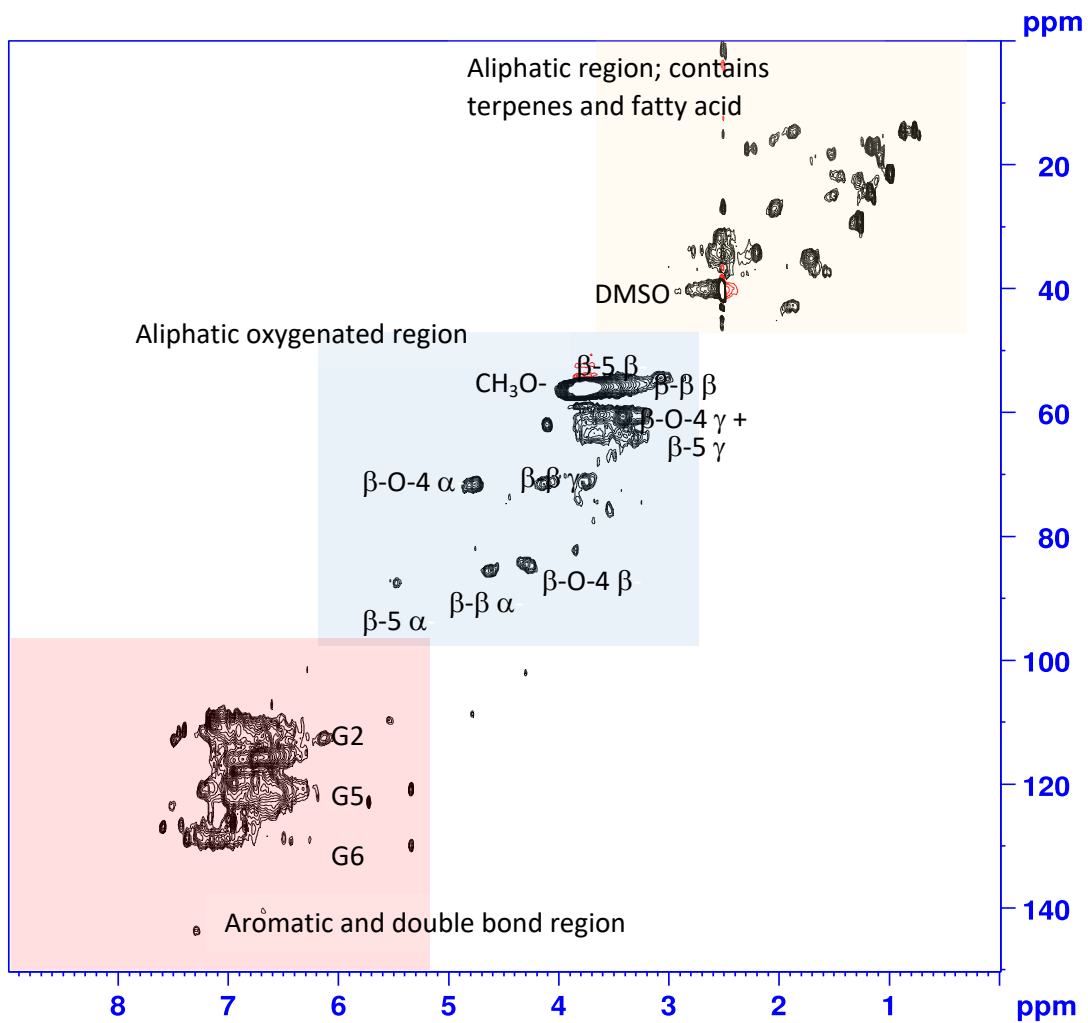


Figure S4. HSQC and ^1H spectra of the kraft lignin BioPiva from softwood shows that the sample contains all typical lignin β -O-4, β - β and β -5 side chain structures with also some fatty acid or terpene signals originating from wood extractives.

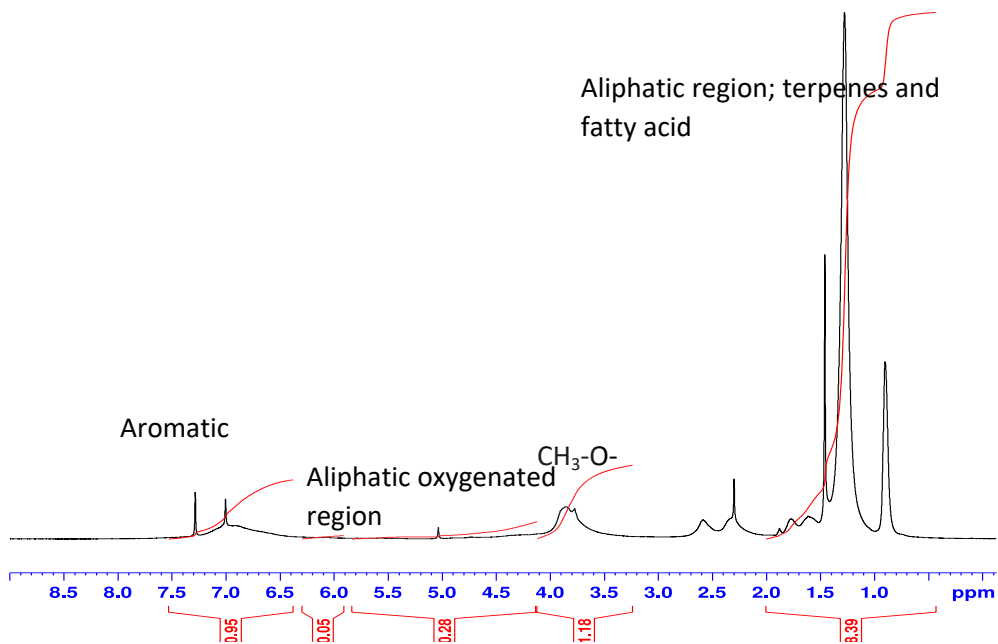
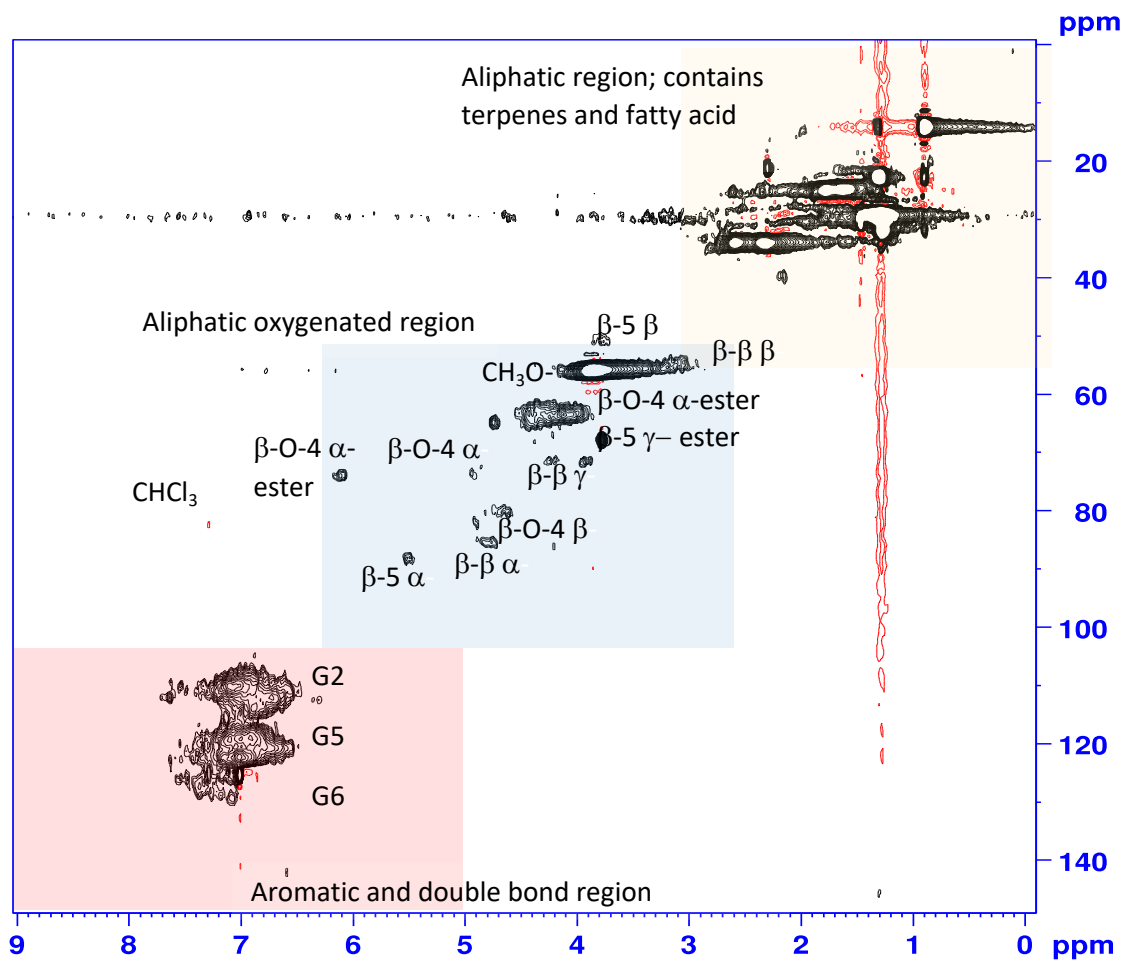
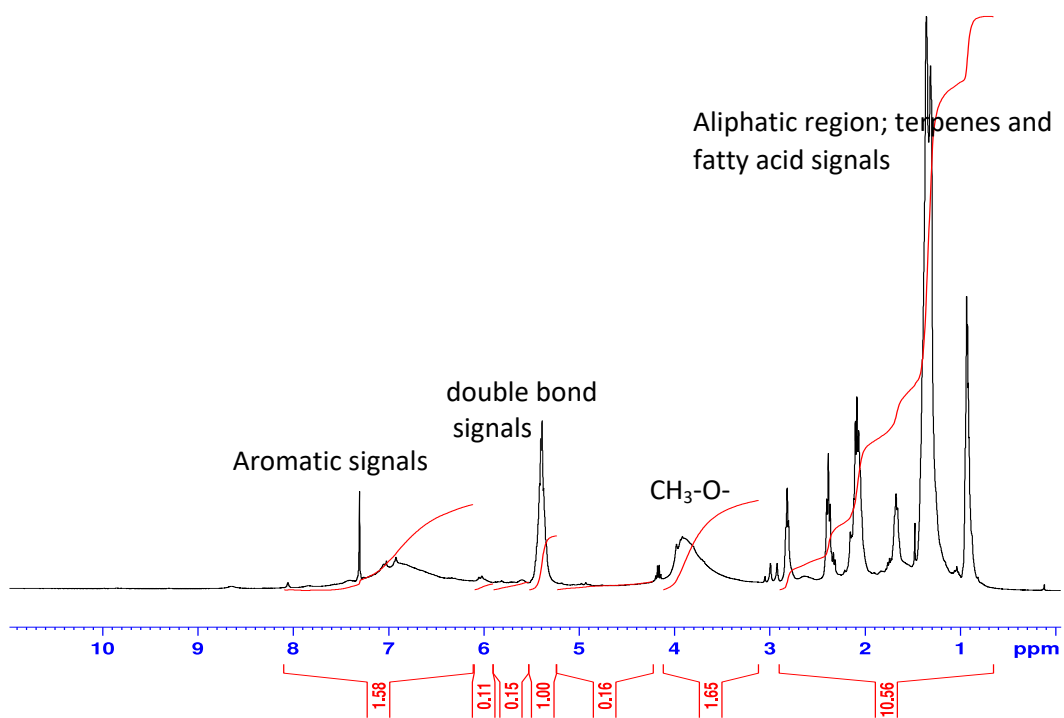
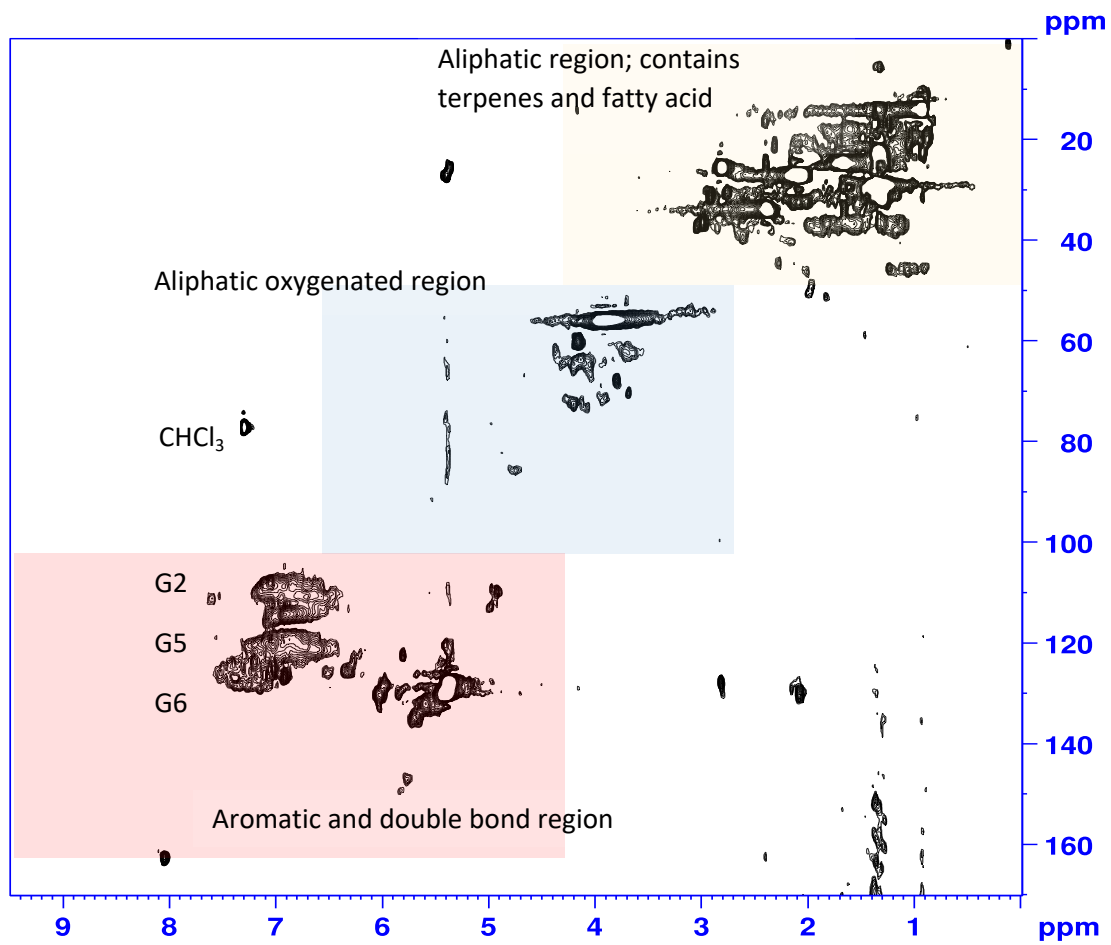


Figure S5. HSQC and ^1H spectra of Lignin-La₁₀₀. The lignin side-chain α and γ CH-signals with -OHs have shifted to left indicating that the esterification on these positions have proceeded successfully.



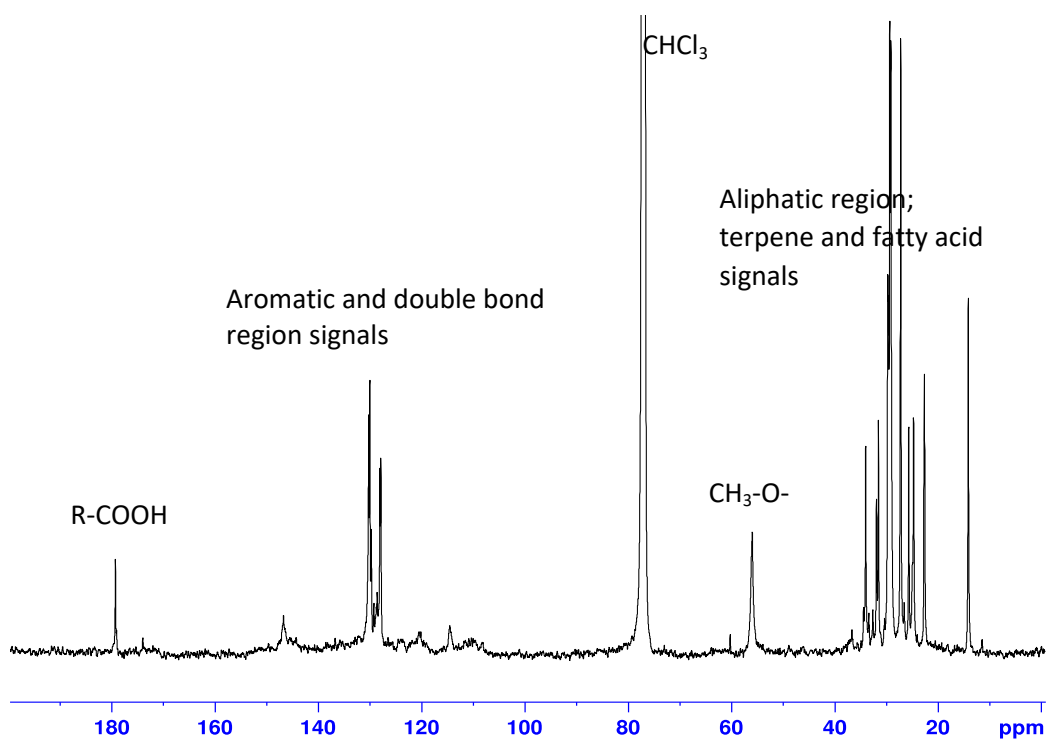


Figure S6. HSQC, ^1H and ^{13}C NMR spectra of TOFA-lignin. The spectral analysis confirms that the sample contains lignin aromatic signals together with the unsaturated fatty acid signals originating from TOFA. The side chain region suggests that the esterification was not complete because the $\gamma\text{-CH}$ -signals contain both underivatized and derivatized signal patterns and the other side-chain signals are too low in intensity to detect. ^{13}C NMR shows both a sharp peak of free carboxylic acid carbonyl signals at 180 ppm and a lower wide peak of the lignin ester carbonyls at approximately 173 ppm.

1.2 The ^{31}P NMR spectral quantification table of lignin hydroxyl groups

Table S1. Quantitative analysis of hydroxyl groups of lignin determined by ^{31}P NMR using n-NHDI as an internal standard. The amount of various hydroxyl groups is expressed as mmol of functional group /g of dry lignin. G= guaiacyl, H= *p*-OH-phenyl.

| | | Lignin | La-L ₃₀ | La-L ₇₀ | La-L ₁₀₀ | TOFA-L |
|---------------------------------|-------------------------------|--------|--------------------|--------------------|---------------------|--------|
| Functionality mmol/g | Aliphatic-OH | 2.08 | 1.27 | 0.86 | 0.06 | 0.80 |
| | 5-Substituted-OH/ syringyl-OH | 1.62 | 0.95 | 0.67 | 0.14 | 0.81 |
| | Non-condensed guaiacyl-OH | 1.67 | 0.82 | 0.63 | 0.10 | 1.32 |
| | H-OH | 0.11 | 0.06 | 0.07 | 0.0 | 0.08 |
| | CO-OH | 0.38 | 0.23 | 0.33 | 0.95* | 3.86* |
| | Total phenolic - OH | 3.41 | 1.8 | 1.37 | 0.24 | 2.13 |
| | Total -OH | 5.88 | 3.33 | 2.57 | 1.25 | 2.93 |
| DS | | 0 | 44 | 60 | 95 | 45 |

* Contains free carboxylic acid groups from TOFA or residual lauric acid

1.3 The GC-MS analysis of the lipophilic fatty acid containing starting materials

Table S2. Composition of TOFA determined by GC-MS analysis from the silylated oil mixture. The oil mixture contained 72% of unsaturated C18 oleic acids and the rest 8% of identified compounds were different chain length fatty acids with varying saturation levels. After GC-MS analysis by using the NIST spectral library, a total of 78% of the compounds could be identified and 22% remained unknown.

| TOFA oil | Average | St Dev | |
|---------------------------|---------|--------|------------|
| | mg/g | mg/g | % of total |
| Palmitic acid, 16:0 | 3,69 | 0,04 | 0,4 |
| Heptadecanoic acid, 17:0 | 8,26 | 0,21 | 0,8 |
| Linolenic acid, 18:3 | 78,85 | 18,39 | 7,9 |
| Linoleic acid, 18:2 | 378,04 | 3,49 | 37,8 |
| Oleic acid, 18:1 | 269,88 | 7,07 | 27,0 |
| Stearic acid, 18:0 | 13,01 | 5,88 | 1,3 |
| Nonadecenoic acid, 19:1 | 12,78 | 5,69 | 1,3 |
| Pimaric acid | 7,12 | 2,00 | 0,7 |
| Eicosatrienoic acid, 20:3 | 8,38 | 0,03 | 0,8 |
| Arachidic acid, 20:0 | 1,06 | 0,07 | 0,1 |
| Total identified | 781,08 | 29,12 | 78,1 |

Table S3a-b. Composition of spruce needle wax (SNW) extract determined by GC-MS analysis from the silylated wax mixture. The identified components of wax consisted of saturated fatty acids with long hydrocarbon chain varying between C16-C30. Only 4% of the mixture was identified using GC-MS analysis referenced to the NIST spectral library.

a.

| Spruce needle wax | Average | St Dev | |
|----------------------------|---------|--------|------------|
| | mg/g | mg/g | % of total |
| Palmitic acid, 16:0 | 1,10 | 0,00 | 0,1 |
| Octadecanoyl alcohol, 18:0 | 0,31 | 0,00 | 0,0 |
| Stearic acid, 18:0 | 1,06 | 0,02 | 0,1 |
| Docosanoic acid, 22:0 | 1,08 | 0,33 | 0,1 |
| Tetracosanoic acid, 24:0 | 1,02 | 0,21 | 0,1 |
| Hexacosanoic acid, 26:0 | 0,92 | 0,09 | 0,1 |
| 10-hydroxynonacosane, 29:0 | 29,70 | 0,70 | 3,0 |
| Nonacosan-10-one, 29:0; 10 | 0,44 | 0,02 | 0,0 |
| Octacosanoic acid, 28:0 | 1,50 | 0,11 | 0,1 |
| Triacontanoate, 30:0 | 3,24 | 0,70 | 0,3 |
| Total identified | 40,36 | 0,69 | 4,0 |

b. Alkaline hydrolysis was utilized to hydrolyze the nonvolatile high molecular weight esters in the SNW to their more volatile counterparts. The procedure was as following: Dried SNW (0.2 g) was

dispersed in 2 ml of 0.5 M KOH in 90% EtOH (v/v). The hydrolysis was carried out at 70 °C for 3 hours. The sample was diluted and acidified using 3 ml water with two drops of bromocresol green and 30 % sulfuric acid. The triplicate samples were each extracted three times in methyl tert-butyl ether (MTBE) containing internal standard, 0.02 mg/ml betulinol. The combined MTBE extracts were evaporated under N₂ and dried in vacuum at 40 °C for 15–20 min. The residue was silylated at 70 °C for 45 min using 150 µl silylation mixture of pyridine, BSTFA, and TMCS in a 1:4:1 ratio. The silylated sample was analysed by GC-MS. The hydrolysate contained C12-C30 saturated long chain fatty acids, diacids, and alcohols with some residual glyceryl esters.

| Spruce needle wax hydrolysate | Average mg/g | St dev mg/g | % of total |
|-------------------------------------|-----------------|----------------|------------|
| Dodecanoic acid, 12:0 | 4,30 | 1,32 | 0,4 |
| Nonanedioic acid | 0,92 | 0,06 | 0,1 |
| Tetradecanoic acid, 14:0 | 7,96 | 0,34 | 0,8 |
| 1,12-Dodecanediol | 12,16 | 0,60 | 1,2 |
| 4-Hydroxycinnamic acid | 0,91 | 0,14 | 0,1 |
| Undecanedioic acid | 24,27 | 0,73 | 2,4 |
| Palmitic acid,16:0 | 5,86 | 0,10 | 0,6 |
| Ferulic acid | 0,77 | 0,03 | 0,1 |
| 1,14-Tetradecanediol | 9,31 | 0,67 | 0,9 |
| 1-Syringylglycerol | 1,40 | 0,30 | 0,1 |
| 14-Hydroxy-tetradecanoic acid, 14:0 | 125,33 | 5,78 | 12,5 |
| Stearic acid, 18:0 | 2,86 | 0,16 | 0,3 |
| Unknown alkane | 1,40 | 0,24 | 0,1 |
| 1,16-Hexadecanediol | 3,59 | 0,32 | 0,4 |
| 16-Hydroxy-palmitic acid, 16:0 | 155,25 | 5,16 | 15,5 |
| Arachidic acid, 20:0 | 2,52 | 0,08 | 0,3 |
| Unidentified fatty alcohol | 1,30 | 0,20 | 0,1 |
| 9,16-Dihydroxy-palmitic acid, 16:0 | 3,05 | 0,13 | 0,3 |
| Glyceryl palmitate | 0,79 | 0,41 | 0,1 |
| Docosanoic acid, 22:0 | 7,10 | 0,34 | 0,7 |
| Tetracosanoic alcohol 24:0 | 2,18 | 0,49 | 0,2 |
| Glyceryl monostearate | 0,79 | 0,03 | 0,1 |
| Tetracosanoic acid, 24:0 | 4,80 | 0,09 | 0,5 |
| Unidentified long alkane | 1,78 | 0,13 | 0,2 |
| Hexacosanoic acid, 26:0 | 2,63 | 0,39 | 0,3 |
| 10-Hydroxynonacosane | 87,52 | 8,76 | 8,8 |
| Octacosanoic acid, 28:0 | 3,29 | 0,22 | 0,3 |
| Triacantanoate, 30:0 | 9,47 | 0,71 | 0,9 |
| Unidentified | 24,05 | 8,92 | 2,4 |
| SUM | 507,55 | 13,32 | 50,8 |
| Total identified | 479,02 | | 47,9 |

1.4 Thermal properties of the starting materials

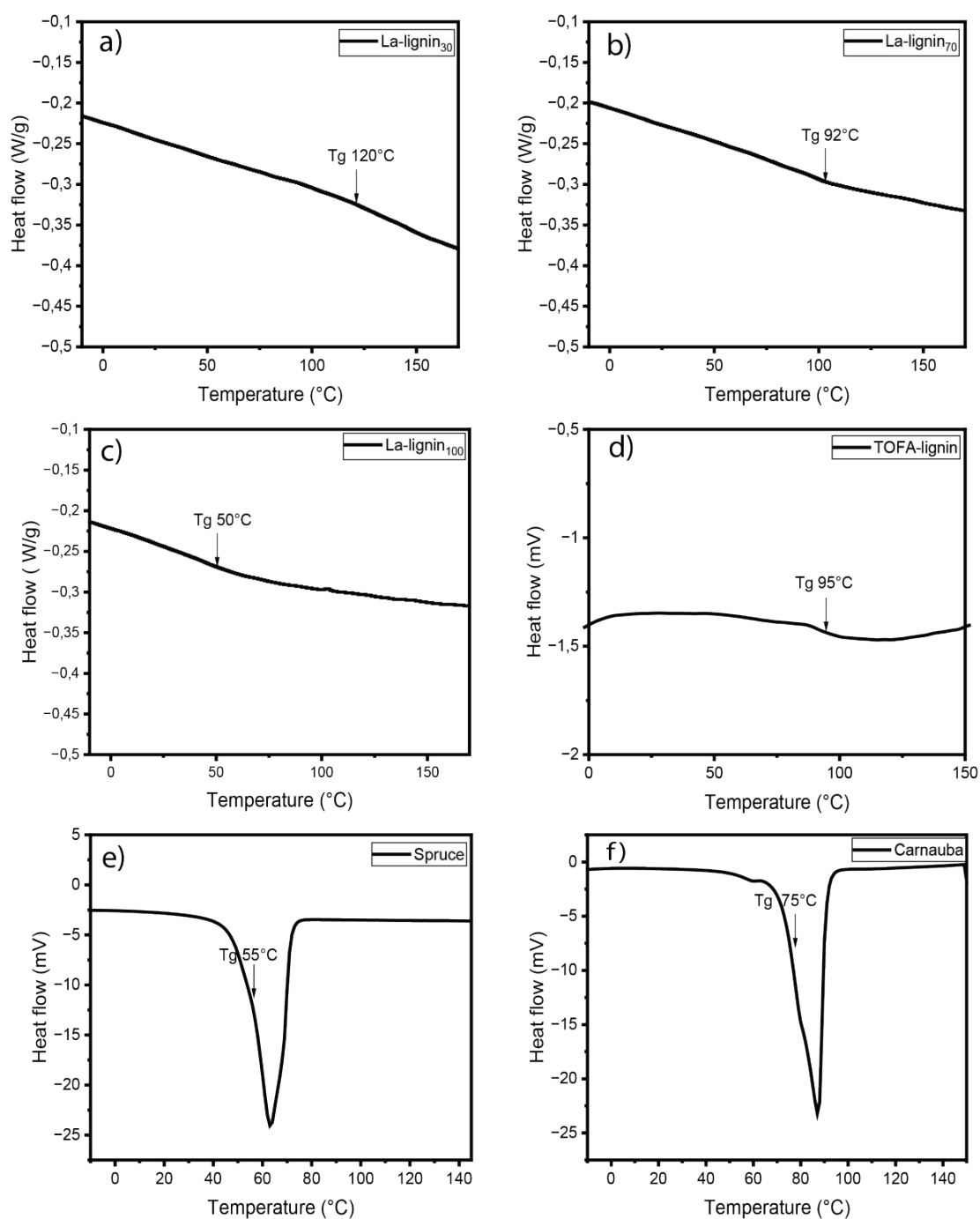


Figure S7. DSC curves of La-lignin₃₀, La-lignin₇₀, La-lignin₁₀₀, TOFA-lignin, spruce needle wax, lignin, carnauba wax. The T_g for each sample is indicated in the figures.

2. Cassie–Baxter equation

Cassie-Baxter equation is used for explaining superhydrophobicity where the mixed surface is comprised of solid surface and air pockets (1).

$$\cos \theta_{CB} = f_m(\cos \theta_c + 1) - 1 \quad (\text{eq 1})$$

In this equation f_m is the solid fraction of water droplets on the micro-scale surface structure and θ_c is the contact angle of the solid substrate.

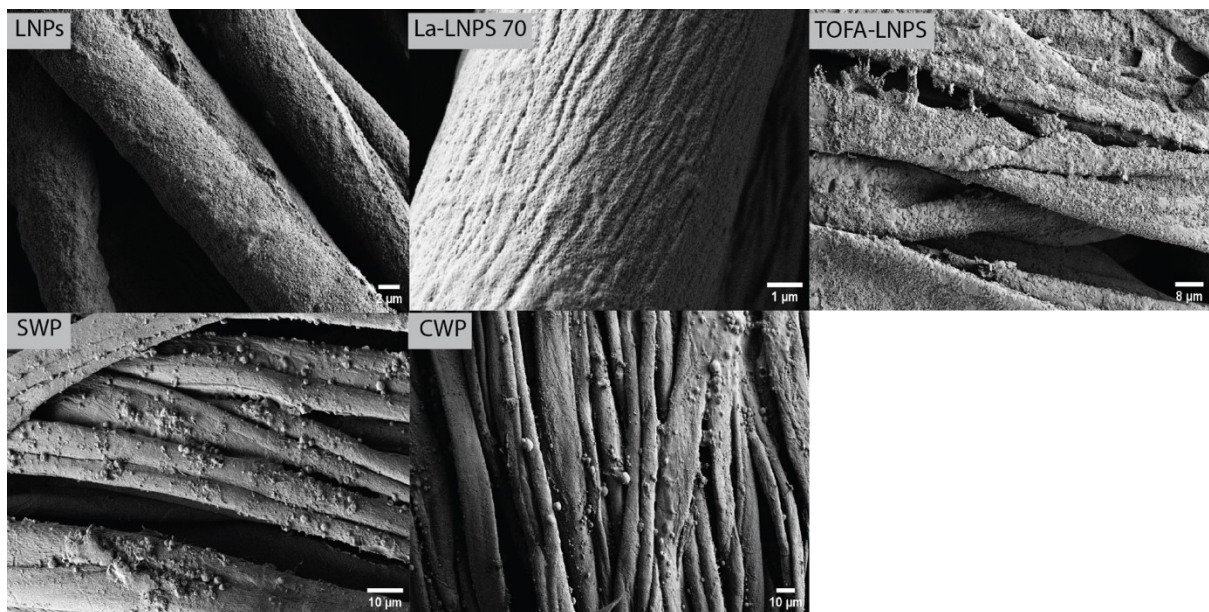


Figure S8. SEM images of cotton functionalized with LNPs, La-LNPs₇₀, TOFA-LNPs, SWPs, and CWPs after heat treatment, the HT temperature was specified for each coated sample at 10 degrees below T_g (Table 1), ranging from 45 degrees for SW to 120 degrees for lignin.

4. Wetting properties - water droplet test

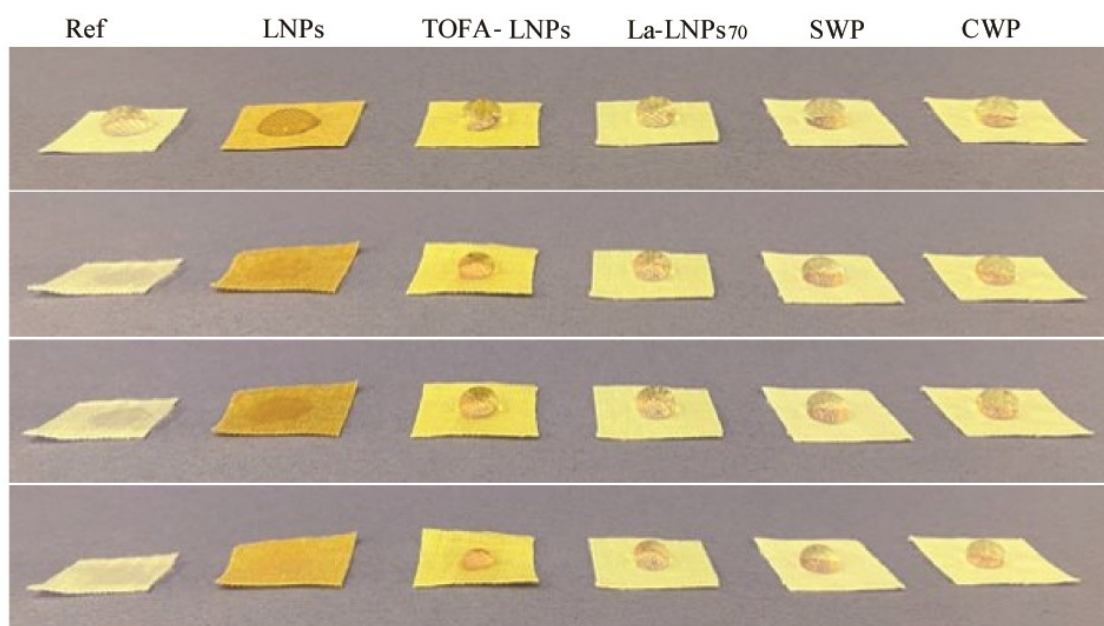


Figure S9. Water droplets on the cotton fabric and coated cotton fabric. Rows from top to bottom: 30 min, 1 hour 1,30 hours, and 3 hours after application, showing possible absorption or spreading.

5. Self-cleaning properties of the coated fabrics

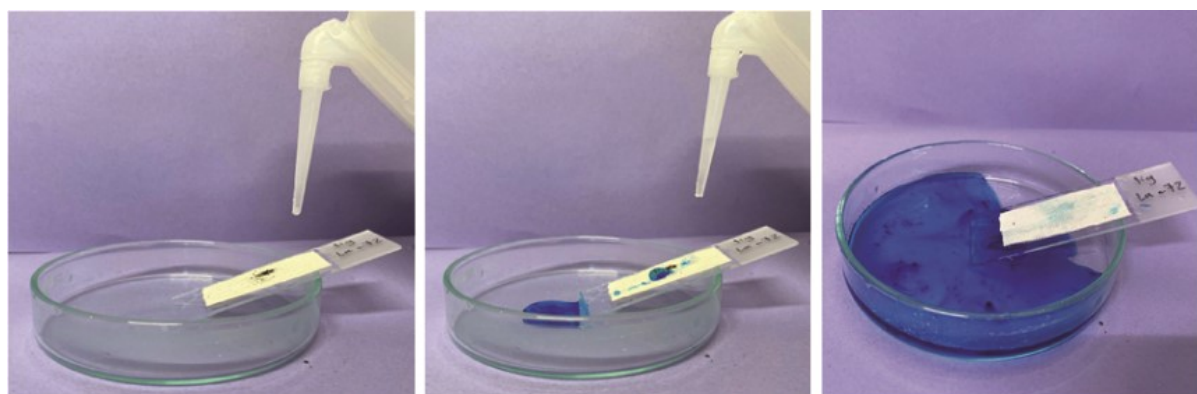


Figure S10. Pictures of the cleaning process of cotton coated cotton with La-LNPs70, where the contamination was methylene blue powder and the fabric was cleaned up by rolling water droplets.

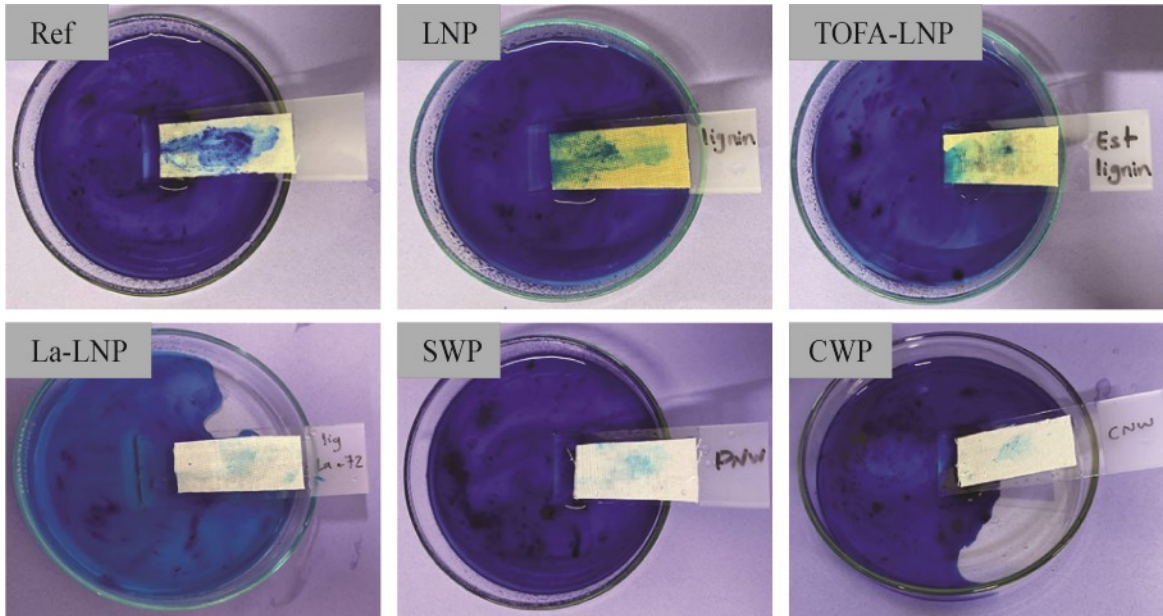
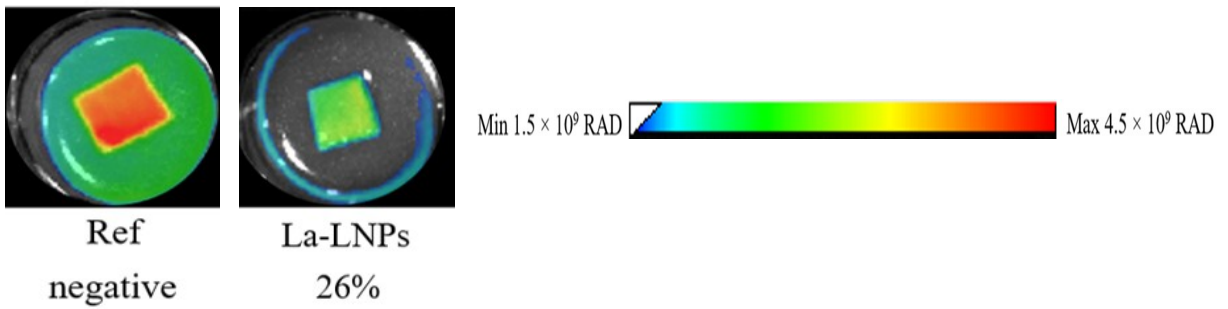


Figure S11. Pictures of the cleaning process of cotton fabrics coated with all NPs, where the contamination was methylene blue powder and the fabric was cleaned by rolling water droplets over the sample.

6. Antibacterial test

E. coli



S. aureus

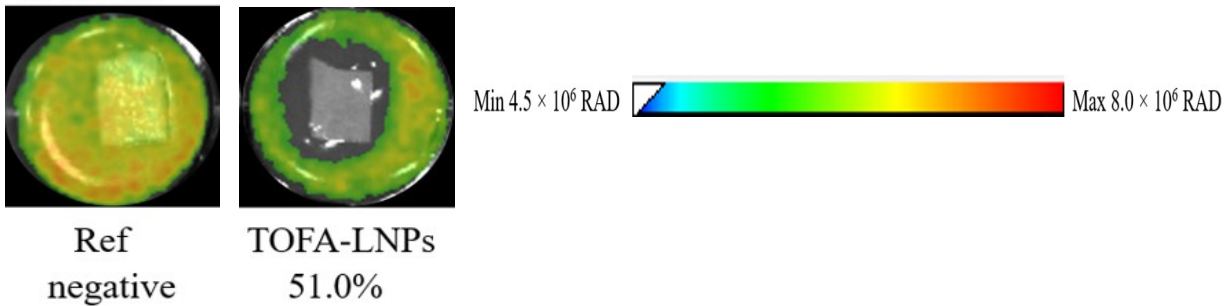


Figure S12. Images of luminescent bacteria plates showing the reference fabric, La-LNP, and TOFA-LNP coated fabric samples against the bacteria *E. coli* and *S. aureus*.

7. SEM images of functionalized cotton fabric after heat treatment and after two washing cycles

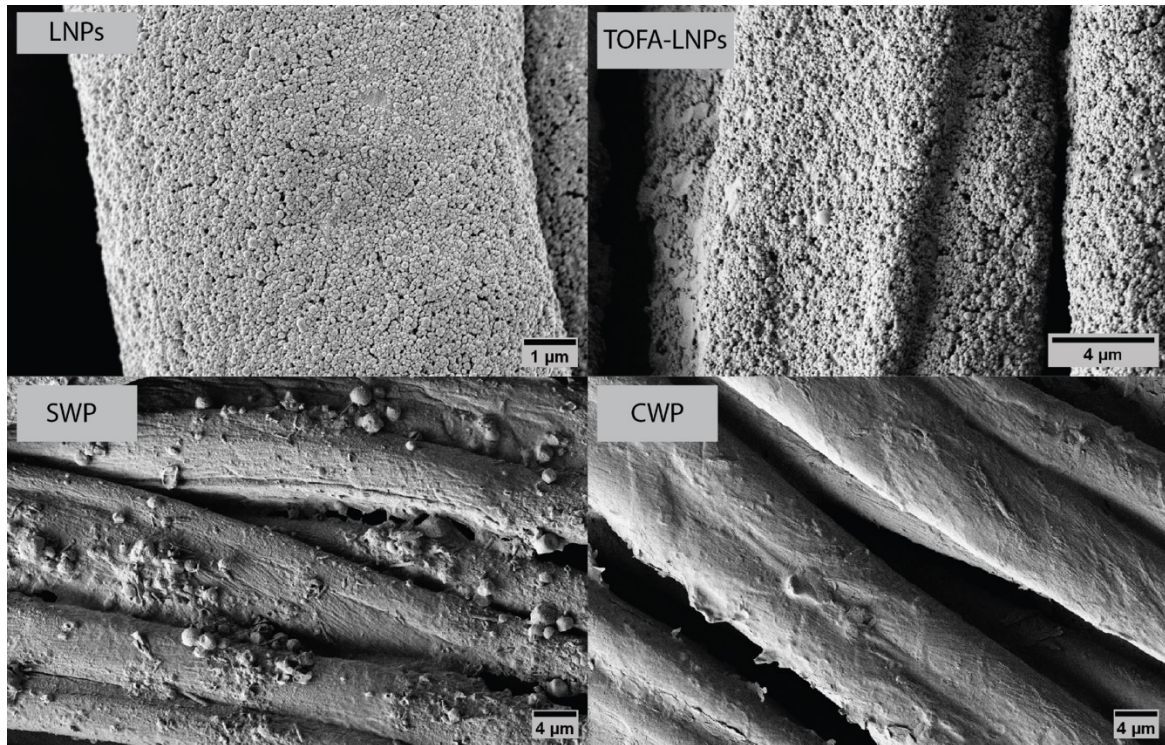


Figure S13. SEM images of cotton functionalized with LNPs, TOFA-LNPs, SWPs, and CWPs after two cycles of washing.

8. Spray testing

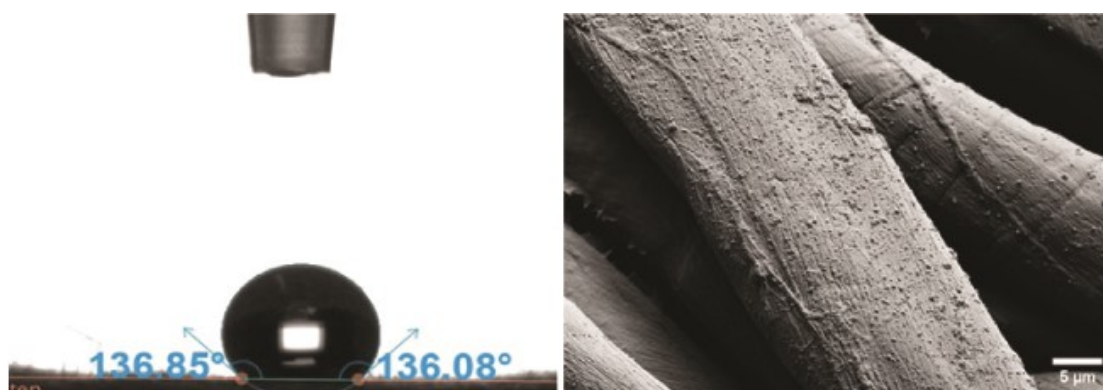


Figure S14. SEM micrograph of La-LNP₁₀₀ coating applied by spraying method to the fabric. The spray coating showed successful attachment to the cotton and improved hydrophobicity.

References

Park S, Kim J, Park CH. Analysis of the wetting state of super-repellent fabrics with liquids of varying surface tension. *RSC Adv.* 2016 May 11 [cited 2023 Dec 7];6(51):45884–93. Available from: <https://pubs.rsc.org/en/content/articlehtml/2016/ra/c5ra27281e>.