Electronic Supplementary Information

Synthesis of Diols from Jojoba Oil via Rhodium-Catalyzed Reductive Hydroformylation: a Smart Way to Access Biobased Polyurethanes

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I) General purpose

I.1 Materials

Jojoba oil is a Sigma-Aldrich Merck (Darmstadt, Germany) product commercialized as "Jojoba oil from Simmondsia chinensis". $Rh(acac)(CO)_2$, triethylamine, toluene and glycerol were purchased from the same society. Silica (Silica gel 60A; 30-70 μm) was purchased from Acros Organics (Geel, Belgium). Tolonate™ X FLO 100 was kindly supplied by Vencorex® Chemicals (Saint Priest, France). Pripol® 2033 was kindly supplied by Croda (East Cowick, United Kingdom). All materials were used as received.

I.2 Instruments

Hydroformylation and hydrohydroxymethylation experiments were carried out in a 25 or a 100 mL **autoclave** (Parr instrument company) equipped with a mechanical stirrer. All reactions involving $Rh(acac)(CO)_2$ or $Rh(acac)(CO)_2$/triethylamine combination were conducted at air atmosphere, under a fume hood, in a room equipped with a CO detector and an explosimeter, both connected to an alarm.

NMR spectra were recorded at 298 K on a Bruker Avance III HD 300 NanoBay spectrometer equipped with a 5 mm broadband probe BBFO with Z-gradients, operating at 7.05 T field strength (300 MHz for ^{1}H nuclei and 75 MHz for ^{13}C nuclei). ^{1}H and ^{13}C chemicals shifts were determined using residual signals of the deuterated solvents. Assignment of the signals was carried out using 1D (^{1}H, $^{13}C\{^{1}H\}$) and 2D (COSY, HSQC) NMR experiments when necessary.

Rhodium concentrations were determined through inductively coupled plasma optical emission spectroscopy experiments using a Thermo Scientific iCAP 7000 Plus Series **ICP**-OES. Samples composed of an aliquot of the organic phase were digested before ICP experiments in a sulfuric-nitric acid/H_2O_2 mixture via microwave mineralization using a MARS 6 microwave digestion system.

Infrared (**IR**) spectra were recorded on a Nicolet 210 Fourier transform infrared (FTIR) spectrometer. Materials analyses were recorded using an ATR accessory.

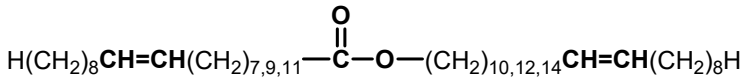
Thermogravimetric analyses (**TGA**) were carried out using a TG 209F1 apparatus (Netzsch). Approximately 10 mg of sample were placed in an aluminum crucible and heated from room temperature to 580 °C, at a heating rate of 20 °C/min, and under nitrogen atmosphere (60 mL/min).

Differential Scanning Calorimetry (**DSC**) analyses were carried out using a NETZSCH DSC200F3 calorimeter, which was calibrated using adamantane, biphenyl, indium, tin, bismuth and zinc standards. Nitrogen was used as purge gas. Approximately 10 mg of sample were placed in a perforated aluminum pan and the thermal properties were recorded between -100 °C and 100 °C at 20 °C/min to observe the glass transition temperature. The Tg values were measured on the second heating ramp to erase the thermal history of the polymer. All the reported temperatures are average values.

Dynamic mechanical analyses (**DMA**) were carried out on a Metravib DMA 25 with Dynatest 6.8 software. Parallelepiped samples were tested in the uniaxial tension mode at a frequency of 1 Hz with a fixed strain of 10^{-5} m, while applying a temperature ramp at a rate of 3 °C/min from -100 °C to 125°C. The Tα was determined as the maximum of the loss modulus E''.

II) Jojoba oil ester analyses

II.1 Jojoba oil ester NMR spectra



Jojoba oil ester

(liquid at room temperature)

^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C, δ(ppm)): 5.36 (*m*, 4 H, =CH-), 4.06 (*t*, *J* = 6.7 Hz, 2 H, -CO_2-CH_2-), 2.30 (*t*, *J* = 7.6 Hz, 2 H, -CH_2-CO_2-), 2.02 (*q*, *J* = 6.5 Hz, 8 H, -C$\underline{H}_2$-CH=), 1.62 (*quintet*, *J* = 6.8 Hz, 4 H, -C$\underline{H}_2$-CH_2-CO_2- *and* -CO_2-CH_2-C$\underline{H}_2$-), 1.28 (*m*, 52 H, other CH_2), 0.89 (*t*, *J* = 6.9 Hz, 6 H, 2 CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, δ(ppm)): 174.0 (-CO_2-), 129.9 (-CH=), 64.4 (-CO_2-$\underline{C}H_2$-), 34.4 (-$\underline{C}H_2$-CO_2-), 31.9, 29.8, 29.5, 29.3, 28.7 (-CO_2-CH_2-$\underline{C}H_2$-), 27.2, 25.9, 25.0 (-$\underline{C}H_2$-CH_2-CO_2-), 22.7 (other CH_2), 14.1 (CH_3).

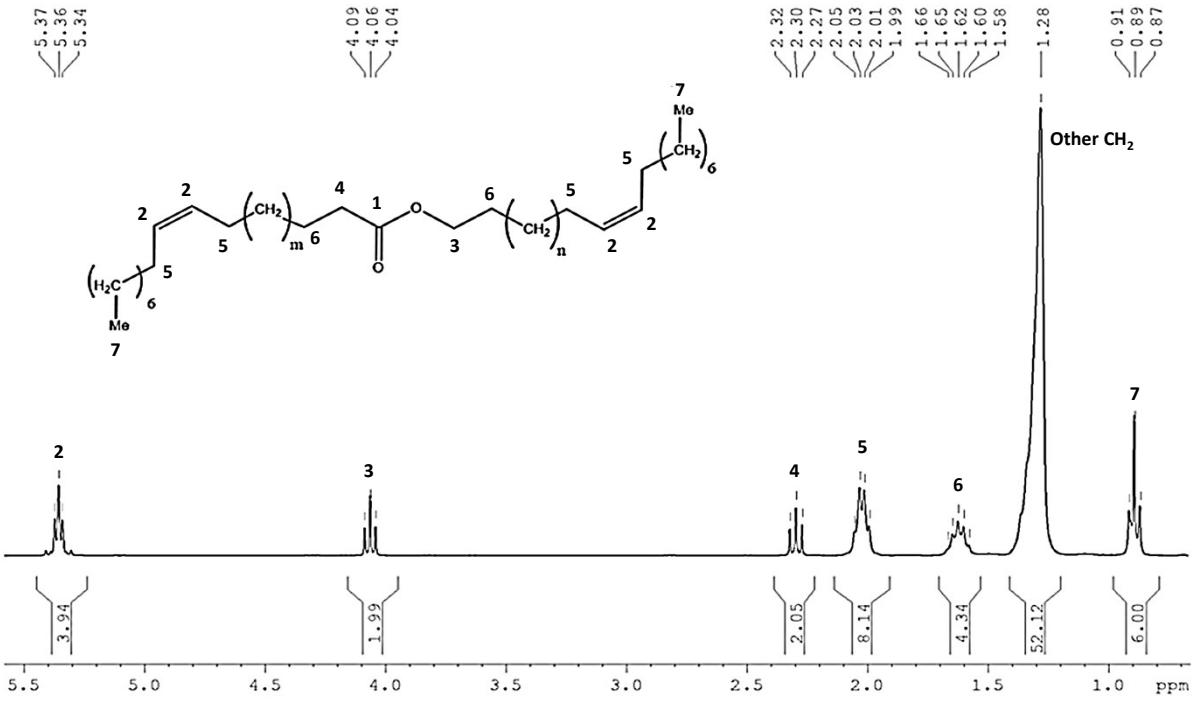


Figure S1. ^{1}H NMR spectrum of jojoba oil ester (300 MHz, $CDCl_3$, 25 °C).

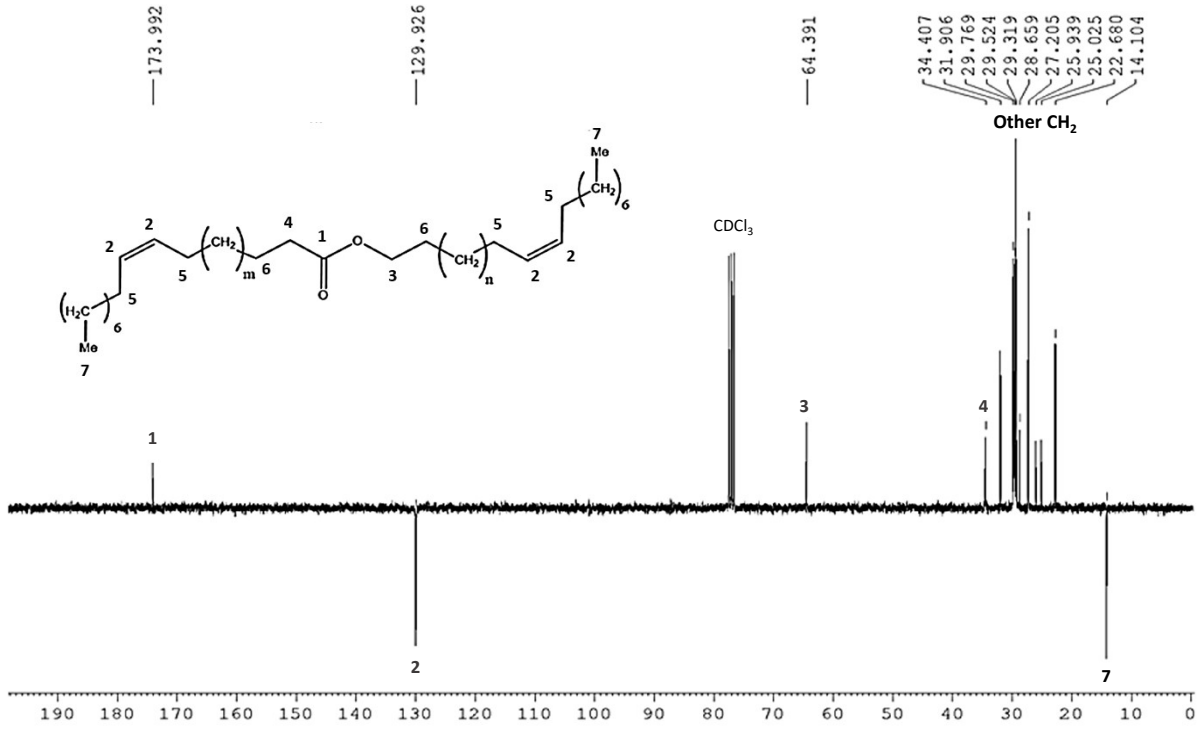


Figure S2. ^{13}C-JMOD NMR spectrum of jojoba oil ester (75 MHz, $CDCl_3$, 25 °C).

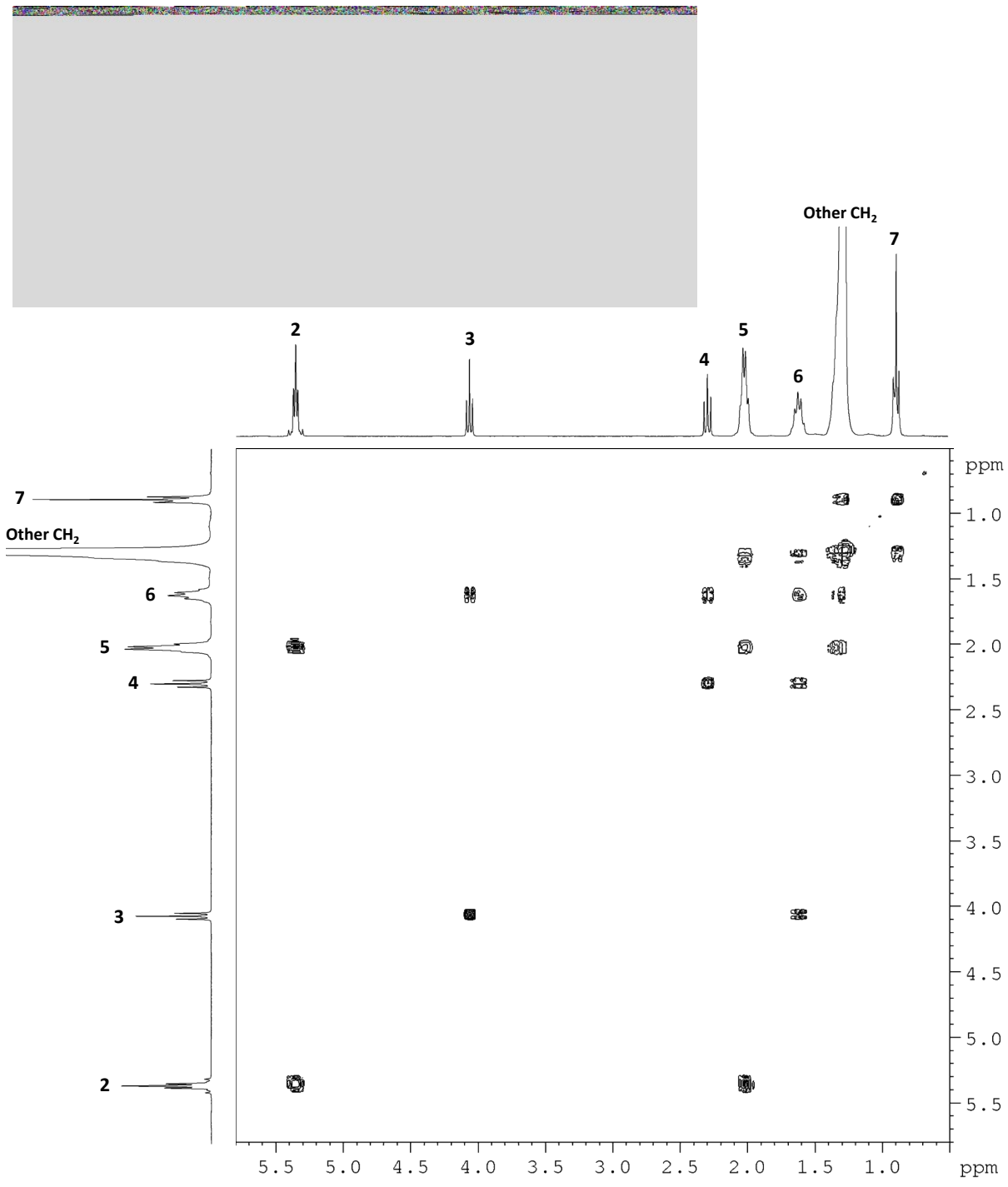


Figure S3. COSY NMR spectrum of jojoba oil ester (300 MHz, $CDCl_3$, 25 °C).

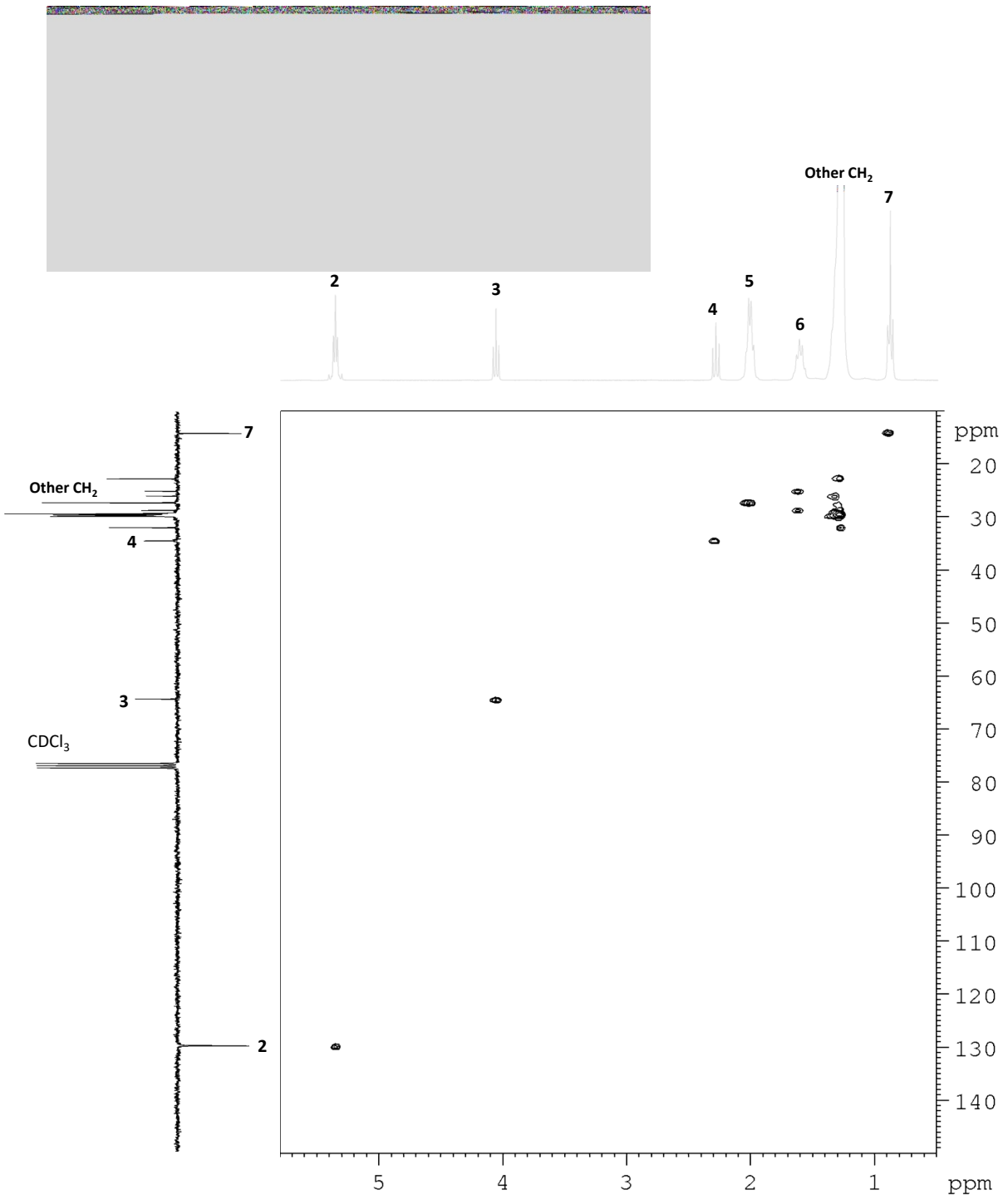
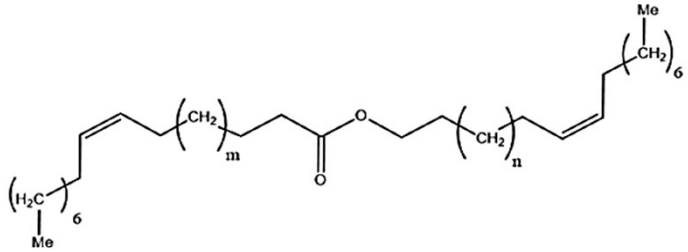


Figure S4. HSQC NMR spectrum of jojoba oil ester (300 MHz, $CDCl_3$, 25 °C).

II.2 Jojoba oil ester average molar mass determination



Jojoba oil ester

From the drawing above, we can deduce that jojoba oil ester has the following chemical formula: $\mathbf{C_{27}H_{50}O_2(CH_2)_{n+m}}$

Normalized ^{1}H NMR spectrum of jojoba oil ester (see Figure S1) shows that the (12 + n + m) CH_2 moieties integrate for 52.12 H.

So, we can write: **12 + n + m = 52.12 / 2**

That means: **n + m = 14.06**

Therefore, the chemical formula of jojoba oil ester is: $\mathbf{C_{27}H_{50}O_2(CH_2)_{14.06}}$

And finally: $\mathbf{C_{41.06}H_{78.12}O_2}$

Considering the molar mass of carbon (12.01 g.mol^{-1}), hydrogen (1.01 g.mol^{-1}) and oxygen (16.00 g.mol^{-1}), the average molar mass of jojoba oil ester can be calculated as follows:

41.06 × 12.01 + 78.12 × 1.01 + 2 × 16.00 = 604.03

So, the value of **604 g.mol^{-1}** was kept for jojoba oil ester.

III) Synthesis and characterization of jojoba oil ester HHM products

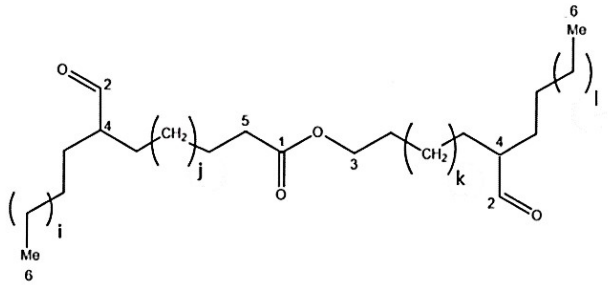
III.1 Catalytic tests

In a typical catalytic experiment (without catalyst recycling), $Rh(acac)(CO)_2$ (6.0 mg, 23.3 μmol, 1 equiv.), triethylamine (0, 1000 or 2000 equiv., values corresponding to 0 mL, 3.25 mL and 6.5 mL, respectively), jojoba oil ester (1.73 g, 2.87 mmol, 125 equiv.), toluene (6.5, 3.25 or 0 mL, respectively, to obtained a total volume of solvent "triethylamine + toluene" equal to 6.5 mL) were introduced in a 25 mL stainless-steel autoclave equipped with a mechanical stirrer. The reactor was sealed, the reaction mixture was stirred and the reactor was heated at the desired temperature. Then, the reactor was pressurized with CO and H_2 at the desired pressure. After the appropriate reaction time, the reactor was cooled to room temperature and depressurized. After removing triethylamine and toluene by evaporation of an aliquot sample, the obtained mixture was then analyzed by NMR spectroscopy.

Hydroformylated jojoba oil ester was obtained in these previous conditions using 6.5 mL of toluene, no triethylamine, after 24 h at 80 °C, under 80 bar of CO/H_2 (1/1) and without further purification. **Hydrohydroxymethylated jojoba oil ester** was obtained in the previous conditions using 3.25 mL of toluene, 3.25 mL of triethylamine, after 24 h at 80 °C, under 80 bar of CO/H_2 (1/1); the product was then purified by flash chromatography using a 88/12 v/v *n*-hexane/ethyl acetate mixture as eluant and a Büchi FlashPure-IDSi40g-20 μm silica cartridge as stationary phase.

For the kinetic follow-up as well as for the catalyst recycling experiments, $Rh(acac)(CO)_2$ (36.0 mg, 140 μmol, 1 equiv.), triethylamine (1000 equiv., 140 mmol, 14.2 g, 19.5 mL), jojoba oil ester (10.53 g, 17.4 mmol, 125 equiv.) and toluene (19.5 mL; same volume as triethylamine) were introduced in a 100 mL stainless-steel autoclave equipped with a mechanical stirrer. The reactor was sealed, the reaction mixture was stirred and the reactor was heated at 80 °C. Then, the reactor was pressurized with CO / H_2 (1:1) at 80 bar. **For the kinetic follow-up**, samples were taken under pressure after 1, 2, 4, 6, 8, 10 and 24 h of reaction and then analyzed by ^{1}H NMR. **For the catalyst recycling experiments**, samples were taken only after 4 and 24 h of reaction and the full mixture obtained at 24 h was percolated on a silica column (4 g of Silica gel 60A (30-70 μm) in a column of 2 cm of internal diameter). The silica was then washed with 200 mL of toluene to remove reaction products and triethylamine. The rhodium was recovered by flushing the silica with 20 mL of acetone, solution directly collected in the preliminary washed 100 mL autoclave. The autoclave was sealed and the acetone was removed under vacuum. After this step, a new charge of jojoba oil ester, triethylamine and toluene was introduced in the autoclave containing the recovered rhodium. The autoclave was heated at 80 °C and then pressurized at 80 bar for a new run. The same silica column was used for all runs. **The hydrohydroxymethylated jojoba oil obtained from the catalyst recycling experiments** has been purified by flash chromatography to obtain an alcohols mixture directly used as **starting monomer for thermosets synthesis**. The flash chromatography was conducted using a 88/12 v/v n-hexane/ethyl acetate mixture as eluant and a Büchi FlashPure-IDSi40g-20 μm silica cartridge as stationary phase.

III.2 Jojoba oil ester hydroformylation products



Hydroformylated jojoba oil ester (liquid at room temperature)

^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C, δ(ppm)): 9.54 (*d*, *J* = 3.0 Hz, 2 H, -CH=O), 4.05 (*t*, *J* = 6.7 Hz, 2 H, $-CO_2-CH_2-$), 2.30 (*t*, *J* = 7.6 Hz, 2 H, $-CH_2-CO_2-$), 2.21 (*m*, 2 H, C<u>H</u>-CH=O), 1.65-1.20 (*m*, 68

H, other CH_2), 0.87 (*t*, *J* = 6.9 Hz, 6 H, 2 CH_3). **^{13}C NMR** ($CDCl_3$, 75 MHz, 25 °C, δ(ppm)): 205.8 (-CH=O), 174.0 (-CO_2-), 64.4 (-CO_2-$\underline{C}H_2$-), 52.0 ($\underline{C}$H-CH=O), 34.4 (-$\underline{C}H_2$-CO_2-), 31.9, 29.7, 29.5, 29.4, 29.2, 28.9, 27.1, 22.7 (other CH_2), 14.1 (CH_3).

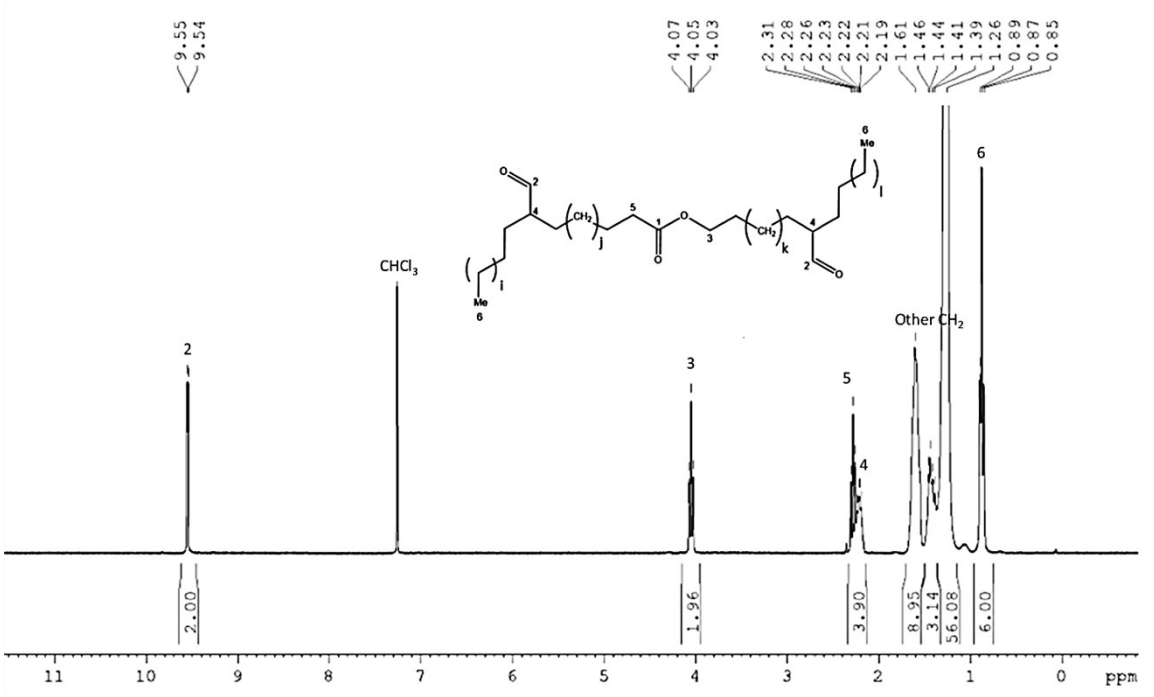


Figure S5. ^{1}H NMR spectrum of hydroformylated jojoba oil ester (300 MHz, $CDCl_3$, 25 °C).

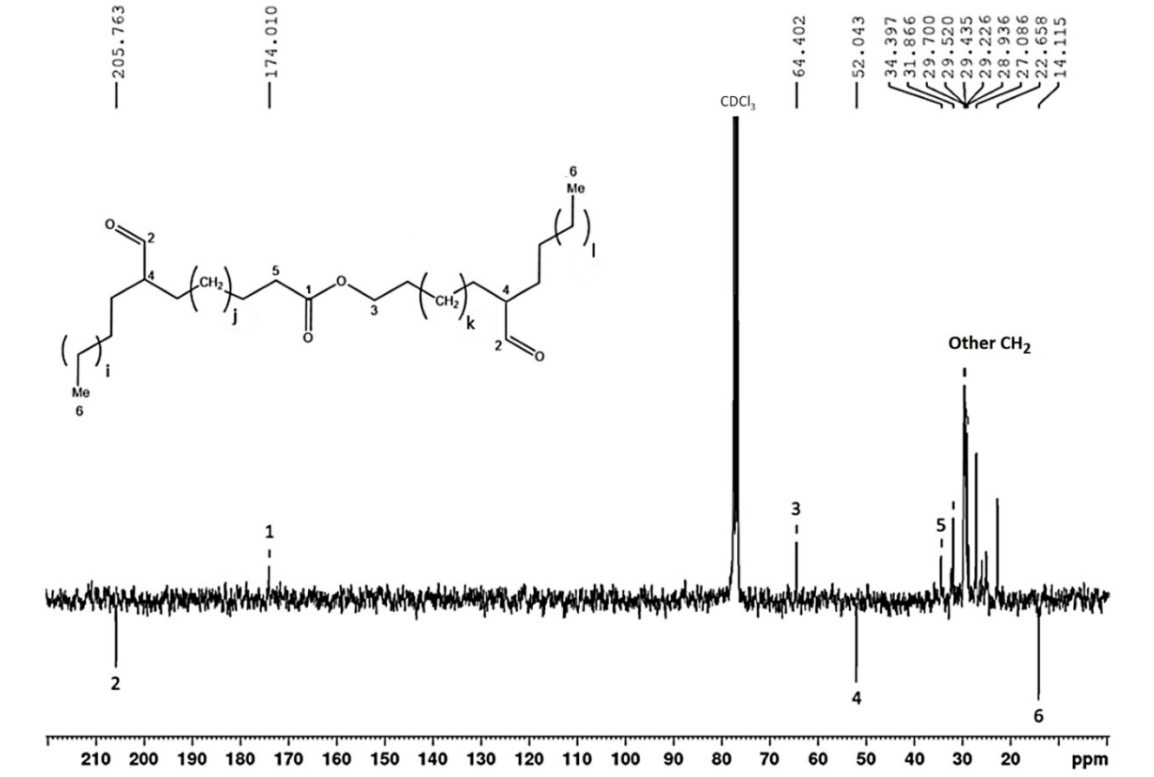
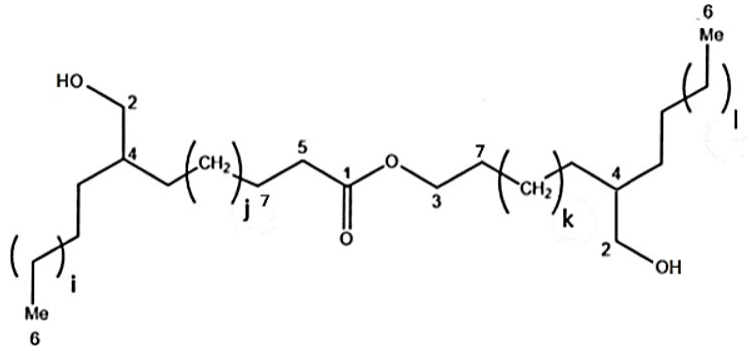


Figure S6. ^{13}C-JMOD NMR spectrum of hydroformylated jojoba oil ester (75 MHz, $CDCl_3$, 25 °C).

III.3 Jojoba oil ester hydrohydroxymethylation products



Hydrohydroxymethylated jojoba oil ester
(liquid at room temperature)

^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C, δ(ppm)): 4.05 (*t*, *J* = 6.7 Hz, 2 H, -CO_2-CH_2-), 3.53 (*d*, *J* = 5.5 Hz, 4 H, -C<u>H</u>$_2$-OH), 2.28 (*t*, *J* = 7.6 Hz, 2 H, -CH_2-CO_2-), 1.61 (*quintet*, *J* = 6.8 Hz, 4 H, -C<u>H</u>$_2$-CH_2-CO_2- *and* -CO_2-CH_2-C<u>H</u>$_2$-), 1.5-1.1 (*m*, C<u>H</u>-CH_2-OH (2 H) and other CH_2 (69 H)), 0.88 (*t*, *J* = 6.9 Hz, 6 H, 2 CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C, δ(ppm)): 174.0 (-CO_2-), 65.7 (-CH_2-OH), 64.4 (-CO_2-<u>C</u>H_2-), 40.5 (<u>C</u>H-CH_2-OH), 34.4 (-<u>C</u>H_2-CO_2-), 31.9, 30.9, 30.1, 29.6, 29.3, 29.2, 28.6 (-CO_2-CH_2-<u>C</u>H_2-), 26.9, 25.9, 25.0 (-<u>C</u>H_2-CH_2-CO_2-), 22.7 (other CH_2), 14.1 (CH_3).

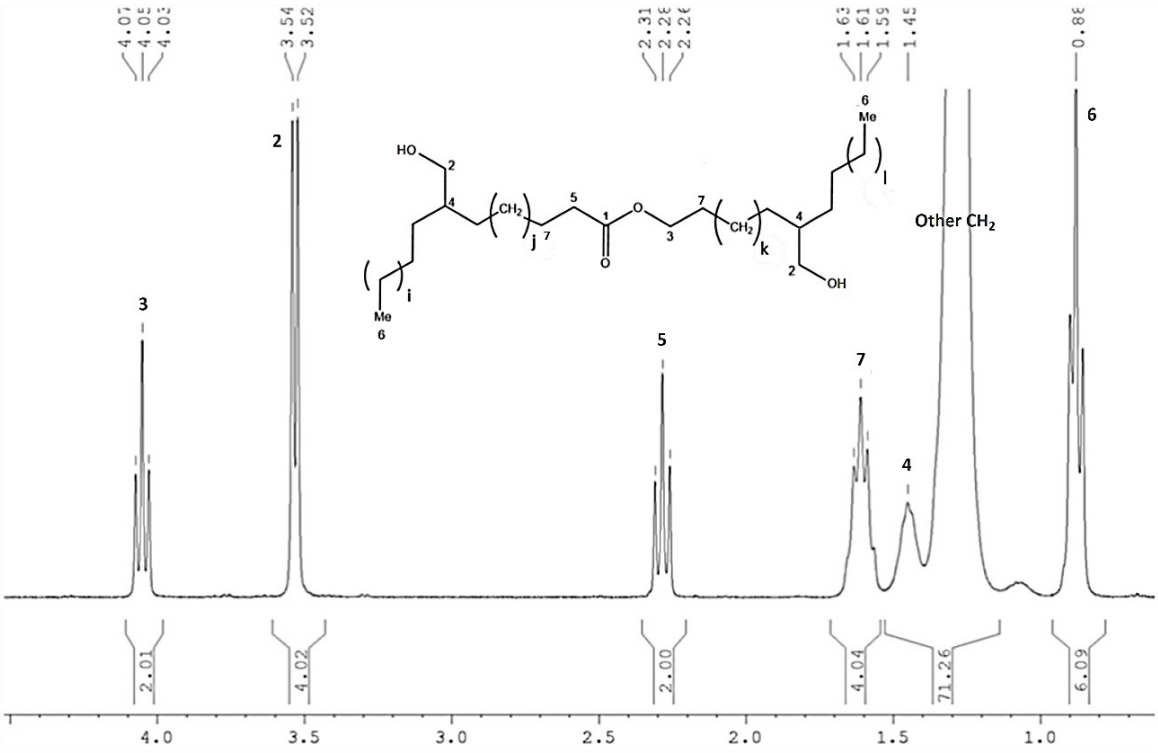


Figure S7. ^{1}H NMR spectrum of hydrohydroxymethylated jojoba oil ester (300 MHz, $CDCl_3$, 25 °C).

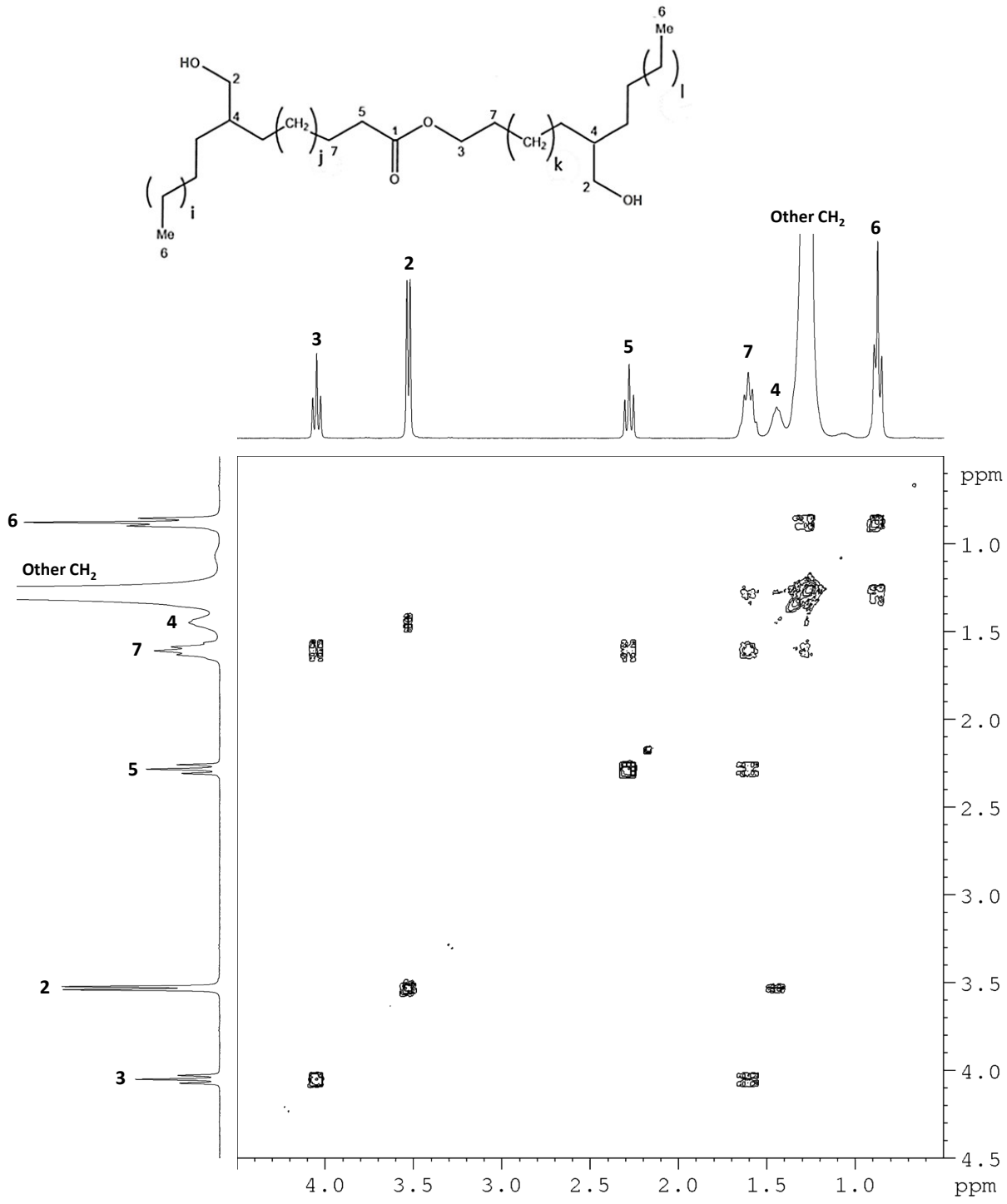


Figure S8. COSY NMR spectrum of hydrohydroxymethylated jojoba oil ester (300 MHz, $CDCl_3$, 25 °C).

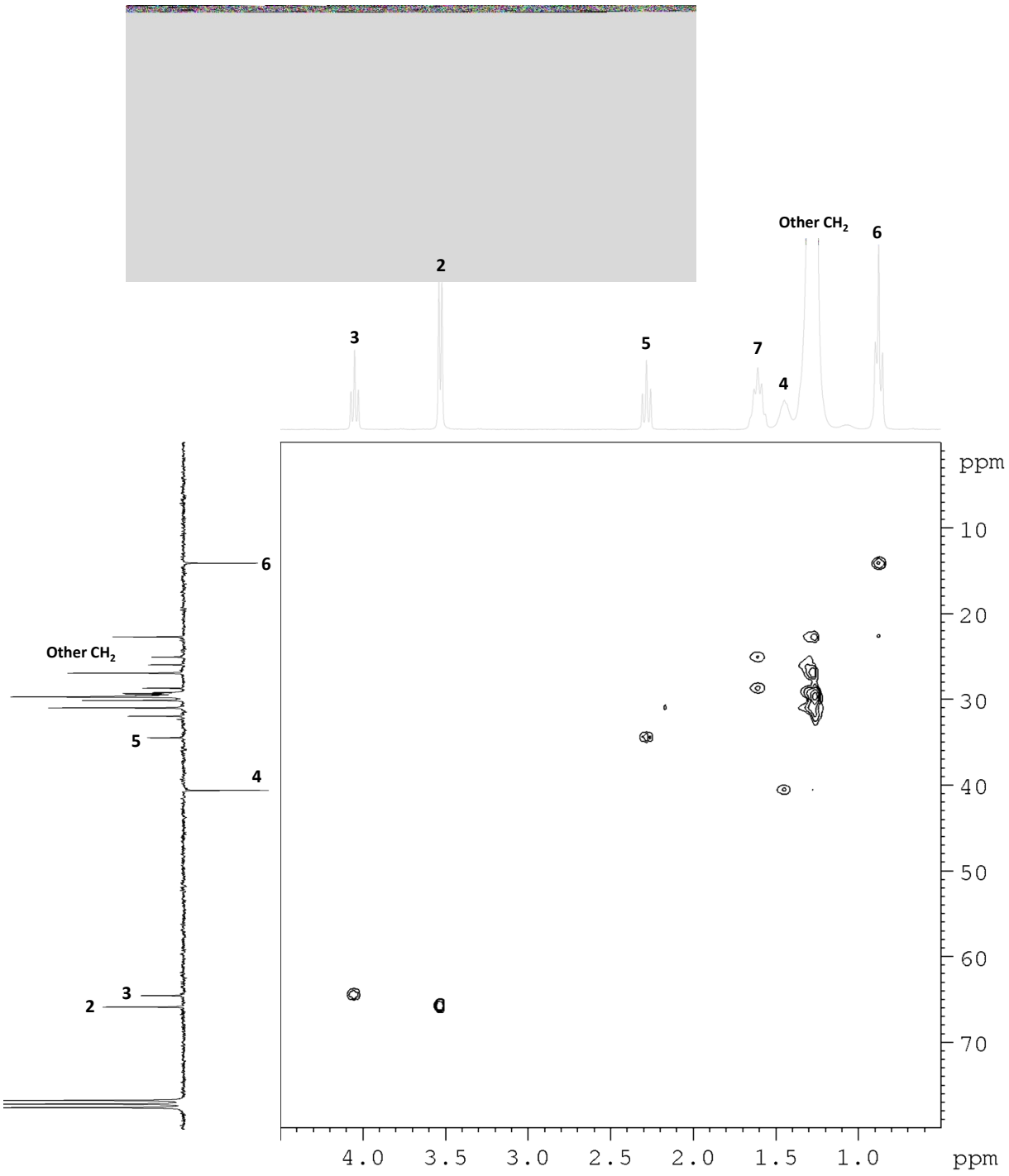


Figure S9. HSQC spectrum of hydrohydroxymethylated jojoba oil ester (300 MHz, $CDCl_3$, 25 °C).

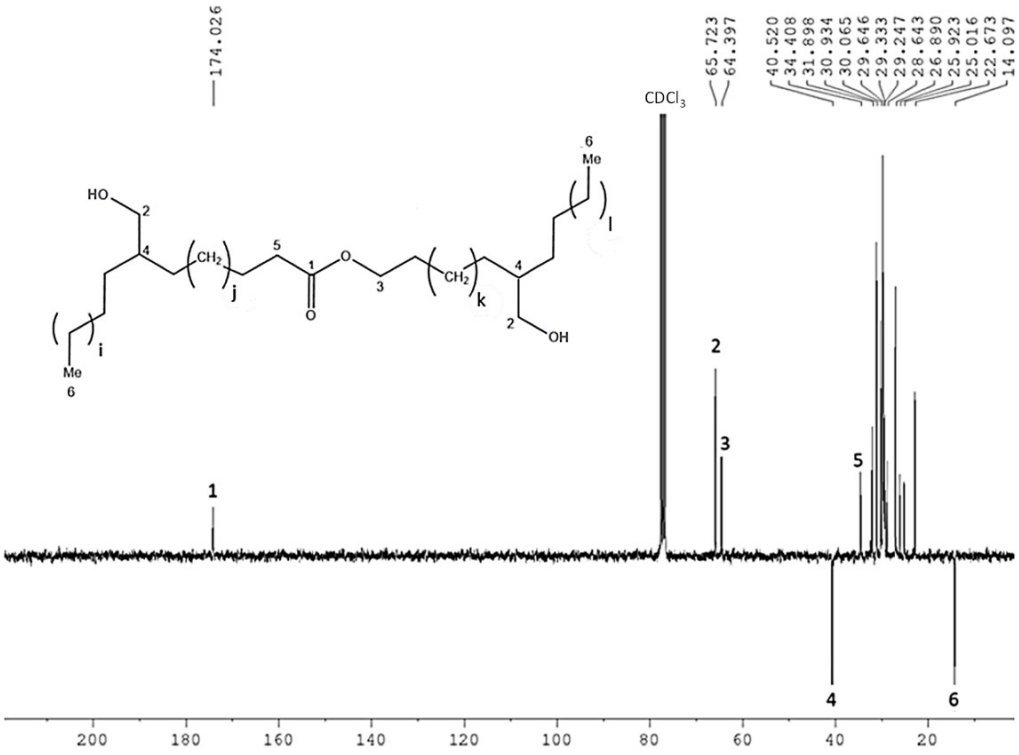
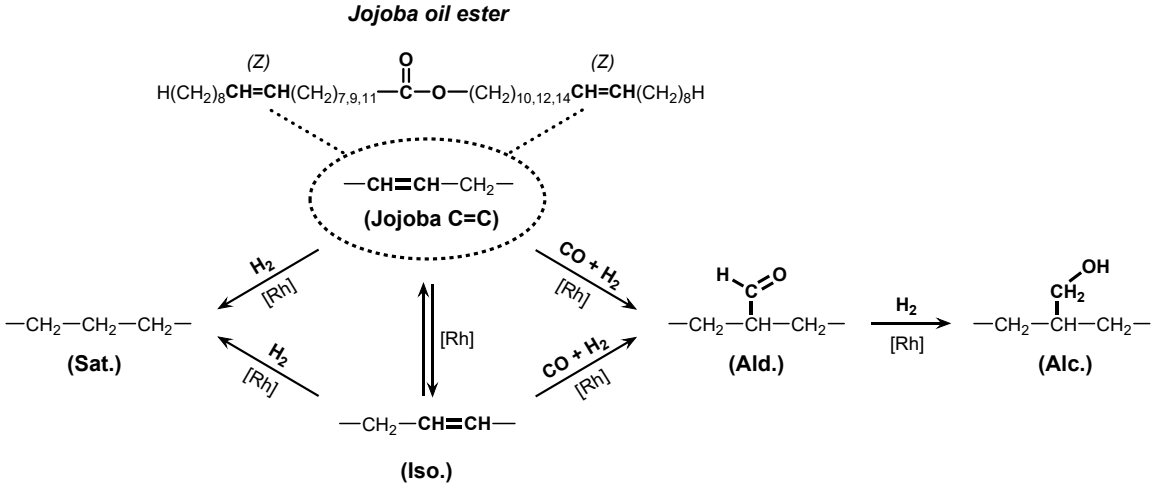


Figure S10. ^{13}C-JMOD NMR spectrum of hydrohydroxymethylated jojoba oil ester (75 MHz, $CDCl_3$, 25 °C).

IV) Determination of conversion and yields for the catalytic experiments

During a catalytic test involving jojoba oil ester as substrate, each of the two C=C double bonds of jojoba oil ester **(Jojoba C=C)** can either be hydrogenated **(Sat.)**, isomerized **(Iso.)**, hydroformylated **(Ald.)** or hydrohydroxymethylated **(Alc.)** (Scheme S1).



Scheme S1. Denomination of the different moieties coming from each double C=C bond of jojoba oil ester.

The **A**, **E**, **R** and **P** signals (for **A**ldehyde, **E**thylenic, **R**eference and **P**rimary alcohol, respectively) present in the ^{1}H NMR spectrum of a reaction medium sample of jojoba oil ester hydrohydroxymethylation (after evaporation of triethylamine and toluene) have been used to calculate global double C=C bond conversion and yields. These signals are presented figure S11 and described in table S1.

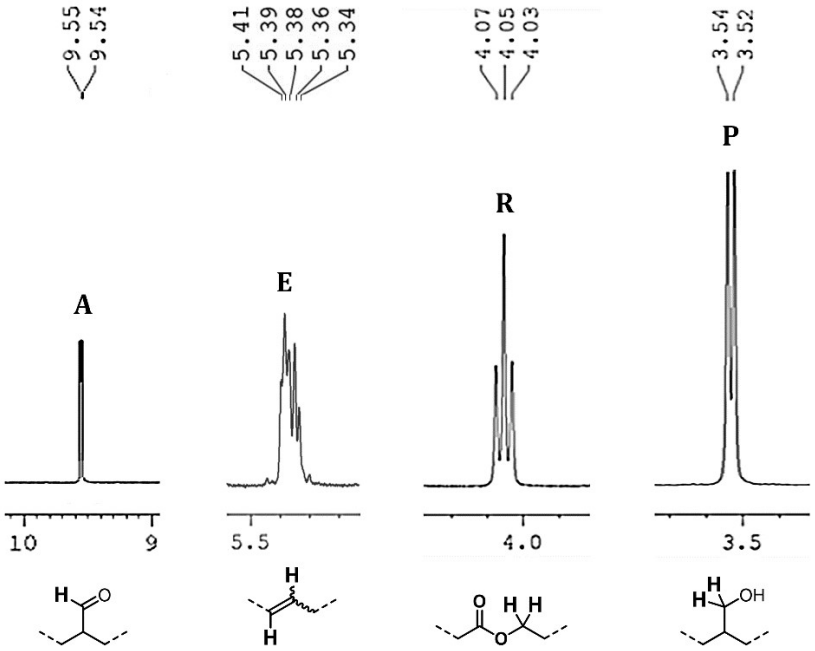
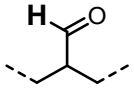
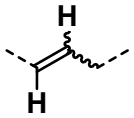
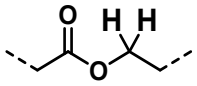
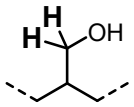


Figure S11. ^{1}H NMR signals whose integration value was used to calculate conversion and yields (300 MHz, $CDCl_3$, 25 °C).

Table S1. Chemical shift zones used for jojoba oil ester C=C bonds conversion and yields determination.

^{1}H NMR signal name	Signal nature	Integration limits (ppm)	Value of integration	Involved moiety	Involved hydrogens on the different moieties	*n* H [a]
A	*d* (9.54 ppm) *J* = 3.0 Hz	9.50-9.60	$\mathbf{I_A}$	**Ald.**		1
E	*m* (5.38 ppm)	5.25-5.45	$\mathbf{I_E}$	**Substrate** and **Iso.**		2
R	*t* (4.05 ppm) *J* = 6.7 Hz	4.00-4.10	$\mathbf{I_R = 100}$ [b]	All compounds		2
P	*d* (3.53 ppm) *J* = 5.5 Hz	3.45-3.60	$\mathbf{I_P}$	**Alc.**		2

[a] ***n* H** = number of hydrogen atoms corresponding to the area defined by the integration limits and per moiety.
[b] **R** NMR signal must be calibrated with the value of $\mathbf{I_R = 100}$.

It is interesting to note that both ethylenic and allylic protons ^{1}H NMR signals (signals **E** and $\mathbf{E_\alpha}$, respectively) undergo a modification of shape during the catalyzed transformation: signals of jojoba oil ester substrate are symmetrical while signals of samples taken during reaction are asymmetrical (Figure S12). So, during the catalytic tests, the *(Z)* C=C double bonds of jojoba oil ester are partially isomerized into *(E) and (Z)* C=C double bonds, with and without migration along aliphatic chains (by classical "association / insertion into Rh-H bond / β-hydride elimination / dissociation" sequence).

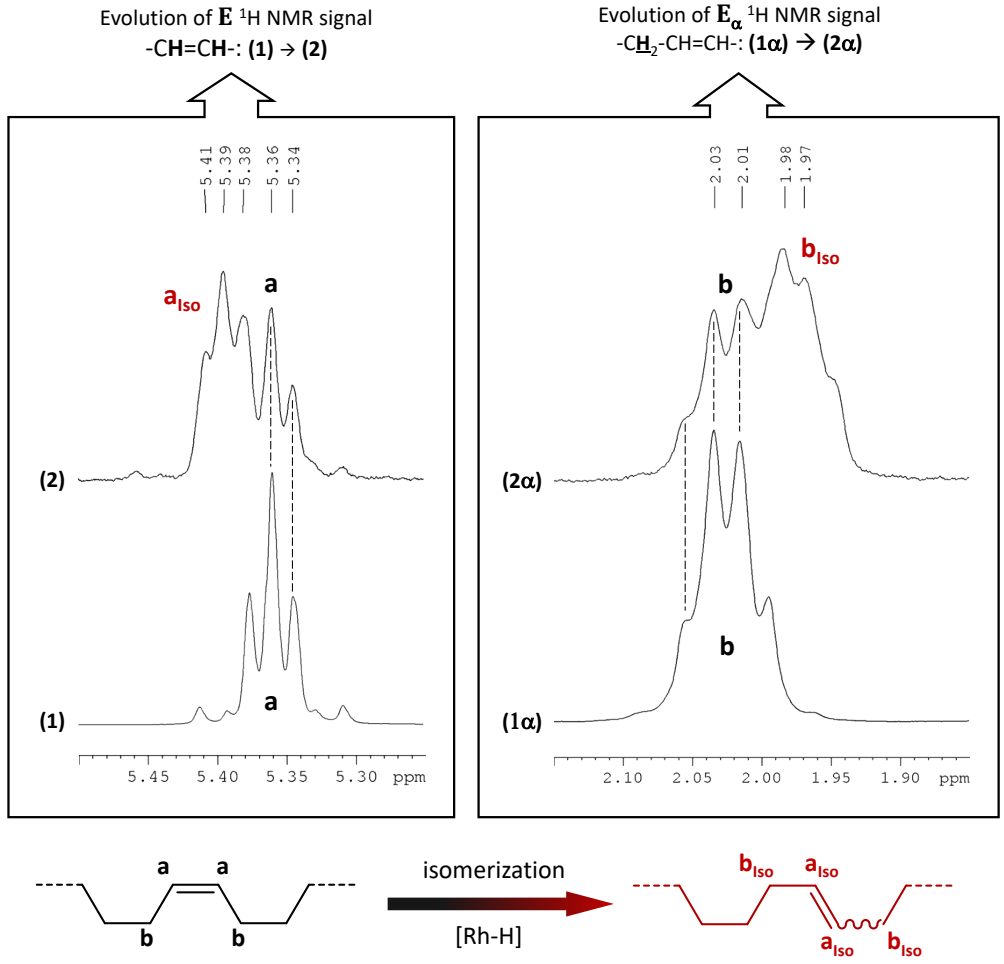


Figure S12. Evolution of ^{1}H NMR signals of jojoba oil ester during the catalytic tests. **(1)** Ethylenic and **(1α)** Allylic hydrogens signals of jojoba oil ester. **(2)** Ethylenic and **(2α)** Allylic hydrogens signals of partially isomerized jojoba oil ester (300 MHz, $CDCl_3$, 25 °C).

The ^{1}H NMR signal taken for normalization of the ^{1}H NMR spectrum of the final reaction medium was the **R** NMR signal (*t* at 4.05 ppm, *J* = 6.7 Hz) whose integration value was called $\mathbf{I_R}$ and which corresponds to the **CH_2** group simply bound to the oxygen of the ester group present in the substrate and in all formed products.

This $\mathbf{I_R}$ integration value must be calibrated at $\mathbf{I_R = 100}$ in the aim to consider a **Total Number** ($\mathbf{N_T}$) of initial C=C double bonds equal to 100, that means a considered transformation of 50 initial jojoba oil ester molecules.

$$\mathbf{N_T = 100} \qquad [1].$$

After this step and from table S1, we can deduce the following equations giving the number $\mathbf{N_{(X)}}$ of each $\mathbf{(X)}$ moiety (among the 100 considered) as a function of the different $\mathbf{I_Y}$ integration values ($\mathbf{Y}$ = $\mathbf{A}$, $\mathbf{E}$ or $\mathbf{P}$).

$$\mathbf{N_{(Ald.)} = I_A} \qquad [2]$$

$$\mathbf{N_{(Jojoba\ C=C)} + N_{(Iso.)} = I_E / 2} \qquad [3]$$

$$\mathbf{N_{(Alc.)} = I_P / 2} \qquad [4].$$

Due to the normalization and by mass conservation, we can write:

$$\mathbf{N_T = N_{(Ald.)} + N_{(Jojoba\ C=C)} + N_{(Iso.)} + N_{(Alc.)} + N_{(Sat.)} = 100} \qquad [5].$$

So, the number of saturated moieties $\mathbf{(Sat.)}$ can be obtained like this:

$$\mathbf{N_{(Sat.)} = 100 - N_{(Ald.)} - N_{(Jojoba\ C=C)} - N_{(Iso.)} - N_{(Alc.)}} \qquad [6].$$

Taking into account the definition of $\mathbf{N_{(X)}}$, the following equations can be written, where **Conv.** represents the global C=C double bonds conversion and $\mathbf{Y_{(X)}}$ the yield in $\mathbf{(X)}$ moiety:

$$\mathbf{Conv.}\,(\%) = \mathbf{100 - N_{(Jojoba\ C=C)} - N_{(Iso.)}} \qquad [7]$$

$$\mathbf{Y_{(Ald.)}}\,(\%) = \mathbf{N_{(Ald.)}} \qquad [8]$$

$$\mathbf{Y_{(Alc.)}}\,(\%) = \mathbf{N_{(Alc.)}} \qquad [9]$$

$$\mathbf{Y_{(Sat.)}}\,(\%) = \mathbf{N_{(Sat.)}} \qquad [10].$$

Introducing equations [2], [3], [4] and [6] into equations [7]-[10] gives expressions of global C=C double bonds conversion and yields in the different aldehyde, alcohol and alkane moieties in function of the integration values $\mathbf{I_A}$, $\mathbf{I_E}$ and $\mathbf{I_P}$ (equations [11]-[14]).

$$Conv.(\%) = 100 - \frac{I_E}{2} \qquad [11]$$

$$Y_{(Ald.)}(\%) = I_A \qquad [12]$$

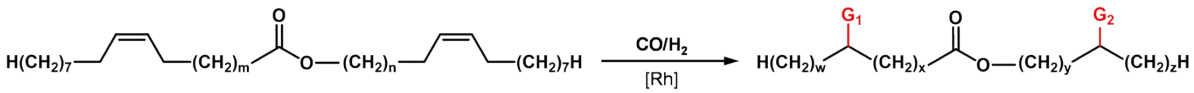
$$Y_{(Alc.)}(\%) = \frac{I_P}{2} \qquad [13]$$

$$Y_{(Sat.)}(\%) = 100 - I_A - \frac{I_E + I_P}{2} \qquad [14].$$

V) Kinetic follow-up of a jojoba oil ester HHM test and catalyst FT-IR and NMR analyses

Table S2 presents the data corresponding to the kinetic follow-up of a jojoba oil ester HHM test (the corresponding curve appears in the manuscript as Figure 1).

Table S2. Rhodium-catalyzed reductive hydroformylation of jojoba oil in various conditions.



Jojoba oil ester

m = 6, 8 or 10; n = 9, 11 or 13

-G_1, -G_2 = -CHO (Ald.), **-CH_2OH** (Alc), or **-H** (Sat.)

w, x, y, z = 0, 1, 2 ... ; w + x = 16, 18 or 20; y + z = 19, 21 or 23

Entry	t(h)	C(%)[b]	$Y_{Ald.}$(%)[c]	$Y_{Alc.}$(%)[c]	$Y_{Sat.}$(%)[c]
1	1	14	5	8	1
2	2	25	6	18	1
3	4	42	4	37	1
4	6	56	2	53	1
5	8	67	1	65	1
6	10	75	1	73	1
7	24	97	0	96	1

Experimental conditions: $Rh(acac)(CO)_2$ (36 mg, 140 µmol, 1 equiv.), jojoba oil ester (10.53 g, 17.4 mmol, 125 equiv.), TEA (14.2 g, 140 mmol, 1000 equiv.), toluene (19.5 mL), 80 bar of $CO:H_2$ (1:1), 80 °C, 1500 rpm [b]C = global CC double bond conversion = total amount of CC double bonds in the starting jojoba oil ester and in the CC double bond isomerized ester that have been transformed into other products (Ald., Alc. and Sat.). [c]Y_x = yield in X with respect to CC double bonds, determined by ^{1}H NMR.

This catalytic test was carried out a second time under the same conditions but without taking intermediate samples. This second test gave exactly the same result after 24 h (96% yield of alcohols). The full mixture obtained at 24 h was then percolated on a silica column (4 g of Silica gel 60A (30-70 µm) in a column of 2 cm of internal diameter). The silica was washed with 200 mL of toluene to remove reaction products and triethylamine. The rhodium was recovered by flushing the silica with 20 mL of acetone.

The obtained solution was concentrated by evaporation to give 105 mg of a dark pasty solid, then analyzed by FT-IR (Figure S13) and NMR (Figure S14). The IR analysis revealed that this solid was composed of a mixture of rhodium carbonyl clusters (presence of stretching bands of terminal CO ligands (t-CO, at 1995 and 2073 cm^{-1}) and of bridging CO ligands (µ-CO, 1680-1720 cm^{-1})) and of residual hydrohydroxymethylated jojoba oil ester (less than 1% of the total amount of diol produced by the test which involved 10.53 g of jojoba oil ester as substrate). The NMR analyses confirmed the presence of jojoba oil ester diol in the solid and no rhodium-hydride bond was evidenced in the ^{1}H NMR spectrum at low chemical shift, in the analysis conditions (Figure S14 (a)).

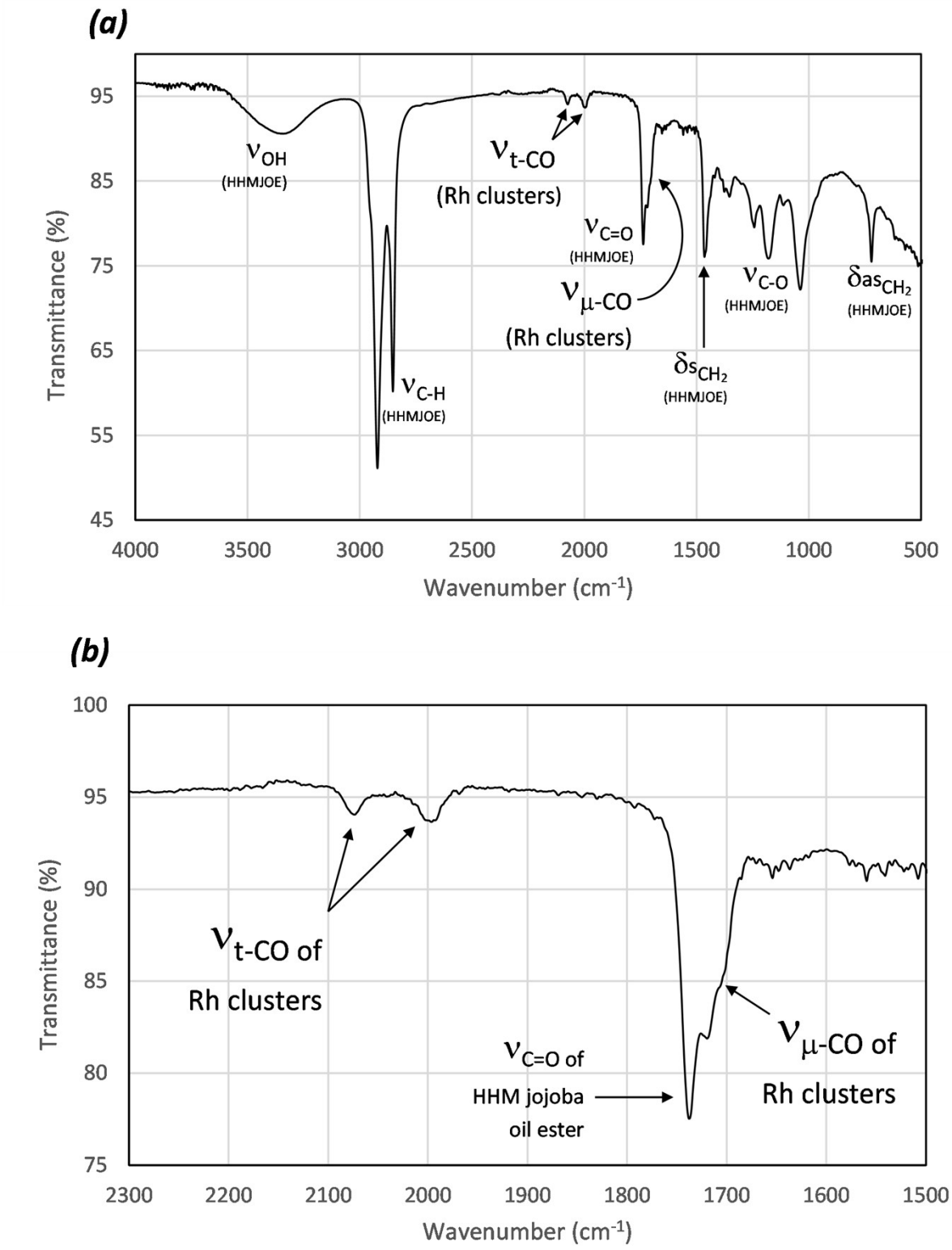


Figure S13. FT-IR spectra of the solid coming from the concentration of the solution obtained after flushing the silica with acetone in the catalyst recovering protocol. (a) full spectrum and (b) zoom between 1500 and 2300 cm^{-1}. HHMJOE = hydrohydroxymethylated jojoba oil ester.

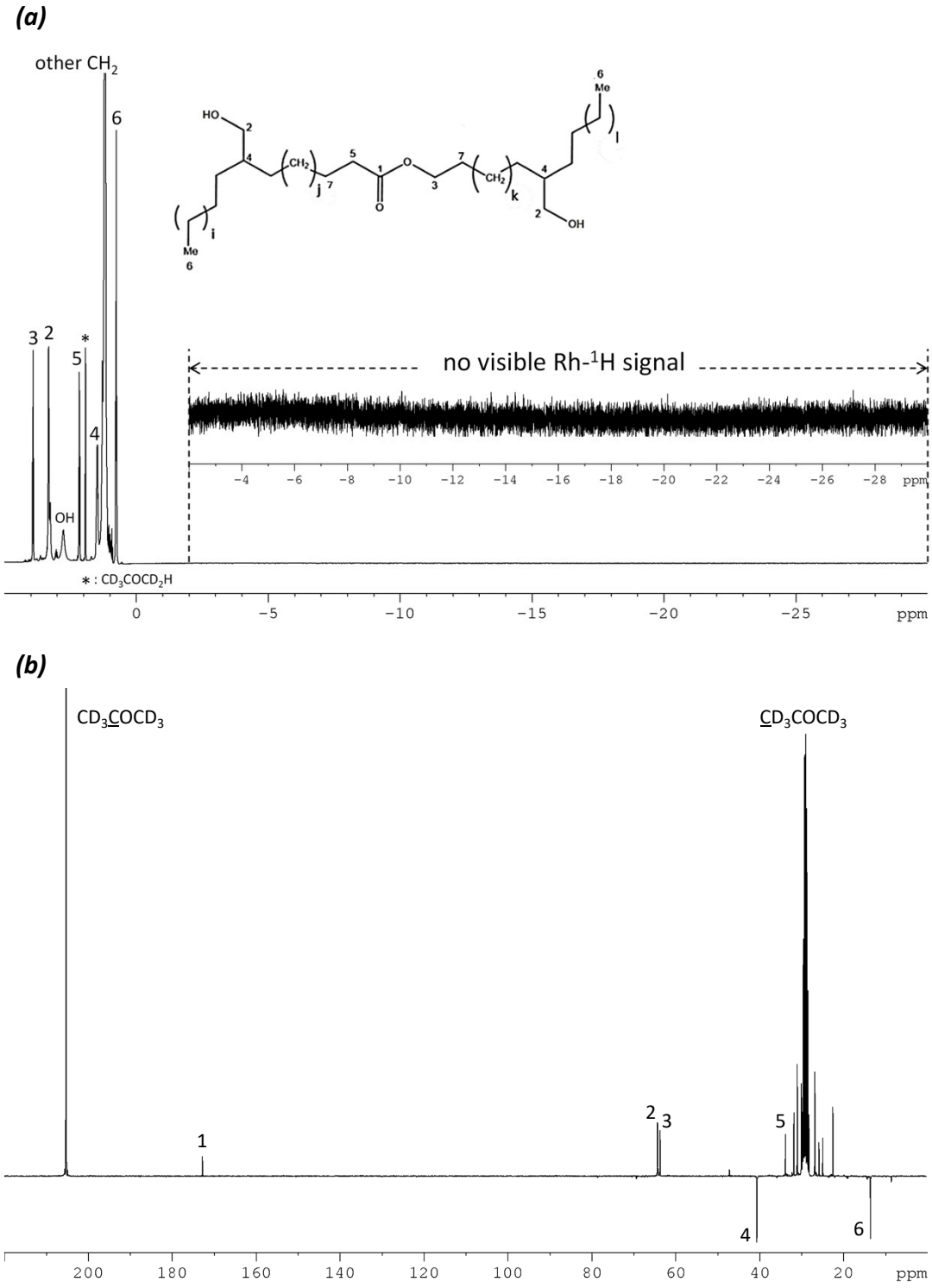


Figure S14. NMR spectra of the solid coming from the concentration of the solution obtained after flushing the silica with acetone in the catalyst recovering protocol. (a) ^{1}H NMR spectrum (300 MHz, acetone-d_6, 25 °C) and (b) $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, acetone-d_6, 25 °C).

VI) Synthesis and characterization of the thermosets

VI.1 Synthesis procedure

For the synthesis of **PU1**, Glycerol (0.041 g, 0.3 equiv. of OH functions) and hydrohydroxymethylated jojoba oil (1 g, 0.7 equiv. of OH functions) were stirred 1 min in a SpeedMixer at 2 500 rpm. Then Tolonate™ X FLO 100 (1.522 g, 1 equiv. of NCO functions) was added and the mixture was stirred 1 min at 2 500 rpm once again. The liquid mixture was then poured in aluminum mold and cured at 100 °C for 15 h then at 140 °C for 2 h.

For the synthesis of **PU2**, the same protocol was used except that hydrohydroxy-methylated jojoba oil was replaced by Pripol®2033 (0.847 g, 0.7 equiv. of OH functions).

VI.2 Characterizations

i. IR, TGA and DSC analyses

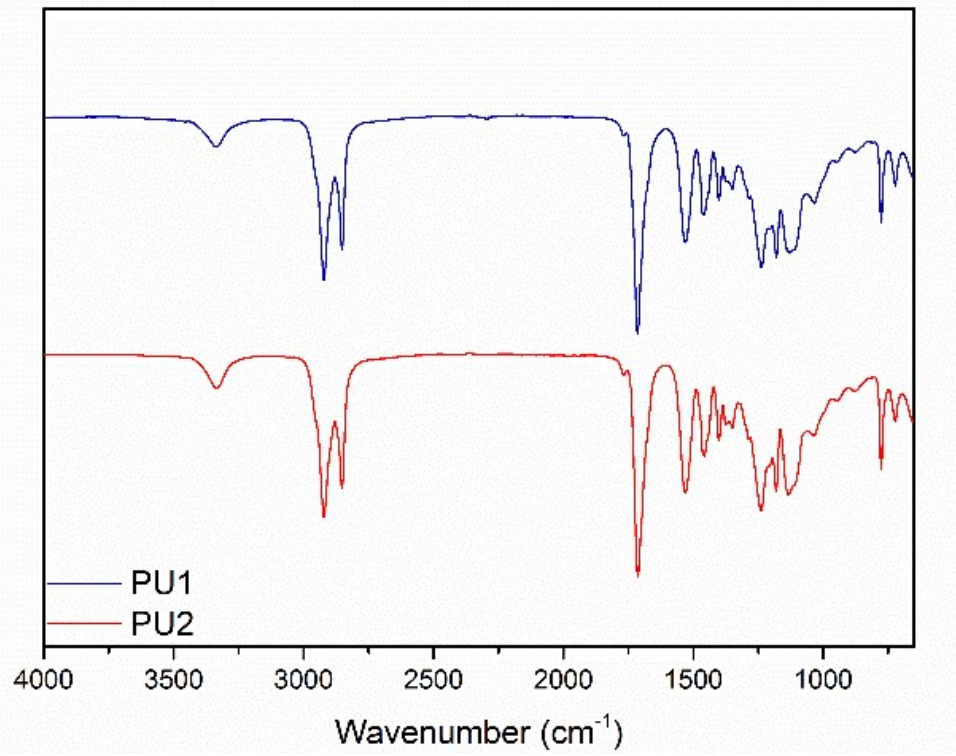


Figure S15. FT-IR spectra of polyurethanes (PUs).

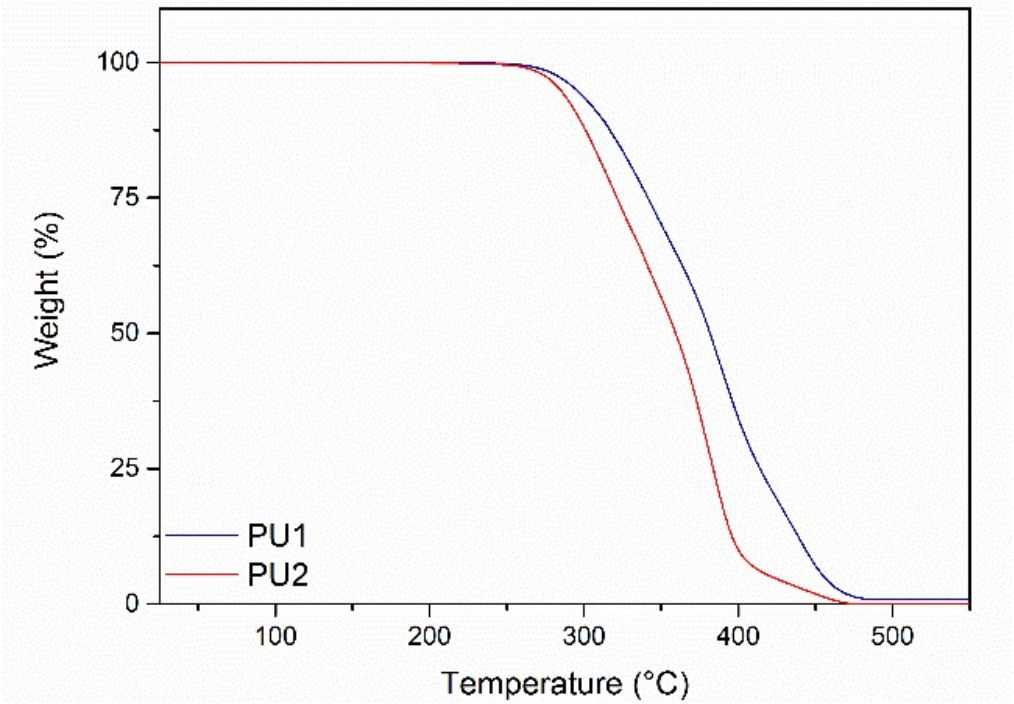


Figure S16. TGA thermograms of PUs.

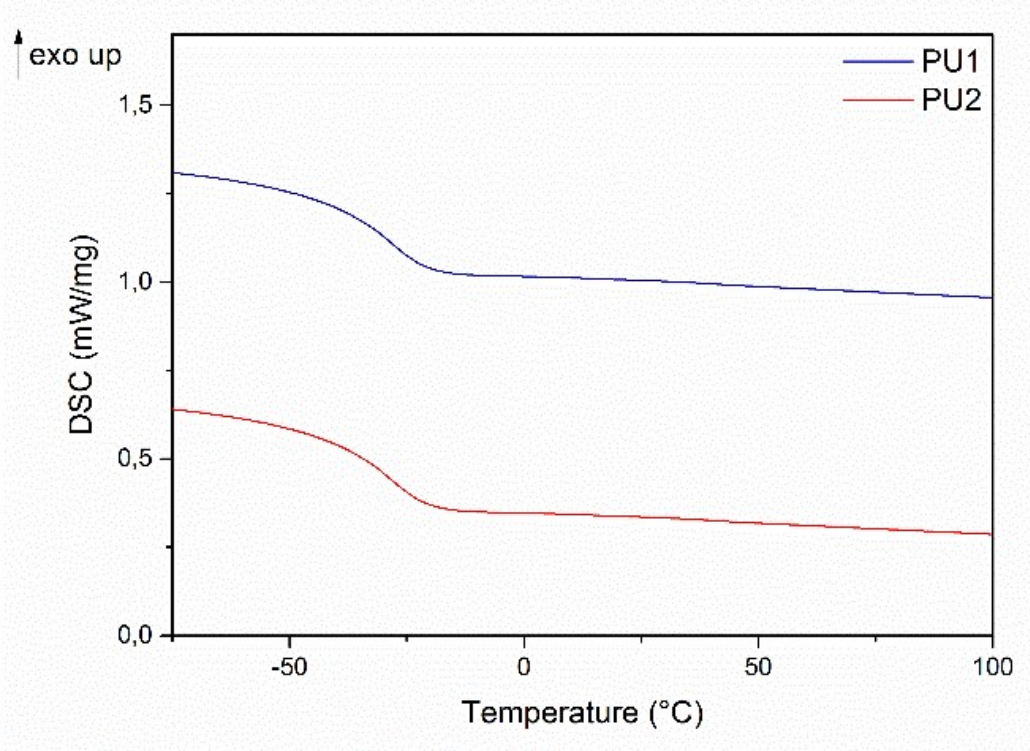


Figure S17. DSC thermograms of PUs.

ii. Titration of the alcohol equivalent weight by ^{1}H NMR

The Alcohol Equivalent Weight (**AEW**, in g.mol^{-1}) is the weight of product needed (in g) to get one mole of reactive alcohol functions. It was determined by ^{1}H NMR using an internal standard (benzophenone). A known weight of product and benzophenone were poured into an NMR tube and 500 µL of $CDCl_3$ were added. AEW was determined using equation [15] by comparing the integral of the protons of the benzophenone (7.5-7.8 ppm) and the integral of the alcohol moiety (3.66 ppm for Pripol® 2033 and 3.53 ppm for primary alcohols obtained from jojoba oil by HHM).

$$AEW = \frac{\int PhCOPh \times H_{alcohol}}{\int alcohol \times H_{PhCOPh}} \times \frac{m_{alcohol}}{m_{PhCOPh}} \times M_{PhCOPh} \quad [15].$$

∫PhCOPh*: integration of the benzophenone protons;* ***∫alcohol****: integration of the protons in α of the alcohol function;* $H_{alcohol}$*: number of protons in α of the alcohol function;* H_{PhCOPh}*: number of protons of the benzophenone;* $m_{alcohol}$*: weight of the product;* m_{PhCOPh}*: weight of the benzophenone;* M_{PhCOPh}*: molecular weight of the benzophenone.*

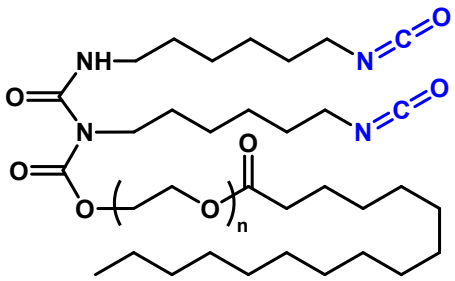
The AEW values found by ^{1}H NMR for the diol monomers (table S3, entry 5) are in good accordance with the theoretical AEW calculated from compound structures (table S3, entry 4). For glycerol, the theoretical value of AEW = 30.7 was taken (table S3, entry 4).

Table S3. Comparison of experimental and theoretical AEW values for polyol monomers.

		HHM Jojoba oil	**Pripol®2033**	**Glycerol**
Entry 1	Formula	$C_{43}H_{86}O_4$ (a)	$C_{36}H_{72}O_2$	$C_3H_8O_3$
Entry 2	Molecular Weight (g.mol^{-1})	668	537	92.1
Entry 3	v = Number of OH / molecule	2	2	3
Entry 4	Theoretical AEW (= MW/v; g.mol^{-1})	334	268.5	30.7
Entry 5	**Experimental AEW (g.mol^{-1}) determined by ^{1}H NMR**	**320**	**271**	**-**

(a) Average molecular formula.

Remark: the Isocyanate Equivalent Weight (**IEW**, in g.mol^{-1}, corresponding to the weight, in g, of product needed to get one mole of reactive isocyanate functions) taken for **Tolonate ™ X FLO 100** was the commercial value: **341 g.mol^{-1}** (source: Vencorex® Chemicals). This commercial value leads to a molecular weight of 682 g.mol^{-1} (Tolonate ™ X FLO 100 being a diisocyanate) and then to the average value of **n = 2** in the following structure of Tolonate ™ X FLO 100.



Tolonate ™ X FLO 100
(**n** average value = **2**)
MW = 682 g.mol^{-1}
$C_{36}H_{64}N_4O_8$

iii. Cross-linking density

From rubber elasticity theory, the uniaxial stretching was studied on the rubbery plateau at T > Tα+50, and at very small deformations. Under these hypotheses, the cross-linking density (ν'), can be obtained from equation [16].

$$\nu' = \frac{E'_{at\ T\alpha + 50}}{3RT_{\alpha + 50}} \qquad [16].$$

E' is the storage modulus (Pa), R is gas constant (8.314 J.K^{-1}.mol^{-1}) and Tα is the temperature, in K, of transition from vitreous to rubber domain of material determined at the maximum of **E"**. Calculated values are given for information purposes and can only be compared.

iv. Swelling index

Three samples of around 10 mg each were separately put in THF for 24 h. The swelling index (**SI**) was calculated using the equation [17] where $\mathbf{m_2}$ is the mass of the material after swelling in THF and $\mathbf{m_1}$ is the initial mass of the material.

$$SI = \frac{m_2 - m_1}{m_1} \times 100 \qquad [17].$$

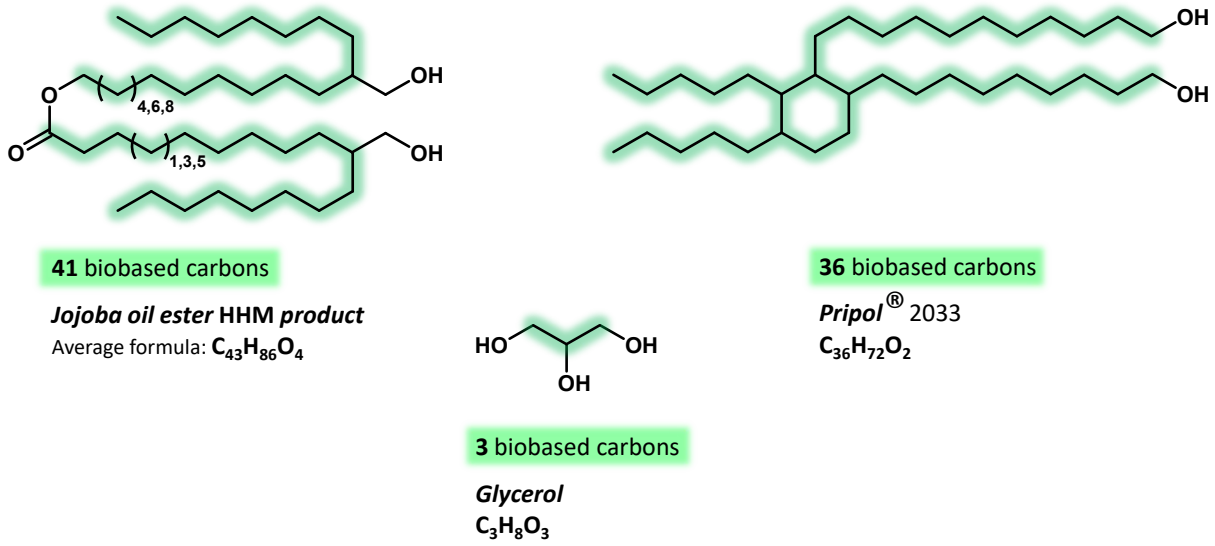
v. Gel Content

After SI measurements, the three samples were dried in a ventilated oven at 70 °C for 24 h. The gel content (**GC**) was calculated using the equation [18], where $\mathbf{m_3}$ is the mass of the material after drying and $\mathbf{m_1}$ is the initial mass of the material.

$$GC = \frac{m_3}{m_1} \times 100 \qquad [18].$$

vi. Determination of the biobased carbon content of PUs

Scheme S2 presents the biobased carbon parts of the polyols used in this study.



41 biobased carbons

Jojoba oil ester* HHM *product
Average formula: $C_{43}H_{86}O_4$

36 biobased carbons

***Pripol*®** 2033
$C_{36}H_{72}O_2$

3 biobased carbons

Glycerol
$C_3H_8O_3$

Scheme S2. Carbon biobased parts of the different polyols used (highlighted in green).

On this basis and taking into account to molar amounts of the monomers used for the polyurethanes' preparation, tables S4 and S5 explain how the biobased carbon contents of **PU1** and **PU2** were calculated. The values found are equal to 61 and 60%, respectively.

Table S4. Determination of the biobased carbon content of **PU1**.

	Tolonate ™ X FLO 100	**HHM Jojoba oil**	**Glycerol**
Formula	$C_{36}H_{64}N_4O_8$ [(a)]	$C_{43}H_{86}O_4$ [(a)]	$C_3H_8O_3$
Total number of carbon ($\mathbf{x_i}$)	$x_1 = 36$	$x_2 = 43$	$x_3 = 3$
Number of biobased carbon ($\mathbf{y_i}$)	$y_1 = 11.5$ [(b)]	$y_2 = 41$	$y_3 = 3$
Molar amounts ($\mathbf{z_i}$) [(c)]	$z_1 = 1$	$z_2 = 0.7$	$z_3 = 0.2$

$$Biobased\ carbon\ content\ of\ PU1\ (\%) = \frac{\sum_{i=1}^{3} y_i \times z_i}{\sum_{i=1}^{3} x_i \times z_i} \times 100 = 61$$

(a) Average molecular formula; (b) Tolonate™ X FLO 100 is known to contain 32% of renewable carbons (source: Vencorex® Chemicals), so $y_1 = 0.32 \times x_1 = 11.5$; (c) z_i is the relative molar amounts of the three involved molecules (z_1=1, z_2=0.7 and z_3=0.2, corresponding to 2 NCO, 1.4 OH and 0.6 OH functions respectively, that means 1 NCO function for 1 OH function and 1.4 / 2 = 70% of the OH functions coming from the HHM Jojoba oil (30% from the glycerol).

Table S5. Determination of the biobased carbon content of **PU2**.

	Tolonate ™ X FLO 100	**Pripol®**2033	**Glycerol**
Formula	$C_{36}H_{64}N_4O_8$ [(a)]	$C_{36}H_{72}O_2$	$C_3H_8O_3$
Total number of carbon ($\mathbf{x_i}$)	$x_1 = 36$	$x_2 = 36$	$x_3 = 3$
Number of biobased carbon ($\mathbf{y_i}$)	$y_1 = 11.5$ [(b)]	$y_2 = 36$	$y_3 = 3$
Molar amounts ($\mathbf{z_i}$) [(c)]	$z_1 = 1$	$z_2 = 0.7$	$z_3 = 0.2$

$$Biobased\ carbon\ content\ of\ PU2\ (\%) = \frac{\sum_{i=1}^{3} y_i \times z_i}{\sum_{i=1}^{3} x_i \times z_i} \times 100 = 60$$

(a) Average molecular formula; (b) Tolonate™ X FLO 100 is known to contain 32% of renewable carbons (source: Vencorex® Chemicals), so $y_1 = 0.32 \times x_1 = 11.5$; (c) z_i is the relative molar amounts of the three involved molecules (z_1=1, z_2=0.7 and z_3=0.2, corresponding to 2 NCO, 1.4 OH and 0.6 OH functions respectively, that means 1 NCO function for 1 OH function and 1.4 / 2 = 70% of the OH functions coming from the HHM Jojoba oil (30% from the glycerol).