Electronic Supplementary Information

Rhodium-catalyzed one pot synthesis of hydroxymethylated triglycerides

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Materials and methods

All chemicals were purchased from Acros, Strem or Aldrich Chemicals in their highest purity. Olive oil was purchased from Aldrich while Very High Oleic Sunflower Oil (VHOSO) was provided by Novance (France). NMR spectra were recorded on a Bruker DRX300 spectrometer operating at 300 MHz for ^{1}H nuclei and 75 MHz for ^{13}C nuclei. $CDCl_3$ (99.50% isotopic purity) were purchased from Eurisotop.

Triolein (European Pharmacopoeia Reference Standard Triolein from Sigma-Aldrich, http://www.sigmaaldrich.com/catalog/product/sial/y0001113) was used as model triglyceride. Compared to technical grade triglycerides, its purity and symmetrical structure derived from glycerol and oleic acid has the significant advantage of facilitating the analysis of the reaction products.

GC-MS analysis were performed using a Shimadzu GC-17A gas chromatograph using a Varian capillary column (length 30 m, internal diameter 0.025 µm) and a Shimadzu GCMS-QP500 mass spectrometer. The products were analyzed using a temperature gradient from 250 °C to 300 °C at 1.5 °C/min.

Mass spectra were recorded on a MALDI-TOF/TOF Ultraflex II Bruker Daltonics spectrometer in positive reflectron or linear mode with 2,5-dihydroxybenzoic acid (DHB) as matrix.

All the hydroformylation experiments were carried out in laboratory reactors from Parr Instrument Company (USA). To prevent oxidation of the catalyst precursors, the reaction mixture was transferred into the reactor using the standard Schlenk technique.

Size-exclusion chromatography (SEC) was performed at the French Institute of Fats and Oils (ITERG – Pessac, France).

^{13}C NMR (JMOD) spectrum

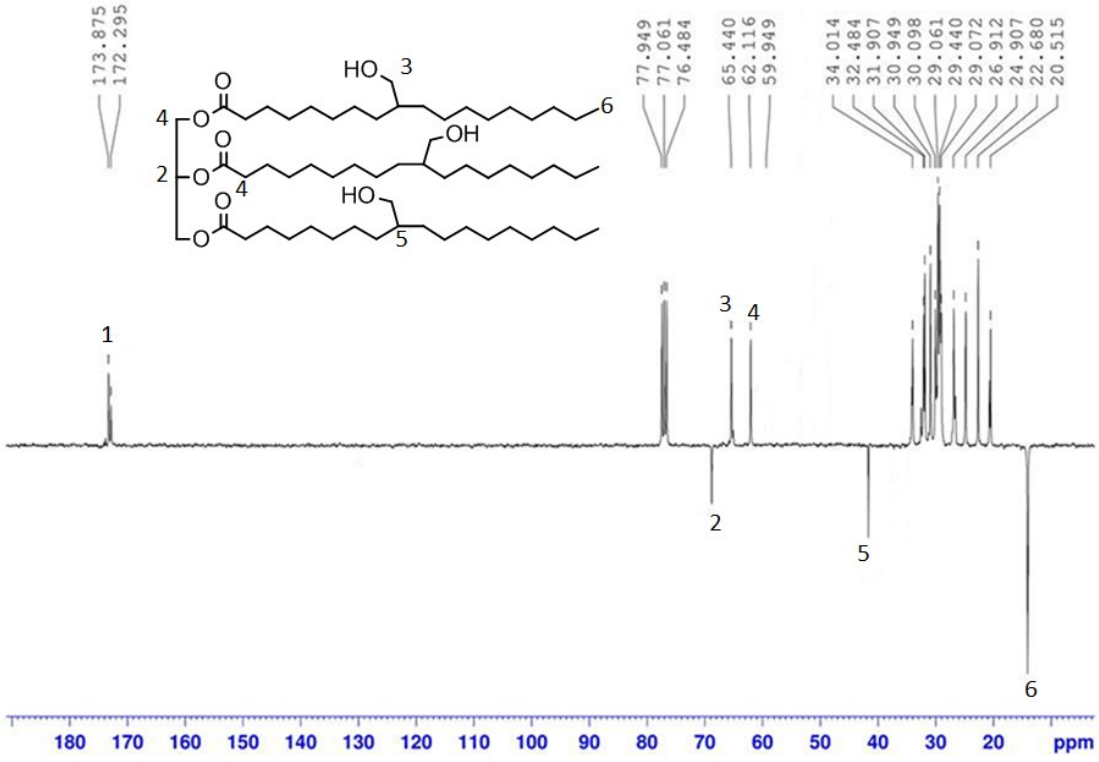


Figure S1. ^{1}H NMR spectrum of hydroxymethylated triolein in $CDCl_3$ at 25 °C.

Transesterification of hydroxymethylated triolein

To ensure the presence of hydroxymethyl groups along the fatty acid chains, the functionalized triolein is transesterified with methanol to form fatty acid methyl ester that are more easily identifiable. The transesterification is performed as follows: 1 g trihydroxymethyl-triolein is dissolved in 10 mL of MeOH with a catalytic amount of sodium methoxide (5 mg). The mixture is vigorously stirred under reflux for 36 h. After solvent evaporation, the products are dissolved in Et_2O and washed three times with water to remove the methanol and the alkaline catalyst. Et_2O is then evaporated and the resulting products are analyzed by NMR.

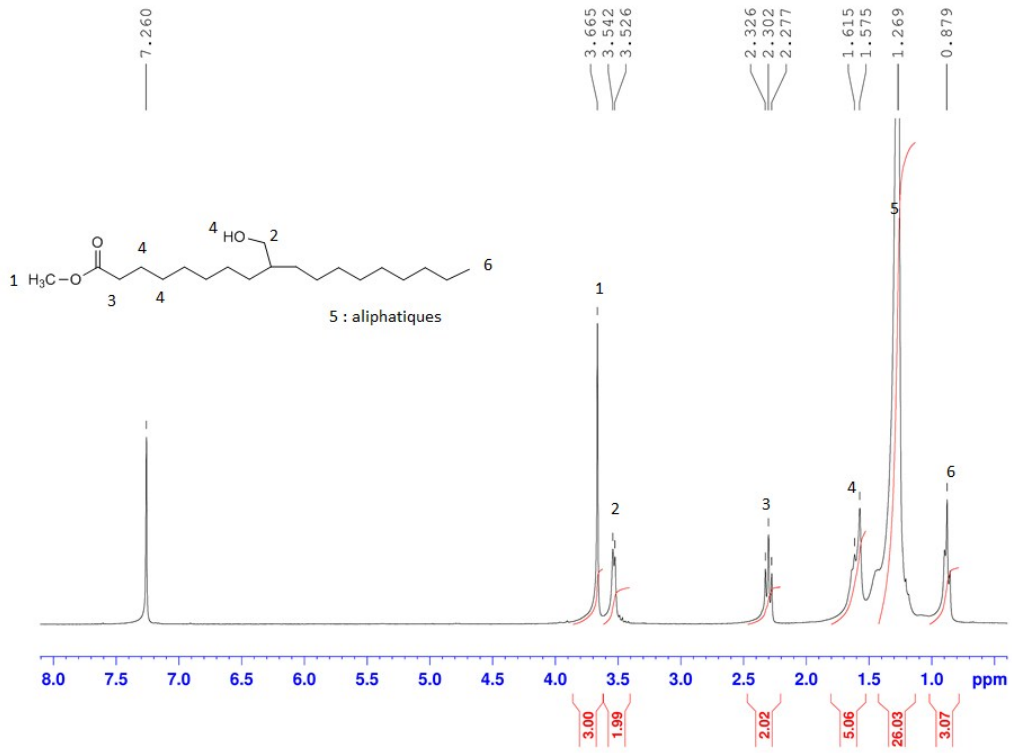


Figure S2. ^1H NMR spectrum of hydroxymethylated fatty acid methyl ester in $CDCl_3$ at 25 °C.

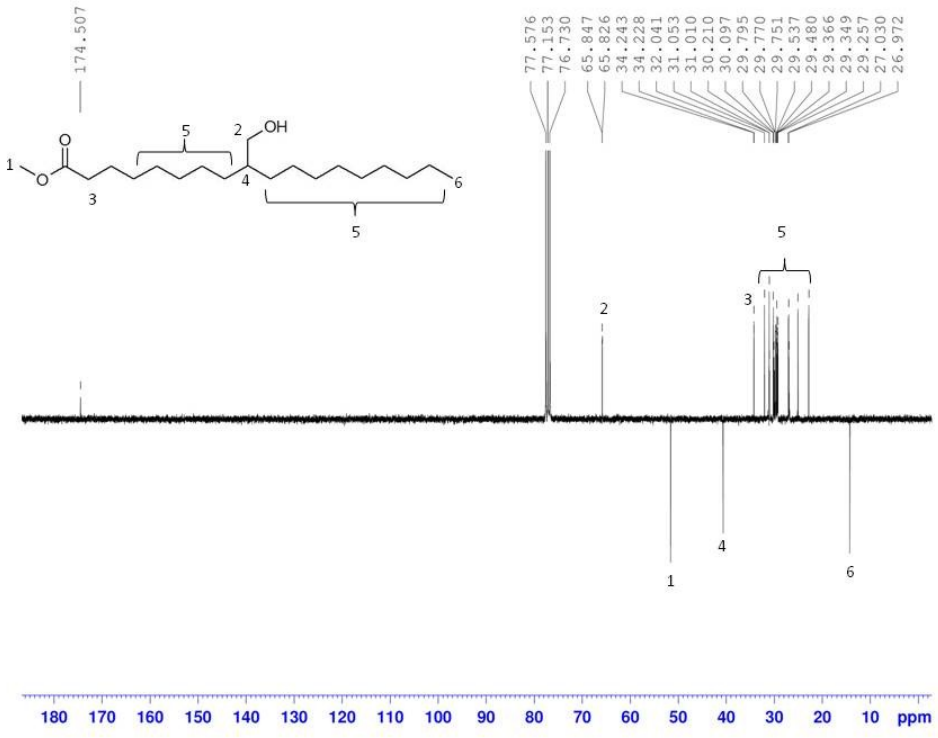


Figure S3. ^{13}C NMR (JMOD) spectrum of hydroxymethylated fatty acid methyl ester in $CDCl_3$ at 25 °C.

Mass spectrometry (MALDI TOF)

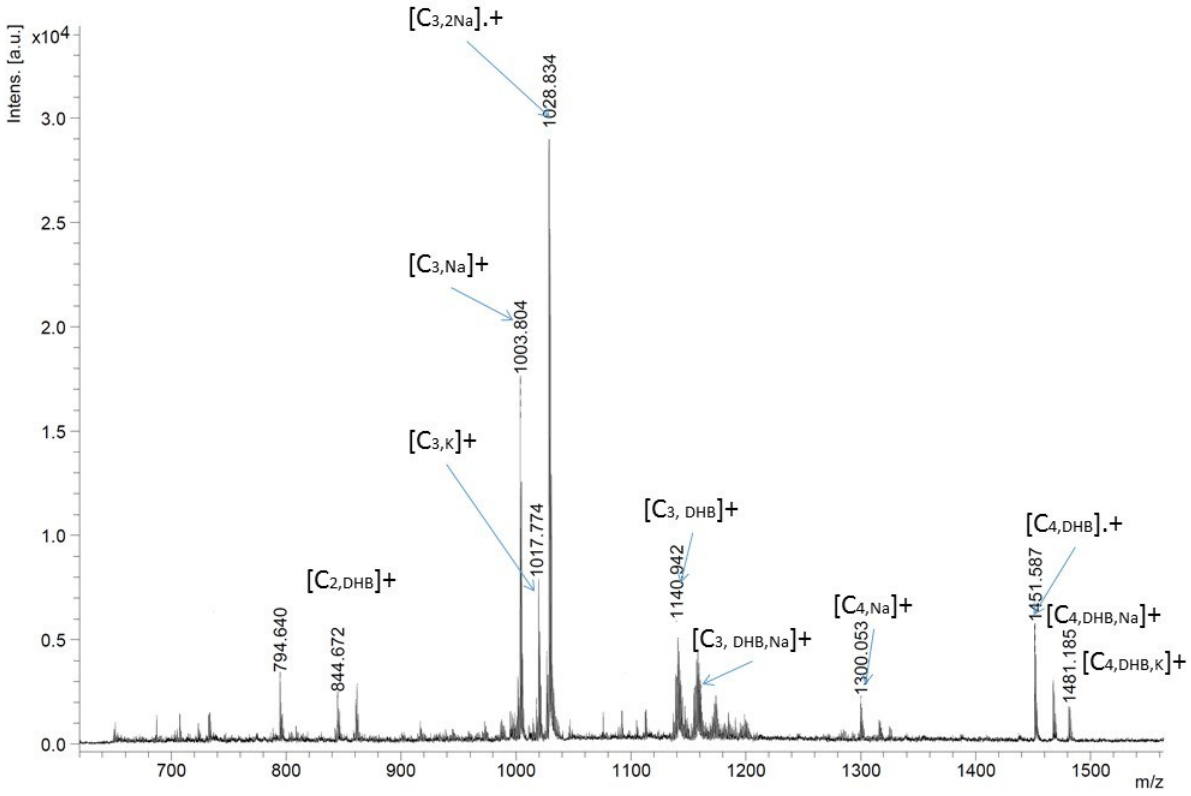
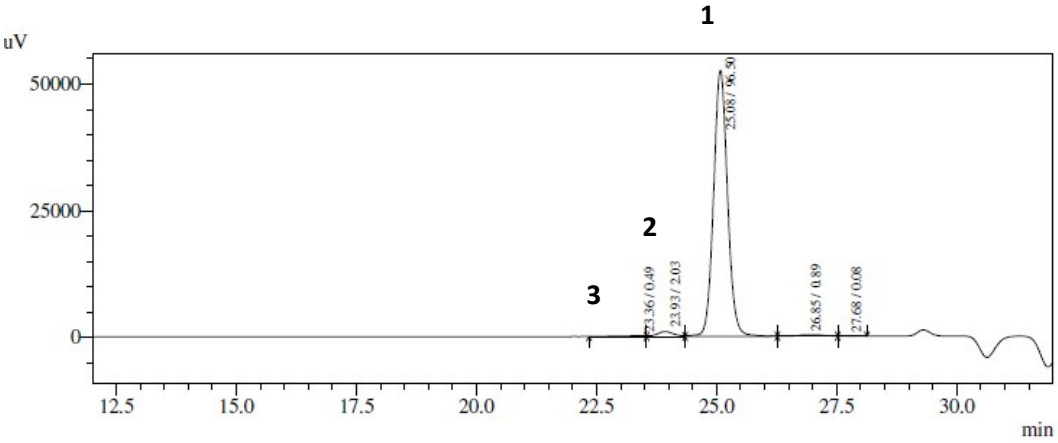
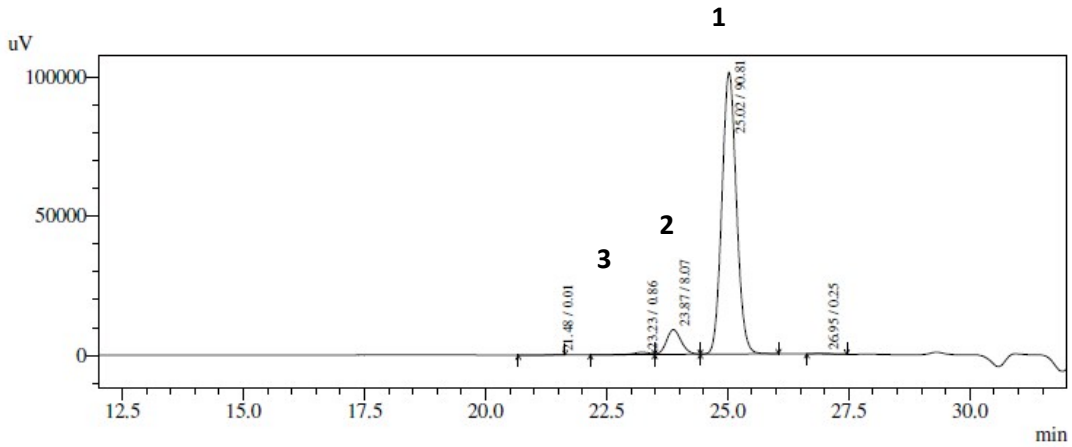


Figure S4. Mass spectrum of the reaction mixture resulting from the hydrohydroxymethylation of **T**. Conditions: **T** (1 mL, 1 mmol), 80 bar CO/H_2 (1/2) at 110 °C in toluene (5 mL), $N(Bu)_3$ (9 mmol) and $Rh(CO)_2(acac)$ (0.015 mmol), t = 8 h. C3: functionalized triolein; C4: estolide (functionalized C3 substituted by one additional chain).

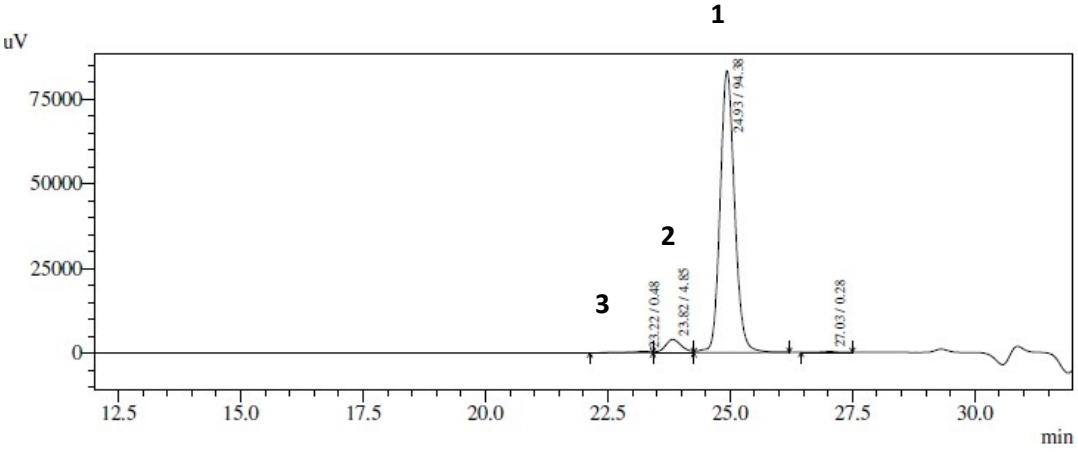
Size-exclusion chromatography (SEC)



*HHM of **T** after 1 h reaction time*



*HHM of **T** after 3 h reaction time*



*HHM of **T** after 6 h reaction time*

Figure S5. SEC chromatograms.

Peak	Retention time (min)	HHM 1h		HHM 3h		HHM 6h	
		%	Mn	%	Mn	%	Mn
1	25.1	**96.5**	1455	**90.8**	1503	**94.4**	1581
2	23.9	**2.0**	2935	**8.1**	3007	**4.9**	3122
3	23.3	**0.5**	4578	**0.9**	4636	**0.5**	4777
4	22.8	**0**	-	**0**	-	**0**	-

Sample	**HHM 1h**	**HHM 3h**	**HHM 6h**
M_n	1441	1566	1612
M_w	1505	1664	1682
$Đ_M$ (M_w/M_n)	1.04	1.06	1.04

^{1}H NMR analysis of vegetable oils

As the four glycerol protons are not involved in the hydroformylation reaction, they are chosen as the reference to determine the normalization integration factor (*NF*), which specifies the integration value of one proton (*NF = B/4* with *B* the integration value of the four glycerol protons). The numbers of initial and final C=C double bonds (DB_i and DB_f, respectively) are:

$$DB_i = \frac{Ai - NF}{2} \qquad DB_f = \frac{Af - NF}{2}$$

with *Ai* and *Af* the peak integrations of olefinic protons plus the internal proton of glycerol before and after reaction, respectively. Once the reaction is complete, the conversion is given by:

$$Conv.(\%) = \frac{DBi - DB_f}{DBi} \times 100 = \frac{Ai - Af}{Ai - NF} \times 100$$

The alcohol selectivity is given by:

$$Alc.\,selec.(\%) = \frac{H/_{6NF}}{DBi - DB_f} \times 100$$

where *H* is the integration value of the signal attributed to the hydroxymethyl group.