Supporting Information

Insights into the hydroformylation of oleochemicals: On the degree of unsaturation

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Table of Contents

1 General methods and reagents

All chemicals used for the experiments were stored under argon, and the liquid chemicals were degassed with argon dispersed by a frit for one hour in an ultrasonic bath (Table S1).

Table S1: Chemicals used in this work.

Chemical	Manufacture	Purity [w%]
High Oleic SunflowerME	Dako Lub AG	91.5
Methyl Linoleate	TCI	> 95
Toluene	Acros Organics	99.85
d8-toluene	Deutero	> 95
Ultrapure Water	generated with PURELAB flex 3	
2- Propanol	TCI	> 99.8
$Rh(acac)(CO)_2$	Umicore AG & Co. KG	> 99.9
L1	Carl Roth	> 99.5
L2	Strem	> 97%
L3	TCI	> 97%
L4	Strem	> 98%
TPPTS	OXEA	> 95
Methyl tert-butyl ether	Merck	≥ 99
Dodecan	Carl Roth GmbH + Co. KG	≥ 99
Syngas (1:1)	Messer SE	50 ± 2 mol% H_2, 50 ± 2 mol% CO, H_2 99.999 , CO 99.997
Argon	Messer SE	99.996
N_2	Messer SE	99.5

1.1 Procedure for hydroformylation experiments

For all batch experiments, a 300 ml overhead stirred autoclave with a pitched blade stirrer at a speed of 1000 rpm, and continuous gassing during the reaction was used. First, 73 g toluene, together with 0.0122 g of the precursor $Rh(acac)(CO)_2$ and the corresponding amount of ligand, were weighed under inert gas atmospheres and dissolved in an ultrasonic bath. The amount of ligand was chosen so that the molar ratio of 10 to 1 phosphorus to rhodium was maintained. The reaction solution was then transferred to the reactor pot and inserted by repeatedly depressurizing and applying 5 bar argon. After applying 10 bar of syngas to the reactor, heat it to 120 °C and stir it at 500 rpm. During heating, 14 g of the substrate mixture under investigation and 6 g of toluene were filled into the feed bomb on the reactor using a syringe. After the reaction solution was heated to 120 °C, the reactor was pressurized to 30 bar with syngas, the stirrer speed was increased to 1000 rpm, and preforming was performed for 30 minutes. After this time, the substrate in the feed bomb was added. During the reaction time, samples are taken via a sampling valve into vials cooled with nitrogen.

At the end of the reaction time, the reactor was cooled in an ice bath with stirring, purged with nitrogen, and degassed. A sample of the reactor contents, along with all samples taken, was submitted to the analytical methods described above. Finally, the reactor was cleaned with isopropanol.

In the case of the experiments with the biphasic reaction mixture, a mixture of 47 g of ultrapure water and 41.96 g of isopropanol was used as the solvent instead of toluene. Another 6 g of isopropanol is filled into the feed bomb instead of toluene and the substrates used. 3,3′,3″-Phosphanetriyltris(benzenesulfonic acid) trisodium salt (TPPTS) was used exclusively as the

ligand. Furthermore, the reaction was conducted at 140 °C and 50 bar synthesis gas. The rest of the procedure was carried out in the same way.

The samples taken during the experiment were first separated into aqueous and organic phases, and then only the organic phase was submitted to the described analysis.

1.2 Procedure for partial hydrogenation of methyl esters

The methyl ester mixtures used were treated as in our previous work to hydrogenate the polyunsaturated to monounsaturated methyl esters. For convenience, the main procedure is described below.

To prepare the nanoparticle solution, 0.05 mMol of $Pd(OAc)_2$ was dissolved in 0.5 mol of propylene carbonate (equivalent to 100 ppm). The solution was then heated to 80 °C, and conditioning was started by stirring the solution. After 2h, the conditioning was stopped by cooling to < 20 °C with further stirring.

To perform the semi-hydrogenation, 5 g of the nanoparticle solution was further diluted with 20 g of the solvent. This stock solution was then pressurized with 10 bar of hydrogen and heated. After reaching the reaction temperature of 80 °C, 0.25 mol of reactant was added. After 2 h, the reaction phase was cooled to <20 °C, excess hydrogen was drained off, and the product phase obtained was analyzed.

2 Analytics

2.1 GC-FID

Experimental samples were analysed on an Agilent Technologies gas chromatograph (7890A) equipped with a flame ionisation detector and an HP-5 capillary column (30 m x 0.32 mm x 0.25 µm, methods in Table S2 and Table S3). Methyl tert-butyl ether (MTBE) 0.6 g solvent, dodecane 0.05 g internal standard and 0.35 g sample were used for the analysis. Using the method on this column, all mono- and polyunsaturated methyl esters appear as a single peak, while good separation of the corresponding aldehydes can be achieved. An additional Agilent Technologies gas chromatograph (8860) with a flame ionisation detector and a DB-FastFAME® capillary column (90 m x 250 µm x 0.25 µm, Methods in Table S4) was used to validate these results and to obtain a clear separation of the methyl esters.

Table S2: Heating profiles for the analysis of hydroformylation using GC-FID with HP-5 column.

	Rate [°C min^{-1}]	**Temperature [°C]**	**Holding time [min]**
T_{Start}		40	2
Ramp 1	50	228	0
Ramp 2	0,2	230	2
Ramp 3	80	320	3

Table S3: Volume flows via a column for the analysis of hydroformylation using GC-FID with HP-5 column.

	Rate [ml min^{-2}]	**Value [ml min^{-1}]**	**Holding time [min]**
n_{Start}		2,19	5
Ramp 1	1	1	10
Ramp 2	1	2,5	0
nEnd		2,5	

Table S4: Heating profiles for the analysis of partial hydrogenation using GC-FID with DB-FastFAME column.

	Rate [°C min^{-1}]	**Temperature [°C]**	**Holding time [min]**
T_{Start}		50	
Ramp 1	50	175	1
Ramp 2	5	185	1
Ramp 3	0,1	188	10
Ramp 4	0,1	192	10
Ramp 5	25	235	5
T_{End}		235	

3 Results

3.1 Used FAME Substrates

Table S 5: FAME Composition of the used substrates

	≤C16	C18:0	C18:1 cis	C18:1 trans	C18:2	C18:3	≥C20
High Oleic SunflowerME	3.2	2	90.9	0	3.6	0.1	0.3
CanolaME	4.6	1.8	61.1	0	20.7	10.6	1.3
P.h. CanolaME	4.6	3.9	69.7	17.2	3.3	0	1.3
P.h. high oleic sunflowerME, “MO”	3.2	5.9	68.8	21.8	0	0	0.2

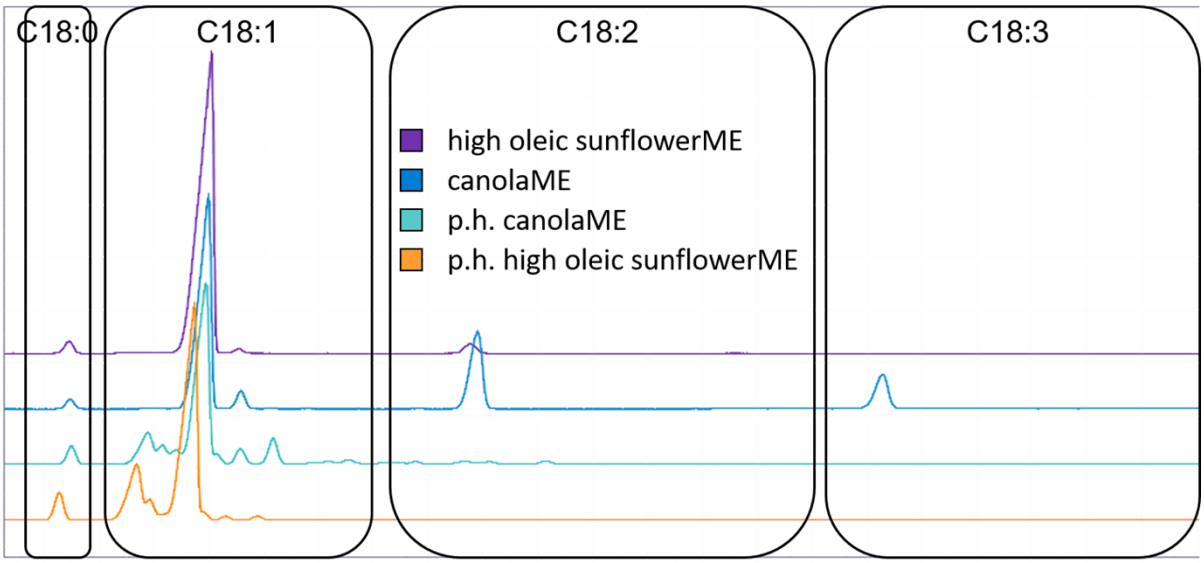

Figure S1: Chromatograms of the substrates, measured on GC-FID with DB-FastFAME column.

3.2 ML influence:

3.2.1 Close up of reaction start

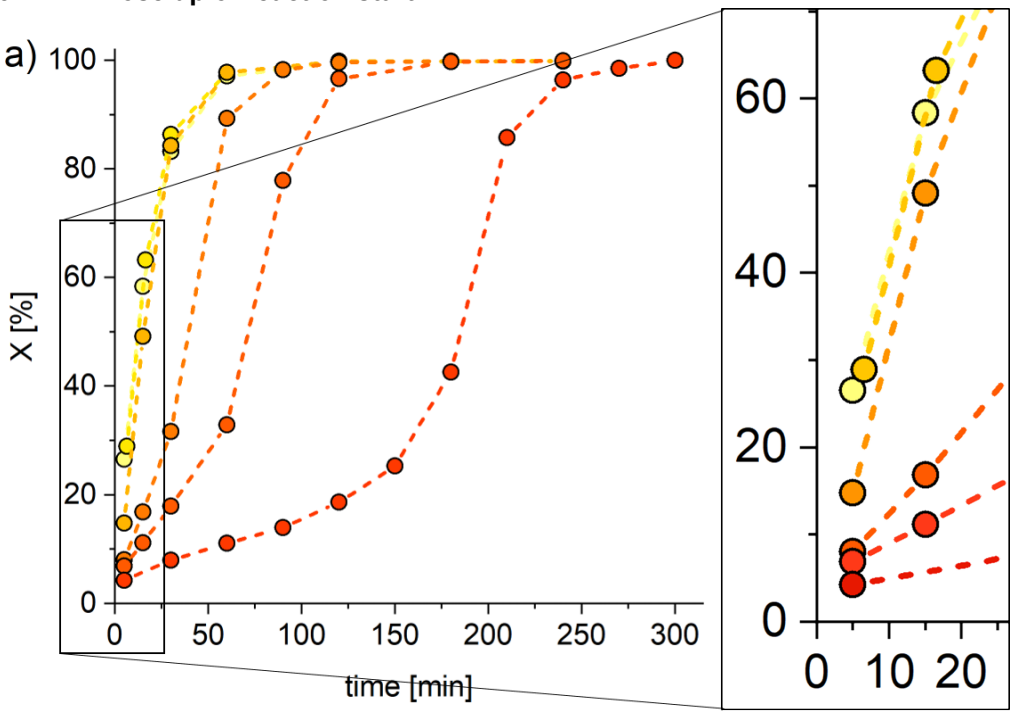

Figure S 2: Close up of the reaction start as presented in Figure 4. For Conditions see Figure 4.

3.2.2 Cis/Trans Ratio

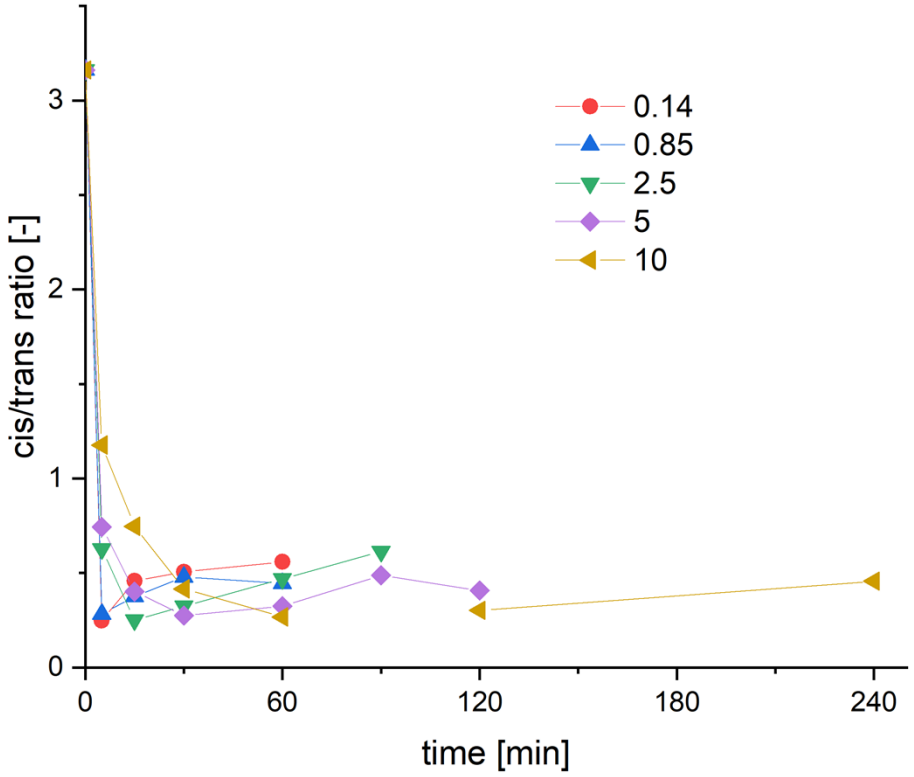

Figure S3: C18:1 cis/trans ratio of the reactions shown in Figure 4. Values are calculated based on GC-FID analysis. Connections between data points are for visualization purposes only. Conditions: T = 120 °C, p = 30 bar, n_{CO}:n_{H2} = 1:1, V_{STR}= 100 ml, U = 1000 rpm, c_{Rh} = 0.5 mmol L^{-1}, n_P:n_{Rh} = 10, $n_{(MO+ML)}$:n_{Rh} = 1000, ligand: **L4**, Preforming: T = 120 °C, p = 30 bar, n_{CO}:n_{H2} = 1:1, U = 1000 rpm, t = 30 min.

3.2.3 Identification of 9,11 conjugated methyl linoleate:

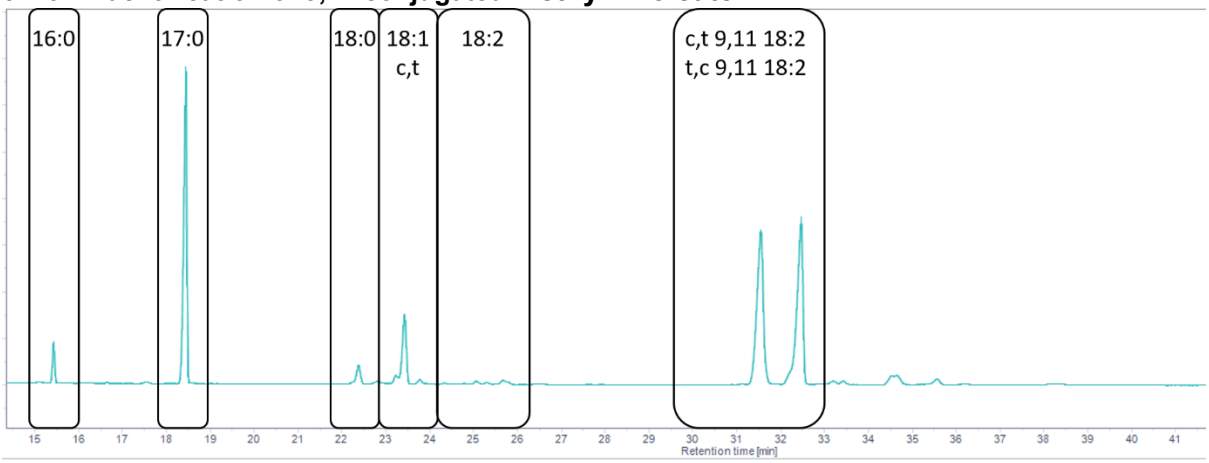

Figure S4: Commercially available ethyl ester of conjugated linoleic acid was transesterified to methyl ester. Chromatogram of the resulting reaction mixture with added C17:0 as internal standard, measured on GC-FID with DB-FastFAME column and methode discribed in Table S4.

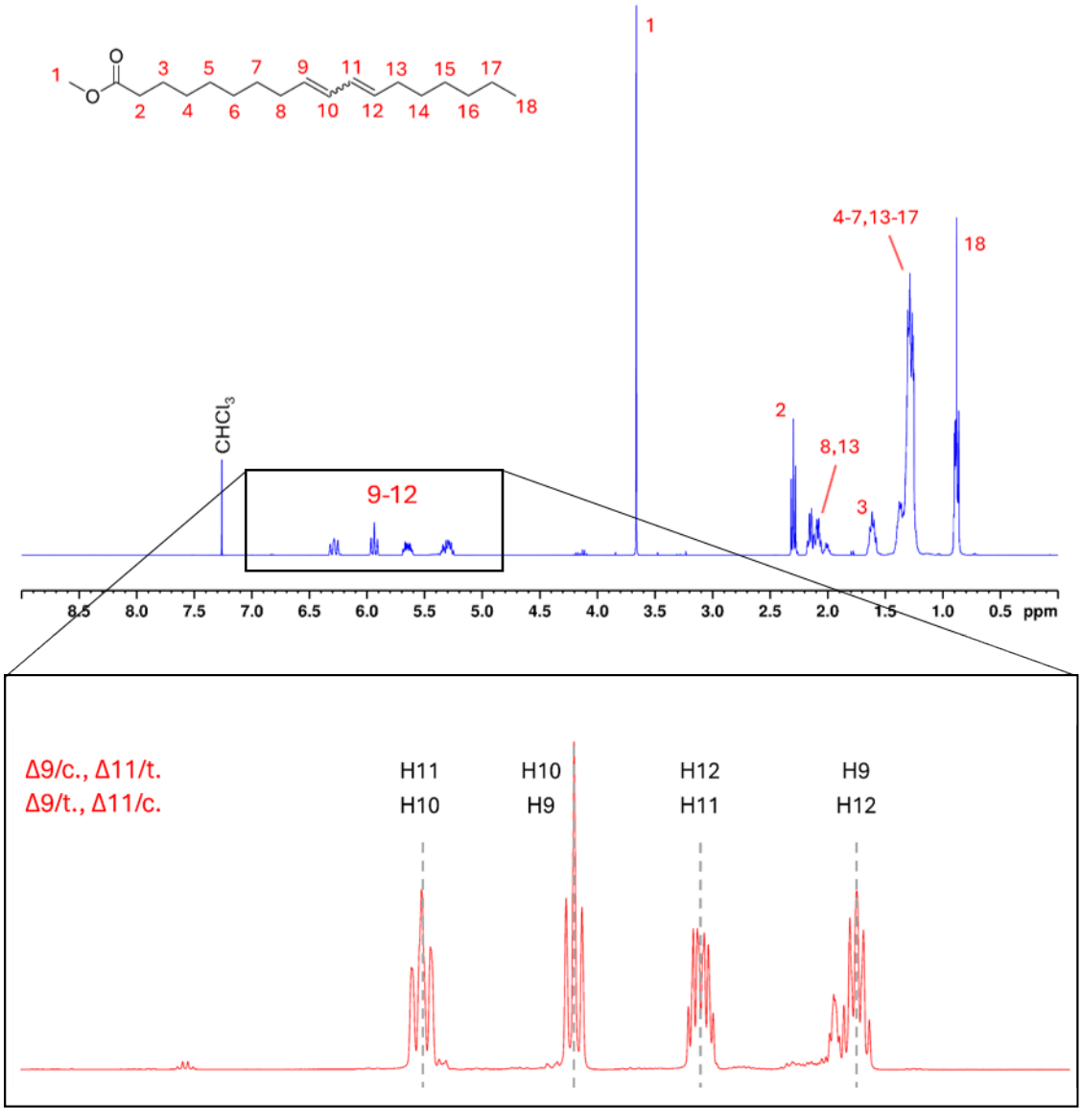

Figure S 5: ^{1}H-NMR (600 MHz, $CDCl_3$) of of commercially available 9,11-CML, measured on Bruker Avance NEO 600. Identification according to literature.[1],[2]

3.2.4 NMR Investigation

The substrate (MO or ML) was filtered through a column of Al_2O_3, then transferred to a centrifuge tube containing Na_2SO_4 and centrifuged at 2000 rpm for 5 minutes. Schlenk tubes with 4Å molecular sieves (activated at 180 °C and approx. 50 mbar for at least two hours) are prepared by inerting by heating the tubes five times in succession with a heat gun under vacuum and flushing with argon after cooling to room temperature. The pre-dried substrate and toluene-d8 were then filled into the prepared Schlenk tubes and degassed by 5 cycles of freeze-pump-thaw with argon.

The precursor $Rh(acac)(CO)_2$ (12,8 mg, 0,05 mmol) and the ligand 2,4-di-tert-butyl-phenylphosphite (324,3 mg, 0,5 mmol, 10 eq. to Rh) were dissolved in toluene-d8 (5 ml) under argon. This solution was then pressurized with syngas (H_2/CO = 1:1, 30 bar) and preforming took place for 1 h at 120 °C. The solution was cool down and depressurized while a NMR-tube was inertized by 5 cycles of Argon pressure and vacuum. With an inertized syringe a sample of the solution was transferred to the NMR-tube in argon counterflow, afterwards the NMR tube was flushed with syngas for 3 cycles and transferred to the ^{1}H and ^{31}P NMR spectroscopy measurments (Figure S6 and Figure S7) within <5 minutes. Afterwards MO or ML (445 mg, 1,5 mmol) was added to the remaining solution and the reaction mixture was left for 30 minutes under the specified reaction conditions. The solutions were then analyzed again using ^{1}H and ^{31}P NMR (Table S6) following the same procedure. Only in the hydroformylation of ML was the formation of a signal at δ = 4.59 ppm (td) observed (Figure S8).

All following measurements were performed on a Bruker Avance III HD - 600 MHz.

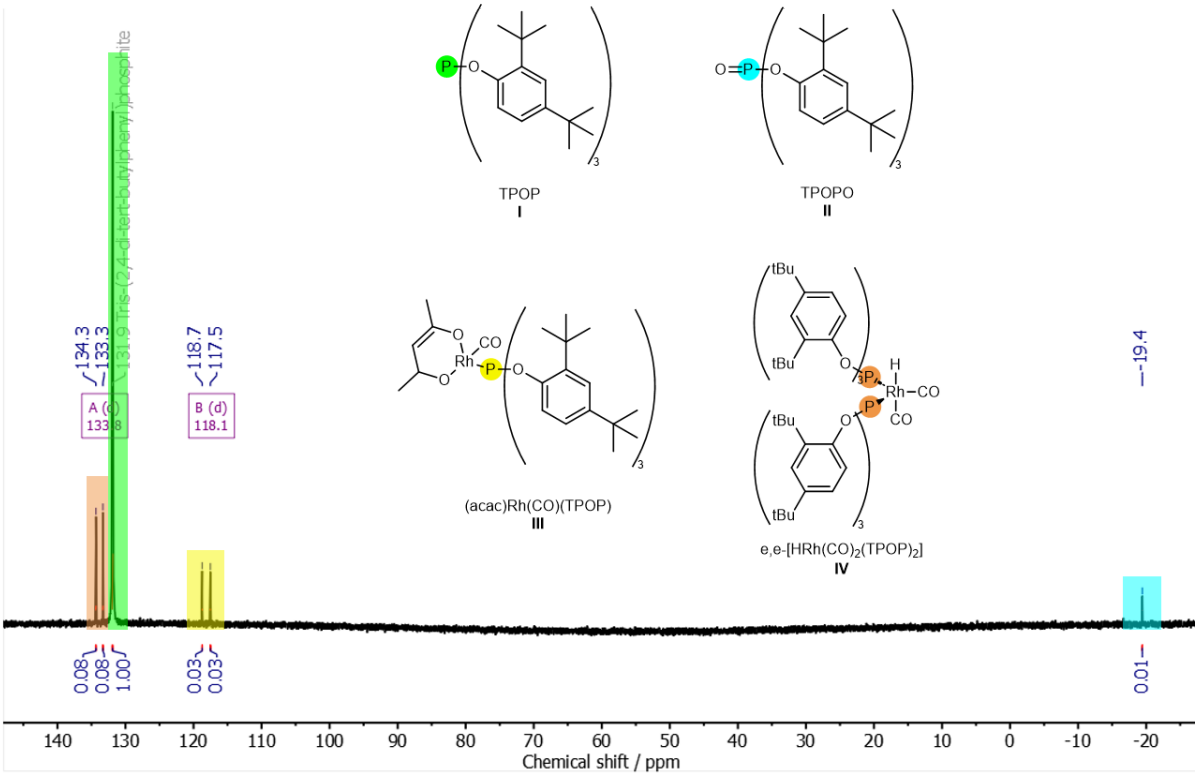

Figure S6: ^{1}H inverse gated decoupled ^{31}P-NMR of the preforming phase. Assignment of the species corresponds to the known literature.[3]–[5]

^{31}P{^{1}H} NMR (243 MHz, toluene-d8, 25 °C): δ/ppm = 133.8 (d, ^{1}J(P,Rh) = 249.5 Hz), 131.9 (s), 118.1 (d, ^{1}J(P,Rh) = 291.5 Hz), -19.4 (s).

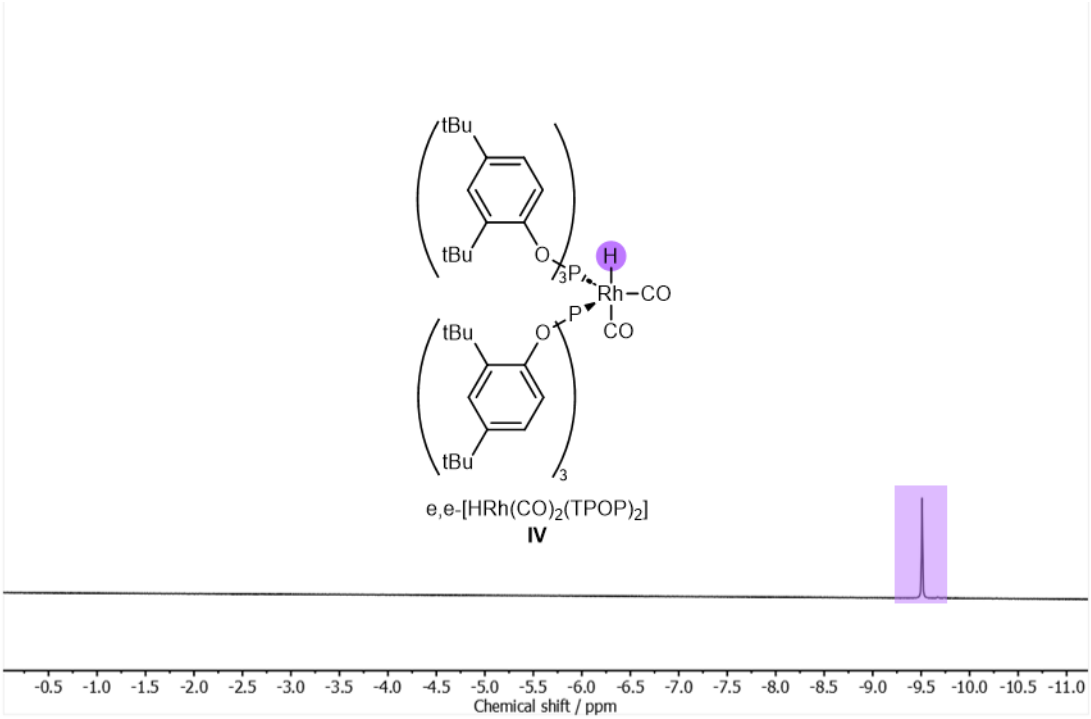

Figure S7: 1H-NMR of the preforming phase. Assignment of the species corresponds to the known literature.[3] [6]

^{1}H NMR (600 MHz, toluene-d8, 25 °C): δ/ppm = -9.5 (s).

Table S6: Selected ^{1}H and ^{31}P NMR data of the reaction solution after hydroformylation of MO and ML. Assignment of the species corresponding to Figure S6 and Figure S7.

Reaction with:	**^{31}P{^{1}H} NMR** (243 MHz, toluene-d8, 25 °C)	**^{1}H NMR** (600 MHz, toluene-d8, 25 °C)
MO	δ/ppm = 133.8 (d, ^{1}J(P,Rh) = 249.5 Hz), 131.9 (s), 118.1 (d, ^{1}J(P,Rh) = 291.2 Hz), -19.4 (s).	δ/ppm = -9.5 (s).
ML	δ/ppm = 131.9 (s), 118.1 (d, ^{1}J(P,Rh) = 291.6 Hz), -19.4 (s).	-

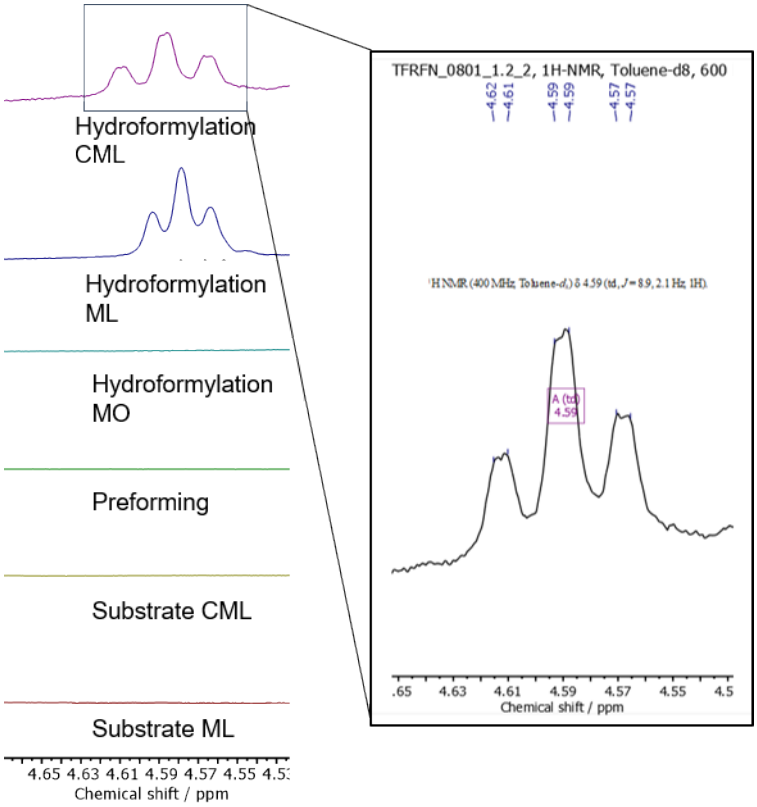

Figure S8: Section of the ^{1}H-NMRs (600 MHz, toluene-d8, 25 °C) of the various substrates and reactions. This signal can be assigned to the central H atom of the Rh-allyl complex.[7]

3.3 Biphasic Hydroformylation

Based on our experience with aqueous biphasic hydroformylations of long-chain FAME, we used a system with the co-solvent isopropanol.[8] Based on our experience from previous publications, we deliberately chose conditions where complete conversion is not achieved to clearly visualize differences between the substrates.

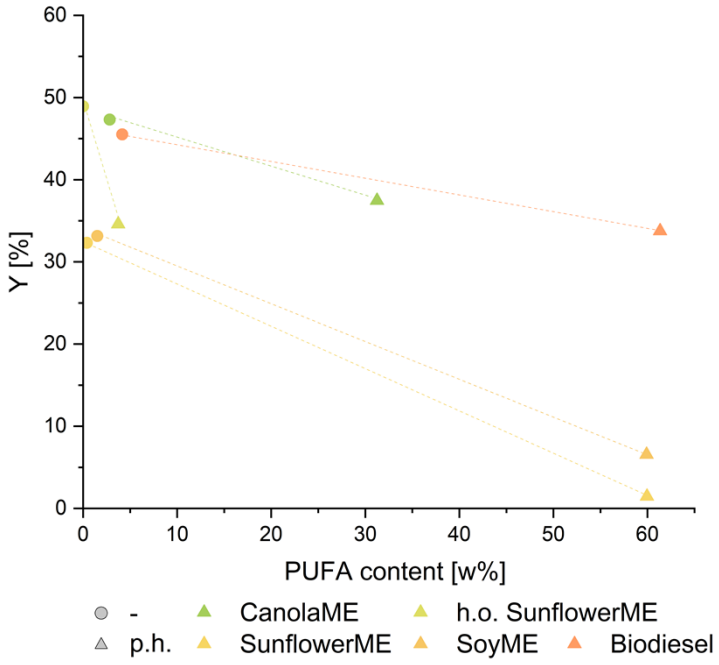

Figure 1: Results of the biphasic Hydroformylation of different FAMEs and partially hydrogenated FAMEs. Yields are calculated based on GC- FID analysis with dodecane as an internal standard. Conditions: T = 140 °C, t = 2 h, n_{CO}/n_{H2} = 1/1, $p_{CO/H2}$= 50 bar, V_{total} =0,3 L, u = 1000 rpm n_{MO}=0,02 mol, n_{MO}/n_{Rh} =100, n_{TPPTS}/n_{Rh} = 10, m_{IPA}/m_{Water} = 1/1. Preforming: T = 120 °C, p = 30 bar, n_{CO}:n_{H2} = 1:1, U = 1000 rpm, t = 30 min.

4 References

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