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# Hydrohydroxymethylation of Ethyl Ricinoleate and Castor Oil

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**Abstract:** The direct functionalization of the carbon–carbon double bonds of castor oil and its derivatives is of major interest to access biosourced building blocks. In particular, polyols derivatives can be produced in this way and find application in the field of bio-based polyesters and polyurethanes. In this study, we described the synthesis of polyhydroxylated derivatives via a hydrohydroxymethylation reaction consisting of two consecutive Rh-catalyzed reactions: a hydroformylation reaction followed by a hydrogenation reaction of formyl groups. A catalytic system based on  $\text{Rh}(\text{acac})(\text{CO})_2$  and a trialkylamine proved to be active both in hydroformylation of carbon–carbon double bonds and reduction of the resulting aldehydes into primary alcohols. By

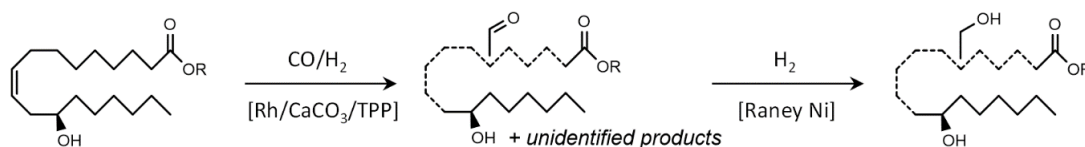
optimizing the reaction conditions, yields in alcohols of 74% and 80% were reached for castor oil and ethyl ricinoleate, respectively.

## **Introduction**

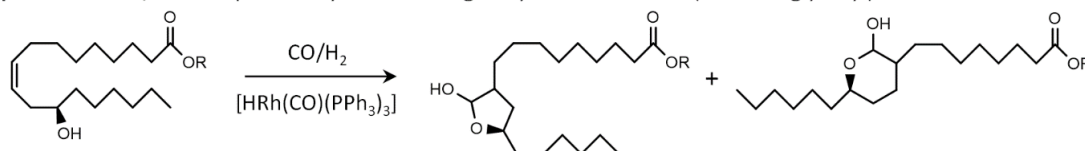
Bio-based feedstocks are valuable resources to produce new molecules and materials. In this context, the unsaturated triglycerides are interesting building blocks owing to the possibility of the carbon-carbon double bonds modification. Among the various possibilities, hydrogenation, hydrosilylation, hydroformylation, hydroaminomethylation, hydrovinylation, metathesis, epoxidation or hydrohydroxymethylation (HHM) can be performed.<sup>1</sup> This last reaction, which consists of the conversion of carbon-carbon double bonds into primary alcohols via a tandem hydroformylation/hydrogenation sequence, was largely less studied. Nevertheless, this reaction is very interesting since polyhydroxylated triglycerides can be produced for the synthesis of bio-based polyesters and polyurethanes. In 2015, the hydrohydroxymethylation reaction was reviewed by Armin Börner and coll.<sup>2</sup> Briefly, different approaches for the production of alcohols can be performed with two-step process or one-pot reaction with a single catalyst or with two catalysts used in different or similar reaction conditions.<sup>3-6</sup> The one-pot reaction with a single catalyst is the best alternative because it simplifies the process by reducing the amount of catalyst, the reaction time and the overall cost. In this way, Rh-catalysts associated to tertiary amines are able to hydroformylate C=C bonds and to hydrogenate the resulting aldehydes into alcohols.<sup>7-15</sup> Contrary to most of the procedures described in the literature, no oxidable phosphane was used to coordinate Rh-species, thus giving to this strategy an industrial potential. This simple Rh/tertiary amine catalytic system has been successfully used to achieve the hydrohydroxymethylation of triglycerides into hydroxylated triglycerides.<sup>16-17</sup> Surprisingly, this one-pot reaction with a single

catalyst was never applied to castor oil and its derivatives. Castor and its derived oil, the so-called “castor oil”, are known from the ancient times, when the oil was used for cosmetics, or as a laxative, or as a fuel in lamps.<sup>18-20</sup> Nowadays, castor oil has a completely renewed interest, not for its direct applications, but thanks to various possibilities in chemical modifications. Indeed, castor oil is a triacylglycerol composed of fatty acids chains bound to glycerol. More precisely, the corresponding fatty acids consist of up to 90% ricinoleic acid and varying small amounts of saturated and unsaturated fatty acids. The high content of ricinoleic acid is the reason for the high value of castor oil and its versatile application possibilities in the chemical industry. The ricinoleic acid is a C18 fatty acid possessing a double carbon-carbon bond in the C-9 position and a hydroxyl group in the C-12 position.

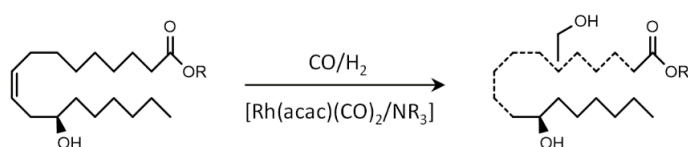
**(a) C.K. Lyon, 1974:** Hydroformylation followed by hydrogenation (R = Me or glyceryl)



**(b) R.G. da Rosa, 2005:** Hydroformylation leading to cyclic hemiacetals (R = Et or glyceryl)



**(c) This work:** One-pot hydrohydroxymethylation (R = Et or glyceryl)



**Scheme 1.** Rhodium-catalyzed functionalization of ricinoleic esters under CO/H<sub>2</sub> atmosphere ((a) 1974, (b) 2005 and (c) this work).

Only two references were published on hydroformylation or hydroformylation-hydrogenation of castor oil and its derivatives. In 1974, the production of primary alcohols from castor oil and methyl ricinoleate was reported in a two-step process (Scheme 1, (a)).<sup>21</sup> A Rh/CaCO<sub>3</sub>/TPP combination was used for the hydroformylation step and the following hydrogenation step was catalyzed by Raney nickel. It should be noted that not only two transition metals but also two different gases were used (CO/H<sub>2</sub> mixture and then H<sub>2</sub>). The distribution of the reaction products was determined only by gas chromatography. The percentages of alcohols were equal to 79% and 84% for castor oil and methyl ricinoleate, respectively. Nevertheless, no extensive characterization of reaction products was reported. In addition, the authors mentioned that hydroformylated methyl ricinoleate showed several peaks which were not identified. In 2005, the hydroformylation of castor oil and ethyl ricinoleate using HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> as catalyst precursor was described and a complete conversion of double bonds was achieved (Scheme 1, (b)).<sup>22</sup> Due to a lactolization reaction involving formyl and hydroxyl groups, cyclic hemiacetals were obtained as major products.

The aim of this work was to produce hydrohydroxymethylated products in the presence of only one transition metal and under the same experimental conditions with the challenge to avoid or displace the formation of hemiacetals (Scheme 1, (c)). A Rh/amine combination was used to promote the hydrohydroxymethylation reaction of ethyl ricinoleate. After an optimization study of the reaction parameters, the best combination was applied to castor oil.

## **Experimental section**

## Catalytic experiments

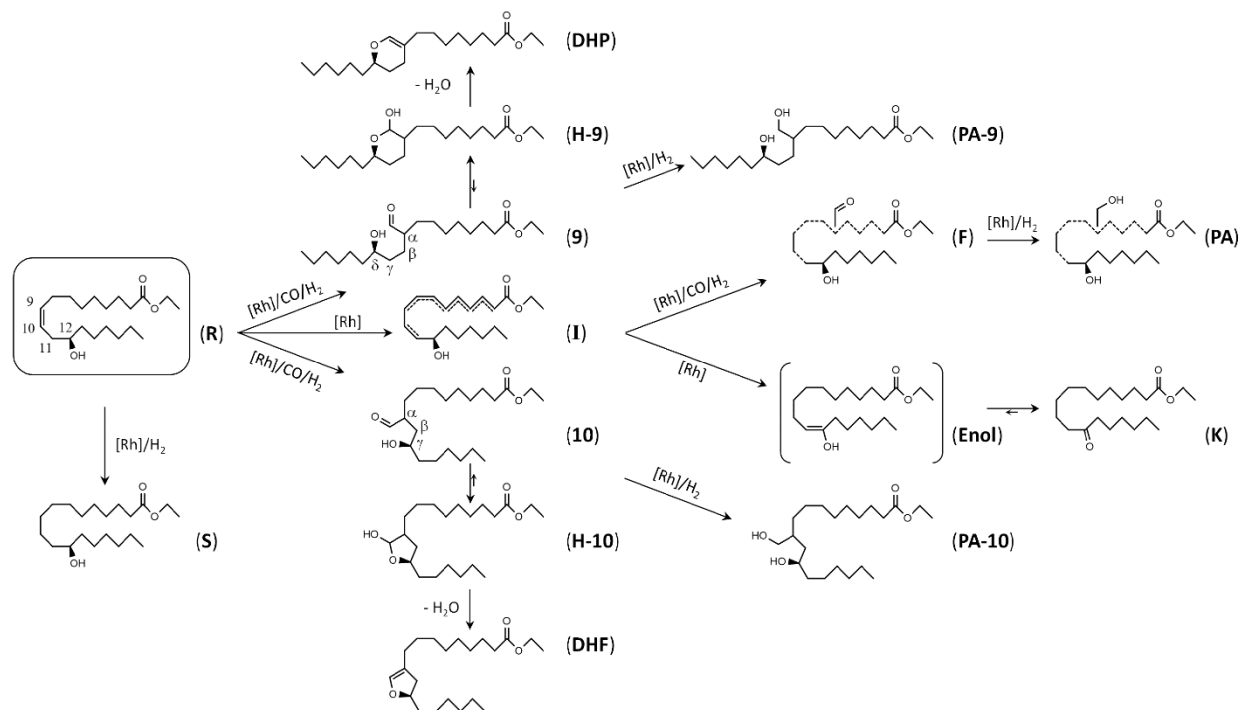
In a typical catalytic experiment, Rh(acac)(CO)<sub>2</sub> (6 mg, 23.3 μmol, 1 eq.) was dissolved under nitrogen in a degassed mixture of triethylamine (2.35 g, 3.2 mL, 23.2 mmol, 1000 eq.), toluene (3.3 mL), and ethyl ricinoleate (1.90 g, 5.81 mmol, 250 eq.) or castor oil (1.79 g, corresponding to 5.81 mmol of ricinoleic chains = 250 eq.). The solution was poured under nitrogen into an autoclave of 25 mL (Parr instrument company) equipped with a mechanical stirrer. The autoclave was then heated under stirring and, once a temperature of 80 °C was reached, the autoclave was charged with 80 bar of CO/H<sub>2</sub> (1:1). After 24 h, the autoclave was allowed to cool down to room temperature and depressurized. Triethylamine and toluene were removed by rotary evaporator and the obtained mixture was analysed by <sup>1</sup>H NMR and quantitative <sup>13</sup>C NMR (inverse-gated-decoupling sequence) on a Bruker DRX300 spectrometer (operating at 300 MHz for <sup>1</sup>H and 75 MHz for <sup>13</sup>C). All runs were performed at least twice in order to ensure reproducibility.

## Results and discussion

### Presentation of the possible reaction products

The hydrohydroxymethylation of ethyl ricinoleate is a complex reaction that can lead to many products. The scheme 2 gathers the different compounds that could be theoretically obtained from ethyl ricinoleate (**R**) in the presence of a [Rh/tertiary amine] catalytic system able to hydroformylate double bonds into aldehydes that can further be hydrogenated into primary alcohols. So, ethyl ricinoleate (**R**) can be hydroformylated into the two aldehydes (**9**) and (**10**) (formyl group at the position 9 and 10, respectively, on the fatty chain). Because these two

aldehydes possess a hydroxyl group in  $\delta$  and  $\gamma$  position, respectively, they should lead quantitatively to the two cyclic hemiacetals (**H-9**) and (**H-10**). These two lactols, symbolized by the letter (**H**) subsequently ((**H**) = (**H-9**) + (**H-10**)), could be further dehydrated into the cyclic enol ethers (**DHP**) and (**DHF**) coming from (**H-9**) and (**H-10**), respectively (**DHP** for dihydropyran and **DHF** for dihydrofuran).<sup>22</sup> The ethyl ricinoleate (**R**) can be hydrogenated into the "saturated" secondary alcohol (**S**). Due to the equilibrium with small quantities of their corresponding (**9**) and (**10**) aldehyde open forms, hemiacetals (**H-9**) and (**H-10**) can also lead to the primary alcohols (**PA-9**) and (**PA-10**), respectively. Of course, the rhodium catalytic system can undergo isomerization reactions, i.e. migration of the C=C double bond initially localized on the 9-10 positions on the fatty chain. This would lead to alkene "isomers" (**I**) for which the C=C double would be at the 8-9, 7-8, 6-7, 5-6, 4-5, 3-4, 2-3 positions as well as the 10-11 position. If, by isomerization, the double C=C bond would reach the 11-12 position, this would lead to an enol ((**Enol**)) that would quickly tautomerize into the ketone (**K**). By hydrogenation, this ketone could lead to the (**S**) compound but in its racemic form. The isomers (**I**) for which the C=C double bond has reached the 8-9 and 10-11 positions can also be hydroformylated into the aldehydes (**9**) and (**10**) that would cyclize into (**H-9**) and (**H-10**), but also into the aldehydes (**8**) and (**11**) (not drawn on the scheme). These two aldehydes (**8**) and (**11**), together with aldehydes (**2**), (**3**), (**4**), (**5**), (**6**) and (**7**), would not form cyclic hemiacetals (lactols with 4 or 7 to 13 atoms in the ring are quite unlikely)<sup>23</sup>. These compounds whose formyl group would stay free will be called (**F**). The term (**PA**) corresponds to the primary alcohols coming from hydrogenation of all the aldehydes: from hydrogenation of (**9**) and (**10**), in equilibrium with hemiacetals (**H-9**) and (**H-10**), but also from hydrogenation of the eight "free" aldehydes (**F**), i.e. (**2**)-(8) and (**11**).



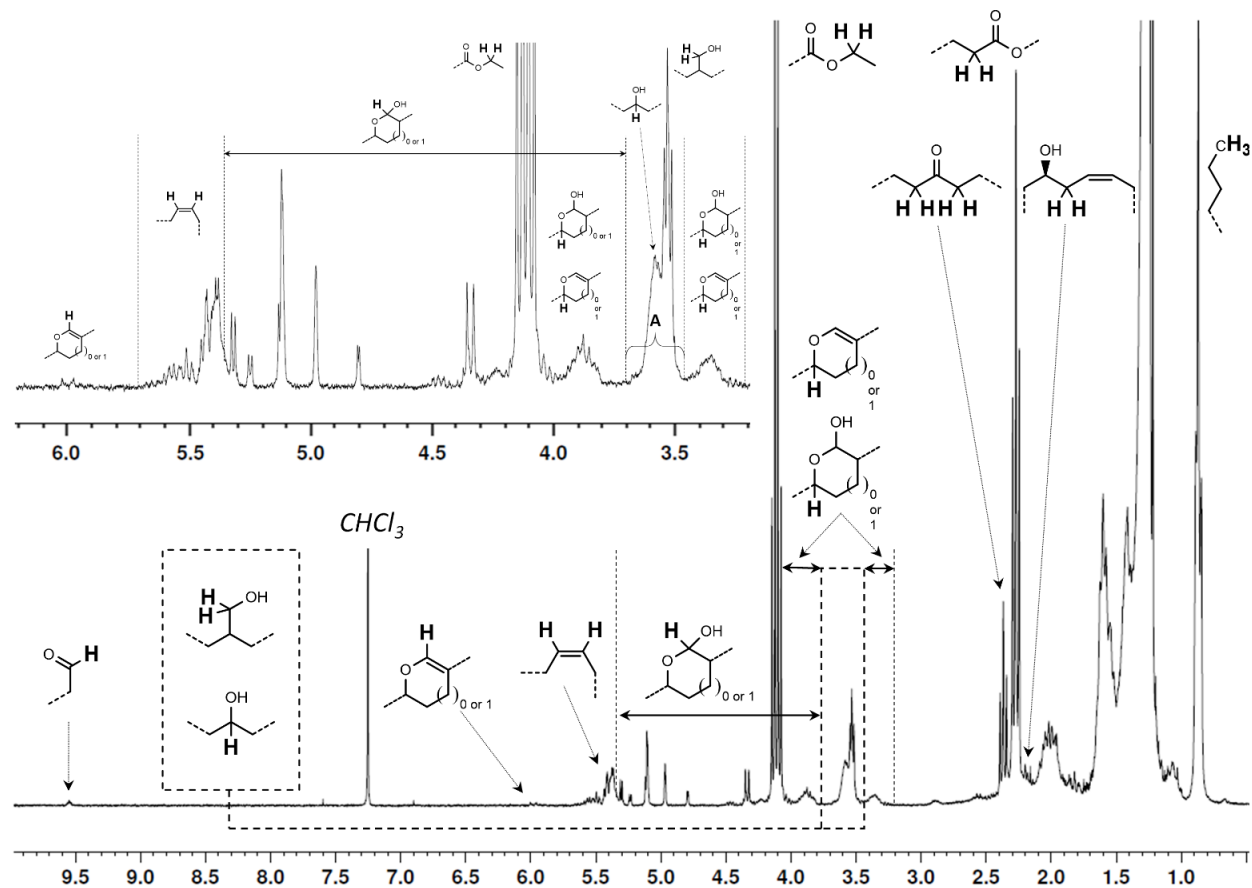
**Scheme 2.** Possible compounds obtained from ethyl ricinoleate under CO/H<sub>2</sub> in the presence of a [Rh/tertiary amine] catalytic system.

### Preliminary reactions

In our first studies, the experimental conditions described by some of us for hydrohydroxymethylation of triglycerides was applied to ethyl ricinoleate.<sup>16</sup> More precisely, the reaction was carried out by using Rh(acac)(CO)<sub>2</sub> as a rhodium precursor, triethylamine (TEA) as ligand, and toluene as solvent under 80 bar of CO/H<sub>2</sub> at 80°C during 24 h (Table 1, entry 1). The aim of this experiment was to identify a maximum of (by)products. At the end of the reaction, the medium was concentrated to remove triethylamine and toluene, and analyzed by <sup>1</sup>H NMR in deuterated chloroform. Figure 1 presents a typical spectrum obtained. Due to the number and the complexity of the products, crude reaction mixture was treated by chromatography on a silica



column with heptane and diethyl ether as eluting solvents. Each isolated compound was analyzed by  $^1\text{H}$ ,  $^{13}\text{C}$ , COSY and HSQC NMR experiments. Thanks to all these analyses, the identification of all the compounds in the  $^1\text{H}$  NMR spectra was achievable. All details for determination of the products structures and for calculation of conversion and yields from the  $^1\text{H}$  NMR spectra are presented in supporting information (SI). On the  $^1\text{H}$  NMR spectrum (Figure 1), C=C double bonds are still present since their conversion was equal to 93%. Peaks relative to aldehydes (**F**), dehydrated compounds (**D**), hemiacetals (**H**), ketone (**K**) and primary alcohols (**PA**) were identified and the different yields were equal to  $Y_{(\text{F})}=1\%$ ,  $Y_{(\text{D})}<0.5\%$ ,  $Y_{(\text{H})}=21\%$ ,  $Y_{(\text{K})}=17\%$  and  $Y_{(\text{PA})}=49\%$ , respectively. The yield of saturated products was obtained by difference ( $Y_{(\text{S})}=5\%$ ). In addition, in order to prove that the cyclisation of the aldehyde (**9**) and (**10**) into the hemiacetals (**H-9**) and (**H-10**) constitutes a lock concerning the primary alcohols production, trimethylsilyl ethyl ricinoleate was used as substrate in the reaction.



**Figure 1.** Typical  $^1\text{H}$  NMR spectrum of the final reaction medium of ethyl ricinoleate hydrohydroxymethylation (reaction conditions:  $\text{Rh}(\text{acac})(\text{CO})_2$  (1 eq.), ethyl ricinoleate (250 eq.), TEA (500 eq.), toluene (4.9 mL),  $\text{P}(\text{CO}/\text{H}_2) = 80$  bar,  $80^\circ\text{C}$ , 24 h) after concentration (300 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ).

Indeed, once silylated, the secondary alcohol function of ricinoleate is not nucleophilic anymore and cannot add to the aldehyde function. The trimethylsilylated ethyl ricinoleate was obtained by reaction of ethyl ricinoleate with trifluoro *N,O*-bis(trimethylsilyl)acetamide (see SI, II.3). By using trimethylsilyl ethyl ricinoleate instead of ethyl ricinoleate under the same reaction conditions (see

Table 1), a higher primary alcohols yield was reached (95% instead of 49%) and a trimethylsilylated version of the (S) product was also formed (yield of 5%). Indeed, neither hemiacetal nor ketone can be obtained. This result undoubtedly proves that the presence of the alcohol function at the position 12 in ethyl ricinoleate hinders the primary alcohols formation. In the following, the aim will be to find the best reaction conditions to reach the higher yields in primary alcohols.

**Table 1.** Ethyl ricinoleate HHM in various solvents.

Entry	Solvent	C. <sup>a</sup> (%)	Y( <b>F</b> ) <sup>b</sup> (%)	Y( <b>D</b> ) <sup>b</sup> (%)	Y( <b>H</b> ) <sup>b</sup> (%)	Y( <b>K</b> ) <sup>b</sup> (%)	Y( <b>PA</b> ) <sup>b</sup> (%)	Y( <b>S</b> ) <sup>b</sup> (%)
1	Toluene	93	1	0	21	17	49	5
2	Isopropanol	86	0	0	38	14	29	5
3	Anisole	94	0	1	18	13	50	12
4	2-Me-THF	95	0	0	40	17	38	0
5	$\gamma$ -valerolactone	0	0	0	0	0	0	0
6	Heptane	90	1	0	30	18	39	2
7 <sup>c</sup>	TEA	95	0	0	34	16	38	7
8 <sup>d</sup>	Acetone	89	0	0	36	13	39	1
9	Ethyl acetate	84	0	0	36	13	29	6

Experimental conditions: Rh(acac)(CO)<sub>2</sub> (6 mg, 23.3  $\mu$ mol, 1 eq.), ethyl ricinoleate (1.90 g, 5.81 mmol, 250 eq.), TEA (1.18 g, 1.6 mL, 11.6 mmol, 500 eq.), solvent (4.9 mL), 80 bar of CO/H<sub>2</sub> (1:1), 80 °C, 24 h. <sup>a</sup> C. = global double CC bond conversion = total amount of C<sub>9</sub>=C<sub>10</sub> double bonds (in (**R**)) and of isomerized other CH=CH double bonds (in (**I**) compounds) that have been transformed into the others products ((**F**), (**D**), (**H**), (**K**), (**PA**) and (**S**)). <sup>b</sup> Y<sub>(X)</sub> = yield in product (**X**). <sup>c</sup> TEA used as ligand and solvent (4.70 g, 6.5 mL, 46.5 mmol, 2000 eq.). <sup>d</sup> Reduction of acetone to isopropanol was observed (10 %).

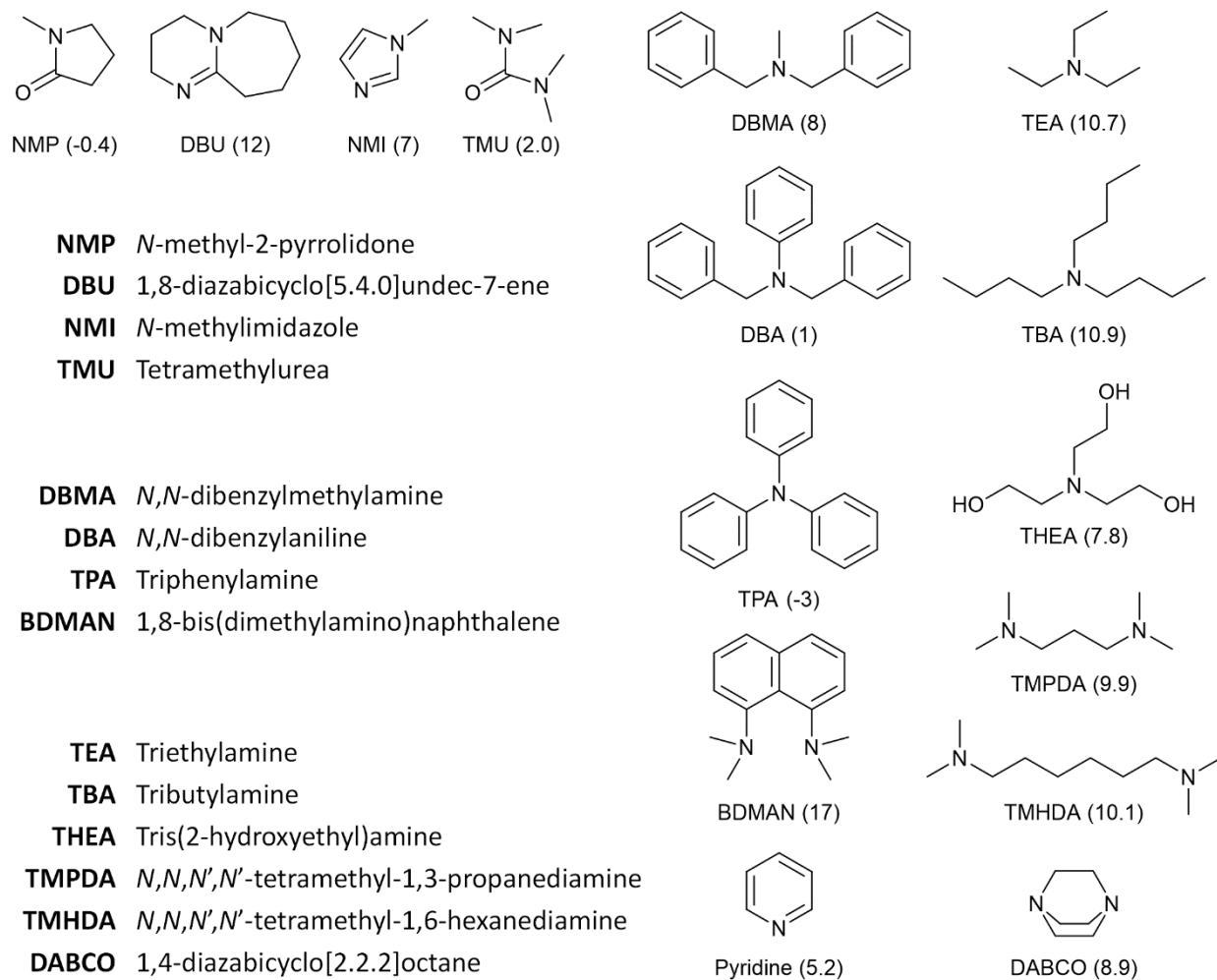
## Effect of the solvent

The rhodium catalyzed hydrohydroxymethylation of ethyl ricinoleate was performed in various solvents to evaluate their influence by using TEA as ligand. These solvents were chosen as a function of their availability or eco-friendly character. For example,  $\gamma$ -valerolactone and 2-methyltetrahydrofuran (2-Me-THF) are solvents derived from biomass, and anisole is a low-cost, non-toxic and biodegradable compound.<sup>24-27</sup> No conversion was observed in  $\gamma$ -valerolactone (Table 1, entry 5). With the other solvents, conversions between 84 and 95% were reached. In the case where TEA was used both as ligand and as solvent, the yield in primary alcohols was equal to 38% (Table 1, entry 7). Toluene and anisole favored the production of alcohols (49% and 50%, respectively) but 12% of saturated product were obtained in anisole against only 5% in toluene (Table 1, entries 1 and 3). Moreover, anisole being less available than toluene, toluene was preferred for the next experiments.

## Effect of the nitrogen ligand

By using toluene as solvent, a series of structurally different nitrogen compounds (trialkylamines, aromatic amines, and other nitrogen compounds such as amidines, amides and urea - scheme 3) were evaluated as Rh-ligands. The catalytic results are summarized in Table 2. Without ligand, a high conversion was reached but no alcohol was produced (Table 2, entry 1). In the presence of NMP or DBU, no conversion was evidenced (Table 2, entries 2-3). For the other nitrogen compounds, the proportions of reaction products depend on their nature. Primary alcohols are mainly produced by using the following trialkylamines: TEA ( $Y_{(PA)}$ =49%; Table 2, entry 11), TBA ( $Y_{(PA)}$ =36%; Table 2, entry 12), THEA ( $Y_{(PA)}$ =22%; Table 2, entry 13), TMPDA ( $Y_{(PA)}$ =46%;

Table 2, entry 14), TMHDA ( $Y_{(PA)}=50\%$ ; Table 2, entry 15) and DABCO ( $Y_{(PA)}=13\%$ ; Table 2, entry 16). By plotting the primary alcohols yields against nitrogen compounds pKa, it appears that the best results were obtained for trialkylamines with pKa values between 7.8-10.9 (Figure 2). These results are in line with the conclusions of Whitehurst who have shown that rhodium/amine complexes catalyze hydrohydroxymethylation of 1-hexene for amines of pKa between 7 and 11.<sup>14</sup> No alcohol was found with very weak or very strong nitrogen compounds, in term of pKa. So, the basicity of the ligand is a key factor to obtain alcohols.



**Scheme 3.** Used nitrogen compounds (pKa value in brackets).

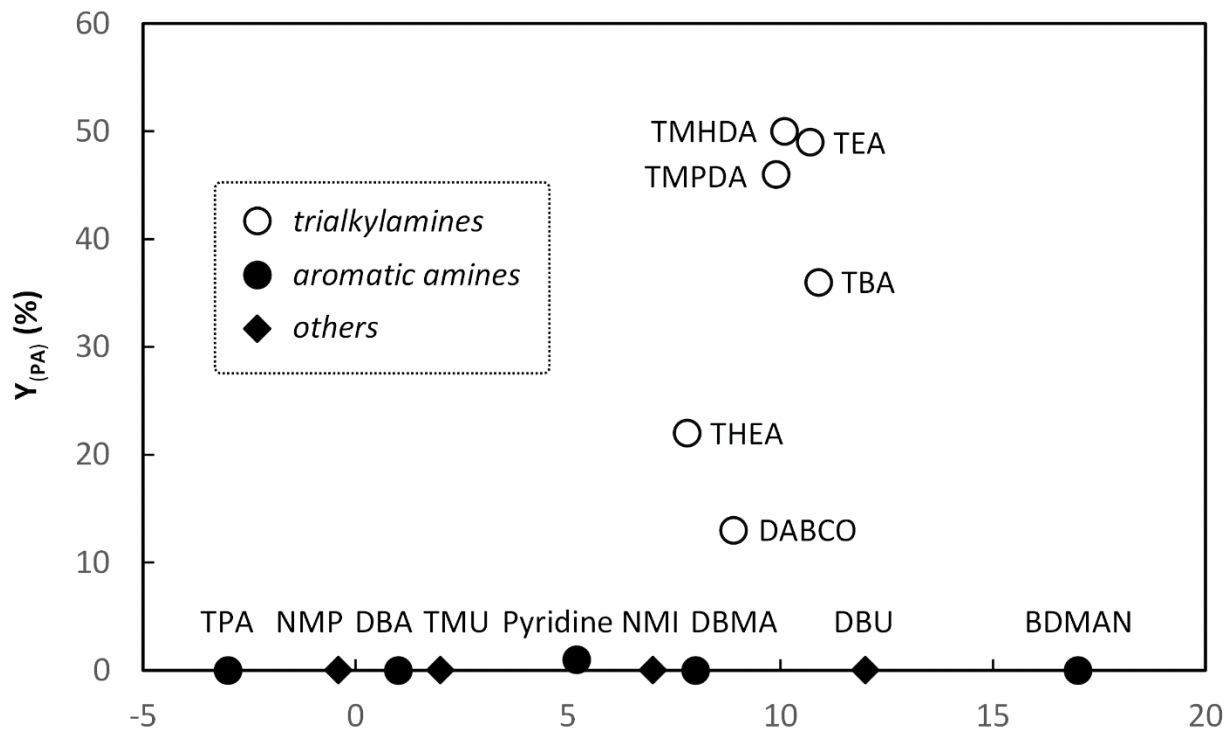
**Table 2.** Ethyl ricinoleate HHM with different nitrogen compounds.

Entry	Nitrogen compound	C. <sup>a</sup> (%)	Y <sub>(F)</sub> <sup>b</sup> (%)	Y <sub>(D)</sub> <sup>b</sup> (%)	Y <sub>(H)</sub> <sup>b</sup> (%)	Y <sub>(K)</sub> <sup>b</sup> (%)	Y <sub>(PA)</sub> <sup>b</sup> (%)	Y <sub>(S)</sub> <sup>b</sup> (%)
1	(-)	95	33	1	45	13	0	3
2	NMP	0	0	0	0	0	0	0
3	DBU	0	0	0	0	0	0	0
4	NMI	100	10	5	74	3	0	8
5	TMU	100	26	2	34	23	0	15
6	DBMA	100	21	0	44	19	0	16
7	DBA	100	33	0	15	16	0	36
8	TPA	100	32	14	29	14	0	11
9	BDMAN	74	20	0	31	17	0	6
10	Pyridine	100	24	0	51	15	1	9
11	TEA	93	1	0	21	17	49	5
12	TBA	100	0	0	35	17	36	12
13	THEA	95	6	1	34	18	22	14
14	TMPDA	100	0	0	38	14	46	2
15	TMHDA	100	0	0	33	15	50	2
16	DABCO	96	10	0	48	16	13	9

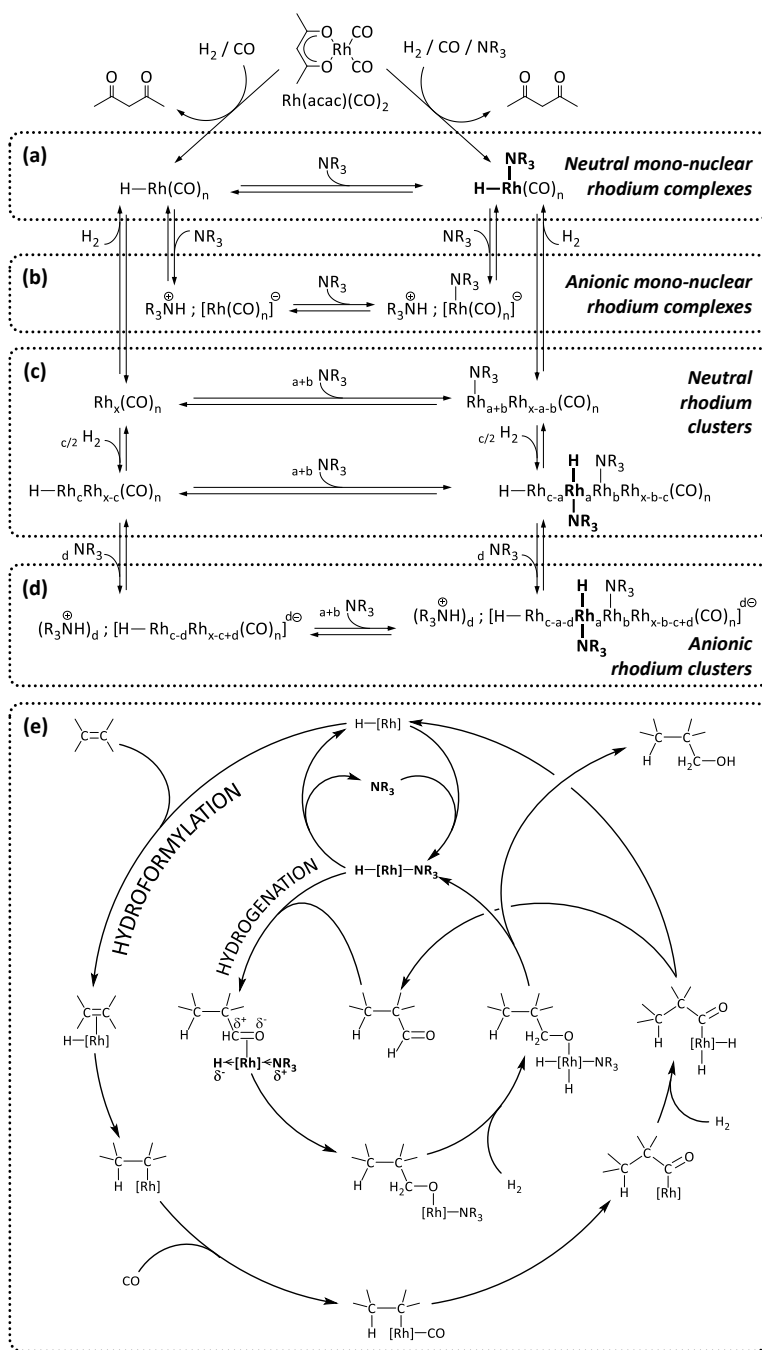
Experimental conditions: Rh(acac)(CO)<sub>2</sub> (6 mg, 23.3 μmol, 1 eq.), ethyl ricinoleate (1.90 g, 5.81 mmol, 250 eq.), nitrogen compound (11.6 mmol, 500 eq.) except for TMPDA, TMHDA, DABCO and BDMAN (5.8 mmol, 250 eq.), toluene (amount to reach a total volume of 8.7 mL in the autoclave), 80 bar of CO/H<sub>2</sub> (1:1), 80 °C, 24 h. <sup>a</sup> C. = global double CC bond conversion = total amount of C<sub>9</sub>=C<sub>10</sub> double bonds (in **(R)**) and of isomerized other CH=CH double bonds (in **(I)** compounds) that have been transformed into the others products (**(F)**, **(D)**, **(H)**, **(K)**, **(PA)** and **(S)**). <sup>b</sup> Y<sub>(X)</sub> = yield in product **(X)**.

Equilibria between different rhodium species could explain the catalytic results (Scheme 4). At the beginning of a catalytic experiment, an initial hydrogenolysis of the Rh-acac bond of the Rh(acac)(CO)<sub>2</sub> precursor should lead firstly to neutral mono-nuclear rhodium complexes, with CO and NR<sub>3</sub> (the amino compound) as possible ligands (Scheme 4, (a)). Depending on the number of coordinated electron-withdrawing CO ligands and on the basicity of the nitrogen compound used, these complexes can then generate anionic mono-nuclear rhodium complexes (Scheme 4, (b)) or lead to neutral rhodium clusters after Rh-Rh bonds and dihydrogen formation (Scheme 4, (c)). Finally, the neutral rhodium clusters can themselves be deprotonated by NR<sub>3</sub> and converted to anionic rhodium clusters (Scheme 4, (d)). The presence of rhodium clusters in the reaction medium was undoubtedly proved by an infra-red study done under CO/H<sub>2</sub> pressure. In particular, rhodium-rhodium bridging carbonyl groups were clearly identified by absorption peaks observed at a wavenumber between 1700 and 1850 cm<sup>-1</sup> (Figure 3). These observations are in good accordance with the Whitehurst works in which the presence of such rhodium clusters was also demonstrated by an infra-red study.<sup>14</sup> Because no primary alcohols were obtained in absence of a NR<sub>3</sub> type compound (Table 2, entry 1), it is probable that only the H-Rh-N moieties of the different possible rhodium species are active in aldehydes hydrogenation. This specificity could be due to an enhanced hydride character induced by the nitrogen ligand presence (polarization such as (δ<sup>-</sup>)H-[Rh]-N(δ<sup>+</sup>) – Scheme 4, (e)). So, the basicity of the nitrogen compound has to be sufficient to coordinate the rhodium center. Nevertheless, if the nitrogen compound is too basic, it can lead to anionic rhodium complexes possessing no H-Rh bonds and being therefore totally inactive. A catalytic cycle gathering the hydroformylation and the hydrogenation reactions is proposed in the Scheme 4 (Scheme 4, (e)).

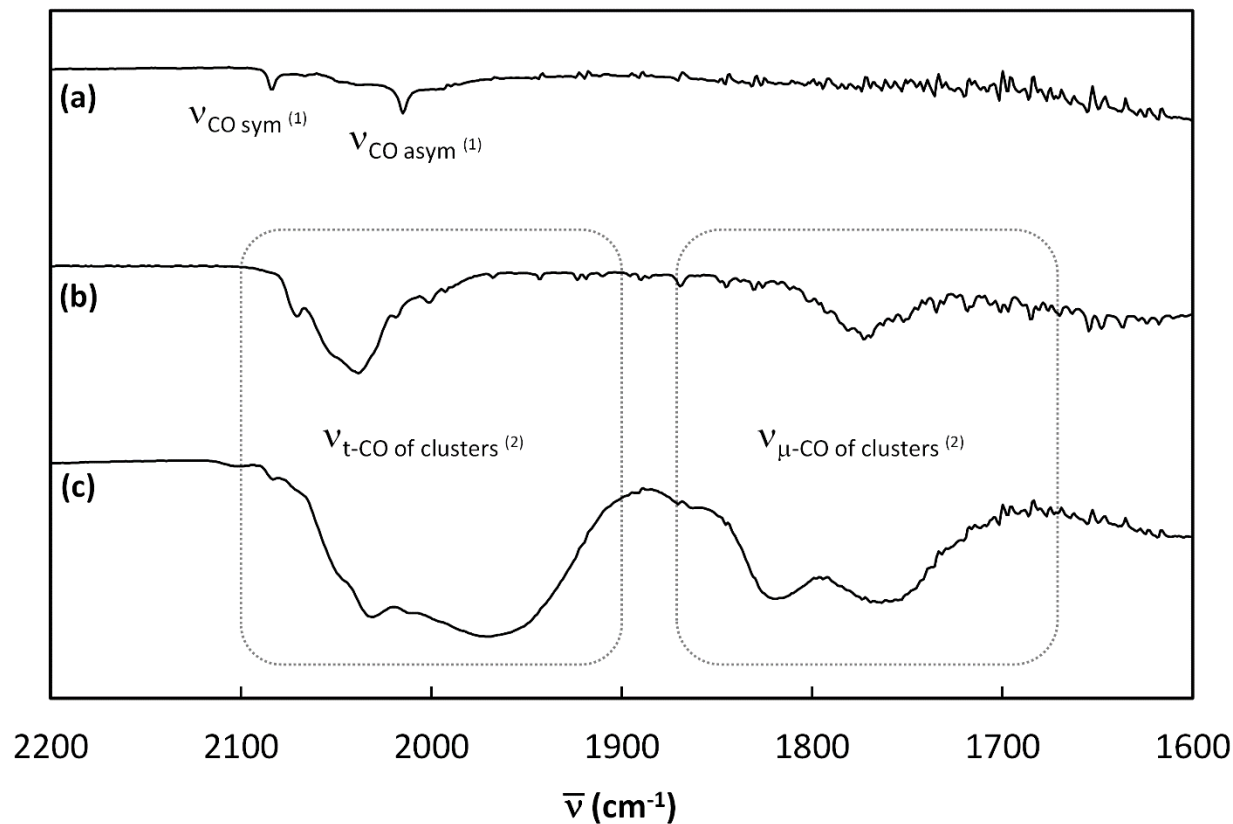




**Figure 2.** Primary alcohols yield ( $Y_{(PA)}(%)$ ), obtained in the experimental conditions of table 2) as a function of nitrogen compounds pKa.



**Scheme 4.** (a)-(d) Possible rhodium species formed from  $\text{Rh}(\text{acac})(\text{CO})_2$  in the presence of the nitrogen compound  $\text{NR}_3$  and under  $\text{CO}/\text{H}_2$  pressure (to simplify writing, equations are not equilibrated in terms of  $\text{CO}$  ligands and, only between (a) and (c) blocks, in terms of rhodium atoms and dihydrogen). (e) Proposed catalytic cycle for the hydrohydroxymethylation reaction explained the role of the nitrogen compound in the aldehydes hydrogenation activity.



**Figure 3.** Infrared spectrum of (a) a solution of  $\text{Rh}(\text{acac})(\text{CO})_2$ , 20 mM in *n*-heptane, at 20 °C, under 20 bar of  $\text{CO}/\text{H}_2$  (1:1), (b) the same solution after a heating of 1 h at 80 °C, under 20 bar of  $\text{CO}/\text{H}_2$  (spectrum recorded at 20 °C, under pressure), and (c) a solution of  $\text{Rh}(\text{acac})(\text{CO})_2$ , 20 mM in a 1:3 (w/w) triethylamine/*n*-heptane mixture, at 20 °C, under 20 bar of  $\text{CO}/\text{H}_2$  (1:1). <sup>(1)</sup> Symmetric and asymmetric stretching of the two CO ligands in  $\text{Rh}(\text{acac})(\text{CO})_2$  ( $2083 \text{ cm}^{-1}$  and  $2015 \text{ cm}^{-1}$ , respectively). <sup>(2)</sup> Stretching of terminal CO ligands (t-CO) and bridging CO ligands ( $\mu$ -CO) in rhodium clusters ( $1900\text{-}2100 \text{ cm}^{-1}$  and  $1700\text{-}1850 \text{ cm}^{-1}$ , respectively).

### Effect of the TEA amount

Among the various nitrogen ligands, TEA was chosen for (i) its efficiency as ligand, (ii) its availability and (iii) its low boiling point facilitating its evaporation at the end of the reaction. The experiment performed without TEA gave high conversion but no production of alcohol. Increasing the amount of TEA slightly affects the conversion and significantly modifies the primary alcohols proportion (Table 3). Indeed, the alcohols proportion reached a maximum of 50% at a ratio 1000 followed by a decrease at 38% for a ratio of 2000 (Table 3, entries 6 and 7). The proportion of free aldehydes decreased with increasing amount of TEA. In the presence of a high amount of TEA, the equilibria are displaced from hydroformylating Rh-carbonyl complexes toward hydrogenating Rh-amino complexes.

**Table 3.** Effect of the TEA amount on the ethyl ricinoleate HHM.

Entry	TEA/Rh <sup>a</sup>	C. <sup>b</sup> (%)	Y( <b>F</b> ) <sup>c</sup> (%)	Y( <b>D</b> ) <sup>c</sup> (%)	Y( <b>H</b> ) <sup>c</sup> (%)	Y( <b>K</b> ) <sup>c</sup> (%)	Y( <b>PA</b> ) <sup>c</sup> (%)	Y( <b>S</b> ) <sup>c</sup> (%)
1	0	95	33	1	45	13	0	3
2	5	100	25	3	37	17	5	13
3	15	80	12	0	27	18	7	16
4	200	85	1	0	35	16	29	4
5	500	93	1	0	21	17	49	5
6	1000	98	0	0	24	16	50	8
7	2000	95	0	0	34	16	38	7
8 <sup>d</sup>	4000	48	0	0	25	11	10	2

Experimental conditions: Rh(acac)(CO)<sub>2</sub> (6 mg, 23.3 μmol, 1 eq.), ethyl ricinoleate (1.90 g, 5.81 mmol, 250 eq.), triethylamine (TEA), toluene (amount to reach a total volume of 8.7 mL in the autoclave: from 6.5 mL (entry 1) to 0 mL (entry 7)), 80 bar of CO/H<sub>2</sub> (1:1), 80 °C, 24 h. <sup>a</sup> TEA/Rh molar ratio. <sup>b</sup> C. = global double CC bond conversion = total amount of C<sub>9</sub>=C<sub>10</sub> double bonds (in (**R**)) and of isomerized other CH=CH double bonds (in (**I**) compounds) that have been transformed

into the others products ((**F**), (**D**), (**H**), (**K**), (**PA**) and (**S**)). <sup>c</sup>  $Y_{(X)}$  = yield in product (**X**). <sup>d</sup> Same experiment as that of entry 7 excepted the Rh(acac)(CO)<sub>2</sub> mass: 3 mg instead of 6.

Actually, CO and TEA compete to coordinate the rhodium center. Primary alcohols being partially formed from hemiacetals, the lower hemiacetals productions were logically observed for the higher alcohols productions. With or without TEA, the percentages of ketone and saturated product are relatively stable (13-18% and 3-16%, respectively).

To evaluate the consequence of a substrate/Rh ratio increase (from 250 to 500), an experiment was done in pure TEA with an amount of introduced Rh(acac)(CO)<sub>2</sub> catalyst precursor divided by 2 (compare entries 7 and 8, Table 3). Expectedly, the conversion decreased (from 95% to 48%) as well as the primary alcohols yield (from 38% to 10%).

### Effect of the reaction pressure

**Table 4.** Effect of the reaction pressure on the ethyl ricinoleate HHM.

Entry	P <sub>CO/H<sub>2</sub></sub> (bar)	C. <sup>a</sup> (%)	Y( <b>F</b> ) <sup>b</sup> (%)	Y( <b>D</b> ) <sup>b</sup> (%)	Y( <b>H</b> ) <sup>b</sup> (%)	Y( <b>K</b> ) <sup>b</sup> (%)	Y( <b>PA</b> ) <sup>b</sup> (%)	Y( <b>S</b> ) <sup>b</sup> (%)
1	20	24	0	0	3	16	1	4
2	40	84	0	0	14	28	26	16
3	60	96	0	0	18	22	43	13
4	80	98	0	0	24	16	50	8
5	100	100	0	0	27	14	53	5
6 <sup>c</sup>	80	100	0	0	22	15	53	10

Experimental conditions: Rh(acac)(CO)<sub>2</sub> (6 mg, 23.3 μmol, 1 eq.), ethyl ricinoleate (1.90 g, 5.81 mmol, 250 eq.), TEA (2.35 g, 3.2 mL, 23.2 mmol, 1000 eq.), toluene (3.3 mL), CO/H<sub>2</sub> (1:1), 80°C,

24 h. <sup>a</sup> C. = global double CC bond conversion = total amount of C<sub>9</sub>=C<sub>10</sub> double bonds (in **(R)**) and of isomerized other CH=CH double bonds (in **(I)** compounds) that have been transformed into the others products (**(F)**, **(D)**, **(H)**, **(K)**, **(PA)** and **(S)**). <sup>b</sup> Y<sub>(X)</sub> = yield in product **(X)**. <sup>c</sup> CO/H<sub>2</sub> (1:2).

The effect of the reaction pressure was studied for the Rh/TEA catalytic system at a ratio of 1/1000 at 80 °C from 20 bar to 100 bar of CO/H<sub>2</sub> (1:1). Upon increasing the total CO/H<sub>2</sub> pressure from 20 bar to 80 bar, the conversion significantly varied from 24% to 100% and the yield of primary alcohols reached a maximum of 53% at 100 bar (Table 4). At 20 bar, no alcohol was produced and the main product was the ketone **(K)**, resulting from isomerization reaction (Y<sub>(K)</sub>=16%; Table 4, entry 1). At 40 bar, the alcohols and ketone production and the hydrogenation of the C=C bonds were both higher (Table 4, entry 2). From 40 to 60 bar, the yield in alcohols was raised from 26% to 43% (Table 4, entry 3). For the experiments performed at 80 and 100 bar (Table 4, entries 4 and 5) or by varying relative proportions of CO/H<sub>2</sub> (from 1/1 to 1/2; Table 4, entries 4 and 6), the various percentages have not been significantly modified. So, a pressure of 80 bar (CO/H<sub>2</sub>: 1/1) was chosen for the remaining experiments.

### **Effect of the reaction temperature**

The effect of the reaction temperature was studied for the catalytic system Rh/TEA at a ratio of 1/1000 from 40 to 140 °C (Table 5). The conversion increased with the temperature. At 40 °C, the conversion was very low (14%) whereas 100% of conversion was reached at 100 °C and beyond. The yield of alcohols was the highest at 100 °C and then decreased. At the same time, the proportions of ketone and saturated product increased, from 100 °C, showing a decrease in selectivity with the temperature. At high temperature, isomerization reaction was facilitated,

leading to the higher production of ketone. The best compromise was achieved at a temperature of 100 °C.

**Table 5.** Effect of the reaction temperature on the ethyl ricinoleate HHM.

Entry	T(°C)	C. <sup>a</sup> (%)	Y <sub>(F)</sub> <sup>b</sup> (%)	Y <sub>(D)</sub> <sup>b</sup> (%)	Y <sub>(H)</sub> <sup>b</sup> (%)	Y <sub>(K)</sub> <sup>b</sup> (%)	Y <sub>(PA)</sub> <sup>b</sup> (%)	Y <sub>(S)</sub> <sup>b</sup> (%)
1	40	14	0	0	12	0	0	2
2	60	70	0	0	42	4	24	0
3	80	98	0	0	24	16	50	8
4	100	100	0	0	16	26	54	4
5	120	100	0	0	10	41	38	11
6	140	100	0	0	5	50	20	25

Experimental conditions: Rh(acac)(CO)<sub>2</sub> (6 mg, 23.3 μmol, 1 eq.), ethyl ricinoleate (1.90 g, 5.81 mmol, 250 eq.), TEA (2.35 g, 3.2 mL, 23.2 mmol, 1000 eq.), toluene (3.3 mL), 80 bar of CO/H<sub>2</sub> (1:1), 24 h. <sup>a</sup> C. = global double CC bond conversion = total amount of C<sub>9</sub>=C<sub>10</sub> double bonds (in **(R)**) and of isomerized other CH=CH double bonds (in **(I)** compounds) that have been transformed into the others products (**(F)**, **(D)**, **(H)**, **(K)**, **(PA)** and **(S)**). <sup>b</sup> Y<sub>(X)</sub> = yield in product **(X)**.

### Effect of a temperature progressive increase

In order to increase the production of alcohols, experiments with a temperature progressive increase were performed (Table 6). An increase in reaction time led to an increase in alcohols amount due to the progressive hydrogenation of the hemiacetals (from Y<sub>(PA)</sub>=50% to Y<sub>(PA)</sub>=63%; Table 6, entries 1-2). In addition, as the formation of ketone is an irreversible step, its production has to be regulated by controlling the reaction temperature. So, a two-step heating was performed

in order to decrease the amount of ketone: 60 °C during 24 h and then 80 °C during 24 h (Table 6, entry 3).

**Table 6.** Effect of a temperature progressive increase on the ethyl ricinoleate HHM.

Entry	T(°C)[t(h)] <sup>a</sup>	C. <sup>b</sup> (%)	Y( <b>F</b> ) <sup>c</sup> (%)	Y( <b>D</b> ) <sup>c</sup> (%)	Y( <b>H</b> ) <sup>c</sup> (%)	Y( <b>K</b> ) <sup>c</sup> (%)	Y( <b>PA</b> ) <sup>c</sup> (%)	Y( <b>S</b> ) <sup>c</sup> (%)
1 <sup>d</sup>	80[24]	98	0	0	24	16	50	8
2 <sup>d</sup>	80[72]	100	0	0	13	16	63	8
3	60[24]-80[24]	100	0	0	29	10	60	1
4	60[48]-100[32]	100	0	0	8	8	75	9
5	80[48]-100[32]	100	0	0	0	12	80	8
6 <sup>e</sup>	80[48]-100[32]	100	0	0	10	13	70	7

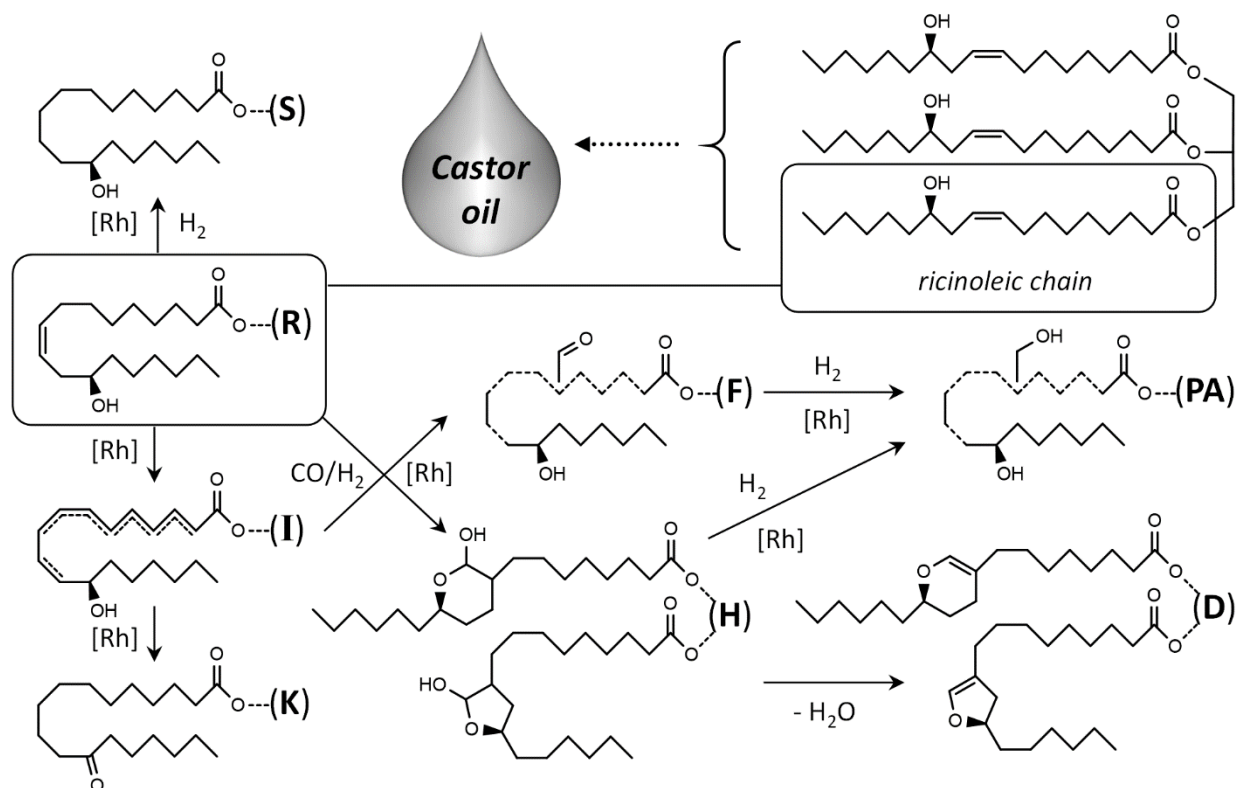
Experimental conditions: Rh(acac)(CO)<sub>2</sub> (6 mg, 23.3 μmol, 1 eq.), ethyl ricinoleate (1.90 g, 5.81 mmol, 250 eq.), TEA (2.35 g, 3.2 mL, 23.2 mmol, 1000 eq.), toluene (3.3 mL), 80 bar of CO/H<sub>2</sub> (1:1). <sup>a</sup> T(°C)[t(h)] means a reaction done at a temperature of T(°C) during a time of t(h); T<sub>1</sub>(°C)[t<sub>1</sub>(h)]-T<sub>2</sub>(°C)[t<sub>2</sub>(h)] means a reaction done at a temperature of T<sub>1</sub>(°C) during a time of t<sub>1</sub>(h), followed by a heating at T<sub>2</sub>(°C) during a time of t<sub>2</sub>(h). <sup>b</sup> C. = global double CC bond conversion = total amount of C<sub>9</sub>=C<sub>10</sub> double bonds (in (**R**)) and of isomerized other CH=CH double bonds (in (**I**) compounds) that have been transformed into the others products ((**F**), (**D**), (**H**), (**K**), (**PA**) and (**S**)). <sup>c</sup> Y<sub>(X)</sub> = yield in product (**X**). <sup>d</sup> A kinetic follow-up corresponding to the experiment done at 80 °C is given in the supporting information (Figure S25). <sup>e</sup> Experiment done without toluene and with TEA as ligand and solvent (4.70 g, 6.5 mL, 46.5 mmol, 2000 eq.).

By this way the percentage of ketone decreased from 16% to 10% and the percentage of alcohols increased from 50% to 60%. This last percentage can reach 75% by increasing both reaction time and second temperature (Table 6, entry 4; 100 °C instead of 80 °C). Unfortunately, this value cannot be improved anymore. The best yield of 80% in alcohols was obtained by a two-step heating (80 °C during 48 h and then 100 °C during 32 h; Table 6, entry 5). The same experiment was



performed in TEA, as ligand and solvent, but the performance was lower, with 70% of alcohols obtained (Table 6, entry 5).

### Hydrohydroxymethylation of castor oil



**Scheme 5.** Carboxylate fatty chains obtained from castor oil under CO/H<sub>2</sub> in the presence of the [Rh/TEA] catalytic system (chains named by the same letters than those used with ethyl ricinoleate).

The hydrohydroxymethylation of castor oil was performed under the best reaction conditions found in the case of ethyl ricinoleate (Scheme 5 and Table 7). The ratios Rh/TEA and Rh/C=C were equal to 1/1000 and 1/250, respectively. As for ethyl ricinoleate, all details for determination

of the products structures and for calculation of conversion and yields from the  $^1\text{H}$  NMR spectra are presented in supporting information (see SI, parts IV-2 and IV-3). The first experiment was performed in the absence of ligand (Table 7, entry 1). The conversion was total after 24 h, but no alcohol was produced. As expected, addition of TEA led to the formation of alcohols ( $Y_{(\text{PA})}=50\%$ ) after 24 h at 80 °C (Table 7, entry 2). A two-step heating (80 °C during 24 h and then 100 °C during 24 h) allowed the formation of 65% of alcohol (Table 7, entry 3). An alcohols yield of 74% was reached after 48 h at 80 °C, followed by 32 h at 100 °C (Table 7, entry 4). In pure TEA, alcohols yields of 10%, 35% and 54% were obtained in 24 h, at 60 °C, 80 °C and after a 80 °C-100 °C (24 h- 24 h) sequence, respectively (Table 7, entries 5-7). Interestingly, the triglyceride structure of castor oil did not prevent to reach yields similar to those obtained with ethyl ricinoleate. Interestingly, the obtained yields with ethyl ricinoleate and castor oil were similar although the structure of castor oil is more complex.

**Table 7.** Castor oil HHM.

Entry	TEA/Rh <sup>a</sup>	T(°C)[t(h)] <sup>b</sup>	C. <sup>c</sup> (%)	Y <sub>(F)</sub> <sup>d</sup> (%)	Y <sub>(D)</sub> <sup>d</sup> (%)	Y <sub>(H)</sub> <sup>d</sup> (%)	Y <sub>(K)</sub> <sup>d</sup> (%)	Y <sub>(PA)</sub> <sup>d</sup> (%)	Y <sub>(S)</sub> <sup>d</sup> (%)
1	0	80[24]	100	31	2	38	15	0	14
2	1000	80[24]	100	0	0	20	19	50	11
3	1000	80[24]-100[24]	100	0	0	4	16	65	15
4	1000	80[48]-100[32]	100	0	0	0	12	74	14
5	2000	60[24]	60	0	0	42	7	10	1
6	2000	80[24]	95	0	0	35	15	35	10
7	2000	80[24]-100[24]	100	0	0	14	15	54	17

Experimental conditions: Rh(acac)(CO)<sub>2</sub> (6 mg, 23.3 μmol, 1 eq.), castor oil (1.79 g, corresponding to 5.81 mmol of ricinoleic chains = 250 eq.), toluene (amount to reach a total volume of 8.7 mL in the autoclave: from 6.5 mL (entry 1) to 0 mL (entry 6-8)), 80 bar of CO/H<sub>2</sub> (1:1). <sup>a</sup> TEA/Rh molar ratio. <sup>b</sup> T(°C)[t(h)] means a reaction done at a temperature of T(°C) during a time of t(h); T<sub>1</sub>(°C)[t<sub>1</sub>(h)]-T<sub>2</sub>(°C)[t<sub>2</sub>(h)] means a reaction done at a temperature of T<sub>1</sub>(°C) during a time of t<sub>1</sub>(h), followed by a heating at T<sub>2</sub>(°C) during a time of t<sub>2</sub>(h). <sup>c</sup> C. = global double CC bond conversion = total amount of C<sub>9</sub>=C<sub>10</sub> double bonds and of isomerized other CH=CH double bonds that have been transformed into the different carboxylate fatty chains called by the same letters used for products from ethyl ricinoleate ((F), (D), (H), (K), (PA) and (S)). <sup>d</sup> Y<sub>(X)</sub> = yield in the different carboxylate fatty chains (X).

## Conclusions

In summary, we succeeded in direct functionalization of ethyl ricinoleate and castor oil with primary alcohol functions. This functionalization of the ricinoleic chain was challenging not only due to the low reactivity of the internal carbon-carbon double bond but also due to the formation of hemiacetal functions by reaction between the secondary alcohol initially present and the formyl group formed by the hydroformylation step. The best yields in primary alcohols were equal to 74%

and 80% for castor oil and ethyl ricinoleate, respectively. For these two results, no more hemiacetal was present in the final medium and the co-products were the ketone and the saturated product, coming from the C=C double bond isomerization and hydrogenation, respectively. Moreover, the developed one-pot tandem reaction proceeds very cleanly and is fully atom-economical. Depending on the substrate used, linear molecules with 2 alcohol functions or branched molecules with 6 alcohol functions can be obtained. Works are in progress to synthesize bio-based polyesters and polyurethanes from these polyhydroxylated compounds.

**Supporting Information.** This part contains an experimental section, the characterization of reaction products and the determination of conversions and yields.

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### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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## Synopsis

Associated with rhodium and under CO/H<sub>2</sub> pressure, trialkylamines promote hydrohydroxymethylation of biosourced ricinoleic derivatives into polyols with high yields (up to 80%).

## Abstract graphic

