

# Supporting Information to “Recycling of a Thermo-responsive ‘Catalyst Pill’: Separation of a Molecular Catalyst in solid Ethylene Carbonate in Various Reactions”

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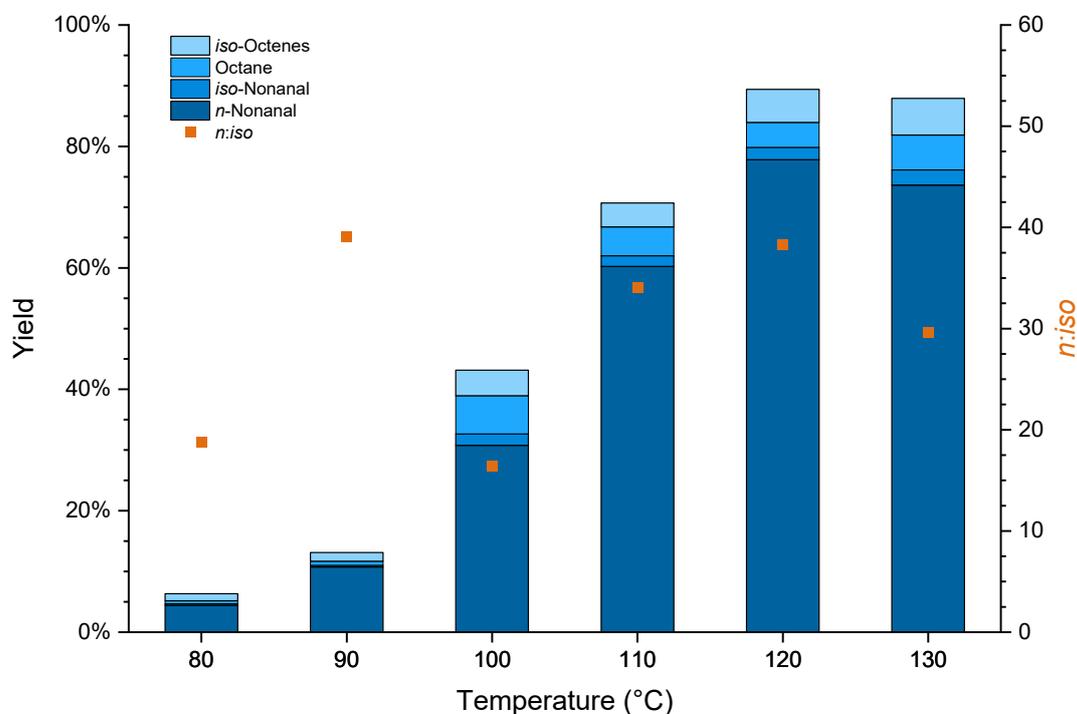
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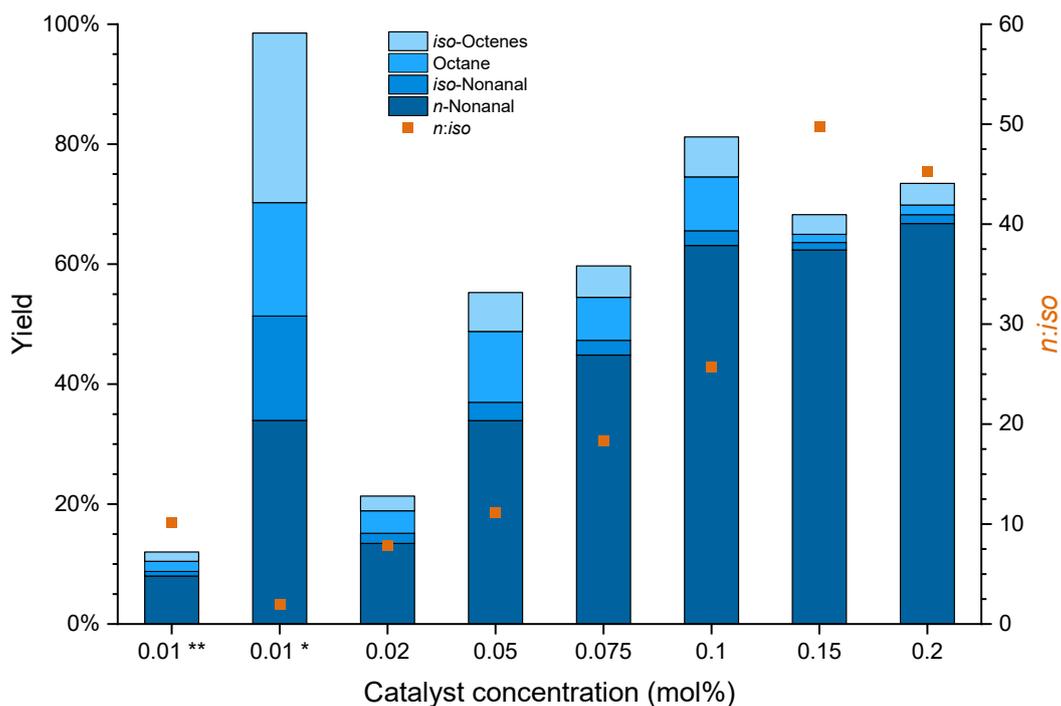
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# 1 Supporting Data and Graphs

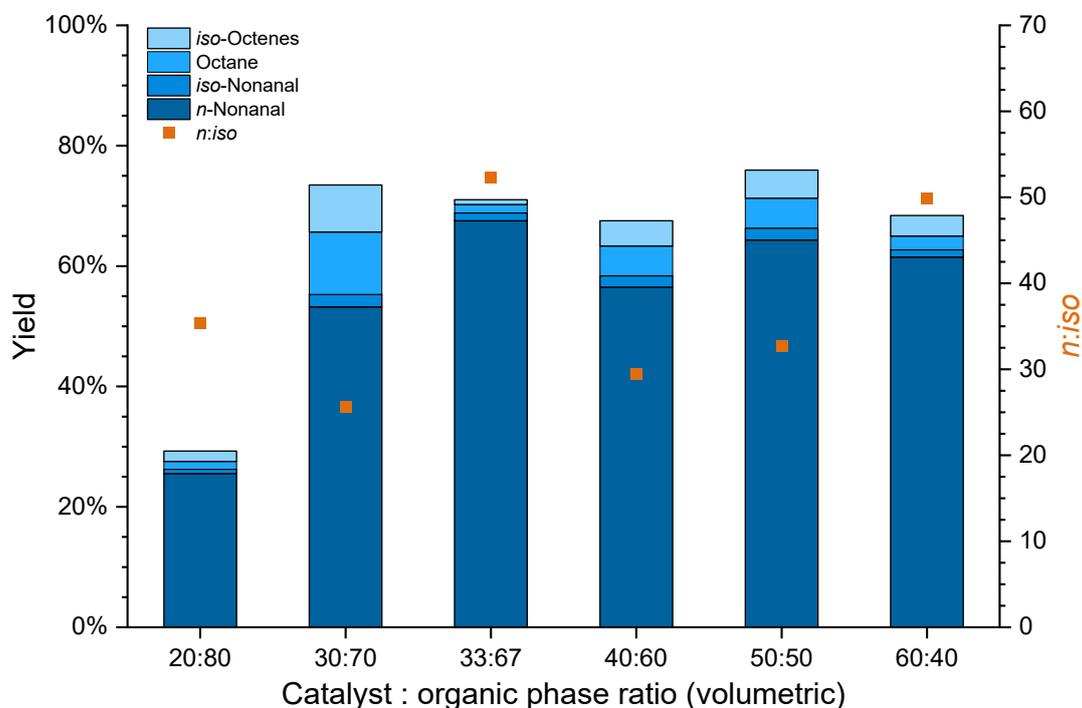
## 1.1 Supporting Data for Screening Reactions with Ethylene Carbonate



**Figure S1:** Yield, conversion and *n:iso* ratios in the hydroformylation of 1-octene (2.0 mL, with 5 vol% mesitylene as internal standard) in ethylene carbonate (1.0 mL) at different temperatures ranging from 80 °C to 130 °C with a Rh/sulfoXantphos catalyst (0.1 mol% relative to 1-octene, Rh:P = 1:4) at 50 bar CO/H<sub>2</sub> (1:1) in 20 mL autoclave reactors and 1000 rpm stirring speed for 2 h reaction time.



**Figure S2:** Yield, conversion and *n:iso* ratios in the hydroformylation of 1-octene (4.0 mL, with 5 vol% mesitylene as internal standard) in ethylene carbonate (2.0 mL) at different Rh/sulfoXantphos (Rh:P = 1:4) catalyst concentrations in mol% relative to the amount of substrate at 110 °C for 2 h reaction time with 80 bar CO/H<sub>2</sub> (1:1) in 20 mL autoclave reactors and 1000 rpm stirring speed. \* Inaccurate Rh:P ratio due to small amounts weighed resulting in a reduced selectivity and higher reaction rates. \*\* Reaction conducted again with a Rh:P of 1:5 instead of 1:4.



**Figure S3:** Yield, conversion and *n:iso* ratios in the hydroformylation of 1-octene (2.0 mL, with 5 vol% mesitylene as internal standard) in ethylene carbonate at different EC:organic phase ratios with Rh/sulfoXantphos (0.1 mol% relative to the substrate, Rh:P = 1:4) at 110 °C for 2 h reaction time with 80 bar CO/H<sub>2</sub> (1:1) in 20 mL autoclave reactors and 1000 rpm stirring speed.

## 1.2 Supporting Data for Recycling Reactions with Ethylene Carbonate

**Table S1:** Rhodium (ppm and % of initial amount), phosphorus (ppm and % of initial amount) and EC (mg) leaching per run in the catalyst recycling in the hydroformylation of 1-octene.

Run	Rh Leaching*		P Leaching*		EC Leaching mg
	ppm	%	ppm	%	
1	0.855	0.124%	0.277	0.031%	0.0634
2	0.173	0.026%	<0.001	<0.001%	0.0889
3	0.524	0.077%	<0.001	<0.001%	0.0620
4	0.296	0.044%	0.306	0.035%	0.0752
5	0.267	0.040%	0.016	0.002%	0.0825
6	0.298	0.045%	<0.001	<0.001%	0.0813
7	0.298	0.044%	<0.001	<0.001%	0.0721
8	0.227	0.034%	0.207	0.024%	0.0812
9	0.192	0.029%	0.009	<0.001%	0.0855
10	0.290	0.043%	<0.001	<0.001%	0.0626
11	0.008	0.001%	0.016	0.002%	0.0478
12	0.259	0.038%	0.050	0.006%	0.0558

**Table S2:** Rhodium (ppm and % of initial amount), phosphorus (ppm and % of initial amount) and EC (mg) leaching per run in the switch catalyst recycling in the hydroformylation of 1-octene and 1-decene.

Run	Substrate	Rh Leaching		P Leaching		EC Leaching
		ppm	%	ppm	%	mg
1	1-octene	0.5	0.077%	0.6	0.016%	0.0714
2	1-decene	0.4	0.062%	0.6	0.016%	0.0215
3	1-octene	0.3	0.045%	0.4	0.010%	0.0367
4	1-decene	0.5	0.076%	0.5	0.013%	0.0077
5	1-octene	0.6	0.087%	0.5	0.012%	0.0122
6	1-decene	0.8	0.124%	0.4	0.011%	0.0272

**Table S3:** Rhodium (ppm and % of initial amount), phosphorus (ppm and % of initial amount) and EC (mg) leaching per run in the switch catalyst recycling in the hydroformylation of 1-octene and hydrogenation of the C<sub>14</sub> Aldol product.

Run	Substrate	Rh Leaching		P Leaching		EC Leaching
		ppm	%	ppm	%	mg
1	1-octene	2.2	0.304%	1.8	0.045%	0.0432
2	C <sub>14</sub> Aldol	0.1	0.014%	0.2	0.005%	0.0853
3	1-octene	0.2	0.028%	0.1	0.003%	0.0513
4	C <sub>14</sub> Aldol	0.2	0.029%	0.2	0.005%	0.0777
5	1-octene	0.6	0.082%	0.8	0.020%	0.0180
6	C <sub>14</sub> Aldol	4.1	0.587%	2.9	0.076%	0.0708

## 2 Experimental

### General considerations

All reactions were conducted under argon inert gas atmosphere unless stated otherwise with argon supplied by *AirLiquide* (99.9999 purity). Air sensitive chemicals were stored in a glovebox and standard Schlenk techniques were applied. Mesitylene was obtained from *Alfa Aesar*, *n*-decane was supplied by *TCI* and 1-octene was obtained from *Across Organics*, *Sigma Aldrich* and *abcr*. All other chemicals were obtained from *Sigma Aldrich*. All chemicals were used as obtained from the vendors and degassed before application in catalytic reactions. Deionized water was obtained from a *MilliQ IQ 7000* device purchased from *Merck Millipore*. Carbon monoxide (99.999% purity) and hydrogen (99.999% purity) for catalytic reactions were obtained from *AirLiquide*.

NMR Measurements were carried out at ambient temperature using a *Bruker AVANCE NEO 400*-spectrometer ( $^1\text{H}$ : 400 MHz,  $^{31}\text{P}$ : 162 MHz). Chemical shifts were given in ppm and the residual solvent signal of deuterated solvent was referenced to trimethyl silane for  $^1\text{H}$  NMR spectra and to phosphoric acid for  $^{31}\text{P}$  NMR spectra.

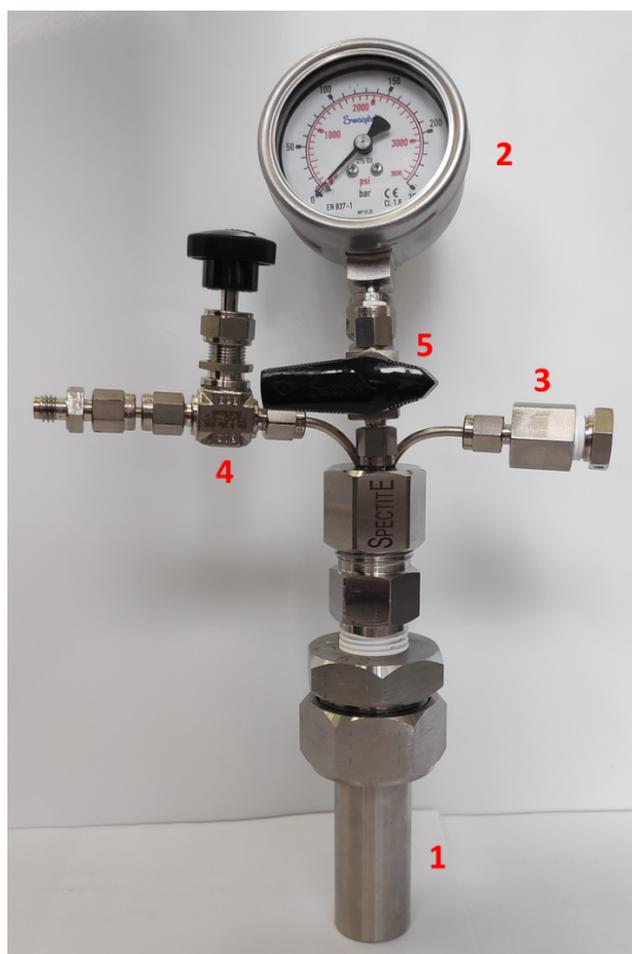
GC measurements were conducted on a *Nexis GC-2030* purchased from *Shimadzu* with a flame ionization detector. A *GCMS-QP2020* by *Shimadzu* was used to conduct GC with in-line mass spectrometry measurements. For both apparatus *Rtx-1* columns of the company *Restek* with a length of 30 m, an inner diameter of 0.25 mm and a particle size of 0.5  $\mu\text{m}$  were installed and helium was used as a carrier gas. A GC FID of the same model with a *CP Wax 52 CB* column with a length of 60 m, an inner diameter of 0.25 mm and a particle size of 0.25  $\mu\text{m}$  was used for measuring the product solution after the Aldol reaction and hydrogenation. The Sternberg method was applied to approximate GC factors for non-calibrated substances.<sup>[1]</sup>

ICP-MS measurements were conducted on an *ICPMS-2030* from *Shimadzu* with a sample preparation carried out using a *Mars 6* microwave by *CEM* and by *Mikroanalytisches Laboratorium Kolbe* on an ICP-OES *Acros Spectro* by the company *Spectro* with a sample preparation carried out on a *Mars 6* microwave by *CEM*. Samples were analyzed for rhodium and phosphorus content.

Mass spectra were measured on an *Advion Expression<sup>L</sup> CMS* purchased from *Advion*. The ESI method was used with the pure or pre-dissolved sample.

### General Procedure for Hydroformylation Autoclave Reactions

Hydroformylation experiments were conducted in 20 mL (total volume) autoclave reactors (Figure S4).  $[\text{Rh}(\text{acac})(\text{CO})_2]$ , sulfoXantphos and EC were weighed into the glass inlet in the glovebox. The inlet was inserted into the autoclave reactor outside the glovebox, which was then closed and placed under inert gas at the Schlenk line. The substrate stock solution was filled into the reactor through the ball valve (5). Most reactions were conducted with a total reaction volume of 3 mL. Synthesis gas was applied through the needle valve (4). The autoclave was placed in a pre-heated cone and the stirring was started 10 min after to ensure that the EC phase had fully melted. After the reaction, the reactor was placed in an ice bath for cooling, the remaining gas was vented and a sample of the organic phase was taken. Mesitylene was used as internal standard in all Hydroformylation reactions. Samples were analyzed using GC FID. Reactions with water as a catalyst phase were carried out using the same reaction conditions.

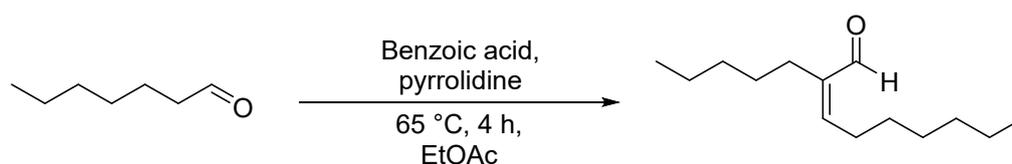


**Figure S4:** Picture of the applied autoclave consisting of a reaction vessel (1), a manometer (2), a rupture disk (3), a needle valve (4) and a ball valve or stopper (5).

## General Procedure for Hydroformylation Recycling Experiments

Recycling reactions were carried out as described for the hydroformylation reactions above. The organic phase was removed under air after the reaction and the inlet with the solid catalyst phase was placed back into the autoclave. Vacuum was applied briefly and the autoclave was placed under inert gas. Fresh substrate stock solution was added, the reactor pressurized and the next run started according to the same procedure as for batch reactions. The organic phase of each run was analyzed by GC FID. The amount of leached EC was determined by the GC FID analysis and ICP-MS measurements of the organic phase were conducted to determine the leached rhodium and phosphorus. Leached EC was resupplied one run later (for example the EC leached in the first run was resupplied before the start of the third run). Recycling reactions were conducted in 20 mL autoclave reactors.

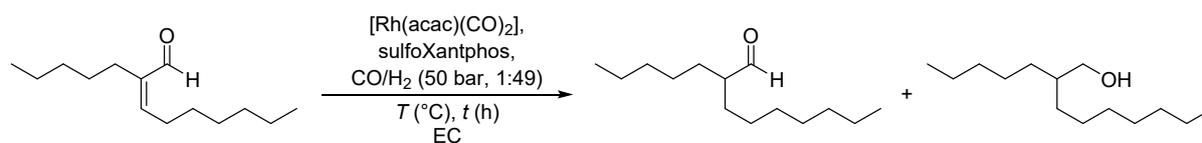
## Synthesis of the C<sub>14</sub>-Aldol Product from Heptanal



**Scheme S1:** Aldol condensation reaction of heptanal to the C<sub>14</sub> Aldol product.

The reaction was conducted based on literature of Vorholt *et al.*<sup>[2]</sup> The aldol product was obtained in 97% purity.

## General Procedure for the Hydrogenation of C<sub>14</sub>-Aldol Product Experiments



**Scheme S2:** Hydrogenation of the C<sub>14</sub> Aldol product to the C<sub>14</sub> compound with a hydrogenated double bond and to the fully hydrogenated product using a rhodium precursor and sulfoxantphos as a ligand with synthesis gas in EC.

The hydrogenation experiments of the Aldol product were carried out in 20 mL stainless steel autoclave reactors in a similar manner to the hydroformylation reactions. The reactors were pressurized with H<sub>2</sub> only. The reaction products were analyzed by GC FID using a *Rtx-1* and a *CpWax* column as mentioned above.

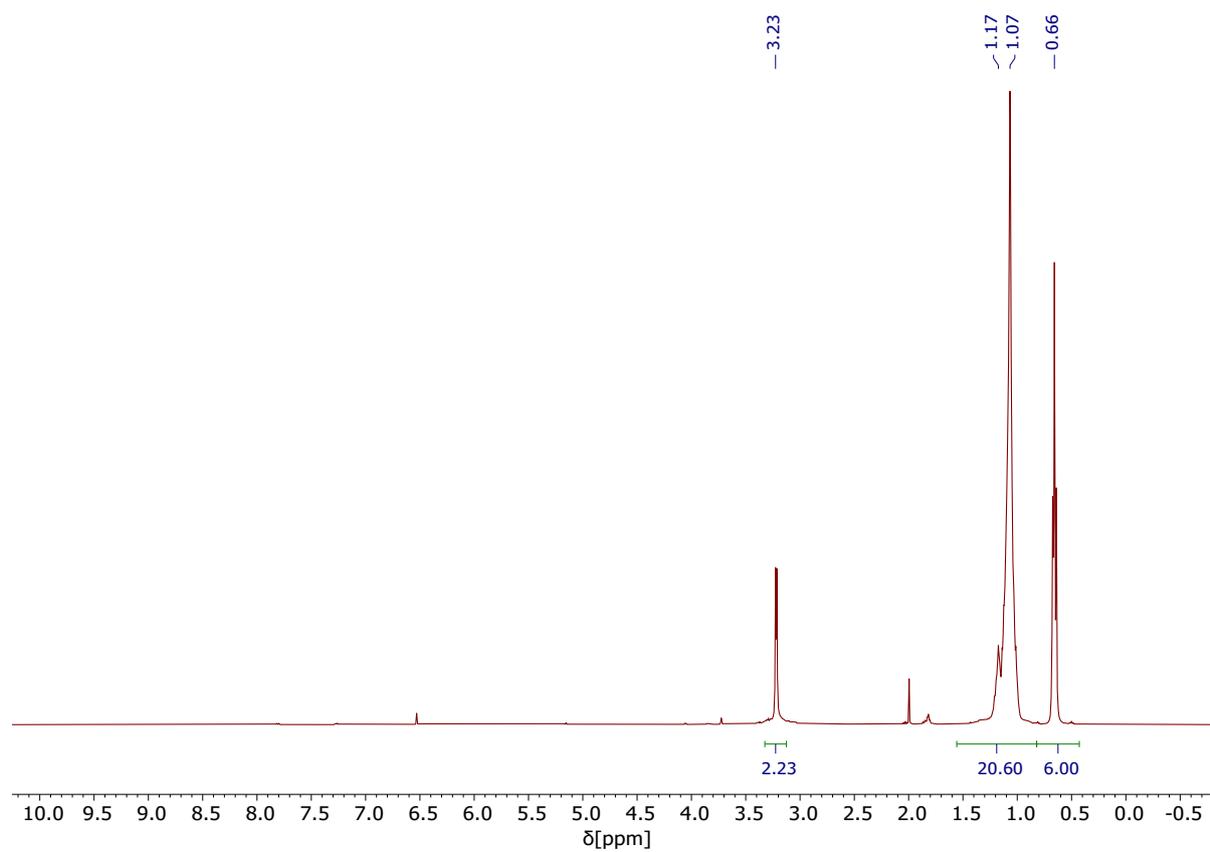
### **General Procedure for the Hydrogenation of C<sub>14</sub> Aldol Product Experiments**

Hydroformylation experiments were conducted in 20 mL (total volume) autoclave reactors (details in the SI). [Rh(acac)(CO)<sub>2</sub>], sulfoXantphos and EC were weighed into the glass inlet in the glovebox. The inlet was inserted into the autoclave reactor outside the glovebox, which was then closed and placed under inert gas at the Schlenk line. The substrate stock solution was filled into the reactor. Most reactions were conducted with a total reaction volume of 3 mL (1 mL EC and 2 mL organic phase). The autoclave was placed in a pre-heated cone after pressurization with CO and H<sub>2</sub> to the designated pressure at ambient temperature and the stirring was started 10 min after to ensure that the EC phase had fully liquified. After the reaction, the reactor was placed in an ice bath for cooling, the remaining gas was vented and the autoclave was opened. The product solution was decanted from the solid catalyst phase and a sample of the organic phase was taken. Mesitylene was used as internal standard in all hydroformylation reactions. Samples were analyzed using GC FID.

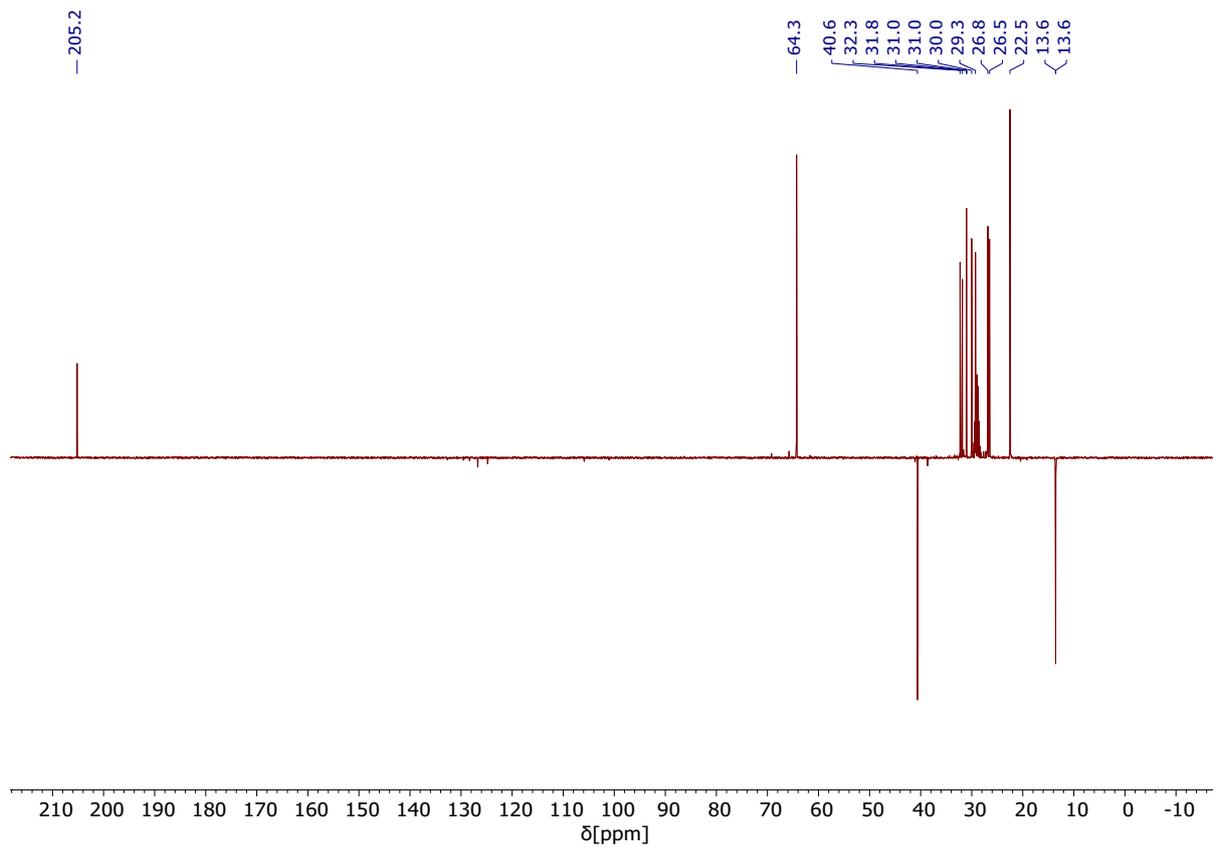
### **General Procedure for Switch Recycling Experiments**

The switch catalyst recycling experiments were carried out in a similar manner to the hydroformylation recycling experiments. Runs with the Aldol product as a substrate were carried out using only H<sub>2</sub> gas according to the procedure for batch hydrogenation reactions.

### 3 NMR Spectra

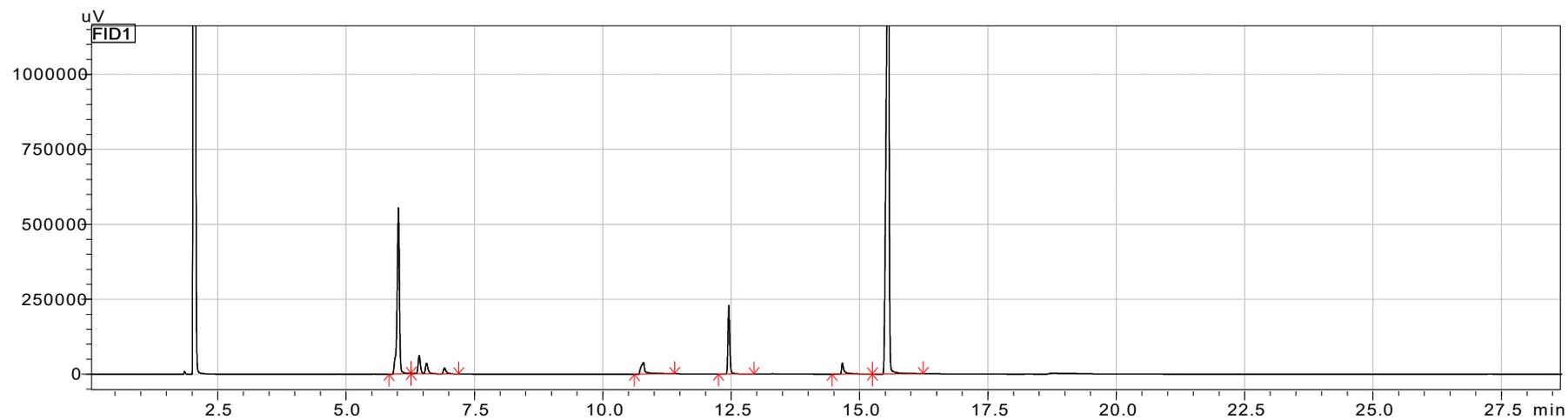


**Figure S5:** <sup>1</sup>H NMR Spectrum (400 MHz, acetone-*d*<sub>6</sub>, AT) of the saturated alcohol from the hydrogenation of the C<sub>14</sub> Aldol product. δ = 0.66 (t, 6 H, CH<sub>3</sub>), 1.07 (m, 20 H, CH<sub>2</sub>), 1.17 (m, 1 H, CH), 2.23 (d, 2 H, CH<sub>2</sub>-OH) ppm. Impurities caused by traces of Mesitylene and the saturated C<sub>14</sub> Aldehyde as an Intermediate in the conversion of the Aldol product.

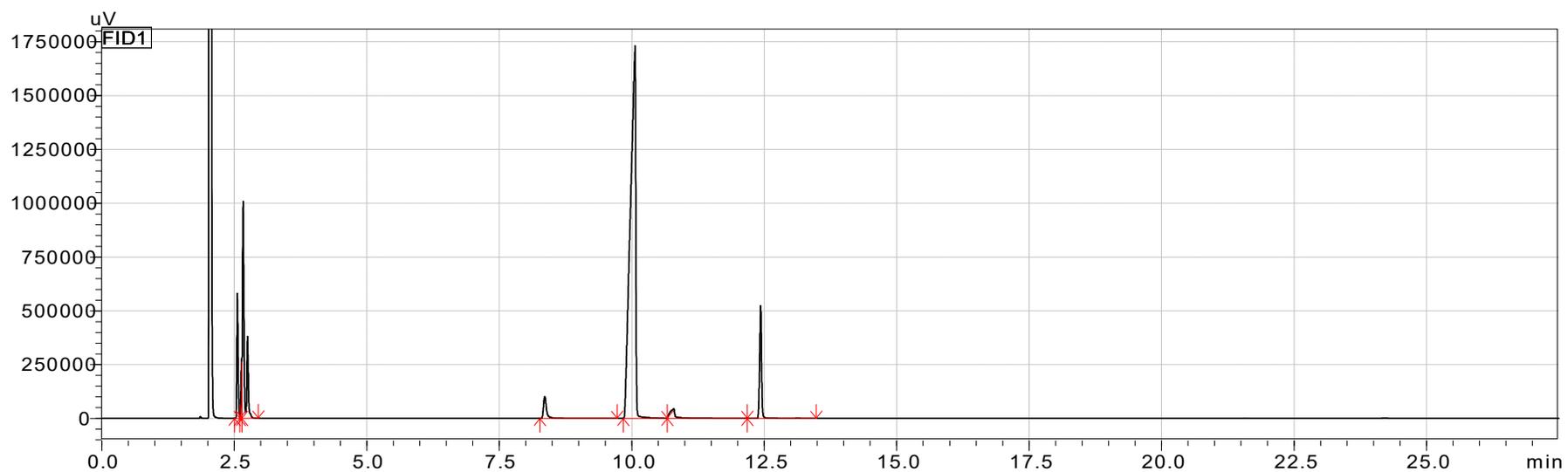


**Figure S6:**  $^{13}\text{C}$  NMR Spectrum (100 MHz, acetone- $d_6$ , AT) of the saturated alcohol from the hydrogenation of the  $\text{C}_{14}$  Aldol product. Impurities caused by traces of Mesitylene and the saturated  $\text{C}_{14}$  Aldehyde as an Intermediate in the conversion of the Aldol product.

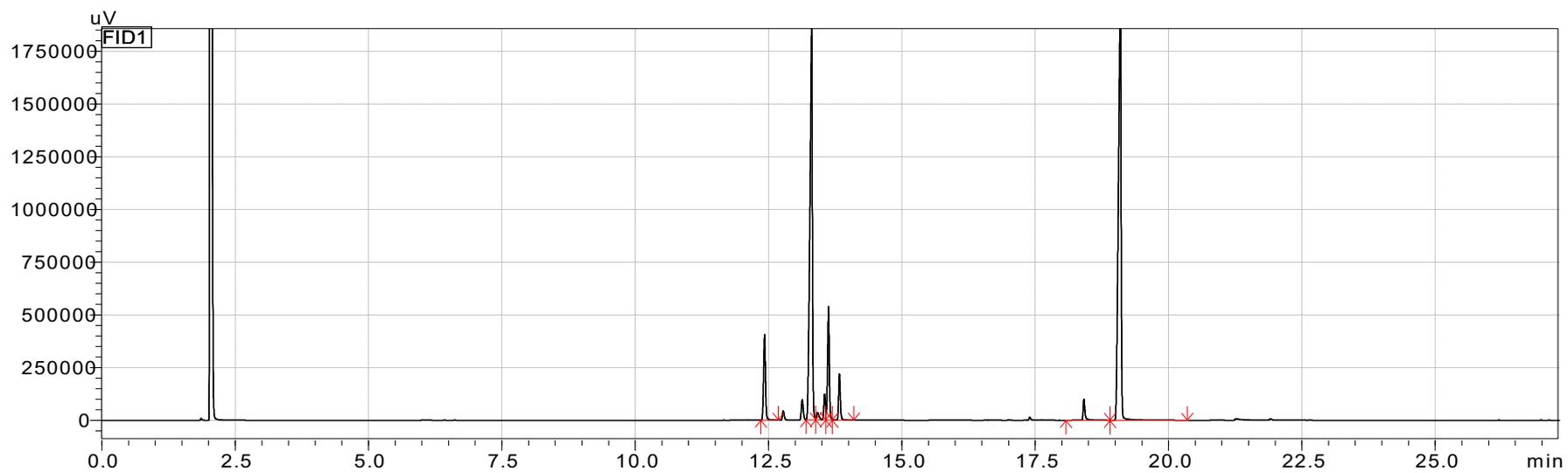
## 4 GC FID Chromatograms



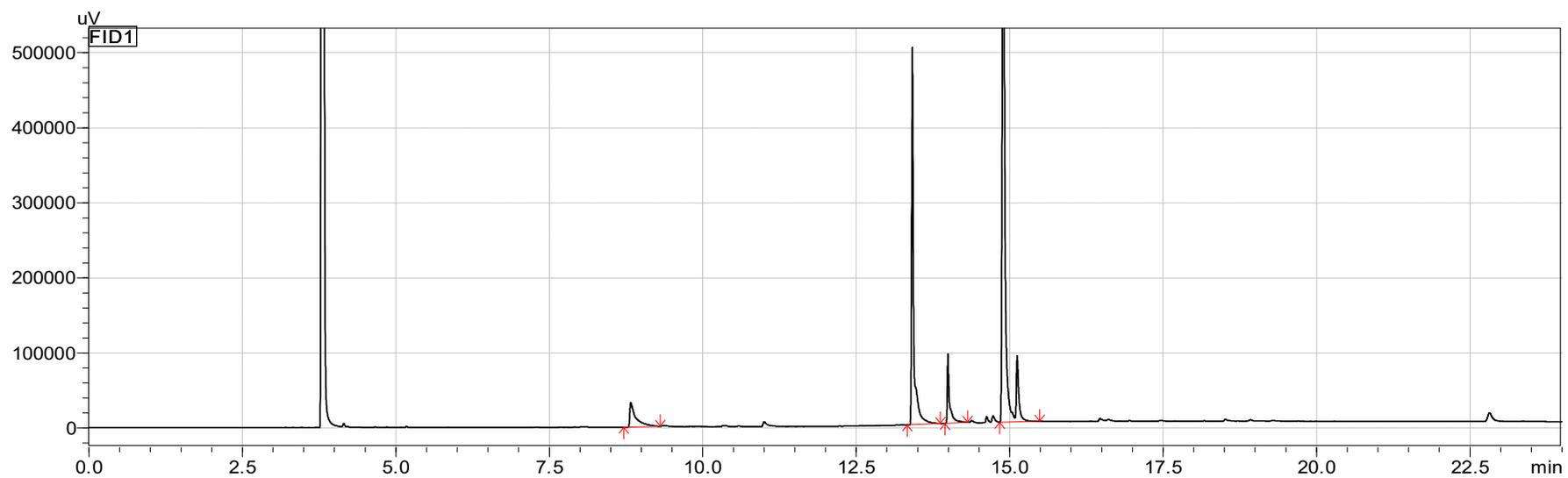
**Figure S7:** Example of a GC FID chromatogram of the product organic phase of the hydroformylation of 1-octene in EC dissolved in acetone. Signals with ascending retention time: 1-octene, internal octenes and octane, ethylene carbonate, mesitylene (standard), *iso*-nonanals, *n*-nonanal.



**Figure S8:** Example of a GC FID chromatogram of the product organic phase of the hydroformylation of 1-hexene in EC dissolved in acetone. Signals with ascending retention time: 1-hexene, internal hexenes and hexane, *iso*-heptanals, *n*-heptanal, ethylene carbonate, mesitylene (standard).



**Figure S9:** Example of a GC FID chromatogram of the product organic phase of the hydroformylation of 1-decene in EC dissolved in acetone. Signals with ascending retention time: ethylene carbonate (not marked as it was not present in this chromatogram), mesitylene (standard), 1-decene, internal decenes and decane, *iso*-undecanals, *n*-undecanal.



**Figure S10:** Example of a GC FID chromatogram of the product organic phase of the hydrogenation of the C<sub>14</sub> Aldol product in EC dissolved in acetone. Signals with ascending retention time: mesitylene, olefin hydrogenated C<sub>14</sub> Aldol product, C<sub>14</sub> Aldol product, fully hydrogenated C<sub>14</sub> Aldol product (C<sub>14</sub> alcohol).

## 5 References

- [1] S. Decker, L. Schubert, F. Schroter, M. Klaas, F. Roessner, *Sorp. Chrom. Proc.* **2013**, *13*, 785-793.
- [2] M. Strohmann, A. J. Vorholt, W. Leitner, *Chem.-Eur. J.* **2022**, *28*, e202202081.