# Supporting Information to: "Catalytic synthesis of carboxylic acids from oxygenated substrates using $CO_2$ and $H_2$ as C1 building block"

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# Supporting Data for Screening Experiments for Various Substrates

**Table S1:** Hydrocarboxylation of 2-BuOH with $CO_2$ and $H_2$: influence of different reaction parameters.

| Entry | Solvent | Volume (ml) | Acidic additive (mol $mol_{Rh}^{-1}$) | Temperature (°C) | $CO_2$ pressure (bar) | Yield (%) |
|-------|---------|-------------|----------------------------------------|------------------|------------------------|-----------|
| 1 | Acetic acid | 1 | 3.5 | 140 | 20 | 45 |
| 2 | Acetic acid | 2 | 3.5 | 140 | 20 | 67 |
| 3 | Acetic acid | 3 | 3.5 | 140 | 20 | 8 |
| 4 | Toluene | 1 | 3.5 | 140 | 20 | 30 |
| 5 | Toluene | 2 | 3.5 | 140 | 20 | 30 |
| 6 | Toluene | 3 | 3.5 | 140 | 20 | 14 |
| 7 | Water | 2 | 3.5 | 140 | 20 | 7 |
| 8 | Xylene | 1 | 3.5 | 140 | 20 | 32 |
| 9 [a) | Dioxane | 1 | 3.5 | 140 | 20 | 2 |
| 10 [b) | Acetonitrile | 2 | 3.5 | 140 | 20 | 2 |
| 11 [c) | Neat | 1 | - | 140 | 20 | 1 |
| 12 | Acetic acid | 1 | - | 140 | 20 | 46 |
| 13 | Toluene | 1 | - | 140 | 20 | 29 |
| 14 | Acetic acid | 2 | 3.5 | 160 | 10 | 62 |
| 15 | Acetic acid | 2 | 3.5 | 160 | 30 | 75 |

If not specified, conversion is over 99%, VA:2-MBA ratio is about 2:1 and MB around or above 80%.

Reaction conditions: 1.88 mmol 2-BuOH, 46 μmol [RhCl(CO)$_2$]$_2$, 2.5 mol $mol_{Rh}^{-1}$ of CHI$_3$ and 5 mol $mol_{Rh}^{-1}$ of PPh$_3$, 10 bar of H$_2$.

a) Conversion = 90%. Solid and unknown products formed.

b) Conversion = 35%;

c) MB = 17%. High amount of not quantified secondary products were identified with GC-MS as ethers. Reaction time = 66h.

**Table S2:** Hydrocarboxylation of 2-BuOH with $CO_2$ and $H_2$: influence of $CHI_3$, $PPh_3$ and Rh precursor.

| Entry | Rh precursor | $CHI_3$ (mol $mol_{Rh}^{-1}$) | $PPh_3$ (mol $mol_{Rh}^{-1}$) | Yield (%) (*n:iso* ratio) |
|-------|--------------|-------------------------------|-------------------------------|---------------------------|
| 1 | $[Rh(CO)_2Cl]_2$ | 2.5 | 5 | 77 (1.8) |
| 2 | $[Rh(COD)Cl]_2$ | 2.5 | 5 | 33 (3.1) |
| 3 | $RhCl(PPh_3)_3$ | 2.5 | 2 | 58 (2.4) |
| 4 | $[HRh(CO)(PPh_3)_3]$ | 2.5 | 2 | 1 (-) |
| 5 | $Rh_2(OAc)_4$ | 2.5 | 5 | 52 (2) |
| 6 | $RhI_3$ | 2.5 | 5 | 4 (1) |
| 7 | $[Rh(CO)_2Cl]_2$ | 0 | 5 | 0 (-) |
| 8 | $[Rh(CO)_2Cl]_2$ | 9.3 | 5 | 7 (1) |
| 9 | $[Rh(CO)_2Cl]_2$ | 2.5 | 0 | 2 (1) |
| 10 | $[Rh(CO)_2Cl]_2$ | 2.5 | 10 | 48 (1.5) |

Reaction conditions: 1.88 mmol of substrate, 92 µm Rh, 2 ml of acetic acid, 3.5 mol $mol_{Rh}^{-1}$ *p*-TsOH•$H_2O$, 20 bar $CO_2$, 10 bar $H_2$, 160 °C. Conversion is always >99%.

**Table S3:** Hydrocarboxylation of 1-BuOH with $CO_2$ and $H_2$: influence of different reaction parameters.

| Entry | Solvent | Volume (ml) | Acidic additive (mol $mol_{Rh}^{-1}$) | Temperature (°C) | $H_2$ pressure (bar) | $CO_2$ pressure (bar) | Yield (%) |
|---|---|---|---|---|---|---|---|
| 4 | Toluene | 1 | 3.5 | 140 | 10 | 20 | 39 |
| 5 | Toluene | 2 | 3.5 | 140 | 10 | 20 | 28 |
| 6 | Toluene | 3 | 3.5 | 140 | 10 | 20 | 19 |
| 7[a] | Water | 2 | 3.5 | 140 | 10 | 20 | 6 |
| 8 | Xylene | 1 | 3.5 | 140 | 10 | 20 | 37 |
| 9[b] | Dioxane | 1 | 3.5 | 140 | 10 | 20 | 3 |
| 10[c] | Acetonitrile | 2 | 3.5 | 140 | 10 | 20 | 2 |
| 11[d] | Neat (66h) | 1 | - | 140 | 10 | 20 | 1.5 |
| 12 | Toluene | 1 | - | 140 | 10 | 20 | 33 |
| 13 | Toluene | 1 | 3.5 | 160 | 10 | 20 | 31 |
| 14 | Acetic acid | 1 | - | 160 | 20 | 10 | 60 |
| 15 | Acetic acid | 1 | - | 160 | 20 | 30 | 48 |

If not specified, conversion is over 99%, VA:2-MBA ratio is about 2:1 and MB around or above 80%.

Reaction conditions: 1.88 mmol 1-BuOH, 46 µmol $[RhCl(CO)_2]_2$, 2.5 mol $mol_{Rh}^{-1}$ of $CHI_3$ and 5 mol $mol_{Rh}^{-1}$ of $PPh_3$.

[a] Conversion = 57%.

[b] Conversion = 85%; solid and unknown products formed.

[c] Conversion = 43%.

[d] High amount of not quantified secondary products were identified with GC-MS as ethers. Reaction time = 66h.

**Table S4:** Hydrocarboxylation of 1-BuOH with $CO_2$ and $H_2$: influence of $CHI_3$, $PPh_3$ and Rh precursor.

| Entry | Rh precursor | $CHI_3$ (mol $mol_{Rh}^{-1}$) | $PPh_3$ (mol $mol_{Rh}^{-1}$) | Conv. (%) | Yield (%) (*n:iso* ratio) |
|-------|--------------|-------------------------------|-------------------------------|-----------|---------------------------|
| 1 | $[Rh(CO)_2Cl]_2$ | 2.5 | 5 | >99 | **65** (2.1) |
| 2 | $[Rh(COD)Cl]_2$ | 2.5 | 5 | 99 | **19** (3.8) |
| 3 | $RhCl(PPh_3)_3$ | 2.5 | 2 | 99 | **41** (2.4) |
| 4 | $[HRh(CO)(PPh_3)_3]$ | 2.5 | 2 | 99 | **1** (-) |
| 5 | $Rh_2(OAc)_4$ | 2.5 | 5 | 99 | **39** (2.5) |
| 6 | $RhI_3$ | 2.5 | 5 | 98 | **22** (1) |
| 7 | $[Rh(CO)_2Cl]_2$ | 0 | 5 | 98 | **0** (-) |
| 8 | $[Rh(CO)_2Cl]_2$ | 9.3 | 5 | 99 | **20** (1.2) |
| 9 | $[Rh(CO)_2Cl]_2$ | 2.5 | 0 | >99 | **2** (-) |
| 10 | $[Rh(CO)_2Cl]_2$ | 2.5 | 10 | 99 | **44** (1.8) |

Standard reaction conditions: 1.88 mmol 1-BuOH, 92 µm Rh, 1 ml acetic acid, 20 bar $CO_2$, 20 bar $H_2$, 160 °C.

**Table S5:** Product distributions as yield, conversion and mass balance obtained as a result of the transformation of 1-BuOH, 2-BuOH, 2-butanone and butanal. Conditions used according to the optimization for the different classes of oxygenated compounds as shown in the manuscript.
Butane and butene are always linear. Butenes are 1-butene and 2-butene.

| Yield (%) | 1-BuOH | 2-BuOH | 2-Butanone | Butanal | 1,4-Butandiol |
|---|---|---|---|---|---|
| *2-Methylbutanoic Acid* | 21 | 27 | 17 | 13 | 11 |
| *Valeric Acid* | 45 | 50 | 37 | 32 | 31 |
| **Acids** (Sum) | 66 | 77 | 54 | 45 | 42 |
| *1-Iodobutane* | 2 | 0 | 0 | 1 | 0.2 |
| *2-Iodobutane* | 1 | 1 | 1 | | 0.2 |
| **Iodobutane** (Sum) | 3 | 1 | 1 | 1 | 0.4 |
| ***n-* or *iso-*butyl acetate** | 6 | 3 | 0.4 | 2 | 1 |
| **Butane** | 8 | 7 | 0.7 | 8 | 6 |
| **Butene** | 1 | 4 | 2 | 2 | 2 |
| *CONVERSION* | >99 | >99 | 98 | >99 | >99 |
| *MB* | 84 | 93 | 60 | 58 | 51 |
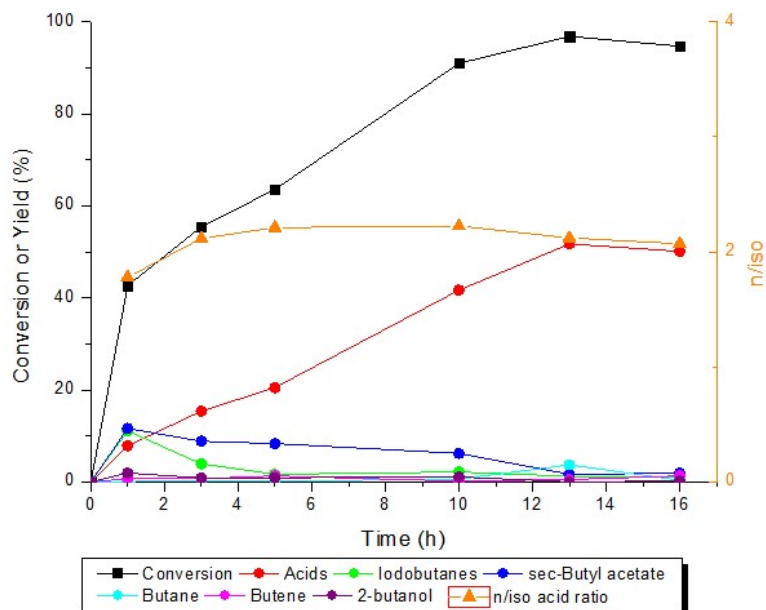
**Figure S1:** Time profile of the reaction of 2-butanone to VA and 2-MBA. Reaction conditions: 1.88 mmol of 2-Butanone, 92 μmol Rh, 2 ml of acetic acid, 2.5 mol $mol_{Rh}^{-1}$ of $CHI_3$, 5 mol $mol_{Rh}^{-1}$ of $PPh_3$, 3.5 mol $mol_{Rh}^{-1}$ $p$-TsOH•$H_2O$, 20 bar $CO_2$, 20 bar $H_2$, 160 °C.

**Table S6:** Product distributions as yield, conversion and mass balance obtained as a result of the transformation of 1-hexanol, 2-hexanol, 2-hexanone and 1-iodohexane. Conditions used according to the optimization for the different classes of oxygenated compounds as shown in the manuscript.

| Yield (%) | 1-Hexanol | 2-Hexanol | 2-Hexanone | 1-Iodohexane |
|---|---|---|---|---|
| Heptanoic Acid | 42 | 43 | 43 | 11 |
| 2-Methyl Hexanoic Acid | 17 | 18 | 26 | 4 |
| 2-Ethyl Pentanoic Acid | 5 | 5 | 6 | 1 |
| **Acids (sum)** | 64 | 66 | 75 | 16 |
| **Hexyl acetate** | 5 | 1 | 0 | 2 |
| 1-Iodohexane | 2 | 0.2 | 0.3 | 8 |
| 2-Iodohexane and 3-Iodohexane | 0.4 | 0.5 | 3 | 2 |
| **Iodohexane (sum)** | 2 | 1 | 3 | 10 |
| **Hexane** | 7 | 6 | 8 | 16 + gas phase[a] |
| **Hexene** | 1 | 1 | 1 | 16 + gas phase[a] |
| **CONVERSION** | >99 | >99 | >99 | 92 |
| **MB** | 79 | 73 | 82 | 47 |

[a] Hexanes and hexenes in the gas phase have not been quantified. Hexane and hexenes are linear. Hexenes are 1-hexene, 2-hexene and 3-hexene.

# Supporting Data for the Reaction Pathway
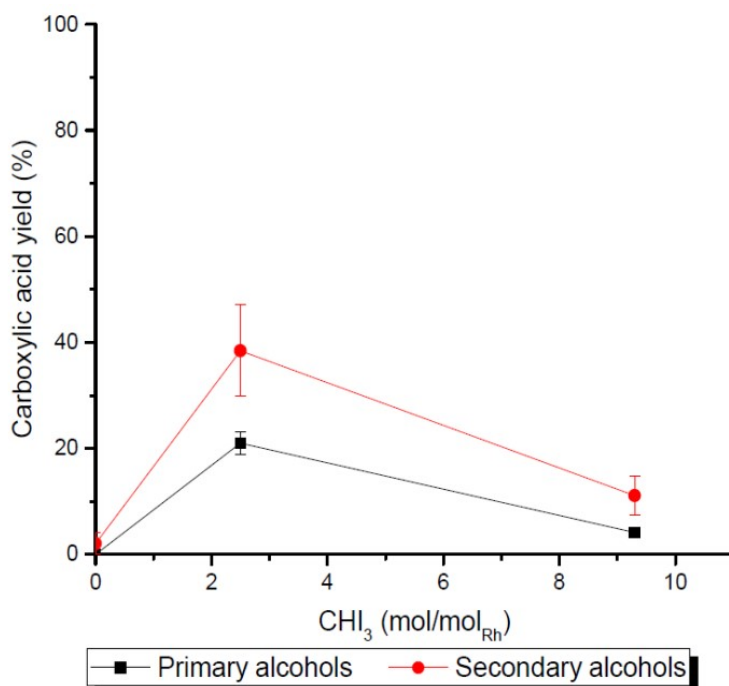


**Figure S2:** Influence of different amount of $CHI_3$ on the carboxylic acids yield using the optimized conditions for primary alcohols and secondary alcohols. CO and $H_2O$ were used instead of $CO_2$ and $H_2$ as explained above.
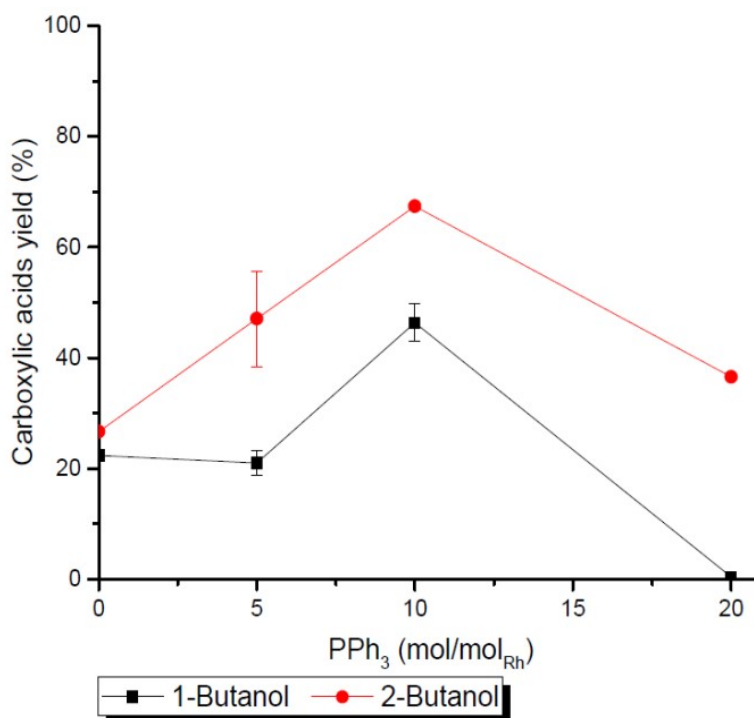


**Figure S3:** Influence of different amounts of $PPh_3$ on the carboxylic acids yield using the optimized conditions for primary and secondary alcohols. CO and $H_2O$ were used instead of $CO_2$ and $H_2$ and the yields were calculated on a total amount of alcohol of 0.5 as explained in the manuscript.

**Table S7:** *r*WGSR activity in different reaction conditions.

$$CO_2 \ + \ H_2 \ \underset{}{\overset{[Rh]}{\rightleftharpoons}} \ CO \ + \ H_2O$$

| Conditions | Absolute amount of CO produced (mmol) | Yield of CO with [Rh] (%) | Yield of CO without [Rh] (%) | Yield of CO without $CO_2$ (%) |
|---|---|---|---|---|
| Primary alcohols[a] | 0.7 | 3.11 | 0.77 | 0.22 |
| Secondary alcohols[b] | 0.6 | 2.58 | 0.08 | 0.35 |

[a] Reaction conditions: 92 µmol [RhCl(CO)$_2$]$_2$, 1 ml of acetic acid, 2.5 mol/mol$_{Rh}$ of CHI$_3$, 5 mol mol$_{Rh}^{-1}$ of PPh$_3$, 20 bar $CO_2$, 20 bar H$_2$, 160 °C, 16 h.

[b] Reaction conditions: 92 µmol [RhCl(CO)$_2$]$_2$, 2 ml of acetic acid, 3.5 mol/mol$_{Rh}$ *p*-TsOH•H$_2$O, 2.5 mol mol$_{Rh}^{-1}$ of CHI$_3$, 5 mol mol$_{Rh}^{-1}$ of PPh$_3$, 20 bar $CO_2$, 10 bar H$_2$, 160 °C, 16 h.

Every result was reproduced at least twice. The maximum error obtained was of ±0.51%. Yields were calculated on the total amount of $CO_2$ pressurized in the reactor (22.7 mmol).
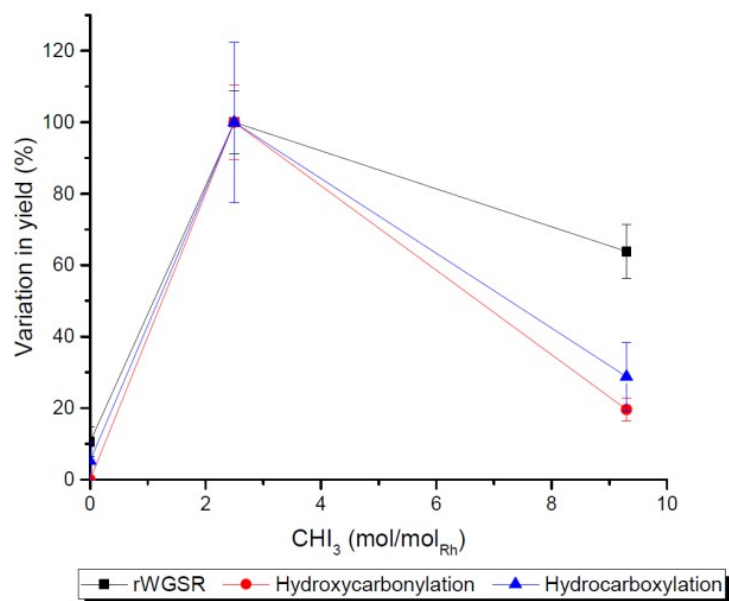
**Figure S4:** Comparison of the effect of the variation of $CHI_3$ amount on the different reaction steps (namely rWGSR and hydroxycarbonylation with $CO + H_2O$) and on the total reaction (hydrocarboxylation with $CO_2 + H_2$) using 1-BuOH at optimized conditions.
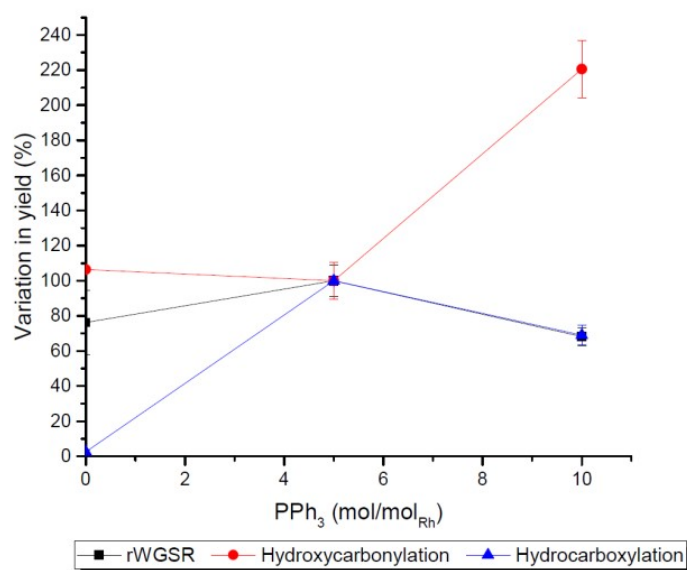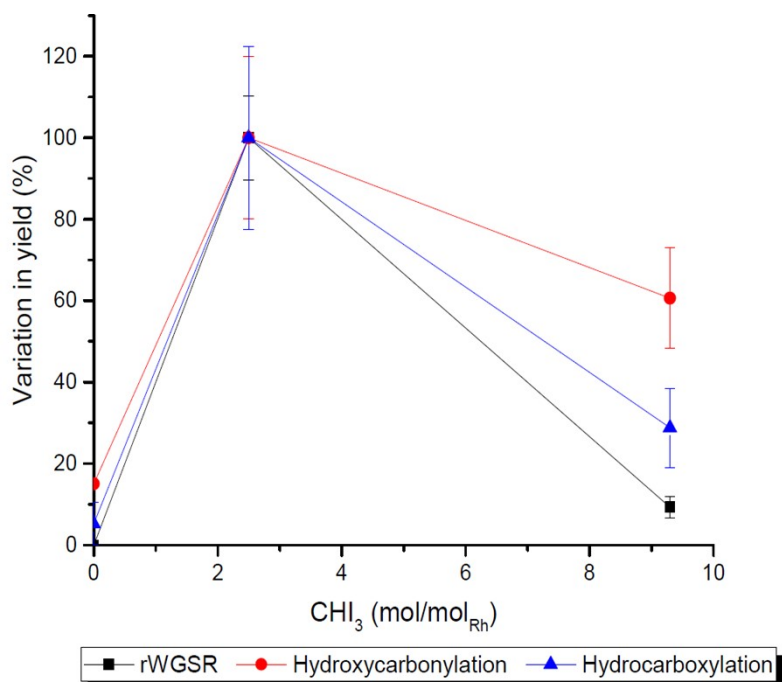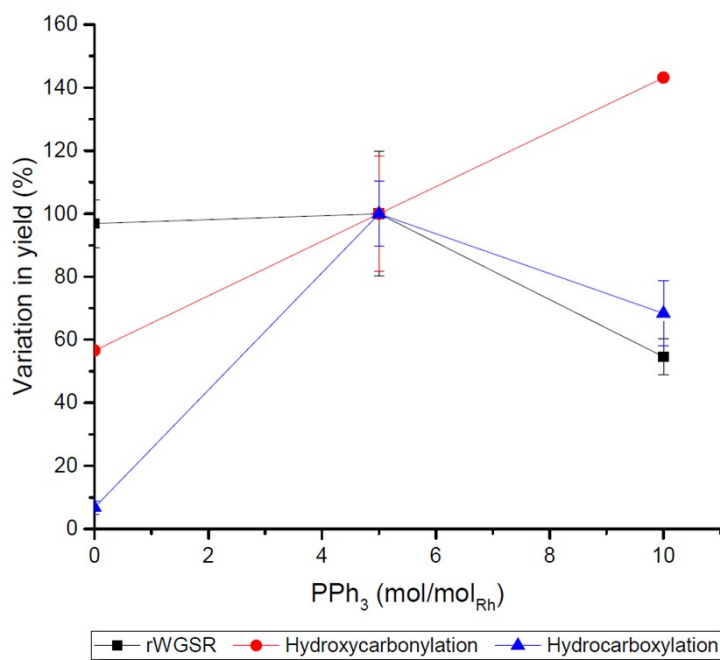


**Figure S5:** Comparison of the effect of the variation of $PPh_3$ amount on the different reaction steps (namely *r*WGSR and hydroxycarbonylation with $CO + H_2O$) and on the total reaction (hydroxycarbonylation with $CO_2 + H_2$) using 1-BuOH or primary alcohols optimized conditions.

**Figure S6:** Comparison of the effect of the variation of $CHI_3$ amounts on different reaction steps (*r*WGSR and hydroxycarbonylation) and on the overall reaction (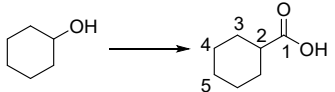hydrocarboxylation) using 2-BuOH under optimized conditions. The percentage variation is shown in the graph, considering 100% as the yield obtained in the optimized reaction conditions reported in the manuscript.



**Figure S7:** Comparison of the effect of the variation of $PPh_3$ amount on the different reaction steps (*r*WGSR and hydroxycarbonylation) and on the overall reaction (hydroxycarbonylation) using 2-BuOH under optimized conditions.
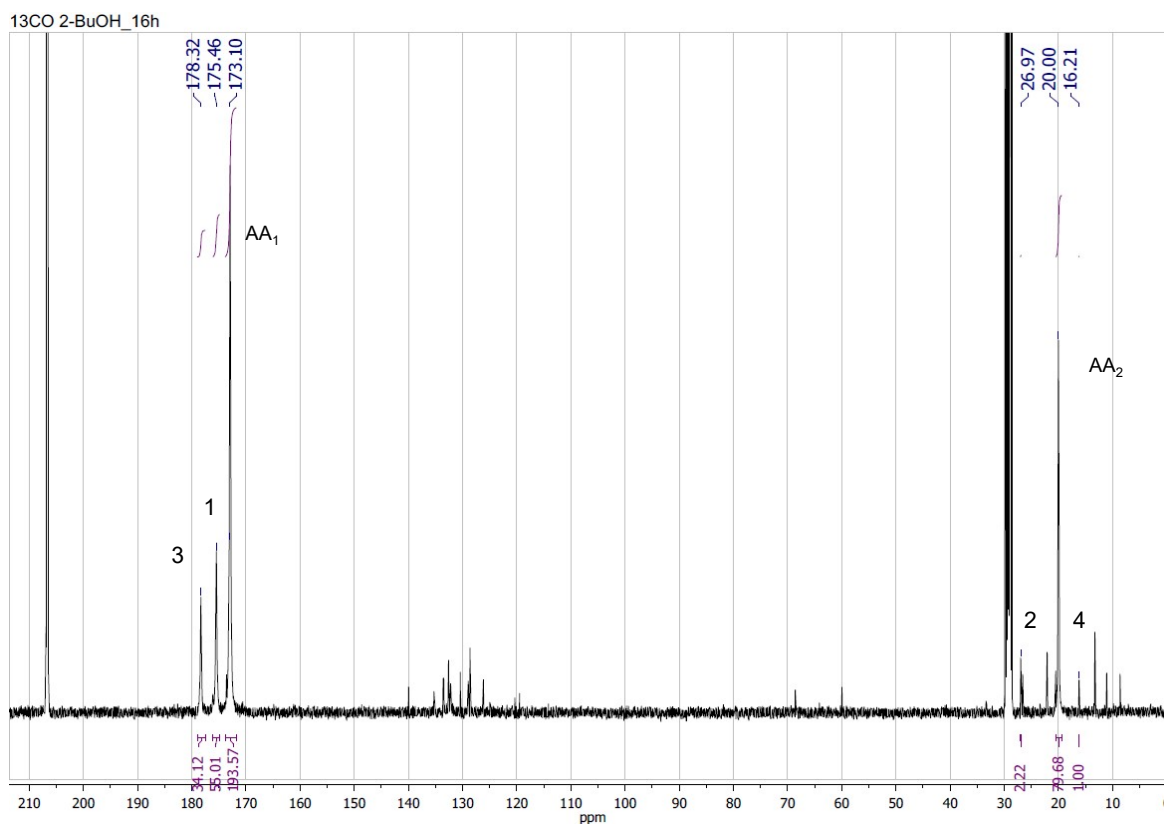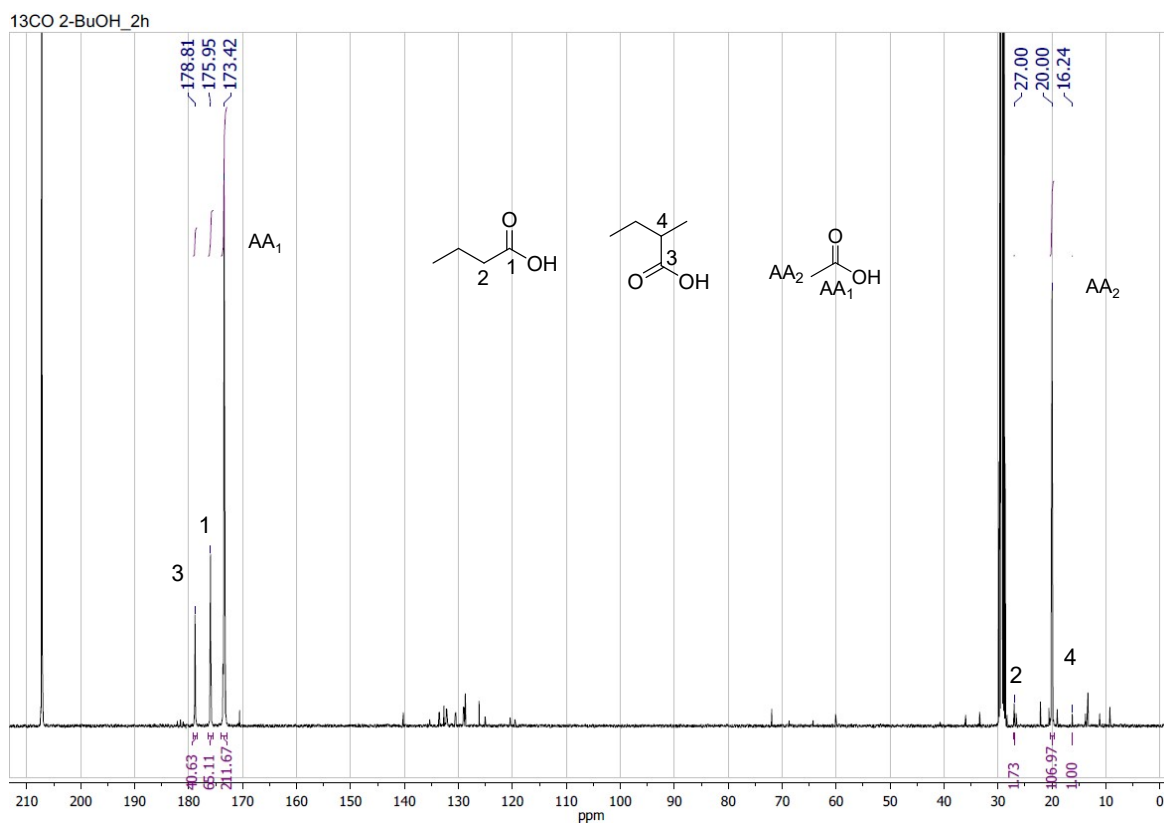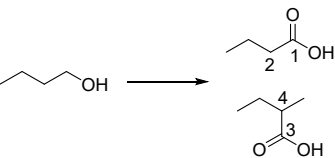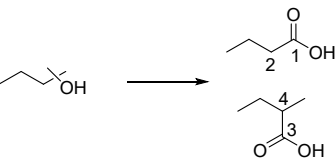
**Figure S8:** Quantitative $^{13}$C-NMR of the reaction mixture obtained from 2-BuOH, $^{13}$CO (2 bar), $H_2O$ (12 µl), $CO_2$ (20 bar) and $H_2$ (10 bar) after 2 h (top) and 16 h (bottom). The other reaction conditions were: 1.88 mmol of substrate, 46 µmol [RhCl(CO)$_2$]$_2$, 2 ml of acetic acid, 2.5 mol mol$_{Rh}^{-1}$ of CHI$_3$, 5 mol mol$_{Rh}^{-1}$ of PPh$_3$, 3.5 mol mol$_{Rh}^{-1}$, $p$-TsOH•$H_2O$ 160 °C.

**Table S8:** NMR study: Ratio between the integrals of the signals obtained in the quantitative $^{13}$C-NMR of the reaction mixtures obtained from the hydroxycarbonylation with *r*WGSR ($CO_2$ and $H_2$) and hydroxycarbonylation ($^{13}CO$ and $H_2O$) of cyclohexanol, 1-BuOH and 2-BuOH. The ratio is obtained using the areas of the carboxyl carbons and the nearby carbons as indicated in the table. The reaction conditions applied are the one optimized reported in the manuscript with the addition of $^{13}CO$ (2 bar) and $H_2O$ (12 □L). [a] **C(AA₂)H₃ - C(AA1)OOH**: $AA_1$ and $AA_2$ refer to the carbon atoms of acetic acid.

| Reaction | Reaction time (h) | Area₁/Area₂ | Area₃/Area₄ | Area$_{AA1}$/Area$_{AA2}$[a] |
|---|---|---|---|---|
| | 2 | 27 | - | 2 |
| | 16 | 24 | - | 2 |
| | 2 | 78 | 168 | 2 |
| | 16 | 90 | 102 | 4 |
| | 2 | 38 | 41 | 2 |
| | 16 | 25 | 34 | 2 |

In the case of butanols, due to isomerization processes, the $^{13}$C-NMR becomes more complex. Through HMBC and HSQC techniques the reference peaks of the products were assigned. Some of the assigned peaks result to be very small (comparable with the noise) and partially overlapped with other signals. For these reasons, the analysis of the integrals of these signals results not as precise as the one done for the cyclohexane carboxylic acid. However, from the analysis of the NMR spectra the same conclusions obtained for cyclohexanol can be drawn. The $^{13}$CO is incorporated in the product already after 2 h of reaction time.
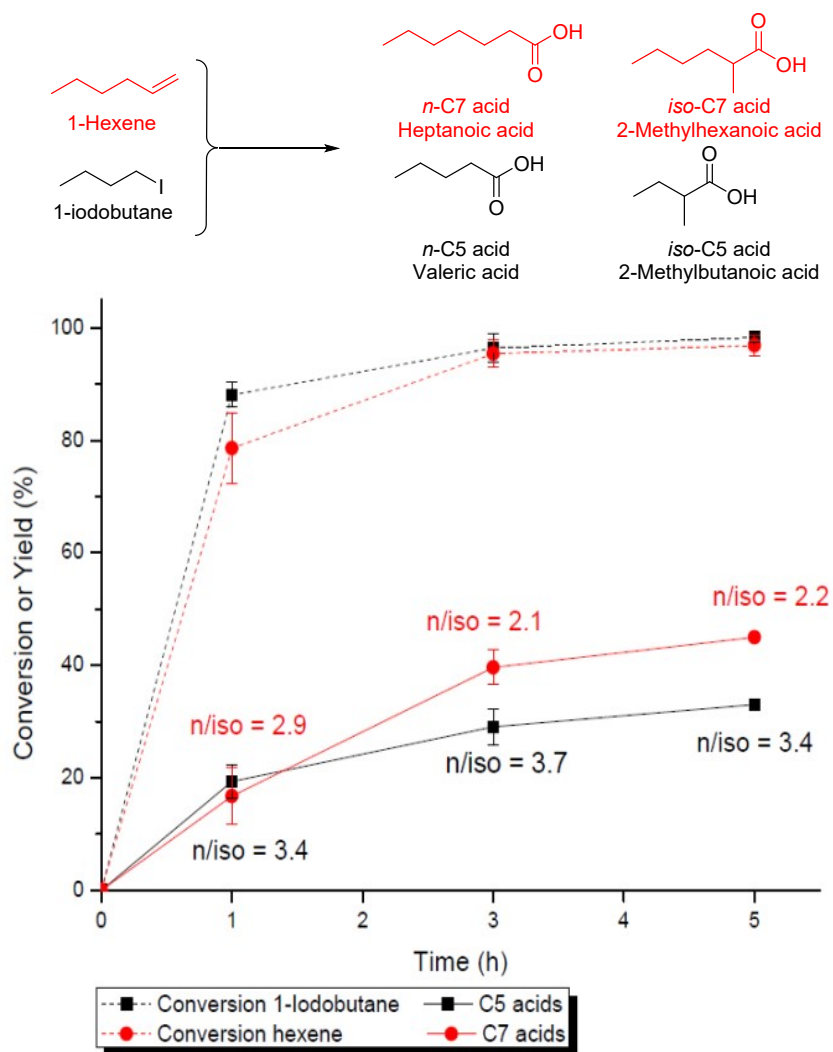
**Figure S9:** Competitive reactions between 1-hexene and 1-iodobutane over the first 5 h of the reaction course. The data shows just the results for the formed acids. Reaction conditions: 0.95 mmol of 1-iodobutane and 0.95 mmol of 1-hexene, 92 μm Rh, 1 ml of acetic acid, 5 mol $mol_{Rh}^{-1}$ of $PPh_3$, 20 bar $CO_2$, 20 bar $H_2$, 160 °C.
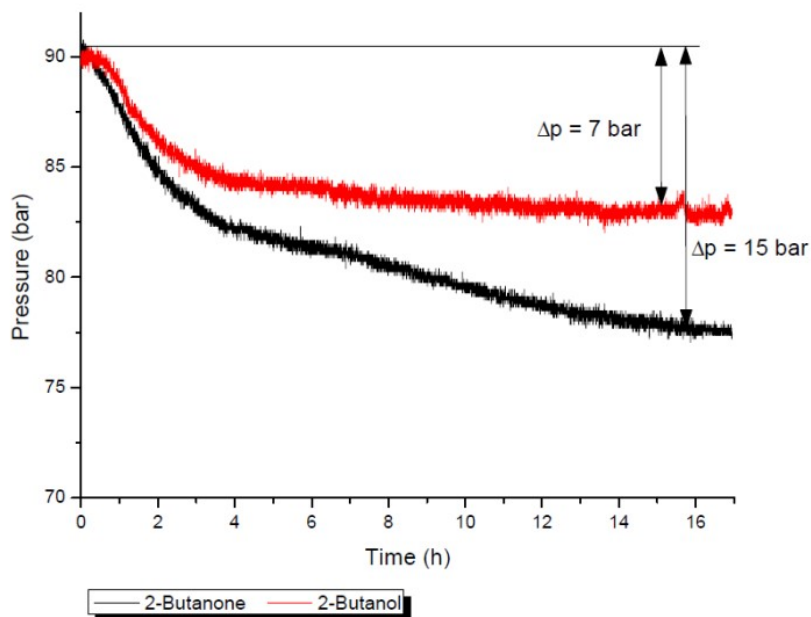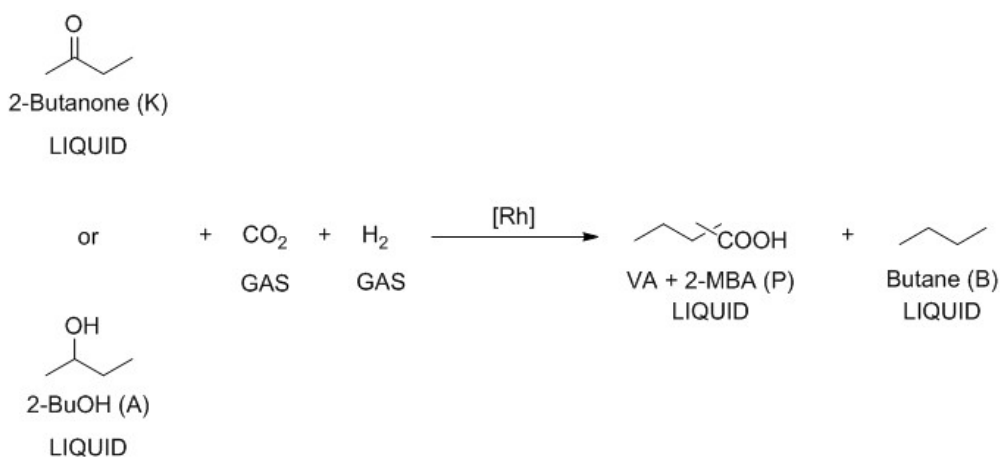
**Figure S10:** Pressure uptake registered for 2-butanone and 2-butanol. The value showed are elaborated and the results of the total pressure uptake normalized by removing the pressure drop due to the system without catalyst (blank value) and the pressure drop due to *r*WGSR activity (presence of the catalyst but no substrate used). Reaction conditions: 1.88 mmol substrate, 92 µm Rh, 3.5 eq. *p*-TsOH•$H_2O$, 2.5 eq. $CHI_3$, 5 eq. $PPh_3$, 2 ml acetic acid, 20 bar $CO_2$, 20 bar $H_2$, 160 °C

2-Butanone (K)
LIQUID

or

+ CO$_2$ + H$_2$  $\xrightarrow{\text{[Rh]}}$  VA + 2-MBA (P) + Butane (B)

GAS    GAS

VA + 2-MBA (P)
LIQUID

Butane (B)
LIQUID

2-BuOH (A)
LIQUID

$$\Delta p_{th} = \underbrace{\frac{(2 \times n_{K\,or\,A} \times Y_P) \times R \times T}{V}}_{\Delta p_{HC}} + \underbrace{\frac{[n_{K\,or\,A}(X_K + Y_B)] \times R \times T}{V}}_{\Delta p_H}$$

$\Delta p_{HC}$ = Pressure drop due to hydrocarboxylation (formation of P)

$\Delta p_H$ = Pressure drop due to hydrogenation (formation of B and of A in the case of Ketones)

$\Delta p_{th}$ = Pressure drop due to hydrocarboxylation and hydrogenation

$n_i$ = mol of reagent A or K

$Y_i$ = yield of product P or by-product B

$X_K$ = conversion of reagent K

$R$ = universal gas constant (8.314 kg m$^2$ s$^{-2}$ mol$^{-1}$ K$^{-1}$)

$T$ = temperature (433 K)

$V$ = volume of the reactor occupied by gases (9.5 · 10$^{-6}$ m$^3$)

**Scheme 1:** Reaction scheme and equation used for calculating the theoretical pressure drop in the transformation of 2-BuOH and 2-Butanone into carboxylic acids. The theoretical pressure drop was calculated with the assumption of the ideal gas law. Reaction conditions: 1.88 mmol substrate, 92 µmol Rh, 3.5 eq. p-TsOH•H$_2$O, 2.5 eq. CHI$_3$, 5 eq. PPh$_3$, 2 ml acetic acid, 20 bar.

## Experimental

### General considerations

All reactions were performed and compounds handled under inert gas atmosphere (Argon 4.8 *Messer*, Germany) if not stated otherwise, using the Schlenk technique or were handled in a glovebox (*MBraun LabMaster SP*).

### Solvents and Chemicals

Acetic acid and other solvents used were dried and stored over molecular sieves (4 Å), then degassed by bubbling argon through a frit for at least 1 h. All liquid substrates were degassed by at least three freeze-pump-thaw cycles and stored over molecular sieves (4 Å) under argon. Cyclohexane oxide was stored under argon and the molecular sieves used for drying were removed after maximum 24 h. Deionized water was taken from a reverse-osmosis purification system (*Werner EasyPure II*) and degassed by bubbling argon with a frit for at least 1 h. Water contents of all organic solvents and substrates were measured by a Karl-Fischer titration (*Metrohm 756 F Coulometer*). All reagents were commercially supplied and used as received, unless stated otherwise.

### Mass Spectrometry

Mass spectroscopy measurements were performed on a *Varian 1200L Quadrupole Ms/ms* using the ESI ionization method. Detected masses are given in *m/z* and correlated to calculated masses of the respective species.

### Gas Chromatography

GC analyses of the liquid phases were performed on a *Trace GC Ultra* (*ThermoScientific*) using a packed *CP-WAX-52-CB* column (length = 60 m, diameter = 0.25 mm) and a flame ionization detector (FID) or mass spectroscopy detector (MS). Analysis of butane and butene gases were performed on a *Sichromat* using a capillary *PLOT $Al_2O_3$* column (length = 50 m) equipped with an FID. GC analysis of CO, $CO_2$ and $H_2$ gases were performed on a *HP6890* using a capillary *Chem Carbon ST* column (length = 2 m) and a thermal conductivity detector (TCD). Examples of the different types of chromatograms are reported in the SI (Figure S11–Figure S13).

Liquid substances were analysed using (±)-1-phenylethanol and/or *n*-dodecane as standard. Acetone was used as a solvent for the work-up procedure (for cyclohexanol reactions acetone was substituted by dichloromethane). The correction factors were calculated preparing solutions with known amounts of substances and standard. The gaseous substances were quantified using ethane as standard. As for the liquid samples, the correction values were obtained from self-made gas solutions with known amounts of gases.

### NMR Analysis

NMR measurements were conducted on a *Bruker AVIII-300* spectrometer (300 MHz) at ambient temperature. The $^2$H-NMR measurements were conducted on a *Bruker AVIII HD-600* spectrometer (600 MHz) at ambient temperature. For $^1$H, $^2$H and $^{13}$C chemical shifts are given in ppm relative to tetramethyl silane. For $^{31}$P{$^1$H} NMR spectra, chemical shifts are given in ppm relative to $H_3PO_4$.

**Autoclave Reactions**

The catalytic runs were performed in 10 ml stainless steel autoclaves. The autoclaves were equipped with glass inlets in which the reactions took place. The autoclaves containing iodoform ($CHI_3$), triphenylphosphine ($PPh_3$) and *para*-toluensulfonic acid monohydrate ($p$-TsOH·$H_2O$) were evacuated at high vacuum for at least one hour and then charged with an argon atmosphere. Stock solutions of the catalyst precursor were prepared and transferred to the autoclave, which was then pressurized with $CO_2$ and $H_2$ (or CO, $^{13}CO$ and $D_2$ in the labelling experiment). The mixture was heated and stirred for the desired reaction time after which the autoclave was cooled down and the pressure relieved. The obtained reaction mixture was analysed *via* gas chromatography with a flame ionization detector (GC FID) and a mass spectroscopy detector (GC MS).

Catalytic tests were repeated two or more times. The corresponding error bars are shown in the graphs or tables or indicated in the text. Errors for side-products are not indicated for simplicity reasons, but they are usually around ±2%.

*Design of Experiment (DoE)*

The Design of Experiment was done using the *Design-Expert 8* software. We used the *Box-Behnken* model since it does not require the measurement of any point outside the selected thresholds. The *DoE* was used optimize the reaction conditions for the highest yield of carboxylic acids. Therefore, a *response surface method* was chosen. This method allowed an estimation of the interactions and quadratic effects between parameters, and give an idea of the shape of the investigated response surface.[71] A quadratic model was chosen for the data elaboration.

The reactions were prepared as explained in the previous section "Autoclave reactions" and the reaction mixtures were analysed *via* gas chromatography.

**Preliminary Experiments**

In a general procedure, 2.5 mol $mol_{Rh}^{-1}$ of $CHI_3$, 5 mol $mol_{Rh}^{-1}$ of $PPh_3$ and 3.5 mol $mol_{Rh}^{-1}$ $p$-TsOH•$H_2O$ were weighted and inserted in the autoclave. The autoclave was evacuated and refilled with Argon as explained in the Experimental part of the paper. Following, 1.88 mmol of substrate, 92 μmol Rh and 1 ml of acetic acid were added. The autoclave was pressurized with 20 bar $CO_2$ and 10 bar $H_2$. The reaction was carried out for 16 h at 140 °C.
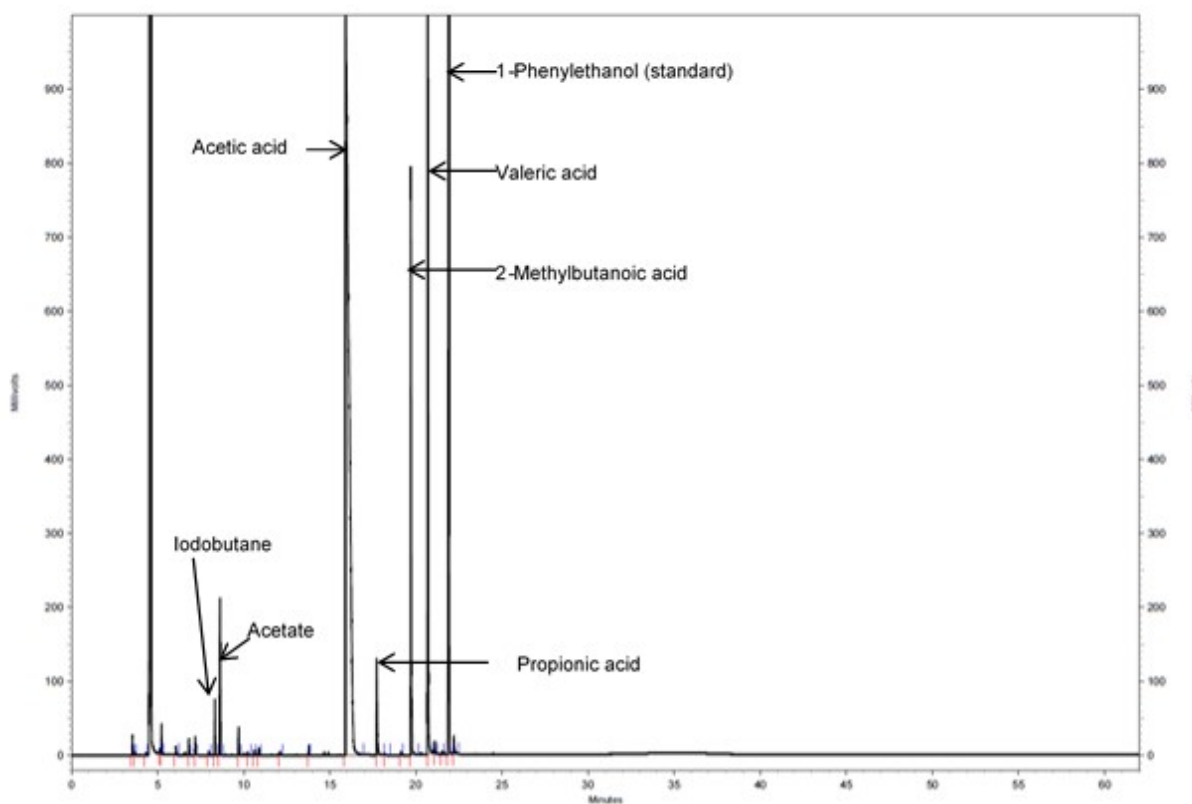
# Examples for GC Chromatograms



**Figure S11:** Example of liquid phase chromatogram obtained from the reaction mixture of 1-BuOH. The same products were detected for 2-BuOH, Butanone, Butanal and 1,4-Butandiol. Traces of propionic acid is present in the reaction mixture probably due to the reduction of acetic acid to ethanol which could hydrocarboxylated to propionic acid. The first signal is associated with acetone which was used as solvent for the analysis.
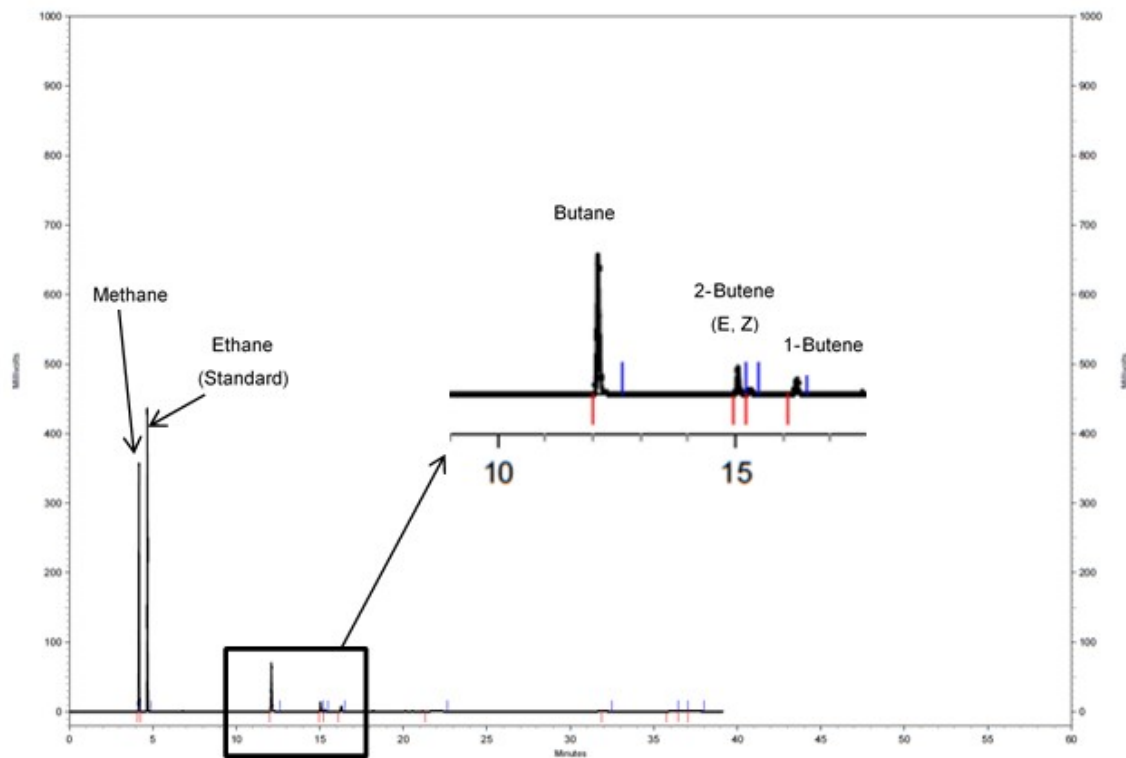
**Figure S12:** Example of the gas phase chromatogram obtained from the reaction mixture of 1-BuOH. The same products were detected for 2-BuOH, Butanone, Butanal and 1,4-Butandiol. Methane is present in the mixture as product of the hydrogenation of $CHI_3$, as well as product of the decarbonylation of acetic acid.
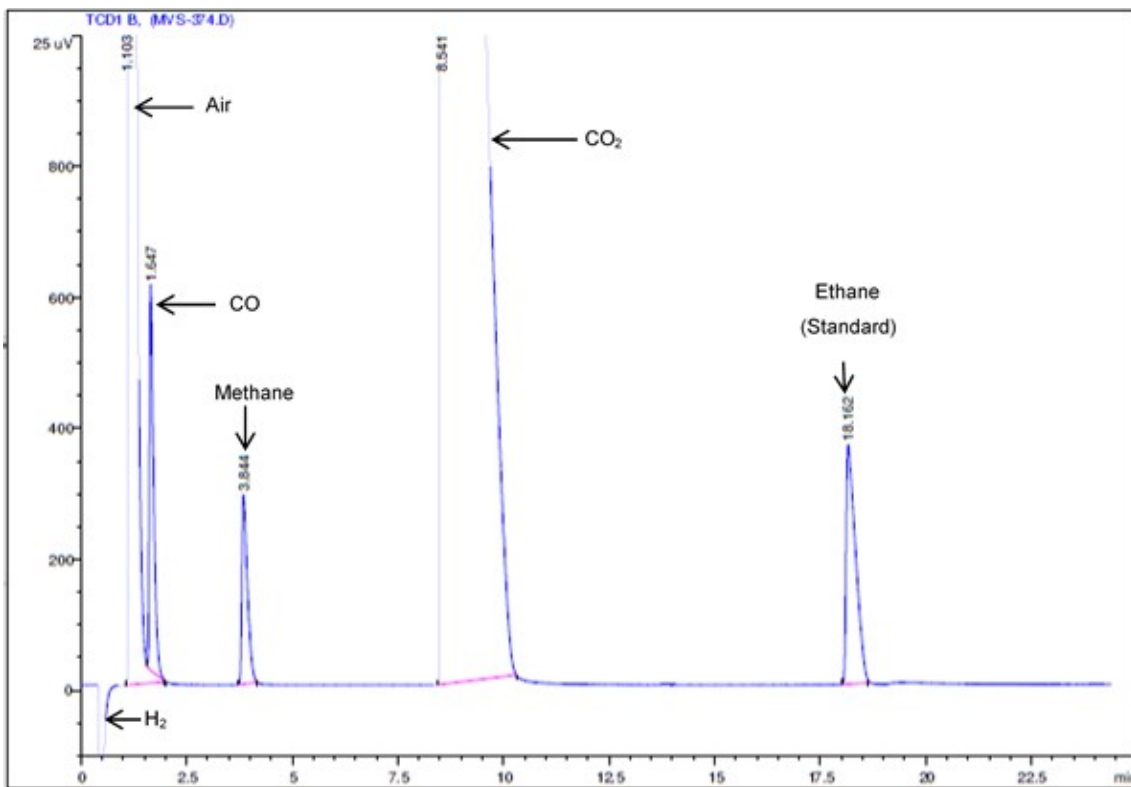
**Figure S13:** Example of gas phase chromatogram obtained from the *r*WGSR.