Supporting Information for:
Mechanistic Investigations on a Homogeneous Ruthenium Guerbet Catalyst in a Flow Reactor

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Table of Contents

1. Reactor Setup and Equipment

Continuously Stirred Tank Reactor Configuration

For ethanol coupling reactions in our continuously stirred tank reactor setup (CSTR), the catalyst and co-catalyst (sodium ethoxide) were dissolved in a polymer solvent and placed within a stainless-steel reactor that was fitted with an aluminum heating jacket. The temperature of the heating jacket was controlled by a hotplate and thermocouple (IKA C-MAG HS7 digital). Ethanol was delivered using a Kd Scientific Legato 100 Syringe Pump, and nitrogen carrier gas was supplied from a pressurized tank whose flow was set by an Alicat mass flow controller (MCS series). Pressurized tubing and fittings were purchased from McMaster-Carr and Swagelok. Attached to this reactor setup, an Agilent 6850 gas chromatograph equipped with an FID was used to analyze the gaseous products. A Restek rxi-1ms column was used for the analysis of ethanol coupling reactions and a J&W DB-Wax column was used for the analysis of transfer hydrogenation reactions.

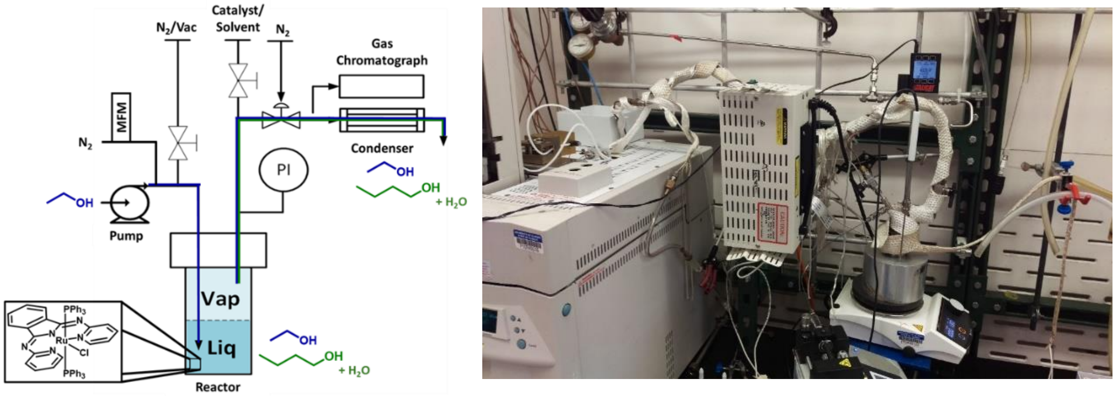

Figure S1 Continuously Stirred Tank Reactor Configuration

2. Catalyst Synthesis and Stability with Polymer

Ru(bpi)(PPh_3)$_2$Cl Synthesis:

Synthesis of the ruthenium complex was taken from literature.[1–3] Confirmation of complex synthesis was performed by ^{1}HNMR and ^{31}PNMR using benzene-d_6 as an internal standard.

1.74 mmol (80 mg) of EtOH was placed in a sealed vessel with 2 mmol (1000 mg) of monomethoxy PEG_{500}, 0.88 mmol (60 mg) of sodium ethoxide, and 5.5e^{-3} mmol (5.5 mg) of ruthenium catalyst. The reaction was carried out at 120°C over 10 hours. The data shows that the catalyst maintains a stable rate even after multiple hours on stream. The conversion throughout the experiment is kept below 7%.

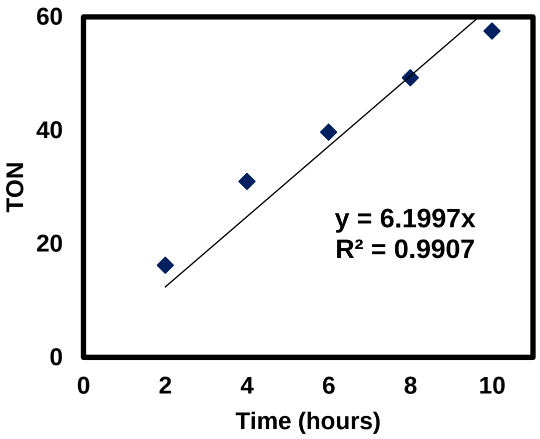

Figure S2 Stability of Catalysts in Batch with PEG (polyethylene glycol)

3e^{-4} mmol (3 mg) of **1-Ru** was dissolved in 8.7 mmol (400 mg) of ethanol and 0.8 mmol (400 mg) of PEG$_{500}$. These mixtures were then heated to 120°C for 30 minutes. Afterwards, the samples were cooled, and 0.5 mL of benzene-d$_6$ was added. The resulting solutions were analyzed using ^{31}P NMR, and the stability of the catalysts was compared. **1-Ru** can be identified by the peak at 25.89 ppm. Additionally, some PPh$_3$ dissociation was observed (-6 ppm). After heating, an unidentified complex (24.95 ppm) was observed in the catalyst-PEG mixture. However, this species was only detected in small quantities (6%), showcasing that the catalyst remains largely inert to the polymer under the reaction conditions.

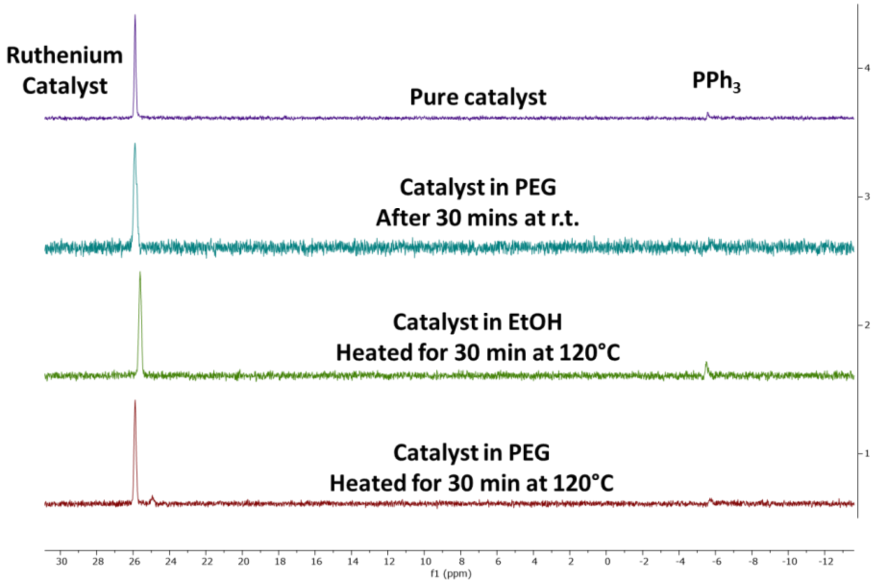

Figure S3 ^{31}P NMR studies for catalyst stability in polymer

3. Mass Balance for Ethanol Coupling Reaction

The mass balance is depicted below for an ethanol coupling experiment performed at 120°C under standard catalyst loadings. Notably, the mass balance does not close initially, due to the transient accumulation of butanol. After 5 hours on stream, we attain a quasi-steady condition, and the mass balance fully closes. The mass balance is calculated by comparing the initial ethanol flow rate to the sum of all volatilized product and substrate formation rates (C_2-C_6).

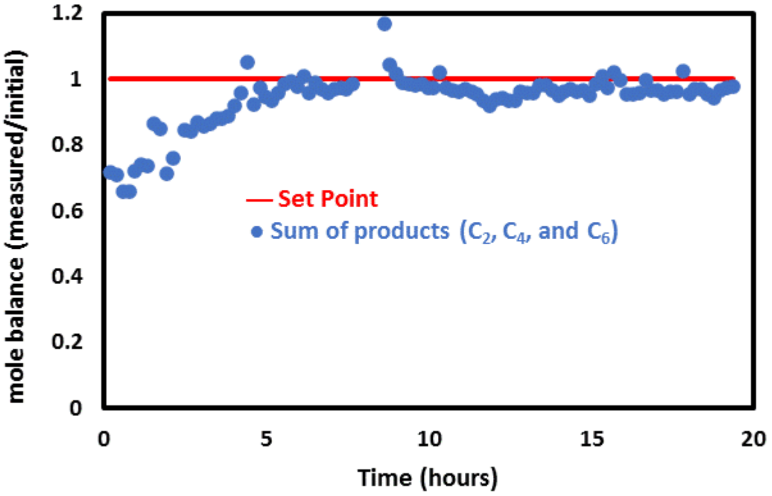

Figure S4 Mass Balance Over Time for Ethanol Coupling Experiment

4. Sample Calculation for Residence Time

Residence times were calculated by dividing the total reaction volume by the total volumetric flowrate. For the CSTR setup, the reactor volume was calculated using the volume of polymer solvent. These residence times are only an approximation, since the calculation of the exact residence time would require knowledge of the ethanol quantity dissolved within the polymer.

Relevant Parameters

$$n_{Ru} = moles\ of\ catalyst\ (mmol)$$

$$\dot{n}_{EtOH} = molar\ flowrate\ of\ ethanol \left(\frac{mmol}{\mathrm{h}}\right)$$

$$\dot{n}_{Tol} = molar\ flowrate\ of\ ethanol\ \left(\frac{mmol}{h}\right)$$

$$x_{Tol} = mole\ fraction\ of\ toluene$$

$$\dot{v}_{EtOH}(l) = liquid\ volumetric\ rate\ of\ ethanol\ \left(\frac{mL}{\mathrm{min}}\right)$$

$$\dot{v}_{EtOH}(g) = gaseous\ volumetric\ rate\ of\ ethanol\ \left(\frac{mL}{\mathrm{min}}\right)$$

$$\dot{v}_{N_2}(g) = gaseous\ volumetric\ rate\ of\ nitrogen\ \left(\frac{mL}{\mathrm{min}}\right)$$

$$\rho_{EtOH} = density\ of\ ethanol\ \left(\frac{g}{mL}\right)$$

$$\rho_{Al} = density\ of\ alumina\ \left(\frac{g}{mL}\right)$$

$$MW_{EtOH} = molecular\ weight\ of\ ethanol\ \left(\frac{g}{mol}\right)$$

$$M_{Al} = mass\ of\ alumina\ (g)$$

$$R = ideal\ gas\ constant\ \left(\frac{L\ atm}{mol\ K}\right)$$

$$T = temperature\ (K)$$

$$V = reaction\ volume\ (mL)$$

$$\tau = residence\ time\ (s)$$

Convert liquid volumetric rate of ethanol to a molar flowrate of ethanol:

$$\dot{n}_{EtOH} = \dot{v}_{EtOH}(l) * \rho_{EtOH} * \frac{1}{MW_{EtOH}}$$

$$\dot{n}_{EtOH} = \left(0.00125 \frac{mL\ (l)}{min}\right) * \left(0.789 \frac{g}{mL}\right) * \left(\frac{1}{46}\frac{mol}{g}\right) * \left(1000 \frac{mmol}{mol}\right) * \left(60 \frac{min}{h}\right) = 1.286 \frac{mmol\ EtOH}{h}$$

Convert the molar rate of ethanol to a gaseous volumetric flowrate:

Note, temperature and pressure are taken from reaction operating conditions.

$$\dot{v}_{EtOH}(g) = \dot{n}_{EtOH} * MW_{EtOH} * \frac{1}{\rho_{EtOH,gas@120°C}}$$

$$\dot{v}_{EtOH} = \left(1.286 \frac{mmol\ EtOH}{h}\right) * \left(46 \frac{mg}{mmol}\right) * \left(\frac{1}{0.001409}\frac{ml}{g}\right) * \left(\frac{1}{1000}\frac{g}{mg}\right) * \left(\frac{1}{60}\frac{h}{min}\right) = 0.7 \frac{ml}{min}\ of\ EtOH\ (g)$$

Calculate residence time:

CSTR**:** Reactor volume is calculated using the volume of PEG used for the reaction.

Ex. for a sample with a 6 g loading of PEG

$$V = \frac{m}{\rho_{PEG}} = \frac{6}{1.12} mL \sim 5.38\, mL$$

Nitrogen flowrate is set by mass flow controller. Ethanol flowrate was calculated above.

$$\tau = \frac{V}{\dot{v}_{EtOH}(g) + \dot{v}_{N_2}(g)} = \frac{5.38}{0.7 + 8.5} \frac{mL}{\frac{mL}{min}} * 60 \frac{s}{min} \sim 35\, s$$

5. Example Rate Calculations

Toluene was used as an internal standard (1 mol% in the ethanol feed) to precisely quantify the rate of product formation during catalysis. The rate of formation was then normalized by the catalyst quantity to calculate the turnover frequencies.

Example calculation for ethanol coupling rate calculations using 1-Ru:

Convert volumetric liquid injection flowrates of ethanol (substrate) and toluene (1 mol%) feed to molar flowrates.

$$\dot{n}_{EtOH} = \dot{v}_{EtOH}(l) * \rho_{EtOH} * \frac{1}{MW_{EtOH}} = 4.11 \frac{mmol\ EtOH}{h}$$

$$\dot{n}_{Tol} = x_{Tol} * \dot{n}_{EtOH} = 0.1 * 4.11 = 0.411 \frac{mmol\ Tol}{h}$$

Calibration curve: mixtures of ethanol butanol and toluene are measured in known quantities and run through the gas chromatograph to produce intensities (areas). Similar calibration curves were created for other species (not shown).

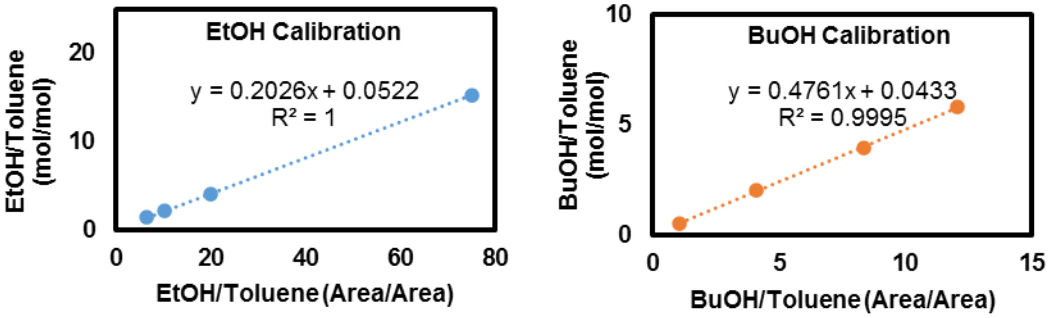

Figure S5 Species Calibration Curves

Use response factor from calibration curves with areas obtained from the gas chromatograph during catalysis to calculate the rate of product formation based upon the molar flowrate of toluene. Finally, normalize by catalyst loading to get turnover rate.

$$\dot{n}_{BuOH} = \frac{Area\ BuOH}{Area\ Toluene} * \dot{n}_{Tol} * \frac{1}{Response\ Factor}$$

$$\dot{n}_{BuOH} = \frac{100}{4500}\left(\frac{Area\ BuOH}{Area\ Toluene}\right) * 0.411\left(\frac{mmol\ Tol}{h}\right) * \frac{1}{0.4761}\left(\frac{Area\ Toluene}{Area\ BuOH} * \frac{mmol\ BuOH}{mmol\ Tol}\right)$$
$$= 0.00192\frac{mmole\ BuOH}{h}$$

$$TOF = \frac{\dot{n}_{BuOH}}{n_{Ru}} = \frac{0.00192\ \frac{mol\ BuOH}{h}}{0.0016\ mol\ Ru} = 1.2\ h^{-1}$$

6. CSTR Mass Transport

EtOH and N_2 were fed into our flow reactor at 1.25 µL/min (l) and 8.4 mL/min (g), respectively. The reactor is held at 120°C and 15.5 psi and is charged with a solution of PEG (4 mL) and EtONa (385 mM). After pre-heating (1-hour), **1-Ru** (0.66 mM) is injected into the system, and the volatile product formation rate is analyzed over time via GC. The stir-rate and stir-bar dimensions were altered to perturb the transfer surface between the ethanol (solvated in PEG) and the reactor headspace. No discontinuity of alcohol formation rate detected upon increasing the stir-rate of the catalyst solution. Moreover, the two near-identical profiles shown below depict no augmentation to alcohol formation rate despite an increase in stir-bar size. These observations suggest that the catalysis performed in our flow reactor is not mass transfer limited.

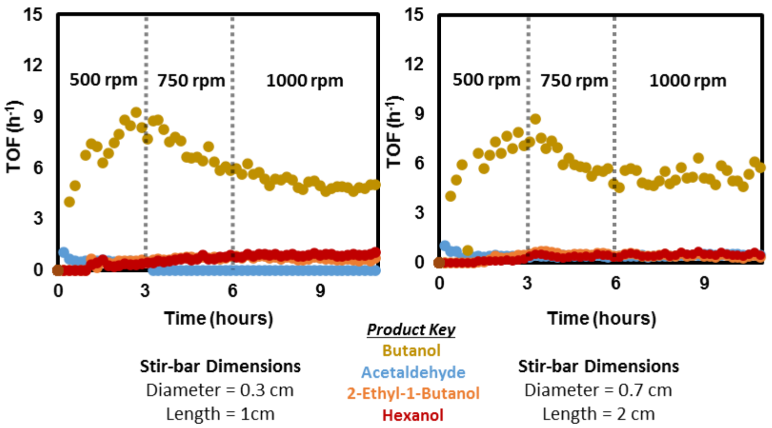

Figure S6. Product profile produced using the flow reactor while varying the stir-rate of the catalyst solution and the stir-bar size.

7. Modeling of Guerbet Reaction in the CSTR

To further validate our mechanistic understanding, we developed a qualitative kinetic model for the reaction in our CSTR. First, several chemical reactions including elimination (k_1 and k_{-4}), condensation (k_2, k_5), and transfer hydrogenation (k_3, k_4, k_6, and k_7) were selected to describe the proposed pathway (**Figure S5**). Elimination was considered the slowest step for the reaction network, and first order dependencies were assumed for all chemical species. Next, a set of differential equations was developed describing their rates of formation (**Figure S7**), and these differential rate expressions were coupled with CSTR design equations while assuming that evaporation rate was directly proportional to the concentration in the liquid phase (instantaneous equilibrium i.e., no mass transfer limitation). Paired with experimental data (**Figure S8 and S9**), the combined reaction and reactor equations were solved simultaneously using Matlab(ODE45) to produce reaction profiles describing the formation rate of products in the gas-phase (**Figure S10**). Examination of the simulated experiment validated the non-linear reaction profile generated experimentally. First, the initial accumulation of butanol was observed; whereafter, butanol was consumed to produce hexanol, which also slowly collected in the reactor. After the transient accumulation of the various products, steady state was attained.

Relevant Parameters

$$N_A = \text{Moles in the CSTR} \ (mole)$$

$$F_{A,in\ or\ out} = \text{Molar flow in or out of the reactor} \left(\frac{mole}{time}\right)$$

$$R_A = \text{Reaction rate} \left(\frac{mol}{volume\ time}\right)$$

$$C_{A,L} = \text{Liquid phase concentration } (M)$$

$$C_{A,V} = \text{Gas phase concentration } (M)$$

$$q = \text{Volumetric flowrate} \left(\frac{volume}{time}\right)$$

$$x_A = \text{Liquid mole fraction}$$

$$y_A = \text{Gas mole fraction}$$

$$P = \text{Overall pressure}$$

$$P_A{}^* = \text{Saturation pressure for species } A$$

$$C_{T,L} = \text{Total liquid phase concentration}(M)$$

$$C_{T,V} = \text{Total gas phase concentration } (M)$$

$$G_A = \text{Lumped paramter}$$

Derived Reaction Equations (R_A)

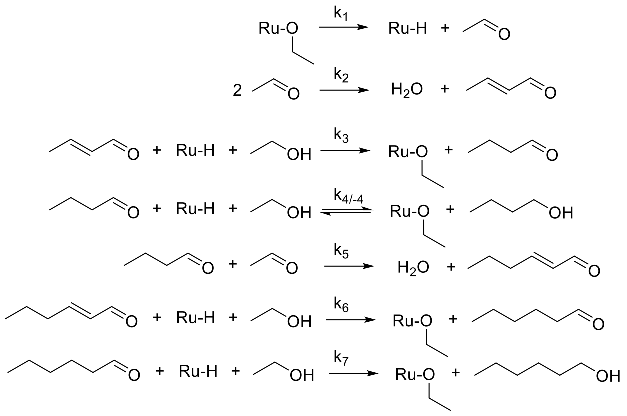

Figure S7 Reactions Considered for Guerbet Model

Parameterized Species

y_1 - Ethanol
y_2 - Acetaldehyde
y_3 - Crotonaldehyde
y_4 - Butanal
y_5 - Butanol
y_6 - 2-hexenal
y_7 - Hexenal
y_8 - Hexanol
y_9 - RuOEt
y_{10} - RuH

Equations for Each Reaction Species

$$dy_1/dt = 0;$$
$$dy_2/dt = k_1y_9-k_2y_2^2-k_5y_2y_4$$
$$dy_3/dt = k_2y_2^2-k_3y_3y_1y_{10}$$
$$dy_4/dt = k_3y_3y_1y_{10}-k_4y_4y_{10}y_1+k_{-4}y_5y_9-k_5y_4y_2$$
$$dy_5/dt = k_4y_4y_{10}y_1-k_{-4}y_5y_9$$
$$dy_6/dt = k_5y_4y_2-k_6y_6y_{10}y_1$$
$$dy_7/dt = k_6y_6y_{10}y_1-k_7y_7y_{10}y_1$$
$$dy_8/dt = k_7y_7y_{10}y_1$$

Equations for Catalyst Concentration

$$dy_9/dt = -k_1y_9+k_3y_3y_{10}y_1+k_4y_4y_{10}y_1 -k_{-4}y_5y_9+k_6y_6y_{10}y_1+k_7y_7y_{10}y_1+k_0y_{10}y_1$$

$$dy_{10}/dt = k_1y_9-k_3y_3y_{10}y_1-k_4y_4y_{10}y_1+k_{-4}y_5y_9-k_6y_6y_{10}y_1 -k_7y_7y_{10}y_1-k_0y_{10}y_1$$

Figure S8 Parameterized Reaction Equations for Each Chemical Species

CSTR Design Equations

The CSTR design equation describes the accumulation in the CSTR as a function of inlet flow, outlet flow, and chemical reaction.

$$\frac{dN_A}{dt} = F_{A,in} - F_{A,out} + R_A$$

Next, we rewrite the design equation to be in terms of concentration. Assuming that the concentration of ethanol is constant in the polymer (low conversion) and considering that ethanol is the only feed, inlet flows are not considered for other reaction species. Thus the accumulation in the liquid polymer ($C_{A,L}$) is a function of the evaporation in the gas phase [$(q/V_L)*C_{A,V}$] and the reaction rate.

$$\frac{dC_{A,L}}{dt} = -\frac{qC_{A,V}}{V_L} + R_A$$

Relating liquid phase concentration (C_L) to gas phase concentration (C_V)

Next a relationship is developed to relate concentration in the liquid phase to the gas phase. Assuming an instantaneous equilibrium, Raoult's law can be rewritten in terms of concentration. The total concentration in the liquid and gas-phase is presumed to be constant since ethanol is the predominant substrate (low conversion assumption).

$$\boldsymbol{y_A P = x_A P_A{}^*}$$

$$\boldsymbol{\left(\frac{C_{A,V}}{C_{T,V}}\right) P = \left(\frac{C_{A,L}}{C_{T,L}}\right) P_A{}^*}$$

Combining reactor design equations and reaction equations

Combining reaction equations with CSTR design equations while assuming an instantaneous evaporation results in the following expression for each volatile reaction species where the lumped parameter G_A includes the residence time (q/V_L) and volatility of the substrate (P^*/P). Combining the reaction and reactor equations results in the final parameterized differential equations which describe the liquid concentration in the CSTR (**Figure S7**).

$$\boldsymbol{\frac{dC_{A,L}}{dt} = -\left[\left(\frac{q}{V_L}\right)\left(\frac{C_{T,V}}{C_{T,L}}\right)\left(\frac{P_A{}^*}{P}\right)\right] C_{A,L} + R_A = -G_A C_{A,L} + R_A}$$

Parameterized Species	**Initial Conditions**
y_1 - Ethanol	$y_1 = 0.04$ M
y_2 - Acetaldehyde	$y_2 = 0$
y_3 - Crotonaldehyde	$y_3 = 0$
y_4 - Butanal	$y_4 = 0$
y_5 - Butanol	$y_5 = 0$
y_6 - 2-Hexenal	$y_6 = 0$
y_7 - Hexenal	$Y_7 = 0$
y_8 - Hexanol	$y_8 = 0$
y_9 - RuOEt	$y_9 = 6.6e^{-4}$ M
y_{10} - RuH	$y_{10} = 0$

Combined differential equations that describe concentration (y) in the CSTR

$dy_1/dt = 0;$

$dy_2/dt = -G_2y_2 + k_1y_9 - k_2y_2{}^2 - k_5y_2y_4$

$dy_3/dt = -G_3y_3 + k_2y_2{}^2 - k_3y_3y_1y_{10}$

$dy_4/dt = -G_4y_4 + k_3y_3y_1y_{10} - k_4y_4y_{10}y_1 + k_{-4}y_5y_9 - k_5y_4y_2$

$dy_5/dt = -G_5y_5 + k_4y_4y_{10}y_1 - k_{-4}y_5y_9$

$dy_6/dt = -G_6y_6 + k_5y_4y_2 - k_6y_6y_{10}y_1$

$dy_7/dt = -G_7y_7 + k_6y_6y_{10}y_1 - k_7y_7y_{10}y_1$

$dy_8/dt = -G_8y_8 + k_7y_7y_{10}y_1$

Equations for Catalyst Concentration

$dy_9/dt = -k_1y_9 + k_3y_3y_{10}y_1 + k_4y_4y_{10}y_1 - k_{-4}y_5y_9$
$+k_6y_6y_{10}y_1 + k_7y_7y_{10}y_1 + k_0y_{10}y_1$

$dy_{10}/dt = k_1y_9 - k_3y_3y_{10}y_1 - k_4y_4y_{10}y_1 + k_{-4}y_5y_9 - k_6y_6y_{10}y_1$
$-k_7y_7y_{10}y_1 - k_0y_{10}y_1$

Figure S9 Combined/Parameterized Reaction and CSTR Design Equations

Estimating $C_{T.L}$ and $C_{T,V}$

($C_{T,L}$) An experiment was designed to determine the concentration of ethanol in the liquid phase at elevated temperatures. A solution of PEG was placed into our stainless-steel flow reactor where ethanol and nitrogen are fed into the heated reactor at rates of 4 µL/min and 8 mL/min, respectively. After 5 hours on stream, the reactor was sealed and cooled. Once the reactor reached room temperature a sample of the reactor solution was analyzed using an external standard (toluene) to calculate the concentration of ethanol in the PEG. The loading of PEG (which correlates to the excess headspace) was varied to determine the impact of condensation on the experiment. The experiment provided an estimate for the concentration of ethanol in the liquid phase to initialize our set of differential equations.

$$C_{T,L} = \frac{\left(\dfrac{10\, mg\, EtOH}{46\dfrac{mg}{mmol}}\right)}{5.33\dfrac{mL}{min}} = 0.0417\, M$$

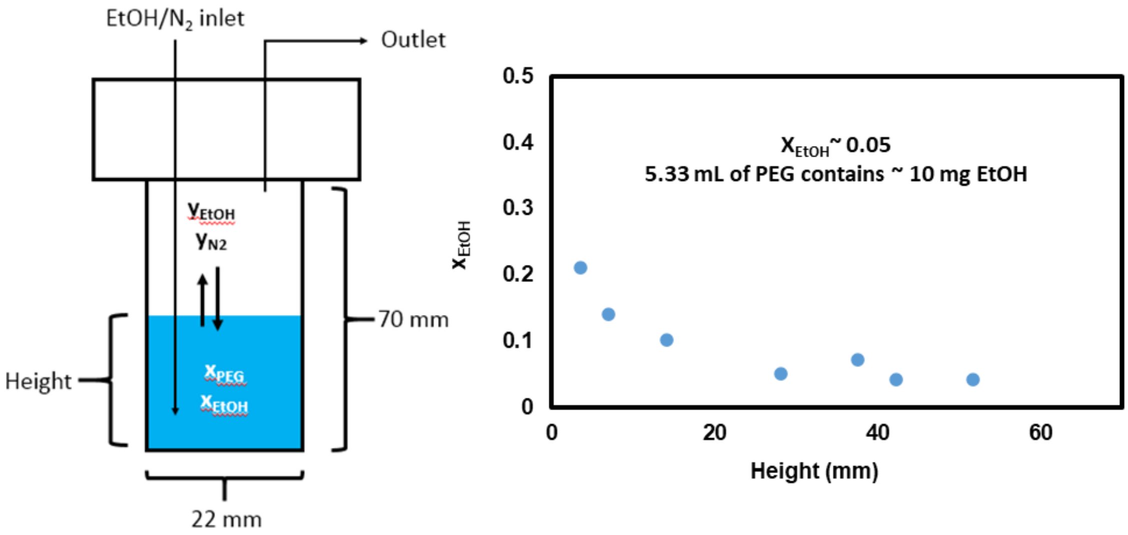

Figure S10 Experimental Setup and Data for Determining $C_{T,L}$

($C_{T,V}$ and q) The total moles of gas in the headspace was estimated using the ideal gas law (1 atm, 120°C). Afterwards the composition of the headspace was calculated based on the molar feed ratios considering ethanol and nitrogen feed rates of 4 µL/min (l) and 8 mL/min (g), respectively. Assuming ethanol concentration remains constant, the gaseous volumetric flowrate (q) of all Guerbet products was set to 4 mL/h (g). This was calculated using the density of ethanol vapor at 120°. Note the solubility of nitrogen gas was not considered.

$$n_T \sim \frac{PV_V}{RT} = \frac{(1\ atm)\left(\frac{35}{1000}\ L\right)\left(1000\frac{mmol}{mol}\right)}{\left(0.082\ \frac{L\ atm}{mol\ K}\right)(120+273\ K)} = 1\ mmol$$

$$x_{EtOH,V} = \frac{\dot{n}_{EtOH}}{\dot{n}_{N2}+\dot{n}_{EtOH}} = \frac{6.86e^{-5}\frac{mol}{min}}{7.14e^{-4}\frac{mol}{min}+6.86e^{-5}\frac{mol}{min}} = 0.088$$

$$C_{T,V} = n_{EtOH,V} * V_V = \frac{0.088\ mmol}{35\ mL} = 0.0025\ M$$

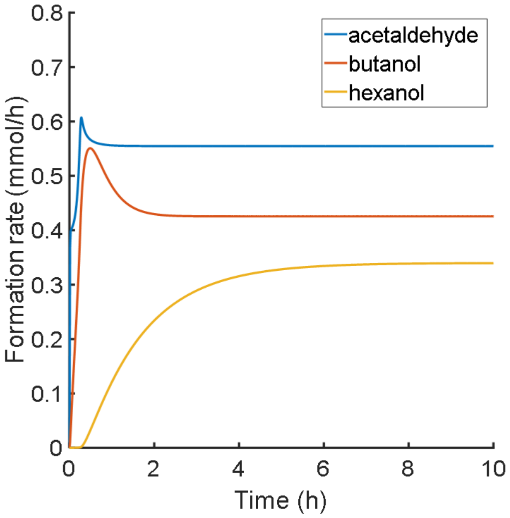

Figure S11 Simulated profile for ethanol coupling reaction in the CSTR flow system. Calculations were based upon ethanol and nitrogen flowrates set at 4 µL/min (l) and 8 mL/min, respectively. Rate constants [elimination: $k_1 = k_{-4} = 75\ h^{-1}$; condensation: $k_2 = k_5 = 1.2e^5\ M^{-1}h^{-1}$; hydrogenation: $k_3 = k_4 = k_6 = k_7 = 4e^8\ M^{-2}h^{-1}$]. Initial Conditions [EtOH] = 0.04 M and [RuOEt] = $6.6e^{-4}$ M.

8. Random Coupling Model (Flory's Equal Reactivity Principle)

Step-growth condensation equation

$$x_i = (1-p)p^{i-1}$$

Relevant Parameters

$$x_i = mole\ fraction$$

$$p = extent\ of\ reaction\ (conversion)$$

$$i = number\ of\ repeat\ units$$

Composition of a random coupling reaction at 2.5 mol% ethanol conversion

$$x_{EtOH} = x_1 = (1-0.025)0.025^{1-1} = 0.975$$

$$x_{BuOH} = x_2 = (1-0.025)0.025^{2-1} = 0.0244$$

$$x_{HexOH} = x_3 = (1-0.025)0.025^{3-1} = 0.00060$$

$$\frac{C_4}{C_6} = \frac{x_{BuOH}}{x_{HexOH}} = \frac{0.0244}{0.0006} = 40.67$$

For the following data, an ethanol coupling reaction was modeled using the step-growth condensation equation shown above. For a specified ethanol conversion, the mol fraction of coupling products ranging from C_2 to C_{28} was calculated.

Selectivity is described as the mol fraction of butanol relative to the total formation of other carbon products [$S_{C4} = C_4/\mathrm{sum}(C_i)$].

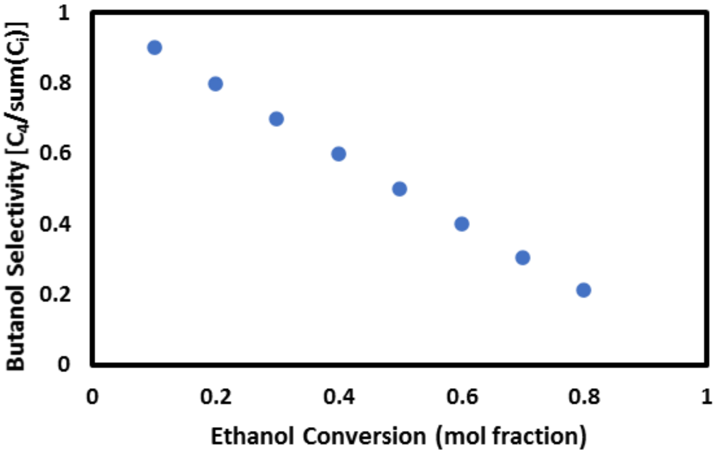

Figure S12 Butanol Selectivity as a Function of Ethanol Conversion

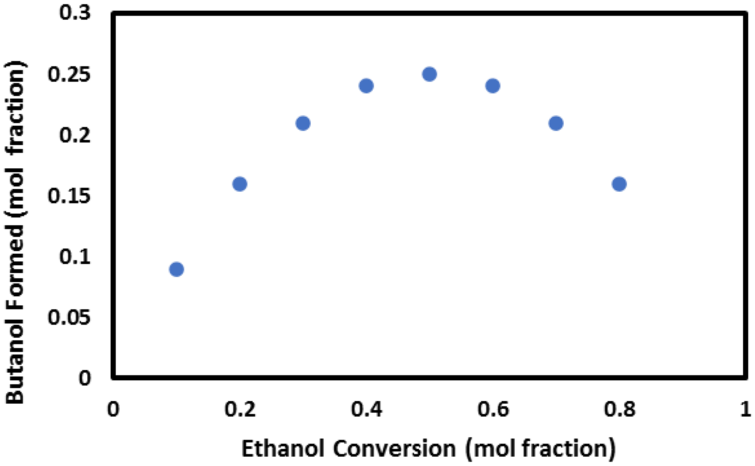

Figure S13 Butanol Formation as a Function of Ethanol Conversion

9. Cannizzaro and Tishchenko Side Products – Batch Condensation Reactions

Diglyme (1 mL), acetaldehyde and butyraldehyde (1:1 molar mixture totaling 1 mL) were reacted in the presence of sodium ethoxide (330 mM) at 120°C in a sealed glass vessel for 1 hour. The resulting product mixture revealed the presence of aldehydes, acids, and esters whose relative compositions have been tabulated below. The range of products showcases competition amongst aldol condensation, Cannizzaro and Tishchenko reactions.

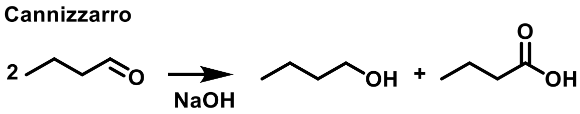

Table S1 Composition for identfied/detected products in the presence of sodium ethoxide.

Species	mol%
Acetaldehyde	35.24
Butyraldehyde	53.39
Butanol	0.41
Crotonaldehyde	0.2
2-ethyl-butanol	0.85
2-ethyl-hexanol	1.42
Butyl Butyrate	0.41
Acetic Acid	7.26
Butyric Acid	0.82

10. Gas-Phase analysis of Transfer Hydrogenations for Unsaturated C_4 Intermediates

^{i}PrOH (spiked with 1 mol% of unsaturated C_4) and He are fed into our flow device at 20 µL/min (l) and 100 mL/min (g), respectively. The reactor is held at 120°C and 15.5 psi. After 3 hours, a solution of PEG (4.9 mL) and EtONa (420 mM) are injected into the reactor where we observe poor mass balance closure in the gas phase for experiments involving butyraldehyde and crotonaldehyde. For aldehyde substrates in the presence of sodium ethoxide, some formation of butanol is observed which is derived from aldehyde disproportionation side reactions (Cannizzaro), which takes two molecules of the corresponding aldehyde and converts it into an acid and an alcohol. Crotyl alcohol which has a carbon-carbon double bond cannot participate in aldehyde side reactions where no side-products are observed in the presence of sodium. After an additional 3 hours on stream, a solution of PEG (0.45 mL) and **1-Ru** (15 mM) are injected into the reactor and mixed with the sodium ethoxide co-catalyst, where high to moderate conversion of unsaturated substrates to butanol is observed.

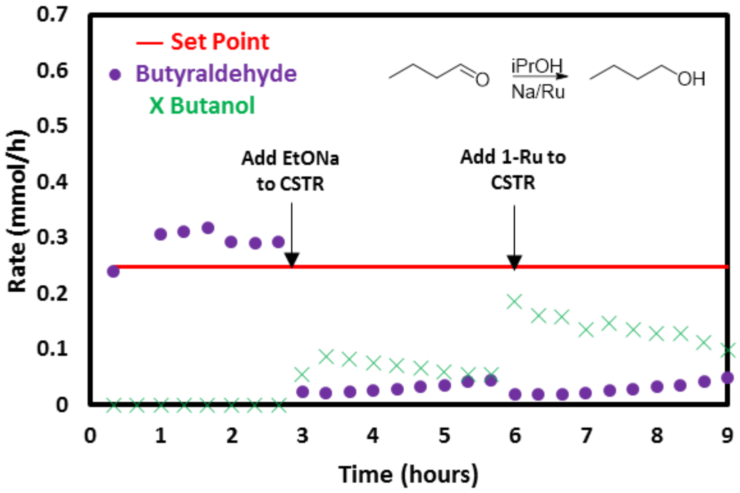

Figure S14 Butyraldehyde Hydrogenation

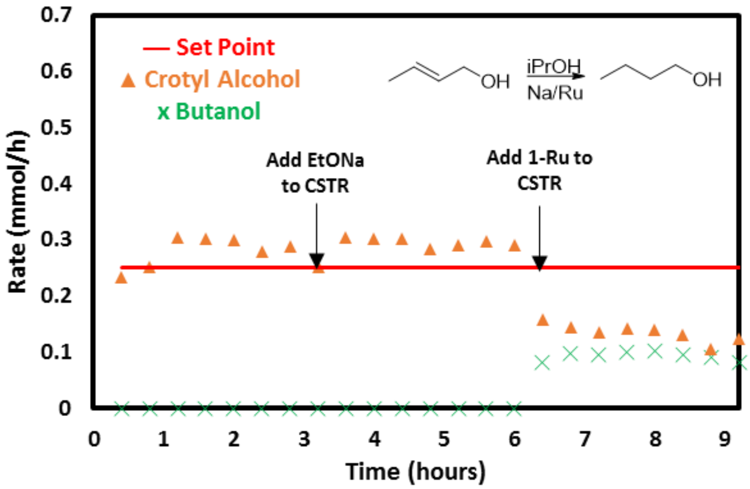

Figure S15 Crotyl Alcohol Hydrogenation

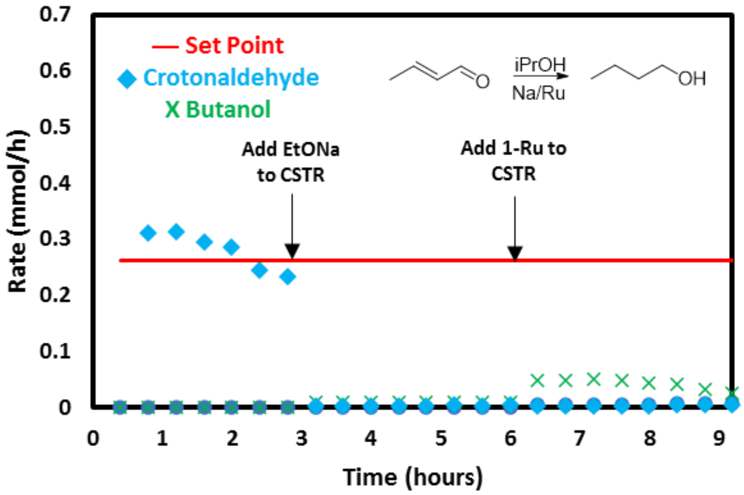

Figure S16 Crotonaldehyde Hydrogenation

11. Comparison of Acetone and Butanol Formation Rates

^{i}PrOH (spiked with 1 mol% of unsaturated C_4) and He are fed into our flow device at 20 µL/min (l) and 100 mL/min (g), respectively. The reactor is held at 120°C and 15.5 psi. After 3 hours, a solution of PEG (4.9 mL) and EtONa (420 mM) are injected into the reactor where no acetone formation is observed. After an additional 3 hours on stream, a solution of PEG (0.45 mL) and **1-Ru** (15 mM) are injected into the reactor and mixed with the sodium ethoxide co-catalyst, whereafter the formation of acetone is detected.

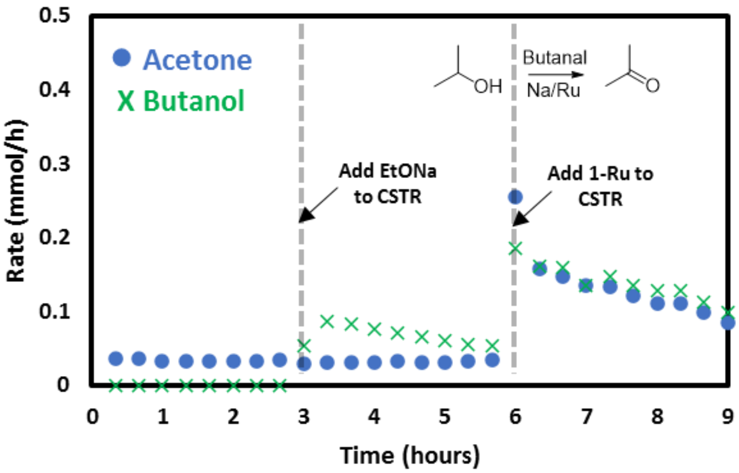

Figure S17 ^{i}PrOH and Butyraldehyde Transfer Hydrogenation

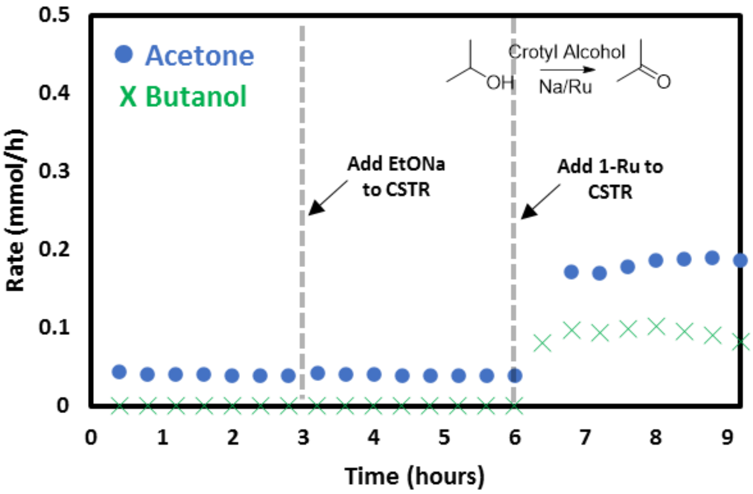

Figure S18 ^{i}PrOH and Crotyl Alcohol Transfer Hydrogenation

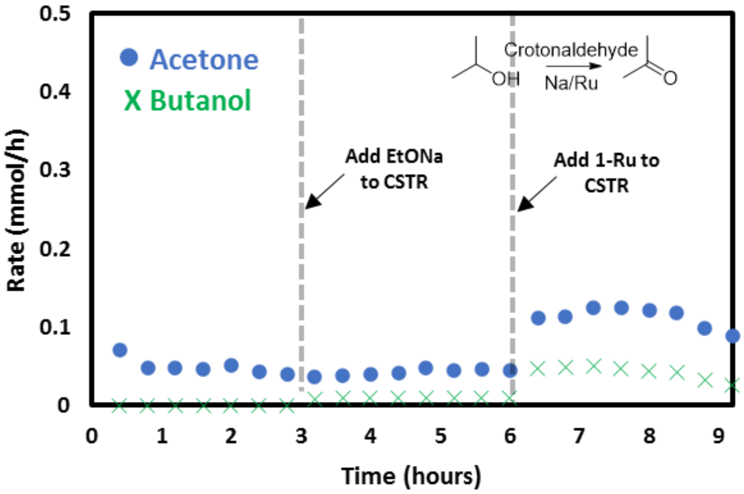

Figure S19 ^{i}PrOH and Crotonaldehyde Transfer Hydrogenation

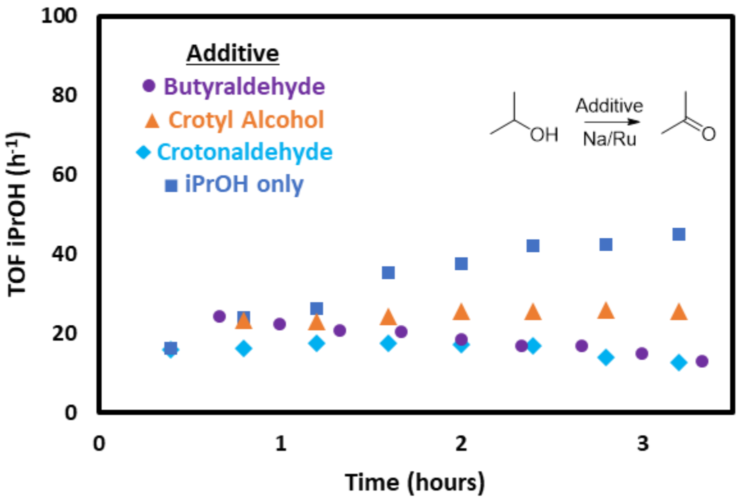

Figure S20 Acetone Formation Rates in the Presence of Various Intermediates

12. Hydrogen Solubility Under Reaction Conditions

A thermodynamic simulation was developed in ChemCad using the SRK equation of state. The solubility of hydrogen gas relative to ethanol in a dimethyl ether PEG (Selexol™) was determined using a simple flash column held at 120°C and 1 atm. Inlet rates were selected to approximate the flowrates into our CSTR. The flowrate of hydrogen gas was selected assuming a maximum hydrogen formation rate which corresponds to the maximum dehydrogenation of ethanol (~10 mol%).

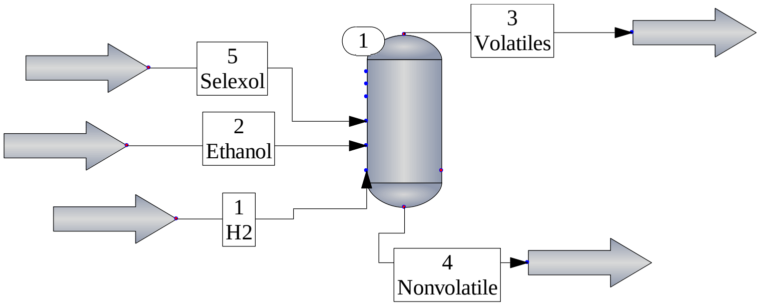

Figure S21 Schematic for Thermodynamic Model

Table S2. Stream Table for Flash Separation of a PEG, Ethanol and Hydrogen Mixture

Species	Inlet Flow (mol/h)	Non-volatiles (mol/h)
Selexol™	10	10
Ethanol	10	2.5
Hydrogen (gas)	1	0.001

13. Product Identification

Retention times for product species were identified using reagents purchased commericially. Analysis is performed using an Agilent 6850 gas chromatograph equipped with either a Restek rxi-1ms column (30m x 0.25mm x 0.5 um film thickness) for ethanol coupling reactions or a J&W DB-WAX GC Column (30m x 0.25 mm x 0.25 ⍰m film thickness) for hydrogen transfer reactions and an FID.

Table S3 GC species retention time for Restek rxi-1ms column. Temperature ramp starts at 50°C and ends at 135°C (15°C/min) with 7psi inlet pressure (helium carrier gas).

Commercially Purchased Product	Retention Time (min)
Acetaldehyde	2.347
Ethanol	2.411
Butanal	2.945
Ethyl acetate	2.979
Butanol	3.389
Crotyl alcohol	3.519
Crotonaldehyde	3.655
2-Ethyl Butanol	7.118
Hexanol	7.775

Table S4 GC species retention time for J&W DB-WAX GC Column. Temperature ramp starts at 50°C and ends at 150°C (15°C/min) with 15psi inlet pressure (helium carrier gas).

Commercially Purchased Product	Retention time (min)
Ethanol	3.825
Acetaldehyde	2.1
Acetone	2.579
Isopropyl Alcohol	3.7
Acetic Acid	15.911
Butyraldehyde	3.034
Crotyl Alcohol	10.808 and 11.3
Crotonaldehyde	5.8
Butanol	9.21
Butyric Acid	18.862
n-hexane	1.9
2-Ethyl butyraldehyde	4.949
Ethyl butyrate	5.929
Butyl acetate	7.29
Hexanal	7.396
Trans-2-hexenal	10.742
2-Ethyl-butanol	12.874
Hexanol	14.027
Butyl Butyrate	10.886
2-Ethyl-Hexanol	16.589
Octanol	17.668

14. Materials, Equipment, and Supplies Summary

Equipment:

Kd Scientific Legato 100 syringe pump
Alicat mass flow controller (MCS series)
IKA C-MAG HS7 digital hotplate
Agilent gas chromatograph 6850

Restek rxi-1ms column 30m, 0.25 mmID 0.25 μm film thickness

Column Conditions: Temperature ramp starts at 50°C and ends at 135°C (15°C/min) with 7psi inlet pressure (helium carrier gas).

J&W DB-WAX GC Column 30m, 0.25 mmID, 0.25 μm film thickness

Column Conditions: Temperature ramp starts at 50°C and ends at 150°C (15°C/min) with 15psi inlet pressure (helium carrier gas).

Stainless steel tubing (1/4th and 1/8th inch) and compression fittings purchsed from Swagelok and McMaster-Carr

NMR spectra were recorded at room temperature on a Varian spectrometer operating at 500 MHz and referenced to C_6D_6. IR spectra were collected at room temperature using a Bruker Alpha ATR Infrared Spectrometer.

Chemicals:

Sigma Aldrich
acetaldehyde, butyraldehyde, crotyl alcohol, crotonaldehyde 2-ethylbutyraldehyde, 2-ethyl-hexanol, butyric acid, acetic acid, ethyl butyrate, butyl acetate, hexanal, trans-2-hexenal, octanol, PEG_{500}, 1,4 dicyanobenzene, 2-aminopyridine, diglyme

Fischer Chemicals
Toluene, iso-propyl alcohol

Alfa Aesar
2-ethyl butanol, hexanol, octanol

Decon labs
Ethanol

TCI Chemicals
Butanol

Acros Organics
Triphenyl Phosphine

J&J Materials
Ru(III) Chloride Hydrate

15. Preparation of chemicals

Solvents were commercially available and purchased from their respective vendors (see above). All chemicals and materials were stored under argon. Ethanol and toluene were dried using 2Å molecular sieves. Polyethylene glycol was sparged with argon prior to storage in a glovebox. Sodium ethoxide was prepared in-house by reacting sodium metal with an excess of dried and degassed ethanol.

16. Notes and References

(1) Fox, M. A.; Harris, J. E.; Heider, S.; Pérez-gregorio, V.; Zakrzewska, M. E.; Farmer, J. D.; Yufit, D. S.; Howard, J. A. K.; Low, P. J. A Simple Synthesis of Trans -RuCl (C „ CR)(Dppe) 2 Complexes and Representative Molecular Structures. *J. Organomet. Chem.* **2009**, *694* (15), 2350–2358.

(2) Siegl, W. Metal Ion Activation of Nitriles . Syntheses of l , 3-Bis (Arylimino) Isoindolines. *J. Org. Chem.* **1977**, *42* (11), 1872–1878.

(3) Zhang, D. Bin; Wang, J. Y.; Wen, H. M.; Chen, Z. N. Electrochemical, Spectroscopic, and Theoretical Studies on Diethynyl Ligand Bridged Ruthenium Complexes with 1,3-Bis(2-Pyridylimino)Isoindolate. *Organometallics* **2014**, *33* (18), 4738–4746.