Supporting Information

Valorisation of Biobased Olefins via Rh-Catalyzed Transfer Hydroformylation and Isomerization using Formaldehyde as CO/H₂ Surrogate

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General

All reagents were used as received without further purification. Anaerobic reactions were run under an argon atmosphere using Schlenk techniques. $^1$H- and $^{31}$P-NMR were recorder at room temperature on a Bruker 400.13 MHz with CHCl$_3$ (7.26 ppm) as an internal standard in deuterated chloroform or in toluene-$d_8$ with phosphoric acid (0 ppm) as an external standard. Gas chromatography measurements were performed on a Shimadzu GC-2014 Plus with a HP-5 column (30 mm x 0.25 mm x 0.25 µm). The corresponding $^1$H-NMR of the products 2a and 3a are in agreement with the literature.$^1$

General procedure for the syngas-free hydroformylation of 1 a-d.

In a 10 mL Schlenk tube with a stir bar were pleased the metal precursor [Rh] (1.0 or 2.0 mol%), decarbonylation ligand rac-BINAP (2.0 mol%) and the hydroformylation ligand (4.0 mol%). After the tube was purged three times with argon, toluene or tetrahydrofuran (5.0 mL) and a solution of the substrate in toluene or tetrahydrofuran (1.0 mL, 1.0 mmol) were added into the tube under argon flow. Once formaldehyde (375 µL, 5.0 mmol) was added an argon flow was maintained for some seconds. The reaction mixture was stirred at 90 ºC for 20 hours. A sample was taken for GC-FID analysis. The reaction mixture was concentrated under pressure and the crude was analyzed by $^1$H NMR. Conversions, yield and ratios were determined by GC.

General procedure for the isomerization of 1 a-d.

In a 10 mL Schlenk tube with a stir bar were pleased the metal precursor [Rh(acac)(CO)$_2$] (5.2 mg, 0.2 mmol), PPh$_3$ (10.5 mg, 0.4 mmol). After the tube was purged three times with argon, toluene (5.0 mL) and a solution of the substrate in toluene (1.0 mL, 1.0 mmol) were added into the tube under argon flow. Once formaldehyde (375 µL, 5.0 mmol) was added an argon flow was maintained for some seconds. The reaction mixture was stirred at 90 ºC for 20 hours. A sample was taken for GC-FID analysis. The reaction mixture was concentrated under pressure and the crude was analyzed by $^1$H NMR. Conversions, yield and ratios were determined by GC. E/Z stereoselectivity was determined by $^1$H NMR.
**31P-NMR Experiments**

[Rh(acac)(CO)₂] (1.3 mg, 0.005 mmol) and/or PPh₃ (10.4 mg, 0.04 mmol) and/or (S)-BINAP (25 mg, 0.04 mmol), were placed into a NMR tube under argon atmosphere. After 5 minutes, the spectrum was immediately recorded. After the addition of formaldehyde (0.019 mL, 0.25 mmol) a new spectrum was measured.

**Generation of syngas for hydroformylation of safrole under isomerization conditions**

In two broad vials (A and B) with screw caps and linked by a glass apparatus was performed the hydroformylations (Figure S2). In vial A was generated syngas *in situ* with the catalytic system [Rh(COD)Cl]₂/rac-BINAP and formaldehyde.

![Figure S1. Glass apparatus used for the hydroformylation of safrole under isomerization conditions.](image)

[Rh(COD)Cl]₂ (9.9 mg, 0.02 mmol), rac-BINAP (25 mg, 0.04 mmol), formaldehyde (0.75 mL, mol) were added into the vial A, which was purged with argon three times and toluene (6 mL) was added to the vial through an argon flow. The reaction mixture was stirred at 90 °C. After 40 minutes the solution C* was added into the vial B though an argon flow and both mixture was stirred at 90 °C for 5 hours. A sample was analyzed by gas chromatography.

*Preparation of solution C:

[Rh(acac)(CO)₂] (5.2 mg, 0.02 mmol), PPh₃ (10.4 mg, 0.04 mmol), safrole (1.0 mmol), toluene (6.0 mL) and formaldehyde (0.36 mL) were added into a Schlenk tube through an argon flow.
$^1$H-NMR spectrum of the crude 4a
E/Z ratio of 4a (93:7).
$^1$H-NMR spectrum of the crude 4b

E/Z ratio of 4b (100:0).
$^1$H-NMR spectrum of the crude 4c
E/Z ratio of 4c (95:5).
$^1$H-NMR spectrum of the crude 4d
E/Z ratio of 4d (93:7).
$^{31}$P-NMR spectrum of the mixture [Rh(acac)(CO)$_2$]/(S)-BINAP/PPh$_3$/HCHO
$^1$H-NMR spectrum of the mixture [Rh(acac)(CO)$_2$]/(S)-BINAP/PPh$_3$/HCHO
$^{31}\text{P}-\text{NMR}$ spectrum of the mixture $[\text{Rh}(\text{acac})(\text{CO})_2/(\text{S})-\text{BINAP}]

$^{31}\text{P}-\text{NMR}$ spectrum of the mixture $[\text{Rh}(\text{acac})(\text{CO})_2/(\text{S})-\text{BINAP}/\text{HCHO}$
$^1$H-NMR spectrum of the mixture [Rh(acac)(CO)$_2$/($S$)-BINAP/HCHO
$^{31}$P-NMR spectrum of the mixture [Rh(acac)(CO)$_2$/ PPh$_3$
$^{31}$P-NMR spectrum of the mixture [Rh(acac)(CO)$_2$/PPh$_3$/HCHO

$^1$H-NMR spectrum of the mixture [Rh(acac)(CO)$_2$/PPh$_3$/HCHO
References