# Homogeneous polymetallic Ruthenium(II)^Zinc(II) complexes: Robust catalysts for the efficient hydrogenation of levulinic acid to *γ*-valerolactone

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## Supporting Information

## Experimental details

### *J Young* NMR tube experiment

The reaction was performed by loading a $CDCl_3$ solution of pre-catalyst **3** (2.0 μmol; 5.3 mg), formic acid (30.0 μmol; 1.1 μL) and triethyl amine (6.7 μmol; 6.1 μL) into a *J Young* NMR tube and heated in an oil bath containing silicon oil at 70 °C. Prior to the heating, the mixture was analyzed by $^{1}H$ NMR and $^{31}P$ $\{^{1}H\}$ spectroscopy. The NMR analyses of the reaction mixture was repeated at regular intervals in the course of the heating.

### Mercury drop test

The mercury drop test or poisoning experiments[1-4] were performed using LA (10 mmol), FA (10 mmol), pre-catalyst **3** (0.01 mmol), elemental mercury (0.06 mmol; 12 mg) in a high pressure reactor at 120 $^{o}C$ for 4 h. After the reaction time, the reactor was cooled to room temperature and the content depressurized and a sample was taken for $^{1}H$ NMR analyses using $CDCl_3$.

**Table S1:** Crystallographic data for complexes **1-3**.

| Compound | 1 | 2 | 3 |
|---|---|---|---|
| Empirical formula | $C_{29}H_{29}Cl_2O_2PRu \cdot H_2O$ | $C_{25}H_{29}Cl_2O_2PRu$ | $C_{121}H_{124}Cl_8O_8P_4Ru_4Zn_2$ |

| | | | |
|---|---|---|---|
| Formula weight | 630.48 | 564.42 | 2551.55 |
| Temperature/K | 99.98 | 99.99 | 100.02 |
| Crystal system | Monoclinic | monoclinic | monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ |
| a/Å | 10.0354(5) | 10.595(2) | 16.387(13) |
| b/Å | 12.4751(12) | 12.873(3) | 27.97(2) |
| c/Å | 22.0590(13) | 18.387(4) | 26.66(2) |
| α/° | 90 | 90 | 90 |
| β/° | 93.550(4) | 106.74 | 101.396(15) |
| γ/° | 90 | 90 | 90 |
| Volume/Å$^3$ | 2756.3(3) | 2401.4(9) | 11980(17) |
| Z | 4 | 4 | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.519 | 1.561 | 1.415 |
| μ/mm$^{-1}$ | 7.169 | 0.962 | 1.169 |
| Radiation | CuKα (λ = 1.54178) | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| Theta range for data collection/° | 8.032 to 144.818 | 3.92 to 57.332 | 2.132 to 38.746 |
| Reflections collected | 39783 | 16618 | 45477 |
| Independent reflections | 5435 [$R_{int}$ = 0.0362, $R_{sigma}$ = 0.0192] | 5026 [$R_{int}$ = 0.1040, $R_{sigma}$ = 0.2111] | 10056 [$R_{int}$ = 0.1918, $R_{sigma}$ = 0.1485] |
| Data/restraints/parameters | 5435/3/341 | 5026/0/287 | 10056/132/729 |
| Goodness-of-fit on $F^2$ | 1.043 | 0.577 | 1.007 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0251, $wR_2$ = 0.0623 | $R_1$ = 0.0420, $wR_2$ = 0.0624 | $R_1$ = 0.0811, $wR_2$ = 0.2024 |
| Final R indexes [all data] | $R_1$ = 0.0279, $wR_2$ = 0.0640 | $R_1$ = 0.0874, $wR_2$ = 0.0715 | $R_1$ = 0.1648, $wR_2$ = 0.2564 |

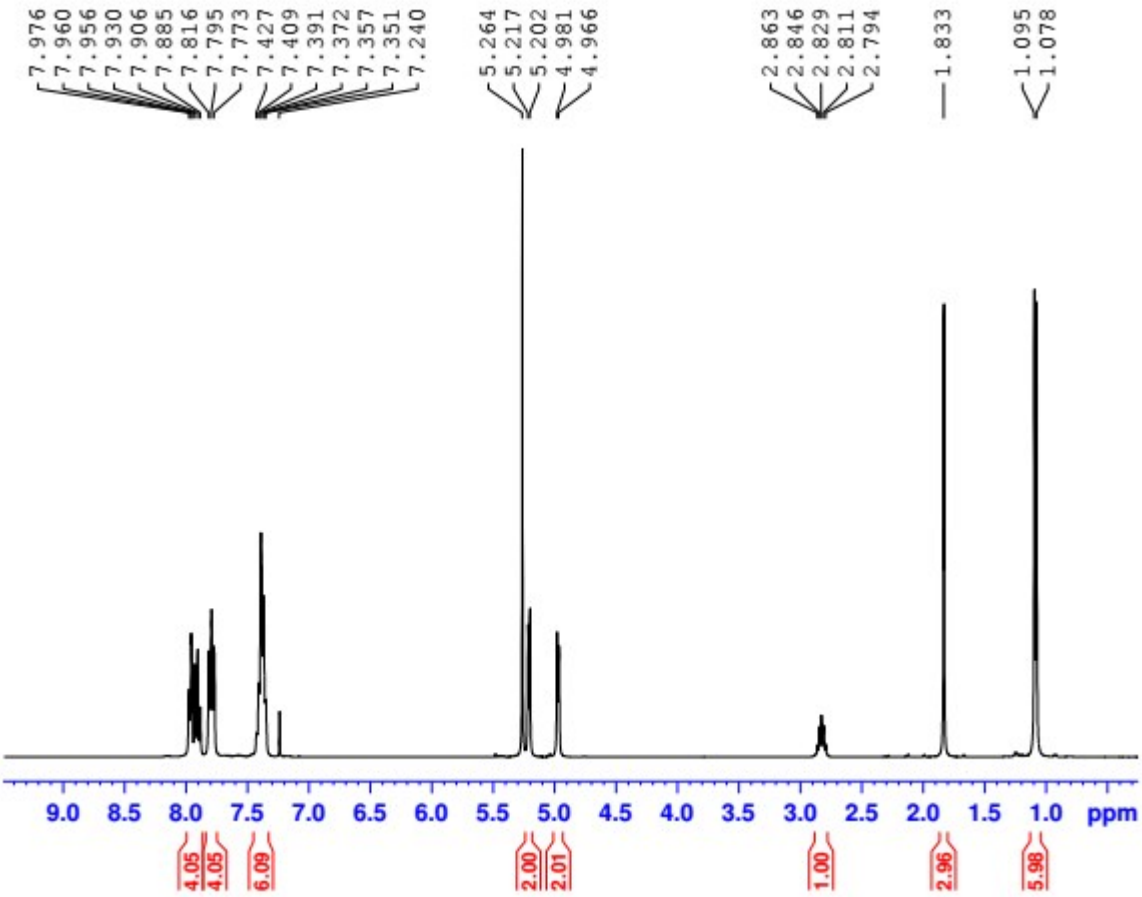


**Figure S1**: $^{1}H$ NMR spectrum of **1**. (400 MHz, $CDCl_3$, 298 K).

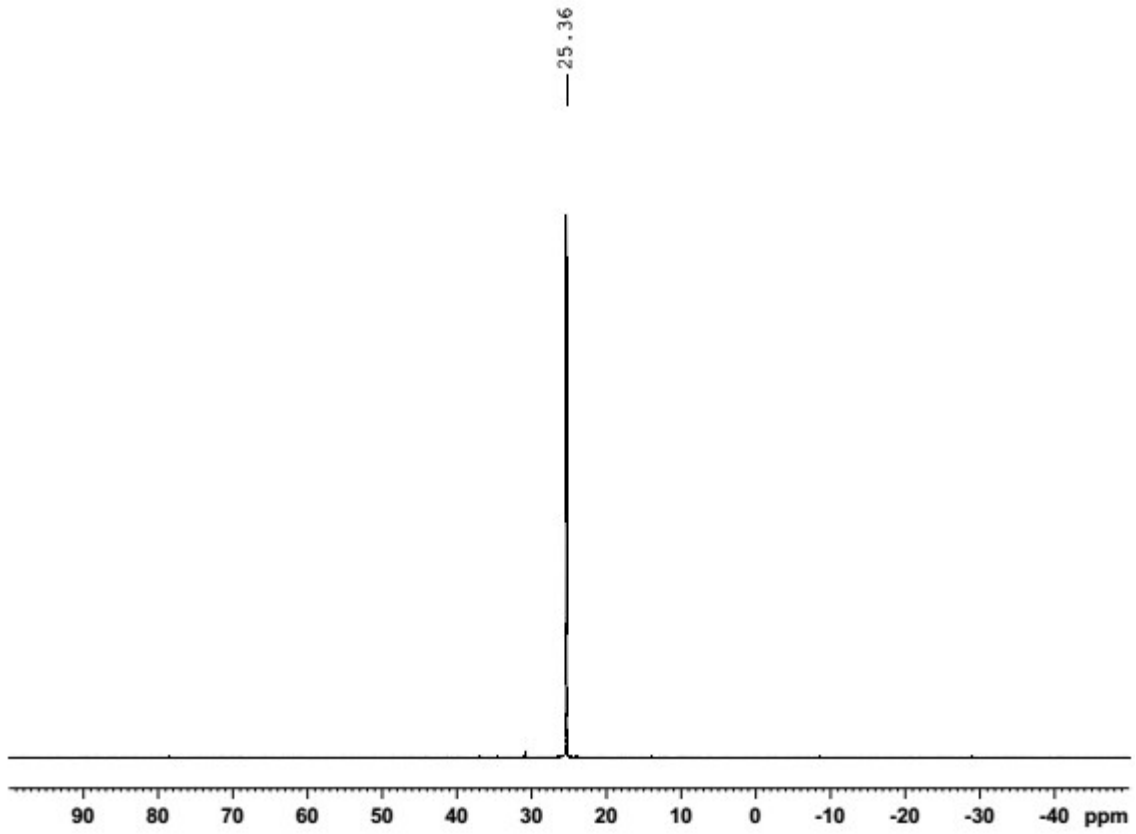


**Figure S2**: $^{31}P$ $\{^{1}H\}$ NMR spectrum of **1**. (400 MHz, $CDCl_3$, 298 K).

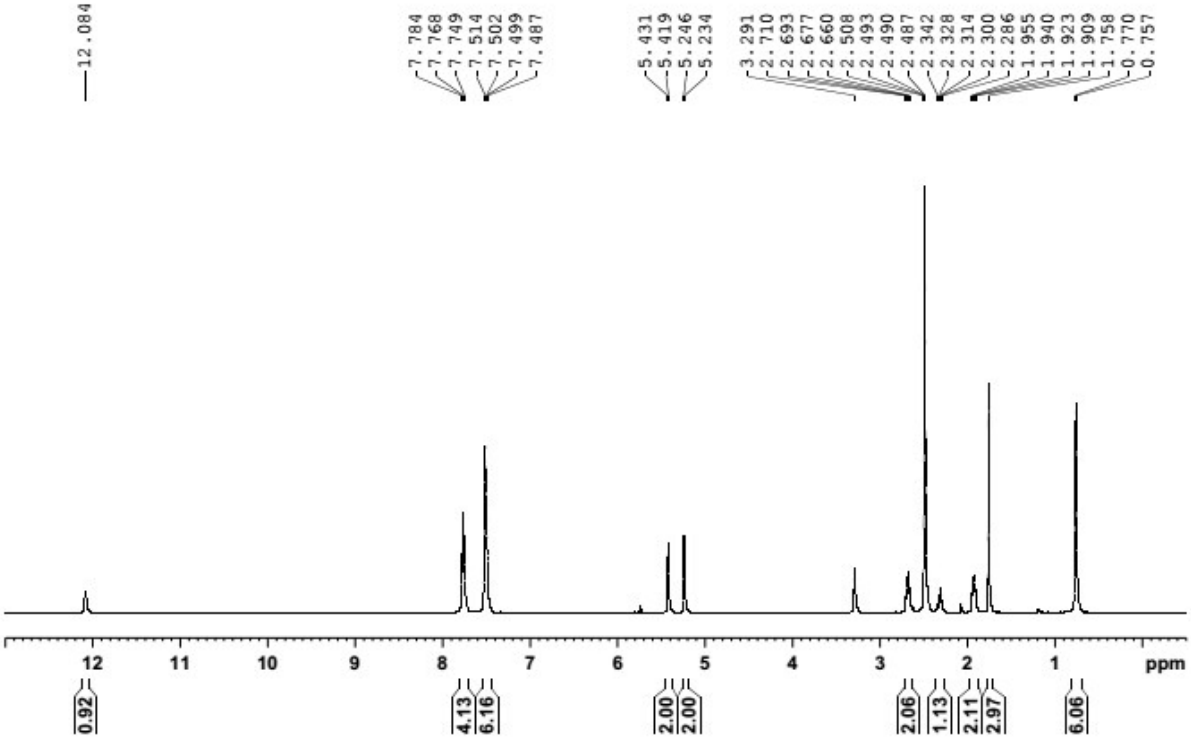


**Figure S3**: $^{1}H$ NMR spectrum of **2**. (400 MHz, DMSO-d6, 298 K).

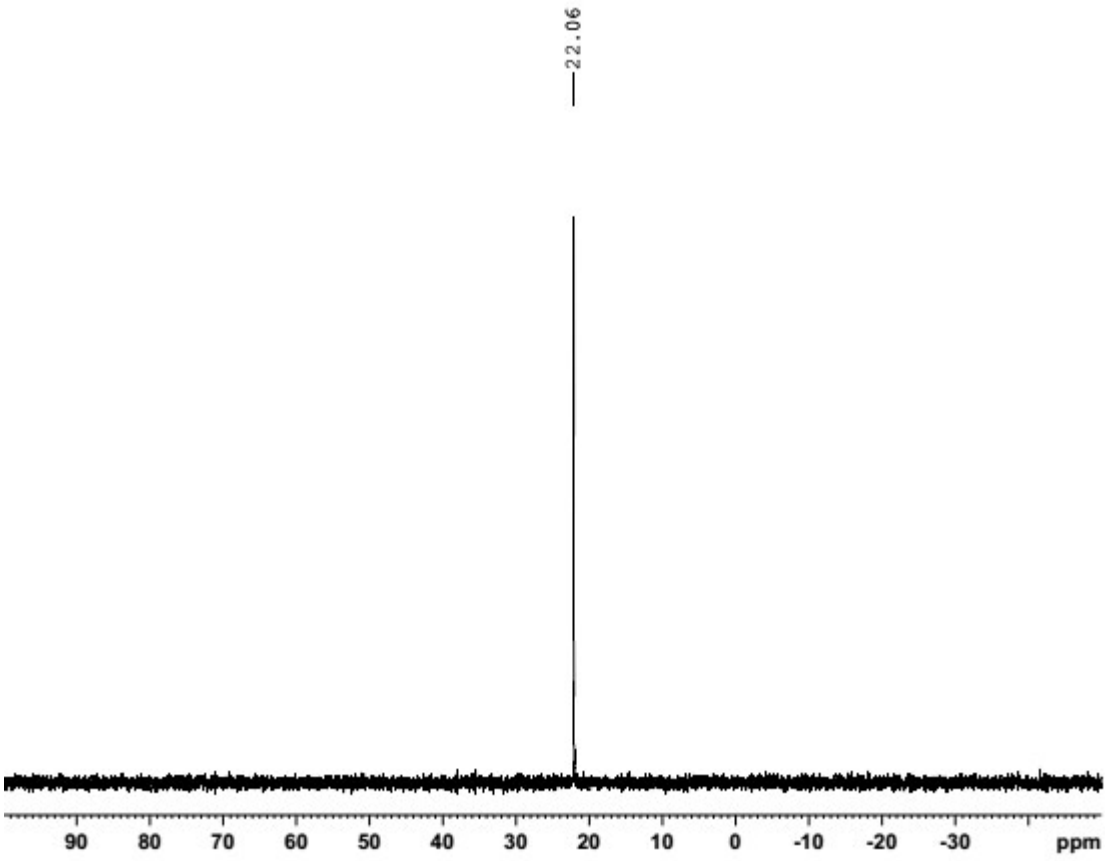


**Figure S4**: $^{31}P$ $\{^{1}H\}$ NMR spectrum of **2**. (400 MHz, DMSO-d6, 298 K).

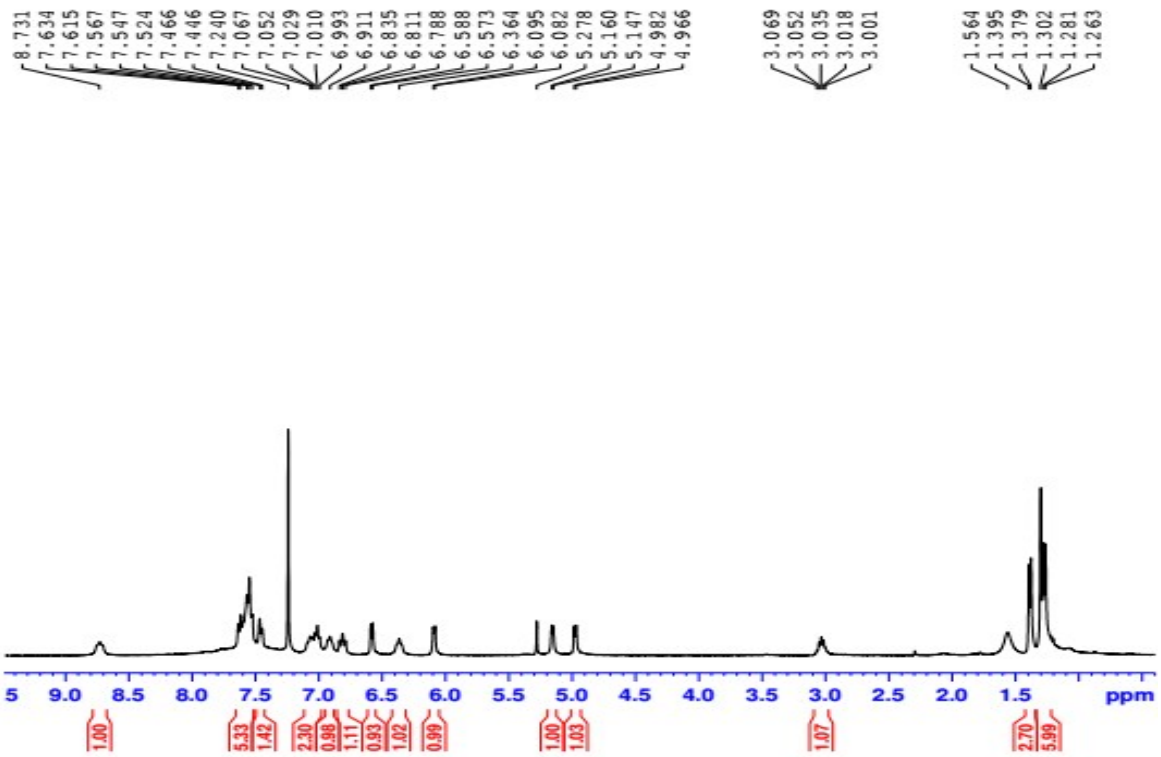


**Figure S5**: $^{1}H$ NMR spectrum of **3**. (400 MHz, $CDCl_3$, 298 K).

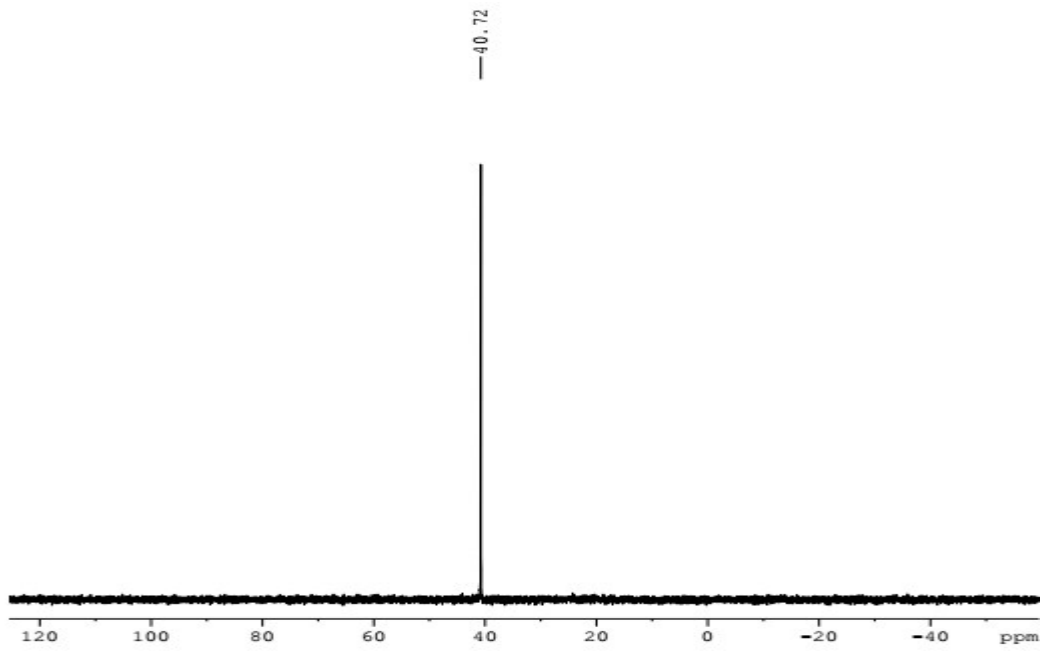


**Figure S6**: $^{31}P$ $\{^{1}H\}$ NMR spectrum of **3**. (400 MHz, $CDCl_3$, 298 K).

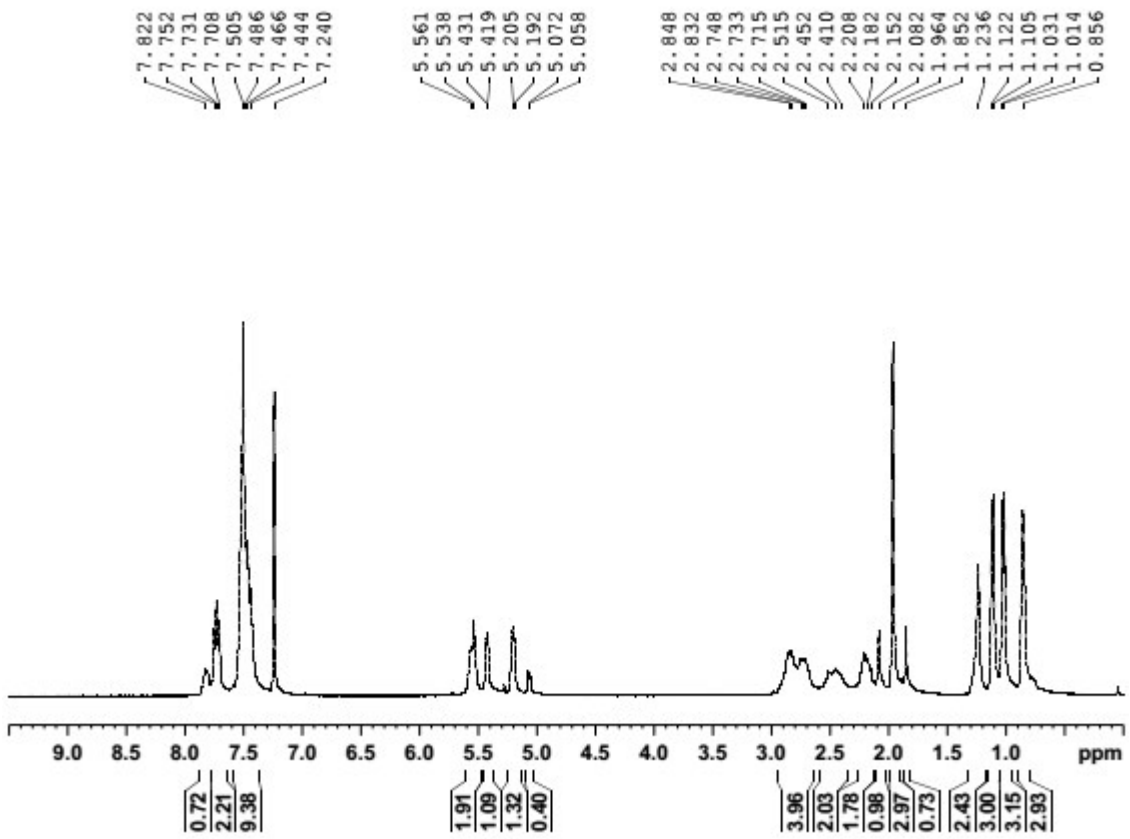


**Figure S7**: $^{1}H$ NMR spectrum of **4**. (400 MHz, $CDCl_3$, 298 K).

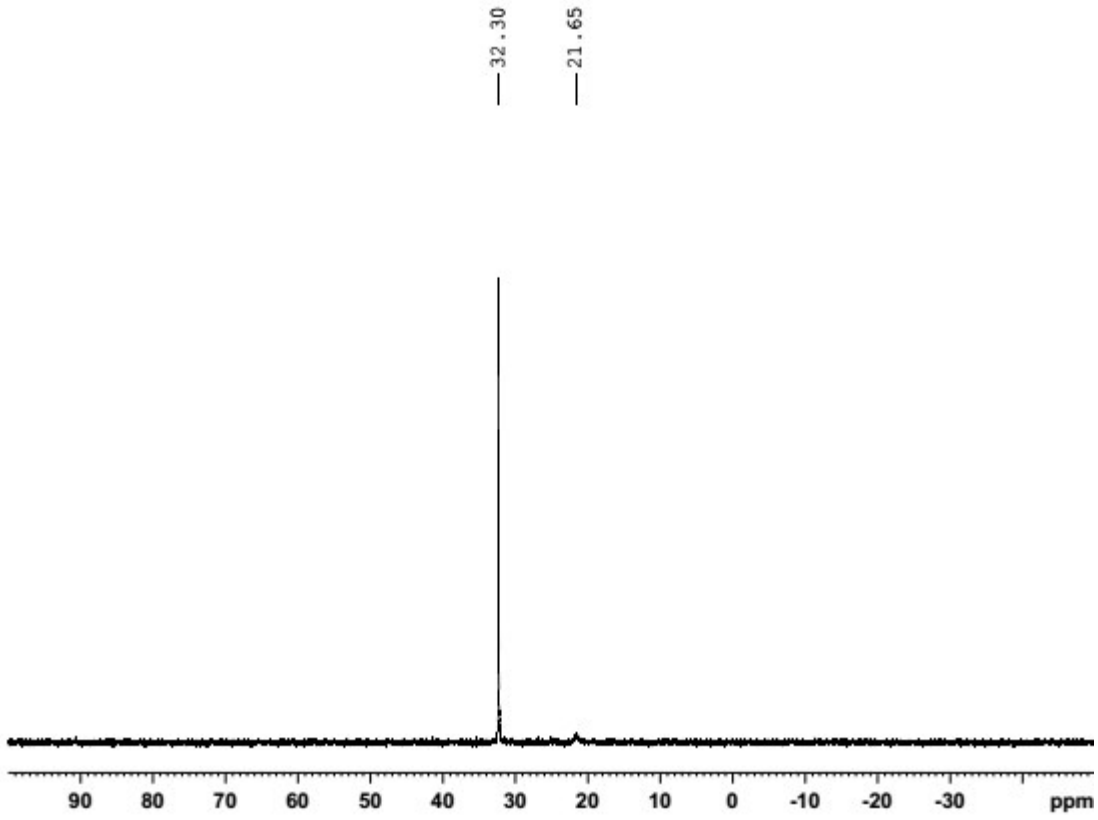


**Figure S8**: $^{31}P$ $\{^{1}H\}$ NMR spectrum of **4**. (400 MHz, $CDCl_3$, 298 K).

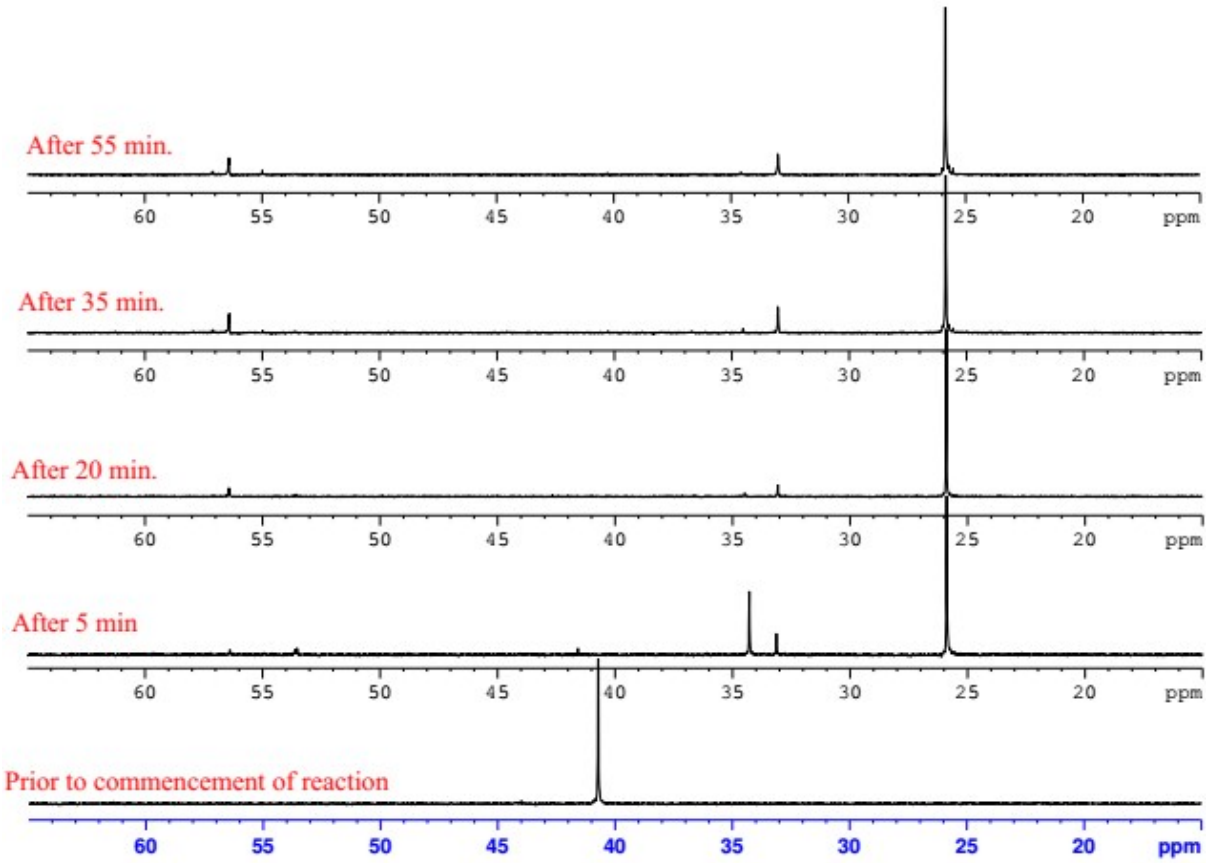


**Figure S9**: $^{31}P$ $\{^{1}H\}$ NMR spectrum of **3** obtained during monitoring of the formation of the active species.

**Table S2: Hydrogenation of LA using 3 at additional conditions**

| Entry | FA (equi.) | Base (equi.) | Conversion (%) | Selectivity (GVL) | TON | TOF ($h^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | 1 | Et3N (1) | 93 | 95 | 930 | 233 |
| 2 | 1.5 | Et3N (0.6) | >99 | 95 | 990 | 248 |
| 3 | 1 | KOH (0.6) | 29 | 93 | 290 | 73 |

Conditions: LA 10 mmol; catalyst precursor 0.01 mmol (0.1 mol%); 120 °C; 4 h. Conversions were determined by from $^{1}H$ NMR spectra. (400 MHz, $CDCl_3$, 298 K)

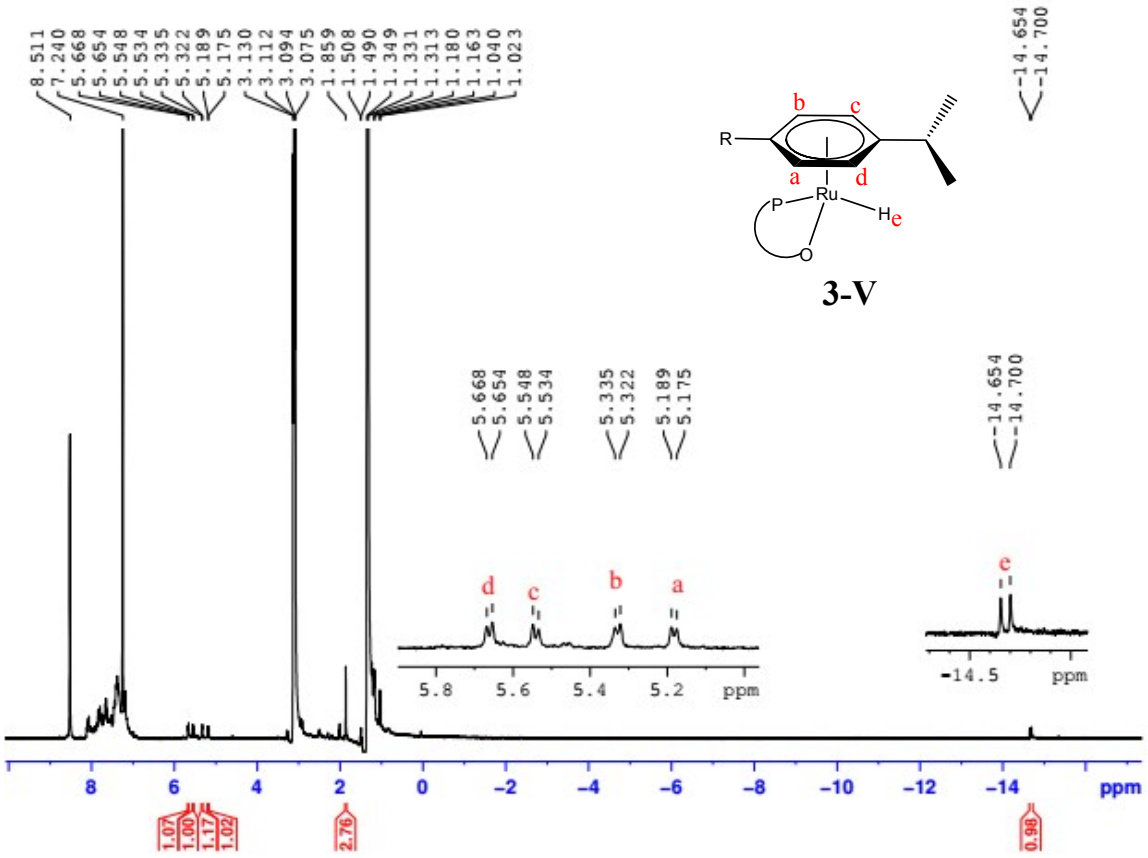


**Figure S10**: $^{1}$H NMR spectrum of **3** showing the hydride proton signal and other unique signals of the metal hydride species after the pressure generated was released. (400 MHz, $CDCl_3$, 298 K).

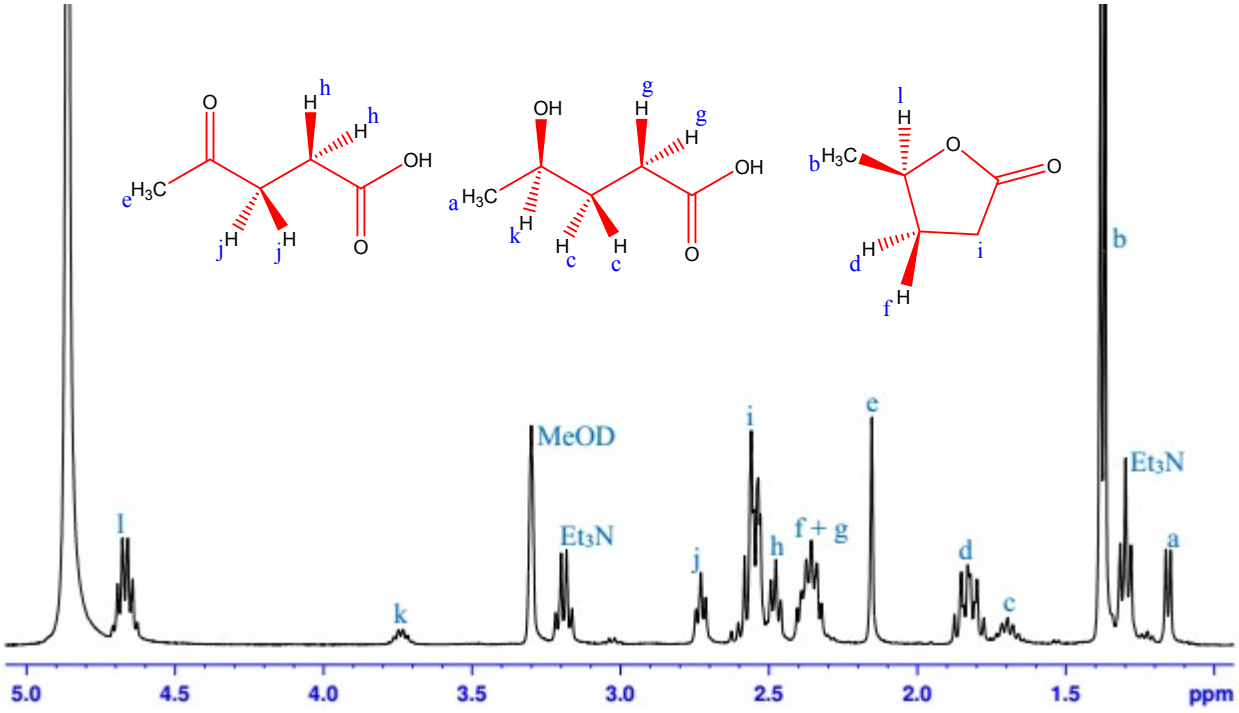


**Figure S11**: $^{1}$H NMR spectrum of a crude mixture obtained from hydrogenation of LA with **3**. (400 MHz, MeOD, 298 K).

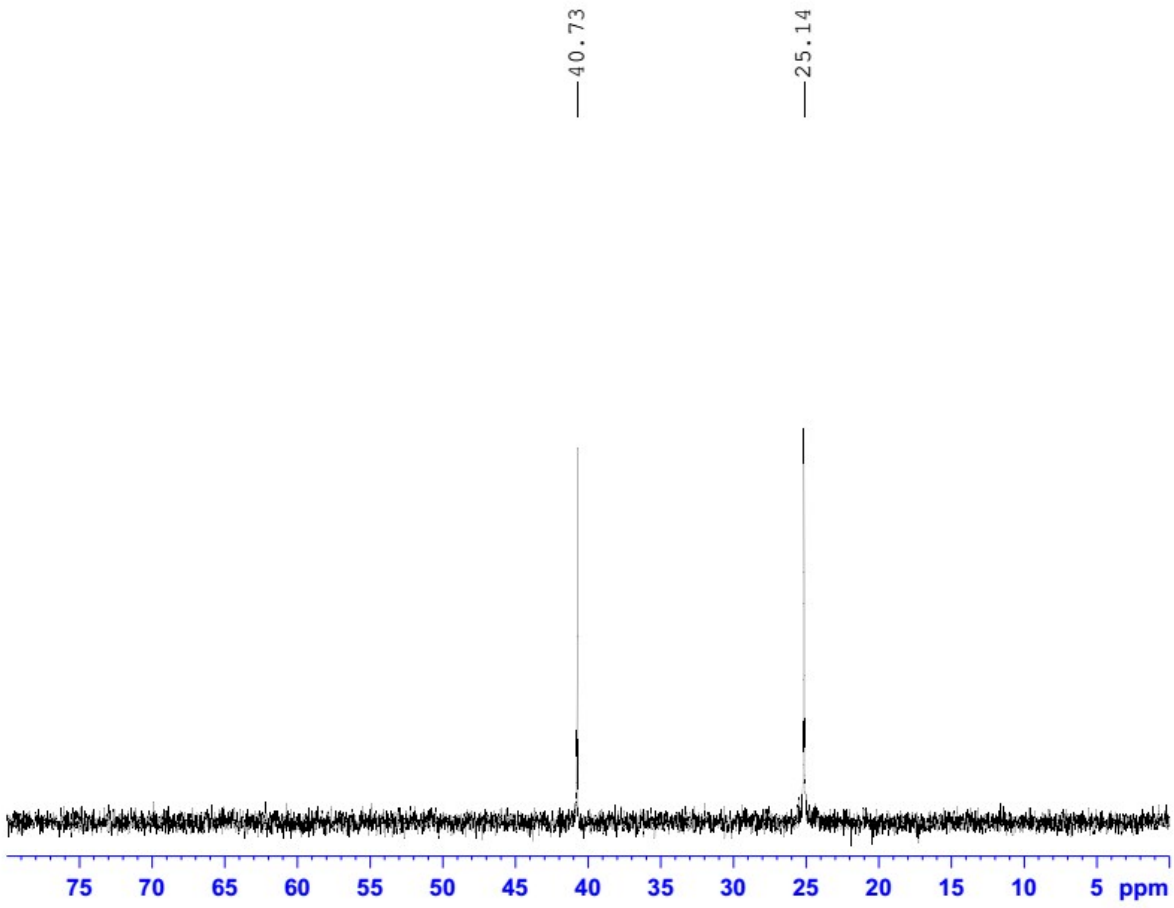


**Figure S12**: $^{31}P$ $\{^{1}H\}$ NMR spectrum of **3** obtained after 2 h during monitoring of the formation of the active species using molecular hydrogen. (400 MHz, $CDCl_3$, 298 K).

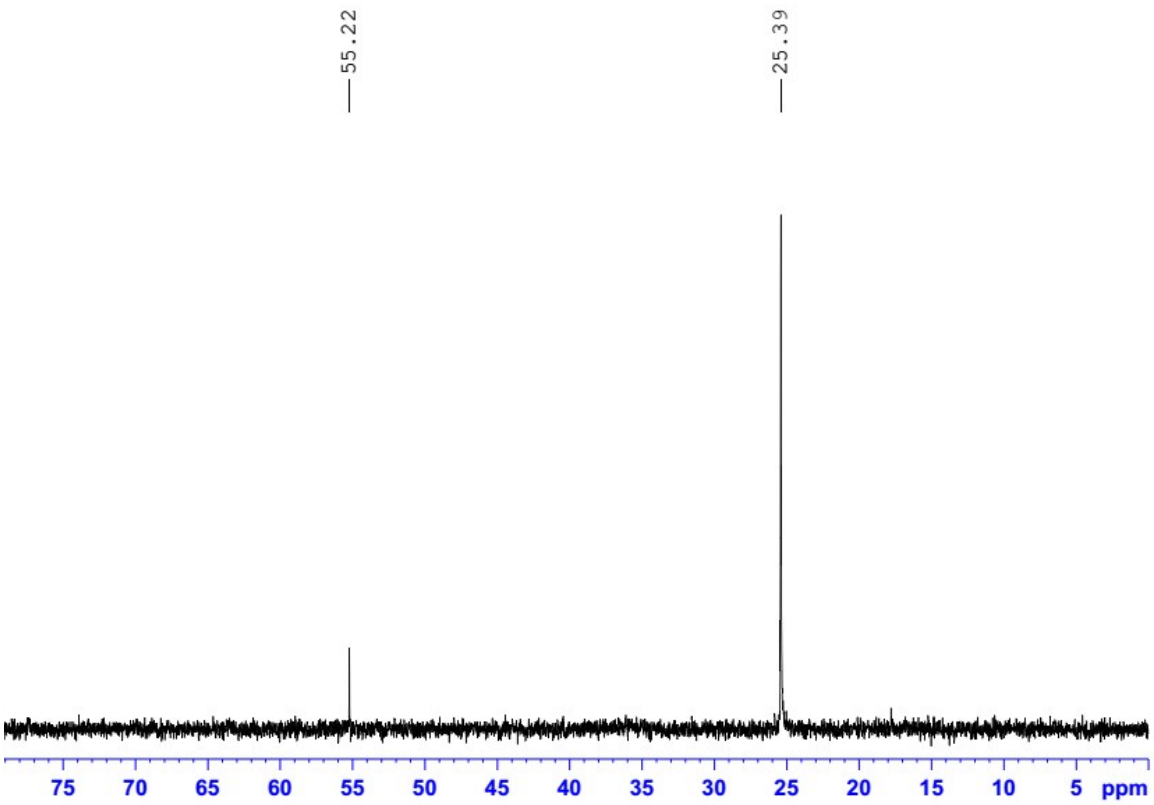


**Figure S13**: $^{31}P$ $\{^{1}H\}$ NMR spectrum of **3** obtained in after 24 h during monitoring of the formation of the active species using molecular hydrogen. (400 MHz, $CDCl_3$, 298 K).

**References**


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