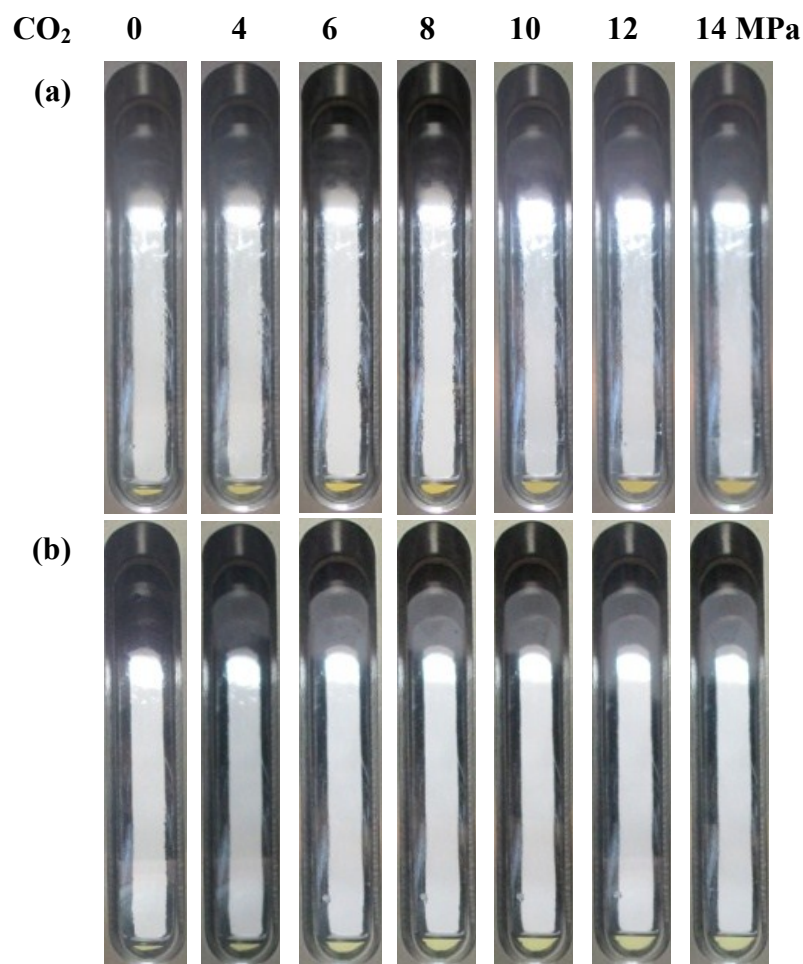


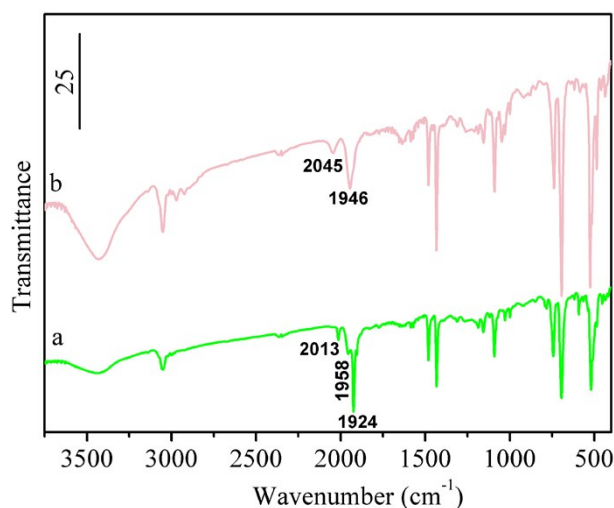
*Supporting Information*

**Hydrogenation of levulinic acid by  $\text{RuCl}_2(\text{PPh}_3)_3$  in supercritical  $\text{CO}_2$ :  
Significance of structural changes of Ru complexes via interaction with  $\text{CO}_2$**

Wenjing Yang, Haiyang Cheng\*, Bin Zhang, Yan Li, Tong Liu, Mingli Lan, Yancun Yu, Chao Zhang, Weiwei Lin, Shin-ichiro Fujita, Masahiko Arai, Fengyu Zhao\*



**Fig. S1** Phase behavior of (a) LA and (b) GVL at 150 °C pressurized by 4 MPa  $\text{H}_2$  and compressed  $\text{CO}_2$  at different pressures given. The relative volume of LA and GVL against the reactor volume was same as used in the hydrogenation runs.



**Fig. S2** FTIR spectra of pre-treated  $\text{RuCl}_2(\text{PPh}_3)_3$  with 4 MPa  $\text{CO}_2$  (a), and 0.05 MPa 10% CO/He (b). Other pretreatment conditions:  $\text{RuCl}_2(\text{PPh}_3)_3$  80 mg, 4 MPa  $\text{H}_2$ , methanol 2.5 mL, 150 °C, 6 h.

**Table 1** Results for the hydrogenation of LA to GVL with different Ru complexes

Entry	Catalyst	Pretreatment conditions <sup>a</sup>	Conversion (%)	Selectivity to GVL (%)	TON
1	$\text{RuCl}_2(\text{PPh}_3)_3$	$\text{CO}_2$ 4 MPa, $\text{H}_2$ 4 MPa	77	98	770
2	$\text{RuCl}_2(\text{PPh}_3)_3$	10% CO/He 0.05 MPa, $\text{H}_2$ 4 MPa	50	82	500

Reaction conditions: LA 20 mmol, catalyst 0.02 mmol,  $\text{H}_2$  4 MPa, 150 °C, 6 h. <sup>a</sup> the catalyst pretreatment under the conditions:  $\text{RuCl}_2(\text{PPh}_3)_3$  80 mg, methanol 2.5 mL, 150 °C, 6 h.