Electronic Supporting Information

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- Fig.S12. 31P NMR (CDCl3) of post-reaction mixture after the hydroformylation of catalyzed by Rh(acac)(CO)$_2$/PPh$_2$(NC$_4$H$_4$)$_2$ with addition, little amount of water to NMR sample.

![Fig. S1](image)

**Fig. S1.** The effect of temperature on hydroformylation of 1-butene
**Fig. S2.** Effect of water on hydroformylation of 1-butene in toluene

**Fig. S3.** Effect of time on hydroformylation of 1-butene in toluene
**Fig. S4.** Effect of [L]/[Rh] ratio on hydroformylation of 1-butene

**Fig. S5.** The effect of water on the hydroformylation of 1-butene catalyzed by Rh(acac)(CO)$_2$ modified with different ligands at 80 °C and 10 bar of syngas using autoclave 50 mL.

**1H, 13C NMR data for post-reaction mixture:**

**1-butene:** $^1$H NMR (500 Hz, CDCl$_3$) $\delta(=\text{CH})$ 5.78 ppm (ddddd, 6.17, 6.81, 10.3, 17.1 Hz); $\delta(=\text{CH}_2)$ 4.9 ppm (dd, 17.2, 1.87Hz); $\delta(=\text{CH}_2)$ 4.82 ppm (dd, 10.2, 2Hz); $\delta(\text{CH}_3)$ 1.2 ppm (d, 7.24 Hz); $^{13}$C NMR (500 Hz, CDCl$_3$): 140.43, 113.04, 26.63, 17.72.
2-butene: $^1$H NMR (500 Hz, CDCl$_3$) $\delta$(=CH$_2$) 5.32 ppm (ddd, 1.4, 4.8, 3.36Hz); $\delta$(=CH$_2$) 5.36 ppm (ddd, 3.1, 7.9, 0.91Hz)

Pentanal: $^1$H NMR (500 Hz, CDCl$_3$): $\delta$(CHO) 9.62 ppm (t, 1.86 Hz); $\delta$(CH$_2$) 2.29 ppm (ddd, 1.85, 7.38, 14.75 Hz); $\delta$(CH$_2$) 2.29 ppm (ddd, 1.85 Hz); $\delta$(CH$_2$) 1.5 ppm (ddd, 7.51Hz); $\delta$(CH$_2$) 1.26 ppm (dddd, 7.57Hz); $\delta$(CH$_3$) 0.83 ppm (t, 7.46 Hz); $^{13}$C NMR (500 Hz, CDCl$_3$): 202.5, 43.53, 24.1, 22.24, 13.68.

2-methylbutanal: $^1$H NMR (500 Hz, CDCl$_3$): $\delta$(CHO) 9.51 ppm (d, 1.88 Hz); $^{13}$C NMR (500 Hz, CDCl$_3$): 204.98, 47.67, 23.46, 12.71, 11.21.

Table S1 the effect of pressure of syngas on n/iso ratio of hydroformylation of 1-butene catalyzed by Rh(acac)(CO)$_2$/PPh(NC$_4$H$_4$)$_2$

<table>
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<th>Entry</th>
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<th>Aldehydes, mol</th>
<th>n/iso (Fid-GC)</th>
<th>n/iso(NMR)</th>
<th>TOF</th>
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</tr>
</tbody>
</table>

Reaction condition: [Rh] = 1.5 x 10$^{-5}$mol, [L]/[Rh] = 13, P$_1$-Butene = 2 bar, P$_{H2:CO}$ = 1:1, toluene (0.5 ml), cyclohexane (0.25 mL), t = 2h, T = 80°C.

Fig.S6. The effect of pressure on hydroformylation of 1-butene catalyzed by Rh(acac)(CO)$_2$/PPh(NC$_4$H$_4$)$_2$
Fig. S7. $^1$H NMR (CDCl$_3$) of post-reaction mixture after the hydroformylation of 1-butene at 8 bar, 80 °C.
**Fig.S8.** $^1$H NMR (a) and $^{13}$C NMR (b) spectra (CDCl$_3$) of post-reaction mixture after the hydroformylation of 1-butene at 6 bar, $80 \, ^\circ$C.

**Fig.S9.** $^1$H NMR (CDCl$_3$) of post-reaction mixture after the hydroformylation of 1-butene at 4 bar, $80 \, ^\circ$C.
Fig. S10. $^{31}$P NMR (CDCl$_3$) of post-reaction mixture after the hydroformylation of catalyzed by Rh(acac)(CO)$_2$/ P(NC$_4$H$_4$)$_3$, without(a) and with(b) addition little amount of water to NMR sample.
Fig. S11. $^{31}$P NMR (CDCl3) of post-reaction mixture after the hydroformylation of catalyzed by Rh(acac)(CO)$_2$/PPh(NC$_4$H$_4$)$_2$, without (a) and with (b) addition little amount of water to NMR sample.
Fig.S12. $^{31}$P NMR (CDCl3) of post-reaction mixture after the hydroformylation of catalyzed by Rh(acac)(CO)$_2$/PPh$_2$(NC$_4$H$_4$) with addition, little amount of water to NMR sample.