

Electronic Supporting Information

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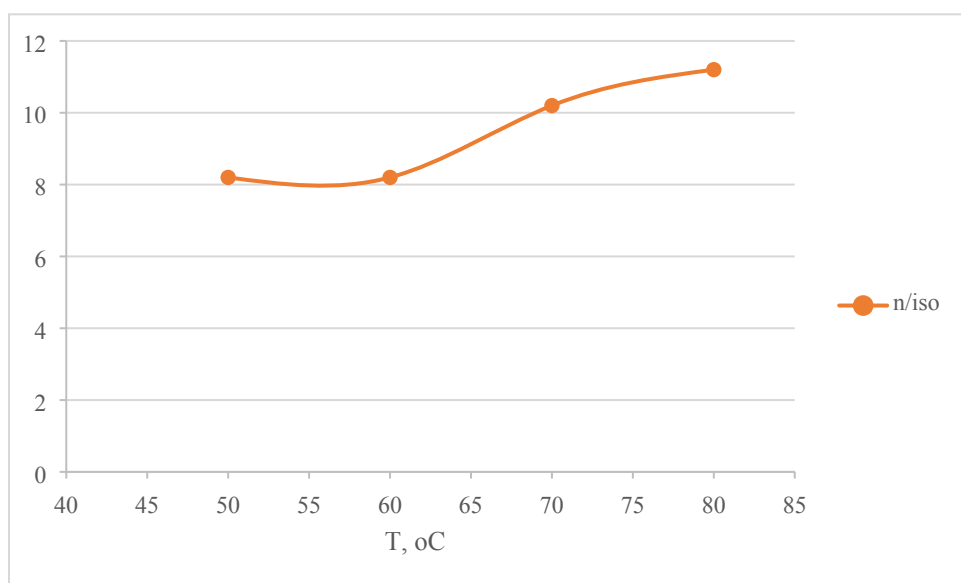


Fig. S1. The effect of temperature on hydroformylation of 1-butene

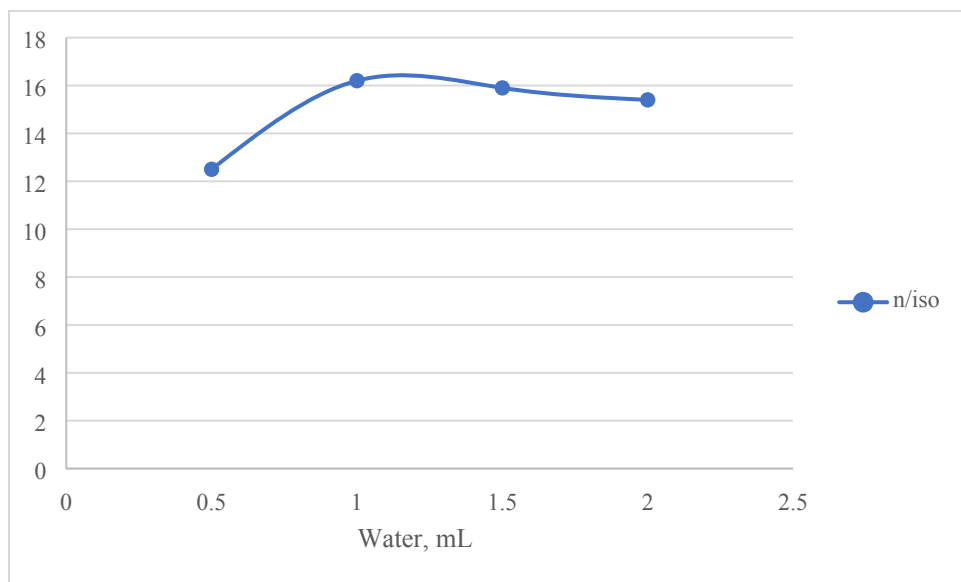


Fig. S2. Effect of water on hydroformylation of 1-butene in toluene

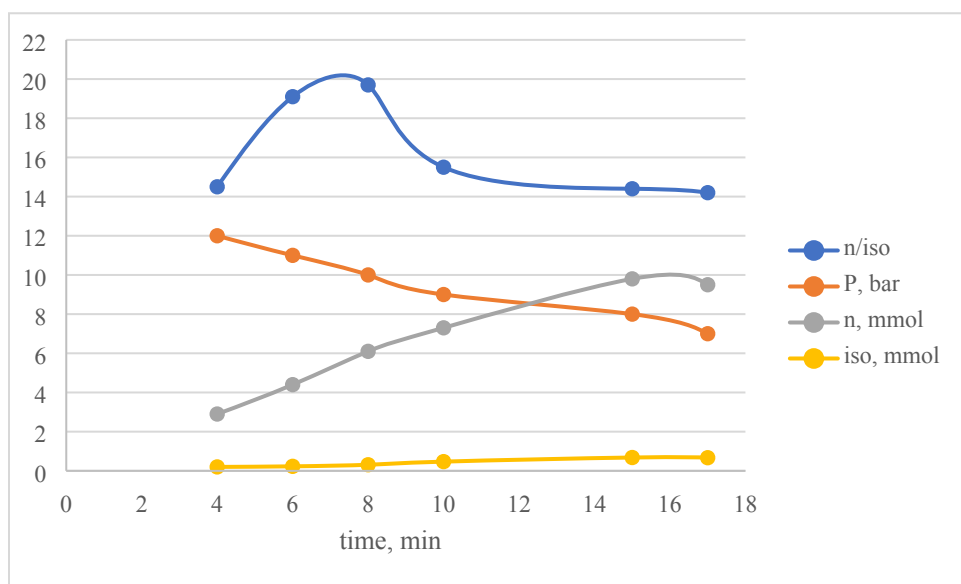


Fig. S3. Effect of time on hydroformylation of 1-butene in toluene

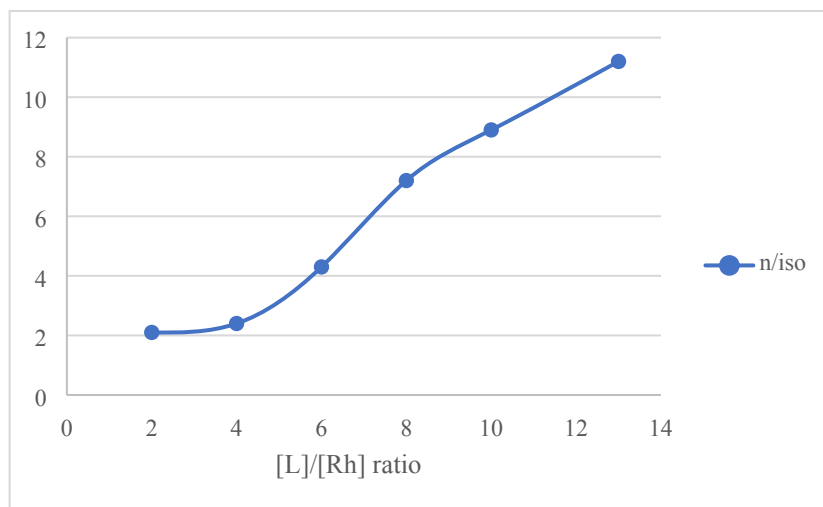


Fig. S4. Effect of [L]/[Rh] ratio on hydroformylation of 1-butene

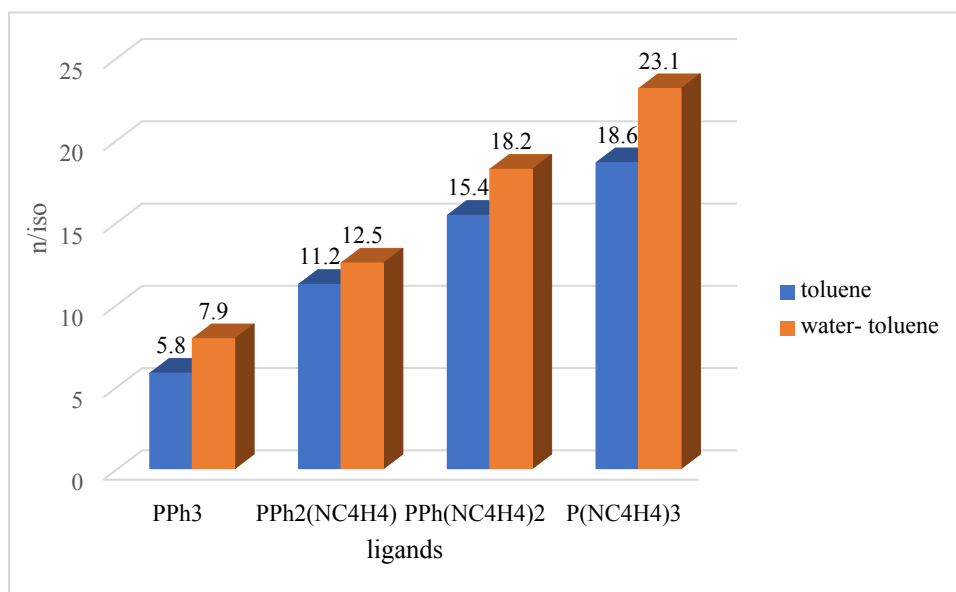


Fig.S5. The effect of water on the hydroformylation of 1-butene catalyzed by Rh(acac)(CO)₂ modified with different ligands at 80 °C and 10 bar of syngas using autoclave 50 mL.

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

1-butene: ¹H NMR (500 Hz, CDCl₃) δ(=CH) 5.78 ppm (dddd, 6.17, 6.81, 10.3, 17.1 Hz); δ(=CH₂) 4.9 ppm (dd, 17.2, 1.87Hz); δ(=CH₂) 4.82 ppm (dd, 10.2, 2Hz); δ(CH₃) 1.2 ppm (d, 7.24 Hz); ¹³C NMR (500 Hz, CDCl₃): 140.43, 113.04, 26.63, 17.72.

2-butene: ^1H NMR (500 Hz, CDCl_3) $\delta(=\text{CH}_2)$ 5.32 ppm (ddd, 1.4, 4.8, 3.36Hz); $\delta(=\text{CH}_2)$ 5.36 ppm (ddd, 3.1, 7.9, 0.91Hz)

Pentanal: ^1H NMR (500 Hz, CDCl_3): $\delta(\text{CHO})$ 9.62 ppm (t, 1.86 Hz); $\delta(\text{CH}_2)$ 2.29 ppm (ddd, 1.85, 7.38, 14.75 Hz); $\delta(\text{CH}_2)$ 2.29 ppm (ddd, 1.85 Hz); $\delta(\text{CH}_2)$ 1.5 ppm (dddd, 7.51Hz); $\delta(\text{CH}_2)$ 1.26 ppm (dddd, 7.57Hz); $\delta(\text{CH}_3)$ 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: ^1H NMR (500 Hz, CDCl_3): $\delta(\text{CHO})$ 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 $\text{Rh}(\text{acac})(\text{CO})_2/\text{PPh}(\text{NC}_4\text{H}_4)_2$

Entry	P, bar	Aldehydes, mol	n/iso (Fid-GC)	n/iso(NMR)	TOF
1	8	0.018	22.5	27.5	600
2	6	0.017	24.2	34.4	566.7
3	4	0.007	20	38.8	233.3

Reaction condition: $[\text{Rh}] = 1.5 \times 10^{-5} \text{ mol}$, $[\text{L}]/[\text{Rh}] = 13$, $P_{1\text{-Butene}} = 2 \text{ bar}$, $P_{(\text{H}_2:\text{CO} = 1:1)}$, toluene (0.5 ml), cyclohexane (0.25 mL), $t = 2 \text{ h}$, $T = 80^\circ\text{C}$.

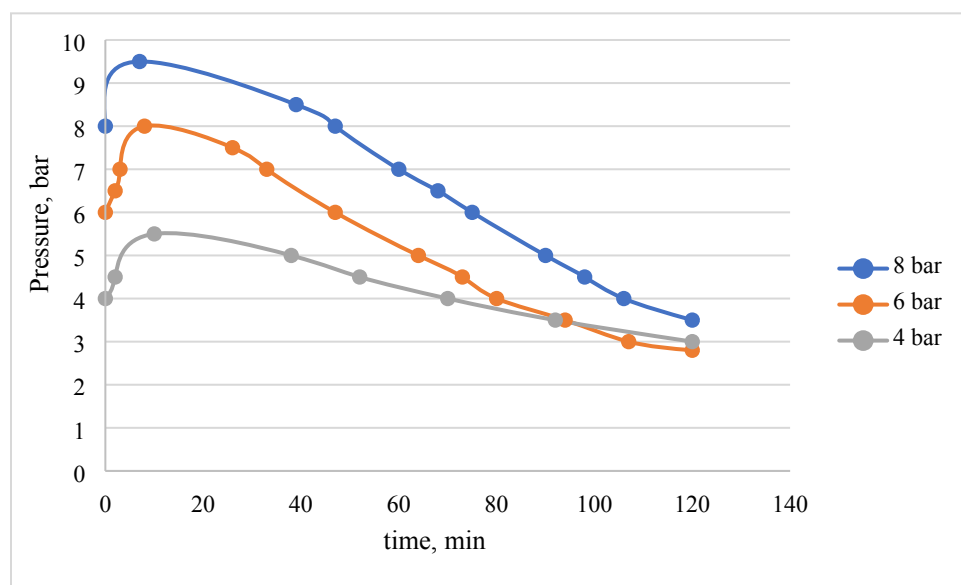
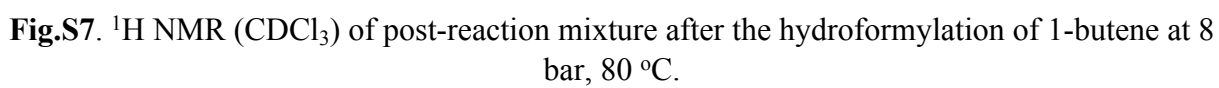


Fig.S6. The effect of pressure on hydroformylation of 1-butene catalyzed by $\text{Rh}(\text{acac})(\text{CO})_2/\text{PPh}(\text{NC}_4\text{H}_4)_2$



1H NMR spectrum of 1,2-dichloroethane in CDCl₃. The spectrum shows a triplet at ~1.2 ppm (3H), a quartet at ~2.3 ppm (2H), and a multiplet at ~7.2 ppm (5H). Integration curves are shown above the peaks.

b

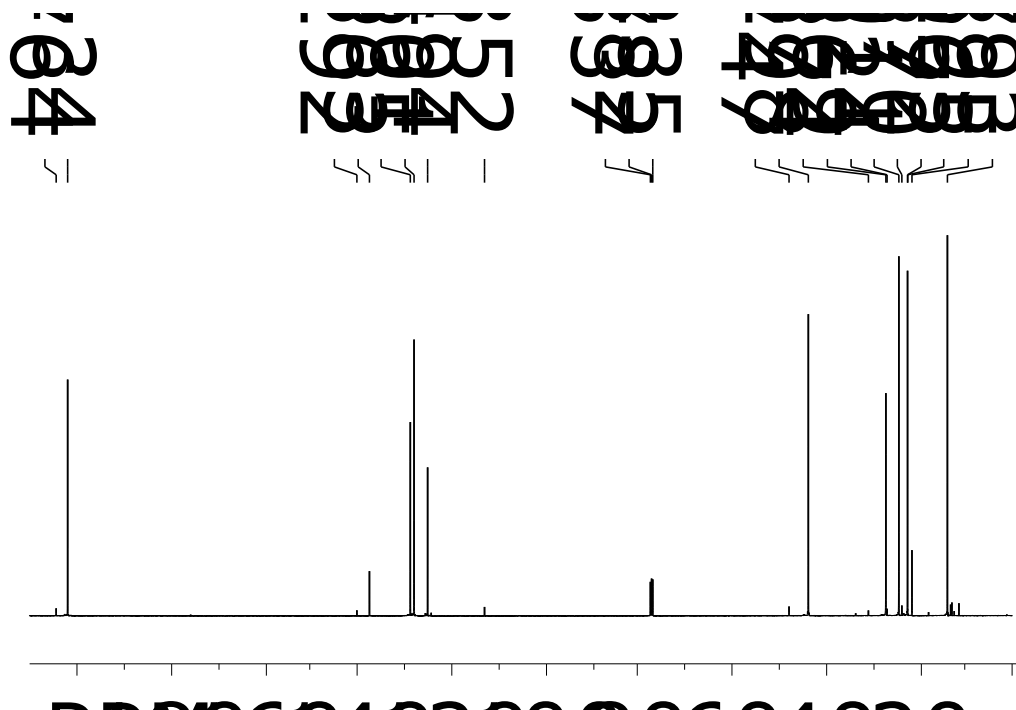


Fig.S8. ^1H NMR (a) and ^{13}C NMR (b) spectra (CDCl_3) of post-reaction mixture after the hydroformylation of 1-butene at 6 bar, 80 C.

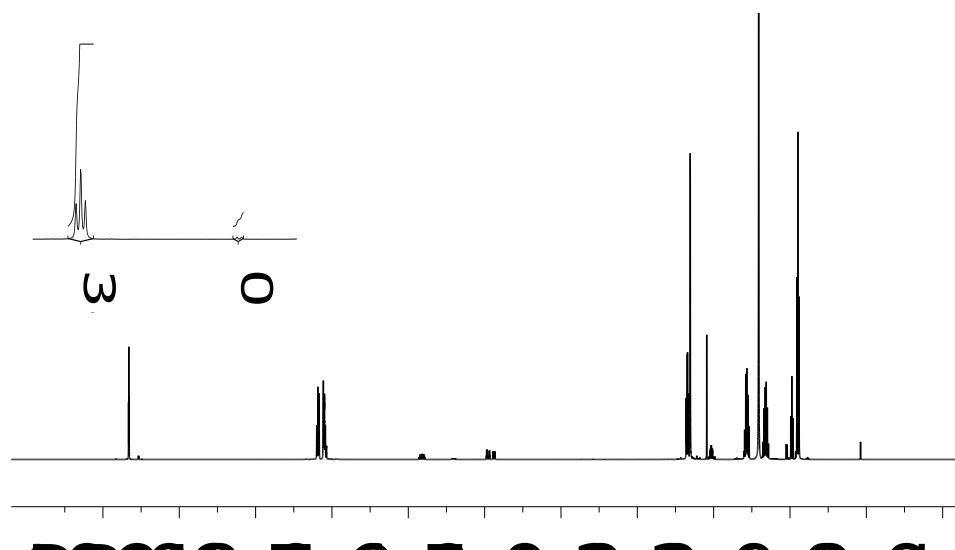
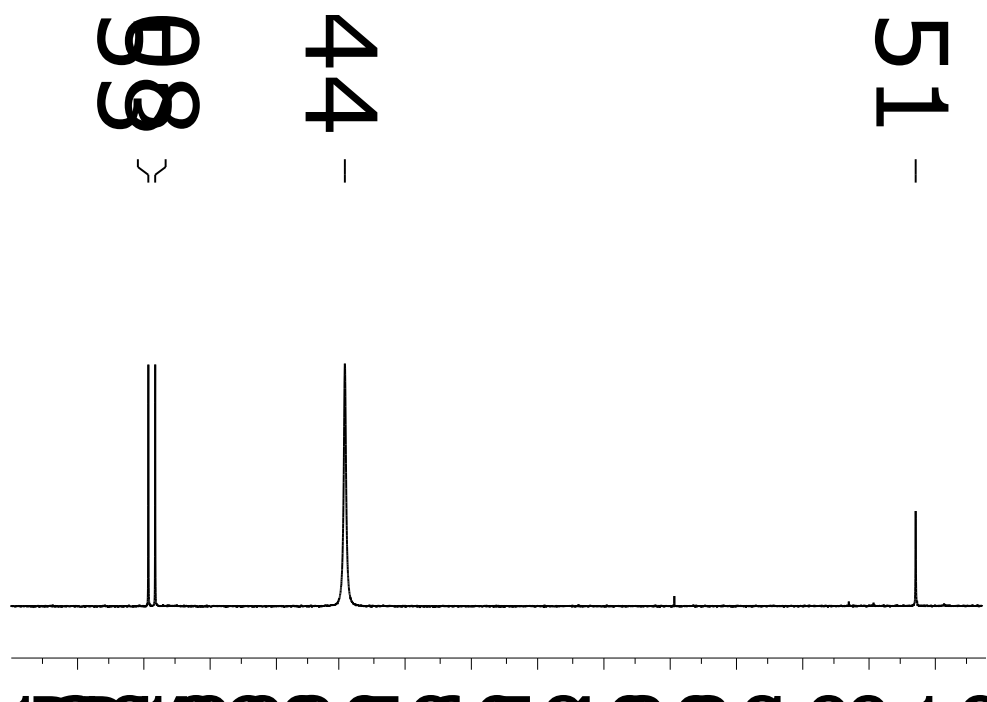


Fig.S9. ^1H NMR (CDCl_3) of post-reaction mixture after the hydroformylation of 1-butene at 4 bar, 80 °C.

a



b

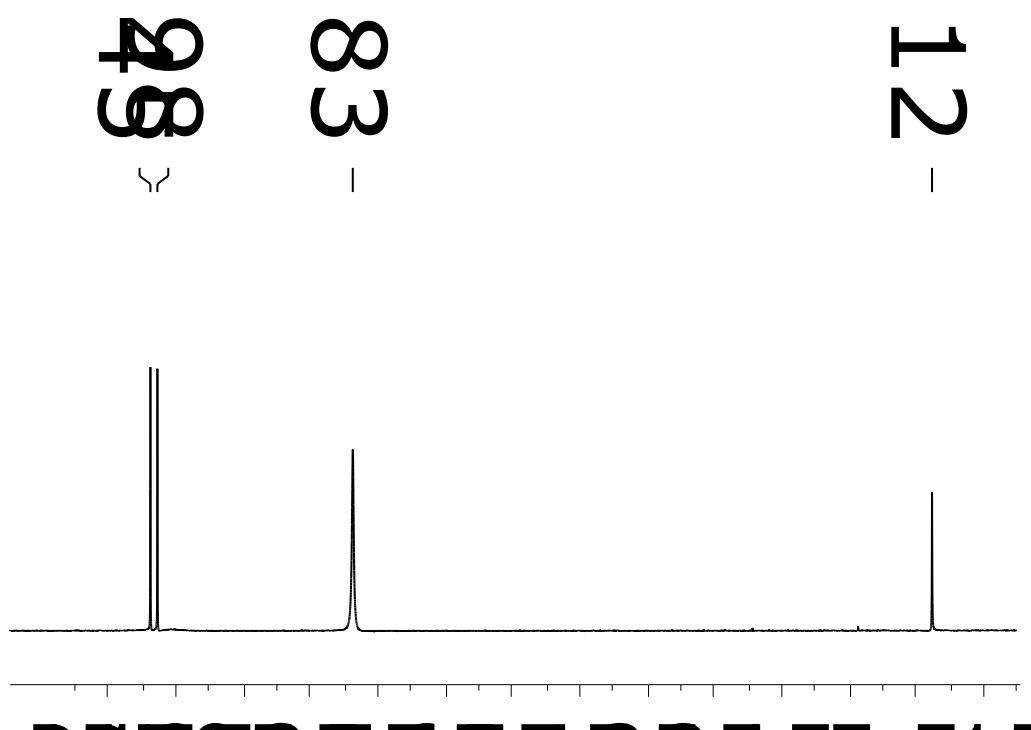
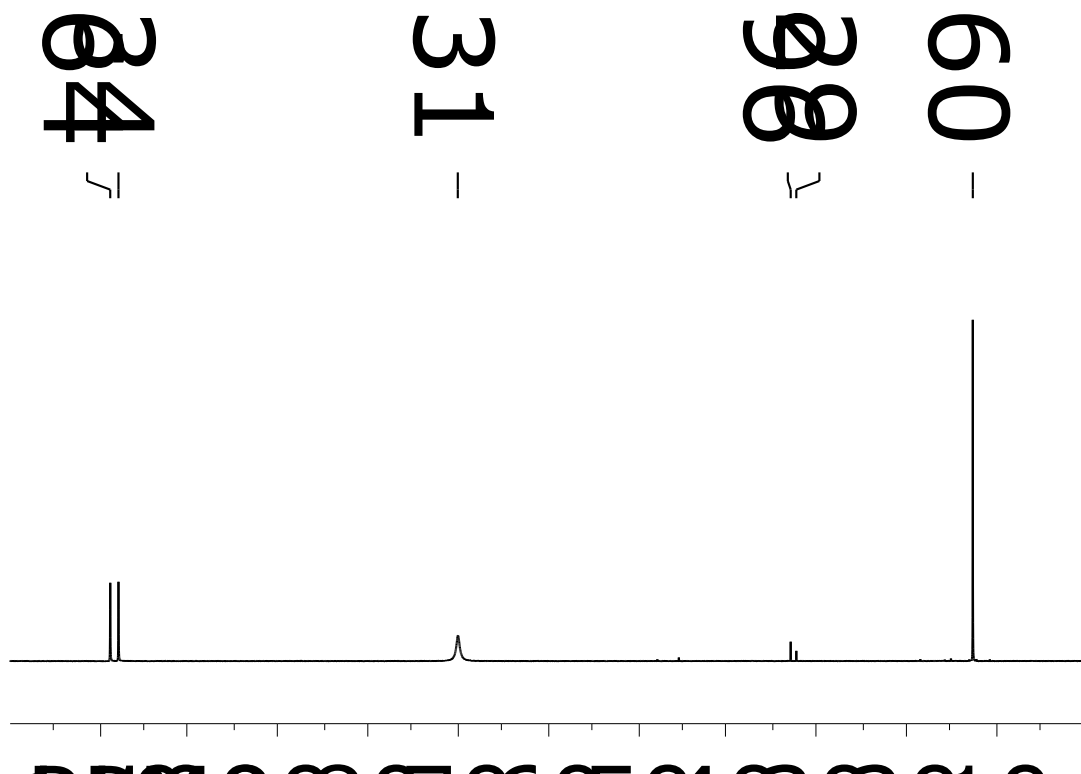


Fig.S10. ^{31}P NMR (CDCl_3) of post-reaction mixture after the hydroformylation of catalyzed by $\text{Rh}(\text{acac})(\text{CO})_2/ \text{P}(\text{NC}_4\text{H}_4)_3$, without(a) and with(b) addition little amount of water to NMR sample.

a



b

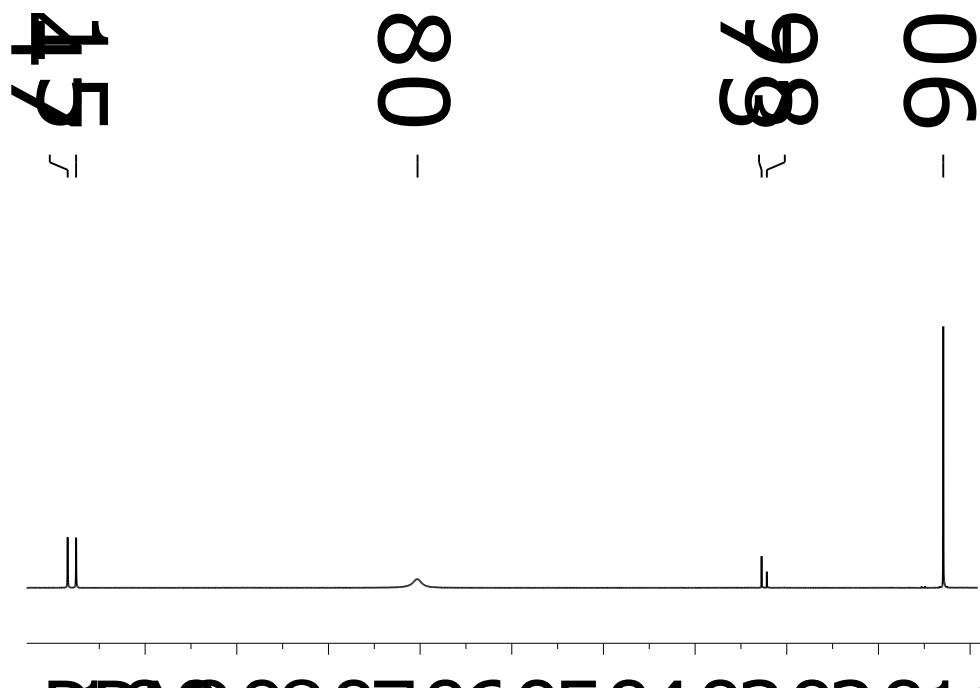


Fig.S11. ^{31}P NMR (CDCl_3) of post-reaction mixture after the hydroformylation of catalyzed by $\text{Rh}(\text{acac})(\text{CO})_2/\text{PPh}(\text{NC}_4\text{H}_4)_2$, without(a) and with(b) addition little amount of water to NMR sample.

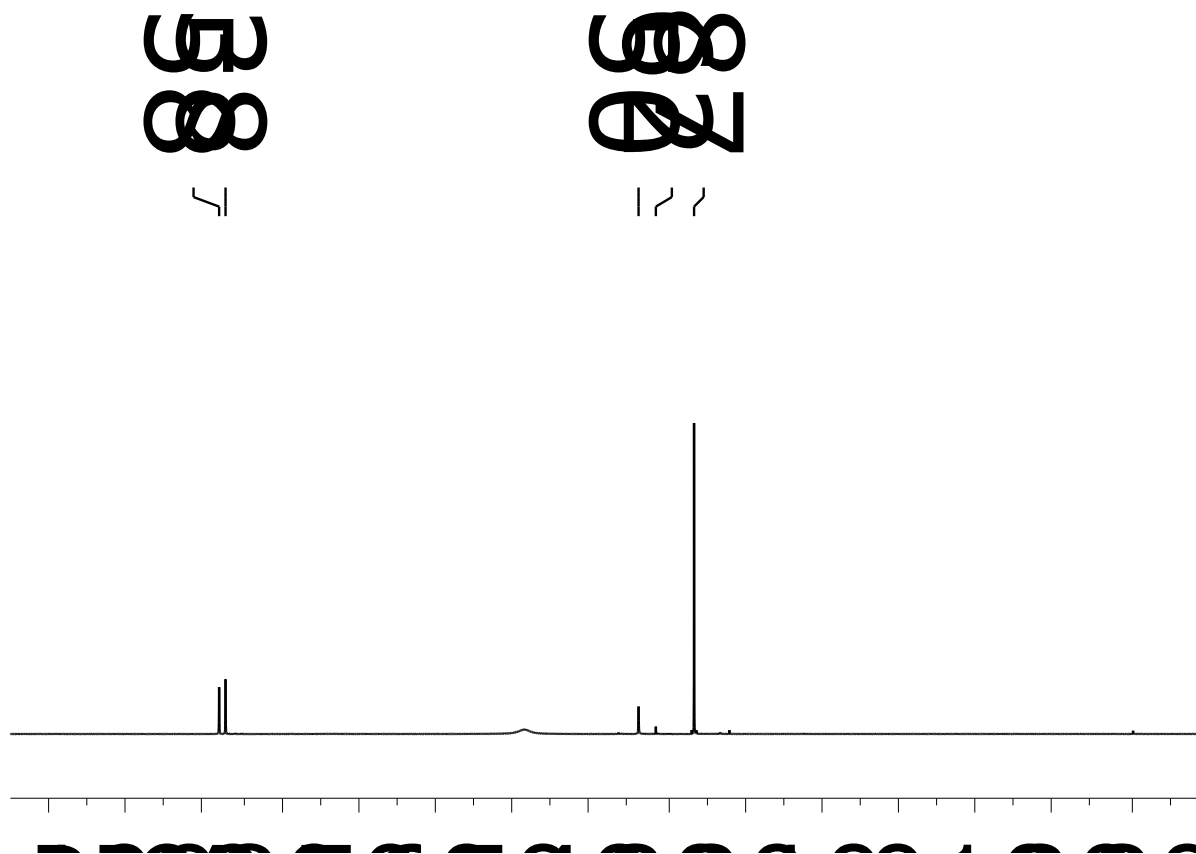


Fig.S12. ^{31}P NMR (CDCl_3) of post-reaction mixture after the hydroformylation of catalyzed by $\text{Rh}(\text{acac})(\text{CO})_2/\text{PPh}_2(\text{NC}_4\text{H}_4)$ with addition, little amount of water to NMR sample.