Electronic Supplementary Material (ESI) for Dalton Transactions.

Enhancing stability via confining Rh-P species in ZIF-8 for hydroformylation of 1-octene

Xiaorui Yan†, Lele Chen†, Haisheng Wei*, Tiantian Liu, Kairui Li, Jing Li*

College of Chemistry and Chemical Engineering, Yantai University, Yantai 264005, Shandong, China

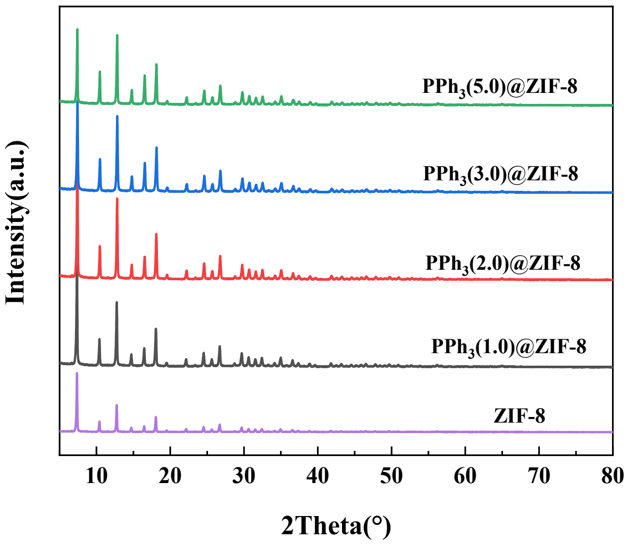

Figure S1. XRD characterizations of the samples with different content of PPh_3 ligand.

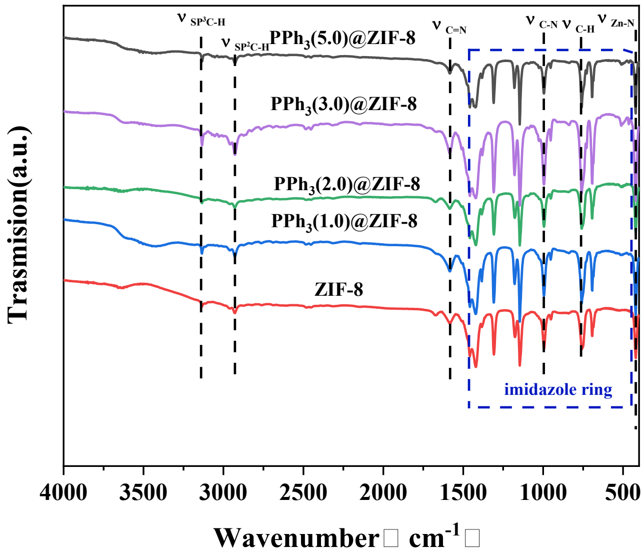

Figure S2. FT-IR patterns for different content of phosphine ligand in PPh_3(x)@ZIF-8 samples

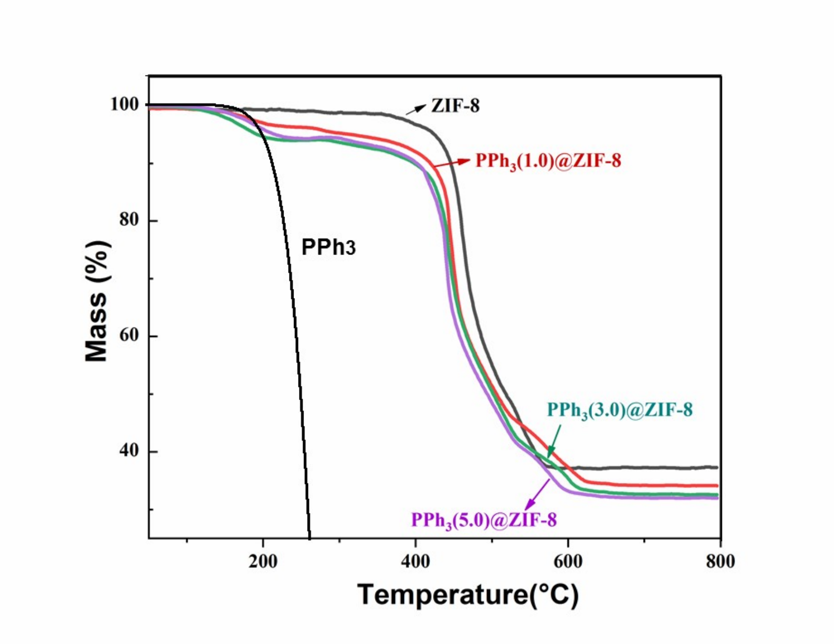

Figure S3. TG curves of different PPh_3(x)@ZIF-8 samples, pure ZIF-8 and PPh_3 ligand.

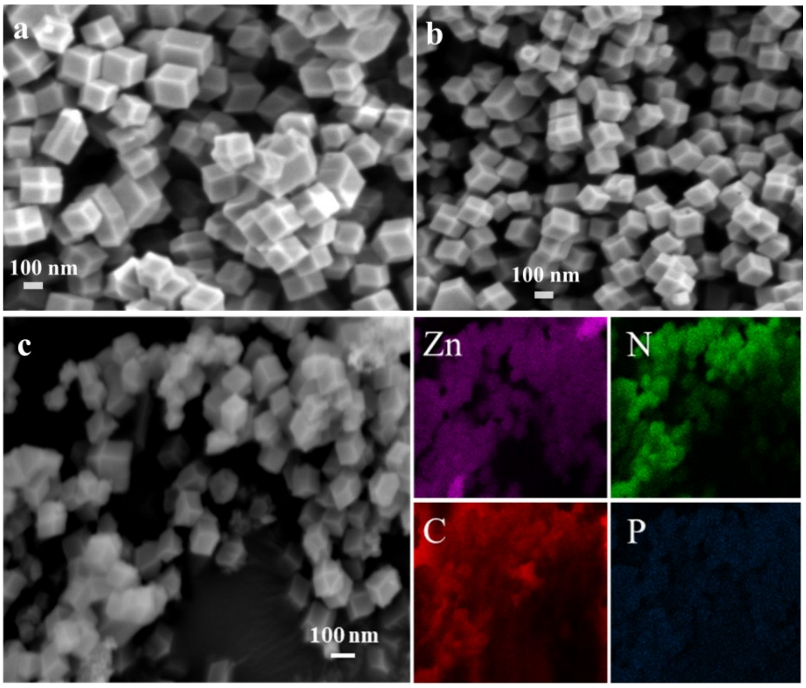

Figure S4. SEM images (a,b) and EDS mapping of PPh_3(3.0)@ZIF-8 sample (c).

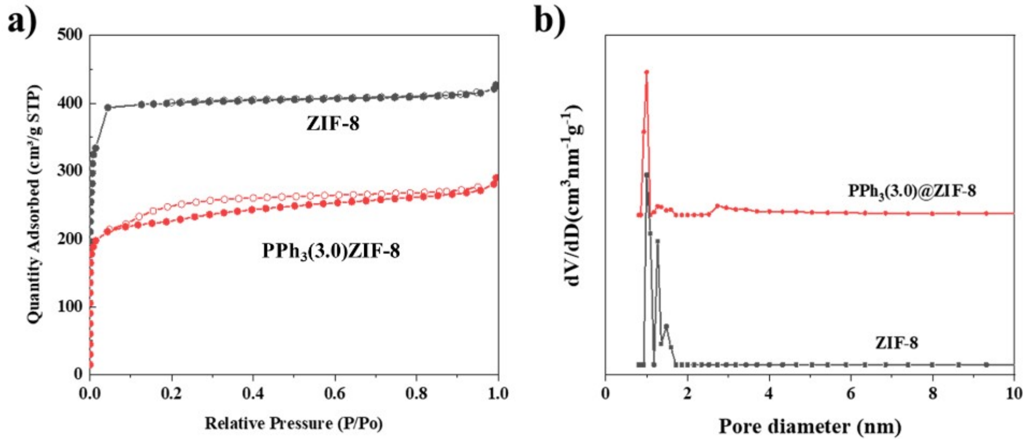

Figure S5. Nitrogen physisorption analysis of PPh_3(3.0)@ZIF-8 and pure ZIF-8 samples.

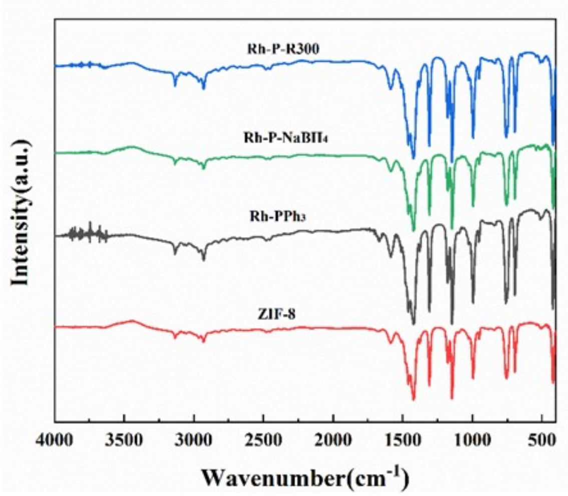

Figure S6. FT-IR results of Rh-PPh_3 samples by different reduction procedure.

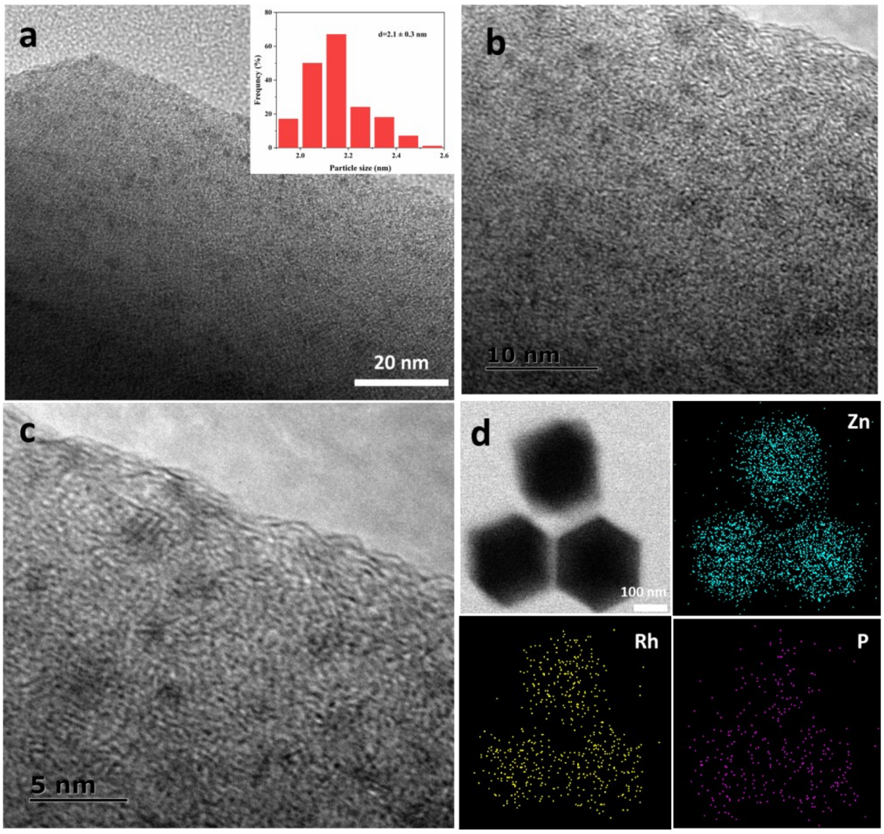

Figure S7. HRTEM (a,b,c) and EDS mapping (d) analyses of Rh-P-$NaBH_4$ catalyst. The inner picture is the size distribution of Rh particles.

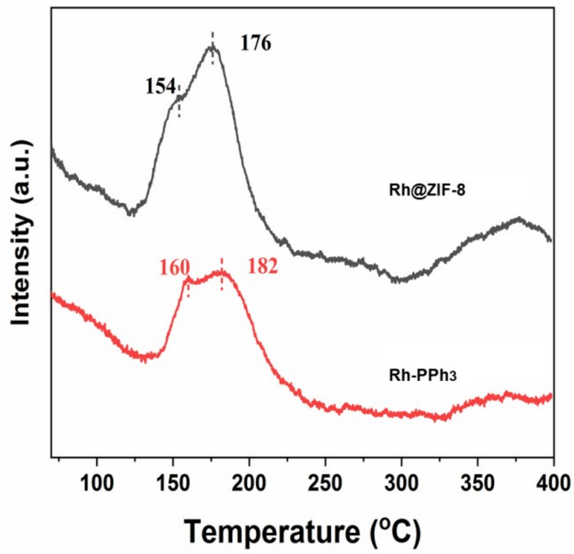

Figure S8. H_2-TPR results of Rh@ZIF-8 and Rh-PPh_3 catalysts.

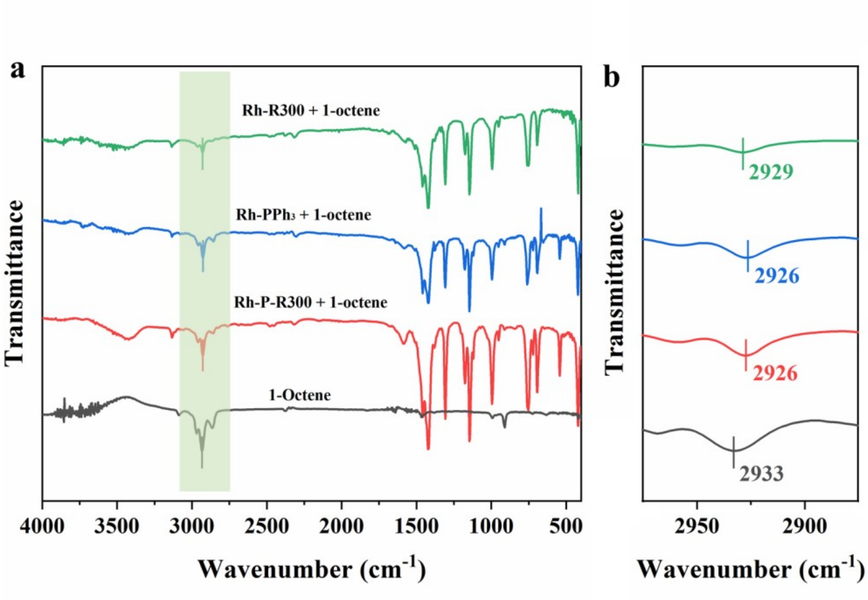

Figure S9 FT-IR analysis of 1-octene adsorption on different catalysts (a) and enlargement of the shadow part (b).

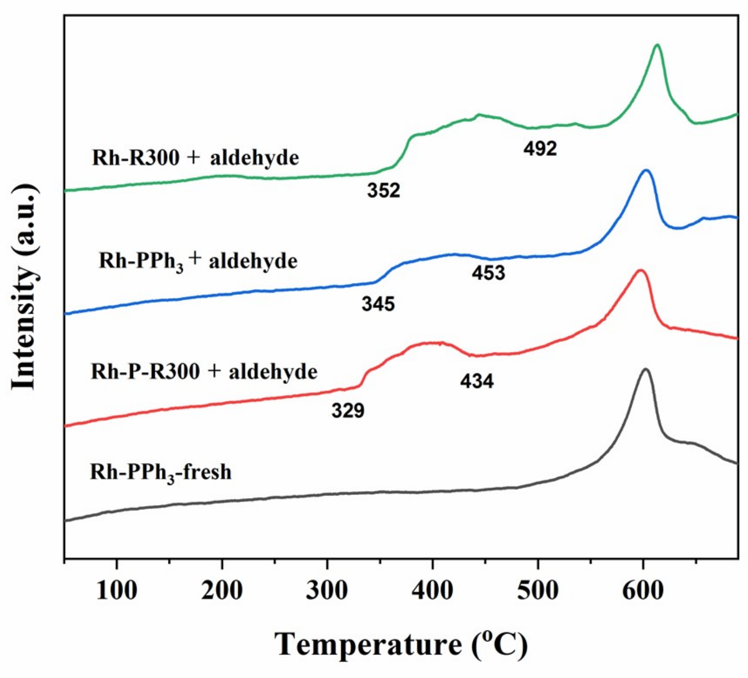

Figure S10 TPD analysis of n-nonaldehyde desorption on different catalysts. The desorption temperature at around 600 °C is due to the decomposition of support, which is confirmed by the TPD results of Rh-PPh_3 catalyst without addition of n-nonaldehyde.

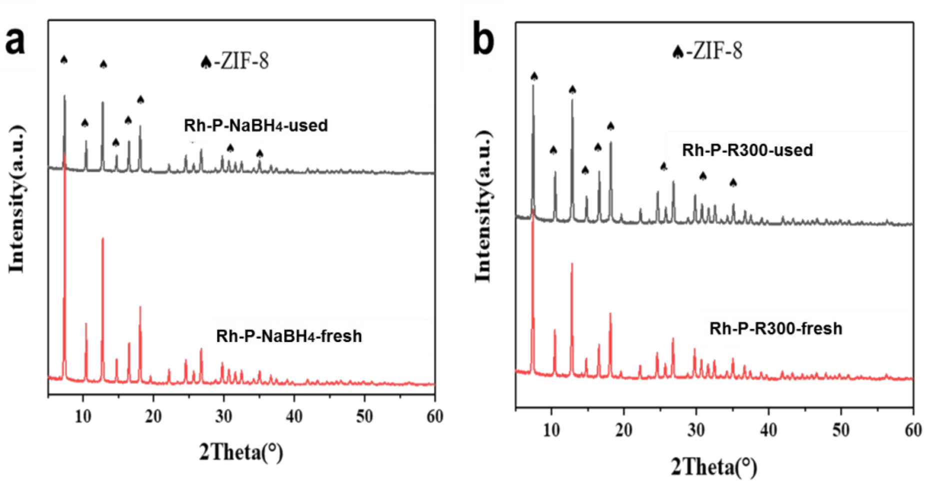

Figure S11. XRD results of Rh-P-$NaBH_4$ (a) and Rh-P-R300 (b) catalysts before and after reaction.

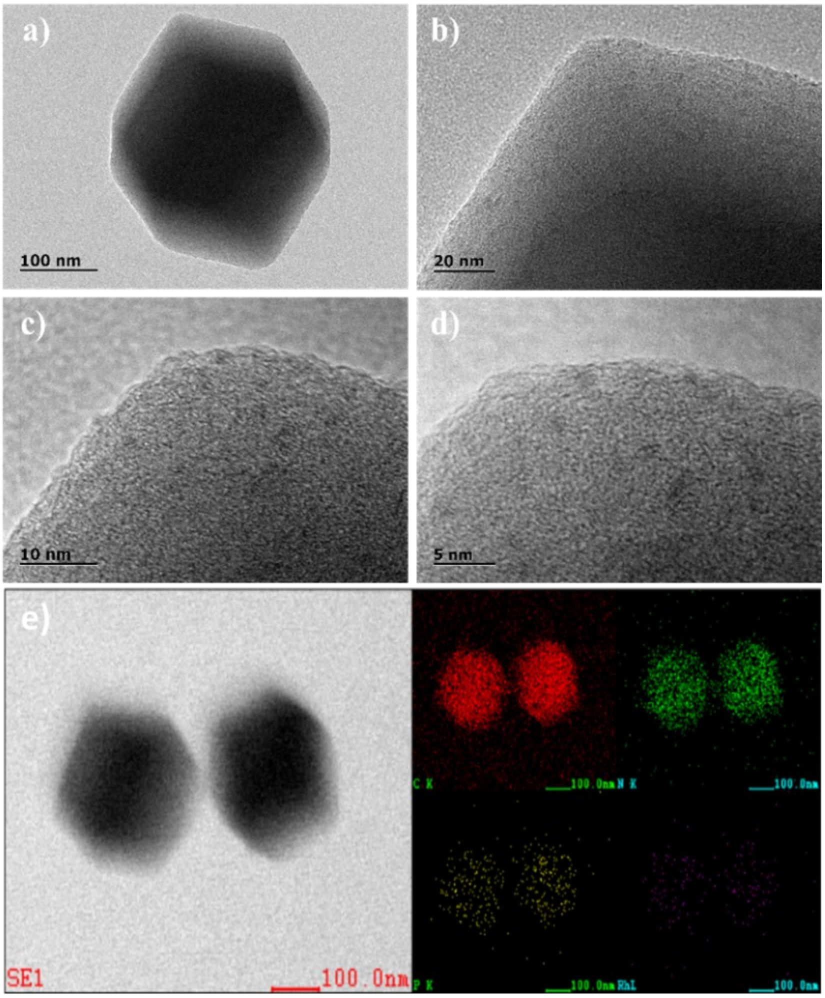

Figure S12. HRTEM (a-d) and EDS mapping (e) analyses of Rh-P-NaBH$_4$ catalyst after reaction.

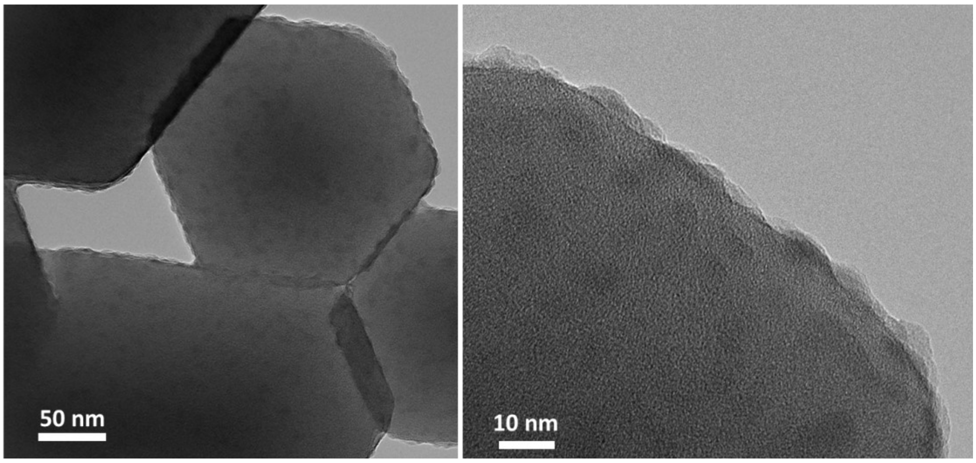

Figure S13. HRTEM images of Rh-P-R300 catalyst after reaction.

Table S1. Nitrogen physisorption analysis for different samples.

Sample	BET surface area (m^2/g)	Micropore volume (cm^3 /g)	Pore diameter (nm)
ZIF-8	1644.0	0.64	2.5
PPh_3(3.0)@ZIF-8	1304.0	0.63	8.7
Rh-PPh_3	1206.0	0.62	9.9
Rh-P-$NaBH_4$	1188.4	0.69	5.9
Rh-P-R300	905.1	0.47	8.5

Table S2 Catalytic result with Wilkinson catalyst in the hydroformylation of 1-octene.

Catalyst	Conv. (%)	Sel. (%)		Yield[a] (%)	L/B[b] ratio
		Aldehydes	Iso-olefins		
$RhCl(PPh_3)_3$	78.3	70.2	29.8	55.0	1.7
Rh-P-R300	99.0	56.5	43.5	56.0	0.7

Reaction condition: 1-octene/Rh=130, 1.25 mmol 1-octene, 0.5 mmol 1-hexanol as internal standard, 5 mL toluene, 90 ^{o}C, 2 MPa, 2 h. a: refer to the yield of aldehyde. b: L/B ratio refer to the ratio of linear to branched aldehyde in the products.

Table S3 The catalytic results of P-Rh-R300 catalysts with different PPh_3 content

PPh_3 content (g)	Conv. (%)	Sel. (%)		Yield[a] (%)	L/B[b] ratio
		Aldehydes	Iso-olefins		
1.0	99.1	29.4	70.6	29.1	0.9
2.0	99.5	35.8	64.2	35.6	0.9
3.0	99.0	56.5	43.5	56.0	0.7
5.0	99.3	53.7	46.3	53.3	0.8

Reaction condition: 1-octene/Rh=130, 1.25 mmol 1-octene, 0.5 mmol 1-hexanol as internal standard, 5 mL toluene, 90 ^oC, 2 MPa, 2 h. a: refer to the yield of aldehyde. b: L/B ratio refer to the ratio of linear to branched aldehyde in the products.

Table S4 The effect of the value of P/Rh in the homogeneous hydroformylation.

PPh_3 ligand	mole ratio of P/Rh	Conv. (%)	Sel. (%)		Yield[a] (%)	L/B[b] ratio
			Aldehydes	Iso-olefins		
no	-	73.9	27.9	72.1	20.6	0.6
0.005g	19	87.8	75.6	24.4	66.4	1.7
0.01g	38	97.1	93.8	6.2	91.1	2.7

Reaction condition: 0.1 mg Rh, 1.25 mmol 1-octene, 0.5 mmol 1-hexanol as internal standard, 5 mL toluene, 90 ^{o}C, 2 MPa, 2 h. a: refer to the yield of aldehyde. b: L/B ratio refer to the ratio of linear to branched aldehyde in the products.

Table S5 The ICP results of Rh-P-$NaBH_4$ and Rh-P-R300 catalysts used for five cycles.

Catalyst	Rh content / wt%		the leaching of metal Rh /wt%
	fresh	used	
Rh-P-$NaBH_4$	1.02	0.82	19.6
Rh-P-R300	1.08	1.06	1.8