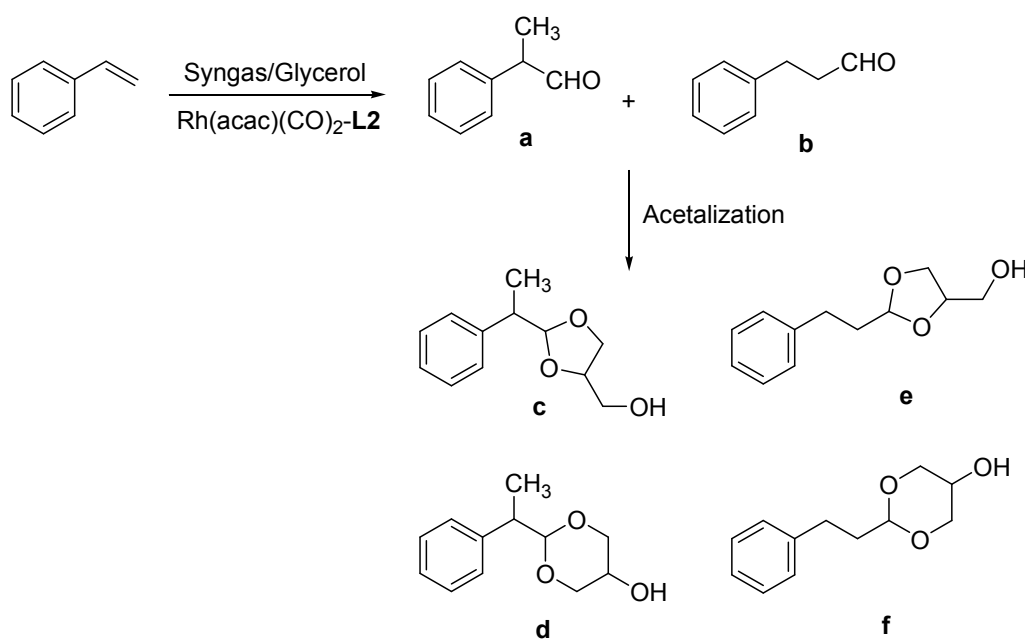
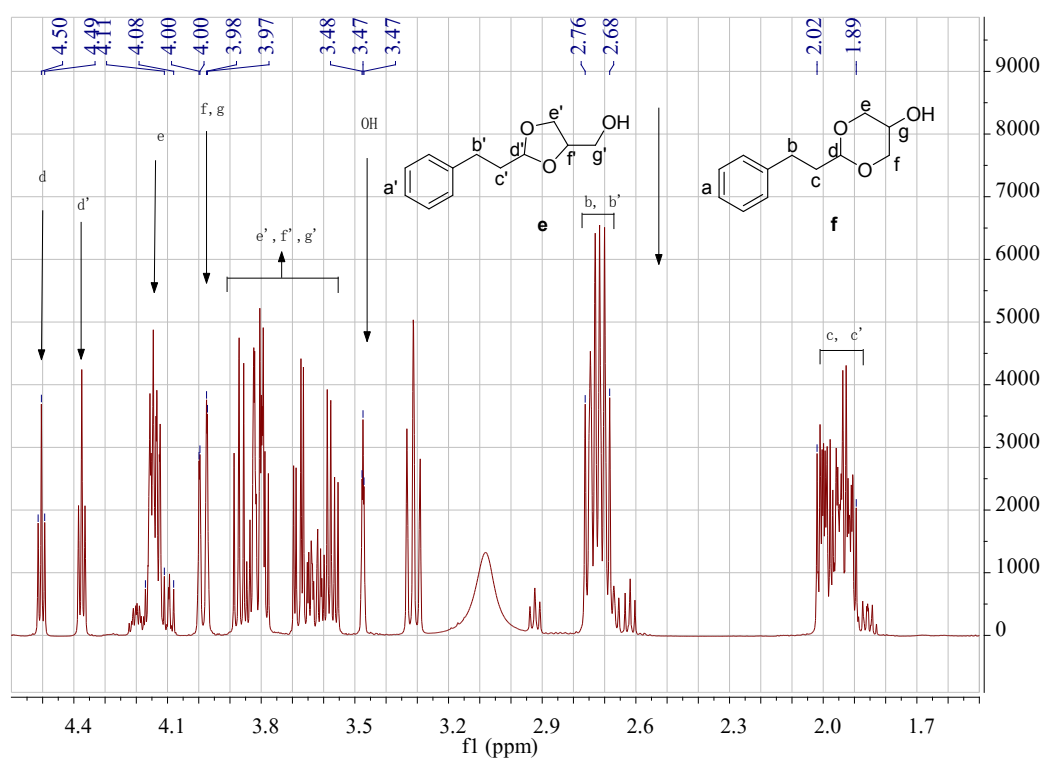
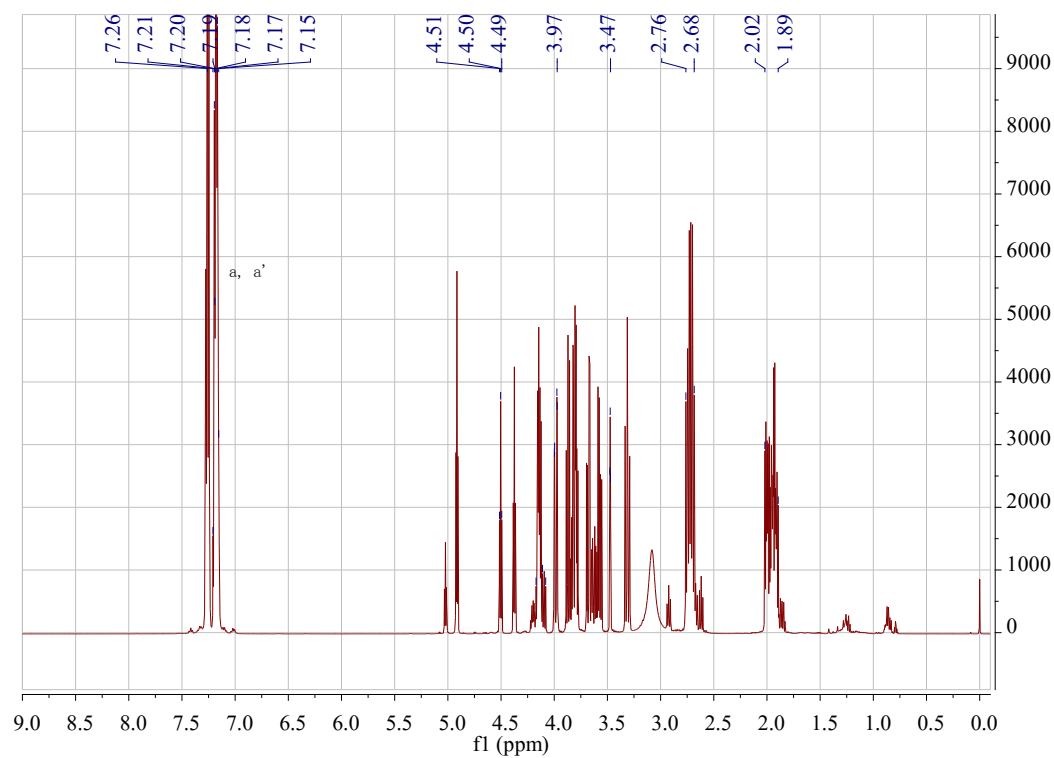


Supplementary Information

The hydroformylation-acetalization of styrene with glycerol was performed under the appointed conditions as indicated in S. Scheme 1 for two times. The combined mixture was purified by column chromatography on silica gel with the eluent of petroleum ether/ ethyl acetate (10:1~4:1). Since besides of the left glycerol, the oxo-products is composed of (linear and branched) phenylpropanals (**a** and **b**) and the corresponding five-member-/six-member-ring acetals (**c-f**) with very similar polarity, it is very difficult to isolate every product. With our best effort, only the mixed acetalized products of **e** ((2-phenethyl-1,3-dioxolan-4-yl)methanol) and **f** (2-phenethyl-1,3-dioxan-5-ol) was obtained in the low yield. ^1H NMR (δ , ppm, CDCl_3) for **f**: 7.19-7.14 (5H, m), 4.51-4.49 (1H, t), 4.17-4.08 (2H, m), 4.00-3.97 (3H, m), 3.48-3.47 (1H, t), 2.76-2.68 (2H, m), 2.02-1.89 (2H, m).

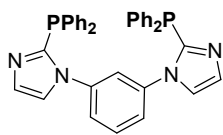
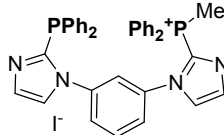
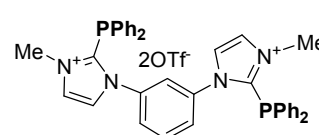
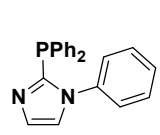


S. Scheme 1 The hydroformylation-acetalization of styrene with glycerol [Reaction conditions: $\text{Rh}(\text{acac})(\text{CO})_2$ 0.01 mmol, olefin 20 mmol (S/C=2000), **L2** 0.06 mmol (P/Rh=6:1), CO/H_2 (1:1) 4.0 MPa, temperature 120 °C, glycerol 5 mL, reaction time 2 h.]



The investigation on the effect of I^- (TABI, tetrabutylammonium iodide) on the performance of **L1**, **L3**, and **L4** was supplemented in S. Table 1. It was shown that the involved I^- had no effect on the reaction results.

S. Table 1 The effect of I⁻ on homogeneous hydroformylation-acetalization with the presence of different ligands ^a

<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p>L1</p> </div> <div style="text-align: center;">  <p>L2</p> </div> <div style="text-align: center;">  <p>L3</p> </div> <div style="text-align: center;">  <p>L4</p> </div> </div>								
Entry	Ligand	TABI (mmol)	Conv. (%) ^b	S _{oxo} (%) ^{b,c}	P _{acetals} (%) ^{b,c}	S _{iso-octenes} (%) ^{b,c}	L/B ^d	TON _{oxo} ^e
1	L2	--	91	94	62	6	1.9	1710
2	L1	0.015	65	88	2	12	2.1	1140
3	L3	0.015	86	90	27	10	2.4	1550
4	L4	0.015	76	88	2	12	1.9	1350

^a Rh(acac)(CO)₂ 0.0025 mmol, 1-octene 5.0 mmol (S/C=2000, Rh 0.05 mol%), P/Rh=6:1 molar ratio (**L1** or **L3** 0.0075 mmol; **L2** or **L4** 0.015 mmol), CO/H₂ (1:1) 4.0 MPa, MeOH 3 mL, 80 °C, reaction time 6 h; ^b Determined by GC; ^c S_{oxo}=(aldehydes+acetals)/(aldehydes+acetals+iso-octenes), P_{acetals} =acetals/(aldehydes+acetals), percentage of acetals in the total oxo-products; S_{iso-octenes}=iso-octenes/(aldehydes+acetals+iso-octenes); ^d L/B, the ratio of linear nonanals and acetals to branched nonanals and acetals; ^e TON_{oxo} (turnover number)=mol of oxo products·(mol of Rh)⁻¹.