Electronic Supplementary Information

Zirconia supported rhenium oxide as an efficient catalyst for the synthesis of biomass-based adipic acid ester

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Experimental & calculation details

Materials

ZrO_2, SiO_2, Al_2O_3, TiO_2 and MgO with purities >99% were purchased from Sinopharam Chemical Reagent Co. Ltd or Alfa Aesar. NH_4ReO_4, CH_3ReO_3, NH_4VO_3, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $(NH_4)_6H_2W_{12}O_{40}\cdot xH_2O$ were purchased from Macklin Co. D-glucaric acid-1,4-lactone was obtained from Sigma Aldrich Co. LLC. All reagents were used without further purification.

Catalyst preparation

ZrO_2-supported rhenium oxide (ReO_x/ZrO_2) was prepared by the following procedure. 1.0 g of ZrO_2 was mixed with an ethanol solution of NH_4ReO_4 at room temperature under continuous stirring. After stirring for 0.5 h, the solvent was evaporated at 393 K to get a solid product. Then, the catalyst was obtained by heating the solid product at a rate of 2 K min^{-1} to 473 K and keeping at 473 K for 3 h under H_2 flow (10 mL/min). ReO_x catalysts loaded on other metal oxides (i.e., SiO_2, TiO_2, Al_2O_3, MgO) were prepared with the same procedure. This procedure was also employed for the preparation of ZrO_2-supported other metal oxides (MO_x/ZrO_2, M = V, Mo, W) by using NH_4VO_3, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $(NH_4)_6H_2W_{12}O_{40}\cdot xH_2O$ as precursors instead of NH_4ReO_4. The loading amount of metal oxides (e.g., ReO_x, VO_x, MoO_x and WO_x) was fixed at 5.0 wt%.

Catalytic reaction and product analysis

Catalytic conversion of D-glucaric acid-1,4-lactone was performed in a two-neck flask under refluxing conditions. Typically, 20 mg of catalyst, 21 mg of D-glucaric acid-1,4-lactone and 5.0 mL of butanol were added into the flask equipped with a condenser. After ultrasonic treatment for 10 min, the flask was purged by N_2 flow (20 mL/min) for 10 min to remove air from the system. Then, the reaction was started by placing the flask into a preheated oil bath at 393 K. After a certain reaction time (typically 24 h), the reaction was stopped by cooling the reactor with water. The catalyst was filtrated and the liquid products were analysed by a gas chromatograph (GC-7890B, Agilent) by using trimethylbenzene as an internal standard.

Because of the high boiling points, some products or intermediates could not be analysed directly by GC. These compounds were identified and quantified using a silylation method. Generally, 1.0 mL of liquid sample was transferred from the reaction solution to a vial, which was pre-charged with 0.7 mL pyridine, 0.7 mL hexamethyldisilazane (HMDS) and 50 μL trifluoroacetic acid. After reaction at 343 K for 2 h, the sample was analysed by GC (GC-7890B, Agilent) and GC-MS (QP2010, Shimadzu).

Characterization

Hydrogen temperature-programmed reduction (H_2-TPR) was performed on a fixed-bed reactor equipped with a thermal conductivity detector (TCD). First, the catalyst (100 mg) was loaded in the reactor, and pretreated by N_2 flow (20 mL/min) at 473 K for 1 h. When the temperature was reduced to 323 K, the carrier gas was changed to 5% H_2/Ar (20 mL/min), and the catalyst was heated from 323 to 1123 K at a rate of 10 K/min. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Quantum 2000 Scanning ESCA Microprobe (Physical Electronics) using Al K_α radiation (1846.6 eV) as the X-ray source. *In situ* Fourier-transform infrared (FT-IR) spectra were recorded with a Mettler-Toledo ReactIR 45 FT-IR spectrophotometer equipped with an AgX fiber conduit and a diamond probe tip. The probe was placed in a vertical position with the probe tip pointing downwards submerged in the liquid reaction mixture together with a magnetic stir bar, the temperature was controlled by an oil bath with an internal thermometer.

DFT calculation

To obtain optimized structures and vibrational frequencies of studied molecules, hybrid density functional theory (DFT) calculations were carried out with Becke's three-parameter exchange functional and Lee-Yang-Parr correlation functional (B3LYP). The basis sets for C, O and H atoms of the investigated molecule were 6-311+G (d, p). For the Re atom, we adopted the small core pseudo-potential basis set, LANL2DZ. To better simulate experimental conditions, the solvation model has been considered in this work. The polarizable continuum model (PCM) includes a solvent

reaction field self-consistent with the solute electrostatic potential by using a solvent of butanol (dielectric constant ε =17.332). Full geometry optimizations and frequency analyse were carried out by using Gaussian 16 package.

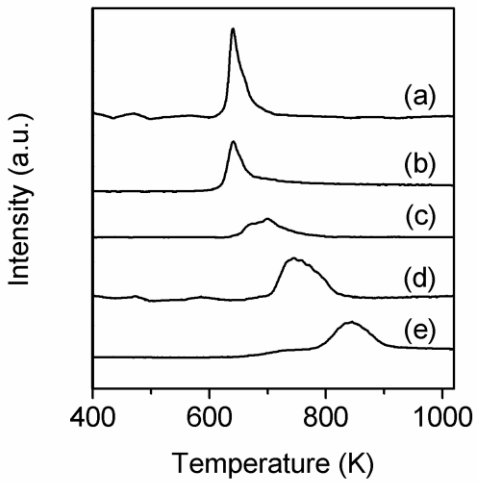

Fig. S1 H_2-TPR profiles. (a) ReO_x/ZrO_2. (b) ReO_x/TiO_2. (c) ReO_x/SiO_2. (d) ReO_x/Al_2O_3. (e) ReO_x/MgO.

Table S1 Summary of TPR results[a]

Catalyst	Re amount (mmol g_{cat}^{-1})	Temperature (K)	Total H_2 consumption (mmol g_{cat}^{-1})
ReO_x/ZrO_2	0.27	608-720	0.79
ReO_x/TiO_2	0.27	595-741	0.69
ReO_x/SiO_2	0.27	634-800	0.89
ReO_x/Al_2O_3	0.27	663-842	0.90
ReO_x/MgO	0.27	670-950	0.93

[a] Calculated from the result in Fig. S1.

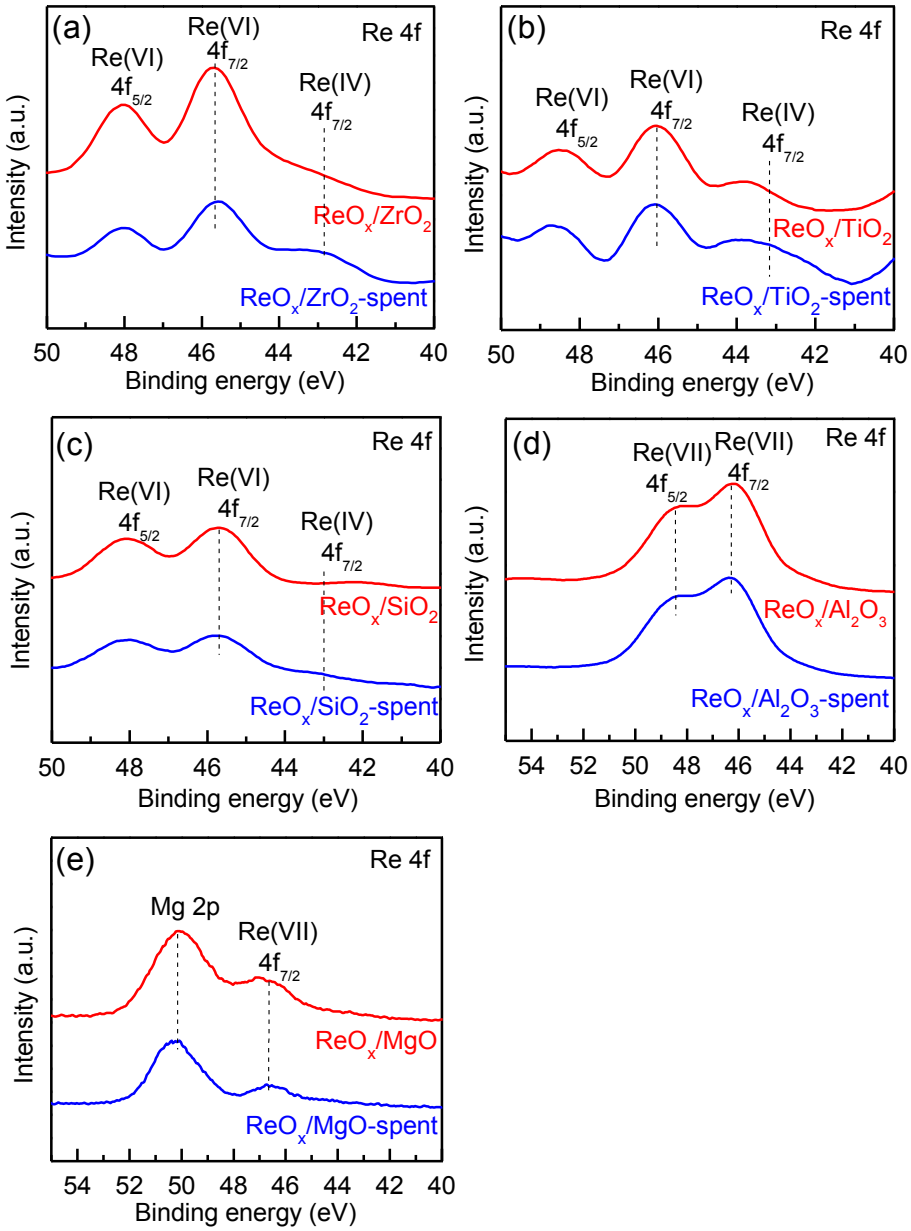

Fig. S2 Re 4f XPS spectra. (a) ReO_x/ZrO_2. (b) ReO_x/TiO_2. (c) ReO_x/SiO_2. (d) ReO_x/Al_2O_3. (e) ReO_x/MgO. The red curve was for the fresh catalyst, while the blue curve was for the catalyst after reaction.

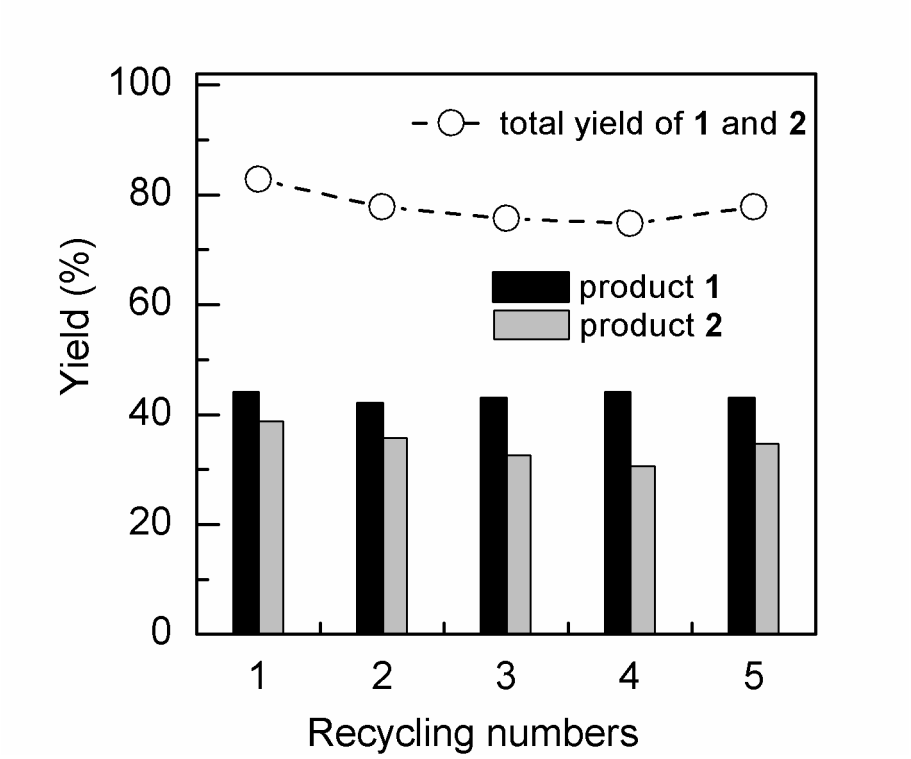

Fig. S3 Recycling uses of ReO_x/ZrO_2 for the conversion of D-glucaric acid-1,4-lactone. Reaction conditions: D-glucaric acid-1,4-lactone, 0.10 mmol; ReO_x/ZrO_2, 20 mg; butanol, 5.0 mL; N_2 flow, 20 mL/min; reaction temperature, 393 K; reaction time 24 h.

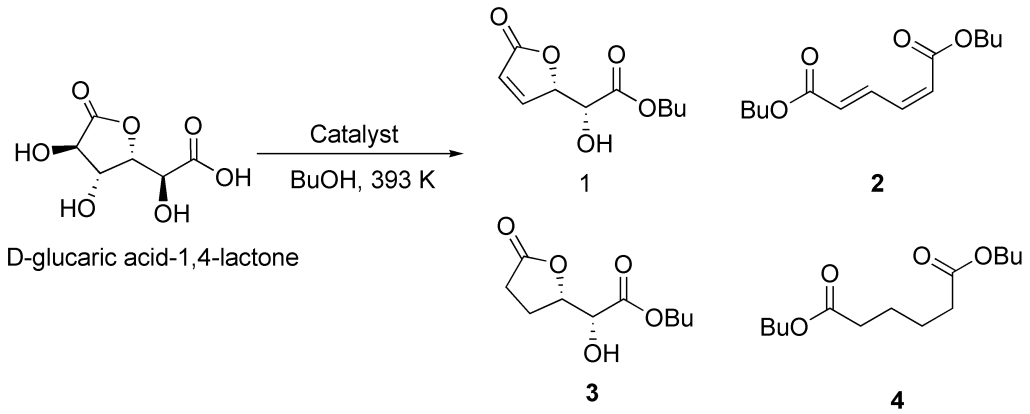

Table S2 Catalytic conversion of D-glucaric acid-1,4-lactone over ReO_x/ZrO_2 and the combination of (ReO_x/ZrO_2 + Pd/C) in butanol[a]

Entry	Catalyst	Flow gas	Yield (%)				Total yield of products (%)
			1	**2**	**3**	**4**	
1	ReO_x/ZrO_2	N_2	52	41	0	0	93
2[b]	ReO_x/ZrO_2 + Pd/C	N_2	53	12	0	0	65
3[b]	ReO_x/ZrO_2 + Pd/C	H_2	36	3.9	3.1	4.0	47
4[c]	ReO_x/ZrO_2 + Pd/C	H_2	0	0	5.0	5.6	10.6

[a] Reaction conditions: D-glucaric acid-1,4-lactone, 0.10 mmol; ReO_x/ZrO_2, 20 mg; butanol, 5.0 mL; flow rate of gas, 20 mL/min; reaction temperature, 393 K; reaction time, 24 h. [b] Pd/C, 5 mg. [c] Pd/C, 10 mg.

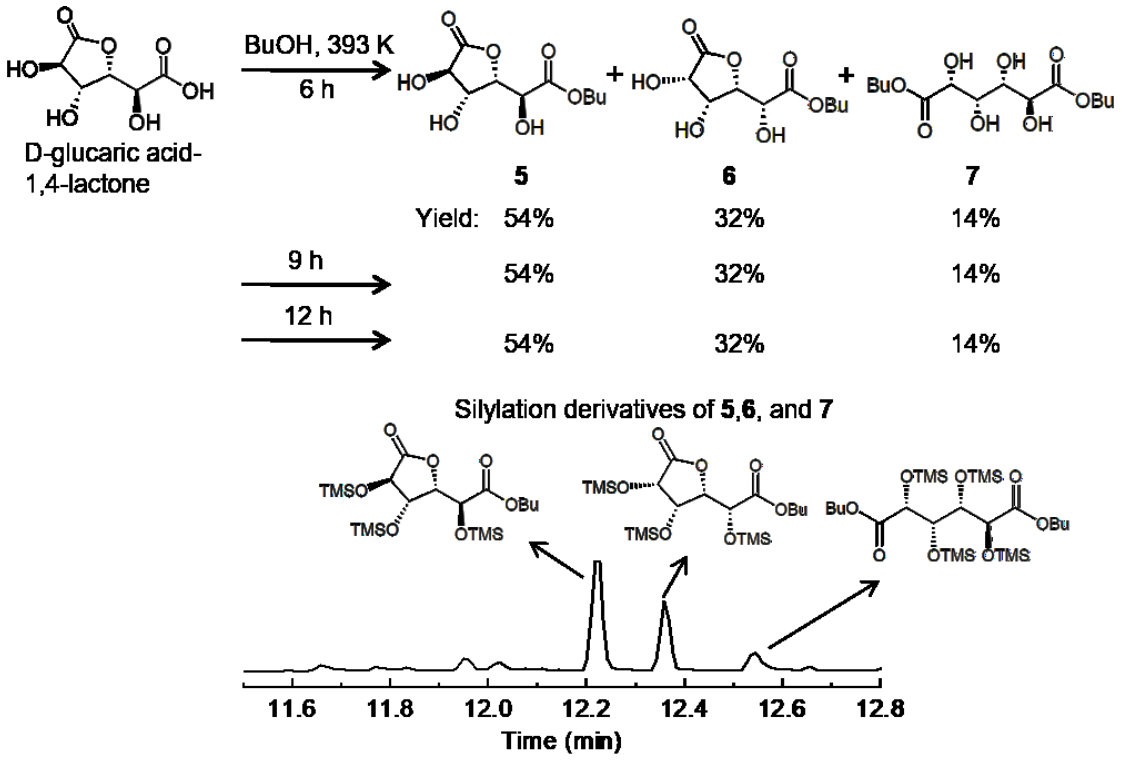

Fig. S4 GC-MS profile of silylation products from the esterification of D-glucaric acid-1,4-lactone in butanol at 393 K and the yields of products.

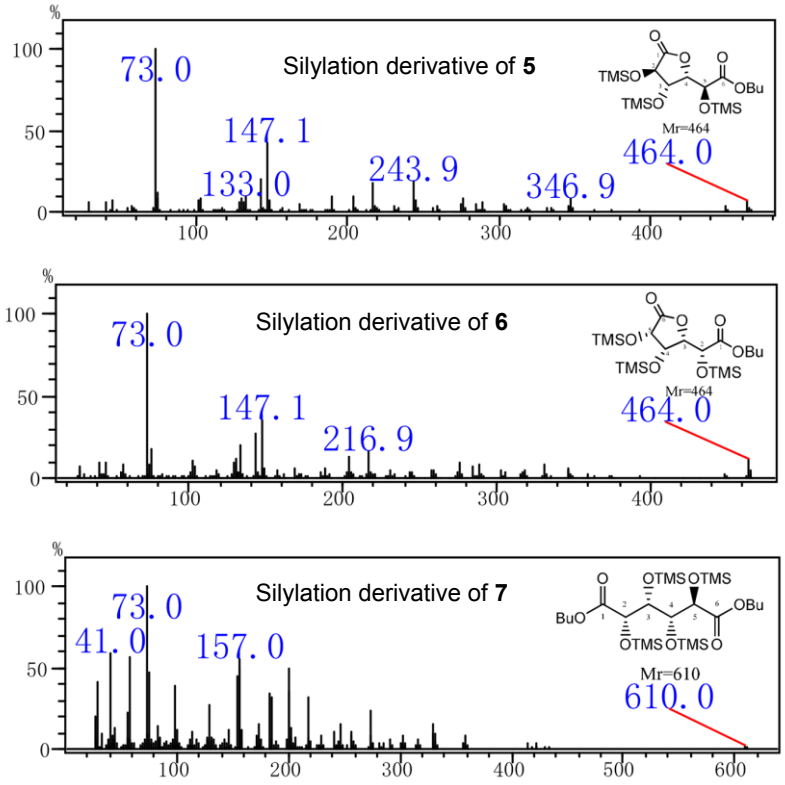

Fig. S5 MS profiles of silylation products from the esterification of D-glucaric acid-1,4-lactone.

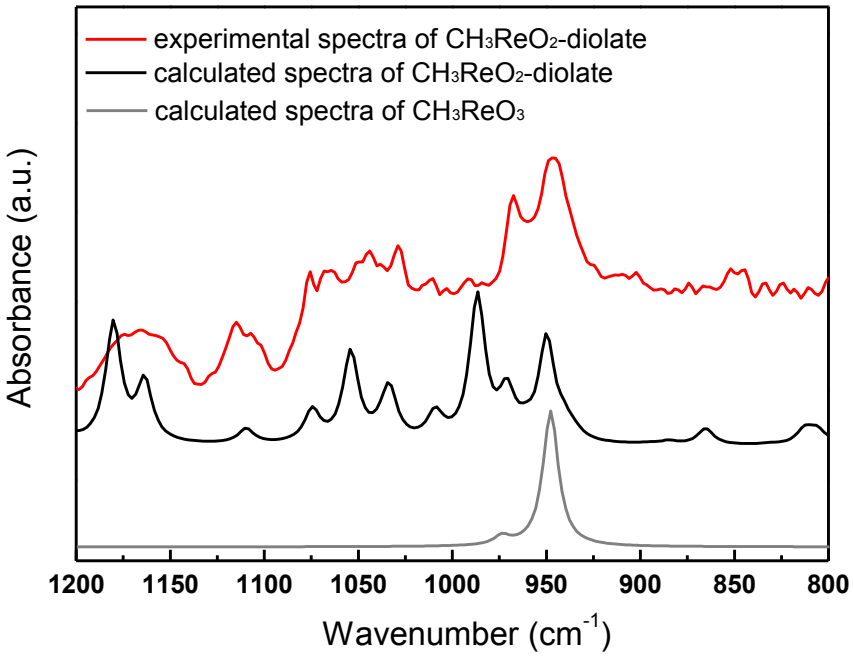

Fig. S6 Calculated and experimental IR spectra of CH_3ReO_2-diolate complex using dibutyl tartrate as a ligand and the calculated spectra of CH_3ReO_3.

Table S3 Comparison of theoretical and experimental vibrational frequencies as well as vibrational assignments for CH_3ReO_2-diolate complex

Freq.	Scale.	Expt.	Vibration analysis
967	948	946	Re-O asymmetric stretching
1005	985	967	Re-O symmetric stretching
1053	1032	1028	C-O stretching in ring
1074	1053	1044	C-C stretching in ring
1131	1110	1115	CH_3 deformation
1202	1162	1165	CH_2 rocking in butyl

To compare the calculated vibrational frequencies with observed IR bands, we used the scaling factors of 0.981 for vibrational frequencies less than 2000 cm^{-1}, and 0.967 for above 2000 cm^{-1}. After the systematic corrections, the mean deviation between theoretical and experimental vibrational frequencies decrease from 39 cm^{-1} to 13 cm^{-1}. For CH_3ReO_2-diolate complex, the calculated IR spectrum is shown in Fig.

S6. This is in good agreement with the experimental IR spectrum. To clearly understand the IR signals observed from the experimental spectrum, we have performed normal-mode analysis for vibrational fundamentals of the molecule (Table S3). The Freq. represents the vibrational frequencies calculated by using B3LYP approach; the symbol "Scale." column denotes the vibrational frequencies scaled by using a scaling factors; the "Expt." column denotes the IR bands experimentally observed in infrared spectra.

The frequency at 948 cm^{-1} arises from the Re-O asymmetric stretching vibration. The frequency at 985 cm^{-1} is due to the Re-O symmetric stretching vibration. They correspond to the observed IR bands at 946 and 967 cm^{-1}, respectively. The frequency at 1032 cm^{-1} is from the C-O stretching vibration in the five-membered ring. The frequency at 1053 cm^{-1} can be attributed to the C-C stretching vibration in the ring.

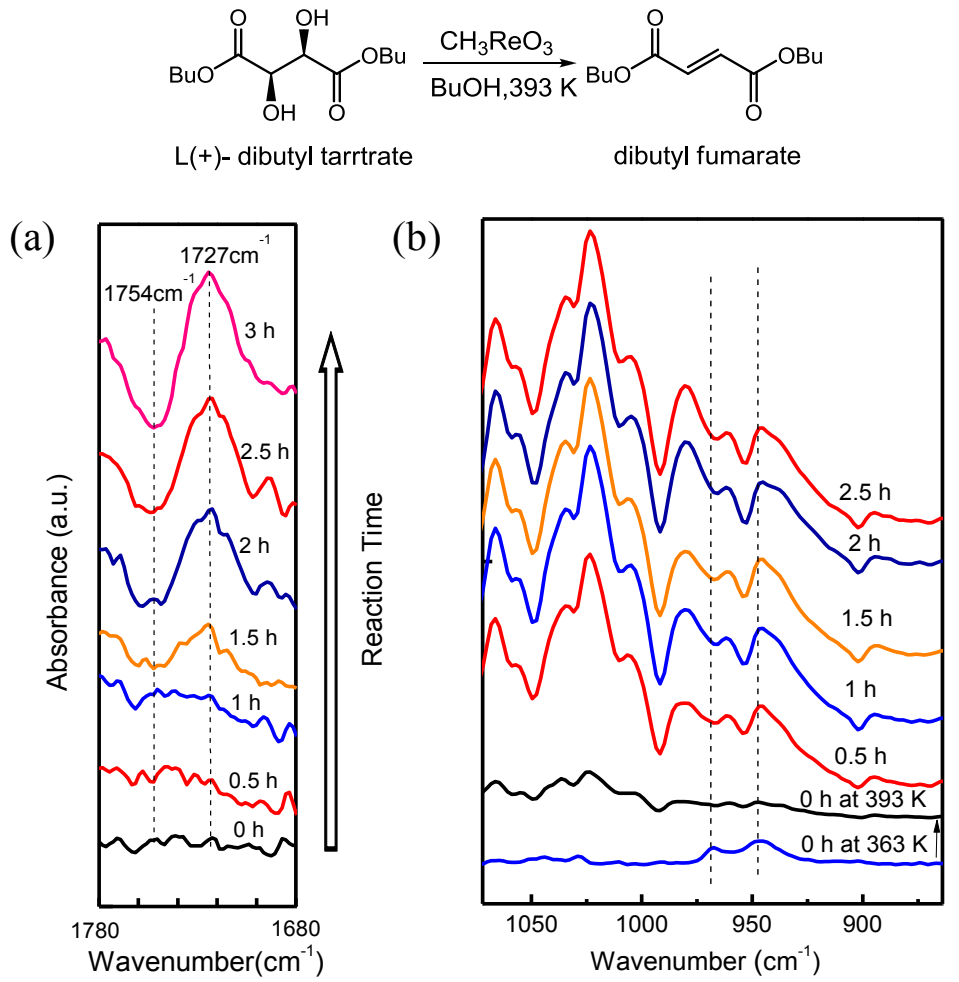

Fig. S7 IR spectra of 0.10 mmol CH_3ReO_3 and 1.0 mmol dibutyl tartrate in butanol at 393 K. (a) Wavenumber range of 1680-1780 cm^{-1}. (b) Wavenumber range of 864-1072 cm^{-1}.

The IR band at 1727 cm^{-1} is assigned to the stretching vibration of C=O in dibutyl fumarate (the product), while the band at 1754 cm^{-1} is attributed to the stretching vibration of C=O in dibutyl tartrate (starting material). The increase in the reaction time led to an increase in the intensity of band at 1727 cm^{-1}, indicating the formation of alkene product. On the other hand, the characteristic band of CH_3ReO_2-diolate complex disappeared when the reaction temperature increased to 393 K. This suggests the transformation of this intermediate. New bands appeared in the range of 900-1040 cm^{-1} with prolonging reaction time. This is probably caused by the formation of both products and by-products.