Supporting Information

Cationic Two-Dimensional Inorganic Network of Antimony Oxide Hydroxide for Lewis Acid Catalysis

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Experimental

General Methods. Starting materials and solvents were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Alfa Aesar, TCI, and others). Proton nuclear magnetic resonance spectra (1H NMR) were recorded on a Varian FT-NMR spectrometer (400 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for TMS. Elemental analysis (EA) for C, H, and S were operated on a (Varian EL III) element analyzer. Thermogravimetric analysis (TGA) were carried out in N_2 stream (60 mL/min) on a TGA Q500 differential thermal analyzer running from room temperature to 800 °C with a heating rate of 10 °C/min. Metallic element content detection for Sb were carried out on a PERKIN ELMER OPTIMA 8300 inductively coupled plasma optical emission spectrometer (ICP-OES), TMOF-3/TMOF-3-Ag samples were degraded in aqua regia. X-ray photoelectron spectra (XPS) were acquired on an AXIS ULTRA DLD spectrometer and the data was analyzed by the PSPEAK 41 software. Gas chromatography-mass spectrum experiments were carried on a Themo Fisher Exactive GC Orbitrap GC-MS instrument.

Hydrothermal Synthesis of TJU-2. A mixture of 0.33 g $Sb(OOCCH_3)_3$ (1.1 mmol), 0.58 g disodium 1,4-butanedisulfonate ($BDSNa_2$, 2.2 mmol), 1 ml perchloric acid ($HClO_4$) and 10 mL deionized water were added into a 15 mL Teflon-lined autoclave reactor. The autoclave was heated statically for 3 days at 150 ℃. Colorless plate-like crystals of $[Sb_2O_2(OH)][O_3S(CH_2)_4SO_3]_{0.5}$ were isolated using vacuum filtration, followed by rinsing with ethanol and deionized water. Yield: 0.20 g (91 % based on Sb content). The phase purity of TJU-2 was confirmed by comparing the experimental powder X-ray diffraction patterns with theoretical pattern simulated from single-crystal data. Elemental analysis for $[Sb_2O_2(OH)][O_3S(CH_2)_4SO_3]_{0.5}$: observed: C, 6.03 %; H, 1.07%; S, 8.09 %, calculated: C,5.99 %; H, 1.24 %; S, 8.01 %.

Thermal and Chemical Stability Test. ~50 mg of as-synthesized TJU-2 were incubated in a specified solution (e.g. boiling organic solvents, boiling water, acid condition or heating in air) for 24 hours. Then, TJU-2 was isolated by filtration, air-dried before performing PXRD and mass balance measurements.

Powder X-ray Diffraction (PXRD). ~20 mg TJU-2 sample was dried under vacuum prior to PXRD analysis. PXRD data was collected at ambient temperature on a Bruker D8 Advance diffractometer at 40 kV, 40 mA for Cu Kα ($\lambda = 1.5418$ Å), with a scan speed of 1 sec/step, a step size of 0.02° in 2θ, and a 2θ range of 5~40°. The experimental backgrounds were corrected using JADE 5.0 software package.

Single Crystal X-ray Diffraction. A single crystal of TJU-2 suitable for X-ray analysis was chosen under an optical microscope, and mounted onto a glass fiber. The diffraction data were collected at 298(2) K using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) from a fine-focus sealed tube operated at 50 kV and 30 mA on a Bruker SMART APEX II CCD area detector X-ray diffractometer. The structure was solved by direct methods and expanded routinely. The model was refined by full-matrix least-squares analysis of F2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Thermal parameters for hydrogen atoms were rebonded. Programs used were APEX-II v2.1.4, SHELXTL v6.14, and Diamond v3.2. Further details of crystallographic data and structural refinement are summarized in Table 1.

Infrared Spectroscopy of Pyridine Adsorption Measurement. ~20 mg TJU-2 were pressed into self-supporting wafer and heated at 523 K in air (300-400 Torr) for 4 h, followed by evacuation at ca. 10^{-5} Torr for 2 h at the same temperature. The thin wafer was cooled to 373K and the IR spectrum was recorded. Pyridine was then introduced into the cell at 5 Torr and contacted with the catalyst for 30 min under 373 K and 473 K, respectively. The sample was then evacuated for 10 min at the same temperature and cooled to room temperature,before recording the spectrum. Spectra were always collected as an average of 60 runs with a 2 cm^{-1} definition.

TJU-2-Catalyzed Cyanosilylation of Benzaldehyde Derivatives. 1.25 mmol of the benzaldehyde derivatives, 2.50 mmol trimethylsilyl cyanide, 6 mol % (based on Sb) catalyst, and 5 mL dichloromethane were added into a 50 ml round-bottom flask under ambient condition. The resulting mixture was placed onto a shaker to shake continuously at 160 rpm for up to 16 h at room temperature. After the reaction, the solution was concentrated, and analyzed by 1H NMR. To test recyclability, the catalyst was separated by filtration, rinsed with dichloromethane, and dried under vacuum. The dried catalysts were directed used for the next round catalysis for the same substrate.

TJU-2-Catalyzed Ketalization of 2-Butanone. 40 mmol of 2-butanone, 80 mmol of ethylene glycol and 1.25 mol % (based on Sb) catalyst were introduced into a 50 ml round-bottom flask. The resulting mixture were heated at 90 oC for 14 h. After the reaction, the solution was concentrated, and analyzed by 1H NMR. To test recyclability, the catalyst was separated by filtration, rinsed with 2-butanone, and dried under vacuum. The dried catalysts were directed used for the next round catalysis.

Supporting Tables and Figures.

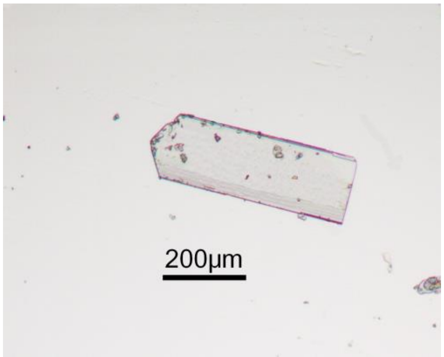

Figure S1. Optical microscope image of a TJU-2 single crystal.

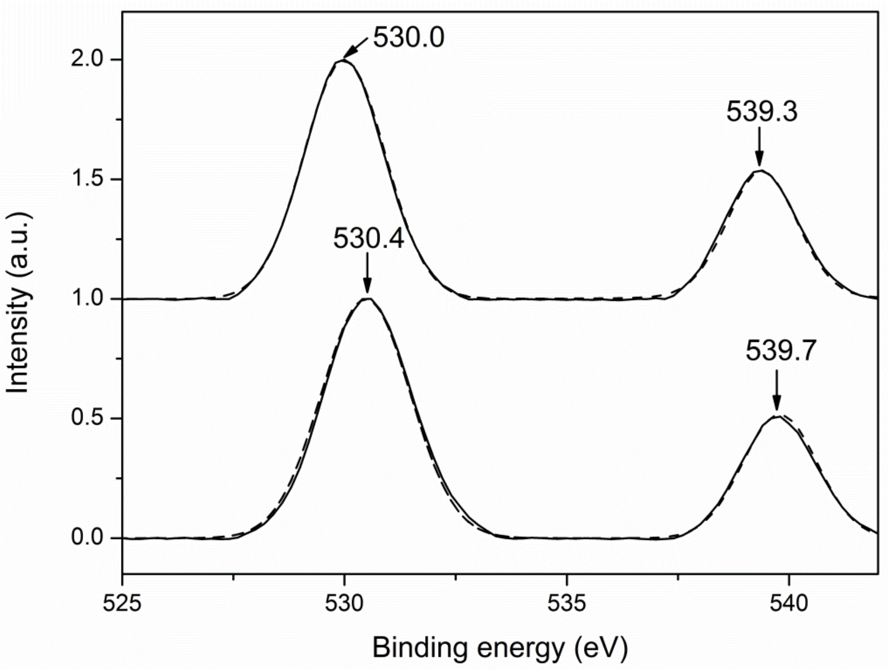

Figure S2. Sb 3d spectra of Sb_2O_3 (top) and TJU-2 (bottom). Dotted Gaussian curves are the results of the digital optimization.

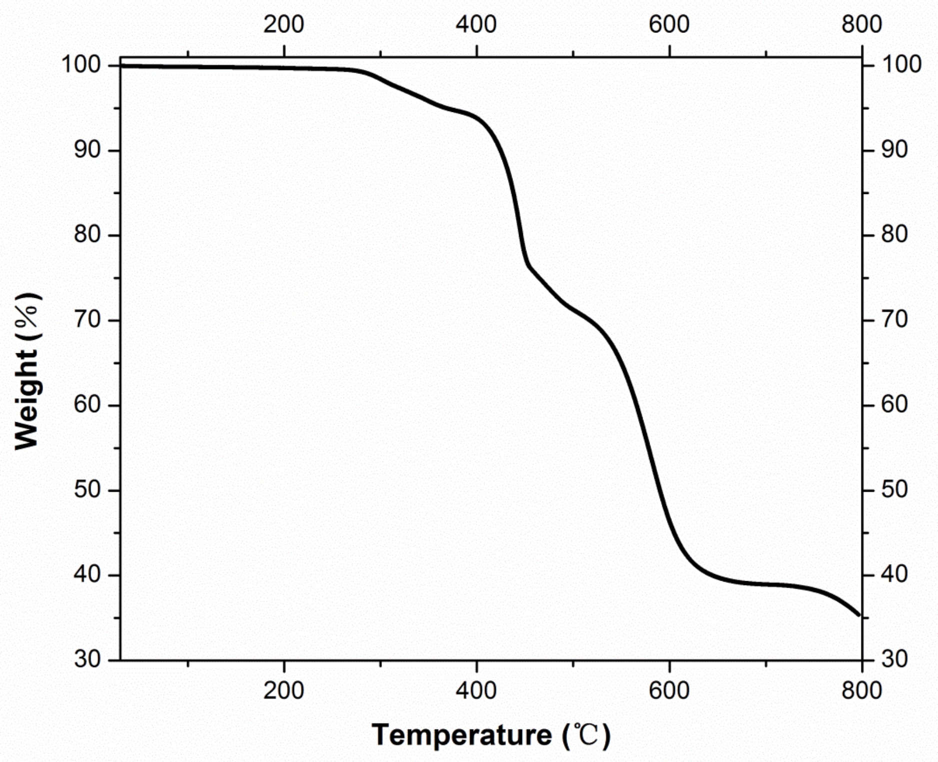

Figure S3. Thermogravimetric analysis of TJU-2.

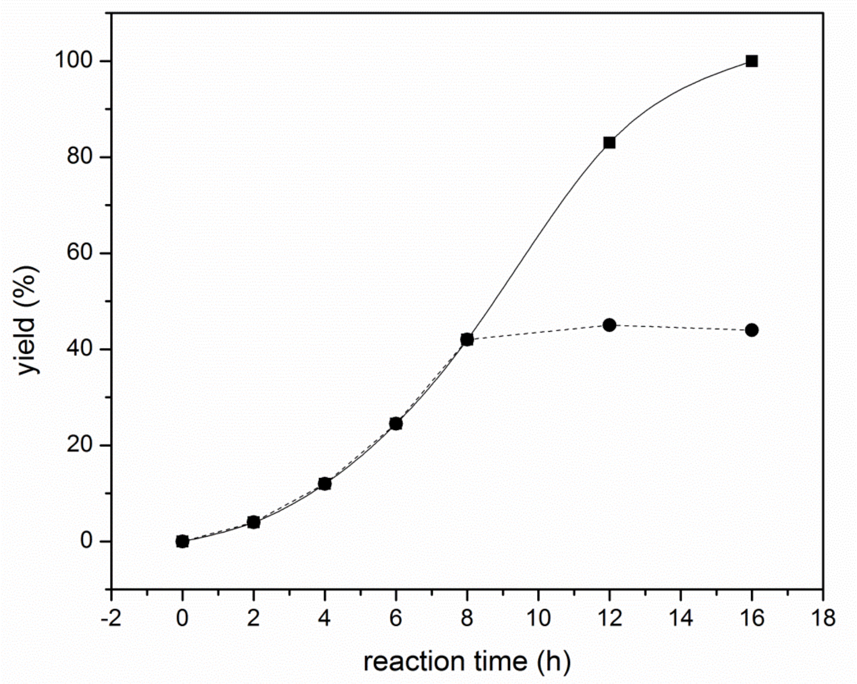

Figure S4. Yield-time plot of TJU-2-catalyzed reaction between benzaldehyde and trimethylsilyl cyanide. Dotted line: TJU-2 catalyst removed at 8 h.

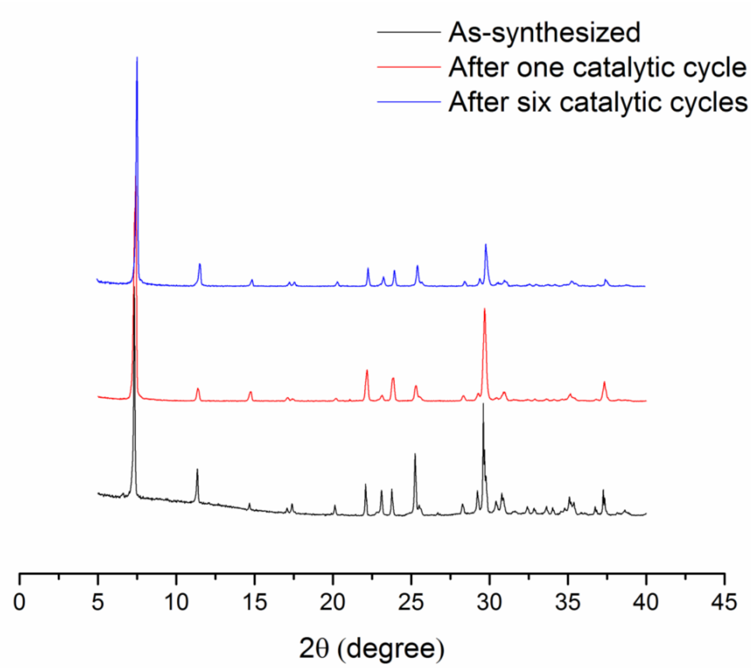

Figure S5. PXRD of TJU-2 before and after catalysis of the cyanosilylation of benzaldehyde.

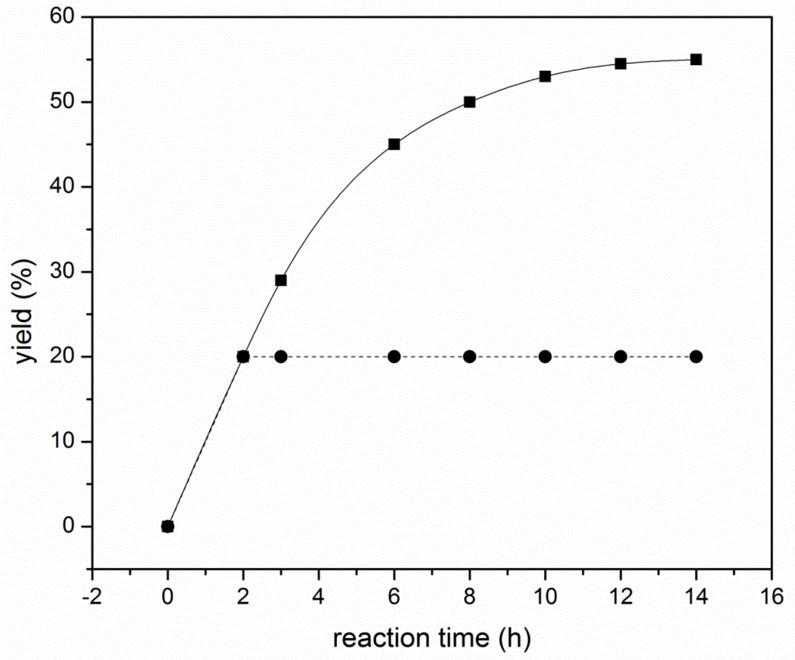

Figure S6. Yield-time plot of TJU-2-catalyzed reaction between 2-butanone and ethylene glycol. Dotted line: TJU-2 catalyst removed at 2 h.

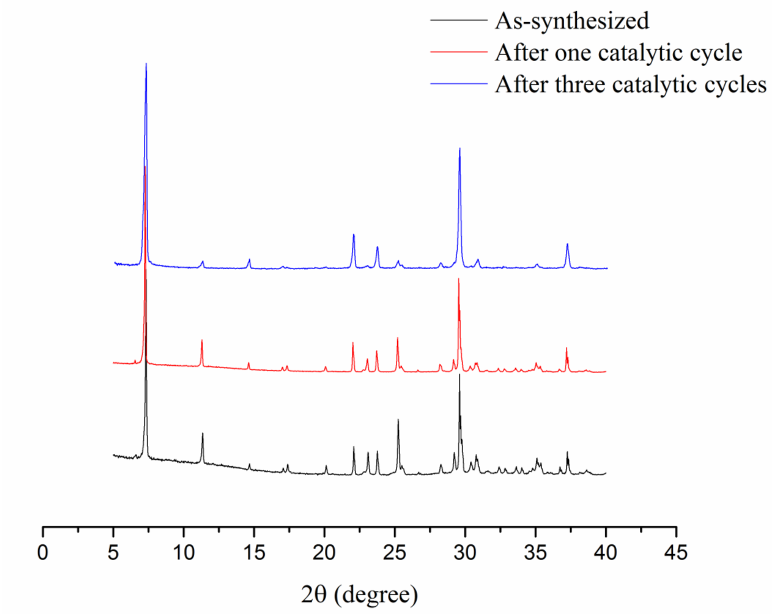

Figure S7. PXRD of TJU-2 before and after catalysis of the ketalization of 2-butanone.

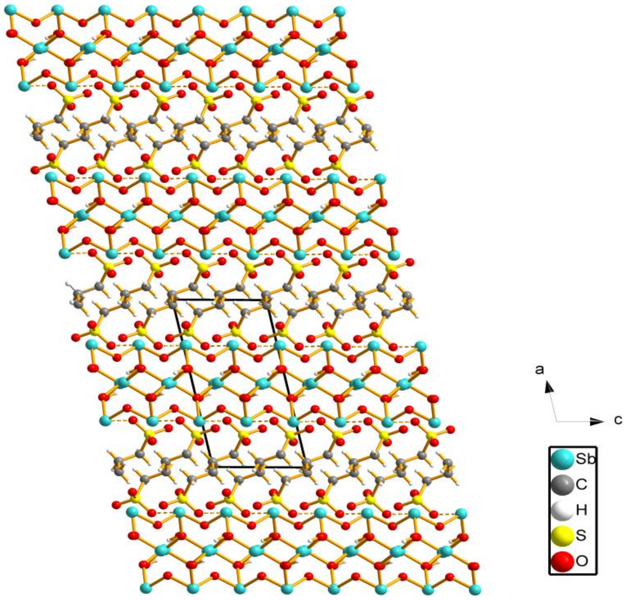

Figure S8. Crystallographic view of TJU-2 along *b*-axis (cyan antimony, red oxygen, grey carbon, white hydrogen). The dashed lines show long intralayer contacts between antimony and oxygen.

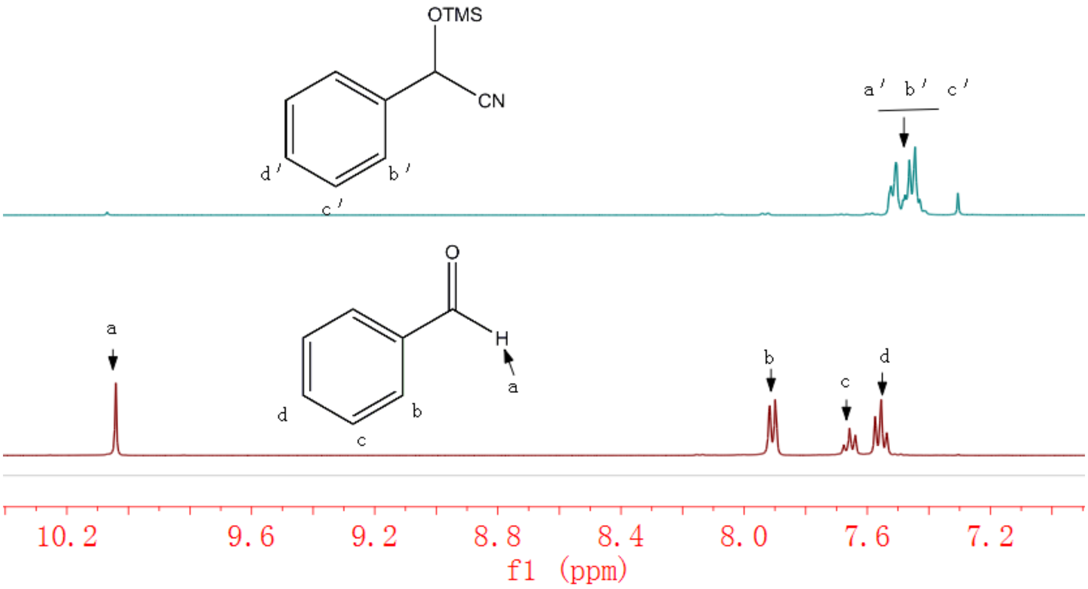

Figure S9. ^{1}H-NMR spectra of cyanosilylation of benzaldehyde before (down) and after (up) TJU-2 catalysis.

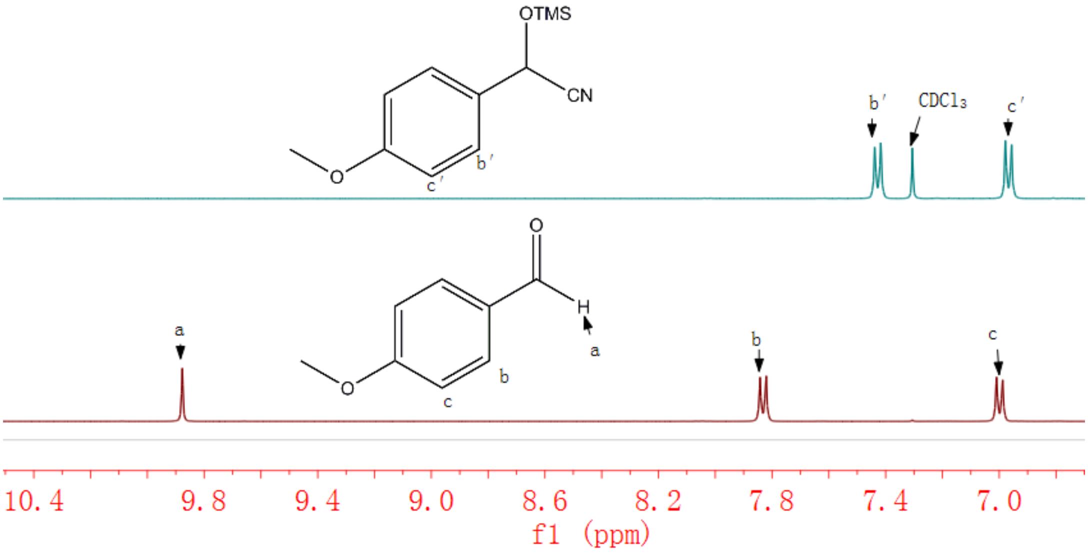

Figure S10. ^{1}H-NMR spectra of cyanosilylation of 4-anisaldehyde before (down) and after (up) TJU-2 catalysis.

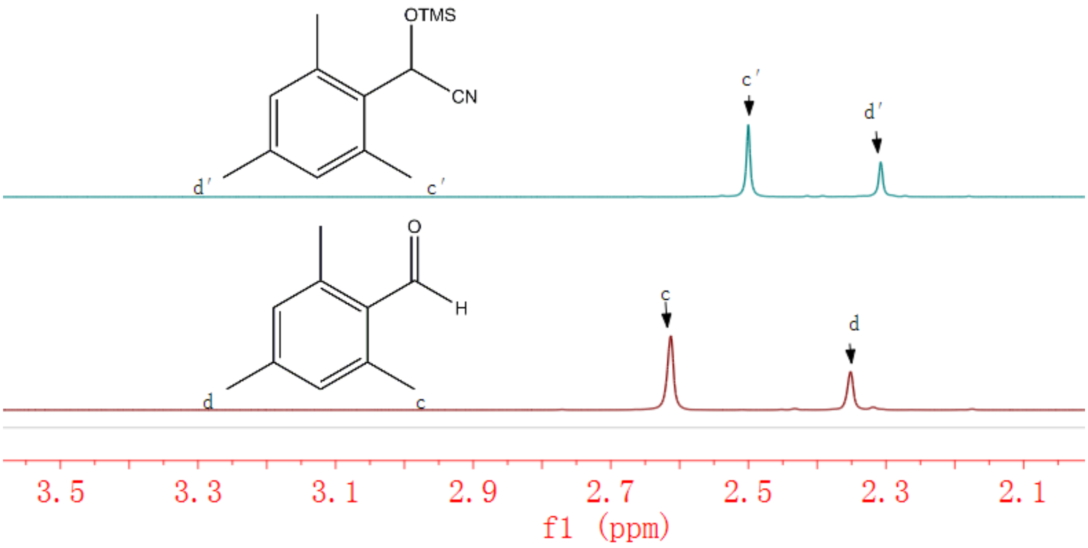

Figure S11. ^{1}H-NMR spectra of cyanosilylation of 2,4,6-trimethylbenzaldehyde before (down) and after (up) TJU-2 catalysis.

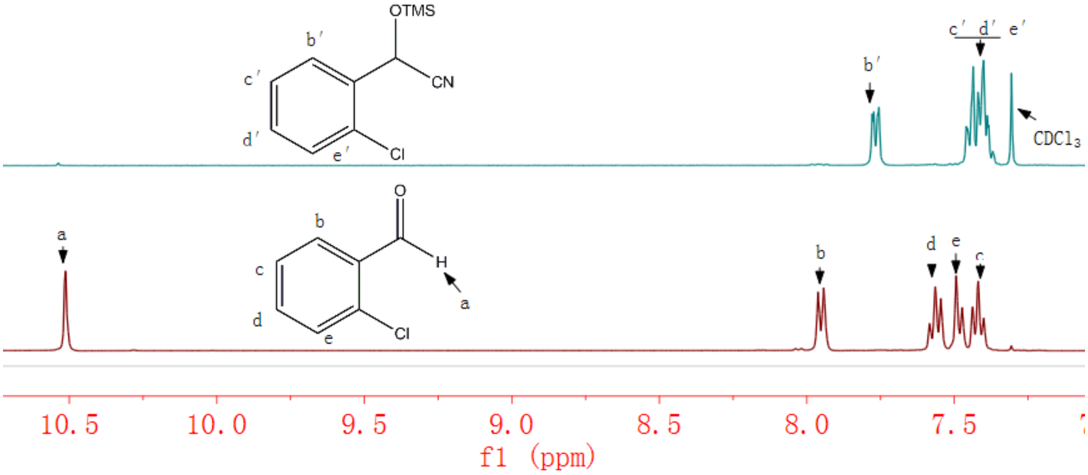

Figure S12. ^{1}H-NMR spectra of cyanosilylation of *o*-chlorobenzaldehyde before (down) and after (up) TJU-2 catalysis.

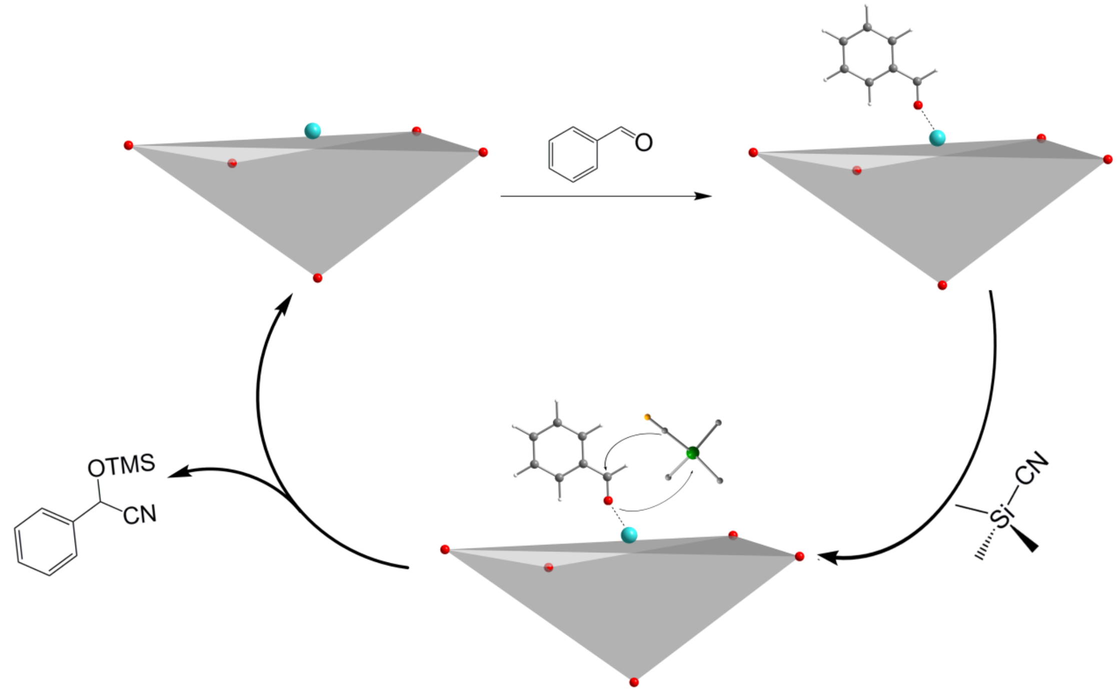

Figure S13. Presumable mechanism of TJU-2-catalyzed cyanosilylation of benzaldehyde.

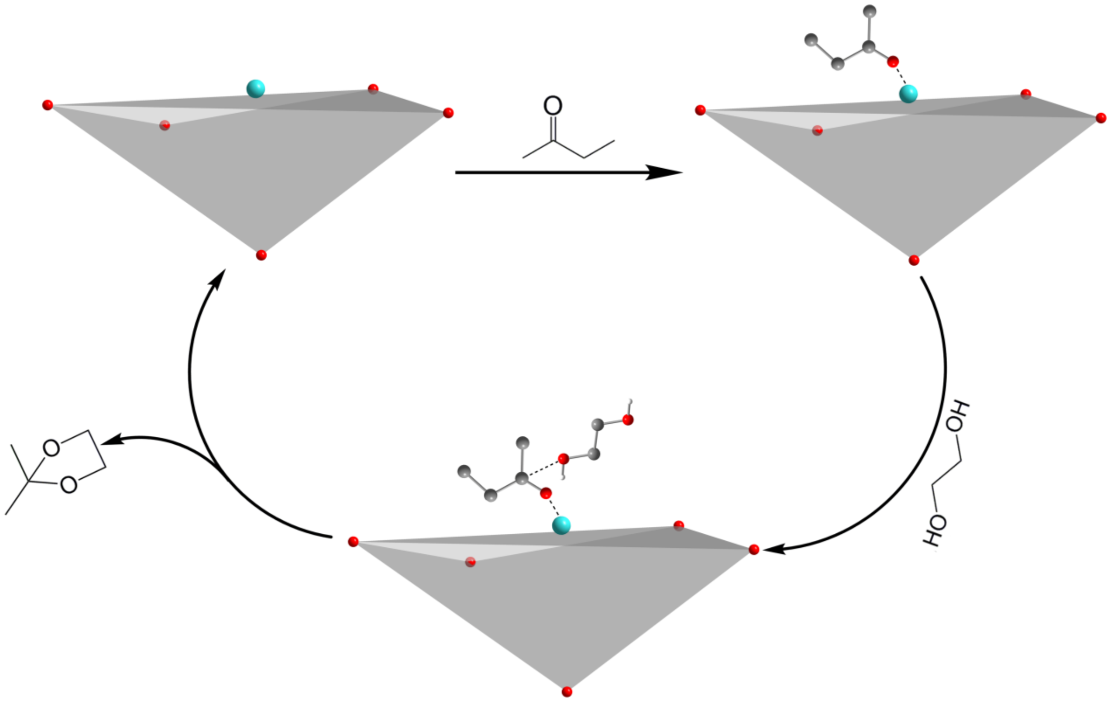

Figure S14. Presumable mechanism of TJU-2-catalyzed ketalization of 2-butanone.

Table S1. Recyclability of TJU-2 in cyanosilylation of benzaldehyde.

cycle	yield (%)
1	>99
2	>99
3	>99
4	>99
5	>99
6	>98

Table S2. Bond lengths [Å] and bond angles [°] around the Sb atoms in TJU-2.

Sb(1)-O(5)	1.981(5)	Sb(1)-O(4)	1.991(6)
Sb(1)-O(4)^a	2.059(7)	Sb(1)-O(1)	2.549(7)
Sb(2)-O(6)	1.941(7)	Sb(2)-O(5)	2.044(7)
Sb(2)-O(6)	1.941(7)	Sb(2)-O(5)	2.044(7)
O(5)-Sb(1)-O(4)	87.3(2)	O(5)-Sb(1)-O(4)#1	76.2(2)
O(4)-Sb(1)-O(4)#1	96.29(14)	O(5)-Sb(1)-O(1)	71.2(2)
O(4)-Sb(1)-O(1)	84.9(2)	O(4)#1-Sb(1)-O(1)	147.3(2)
O(6)-Sb(2)-O(5)	91.4(3)	O(6)-Sb(2)-O(5)#2	90.5(3)
O(5)-Sb(2)-O(5)#2	70.0(2)	O(6)-Sb(2)-O(4)#1	86.5(3)
O(5)-Sb(2)-O(4)#1	68.8(2)	O(5)#2-Sb(2)-O(4)#1	138.6(3)

Symmetry transformations used to generate equivalent atoms: #1 x,-y+3/2,z+1/2; #2 -x+2,-y+1,-z+1

Table S3. Crystallographic information of TJU-2.

empirical formula	$C_2H_5O_6SSb_2$
formula weight ［g/mol］	400.62
Wavelength	0.71073 Å
crystal system	Monoclinic
space group	P2(1)/c
Unit cell dimensions	a = 12.330(3) Å b = 10.154(3) Å c = 6.0161(15) Å β = 102.499(9)°
Z	4
temperature	273(2) K
R_1 ［I>2σ(I)］	0.0354
wR_2(all data)	0.0939
Goodness-of-fit on F2	1.056
Density (calculated)	3.619 $g.cm^{-3}$
ω range for data collection	3.38 to 27.50 °
Index ranges	$0 \leq h \leq 16$, $-13 \leq k \leq 0$, $-7 \leq l \leq 7$
Reflections collected	1620
Absorption correction	Empirical
Max. and min. transmission	0.09491 and 0.06185
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1620 / 7 / 105
Largest diff. peak and hole	1.512 and -1.303 $e^{-}.Å^{-3}$