

Supporting information

An open-framework coordination network that catalyzes O₂-based oxidations

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Experimental section

General method and materials. All chemicals, except 4-(chloromethyl)benzoic acid purchased from Alfa Aesar, were obtained from Aldrich. Dimethylacetamide (DMA) was dried with 3 Å molecular sieves prior to use. Other chemicals were used as received. ^1H and ^{13}C NMR spectra were referenced to the deuterated solvent itself, and chemical shifts were reported relative to $(\text{CH}_3)_4\text{Si}$. ^{51}V NMR spectra were recorded on a Varian Unity 600 MHz instrument. ^1H NMR spectra were referenced to the deuterated solvent itself, and chemical shifts were reported relative to $(\text{CH}_3)_4\text{Si}$. ^{51}V NMR spectra were referenced externally by the sample replacement method to a 10 mM solution of $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$ in 0.60 M NaCl (-533.6 ppm relative to neat VOCl_3), and chemical shifts were reported relative to VOCl_3 . IR spectra were recorded on Nicolet 510 FT-IR instrument. Electronic absorption spectra were obtained using a Hewlett-packard 8452A UV/Vis spectrophotometer. Thermal gravimetric analyses (TGA) were performed on an ISI TGA 1000 under N_2 flow from 25 to 400 °C at a rate of 10 °C/min. Differential scanning calorimetry (DSC) were recorded on ISI DSC 100 under N_2 flow from 25 to 400 °C at a rate of 10 °C/min. Powder X-ray diffraction data were carried out by Ashland Ashland Specialty Chemical Co. Each sample was placed in 0.3mm (diameter) hollow capillary tube and analyzed with a Panalytical X'Pert Pro MPD system using an 1800W Cu x-ray tube. Samples were analyzed from 4-25 degrees (two-theta) using a step size of 0.0167 and a dwell time of 9 seconds per step. Oxidation reactions were quantified by gas chromatography (GC; Hewlett Packard 6890 series gas chromatograph equipped with a flame ionization detector, 5% phenyl methyl silicone capillary column, N_2 carrier gas, and a Hewlett Packard 3396 series III integrator). Elemental analyses for C, H and, N were performed by Atlantic Microlab, Norcross, GA, and elemental analyses for all other elements were performed either by Desert Analytics, Tucson, AZ or by Kanti Lab Ltd, Mississauga, Ontario.

Preparation of (4-HOCC₆H₄)CH₂NHC(CH₂OH)₃ (Acid-Tris). To the solution of tris(hydroxymethyl)amino methane (35.6 g, 0.294 mol) in 300 mL of water, solid chloromethyl benzoic acid (10.0 g, 0.0586 mol) was added over a period of *ca.* 2 min. The mixture was stirred for 20h at room temperature. 4-(Chloromethyl)benzoic acid was completely dissolved in 30 min, and white precipitate began to appear about 7h after the addition. The white precipitate was filtered and washed with water (2 × 20 mL) and acetone (2 × 15 mL) and dried under vacuum for 24 h to yield 10.2 g of product (68.0 %). ¹H NMR (DMSO-d₆): δ = 3.21 (s, 6H), 3.82 (s, 2H), 7.43 (d, 2H), 7.81 (d, 2H). ¹³C NMR (DMSO-d₆): δ = 45.88 (CH₂NH), 61.28 (HOCH₂), 61.95(CNH), 128.88 (o-Bz), 129.76 (m-Bz), 131.73 (p-Bz), 145.23 (CCOOH), 168.61 (COOH). Anal. Calcd. for C₁₂H₁₇NO₅: H, 6.23; C, 53.09; N, 12.38. Found: H, 6.13; C, 52.58; N, 12.13.

Preparation of [(*n*-C₄H₉)₄N]₂[V₆O₁₃{(CH₂O)₃C(NHCH₂C₆H₄-4-COOH)₂] (TBA₂[H₂1]). Acid-Tris (6.00 g, 23.5 mmol) and [(*n*-C₄H₉)₄N]₂[H₃V₁₀O₂₈] (13.2g, 7.83 mmol) were dissolved in 240 ml of dry dimethyl acetamide (DMA). The orange solution was stirred at 85 °C for 24 h under an O₂ atmosphere. The dark brown solution was cooled to room temperature and then added to 720 mL of diethyl ether. The resulting sticky precipitate was obtained by decanting the solvent. To the precipitate, 120 mL of acetone was added, and the mixture was stirred for 1h to produce a powder that was filtered and washed with acetone (3 × 10 mL). The filtrate was concentrated to *ca.* 30 mL, left undisturbed for 6 h, and the resulting powder was filtered and washed with a small amount of acetone. The crude powdery product was redissolved in 70 mL of a 1/1 v/v acetonitrile/dimethyl formamide (DMF) solvent system, and then 150 mL of diethyl ether was added to re-precipitate the product. The material was filtered and washed with diethyl ether (2 × 10 mL) and purified by a crystallization from acetonitrile/DMF/ diethyl ether (v/v/v = 1/1/4) (yield. 6.01g, 29.2 % based on vanadium). (Note: when the reaction is run under N₂, the color of solution changes to a deep green, and the yield is lower 10-11%. Reduced POMs are blue from combined d-d transitions (weak) and intervalence

charge transfer transitions (strong); slight reduction results in a green color from a superposition of oxidized (orange) and a small quantity of reduced (blue) hexavanadate units. Under O₂ the green color changes back to the orange color of the initial fully oxidized hexavanadate, a finding consistent with the point in the previous sentence, and the yield of the reaction improves. ¹H NMR (DMSO-d₆): δ = 0.92 (t, 24H), 1.30 (sextet, 16H), 1.55 (quintet, 16H), 3.15 (t, 16H), 3.77 (s, 4H), 4.88 (d, 12H), 7.26 (d, 4H), 7.72 (d, 4H). ⁵¹V NMR (DMSO-d₆): δ = -493.6. FT-IR (KBr, 400-4000 cm⁻¹): 3436 (s, br), 2961 (s), 2931 (m), 2874 (m), 1710 (m), 1657 (s), 1610 (w), 1482 (m), 1419 (w), 1383 (m), 1254 (m), 1174 (w), 1080 (s), 953 (s), 810 (s), 796 (s), 720 (s), 584(m), 420 (m). Anal. Calcd. for C₆₂H₁₁₄N₆O₂₅V₆ (TBA₂[H₂1]·2DMF): H, 6.97; C, 45.15; N, 5.10; V, 18.5. Found: H, 6.91; C, 44.97; N, 5.14; V, 18.2.

Because of the disorder in the tetrabutylammonium cations, TBA₂[H₂1] was not optimally modeled by a single-crystal X-ray diffraction study. Thus, a protonated form, H₄1, was prepared for a single-crystal X-ray diffraction study. Several drops of 6N HCl (aq) were added to 5 mL of a solution of TBA₂[H₂1] in DMA (20.0 mM), and the solution was left undisturbed for 72h to produce single crystals suitable for X-ray diffraction. Anal. Calcd. for C₄₂H₇₂N₈O₃₁V₆ (H₄1·6DMA·2H₂O): H, 5.49; C, 37.37; N, 7.26. Found: H, 5.43; C, 37.70; N, 7.41.

Preparation of [Tb(bpdo)₂(H1)]·1.5DMF·3.0EG (Tb1, bpdo = 4,4'-bipyridyl-N,N'-dioxide and EG = ethylene glycol). Crystalline **Tb1** was prepared by a slow diffusion of reactants by making three liquid layers: a Tb(NO₃)₃ solution (DMF/EG = 1:1) on the bottom, a mixed solvent (DMF/EG = 2/1) separating phase in the middle, and a bpdo and TBA₂[H₂1] solution in DMF on top of the mixed solvent layer. The crystallization conditions were optimized by varying the density of the three layers and the height of the solvent layer. The actual procedure entailed initial layering of the DMF/EG; v/v = 2/1 mixed solvent (32 mL) on top of a Tb(NO₃)₃ solution (2.5 mM, 32.0 mL in a DMF/EG; v/v = 1/1). A mixed solution of TBA₂[H₂1] (5.0 mM in 16 mL of

DMF) and bpdo (6.0 mM in 38 mL of DMF) was then slowly layered on top of the middle separation phase using a Pasteur pipette. The three-layer system was allowed to stand undisturbed for 5 days. Red crystals were filtered, washed with MeOH and ether (yield: 64 mg, 43%), and air-dried. FT-IR (KBr, 400-4000 cm^{-1}): 3402 (s, br), 3111 (w), 2924 (m), 2853 (w), 1654 (s), 1531 (w), 1470 (s), 1419 (s), 1228 (s), 1179 (m), 1074 (m), 1031 (m), 955 (s), 838 (m), 807 (m), 797 (m), 584 (w), 558 (w), 421 (m). Anal. Calcd. for $\text{C}_{54.5}\text{H}_{71.5}\text{N}_{7.5}\text{O}_{34.5}\text{V}_6\text{Tb}$: C, 35.42; H, 3.90; N, 5.68; V, 16.5; Tb, 8.6. Found: C, 35.51; H, 4.02; N, 5.60; V, 16.0; Tb, 8.5

Gas adsorption isotherms. Gas adsorption isotherms were collected on a Micrometrics ASAP 2010 instrument for nitrogen (at 77 K) and a Quantachrome NOVA 2200 instrument for carbon dioxide (at 273K) by a volumetric method. The gases used were supplied by Specialty Gas Southeast Inc. and were of the following purity: nitrogen (UHP grade) and carbon dioxide (ultra laser grade, 99.996%). A known weight (120-130 mg) of the as-synthesized sample was placed in a standard 9 mm cell, then prior to measurements, the sample was dried under vacuum (*ca.* 10^{-3} torr) at 333 K for 1 day to remove the solvent molecules. The adsorbate was placed into the sample tube, then the change in pressure was monitored and the degree of adsorption was determined by the decrease in pressure at equilibrium. ^1H NMR analysis indicated that some DMF molecules remained in the pores of the sample after the evacuation. The DMF molecules could not be removed even after an extensive treatment at 373 K under vacuum (*ca.* 10^{-3} torr).

Solvent-exchange experiment. The as-made **Tb1** (200 mg) was suspended in acetonitrile for 4 days, and the solvent was replaced with fresh solvent every 24 h. ^1H NMR established that other solvents including methanol, chloroform, acetone, and dichloroethane were unable to completely replace the pore-filling DMF molecules. The solvent-exchanged **Tb1** was air-dried for 48 h, and then elemental analysis of **Tb1** was

performed to determine the amount of acetonitrile in the material. Anal. Calcd. for $C_{50}H_{57}N_9O_{27}V_6Tb$: C, 35.73; H, 3.47; N, 7.50. Found: C, 35.51; H, 3.42; N, 7.60.

Catalytic studies. In a typical PrSH oxidation experiment, 30.0 μ L (3.31×10^{-4} mol) of PrSH, 6.0 μ L (3.1×10^{-5} mol) of decane (internal standard), and 14 mg (7.4×10^{-6} mol) of the catalyst (molar equivalents of V_6 groups in **Tb1**) were stirred in 2.94 mL of chlorobenzene in a schlenk tube fitted with a plug made of PTFE under air at 45 °C. Aliquots were taken over a period of 70h, and the products were quantified by GC. For the recovery-and-reuse experiment, **Tb1** was separated by centrifugation after reaction, rinsed thoroughly, and then re-suspended in a freshly-prepared reaction mixture. In a higher turnover study, 60.0 μ L (6.62×10^{-4} mol) of PrSH, 18.0 μ L (6.2×10^{-5} mol) of decane (internal standard), and 14 mg (7.4×10^{-6} mol) of the catalyst were stirred in 2.92 mL of chlorobenzene in a schlenk tube fitted with a plug made of PTFE under dioxygen at 45 °C for 30 days. In a tetrahydrothiophene (THT) oxidation experiment, 30.0 μ L (3.37×10^{-4} mol) of THT, 9.0 μ L (4.62×10^{-5} mol) of decane (internal standard), 52.0 μ L, (3.76×10^{-4} mol) of TBHP (70% in water), and the catalyst 14 mg (7.4×10^{-6} mol; molar equivalents of V_6 groups in **Tb1**) were stirred in 2.9 mL of acetonitrile in a vial fitted with a PTFE septum at 50 °C. Aliquots were taken over a period of 70 h, and the products were quantified by GC.

X-ray Crystallography. Suitable crystals of **H41** and **Tb1** were coated with Paratone N oil, suspended on a small fiber loop, and placed in a cooled nitrogen stream at 100 K on a Bruker D8 SMART APEX CCD sealed tube diffractometer with graphite monochromated Mo $K\alpha$ (0.71073 Å) radiation. Redundant data were measured using a series of combinations of ϕ and ω scans with 10 s frame exposures and 0.3° frame widths. Data collection, indexing, and initial cell refinements were handled using SMART software (Version 5.628, Bruker AXS, Inc.) Frame integration and final cell refinements were carried out using SAINT software (Version 6.36A, Bruker AXS, Inc.). The final

cell parameters were determined from least-squares refinements and the SADABS program (Version 2.10, George Sheldrick, University of Göttingen) was used to carry out absorption corrections. The structures were solved using direct methods and difference Fourier techniques. In the case of **H41**, all atoms were refined anisotropically, and hydrogens were located on the calculated position as a riding model. In the case of **Tb1**, all non-hydrogen atoms in the framework structure except the two benzene ring moieties from the polyoxovanadate unit were refined anisotropically. The carbons in the two benzene ring moieties were refined isotropically. Only one solvent DMF molecule in the void space was reasonably modeled. The high R value reflects the large number of disordered and dynamic solvent molecules in the channels, a situation that is common for crystals of highly porous materials. The contribution from the solvent molecules to the R value was largely removed by using the SQUEEZE subroutine of PLATON. The improved R value and reduced residual electron density for the “SQUEEZED” structure also indicate that the primary uncertainty in the structure clearly originates from the disordered DMF molecules in the pores of **Tb1**. Table S1 gives the structural parameters and data for **Tb1** determination before and after being subjected to the SQUEEZE subroutine of PLATON (see Table S1).

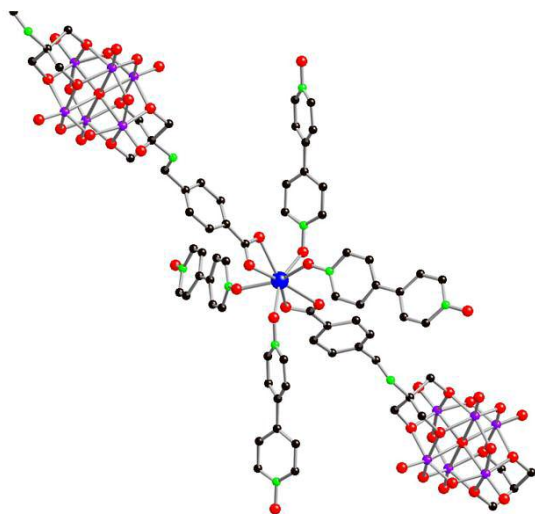


Figure S1. The terbium coordination environment in **Tb1**. Hydrogen atoms are omitted for clarity. Atom coding: terbium (blue), nitrogen (green), oxygen (red), carbon (black), and vanadium (purple).

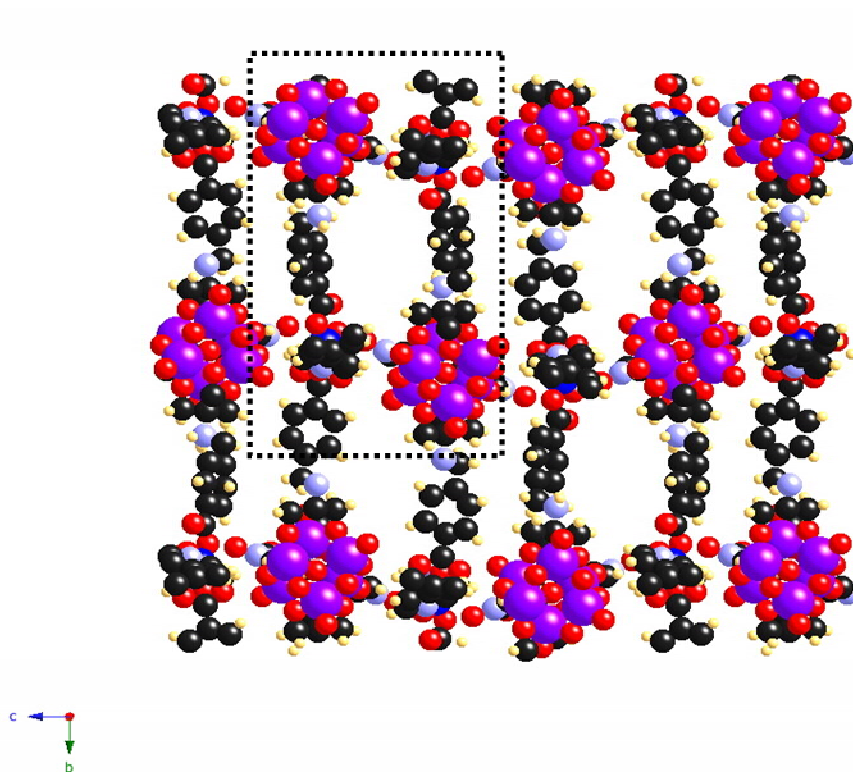


Figure S2. Space-filling model showing the channel structure in **Tb1** viewed down the crystallographic a axis. In the largest channel marked by a dotted line, the longest dimension is 8.0 Å and the shortest dimension is 5.2 Å. Color coding: red (oxygen), black (carbon), orange-yellow (hydrogen), light blue (nitrogen), blue (terbium), and purple (vanadium).

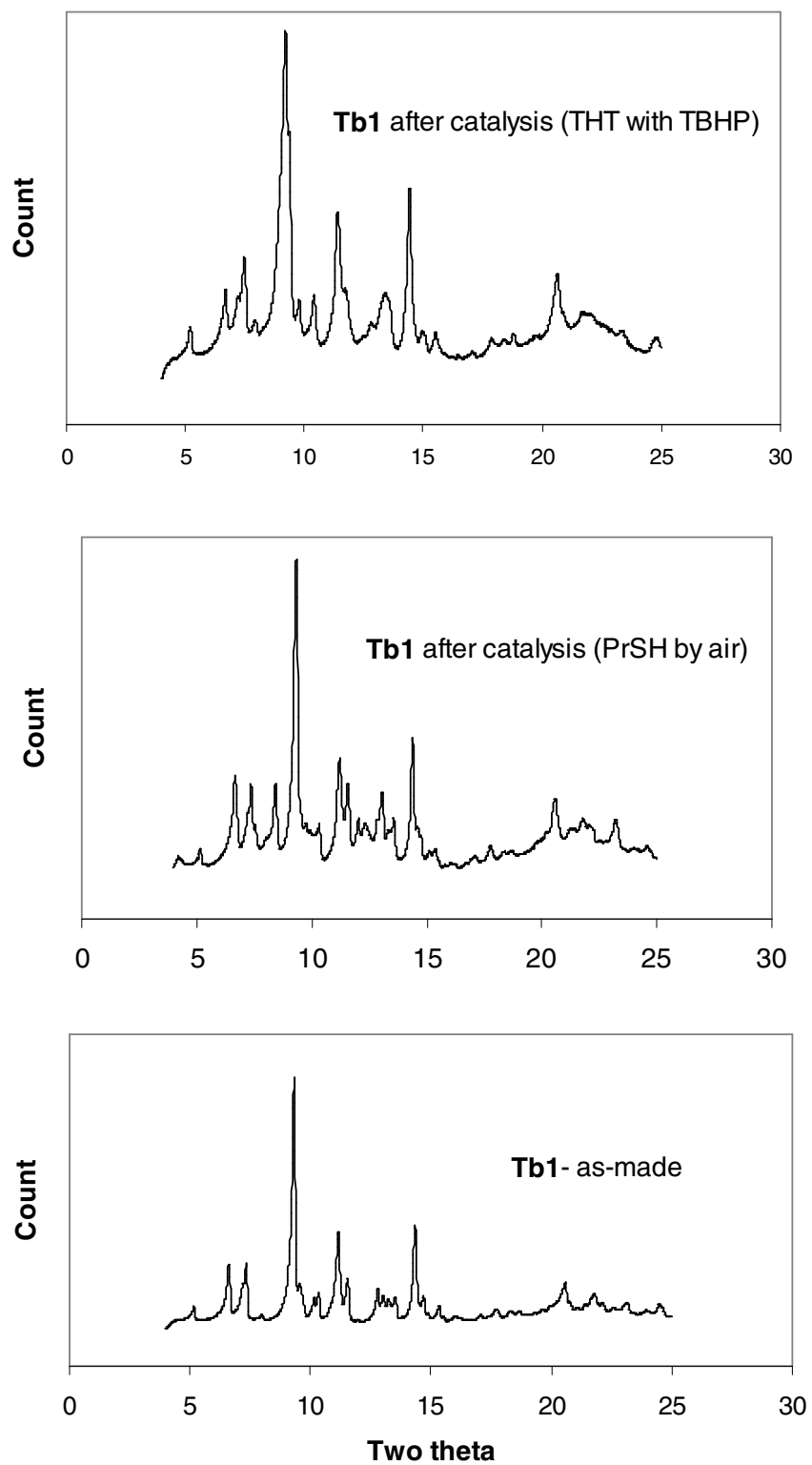


Figure S3. Powder XRD before and after catalysis.

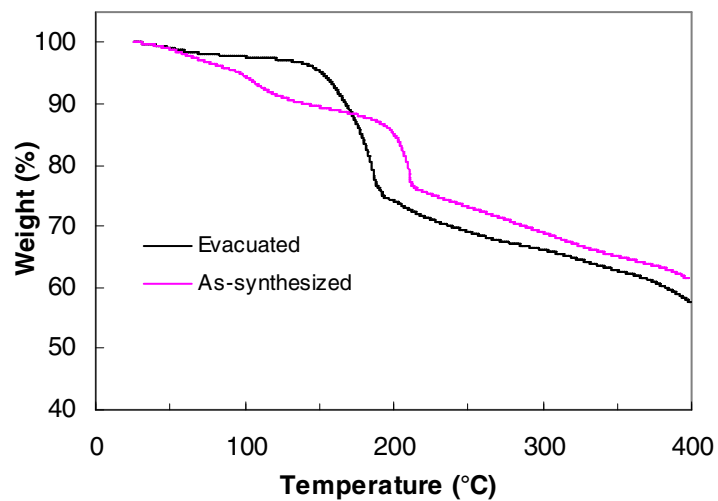


Figure S4. Thermogravimetric analysis (TGA) traces for the as-synthesized and the (partially) pore-evacuated **Tb1**.

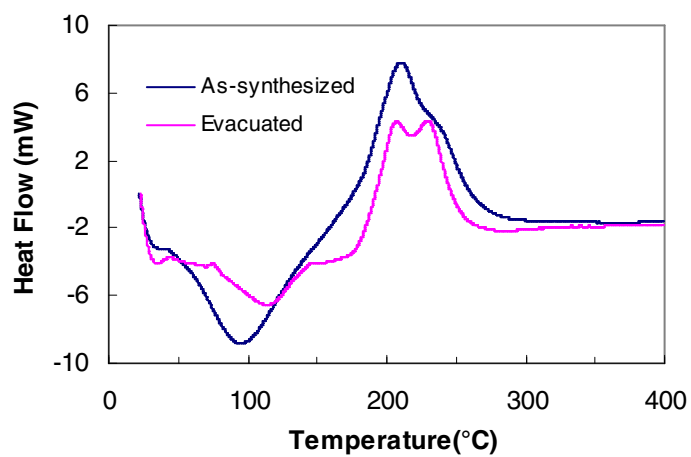


Figure S5. Differential scanning calorimetry (DSC) traces for the as-synthesized and the (partially) pore-evacuated **Tb1**.

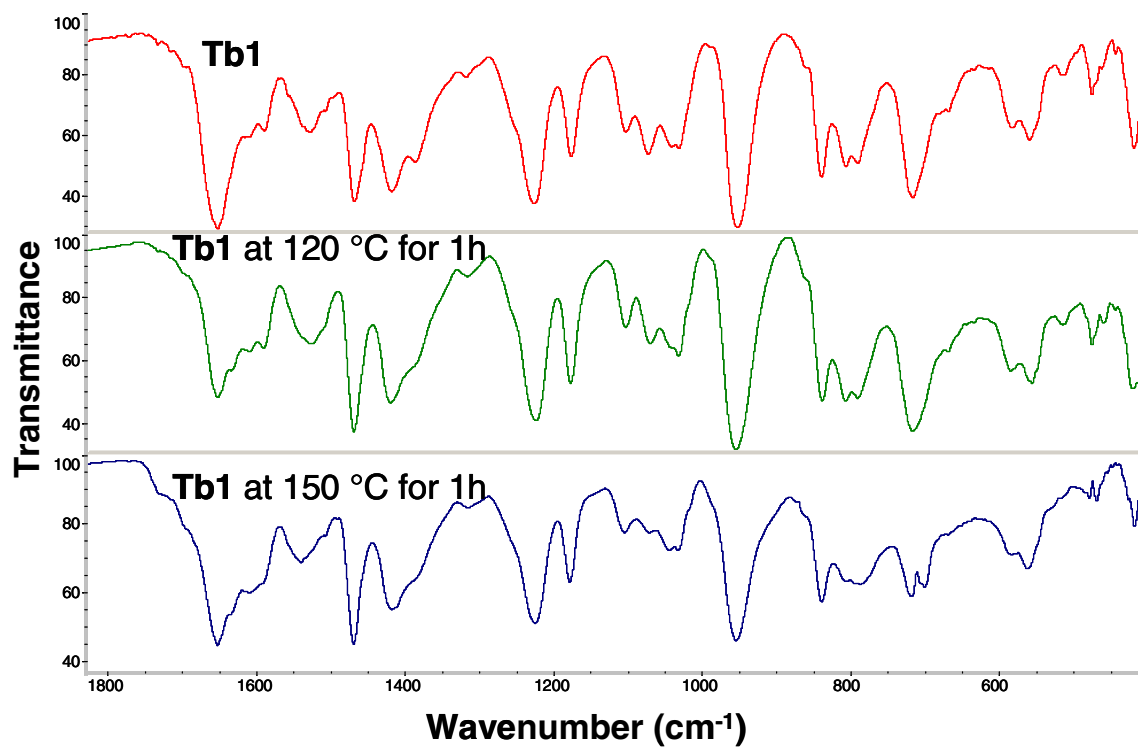


Figure S6. Infrared spectra of **Tb1** as a function of temperature.

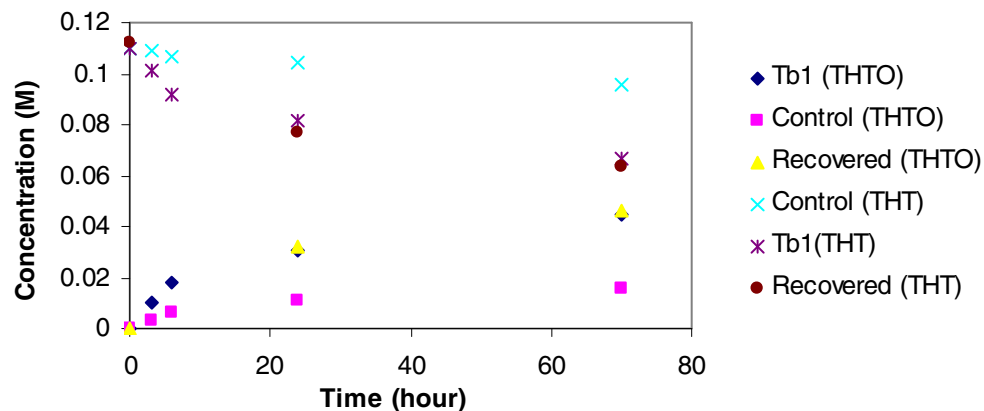


Figure S7. Oxidation of tetrahydrothiophene (THT) by *tert*-butylhydroperoxide (TBHP) catalyzed by **Tb1** (**Tb1** = [Tb(bpdo)₂(**H1**)]·1.5 DMF·3.5EG). The catalyst (0.0074 mmol or milli-equivalents of V₆ units in **Tb1**), THT (0.337 mmol, 0.112 M), decane (internal standard), and TBHP (70% in water, 0.376 mmol, 0.125 M) were stirred in acetonitrile in a vial fitted with a PTFE septum at 50 °C. A control reaction was run under identical reaction conditions except without the catalyst, **Tb1**. Yield 40.7% (41.0 % with recovered **Tb1**).

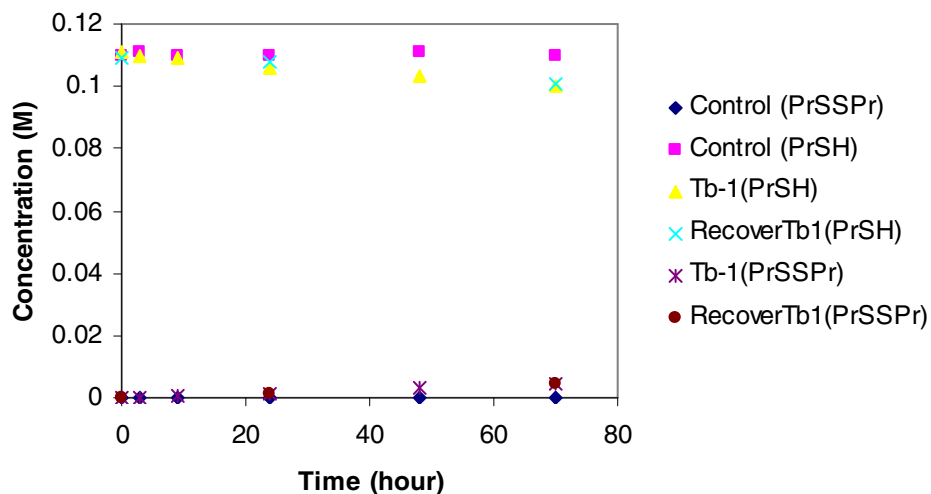


Figure S8. Aerobic oxidation of PrSH catalyzed by **Tb1**. PrSH (0.662 mmol, 0.220 M) decane (internal standard), and the catalyst (0.0074 mmol or milli-equivalents of V_6 units in **Tb1**), were stirred in chlorobenzene in a schlenk tube fitted with a PTFE plug under air at 45 °C. A control reaction was run under identical reaction conditions except without the catalyst, **Tb1**. Yield 8.8% (8.6% with recovered **Tb1**).

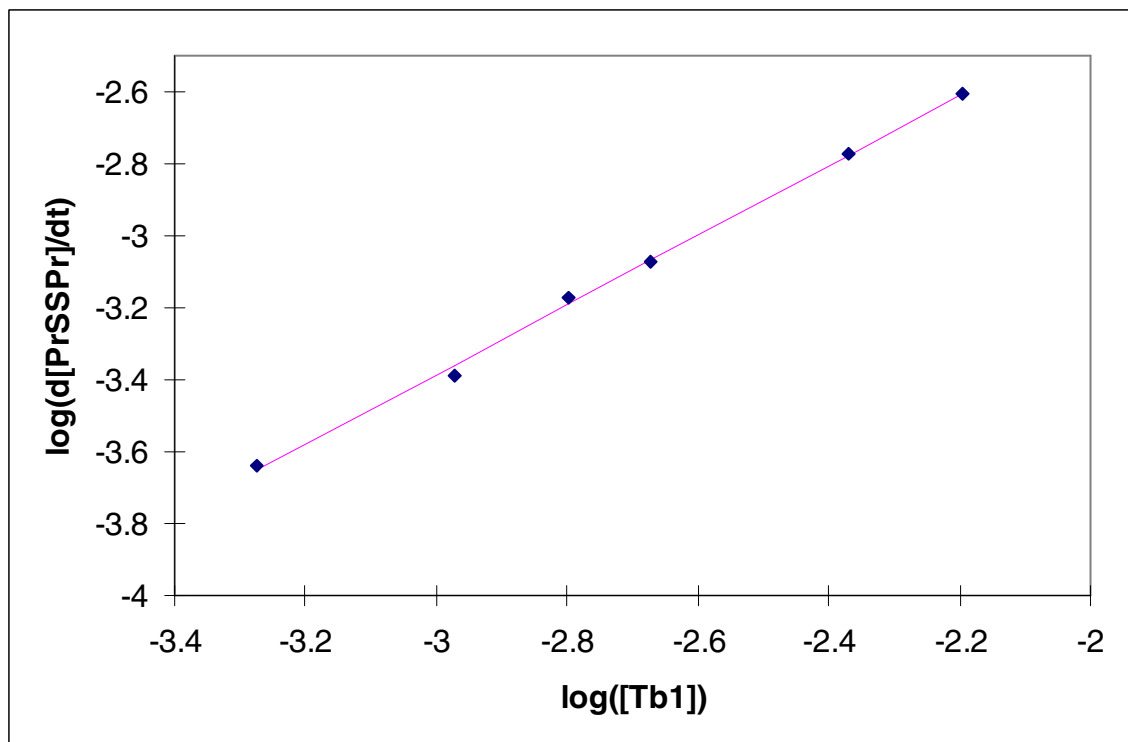


Figure S9. Kinetic van't Hoff plot for the formation of PrSSPr as a function of **[Tb1]**. Conditions for all 6 reactions: $[\text{PrSH}] = 0.20 \text{ M}$; 45°C ; 1 atm of air; 48 h. The points are based on initial rates. The slope is 0.968 with $R^2 = 0.998$ establishing that the reaction is first order in **Tb1**.

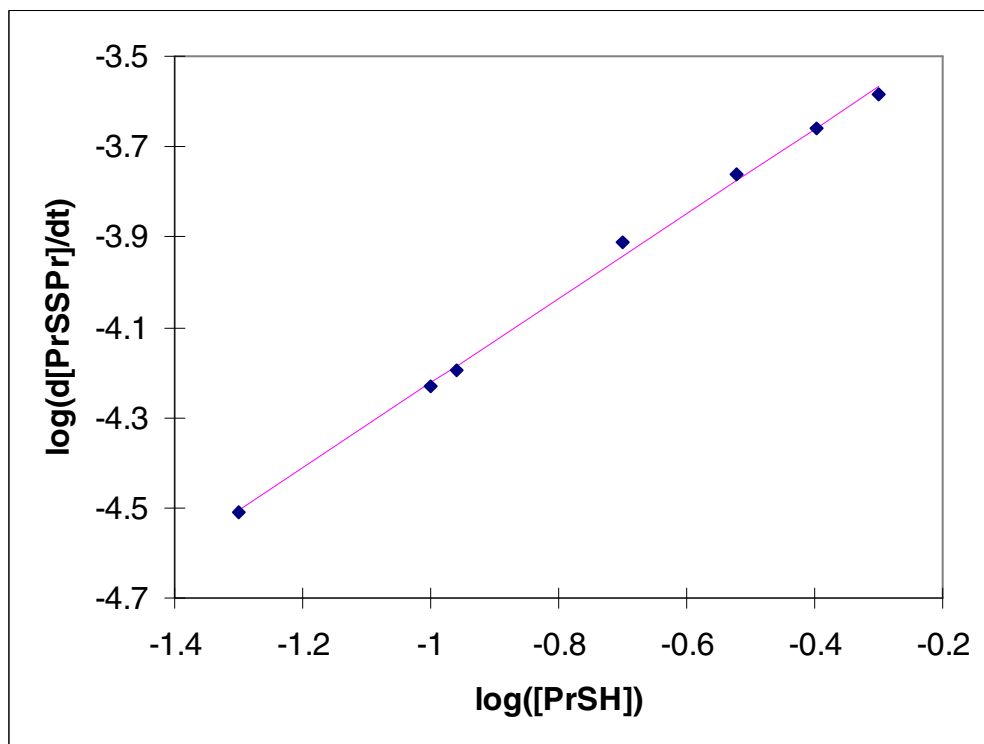


Figure S10. Kinetic van't Hoff plot for the formation of PrSSPr as a function of [PrSH]. Conditions for all 6 reactions: [Tb1] = 0.00030 M; 45 °C; 1 atm of air; 48 h. The points are based on initial rates. The slope is 0.960 with $R^2 = 0.998$ establishing that the reaction is first order in PrSH substrate.

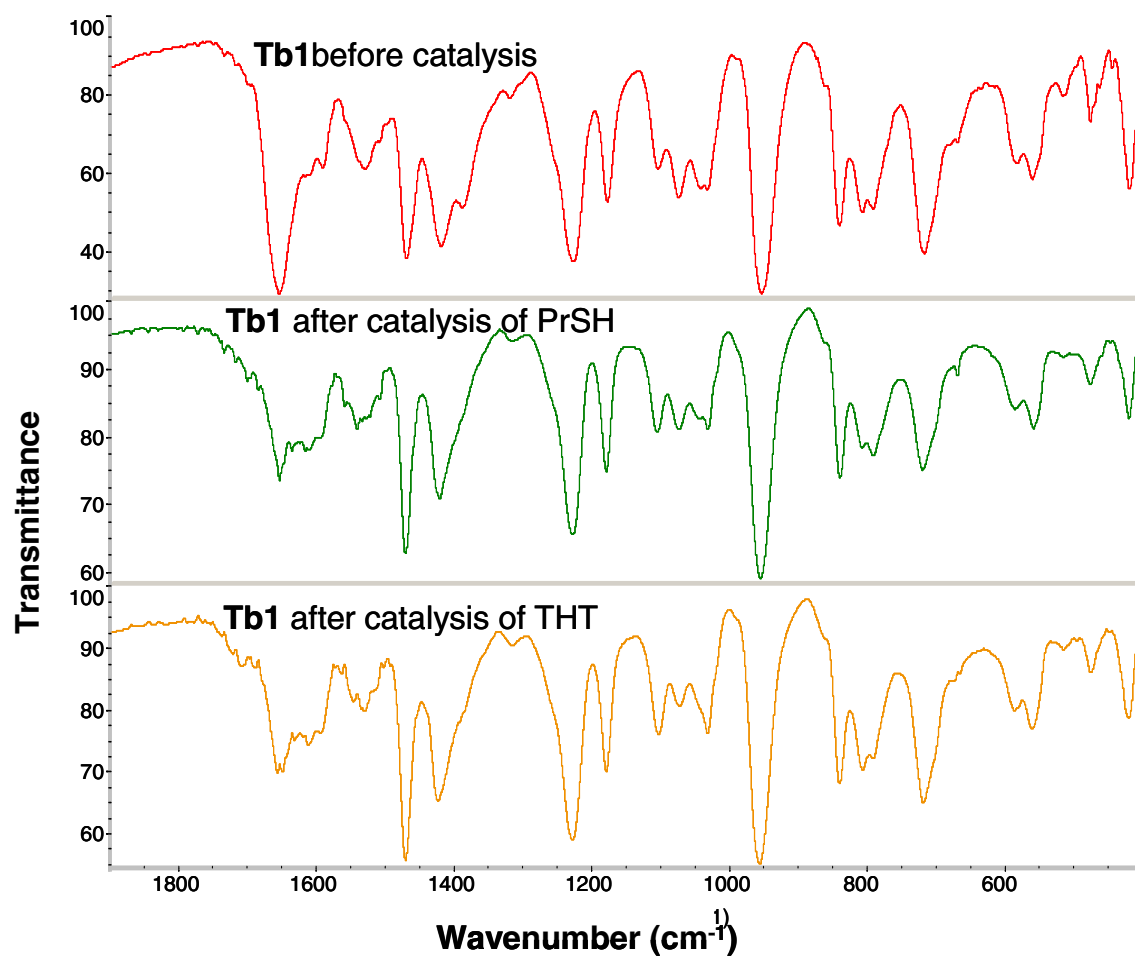


Figure S11. IR spectra of **Tb1** before and after catalysis

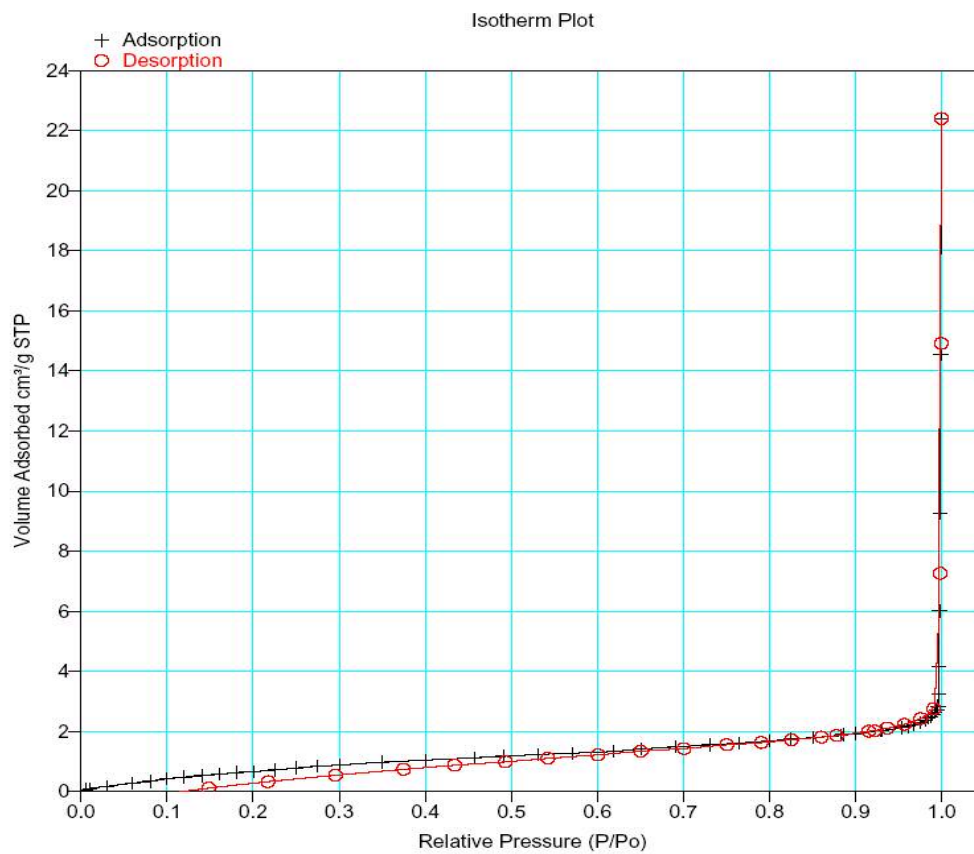


Figure S12. N₂ adsorption isotherm for **Tb1** at 78 K

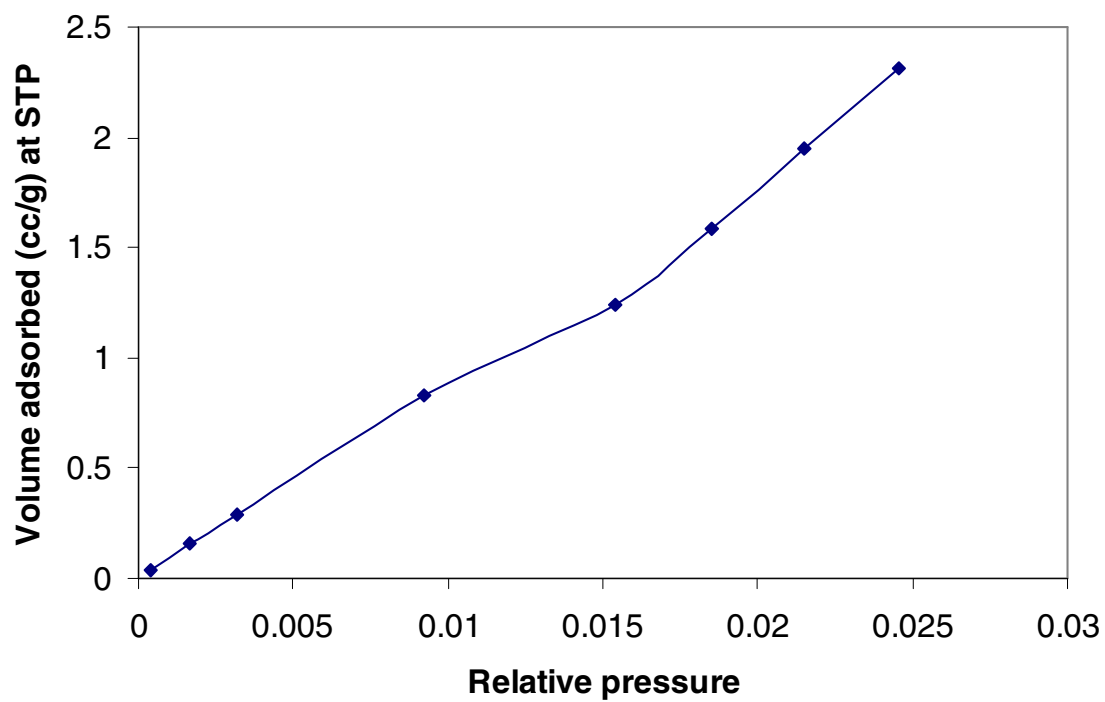


Figure S13. CO₂ adsorption isotherm of **Tb1** at 273 K

	H₄1	Tb1
Empirical formula	C ₄₀ H ₆₆ N ₆ O ₂₇ V ₆	C _{45.20} H _{44.80} N _{6.40} O _{27.40} Tb V ₆
Formula mass	1368.63	1580.65
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /n	P2 ₁ /c
a (Å)	15.6765(11)	13.102(4)
b (Å)	9.0718(7)	26.279(9)
c (Å)	19.8944(14)	26.104(6)
α (°)	90	90
β (°)	108.464(2)	93.923(5)
γ (°)	90	90
V (Å ³)	2683.6(3)	8967(5)
Z	4	4
D _{calcd} (Mg/m ³)	1.694	1.646
μ (mm ⁻¹)	1.095	1.171
Refl. collected	46422	34327
Independent reflections	9783	10930
R(int)	0.1018	0.0988
GOF on F^2	1.009	1.136
R1 (I > 2 σ (I)) ^a	0.0545	0.1378 [0.0879]
wR2 (I > 2 σ (I)) ^a	0.1016	0.3474 [0.2295]

Table S1. Crystallographic information on **H₄1** and **Tb1** (before and after SQUEEZE treatment). ^a Statistics following treatment of the data using the SQUEEZE subroutine of PLATON are bracketed.