

Supporting Information:

Stabilizing Single Sites on Solid Supports: Robust Grafted Ti(IV)-Calixarene Olefin Epoxidation Catalysts via Surface Polymerization and Crosslinking

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Supporting information

Materials and General Methods.

Mesoporous SiO₂ (Selecto Scientist) support consists of a 32-63 μm silica particle size, possesses a N₂ BET surface area of 498 m²/g, and produces pH ~ 7 as a 5% suspension in H₂O

(0.877 mol/L). Before being used as a catalyst support, the mesoporous SiO₂ was dehydroxylated in a quartz Schlenk tube at 800 °C for 4 h by flowing a mixture of dry air and Ar, and was subsequently stored in a N₂-filled glovebox prior to use. The resulting hydroxylated material is denoted as SiO₂@800. Toluene (Aldrich) and octane (Aldrich) were freshly distilled over Na prior to use. Styrene ($\geq 99\%$, Aldrich) and 1,3-diisopropenylbenzene (97%, Aldrich) were passed through a basic Al₂O₃ column, dried with CaH₂, and purified via vapor transfer. B(C₆F₅)₃ ($\geq 95\%$, Aldrich), Ti(O^{*i*}Pr)₄ (97%, Aldrich) and poly(tetrafluoroethylene) (powder, Aldrich) were used as received.

The content of grafted organic species (i.e. grafted calixarene ligands and their polymerized derivatives) in catalysts was determined by thermogravimetric analysis (TGA; Netzsch 449C Jupiter TGA) in a mixed gas flow consisting of 20% O₂ and 80% Ar. The temperature program consists of: (i) heating at 5 °C/min to 120 °C and holding for 60 min and (ii) heating at 5 °C/min up to a final temperature of 800 °C. Ti loadings in the catalysts were measured using a UV-Vis spectrophotometric technique as previously described,²⁷ along with confirmatory ICP/MS^{17,18} for Ia and IIa. The spectrophotometric technique consisted of four steps: (1) extract Ti from ~ 10 mg of calcined samples (after TGA) using 1 mL of H₂SO₄ for 1 h, (2) add 0.14 mL of H₂O₂ (30 wt% in H₂O, Aldrich), (3) dilute the solution to a desired range of Ti concentrations with deionized H₂O, and (4) measure the concentration of extracted Ti using Ultraviolet-Visible (UV-Vis) spectroscopy (Varian Cary 4000 Bio UV-visible spectrometer) at the absorption of $\lambda_{\text{max}} = 408$ nm, and calculated the Ti loadings of the catalysts based on the UV-Vis data. Diffuse reflectance UV-Vis spectra were collected on the same Varian Cary 4000 Bio UV-visible spectrometer. We used poly(tetrafluoroethylene) for baseline correction. Solid-state ¹³C CP/MAS NMR spectroscopy was performed at the Caltech Solid-State NMR facility

using a Bruker DSX500 spectrometer and a Bruker 4 mm magic angle spinning probe. The spectral frequencies were 125.5 MHz for ^{13}C nuclei. Typically about 70 mg of samples were packed into zirconia rotors and spun at 8 kHz at ambient condition. Nitrogen physisorption isotherms were measured on a Micromeritics ASAP2020 instrument at 77 K. Prior to measurement, samples were evacuated at 120 °C for 2 h. The pore size distributions were calculated by the non-local density functional (NLDFT) method based on measured nitrogen adsorption data.

Synthesis and Grafting of Ti(OⁱPr)-Calixarene Complex.

[Ti(OⁱPr)(Methoxycalix)] was synthesized and grafted onto SiO₂@800 according to published procedures.⁸ The synthesis of the vinyl-calixarene ligand proceeded as follows. To a stirred suspension of CsF (0.61g, 4 mmol) in 15 mL of DMF, tetra-tert-butyl-calix[4]arene (2.0g, 3.08 mmol) was added. After 20 min at 60 °C, 5-bromo-1-pentene (0.46g, 4.0 mmol) was added to the suspension, and allowed to stir for an additional 18 h. The reaction mixture was poured into 100 mL of deionized H₂O and extracted with chloroform. The chloroform phase was separated and dried over Na₂SO₄ overnight. After filtration and evaporation of organic solvent, a white solid was produced. Final purification was performed with column chromatography using a mixture of dichloromethane/n-hexane (1:0.6 v/v) as an eluent (R_f 0.8, 2nd spot). A white solid was finally recrystallized using acetonitrile. Yield 47 % (1.04g). ¹H NMR (CDCl₃) δ 10.19 (s, 1H, OH), 9.59 (s, 2H, OH), 7.08 (s, 2H, ArH), 7.05 (m, 4H, ArH), 6.98 (s, 2H, ArH), 5.95 (m, 1H, CH), 5.21 (m, 1H, CH₂=), 5.08 (m, 1H, CH₂=), 4.34 (d, 2H, 2J = 13.2 Hz, ArCH₂Ar), 4.27

(d, 2H, 2J = 13.8 Hz, ArCH₂Ar), 4.13 (t, 2H, 3J = 7.2 Hz, OCH₂), 3.42 (m, 4H, ArCH₂Ar), 2.46 (m, 2H, CH₂), 2.26 (m, 2H, CH₂), 1.20, 1.21, 1.22 (three s, 36H, t-C₄H₉).

Synthesis of [TiOⁱPr(Vinylcalix)]. Ti(OⁱPr)₄ (100.0 mg, 0.35 mmol) was added to a stirred toluene solution (3 mL) of 5,11,17,23-Tetra-tert-butyl-25,26,27-trihydroxy-28-pentenoxy-calix[4]arene (252.4 mg, 0.35 mmol). The resulting solution was stirred at 28 °C for 16 h. The resulting solid product, [TiOⁱPr(Pentenoxycalix)], was recovered by removing the solvent under vacuum. The obtained Ti(IV)-vinyl-calixarene was grafted onto SiO₂@800 using a similar procedure as previously described for alkyl-substituted calixarenes.^{16,17} 1 g of SiO₂@800 and a magnetic stir bar were first loaded in a 25 mL air-free glass reactor in an air- and moisture-free glovebox. This reaction flask was then transferred to the Schlenk line which was filled with Ar. Ti(IV)-vinyl-calixarene (115 mg, 0.14 mmol) in 8 mL of toluene solution was added to the reactor and the resulting silica slurry was stirred under Ar for 4 h. The solution was then decanted with freshly distilled toluene for at least five times until the supernatant solution is colorless. Finally, the resulting solid product (**IIa**) was recovered by filtration and dried under vacuum at RT overnight and at 120 °C for 1 h.

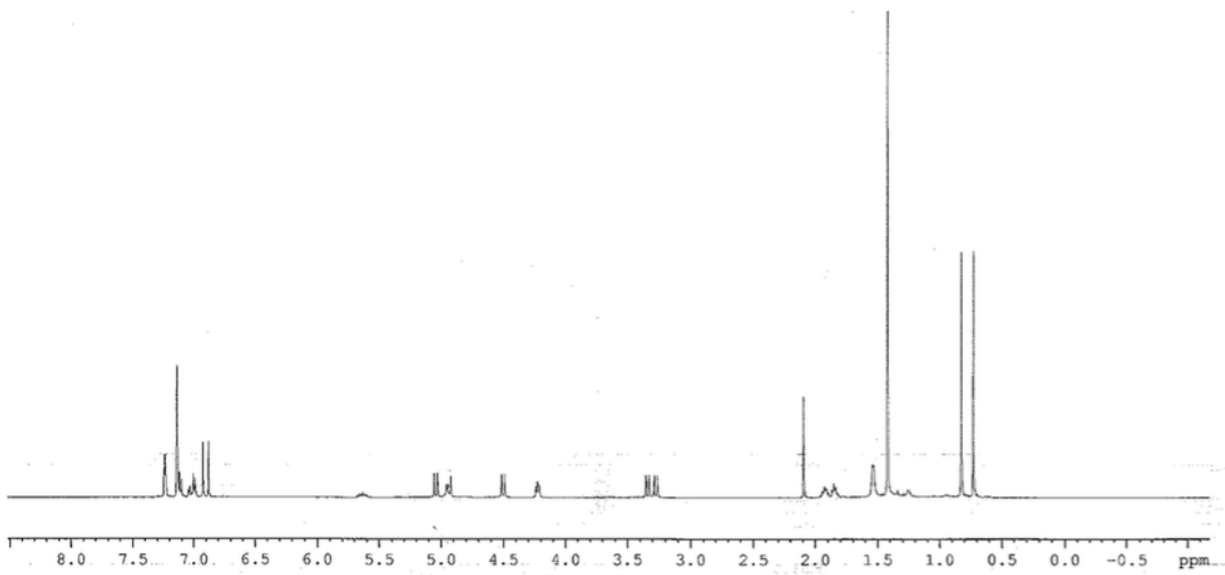


Figure S1. ^1H NMR spectrum of 5,11,17,23-Tetra-tert-butyl-25,26,27-trihydroxy-28-pentenoxy-Ti(IV)-calix[4]arene (**TiO¹Pr(vinylcalix)**) precursor.

NMR spectra were recorded on either a Bruker AVQ-400 or DRX-500 instrument. Solvent residual peak of benzene (7.16 ppm) in benzene- d_6 was used as internal standard.

^1H NMR (benzene- d_6): δ 7.34 (m, 4H, ArH), 7.02 (s, 2H, ArH), 6.98 (s, 2H, ArH), 5.71 (m, 1H, $\text{CH}=\text{CH}_2$), 5.14 (d, 2H, $^2J = 12.0$ Hz, ArCH_2Ar), 5.04 (m, 3H, $\text{TiOCH}(\text{CH}_3)_2 + \text{CH}=\text{CH}_2$), 4.60 (d, 2H, $^2J = 12.0$ Hz, ArCH_2Ar), 4.23 (m, 2H, OCH_2), 3.44 (d, 2H, $^2J = 12.0$ Hz, ArCH_2Ar), 3.37 (d, 2H, $^2J = 12.0$ Hz, ArCH_2Ar), 1.92 (m, 2H, CH_2), 1.86 (m, 2H, CH_2), 1.53 (m, 6H, CH_3CH), 1.43 (s, 18H, t-Bu), 0.82 (s, 9H, t-Bu), 0.76 (s, 9H, t-Bu).

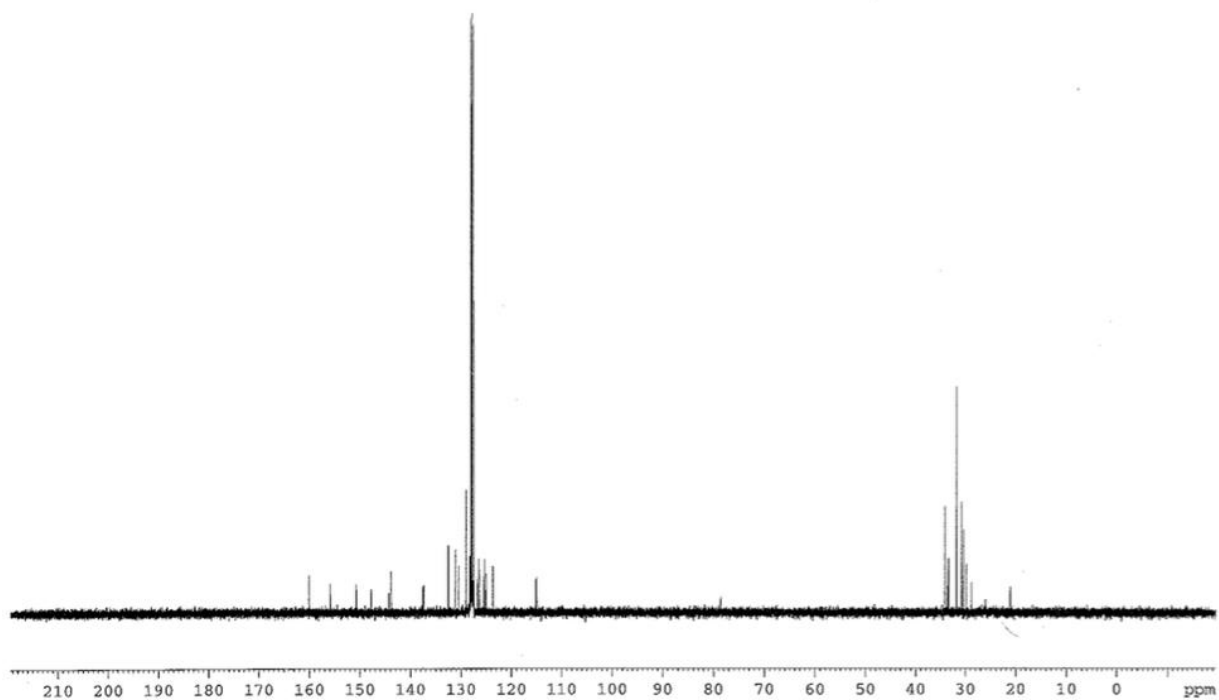


Figure S2. ^{13}C NMR spectrum of 5,11,17,23-Tetra-tert-butyl-25,26,27-trihydroxy-28-pentenoxy-Ti(IV)-calix[4]arene.

^{13}C NMR (benzene- d_6): δ 160.01, 155.87, 150.68, 147.77, 144.21, 143.81, 137.57, 132.47, 131.10, 130.49, 129.02, 128.25, 127.98, 126.80, 126.44, 125.42, 125.38, 125.03, 123.65, 115.08, 78.57, 34.13, 34.10, 33.61, 33.42, 33.34, 31.78, 30.78, 30.40, 29.79, 28.77, 26.04, 21.12.

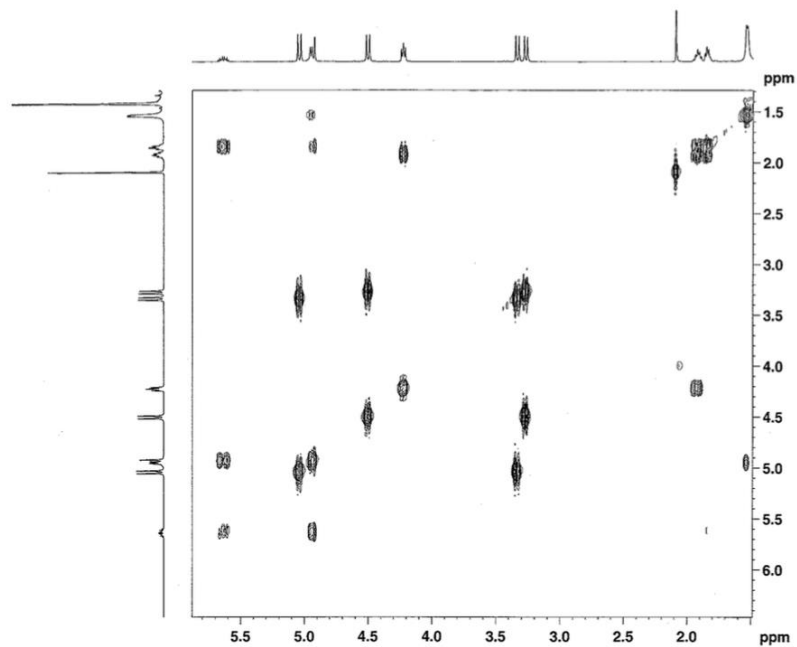
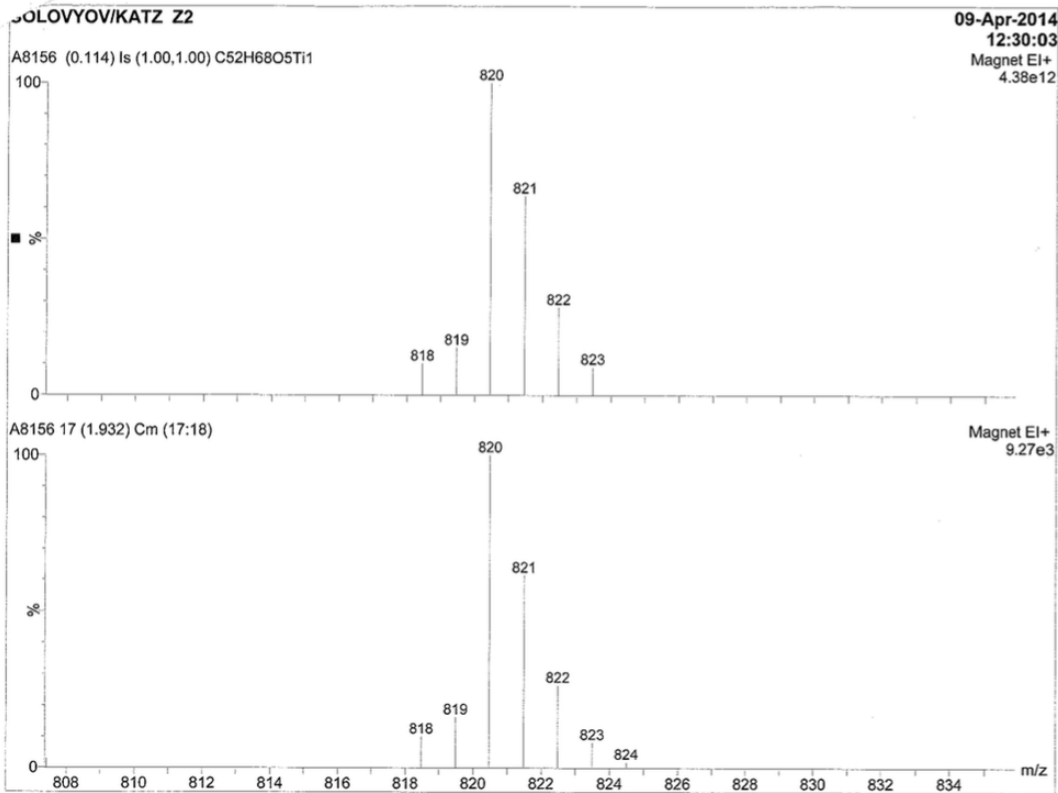
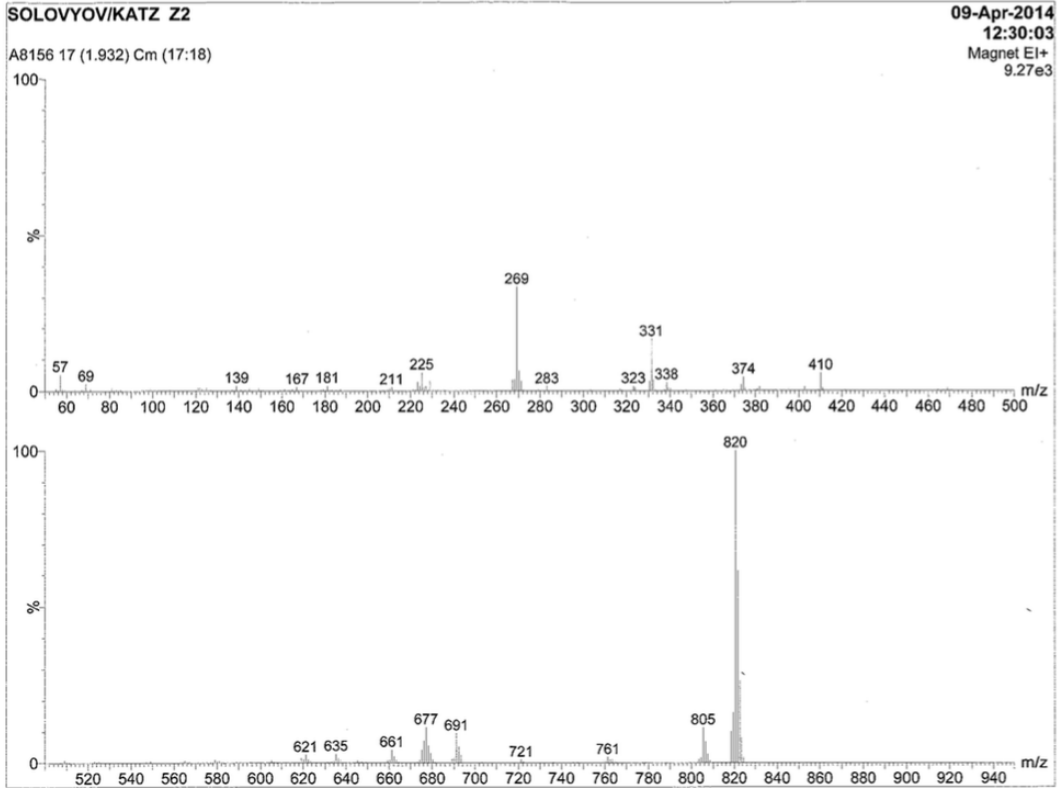


Figure S3. ^1H - ^1H 2D COSY NMR spectrum of 5,11,17,23-Tetra-tert-butyl-25,26,27-trihydroxy-28-pentenoxy-Ti(IV)-calix[4]arene.



Multiple Mass Analysis: 2 mass(es) processed

Tolerance = 200.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

6614 formula(e) evaluated with 359 results within limits (up to 50 closest results for each mass)

Elements Used:

12C: 0-60 13C: 0-1 H: 0-200 O: 0-6 48Ti: 0-1 49Ti: 0-1

SOLOVYOV/KATZ Z2

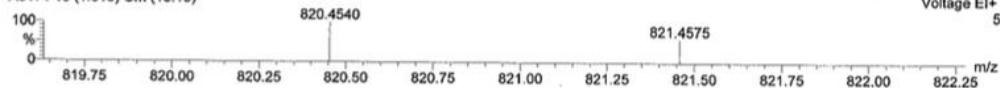
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11:38:50

Voltage EI+

5

A8171 19 (1.616) Cm (18:19)



Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
820.4540	100.00	820.4546	-0.6	-0.7	19.0	12.8	12C52 H68 O5 48Ti
		820.4522	1.8	2.2	9.5	12.9	12C46 H75 O6 48Ti 49Ti
		820.4575	-3.5	-4.3	24.0	13.8	12C55 13C H66 O2 49Ti
		820.4502	3.8	4.6	19.5	13.1	12C51 13C H67 O5 48Ti
		820.4492	4.8	5.9	29.0	12.9	12C58 H60 O4
		820.4487	5.3	6.5	28.0	12.6	12C59 H64 48Ti
		820.4477	6.3	7.7	10.0	13.2	12C45 13C H74 O6 48Ti
							49Ti
		820.4467	7.3	8.9	19.5	13.1	12C52 H67 O5 49Ti
		820.4463	7.7	9.4	18.5	12.8	12C53 H71 O 48Ti 49Ti
		820.4620	-8.0	-9.8	23.5	13.5	12C56 H67 O2 49Ti
		820.4630	-9.0	-11.0	14.0	13.6	12C49 13C H74 O3 48Ti
							49Ti
		820.4447	9.3	11.3	29.5	13.5	12C57 13C H59 O4
		820.4443	9.7	11.8	28.5	12.9	12C58 13C H63 48Ti
		820.4654	-11.4	-13.9	23.5	13.5	12C55 13C H67 O2 48Ti
		820.4423	11.7	14.3	20.0	13.4	12C51 13C H66 O5 49Ti
		820.4658	-11.8	-14.4	24.5	14.1	12C54 13C H63 O6
		820.4418	12.2	14.9	19.0	13.0	12C52 13C H70 O 48Ti
							49Ti
		820.4408	13.2	16.1	28.5	12.9	12C59 H63 49Ti
		820.4674	-13.4	-16.3	13.5	13.3	12C50 H75 O3 48Ti 49Ti
		820.4699	-15.9	-19.4	23.0	13.1	12C56 H68 O2 48Ti
		820.4703	-16.3	-19.9	24.0	13.5	12C55 H64 O6
		820.4364	17.6	21.5	29.0	13.3	12C58 13C H62 49Ti
		820.4335	20.5	25.0	24.0	12.3	12C55 H64 O3 48Ti
		820.4311	22.9	27.9	14.5	12.4	12C49 H71 O4 48Ti 49Ti
		820.4782	-24.2	-29.5	18.0	14.0	12C53 13C H74 48Ti 49Ti
		820.4786	-24.6	-30.0	19.0	14.4	12C52 13C H70 O4 49Ti
		820.4290	25.0	30.5	24.5	12.6	12C54 13C H63 O3 48Ti
		820.4811	-27.1	-33.0	28.5	14.4	12C58 13C H63 O3
		820.4266	27.4	33.4	15.0	12.7	12C48 13C H70 O4 48Ti
							49Ti
		820.4256	28.4	34.6	24.5	12.6	12C55 H63 O3 49Ti
		820.4827	-28.7	-35.0	17.5	13.7	12C54 H75 48Ti 49Ti
		820.4831	-29.1	-35.5	18.5	14.0	12C53 H71 O4 49Ti
		820.4841	-30.1	-36.7	9.0	14.1	12C46 13C H78 O5 48Ti
							49Ti
		820.4236	30.4	37.1	34.5	13.0	12C60 13C H55 O2
		820.4855	-31.5	-38.4	28.0	13.8	12C59 H64 O3
		820.4865	-32.5	-39.6	18.5	14.0	12C52 13C H71 O4 48Ti
		820.4211	32.9	40.1	25.0	12.9	12C54 13C H62 O3 49Ti
		820.4886	-34.6	-42.2	8.5	13.9	12C47 H79 O5 48Ti 49Ti
		820.4182	35.8	43.6	20.0	11.9	12C51 H64 O6 48Ti
		820.4910	-37.0	-45.1	18.0	13.7	12C53 H72 O4 48Ti
		820.4939	-39.9	-48.6	23.0	14.8	12C56 13C H70 O 49Ti
		820.4138	40.2	49.0	20.5	12.3	12C50 13C H63 O6 48Ti
		820.4128	41.2	50.2	30.0	12.1	12C57 H56 O5
		820.4124	41.6	50.7	29.0	11.8	12C58 H60 O 48Ti
		820.4103	43.7	53.3	20.5	12.3	12C51 H63 O6 49Ti
		820.4099	44.1	53.8	19.5	11.9	12C52 H67 O2 48Ti 49Ti

Figure S4. High-resolution mass spectrum of 5,11,17,23-Tetra-tert-butyl-25,26,27-trihydroxy-28-pentenoxy-Ti(IV)-calix[4]arene.

HR EI+ mass spectra were recorded at the UC Berkeley Mass Spectrometry Facility. High resolution EI+ MS calculated for $C_{52}H_{68}O_5Ti$ was 820.4546, found 820.4540.

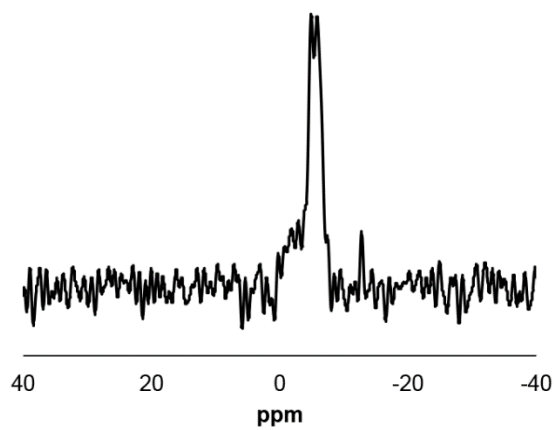


Figure S5. ^{11}B MAS NMR spectrum of **IIc**.

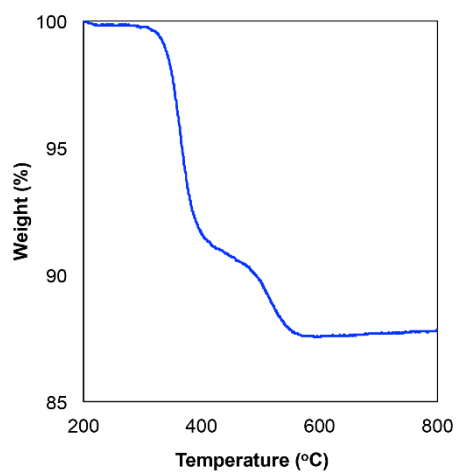


Figure S6. TGA of $\text{SiO}_2@800$ after polymerization with styrene/diisopropenylbenzene.

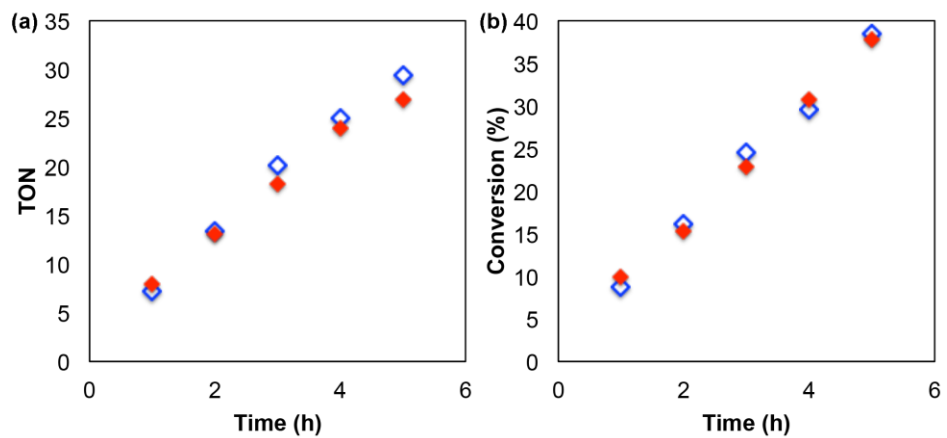


Figure S7. Comparison of **IIa** (hollow blue diamond) with **IIc** (solid red diamond) on SiO_2 support for the 1-octene epoxidation reaction. TON = mol oxidation products / mol Ti.
Conversion (%) = mol TBHP consumed / mol initial TBHP.

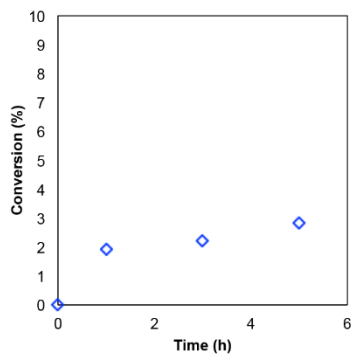


Figure S8. 1-octene epoxidation conversions with $\text{B}(\text{C}_6\text{F}_5)_3$ modified $\text{SiO}_2@800$.

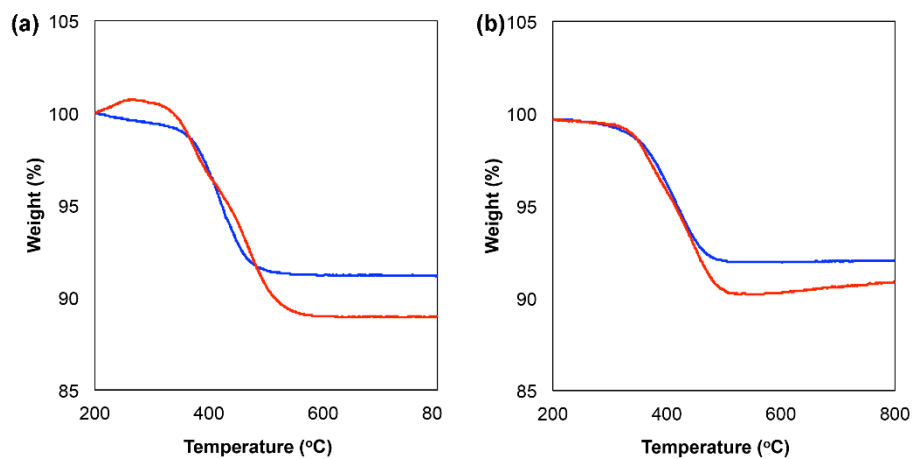


Figure S9. (a) TGA of **Ia** (blue) and **Ic** (red). (b) TGA of **IIa** (blue) and **IIc** (red).

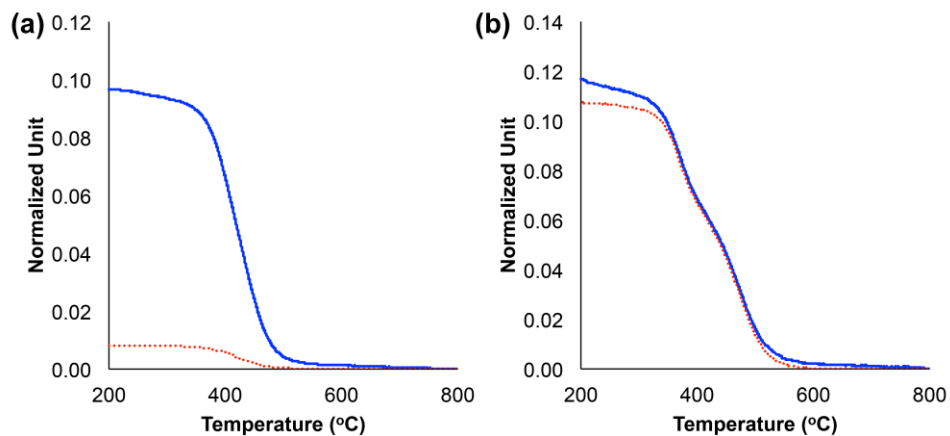


Figure S10. Thermogravimetric analysis of **IIa** and **IIc** before (solid blue line) and after (dashed red line) treated with a mixture of 5 mL isopropanol and 5 mL DI water for 4 h.

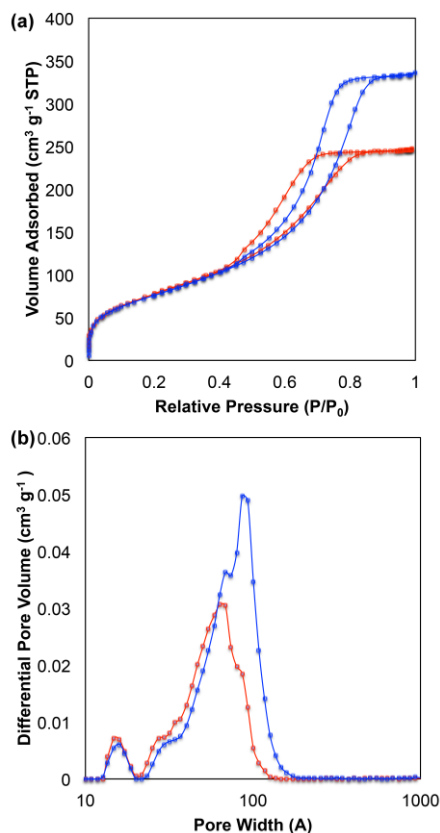


Figure S11. Nitrogen physisorption isotherms of SiO₂@800 before (blue) and after (red) polymerization with styrene/diisopropenylbenzene (a), and their pore size distributions calculated from the NLDFT model using desorption isotherms (b).

$$\text{TGA Normalized Unit} = \frac{1}{100} \left(\frac{\text{Sample mass @ T}}{\text{Sample mass @ 800 } ^\circ\text{C}} - \frac{\text{Control mass @ T}}{\text{Control mass @ 800 } ^\circ\text{C}} \right)$$

Figure S12. TGA normalized unit.

In order to minimize the uncertainty brought by organic adsorption on silica surface, we normalized TGA units following the equation shown above (Fig. S11). The control material refers to a blank silica support that has been dehydroxylated at 800 °C, SiO₂@800, which has no calixarene ligand on the surface. We treat this control sample under the same hydrolytic stress

test conditions mentioned in the experimental section (flow or batch leaching tests) to allow for chemisorption of any protic species as alkoxides on this silica, as would occur in a real catalyst sample.

Sample mass at certain temperature (T) was divided by the sample mass at 800 °C. This results in a relative weight that is referenced to bone-dry silica – a common basis. We did the same calculation for the control sample, where the control mass at certain temperature (T) was divided by the control mass at 800 °C. We then take the difference between these two values and divide it by 100. This yields organic content as a percentage of the amount of bone dry silica in the sample – corrected for any chemisorption that may occur from the protic species in the leaching stress-test solvent.

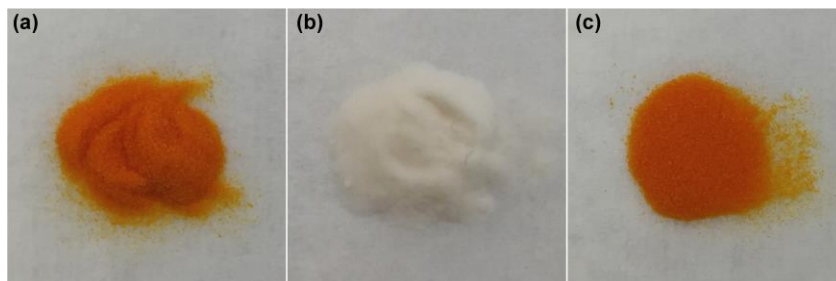


Figure S13. Pictures of catalyst (a) **Ia**, (b) **Ial** and (c) **Icl**.