

## Supporting Information

# Efficient Mukaiyama Aldol Reaction in Water with TiO<sub>4</sub> Tetrahedra on Hydrophobic Mesoporous Silica Surface

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**Figure S1.** (A) Small-angle and (B) wide-angle XRD patterns for (a) TDMS, (b) Propyl-TDMS, (c) Dodecyl-TDMS, (d) Benzyl-TDMS, and (e) Tridecafluoro-TDMS.

**Figure S2.** N<sub>2</sub> adsorption-desorption isotherms for (a) TDMS, (b) Propyl-TDMS, (c) Dodecyl-TDMS, (d) Benzyl-TDMS, and (e) Tridecafluoro-TDMS. Each isotherm is vertically offset by 250 cm<sup>3</sup> g<sup>-1</sup> for clarity.

**Figure S3.** Difference FTIR spectra of CO-adsorbed hydrated SBA-15 and TDMS samples. (a) SBA-15, (b) Propyl-TDMS, (c) Dodecyl-TDMS, (d) Benzyl-TDMS, and (e) Tridecafluoro-TDMS.

**Figure S4.** Catalyst reuse experiment using Tridecafluoro-TDMS for the surfactant-free Mukaiyama-aldol reaction of benzaldehyde with 1-(trimethylsilyloxy)cyclohexene in water.

**Figure S5.** H<sub>2</sub>O adsorption isotherms for the SBA-15 and TDMS samples. (a) SBA-15, (b) bare TDMS, (c) Propyl-TDMS, (d) Dodecyl-TDMS, (e) Benzyl-TDMS, and (f) Tridecafluoro-TDMS.

**Figure S6.** Photograph of TDMS samples suspended in water-ethanol (4:1 vol%) solution. (a) Dodecyl-TDMS, (b) Tridecafluoro--TDMS.

**Figure S7.** Dependence of product yield of bare TDMS for the Mukaiyama-aldol reaction in THF on various water contents.

## **1. EXPERIMENTAL SECTION**

### **1.1 Catalyst Preparation.**

Titanium-deposited mesoporous silica (TDMS) was prepared by the simple impregnation of a titanium complex on mesoporous silica (SBA-15). SBA-15 (5 g) was added to a mixture of distilled water (145 g) and ethanol (15 g). After pH adjustment of the suspension to 10 with diluted ammonia, a mixture of ethanol (5 g), titanium isopropoxide ( $\text{Ti}(i\text{-pro})_4$ ; TTIP), and acetyl acetone (AA) ( $\text{AA}/\text{TTIP} = 3.1$ ) was slowly added to the mixture at 278 K and stirred for 2 h. The solid material recovered by filtration was washed repeatedly with ethanol and then calcined at 823 K for 3 h in air to produce TDMS ( $\text{Ti}/\text{Si} = 1.8 \text{ mol}\%$ ).

Surface modification with hydrophobic organic groups was performed by treatment of the TDMS with various silane coupling agents:  $\text{CH}_3(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$  (propyltrimethoxysilane; Propyl),  $\text{CH}_3(\text{CH}_2)_{11}\text{Si}(\text{OCH}_3)_3$  (dodecyltrimethoxysilane; Dodecyl),  $\text{C}_6\text{H}_5\text{CH}_2\text{Si}(\text{OCH}_3)_3$  (benzyltrimethoxysilane; Benzyl), or  $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{SiCl}_3$  ((1H,1H,2H,2H-tridecafluoro-n-octyl)trichlorosilane; Tridecafluoro). In a typical synthesis, TDMS was heated at 573 K for 1 h to remove physisorbed water. The dehydrated TDMS was then added to a mixture of toluene (25 ml) and an adequate amount of silane coupling agent (0.2-0.4 mmol). After the solution was stirred under reflux for 12 h, the resulting material was recovered by filtration and washed repeatedly with toluene, ethanol, and water, and dried in air at 353 K overnight. The TDMS samples modified with propyl, benzyl, dodecyl, and tridecafluoro-n-octyl groups are denoted as Propyl-TDMS, Benzyl-TDMS, Dodecyl-TDMS, and Tridecafluoro-TDMS, respectively.

## 1.2 Catalyst Characterization.

The titanium content of the samples was determined using X-ray fluorescence spectroscopy (XRF; ZSX100e, Rigaku). Powder X-ray diffraction patterns were obtained with a diffractometer (Ultima IV, Rigaku) using Cu  $K\alpha$  radiation (40 kV, 40 mA) over the  $2\theta$  range of  $0.7\text{--}70^\circ$ . Nitrogen adsorption-desorption isotherms were measured at 77 K with a surface area analyzer (Nova-4200e, Quantachrome). Prior to measurement, the samples were heated at 473 K for 1 h under vacuum to remove physisorbed water. The Brunauer-Emmett-Teller (BET) surface areas were estimated over a relative pressure ( $P/P_0$ ) range of 0.05-0.30. Pore size distributions were obtained from the adsorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) method. Ultraviolet-visible diffuse reflectance spectra (UV-Vis DRS) of the TDMS samples were measured with spectrophotometer (V-670, Jasco). The densities of organic functional groups were estimated from the carbon content determined by elemental analysis (varioMICRO cube, Elementar). The acid site densities of the samples were examined by  $\text{NH}_3$  temperature-programmed desorption (TPD; BEL-CAT, BEL JAPAN) with helium as a carrier gas. Fourier transform-infrared (FTIR) spectra were obtained at a resolution of  $4\text{ cm}^{-1}$  using a spectrometer (FT/IR-6100, Jasco) equipped with an extended KBr beam splitting device and a mercury cadmium telluride (MCT) detector. The samples were pressed into self-supporting disks (20 mm diameter, 0.02 g), placed in an IR cell attached to a closed glass-circulation system and dehydrated by heating at 473 K for 1 h under vacuum. Prior to CO-adsorbed FT-IR measurements, all samples were exposed to water

vapor (20 Torr), followed by evacuation for 5 min to remove weakly physisorbed water, and then exposed to CO (1.0 Torr) for adsorption.

### **1.3 Catalytic Reactions.**

Lewis acid catalyst (0.1 g) was added to a mixture of benzaldehyde (0.4 mmol), 1-(trimethylsilyloxy)cyclohexene (0.6 mmol), and water (3 mL) at 298 K. After stirring the solution at 298 K for 2 h, the product was isolated by extraction with ethyl acetate and analyzed using  $^1\text{H}$  nuclear magnetic resonance (NMR) spectroscopy (Biospin AvanceIII 400 MHz, Bruker) with dioxane used as an internal standard.

## 2. Physicochemical properties of TDMS samples.

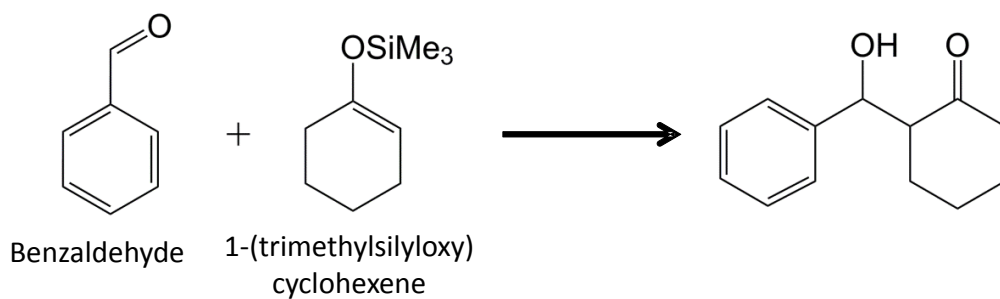
**Table S1.** Physicochemical properties of the TDMS samples.

<b>Catalyst</b>	<b>S<sub>BET</sub> / m<sup>2</sup> g<sup>-1</sup></b>	<b>Pore volume / cm<sup>3</sup> g<sup>-1</sup></b>	<b>Pore diameter / nm</b>	<b>Organic functional group density<sup>a</sup> / nm<sup>-2</sup></b>	<b>Lewis acid site density<sup>b</sup> / mmol g<sup>-1</sup></b>
<b>TDMS</b>	535	0.74	9.3	-	0.16
<b>Propyl-TDMS</b>	485	0.73	8.4	0.28	0.17
<b>Dodecyl-TDMS</b>	436	0.66	7.8	0.32	0.16
<b>Benzyl-TDMS</b>	493	0.71	9.1	0.31	0.16
<b>Tridecafluoro-TDMS</b>	419	0.68	9.1	0.33	0.17

<sup>a</sup>Determined by elemental analysis. <sup>b</sup>Determined by NH<sub>3</sub> TPD measurement.

### 3. Catalytic activities of bare TDMS for the Mukaiyama-aldol reaction in various solvents.

**Table S2.** Influence of solvent on the Mukaiyama-aldol reaction of benzaldehyde with 1-(trimethylsilyloxy)cyclohexene.



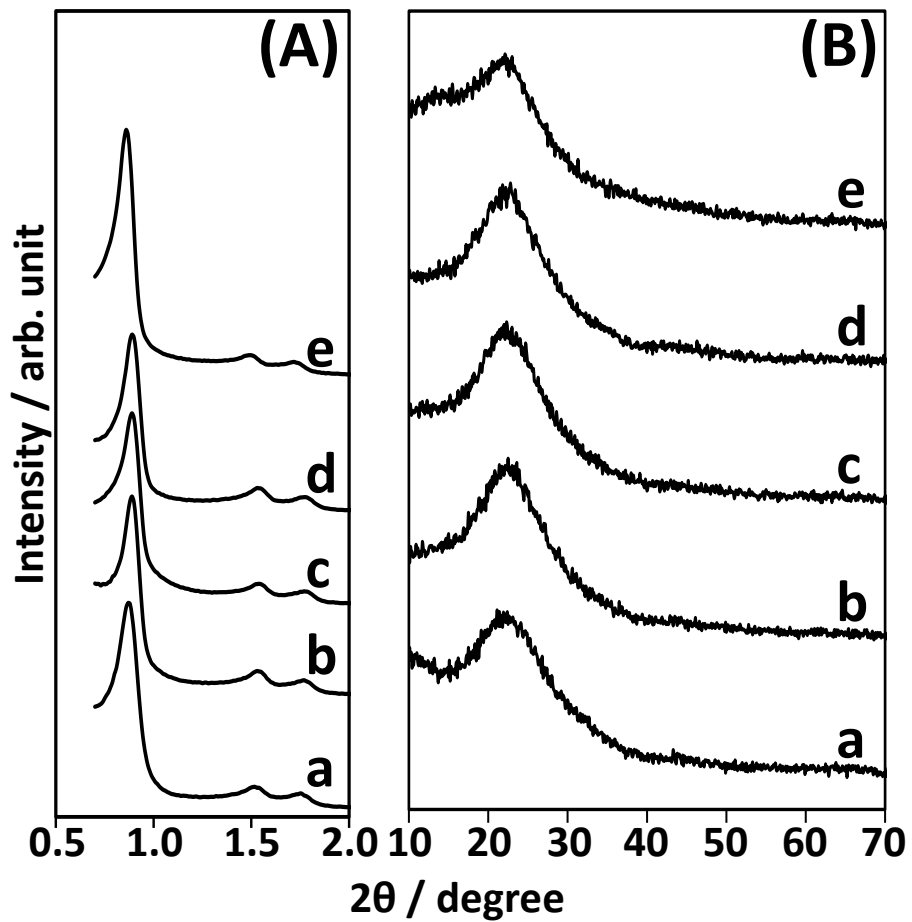
Solvent	Yield <sup>a</sup> (%)
Water	3
Water-SDS <sup>b</sup>	14
Ethanol	1
Tetrahydrofuran	1
Acetonitrile	0
Dichloromethane	0
Toluene	0
Neat	0

Reagents and conditions: benzaldehyde, 0.4 mmol; 1-(trimethylsilyloxy)cyclohexene, 0.6 mmol; water, 3 mL;

catalyst, 0.02 g; temperature, 298 K; time, 1 h. <sup>a</sup>Syn/anti ratio for all tested catalysts was estimated to be ca.

7/3. <sup>b</sup>Reaction in the presence of dodecyl sodium sulfate (SDS) (0.023 g) in reaction solution.

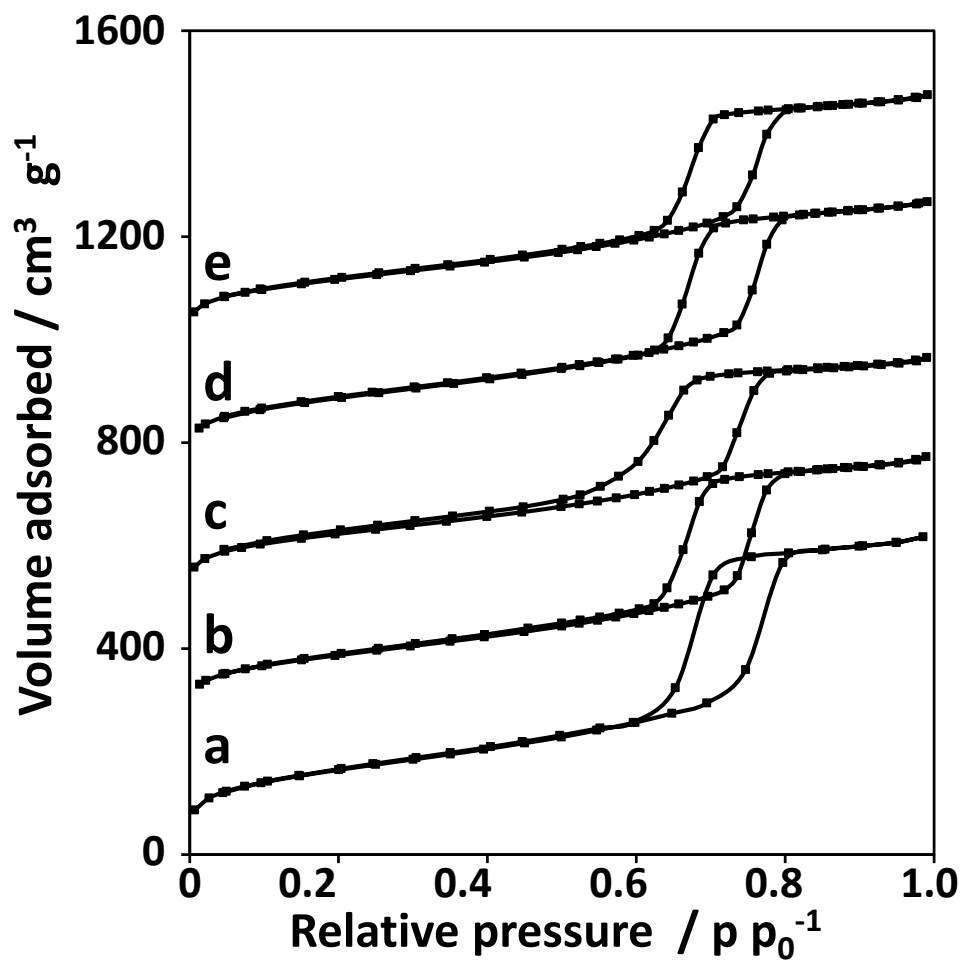
#### 4. XRD patterns.



**Figure S1.** (A) Small-angle and (B) wide-angle XRD patterns for (a) TDMS, (b) Propyl-TDMS, (c) Dodecyl-TDMS, (d) Benzyl-TDMS, and (e) Tridecafluoro-TDMS.



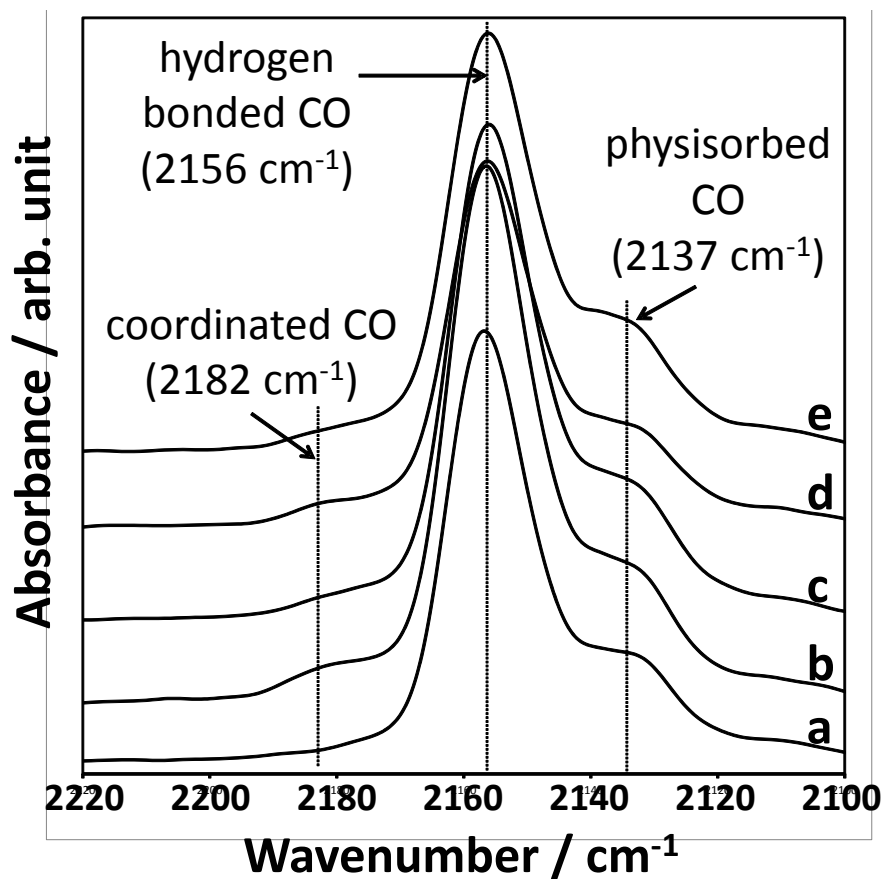
**5. N<sub>2</sub> adsorption-desorption isotherms.**



**Figure S2.** N<sub>2</sub> adsorption-desorption isotherms for (a) TDMS, (b) Propyl-TDMS, (c) Dodecyl-TDMS, (d)

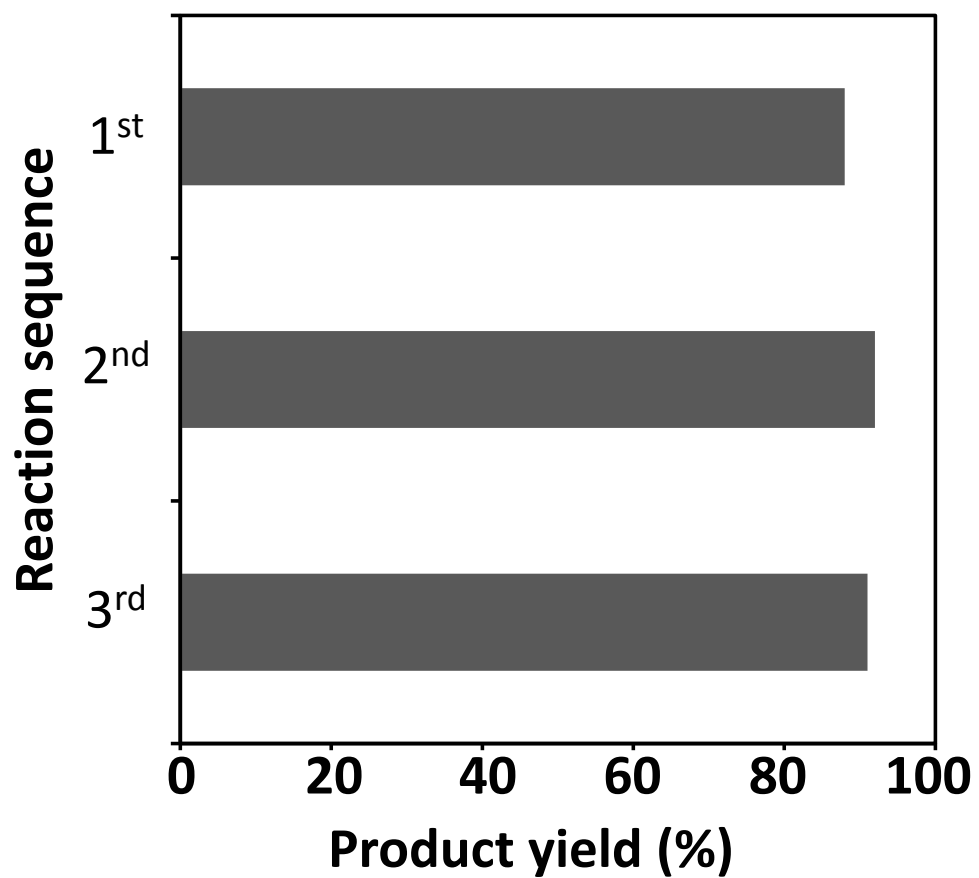
Benzyl-TDMS, and (e) Tridecafluoro-TDMS. Each isotherm is vertically offset by 250 cm<sup>3</sup> g<sup>-1</sup> for clarity.

## 6. CO adsorption experiment for TDMS samples.



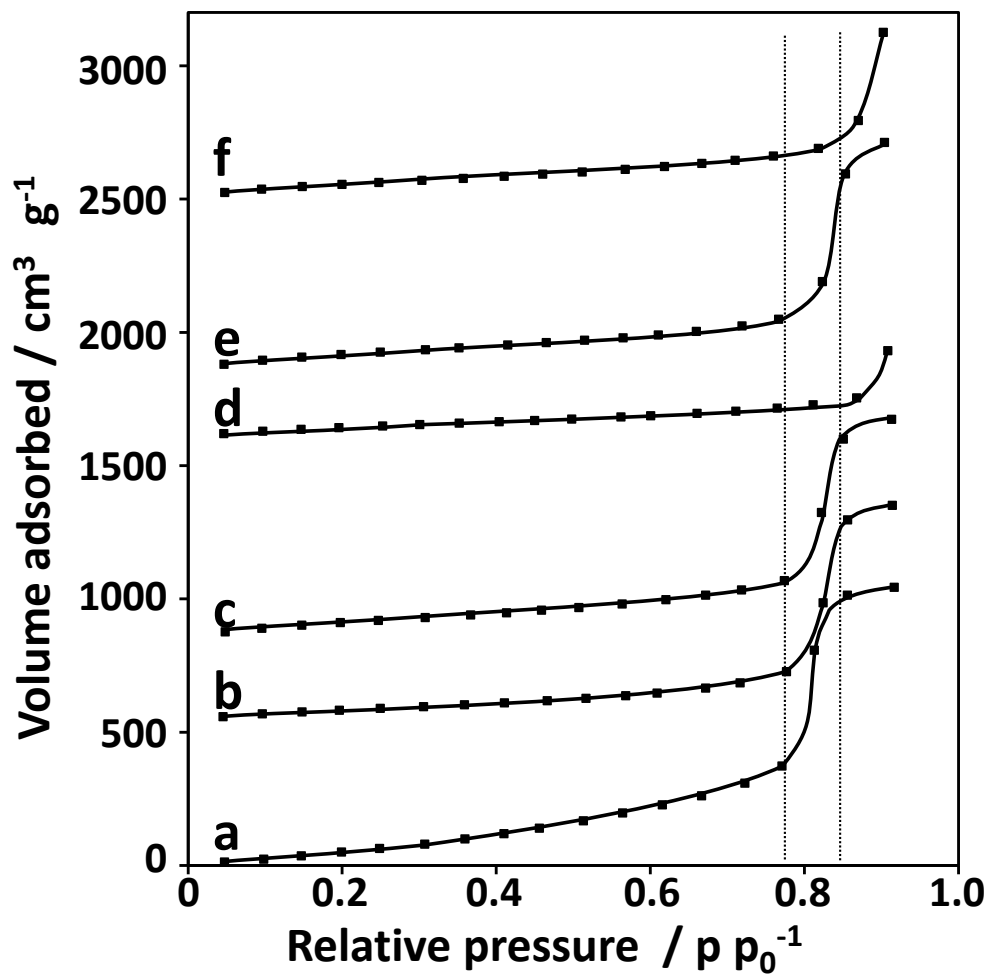
**Figure S3.** Difference FTIR spectra for CO-adsorbed hydrated SBA-15 and TDMS samples. (a) SBA-15, (b) Propyl-TDMS, (c) Dodecyl-TDMS, (d) Benzyl-TDMS, and (e) Tridecafluoro-TDMS. Prior to measurements, all samples were exposed to water vapor (20 Torr) followed by evacuation for 5 min.

**7. Catalyst reuse experiment.**



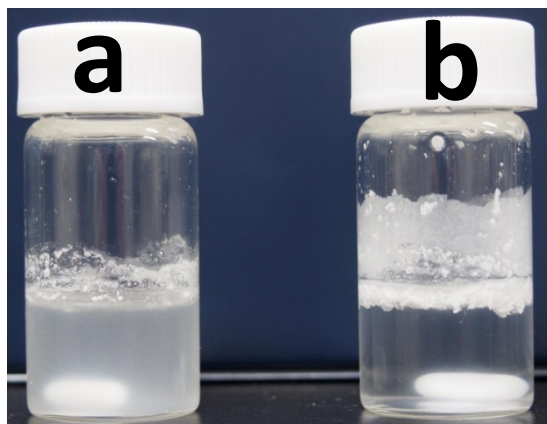
**Figure S4.** Catalytic activities of fresh and reused Tridecafluoro-TDMS for the surfactant-free Mukaiyama-aldol reaction of benzaldehyde with 1-(trimethylsilyloxy)cyclohexene in water.

**8. H<sub>2</sub>O adsorption isotherms for TDMS samples at 298 K.**



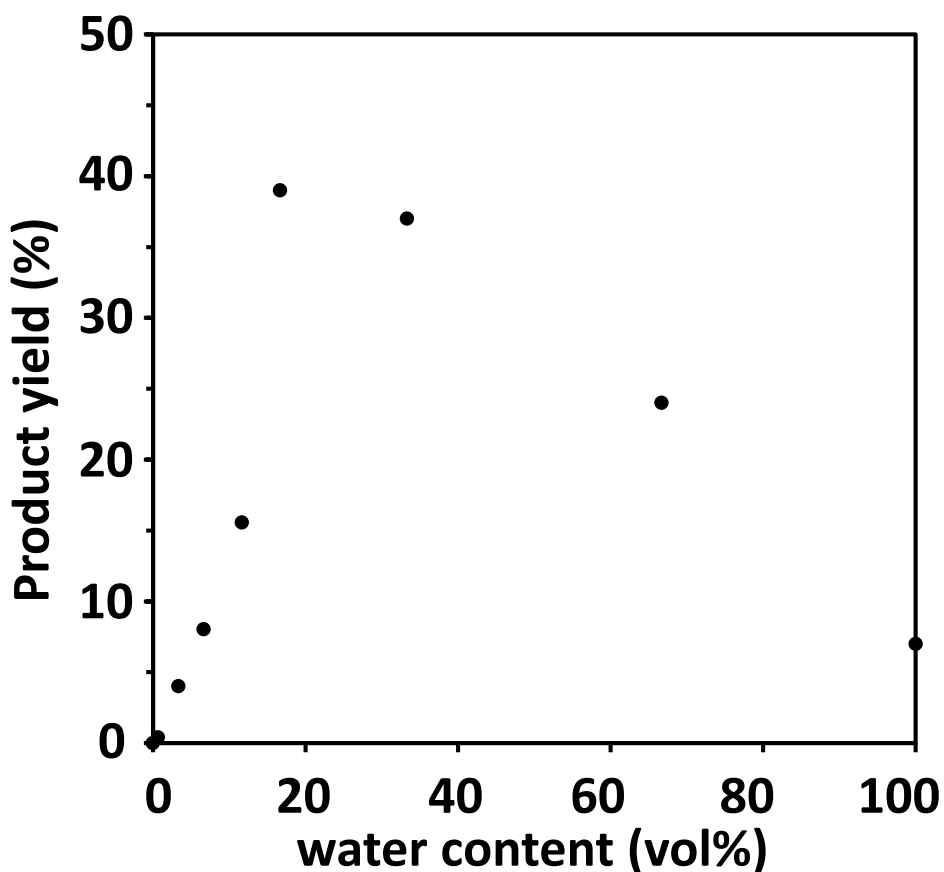
**Figure S5.** H<sub>2</sub>O adsorption isotherms for SBA-15 and TDMS samples measured at 298 K. (a) SBA-15, (b) bare TDMS, (c) Propyl-TDMS, (d) Dodecyl-TDMS, (e) Benzyl-TDMS, and (f) Tridecafluoro-TDMS.

**9. Photograph of Dodecyl and Tridecafluoro-TDMS suspended in ethanol-water mixture.**



**Figure S6.** Photograph of TDMS samples suspended in water-ethanol (4:1 vol%) solution. (a) Dodecyl-TDMS,  
(b) Tridecafluoro-TDMS.

**10. Effect of H<sub>2</sub>O for the Mukaiyama-aldol reaction in organic solvent.**



**Figure S7.** Dependence of product yield of bare TDMS for the Mukaiyama-aldol reaction in THF on various water contents.

Dehydrated TDMS (0.1 g, prepared by heating at 473 K under vacuum) was added to a mixture of benzaldehyde (0.4 mmol), 1-(trimethylsilyloxy)cyclohexene (0.6 mmol), water (x mL) and THF (3-x mL) under argon. After stirring the mixture at 298 K for 2 h, TDMS was separated by centrifugation. THF (10mL) and 1 M HCl (0.5mL) were added, and then stirred for 1 h at 298 K for desilylation of product. THF was removed under reduced pressure and water (7 mL) was added. The product was extracted with ethyl acetate

and organic solvent was removed under reduced pressure. The product yield was analyzed using  $^1\text{H}$  NMR spectroscopy with dioxane used as an internal standard.