

Electronic Supplementary Information
**Formation of Nanostructured Silicas through the Fluoride Catalysed
Self-Polymerization of Q-type Functional Silica Cages**

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Acronyms

SSA – specific surface area

POSS – polyhedral oligomeric silsesquioxanes

BET – Brunauer Emmett Teller

DCM – dichloromethane

ACN – acetonitrile

THF – tetrahydrofuran

DMF – dimethylformamide

TBAF – tetra-n-butylammonium fluoride

TBA – tetra-n-butylammonium

TMAH – tetramethylammonium hydroxide

MeOH – methanol

SEM – scanning electron microscopy

TGA – thermal gravimetric analysis

*p*XRD – powder x-ray diffraction

NMR – nuclear magnetic resonance

MAS/SS NMR – magic angle spinning/solid state NMR

Materials

Octakis(dimethylsiloxy)silsesquioxane ($Q_8M_8^H$) and tetramethylammonium octa-anion (OA, octakis-tetramethylammonium silicate) methanol solution were gifts from Mayaterials Inc. Ann Arbor, MI. Dichloromethane (DCM), Acetonitrile (ACN), methanol (MeOH), toluene, acetone, and Hexanes were purchased from Millipore-Sigma Corporation. TBAF (1 M in THF) was purchased from Acros Organics. Tetramethylammonium hydroxide pentahydrate (TMAH) was obtained from Alfa Aesar. CsF was obtained from Sigma Aldrich. Trimethylsilylchloride was obtained from Acros Organics. All chemicals were used as received.

General reaction toward network materials

1 g (0.98 mmol) of octakis(dimethylsiloxy)silsesquioxane ($Q_8M_8^H$) or (0.89 mmol) octakis(trimethylsiloxy)silsesquioxane ($Q_8M_8^{Me}$) was dissolved in 30 mL of solvent (dichloromethane (DCM), acetonitrile (ACN), methanol (MeOH), toluene, acetone, or 1:1 ACN:DCM). Then 0.3 mmol of catalyst (TBAF, TMAH, CsF) was added into the mixture. Water 0, 33.3, 66.6, or 100 mmol was added as specified. The products were directly collected from the reaction mixture after 24 hours, rinsed with solvent, air dried overnight then vacuumed for 4 hours before analyses (See Table S1 and Figures S1-S20 for setup and characterization). Samples for $Q_8M_8^{Me}$ were evacuated for longer periods of time as specified in the data for those materials (See Figures S21-24, and Table S1 for setup and characterization). Further details and modifications are given in the text.

Reaction to form $Q_8M_8^{Me}$

Octakis(trimethylsiloxy)silsesquioxane ($Q_8M_8^{Me}$) was synthesized using a method from Hasegawa and Motojima.¹ Briefly 15 mL tetramethylammonium octa-anion cage in methanol (~1 M by Si) was added dropwise to a mixture of trimethylchlorosilane (10 mL) in 55 mL of hexanes in an ice bath. The mixture was stirred for 1 h and then extracted using 3x water wash, and then three more aliquots of hexane were used to pull additional product from the water. The hexane layers were combined, dried over Na_2SO_4 , filtered and solvent removed to give a white powder. The crude product was then recrystallized from DCM/methanol to give a 1.8 g batch 1, and 2.1 g batch 2. Batches were combined for characterization (Figure S21).

Instrumental

Thermogravimetric analysis (TGA)

Thermal degradation of the materials was measured with an STA 7200 (Hitachi, Santa Clara, CA, USA). Before measuring, samples were air-dried for 24 hours then vacuumed for 5 hours, ground to powder, then vacuum dried for another 5 hours. 10-20 mg of sample were placed in an alumina pan and then heated from 25 to 1000 °C with 10 °C/min heating rate and 200 cc/min airflow. The degradation graph was then recorded.

Fourier–transform infrared spectroscopy (FTIR)

FTIR was measured by Thermo Scientific Nicolet iS5 (Waltham, Massachusetts, MA, USA) with Attenuated total reflection (ATR) method. Samples were scanned from 4000 to 400 cm^{-1} with 0.121 cm^{-1} spacing on a ZnSe crystal 16 times.

Scanning Electron Microscopy (SEM)

SEM images were taken with a lanthanum hexaboride source Hitachi S2700 (Hitachi High-Tech America, Schaumburg, IL, USA). Materials were placed on a sample spaceman then sputter coated with Au/Pd. Images were collected with 20 kV Voltage.

Powder X-ray Diffraction

XRD patterns were measure by a Rigaku Rotating Anode Goniometer (Rigaku Denki., LTD., Tokyo, Japan). The presence of crystallographic phases was determined by Jade Program 2010 (Version 1.1.5 Materials Data, Inc., Livermore CA). Samples were scanned from 5 to 40° 2 θ with 0.58min⁻¹ in 0.01° increments scan rate. CuK α radiation (1.541 Å) was use for operation at 40 kV and 100 mA.

Specific surface area (SSA) and porosity analyses.

Surface areas and pore size distributions were measured by a Micromeritics 3FLEX surface and catalyst characterization analyzer (Micromeritics Inc., Norcross, GA). Samples collected from the reaction were air-dried for 24 hours then vacuumed for 5 hours, ground to powder then vacuumed for another 5 hours for degassing. The sample then was flushed with nitrogen gas for 30 minutes to eliminate unwanted gases. Measurements were conducted with 12 data points increasing at 0.05 (P/P₀) relative pressure at -196°C (77 K). The instrument then calculated surface areas and pore size distributions by Brunauer Emmet Teller (BET) and Density Functional Theory (DFT) methods respectively.

Universal Gas Analyzer

Gas from the reaction was analyzed by a RGA100 Residue Gas Analyzer (Stanford Research Systems, Sunnyvale, CA). Reactants were put in a 250mL round bottom

flask then TBAF was added into the reaction mixture. Once the reaction start bubbling, the flask was capped with septum, slightly vacuumed, then the probe was inserted into the flask. An analog scan was performed to identify gas molecular weights, then a P vs T scan was applied to identify gas amount the reaction released.

MALDI-TOF Mass Spectrometry

Matrix Assisted Laser Desorption Time of Flight mass spectrometry was carried out using a Shimadzu Axima Performance MALDI-TOF mass spectrometer (Shimadzu Scientific Instruments, Columbia, MD) with dithranol as the matrix cast out of THF.

GCMS Mass Spectrometry

GCMS conducted on a Shimadzu GC-2010 gas chromatograph (30 m ZB-5ms column, 60 – 350 °C, Shimadzu Scientific Instruments, Columbia, MD) linked to a Shimadzu GCMA-QP 2010 Plus mass spectrometer. Headspace analysis was conducted by using an air-tight syringe to extract gas out of the reactions. It was then immediately injected on the GCMS with the solvent delay removed from the program to see fast flowing components.

NMR Spectrometry

Solution: ^1H (300 MHz) and ^{29}Si (59.6 MHz) NMR were performed on a Bruker 300 MHz spectrometer (Bruker Corp. Billerica, MA) at 25 °C in chloroform-*d*. Proton NMR used standard conditions, silicon NMR used a delay of 15 seconds between scans and at

least 5,000 scans to ensure adequate relaxation of the nuclei and data acquisition times.

Solid State: Powdered samples were packed into 3.2 mm zirconium rotors. Samples are spun at 10kHz MAS and 298K. Data was acquired on a Bruker Avance IIIHD Ascend Wide-Bore 600MHz spectrometer. ^{29}Si -detected cross polarization experiments were acquired at a frequency of 119.25 MHz with a 7 sec. recycle delay and 256 scans.

GPC Spectroscopy

Gel Permeation Chromatography was conducted on a Shimadzu LC-10 system (Shimadzu Scientific Instruments, Columbia, MD) with refractive index and UV/Vis detectors. THF was used as the carrier solvent with a set of four Waters Styrogel columns (HR 0.5, 1, 3, 4) over a run time of 50 min. The instrument was calibrated with polystyrene standards and toluene was used as an internal standard to verify calibration.

Table S1. Formulation Surface area, decomposition 5%, and ceramic yield for all samples. *(f) indicates solid foam product collected from corresponding reaction mixture. $Q_8M_8^H$ unless specified.

Solvent	H ₂ O (mmol)	Catalyst (0.3 mmol)	Surface area (m ² g ⁻¹)	Decomposition 5% (°C)	Ceramic Yield (%)
DCM	0*	TBAF	26	201.6	77.9
DCM	16.7	TBAF	13	168.8	75.9
DCM	33.3	TBAF	0	144.0	65.5
DCM	16.7	TMAH	0	179.6	84.6
ACN	0*	TBAF	15	127.8	59.0
ACN(crystal)			59	222.2	81.8
ACN	33.3	TBAF	65	149.4	75.4
ACN(f)			657	422.4	89.0
ACN	66.6	TBAF	230	177.2	82.5
ACN(f)			372	381.7	86.7
Acetone	0*	TBAF	293	149.4	70.2
Toluene	0*	TBAF	279	31.3 [#]	59.7 [#]
Methanol	0*	TBAF	107	160.0	80.6
1:1 DCM:ACN	0*	TBAF	383	196.1	83.1
1:1 DCM:ACN(f)			N/A	196.1	80.5
ACN	0*	TMAH	528	183.0	81.3
ACN(f)			91	203.4	83.0
ACN	0*	CsF	264	313.9	74.9
ACN(f)			108	207.6	78.0
ACN ($Q_8M_8^{Me}$)	0*	TBAF	N/A (Syrup)	142.2	24.0
DCM ($Q_8M_8^{Me}$)	0*	TBAF	N/A (Syrup)	140.1	19.7
ACN ($Q_8M_8^{Me}$)	100	TBAF	0	140.0	19.6

* No additional water added over the ~5 vol% in tetrabutylammonium fluoride solution. [#] Trapped solvent

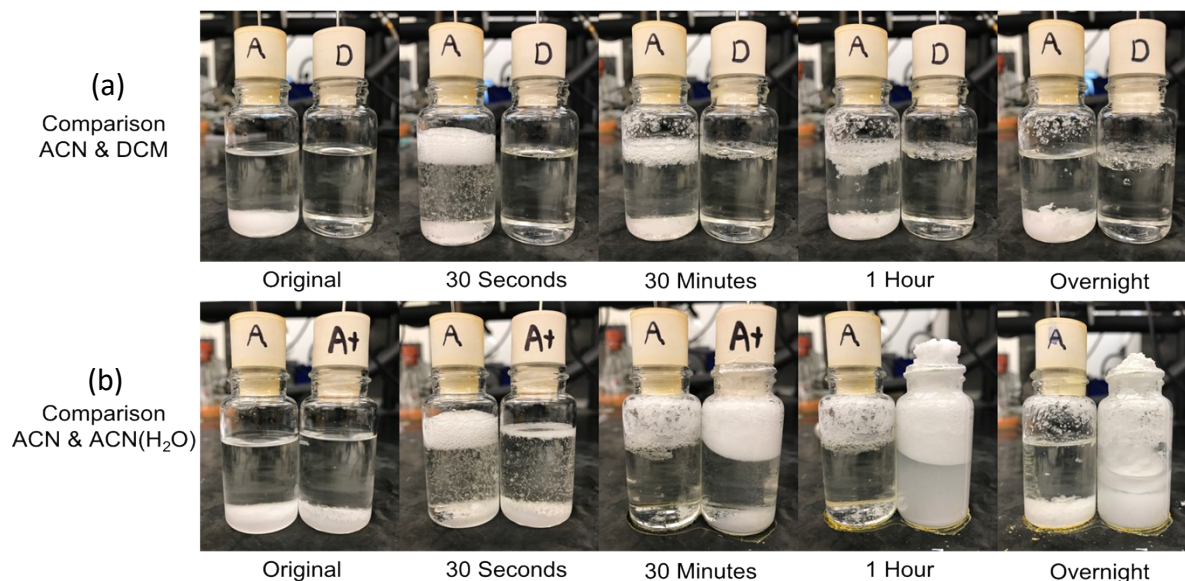
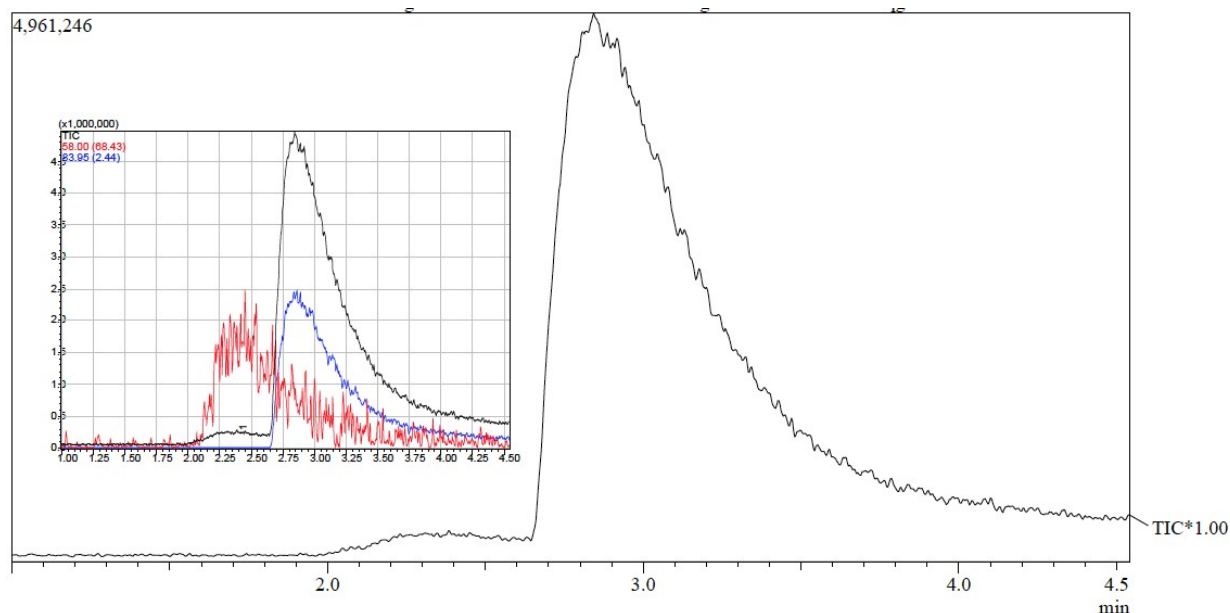


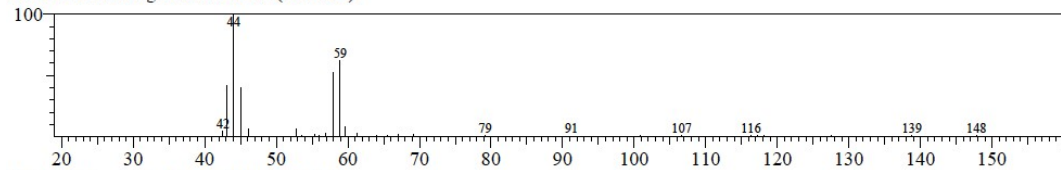
Figure S1. Comparisons between a) reaction in DCM(D) and ACN(A). b) reaction in ACN(A) and with water.



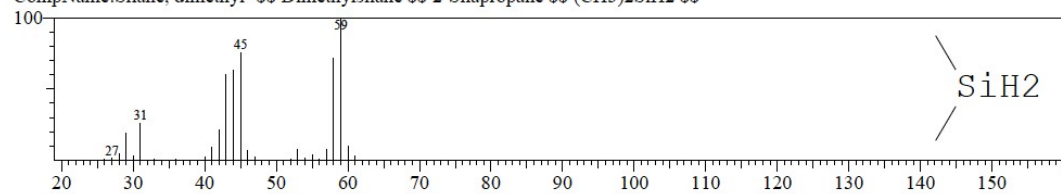
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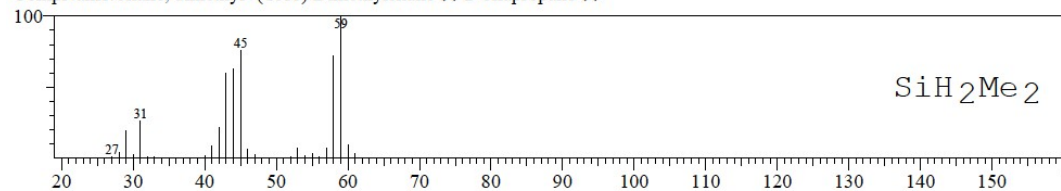


Figure S2. GC-Mass analysis of gas released from the reactions.

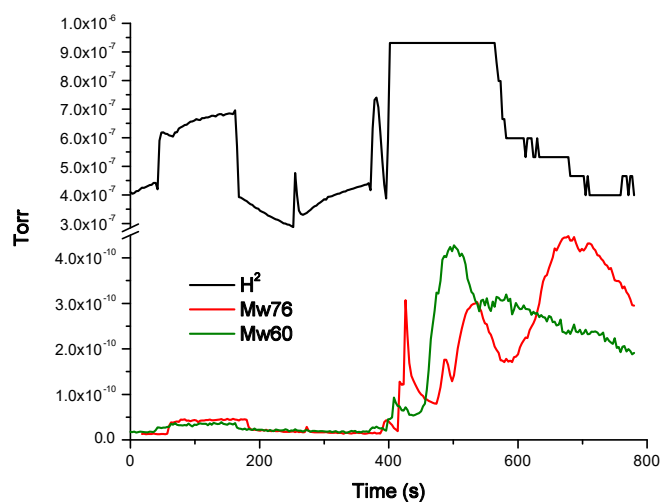


Figure S3. Gas analysis of gas released from the reactions (Note H₂ reaches saturation at 400 s).

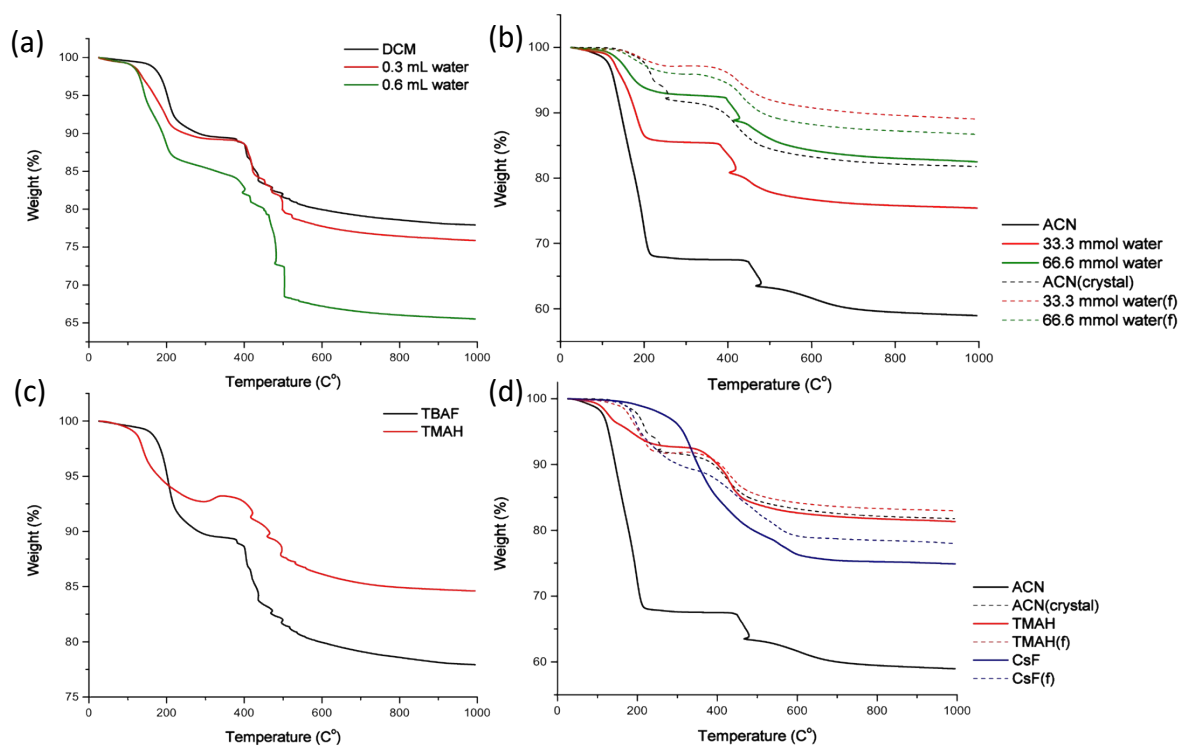


Figure S4. TGA graphs for (a) reactions in DCM. (b) reactions in ACN. (c) reaction with different starting catalyst in DCM. (d) reaction with different starting catalyst in ACN. *(f) indicates foam-like product from corresponding reaction mixture.

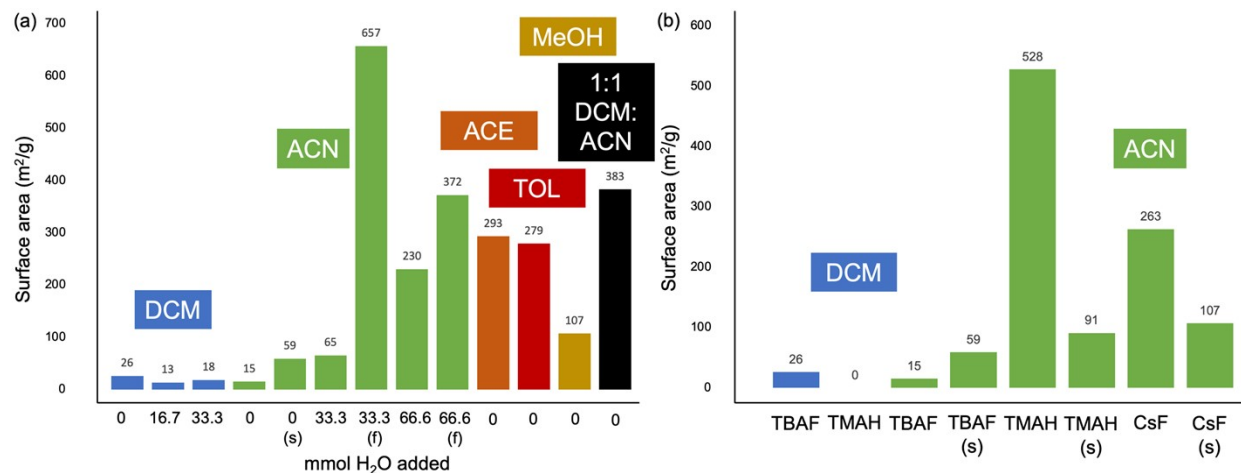


Figure S5. Surface area for reactions in (a) Solvents with different water additions (b) DCM and ACN with different catalyst. *(f) indicates foam-like product from corresponding reaction mixture, (s) is crystalline solid.

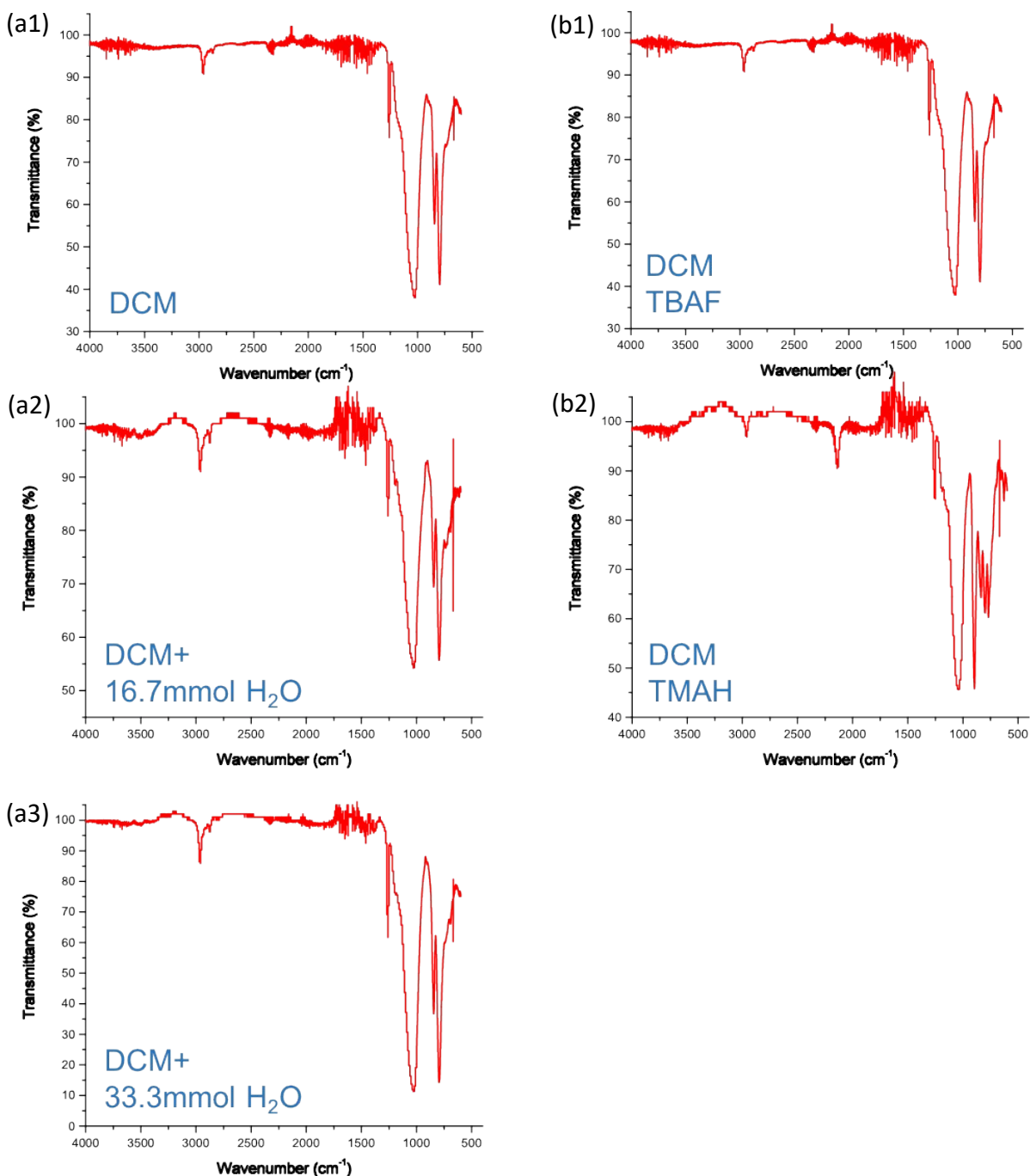


Figure S6. IR spectrum for reaction in DCM (a) with varying amounts of water (b) with different catalyst. Note that little OH and SiH remains in most systems, while CH aliphatic $\sim 2900\text{ cm}^{-1}$ remains verifying that some SiMe_2 remains intact for each reaction. Note CsF solubility in DCM is very low, limiting its reactivity in forming network materials and therefore the data is not included here.

HXY_29Si_Furgal
Jul 18 2022
29Si CPMAS
21-C2-0%H2O (Furgal)
10kHz MAS, 300K
d1=7s, 256ns

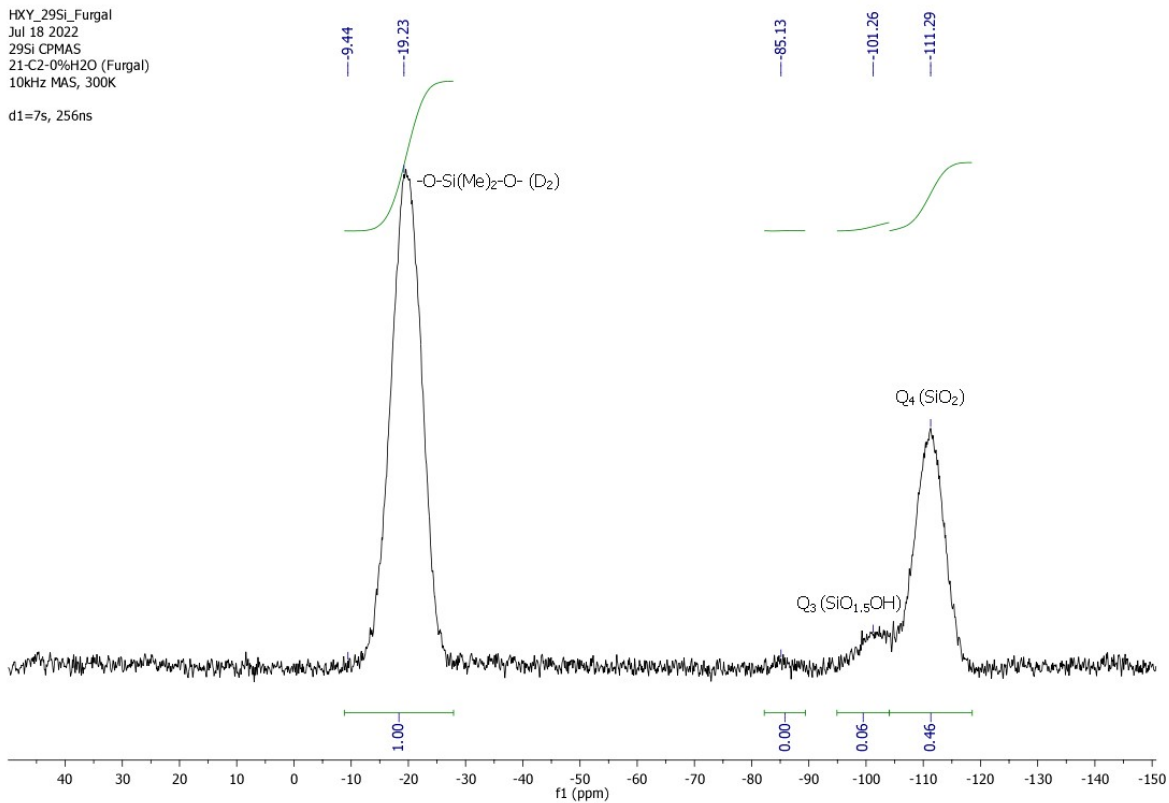


Figure S7. Solid State ²⁹Si NMR of dried solid from the DCM (0 mmol H₂O added) reaction.

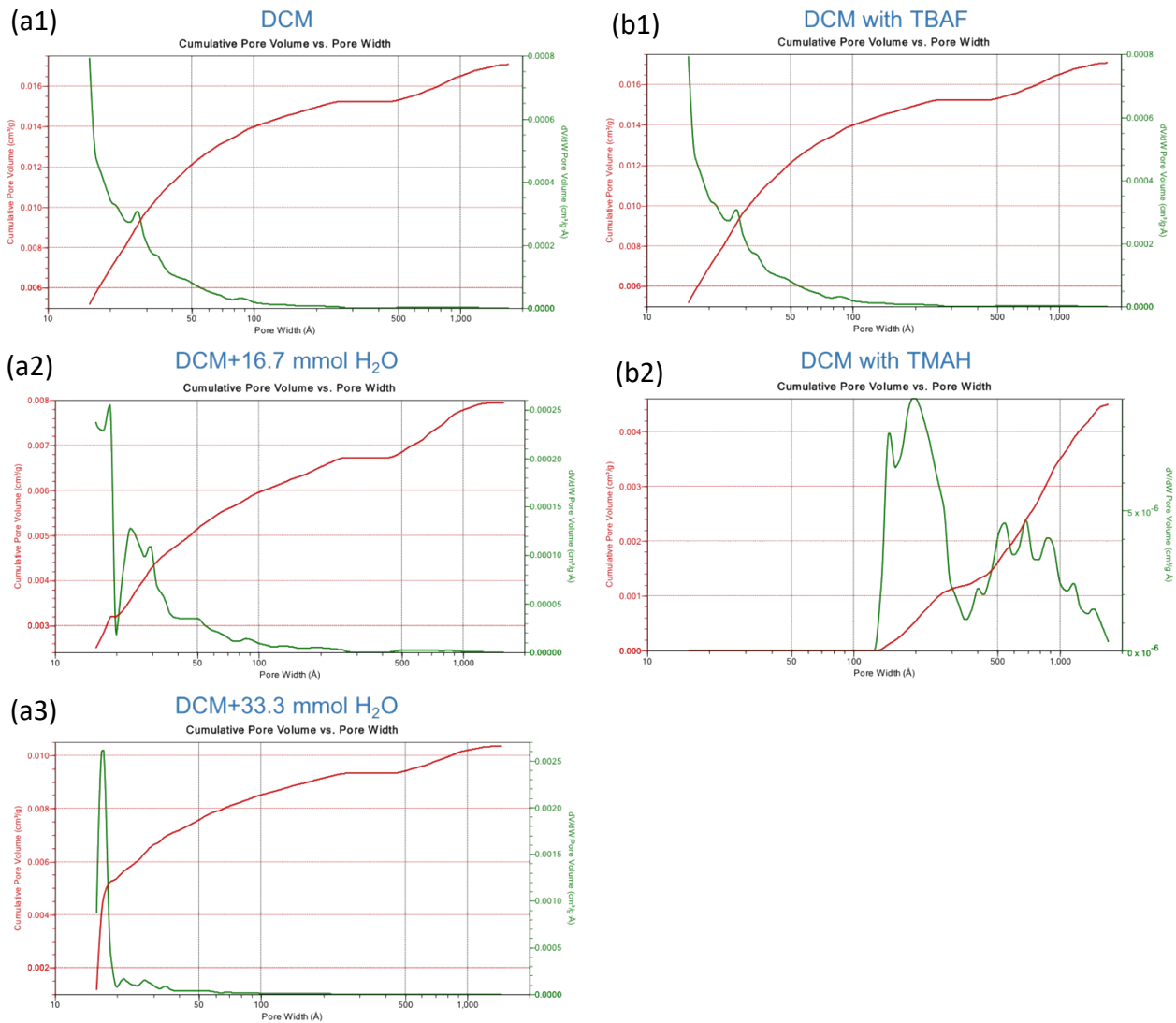


Figure S8. Pore size distributions for reaction in DCM (a) with varying amounts of water (b) with different starting catalysts.

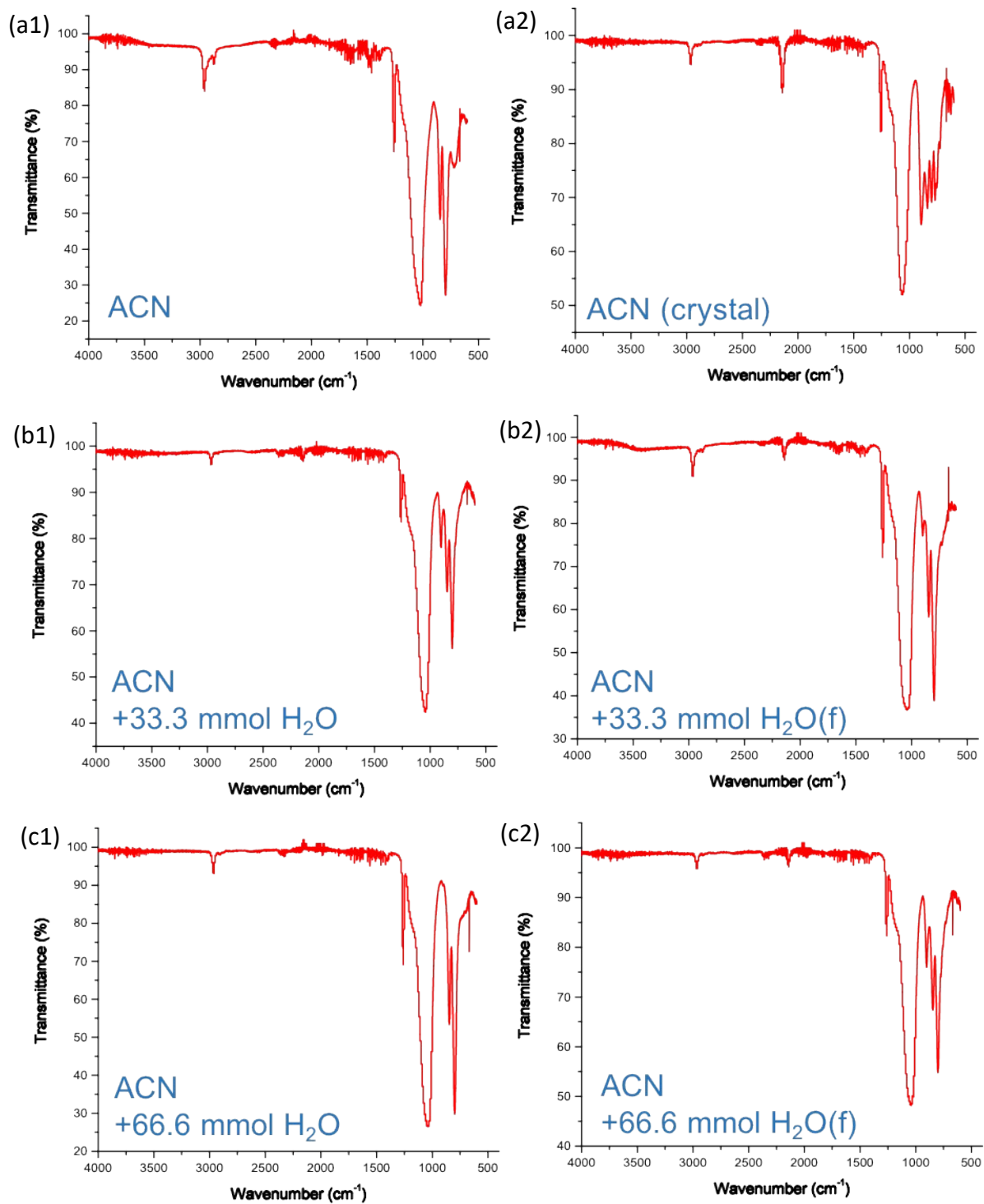


Figure S9. IR spectrum for reaction in ACN with different adding amount of water. *(f) indicates foam-like product from corresponding reaction mixture. Note that little OH and SiH remains in most systems, while CH aliphatic $\sim 2900 \text{ cm}^{-1}$ remains verifying that some SiMe_2 remains intact for each reaction.

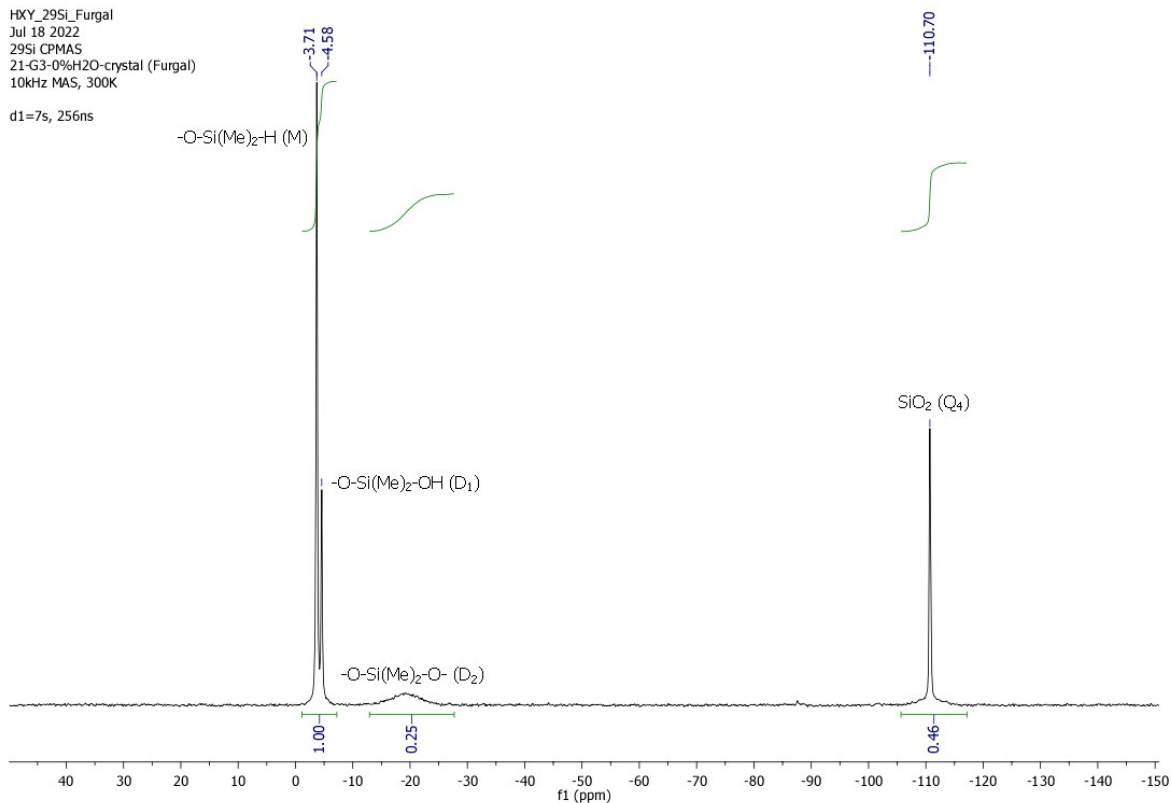


Figure S10. Solid State ^{29}Si NMR of crystalline solid (s) from the ACN (0 mmol H_2O added) reaction.

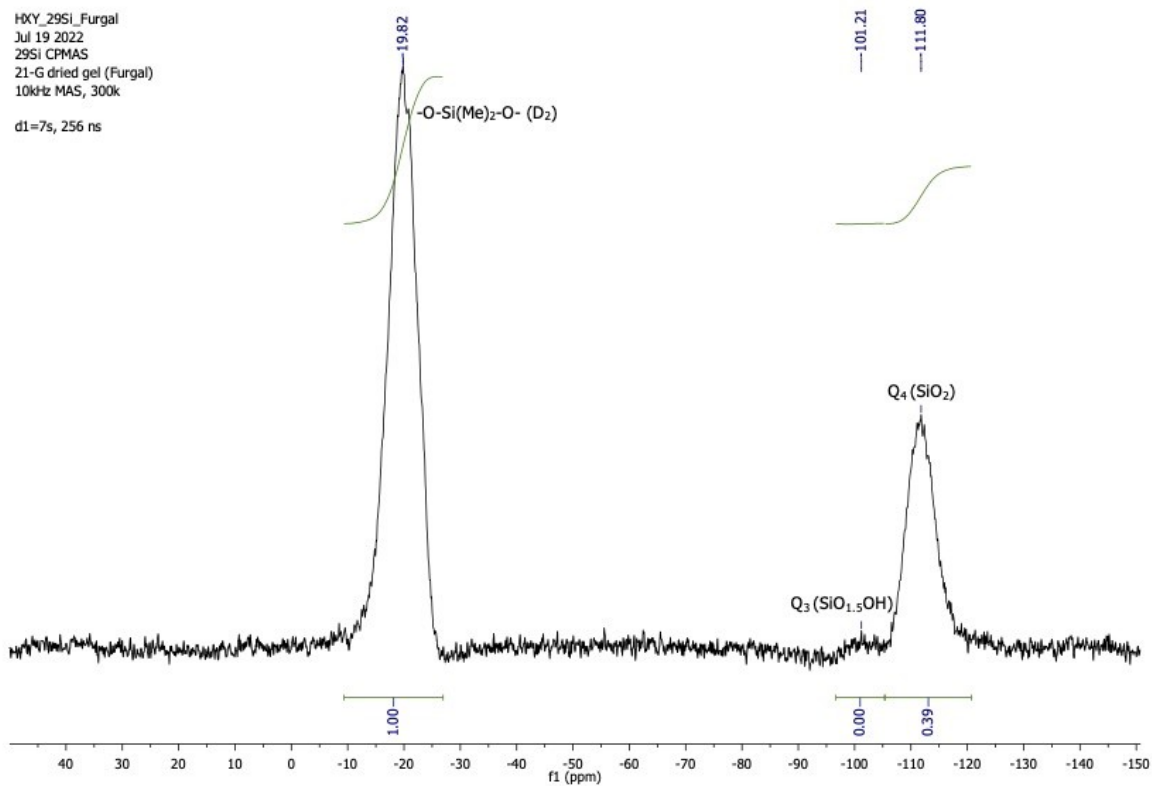


Figure S11. Solid State ^{29}Si NMR of dried gel from the ACN (0 mmol H_2O added) reaction.

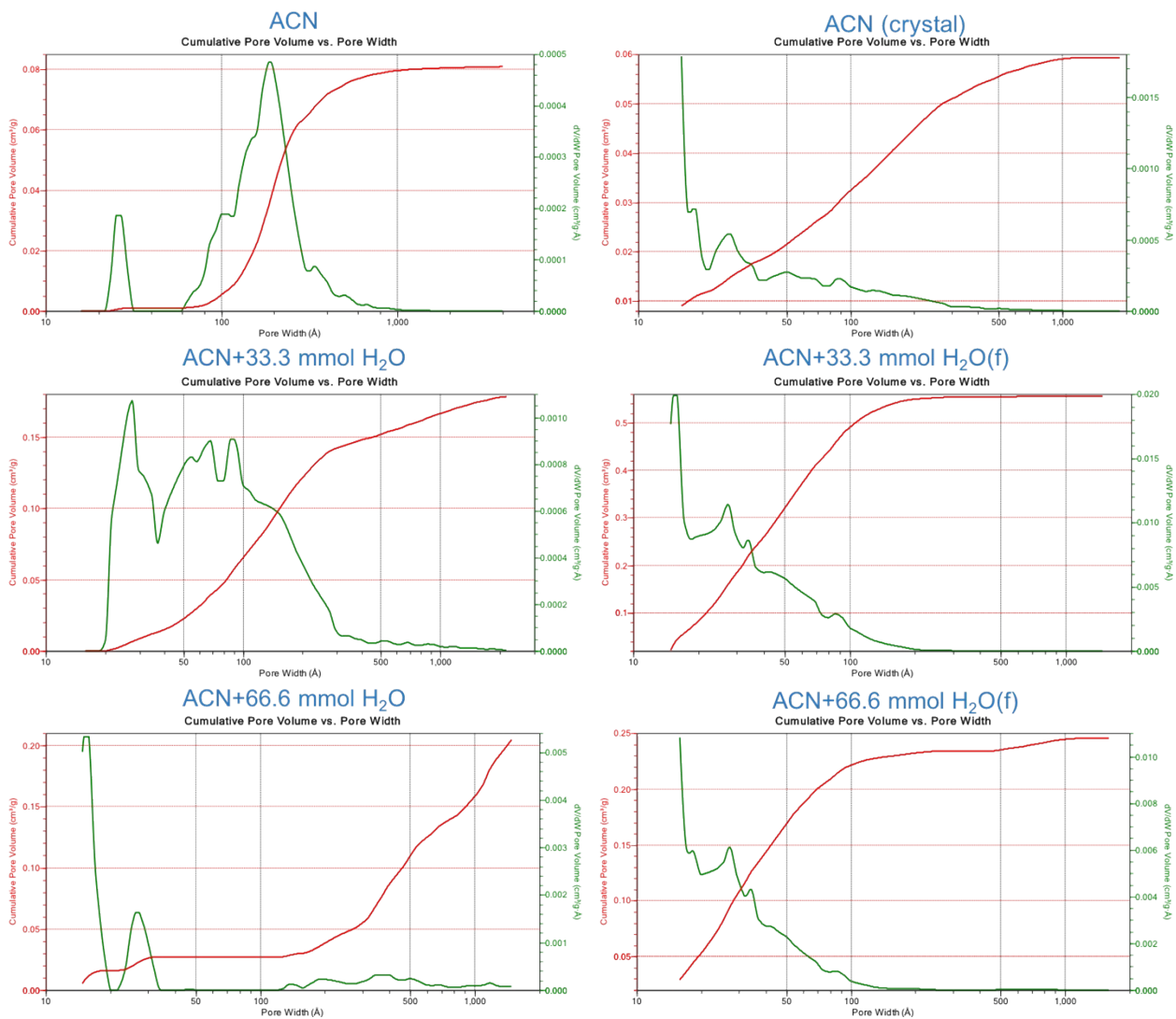


Figure S12. Pore size distributions for reaction in ACN with different adding amount of water. *(f) indicates foam-like product from corresponding reaction mixture.

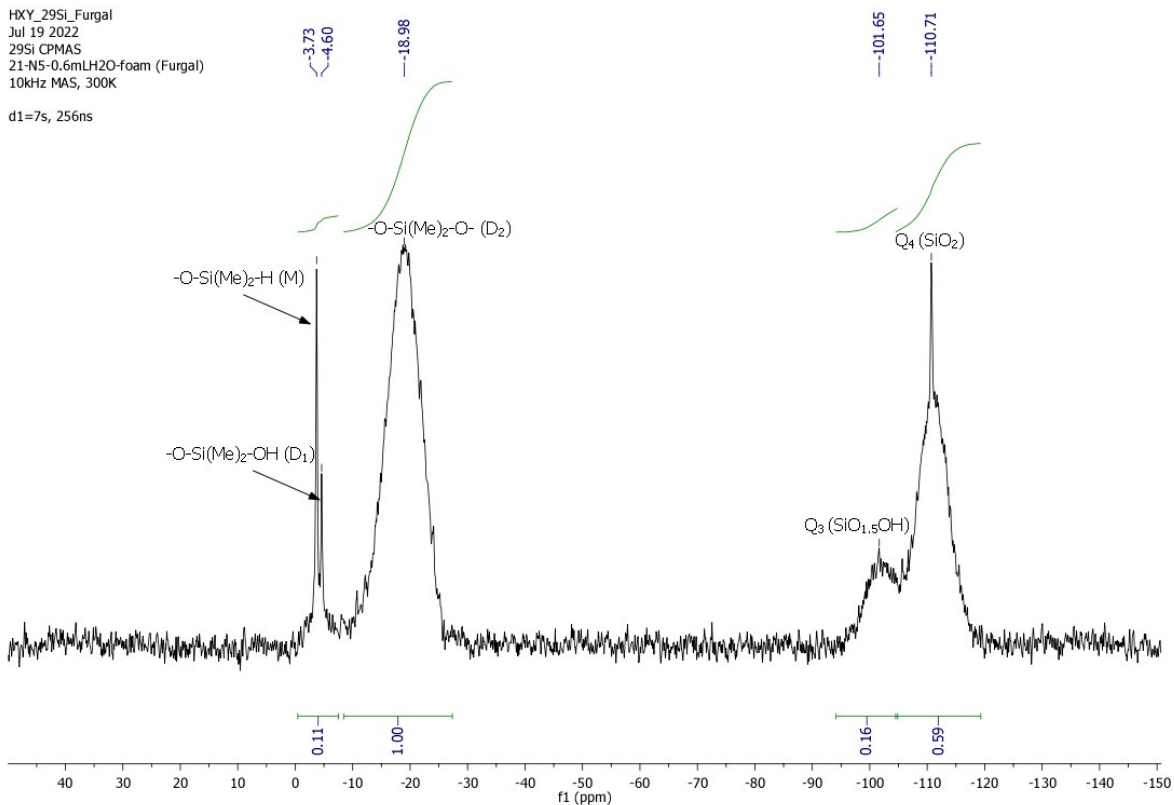


Figure S13. Solid State ²⁹Si NMR of the foam (f) from the ACN (33.3 mmol H₂O added) reaction.

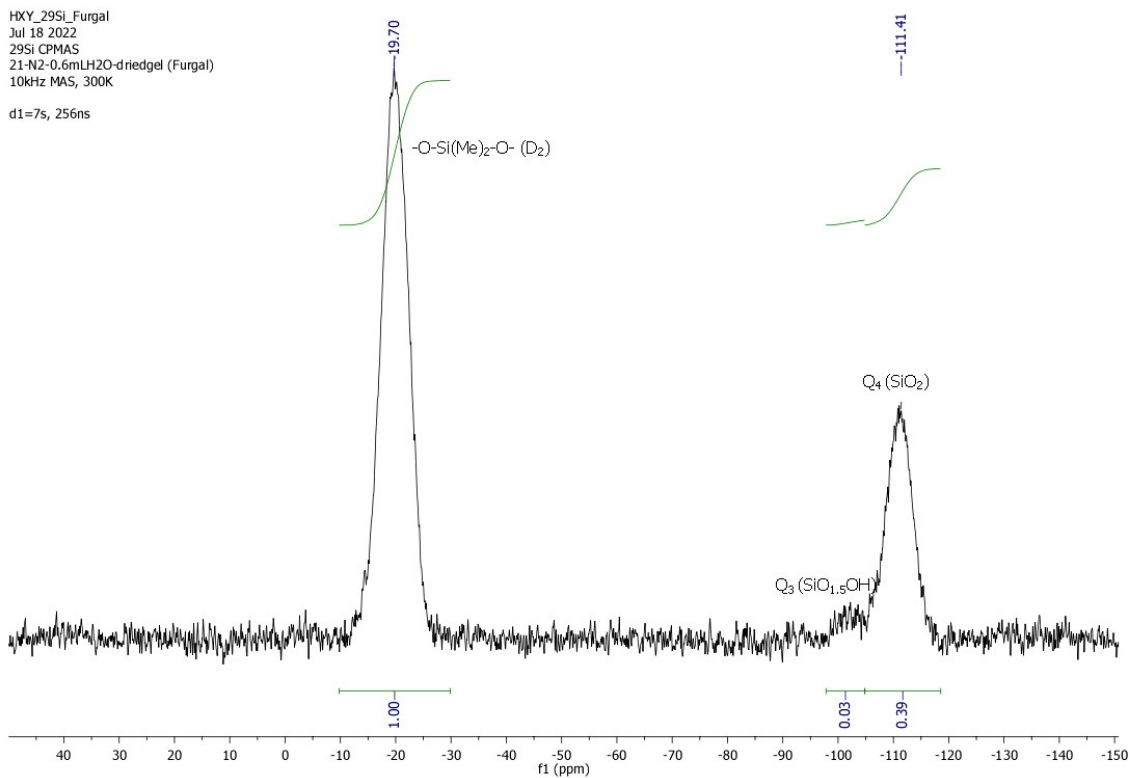


Figure S14. Solid State ²⁹Si NMR of the dried gel from the ACN (33.3 mmol H₂O added) reaction.

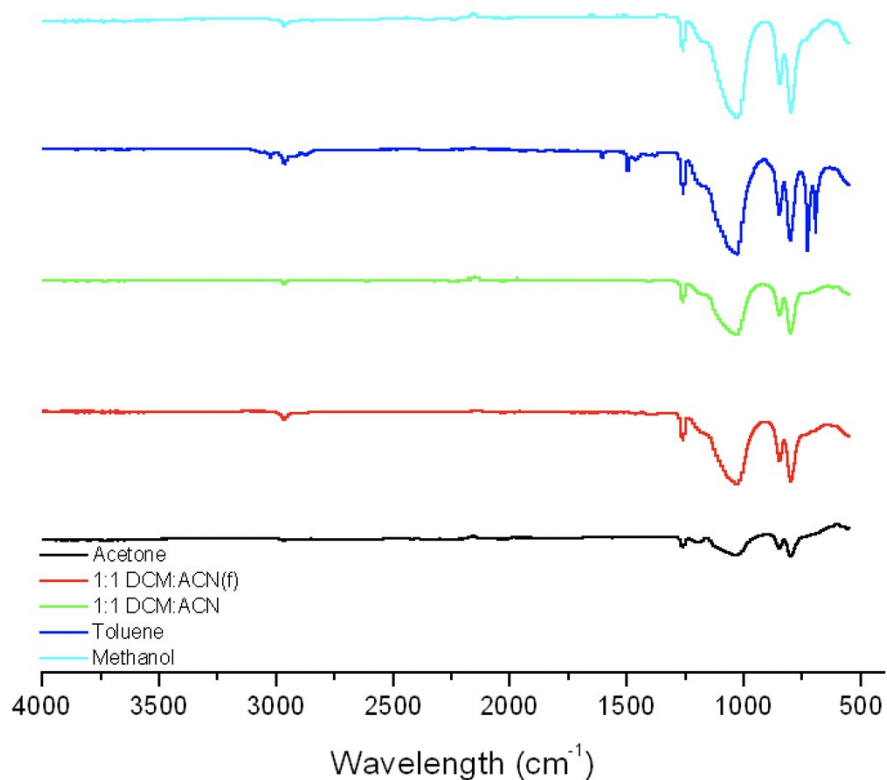


Figure S15. FTIR data for alternative solvent samples. *(f) indicates foam-like product from corresponding reaction mixture.

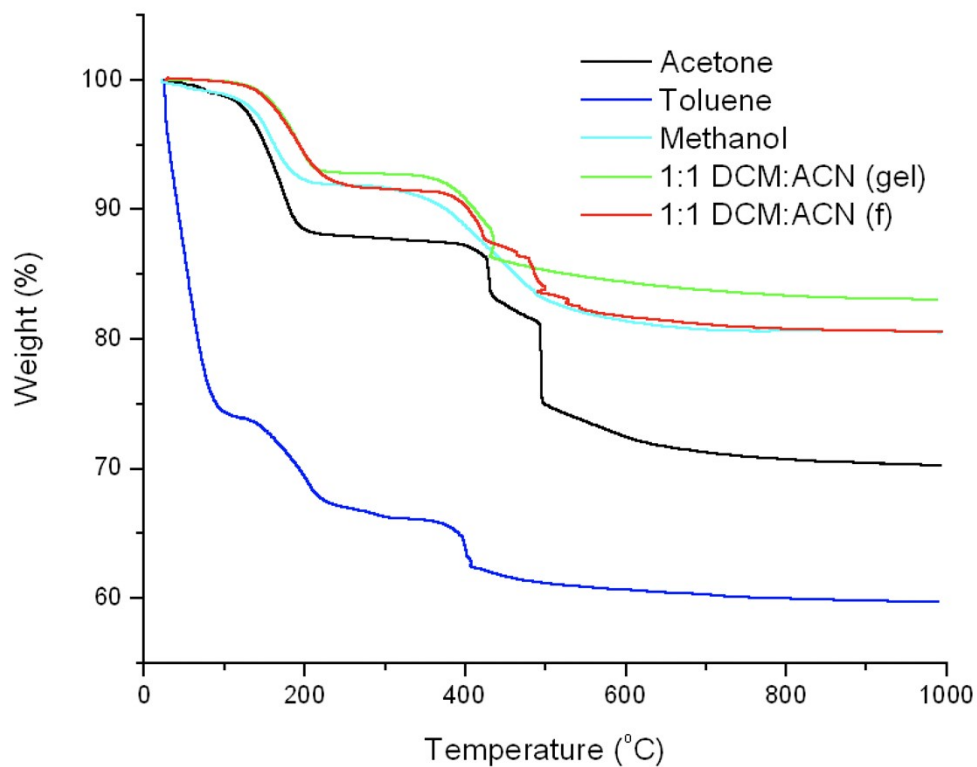


Figure S16. TGA data for alternative solvent samples, *(f) indicates foam-like product from corresponding reaction mixture.

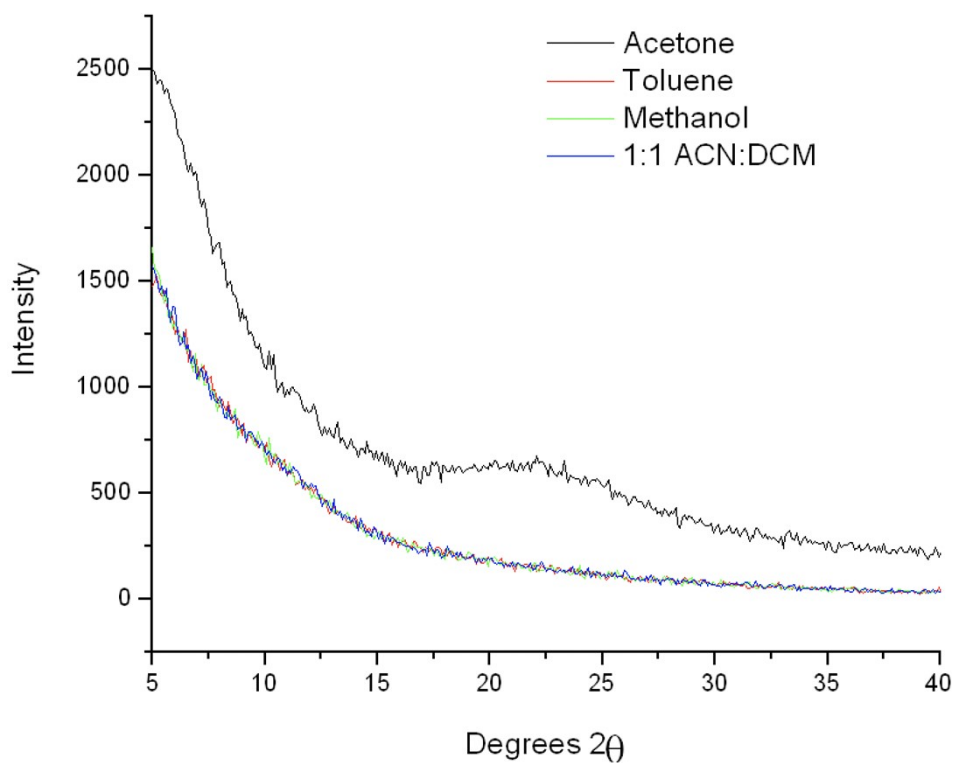


Figure S17. *p*-XRD data for alternative solvent system reactions.

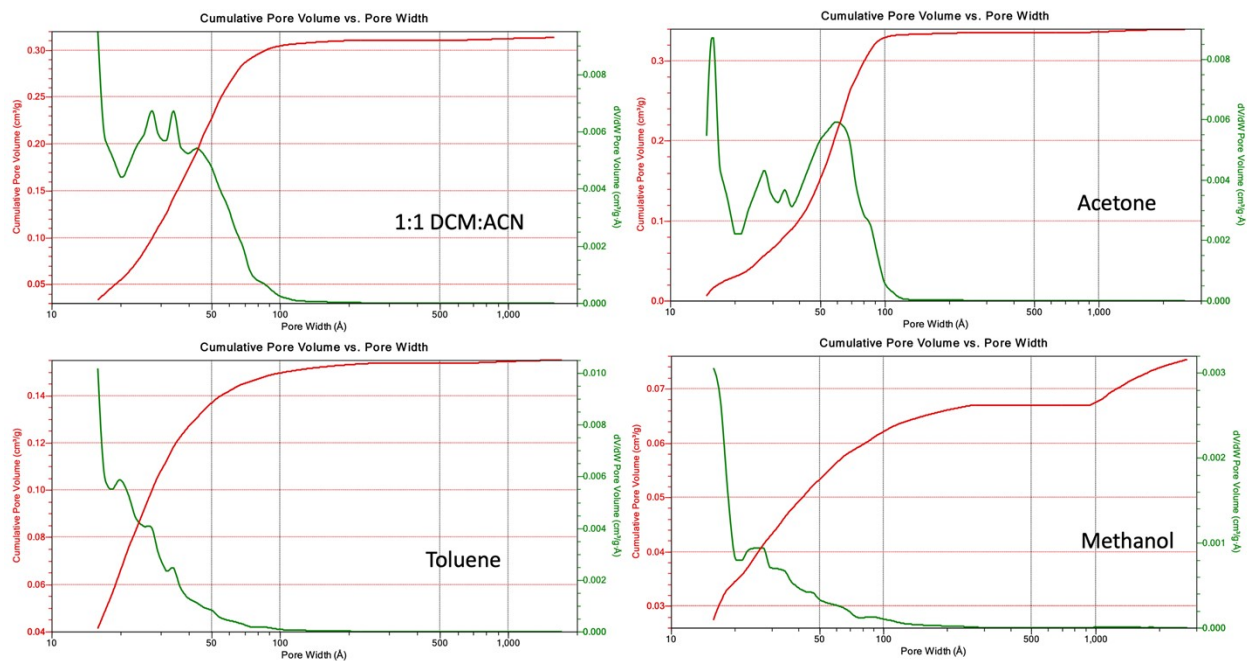


Figure S18. Pore size distributions for reactions in alternative solvents.

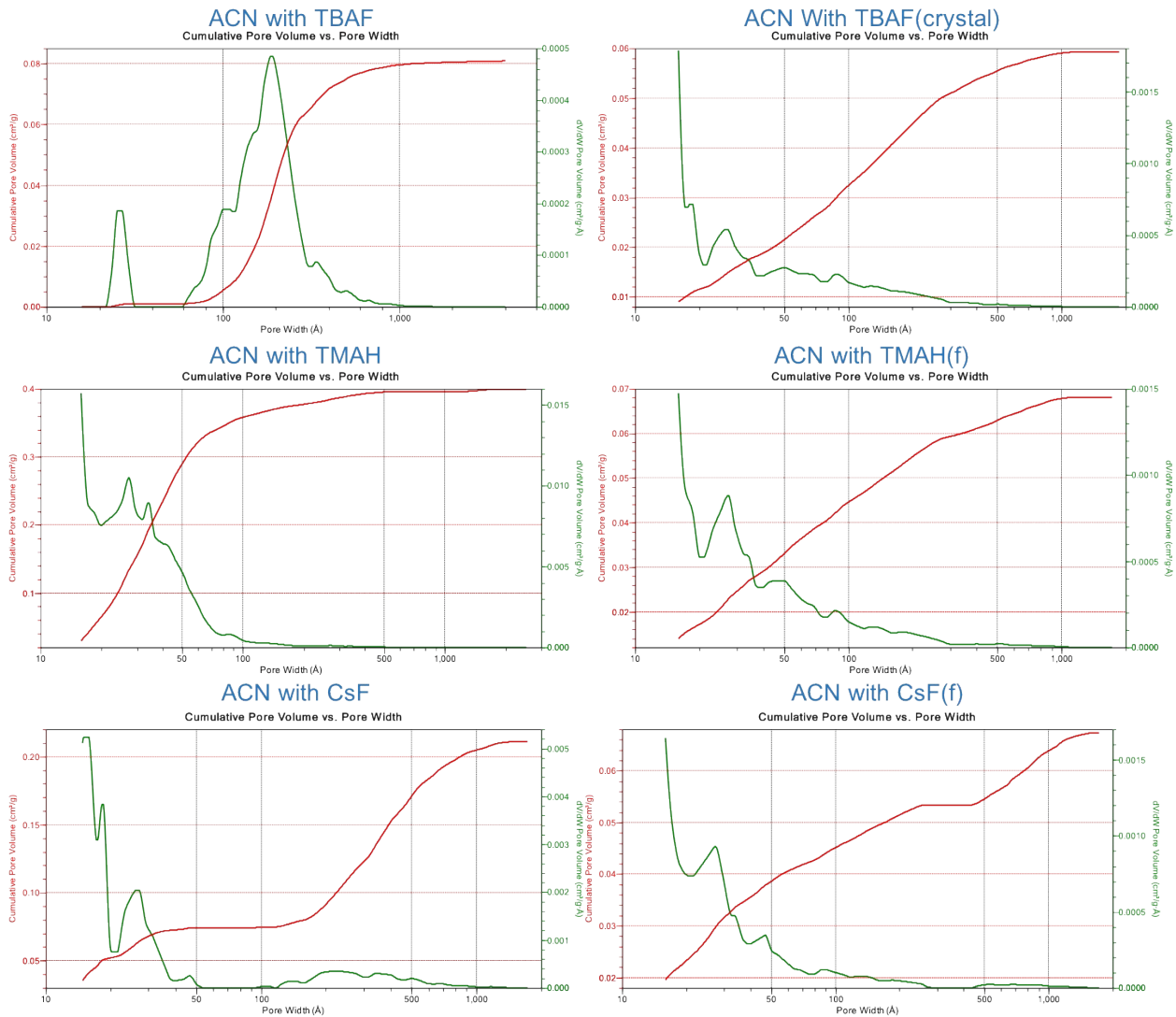


Figure S19. Pore size distributions for reaction in ACN with different starting catalyst. *(f) indicates foam-like product from corresponding reaction mixture. In general reactions are less complete with alternative catalysts and result in greater pore size distributions than TBAF.

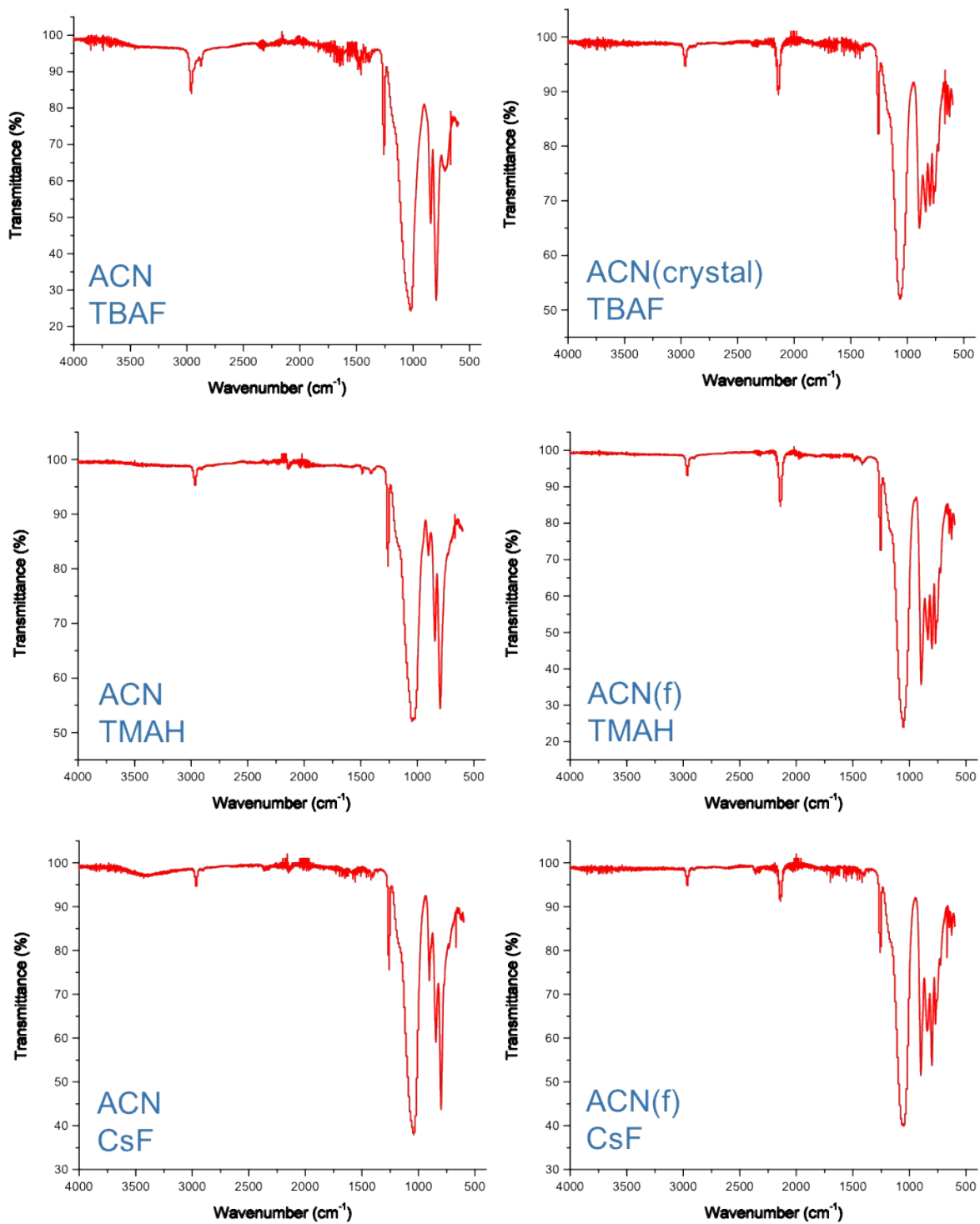


Figure S20. IR spectrum for reaction in ACN with different starting catalyst. *(f) indicates foam-like product from corresponding reaction mixture.

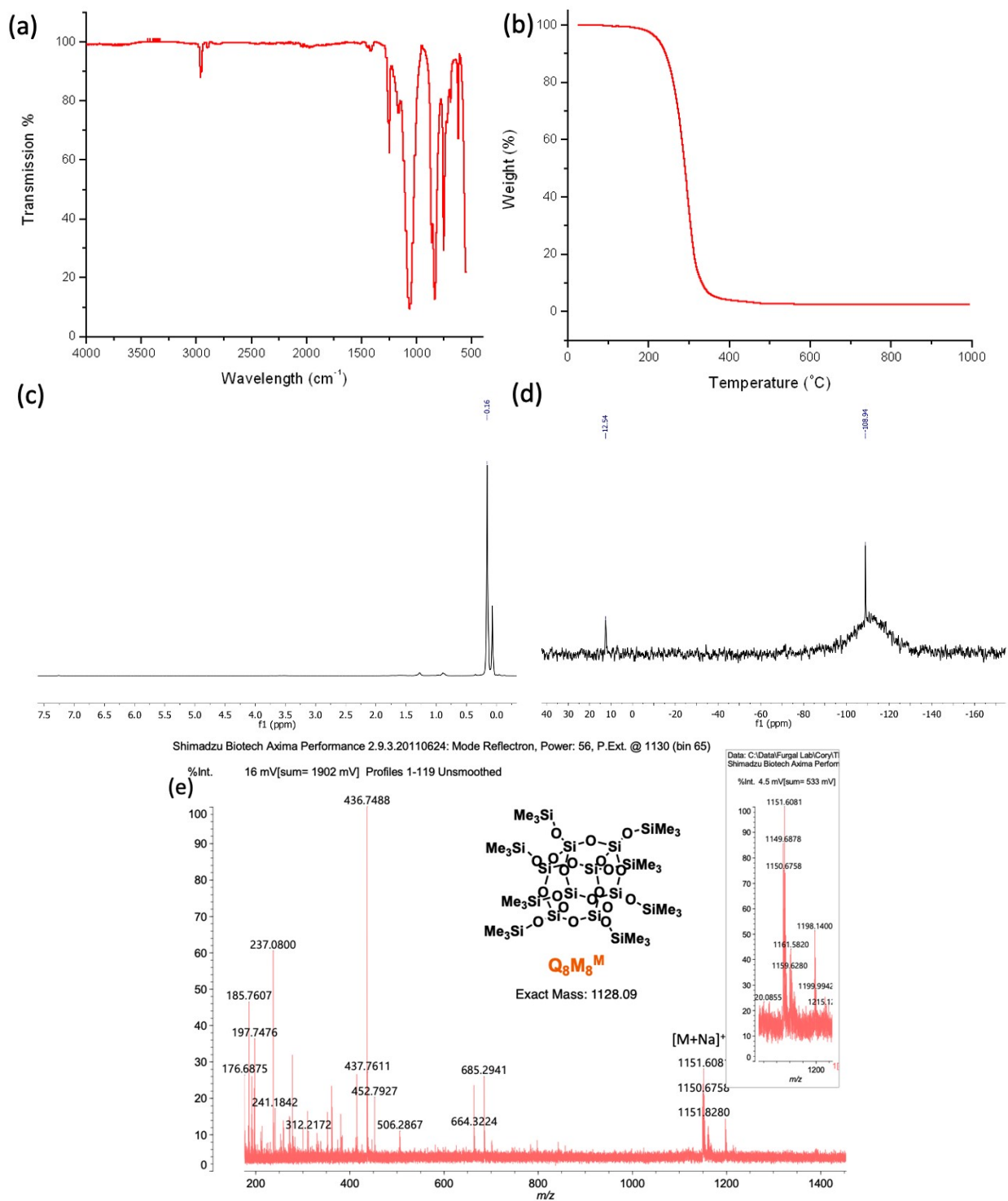


Figure S21. Octadimethylsiloxo-silsesquioxane ($Q_8M_8^M$) Q-cage synthesized by a procedure from Hasegawa and Motojima:¹ (a) FTIR, (b) TGA [$CY = 2.5\%$, $T_{d5\%} = 221\text{ }^{\circ}C$], (c) 1H NMR in $CDCl_3$, (d) ^{29}Si NMR in $CDCl_3$, (e) MALDI-ToF spectrum.

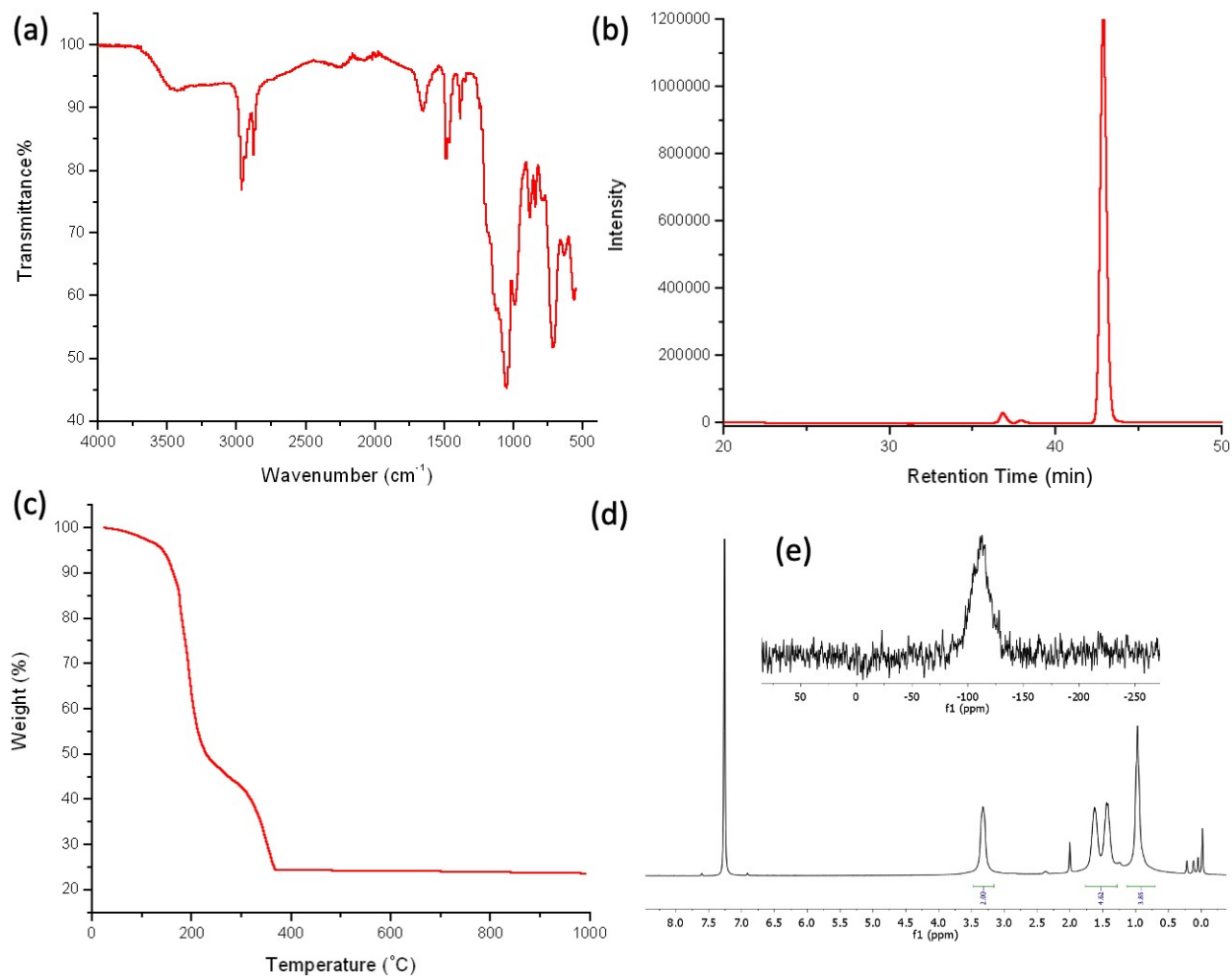


Figure S22. $Q_8M_8^M$ reaction with TBAF in ACN, no added water, resulted in a syrup after 48h high vacuum drying. (a) FTIR, (b) GPC [peak at 43 min is toluene reference, peaks at 36 and 37 min associated with reaction], (c) TGA [CY = 24%, $T_{d5\%} = 142$ °C], (d) ¹H NMR in CDCl₃ [primarily shows tetrabutylammonium peaks due to low miscibility of reaction product in solvents], (e) ²⁹Si NMR in CDCl₃ [only shows glass due to low miscibility of reaction product in solvents].

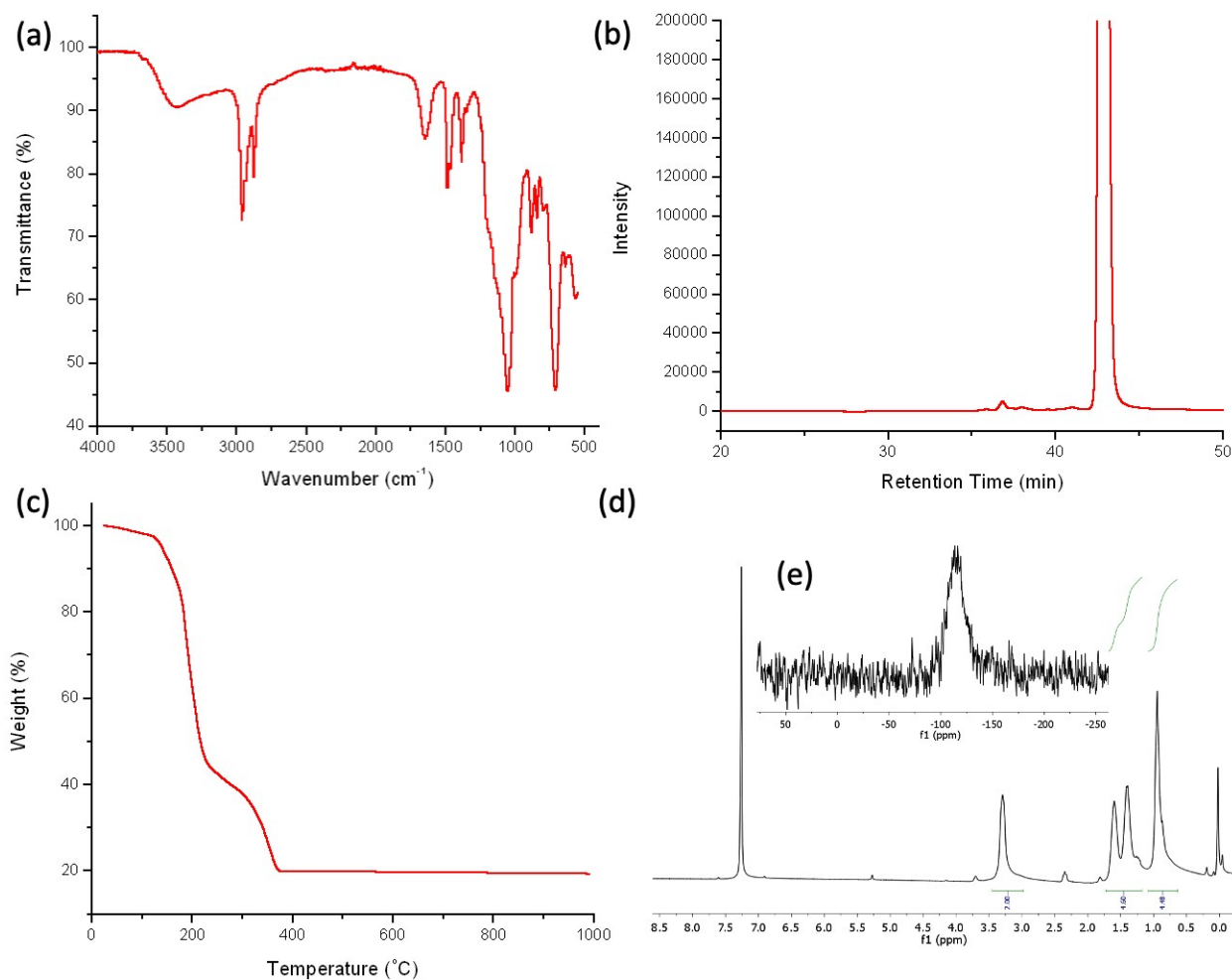


Figure S23. $Q_8M_8^M$ reaction with TBAF in DCM, no added water, resulted in a syrup after 48h high vacuum drying. (a) FTIR, (b) GPC [peak at 43 min is toluene reference, peak at 36 min associated with reaction], (c) TGA [CY = 19.7%, $T_{d5\%}$ = 140 °C], (d) ¹H NMR in CDCl₃ [primarily shows tetrabutylammonium peaks due to low miscibility of reaction product in solvents], (e) ²⁹Si NMR in CDCl₃ [only shows glass due to low miscibility of reaction product in solvents].

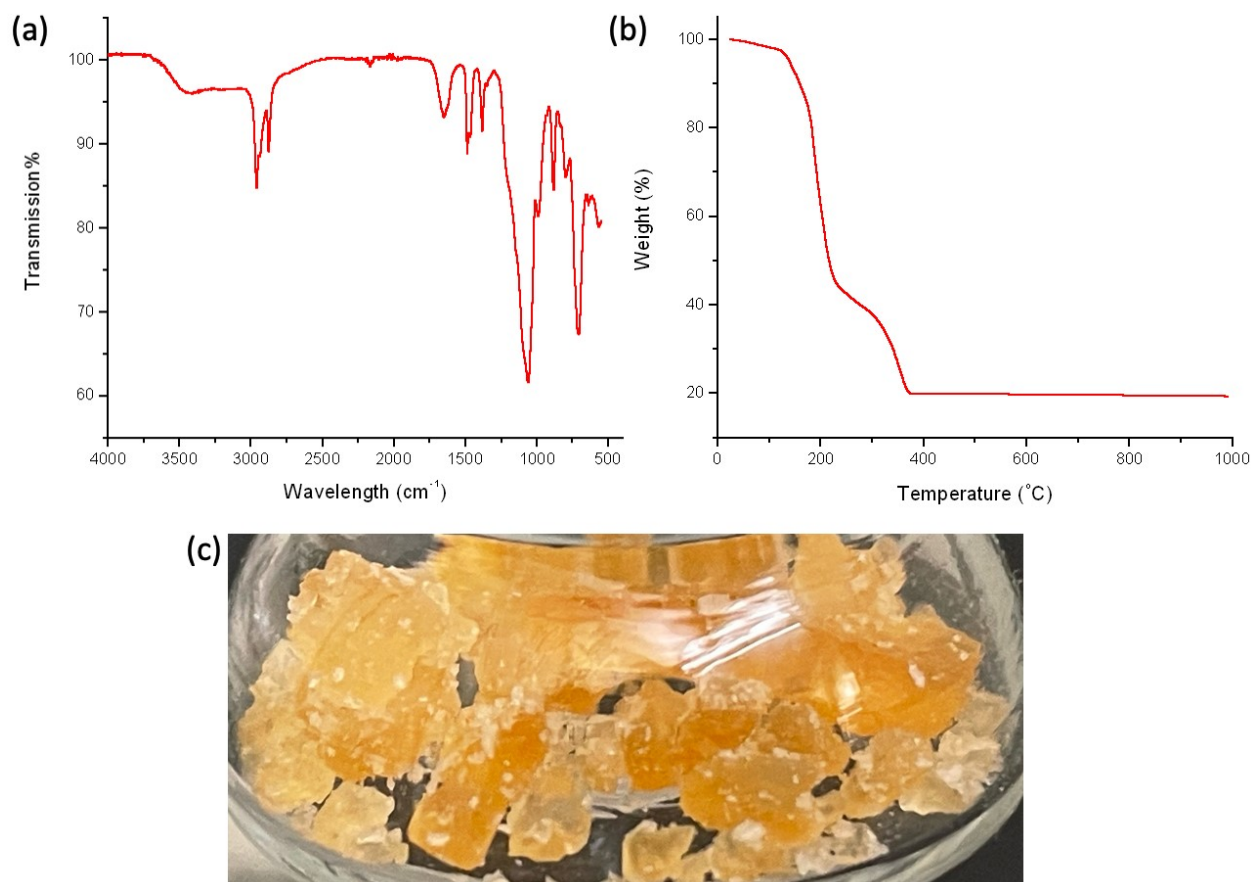


Figure S24. Q₈M₈^M reaction with TBAF in ACN, 100 mmol water added, resulted in a solid yellow-orange soft insoluble gel that contains no porosity [dried 72 hours under high vacuum, then 24 hours at 60 °C in vacuum oven]. (a) FTIR, (b) TGA [CY = 19.6%, T_{d5%} = 140 °C].

Reference:

- 1 I. Hasegawa and S. Motojima, *J. Organomet. Chem.*, 1992, **441**, 373–380.