Electronic Supplementary Material (ESI) for Chemical Science
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Electronic Supplementary Information for: One-Hundred Fold Overall Sensitivity Enhancements for Silicon-29 NMR Spectroscopy of Surfaces by Dynamic Nuclear Polarisation with CPMG Acquisition.

Aaron J. Rossini,[a] Alexandre Zagdoun,[a] Moreno Lelli,[a] David Gajan,[b] Fernando Rascon,[b] Melanie Rosay,[c] Werner E. Maas,[c] Christophe Copéret,[b] Anne Lesage,[a] and Lyndon Emsley*[a]

[a]*Centre de RMN à Très Hauts Champs, University of Lyon (CNRS/ENS Lyon/UCB Lyon 1), 5 Rue de la Doua, 69100, Villeurbanne, France. Fax: +33 4 78 89 67 61; E-mail: lyndon.emsley@ens-lyon.fr*
[b]*Department of Chemistry, ETH Zürich, Laboratory of Inorganic Chemistry, 10 Wolfgang Pauli Strasse, CH-8093, Zürich, Switzerland*
[c] *Bruker BioSpin Corporation, 15 Fortune Drive, Billerica, MA 01821, USA*

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Table S1. Determination of the Mass of Mesoporous Silica Material Inside Each Rotor

Biradical Concentration (mM)	$m_{\mathrm{SiO2\ Total}}$ (mg)^a	m_{H2O} (mg)^b	m_{full} (mg)^c	m_{SiO2} (mg)^d	m_{left} (mg)^e
Pure H_2O	9.0(2)^f	11.6(4)	18.6(4)	8.1(3)	2.0(1)
4.0	8.8(2)	11.4(4)	18.2(4)	7.9(3)	2.0(1)
7.8	9.2(2)	11.8(4)	18.3(4)	8.0(3)	2.7(1)
12.1	8.9(2)	11.4(4)	18.5(4)	8.1(3)	1.8(1)
16.1	8.8(2)	11.8(4)	18.0(4)	7.7(3)	2.6(1)
20.3	9.5(2)	14.6(4)	21.9(4)	8.6(3)	2.2(1)
23.9	8.9(2)	12.1(4)	16.7(4)	7.1(3)	4.3(1)

[a] This is the mass of dry material which was initially added to the weigh boat.

[b] This is the mass of pure water which was added to the dry material in the weigh boat. A micro-pipette set to 12 μL was used to add the water.

[c] This is the total mass of wetted material which was packed into the rotor. This was found by subtracting the mass of the empty rotor from that of the packed rotor.

[d] This is the total mass of dry material in the rotor, which was calcuated as,

$$m_{\mathrm{SiO2}} = m_{\mathrm{full}}\left(\frac{m_{\mathrm{SiO2\ TOTAL}}}{m_{\mathrm{SiO2\ TOTAL}} + m_{\mathrm{H2O}}}\right).$$

[e] This is mass of wet material that was not transferred into the rotor,

$m_{\mathrm{left}} = (m_{\mathrm{H2O}} + m_{\mathrm{SiO2\ Total}}) - (m_{\mathrm{full}})$.

[f] The uncertainty of the analytical balance was ±0.2 mg. This uncertainty was propagated in order to determine the uncertainties associated with the calculated masses.

Table S2. Acquisition Parameters of ^{29}Si SSNMR Spectra.

Pulse Sequence	**CP/MAS**	**CP/MAS**	**CP/CPMG**
MW on/ MW off	MW on	MW off	MW on
Number of scans	128/8	384	128
Recycle Delay (s)	2.0/30.0	2.0	2.0
Dwell (μs)	11.2	11.2	10.0
Spectral width (kHz)	89.3	89.3	100.0
Sample Spinning Rate [ν_{rot}] (Hz)	8000	8000	8000
Acquisition length (number of points)	800	800	9300
^{1}H 90º pulse width [π/2] (μs)	2.80	2.80	2.80
CP contact time (ms)	2.5	2.5	2.5
^{1}H rf field during contact pulse (kHz)	80	80	80
^{29}Si rf field during contact pulse (kHz)	50	50	50
^{1}H rf field during decoupling (kHz)	89	89	89
180º pulse widths [π] (μs)	-	-	10.00
Number of Meiboom-Gill loops [N]	-	-	12
Real points per echo	-	-	350

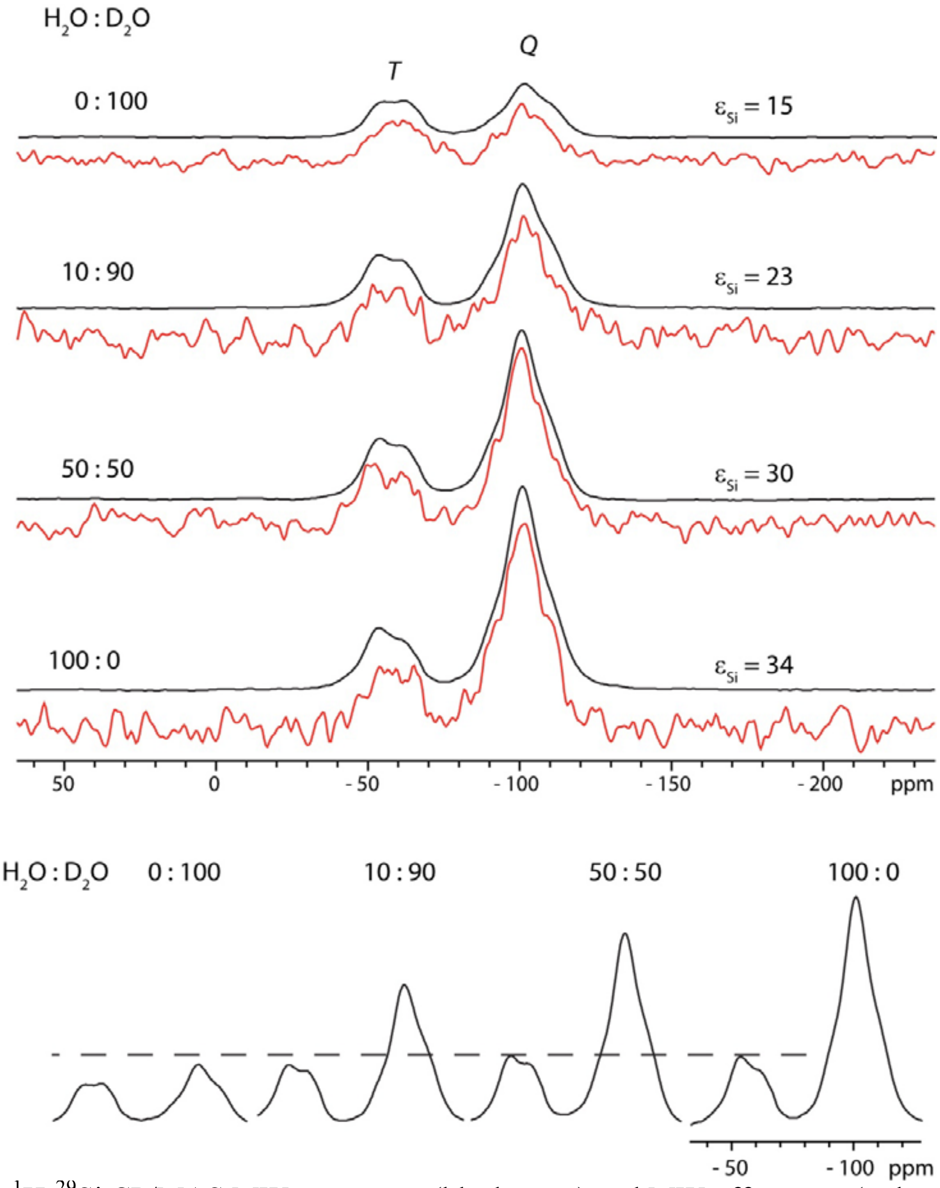

Figure S1. ^{1}H-^{29}Si CP/MAS MW on spectra (black trace) and MW off spectra (red trace) of a methyl passivated mesoporous silica material impregnated with 10 mM TOTAPOL solutions. The structure of the material is identical to that of **I** in Figure 1 (main text), however, the surface of the material is passivated with methyl groups rather than phenol groups. The influence of H_2O:D_2O ratio on ε_{Si} is illustrated in the top portion of the figure. ε is the same for both the *T* and *Q* sites. The intensity of the MW off spectra has been increased by the corresponding value of ε_{Si}. In the bottom portion of the figure the signals of the *T*-sites of the MW on ^{29}Si SSNMR spectra are compared. The decrease in *Q*-site intensity with higher deuteration ratios is attributed to exchange of surface hydroxyl protons for deuterons. Clearly the material impregnated with the 100% H_2O solution provides the best DNP signal enhancement and the largest absolute signal enhancement. All spectra were acquired with 512 scans, a 1.5 s recycle delay in between scans, and ν_{rot} = 8000 Hz.

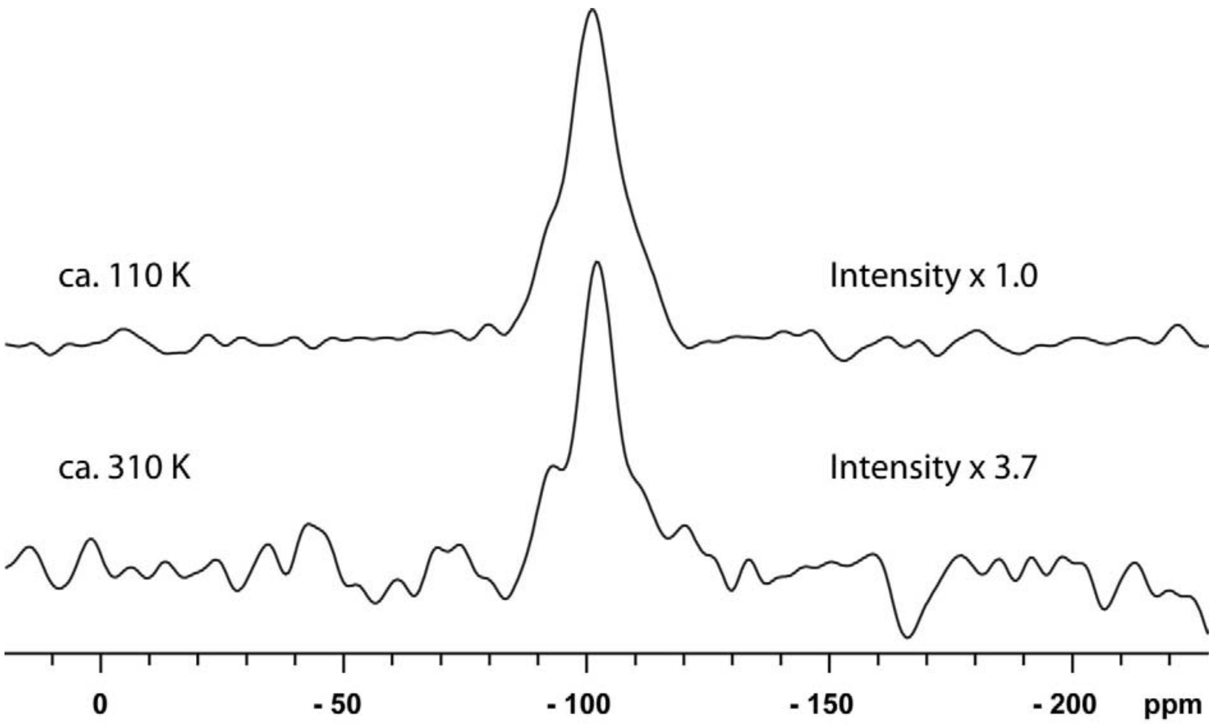

Figure S2. ^{29}Si CP/MAS spectra of **I** acquired at sample temperatures of ca. 110 K and ca. 310 K. Spectra were acquired on a 11.7 T magnet equipped with a low temperature MAS probe similar in design to that employed for DNP experiments. Both spectra were acquired with 100 scans, 2.0 s recycle delays and sample spinning rates of 8000 Hz. All pulse powers (π/2 pulse, contact pulse and decoupling pulses) were re-optimized at each temperature to account for the variation in probe performance with temperature. Saturation recovery measurements indicate that the longitudinal magnetization was fully recovered after ca. 1.2 s at both sample temperatures. The signal of the low temperature spectrum is 3.7(2) times larger than that of the room temperature spectrum. The expected Boltzmann enhancement factor is ca. 2.8. The additional signal enhancement is attributed to increased CP efficiency at lower temperature as well as an increase in the probe quality factor (Q).

Synthesis and Characterization of Methyl Passivated Silica

*General Methods***.** Syntheses and treatments of the surface species were carried out using high vacuum lines (10^{-5} mbar) and glove-box techniques. $(CH_3O)_3SiCH_3$ was purchased from Aldrich. SBA-15 was prepared from $Si(OEt)_4$ according to literature conditions,[1] calcined at 500 °C under air for 5 h and then treated under vacuum at 500 °C for 15 h (support referred as SBA-15_{500}). Pentane was collected from a MBraun SPS-800 solvent purifying unit, dioxane was distilled from Na/K under argon. Elemental analyses were performed at the University of Bourgogne (C, H). Infrared spectra were recorded on a Nicolet 5700 FT-IR spectrometer by using a diffuse reflectance (DRIFT) device. Typically, 32 scans were accumulated for each spectrum (resolution 4 cm^{-1}). Nitrogen adsorption measurements were performed on a Bel-Sorp Max apparatus (Bel Japan Inc.).

*Preparation of methyl-passivated silica***.** A 250mL three necked round bottom flask equipped with a reflux condensor, a dropping funnel and a magnetic stirring bar was charged with SBA-15 (1.2 g), Dioxane (120 mL), and aqueous HCl solution (26 mL, 2.3 N). The mixture was heated to 75 °C under vigourous stirring, and then $(CH_3O)_3SiCH_3$ (1 mL, *ca.* 7.5 mmol) in dry dioxane (35 mL) was added dropwise over a period of 20 min. The mixture was then refluxed for 1.5 h, and then it was allowed to cool down to room temperature. The solid was filtered through a frit (pore type 4) and washed consecutively with 3 X 50mL portions of 20:80 water/THF, THF and diethyl ether (twice with each solvent). The resulting solid was dried at room temperature under vacuum (10^{-5} torr) for 1 h and then under high vacuum at 140 °C during 12 h.

Characterization of methyl-passivated silica

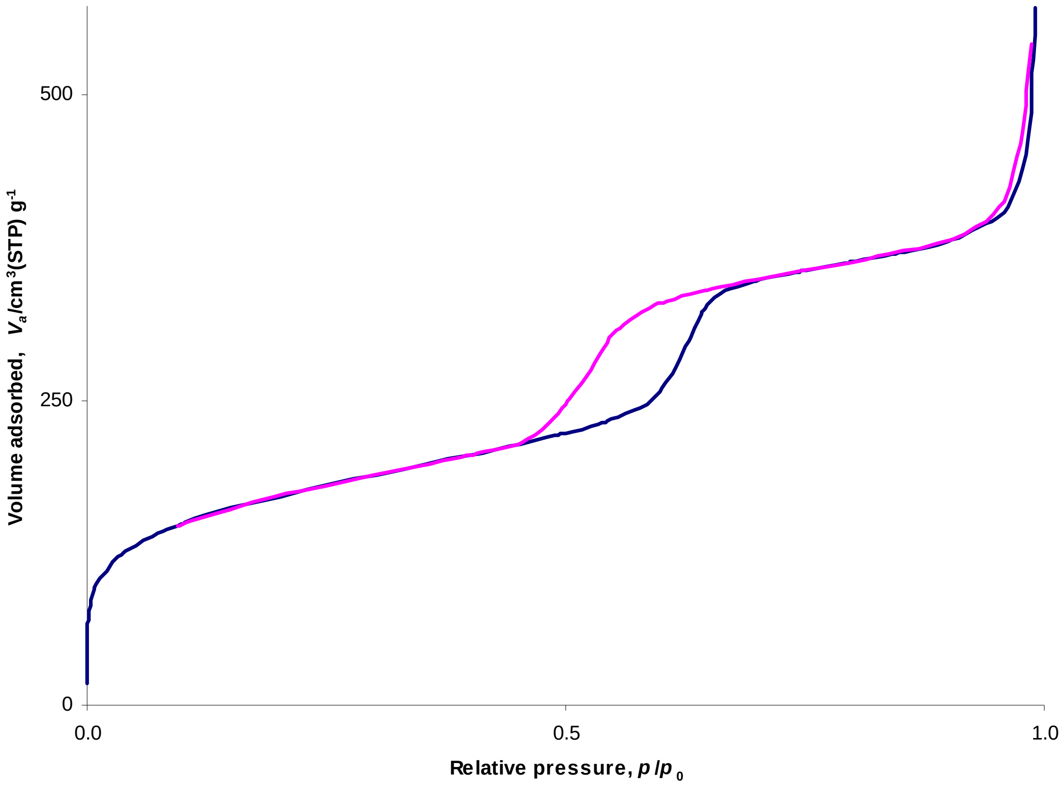

Figure S3. Nitrogen adsorption-desorption isotherm of methyl passivated silica (SBA-15). Isotherm type IV, characteristic of a mesoporous material. Surface (BET) Area = 888 ± 4 m^2 g^{-1}, Pore diameter (BJH) = 4.61 nm, Total pore volume (BET) = 1.16 cm^3 g^{-1}.

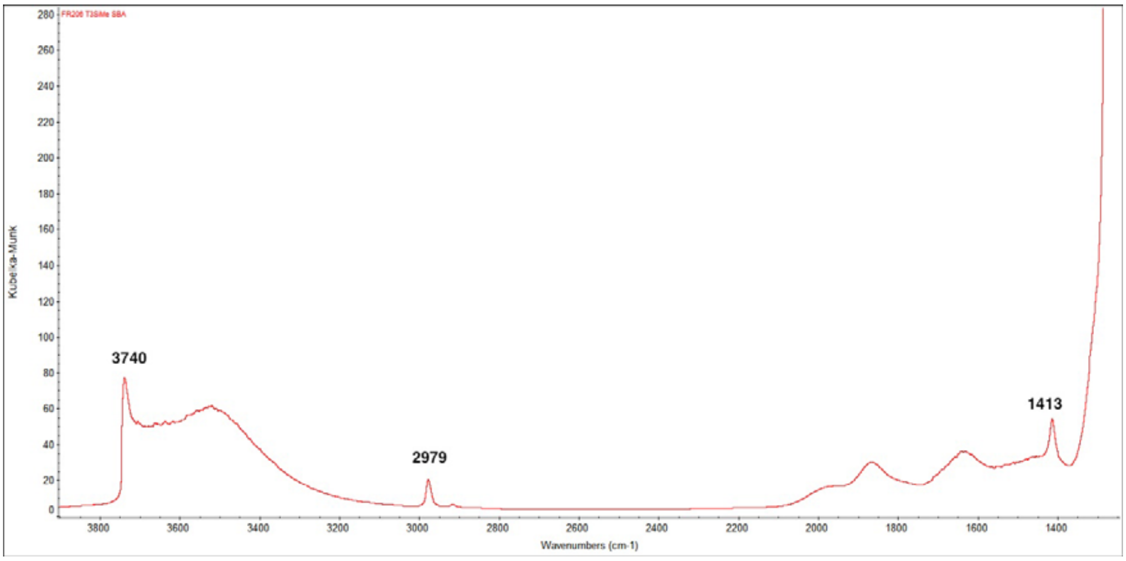

Figure S4. Diffuse reflectance infrared spectrum (DRIFT) of methyl-passivated silica (SBA-15).

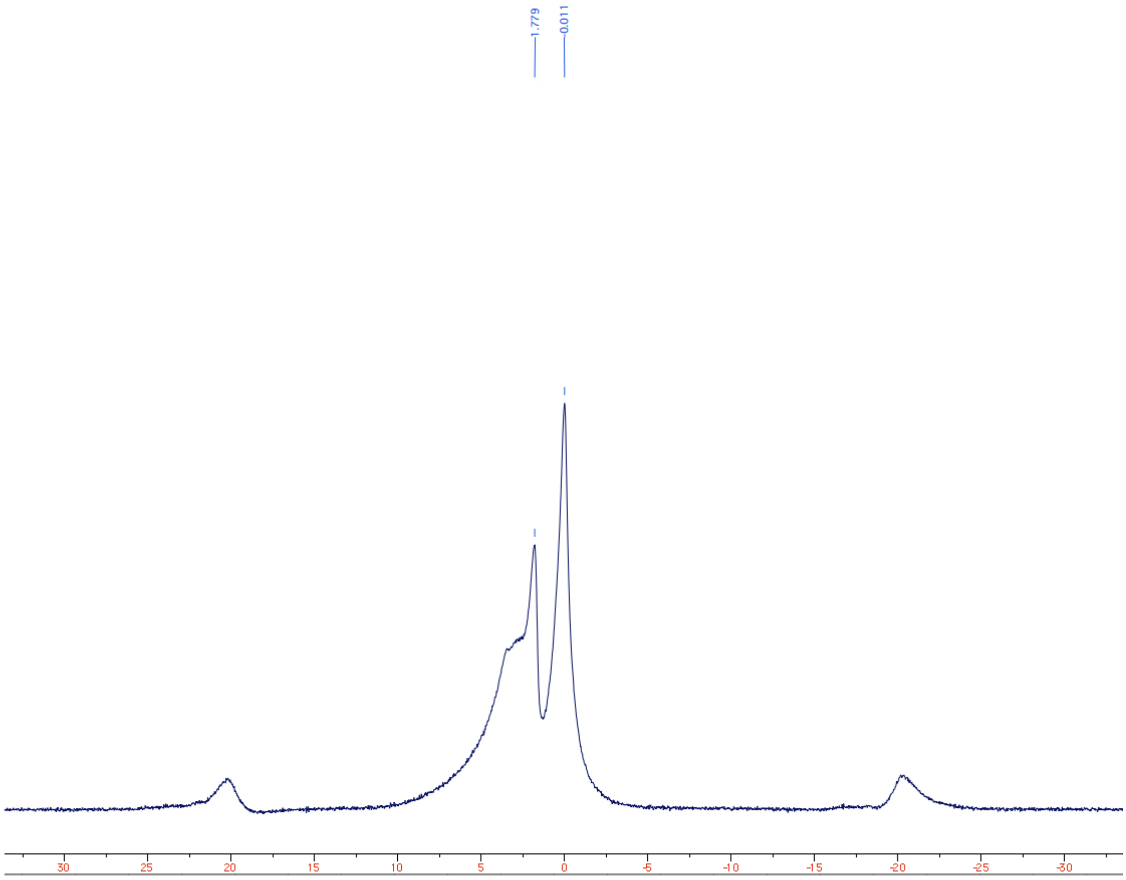

Figure S5. ^{1}H Solid-state nuclear magnetic resonance spectrum of methyl-passivated silica (SBA-15) acquired with a sample spinning rate of 10 kHz with a total of 8 scans and a recycle delay of 256 s.

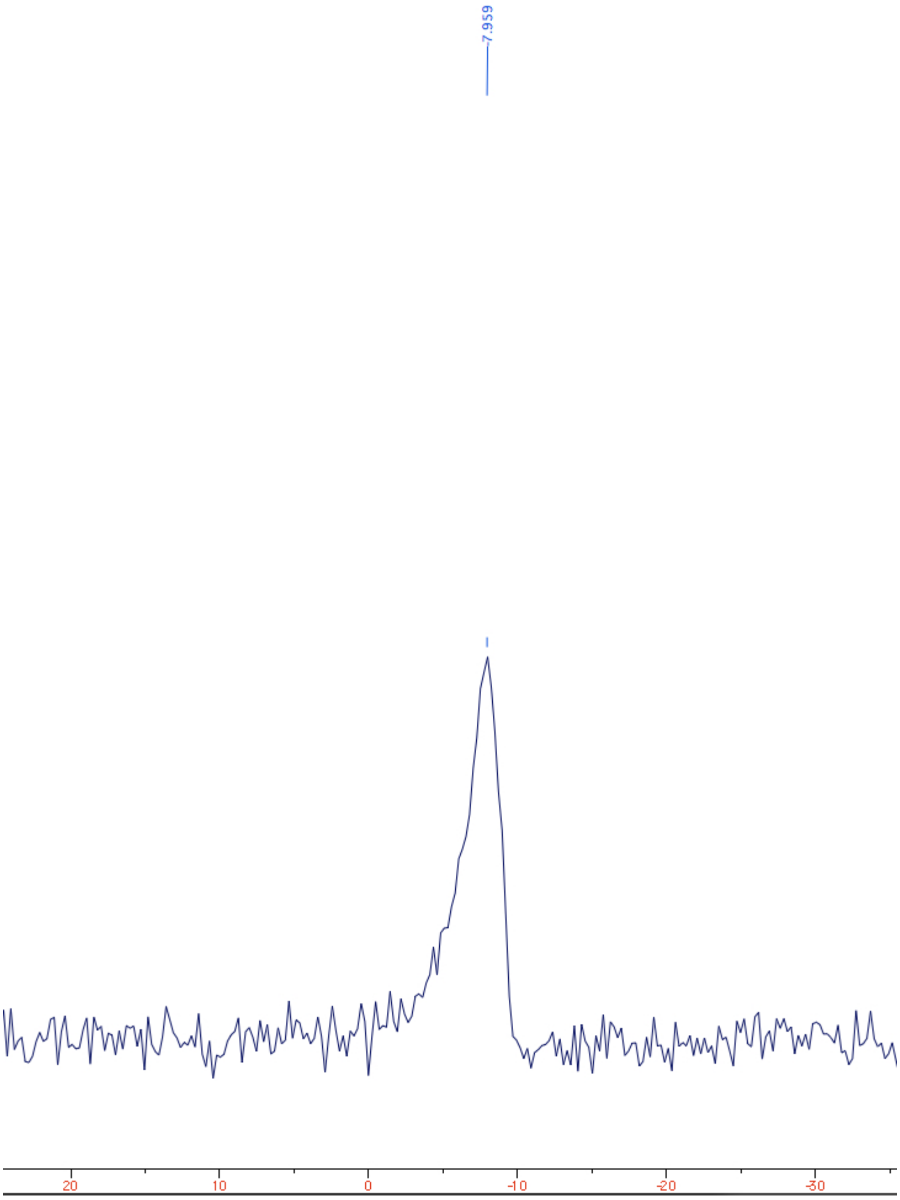

Figure S6. ^{1}H-^{13}C CP/MAS solid-state NMR spectrum of methyl-passivated silica (SBA-15), acquired with a sample spinning rate of 10 kHz.

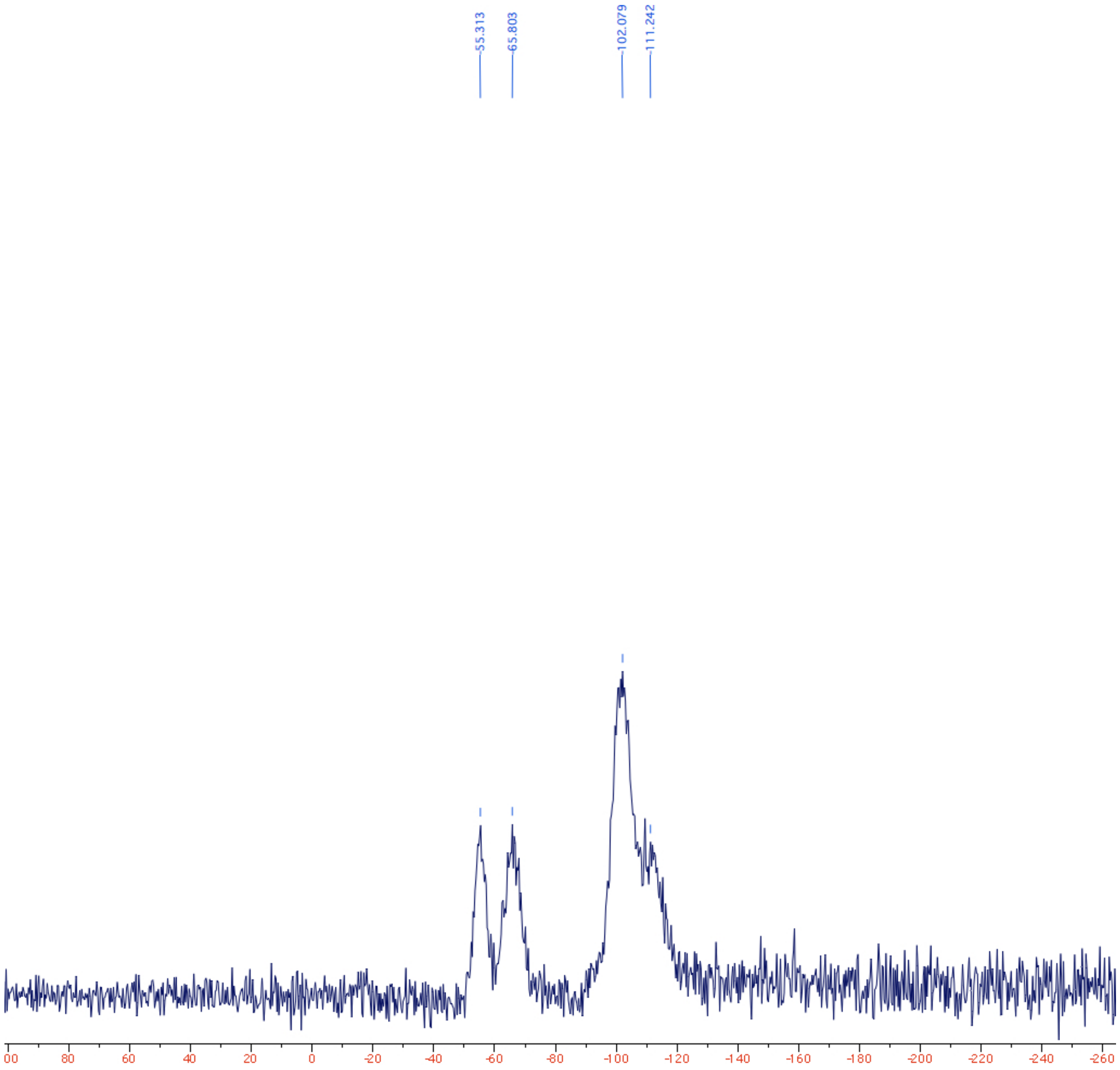

Figure S7. 1H-^{29}Si CP/MAS solid-state NMR spectrum of methyl-passivated silica (SBA-15) acquired with a sample spinning rate of 5 kHz with a total of 9060 scans, a contact time of 5 ms and a recycle delay of 16 s**.**

References

[1] D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc.* **1998**, *120*, 6024-6036.