Electronic Supplementary Information

Silica materials with wall-embedded nitroxides provide efficient polarisation matrices for dynamic nuclear polarization NMR

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1. Experimental procedures for organic precursors

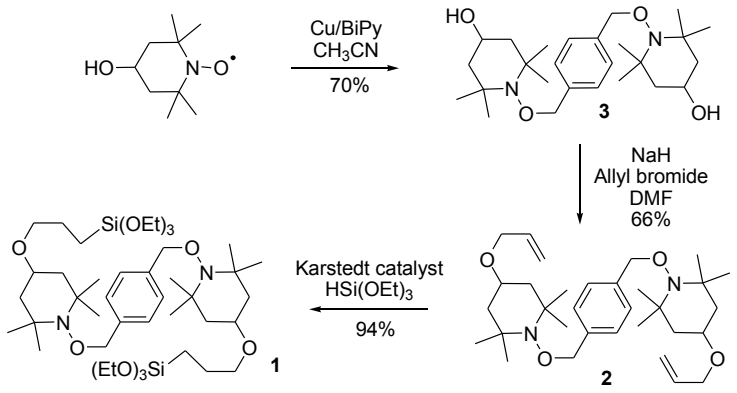
1.1. General procedures

All reactions were carried out in dry glassware using magnetic stirring and a positive pressure of argon. Commercially available solvents were used as purchased, without further purification. CH_2Cl_2 was distilled over CaH_2 and stored under dry conditions. THF was distilled over sodium benzophenone ketyl prior to use. Dry state adsorption conditions and purification were performed on Macherey Nagel silica gel 60 Å (70-230 mesh). Analytical thin layer chromatography was performed on pre-coated silica gel plates. Visualization was accomplished by UV (254 nm) and with phosphomolybdic acid in ethanol. ^{1}H and ^{13}C NMR spectra were recorded on 300 or 400 MHz Bruker NMR Avance III (Nanobay) spectrometers. Chemical shifts (δ) are reported in ppm downfield of TMS. Signals due to residual protonated solvent (^{1}H NMR) or to the solvent (^{13}C NMR) served as the internal standard: $CDCl_3$ (7.27 ppm and 77.0 ppm). Multiplicity is indicated by one or more of the following: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), br (broad). The lists of coupling constants (*J*) correspond to the order of multiplicity assignment and are reported in Hertz (Hz). The APT pulse sequence was used for assigning ^{13}C NMR spectra. All melting points were uncorrected and were recorded in open capillary tubes using a melting point apparatus.

1.2. Chemicals

1,4-Bis(bromomethyl)benzene and 4-Hydroxy-TEMPO (4-Hydroxy-2,2,6,6-tetramethylpiperidine) are commercially available and were used as purchased without purification.

1.3. Synthesis of precursor 1



1-[(4-{[(4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yl)oxy]methyl}phenyl)methoxy]-2,2,6,6-tetramethylpiperidin-4-ol (3).[1] A solution of 1,4-bis(bromomethyl)benzene (1.32 g, 5.0 mmol, 1 equiv), 4-hydroxy-TEMPO (1.72 g, 10.0 mmol, 2 equiv), 2,2′-bipyridine (3.12 g, 20.0 mmol, 4 equiv) in acetonitrile (25 mL) under argon was degassed 5 min by bubbling with argon. Then copper (630 mg, 10.0 mmol, 2 equiv) was added and the mixture stirred overnight at room temperature. After addition of AcOEt (50 mL), the mixture was filtrated and the organic phase washed with a solution of $CuSO_4$ (5%), water (3 times) and brine. After drying over $MgSO_4$, the solution was evaporated to give **3** (1.57 g, 3.5 mmol, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (s, 4 H, Ar*H*), 4.81 (s, 4 H, CH_2O), 3.98 (m, 2 H, C*H*OH), 1.84 (dd, *J* = 12.5 and 4.2 Hz, 4 H, CH_{eq}H), 1.51 (t, *J* = 11.9 Hz, 4 H, CH_{ax}H), 1.30 (s, 12 H, CH_3), 1.20 (s, 12 H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.2 (C_{Ar}), 127.5 (CH$_{Ar}$), 78.7 (*C*), 63.3 (HO*C*H), 60.3 (O*C*H$_2$Ph), 48.3 (*C*H$_2$), 33.2 (*C*H$_3$), 21.2 (*C*H$_3$). (ESI): *m/z*: calculated for $[M+H]^+$ $C_{26}H_{45}N_2O_4$: 449.3374, found: 449.3369.

2,2,6,6-tetramethyl-4-(prop-2-en-1-yloxy)-1-{[4-({[2,2,6,6-tetramethyl-4-(prop-2-en-1-yloxy)piperidin-1-yl]oxy}methyl)phenyl]methoxy}piperidine (2). To a 0°C solution of **3** (0.93 g, 2.0 mmol, 1 equiv) in dry DMF (12 mL) was added NaH (192 mg, 8 mmol, 4 equiv). The suspension was stirred 30 min then allylbromide (968 mg, 8 mmol, 4 equiv) was added. The resulting mixture was stirred one night. The reaction was monitored by TLC. After completion, the mixture was diluted with water, and extracted three times with AcOEt. Organic extracts were washed with water and brine, dried over $MgSO_4$ and concentrated. The residue was purified using silica gel column (5/95 EtOAc /pentane) to give **2** (0.7 g, 1.3 mmol, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (s, 4 H, Ar*H*), 5.93 (ddt, *J* = 17.2, 10.4, 5.6 Hz, 2H, C*H*=CH$_2$), 5.40 (dt, *J* = 17.2, 1.5 Hz, 2H, CH=CH_2), 5.16 (dd, *J* = 10.4, 1.5 Hz, 2H, CH=CH_2), 4.81 (s, 4 H, CH_2O), 4.00 (br d, *J* = 5.6 Hz, 4H, OCH_2), 3.62 (m, 2 H, C*H*OCH$_2$), 1.87 (dd, *J* = 12.5, 3.9 Hz, 4 H, CH_{eq}H), 1.50 (t, *J* = 11.8 Hz, 4 H, CH_{ax}H), 1.29 (s, 12 H, CH_3), 1.18 (s, 12 H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.2 (C_{Ar}), 135.3 (*C*H=CH$_2$), 127.5 (CH$_{Ar}$), 116.6 (CH=*C*H$_2$), 78.7 (*C*), 69.9 (O*C*H), 69.1 (O*C*H$_2$), 60.3 (O*C*H$_2$Ph), 45.1(*C*H$_2$), 33.3 (*C*H$_3$), 21.3 (*C*H$_3$). HRMS (ESI): *m/z*: calculated for $[M+H]^+$ $C_{32}H_{53}N_2O_4$: 529.4000, found: 529.4001.

[1] S. Harrisson, P. Couvreur and J. Nicolas *Polym. Chem.*, 2011, **2**, 1859-1865.

2,2,6,6-tetramethyl-1-({4-[({2,2,6,6-tetramethyl-4-[3-(triethoxysilyl)propoxy]piperidin-1-yl}oxy)methyl]phenyl}methoxy)-4-[3-(triethoxysilyl)propoxy]piperidine (1). To compound **2** (0.7 g, 1.3 mmol, 1 equiv) under argon was added triethoxysilane (0.9 g, 5.5 mmol, 4 equiv) and Karstedt catalyst. The medium was stirred at room temperature for one night (^{1}H NMR monitoring). Then, the mixture was concentrated, pentane was added and the resulting solution filtrated under argon and concentrated. The product was used without further purification (1.05 g, 1.2 mmol, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (s, 4 H, Ar*H*), 4.80 (s, 4 H, CH_2O), 3.81 (q, *J* = 7.0 Hz, 12H, SiOCH_2), 3.54 (m, 2 H, C*H*OCH$_2$), 3.40 (t, *J* = 6.9 Hz, 4H, OCH_2), 1.84 (m, 4 H, CH_2), 1.69 (m, 4H, OCH$_2$CH_2), 1.46 (t, *J* = 11.8 Hz, 4 H, CH_{ax}H), 1.28 (s, 12 H, CH_3), 1.23 (t, *J* = 7.0 Hz, 18H, 6 x CH_3), 1.18 (s, 12 H, CH_3), 0.64 (m, 2H, SiCH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.2 (C_{Ar}), 127.5 (CH_{Ar}), 78.7 (*C*), 70.4 (O*C*H$_2$), 70.2 (O*C*H), 60.3 (O*C*H$_2$Ph), 58.4 (O*C*H$_2$), 45.2(*C*H$_2$), 33.3 (*C*H$_3$), 23.5 (*C*H$_2$), 21.2 (*C*H$_3$), 18.3 (*C*H$_3$), 6.5 (Si*C*H$_2$). HRMS (ESI): *m/z*: calculated for $[M+H]^+$ $C_{44}H_{85}N_2O_{10}Si_2$: 857.5737, found: 857.5739.

2. Experimental procedures for materials

2.1. Thermogravimetric analysis (TGA), X-rays and Nitrogen adsorption/desorption

TGA measurements were carried out with a TGA Q500 apparatus (TA Instruments) under dynamic air atmosphere (sample flow rate 40 mL min^{-1}). SAXS experiments were performed on SAXSess-MC2 (Anton-Paar, GmbH, Austria) with a sealed copper tube as a X-ray source (wavelength is 0.15417 nm (Cu K-α)) and CCD camera as a detection system. The N_2 adsorption/desorption isotherms were obtained at 77 K on a Micrometrics ASAP2010. The specific surface area was determined with the Brunauer, Emmett, and Teller (BET) method and the pore size distribution was calculated from the desorption isotherms using the Barrett Joyner Halenda (BJH) method.[2] Prior to adsorption, the samples were outgassed at 373 K overnight under a vacuum pressure of 2 10^{-3} mbar.

2.2. Solid-state NMR

All solid-state cross polarization magic angle spinning (CPMAS) NMR spectra were obtained on a Bruker Avance III 400 MHz NMR spectrometer operating at a ^{13}C and ^{29}Si Larmor resonance frequency of 101.6 MHz and 79.5 MHz, respectively. ^{13}C and ^{29}Si CPMAS experiments were performed with a commercial Bruker double-bearing probehead. About 100

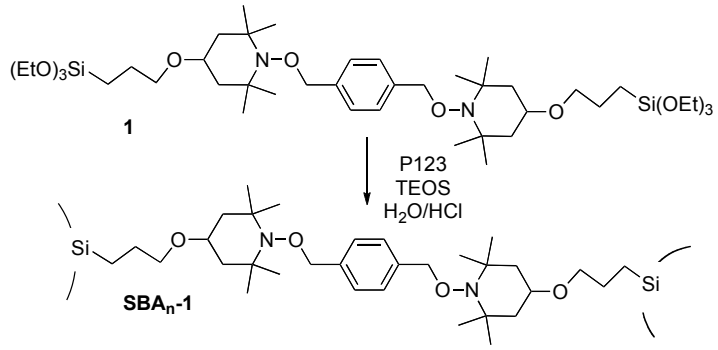
[2] Rouquerol, F., Rouquerol, J., Llewellyn, P., Maurin, G. & Sing, K. S. W. Adsorption by Powders and Porous Solids: Principles, Methodology and Applications 2nd edition (Academic Press: London, 2013).

mg of samples were placed in zirconium dioxide rotors of 4-mm outer diameter and spun at a magic-angle spinning rate of 10 kHz. The CP technique[3] was applied with a ramped ^{1}H-pulse starting at 100% power and decreasing until 50% during the contact time in order to circumvent Hartmann-Hahn mismatches.[4,5] The contact times were 2 ms for ^{13}C CPMAS and 5 ms for ^{29}Si CPMAS. To improve the resolution, a dipolar decoupling GT8 pulse sequence[6] was applied during the acquisition time. To obtain a good signal-to-noise ratio, 6144 scans were accumulated using a delay of 2 s in ^{13}C CPMAS experiment, and 4096 scans with a delay of 5 s in ^{29}Si CPMAS experiment. The ^{13}C and ^{29}Si chemical shifts were externally referenced to tetramethylsilane.

2.3. Chemicals

Tetraethylorthosilicate is commercially available and was distilled before used.

2.4. Synthesis of SBA_n-1 silicas



SBA_{39}-1. In a typical procedure, 2 g of pluronic P-123 ($EO_{20}PO_{70}EO_{20}$) were dissolved in deionized water (14 mL) and 2 M hydrochloric acid solution (60 mL) by stirring for 3 h at 40 °C. Tetraethoxysilane (4.14 g, 20 mmol, 40 equiv) and precursor **1** (436 mg, 0.5 mmol, 1 equiv), previously dissolved in a few milliliters of ethanol, were then added. The mixture was stirred 24 h at 40 °C, then warmed without stirring at 100 °C for 2 days, filtrated, washed twice with water, once with ethanol and finally extracted with a Soxlhet apparatus (ethanol) for one day. The wet powder was filtrated, washed twice with ethanol, acetone and diethylether. After one night at 80 °C under vacuum, a white powder was recovered. The molar composition of the synthesis mixture was as follows: (1-x) M TEOS : x M **1** :0.017 M P123 Polymer : 188 M H_2O : 5.8 M HCl, where x denotes the number of moles of precursor

[3] J. Schaefer and E. O. R. Stejskal, *J. Am. Chem. Soc*. 1976, **98**, 1031–1032.
[4] O. B. Peersen, X. Wu, I. Kustanovich and S. O. Smith, *J. Magn. Reson.* 1993, **104**, 334–339.
[5] R. L. Cook, C. H. Langford, R. Yamdagni and C. M. Preston, *Anal. Chem.* 1996, **68**, 3979–3986.
[6] G. Gerbaud, F. Ziarelli and S. Caldarelli, *Chem. Phys. Lett.* 2003, **377,** 1–5.

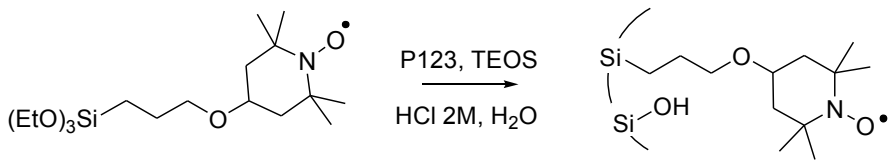
1. ^{13}C CPMAS NMR (101.6 MHz) δ: 136.1, 127.3, 77.6, 69.4, 59.9, 43.7, 30.8, 20.0, 16.2, 7.2. ^{29}Si CPMAS NMR (79.5 MHz) δ: -59.0 (T^2), -67.2 (T^3), -93.6 (Q^2), -103.0 (Q^3), -111.9 (Q^4). BET Surface Area: 679 m²/g. BJH Desorption Average Pore Diameter: 6.4 nm. Vp : 0.973 cm^3/g. SAXS: d = 11.4 nm; a = 9.8 nm.

SBA_{56}-1. The material was prepared by following the previous procedure from tetraethoxysilane (4.19 g, 20.1 mmol, 80 equiv) and precursor **1** (219 mg, 0.25 mmol, 1 equiv). ^{13}C CPMAS NMR (101.6 MHz) δ: 136.0, 127.1, 77.6, 69.2, 60.2, 43.6, 30.8, 20.1, 15.0, 7.4. ^{29}Si CPMAS NMR (79.5 MHz) δ: -67.7 (T^3), -94.5 (Q^2), -103.7 (Q^3), -112.7 (Q^4). BET Surface Area: 661 m²/g. BJH Desorption Average Pore Diameter: 7.2 nm. Vp : 0.976 cm^3/g. SAXS: d = 11.2 nm; a = 9.7 nm.

SBA_{63}-1. The material was prepared by following the previous procedure from tetraethoxysilane (4.21 g, 20 mmol, 39 equiv) and precursor **1** (145 mg, 0.17 mmol, 1 equiv). ^{13}C CPMAS NMR (101.6 MHz) δ: 135.5, 127.6, 77.6, 69.1, 60.0, 43.2, 30.7, 20.1, 14.7, 7.1. ^{29}Si CPMAS NMR (79.5 MHz) δ: -67.6 (T^3), -94.6 (Q^2), -103.8 (Q^3), -113.1 (Q^4). BET Surface Area: 651 m²/g. BJH Desorption Average Pore Diameter: 7.2 nm. Vp : 1.011 cm^3/g. SAXS: d = 11.5 nm; a = 9.9 nm.

2.5. Synthesis of silica of reference with TEMPO moieties in the pores

In order to determine the concentration of radicals after thermolysis, a silica SBA material functionalized with TEMPO moieties was synthesized (**SBA_{30}-3**). Precisely, the double integral of the EPR spectrum of **SBA_{30}-3** was used as a calibrating reference to estimate the radical concentrations of **SBA_m-2** materials from their respective EPR double integrals.



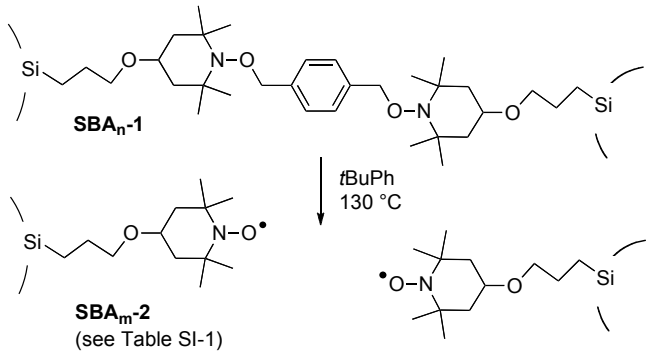
3 **SBA_{30}-3**

SBA_{30}-3. The material was prepared by following the previous procedure from tetraethoxysilane (4.14 g, 19.9 mmol, 39 equiv) and precursor **3**[7] (192 mg, 0.51 mmol, 1 equiv).

[7] F. Behrends, H. Wagner, A. Studer, O. Niehaus, R. Pöttgen and H. Eckert, *Macromolecules* 2013, **46**, 2553−2561.

BET Surface Area: 721 m²/g. BJH Desorption Average Pore Diameter: 7.3 nm. Vp : 1.149 cm^3/g. SAXS: d = 10.6 nm; a = 9.1 nm.

2.6. Synthesis of SBA_m-2 silicas



The homolysis of C-O bonds was triggered by warming a suspension of **SBA_n-1** silicas in *tert*-butylbenzene at 130°C. Specifically, in order to obtain **SBA_m-2** materials displaying different concentrations in nitroxide, the thermolysis reaction time was adjusted by considering the fragmentation kinetics of **SBA_{63}-1** and **SBA_{39}-1** silicas as obtained by EPR studies (Figure S1 and Figure S2, respectively). After filtration, **SBA_m-2** silicas were washed with ethanol and acetone. The concentration in nitroxides in **SBA_m-2** materials (Table S1) was estimated by comparing their EPR signal integral with that of a SBA silica material functionalized in the pores with TEMPO radicals (for which the loading was determined by TGA).

Table S1. References and concentrations in nitroxide of the different materials.

Starting silica (**SBA_n-1**)	**SBA_{63}-1**	**SBA_{63}-1**	**SBA_{63}-1**	**SBA_{63}-1**	**SBA_{63}-1**	**SBA_{63}-1**	**SBA_{56}-1**	**SBA_{39}-1**
Concentration in radical precursors (μmol g^{-1})	229	229	229	229	229	229	252	331
Theoretical maximum concentration in TEMPO (μmol g^{-1})	458	458	458	458	458	458	504	662
Nitroxide functionalized silica (**SBA_m-2**)	**SBA_{485}-2**	**SBA_{350}-2**	**SBA_{282}-2**	**SBA_{165}-2**	**SBA_{89}-2**	**SBA_{43}-2**	**SBA_{34}-2**	**SBA_{22}-2**
Concentration in nitroxide (μmol g^{-1})	34	47	58	98	127	350	434	640

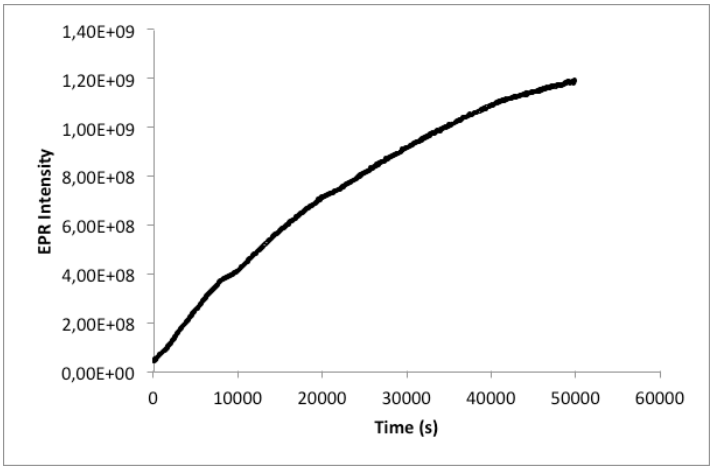


Figure S1. Fragmentation kinetics of **SBA_{63}-1** in *tert*-butylbenzene at 130°C

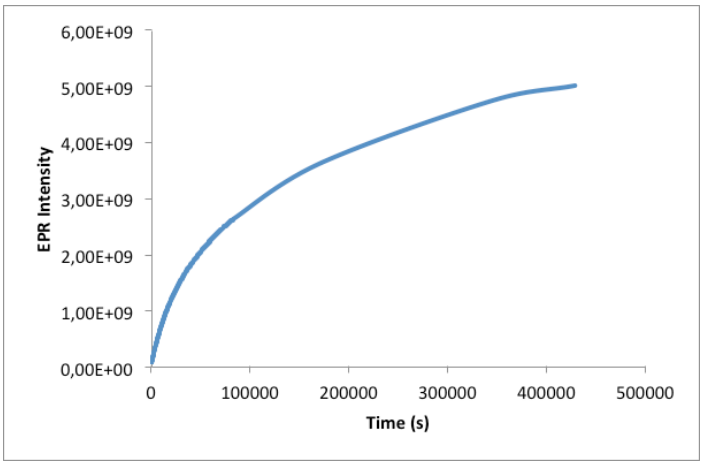


Figure S2. Fragmentation kinetics of **SBA_{39}-1** in *tert*-butylbenzene at 130°C

3. Experimental Procedures for EPR Analysis

3.1. EPR Spectroscopy

EPR experiments were performed in the CW mode with commercially available HPLC grade solvents and reactants, which were used as received. EPR experiments were performed on an ELEXSYS Bruker instrument and the Bruker BVT 3000 set-up was utilized to control the temperature. In a 4 mm quartz-glass tube, 10 mg of functionalized silica were degassed with three freeze-pump-thaw cycles with a 10^{-5} mbar vacuum pump. EPR spectra for direct observation of sulfur centered radicals experiments were recorded with the parameters: modulation amplitude = 1 G, receiver gain = 51 dB, modulation frequency = 100 kHz, power = 0.63 mW, sweep width = 500 G, conversion time = 87.9 ms, sweep time = 90 s, number of scans = 1.

3.2. Pulsed EPR spectroscopy

X band pulsed EPR experiments were carried out on a Bruker Elexsys E580 spectrometer equipped with a dielectric ring resonator (ER4118X-MD5) and a helium flow cryostat (Oxford CF935). All measurements were performed at a temperature of 110 K. The microwave pulses were amplified with a 1 kW TWT. Field sweep ESE two-pulse experiments (π/2–τ–π–τ–echo) were measured as a function of the magnetic field at fixed time interval of 200ns between the two microwave pulses. The phase memory times (τ_m) were measured using the same two-pulse sequence. The integrated echo intensity was measured as a function of τ, incremented in steps of 4 ns from an initial value of 200 ns. Experiments were recorded at magnetic field corresponding to the maximum intensity in the field sweep spectra. A conventional inversion-recovery sequence (π–t–π/2–τ–π–τ–echo) was applied to determine the longitudinal relaxation time, T_{1e}, with a τ delay of 250 ns and a 32 ns detector gate, centered at the maximum of the echo signal. The inversion pulse length was 32 ns and the π/2 and the refocusing π pulses were 52 ns and 104 ns, respectively. Initial delay t was 2000 ns. Experiments were recorded at magnetic field corresponding to the maximum intensity in the field sweep spectra. The resulting inversion recovery curves were fitted[8] with a stretched exponential function such as:

$$I(t) = I_0 + I_1 \, exp\left[-\left(\frac{t}{T_{1e}}\right)^{\beta}\right]$$

[8] D. Gajan, M. Schwarzwalder, M. P. Conley, W. R. Gruning, A. J. Rossini, A. Zagdoun, M. Lelli, M. Yulikov, G. Jeschke, C. Sauvée, O. Ouari, P. Tordo, L. Veyre, A. Lesage, C. Thieuleux, L. Emsley and C. Copéret, *J. Am. Chem. Soc.*, 2013, **135**, 15459-15466.

Accordingly, the electron mean relaxation time $<T_{1e}>$ was obtained using:

$$\langle T_{1e} \rangle = \frac{T_{1e}}{\beta} \Gamma\left(\frac{1}{\beta}\right)$$

where Γ is the Euler Gamma function.

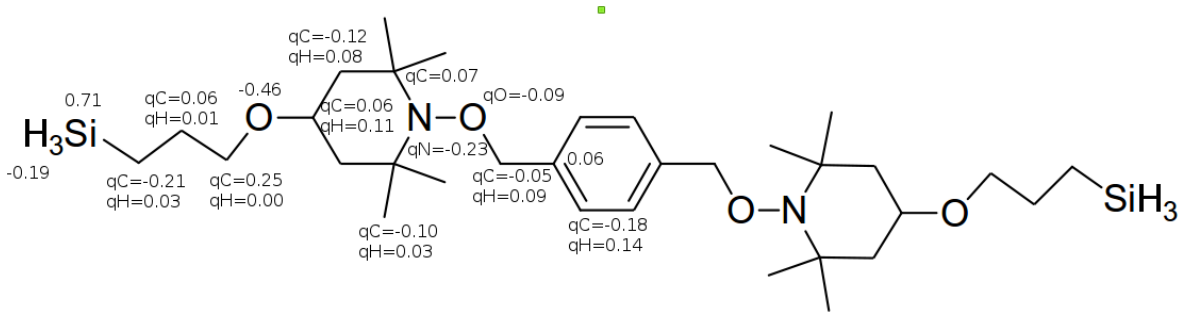
3.3. Main EPR results for TCE-impregnated SBA_m-2 samples

Samples	Radical (μmol g^{-1})	$\Delta\nu_{1/2}$ (G)	T_{1e}	β	$<T_{1e}>$
SBA_{485}-2	34	11.9	105.9	0.73(5)	128.5
SBA_{350}-2	47	12.2	-	-	-
SBA_{282}-2	58	12.3	-	-	-
SBA_{165}-2	98	12.3	76.2	0.69(9)	96.6
SBA_{89}-2	127	11.9	-	-	-
SBA_{43}-2	350	12.8	46.6	0.65(2)	63.4
SBA_{34}-2	434	13.3	-	-	-
SBA_{22}-2	640	14.5	29.4	0.53(1)	53.0

4. MD simulations

In order to study the distance between the two oxygen atoms in precursor (**1**) in all possible conformations, molecular dynamics simulations were performed with the DLPOLY_4 software.[9] Precursor (**1**), where $Si(OEt)_3$ end-groups were replaced by SiH_3 end-groups, was immersed in a box of 2744 water molecules. This system was first submitted to a NPT equilibration run (at 300 K and 1 atm) using the Melchionna modification of the Nosé-Hoover algorithm[10] (thermostat relaxation time: 0.5 ps, barostat relaxation time: 5 ps). Then the NVT production runs were performed at 300 K during 5 ns, using a Nosé-Hoover type thermostat with a relaxation time of 0.5 ps. The time step was 1 fs. Long-range interactions were cut-off after 14 Å. Electrostatics interactions were handled with Ewald summations (precision 10^{-6}). Trajectory snapshots and system properties were recorded every ps for future analysis. The simulation box was cubic and its size settled to 44 Å side after relaxation. These classical simulations used DREIDING[11] force field for the precursor and SPCE[12] for the water. The charges for the precursor were obtained following the RESP procedure[13] using Gaussian 09 software.

[9] W. G. Hoover, *Phys. Rev. A* 1985, **31**, 1695–1697.
[10] S. Melchionna, G. Ciccotti and B. L. Holian, *Mol. Phys.,* 1993, **78**, 533–544.
[11] S. Mayo, B. Olafson and W. A. Goddard III, *J. Phys. Chem*., 1990, **94**, 8897–8909.
[12] H. J. C. Berendsen, J. R. Grigera and T. P. Straatsma, *J. Phys. Chem.*, 1987, **91**, 6269–6271.
[13] J. Wang, R. M. Wolf, J. W. Caldwell, P. A. Kollman and D. A. Case, *J. Comput. Chem.* 2004, **25**, 1157–1174; Erratum in *J. Comput. Chem.* 2005, **26**, 114.



5. Experimental Procedures for DNP NMR Analysis

5.1. Experimental parameters

All DNP SSNMR experiments described in this work were recorded on a commercially available Bruker AVANCE-III spectrometer operating at 9.4 T (400 MHz for the ^{1}H Larmor frequency), which was located at Bruker Biospin (Wissembourg, France). This spectrometer was equipped with a 3.2 mm low-temperature DNP ^{1}H/X double-resonance MAS probe manufactured by Bruker. The sample temperature was roughly 110 K. The DNP SSNMR spectrometer was equipped with a gyrotron that provided microwave (MW) irradiation of the sample. Specifically, the field sweep coil of the NMR magnet was set so that MW irradiation occurred at the maximum DNP enhancement of TOTAPOL (263.334 GHz).[14] The estimated power of the MW beam at the output of the probe waveguide was ~6 W. The pulse sequence used for CPMAS experiment was as described in the work by Lesage et al.,[15] with the MW irradiation field that was either turned *off* or continuously *on*. During Cross Polarization (CP), the amplitude of the ^{1}H contact pulse was linearly ramped in order to improve CP efficiency.[16] Hartmann–Hahn matching conditions and CP contact times were optimized directly on the samples under study. Detailed experimental parameters are reported Table S2. Sapphire rotors were used for all DNP experiments. They were sealed with a Teflon insert and capped with zirconia caps. Typically, 20 mg of SBA_m-2 silicas were impregnated with 40 µL of solution according to the protocol described by Lesage et al.[15]

[14] C. S. Song, K. N. Hu, C. G. Joo, T. M. Swager and R. G. Griffin, *J. Am. Chem. Soc.*, 2006, **128**, 11385-11390.
[15] A. Lesage, M. Lelli, D. Gajan, M. A. Caporini, V. Vitzthum, P. Mieville, J. Alauzun, A. Roussey, C. Thieuleux, A. Mehdi, G. Bodenhausen, C. Copéret and L. Emsley, *J. Am. Chem. Soc.*, 2010, **132**, 15459-15461.
[16] G. Metz, X. Wu and S. O. Smith, *J. Magn. Reson. Ser. A*, 1994, **110**, 219-227.

Table S2. Parameters used to record the ^{13}C DNP CPMAS experiments (with the microwave field *on* or *off*).

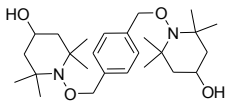
Parameters	
Number of scans	8
Recycle delay (s)	15 (*)
Sample spinning rate (Hz)	10000
Sweep width (ppm)	295.8
Acquisition length (ms)	34.4
^{1}H 90° pulse (μs)	2.8
^{1}H SPINAL-64 decoupling pulse length (μs)	5.8
Cross-polarization: ^{1}H ➔ ^{13}C	
CP contact time (ms)	1.0
^{1}H RF field (kHz)	50 (Ramp: 50%-> 100%)
^{13}C RF field (kHz)	50

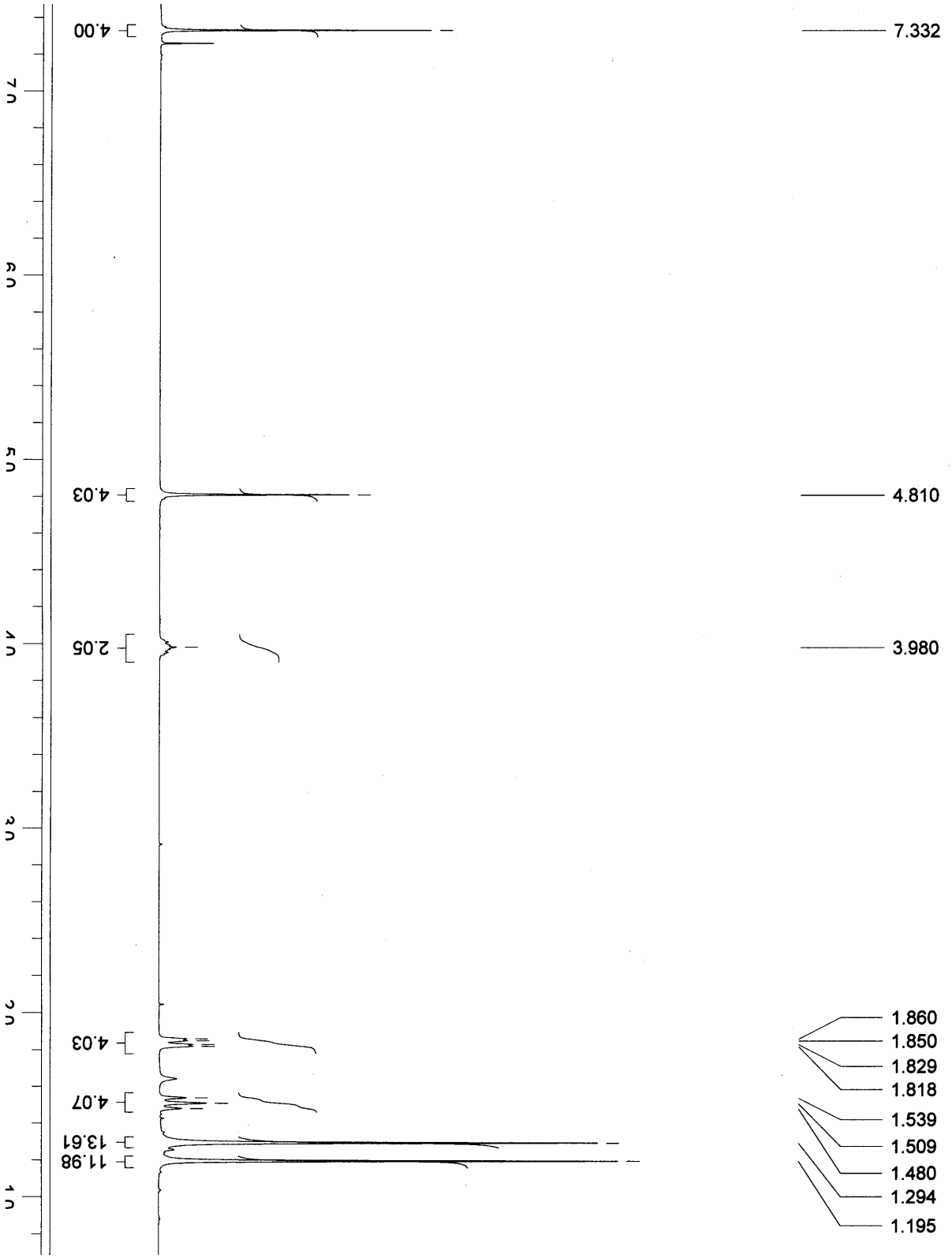
5.2. Main experimental results for DNP SSNMR experiments

Sample	Radical (μmol g^{-1})	ε_{H}	$\varepsilon_{C,CP}$
SBA_{485}-2	34	5	5
SBA_{350}-2	47	8	8
SBA_{282}-2	58	8	8
SBA_{165}-2	98	11	11
SBA_{89}-2	127	18	18
SBA_{43}-2	350	34	34
SBA_{34}-2	434	24	24
SBA_{22}-2	640	16	16

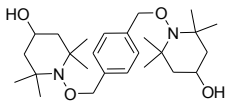
6. ^{1}H and ^{13}C liquid-state NMR spectra

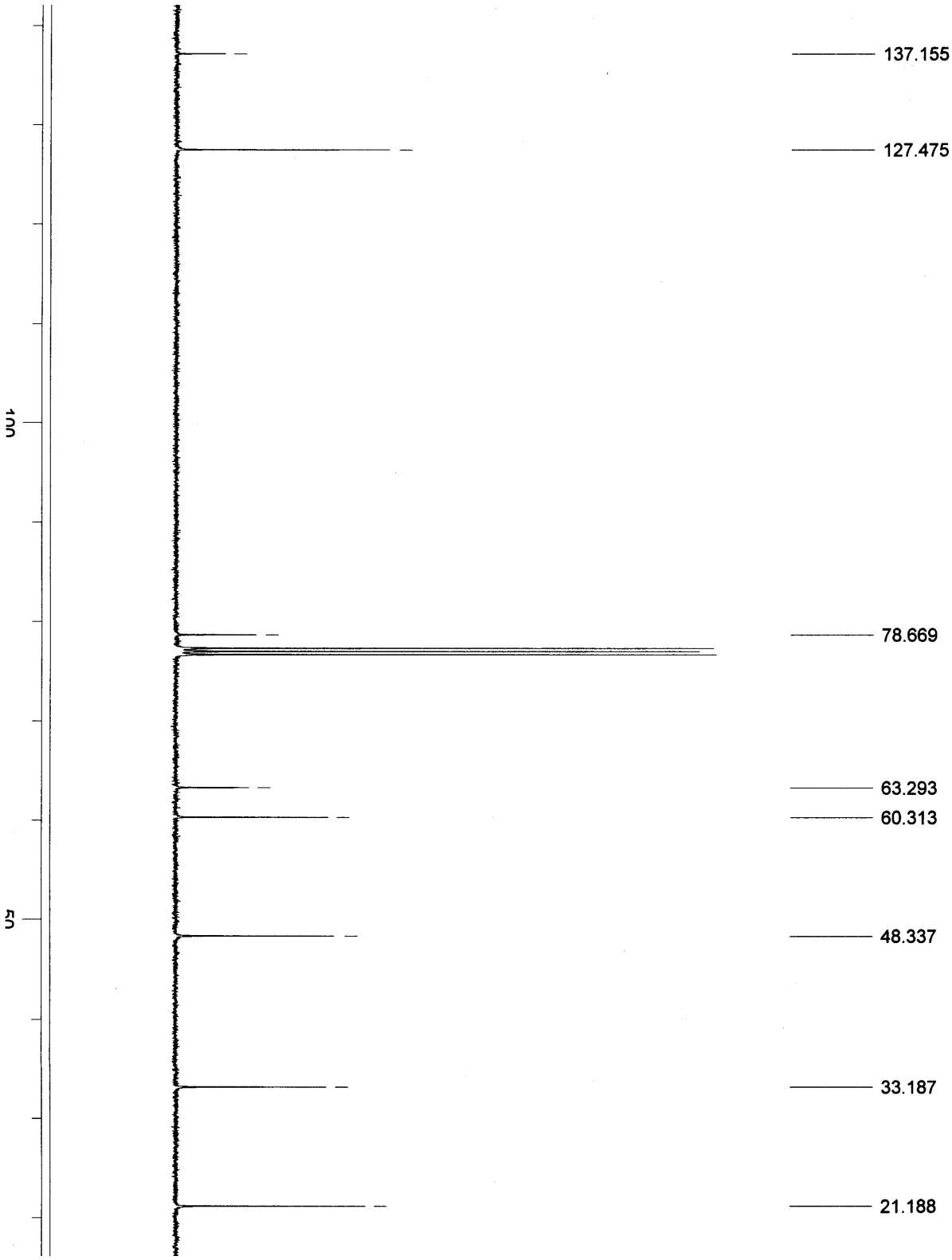
6.1. 1-[(4-{[(4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yl)oxy]methyl}phenyl)methoxy]-2,2,6,6-tetramethylpiperidin-4-ol (3): ^{1}H NMR



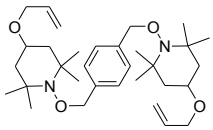


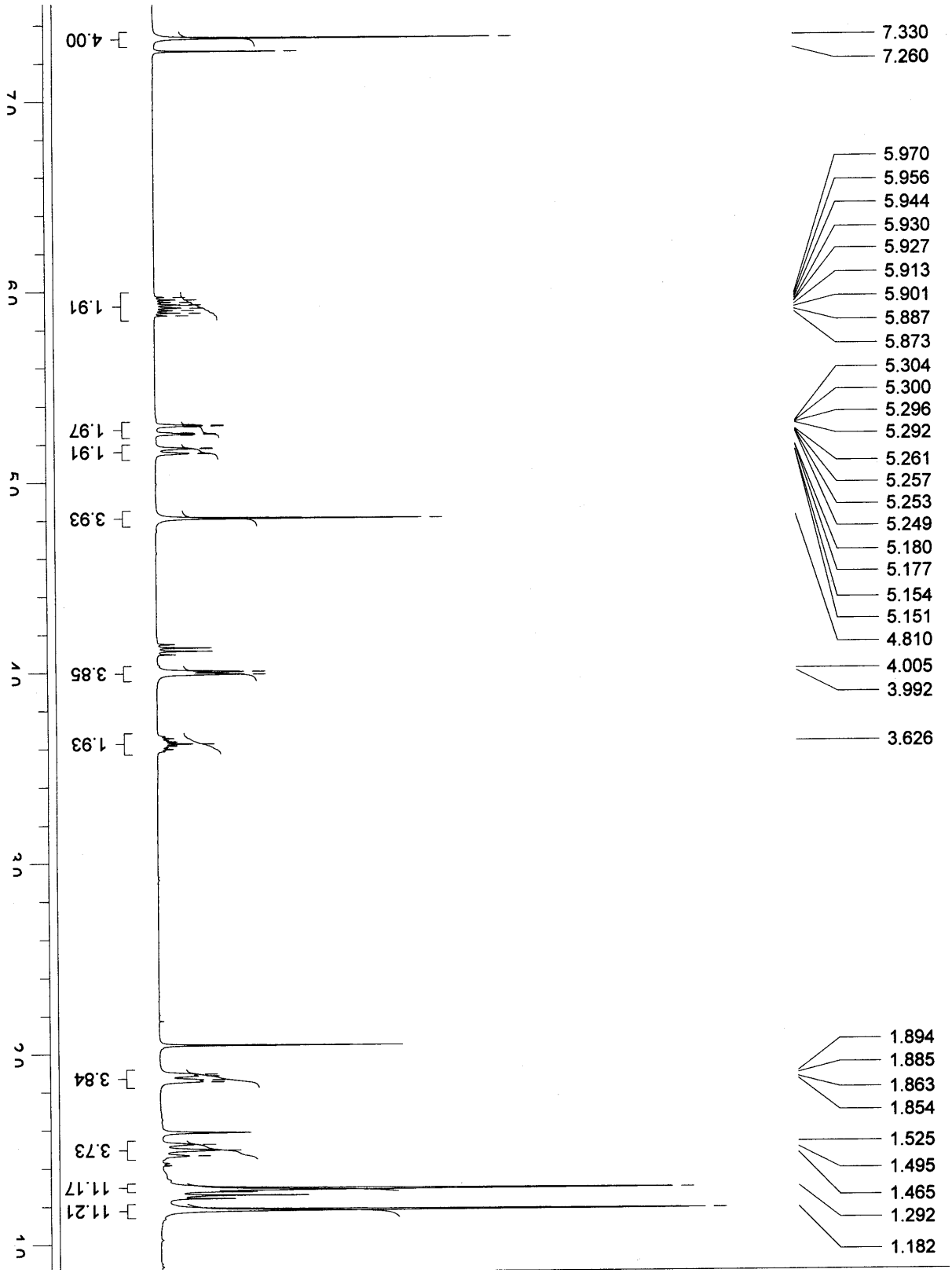
6.2. 1-[(4-{[(4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yl)oxy]methyl}phenyl)methoxy]-2,2,6,6-tetramethylpiperidin-4-ol (3): ^{13}C NMR



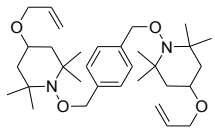


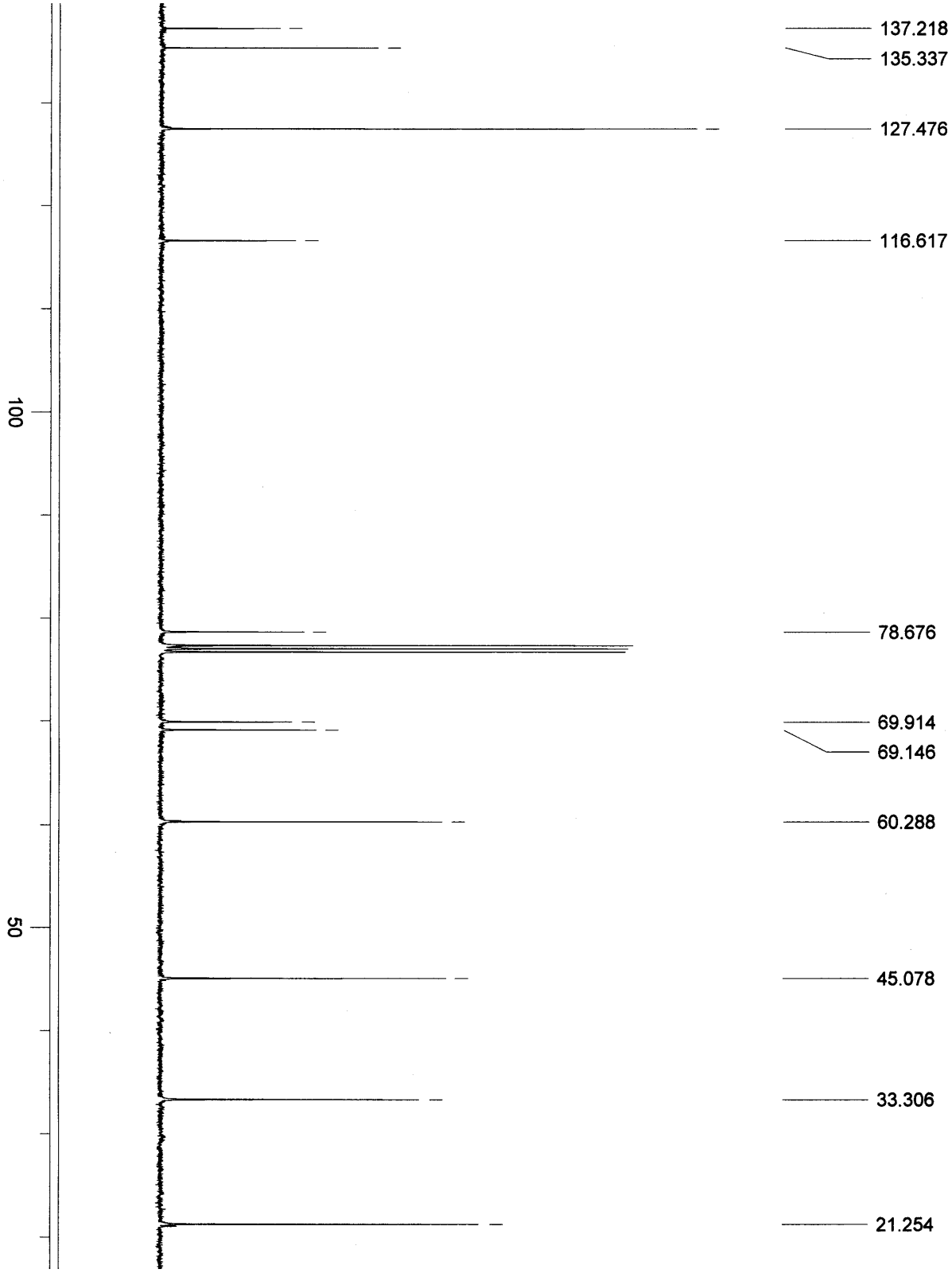
6.3. 2,2,6,6-tetramethyl-4-(prop-2-en-1-yloxy)-1-{[4-({[2,2,6,6-tetramethyl-4-(prop-2-en-1-yloxy)piperidin-1-yl]oxy}methyl)phenyl]methoxy}piperidine (2): ^{1}H NMR



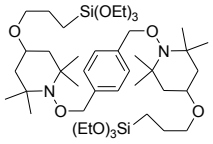


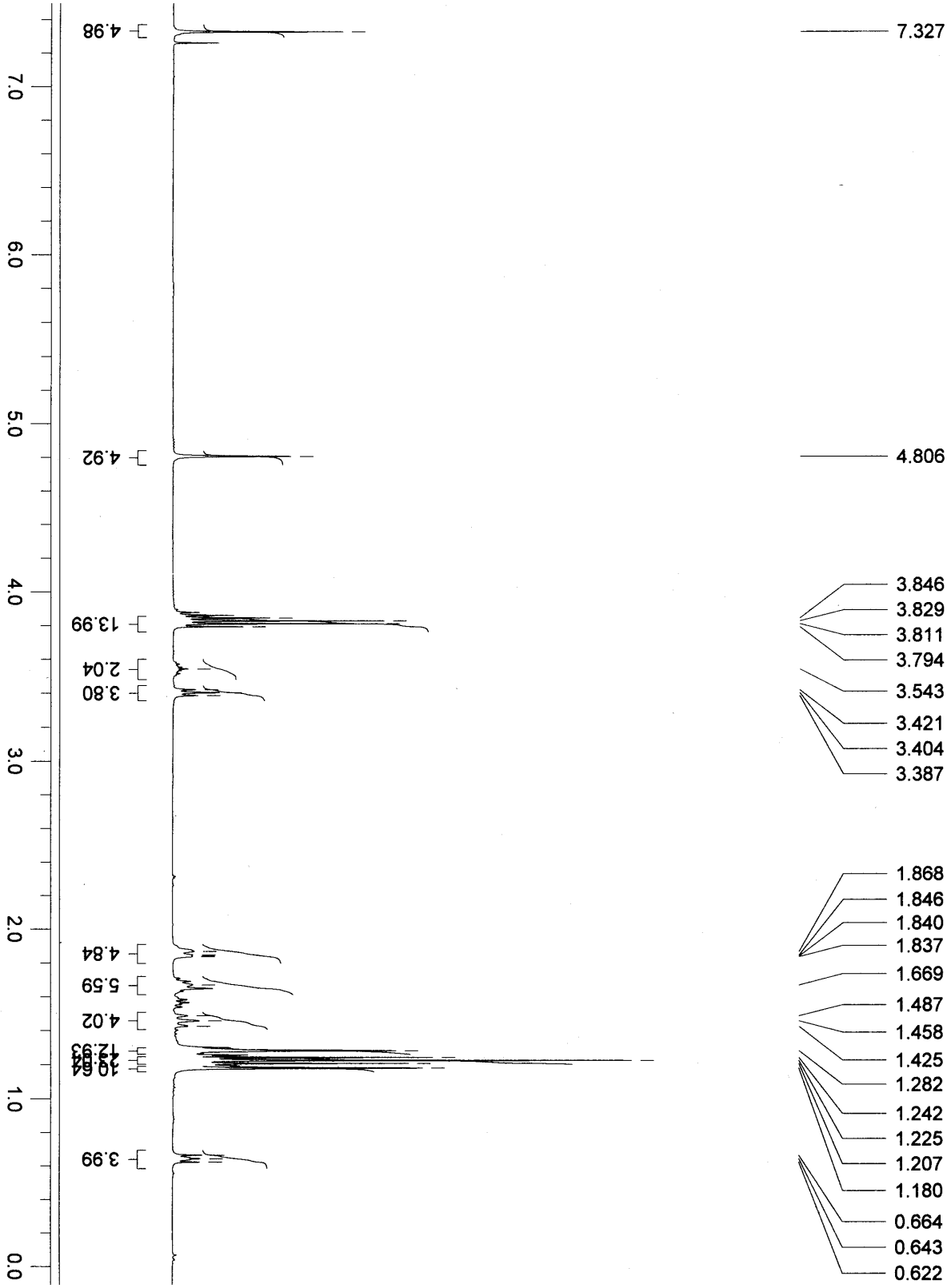
6.4. 2,2,6,6-tetramethyl-4-(prop-2-en-1-yloxy)-1-{[4-({[2,2,6,6-tetramethyl-4-(prop-2-en-1-yloxy)piperidin-1-yl]oxy}methyl)phenyl]methoxy}piperidine (2): ^{13}C NMR



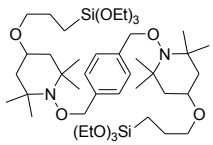


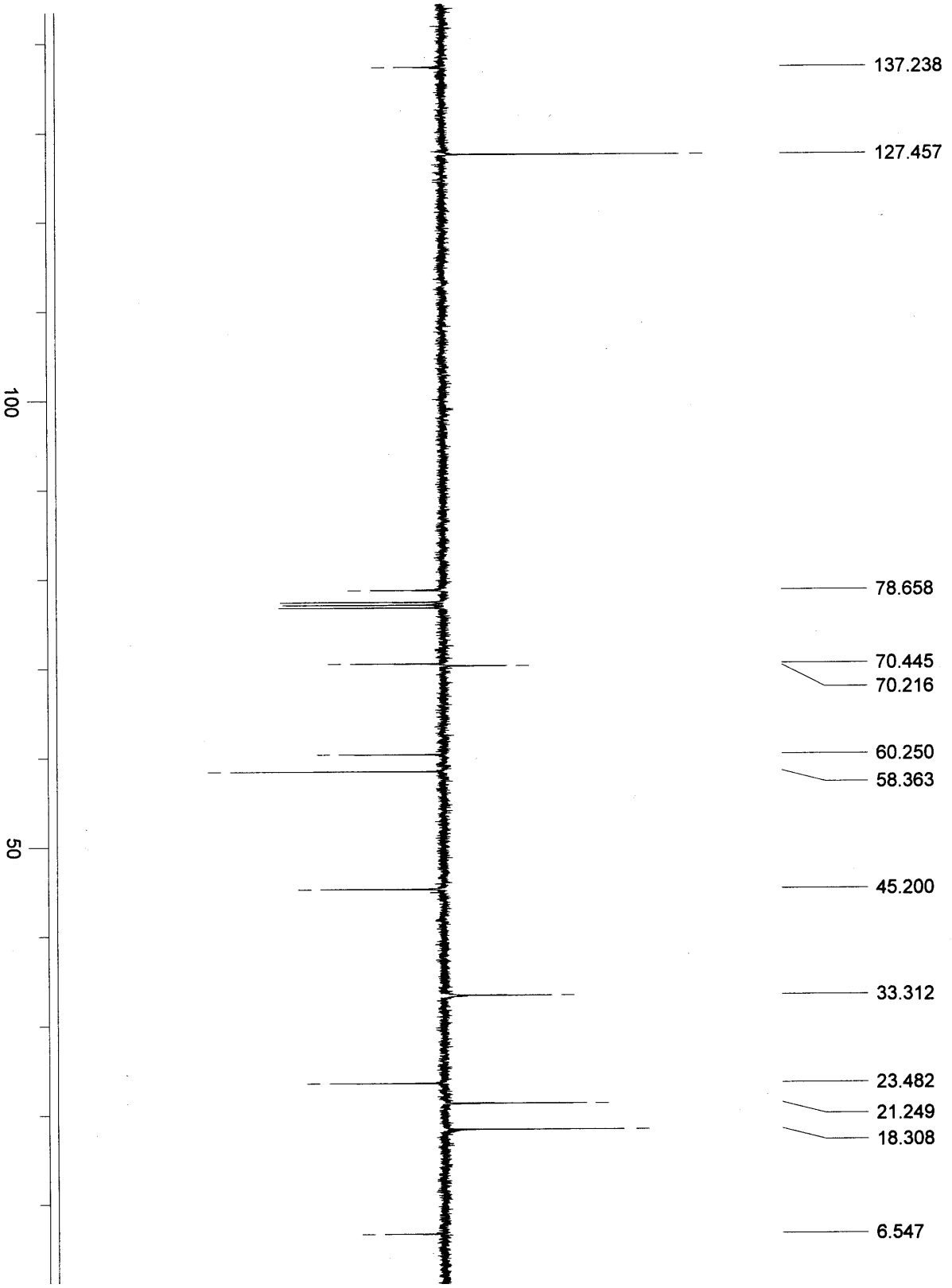
6.5. 2,2,6,6-tetramethyl-1-({4-[({2,2,6,6-tetramethyl-4-[3-(triethoxysilyl)propoxy]piperidin-1-yl}oxy)methyl]phenyl}methoxy)-4-[3-(triethoxysilyl)propoxy]piperidine (1): ^{1}H NMR





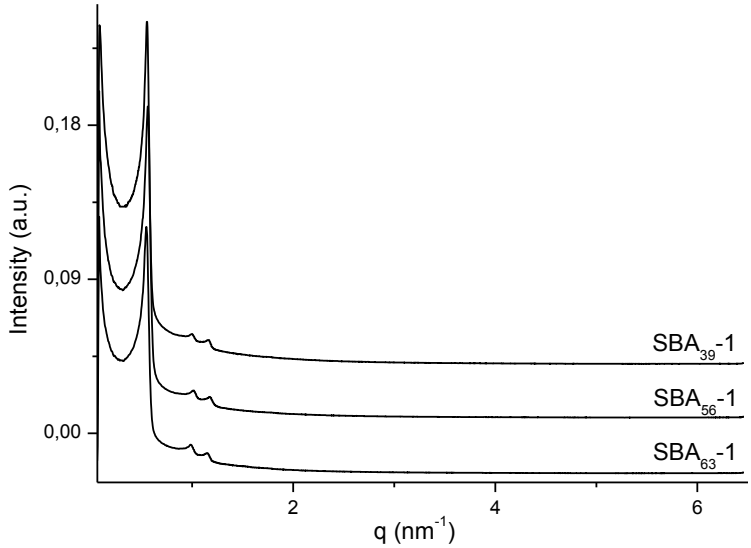
6.6. 2,2,6,6-tetramethyl-1-({4-[({2,2,6,6-tetramethyl-4-[3-(triethoxysilyl)propoxy]piperidin-1-yl}oxy)methyl]phenyl}methoxy)-4-[3-(triethoxysilyl)propoxy]piperidine (1): ^{13}C NMR (APT)



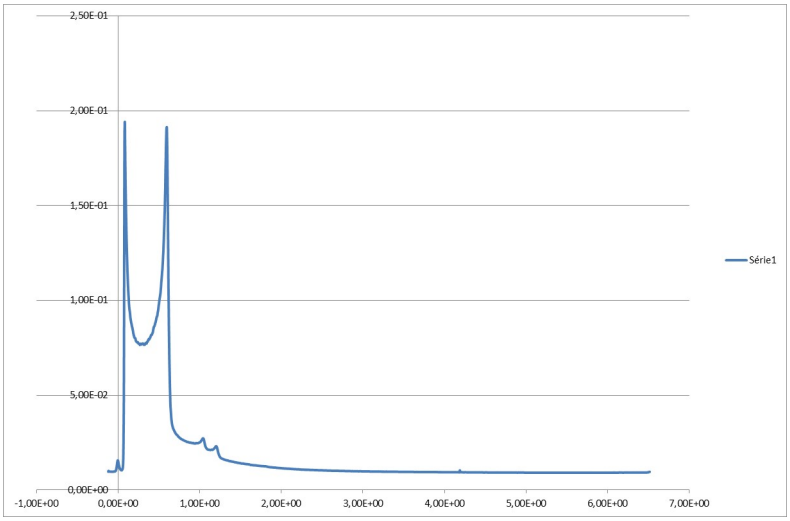


7. Small Angle X-Ray Scattering (SAXS) of SBA_n-1 silicas and SBA_{30}-3

7.1. SBA_n-1

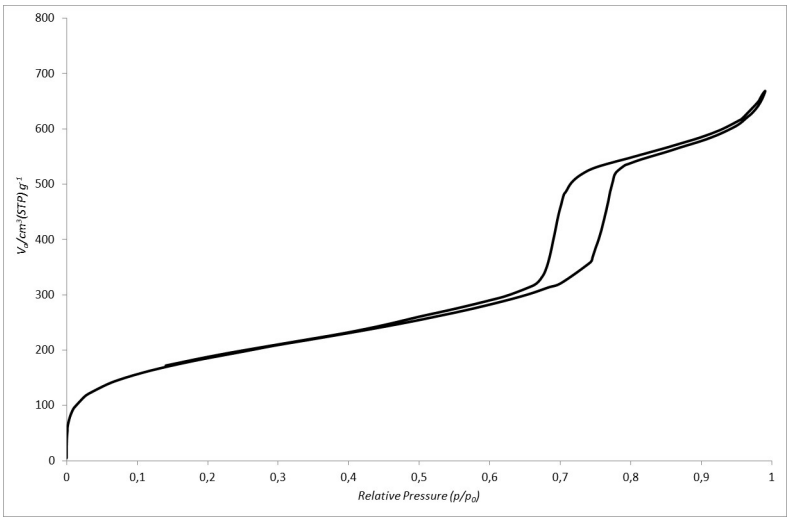


7.2. SBA_{30}-3

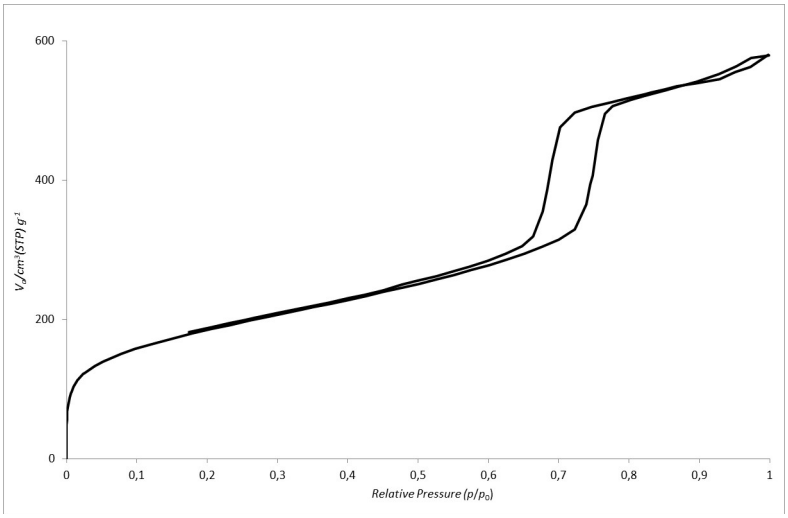


8. Nitrogen adsorption/desorption analysis

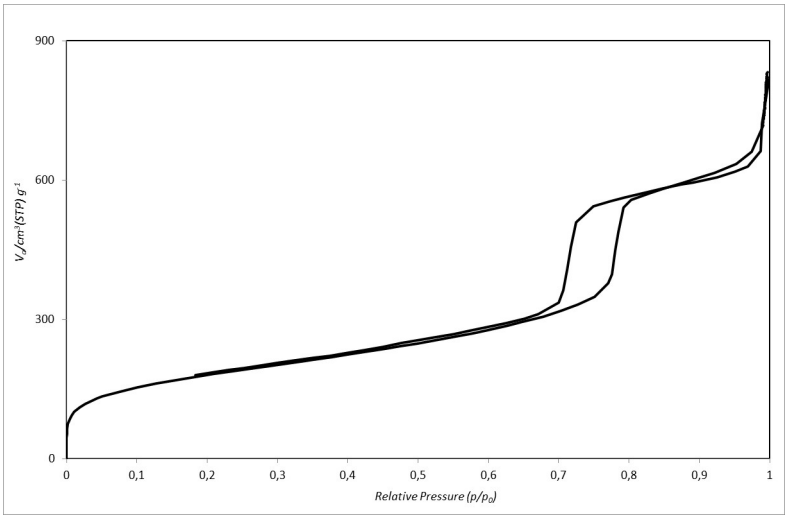
8.1. SBA_{39}-1



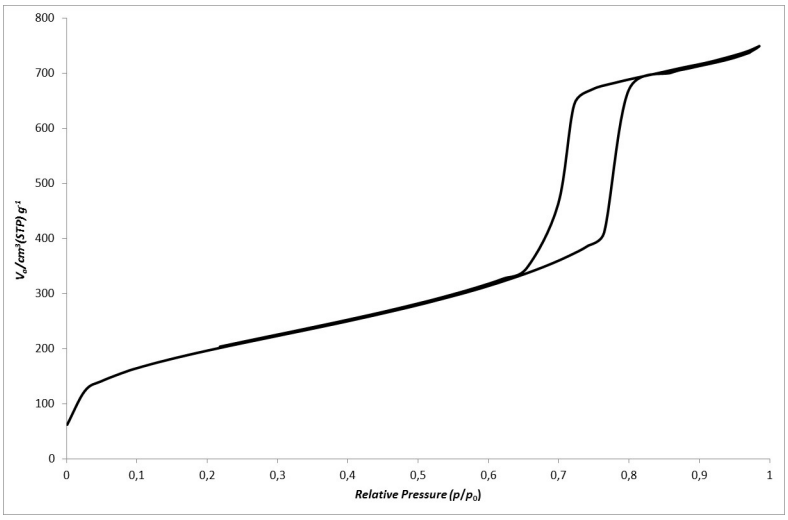
8.2. SBA_{56}-1



8.3. SBA_{63}-1

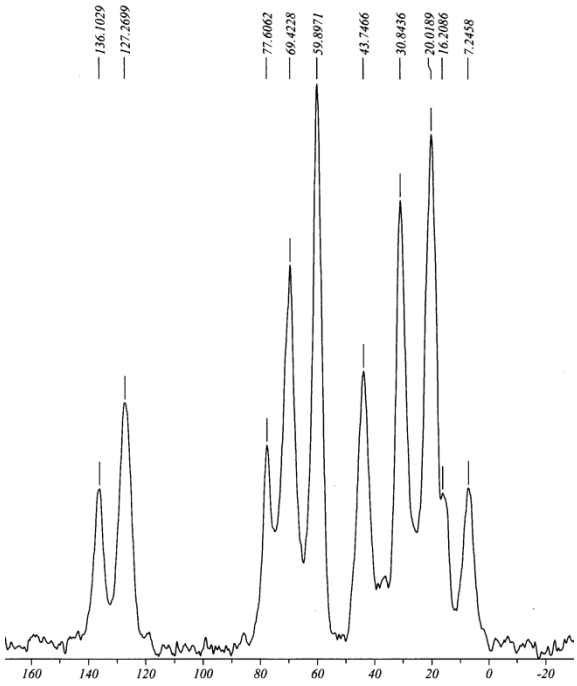


8.4. SBA_{30}-3

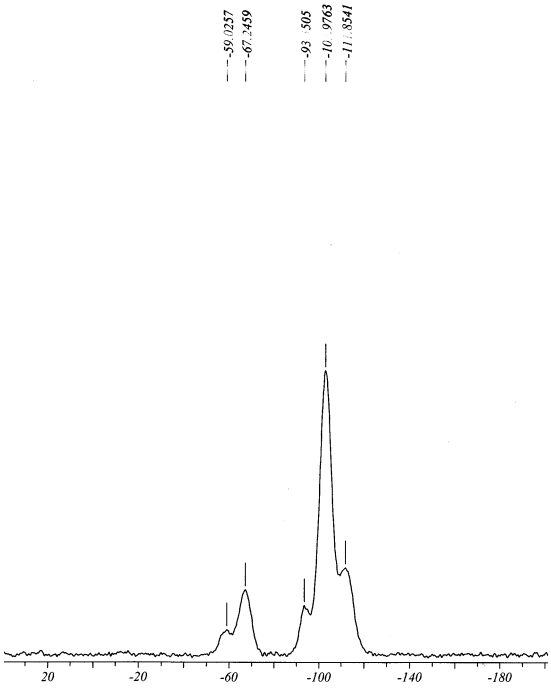


9. ^{13}C and ^{29}Si CPMAS solid-state NMR of SBA$_n$-1 silicas

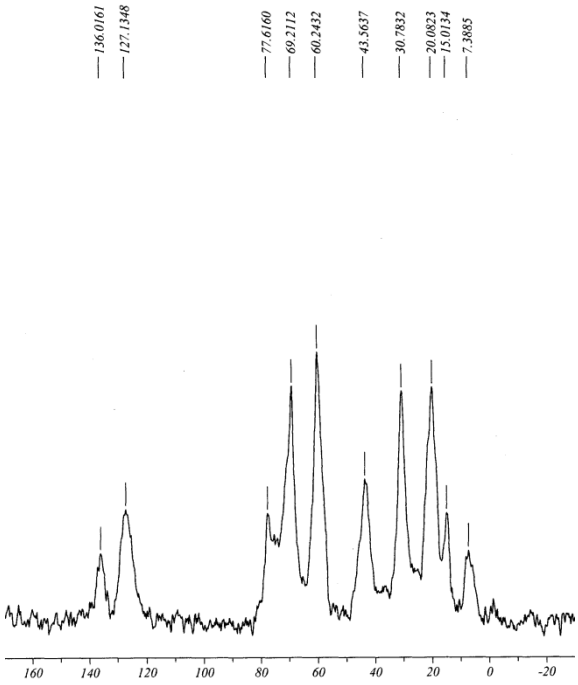
9.1. ^{13}C CPMAS of SBA$_{39}$-1



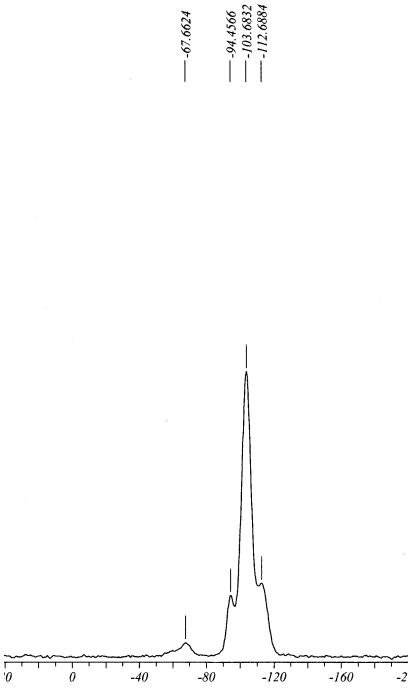
9.2. ^{29}Si CPMAS of SBA$_{39}$-1



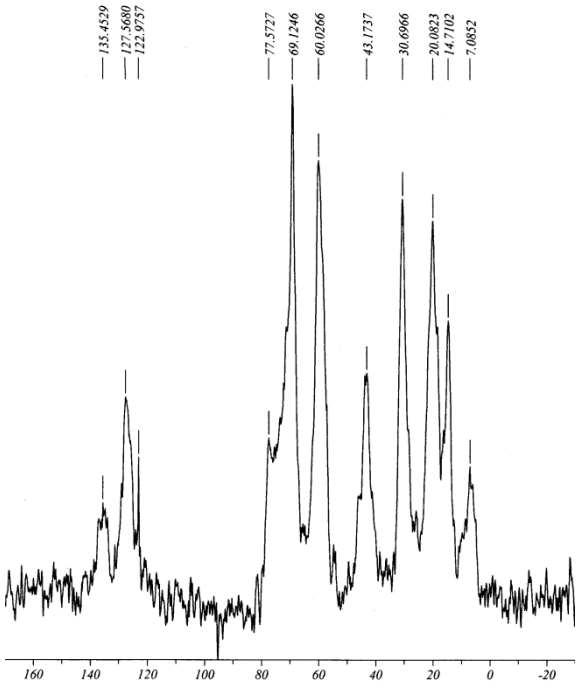
9.3. ^{13}C CPMAS of SBA$_{56}$-1



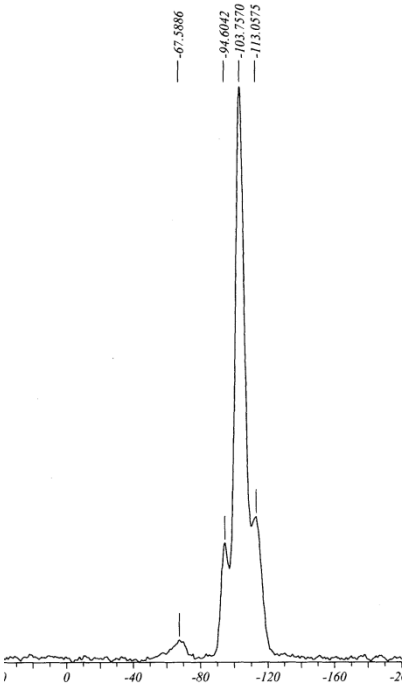
9.4. ^{29}Si CPMAS of SBA$_{56}$-1



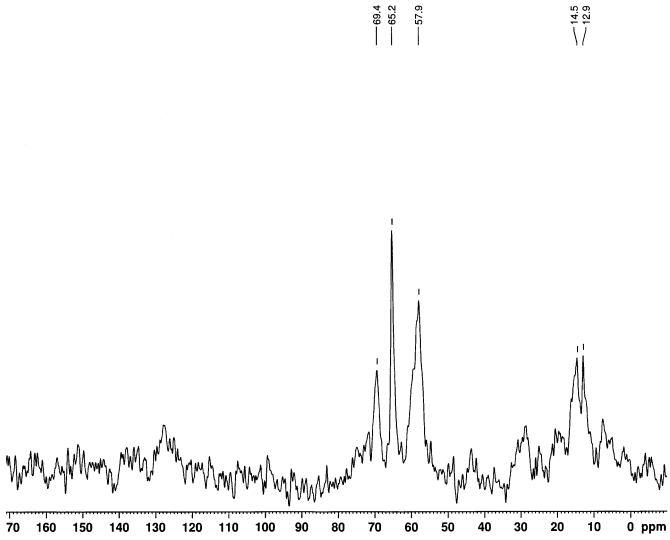
9.5. ^{13}C CPMAS of SBA$_{63}$-1



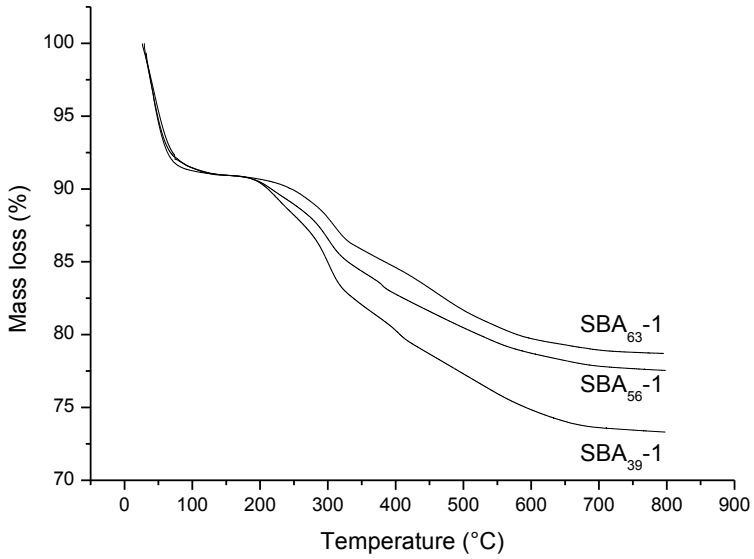
9.6. ^{29}Si CPMAS of SBA$_{63}$-1



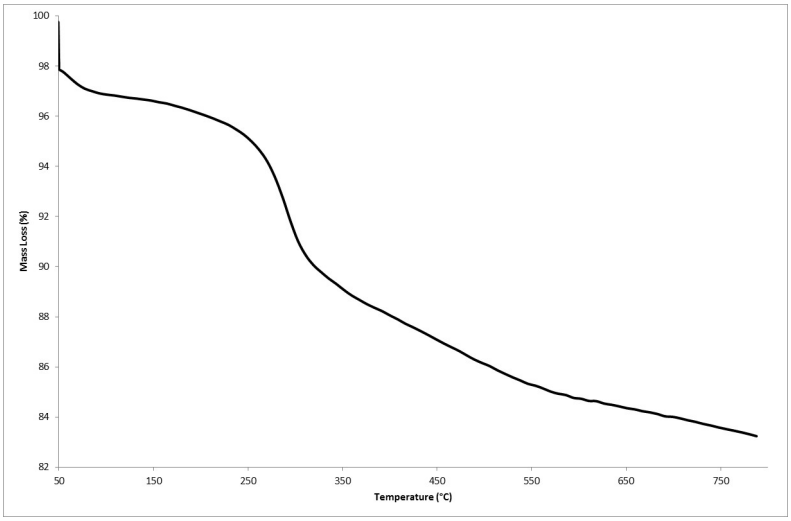
9.7. ^{13}C CPMAS of SBA_{43}-2



10. TGA for SBA_n-1 silicas



11. TGA for SBA_{30}-3



12. TGA for SBA_{22}-2 and SBA_{34}-2