Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Modulating lifetimes and relaxation times of phenoxyl radicals through their incorporation into different hybrid nanostructures

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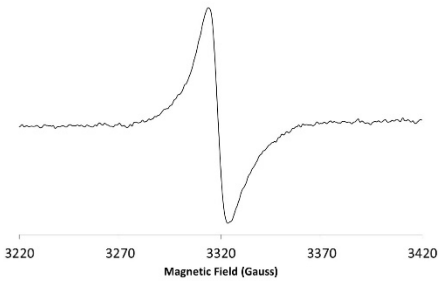

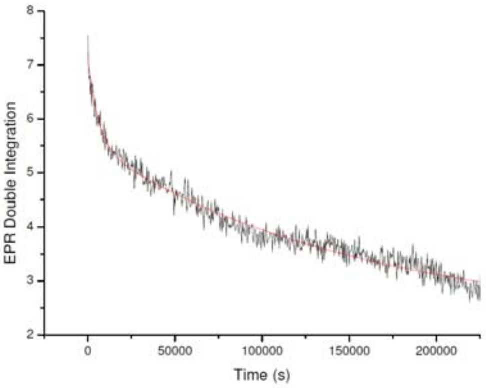

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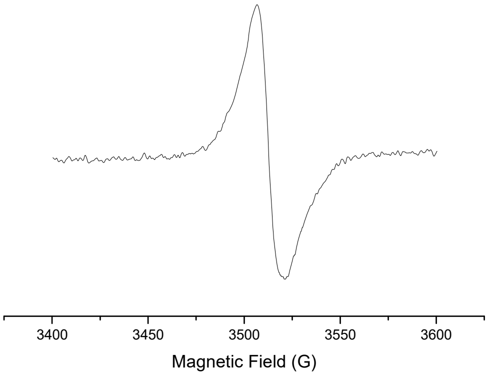

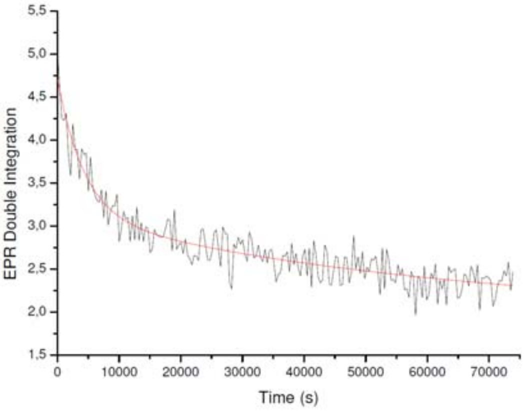

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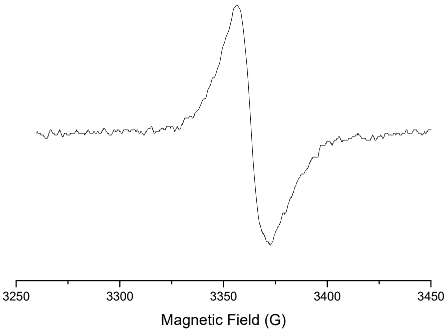

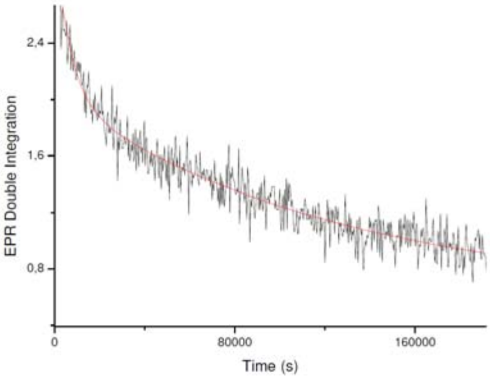

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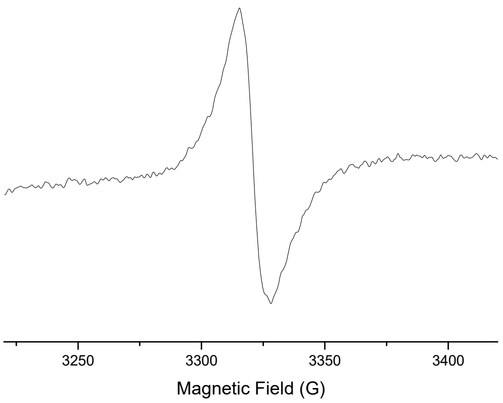

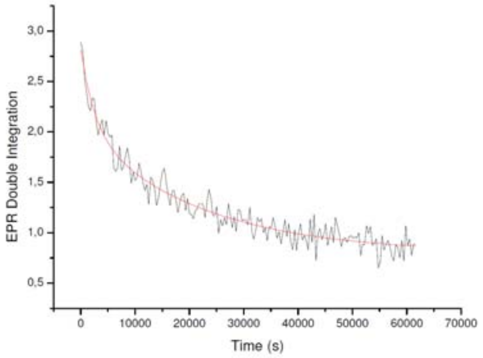

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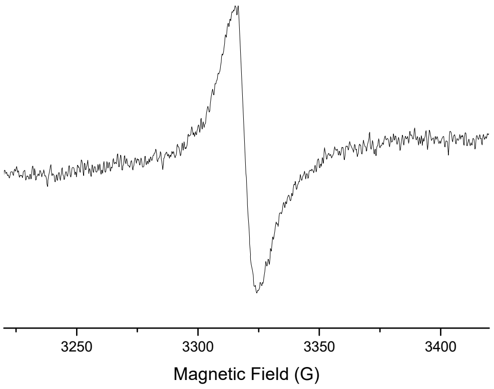

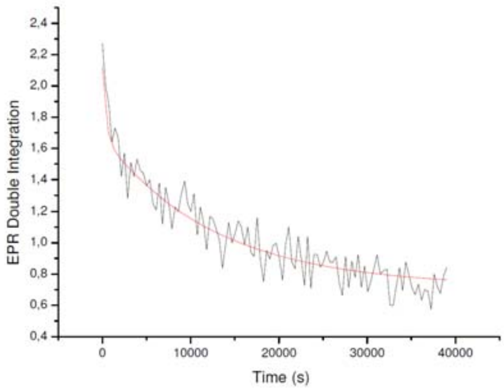

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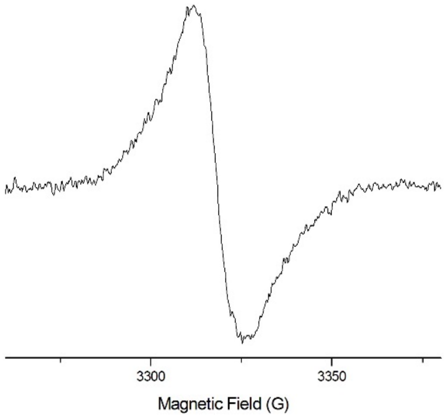

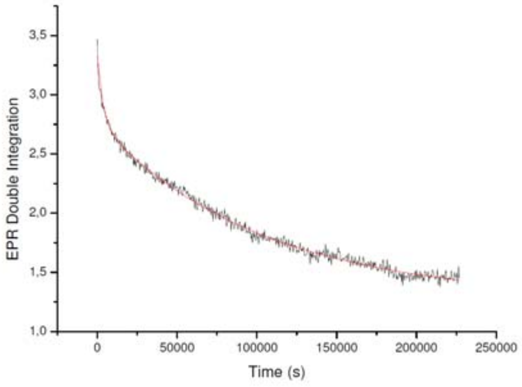

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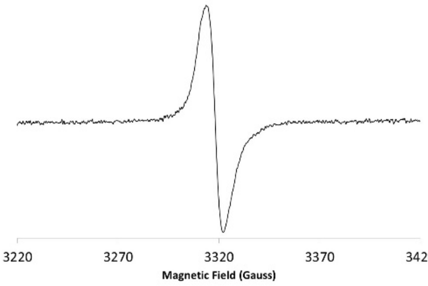

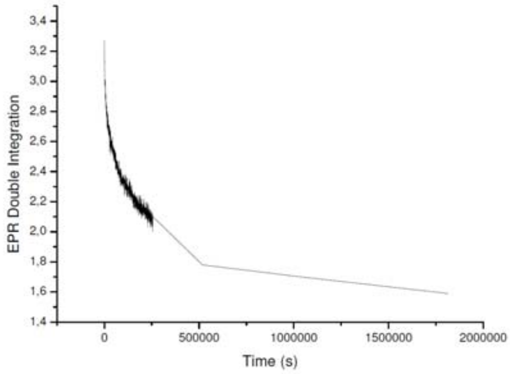

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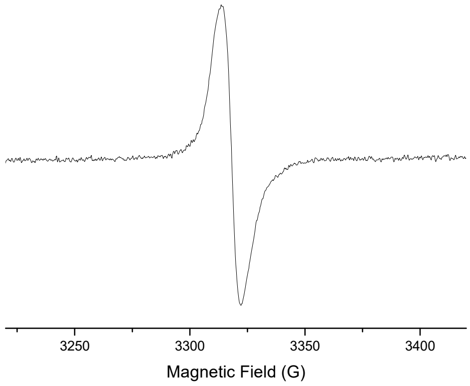

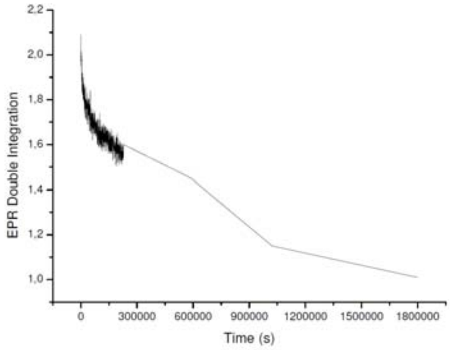

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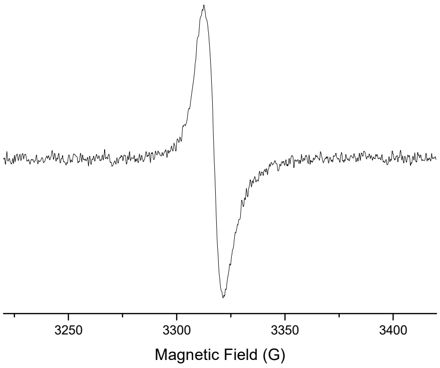

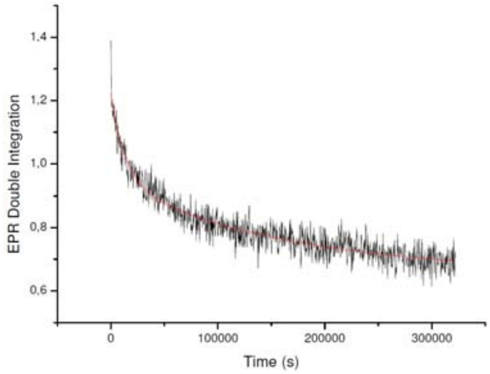

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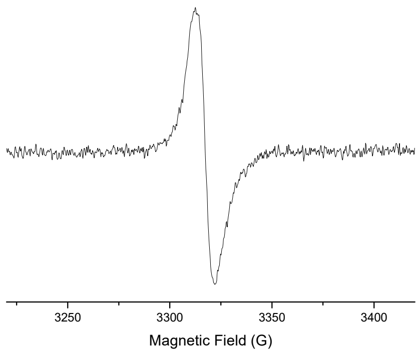

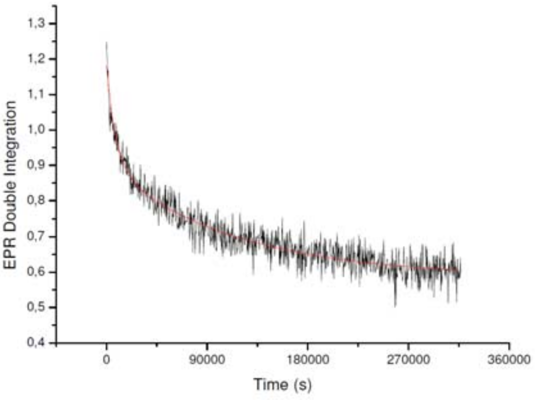

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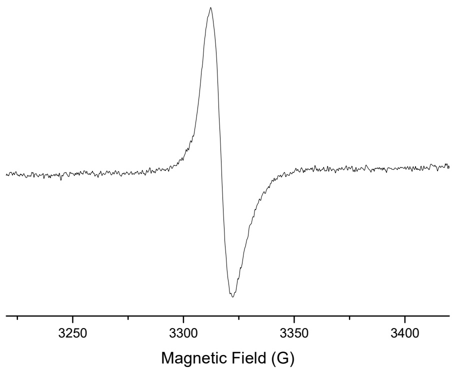

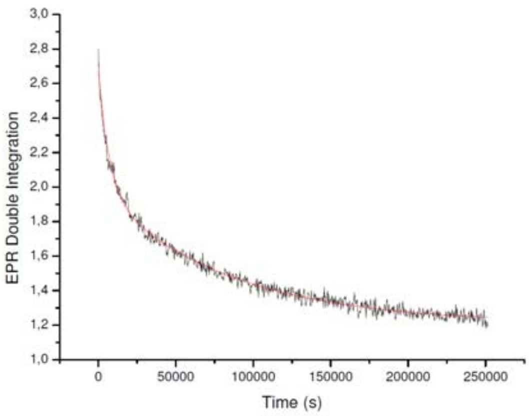

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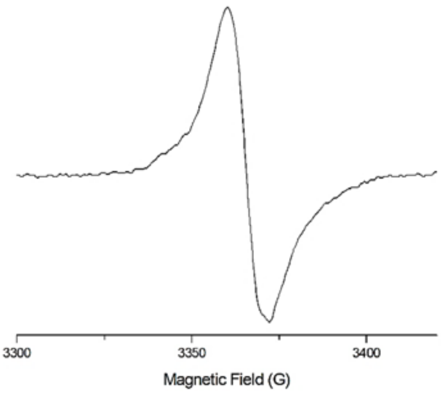

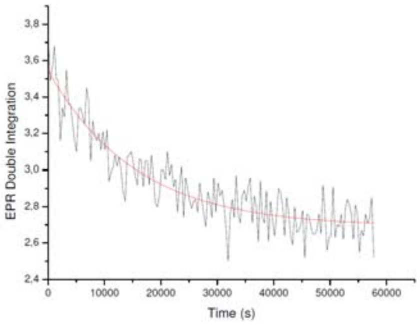

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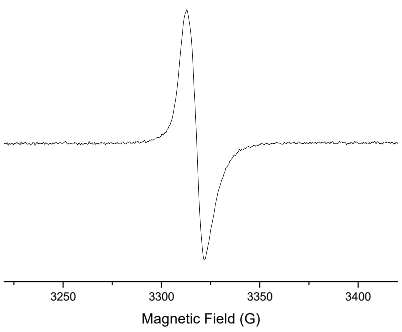

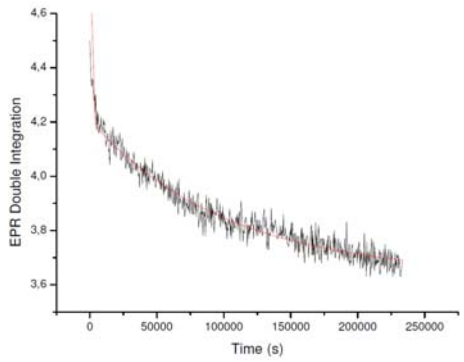

Experimental procedures for organic precursors

General procedure. 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 and THF were dried over molecular sieves 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 NMR, ^{13}C NMR spectra were recorded on 300 or 400 MHz spectrometers. Chemical shifts (δ) are reported in ppm. Signals due to residual protonated solvent (^{1}H NMR) or to the solvent (^{13}C NMR) served as the internal standard: $CDCl_3$ (7.26 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). APT was used for ^{13}C spectra assignment.

1,3-dichloro-2-fluoro-5-nitrobenzene, 3-(triethoxysilyl)propyl isocyanate are commercially available, they were used as purchased without purification. 2-[(*E*)-2-(1-Hydroxy-2-methylpropan-2-yl)diazen-1-yl]-2-methylpropan-1-ol (**7**)[1] and precursors (**5**, **3** and **1)** were prepared according to a literature procedure.[2]

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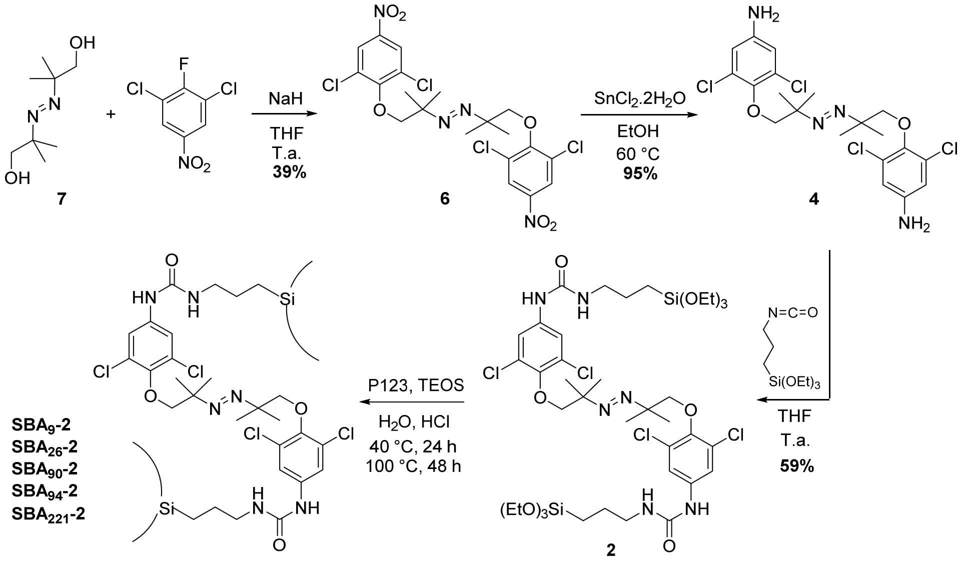
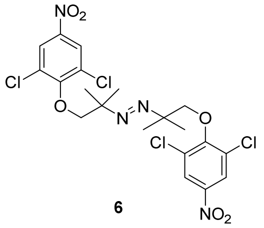
[1] Vibert, F.; Marque, S. R. A.; Bloch, E.; Queyroy, S.; Bertrand, M. P.; Gastaldi, S.; Besson, E. *J. Phys. Chem. C* 2015, **119**, 5434–5439.

[2] a) Dol, C.; Bertrand, M. P.; Gastaldi, S.; Besson, E. *Tetrahedron* 2016, **72**, 7744–7748. b) Dol, C.; Vibert, F.; Bertrand, M. P.; Lalevée, J.; Gastaldi, S.; Besson E. *ACS Macro Lett.* 2017, **6**, 117–120.

Synthesis of precursor 2 and SBA$_n$-2 silicas:



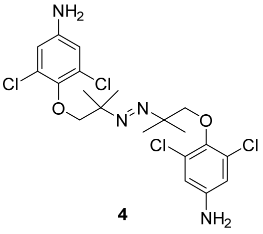
(*E*)-1,2-bis(1-(2,6-dichloro-4-nitrophenoxy)-2-methylpropan-2-yl)diazene (6).



6

To a solution of diol **7** (2.14 g, 12.29 mmol, 1 eq.) in THF (13 mL) under argon was slowly added NaH (1.38 g, 34.42 mmol, 2.8 eq.) at 0 °C. After 30 min of stirring, a solution of 1,3-dichloro-2-fluoro-5-nitrobenzene (5.68 g, 27.04 mmol, 2.2 eq.) in THF (5 mL) was added at 0 °C. The mixture was stirred overnight at 60 °C. The reaction was monitored by TLC (pentane/EtOAc : 95/5). After completion, the THF was concentrated and the mixture was diluted with water and extracted three times with EtOAc. Organic phase was washed with water and brine, dried over $MgSO_4$ and concentrated. The residue was taken on diisopropylethylether, stirred for 1 night, and filtrated to give **6** as a yellow powder (2.63 g, 4.75 mmol, 39 %). ^1H NMR (300 MHz, $CDCl_3$) δ: 8.18 (s, 4H, ArH), 4.28 (s, 4H, CH_2), 1.35 (s, 12H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 156.9 (C_{ar}-O), 143.3 (C_{ar}-N), 130.0 (C_{ar}-Cl), 124.5 (HC_{ar}), 79.2 (CH_2), 70.0 (C-N), 21.9 (CH_3). HRMS (ESI): *m/z*: calcd for $[M+H]^+$ $C_{20}H_{21}N_4O_6Cl_4^+$: 553.0210 Da, found : 553.0208 Da.

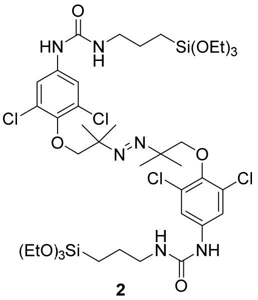
(*E*)-4,4'-((diazene-1,2-diylbis(2-methylpropane-2,1-diyl))bis(oxy))bis(3,5-dichloroaniline) (4).



4

To a solution of **6** (0.72 g, 1.29 mmol, 1 eq.) in EtOH (16 mL) was added $SnCl_2.2H_2O$ (2.91 g, 12.90 mmol, 10 eq.). The resulting mixture was stirred overnight at 60 °C. The reaction was monitored by TLC (pentane/EtOAc : 70/30). After completion, the mixture was diluted with iced water and a saturated solution of $NaHCO_3$ was added until pH=7-8. The mixture was extracted three times with EtOAc, washed with brine, dried over $MgSO_4$ and concentrated to give **4** as a brown oil (0.60 g, 1.21 mmol, 95 %). The residue was used without further purification. ^1H NMR (400 MHz, DMSO d^6) δ: 6.57 (s, 4H, ArH), 5.39 (br s, 4H, NH_2), 3.92 (s, 4H, CH_2), 1.26 (s, 12H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 143.4 (C_{ar}), 143.3 (C_{ar}), 129.9 (C_{ar}-Cl), 115.2 (HC_{ar}), 78.9 (CH_2), 70.0 (C-N), 22.2 (CH_3). HRMS (ESI): *m/z*: calcd for $[M+H]^+$ $C_{20}H_{25}N_4O_2Cl_4^+$: 493.0726 Da, found : 493.0726 Da.

(*E*)-1,1'-(((diazene-1,2-diylbis(2-methylpropane-2,1-diyl))bis(oxy))bis(3,5-dichloro-4,1-phenylene))bis(3-(3-(triethoxysilyl)propyl)urea) (2).



2

To a solution of **4** (2.04 g, 4.13 mmol, 1 eq.) in anhydrous THF (28 mL) under argon was slowly added 3-(triethoxysilyl)propyl isocyanate (2.30 mL, 11.15 mmol, 2.7 eq.). The mixture was stirred thirteen days at room temperature. The reaction was monitored by ^1H NMR. After completion, the mixture was evaporated, the residue was taken on pentane and filtrated three times under argon. Then, the residue was taken in a minimum of THF and pentane was added in order to precipitate. The mixture was filtrated under argon and dried under vacuum to give **2** as a brown oil (2.42 g, 2.45 mmol, 59 %). ^1H NMR (400 MHz, DMSO d_6) δ: 8.64 (br s, 2H, NH), 7.48 (s, 4H, ArH), 6.33 (t, J=5.4 Hz, 2H, NH), 4.02 (s, 4H, OCH_2), 3.75 (q, J=6.9 Hz, 12H, OCH_2CH_3), 3.03 (q, J=6.2 Hz, 4H, $HNCH_2$), 1.47 (m, 4H, $CH_2CH_2CH_2$), 1.28 (s, 12H, CH_3), 1.15 (t, 18H, J=6.9 Hz, OCH_2CH_3), 0.54 (m, 4H, CH_2-Si). ^{13}C NMR (75 MHz, DMSO d_6) δ: 154.7 (HNCONH), 143.7 (C_{ar}-O), 138.0 (C_{ar}-NH), 127.9 (C_{ar}-Cl), 117.5 (HC_{ar}), 78.2 (CH_2-O), 69.5 (C_{quat}-N), 57.7 (OCH_2CH_3), 41.8 ($HNCH_2$), 23.1 ($CH_2CH_2CH_2$), 21.7 (CH_3-C_{quat}), 18.1 (OCH_2CH_3), 7.2 (CH_2-Si). HRMS (ESI): *m/z*: calcd for $[M+H]^+$ $C_{40}H_{67}N_6O_{10}Si_2Cl_4^+$: 987.3206 Da, found : 987.3207 Da.

Experimental procedures for materials

General procedure. Thermogravimetric (TGA) measurements were carried out with a TGA Q500 apparatus (TA Instruments) under dynamic air atmosphere (sample flow rate 40 ml/min). SAXS experiments were performed on SAXSess-MC2 (Anton-Paar, GmbH, Austria) with a sealed copper tube as X-ray source (wavelength is 0.15417 nm (Cu K-α)) and CCD camera as 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.[3] Prior to adsorption, the samples were outgassed at 373 K overnight under a vacuum pressure of 2×10^{-3} mbar. All solid-state Cross Polarization Magic Angle Spinning (CPMAS) NMR spectra were obtained on a Bruker Avance-400 MHz NMR spectrometer operating at a ^{13}C and ^{29}Si 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 probe. About 100 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[4] 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.[5,6] 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[7] 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 referenced to tetramethylsilane. Tetraethylorthosilicate is commercially available. Tetraethylorthosilicate was distilled before used. LAM-1 was prepared according to a literature procedure.[2b]

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[3] Rouquerol, F., Rouquerol, J., Llewellyn, P., Maurin, G. & Sing, K. S. W., *Academic Press: London*, 2013

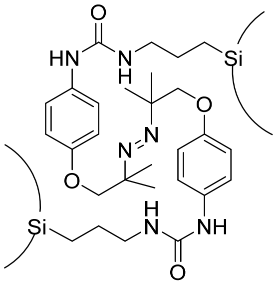
[4] Schaefer, J.; Stejskal, *J. Am. Chem. Soc.* 1976, **98**, 1031–1032.

[5] Peersen, O. B.; Wu, X.; Kustanovich, I.; Smith, 1993, **104**, 334–339.

[6] Cook, R. L.; Langford, C. H.; Yamdagni, R.; Preston, *Anal. Chem.,* 1996, **68**, 3979–3986.

[7] Gerbaud, G.; Ziarelli, F.; Caldarelli, S., *Chem. Phys. Lett.,* 2003, **377,** 1–5.

Synthesis of SBA$_n$-1.



SBA$_{11}$-1: In a typical procedure, pluronic P-123 (1 g) in deionized water (7 mL) and 2 M hydrochloric acid solution (30 mL) was stirred for 3h at 40 °C. Tetraethoxysilane (1.90 g, 9.1 mmol, 18 equiv) and organic precursor **1** (432 mg, 0.51 mmol, 1 equiv) in DMSO (1 mL) were 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 acetone and finally extracted with a Soxhlet apparatus (acetone) for one day. The wet powder was filtrated, washed twice with acetone and diethylether. After one night at 80 °C under vacuum, a pale brown 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 **1**.^{13}C CPMAS NMR (101.6 MHz) δ: 157.4, 153.5, 131.8, 119.9, 114.8, 74.1, 74.1 (P123), 69.1, 69.1 (P123), 42.7, 24.3, 21.5, 15.5 (P123), 10.4. ^{29}Si CPMAS NMR (79.5 MHz) δ: -59.4 (T^2), -66.3 (T^3), -92.5 (Q^2), -101.8 (Q^3), -110.8 (Q^4). BET Surface Area: 498 m²/g. BJH Desorption Average Pore Diameter: 5.9 nm. TGA: Mass Loss = 10.8%. SAXS: d = 11.0 nm.

SBA$_{26}$-1: Following the previous procedure, tetraethoxysilane (2.01 g, 9.63 mmol, 38 equiv) and organic precursor **1** (216 mg, 0.25 mmol, 1 equiv). ^{13}C CPMAS NMR (101.6 MHz) δ: 157.2, 153.4, 131.6, 119.3, 114.5, 74.2, 74.2 (P123), 69.4, 69.4 (P123), 42.8, 24.3, 21.1, 15.4 (P123), 10.4. ^{29}Si CPMAS NMR (79.5 MHz) δ: -68.7 (T^3), -92.1 (Q^2), -101.7 (Q^3), -110.8 (Q^4). BET Surface Area: 652 m²/g. BJH Desorption Average Pore Diameter: 6.5 nm. TGA: Mass Loss = 6.5%. SAXS: d = 10.7 nm, a = 9.1 nm.

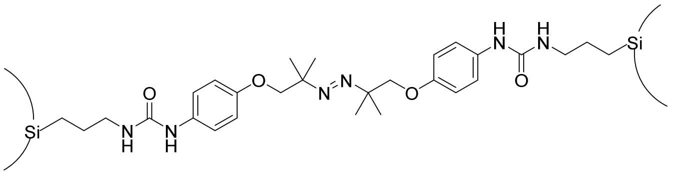
SBA$_{73}$-1: Following the previous procedure, tetraethoxysilane (2.07 g, 9.91 mmol, 88 equiv) and organic precursor **1** (96 mg, 0.11 mmol, 1 equiv). ^{13}C CPMAS NMR (101.6 MHz) δ: 157.4, 131.8, 120.4, 114.4, 73.8, 73.8 (P123), 70.0, 70.0 (P123), 60.4 (OEt), 42.5, 24.2, 21.0, 15.5 (P123), 9.8. ^{29}Si CPMAS NMR (79.5 MHz) δ: -66.7 (T^3), -93.5 (Q^2), -102.4 (Q^3), -111.4 (Q^4). BET Surface Area: 748 m²/g. BJH Desorption Average Pore Diameter: 6.7 nm. TGA: Mass Loss = 2.8%. SAXS: d = 10.3 nm, a = 8.9 nm.

SBA$_{126}$-1: Following the previous procedure, tetraethoxysilane (2.08 g, 9.97 mmol, 118 equiv) and organic precursor **1** (72 mg, 0.085 mmol, 1 equiv). ^{13}C CPMAS NMR (101.6 MHz) δ: 156.6, 153.3, 131.9, 119.5, 114.2, 75.3, 75.3 (P123), 69.6, 69.6 (P123), 42.4, 23.9, 21.0, 15.1

(P123). ^{29}Si CPMAS NMR (79.5 MHz) δ: -61.6 (T^2), -68.6 (T^3), -93.0 (Q^2), -102.7 (Q^3), -112.1 (Q^4). BET Surface Area: 620 m²/g. BJH Desorption Average Pore Diameter: 6.7 nm. TGA: Mass Loss = 1.7%. SAXS: d = 10.2 nm, a = 8.8 nm.

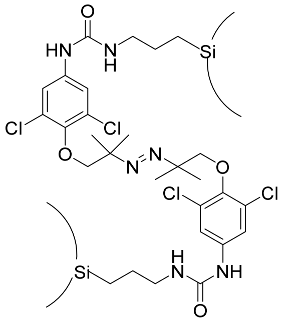
SBA_{194}-1 : Following the previous procedure, tetraethoxysilane (2.09 g, 10.03 mmol, 178 equiv) and organic precursor **1** (48 mg, 0.056 mmol, 1 equiv). ^{13}C CPMAS NMR (101.6 MHz) δ: 157.9, 155.5, 131.5, 114.1, 75.0, 75.0 (P123), 69.7, 69.7 (P123), 41.9, 24.0, 20.6, 14.9 (P123). ^{29}Si CPMAS NMR (79.5 MHz) δ: -66.8 (T^2), -69.8 (T^3), -93.2 (Q^2), -102.9 (Q^3), -111.6 (Q^4). BET Surface Area: 534 m²/g. BJH Desorption Average Pore Diameter: 6.5 nm. TGA: Mass Loss = 1.1%. SAXS: d = 10.4 nm, a = 9.0 nm.

Synthesis of PMOs-1.



Pluronic P-123 (0.43 g), sodium chloride (1.20 g) and ammonium fluoride (5.23 mg, 0.14 mmol, 0.066 equiv) in 0.1 M hydrochloric acid solution (14 mL) were stirred for 5 h at 37 °C. Organic precursor **1** (1.82 g, 2.14 mmol, 1 equiv) in DMSO (4 mL) was added. The mixture was stirred 20 h at 37 °C, then warmed without stirring at 60 °C for 24 h and then at 90 °C for 24h. The mixture was filtrated, washed twice with water, once with ethanol and acetone and finally extracted with a Soxhlet apparatus (acetone) for 6 h. The wet powder was filtrated, washed twice with acetone and diethylether. After one night at 60 °C, a brown powder was recovered. ^{13}C CPMAS NMR (101.6 MHz) δ: 156.0, 130.9, 118.4, 113.7, 72.5, 68.4, 42.0, 23.1, 9.6. ^{29}Si CPMAS NMR (79.5 MHz) δ: -48.3 (T^1), -57.8 (T^2), -65.4 (T^3). BET Surface Area: 50 m²/g. BJH Desorption Average Pore Diameter: 9.7 nm. TGA: Mass Loss = 74.8%. SAXS : no peak.

Synthesis of SBA$_n$-2.



SBA$_9$-2: In a typical procedure, pluronic P-123 (2 g) in deionized water (14 mL) and 2 M hydrochloric acid solution (60 mL) was stirred for 3 h at 40 °C. Tetraethoxysilane (3.80 g, 18.25 mmol, 18 equiv) and organic precursor **2** (1.00 g, 1.01 mmol, 1 equiv) in EtOH (1 mL) were 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 acetone and finally extracted with a Soxhlet apparatus (acetone) for one day. The wet powder was filtrated, washed twice with 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 **2** : 0.017 M P123 Polymer : 188 M H_2O : 5.8 M HCl, where x denotes the number of moles of precursor **2**. ^{13}C CPMAS NMR (101.6 MHz) δ: 155.8, 145.3, 135.3, 128.2, 116.5, 77.2, 69.1, 41.9, 21.8, 9.3. ^{29}Si CPMAS NMR (79.5 MHz) δ: -57.3 (T^2), -66.2 (T^3), -91.2 (Q^2), -100.3 (Q^3), -108.4 (Q^4). BET Surface Area: 578 m²/g. BJH Desorption Average Pore Diameter: 7.1 nm. TGA: Mass Loss = 10.7%. SAXS: d = 11.0 nm, a = 9.6 nm.

SBA$_{26}$-2: Following the previous procedure, tetraethoxysilane (4.01 g, 19.27 mmol, 38 equiv) and organic precursor **2** (501 mg, 0.51 mmol, 1 equiv). ^{13}C CPMAS NMR (101.6 MHz) δ: 155.5, 145.0, 135.0, 127.9, 116.0, 75.3, 75.3 (P123), 69.0, 69.0 (P123), 40.7, 21.7, 14.6 (P123), 10.3. ^{29}Si CPMAS NMR (79.5 MHz) δ: -65.0 (T^3), -90.5 (Q^2), -100.5 (Q^3), -109.2 (Q^4). BET Surface Area: 439 m²/g. BJH Desorption Average Pore Diameter: 7.0 nm. TGA: Mass Loss = 6.0%. SAXS: d = 11.5 nm, a = 9.9 nm.

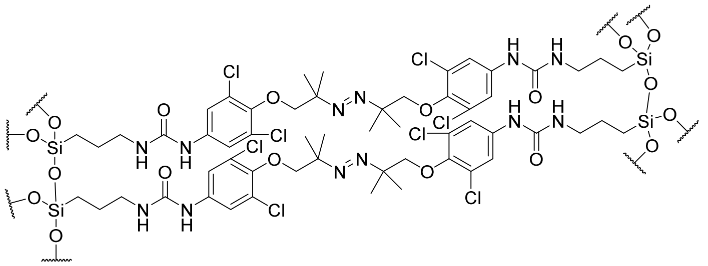
SBA$_{90}$-2: Following the previous procedure, tetraethoxysilane (4.15 g, 19.94 mmol, 118 equiv) and organic precursor **2** (167 mg, 0.17 mmol, 1 equiv). ^{13}C CPMAS NMR (101.6 MHz) δ: 155.0, 144.9, 128.1, 117.0, 74.1, 74.1 (P123), 69.2, 69.2 (P123), 41.2, 20.7, 14.9 (P123), 10.8. ^{29}Si CPMAS NMR (79.5 MHz) δ: -66.7 (T^3), -91.2 (Q^2), -100.5 (Q^3), -110.1 (Q^4). BET Surface Area: 502 m²/g. BJH Desorption Average Pore Diameter: 6.8 nm. TGA: Mass Loss = 2.3%. SAXS: d = 11.6 nm, a = 10.0 nm.

SBA$_{94}$-2: Following the previous procedure, tetraethoxysilane (4.13 g, 19.83 mmol, 88 equiv) and organic precursor **2** (223 mg, 0.23 mmol, 1 equiv). ^{13}C CPMAS NMR (101.6 MHz) δ:

154.0, 144.5, 139.2, 128.1, 117.6, 74.7, 74.7 (P123), 69.1, 69.1 (P123), 41.4, 28.5, 20.3, 14.9 (P123), 9.0. ^{29}Si CPMAS NMR (79.5 MHz) δ: -65.2 (T^3), -90.3 (Q^2), -100.3 (Q^3), -109.9 (Q^4). BET Surface Area: 331 m²/g. BJH Desorption Average Pore Diameter: 6.6 nm. TGA: Mass Loss = 2.1%. SAXS: d = 11.3 nm, a = 9.8 nm.

SBA$_{221}$-2: Following the previous procedure, tetraethoxysilane (4.17 g, 20.04 mmol, 166 equiv) and organic precursor **2** (120 mg, 0.12 mmol, 1 equiv). ^{13}C CPMAS NMR (101.6 MHz) δ: 156.1, 147.3, 137.7, 126.2, 117.4, 75.1, 75.1 (P123), 69.2, 69.2 (P123), 57.8 (OEt), 45.2, 23.6, 20.3, 14.4 (P123), 7.4. ^{29}Si CPMAS NMR (79.5 MHz) δ: -90.6 (Q^2), -100.6 (Q^3), -110.3 (Q^4). BET Surface Area: 648 m²/g. BJH Desorption Average Pore Diameter: 6.3 nm. TGA: Mass Loss = 1.0%. SAXS: d = 11.3 nm, a = 9.8 nm.

Synthesis of LAM-2.



A suspension of **2** (641 mg) in 30 mL of water at pH = 1.5 (acidified with hydrochloric acid) was stirred two weeks at room temperature, then warmed without stirring at 100 °C for 2 days. The mixture was filtrated and the solid residue milled first dried up and then in ethanol before being filtrated again. This operation was repeated three times. The solid was washed two times with acetone and Et_2O. After one night under vacuum at 80 °C, a brown solid was recovered. ^{13}C CPMAS NMR (101.6 MHz) δ: 155.9, 144.9, 134.9, 128.4, 116.8, 77.8, 69.0, 41.7, 21.7, 9.6. ^{29}Si CPMAS NMR (79.5 MHz) δ: -47.7 (T^1), -57.3 (T^2), -65.8 (T^3). TGA: Mass Loss = 74.7%. WAXS: 9.18, 9.99, 12.10, 13.20, 15.00, 16.45, 18.08, 19.98.

Experimental Procedures for EPR Analysis

CW EPR Spectroscopy: EPR experiments were performed on a Bruker Elexsys E500 spectrometer and the Bruker BVT 3000 set-up was utilized to control the temperature. The photolysis was directly performed in the cavity of the EPR spectrometer with a Hamamatsu LC8 01A light source with a 360-370 nm filter.

In a 4 mm quartz-glass tube, 5 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 oxygen centered radical experiments were recorded with the parameters: modulation amplitude = 2 G, receiver gain = 99 dB, modulation frequency = 100 kHz, power = 0.2 mW, sweep width = 200 G, conversion time = 29.3 ms, sweep time = 30 s, number of scans = 2.

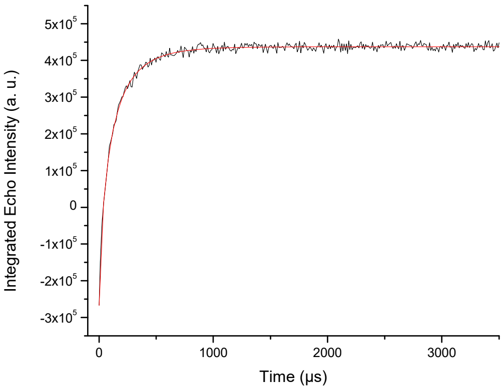
Pulse EPR spectroscopy: X band pulsed EPR experiments were carried out on a Bruker Elexsys E580 spectrometer equipped with a dielectric ring resonator (ER4118X-MD5) and a helium flow cryostat (Oxford CF935). The microwave pulses were amplified with a 1kW TWT. A 3 mm external diameter quartz-glass tube was filled with 5 mg of functionalized silica. The tube was degassed with three freeze-pump-thaw cycles with a 10^{-5} mbar vacuum pump and finally filled with argon. The sample irradiation was performed before the introduction of the EPR tube in the cavity with a Rayonet apparatus (RPR-200, 16 UV lamps (360 nm)). Temperatures and relaxation times are listed in Tables S1 and S2 (see below).

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.

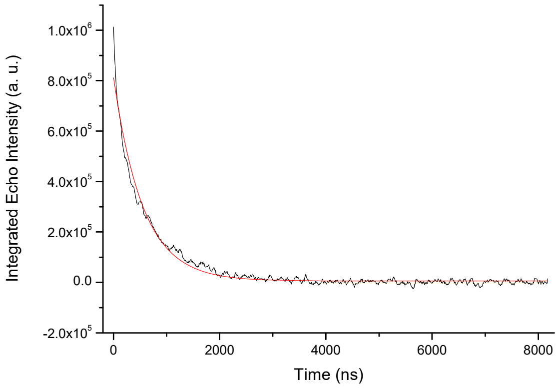
The phase memory time, T_m, were measured using the same two-pulse sequence. The integrated echo intensity was measured as a function of τ, incremented in steps of 4ns from a initial value of 200ns. Experiments were recorded at magnetic field corresponding to the maximum intensity in the field sweep spectra. Single exponential decay fit ($I(t) = I_0 + I_1\ exp\left[-\left(\frac{t}{T_m}\right)\right]$) was used to extract τ_m.

A conventional inversion-recovery sequence (π–t–π/2–τ–π–τ–echo) was applied to determine the electron relaxation time, T_{1e}, with a τ delay of 200ns and a 32ns detector gate, centered at the maximum of the echo signal. The inversion pulse length and the refocusing π pulses were 32ns. Initial delay t was adjusted depending on the T_{1e}. Experiments were recorded at magnetic field corresponding to the maximum intensity in the field sweep spectra. Experimental curves were adjusted using a stretched exponential function ($I(t) = I_0 + I_1\, exp\left[-\left(\frac{t}{T_{1e}}\right)^{\beta}\right]$). Gamma function was used ($\langle T_{1e}\rangle = \frac{T_{1e}}{\beta}\Gamma\left(\frac{1}{\beta}\right)$) in order to obtain the mean longitudinal relaxation times $<T_{1e}>$ which is the first moment of the distribution and describes a mean recovery time.[8]

An example of experimental data (black curve) together with the fit obtained (red curve) using the equations above both for T_{1e} and T_m is given for **LAM-2** at 180K in Figure S1-A and B, respectively.



A)



B)

Figure S1

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[8] a) E. Besson, F. Ziarelli, E. Bloch, G. Gerbaud, S. Queyroy, S. Viel and S. Gastaldi, *Chem. Commun.*, 2016, **52**, 5531-5533. b) 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.

Table S1. Relaxation times for porous materials **SBA$_n$-1**, **SBA$_n$-2** and **PMOs-1**.

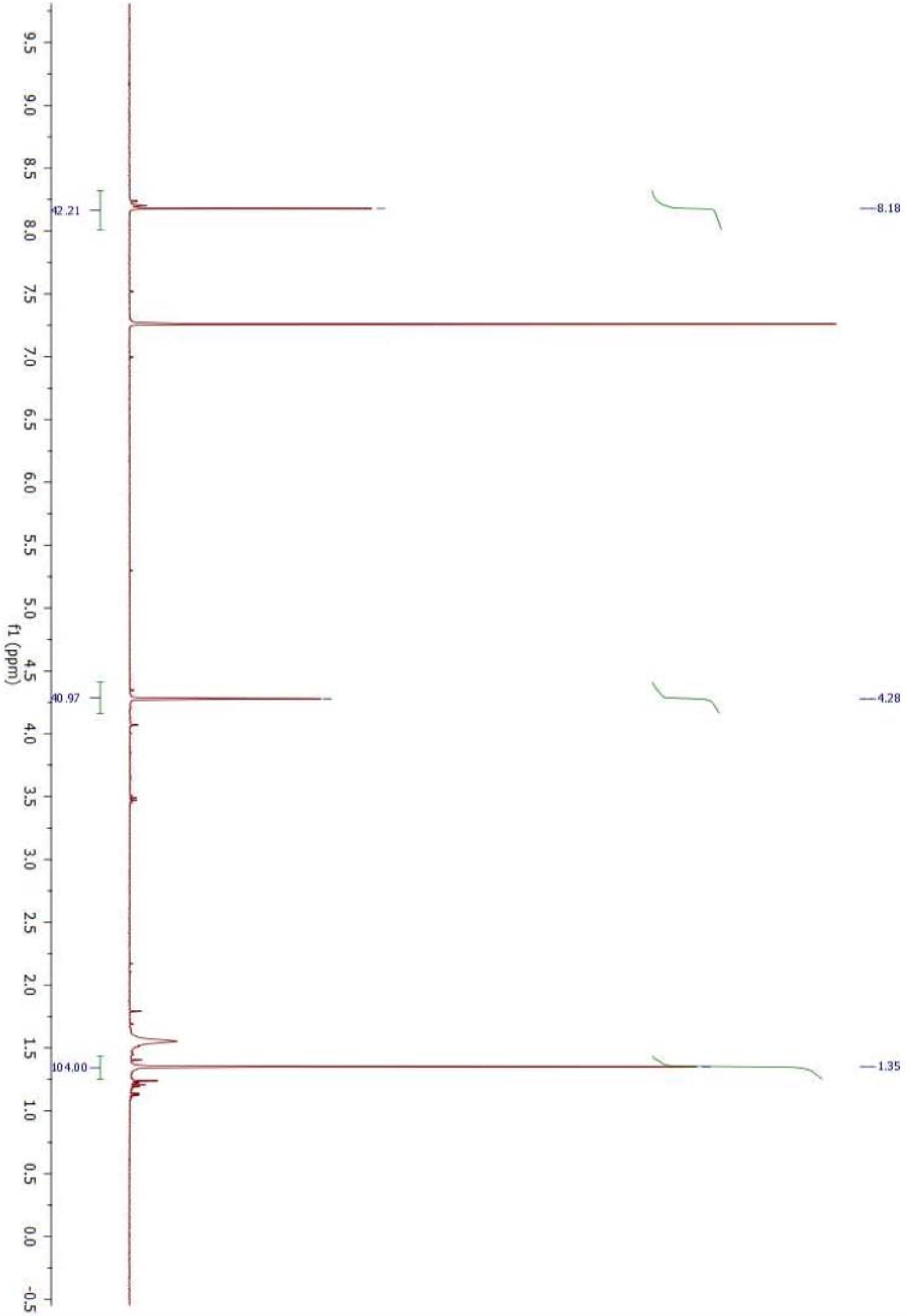
Entry		T °C	$<T_{1e}>$ (μs)	Error (μs)	T_m (ns)	Error (ns)
1	**SBA$_{11}$-1**	50 K	2200	300	1470	15
2	**SBA$_{26}$-1**	50 K	370	60	1435	15
3		110 K	170	25	1370	25
4	**SBA$_{73}$-1**	50 K	270	120	1280	15
5		50 K, TCE	> 4000[b]		1380	75
6	**SBA$_{126}$-1**	50 K	190	50	1150	25
7	**PMOs-1**	50 K	800	30	1420	15
8		110 K, TCE	1900	120	1830	40
9	**SBA-$_{9}$-2**	50 K	1690	65	1410	20
10		50 K, TCE	2430	90	1340	20
11	**SBA$_{26}$-2**	50 K	1150	70	1125	15
12	**SBA$_{94}$-2**	50 K	970	90	880	20
13	**SBA$_{221}$-2**	50 K	945	220	870	15

[a] Not determined. [b] Estimated on the echo intensity by varying the shot repetition time.

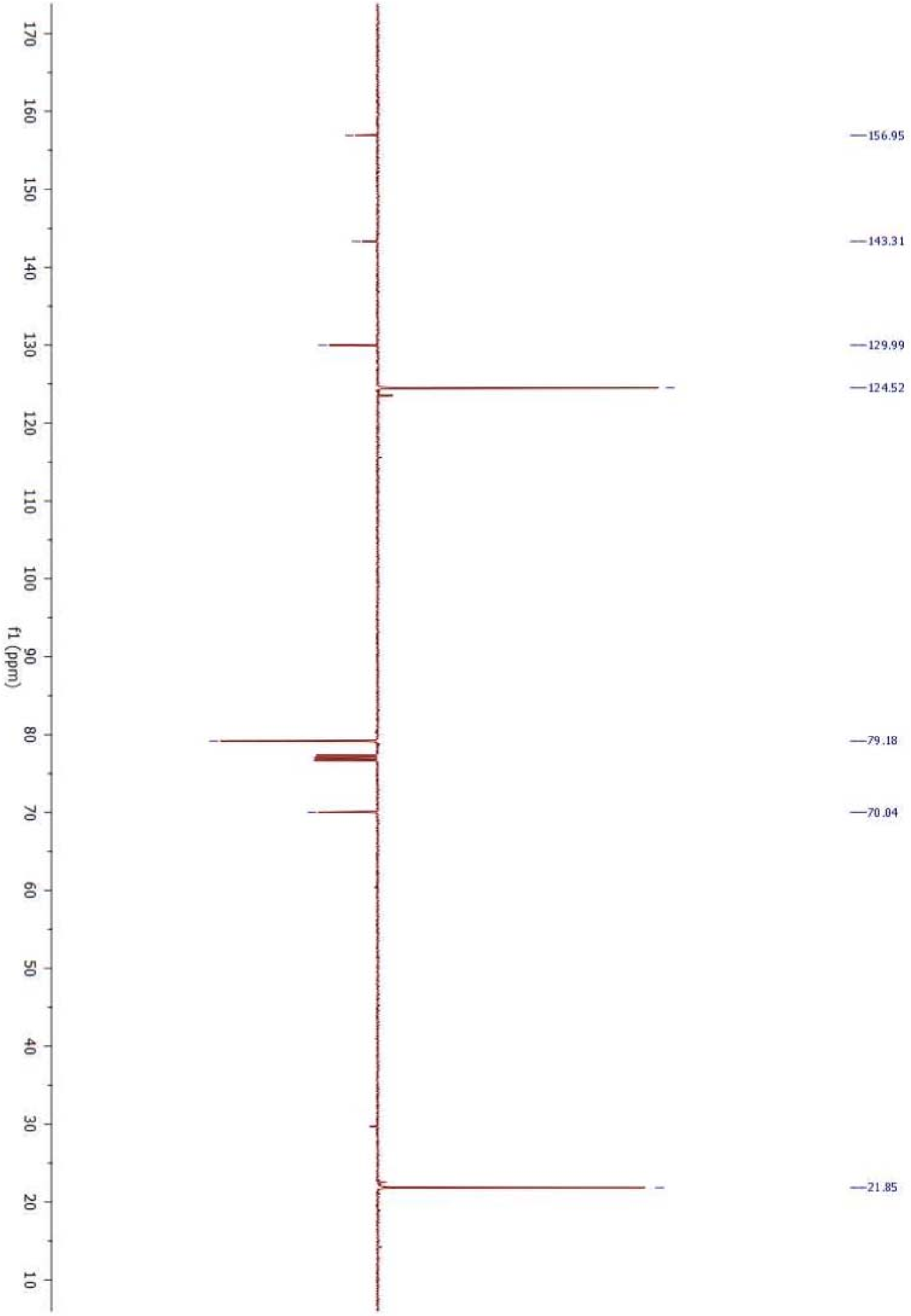
Table S2. Relaxation times for lamellar polysilsesquioxanes **LAM-1** and **LAM-2**.

Entry		T °C	$<T_{1e}>$ (μs)	Error (μs)	T_m (ns)	Error (ns)
1	**LAM-1**	50 K	1225	20	1480	10
2	**LAM-1**	110 K	490	20	1360	15
3	**LAM-1**	180 K	160	20	1230	20
4	**LAM-1**	240 K	75	5	1020	30
5	**LAM-1**	295 K	40	2	560	10
6	**LAM-1**	110 K, TCE	1220	60	1450	25
7	**LAM-1**	180 K, TCE	270	10	1250	20
8	**LAM-1**	240 K, TCE	100	10	1000	20
9	**LAM-1**	295 K,TCE	60	2	550	10
10	**LAM-2**	110 K	120	25	1010	15
11	**LAM-2**	180 K	55	15	920	10
12	**LAM-2**	240 K	40	10	740	10
13	**LAM-2**	295 K	30	5	490	5
14	**LAM-2**	110 K, TCE	380	60	1390	15
15	**LAM-2**	180 K, TCE	130	25	1215	15
16	**LAM-2**	240 K, TCE	60	15	980	15
17	**LAM-2**	295 K,TCE	30	5	555	10

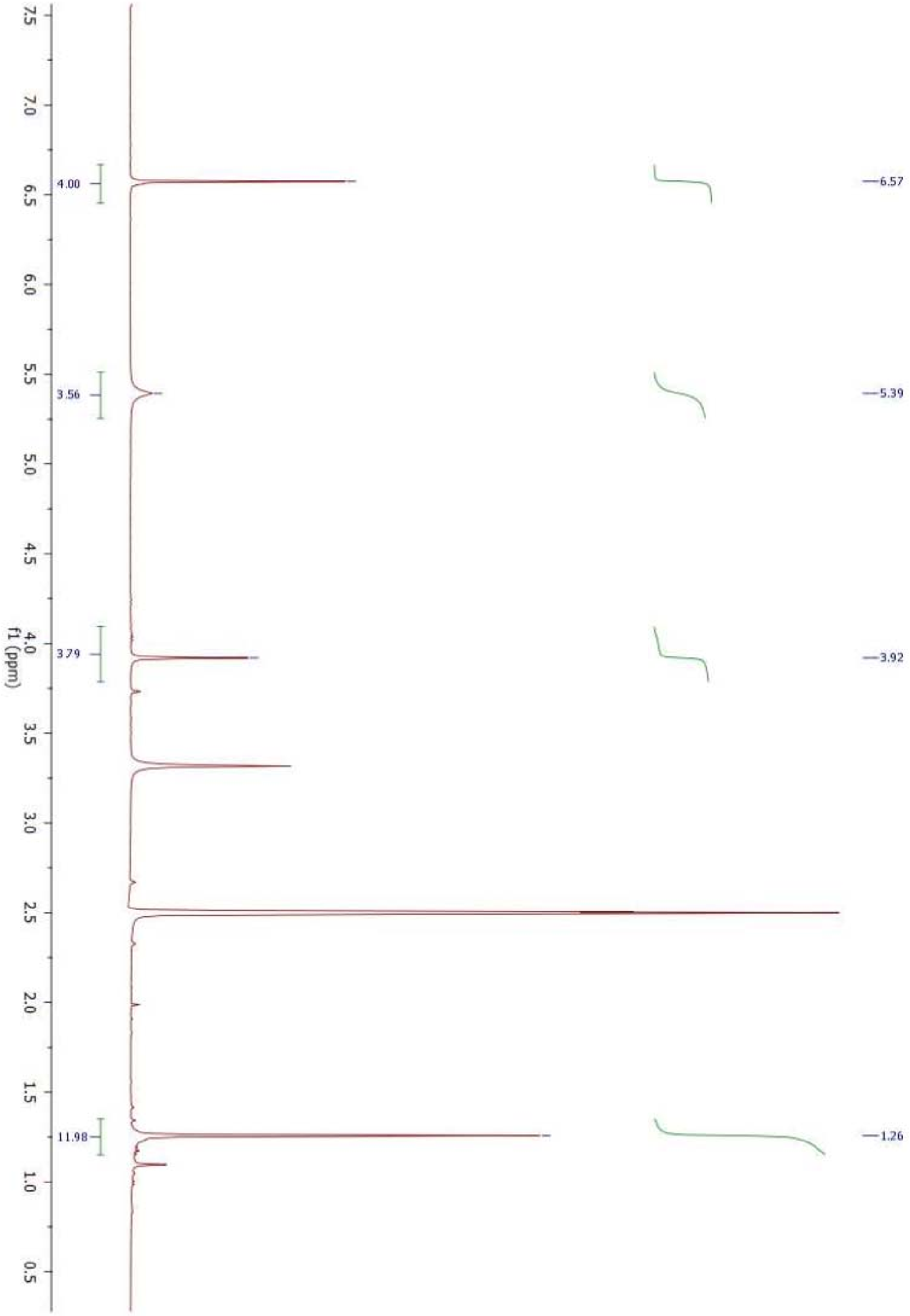
(*E*)-1,2-bis(1-(2,6-dichloro-4-nitrophenoxy)-2-methylpropan-2-yl)diazene (6): ^{1}H NMR



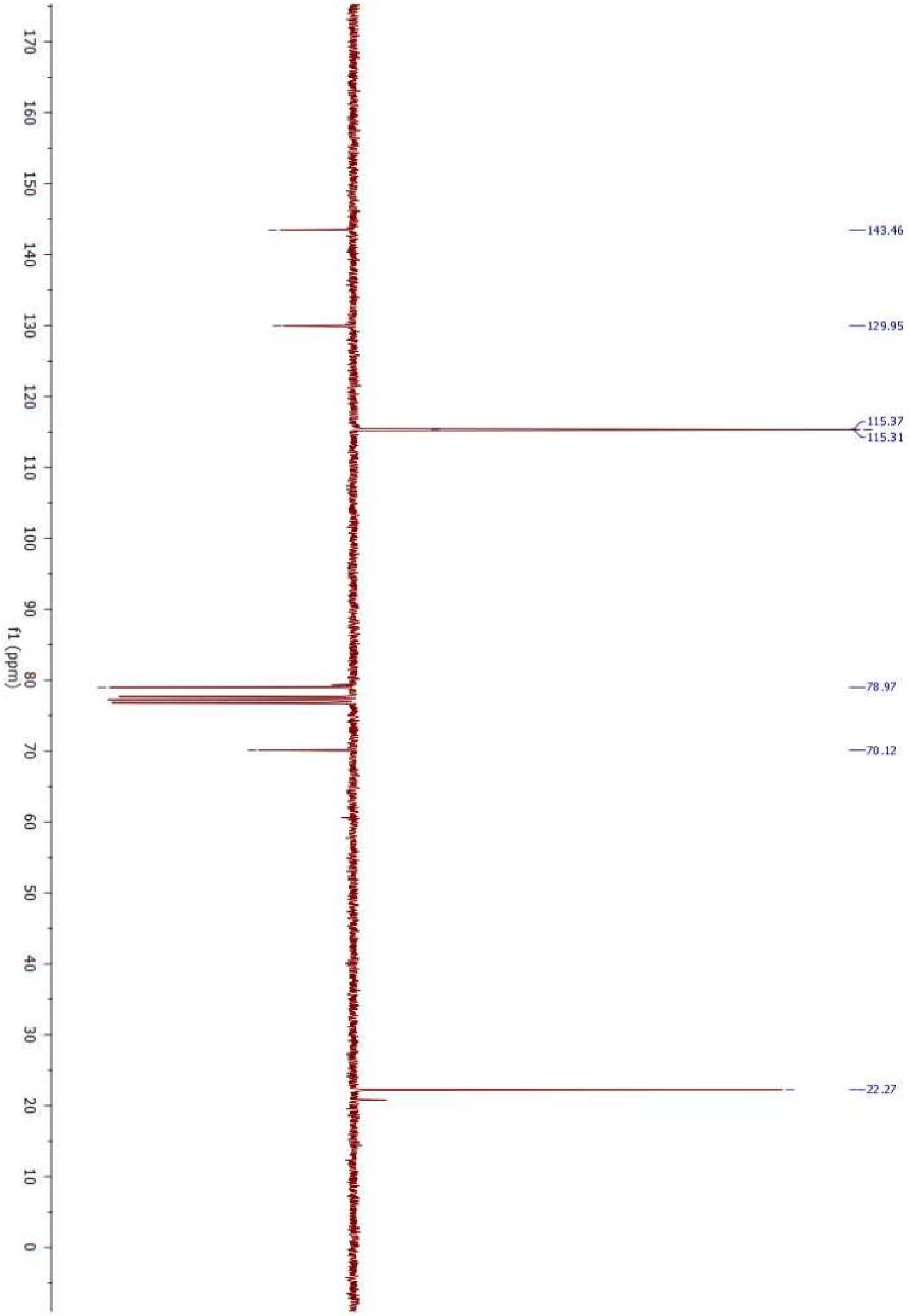
(*E*)-1,2-bis(1-(2,6-dichloro-4-nitrophenoxy)-2-methylpropan-2-yl)diazene (6): ^{13}C APT



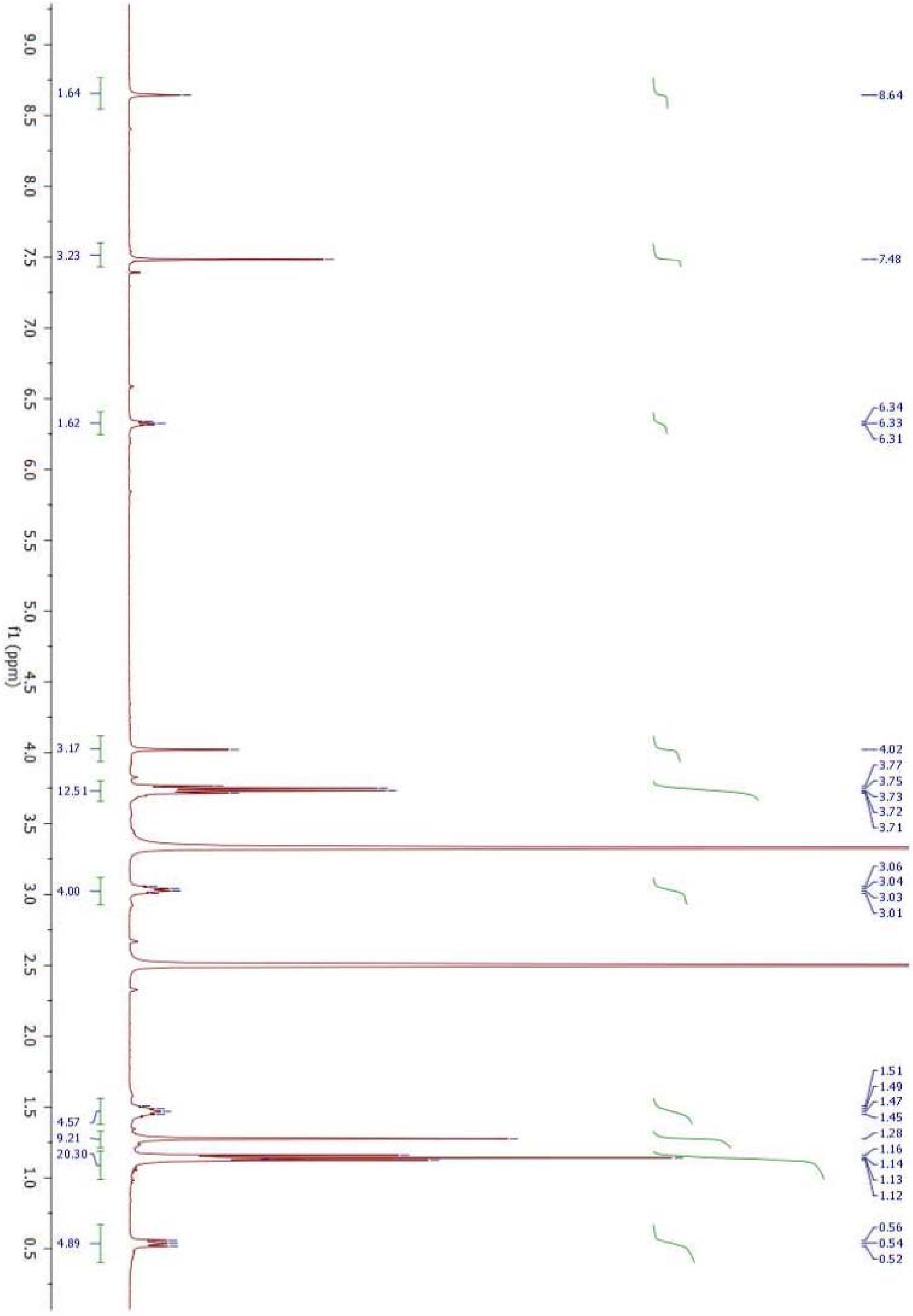
(*E*)-4,4'-((diazene-1,2-diylbis(2-methylpropane-2,1-diyl))bis(oxy))bis(3,5-dichloroaniline) (4): ^{1}H NMR



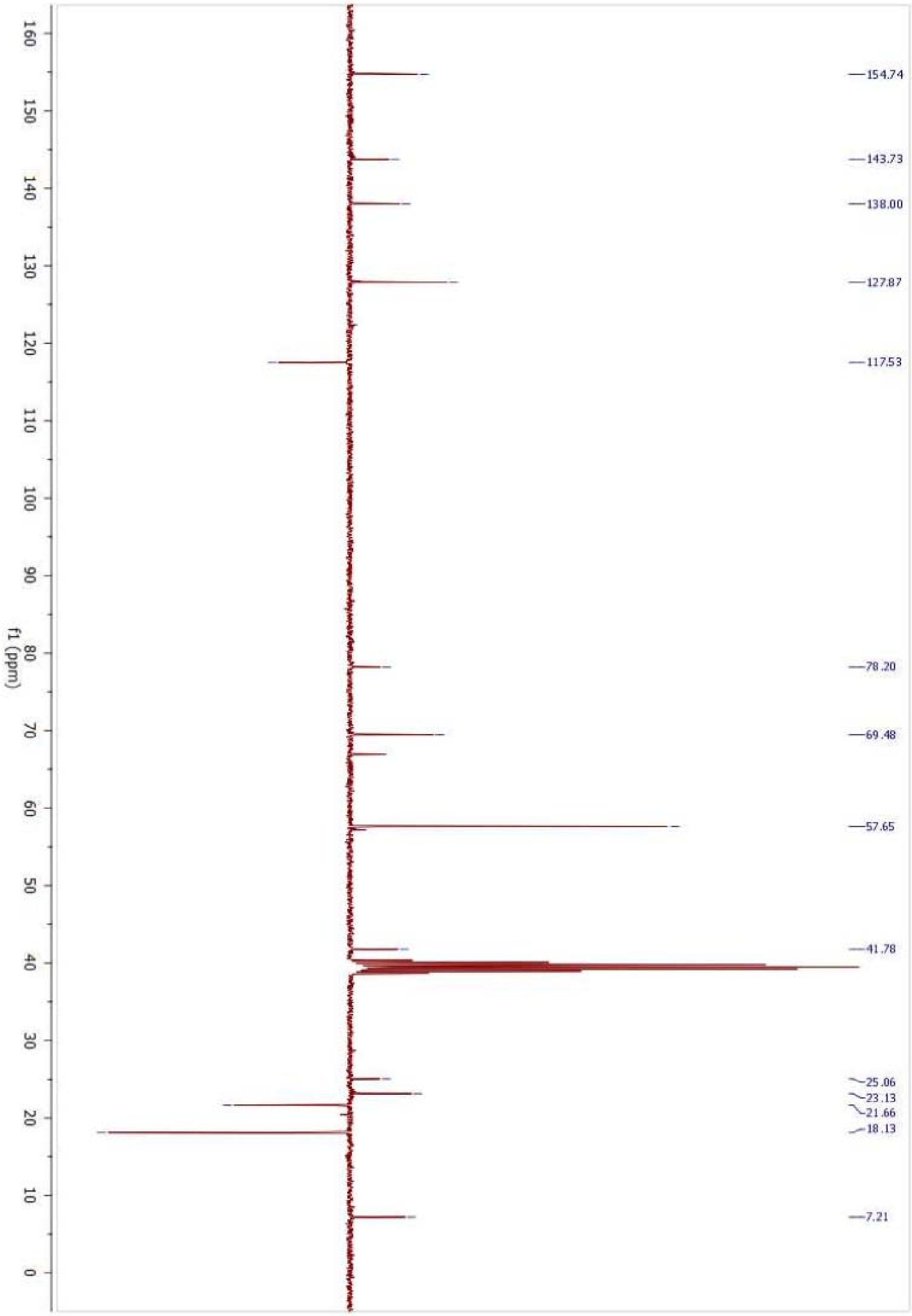
(*E*)-4,4'-((diazene-1,2-diylbis(2-methylpropane-2,1-diyl))bis(oxy))bis(3,5-dichloroaniline) (4): ^{13}C APT



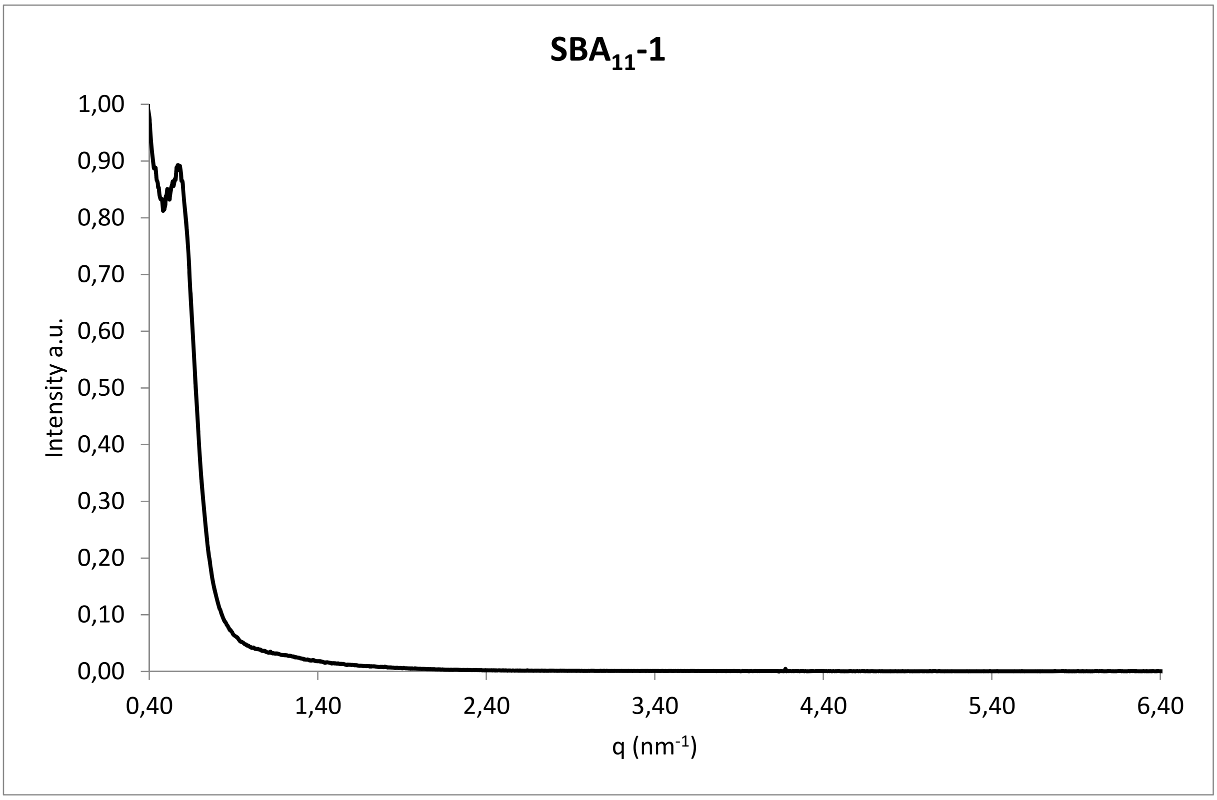
(*E*)-1,1'-(((diazene-1,2-diylbis(2-methylpropane-2,1-diyl))bis(oxy))bis(3,5-dichloro-4,1-phenylene))bis(3-(3-(triethoxysilyl)propyl)urea) (2): ^{1}H NMR

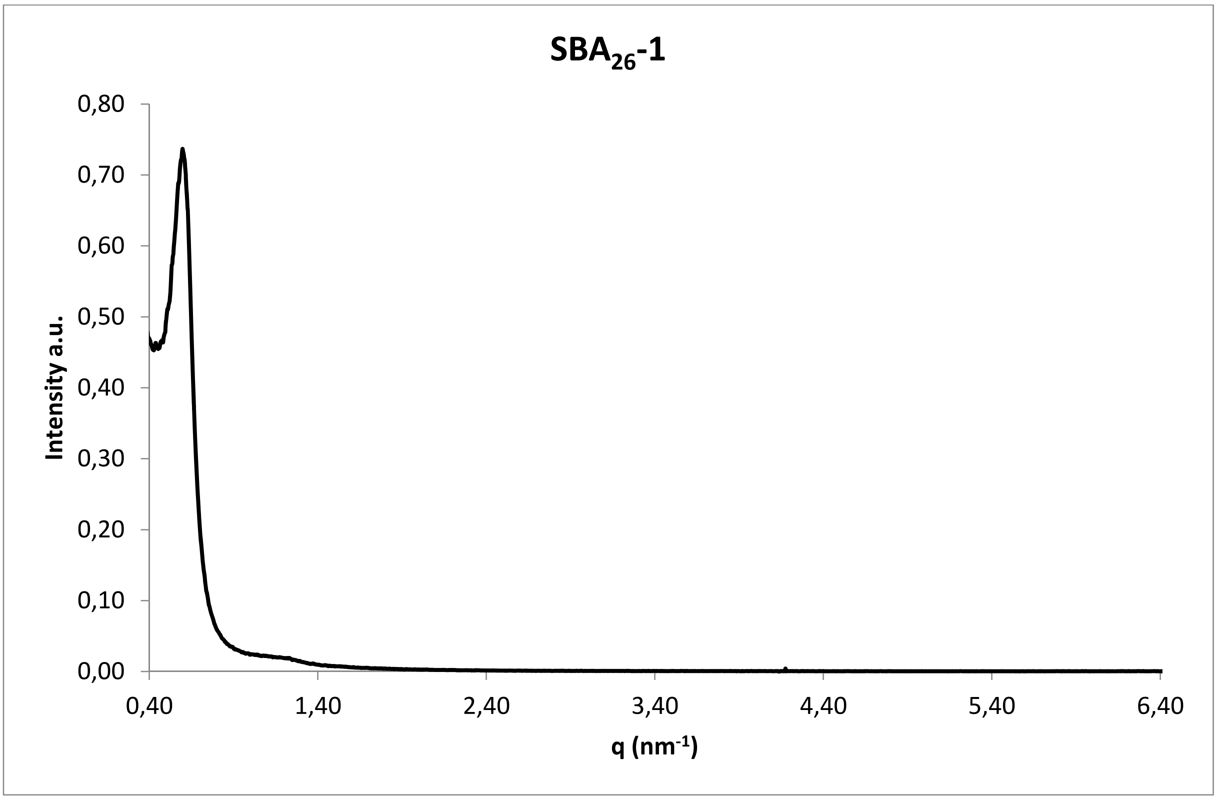


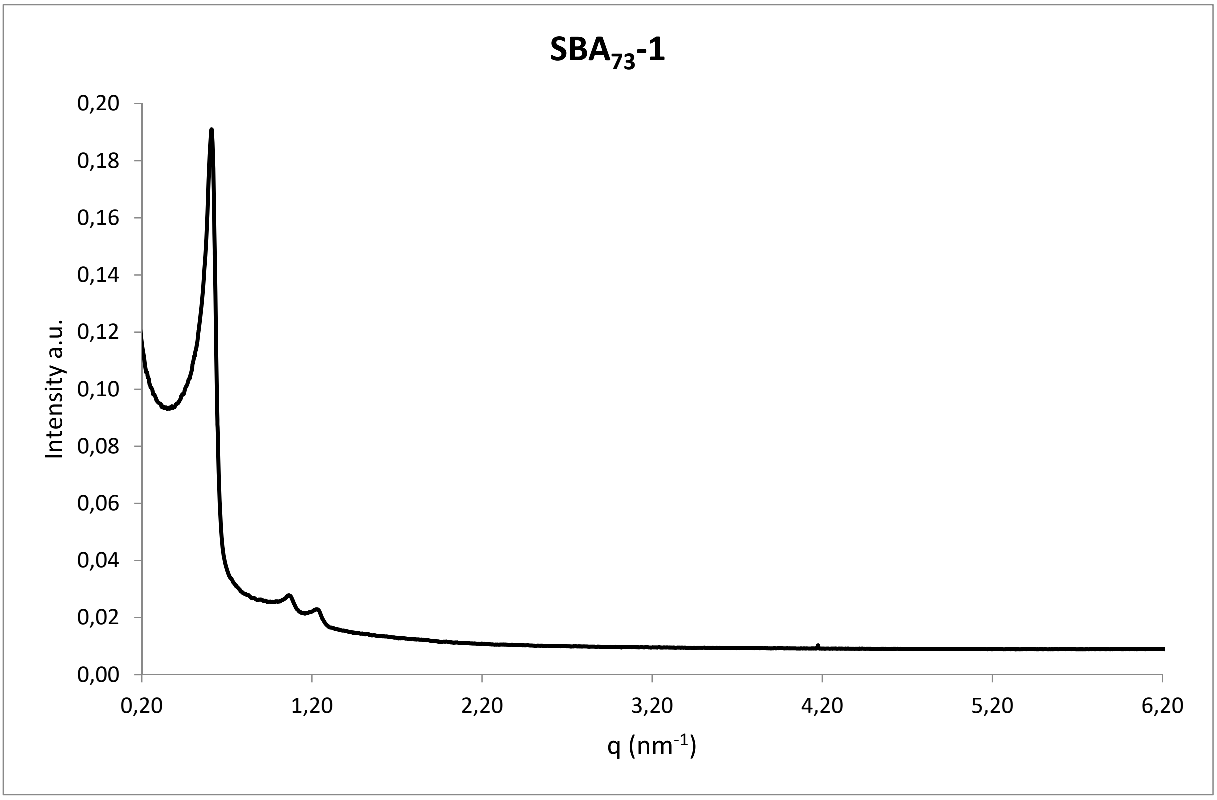
(*E*)-1,1'-(((diazene-1,2-diylbis(2-methylpropane-2,1-diyl))bis(oxy))bis(3,5-dichloro-4,1-phenylene))bis(3-(3-(triethoxysilyl)propyl)urea) (2): ^{13}C APT



Small Angle X-Ray Scattering (SAXS): SBA$_{11}$-1, SBA$_{26}$-1, SBA$_{73}$-1, SBA$_{126}$-1, SBA$_{194}$-1







SBA$_{73}$-1
Intensity a.u.
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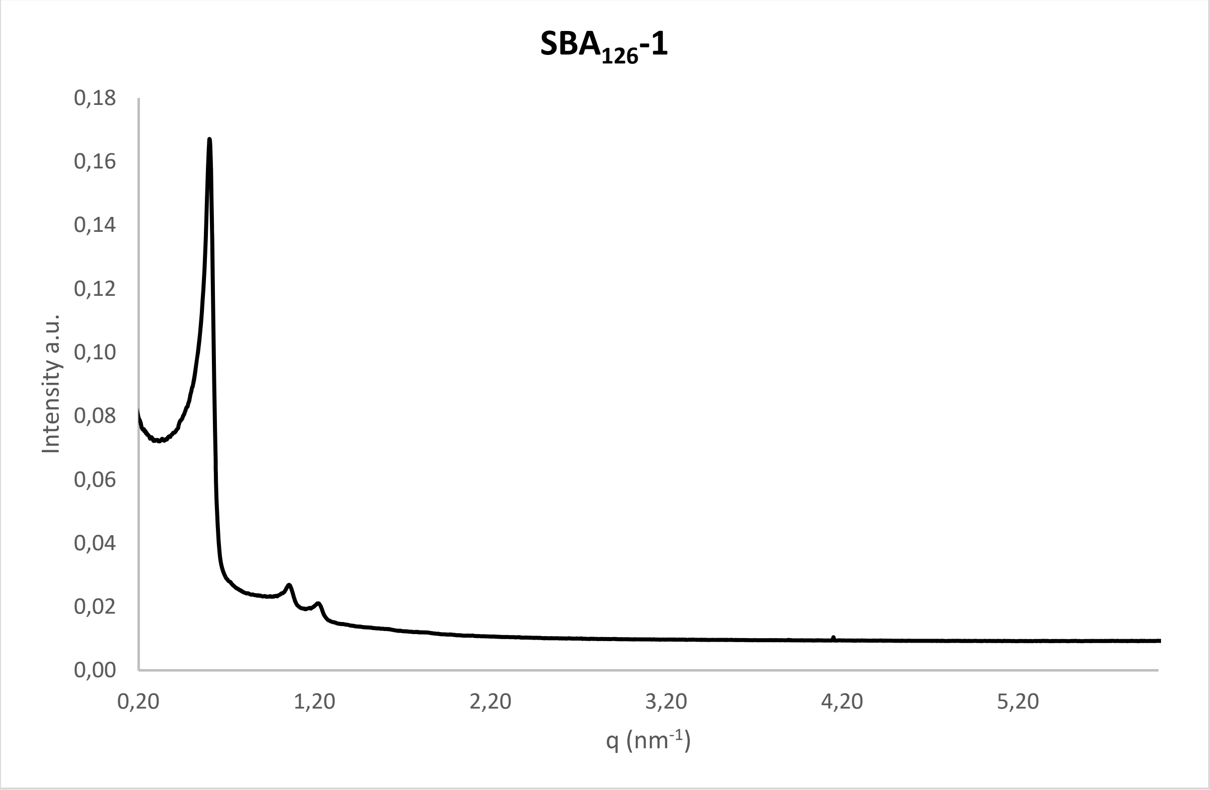
0,16
0,14
0,12
0,10
0,08
0,06
0,04
0,02
0,00
0,20
1,20
2,20
3,20
4,20
5,20
6,20
q (nm^{-1})



SBA$_{126}$-1
Intensity a.u.
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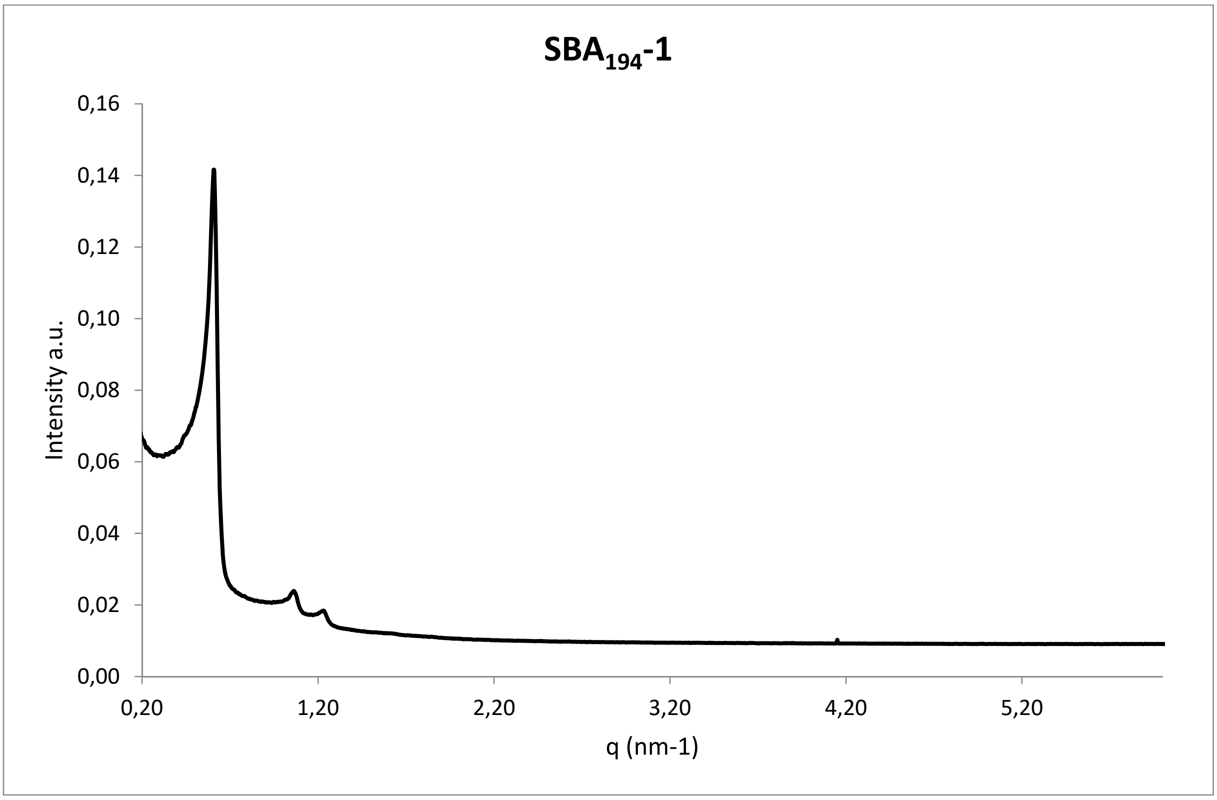
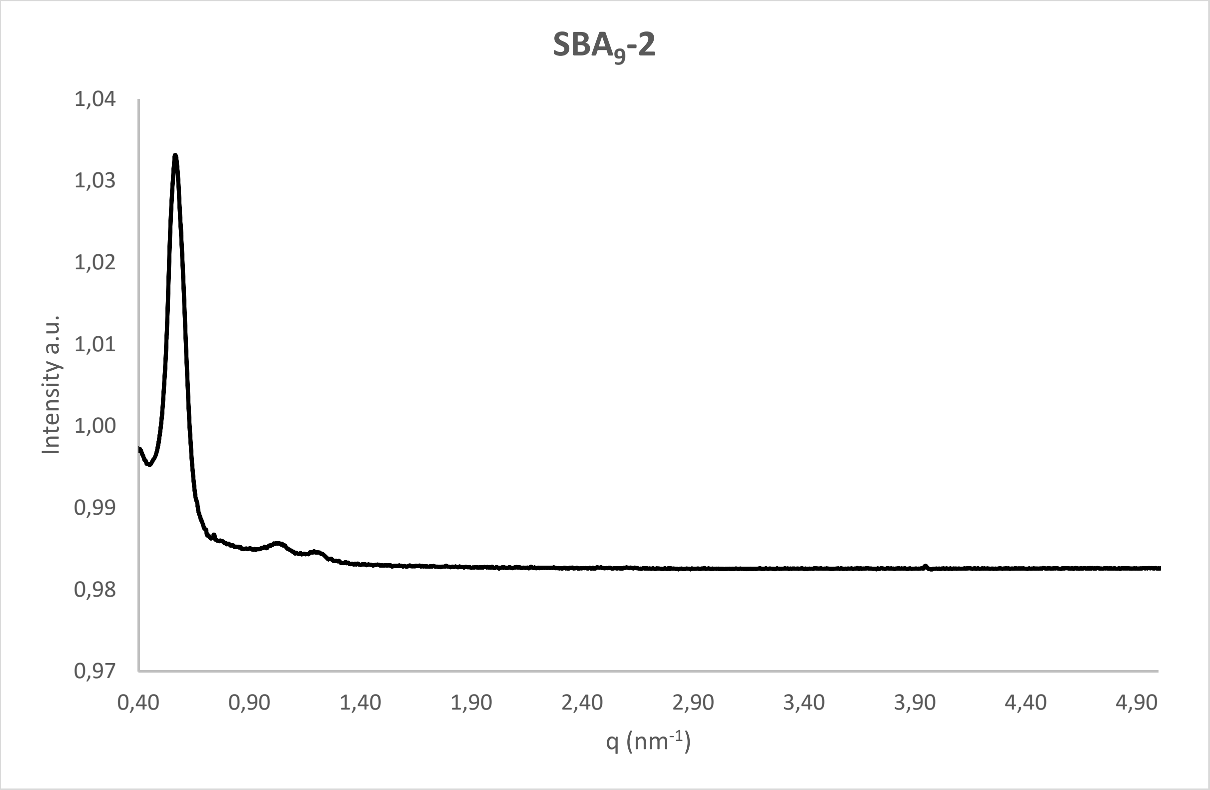
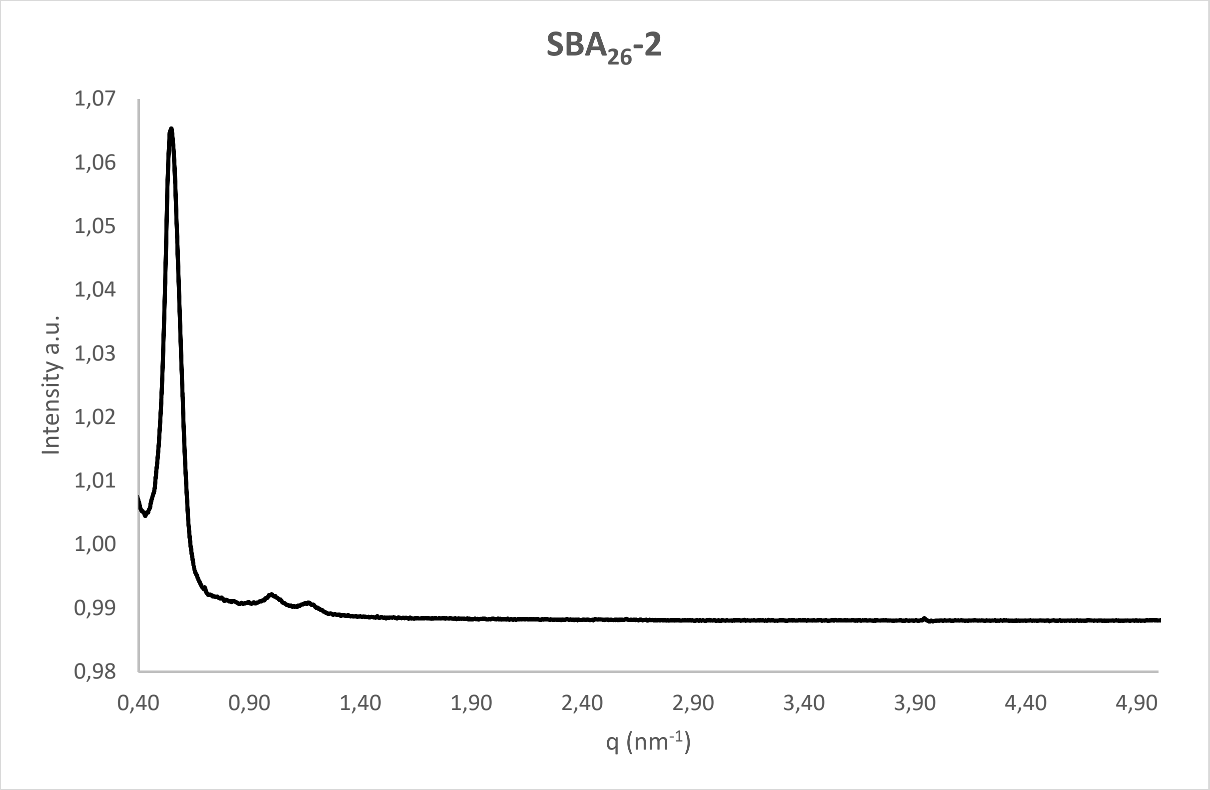
3,20
4,20
5,20
q (nm^{-1})



Small Angle X-Ray Scattering (SAXS): SBA$_9$-2, SBA$_{26}$-2, SBA$_{94}$-2, SBA$_{221}$-2

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1,03
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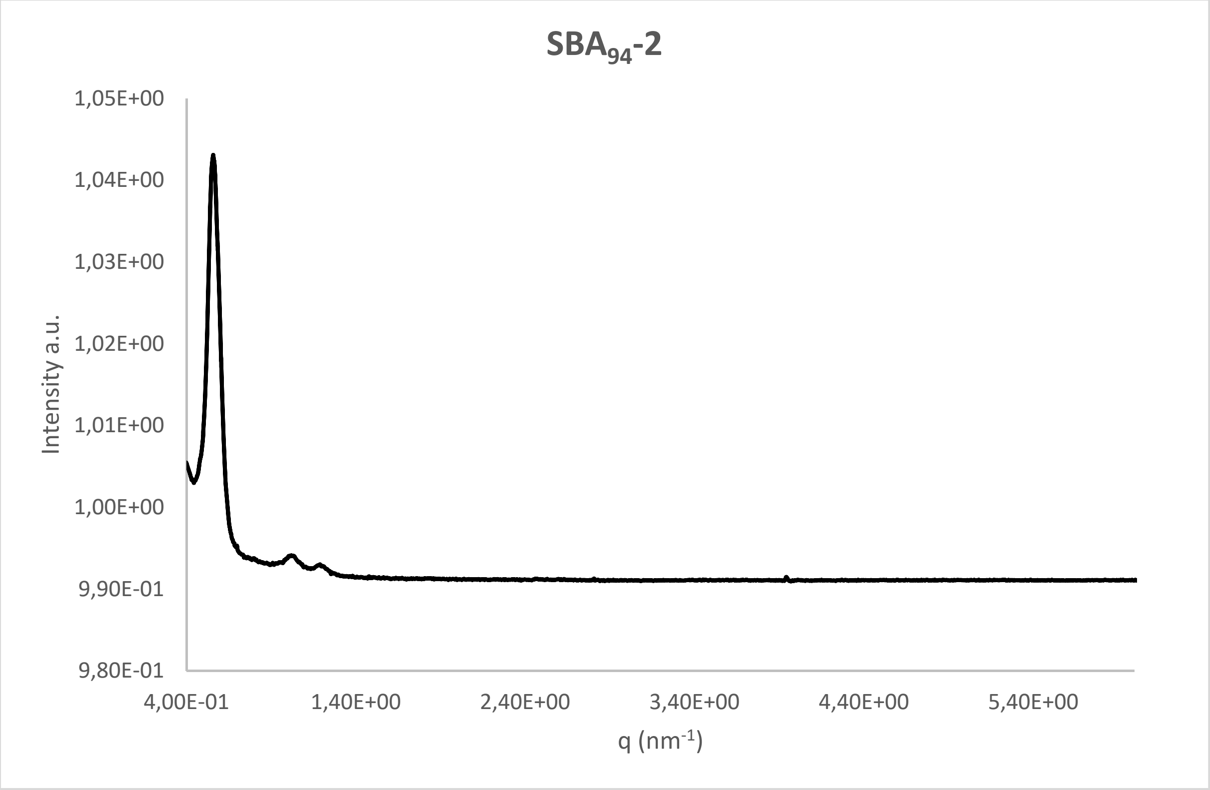
1,90
2,40
2,90
3,40
3,90
4,40
4,90
q (nm^{-1})


SBA$_{94}$-2
Intensity a.u.
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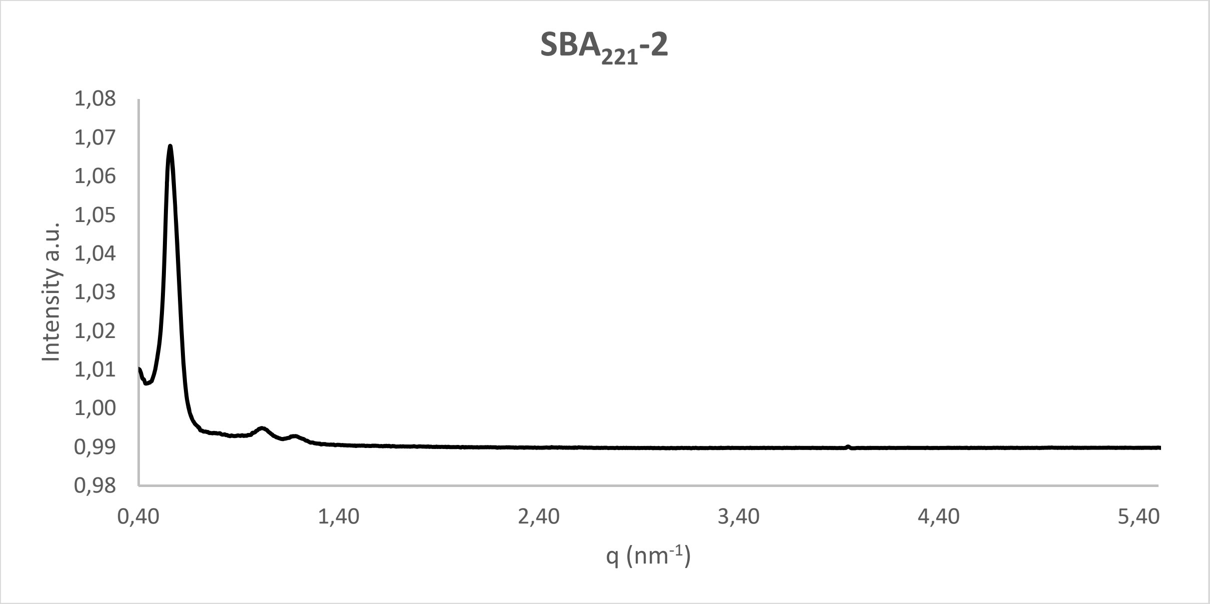
5,40E+00
q (nm^{-1})


SBA$_{221}$-2
Intensity a.u.
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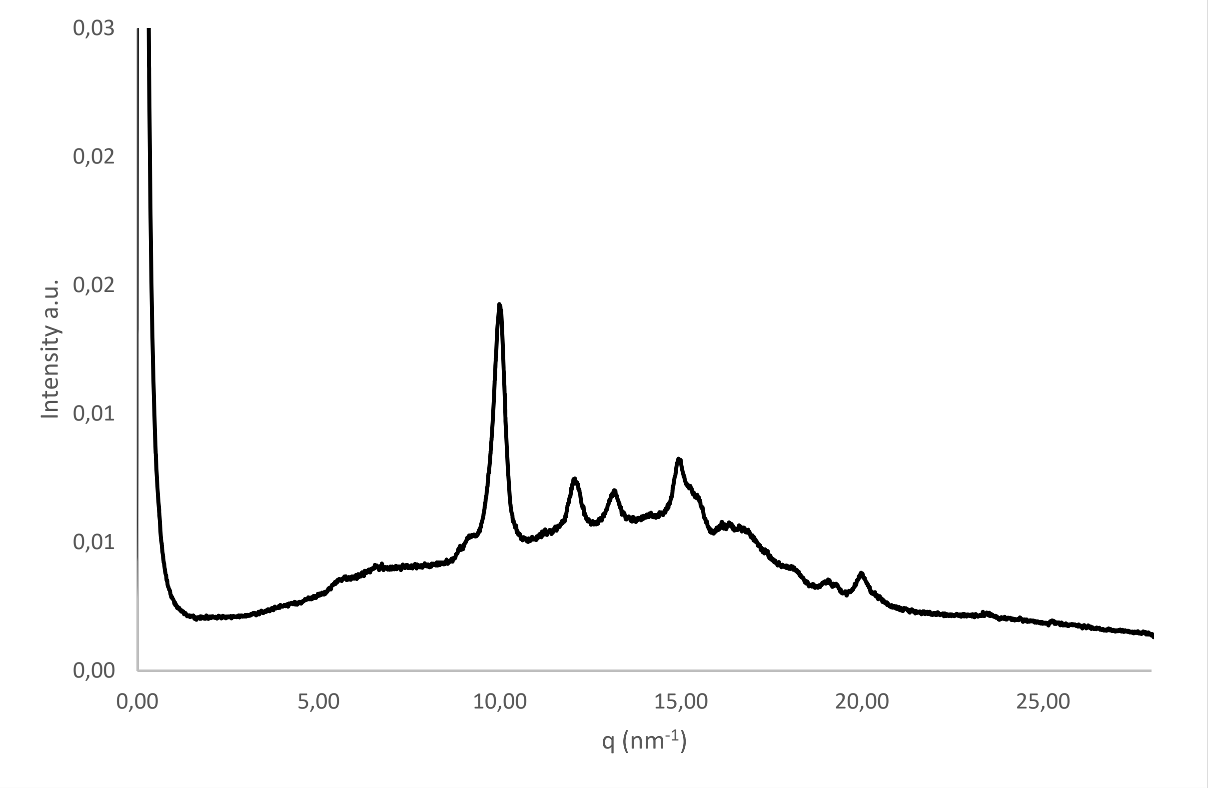
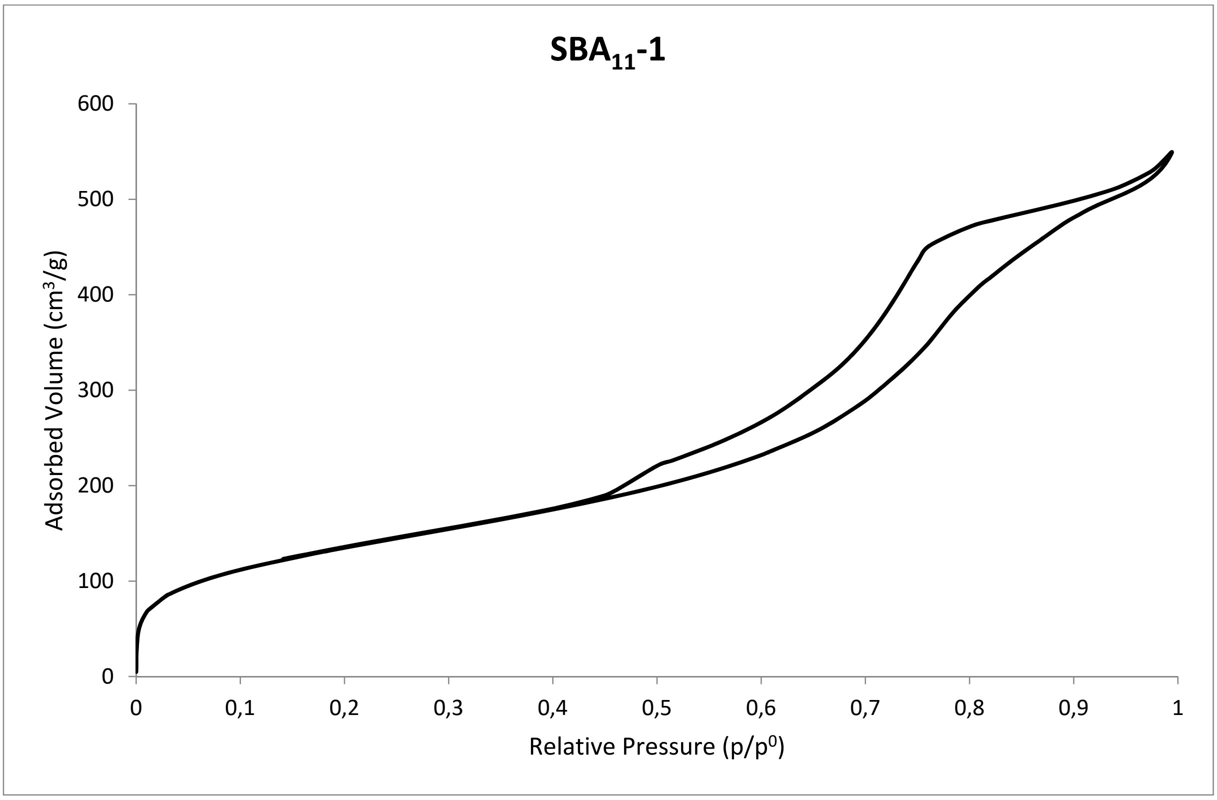
4,40
5,40
q (nm^{-1})

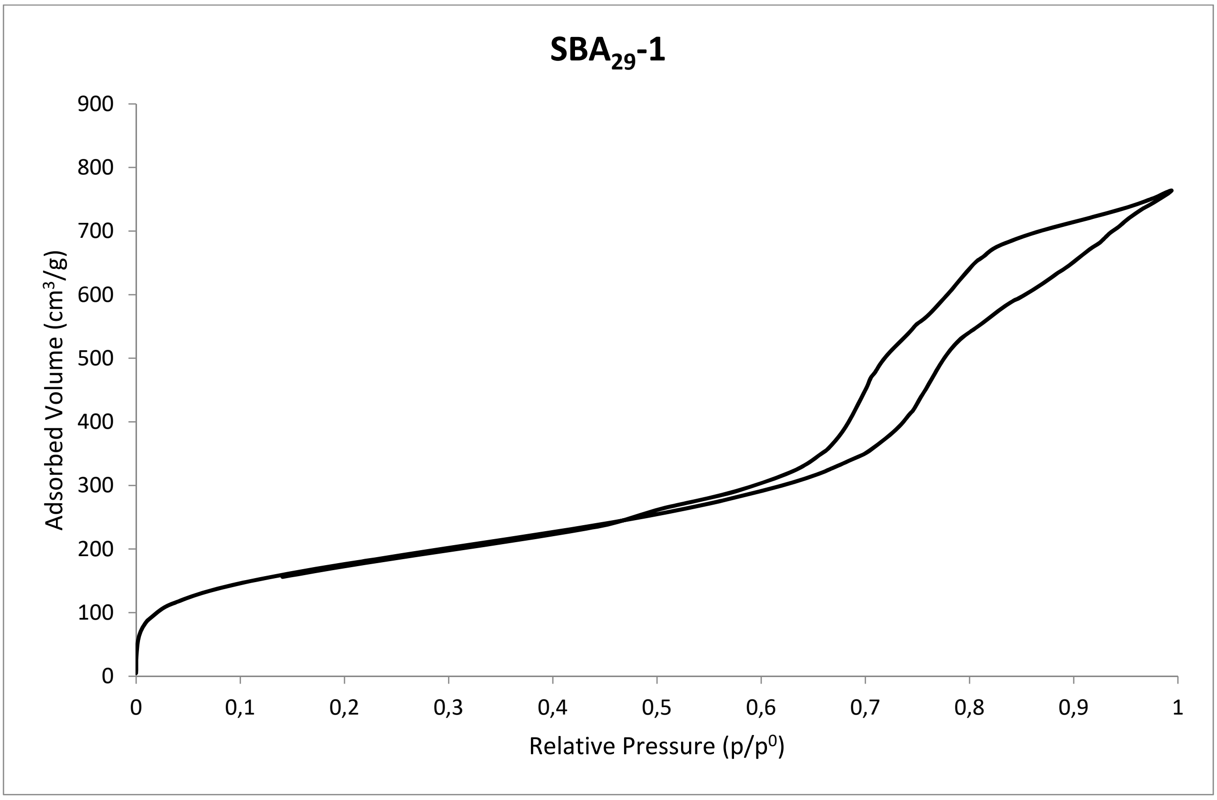
Wide Angle X-Ray Scattering (SAXS): LAM-2



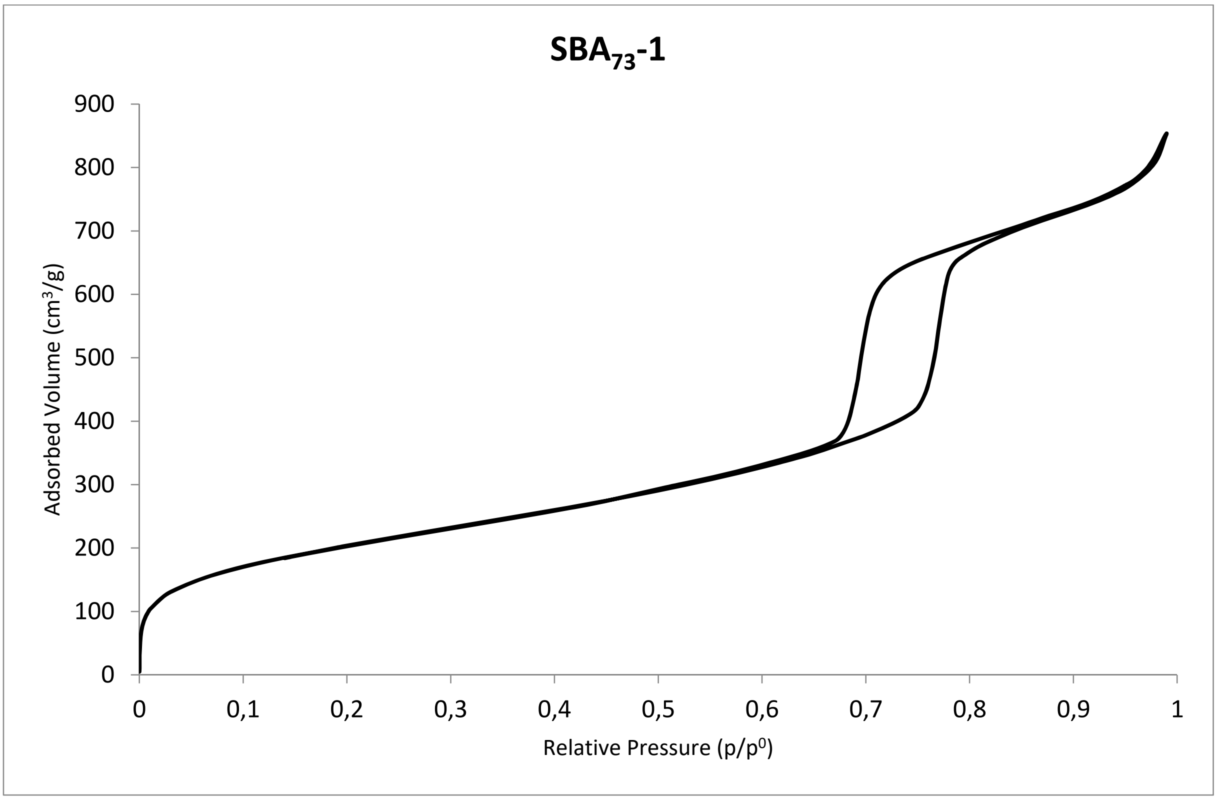
Nitrogen adsorption/desorption analysis: SBA$_{11}$-1



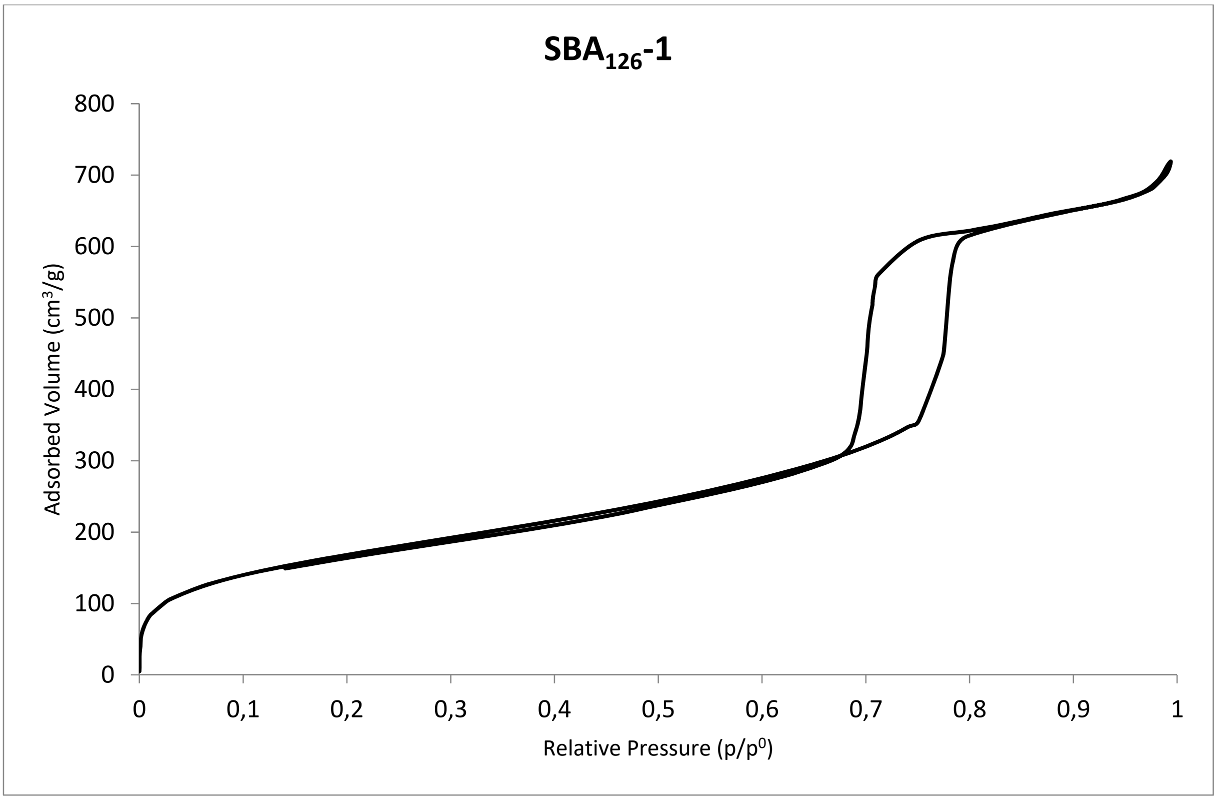
Nitrogen adsorption/desorption analysis: SBA$_{26}$-1



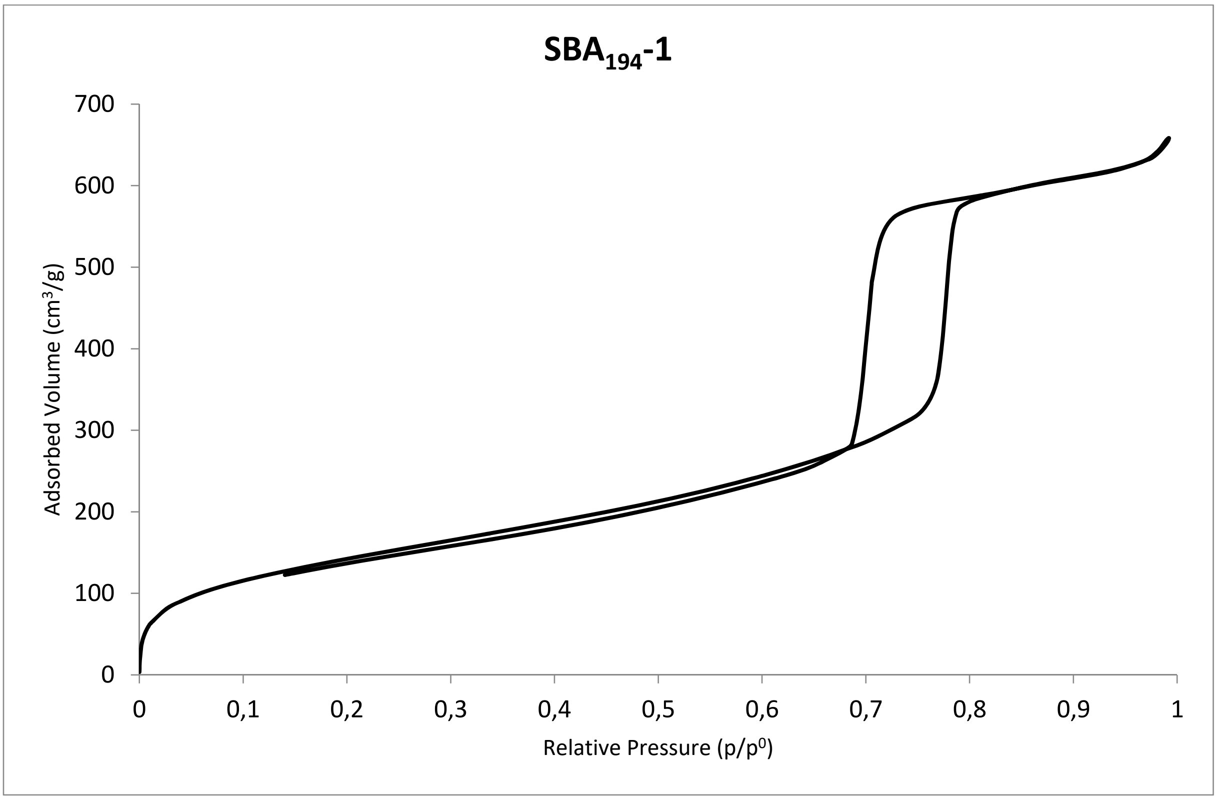
Nitrogen adsorption/desorption analysis: SBA$_{73}$-1



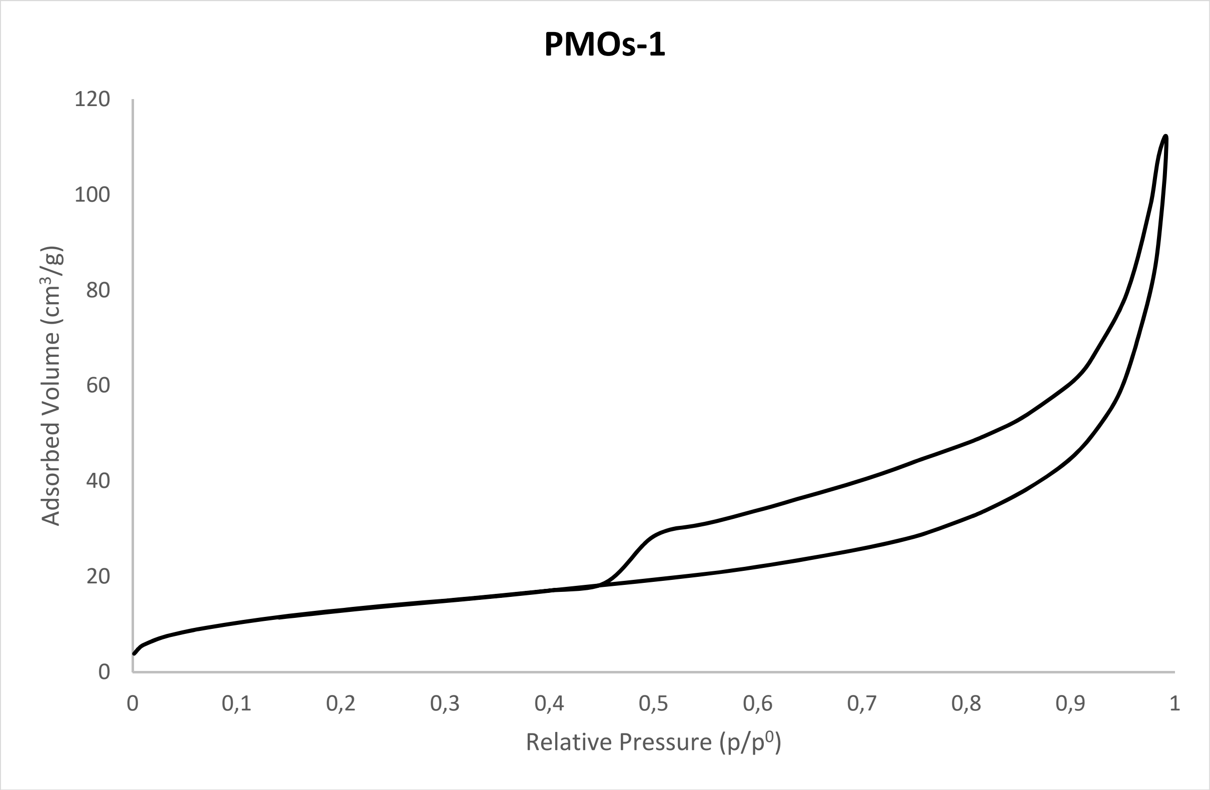
Nitrogen adsorption/desorption analysis: SBA$_{126}$-1



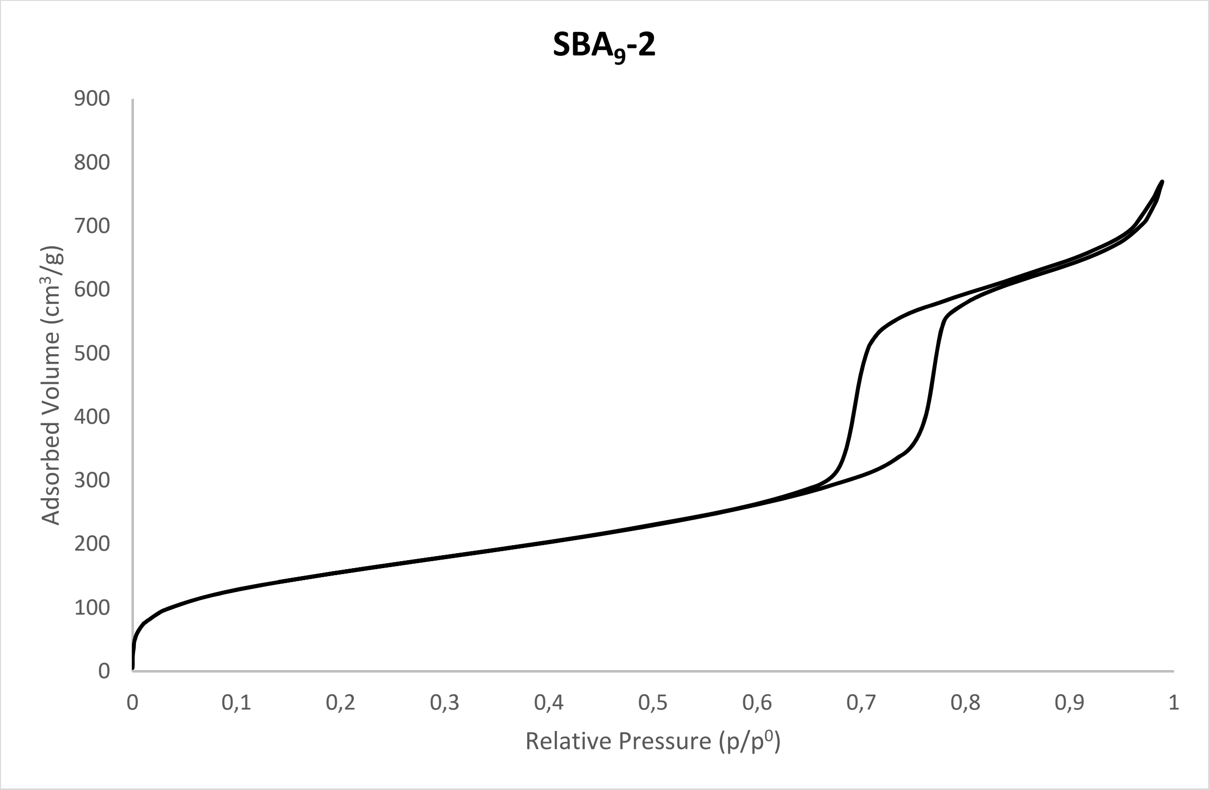
Nitrogen adsorption/desorption analysis: SBA_{194}-1



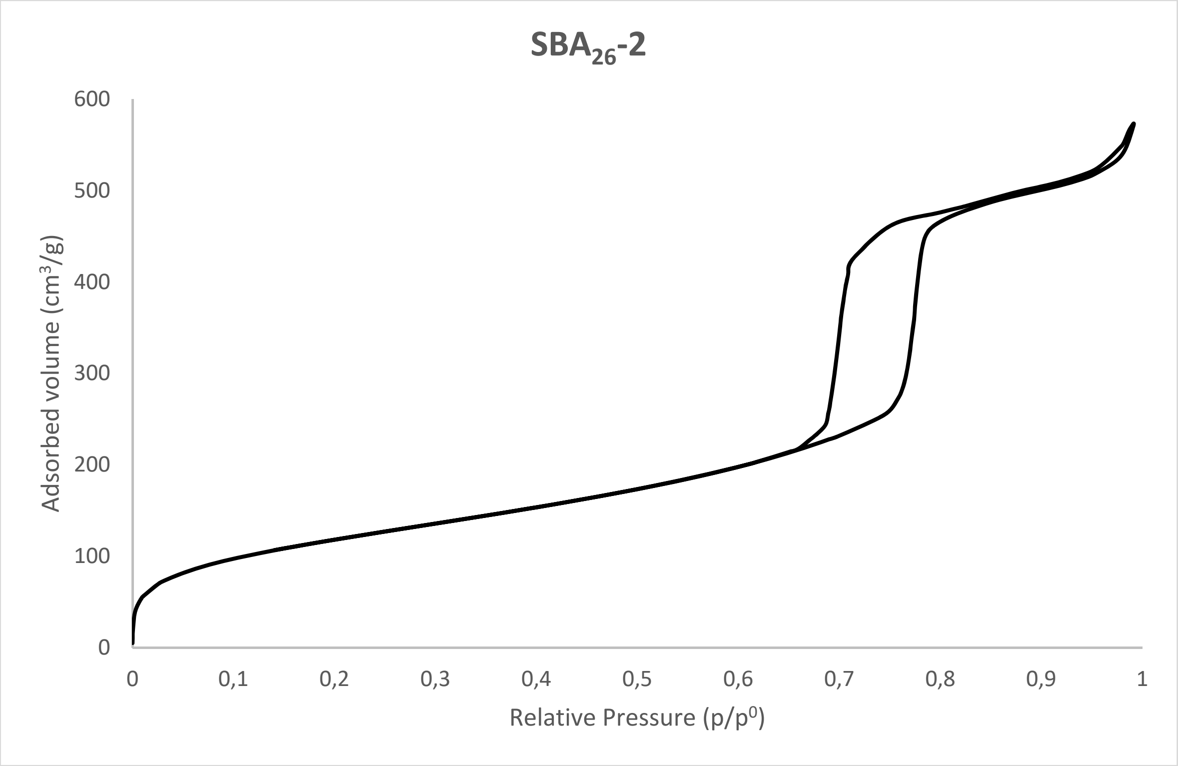
Nitrogen adsorption/desorption analysis: PMOs-1



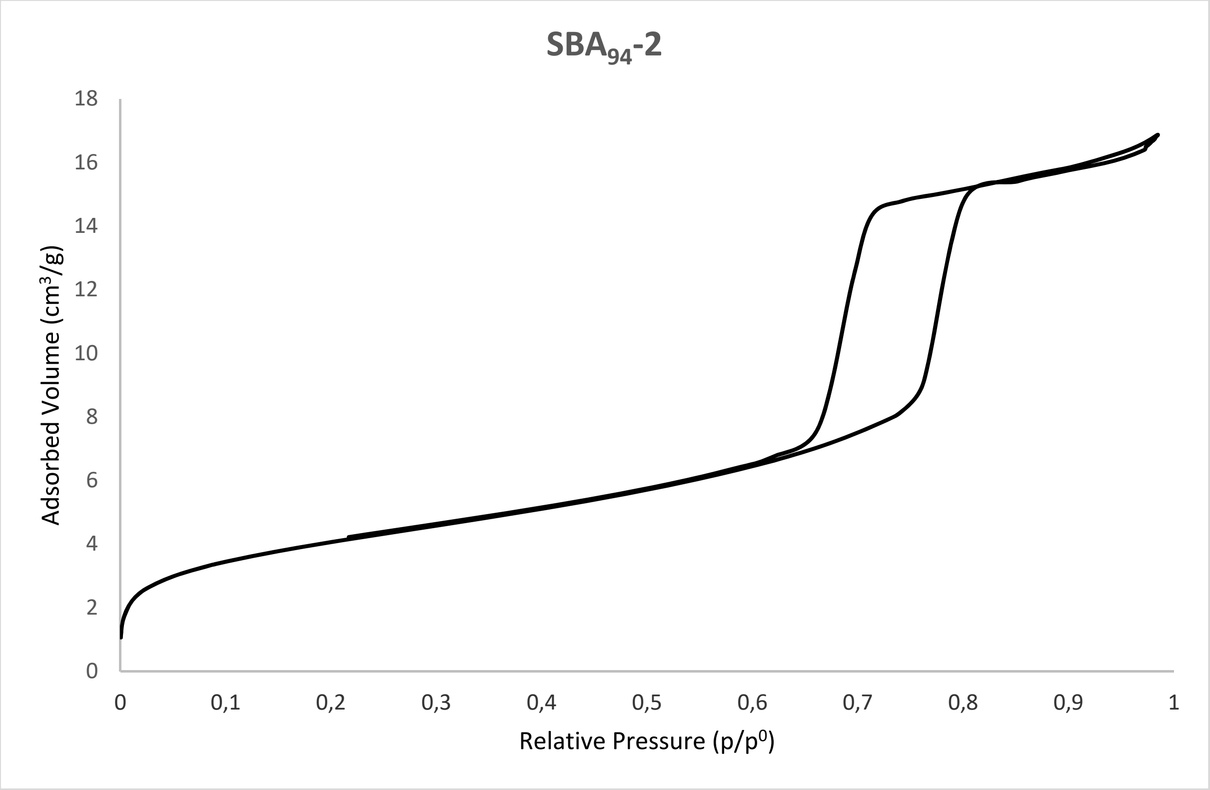
Nitrogen adsorption/desorption analysis: **SBA$_9$-2**



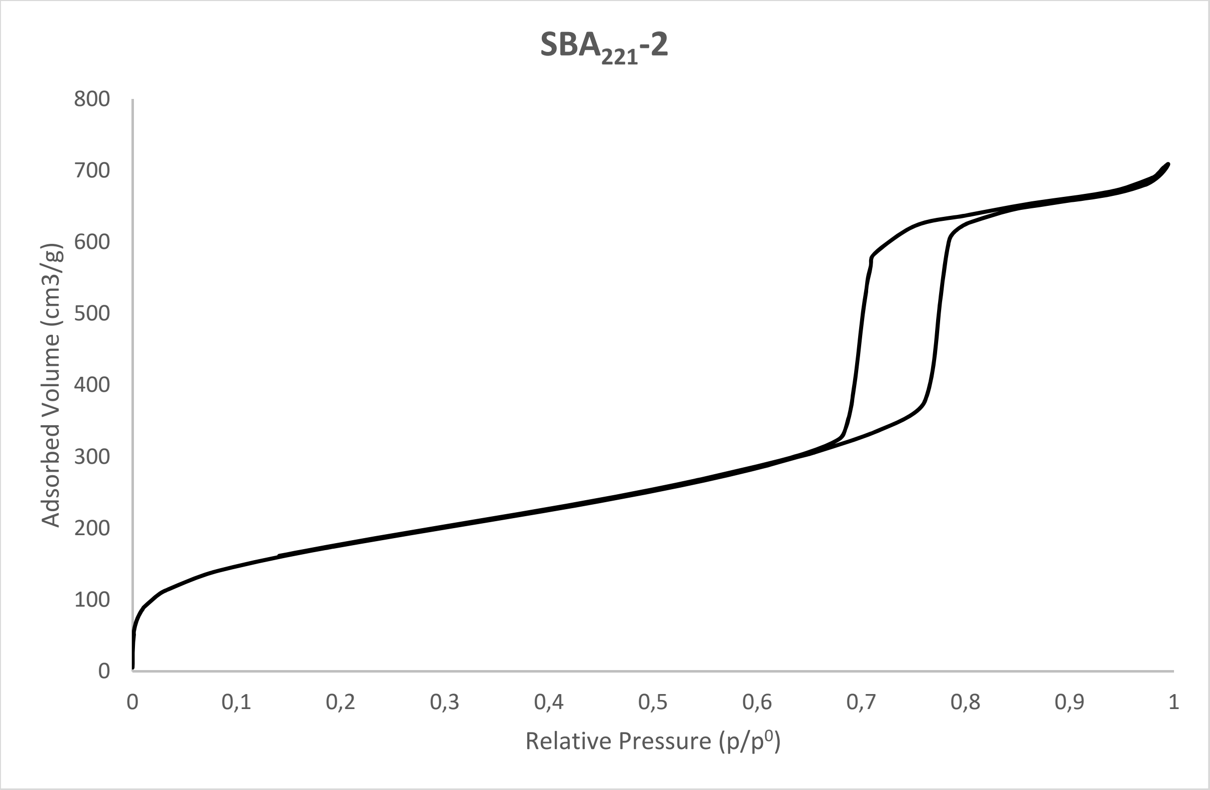
Nitrogen adsorption/desorption analysis: **SBA$_{26}$-2**



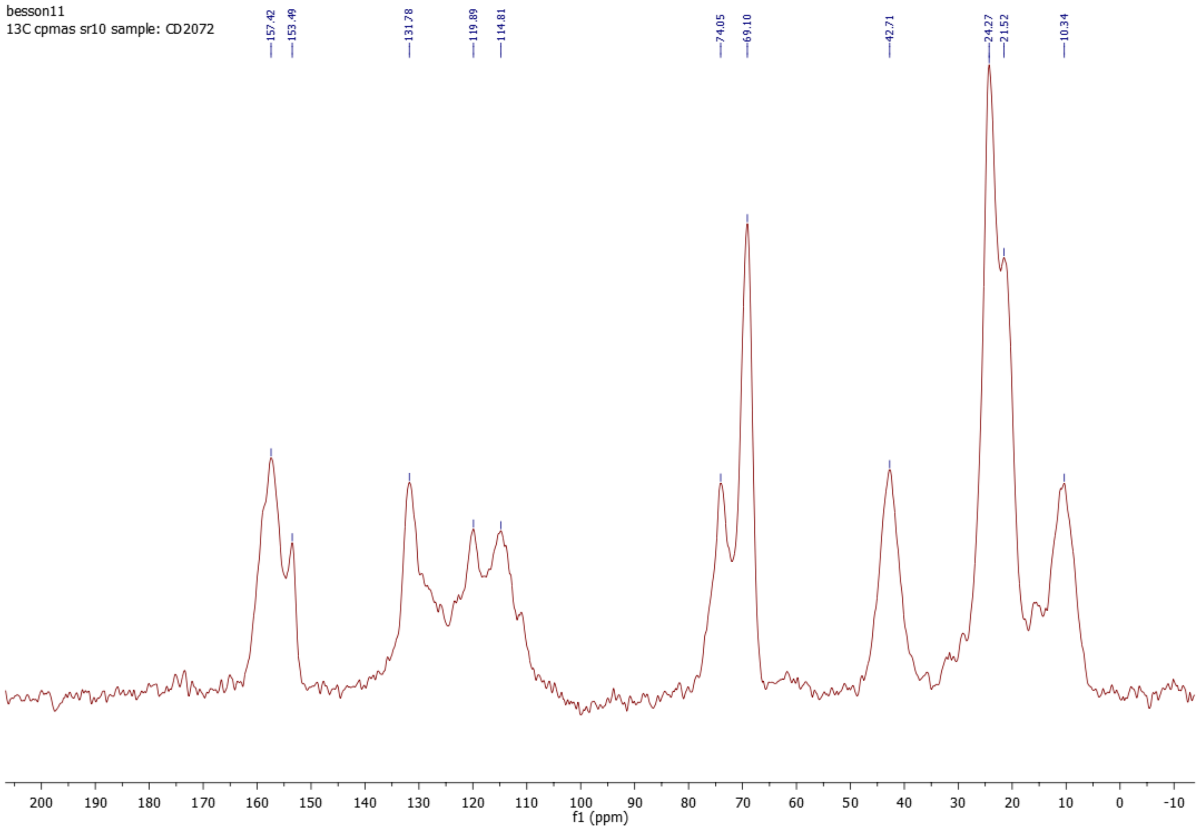
Nitrogen adsorption/desorption analysis: SBA$_{94}$-2



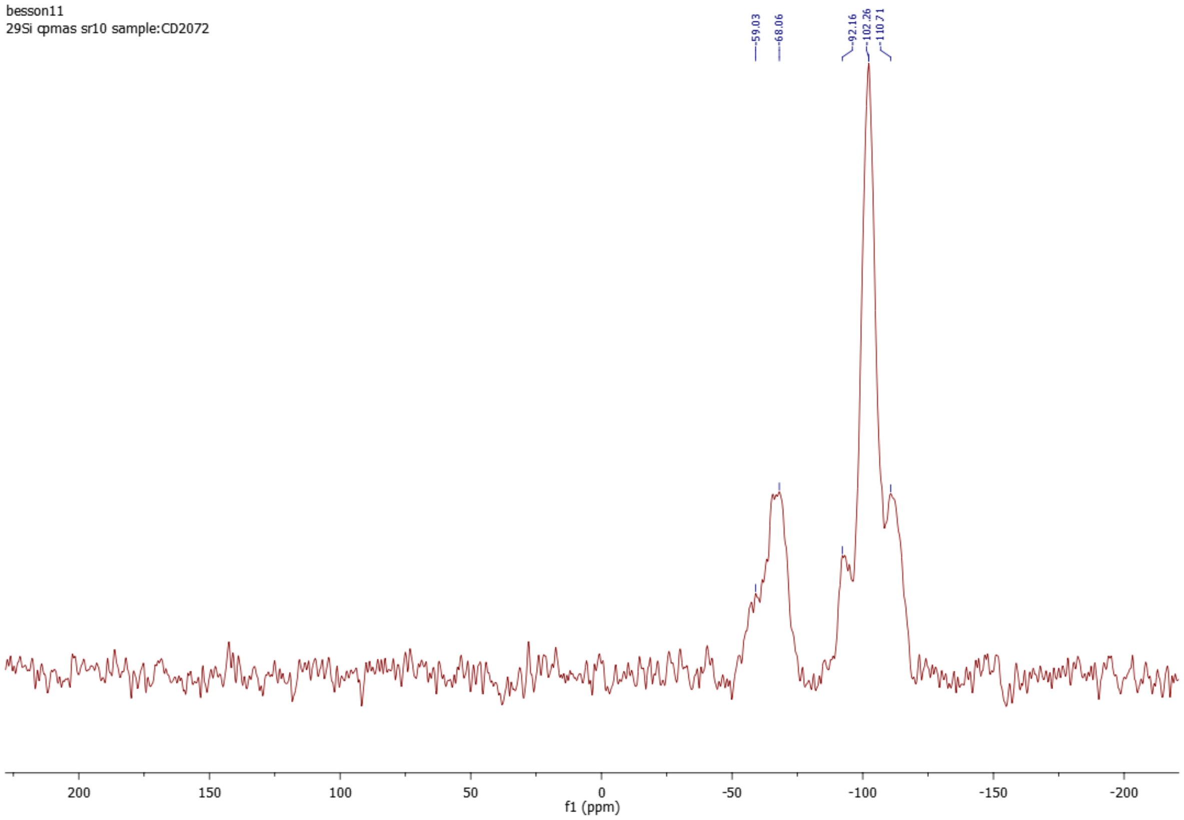
Nitrogen adsorption/desorption analysis: SBA$_{221}$-2



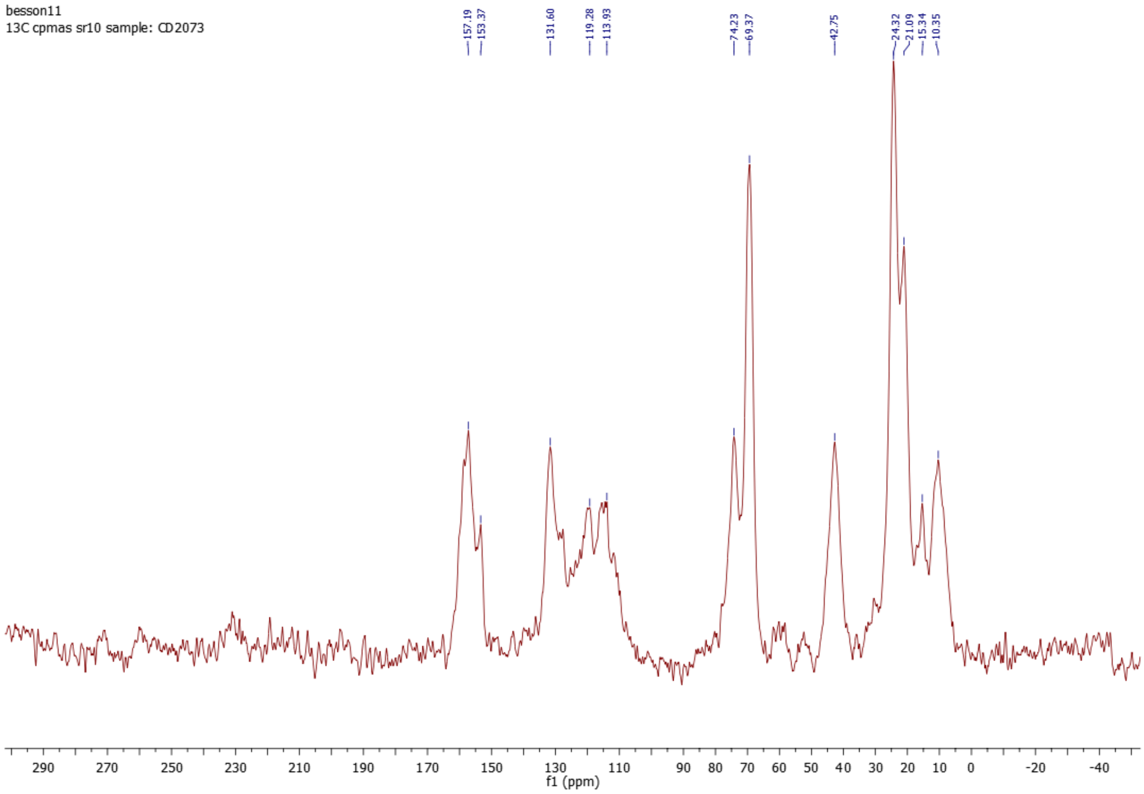
^{13}C CP-MAS solid state NMR of SBA$_{11}$-1:



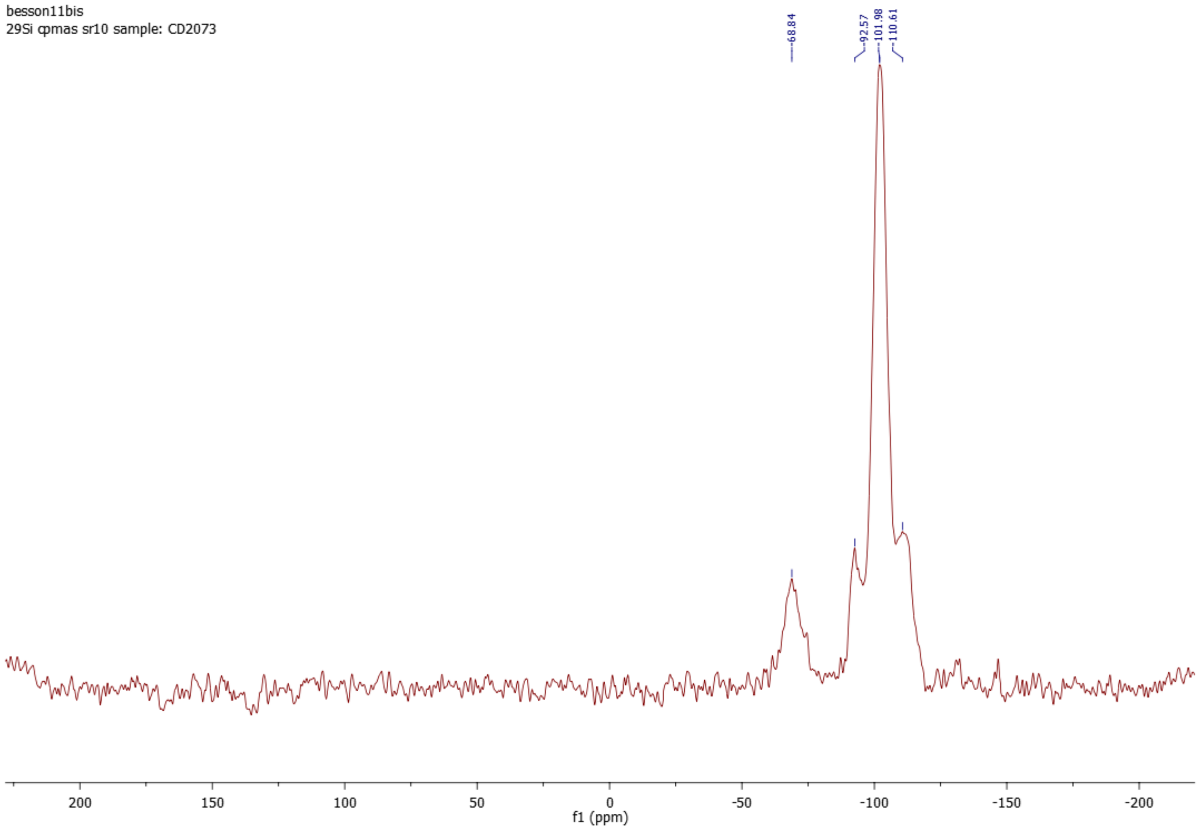
^{29}Si CP-MAS solid state NMR of SBA$_{11}$-1:



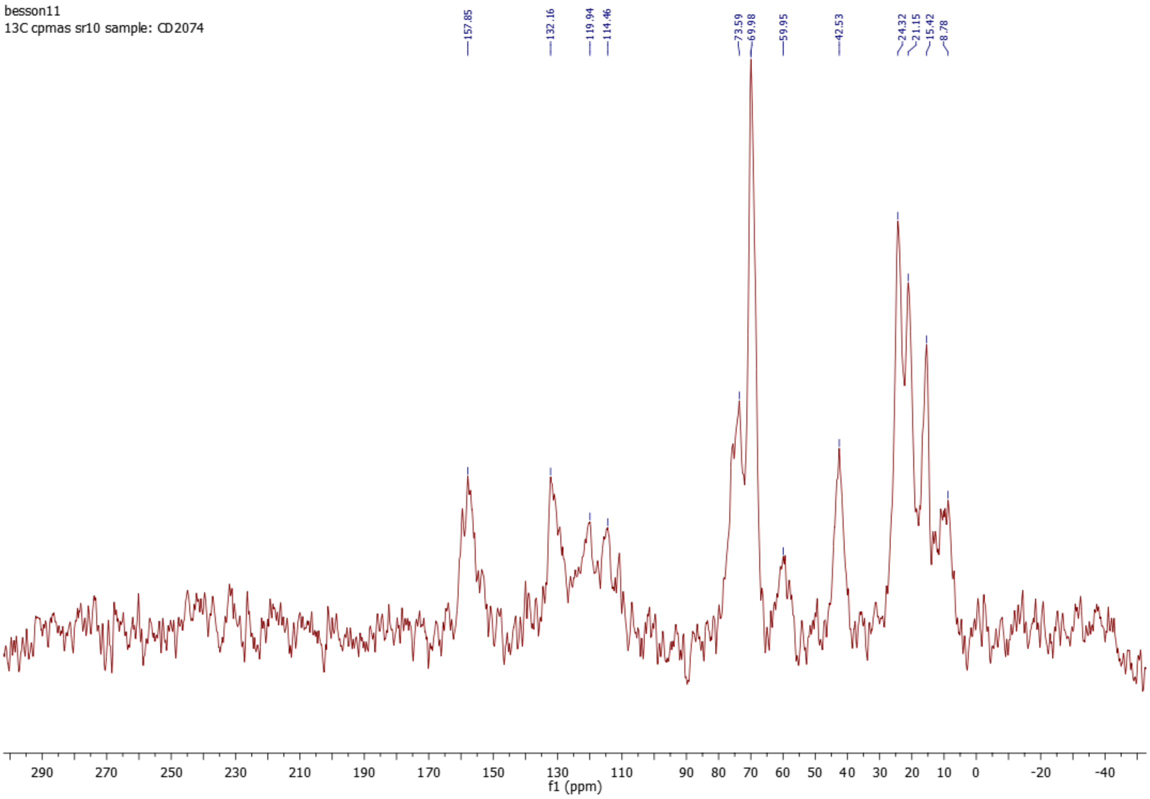
^{13}C CP-MAS solid state NMR of SBA$_{26}$-1:



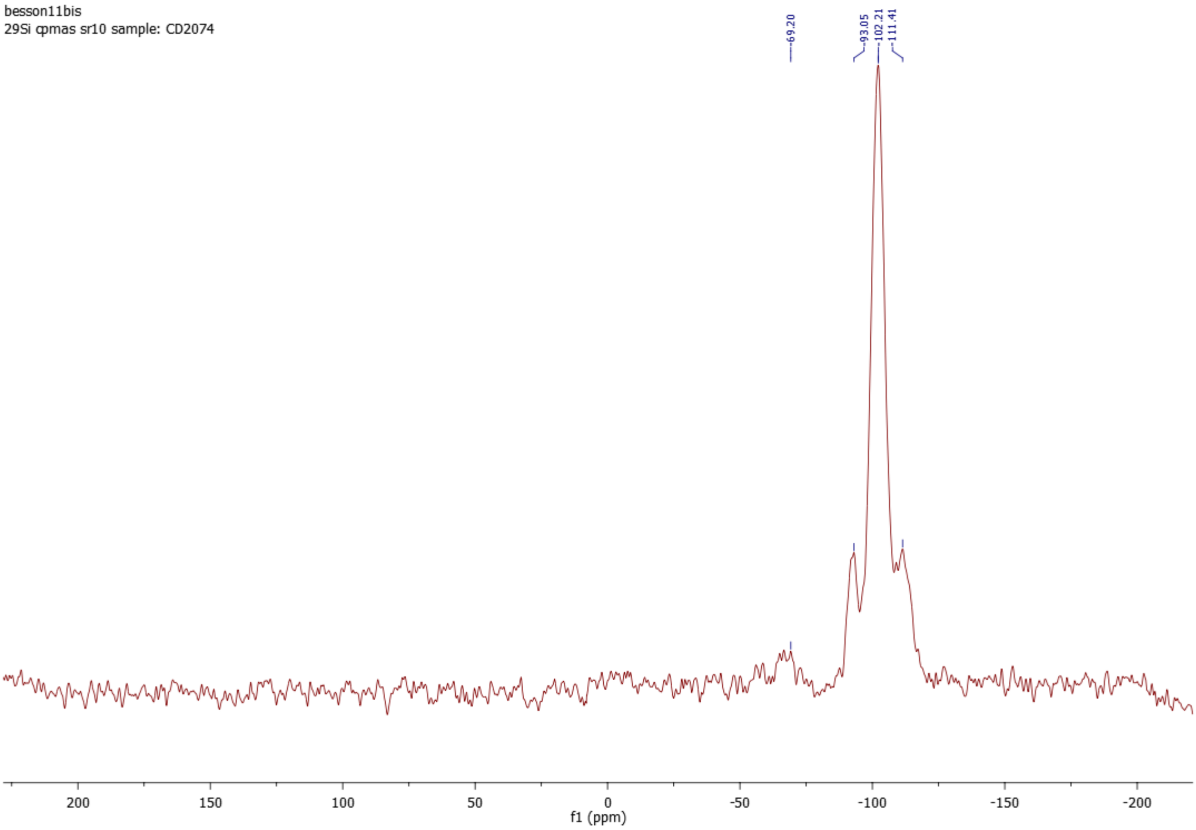
^{29}Si CP-MAS solid state NMR of SBA$_{26}$-1:



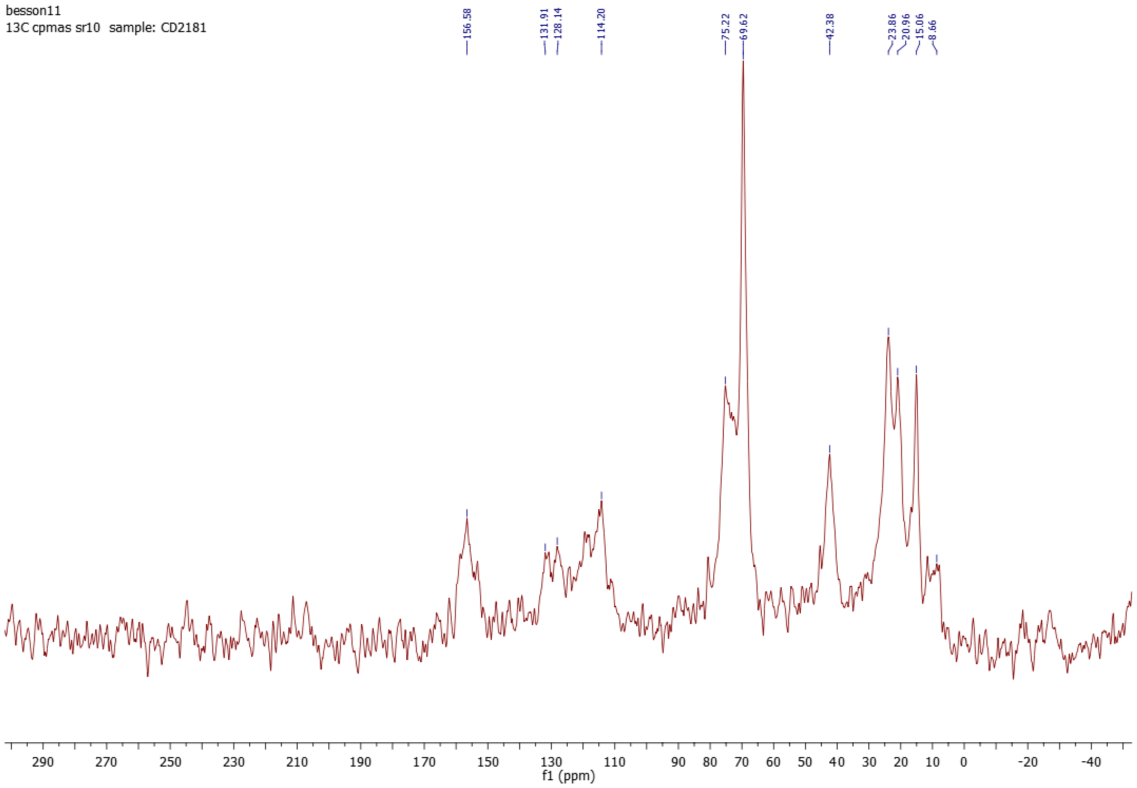
^{13}C CP-MAS solid state NMR of SBA$_{73}$-1:



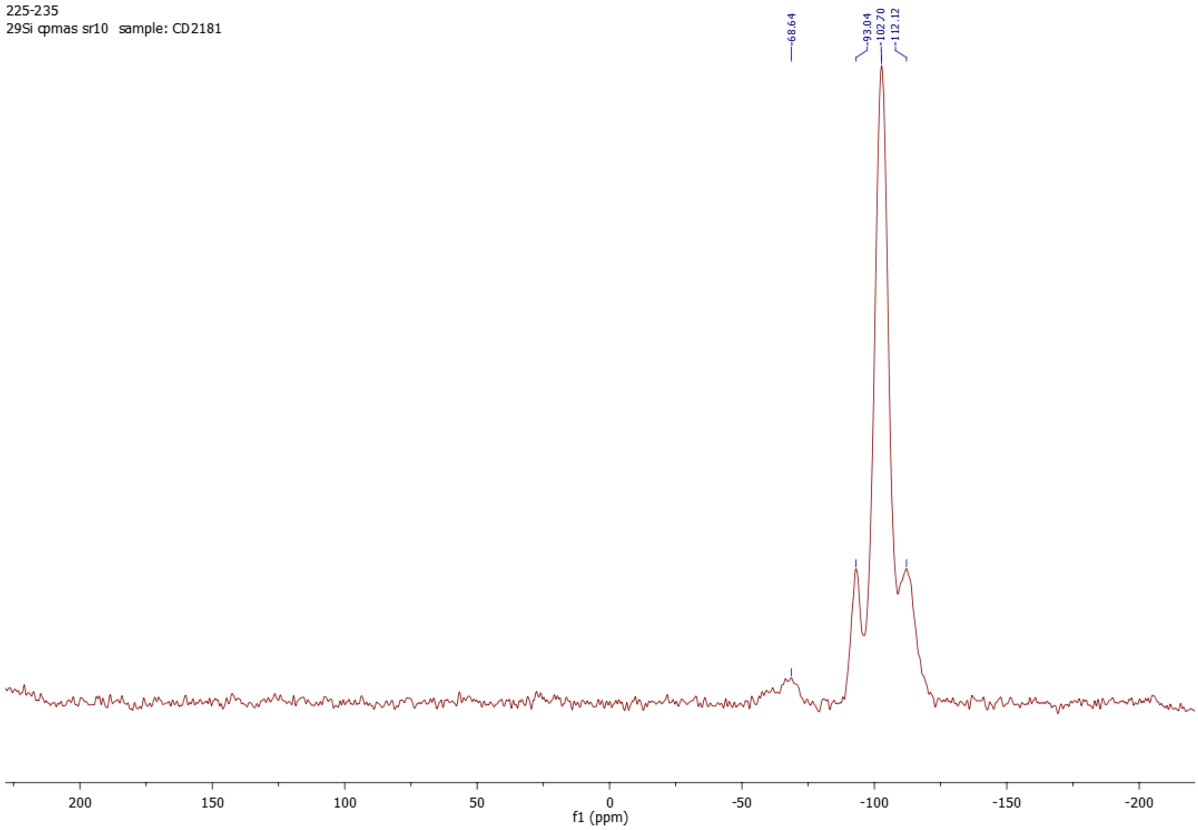
^{29}Si CP-MAS solid state NMR of SBA$_{73}$-1:



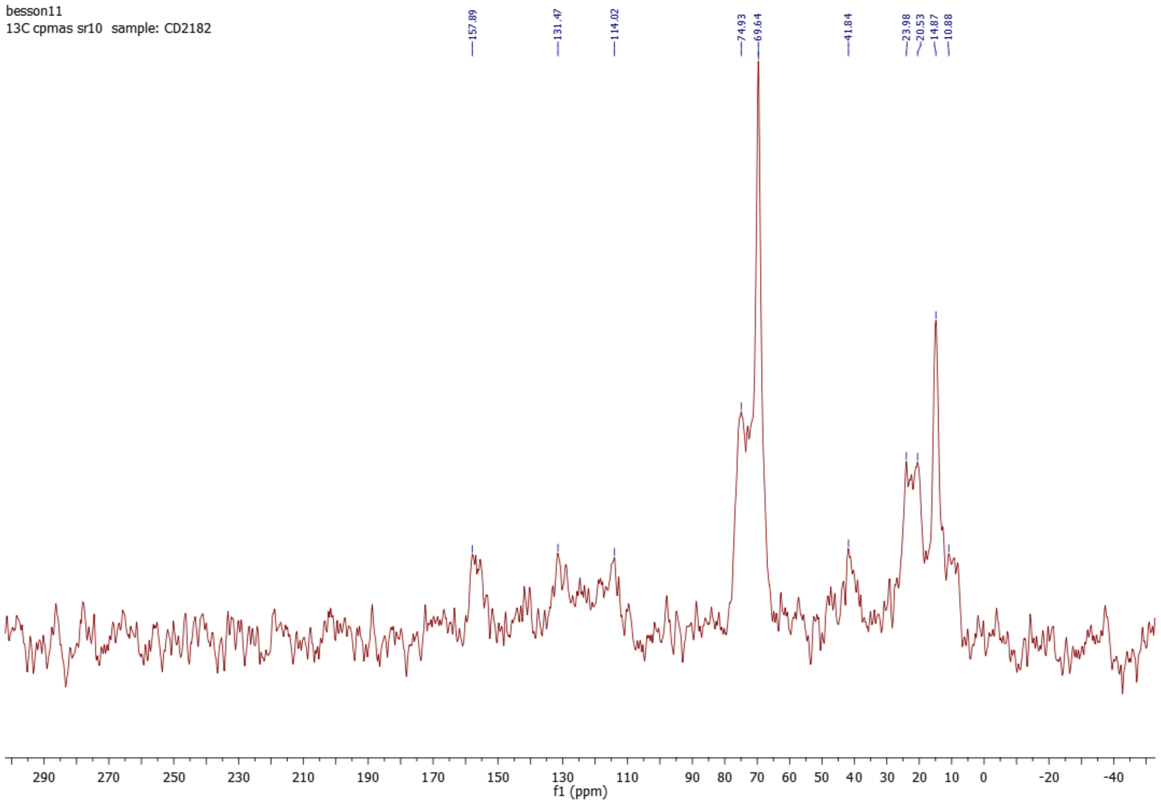
^{13}C CP-MAS solid state NMR of SBA$_{126}$-1:



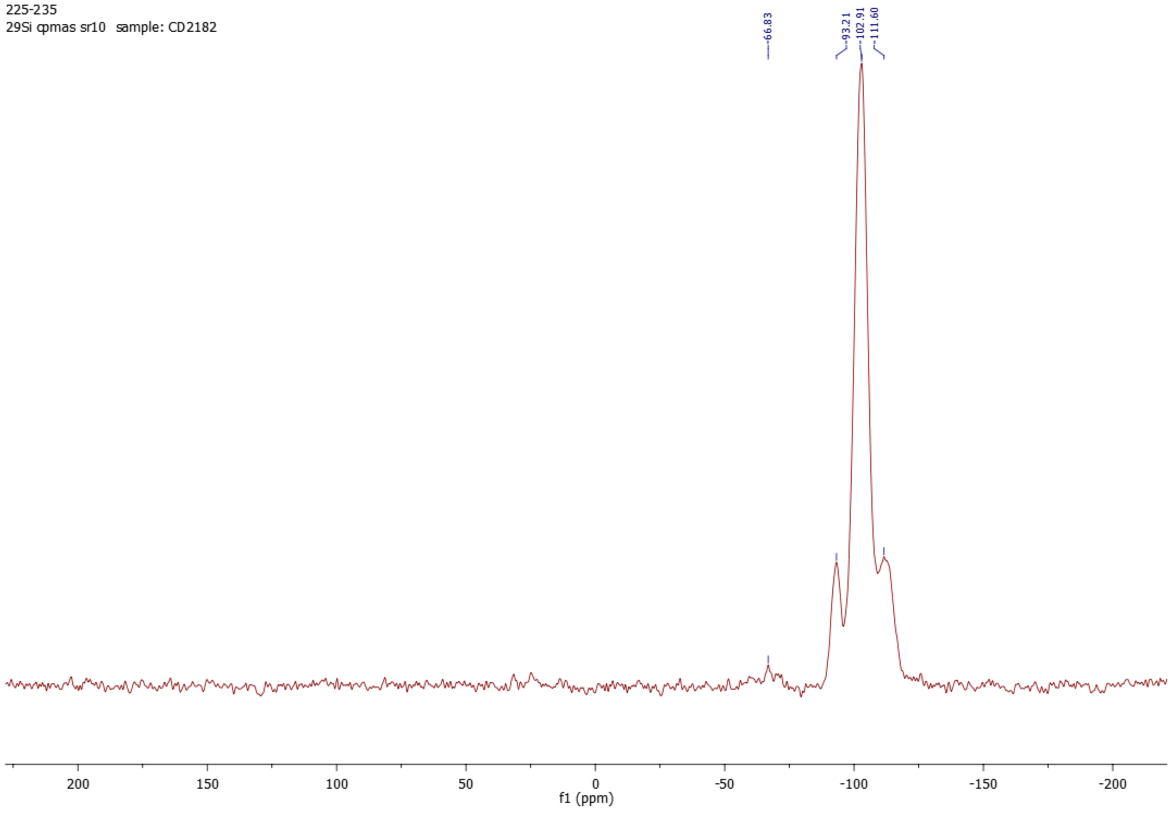
^{29}Si CP-MAS solid state NMR of SBA$_{126}$-1:



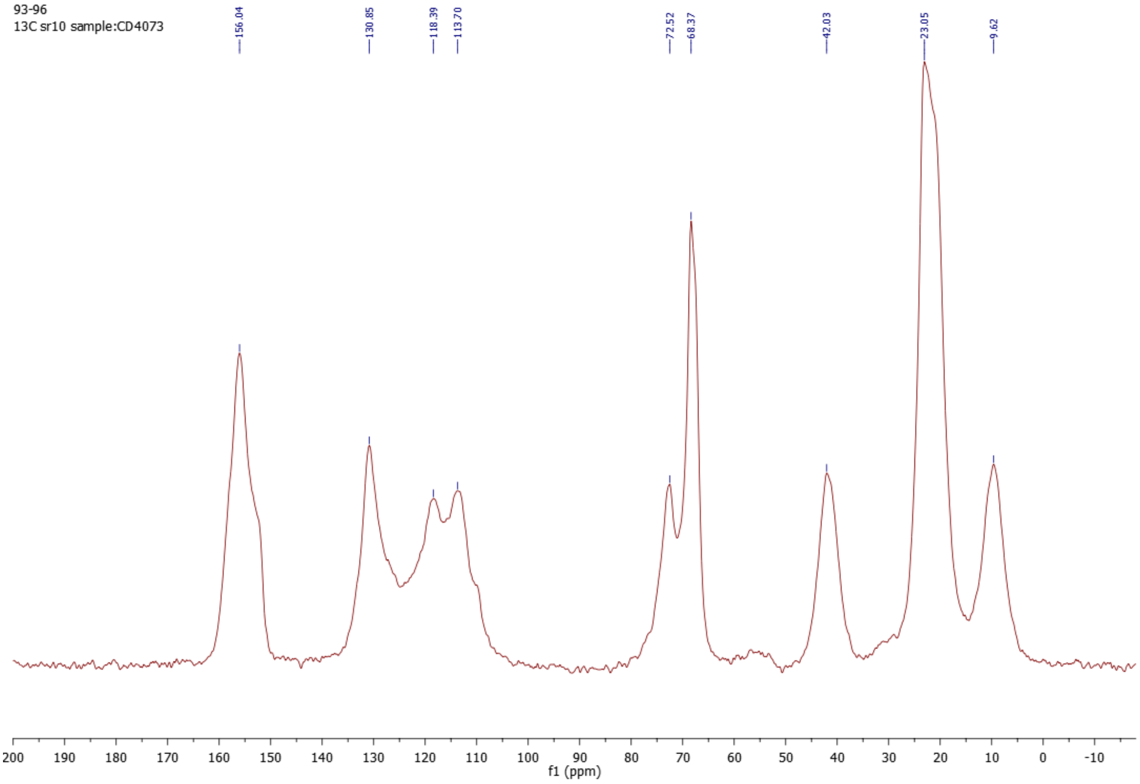
^{13}C CP-MAS solid state NMR of SBA$_{194}$-1:



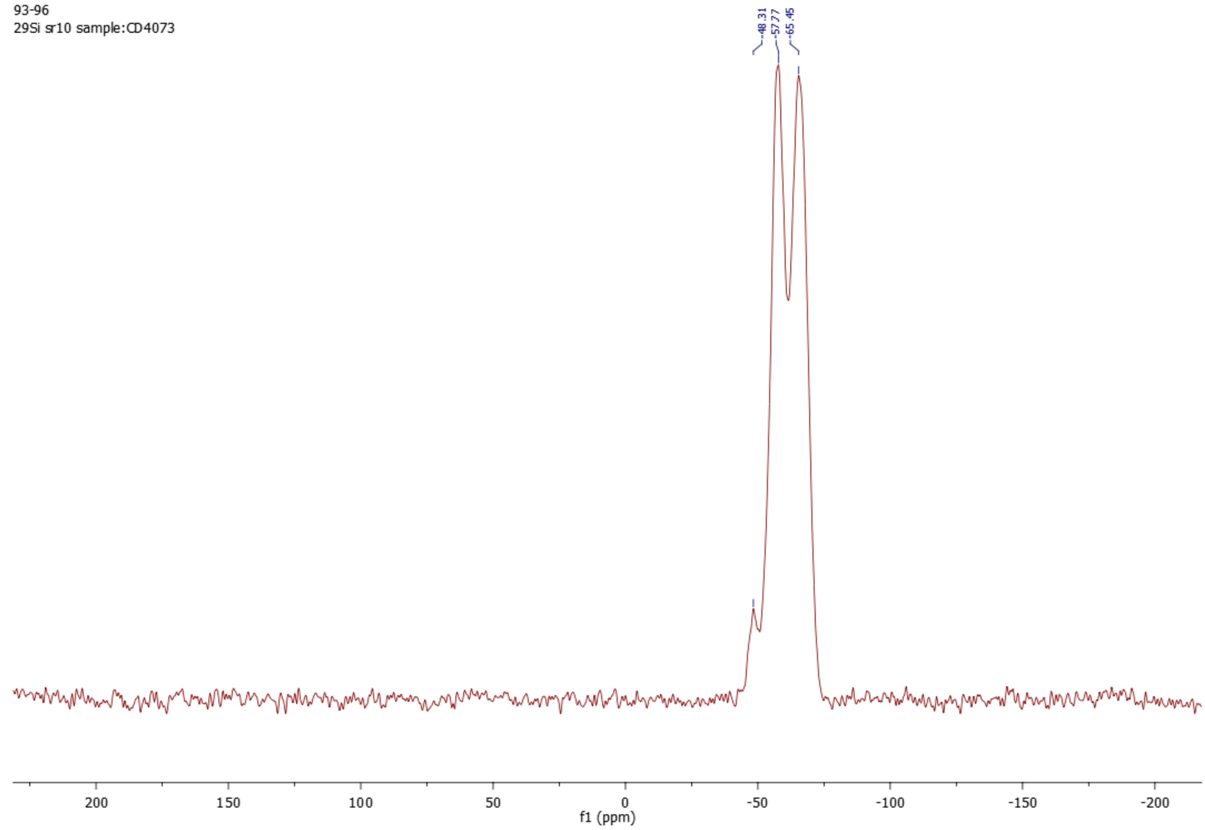
^{29}Si CP-MAS solid state NMR of SBA$_{194}$-1:



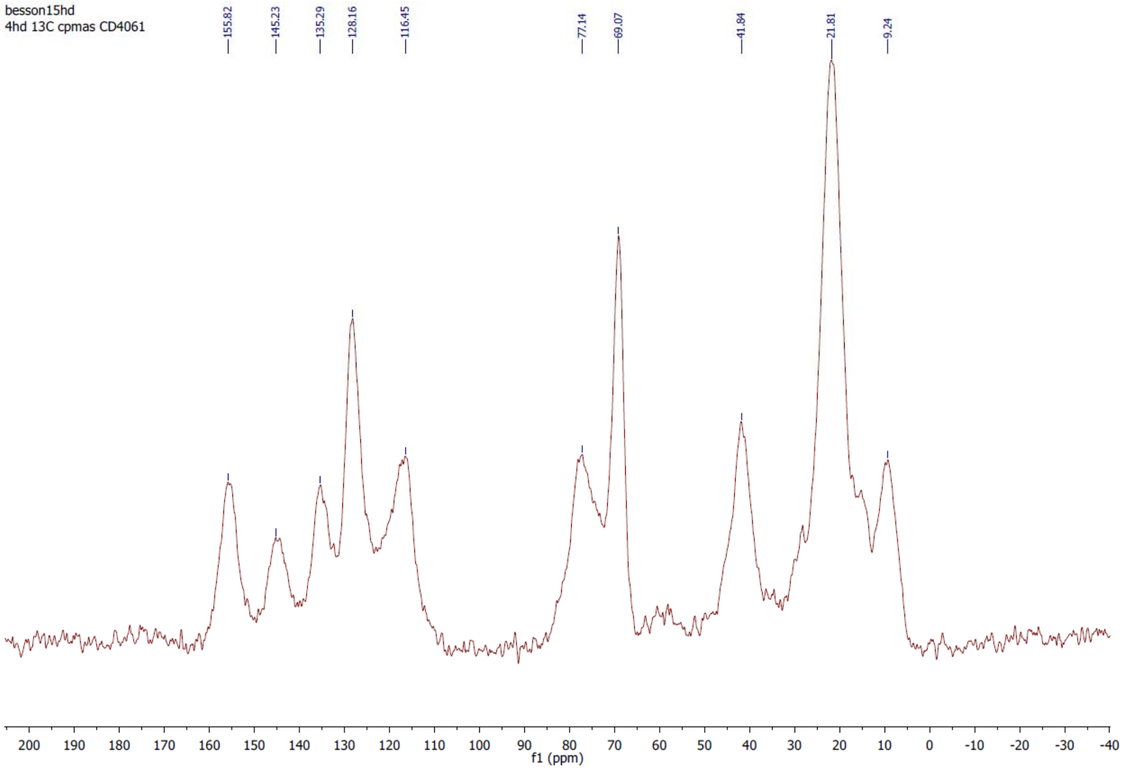
^{13}C CP-MAS solid state NMR of PMOs-1:



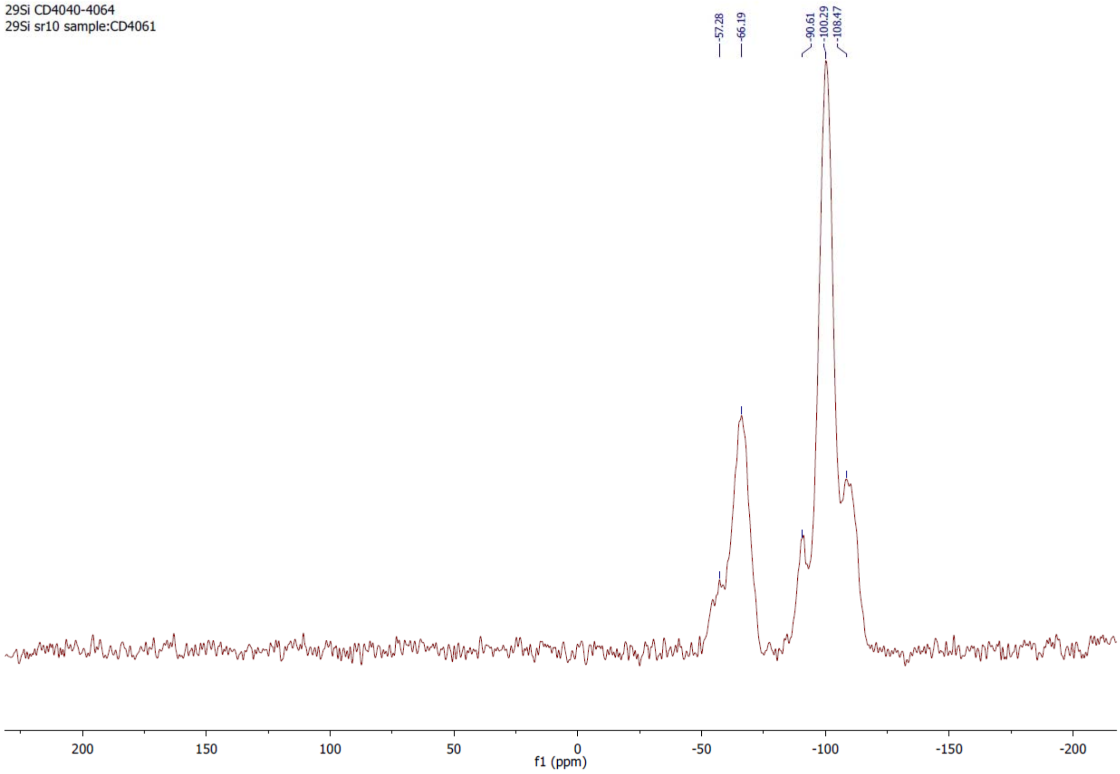
^{29}Si CP-MAS solid state NMR of PMOs-1:



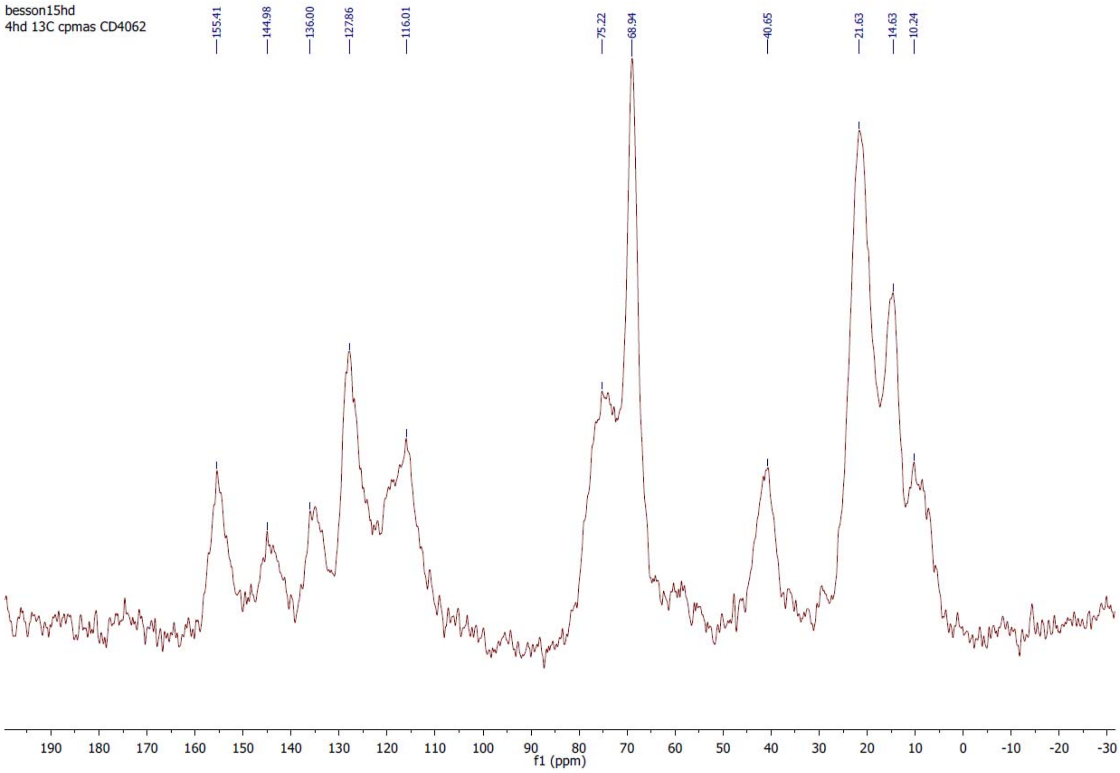
^{13}C CP-MAS solid state NMR of SBA$_9$-2:



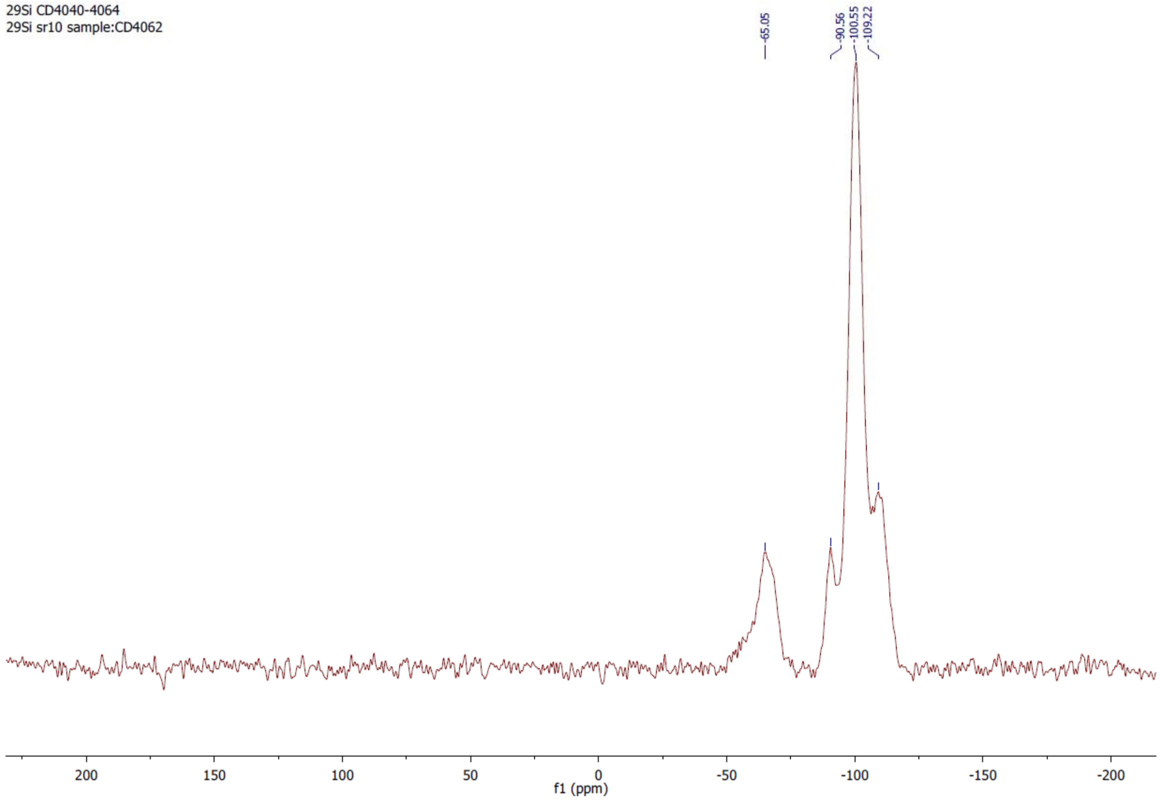
^{29}Si CP-MAS solid state NMR of SBA$_9$-2:



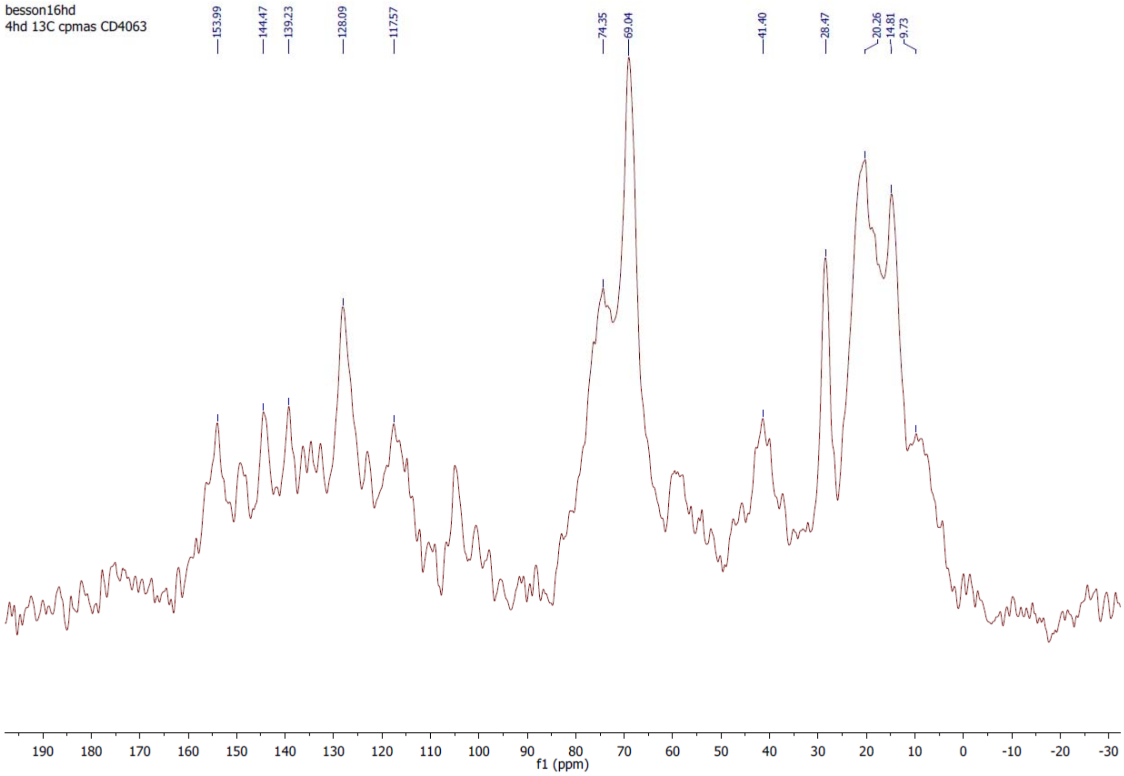
^{13}C CP-MAS solid state NMR of SBA$_{26}$-2:



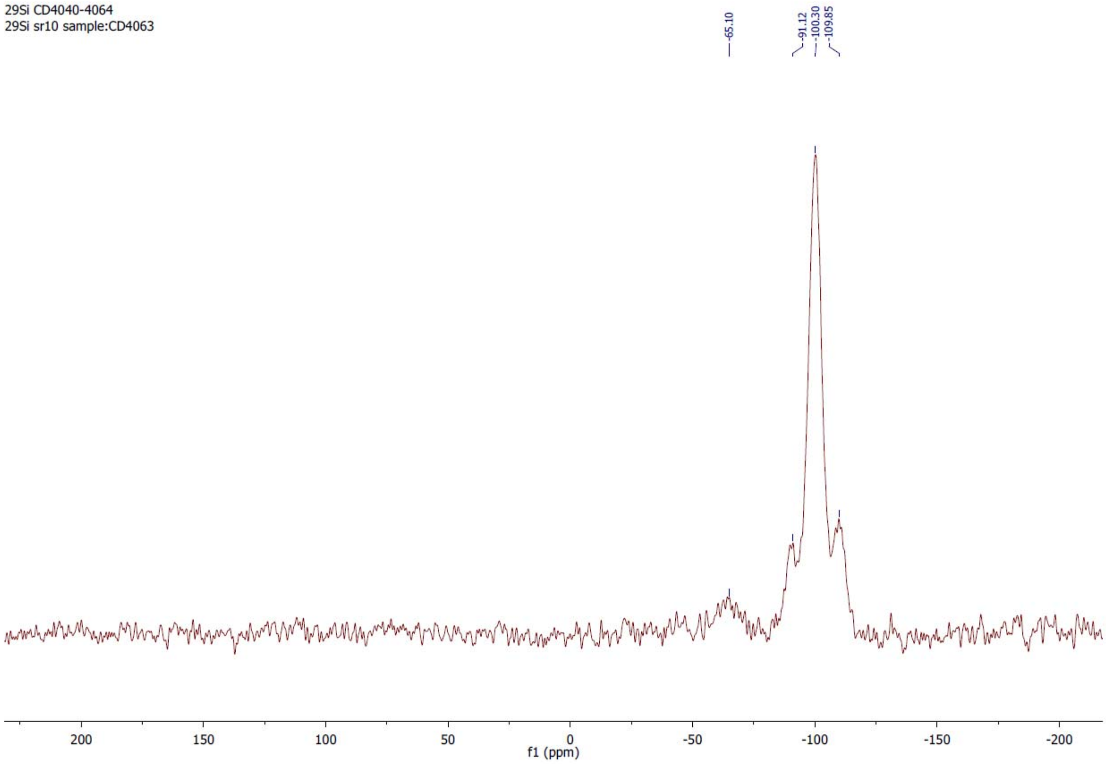
^{29}Si CP-MAS solid state NMR of SBA$_{26}$-2:



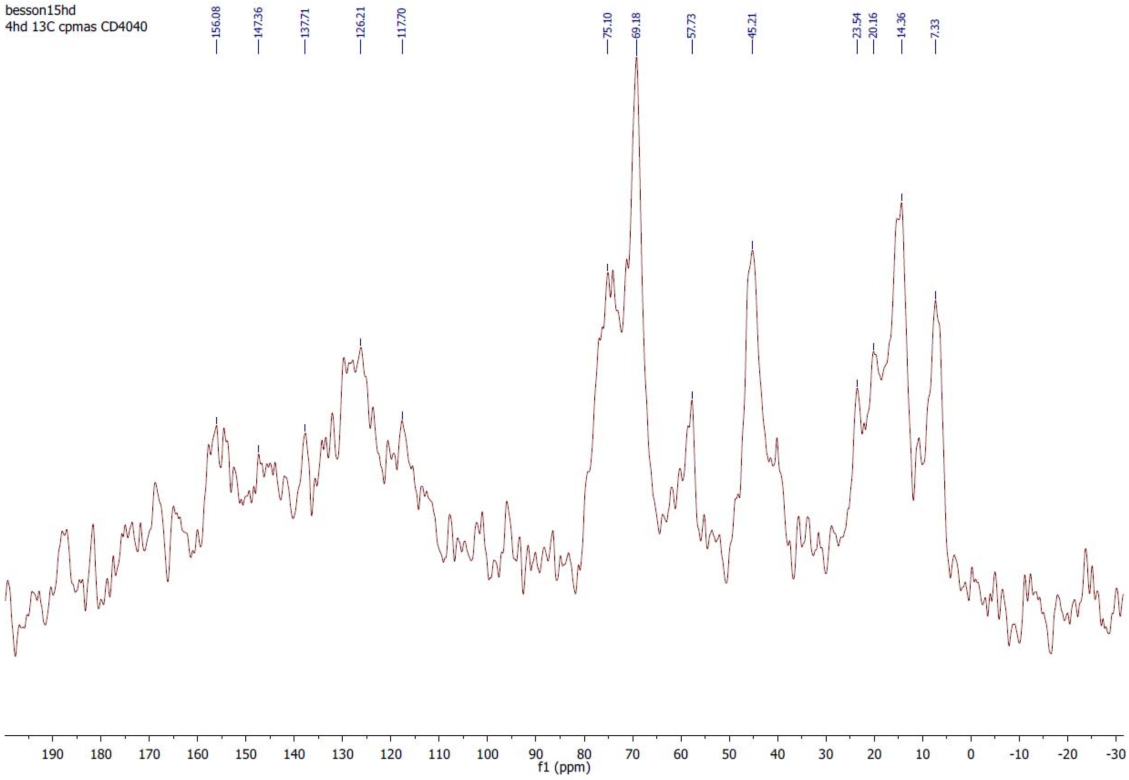
^{13}C CP-MAS solid state NMR of SBA$_{94}$-2:



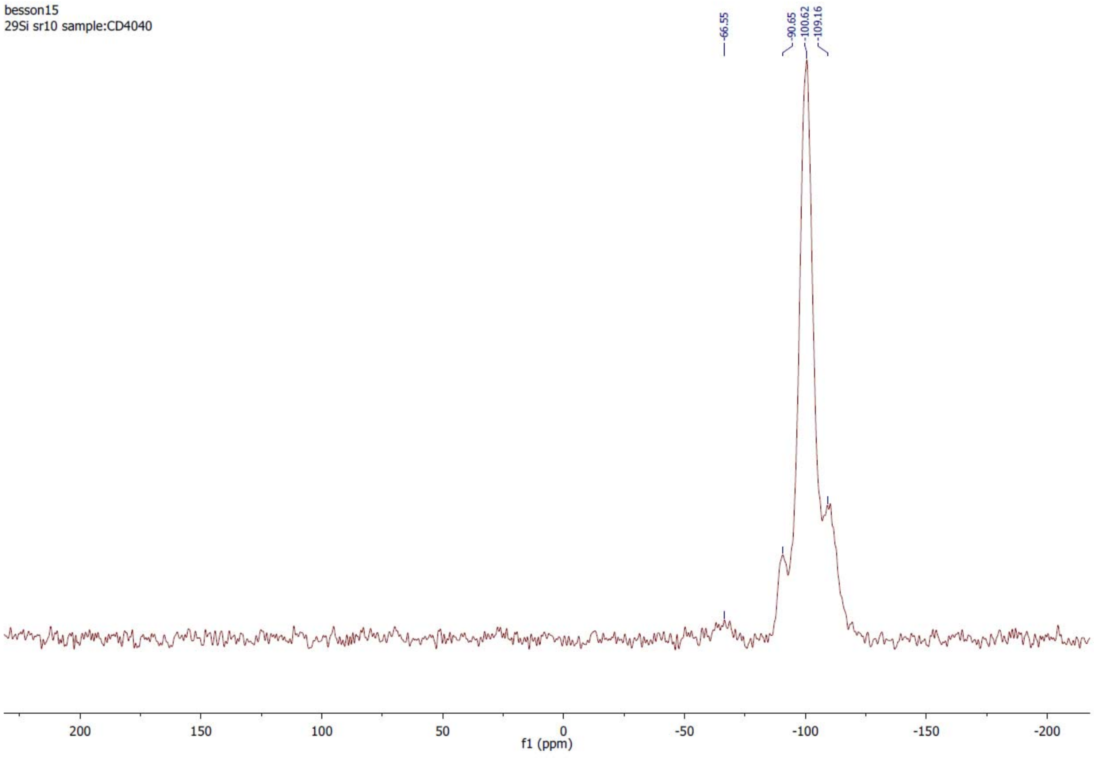
^{29}Si CP-MAS solid state NMR of SBA$_{94}$-2:



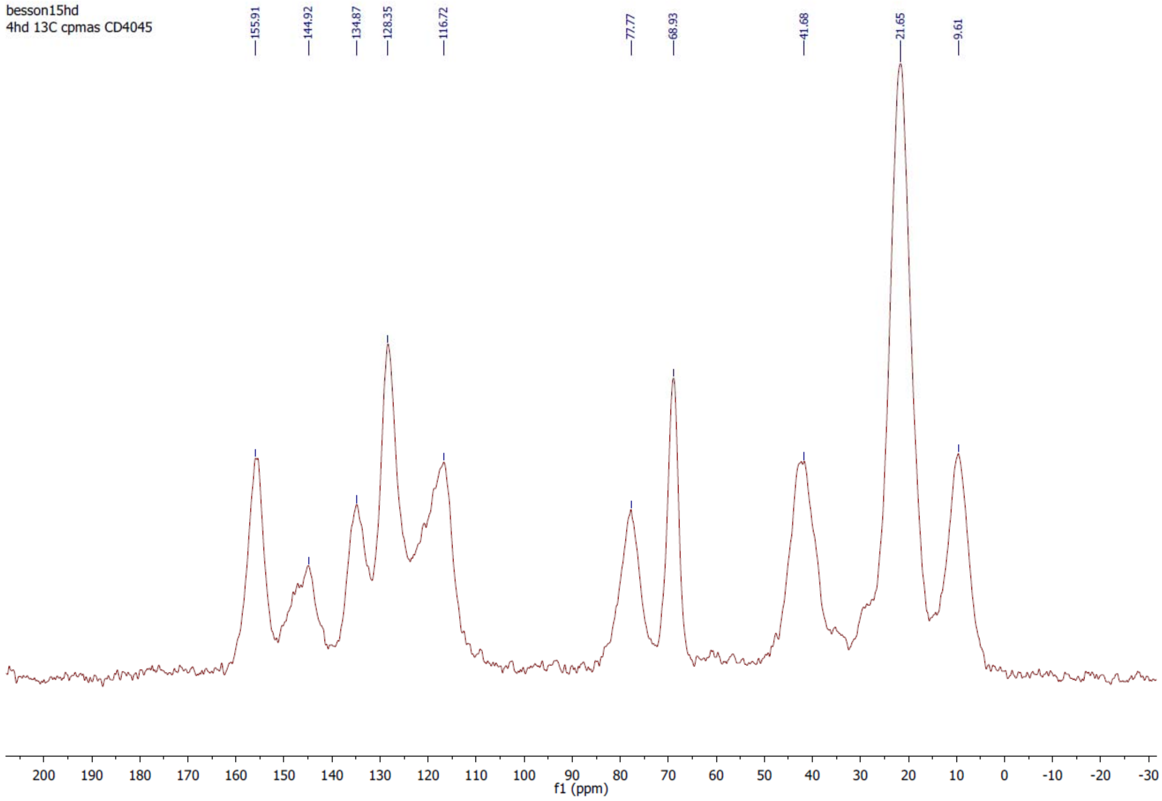
^{13}C CP-MAS solid state NMR of SBA$_{221}$-2:



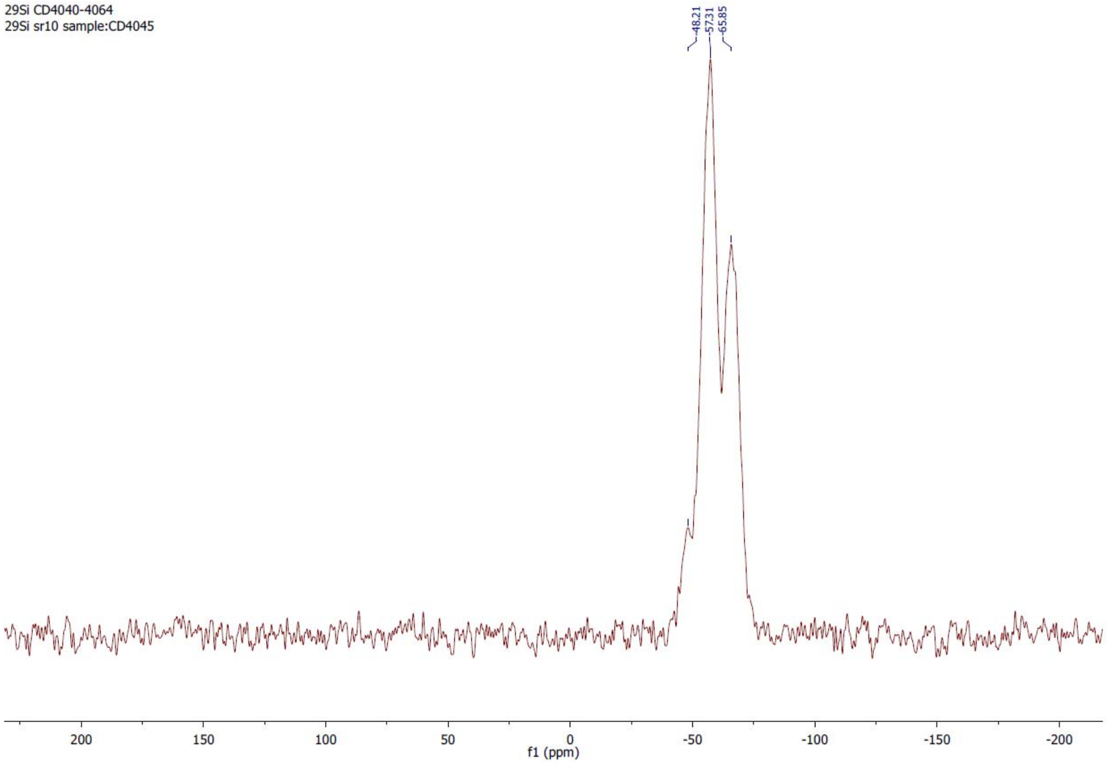
^{29}Si CP-MAS solid state NMR of SBA$_{221}$-2:



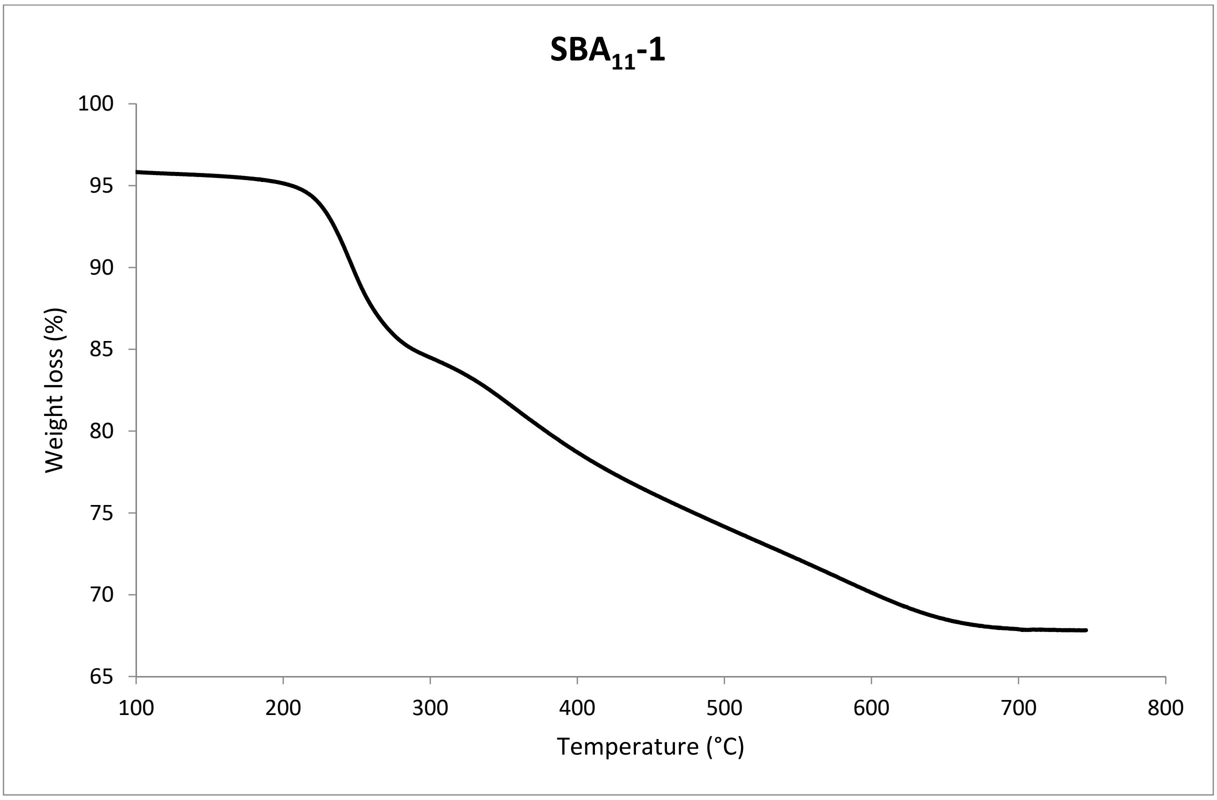
^{13}C CP-MAS solid state NMR of LAM-2:

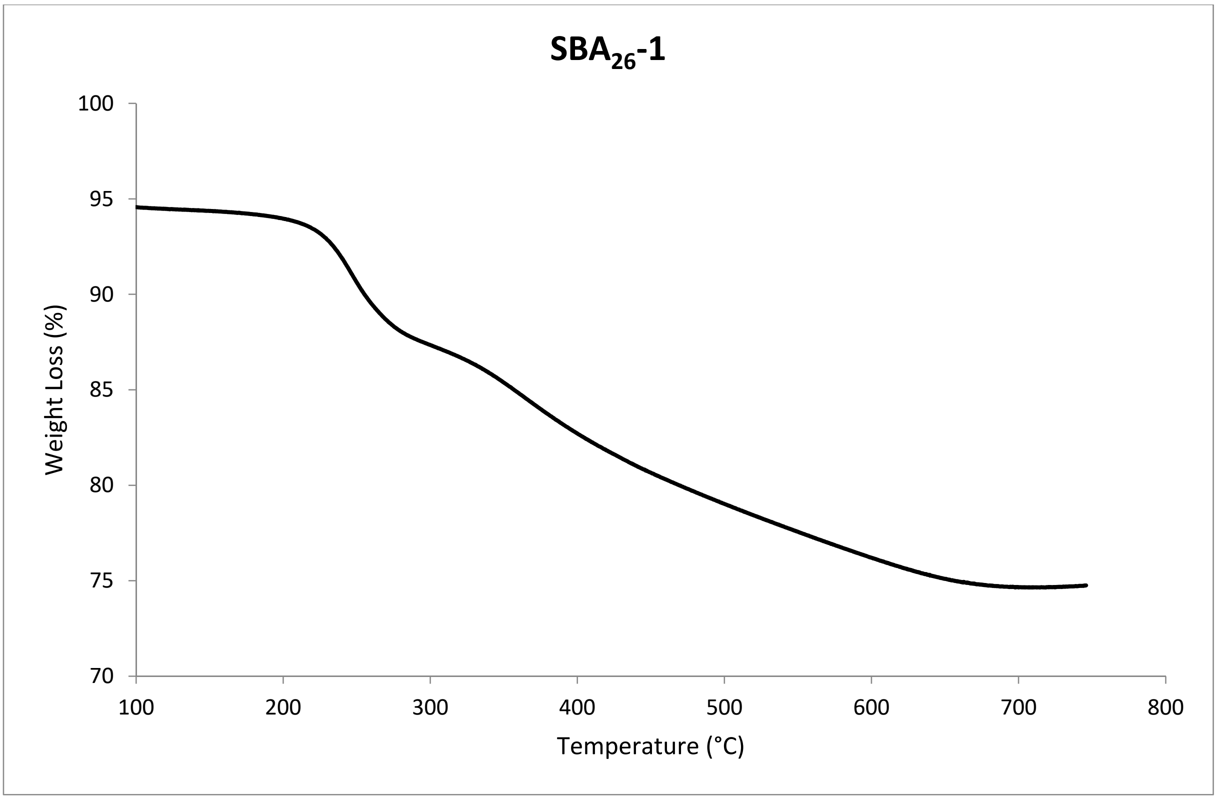


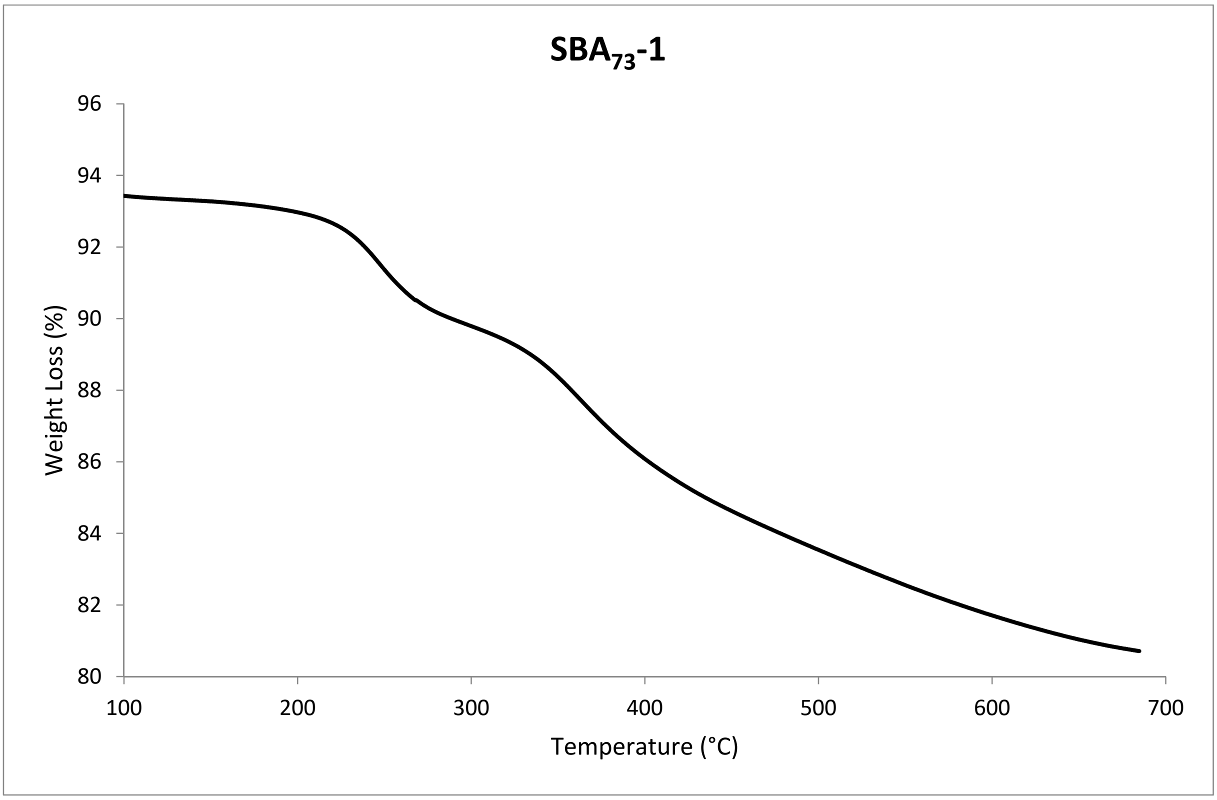
^{29}Si CP-MAS solid state NMR of LAM-2:

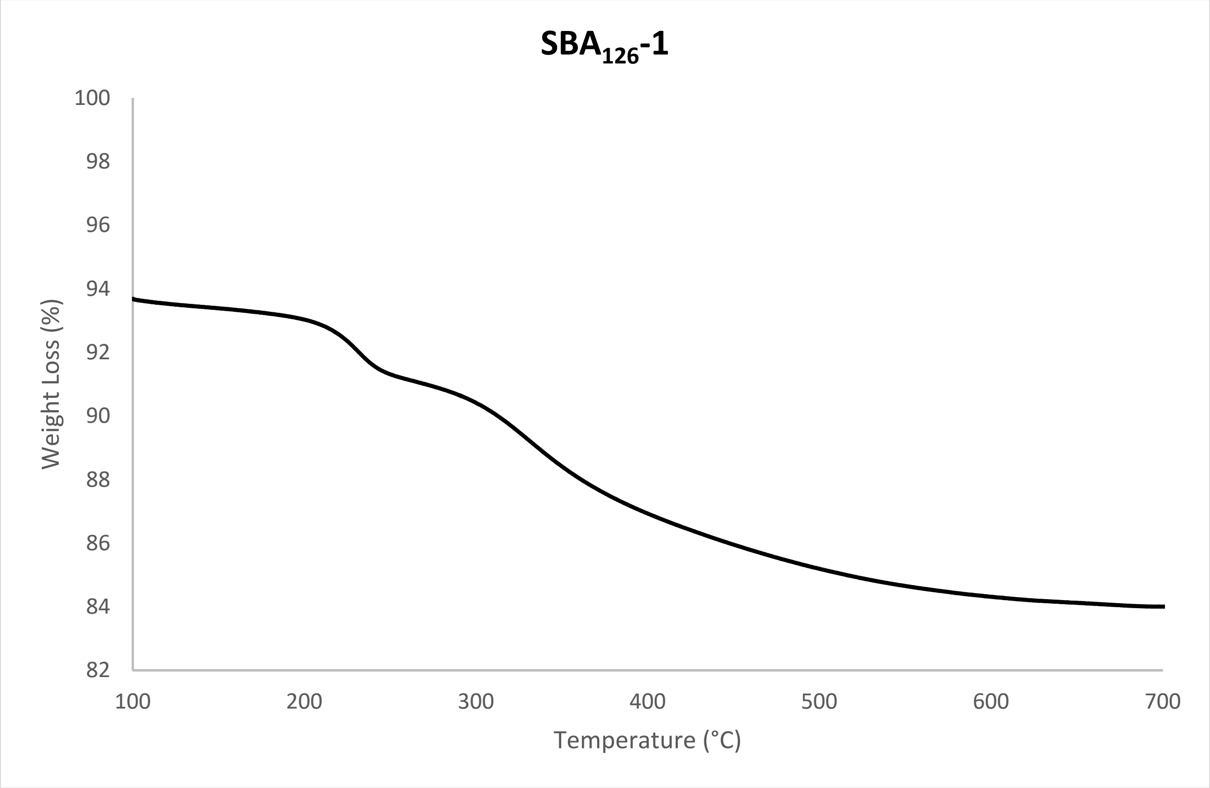


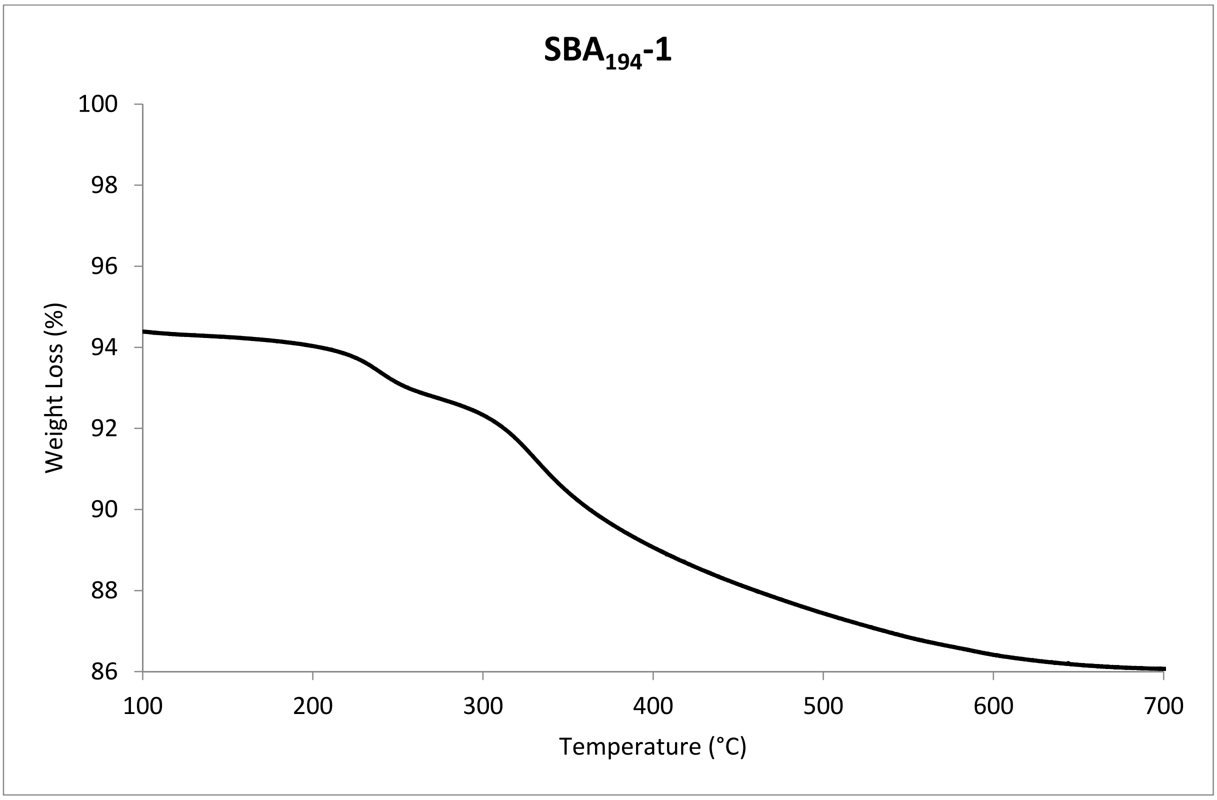
TGA for SBA_{11}-1, SBA_{26}-1, SBA_{73}-1, SBA_{126}-1, SBA_{194}-1, PMOs-1

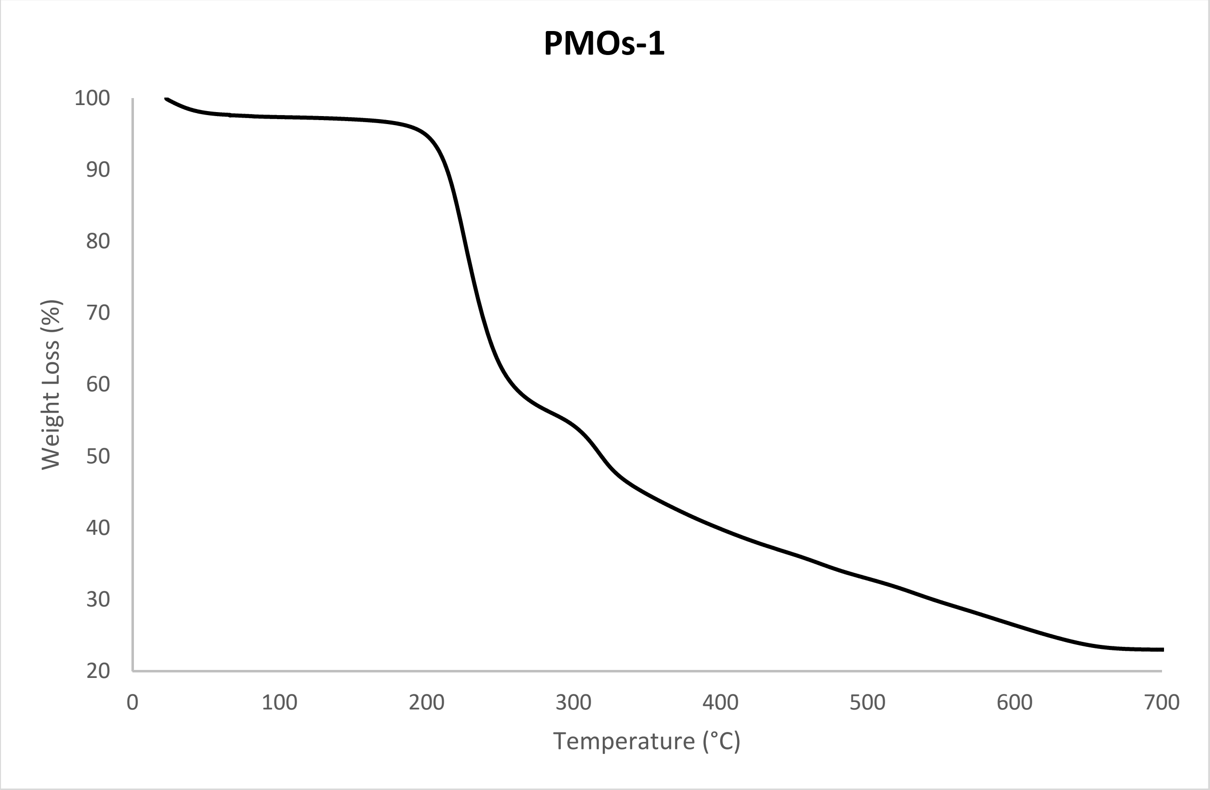




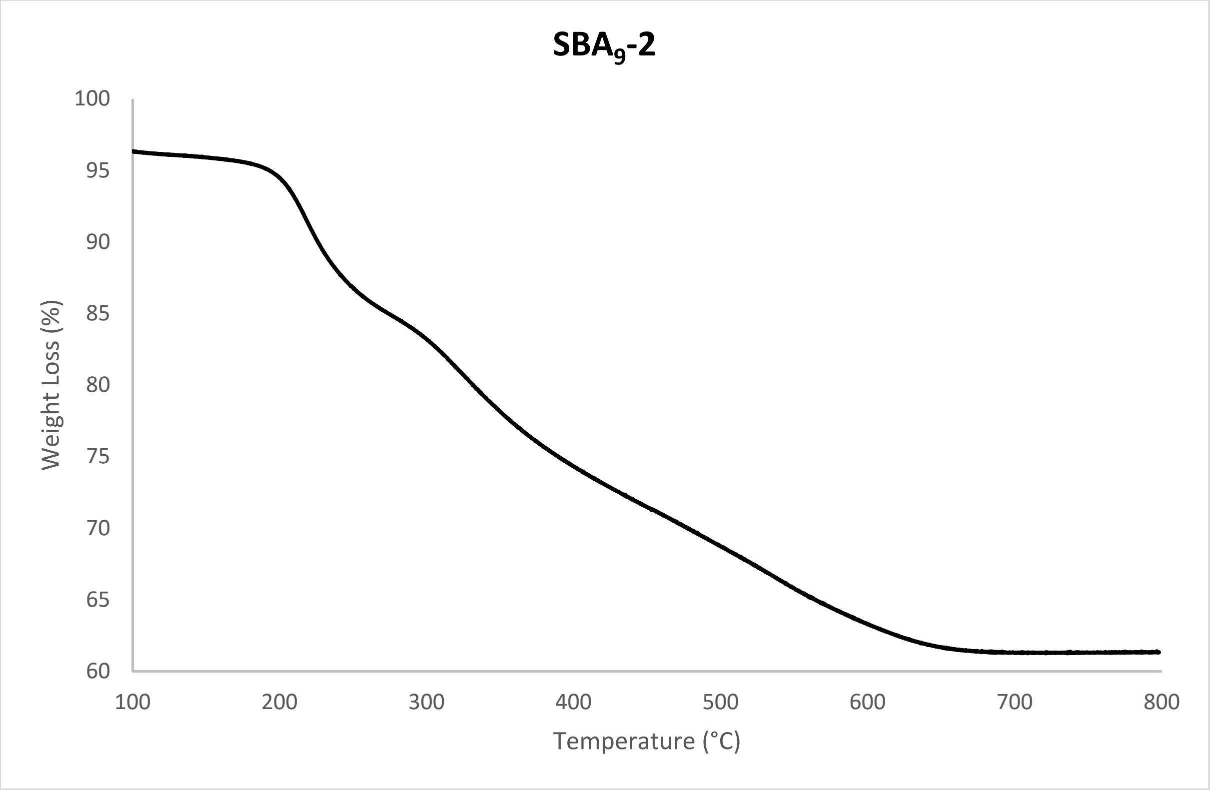

SBA$_{73}$-1
96
94
92
90
88
86
84
82
80
Weight Loss (%)
100
200
300
400
500
600
700
Temperature (°C)

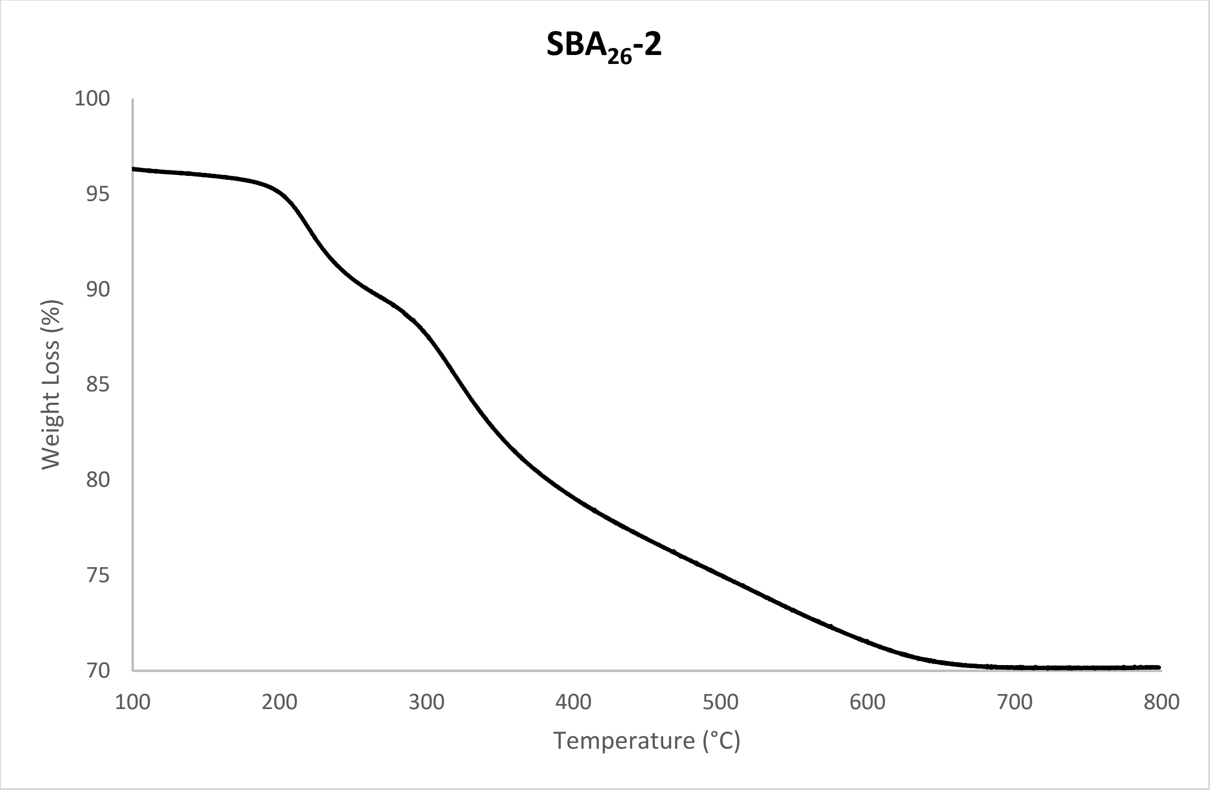

SBA$_{126}$-1
100
98
96
94
92
90
88
86
84
82
Weight Loss (%)
100
200
300
400
500
600
700
Temperature (°C)

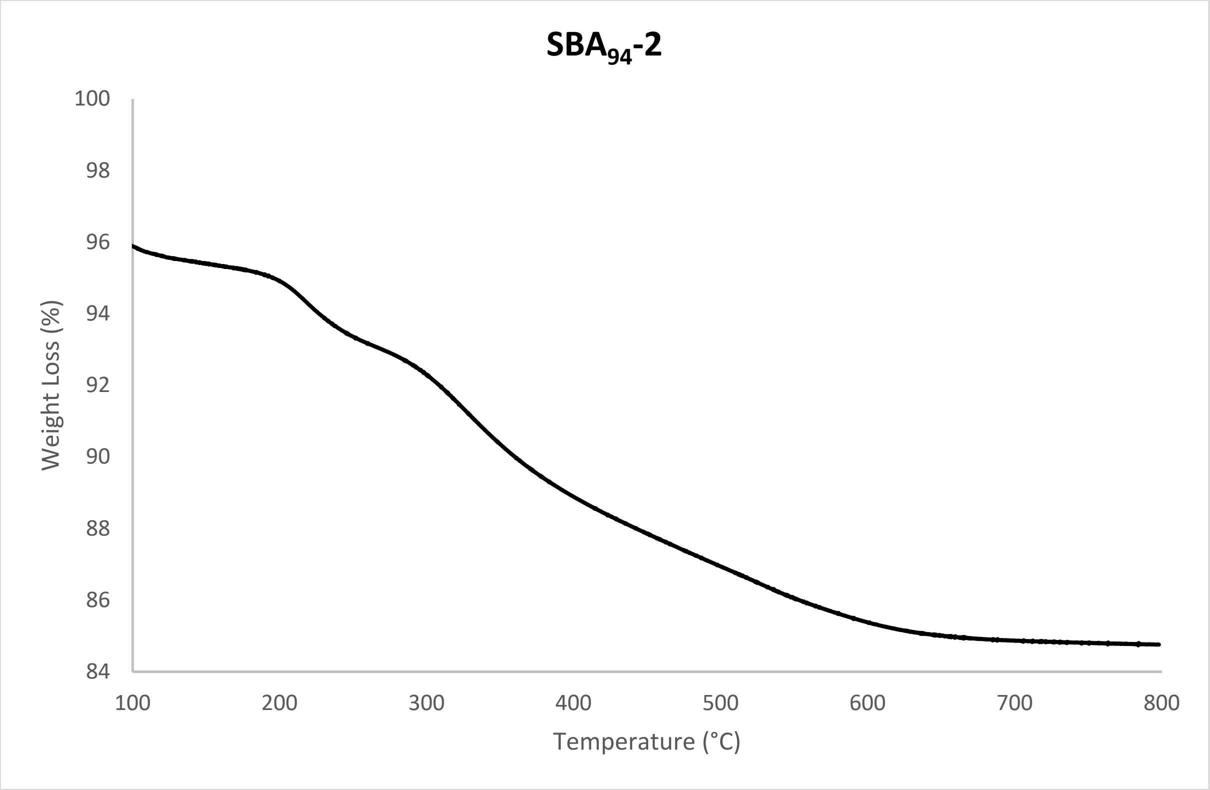

SBA$_{194}$-1
Weight Loss (%)
100
98
96
94
92
90
88
86
100
200
300
400
500
600
700
Temperature (°C)

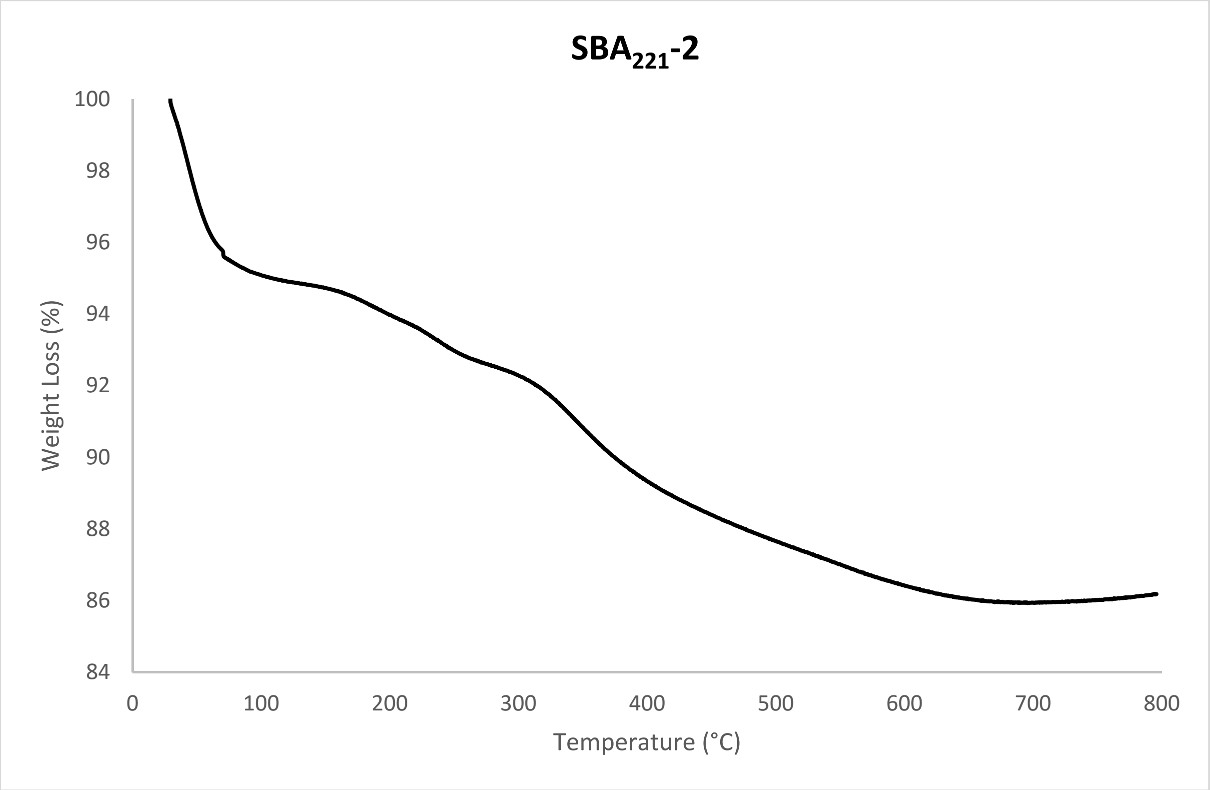

PMOs-1
Weight Loss (%)
100
90
80
70
60
50
40
30
20
0
100
200
300
400
500
600
700
Temperature (°C)

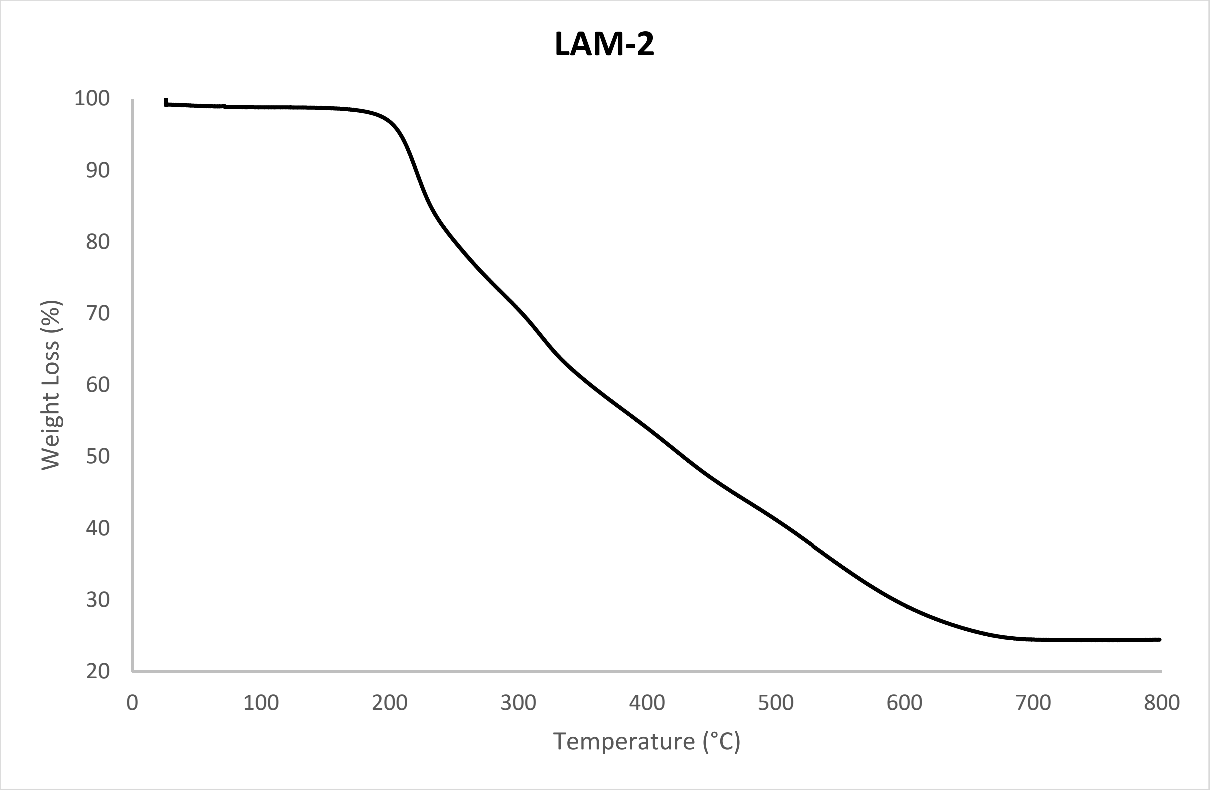
TGA for SBA_9-2, SBA_{26}-2, SBA_{94}-2, SBA_{221}-2, LAM-2






SBA$_{94}$-2
Weight Loss (%)
100
98
96
94
92
90
88
86
84
100
200
300
400
500
600
700
800
Temperature (°C)


SBA$_{221}$-2
Weight Loss (%)
100
98
96
94
92
90
88
86
84
0
100
200
300
400
500
600
700
800
Temperature (°C)


LAM-2
Weight Loss (%)
100
90
80
70
60
50
40
30
20
0
100
200
300
400
500
600
700
800
Temperature (°C)