Electronic Supplementary Information

Investigating the efficiency of silica materials with wall-embedded nitroxide radicals for dynamic nuclear polarisation NMR

Eric Besson,[a] Aurelien Vebr,[a] Fabio Ziarelli,[b] Emily Bloch,[c] Guillaume Gerbaud,[d] Séverine Queyroy,[a] Pierre Thureau,[a] Stéphane Viel*[ae] and Stéphane Gastaldi*[a]*

[a]Aix Marseille Univ, CNRS, ICR, Marseille, France
[b]Aix Marseille Univ, CNRS, Centrale Marseille, FSCM, Marseille, France
[c]Aix Marseille Univ, CNRS, MADIREL, Marseille, France
[d]Aix Marseille Univ, CNRS, BIP, Marseille, France
[e]Institut Universitaire de France, Paris, France

To whom correspondence should be sent:
E-mails: eric.besson@univ-amu.fr, s.viel@univ-amu.fr, stephane.gastaldi@univ-amu.fr

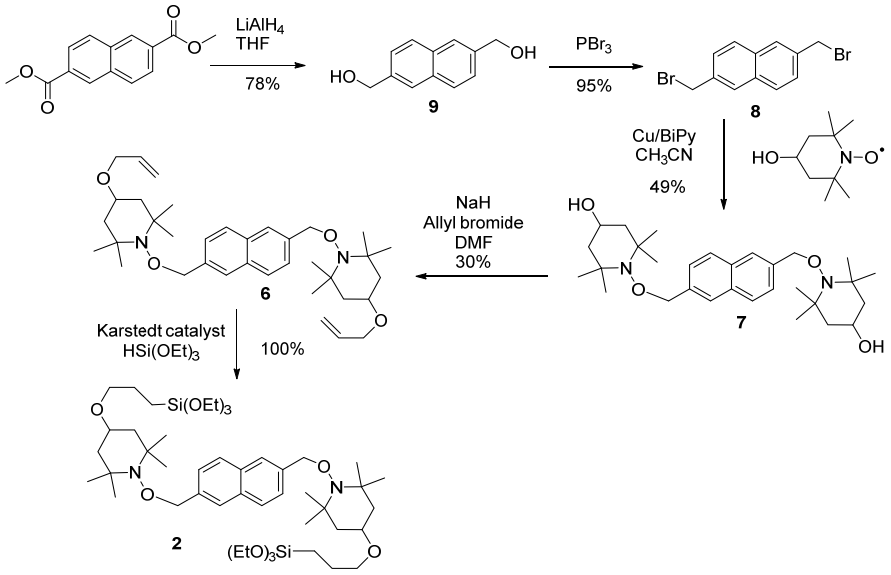
Table of contents:

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. All melting points were uncorrected and were recorded in open capillary tubes using a melting point apparatus.

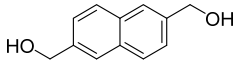
4-Hydroxy-TEMPO (4-Hydroxy-2,2,6,6-tetramethylpiperidine) and 4,4′-bis(bromomethyl)biphenyl are commercially available, they were used as purchased without purification. Precursor **1** was prepared according to literature procedures.[1]

Synthesis of precursor 2:



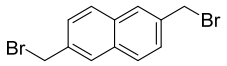
[1] E. Besson, F. Ziarelli, E. Bloch, G. Gerbaud, S. Queyroy, S. Viel, S. Gastaldi, *Chem. Commun.* **2016**, *52*, 5531-5533.

Naphthalene-2,6-diyldimethanol (9).[2]



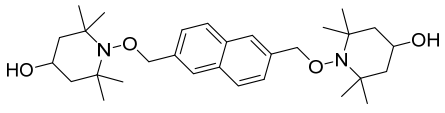
To a 0°C solution of dimethyl naphthalene-2,6-dicarboxylate (5.0 g, 20.0 mmol, 1 equiv) in dry THF (25 mL) was added $LiAlH_4$ (1.55 g, 41 mmol, 2 equiv). The suspension was stirred 3 hours at room temperature then sodium sulfate decahydrate (13.2 g, 41 mmol, 2 equiv) was added. The resulting mixture was stirred one night. The mixture was filtrated over Celite, and evaporated to give **9** (3.3 g, 15.6 mmol, 78%). ^{1}H NMR (300 MHz, DMSO) δ: 7.84 (d, *J* = 8.5, 2 H, Ar*H*), 7.79 (s, 2H, Ar*H*), 7.46 (d, *J* = 8.5, 2 H, Ar*H*), 5.27 (t, J = 5.3, 2 H, O*H*), 4.67 (d, *J* = 5.3, 4 H, O-C*H*$_2$). ^{13}C NMR (75 MHz, DMSO) δ: 140.2 (*C*$_{Ar}$), 132.6 (*C*$_{Ar}$), 127.9 (*C*H$_{Ar}$), 125.8 (CH$_{Ar}$), 124.7 (CH$_{Ar}$), 63.5 (O-*C*H$_2$).

2,6-Bis(bromomethyl)naphthalene (8).[3]



Compound **9** (3.0 g, 14.2 mmol, 1 equiv) was solubilized with THF at 0°C then PBr_3 (6 mL, 60 mmol, 11 equiv) was added under stirring. After three hours, the mixture was diluted with chloroform (10mL) and cooled at 0°C. A solution of $NaHCO_3$ was then added dropwise until there is no emulsion. The aqueous sphase was washed with chloroform (3x). The organic phase was washed with brine, dried over $MgSO_4$ and concentrated to give **8** (3.18 g, 13.5 mmol, 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.82 (s, 2H, Ar*H*), 7.80 (d, *J* = 8.6, 2 H, Ar*H*), 7.52 (d, *J* = 8.6, 2 H, Ar*H*), 4.66 (s, 4 H, BrCH$_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 135.9 (*C*$_{Ar}$), 132.9 (*C*$_{Ar}$), 128.8 (*C*H$_{Ar}$), 127.7 (*C*H$_{Ar}$), 127.4 (*C*H$_{Ar}$), 33.7 (Br*C*H$_2$).

(1,1'-((Naphthalene-2,6-diylbis(methylene))bis(oxy))bis(2,2,6,6-tetramethylpiperidin-4-ol) (7).

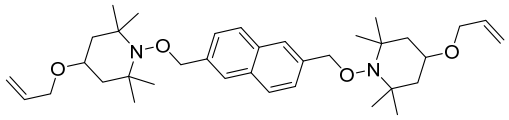


A solution of **8** (3.06 g, 9.4 mmol, 1 equiv.), 4-hydroxy-TEMPO (4.84 g, 28.2 mmol, 3 equiv), 2,2′-bipyridine (5.85 g, 37.5 mmol, 4 equiv) in acetonitrile (70 mL) was degassed 15 min by

[2] Z. Yu, T. Y. Ohulchanskyy, P. An, P. N. Prasad, Q. Lin, *J. Am. Chem. Soc.*, **2013**, *135*, 16766-16769.
[3] J. C. Rosa, D. Galanakis, C. R. Ganellin, P. M. Dunn, *J. Med. Chem.*, **1996**, *39*, 4247-4254

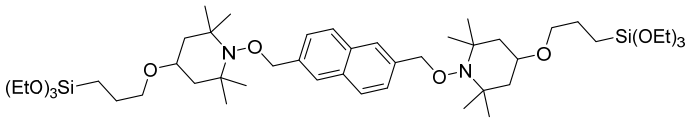
bubbling with argon. Then copper (1.79 g, 28.2 mmol, 3 equiv) was added and the mixture stirred overnight at room temperature under argon. After addition of AcOEt (50 mL), the mixture was filtrated and the organic phase washed with a solution of $CuSO_4$ (5%), water (3 times) and brine. After drying over $MgSO_4$, the solution was evaporated to give **7** (2.53 g, 4.52 mmol, 49%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (d, *J* = 8.3, 2 H, Ar*H*), 7.80 (s, 2H, Ar*H*), 7.48 (d, *J* = 8.3, 2 H, Ar*H*), 4.99 (s, 4 H, OCH_2), 4.04 (m, 2 H, HO-C*H*), 1.89 (broad d, *J* = 11.5 Hz, 4 H, CH_2), 1.56 (t, *J* = 11.5 Hz, 4 H, CH_2), 1.35 (s, 12 H, CH_3), 1.24 (s, 12 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 134.7 (*C*$_{Ar}$), 132.1 (*C*$_{Ar}$), 127.7 (*C*H$_{Ar}$), 125.6 (*C*H$_{Ar}$), 125.5 (*C*H$_{Ar}$), 78.6 (O-*C*H_2), 62.4 (O-*C*H), 59.8 (N-*C*), 48.9 (*C*H_2), 33.1 (*C*H_3), 21.0 (*C*H_3). HRMS (ESI): *m/z*: calculated for $[M+H]^+$ $C_{30}H_{47}N_2O_4$: 499.3530, found: 499.3529.

2,6-Bis(((4-(allyloxy)-2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)naphthalene (6).



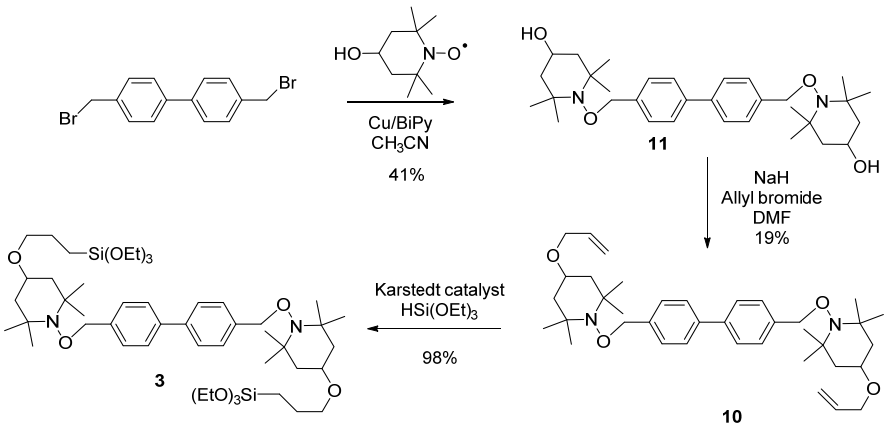
To a 0°C solution of **7** (750 mg, 1.34 mmol, 1 equiv) in dry DMF (11 mL) was added NaH (96 mg, 4 mmol, 3 equiv). The suspension was stirred 30 min then allylbromide (0.65 g, 5.4 mmol, 4 equiv) was added. The resulting mixture was stirred one night. The reaction was monitored by TLC. After completion, 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 by flash chromatography on silicagel (5/95 EtOAc /pentane) to give **6** (234 mg, 0.37 mmol, 30%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.3, 2 H, Ar*H*), 7.85 (s, 2H, Ar*H*), 7.55 (d, *J* = 8.3, 2 H, Ar*H*), 6.03 (ddt, *J* = 17.3, 10.5, 5.1 Hz, 2 H, CH_2=C*H*-CH_2), 5.37 (d, *J* = 17.3 Hz, 2 H, *H*C=), 5.26 (d, *J* = 10.5 Hz, 2 H, *H*C=), 5.06 (s, 4 H, O-CH_2-C$_{Ar}$), 4.10 (d, *J* = 5.1 Hz, 4 H, O-CH_2-C=), 3.73 (tt, *J* = 3.4, 11.5 Hz, 2H, O-C*H*), 1.98 (broad d, *J* = 11.6 Hz, 4 H, CH_2), 1.46 (t, *J* = 11.6 Hz, 4 H, CH_2), 1.42 (s, 12 H, CH_3), 1.31 (s, 12 H, CH_3).^{13}C NMR (75 MHz, $CDCl_3$) δ: 130.8 (*C*$_{Ar}$), 130.8 (*C*H=), 128.1 (*C*$_{Ar}$), 123.3 (H*C*$_{Ar}$), 121.4 (H*C*$_{Ar}$), 121.3 (H*C*$_{Ar}$), 112.9 (=*C*H_2), 74.4 (O-*C*H_2-C$_{Ar}$), 65.2 (O-*C*H), 64.6 (O-*C*H_2), 63.6 (N-*C*), 40.5 (*C*H_2), 28.8 (*C*H_3), 16.7 (*C*H_3). HRMS (ESI): *m/z*: calculated for $[M+H]^+$ $C_{36}H_{55}N_2O_4$: 579.4156, found: 579.4156.

2,6-bis(((2,2,6,6-tetramethyl-4-(3-(triethoxysilyl)propoxy)piperidin-1-yl)oxy)methyl)naphthalene (2).

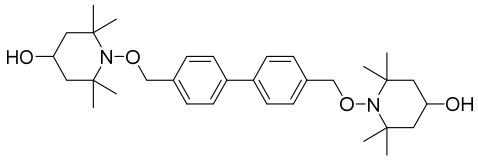


To compound **6** (0.234 g, 0.4 mmol, 1 equiv) under argon was added triethoxysilane (0.261 g, 1.6 mmol, 4 equiv) and Karstedt catalyst. The medium was stirred at room temperature for one night (^{1}H NMR monitoring). Then, the mixture was concentrated, pentane was added and the resulting solution filtrated under argon and concentrated. The product **2** was used without further purification (0.366 g, 0.4 mmol, 100%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.80 (d, *J* = 7.8 Hz, 4 H, Ar*H*), 7.78 (s, 2 H, =C*H*), 7.46 (d, *J* = 7.8 Hz, 4 H, Ar*H*), 4.97 (s, 4 H, CH_2O), 3.84 (q, *J* = 7.1 Hz, 12H, SiOCH_2), 3.57 (m, 2 H, C*H*OCH$_2$), 3.42 (t, *J* = 7.0 Hz, 4H, OCH_2), 1.88 (m, 4 H, CH_2), 1.69 (m, 4H, OCH$_2$CH_2), 1.49 (t, *J* = 11.7 Hz, 4 H, CH_{ax}H), 1.33 (s, 12 H, CH_3), 1.24 (t, *J* = 7.1 Hz, 18H, 6 x CH_3), 1.22 (s, 12 H, CH_3), 0.66 (m, 4H, SiCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 135.4 (*C*$_{Ar}$), 132.6 (*C*$_{Ar}$), 127.7 (H*C*$_{Ar}$), 125.8 (H*C*$_{Ar}$), 125.7 (H*C*$_{Ar}$), 78.9 (O-*C*H$_2$-C$_{Ar}$), 70.3 (O-*C*H$_2$), 70.1 (O-*C*H), 60.1 (N-*C*), 58.2 (O*C*H$_2$), 45.1 (*C*H$_2$), 33.2 (*C*H$_3$), 23.4 (*C*H$_2$), 21.1 (*C*H$_3$), 18.1 (*C*H$_3$), 6.4 (Si*C*H$_2$). HRMS (ESI): *m/z*: calculated for $[M+H]^+$ $C_{48}H_{87}N_2O_{10}Si_2$: 907.5894, found: 907.5896.

Synthesis of precursor 3:

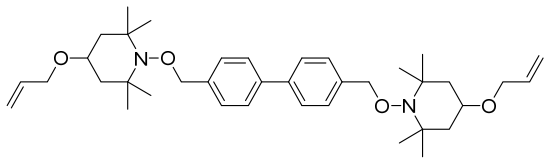


1,1'-(([1,1'-biphenyl]-4,4'-diylbis(methylene))bis(oxy))bis(2,2,6,6-tetramethylpiperidin-4-ol) (11).



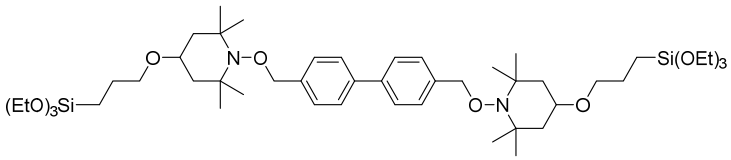
A solution of 4,4′-bis(bromomethyl)biphenyl (3.0 g, 8.82 mmol, 1 equiv.), 4-hydroxy-TEMPO (4.54 g, 26.4 mmol, 3 equiv), 2,2′-bipyridine (5.5 g, 35.2 mmol, 4 equiv) in acetonitrile (40 mL) was degassed 15 min by bubbling with argon. Then copper (1.7 g, 26.4 mmol, 3 equiv) was added and the mixture stirred overnight at room temperature under argon. After addition of AcOEt (100 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. The residue was purified using silica gel column (20/80 to 80/20 AcOEt/pentane to give **11** (1.87 g, 3.57 mmol, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (d, *J* = 8.1 Hz, 4H, Ar*H*), 7.44 (d, *J* = 8.1 Hz, 4H, Ar*H*), 4.86 (s, 4H, OCH_2), 4.00 (m, 2 H, HO-C*H*), 1.85 (broad d, *J* = 12.58 Hz, 4 H, CH_2), 1.54 (t, *J* = 11.6 Hz, 4 H, CH_2), 1.32 (s, 12 H, CH_3), 1.22 (s, 12 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 139.6 (C_{Ar}), 136.4 (C_{Ar}), 127.3 (C_{Ar}H), 126.4 (C_{Ar}H), 78.0 (O-*C*H_2-Ph), 62.7 (HO-*C*H), 59.8 (N-*C*), 47.9 (*C*H_2), 32.7 (*C*H_3), 20.7 (*C*H_3). HRMS (ESI): *m/z*: calculated for $[M+H]^+$ $C_{32}H_{49}N_2O_4$: 525.3687, found: 525.3687.

4,4'-bis(((4-(allyloxy)-2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-1,1'-biphenyl (10).



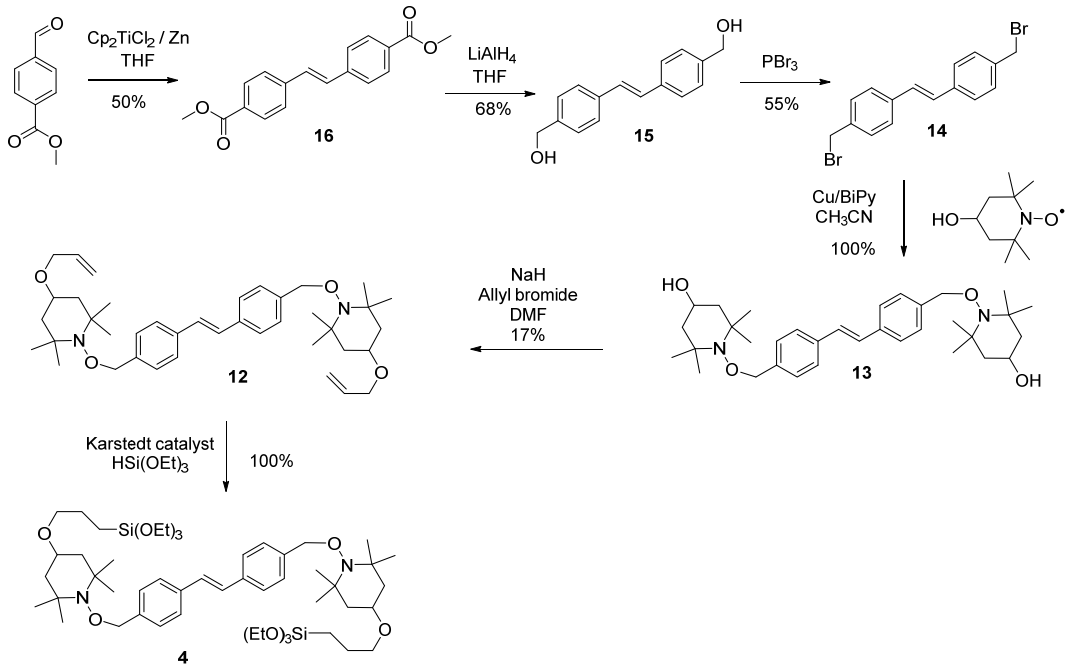
To a 0°C solution of **11** (1.87 g, 3.6 mmol, 1 equiv) in dry DMF (35 mL) was added NaH (350 mg, 10.2 mmol, 3 equiv). The suspension was stirred 30 min then allylbromide (1.26 mL, 14.6 mmol, 4 equiv) was added. The resulting mixture was stirred overnight. The reaction was monitored by TLC. After completion, 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 by flash chromatography on silicagel (0/100 to 10/90 EtOAc /pentane) to give **10** (425 mg, 0.68 mmol, 19%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.57 (d, *J* = 8.4 Hz, 4 H, Ar*H*), 7.42 (d, *J* = 8.4 Hz, 4 H, Ar*H*), 5.93 (ddt, *J* = 17.2, 10.3, 5.5 Hz, 2 H, C*H*=), 5.29 (dd, *J* = 1.6, 17.2 Hz, 2 H, =CH_2), 5.17 (dd, *J* = 1.0, 10.3 Hz, 2 H, =CH_2), 4.87 (s, 4 H, OCH_2), 4.01 (d, *J* = 5.5 Hz, 4 H, O-CH_2-C=), 3.64 (tt, *J* = 4.2, 11.1 Hz, 2 H, O-C*H*), 1.90 (dd, *J* = 2.5, 11.8 Hz, 4 H, CH_2), 1.52 (t, *J* = 11.6 Hz 4 H, CH_2), 1.33 (s, 12 H, CH_3), 1.22 (s, 12 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 139.0 (C_{Ar}), 135.9 (C_{Ar}), 134.2 (*C*H=), 126.7 (C_{Ar}H), 125.8 (C_{Ar}H), 115.4 (CH_2=), 77.4 (O-*C*H_2-Ph), 68.7 (O-*C*H), 68.0 (O-*C*H_2), 59.1 (N-*C*), 43.9 (*C*H_2), 32.2 (*C*H_3), 20.1 (*C*H_3). HRMS (ESI): *m/z*: calculated for $[M+H]^+$ $C_{38}H_{57}N_2O_4$: 605.4313, found: 605.4314.

4,4'-bis(((2,2,6,6-tetramethyl-4-(3-(triethoxysilyl)propoxy)piperidin-1-yl)oxy)methyl)-1,1'-biphenyl (3).

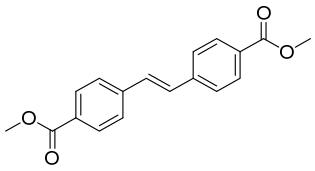


To compound **10** (232 mg, 0.38 mmol, 1 equiv) under argon was added triethoxysilane (251 mg, 1.53 mmol, 4 equiv) and Karstedt catalyst. The medium was stirred at room temperature for one hour (^{1}H NMR monitoring). Then pentane was added and the resulting solution filtrated under argon and concentrated. The product **3** was used without further purification (350 mg, 0.83 mmol, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (d, *J* = 8.1 Hz, 4 H, Ar*H*), 7.43 (d, *J* = 8.1 Hz, 4 H, Ar*H*), 4.87 (s, 4 H, OCH_2), 3.84 (q, *J* = 7.0 Hz, 12 H, Si-O-CH_2), 3.57 (m, 2 H, O-C*H*), 3.42 (t, *J* = 6.8 Hz, 4 H, O-CH_2), 1.88 (dd, *J* = 3.2, 12.0 Hz, 4 H, CH_2), 1.69 (m, 4 H, CH_2), 1.49 (t, *J* = 11.9 Hz, 4 H, CH_2-C), 1.32 (s, 12 H, CH_3), 1.24 (t, *J* = 7.0 Hz, 18 H, CH_3), 1.22 (superimposed s, 12 H, CH_3), 0.65 (m, 4 H, CH_2-Si). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.9 (*C*$_{Ar}$), 136.8 (*C*$_{Ar}$), 127.7 (*C*$_{Ar}$H), 126.7 (*C*$_{Ar}$H), 78.3 (O-*C*H$_2$-Ph), 70.2 (O-*C*H$_2$), 69.9 (O-*C*H$_2$), 60.0 (N-*C*), 58.1 (Si-O-*C*H$_2$), 44.9 (*C*H$_2$), 33.1 (*C*H$_3$), 23.2 (Si-CH$_2$-*C*H$_2$), 21.0 (*C*H$_3$), 18.0 (*C*H$_3$), 6.3 (Si-*C*H$_2$). HRMS (ESI): *m/z*: calculated for $[M+H]^+$ $C_{50}H_{89}N_2O_{10}Si_2$: 933.6050, found: 933.6049.

Synthesis of precursor 4:

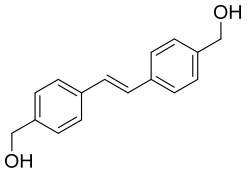


(*E*)-1,1'-(Ethene-1,2-diylbis(4,1-phenylene))bis(ethan-1-one) (16).[4]



Zinc (7.5g) was activated by washing with a HCl (1M) solution, water, EtOH, Et_2O, and finaly dry under vacuum. A solution of methyl 4-formylbenzoate (3,225 g, 19.65 mmol, 1 equiv) in THF (36 mL) was degassed three times (freeze thaw cycle). Titanocene dichloride (5.880 g, 23.55 mmol, 1.2 equiv) in THF (84.5 mL) was degassed three times (freeze thaw cycle), then activated zinc (3.020 g, 47.25 mmol, 2.2 equiv.) was added. The mixture was stirred until it turns green. The solution of methyl 4-formylbenzoate was then added onto the catalyst solution and this mixture was stirred at 80°C overnight. The solution was diluted with MTBE, washed with HCl (1M) and brine. The organic phase was washed with water. After drying over $MgSO_4$, the solution was evaporated to give **16** (1.43 g, 5.0 mmol, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04 (d, *J* = 8.5 Hz, 4 H, Ar*H*), 7.58 (d, *J* = 8.5 Hz, 4 H, Ar*H*), 7.23 (s, 2 H, =C*H*), 3.93 (s, 6 H, O-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.7 (CO_2), 141.2 (C_{Ar}), 130.1 (CH_{Ar}), 129.5 (C_{Ar}), 126.6 (CH_{Ar}), 116.7 (=*C*H), 52.1 (O-*C*H_3).

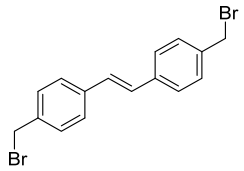
(*E*)-(Ethene-1,2-diylbis(4,1-phenylene))dimethanol (15).[3]



To a 0°C solution of **16** (2.1 g, 7.0 mmol, 1 equiv) in dry THF (100 mL) was added $LiAlH_4$ (531 mg, 14 mmol, 2 equiv). The suspension was stirred 2 hours then sodium sulfate decahydrate (4.5 g, 14 mmol, 2 equiv) was added. The resulting mixture was stirred overnight. The mixture was filtrated over Celite, and evaporated to give **15** (1.3 g, 4.8 mmol, 68%). ^{1}H NMR (300 MHz, DMSO-d6) δ: 7.56 (d, *J* = 8.0 Hz, 4 H, Ar*H*), 7.34 (d, *J* = 8.0 Hz, 4 H, Ar*H*), 7.22 (s, 2 H, =C*H*), 5.16 (t, *J* = 5.5 Hz, 2 H, O*H*), 4.52 (d, *J* = 5.5 Hz, 4 H, O-CH_2). ^{13}C NMR (75 MHz, DMSO) δ: 143.6 (C_{Ar}), 137.2 (C_{Ar}), 129.3 (=*C*H), 128.4 (CH_{Ar}), 127.7 (CH_{Ar}), 64.4 (O-*C*H_2).

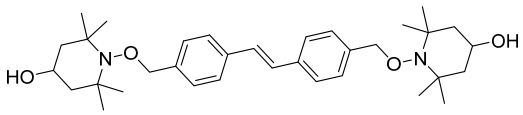
[4] H. R. Dieguez, A. Lopez, V. Domingo, J. F. Arteaga, J. A. Dobado, M. M. Herrador, J. F. Quilez Del Moral, A. F. Barrero, *J. Am. Chem. Soc.*, **2010**, *132*, 254-259.

(*E*)-1,2-bis(4-(Bromomethyl)phenyl)ethane (14).[3]



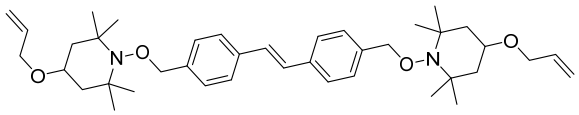
Compound **15** (1.3 g, 4.8 mmol, 1 equiv) was solubilized with THF at 0°C. Was added under stirring PBr_3 (3mL, 30 mmol, 6 equiv). After three hours was added 10mL of chloroform. Then was added dropwise a solution of $NaHCO_3$ until there is no emulsion. The mixture was washed with chloroform and brine. dried over $MgSO_4$ and concentrated. The residue was purified using silica gel column (2/95 → 15/85 Et_2O/pentane, then 50/50 → 100/0 AcOEt/pentane) to give **14** (0.96 g, 2.6 mmol, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50 (d, *J* = 8.2 Hz, 4 H, Ar*H*), 7.39 (d, *J* = 8.2 Hz, 4 H, Ar*H*), 7.10 (s, 2 H, =C*H*), 4.52 (s, 4 H, C*H*), .^{13}C NMR (75 MHz, $CDCl_3$) δ: 137.6 (C_{Ar}), 137.5 (C_{Ar}), 129.7 (=*C*H), 128.9 (CH_{Ar}), 127.1 (CH_{Ar}), 33.6 (*C*Br).

(*E*)-1,1'-(((Ethene-1,2-diylbis(4,1-phenylene))bis(methylene))bis(oxy))bis(2,2,6,6-tetramethylpiperidin-4-ol) (13).



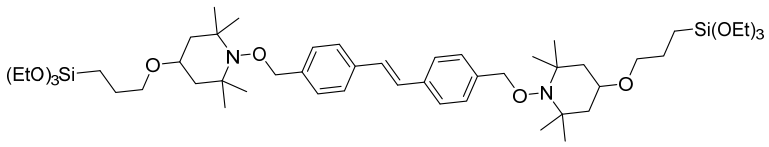
A solution of compound **14** (955 mg, 2.6 mmol, 1 equiv.), 4-hydroxy-TEMPO (1.35 g, 7.8 mmol, 3 equiv), 2,2′-bipyridine (1.63 mg, 10.4 mmol, 4 equiv) in acetonitrile (20 mL) under argon was degassed 15 min by bubbling with argon. Then copper (500 mg, 7.8 mmol, 3 equiv) was added and the mixture stirred 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 **13** (1.48 g, 2.6 mmol, 100%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 7.6 Hz, 4 H, Ar*H*), 7.38 (d, *J* = 7.4 Hz, 4 H, Ar*H*), 7.14 (s, 2 H, =C*H*), 4.86 (s, 4 H, O-CH_2), 4.07 (m, 2 H, HO-C*H*), 1.91 (d, *J* = 17.4 Hz, 4 H, CH_2), 1.57 (s, 4 H, CH_2), 1.34 (s, 12H, CH_3), 1.25 (s, 12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.3 (C_{Ar}), 134.5 (C_{Ar}), 126.2 (=*C*H), 125.8 (C_{Ar}), 124.3 (C_{Ar}), 76.6 (O-*C*H_2-Ph), 61.1 (O-*C*H), 58.2 (N-*C*), 46.5 (*C*H_2), 31.2 (*C*H_3), 19.1 (*C*H_3). HRMS (ESI): *m/z*: calculated for $[M+H]^+$ $C_{34}H_{51}N_2O_4$: 551.38434, found: 551.3842.

(*E*)-1,2-Bis(4-(((4-(allyloxy)-2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)phenyl)ethane (12).



To a 0°C solution of **13** (1.47 g, 2.67 mmol, 1 equiv) in dry DMF (22 mL) was added NaH (192 mg, 8 mmol, 3 equiv). The suspension was stirred 30 min then allylbromide (1.3 g, 10.7 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 **12** (140 mg, 0.22 mmol, 17%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (d, *J* = 8.1 Hz, 4 H, Ar*H*), 7.34 (d, *J* = 8.0 Hz, 4 H, Ar*H*), 7.09 (s, 2 H, =C*H*), 5.93 (ddt, *J* = 5.24, 10.5, 17.3 Hz, 2 H, CH_2=C*H*-CH_2), 5.31 (dd, *J* = 1.6, 17.3 Hz, 2 H, *H*C=), 5.17 (dd, *J* = 1.6, 8.9 Hz, 2 H, *H*C=), 4.83 (s, 4 H, O-CH_2-C_{Ar}), 4.00 (d, *J* = 5.6 Hz, 4 H, O-CH_2-C=), 3.63 (tt, *J* = 3.9, 11.1 Hz, 2H, O-C*H*), 1.87 (d, *J* = 17.4 Hz, 4 H, CH_2), 1.52 (s, 4 H, CH_2), 1.30 (s, 12H, CH_3), 1.20 (s, 12 H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.6 (C_{Ar}), 136.7 (C_{Ar}), 135.4 (=*C*-CH_2), 128.4 (=*C*H), 127.9 (C_{Ar}), 126.4 (C_{Ar}), 116.6 (*C*=), 78.7 (O-*C*H_2-Ph), 70.0 (O-*C*H), 69.2 (O-*C*H_2-C=), 60.32 (N-*C*), 45.1 (*C*H_2), 33.4 (*C*H_3), 21.4 (*C*H_3). HRMS (ESI): *m/z*: calculated for $[M+H]^+$ $C_{40}H_{59}N_2O_4$: 631.4469, found: 631.4470.

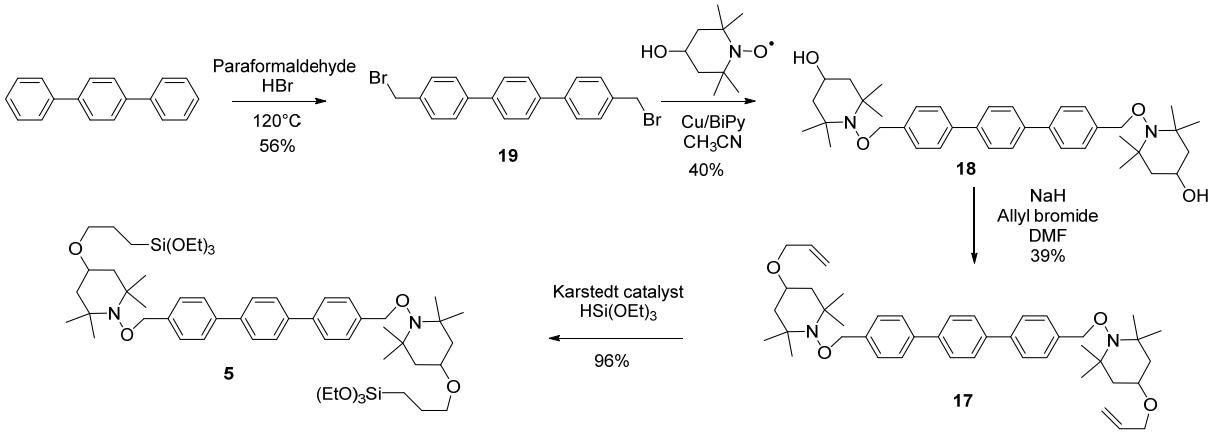
(*E*)-1,2-bis(4-(((2,2,6,6-tetramethyl-4-(3-(triethoxysilyl)propoxy)piperidin-1-yl)oxy)methyl)phenyl)ethene (4).



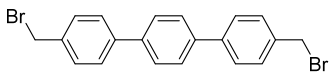
To compound **12** (0.14 g, 0.22 mmol, 1 equiv) under argon was added triethoxysilane (0.145 g, 0.88 mmol, 4 equiv) and Karstedt catalyst. The medium was stirred at room temperature for one night (^{1}H NMR monitoring). Then, the mixture was concentrated, pentane was added and the resulting solution filtrated under argon and concentrated. The product **4** was used without further purification (0.12 g, 0.22 mmol, 100%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.49 (d, *J* = 7.8 Hz, 4 H, Ar*H*), 7.34 (d, *J* = 7.8 Hz, 4 H, Ar*H*), 7.10 (s, 2 H, =C*H*), 4.82 (s, 4 H, CH_2O), 3.82 (q, *J* = 7.1 Hz, 12H, SiOCH_2), 3.56 (m, 2 H, C*H*OCH_2), 3.42 (t, *J* = 7.0 Hz, 4H, OCH_2), 1.87 (m, 4 H, CH_2), 1.68 (m, 4H, OCH_2CH_2), 1.47 (t, *J* = 11.7 Hz, 4 H, CH_{ax}H), 1.30 (s, 12 H, CH_3),

1.24 (t, *J* = 7.1 Hz, 18H, 6 x C*H*$_3$), 1.20 (s, 12 H, C*H*$_3$), 0.65 (m, 4H, SiC*H*$_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 137.5 (*C*$_{Ar}$), 136.5 (*C*$_{Ar}$), 128.2 (*C*H=), 127.8 (*C*H$_{Ar}$), 126.3 (*C*H$_{Ar}$), 78.6 (O*C*H$_2$), 70.4 (O*C*H$_2$), 70.1 (O*C*H), 60.2 (N*C*), 58.3 (O*C*H$_2$), 45.2(*C*H$_2$), 33.3 (*C*H$_3$), 23.4 (*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 $[M+H]^+$ $C_{52}H_{91}N_2O_{10}Si_2$: 959.6207, found: 959.6210.

Synthesis of precursor 5:

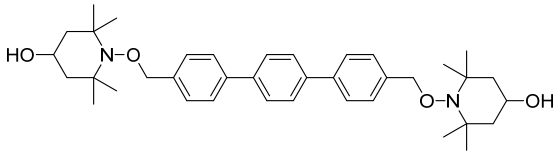


4,4''-Bis(bromomethyl)-1,1':4',1''-terphenyl (19).[5]



A solution of 1,1':4',1''-terphenyl (6.0 g, 26.0 mmol, 1 equiv), paraformaldehyde (4.31 g, 143.5 mmol, 5.5 equiv), HBr 33% in acetic acid (42.4 mL, 244 mmol) was stirred at 120°C overnight. The mixture was poured into iced water. The white solid was then washed with AcOEt and hot water (70°C). The solid was dried under vacuum to give **19** (4.6 g, 14.5 mmol, 56%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.67 (s, 4 H, Ar*H*), 7.62 (d, *J* = 8.1 Hz, 4 H, Ar*H*), 7.49 (d, *J* = 8.2 Hz, 4H, Ar*H*), 4.56 (s, 4H, BrC*H*$_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 139.6 (*C*$_{Ar}$), 139.5 (*C*$_{Ar}$), 137.0 (*C*$_{Ar}$), 129.6 (*C*H$_{Ar}$), 127.5 (*C*H$_{Ar}$), 127.4 (*C*H$_{Ar}$), 33.3 (Br*C*H$_2$).

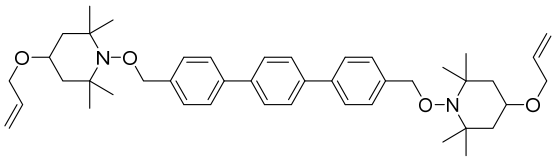
1,1'-(([1,1':4',1''-Terphenyl]-4,4''-diylbis(methylene))bis(oxy))bis(2,2,6,6-tetramethylpiperidin-4-ol) (18).



[5] A. Helms, D. Heiler, G. McLendon, *J. Am. Chem. Soc.*, **1992**, *114*, 6227-6238.

A solution of **19** (4.0 g, 12.5 mmol, 1 equiv.), 4-hydroxy-TEMPO (6.48 g, 37.7 mmol, 3 equiv), 2,2′-bipyridine (7.8 g, 50.0 mmol, 4 equiv) in acetonitrile (93 mL) was degassed 15 min by bubbling with argon. Then copper (2.4 g, 37.7 mmol, 3 equiv) was added and the mixture stirred overnight at room temperature under argon. After addition of AcOEt (150 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. The residue was purified using silica gel column (20/80 to 80/20 AcOEt/pentane to give **18** (2.93 g, 4.98 mmol, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (s, 4 H, Ar*H*), 7.62 (d, *J* = 8.1 Hz, 4H, Ar*H*), 7.44 (d, *J* = 8.2 Hz, 4H, Ar*H*), 4.88 (s, 4H, OCH_2), 4.00 (m, 2 H, HO-C*H*), 1.87 (dd, *J* = 2.5 and 11.8 Hz, 4 H, CH_2-C), 1.54 (t, *J* = 11.9 Hz, 4 H, CH_2-C), 1.33 (s, 12 H, CH_3), 1.24 (s, 12 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 139.9 (*C*$_{Ar}$), 139.9 (*C*$_{Ar}$), 137.1 (*C*$_{Ar}$), 128.0 (*C*$_{Ar}$H), 127.4 (*C*$_{Ar}$H), 126.9 (*C*$_{Ar}$H), 78.6 (O-*C*H_2-Ph), 63.3 (HO-*C*H), 60.4 (N-*C*), 48.4 (*C*H_2), 33.2 (*C*H_3), 21.2 (*C*H_3). HRMS (ESI): *m/z*: calculated for $[M+H]^+$ $C_{38}H_{53}N_2O_4$: 601.4000, found: 601.4008.

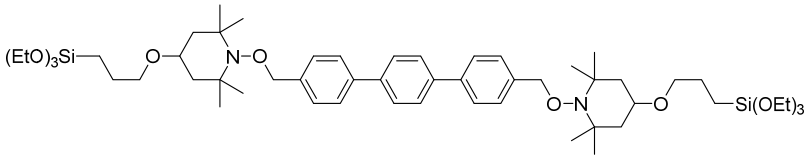
4,4''-Bis(((4-(allyloxy)-2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-1,1':4',1''-terphenyl (17).



To a 0°C solution of **18** (2.0 g, 3.4 mmol, 1 equiv) in dry DMF (26 mL) was added NaH (245 mg, 10.2 mmol, 3 equiv). The suspension was stirred 30 min then allylbromide (1.17 mL, 13.6 mmol, 4 equiv) was added. The resulting mixture was stirred overnight. 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 by flash chromatography on silicagel (5/95 EtOAc /pentane) to give **17** (880 mg, 1.32 mmol, 39%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (s, 4 H, Ar*H*), 7.62 (d, *J* = 8.1 Hz, 4 H, Ar*H*), 7.45 (d, *J* = 8.1 Hz, 4 H, Ar*H*), 5.93 (ddt, *J* = 17.4, 10.5, 5.6 Hz, 2 H, C*H*=), 5.29 (dd, *J* = 1.6, 17.4 Hz, 2 H, =CH_2), 5.17 (dd, *J* = 0.8, 10.5 Hz, 2 H, =CH_2), 4.88 (s, 4 H, OCH_2), 4.01 (d, *J* = 5.6 Hz, 4 H, O-CH_2-C=), 3.64 (tt, *J* = 4.0, 10.9 Hz, 2 H, O-C*H*), 1.90 (dd, *J* = 2.5, 11.5 Hz, 4 H, CH_2), 1.52 (m, 4 H, CH_2), 1.33 (s, 12 H, CH_3), 1.22 (s, 12 H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.1 (*C*$_{Ar}$), 139.9 (*C*$_{Ar}$), 137.2 (*C*$_{Ar}$), 135.4 (*C*H=), 128.0 (*C*$_{Ar}$H), 127.4 (*C*$_{Ar}$H), 126.9 (*C*$_{Ar}$H), 116.5 (CH_2=), 78.6 (O-*C*H_2-Ph), 69.9 (O-

*C*H), 69.1 (O-*C*H$_2$), 60.3 (N-*C*), 45.1 (*C*H$_2$), 33.3 (*C*H$_3$), 21.3 (*C*H$_3$). HRMS (ESI): *m/z*: calculated for $[M+H]^+$ $C_{44}H_{61}N_2O_4$: 681.4626, found: 681.4631.

4,4''-Bis(((2,2,6,6-tetramethyl-4-(3-(triethoxysilyl)propoxy)piperidin-1-yl)oxy)methyl)-1,1':4',1''-terphenyl (5).



To compound **17** (581 mg, 0.87 mmol, 1 equiv) under argon was added triethoxysilane (571 mg, 3.48 mmol, 4 equiv) and Karstedt catalyst. The medium was stirred at room temperature for one hour (^{1}H NMR monitoring). Then pentane was added and the resulting solution filtrated under argon and concentrated. The product **5** was used without further purification (827 mg, 0.83 mmol, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (s, 4 H, Ar*H*), 7.62 (d, *J* = 8.1 Hz, 4 H, Ar*H*), 7.45 (d, *J* = 8.1 Hz, 4 H, Ar*H*), 4.88 (s, 4 H, OC*H*$_2$), 3.83 (q, *J* = 7.0 Hz, 12 H, Si-O-C*H*$_2$), 3.57 (tt, *J* = 4.1, 11.1 Hz, 2 H, O-C*H*), 3.42 (t, *J* = 6.9 Hz, 4 H, O-C*H*$_2$), 1.87 (dd, *J* = 3.0, 8.6 Hz, 4 H, C*H*$_2$), 1.67 (m, 4 H, C*H*$_2$), 1.48 (t, *J* = 11.9 Hz, 4 H, C*H*$_2$-C), 1.32 (s, 12 H, C*H*$_3$), 1.23 (t, *J* = 7.0 Hz, 18 H, C*H*$_3$), 1.22 (superimposed s, 12 H, C*H*$_3$), 0.65 (m, 4 H, C*H*$_2$-Si). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 139.9 (*C*$_{Ar}$), 139.8 (*C*$_{Ar}$), 137.2 (*C*$_{Ar}$), 128.0 (*C*$_{Ar}$H), 127.4 (*C*$_{Ar}$H), 126.9 (*C*$_{Ar}$H), 78.6 (O-*C*H$_2$-Ph), 70.4 (O-*C*H$_2$), 60.3 (N-*C*), 58.3 (Si-O-*C*H$_2$), 45.2 (*C*H$_2$), 33.5 (*C*H$_3$), 23.5 (Si-CH$_2$-*C*H$_2$), 21.3 (*C*H$_3$), 18.3 (*C*H$_3$), 6.6 (Si-*C*H$_2$). HRMS (ESI): *m/z*: calculated for $[M+H]^+$ $C_{56}H_{93}N_2O_{10}Si_2$: 1009.6363, found: 1009.6367.

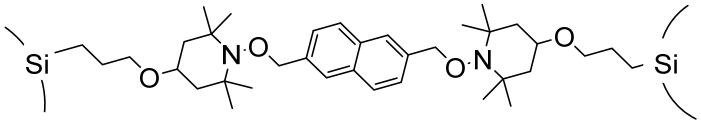
Experimental procedures for materials

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 and pore volume were calculated from the desorption isotherms using the Barrett Joyner Halenda (BJH) method.[6] Prior to adsorption, the samples were outgassed at 373 K overnight under a vacuum pressure of $2\times10^{-}$

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

^{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[7] 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.[8,9] 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[10] 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. **SBA$_n$-1** was prepared according to literature procedures.[1]

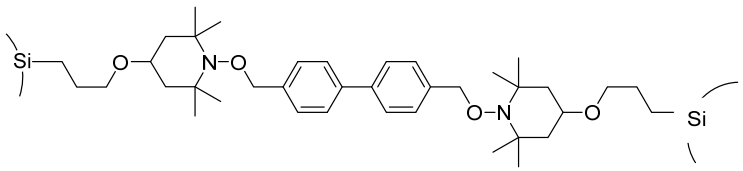
SBA$_{56}$-2.



In a typical procedure, 3.13 g of pluronic P-123 ($PEO_{20}PPO_{70}PEO_{20}$) were dissolved in deionized water (23 mL) and 2M hydrochloric acid solution (94 mL) by stirring for 3 h at 40 °C. Tetraethoxysilane (6.5 g, 31.4 mmol, 79 equiv) and precursor **2** (360 mg, 0.25 mmol, 1 equiv) were then added. The mixture was stirred 24 h at 40 °C, then warmed without stirring at 95 °C for 2 days, filtrated, washed twice with water, once with ethanol and finally extracted with a Soxhlet 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.^{13}C CPMAS NMR (101.6 MHz) δ: 134.6, 132.0, 126.2, 77.7, 74.8, 74.1, 69.0, 58.6, 43.6, 30.7, 26.0, 19.1, 14.4, 7.0. ^{29}Si CPMAS NMR (79.5 MHz) δ: -63.9 (T^3), -91.8 (Q^2), -100.3 (Q^3), -109.5 (Q^4). BET Surface Area: 842 m^2/g. BJH Desorption Average Pore Diameter: 6.9 nm. Vp = 1.31 cm^3/g. SAXS: d = 10.4 nm; a = 12.0 nm.

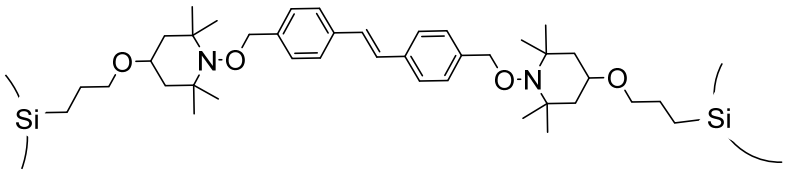
[7] J. Schaefer, E. O. Stejskal, *J. Am. Chem. Soc*. **1976**, *98*, 1031-1032.
[8] O. B. Peersen, X. Wu, I. Kustanovich, S. O. Smith, *J. Magn. Reson.* **1993**, *104*, 334-339.
[9] R. L. Cook, C. H. Langford, R. Yamdagni, C. M. A. Preston, *Anal. Chem.,* **1996**, *68*, 3979-3986.
[10] G. Gerbaud,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

SBA_{55}-3.



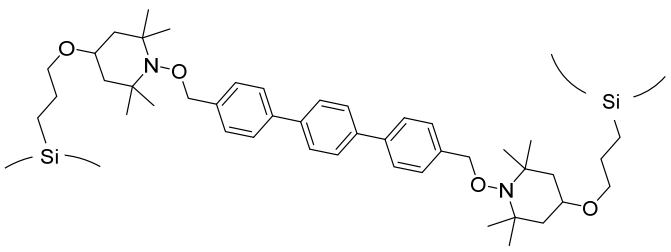
The material was prepared by following the previous procedure from tetraethoxysilane (5.50 g, 20 mmol, 79 equiv) and precursor **3** (313 mg, 0.33 mmol, 1 equiv) 2.69 g of pluronic P-123 ($PEO_{20}PPO_{70}PEO_{20}$), deionized water (20 mL) and 2M hydrochloric acid solution (81 mL). ^{13}C CPMAS NMR (101.6 MHz) δ: 136.8, 125.3, 77.1, 76.5, 39.1, 58.2, 43.2, 30.5, 18.6, 14.4, 6.6. ^{29}Si CPMAS NMR (79.5 MHz) δ: -63.5 (T^3), -100.4 (Q^3), -109.7 (Q^4). BET Surface Area: 831 m^2/g. BJH Desorption Average Pore Diameter: 7.1 nm. Vp = 1.44 cm^3/g. SAXS: d = 10.7 nm; a = 12.3 nm.

SBA_{60}-4.



The material was prepared by following the previous procedure from tetraethoxysilane (3.64 g, 17.5 mmol, 79 equiv) and precursor **4** (213 mg, 0.22 mmol, 1 equiv) 1.76 g of pluronic P-123 ($PEO_{20}PPO_{70}PEO_{20}$), deionized water (13 mL) and 2M hydrochloric acid solution (53 mL). ^{13}C CPMAS NMR (101.6 MHz) δ: 136.0, 126.7, 125.1, 77.5, 75.5, 74.6, 69.1, 64.8, 58.1, 44.3, 43.2, 30.7, 28.1, 25.4, 19.6, 14.8, 12.3, 7.2, 5.9. ^{29}Si CPMAS NMR (79.5 MHz) δ: -63.5 (T^3), -100.4 (Q^3), -109.7 (Q^4). BET Surface Area: 657 m^2/g. BJH Desorption Average Pore Diameter: 6.8 nm. Vp = 1.10 cm^3/g. SAXS: d = 10.4 nm; a = 12.0 nm.

SBA_{60}-5.



The material was prepared by following the previous procedure from tetraethoxysilane (3.64 g, 17.5 mmol, 79 equiv) and precursor **5** (0.257 mg, 0.25 mmol, 1 equiv) 2 g of pluronic P-123

($PEO_{20}PPO_{70}PEO_{20}$), deionized water (15 mL) and 2M hydrochloric acid solution (60 mL). ^{13}C CPMAS NMR (101.6 MHz) δ: 138.7, 125.7, 7404, 68.9, 59.0, 43.8 31.5, 19.8 14.2 7.7, 6.4. ^{29}Si CPMAS NMR (79.5 MHz) δ: -72.0 (T^3), -98.0 (Q^2), -107.3 (Q^3), -115.9 (Q^4). BET Surface Area: 759 m^2/g. BJH Desorption Average Pore Diameter: 7.2 nm. Vp = 1.25 cm^3/g. SAXS: d = 10.4 nm; a = 12.0 nm.

Silicas functionalized with nitroxides SBA_m-B, SBA_m-C, SBA_m-D and SBA_m-E:

The homolysis of C-O bond was triggered by warming a suspension of silica in *tert*-butylbenzene at 130°C. In order to have different concentrations in nitroxide, the reaction time was determined with the kinetic fragmentation curves set from the EPR studies of the behavior of silicas **SBA_{56}-2**, **SBA_{55}-3**, **SBA_{60}-4** and **SBA_{60}-5** (Figure 1). After filtration, the silica was washed with ethanol and acetone. The concentration (Tables 1 to 4) was estimated by comparison with the integration of the EPR signal of a SBA silica functionalized in the pore with TEMPO moieties for which the loading was determined by TGA.

Figure S1: Kinetic of fragmentation of **SBA_{56}-2**, **SBA_{55}-3**, **SBA_{60}-4** and **SBA_{60}-5** in *tert*-butylbenzene at 130°C

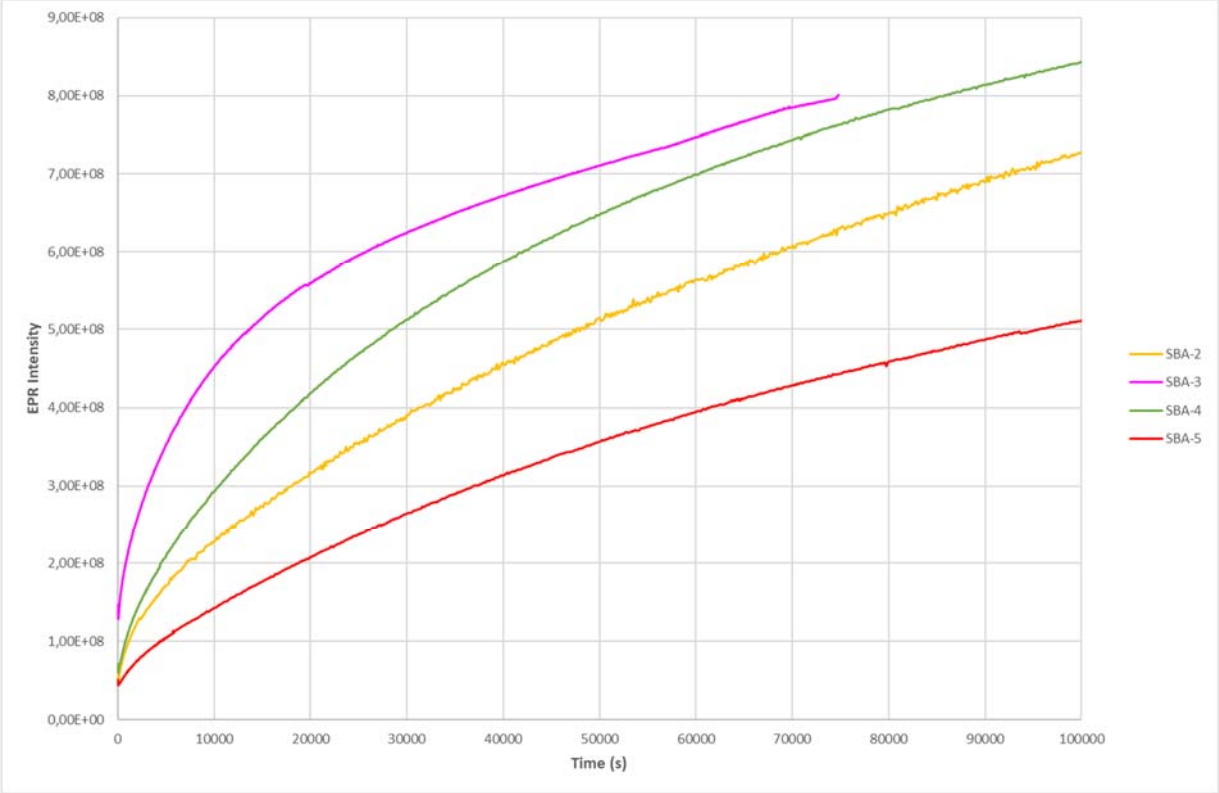


Table SI-1: References and concentrations in nitroxide for **SBA_{56}-2**.

Starting silica	**SBA_{56}-2**	**SBA_{56}-2**	**SBA_{56}-2**	**SBA_{56}-2**	**SBA_{56}-2**	**SBA_{56}-2**	**SBA_{56}-2**
Nitroxide functionalized silica	**SBA_{221}-B**	**SBA_{94}-B**	**SBA_{61}-B**	**SBA_{41}-B**	**SBA_{22}-B**	**SBA_{21}-B**	**SBA_{22}-B**
Concentration in nitoxide ($\mu mol\ g^{-1}$)	69	154	226	316	498	515	504

Table SI-2: References and concentrations in nitroxide for **SBA_{55}-3**.

Starting silica	**SBA_{55}-3**	**SBA_{55}-3**	**SBA_{55}-3**	**SBA_{55}-3**	**SBA_{55}-3**	**SBA_{55}-3**	**SBA_{55}-3**
Nitroxide functionalized silica	**SBA_{116}-C**	**SBA_{80}-C**	**SBA_{54}-C**	**SBA_{34}-C**	**SBA_{29}-C**	**SBA_{21}-C**	**SBA_{15}-C**
Concentration in nitoxide ($\mu mol\ g^{-1}$)	132	185	259	377	417	532	656

Table SI-3: References and concentrations in nitroxide for **SBA_{60}-4**.

Starting silica	**SBA_{60}-4**	**SBA_{60}-4**	**SBA_{60}-4**	**SBA_{60}-4**	**SBA_{60}-4**	**SBA_{60}-4**	**SBA_{60}-4**	**SBA_{60}-4**
Nitroxide functionalized silica	**SBA_{156}-D**	**SBA_{119}-D**	**SBA_{50}-D**	**SBA_{38}-D**	**SBA_{25}-D**	**SBA_{35}-D**	**SBA_{21}-D**	**SBA_{27}-D**
Concentration in nitoxide ($\mu mol\ g^{-1}$)	100	119	257	318	439	336	502	415

Table SI-4: References and concentrations in nitroxide for **SBA_{60}-5**.

Starting silica	**SBA_{60}-5**	**SBA_{60}-5**	**SBA_{60}-5**	**SBA_{60}-5**	**SBA_{60}-5**	**SBA_{60}-5**	**SBA_{60}-5**	**SBA_{60}-5**
Nitroxide functionalized silica	**SBA_{510}-E**	**SBA_{243}-E**	**SBA_{118}-E**	**SBA_{106}-E**	**SBA_{75}-E**	**SBA_{44}-E**	**SBA_{31}-E**	**SBA_{30}-E**
Concentration in nitoxide ($\mu mol\ g^{-1}$)	32	68	134	147	201	315	415	450

Experimental Procedures for EPR Analysis

CW EPR Spectroscopy : EPR experiments were performed 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.

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 110K. The microwave pulses were amplified with a 1kW TWT.

Field sweep ESE two-pulse experiments ($\pi/2$–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.

A conventional inversion-recovery sequence (π–t–$\pi/2$–τ–π–τ–echo) was applied to determine T_{1e} with a τ delay of 250ns and a 32ns detector gate, centered at the maximum of the echo signal. The inversion pulse length was 32ns and the $\pi/2$ and the refocusing π pulses were 52ns and 104ns, respectively. Initial delay t was 2000ns. Experiments were recorded at magnetic field corresponding to the maximum intensity in the field sweep spectra.

Table SI-5: Mean longitudinal relaxation time (T_{1e}) and phase memory time (T_m) for **SBA_n-B**.

Reference	Radical contents	Pulsed EPR			
	µmol/g	T_{1e} (µs)	β	$<T_{1e}>$ (µs)	T_m (ns)
SBA_{221}-B	69	90.9	0.64	125.3	349
SBA_{94}-B	154	68.0	0.65	92.2	280
SBA_{61}-B	226	54.4	0.69	69.5	236
SBA_{41}-B	316	49.5	0.63	70.6	232
SBA_{22}-B	498	36.6	0.58	57.6	204
SBA_{21}-B	504	36.3	0.58	56.5	207
SBA_{22}-B	515	37.0	0.55	63.3	207

Table SI-6: Mean longitudinal relaxation time (T_{1e}) and phase memory time (T_m) for **SBA_n-C**.

Reference	Radical contents	Pulsed EPR			
	µmol/g	T_{1e} (µs)	β	$<T_{1e}>$ (µs)	T_m (ns)
SBA_{116}-C	132	60.8	0.65	83.0	255
SBA_{80}-C	185	51.28	0.62	73.3	230
SBA_{54}-C	259	46.21	0.63	65.7	211
SBA_{34}-C	377	40.21	0.59	61.2	206
SBA_{29}-C	417	39.22	0.63	55.9	204
SBA_{21}-C	532	35.25	0.60	53.5	209
SBA_{15}-C	656	39.37	0.60	58.6	224

Table SI-7: Mean longitudinal relaxation time (T_{1e}) and phase memory time (T_m) for **SBA_n-D**.

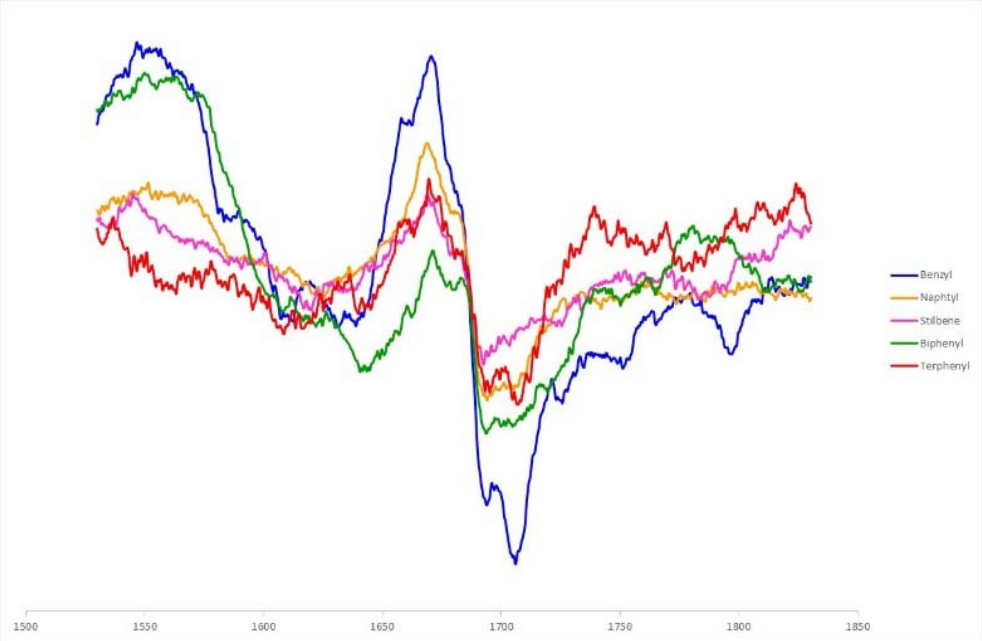
Reference	Radical contents	Pulsed EPR			
	µmol/g	T_{1e} (µs)	β	$<T_{1e}>$ (µs)	T_m (ns)
SBA_{156}-D	100	83.8	0.67	111.1	334
SBA_{119}-D	119	72.2	0.60	108.3	306
SBA_{50}-D	257	47.2	0.62	68.3	220
SBA_{38}-D	318	40.8	0.53	73.5	210
SBA_{35}-D	336	46.8	0.51	89.6	234
SBA_{27}-D	415	38.6	0.50	76.5	223
SBA_{25}-D	439	44.7	0.61	65.5	212
SBA_{21}-D	502	35.2	0.55	60.3	215

Table SI-8: Mean longitudinal relaxation time (T_{1e}) and phase memory time (T_m) for **SBA_n-E**.

Reference	Radical contents	Pulsed EPR			
	µmol/g	T_{1e} (µs)	β	$<T_{1e}>$ (µs)	T_m (ns)
SBA_{510}-E	32	99.8	0.71	124.1	526
SBA_{243}-E	68	82.9	0.74	99.4	386
SBA_{118}-E	134	67.5	0.68	87.8	346
SBA_{106}-E	147	71.8	0.68	92.7	299
SBA_{75}-E	201	53.6	0.68	69.9	260
SBA_{44}-E	315	49.5	0.66	66.2	223
SBA_{31}-E	415	39.1	0.63	55.2	192
SBA_{30}-E	450	44.9	0.62	64.0	234

Half-field adsorption EPR signal for SBA_{434}-A, SBA_{498}-B, SBA_{532}-C, SBA_{439}-D and SBA_{415}-E.

EPR spectra of **SBA_{434}-A, SBA_{498}-B, SBA_{532}-C, SBA_{439}-D and SBA_{415}-E**. Half-field transition. The EPR spectra were recorded at 9.4 GHz at 110 K in TCE.



Experimental Procedures for DNP NMR Analysis

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 (263.334 GHz) occurred at the maximum DNP enhancement of TOTAPOL.[11] 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.,[12] 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.[13] Hartmann–Hahn matching conditions and CP contact times were optimized directly on the samples under study. Detailed experimental parameters are reported Table SI-NMR-1. Sapphire rotors were used for all DNP experiments. They were sealed with a Teflon insert and capped with zirconia caps.

Table SI-NMR-1. Parameters used to record the ^{13}C CPMAS experiments (with the microwave field *on* or *off*).

Parameters	
Number of scans	8
Recycle delay (s)	(*)
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)	5.6
Δt_1 (μs)	-
Number of increments	-
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

(*) Systematically adjusted to 5 times the proton T1 relaxation time (measured with a saturation-recovery experiment)

[11] C. S. Song, K. N. Hu, C. G. Joo, T. M. Swager and R. G. Griffin, *J. Am. Chem. Soc.*, 2006, **128**, 11385-11390.
[12] 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.
[13] G. Metz, X. Wu and S. O. Smith, *J. Magn. Reson. Ser. A*, 1994, **110**, 219-227.

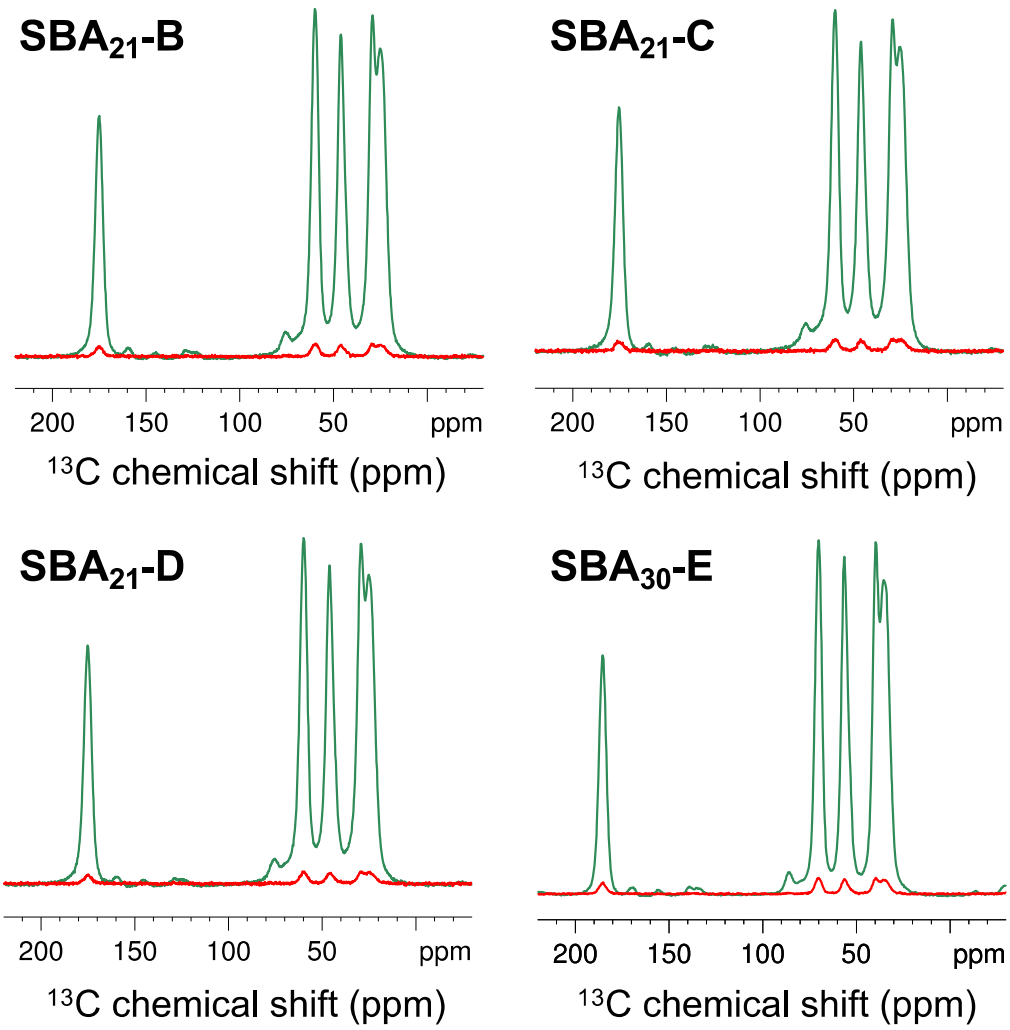
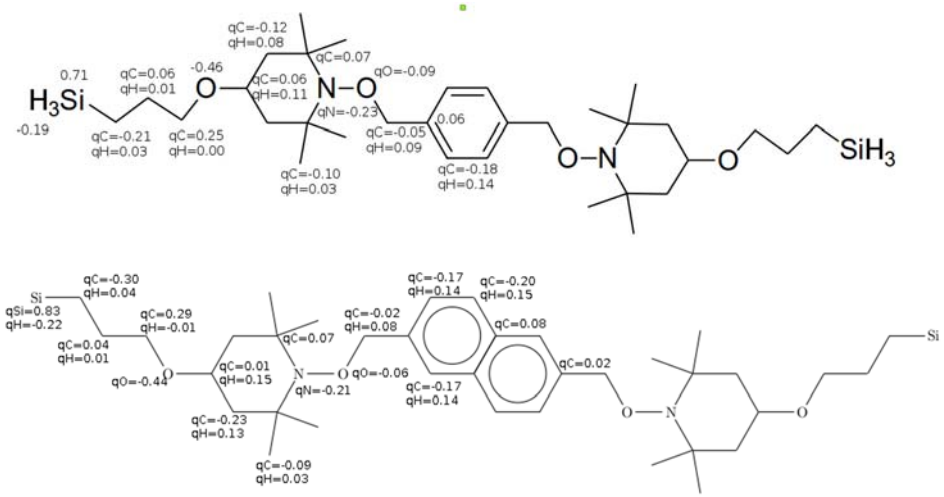


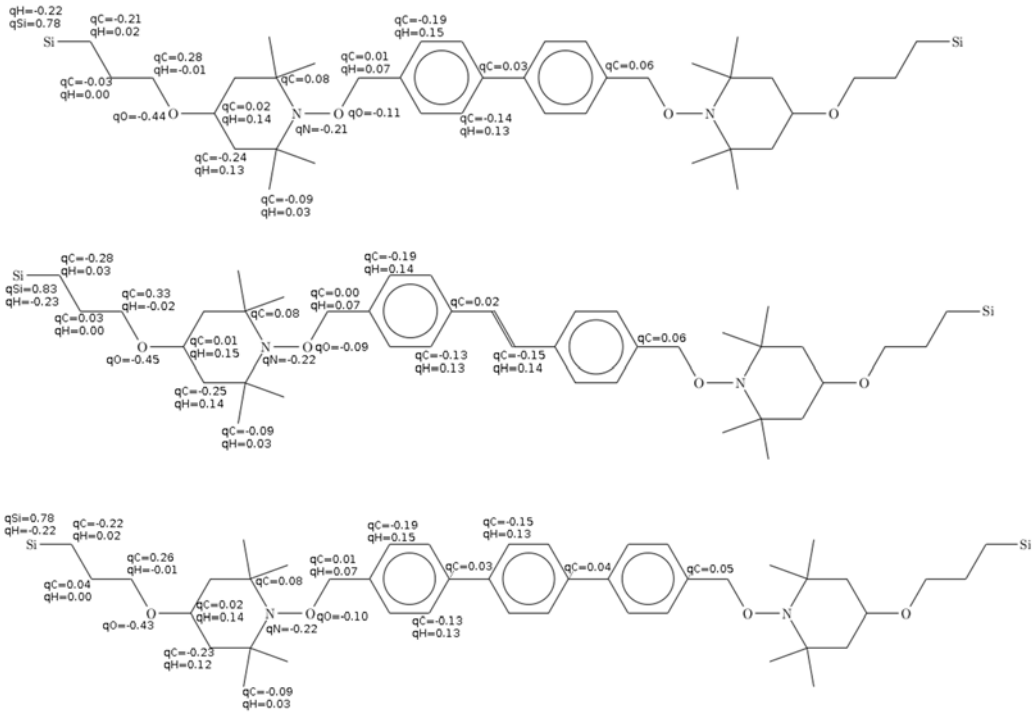
Figure S2. $^{1}H \rightarrow ^{13}C$ CP MAS spectra recorded with (green) and without (red) microwave irradiation at 9.4 T and ~105K of 4 **SBA$_m$-*x*** samples (where *x* is B, C, D, or E) impregnated with a 0.2 M aqueous solution of U-$^{13}C/^{15}N$ proline. These samples correspond to the maximum ^{13}C CP DNP signal enhancements obtained for each of the 4 families of materials (B, C, D, or E).

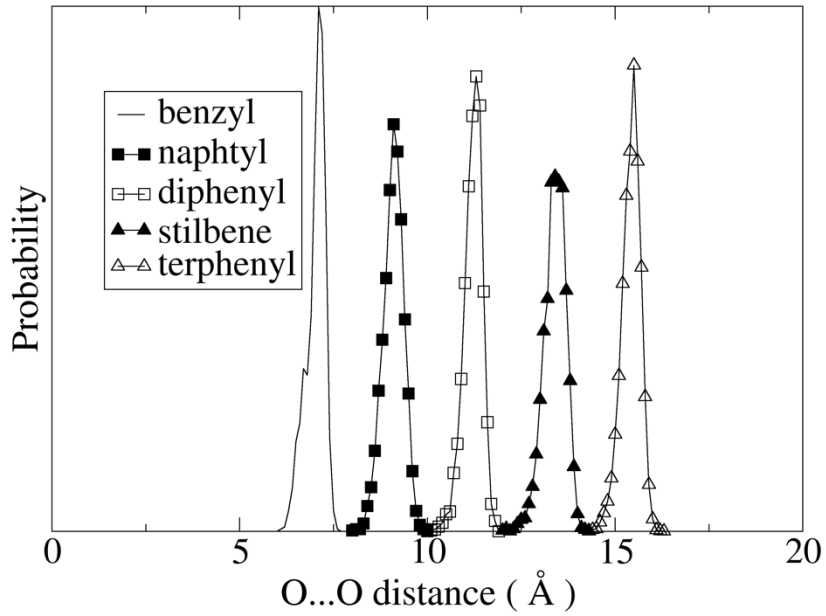
MD Simulations

In order to study the distance between the two oxygen atoms for precursors (**1** to **5**) in all possible conformations, molecular dynamics simulations were performed with the DLPOLY_4 software.[14] Precursors, where $Si(OEt)_3$ end-groups were replaced by SiH_3 end-groups, were separately immersed in a box of water molecules (the number of water molecules varied between 2680 and 2744 depending on the precursor). These boxes were first submitted to a NPT equilibration run (at 300 K and 1 atm) using the Melchionna modification of the Nosé-Hoover algorithm[15] (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 side length settled between 43 and 44 Å after relaxation. These classical simulations used DREIDING[16] force field for the precursor and SPCE[17] for the water. The charges for the precursor were obtained following the RESP procedure[18] using Gaussian 09 software.

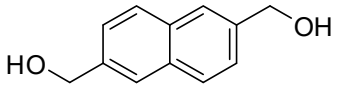


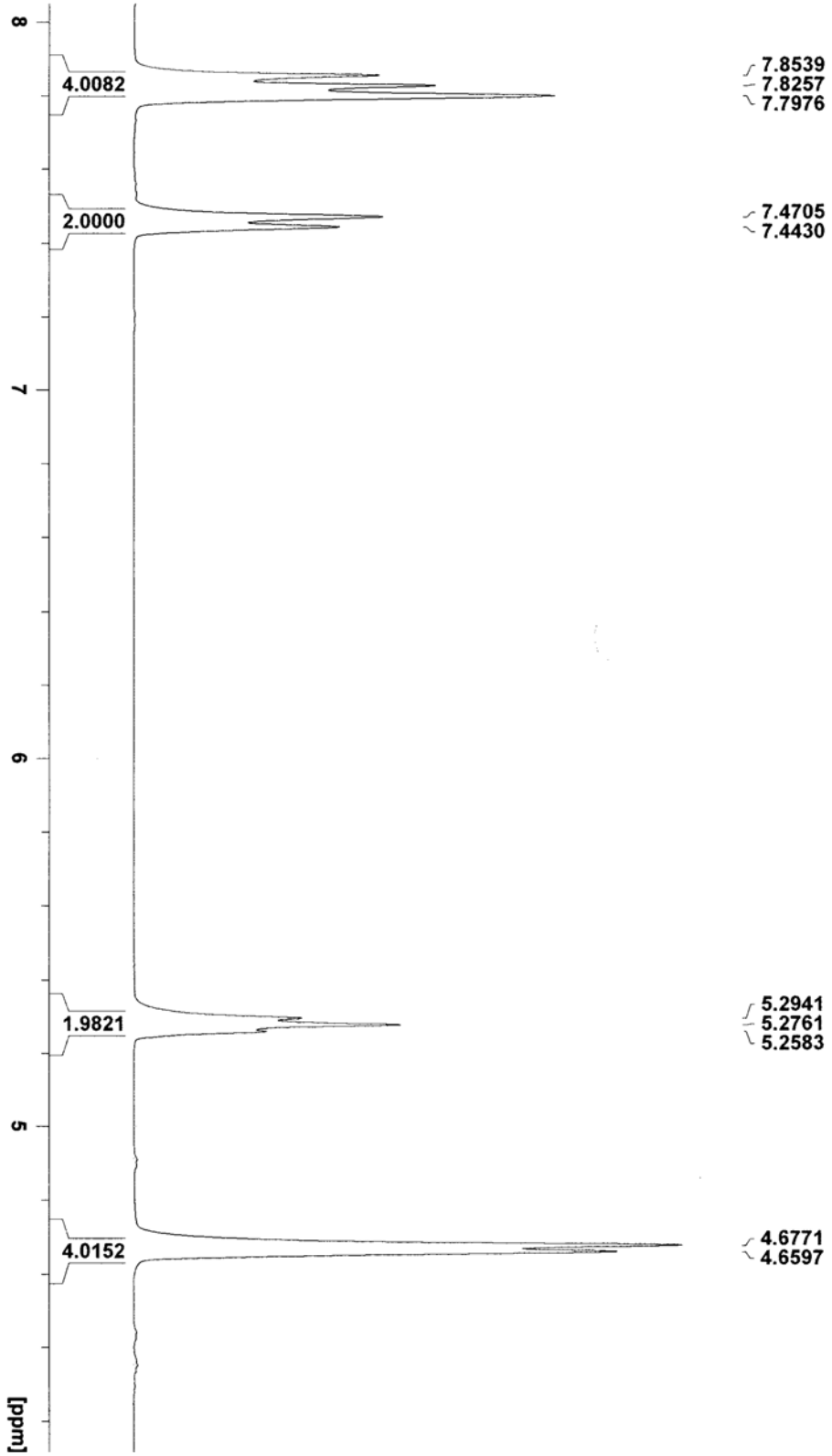
[14] I.T. Todorov, W. Smith, K. Trachenko, M.T. Dove, *J. Mat. Chem.*, **2006**, *16*, 1911-1918.
[15] S. Melchionna, G. Ciccotti, B. L. Holian, *Mol. Phys.,* **1993**, *78*, 533-544.
[16] S. Mayo, B. Olafson, W. A. Goddard III, *J. Phys. Chem.*, **1990**, *94*, 8897-8909.
[17] H. J. C. Berendsen, J. R. Grigera, T. P. Straatsma, *J. Phys. Chem.*, **1987**, *91*, 6269-6271.
[18] J. Wang, R. M. Wolf, J. W. Caldwell, P. A. Kollman, D. A. Case, *J. Comput. Chem.* **2004**, *25*, 1157-1174; Erratum in *J. Comput. Chem.* **2005**, *26*, 114.


qH=-0.22
qSi=0.78
Si
qC=-0.21
qH=0.02
qC=0.28
qH=-0.01
qC=-0.03
qH=0.00
qO=-0.44
O
qC=0.02
qH=0.14
N
O
qO=-0.11
qN=-0.21
qC=0.08
qC=-0.24
qH=0.13
qC=-0.09
qH=0.03
qC=-0.19
qH=0.15
qC=0.01
qH=0.07
qC=0.03
qC=0.06
qC=-0.14
qH=0.13
O
N
O
Si
qC=-0.28
qH=0.03
Si
qSi=0.83
qH=-0.23
qC=0.33
qH=-0.02
qC=0.03
qH=0.00
O
qO=-0.45
qC=0.01
qH=0.15
N
O
qO=-0.09
qN=-0.22
qC=0.08
qC=-0.25
qH=0.14
qC=-0.09
qH=0.03
qC=-0.19
qH=0.14
qC=0.00
qH=0.07
qC=0.02
qC=-0.13
qH=0.13
qC=-0.15
qH=0.14
qC=0.06
O
N
O
Si
qSi=0.78
qH=-0.22
Si
qC=-0.22
qH=0.02
qC=0.26
qH=-0.01
qC=0.04
qH=0.00
O
qO=-0.43
qC=0.02
qH=0.14
N
O
qO=-0.10
qN=-0.22
qC=0.08
qC=-0.23
qH=0.12
qC=-0.09
qH=0.03
qC=-0.19
qH=0.15
qC=0.01
qH=0.07
qC=0.03
qC=-0.13
qH=0.13
qC=-0.15
qH=0.13
qC=0.04
qC=0.05
O
N
O
Si

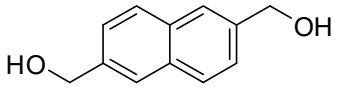

benzyl
naphtyl
diphenyl
stilbene
terphenyl
Probability
0
5
10
15
20
O...O distance (Å)

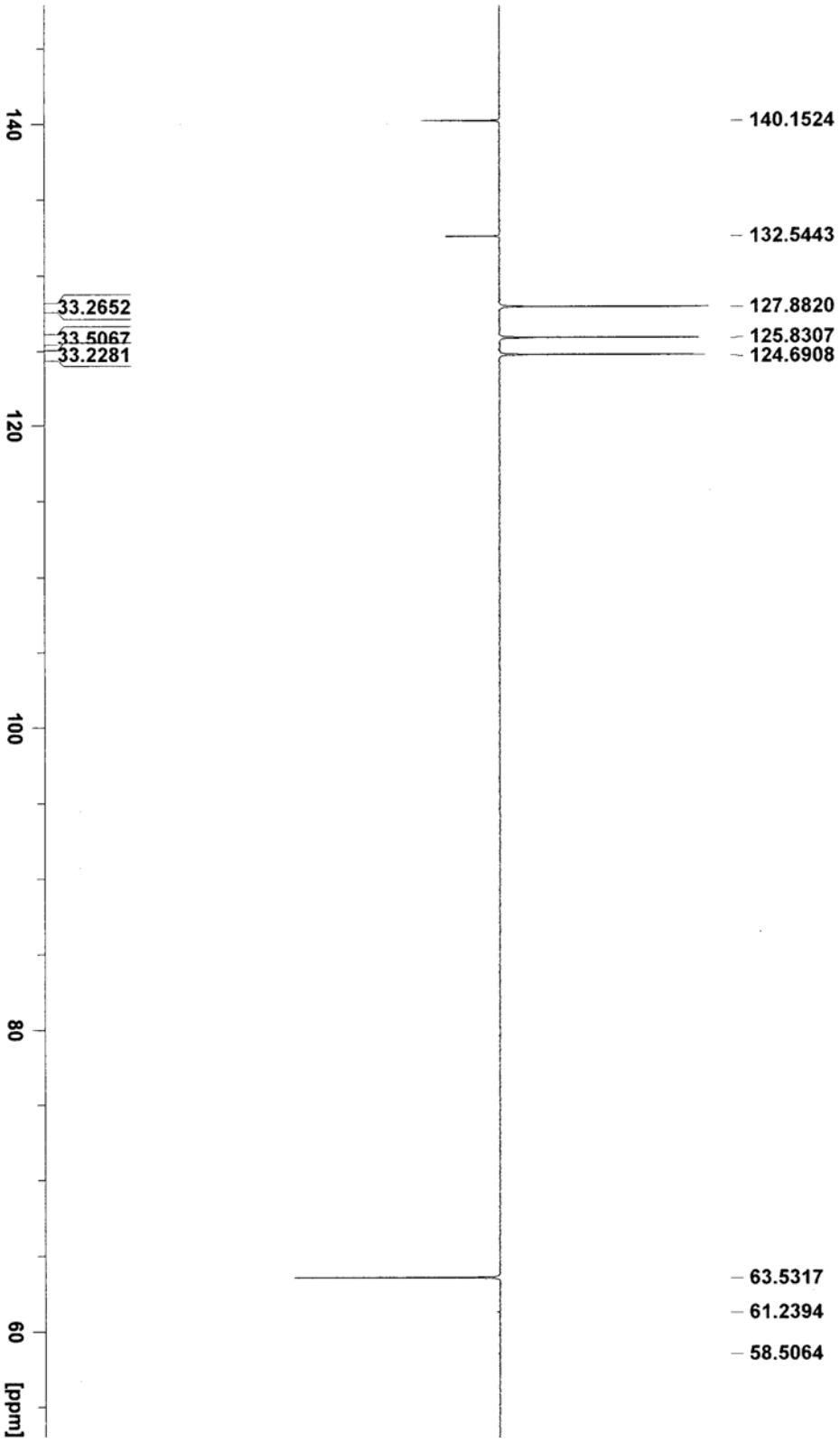
Naphthalene-2,6-diyldimethanol (9): ^{1}H NMR



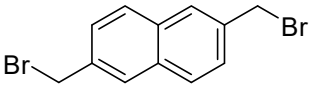


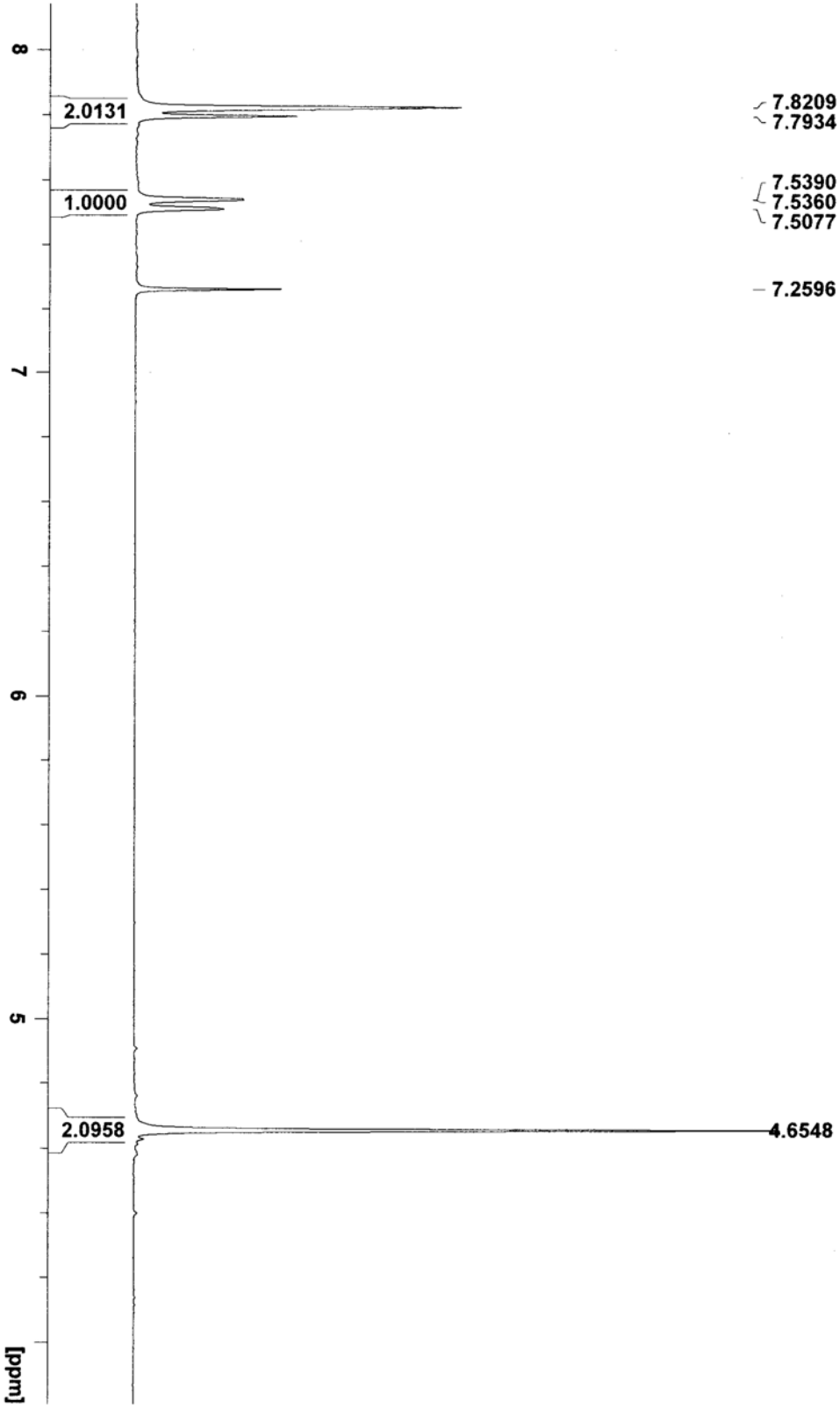
Naphthalene-2,6-diyldimethanol (9): ^{13}C APT



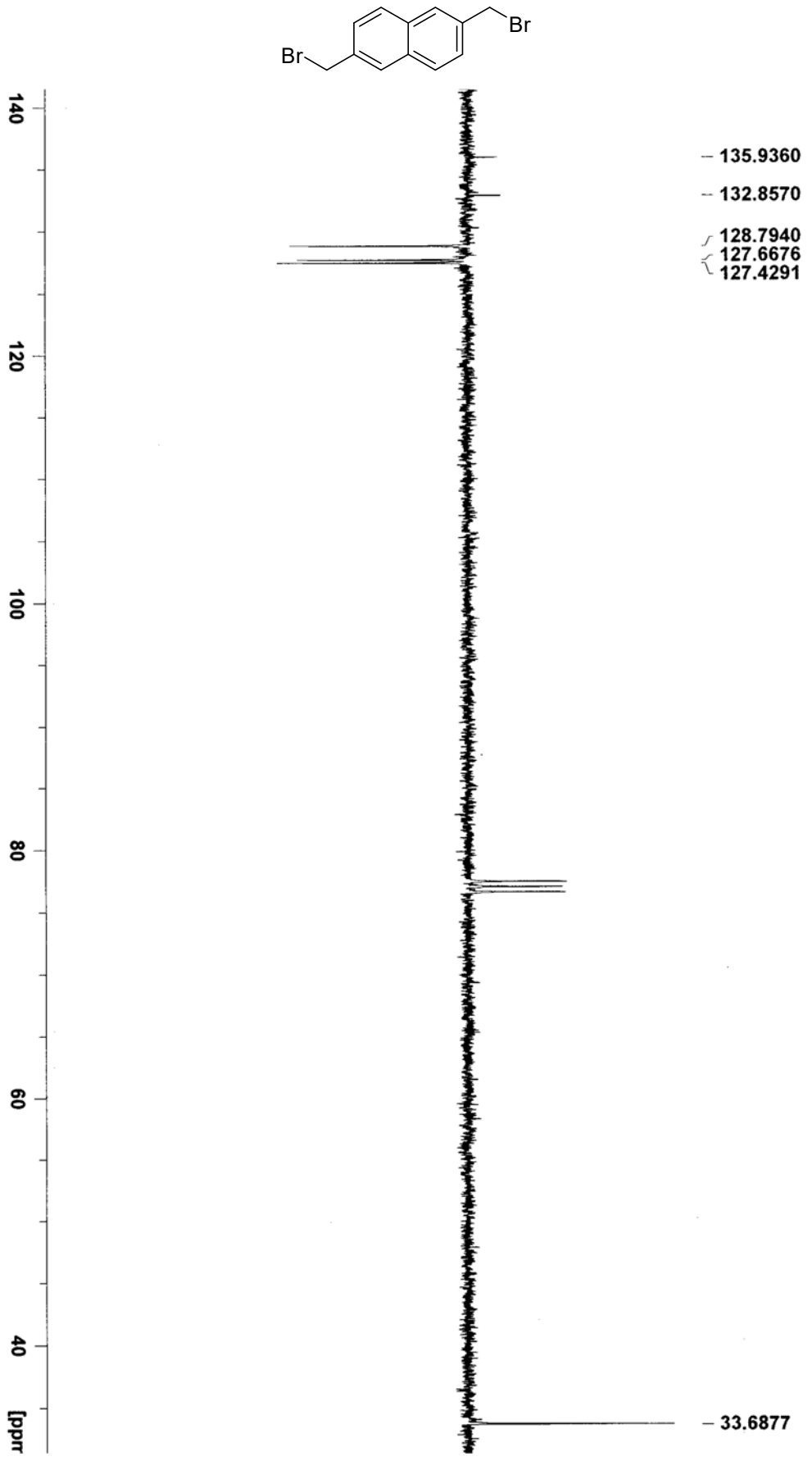


2,6-Bis(bromomethyl)naphthalene (8) : ^{1}H NMR

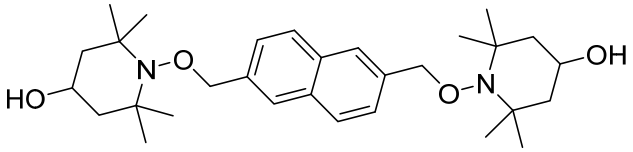


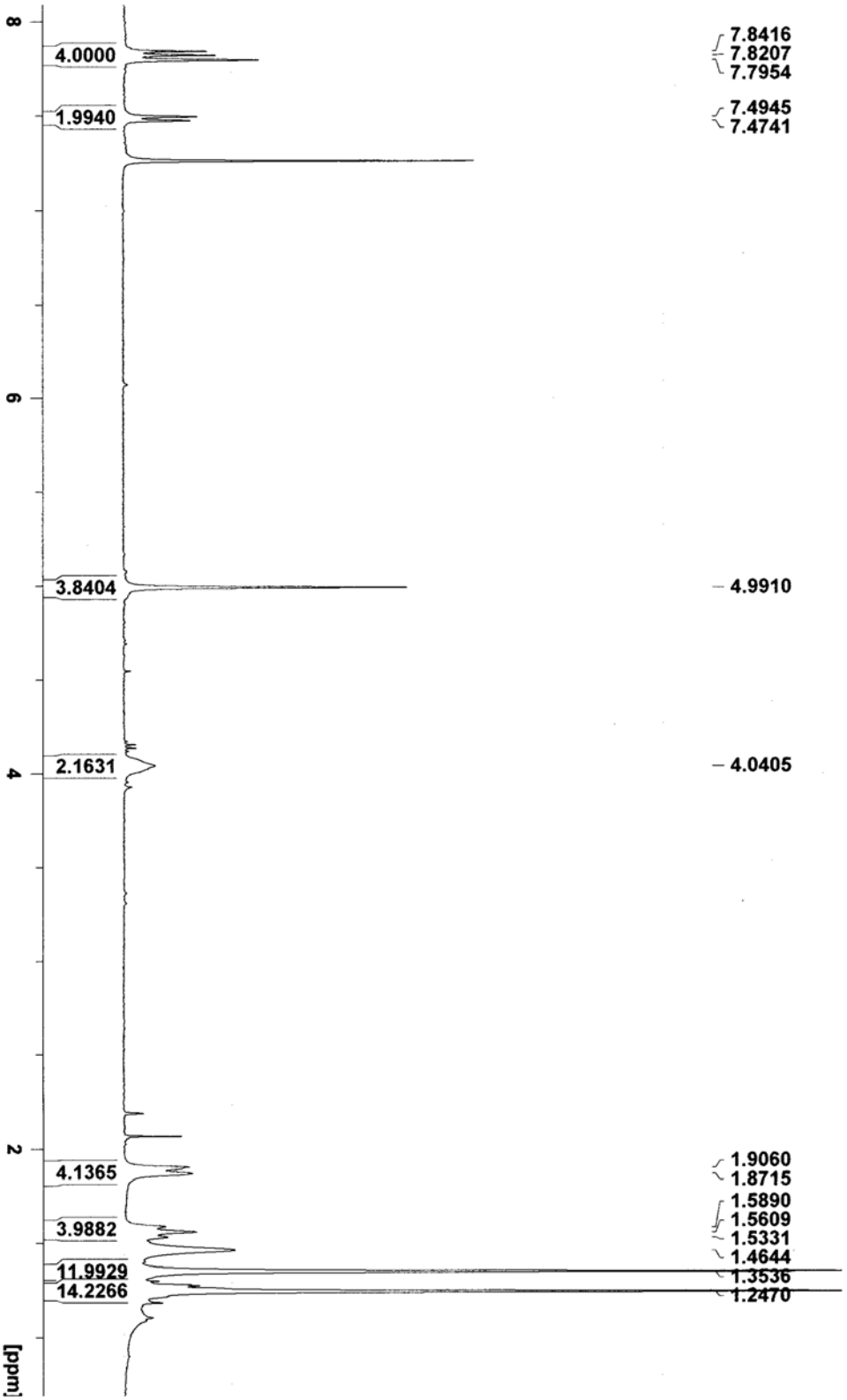


2,6-Bis(bromomethyl)naphthalene (8) : ^{13}C APT

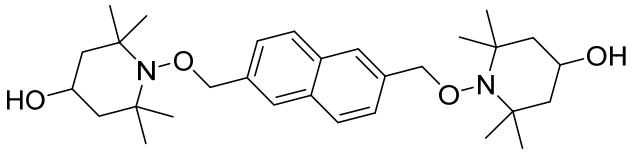


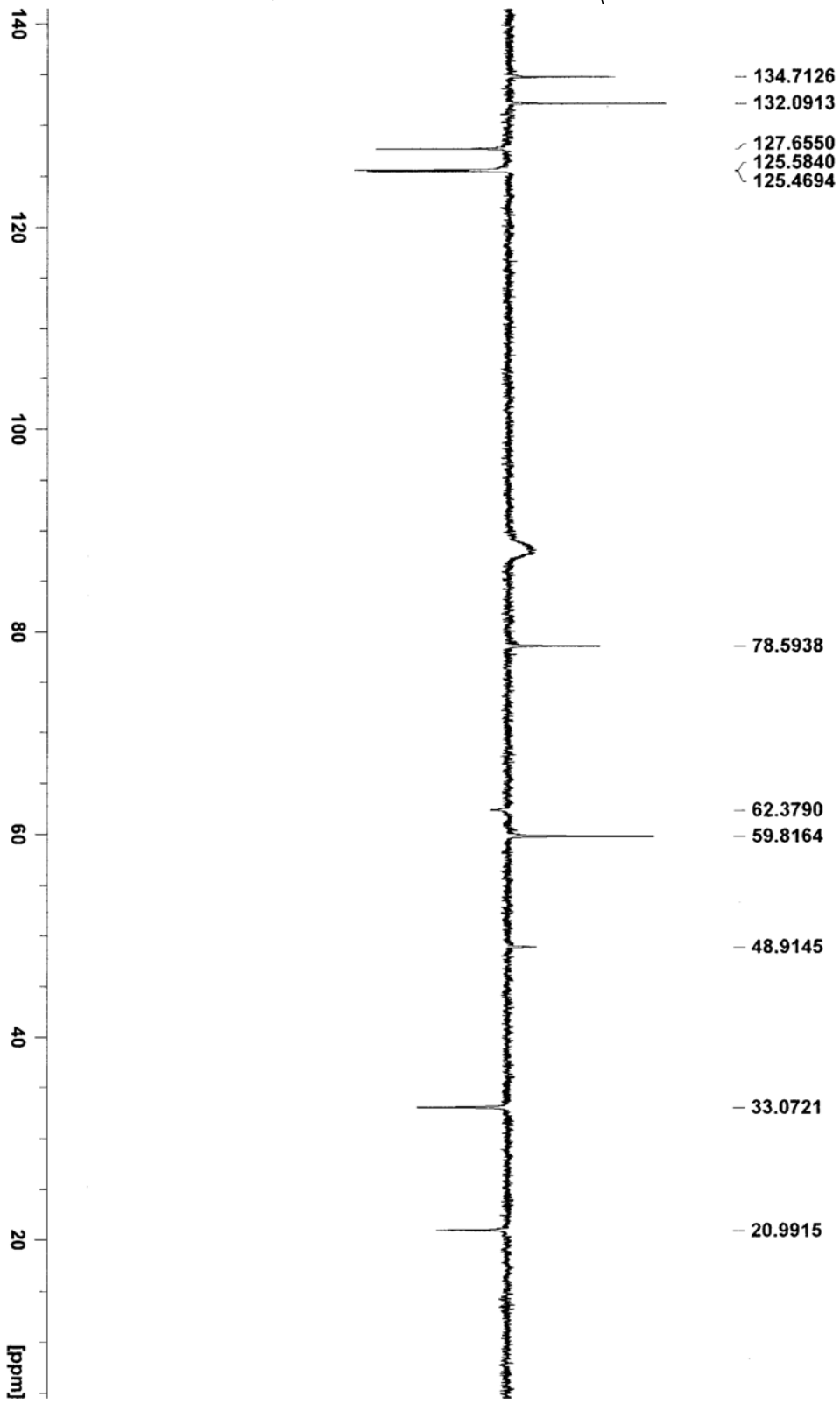
(1,1'-((Naphthalene-2,6-diylbis(methylene))bis(oxy))bis(2,2,6,6-tetramethylpiperidin-4-ol) (7) : ^{1}H NMR



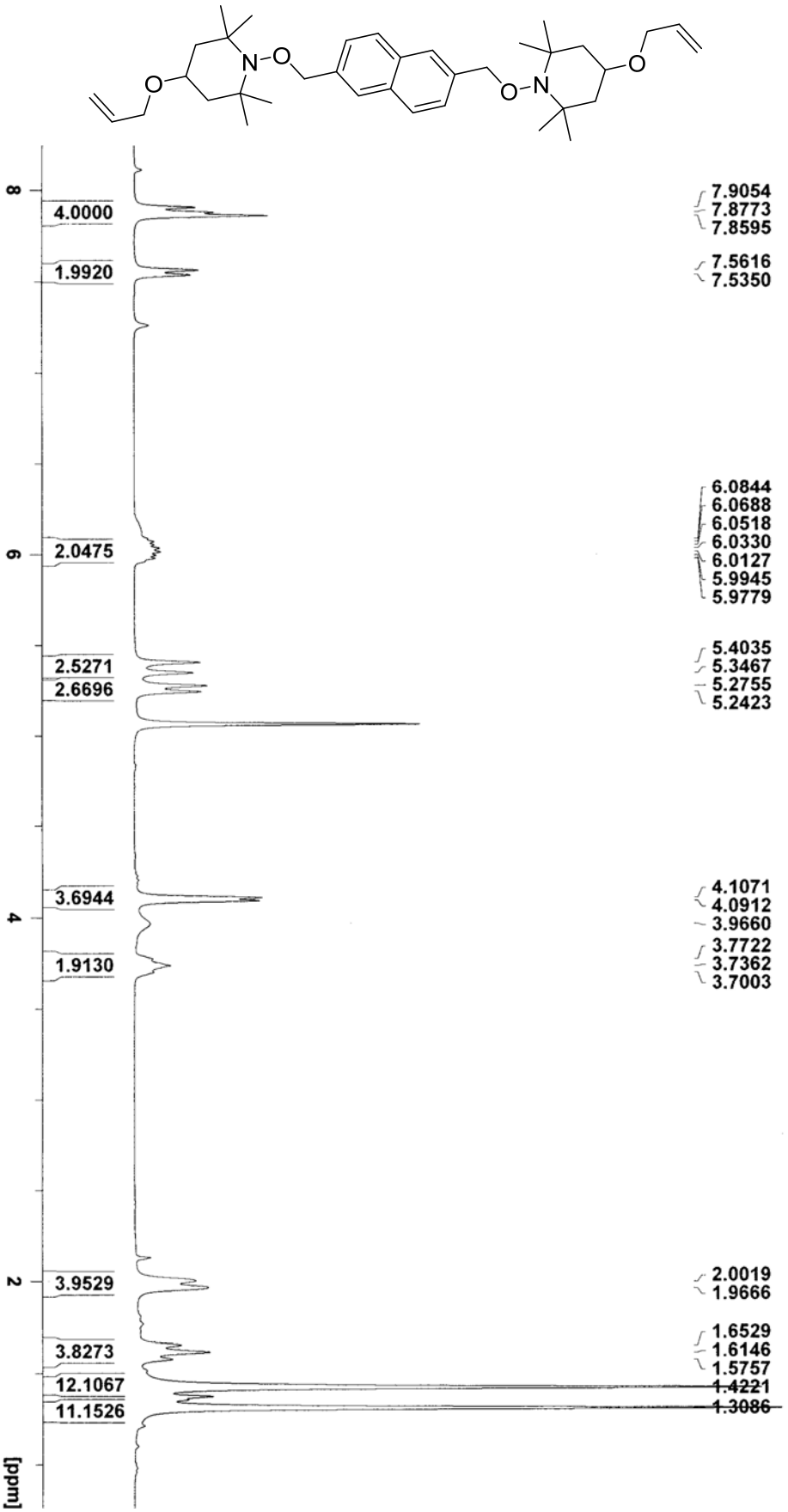


(1,1'-((Naphthalene-2,6-diylbis(methylene))bis(oxy))bis(2,2,6,6-tetramethylpiperidin-4-ol) (7) : ^{13}C APT

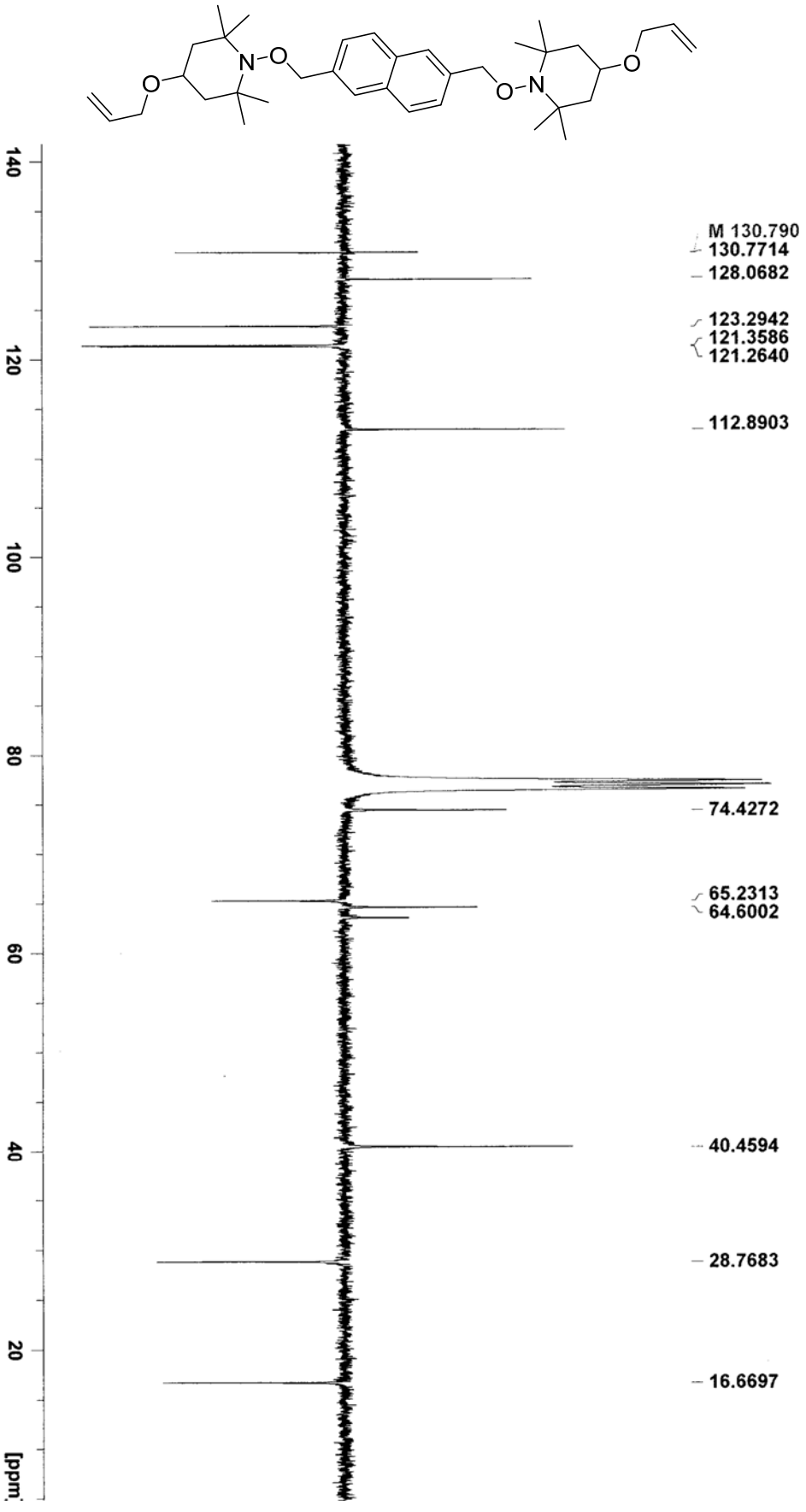




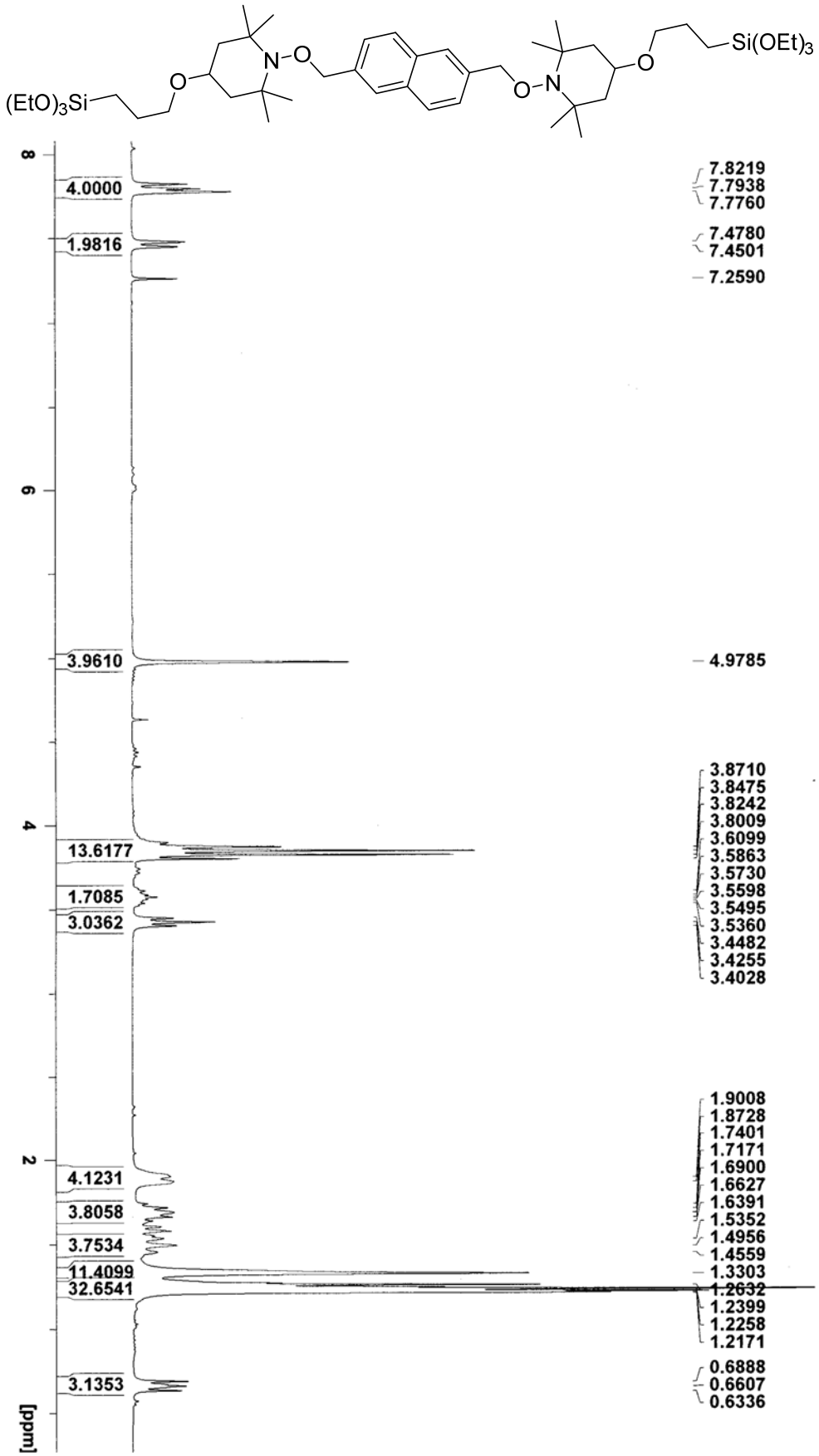
2,6-Bis(((4-(allyloxy)-2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)naphthalene (6) : ^{1}H NMR



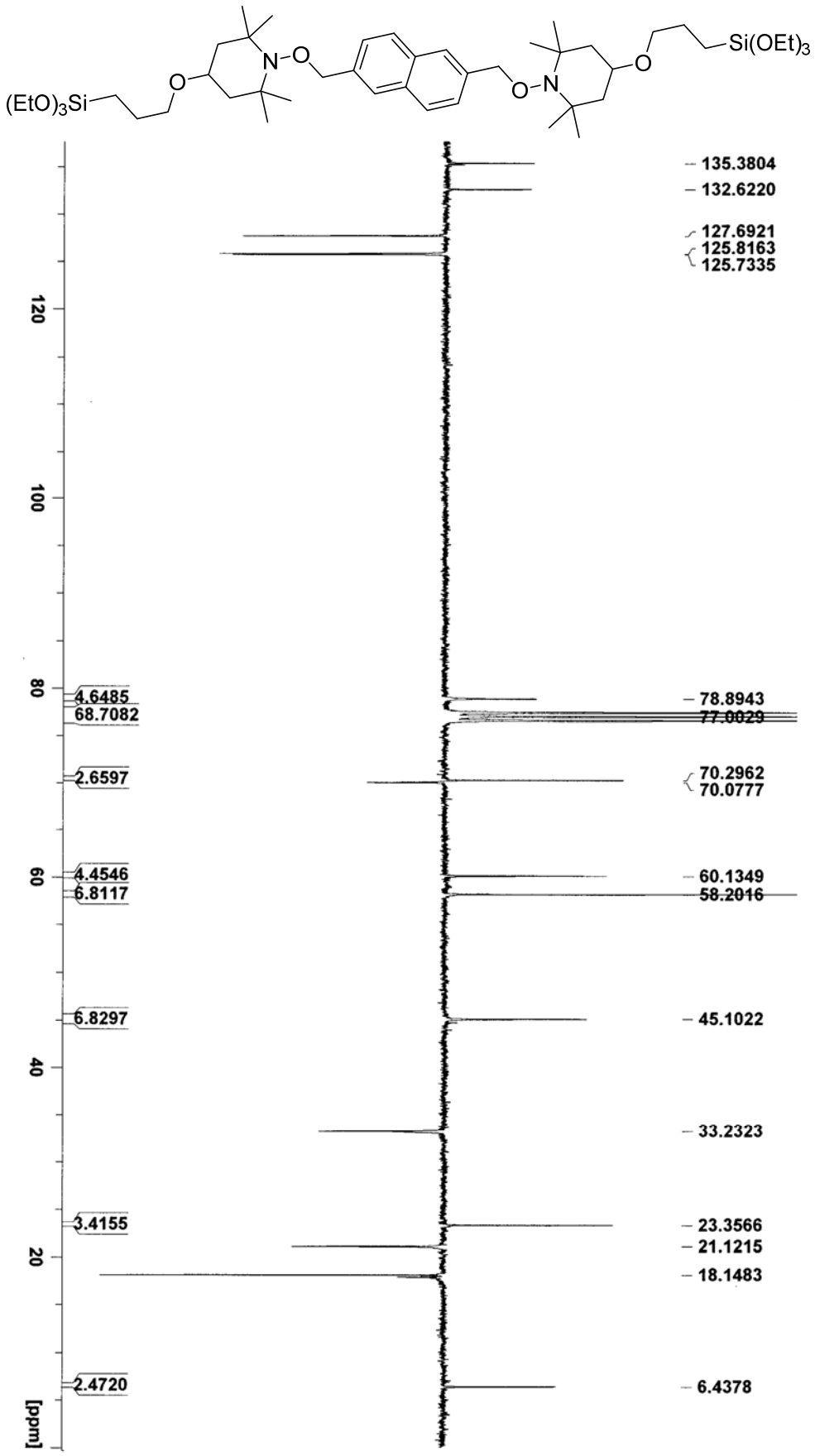
2,6-Bis(((4-(allyloxy)-2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)naphthalene (6) : ^{13}C APT



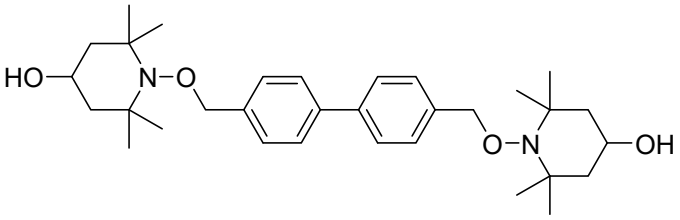
2,6-bis(((2,2,6,6-tetramethyl-4-(3-(triethoxysilyl)propoxy)piperidin-1-yl)oxy)methyl)naphthalene (2) : ^{1}H NMR

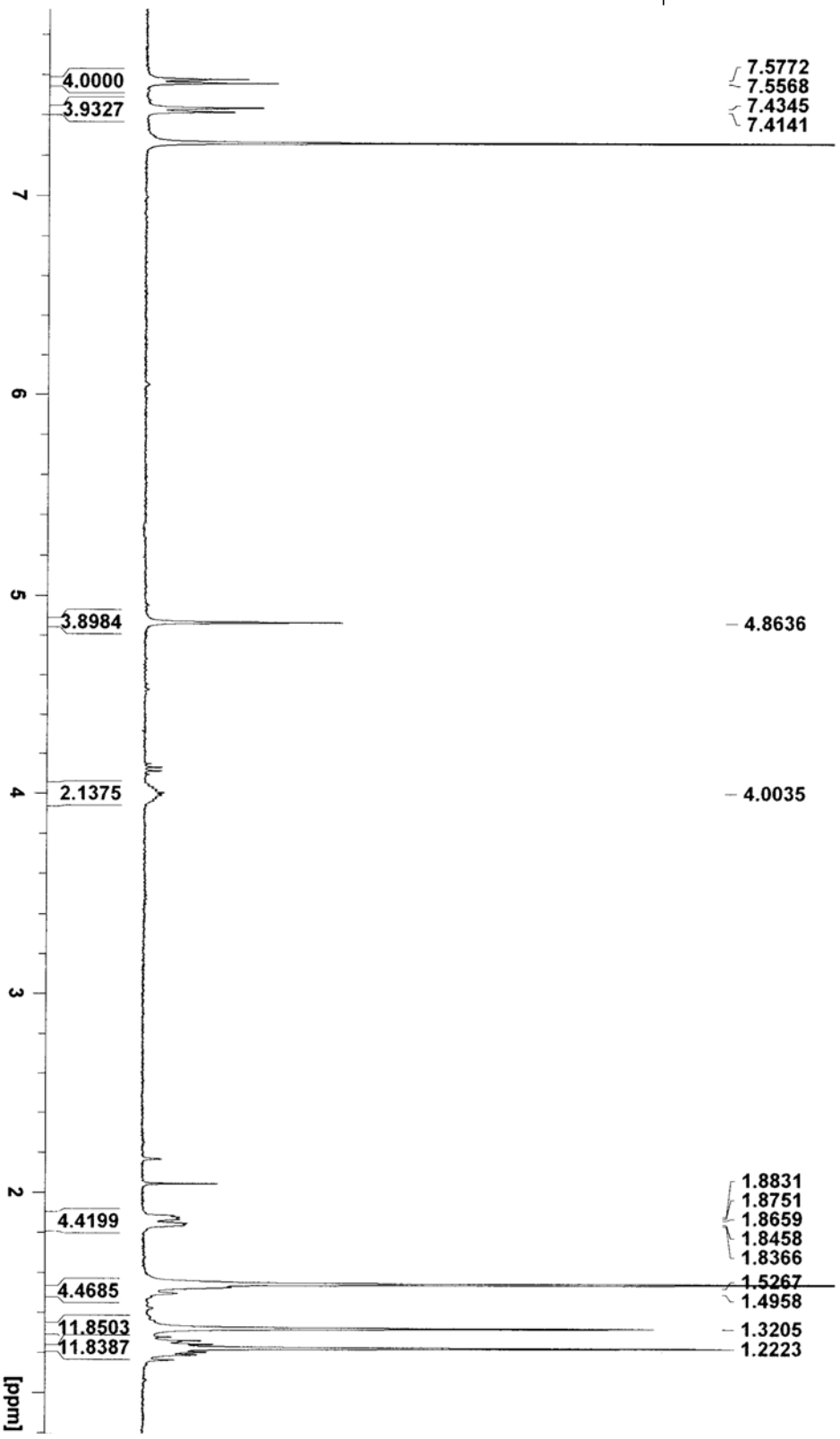


2,6-bis(((2,2,6,6-tetramethyl-4-(3-(triethoxysilyl)propoxy)piperidin-1-yl)oxy)methyl)naphthalene (2) : ^{13}C APT

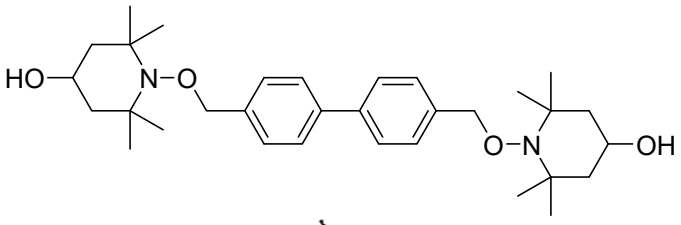


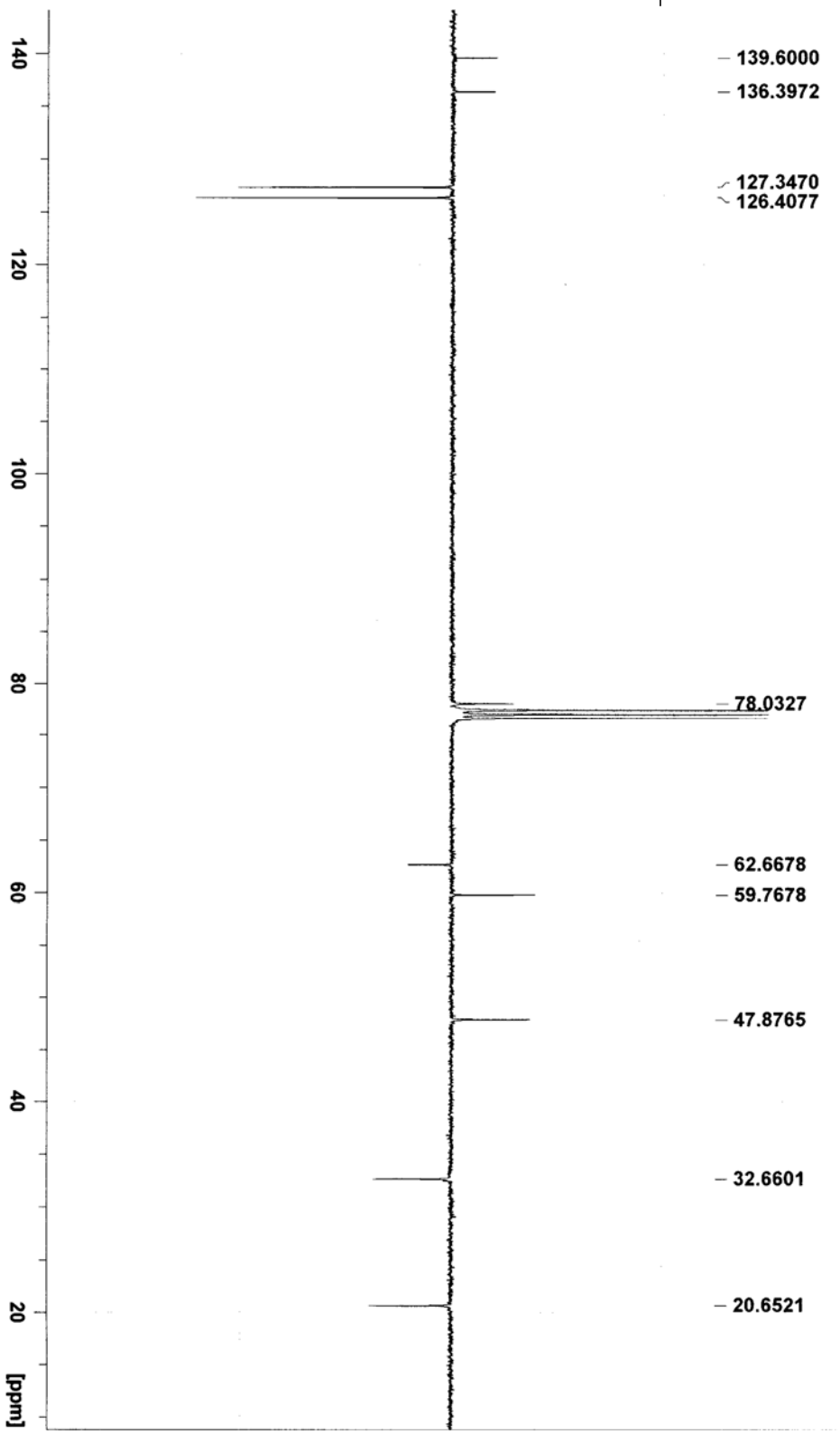
1,1'-(([1,1'-biphenyl]-4,4'-diylbis(methylene))bis(oxy))bis(2,2,6,6-tetramethylpiperidin-4-ol) (11) : ^{1}H NMR



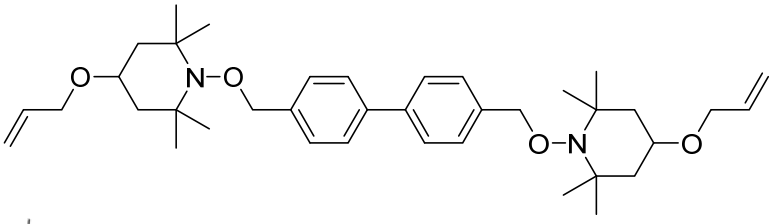


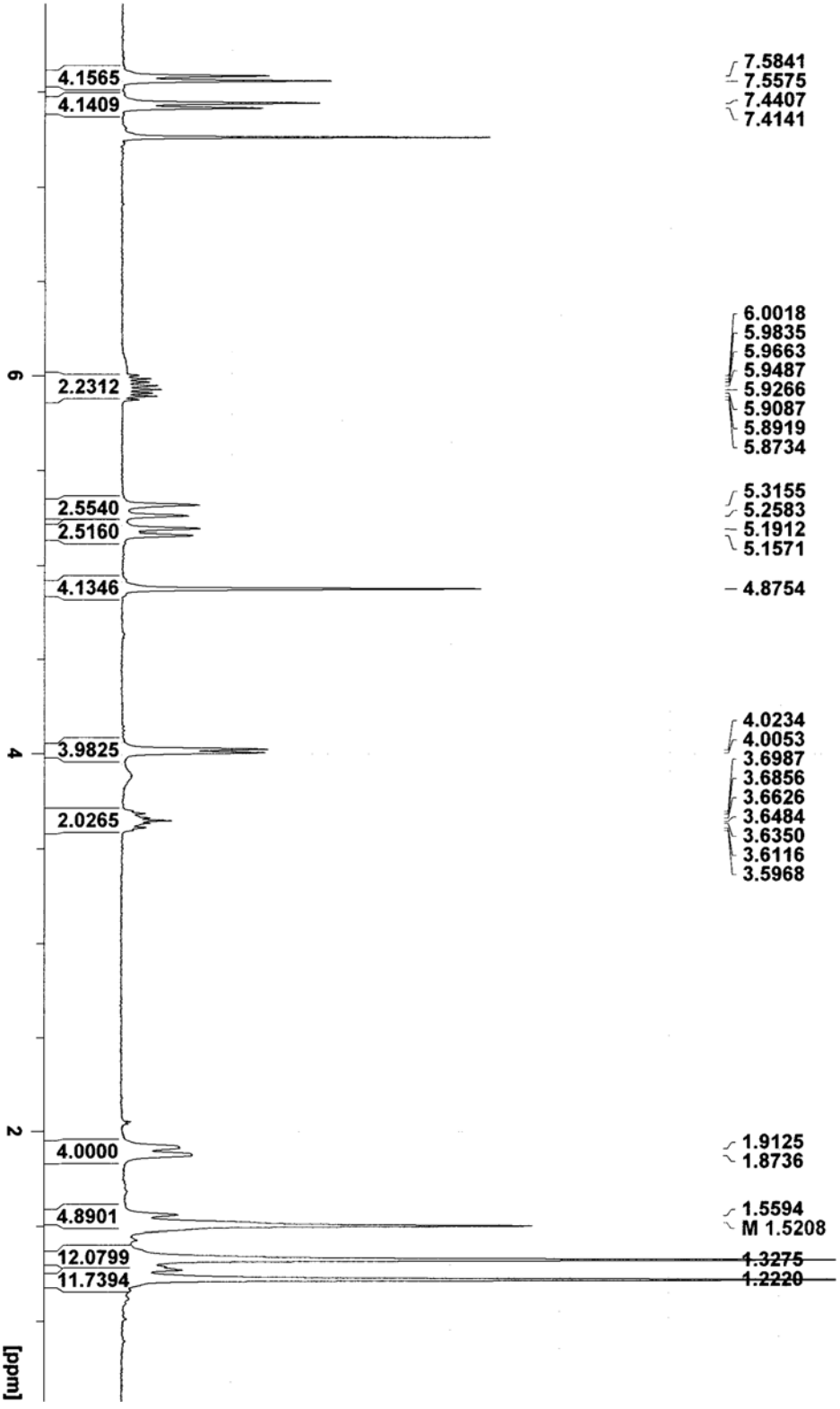
1,1'-(([1,1'-biphenyl]-4,4'-diylbis(methylene))bis(oxy))bis(2,2,6,6-tetramethylpiperidin-4-ol) (11) : ^{13}C APT



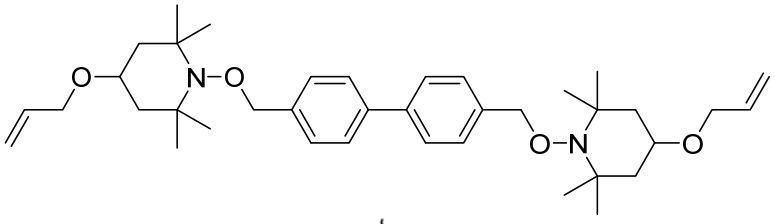


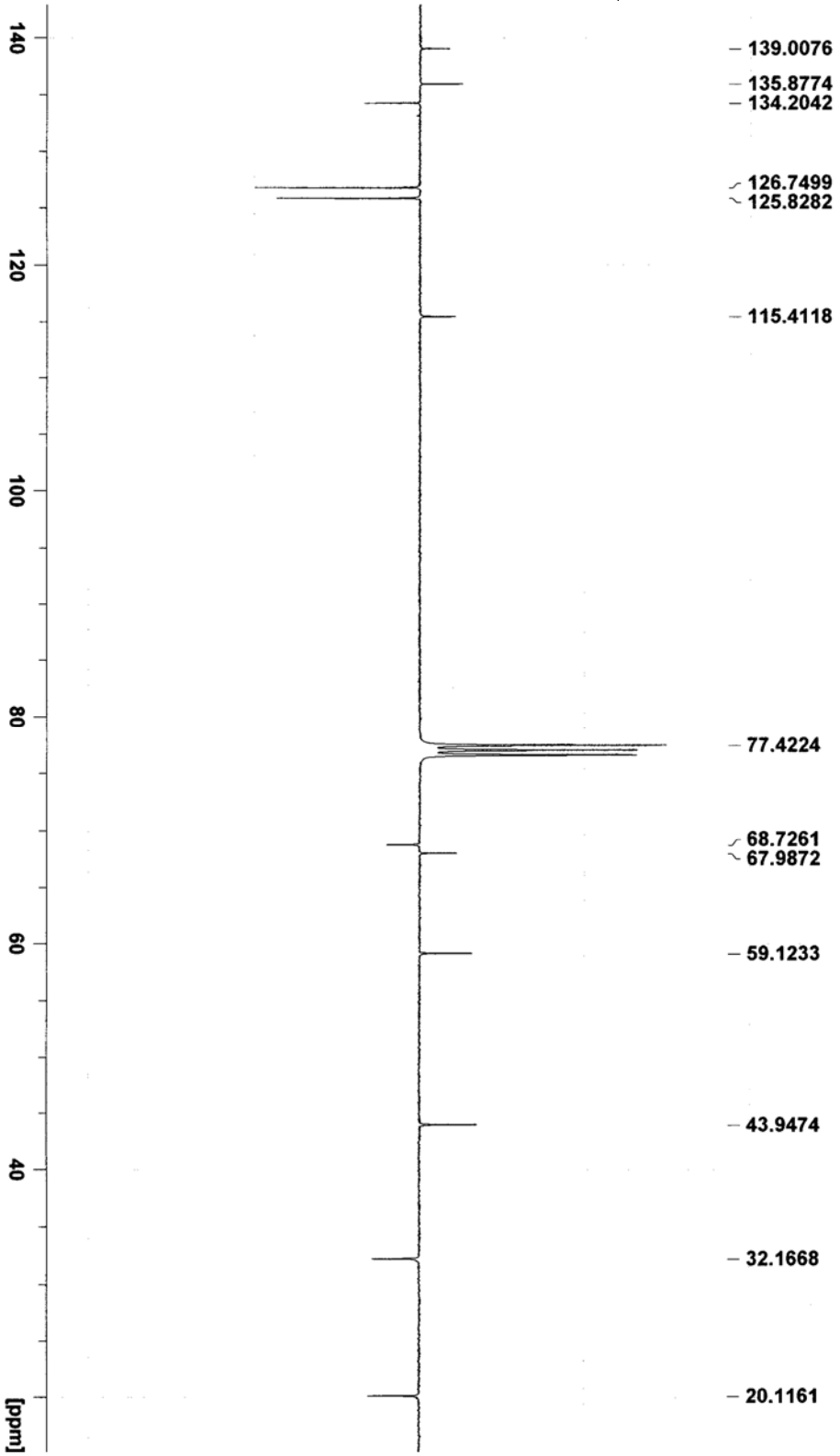
4,4'-bis(((4-(allyloxy)-2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-1,1'-biphenyl (10) : ^{1}H NMR



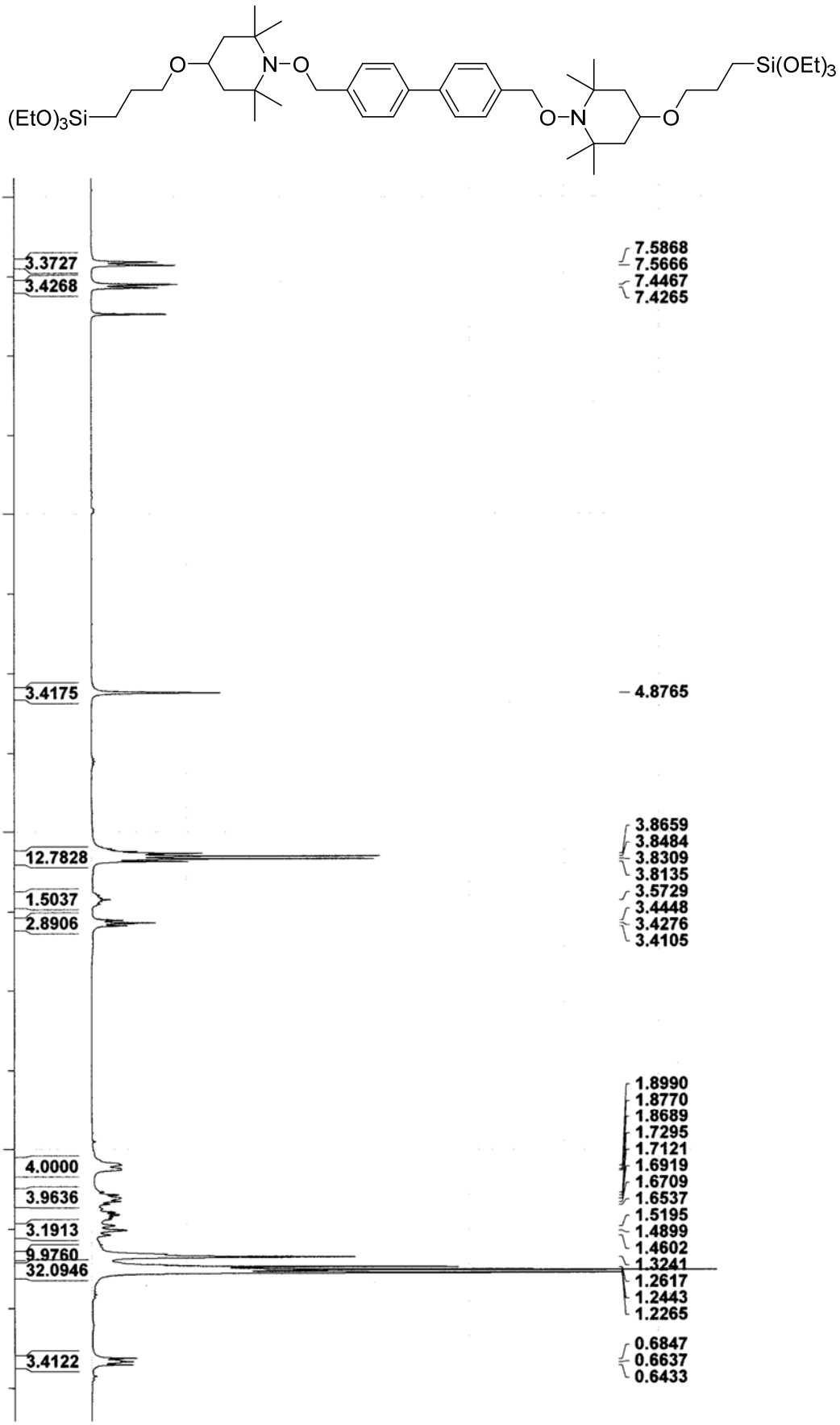


4,4'-bis(((4-(allyloxy)-2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-1,1'-biphenyl (10) : ^{13}C APT

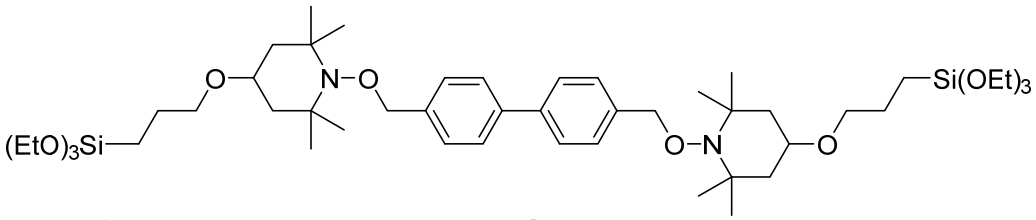


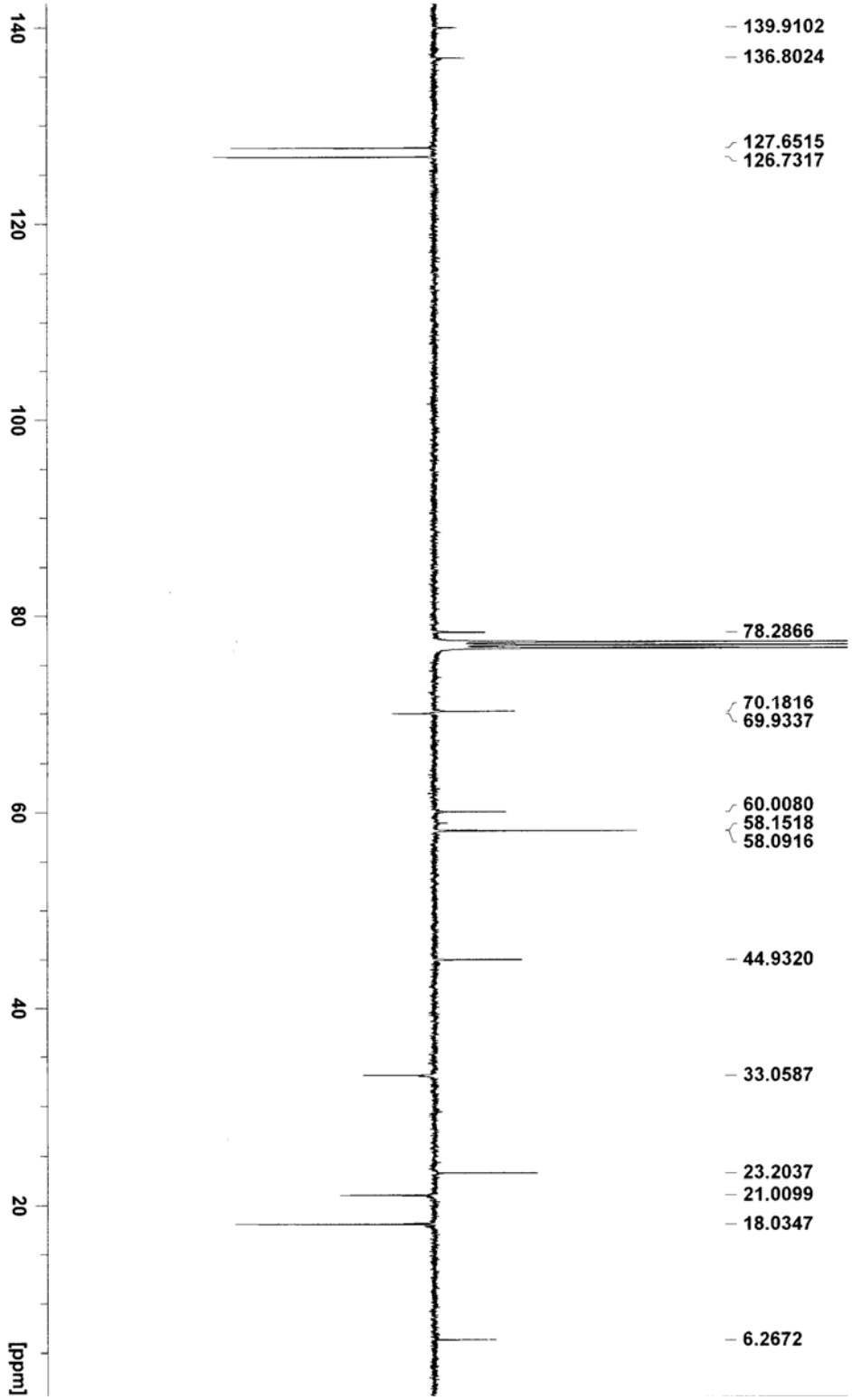


4,4'-bis(((2,2,6,6-tetramethyl-4-(3-(triethoxysilyl)propoxy)piperidin-1-yl)oxy)methyl)-1,1'-biphenyl (3) : ^{1}H NMR

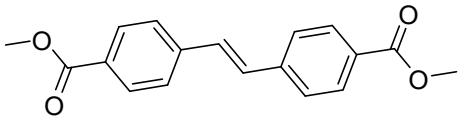


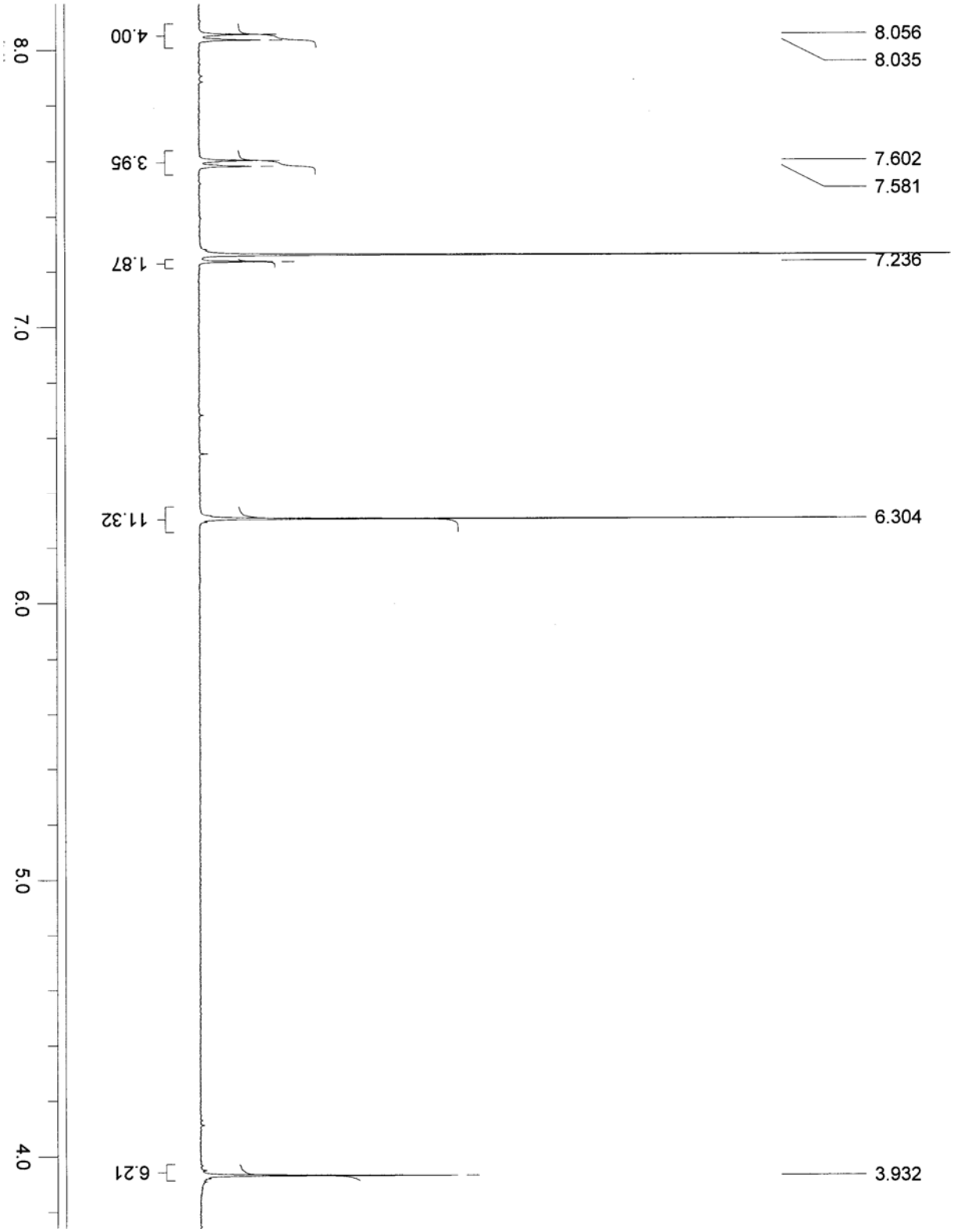
4,4'-bis(((2,2,6,6-tetramethyl-4-(3-(triethoxysilyl)propoxy)piperidin-1-yl)oxy)methyl)-1,1'-biphenyl (3) : ^{13}C APT



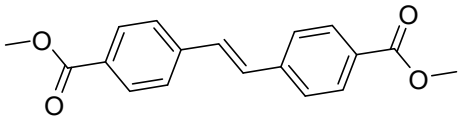


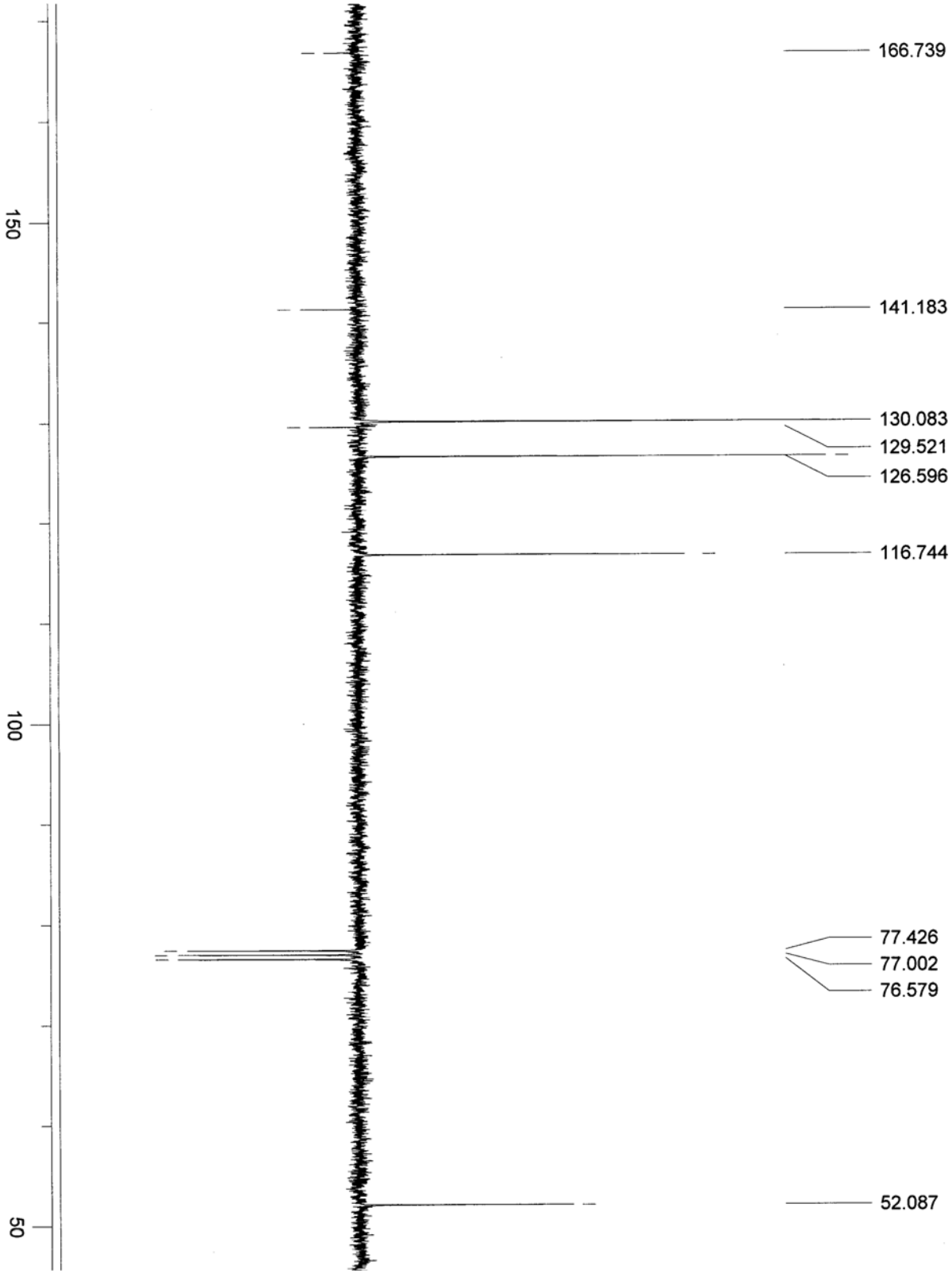
(*E*)-1,1'-(Ethene-1,2-diylbis(4,1-phenylene))bis(ethan-1-one) (16) : ^{1}H NMR



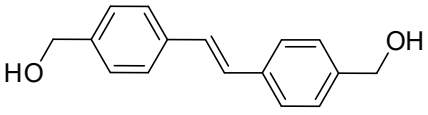


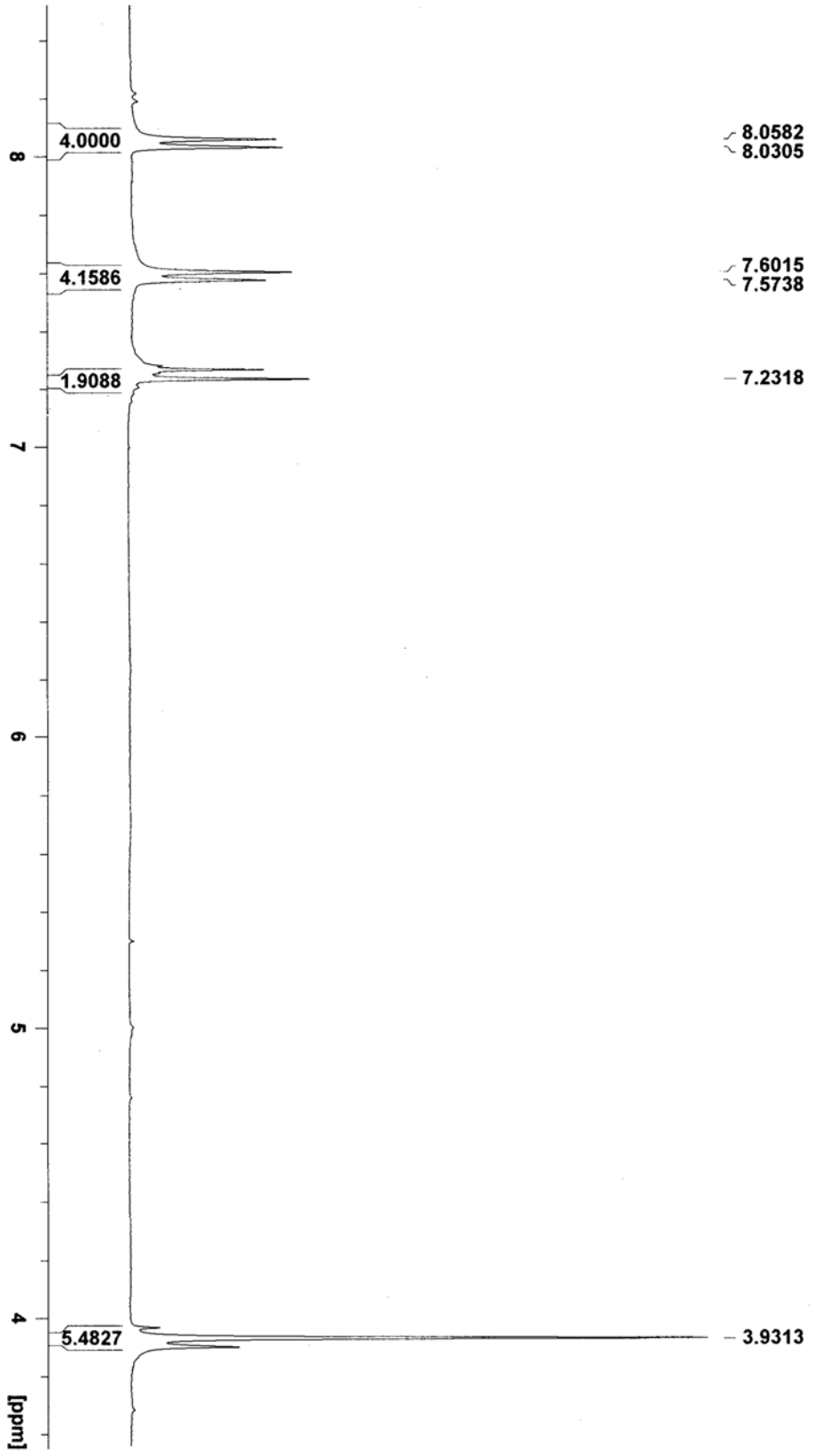
(*E*)-1,1'-(Ethene-1,2-diylbis(4,1-phenylene))bis(ethan-1-one) (16) : ^{13}C APT



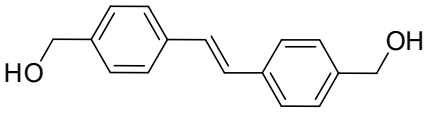


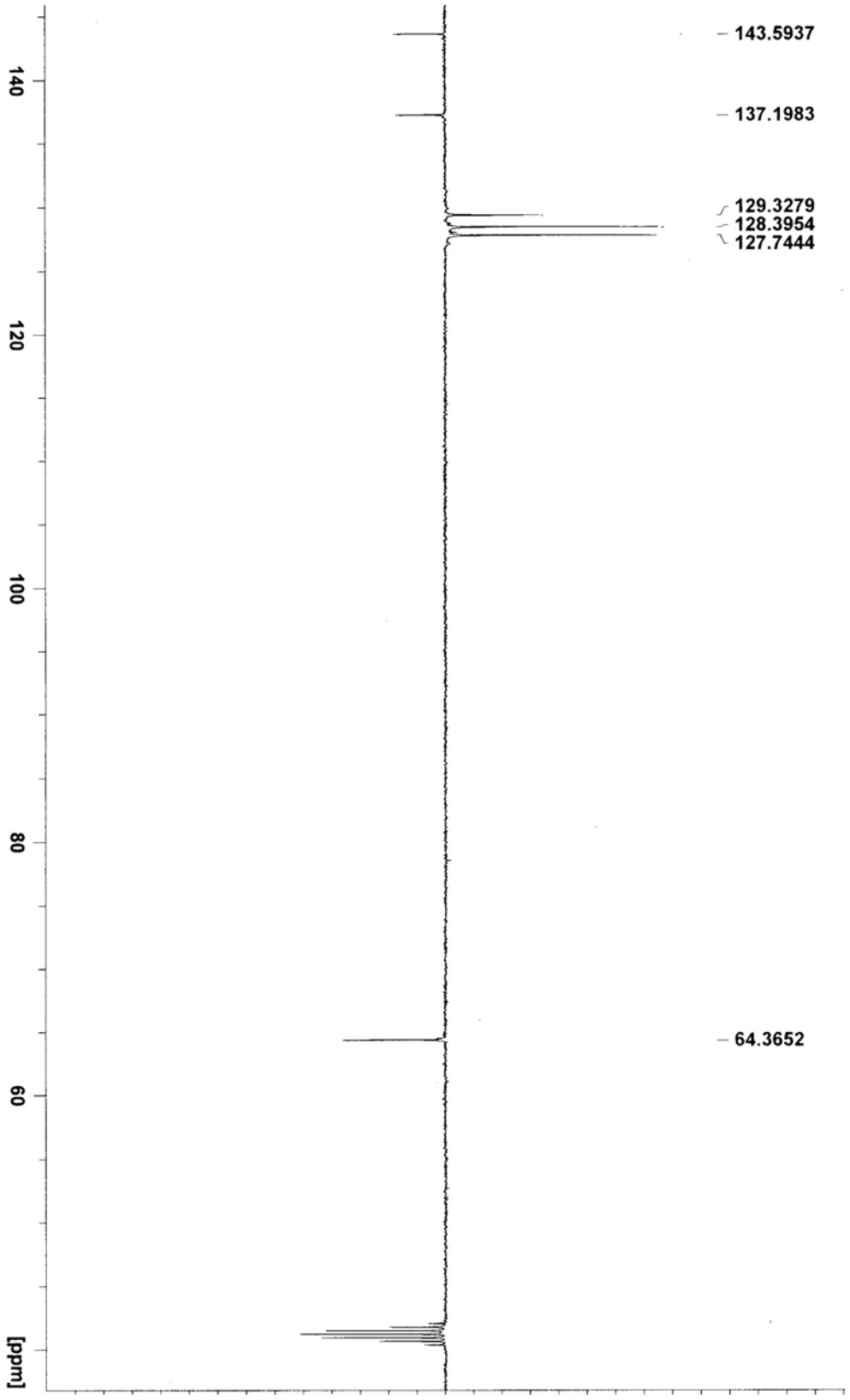
(*E*)-(Ethene-1,2-diylbis(4,1-phenylene))dimethanol (15) : ^{1}H NMR



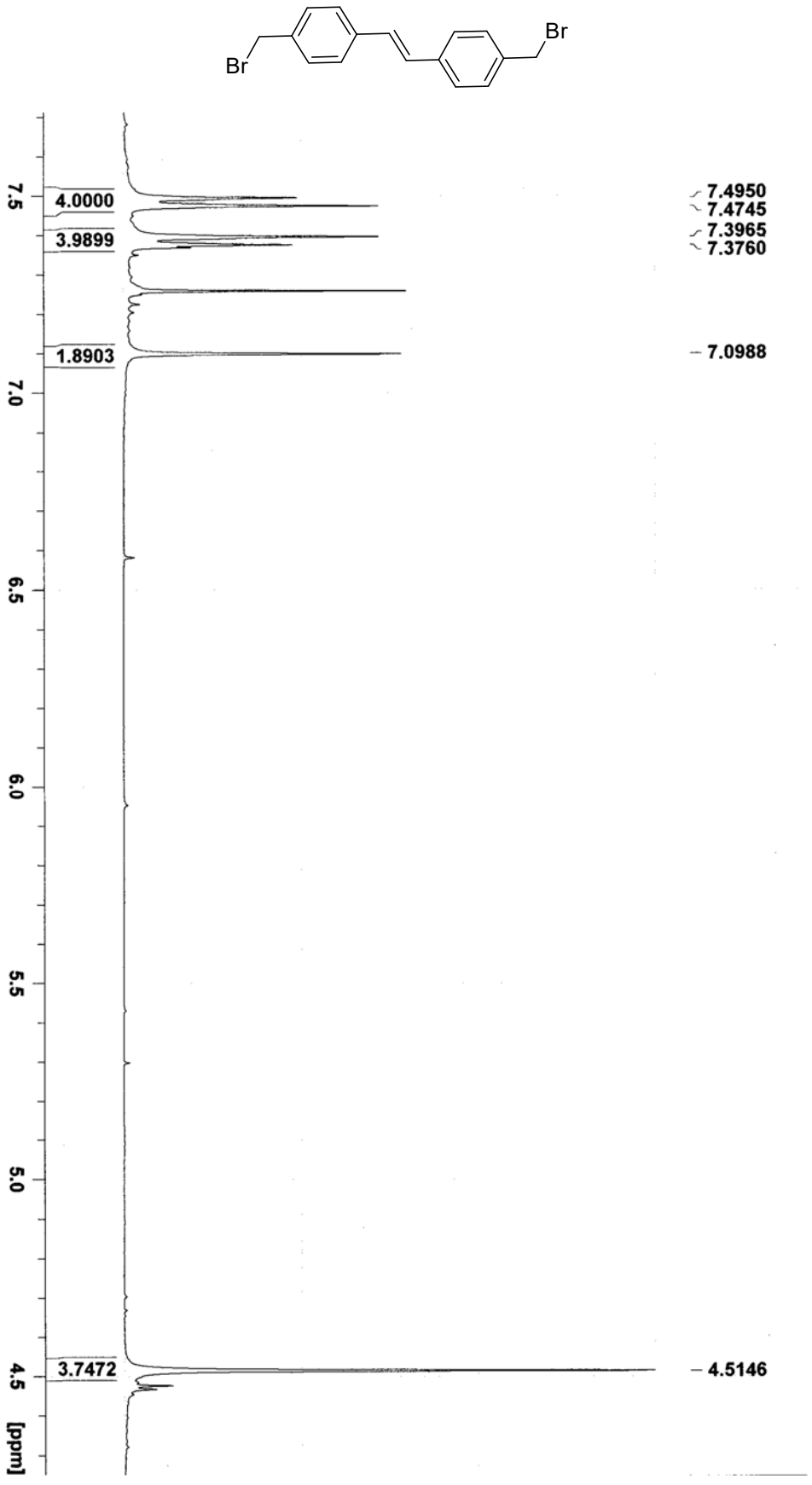


(*E*)-(Ethene-1,2-diylbis(4,1-phenylene))dimethanol (15) : ^{13}C APT

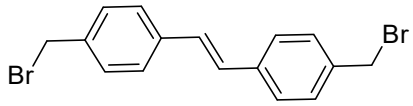


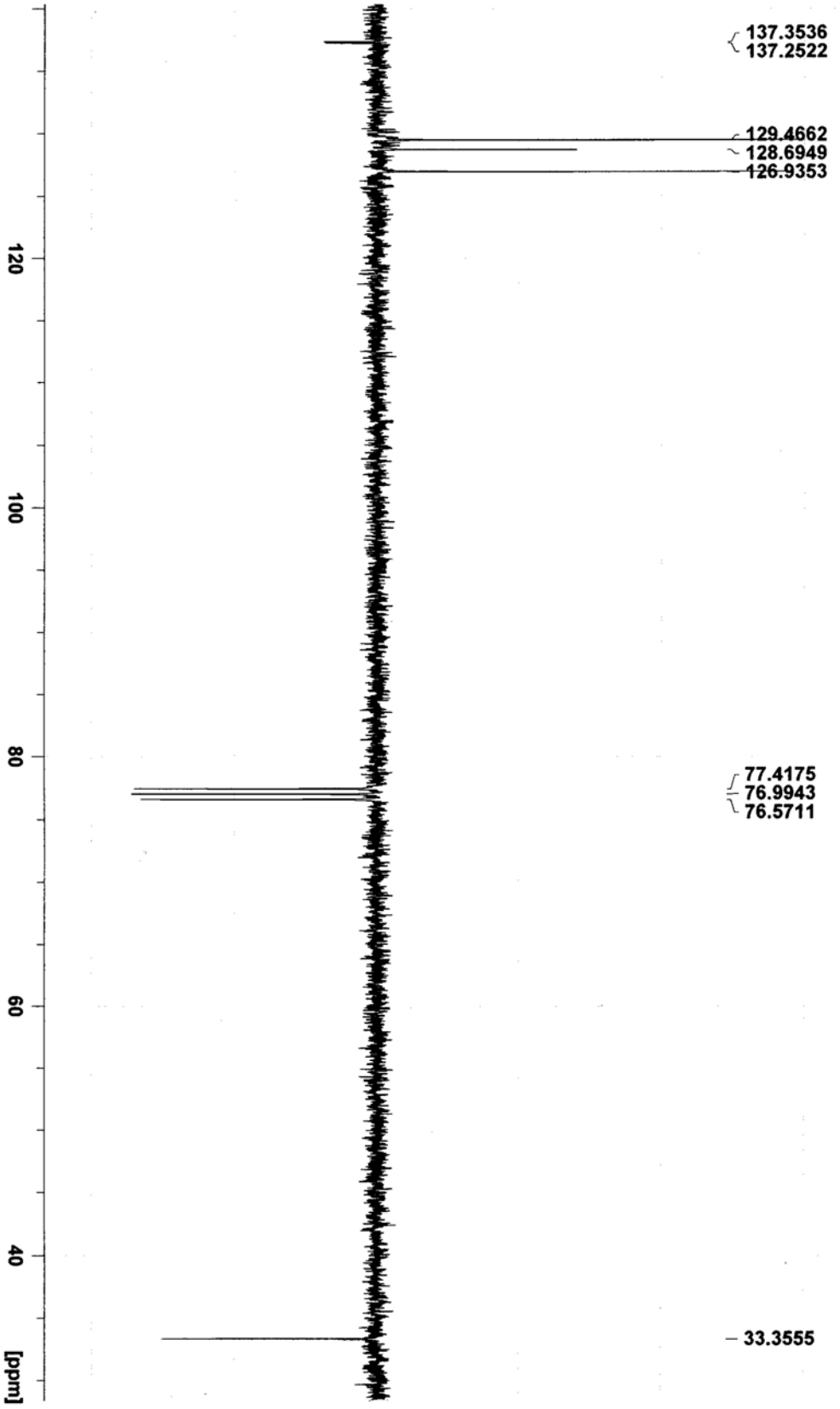


(*E*)-1,2-bis(4-(Bromomethyl)phenyl)ethane (14) : ^{1}H NMR

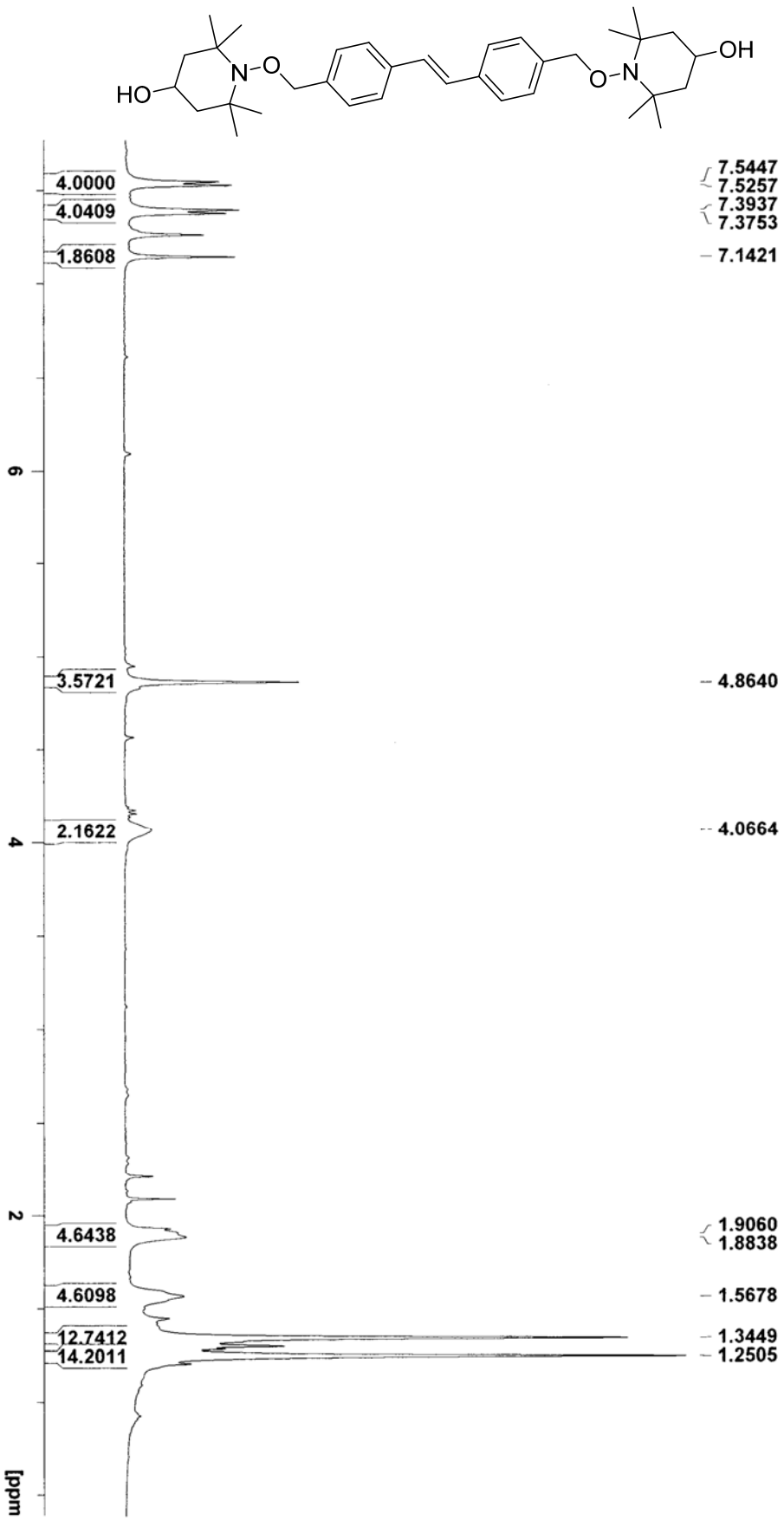


(*E*)-1,2-bis(4-(Bromomethyl)phenyl)ethane (14) : ^{13}C APT

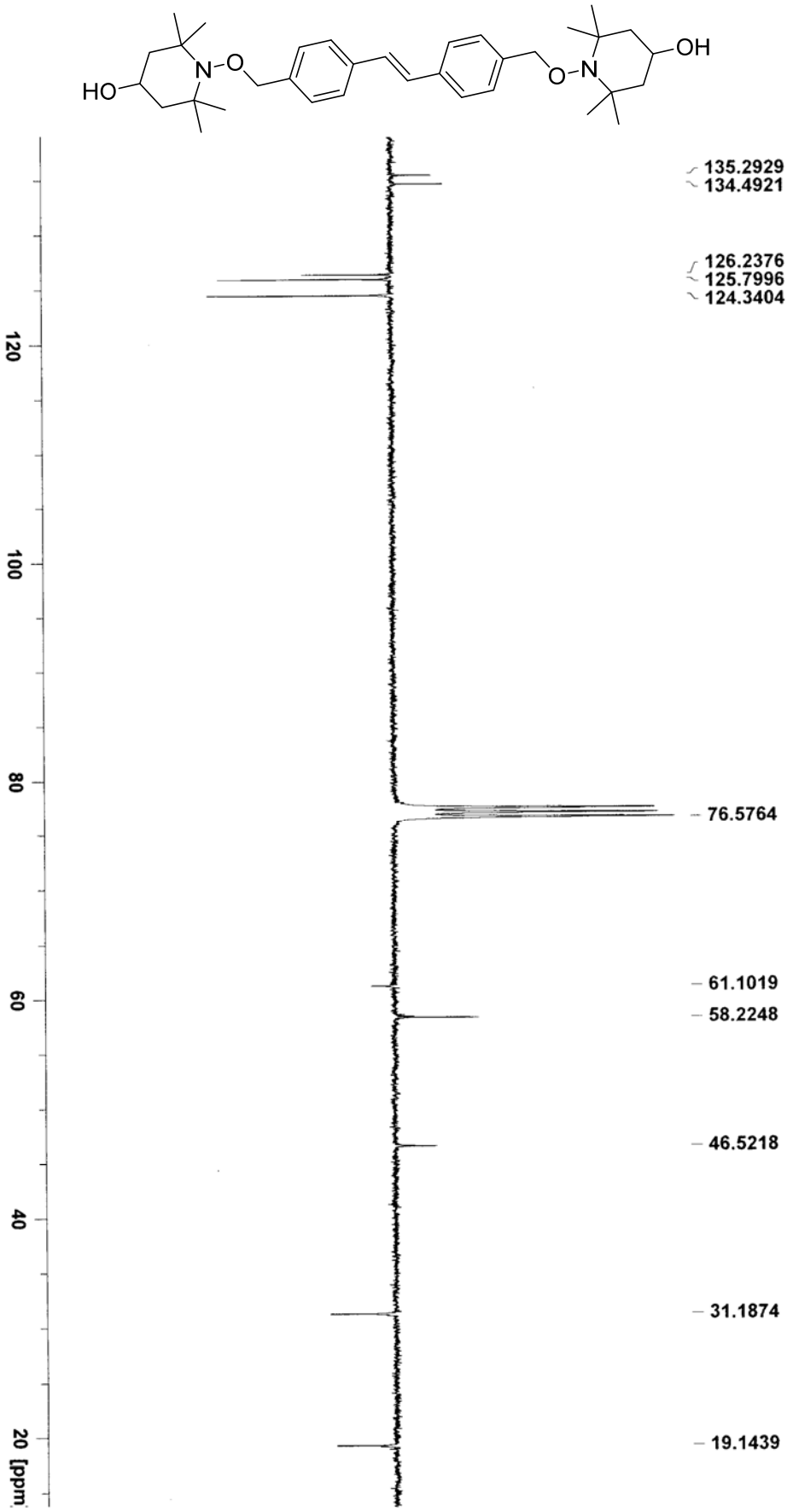




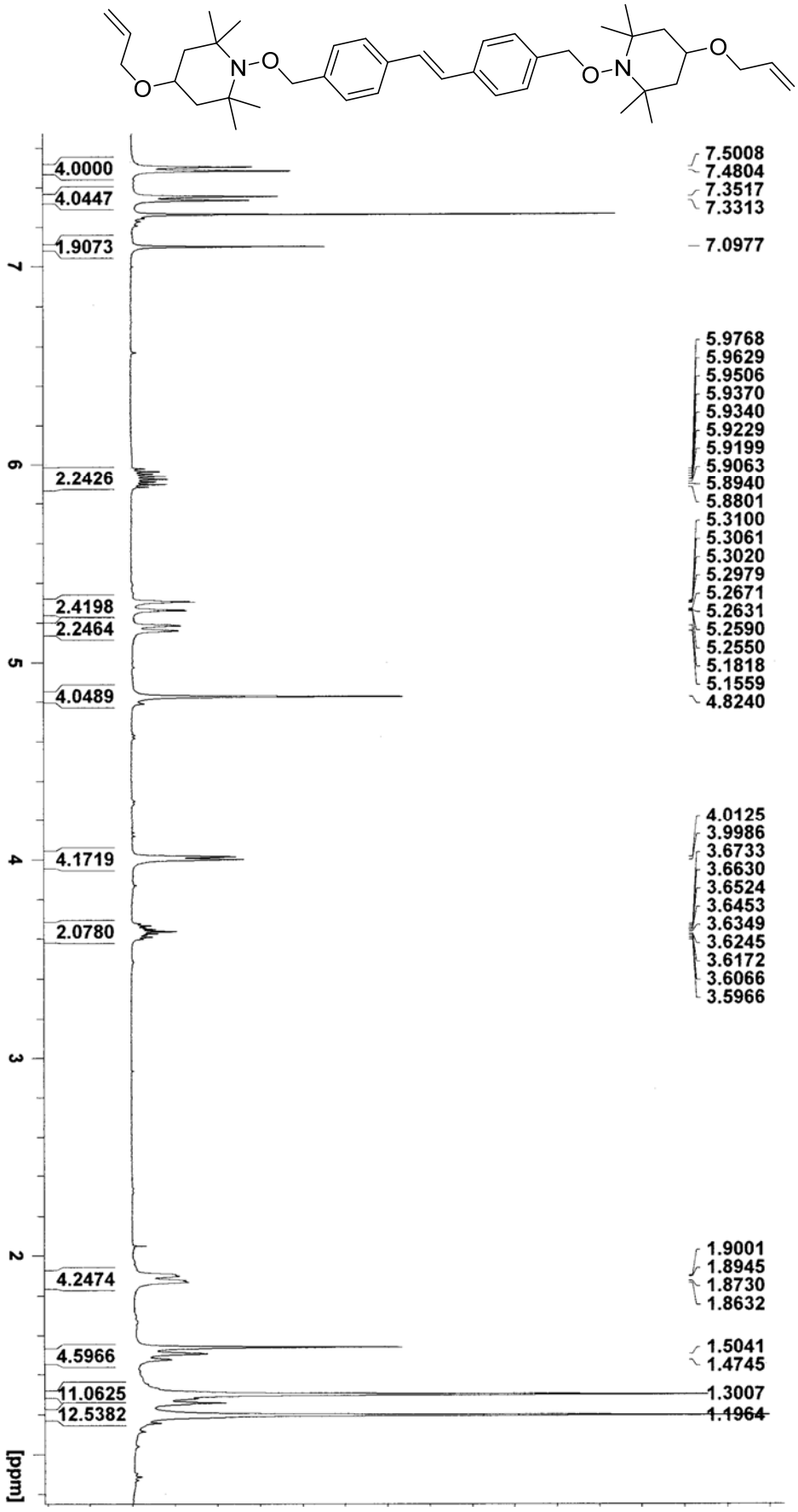
(*E*)-1,1'-(((Ethene-1,2-diylbis(4,1-phenylene))bis(methylene))bis(oxy))bis(2,2,6,6-tetramethylpiperidin-4-ol) (13) : ^{1}H NMR



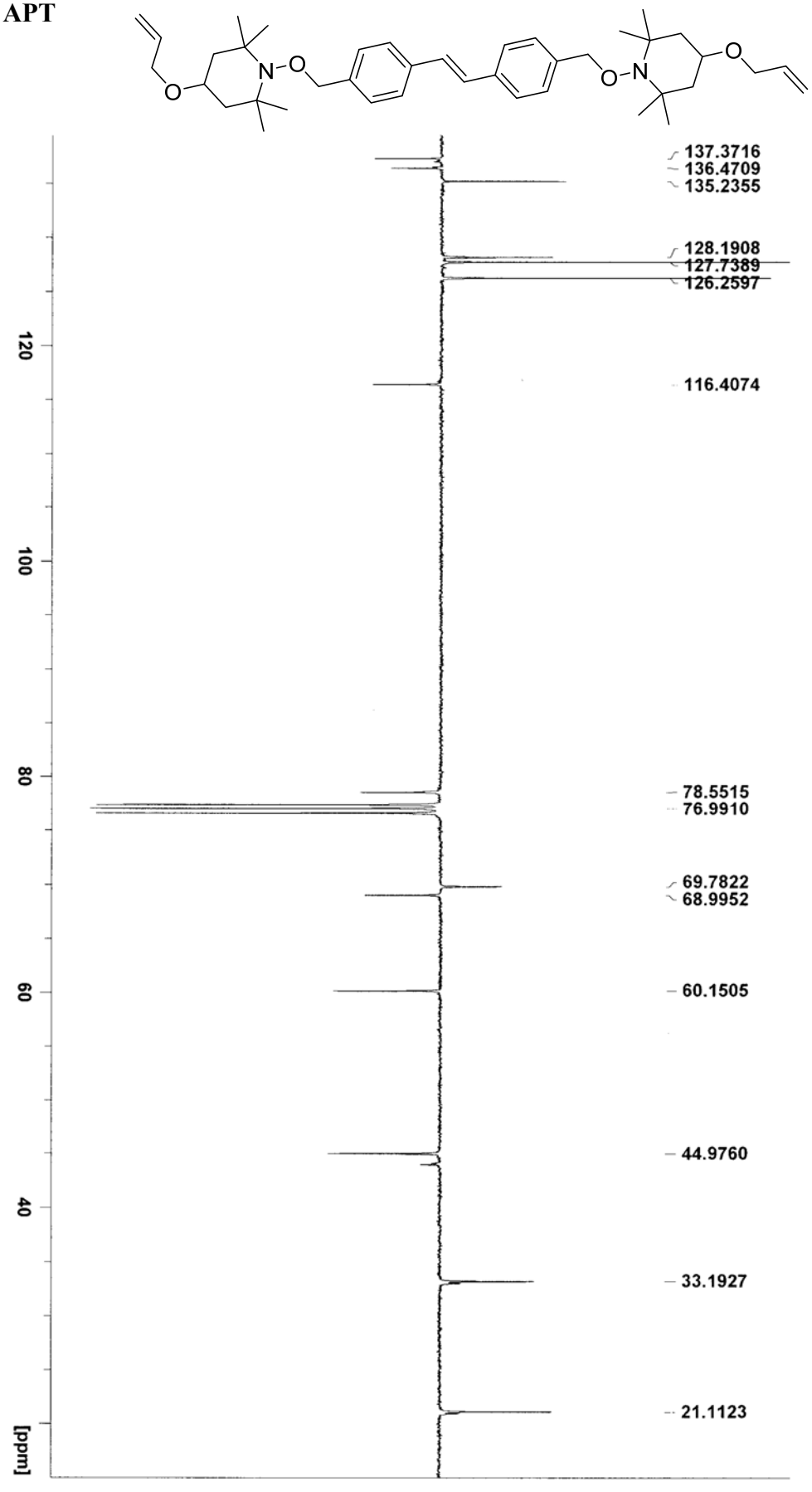
(*E*)-1,1'-(((Ethene-1,2-diylbis(4,1-phenylene))bis(methylene))bis(oxy))bis(2,2,6,6-tetramethylpiperidin-4-ol) (13) : ^{13}C APT



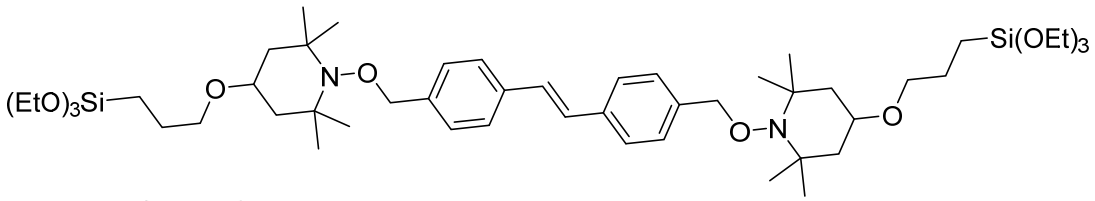
(*E*)-1,2-Bis(4-(((4-(allyloxy)-2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)phenyl)ethane (12) : ^{1}H NMR

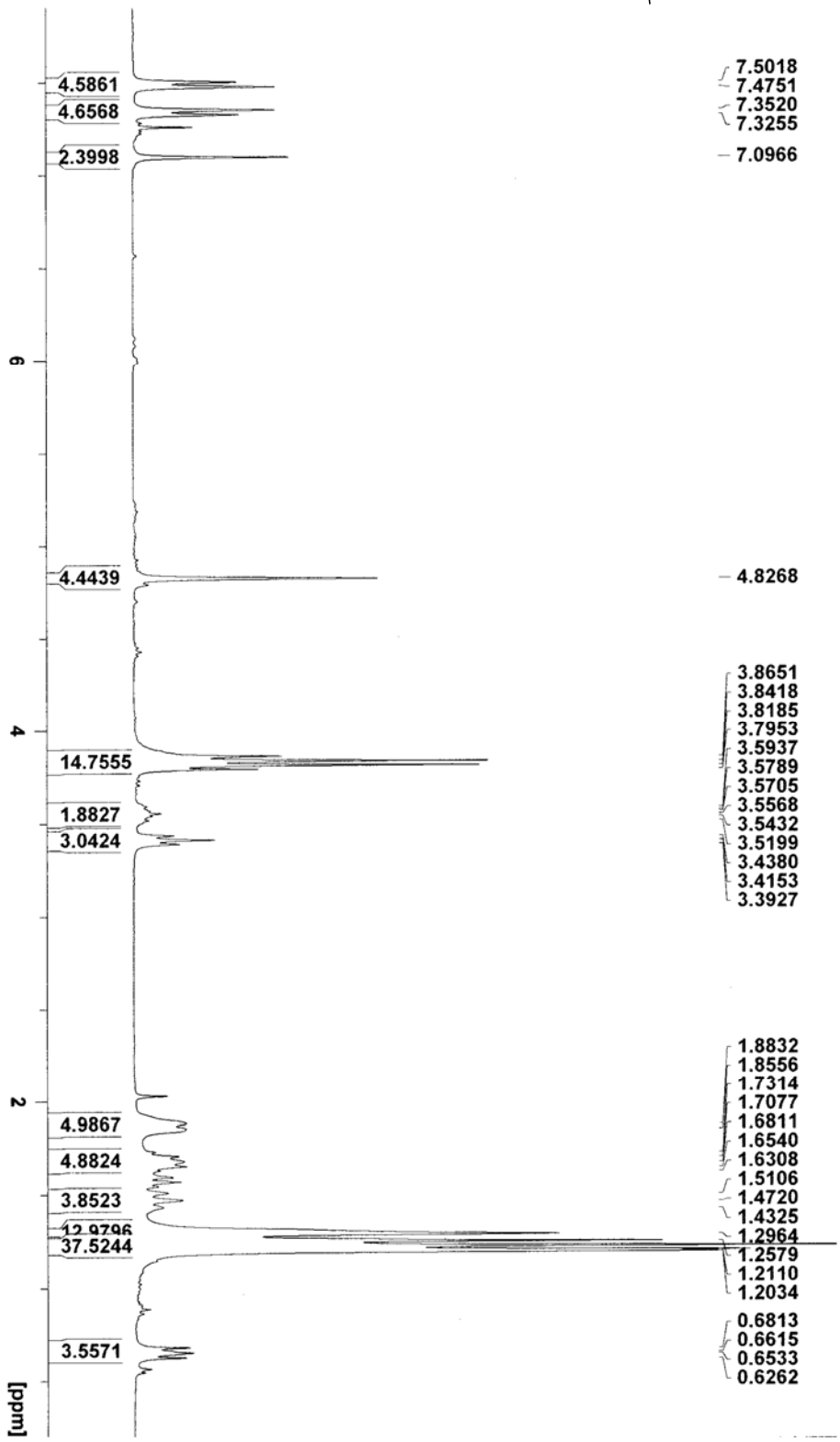


(*E*)-1,2-Bis(4-(((4-(allyloxy)-2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)phenyl)ethane (12) : ^{13}C APT

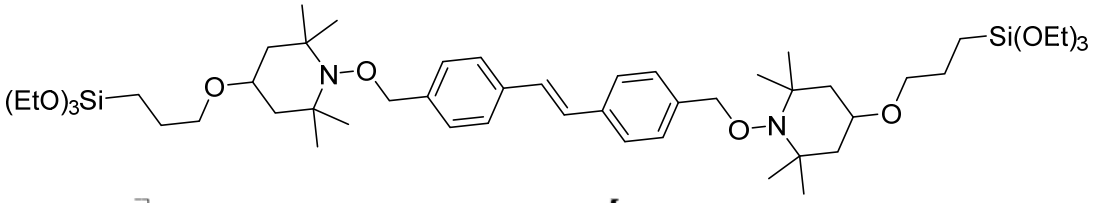


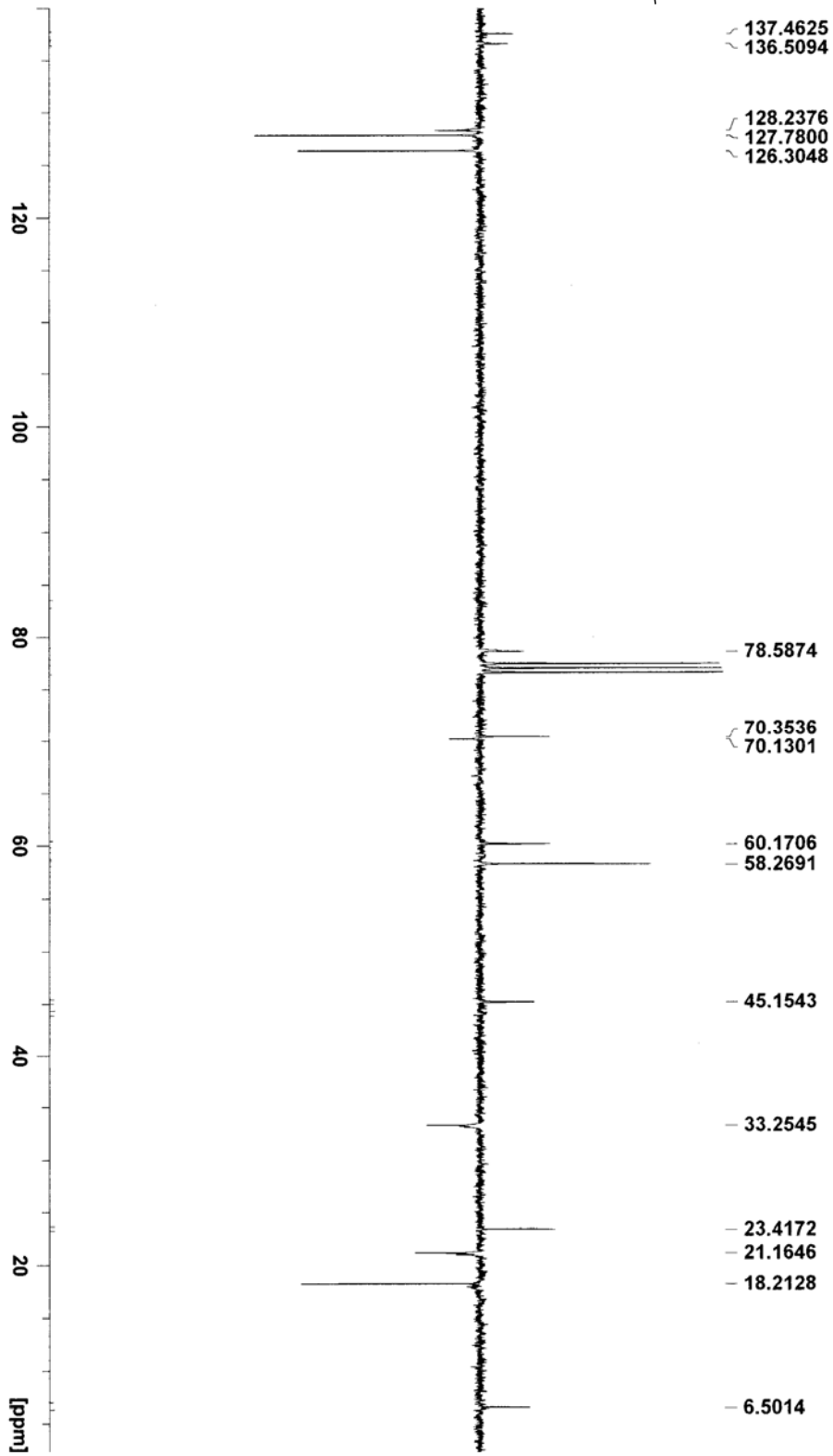
(*E*)-1,2-bis(4-(((2,2,6,6-tetramethyl-4-(3-(triethoxysilyl)propoxy)piperidin-1-yl)oxy)methyl)phenyl)ethene (4) : ^{1}H NMR



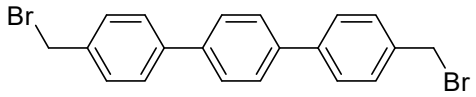


(*E*)-1,2-bis(4-(((2,2,6,6-tetramethyl-4-(3-(triethoxysilyl)propoxy)piperidin-1-yl)oxy)methyl)phenyl)ethene (4) : ^{13}C APT

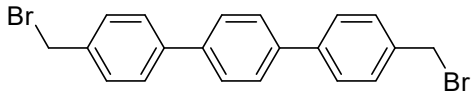


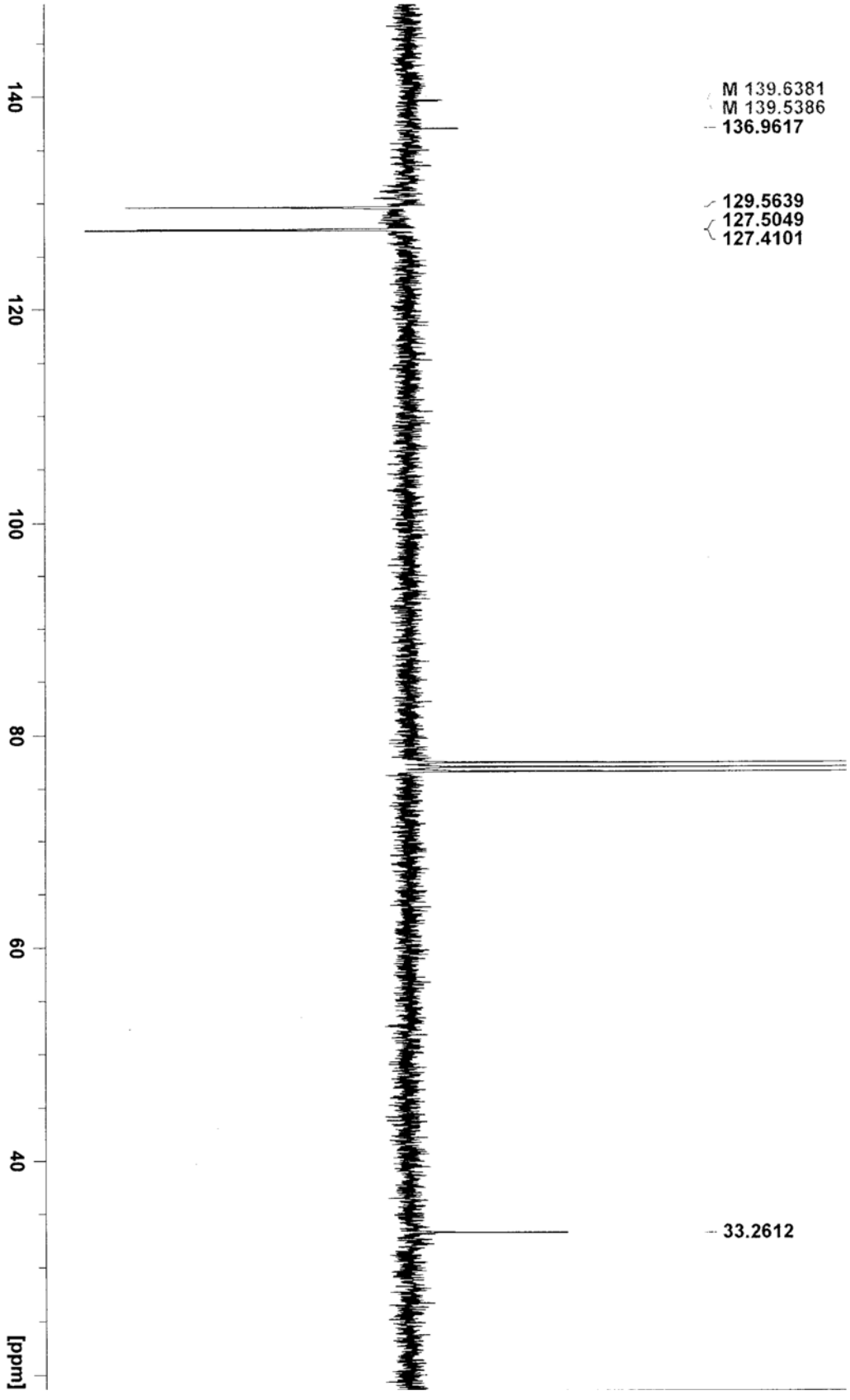


4,4''-Bis(bromomethyl)-1,1':4',1''-terphenyl (19) : ^{1}H NMR

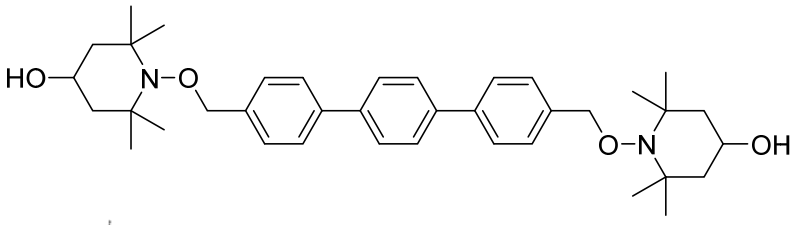


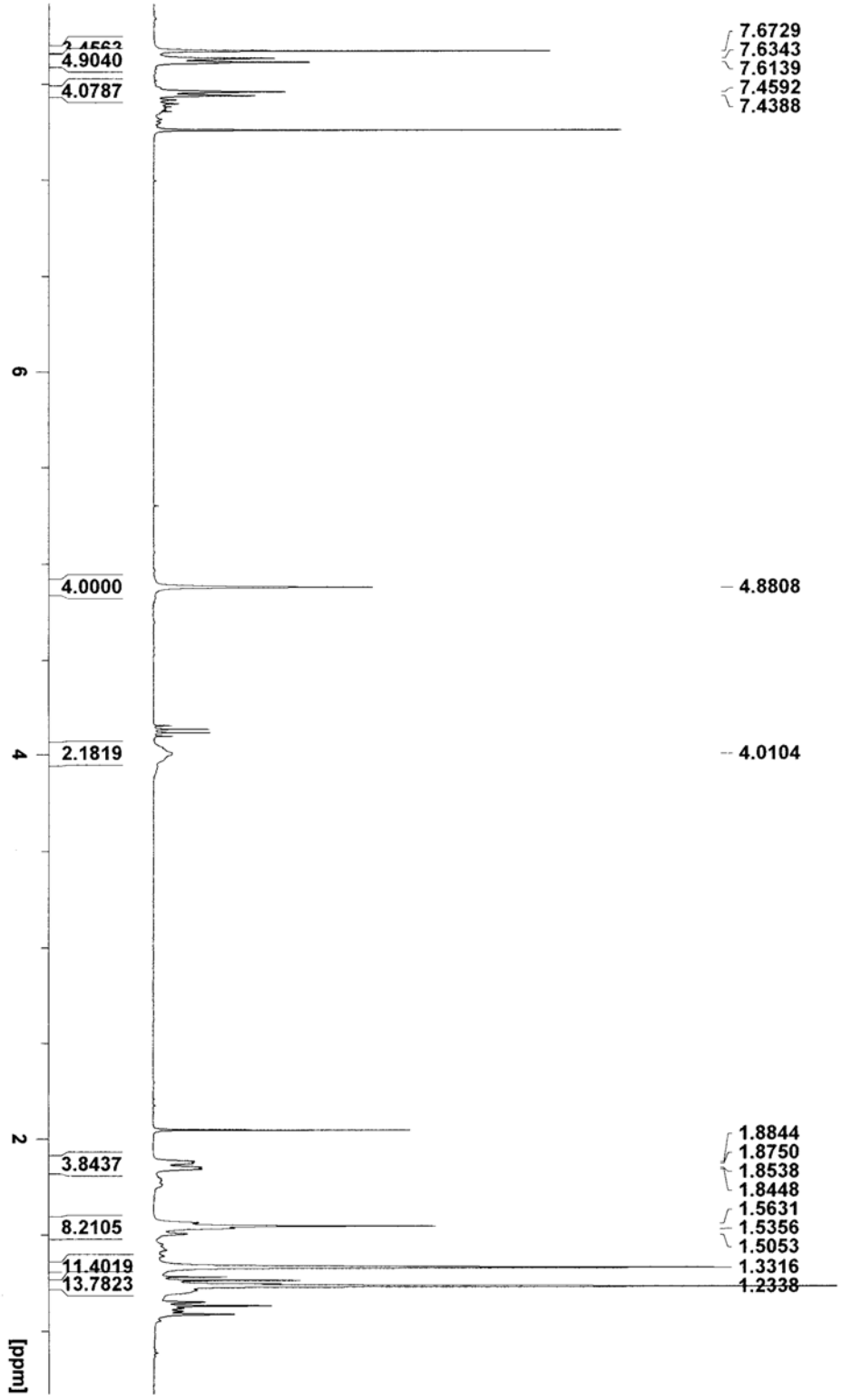
4,4''-Bis(bromomethyl)-1,1':4',1''-terphenyl (19) : ^{13}C APT



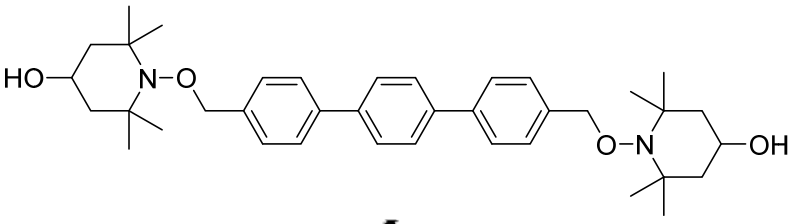


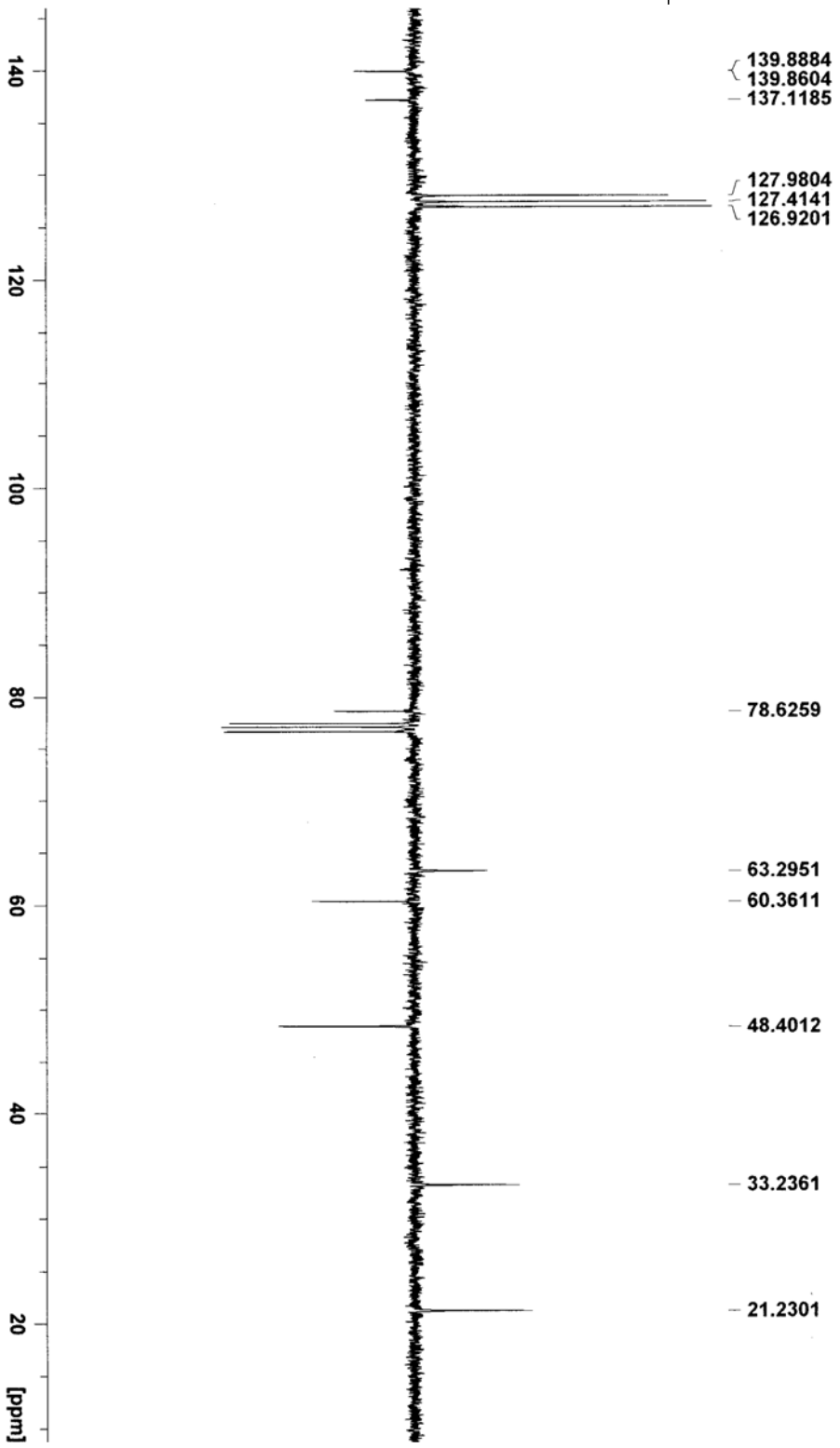
1,1'-(([1,1':4',1''-Terphenyl]-4,4''-diylbis(methylene))bis(oxy))bis(2,2,6,6-tetramethylpiperidin-4-ol) (18) : ^{1}H NMR



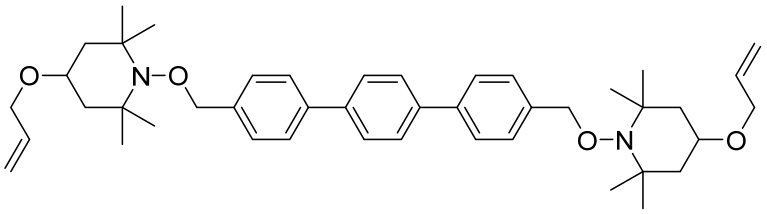


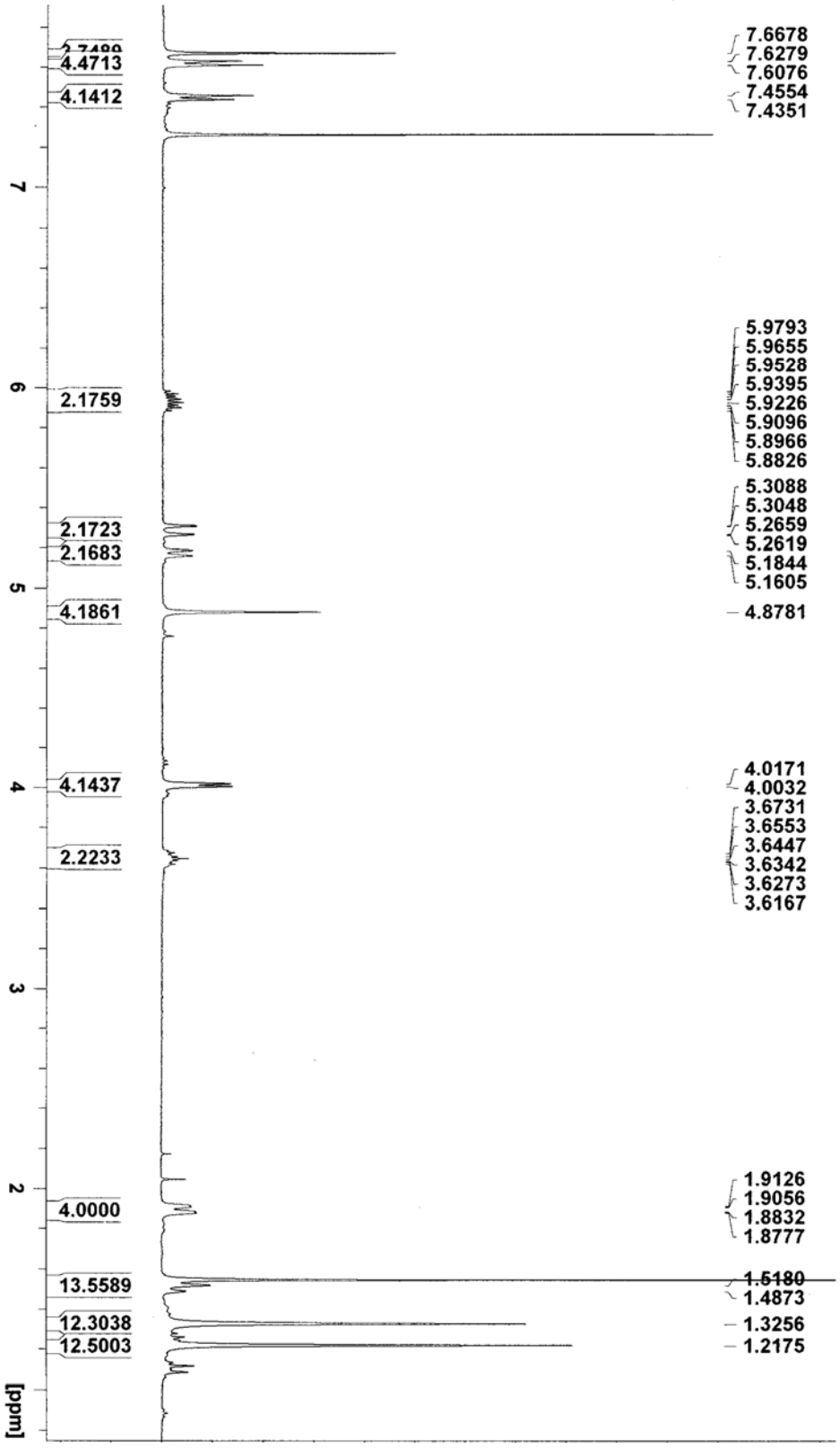
1,1'-(([1,1':4',1''-Terphenyl]-4,4''-diylbis(methylene))bis(oxy))bis(2,2,6,6-tetramethylpiperidin-4-ol) (18) : ^{13}C APT



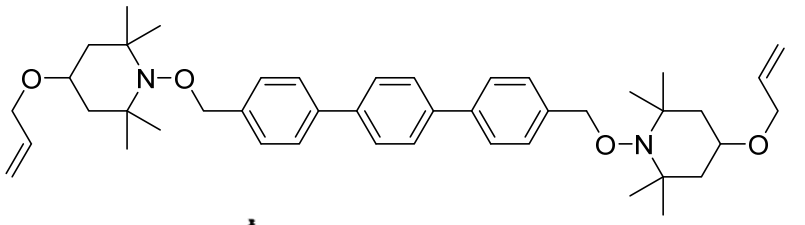


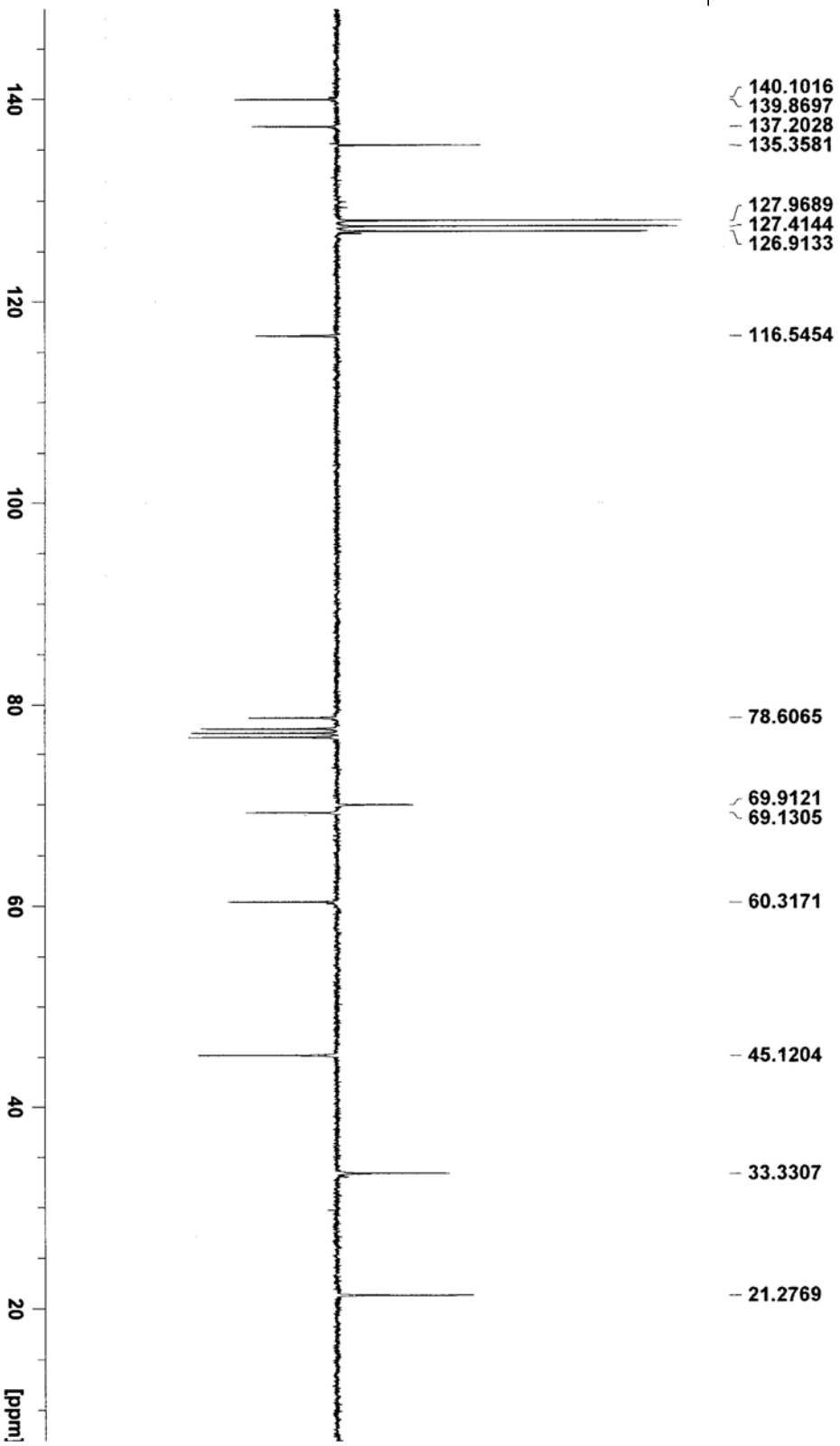
4,4''-Bis(((4-(allyloxy)-2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-1,1':4',1''-terphenyl (17) : ^{1}H NMR



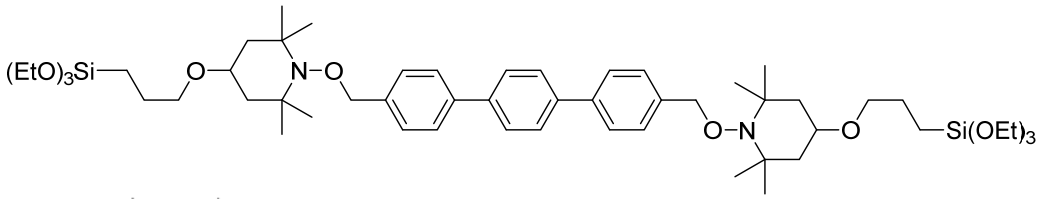


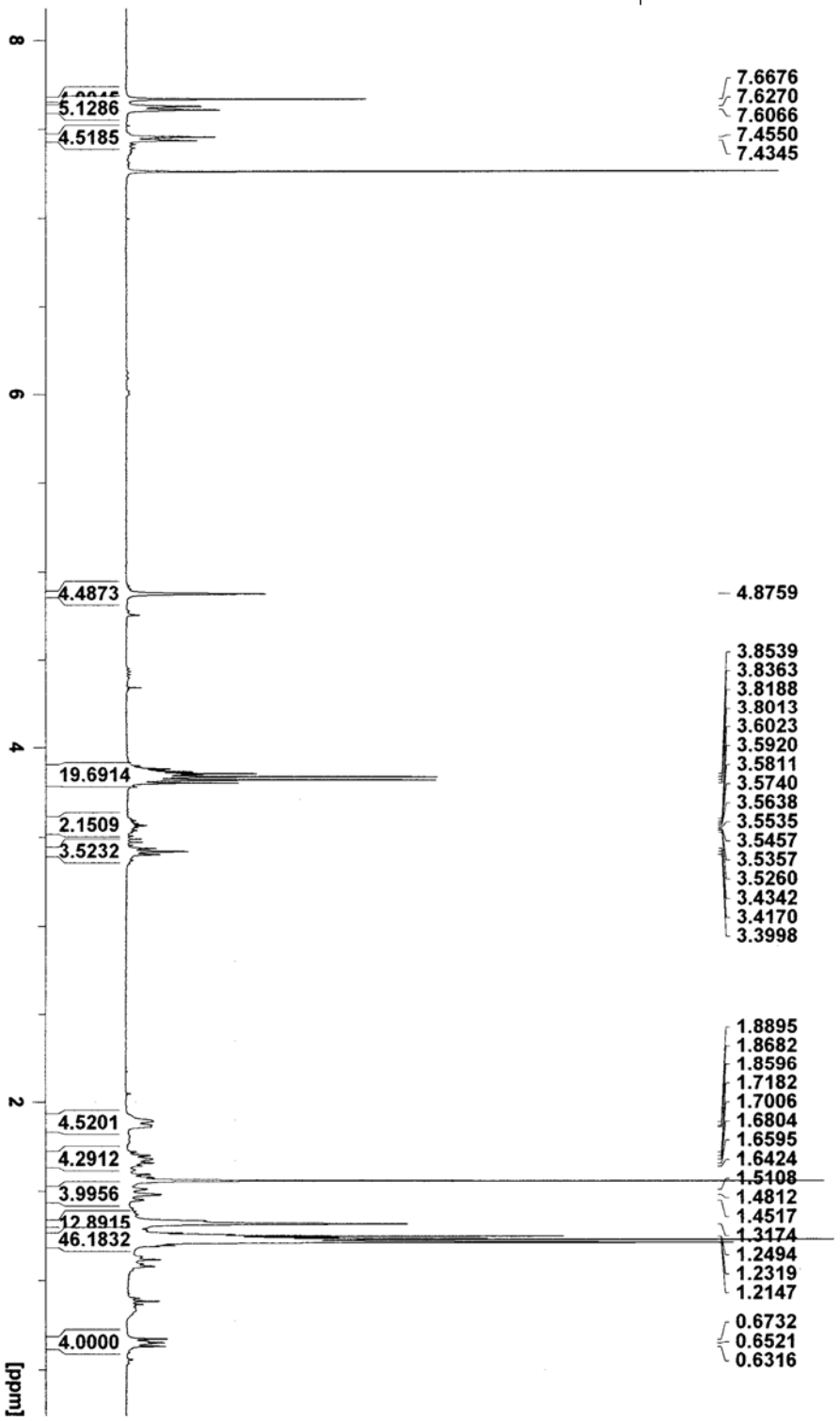
4,4''-Bis(((4-(allyloxy)-2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-1,1':4',1''-terphenyl (17) : ^{13}C APT



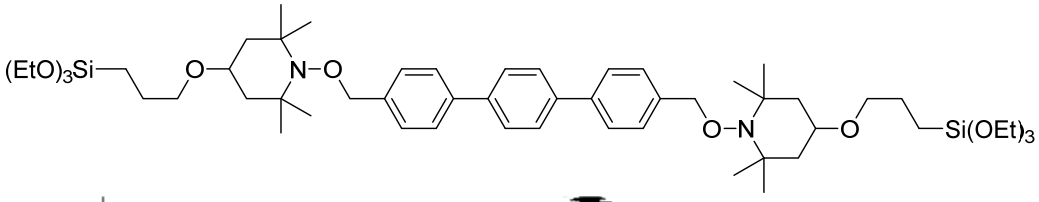


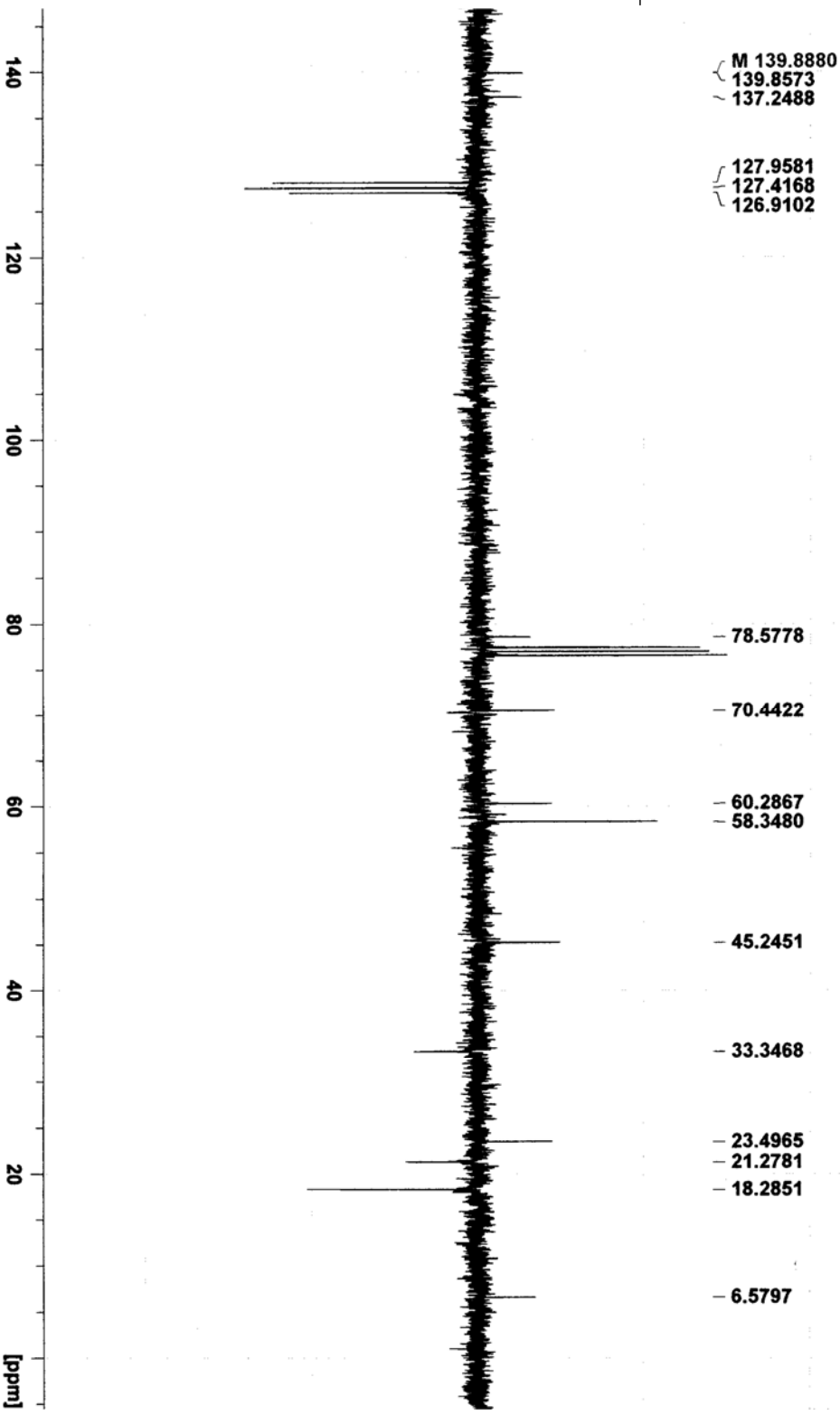
4,4''-Bis(((2,2,6,6-tetramethyl-4-(3-(triethoxysilyl)propoxy)piperidin-1-yl)oxy)methyl)-1,1':4',1''-terphenyl (5) : ^{1}H NMR



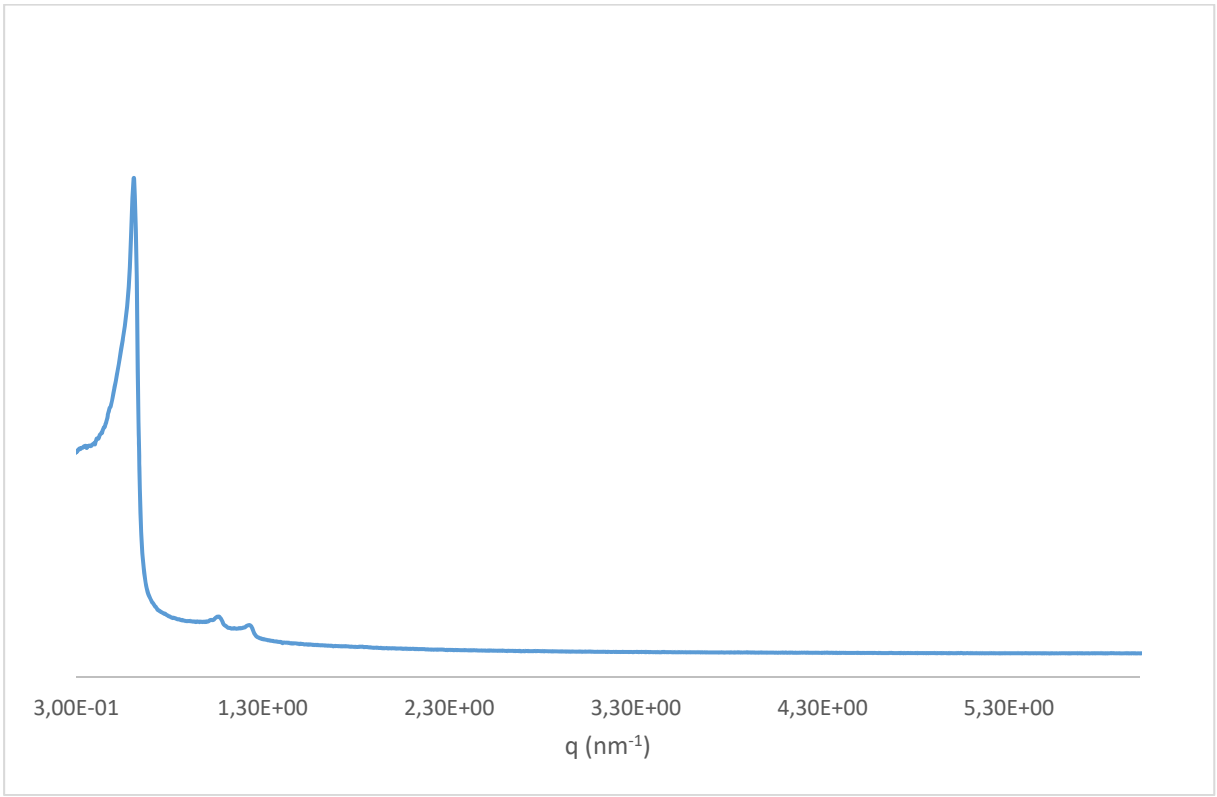


4,4''-Bis(((2,2,6,6-tetramethyl-4-(3-(triethoxysilyl)propoxy)piperidin-1-yl)oxy)methyl)-1,1':4',1''-terphenyl (5) : ^{13}C APT

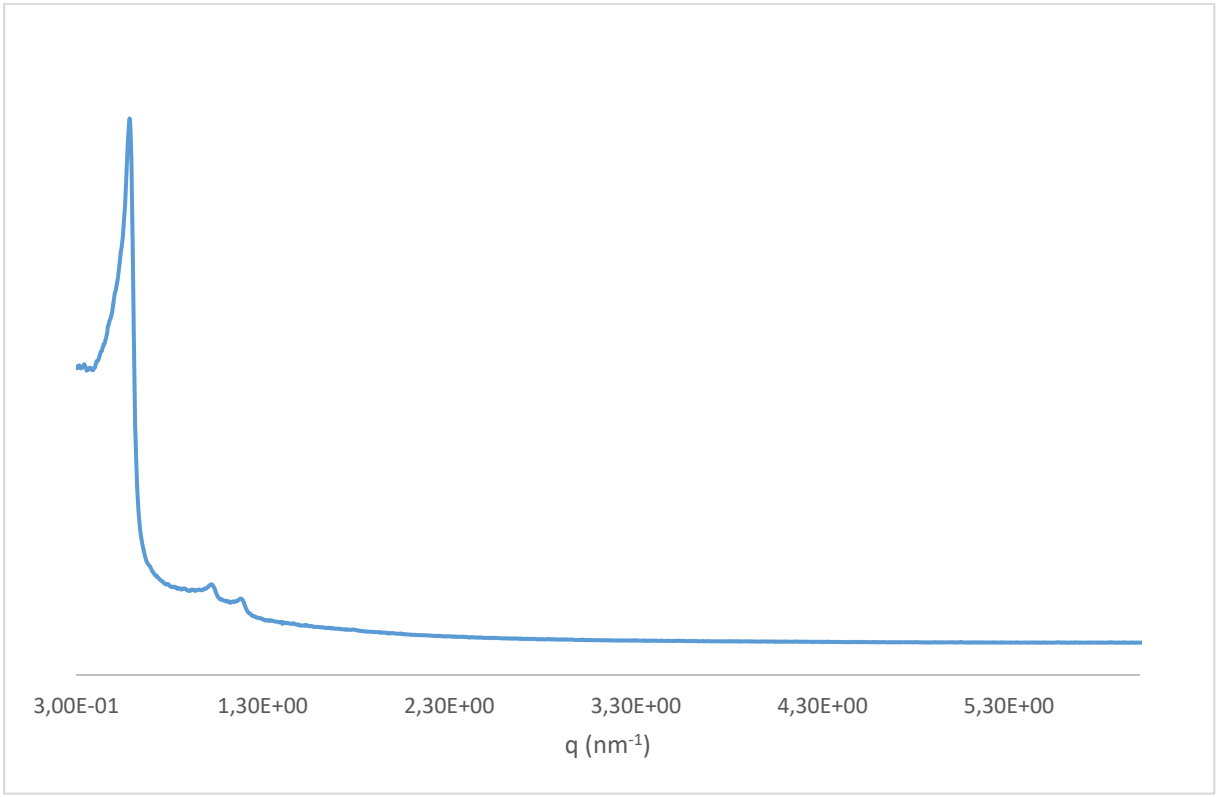




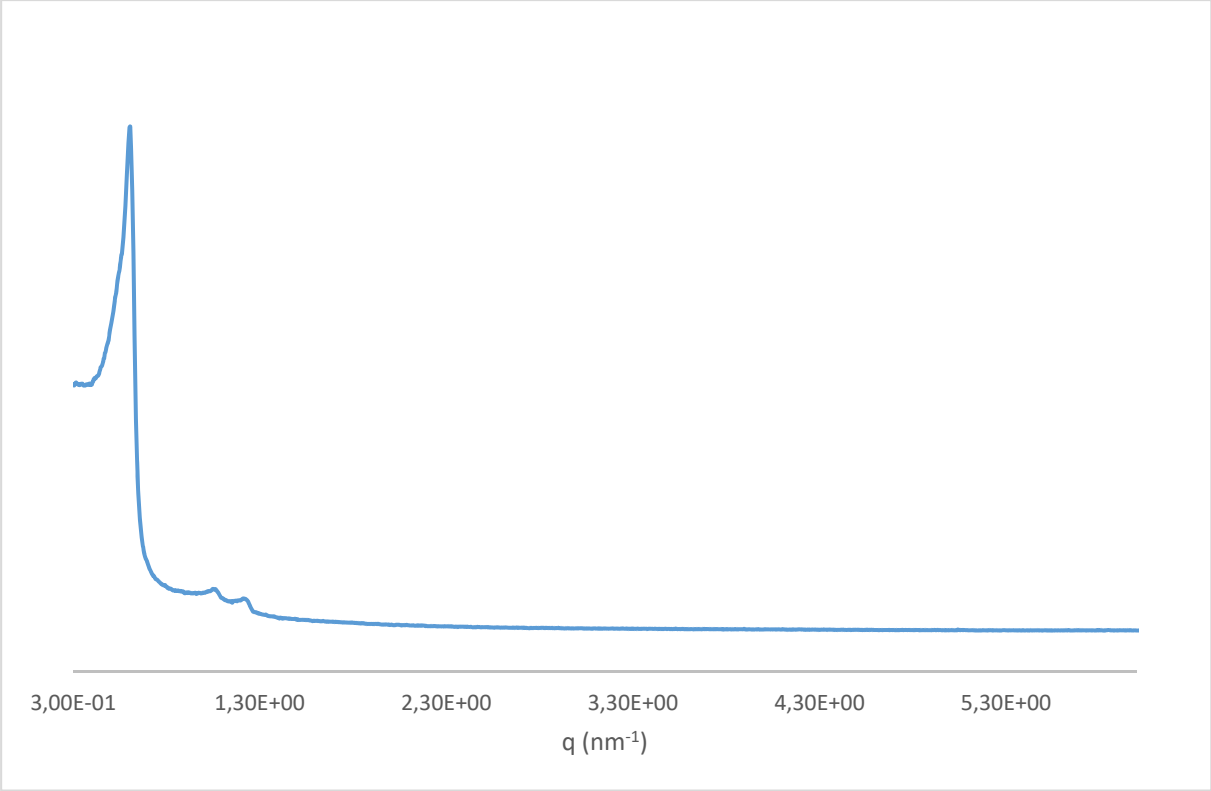
Small Angle X-Ray Scattering (SAXS): SBA_{56}-2



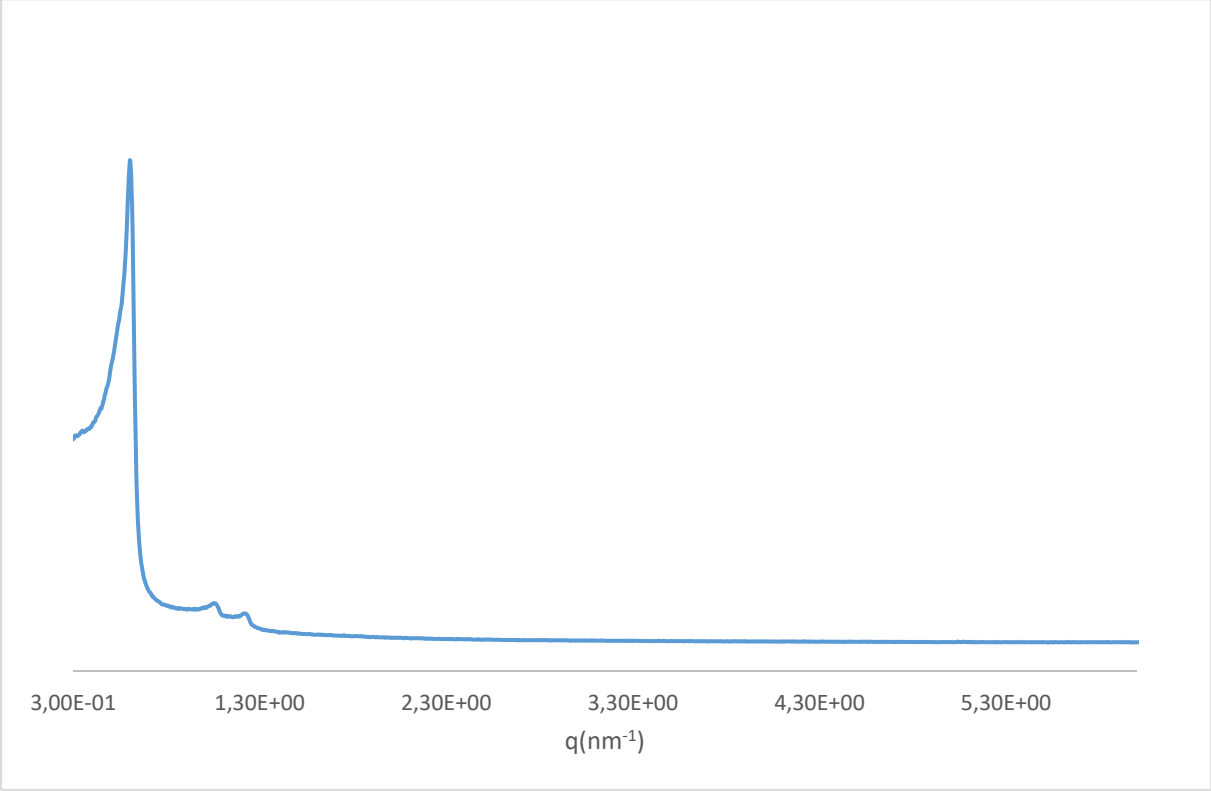
Small Angle X-Ray Scattering (SAXS): SBA_{55}-3



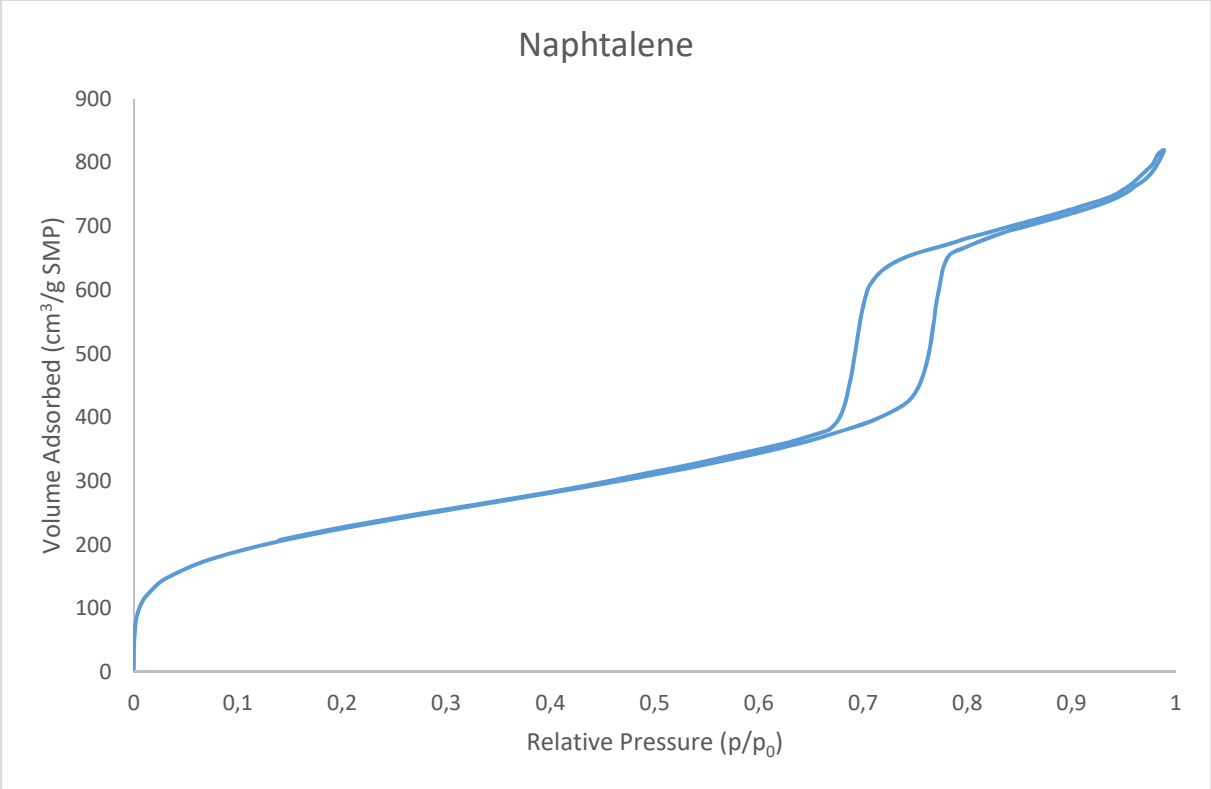
Small Angle X-Ray Scattering (SAXS): SBA_{60}-4



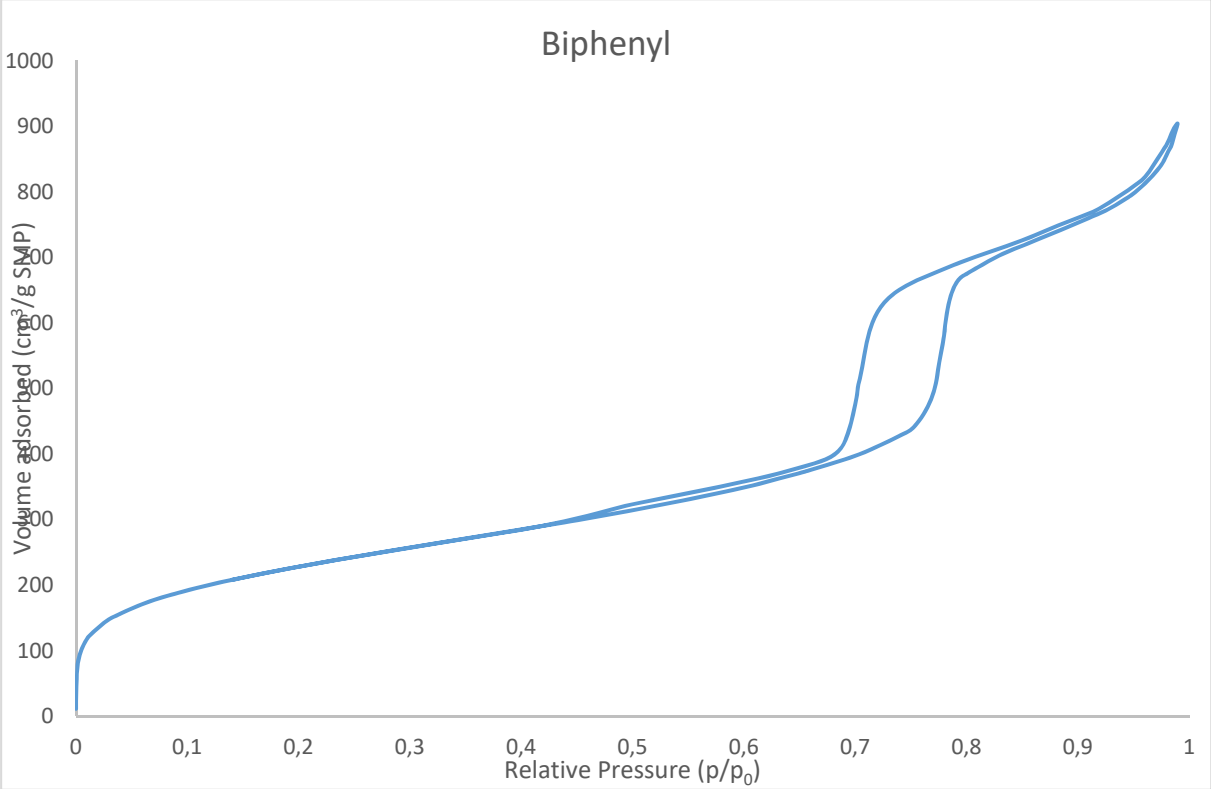
Small Angle X-Ray Scattering (SAXS): SBA_{60}-5



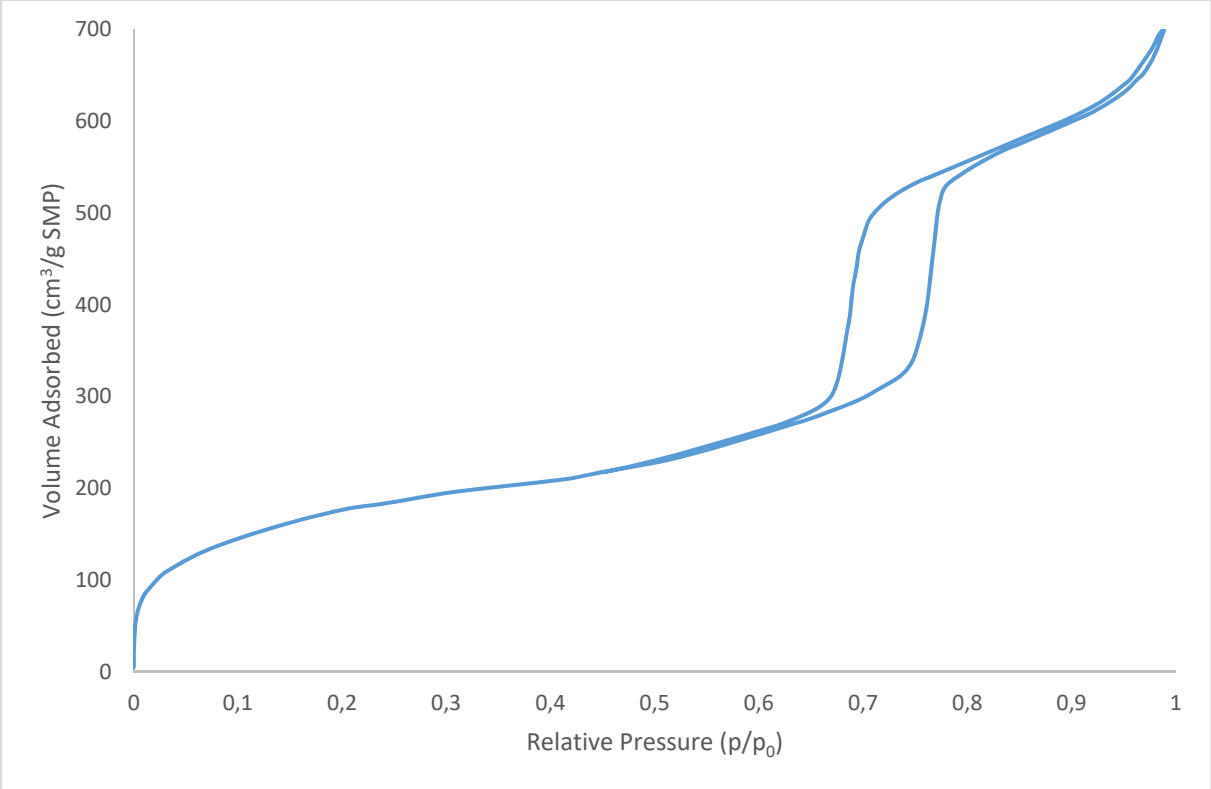
Nitrogen adsorption/desorption analysis: SBA_{56}-2



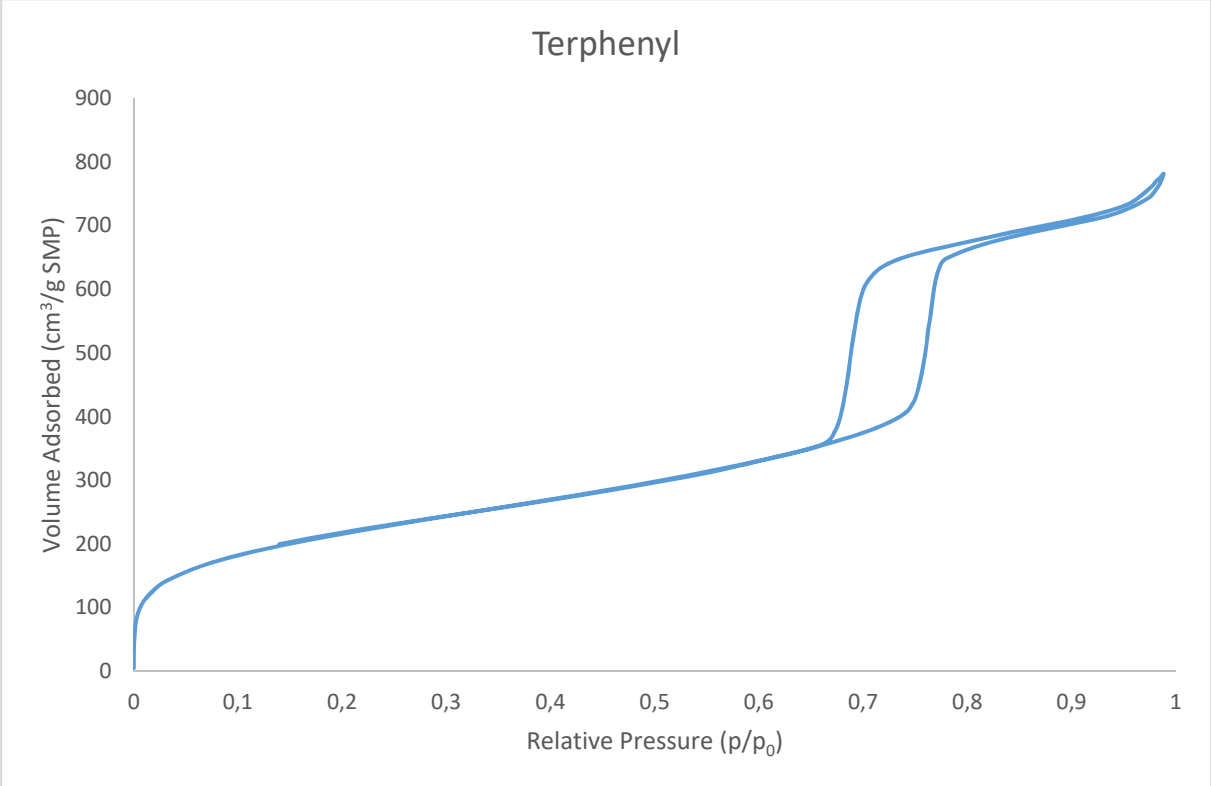
Nitrogen adsorption/desorption analysis: SBA_{55}-3



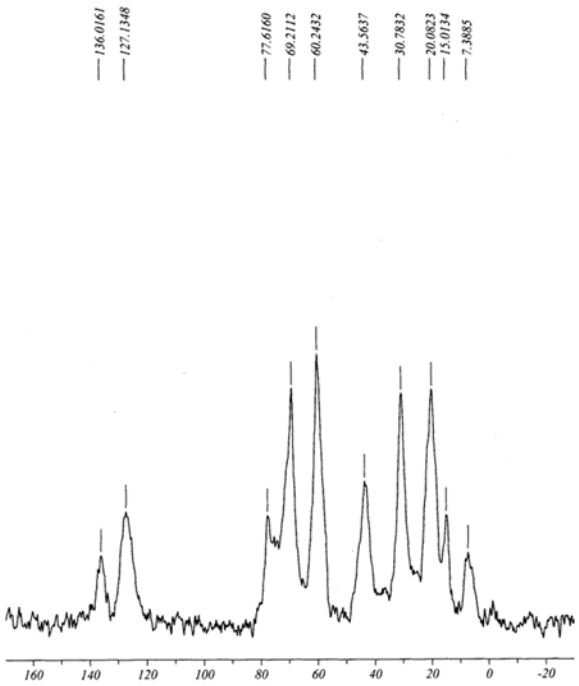
Nitrogen adsorption/desorption analysis: SBA_{60}-4



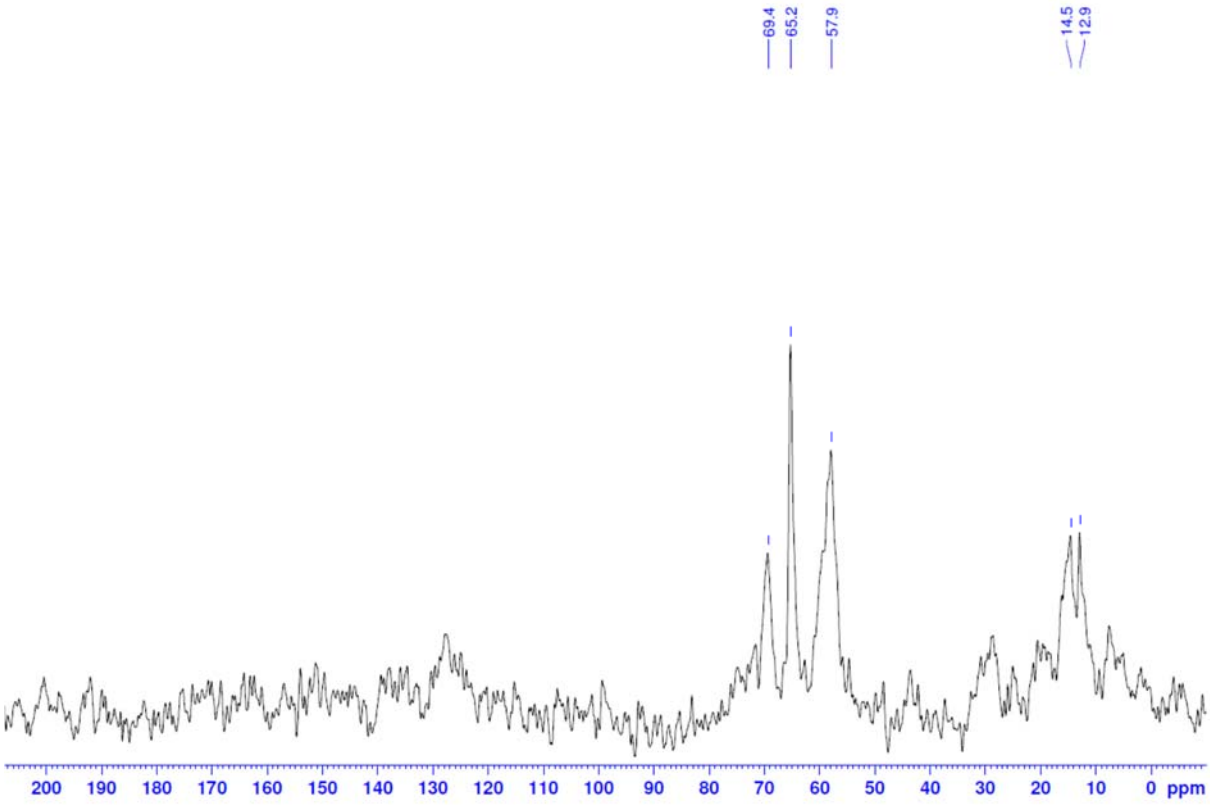
Nitrogen adsorption/desorption analysis: SBA_{60}-5



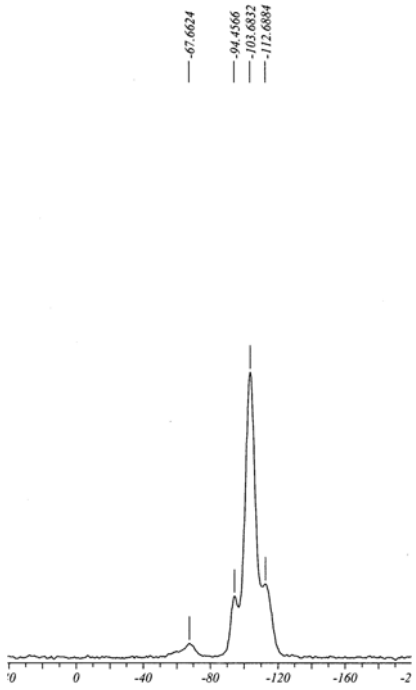
^{13}C CP-MAS solid state NMR of SBA_{56}-1:



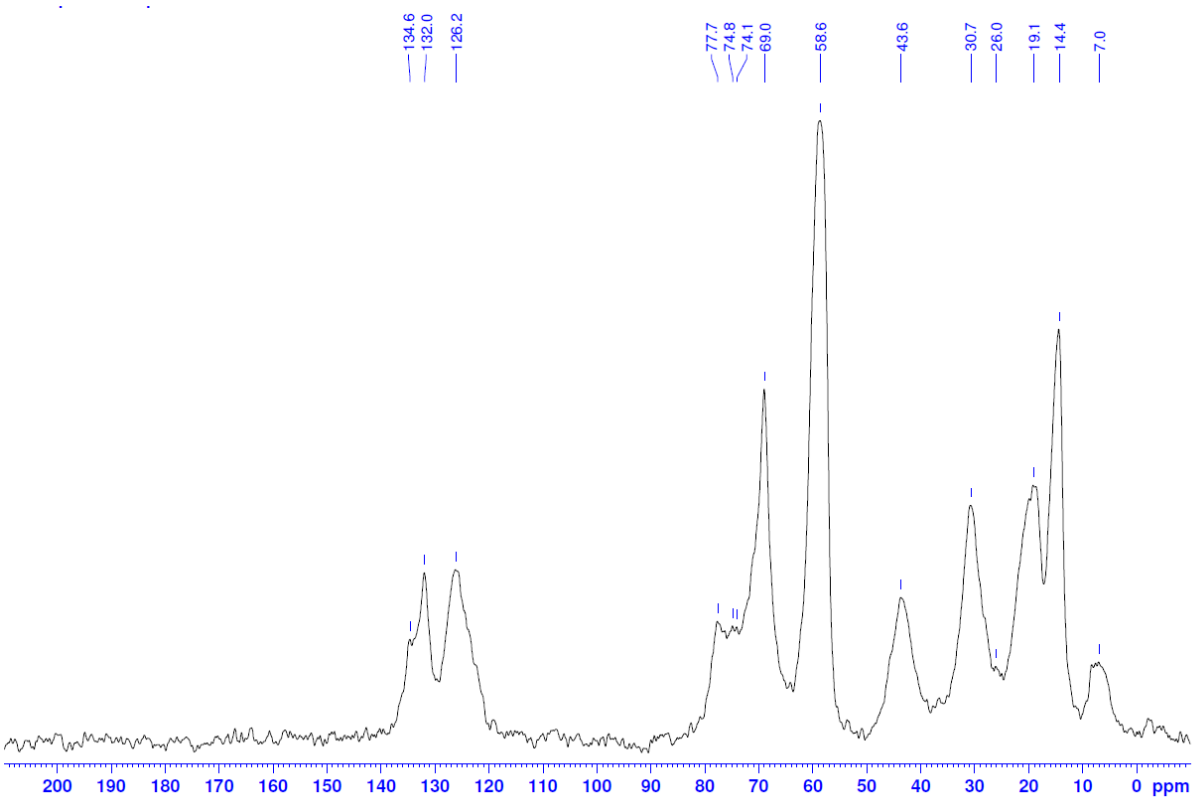
^{13}C CP-MAS solid state NMR of SBA_{56}-1 after 5days heating at 130°C in tert-butylbenzene:



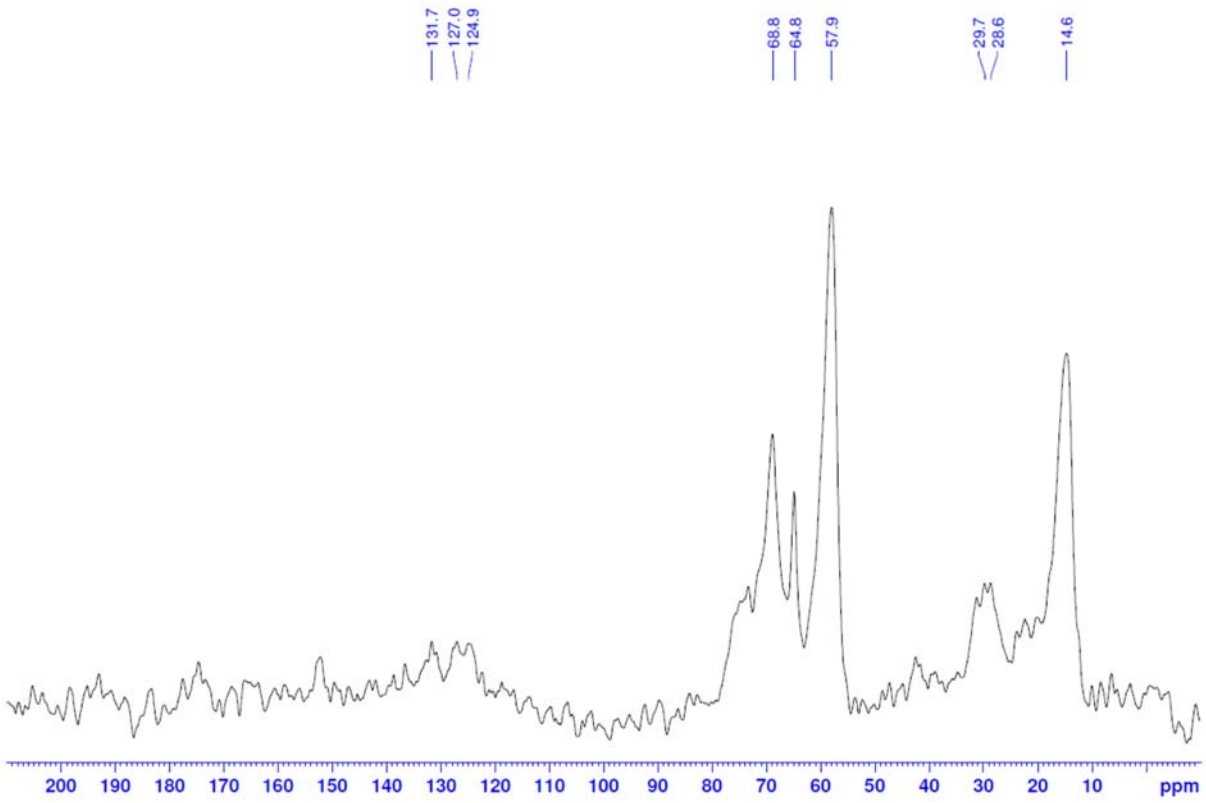
^{29}Si CP-MAS solid state NMR of SBA$_{56}$-1:



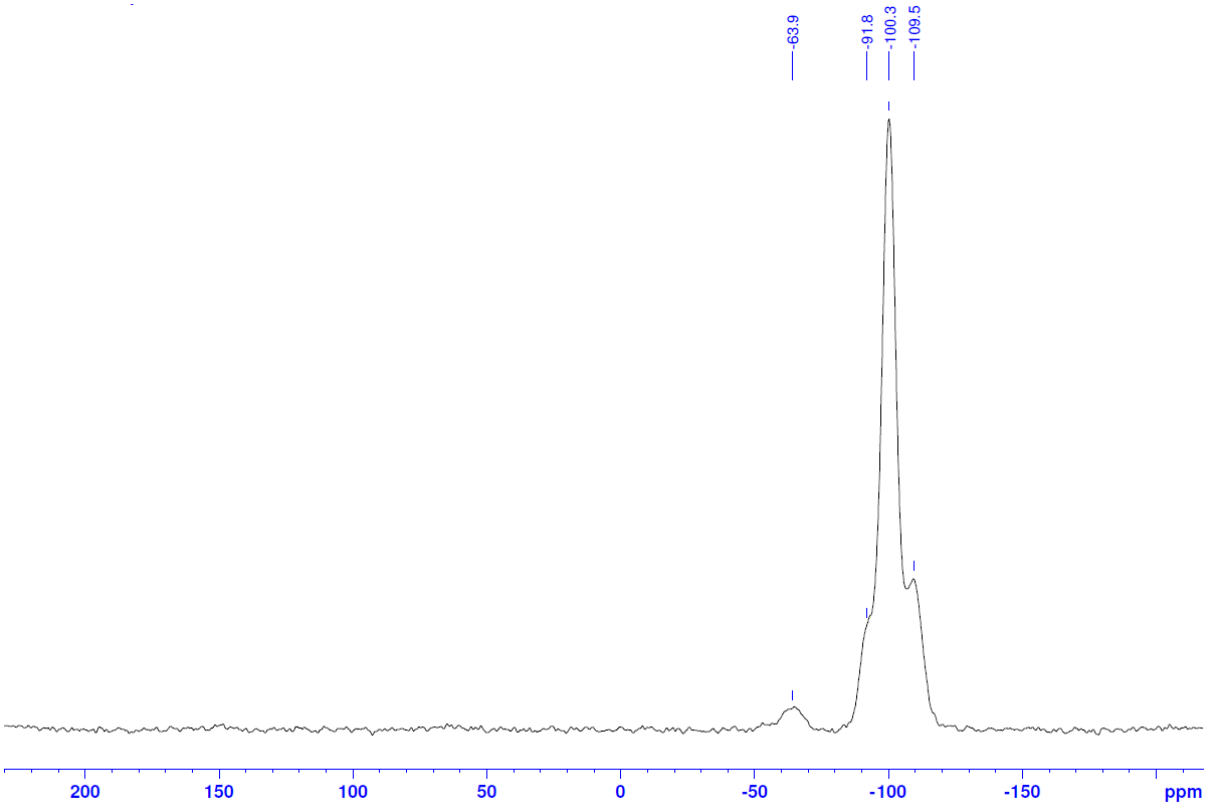
^{13}C CP-MAS solid state NMR of SBA$_{56}$-2:



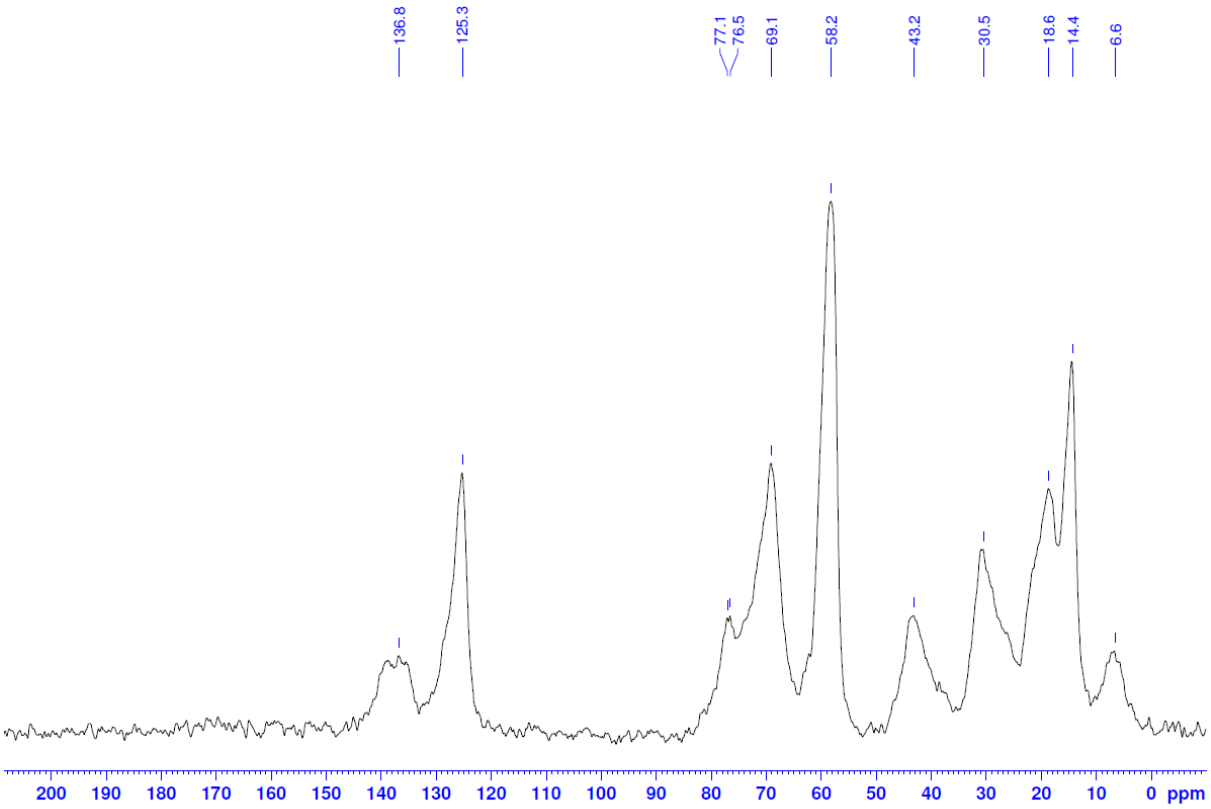
^{13}C CP-MAS solid state NMR of SBA$_{56}$-2 after 7days heating at 130°C in tert-butylbenzene:



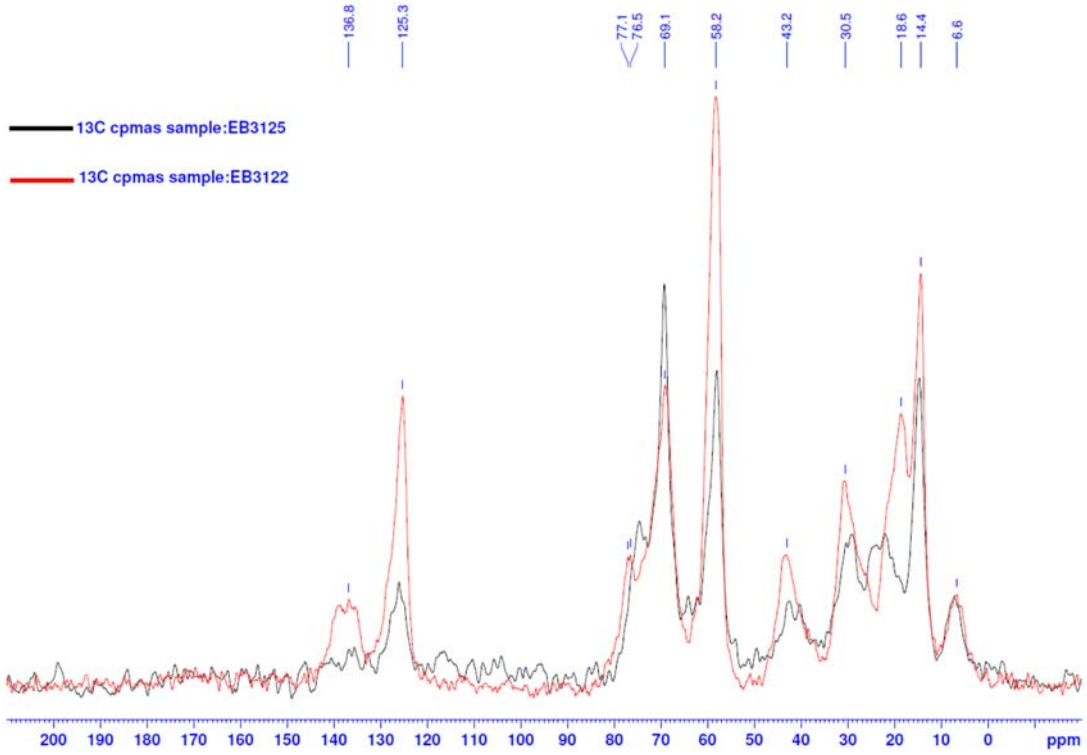
^{29}Si CP-MAS solid state NMR of SBA$_{56}$-2:



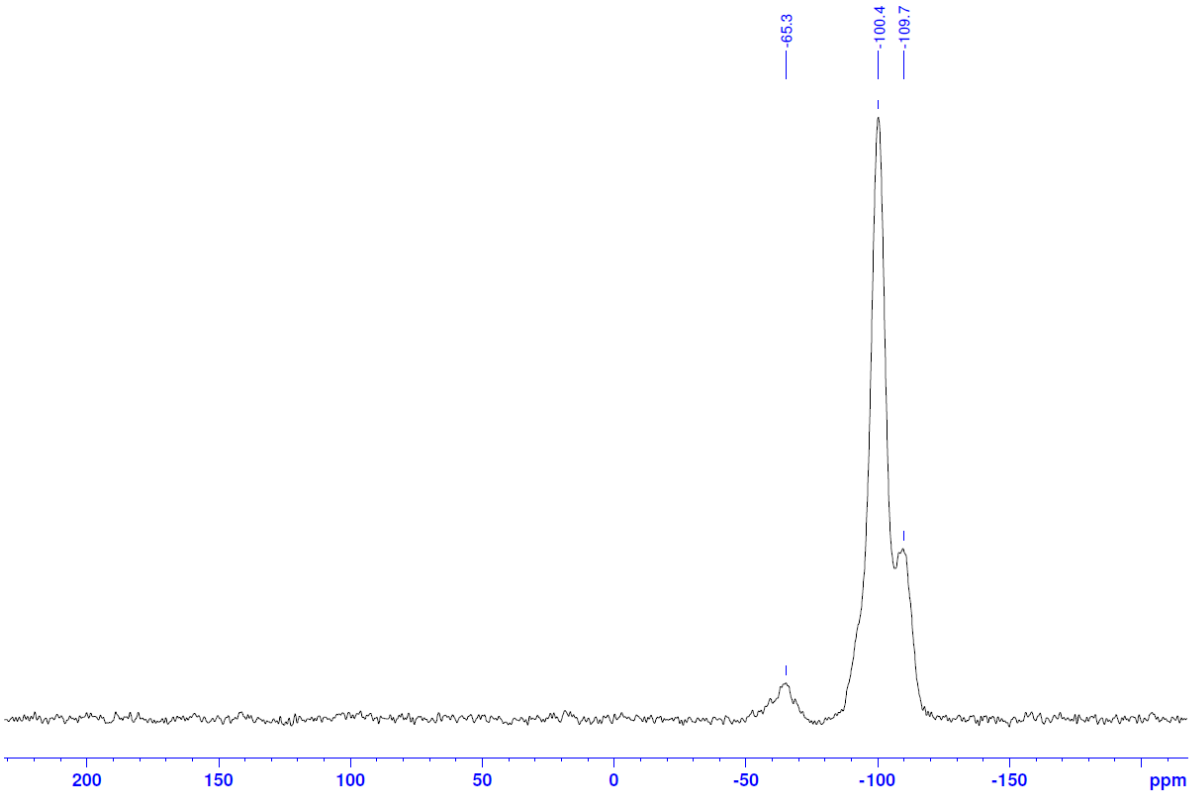
^{13}C CP-MAS solid state NMR of SBA$_{55}$-3:



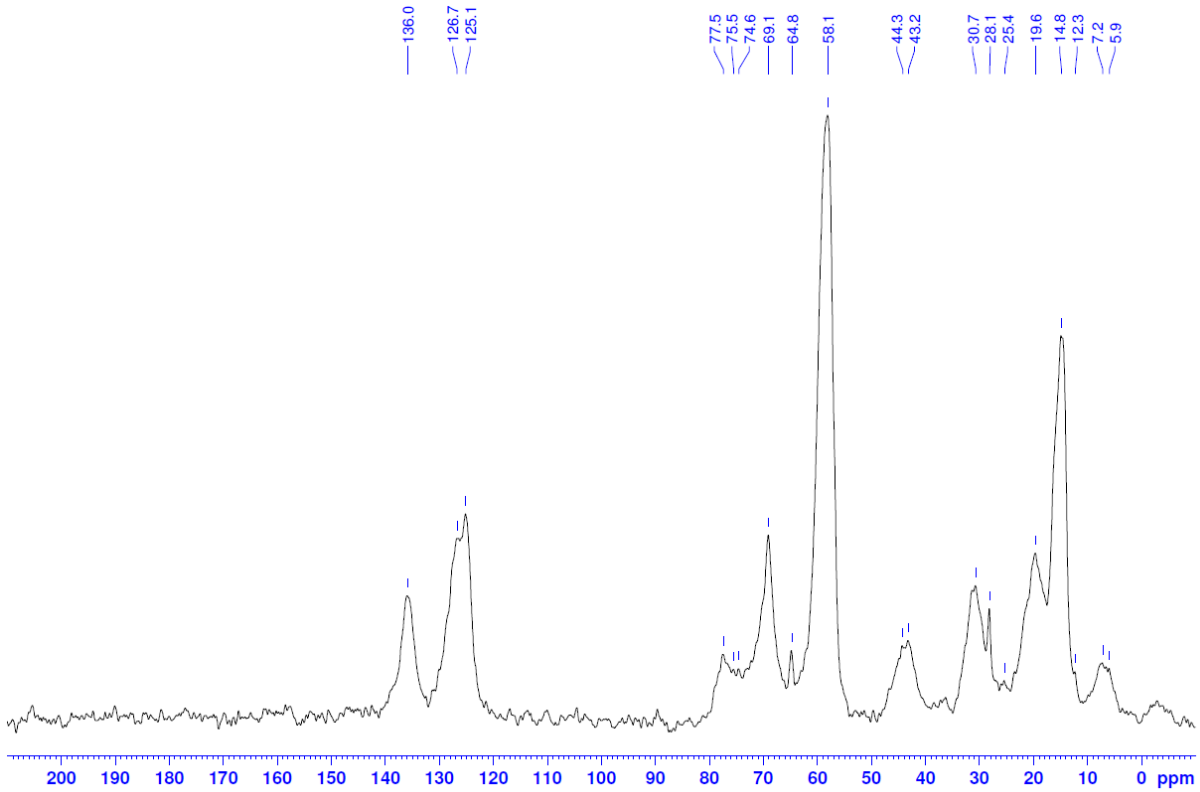
^{13}C CP-MAS solid state NMR of SBA$_{55}$-3 after 5days heating at 130°C in tert-butylbenzene:



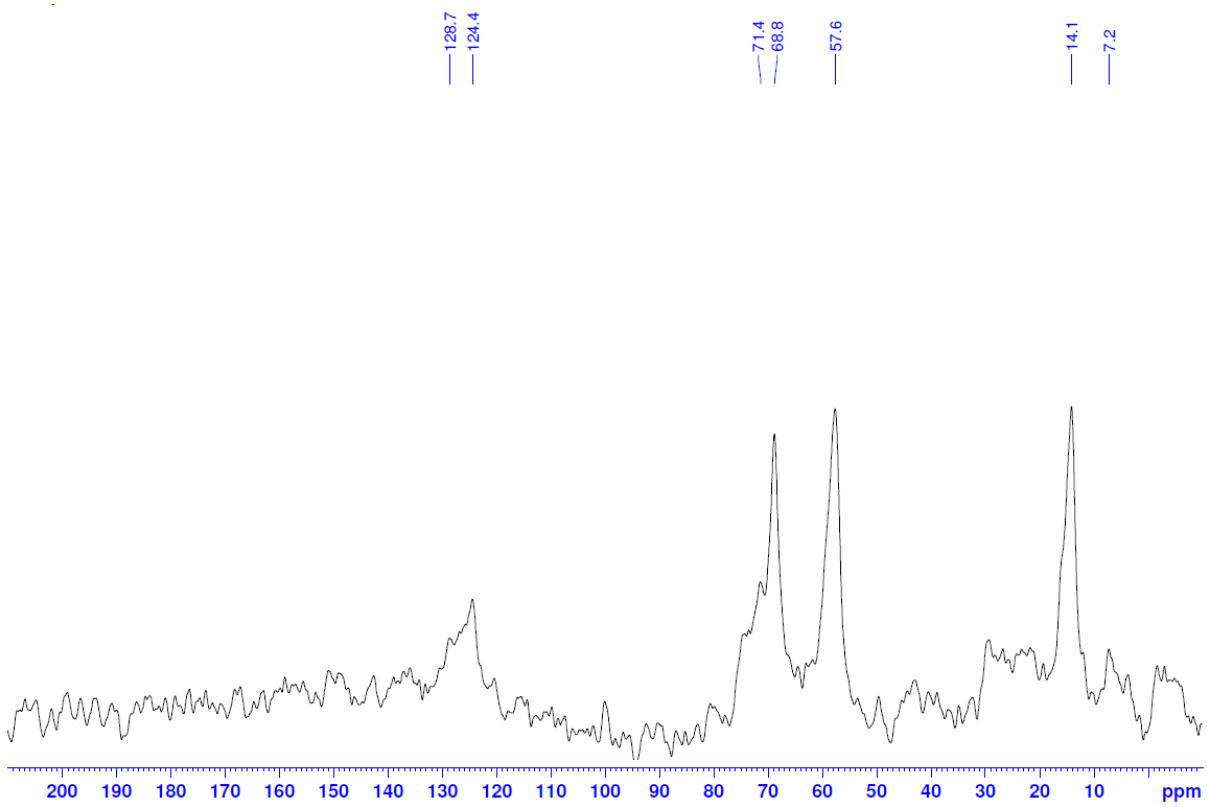
^{29}Si CP-MAS solid state NMR of SBA_{55}-3:



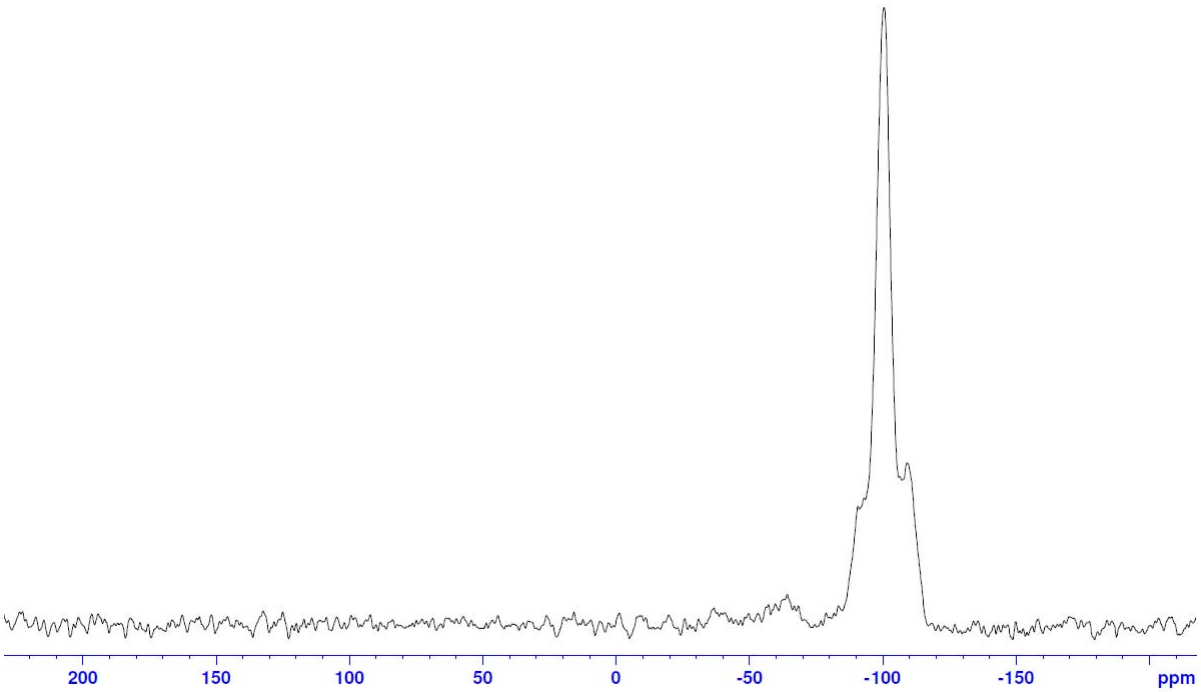
^{13}C CP-MAS solid state NMR of SBA_{60}-4:



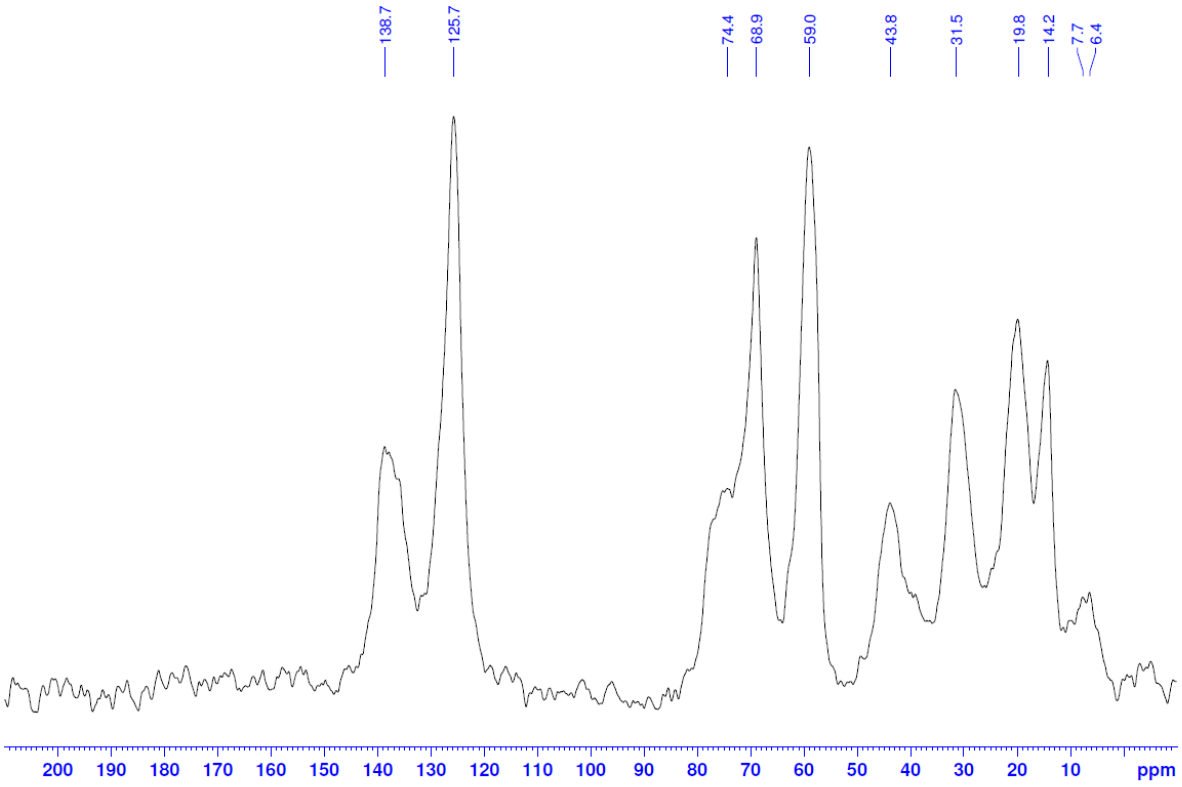
^{13}C CP-MAS solid state NMR of SBA_{60}-4 after 5days heating at 130°C in tert-butylbenzene:



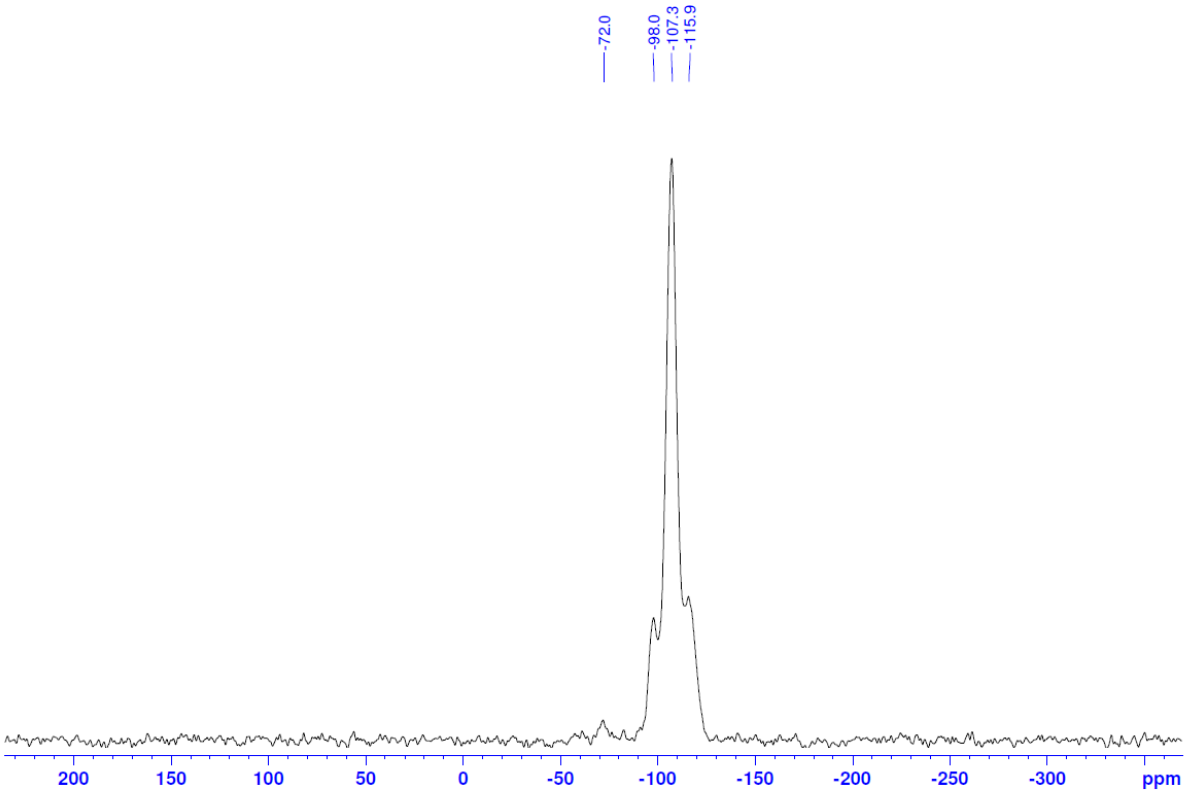
^{29}Si CP-MAS solid state NMR of SBA_{60}-4:



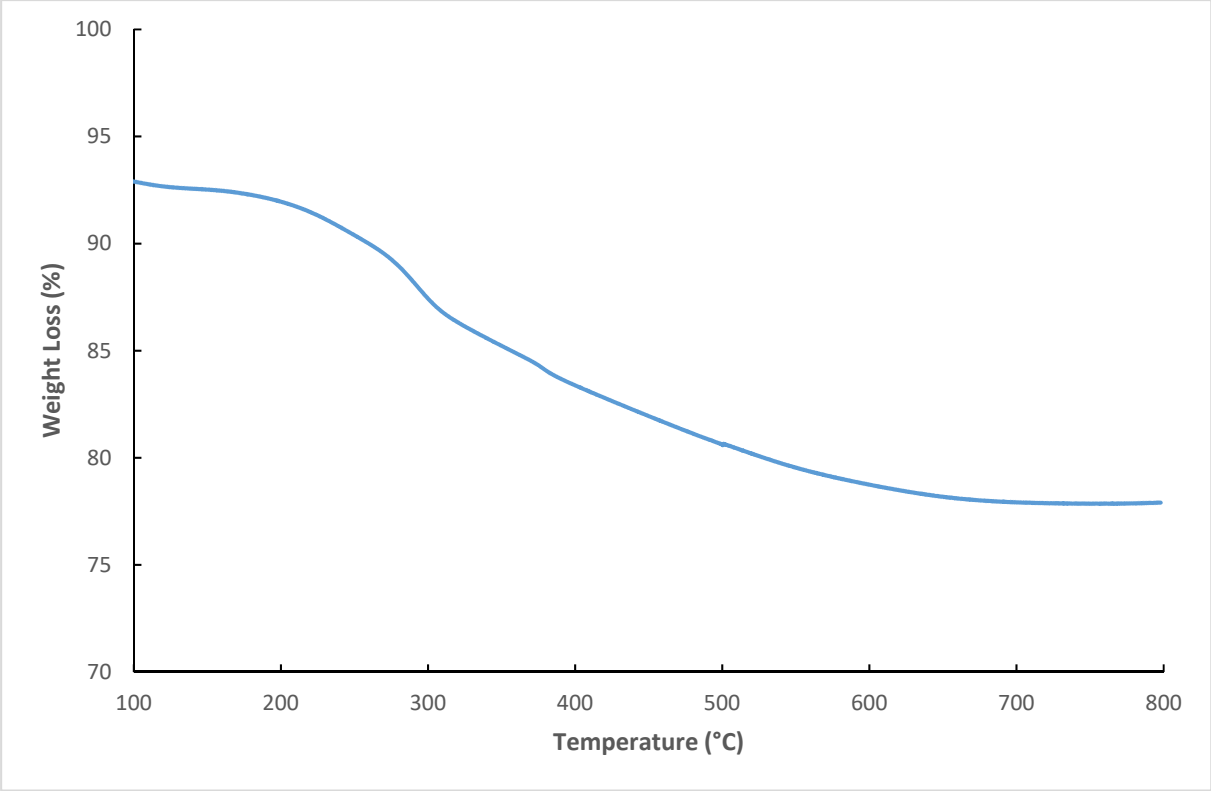
^{13}C CP-MAS solid state NMR of SBA$_{60}$-5:



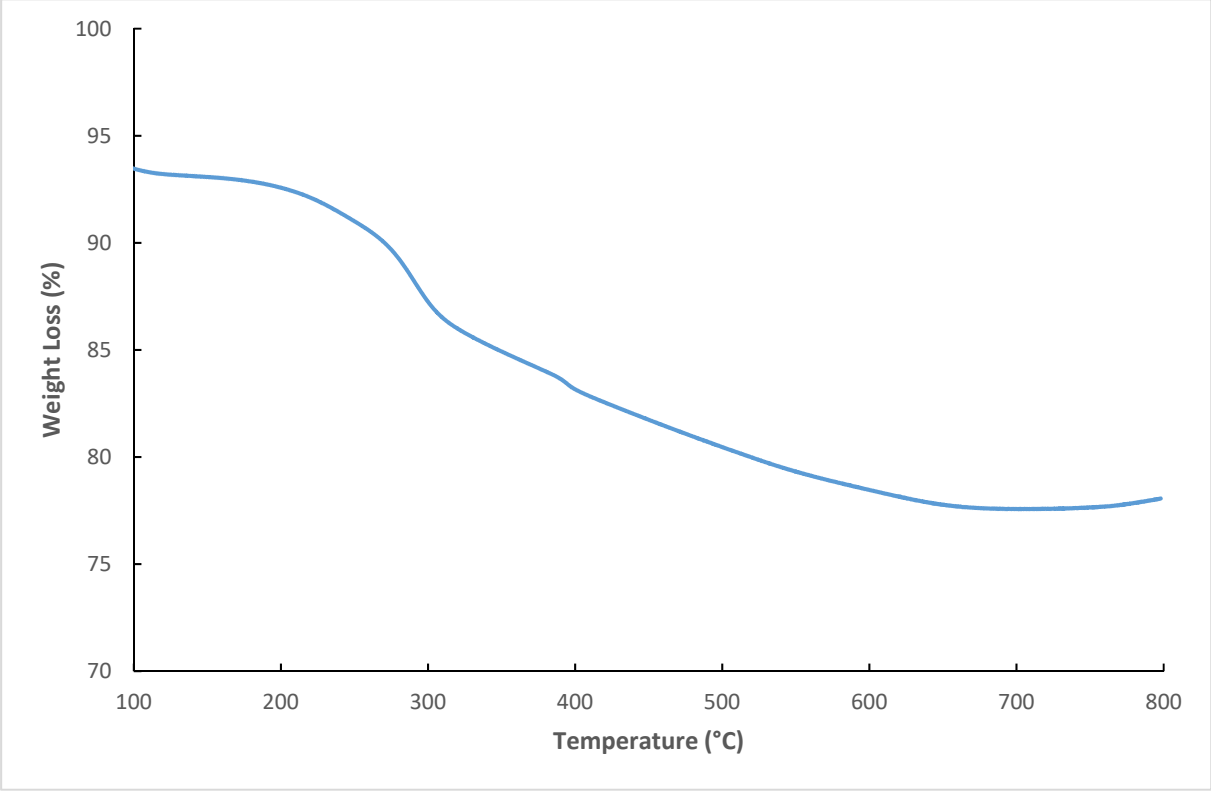
^{29}Si CP-MAS solid state NMR of SBA$_{60}$-5:



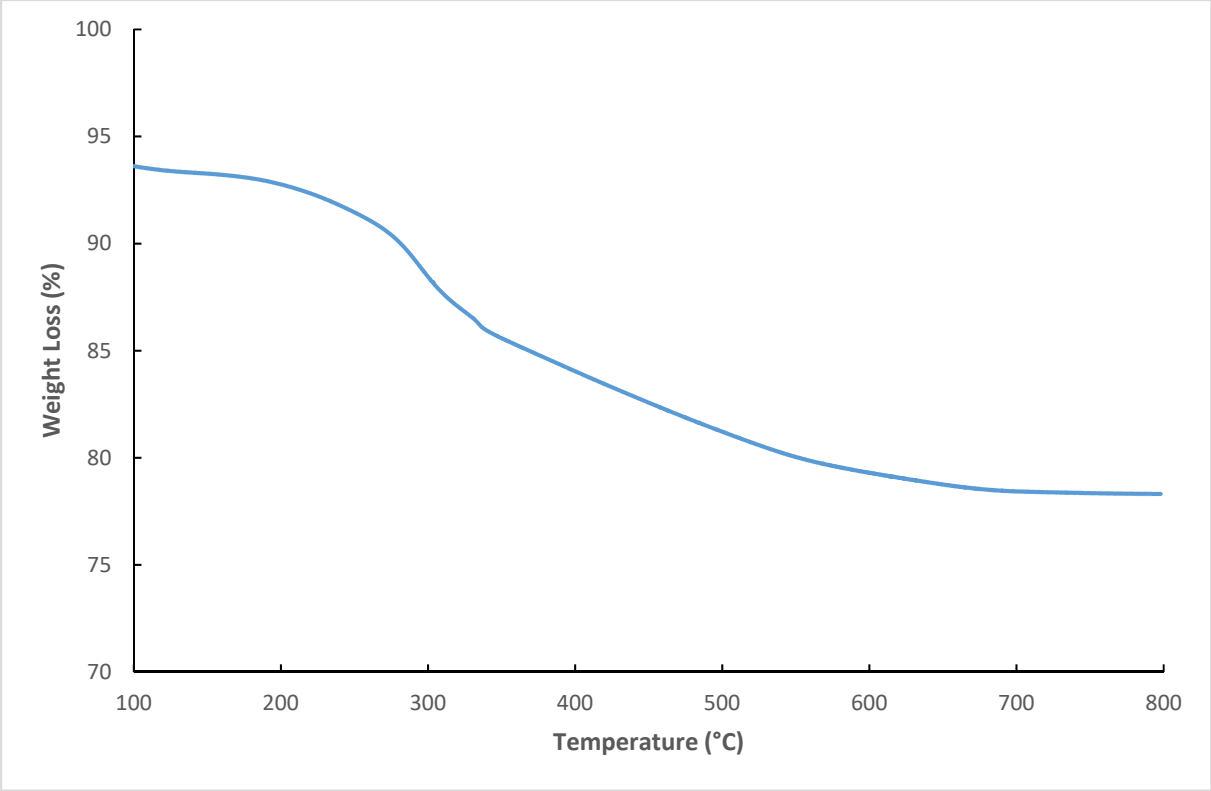
TGA for SBA_{56}-2,



TGA for SBA_{55}-3



TGA for SBA_{60}-4



TGA for SBA_{60}-5