

Supporting Information for
**A Bimolecular Micelle Constructed Amphiphilic
Pillar[5]arene Molecules**

*Tomoki Nishimura, Takuma Matsuo, Yusuke Sanada, and Kazuo Sakurai**

Tadashi Okobira

Efstratios Mylonas and Naoto Yagi

*The University of Kitakyushu, Department of Chemistry and Biochemistry, 1-1
Hibikino, Kitakyushu, Fukuoka, Japan 808-0135*

*Ariake National Colleges of Technology, Department of Chemical Science and
Engineering, 150 Higashihagio, Omuta, Fukuoka, Japan 836-8585*

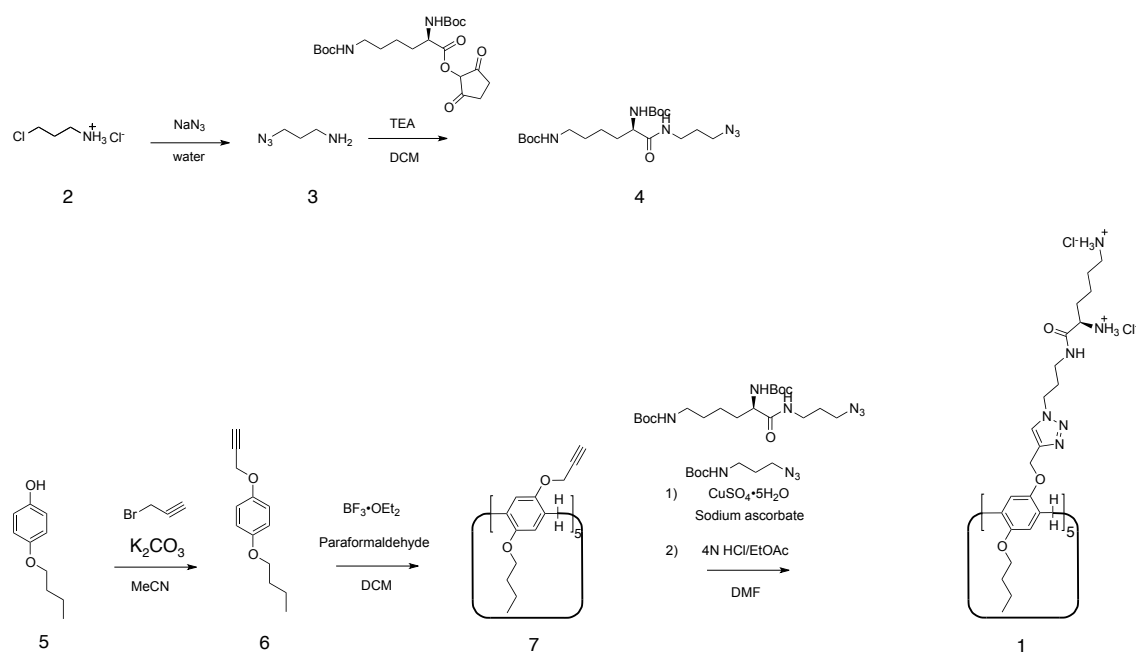
*Japan Synchrotron Radiation Research Institute (JASRI/SPring-8), 1-1-1 Koto,
Sayo, Hyogo, Japan 679-5198*

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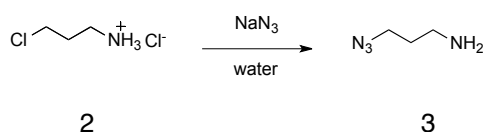
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Synthesis

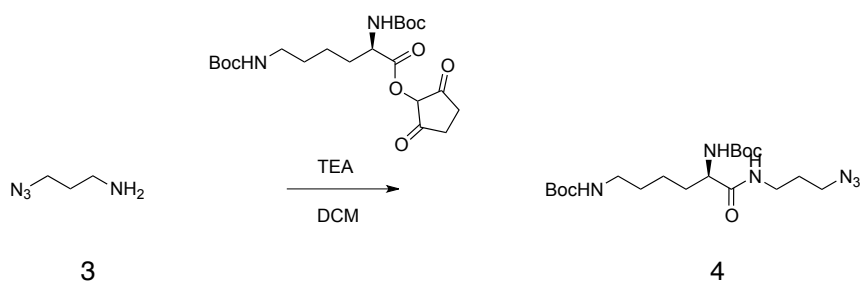
All starting materials were commercially available and were used without further purification. All solvents were reagent grade and were used as received. The progress of the reactions was monitored by thin layer chromatography (TLC, Merck254, silica) and the compounds were detected either by exposure to UV or by spraying with a basic solution of potassium permanganate. Flash column chromatography purifications were carried out on silica gel 60 (Kanto Chemical Co. Inc., 40—50 μm). Nuclear magnetic resonance spectra were run in chloroform-*d* or dimethylsulfoxide-*d*₆ using JEOL ECP-500 spectrometers to acquire ¹H and ¹³C NMR spectra. Chemical shifts (δ) are expressed in parts per million and are reported relative to trimethylsilane (TMS) as an internal standard in ¹H and ¹³C NMR spectra, with coupling constants (*J*) expressed in Hertz. All Mass spectrums were recorded on a micrOTOF electrospray time-of-flight (ESI-TOF) mass spectrometer (Bruker Daltonics) coupled to an Agilent Technologies 1200 LC system. Elemental analyses were performed on a YANAKO MT-6 CHN Corder.



Scheme S1 synthetic route for compound 1



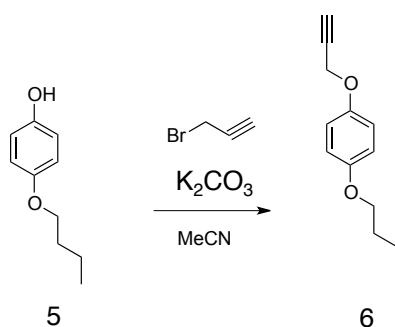
3-azidopropan-1-amine **3** was synthesized according to literature procedure.^[1]



Synthesis of (S) - di - tert-butyl (6-((3-azidopropyl) amino) -6- oxohexane -1,5-diy) dicarbamate 4

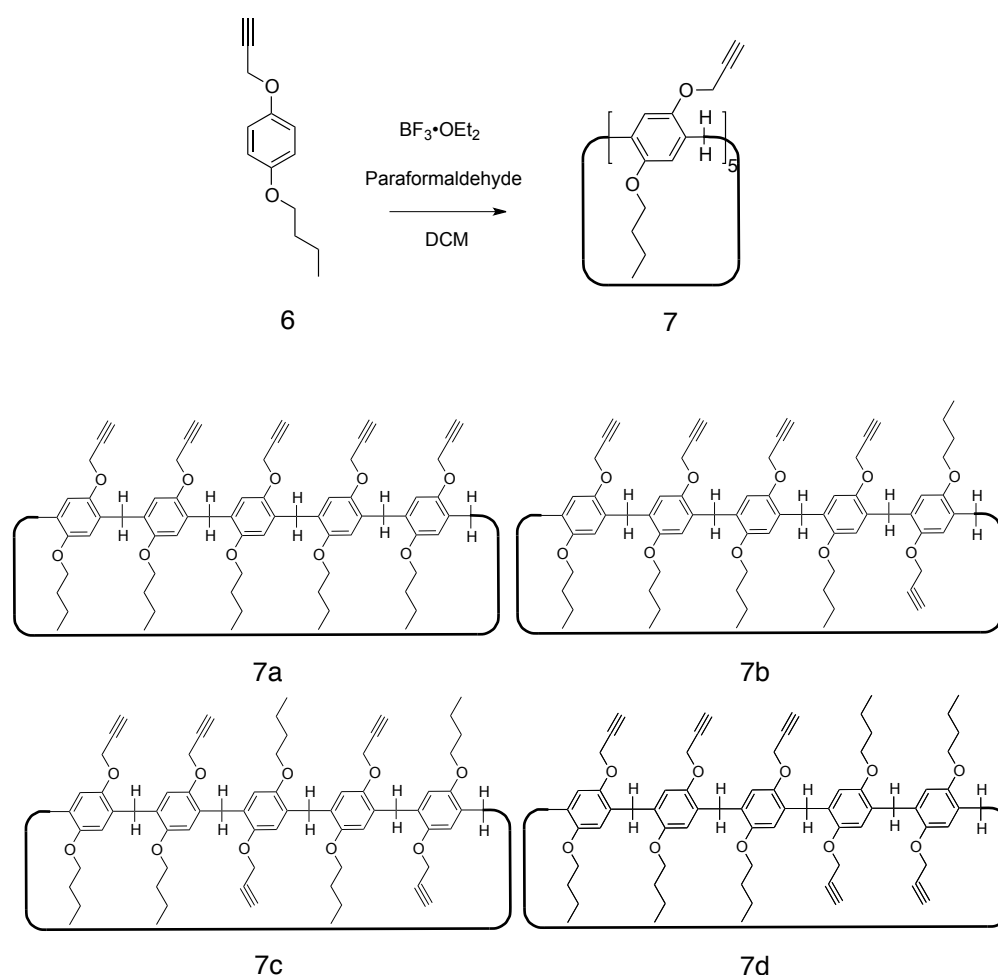
Boc-Lys(Boc)-OSu (2.39 g, 5.34 mmol) was added portionwise to a solution of **3** (0.61 g, 6.12 mmol) and triethylamine (1.16, 11.1 mmol) in DCM (100 mL) at 0 °C. The mixture was stirred for 3 hr at RT. The reaction was quenched with

sat. NaHCO_3 solution. Organic layers was washed with water and brine, dried over MgSO_4 and filtered. The solution was concentrated to give **4** as transparent viscous oil (1.99 g, 87% yield). $^1\text{H-NMR}$ (500 MHz; $[\text{CDCl}_3]$): δ 6.59 (s, 1H), 5.25-5.24 (m, 1H), 4.68 (m, 1H), 4.02 (m, 1H), 3.38-3.32 (m, 6H), 3.11 (m, 3H), 1.79 (dt, $J = 13.4, 6.7$ Hz, 4H), 1.65-1.59 (m, 1H), 1.44 (s, 18H). $^{13}\text{C-NMR}$ (126 MHz; $[\text{CDCl}_3]$): δ 149.8, 149.1, 143.9, 128.3, 124.92, 124.90, 114.59, 114.57, 68.1, 61.7, 47.2, 36.7, 32.0, 28.34, 28.29, 19.5, 14.4 HRMS: $[\text{M}+\text{Na}]^+$, m/z , (ESI, positive) found 451.2720. $\text{C}_{19}\text{H}_{36}\text{N}_6\text{O}_5\text{Na}$ requires 451.2640



Synthesis of 1-butoxy-4-(prop-2-yn-1-yloxy)benzene 6

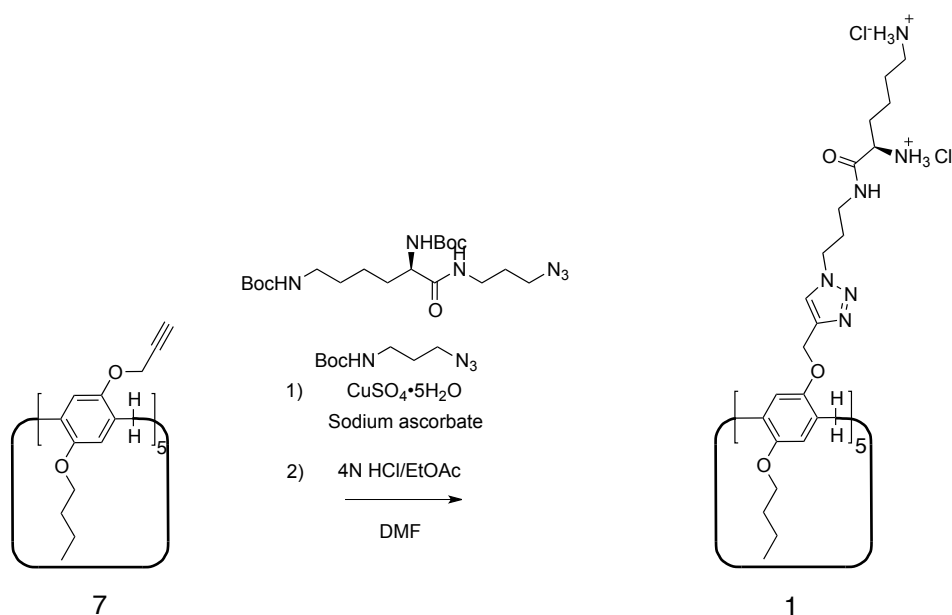
A mixture of **5** (5.83 g, 35.0 mmol), propargyl bromide (6.26g, 52.6 mmol), and potassium carbonate (14.53 g, 105.1 mmol) in dry acetonitrile (50 mL) were stirred at 60 °C for 3 h under N_2 . The reaction mixture was cooled to RT. After dilution with DCM, organic layer was washed with 2.5 M NaOH aqueous solution, water and brine and dried over MgSO_4 and filtered. The solvent was removed *in vacuo*. The crude product was purified by column chromatography on silica using Hexane/Ethyl acetate=10/1 as the eluent to yield 6.43 g (90%) of **6** as a yellow oil. $^1\text{H-NMR}$ (500 MHz; $[\text{CDCl}_3]$): δ 6.93-6.82 (m, 4H), 4.63 (d, $J = 2.3$ Hz, 2H), 3.91 (t, $J = 6.5$ Hz, 2H), 2.50 (ddt, $J = 2.4, 1.6, 0.7$ Hz, 1H), 1.77-1.71 (m, 2H), 1.48 (sextet, $J = 7.5$ Hz, 2H), 0.97 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C-NMR}$ (126 MHz; $[\text{CDCl}_3]$): δ 150.0, 149.1, 143.9, 128.48, 128.35, 124.9, 114.9, 114.5, 68.6, 61.8, 47.2, 36.77, 36.69, 31.8, 29.9, 28.36, 28.31, 25.9, 22.6, 14.4. Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2$: C, 76.44; H, 7.90. Found: C, 76.28; H, 7.92.



Synthesis of Butoxy propynyloxy Pillar[5]arene 7a

To a solution of **6** (3.04 g, 14.9 mmol) and paraformaldehyde (1.34g, 44.7 mmol) in 1,2-dichloroethane (150 mL) was added boron trifluoride diethylether complex (2.21 g, 15.6 mmol) under N_2 . The solution was stirred for 3 h at RT. The reaction was quenched with methanol. Organic layer was washed with water and brine and dried over MgSO_4 and filtered. The crude product was purified by column chromatography on silica using Hexane/Ethyl acetate=5/1 as the eluent to yield 1.81 g (56 %) of **7** as a white powder. Non-symmetric pillar[5]arene **7** has four constitutional isomers **7a**, **7b**, **7c**, and **7d**. The desired compound **7a** could be separated here (0.13 g, 4%). $^1\text{H-NMR}$ (500 MHz; $[\text{CDCl}_3]$): δ 6.94 (s, 1H), 6.76 (s, 1H), 4.57 (d, $J = 2.2$ Hz, 2H), 3.87 (t, $J = 6.5$ Hz, 2H), 3.80 (s, 2H), 2.29-2.28 (m, 1H), 1.83-1.77 (m, 2H), 1.56 (dq, $J = 14.9, 7.4$ Hz,

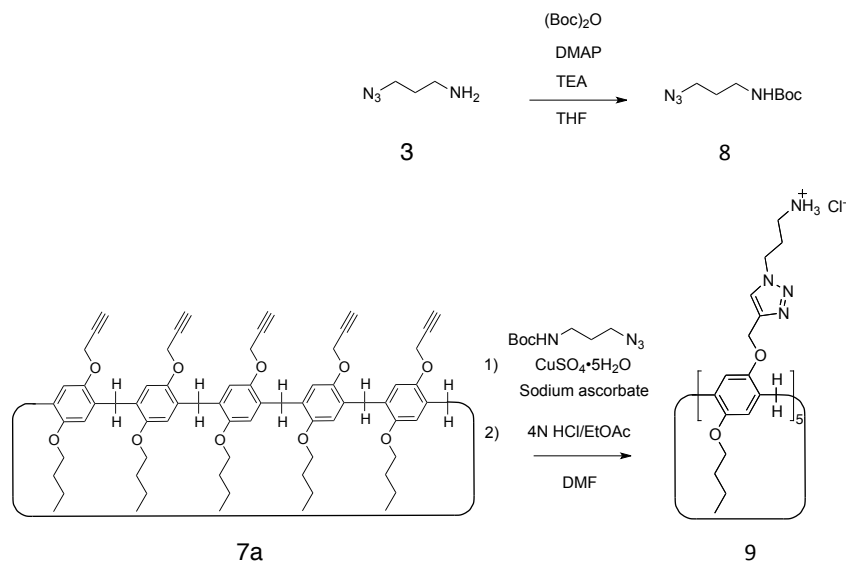
2H), 1.00 (t, $J = 7.4$ Hz, 3H). ^{13}C -NMR (126 MHz; $[\text{CDCl}_3]$): δ 14.10, 14.20, 19.61, 22.70, 29.57, 31.64, 32.07, 56.47, 67.97, 74.79, 79.57, 114.62, 115.15, 128.16, 128.77, 148.66, 150.53 HRMS: $[\text{M}+\text{Na}]^+$, m/z , (ESI, positive) found 1103.5625. $\text{C}_{70}\text{H}_{80}\text{O}_{10}\text{Na}$ requires 1103.5644



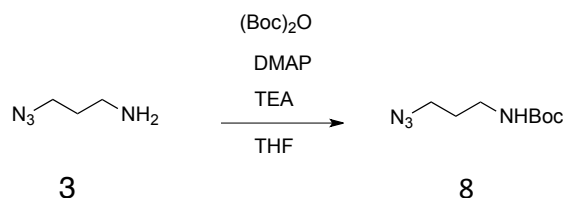
Synthesis of 1

A mixture of **7a** (0.133 g, 0.123 mmol), copper sulfate pentahydrate (0.003 g, 0.012 mmol), sodium ascorbate (0.005 g, 0.025 mmol) and (S)-di-tert-butyl (6-((3-azidopropyl)amino)-6-oxohexane-1,5-diyl) dicarbamate (0.267 g, 0.616 mmol) in dry *N,N*-dimethylformamide (6 mL) were stirred at 50 °C for 15 h under N_2 . The reaction mixture was cooled to RT. The solvent was removed *in vacuo*. The Boc protected product was isolated by flash column chromatography on silica using ethyl acetate as the eluent. The Boc protected compound was dissolved in 4N HCl/EtOAc. The solution was stirred for 2 hr at RT. The solvent was removed *in vacuo*. The residue was washed with dichloromethane to give the desired product as pale yellow solid (0.233 g, 75 % in 2 steps) ^1H -NMR (500 MHz; $[\text{DMSO}-d_6]$): δ 9.08 (s, 1H), 8.47-8.44 (m, 4H), 8.21 (s, 3H), 6.88 (d, $J = 16.0$ Hz, 2H), 5.02-4.73 (m, 2H), 4.43 (s, 2H), 3.85 (s, 3H), 3.65 (s, 2H), 3.17-3.08 (m, 2H), 2.77 (s, 2H), 1.98-1.97 (m, 2H), 1.78-1.74 (m, 4H), 1.64-1.62 (m, 2H), 1.50-1.46 (m, 2H), 1.41 (m, 2H), 0.92 (q, $J = 8.8$ Hz, 3H). ^{13}C -NMR (126 MHz; $[\text{DMSO}-d_6]$): δ 169.1, 149.8, 149.1, 143.7, 128.4, 124.9,

114.9, 68.1, 61.8, 55.5, 52.5, 47.7, 40.1, 36.5, 32.0, 30.8, 30.2, 26.8, 21.8,
19.5, 14.4 HRMS: $[M+Na]^+$, m/z , (ESI, positive) found 2245.4177.
C₁₁₅H₁₈₀N₃₀O₁₅Na requires 2245.4171

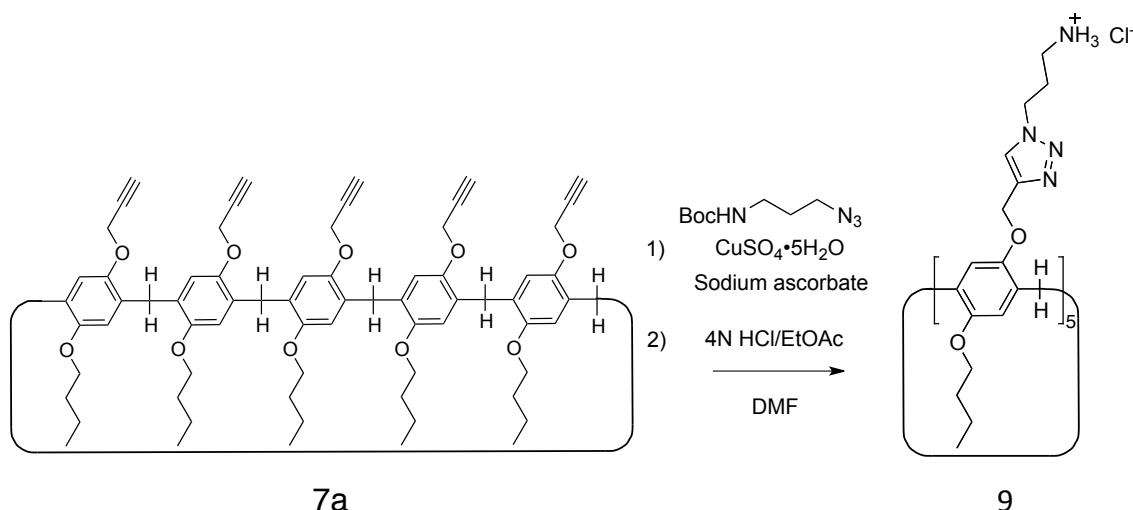


Scheme S2 synthetic route for compound 9



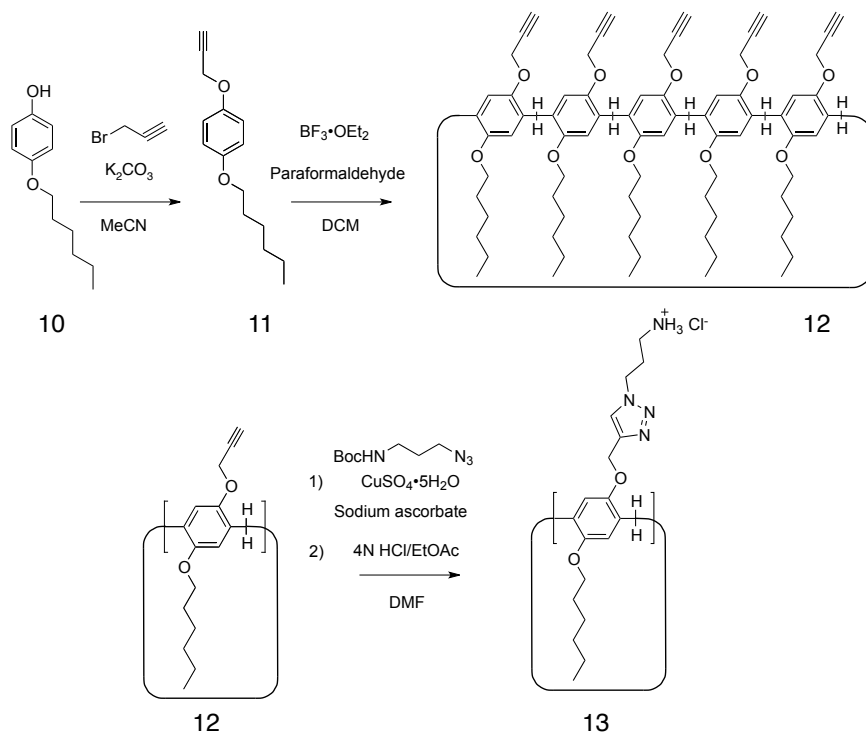
Synthesis of amino propyl azido 8

(Boc)₂O (3.78 g, 13.8 mmol) was added portionwise to a solution of **3** (0.92 g, 9.19 mmol), triethylamine (1.02 g, 10.1 mmol), and Dimethylaminopyridine (0.142g, 0.92 mmol) in THF (5 mL) at 0 °C. The mixture was stirred for overnight at RT. The solvent was removed in vacuo. Diethylether (20 mL) was added. The organic layer was washed with 10 % NaHCO₃ aqueous solution, brine, and water, dried over MgSO₄ and filtered. The solution was concentrated to give **8** as yellow oil (1.56 g, 83% yield). ¹H-NMR (500 MHz; [CDCl₃]): δ 3.36 (t, J = 6.7 Hz, 2H), 3.22 (q, J = 6.3 Hz, 2H), 1.78 (m, 2H), 1.44 (s, 9H). ¹³C-NMR (126 MHz; [CDCl₃]): δ 156.0, 49.2, 38.1, 29.4, 28.5, 28.1 HRMS: [M+Na]⁺, *m/z*, (ESI, positive) found 223.1149. C₈H₁₆N₄O₂Na requires 223.1171

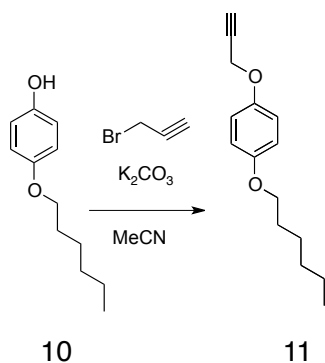


Synthesis of 9

A mixture of **7a** (0.131 g, 0.121 mmol), copper sulfate pentahydrate (0.003 g, 0.012 mmol), sodium ascorbate (0.005 g, 0.025 mmol) and (*S*)-di-tert-butyl (6-((3-azidopropyl)amino)-6-oxohexane-1,5-diyl) dicarbamate (0.242 g, 1.21 mmol) in dry *N,N*-dimethylformamide (2.5 mL) were stirred at 50 °C for 15 h under N₂. The reaction mixture was cooled to RT. The solvent was removed *in vacuo*. The Boc protected product was isolated by flash column chromatography on silica using ethyl acetate as the eluent. The Boc protected compound was dissolved in 4N HCl/EtOAc. The solution was stirred for 3 hr at RT. The solvent was removed *in vacuo*. The residue was washed with dichloromethane to give the desired product as pale yellow solid (0.173 g, 81 % in 2 steps) 1H-NMR (500 MHz; [DMSO-d₆]): δ 8.39 (m, 3H), 7.58 (s, 1H), 6.88 (d, J = 13.6 Hz, 2H), 4.88 (m, 1H), 4.48 (t, J = 6.6 Hz, 2H), 3.84 (m, 2H), 3.64 (s, 2H), 2.80 (s, 2H), 2.16 (quintet, J = 7.0 Hz, 2H), 1.72 (s, 2H), 1.47 (dq, J = 14.9, 7.4 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H). 13C-NMR (126 MHz; [DMSO-d₆]): δ 149.8, 149.1, 143.9, 128.3, 124.92, 124.90, 114.59, 114.57, 68.1, 61.7, 47.2, 36.7, 32.0, 28.34, 28.29, 19.5, 14.4 HRMS: [M+Na]⁺, *m/z*, (ESI, positive) found 1604.9521. C₈₅H₁₂₀N₂₀O₁₀Na requires 1604.9423



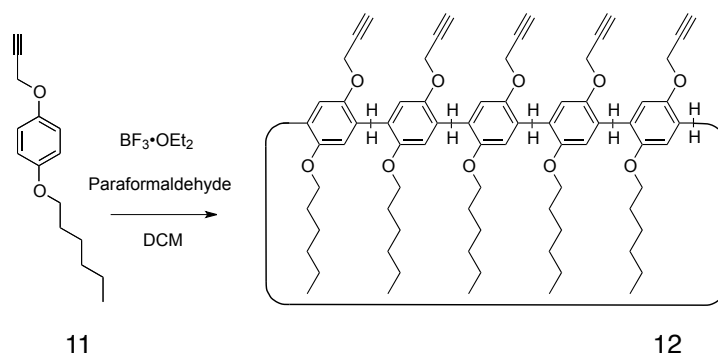
Scheme S3 synthetic route for compound **13**



Synthesis of 1-hexyloxy-4-(prop-2-yn-1-yloxy)benzene **11**

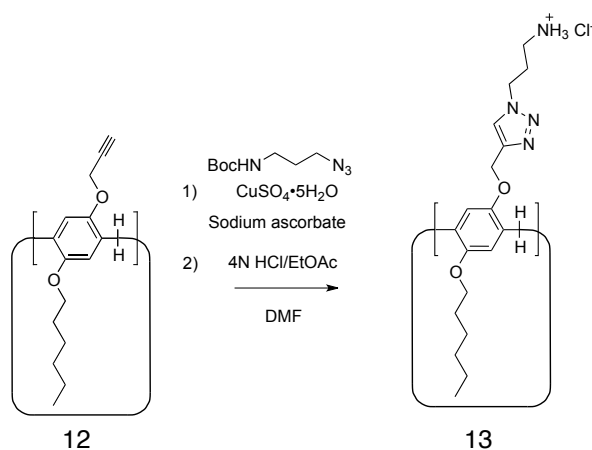
A mixture of **10** (5.20 g, 26.8 mmol), propargyl bromide (4.78g, 40.2 mmol), and potassium carbonate (11.4 g, 80.3 mmol) in dry acetonitrile (50 mL) were stirred at 80 °C for 3 h under N₂. The reaction mixture was cooled to RT. After dilution with DCM, organic layer was washed with 2.5 M NaOH aqueous solution, water and brine and dried over MgSO₄ and filtered. The solvent was removed *in vacuo*. The crude product was purified by column chromatography on silica using Hexane/Ethyl acetate=100/1 as the eluent to yield 4.81 g (77 %) of **6** as a yellow oil. ¹H-NMR (500 MHz; [CDCl₃]): δ 6.93-6.83 (m, 4H), 4.63 (d, J = 2.4 Hz,

2H), 3.90 (t, $J = 6.6$ Hz, 2H), 2.50 (t, $J = 2.3$ Hz, 1H), 1.75 (quintet, $J = 7.4$ Hz, 2H), 1.48-1.42 (m, 2H), 1.35-1.33 (m, 4H), 0.91 (t, $J = 6.5$ Hz, 3H). $^{13}\text{C-NMR}$ (126 MHz; $[\text{CDCl}_3]$): δ 154.2, 151.7, 116.2, 115.4, 79.0, 75.3, 68.7, 56.7, 31.7, 29.4, 25.8, 22.7, 14.1. Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2$: C, 77.55; H, 8.68. Found: C, 77.30; H, 8.71.



Synthesis of Hexyloxy propynyloxy Pillar[5]arene 12

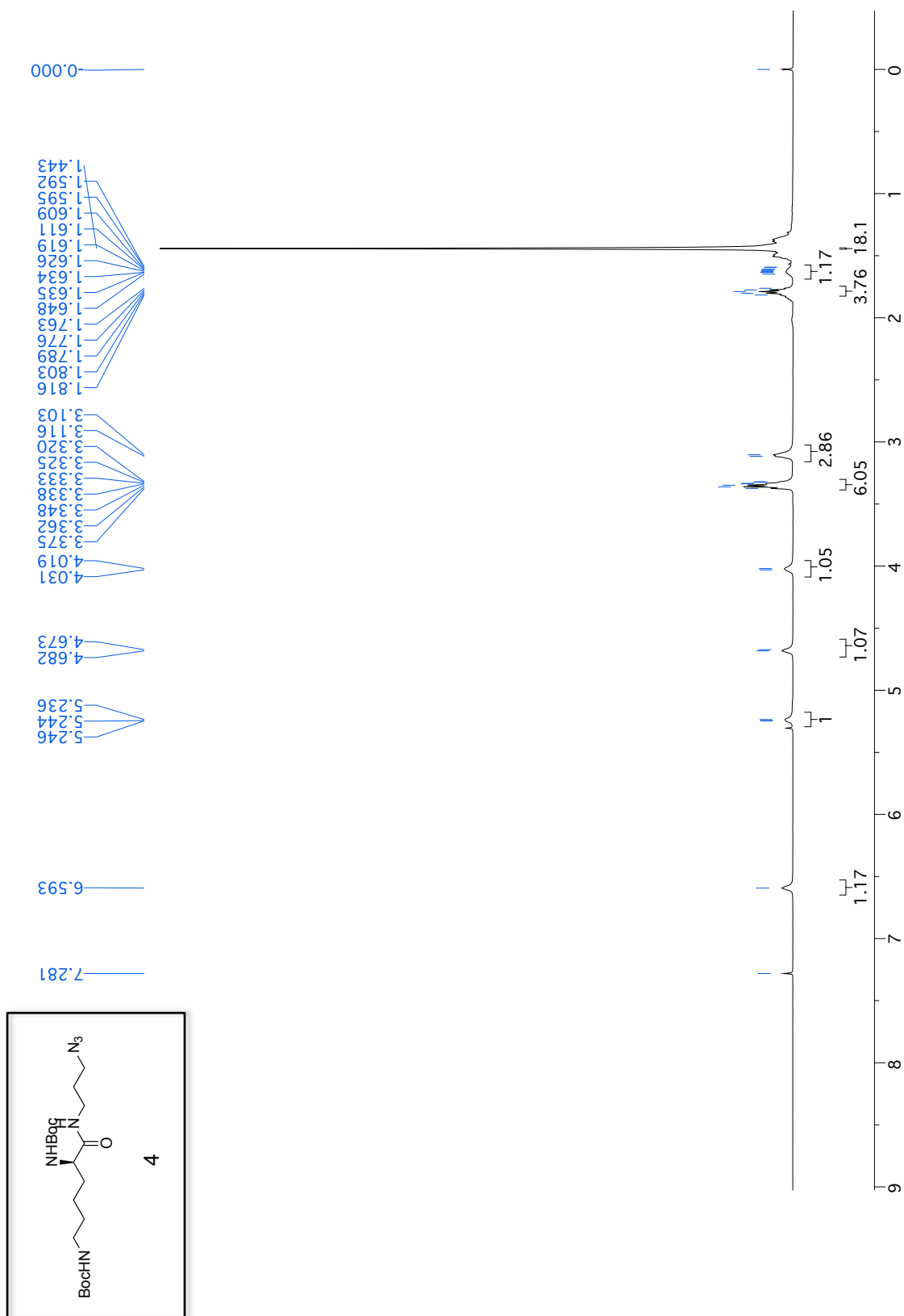
To a solution of **11** (4.75 g, 20.4 mmol) and paraformaldehyde (1.84 g, 61.2 mmol) in 1,2-dichloroethane (210 mL) was added boron trifluoride diethylether complex (3.64 g, 21.4 mmol) under N_2 . The solution was stirred for 3 h at RT. The reaction was quenched with methanol. Organic layer was washed with water and brine and dried over MgSO_4 and filtered. The crude product was purified by column chromatography on silica using Hexane/Ethyl acetate=5/1 as the eluent to yield 0.33 g (7 %) of **12** as a white powder. $^1\text{H-NMR}$ (500 MHz; $[\text{CDCl}_3]$): δ 6.94 (s, 1H), 6.75 (s, 1H), 4.56 (d, $J = 2.4$ Hz, 2H), 3.85 (t, $J = 6.5$ Hz, 2H), 3.78 (s, 2H), 2.28 (t, $J = 2.4$ Hz, 1H), 1.80 (dt, $J = 14.7, 7.1$ Hz, 2H), 1.55-1.49 (m, 2H), 1.36-1.33 (m, 4H), 0.90 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C-NMR}$ (126 MHz; $[\text{CDCl}_3]$): δ 150.6, 148.7, 128.8, 128.1, 115.2, 114.7, 79.6, 74.8, 68.4, 56.5, 31.9, 31.6, 29.9, 29.6, 26.1, 22.7, 14.22, 14.16 HRMS: $[\text{M}+\text{Na}]^+$, m/z , (ESI, positive) found 1243.7271. $\text{C}_{80}\text{H}_{100}\text{O}_{10}\text{Na}$ requires 1243.7209



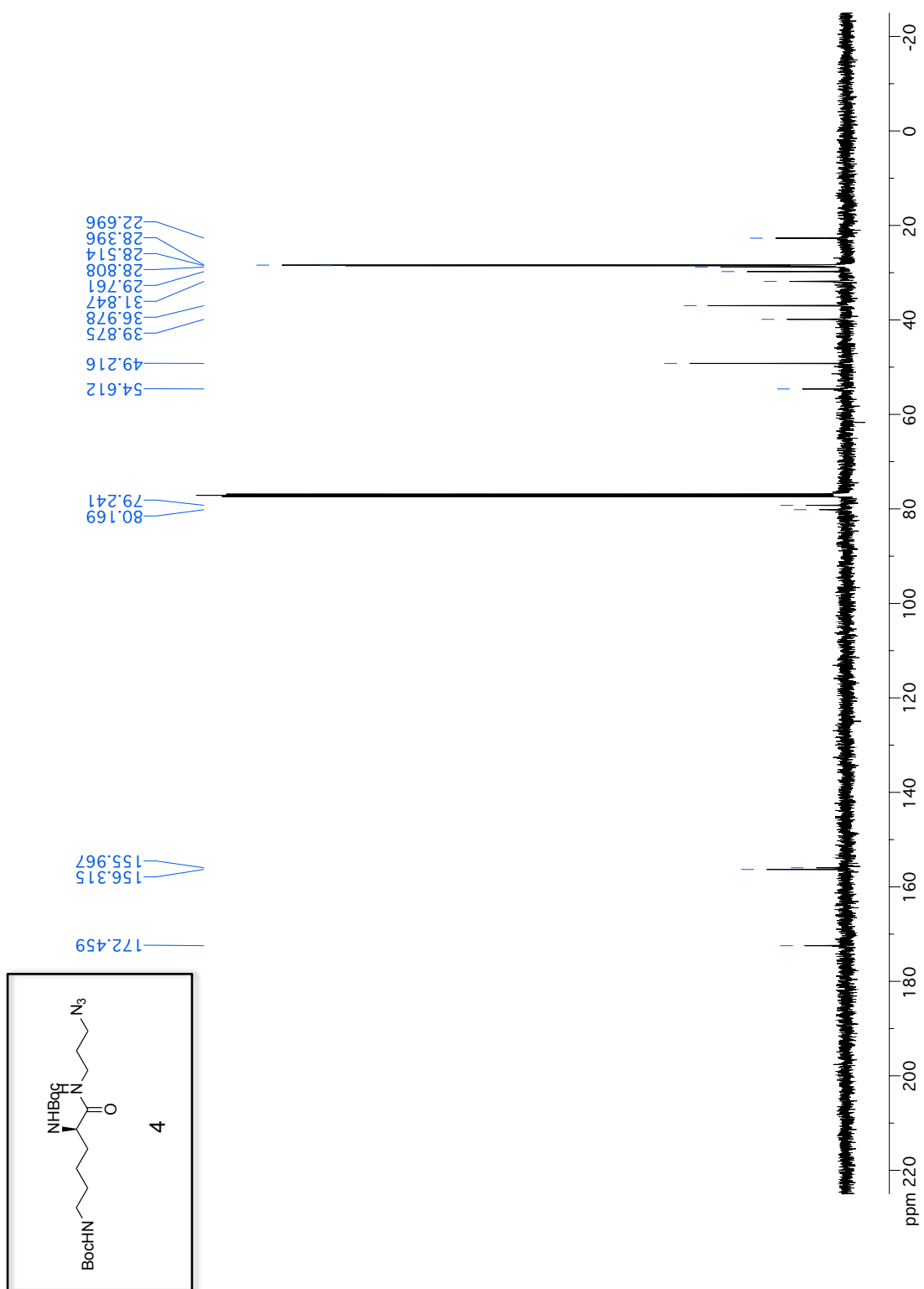
Synthesis of 13

A mixture of **12** (0.101 g, 0.083 mmol), copper sulfate pentahydrate (0.002 g, 0.008 mmol), sodium ascorbate (0.003 g, 0.016 mmol) and (*S*)-di-*tert*-butyl (6-((3-azidopropyl)amino)-6-oxohexane-1,5-diyl) dicarbamate (0.166 g, 0.83 mmol) in dry *N,N*-dimethylformamide (4 mL) were stirred at 50 °C for 24 h under N₂. The reaction mixture was cooled to RT. The solvent was removed *in vacuo*. The Boc protected product was isolated by flash column chromatography on silica using ethyl acetate as the eluent. The Boc protected compound was dissolved in 4N HCl/EtOAc. The solution was stirred for 2 hr at RT. The solvent was removed *in vacuo*. The residue was washed with dichloromethane to give the desired product as pale yellow solid (0.127 g, 80 % in 2 steps) ¹H-NMR (500 MHz; [DMSO-*d*₆]): δ 8.40 (s, 1H), 8.31 (s, 3H), 6.92-6.85 (m, 2H), 5.02 (s, 1H), 4.74 (s, 1H), 4.52-4.47 (m, 7H), 3.93 (s, 1H), 3.73 (s, 1H), 3.65 (s, 2H), 2.81-2.80 (m, 2H), 2.16 (dt, *J* = 14.4, 7.2 Hz, 2H), 1.78 (s, 2H), 1.49 (s, 3H), 1.34-1.33 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H). ¹³C-NMR (126 MHz; [DMSO-*d*₆]): δ 150.0, 149.1, 143.9, 128.48, 128.35, 124.9, 114.9, 114.5, 68.6, 61.8, 47.2, 36.77, 36.69, 31.8, 29.9, 28.36, 28.31, 25.9, 22.6, 14.4 HRMS: [M+Na]⁺, *m/z*, (ESI, positive) found 1745.1201. C₉₅H₁₄₀N₂₀O₁₀Na requires 1745.0988

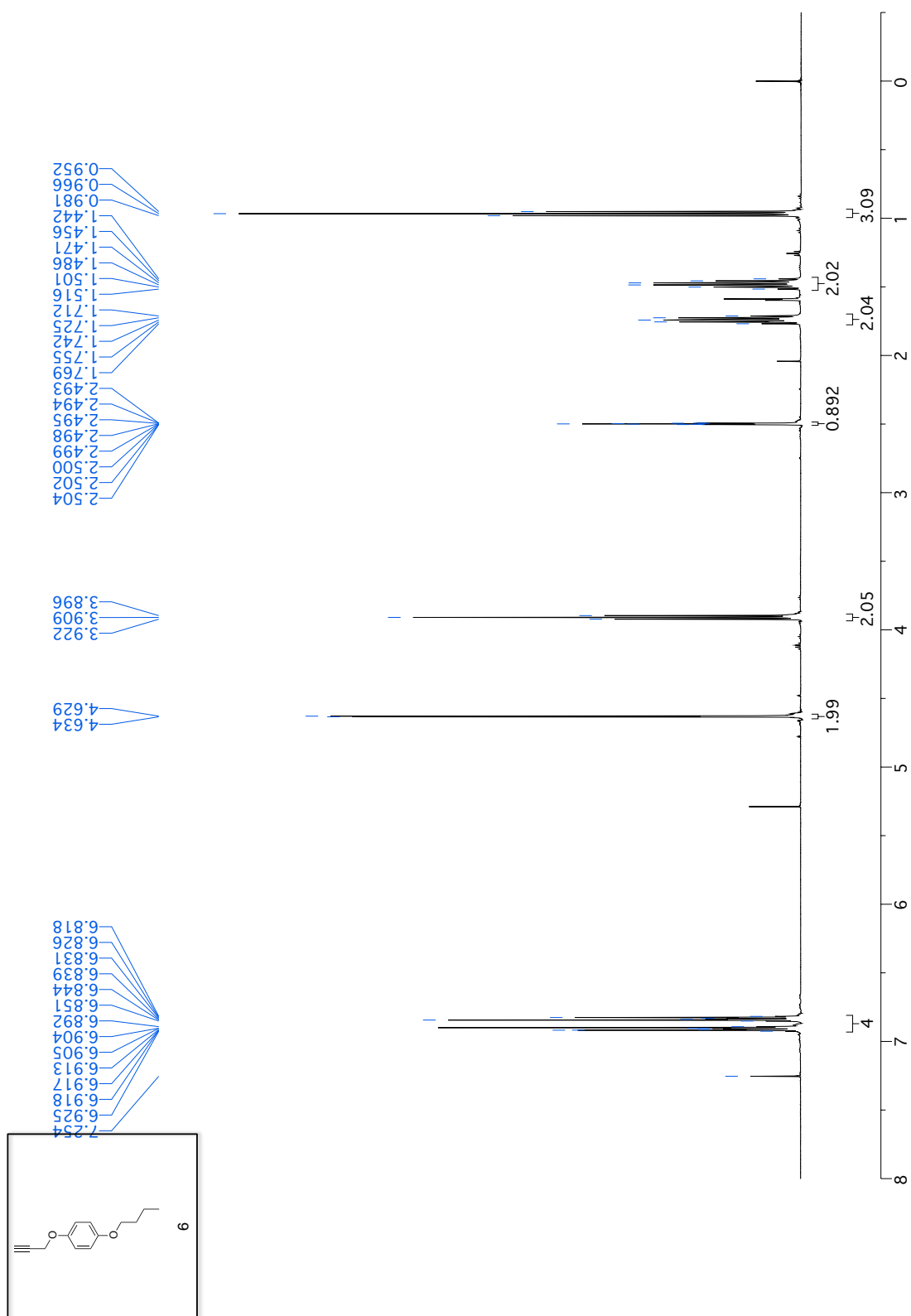
¹H-NMR spectrum of 4



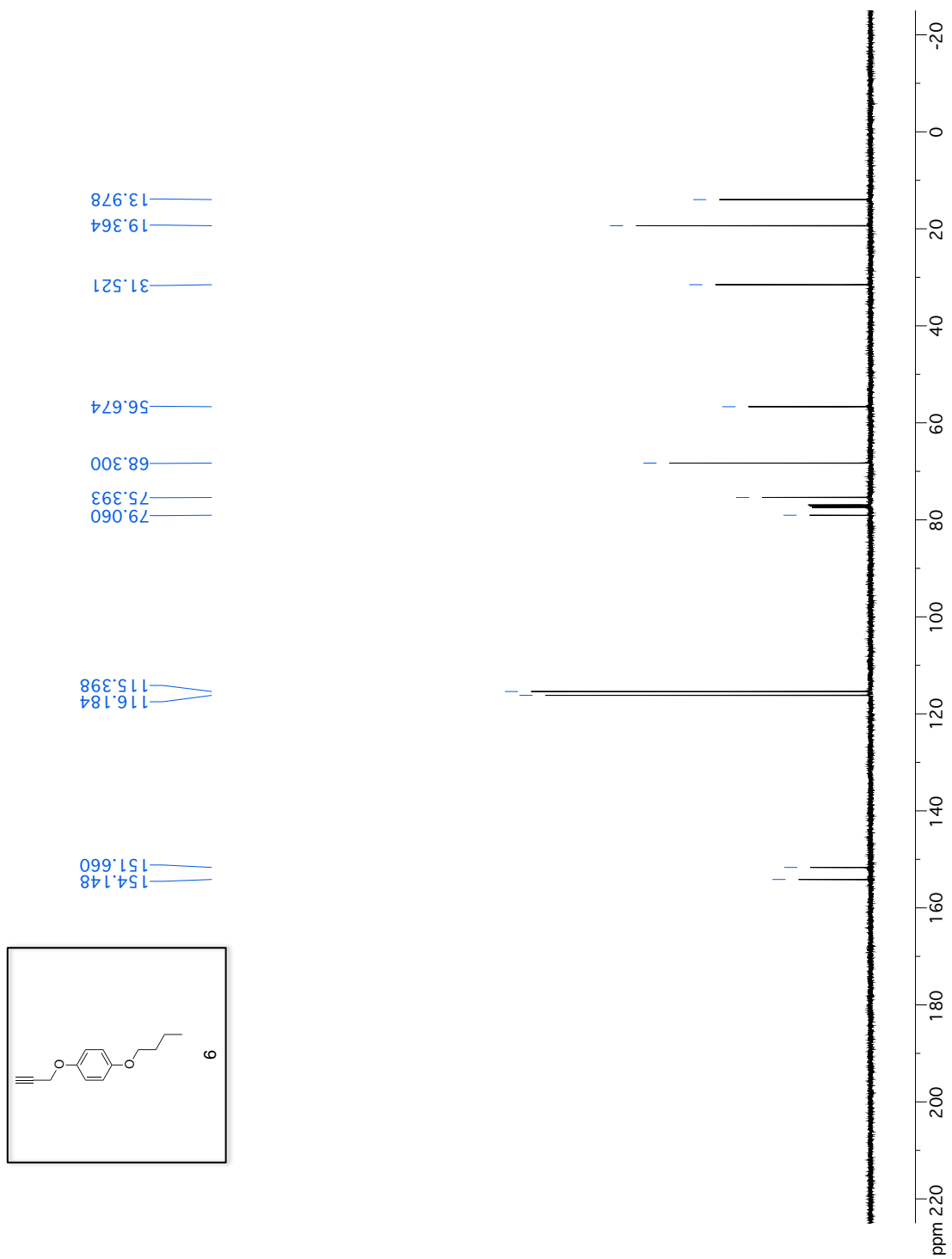
^{13}C -NMR spectrum of **4**



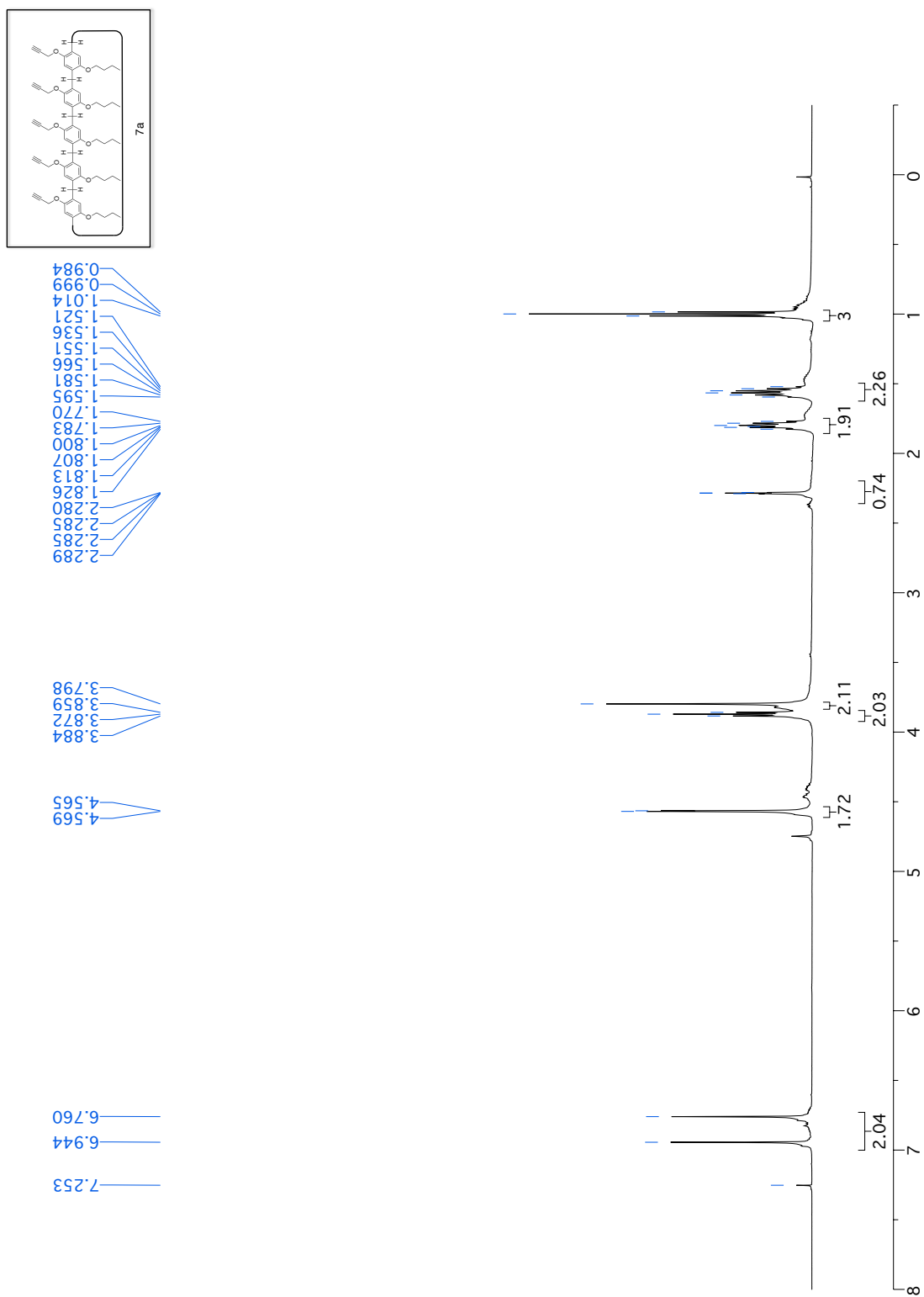
¹H-NMR spectrum of **6**



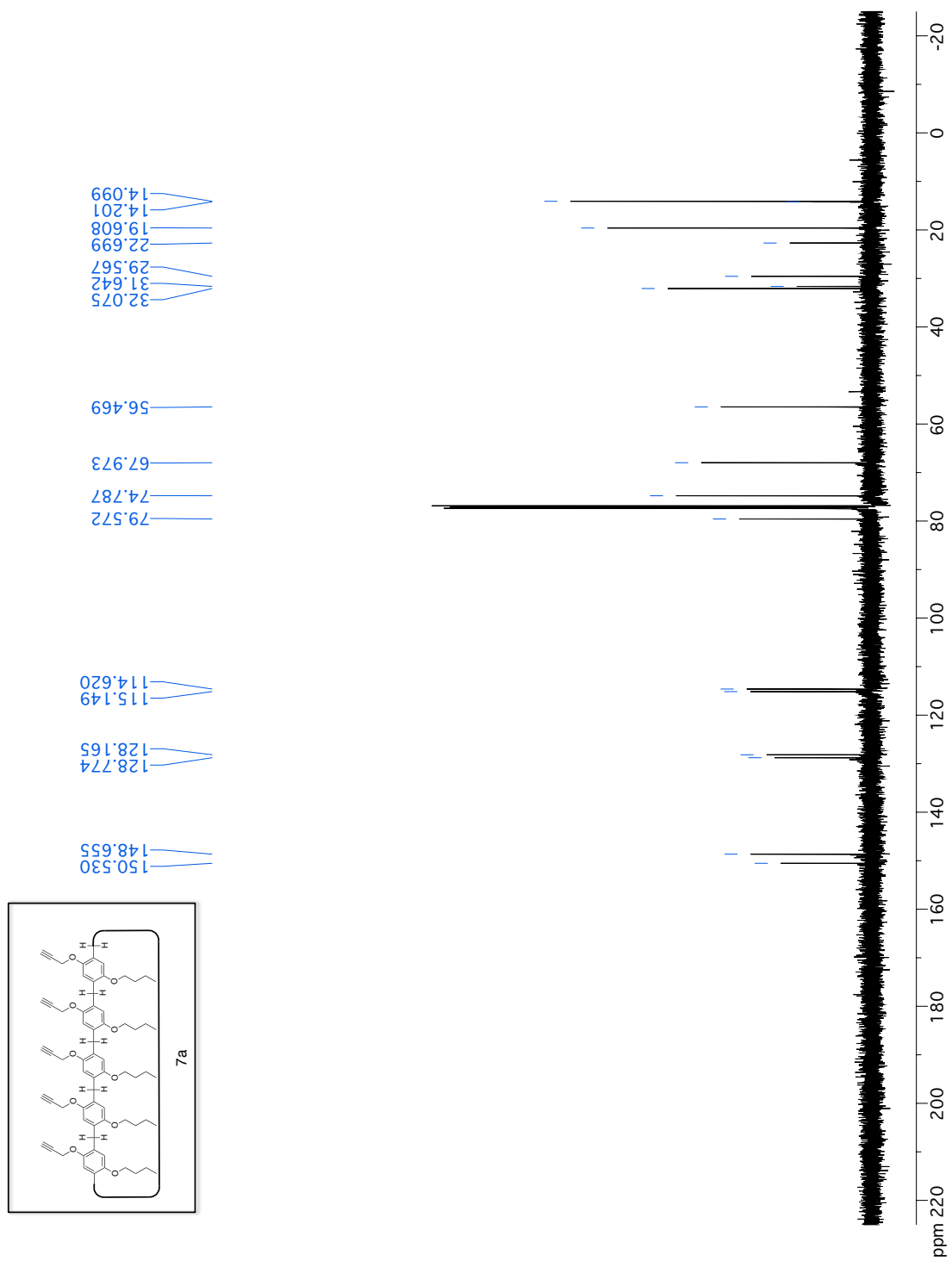
^{13}C -NMR spectrum of **6**



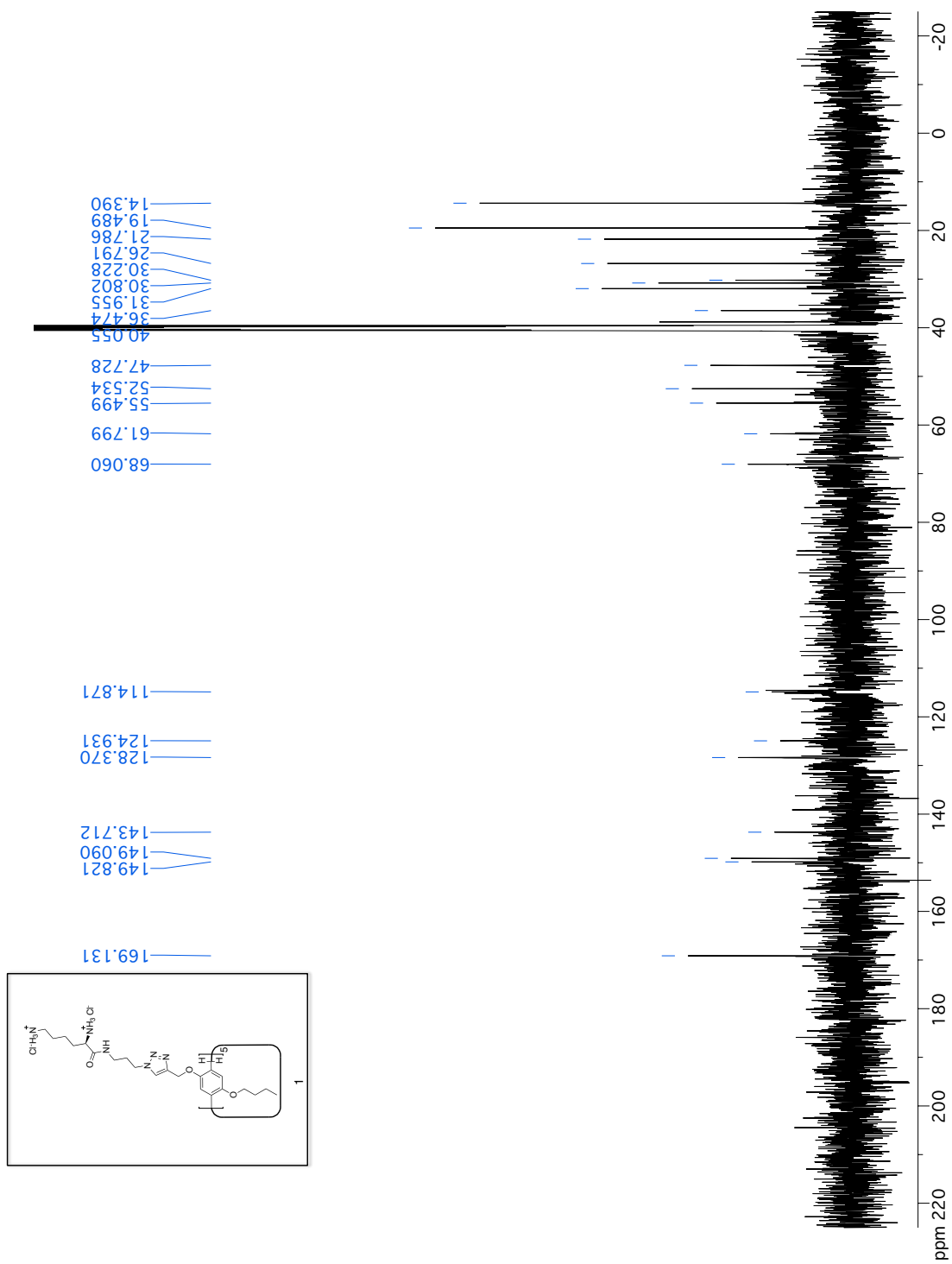
$^1\text{H-NMR}$ spectrum of **7a**



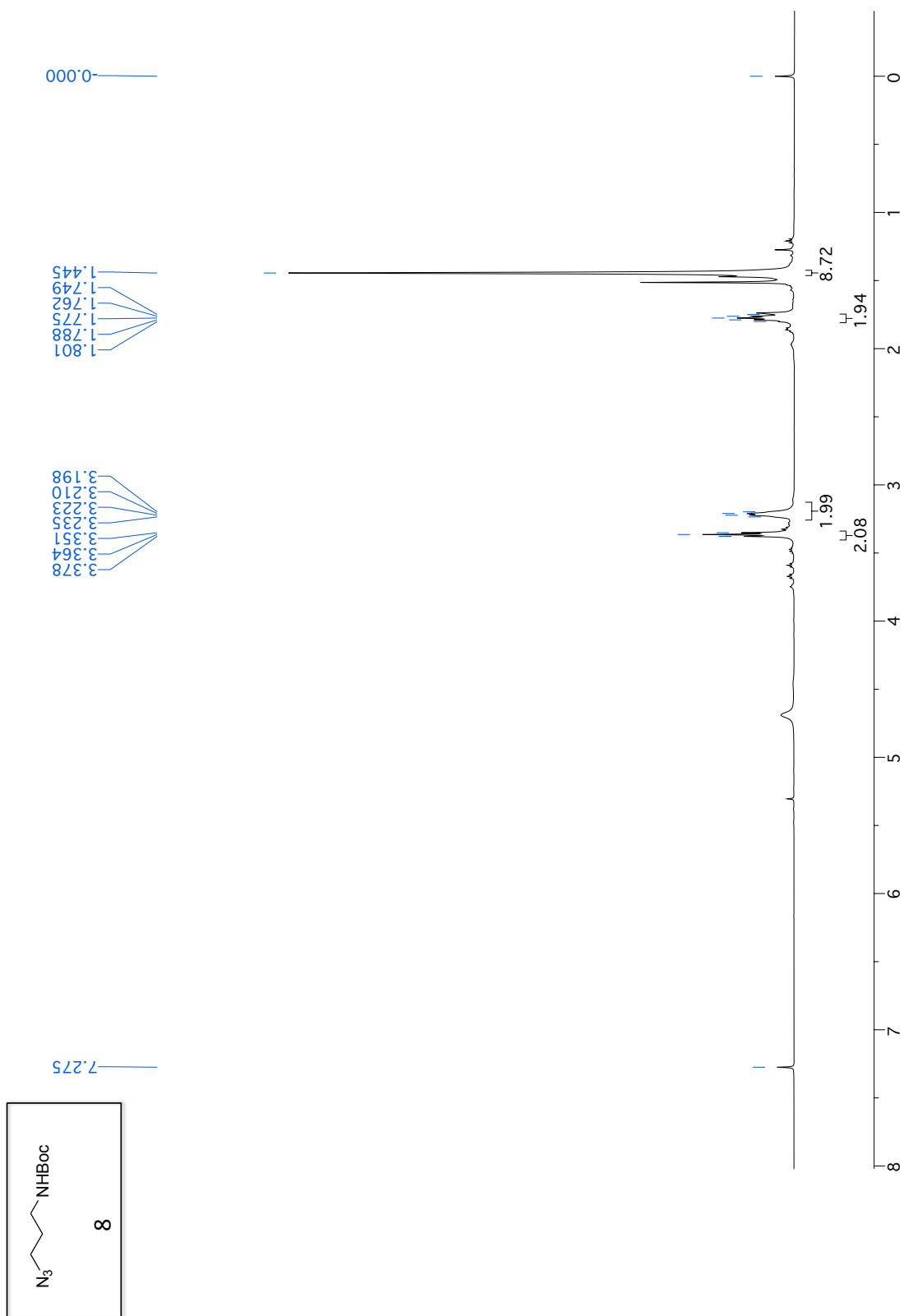
^{13}C -NMR spectrum of **7a**



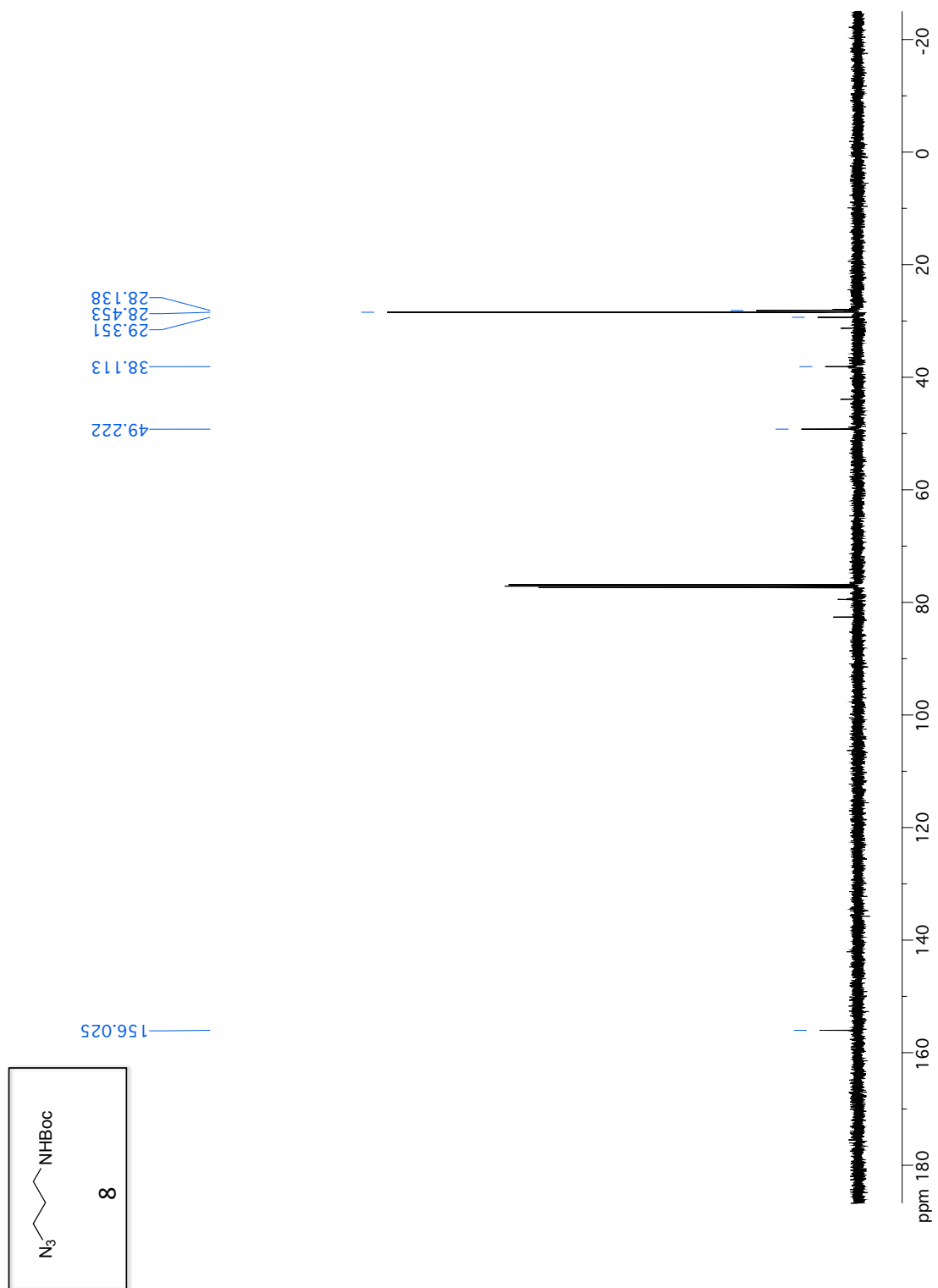
^{13}C -NMR spectrum of **1**



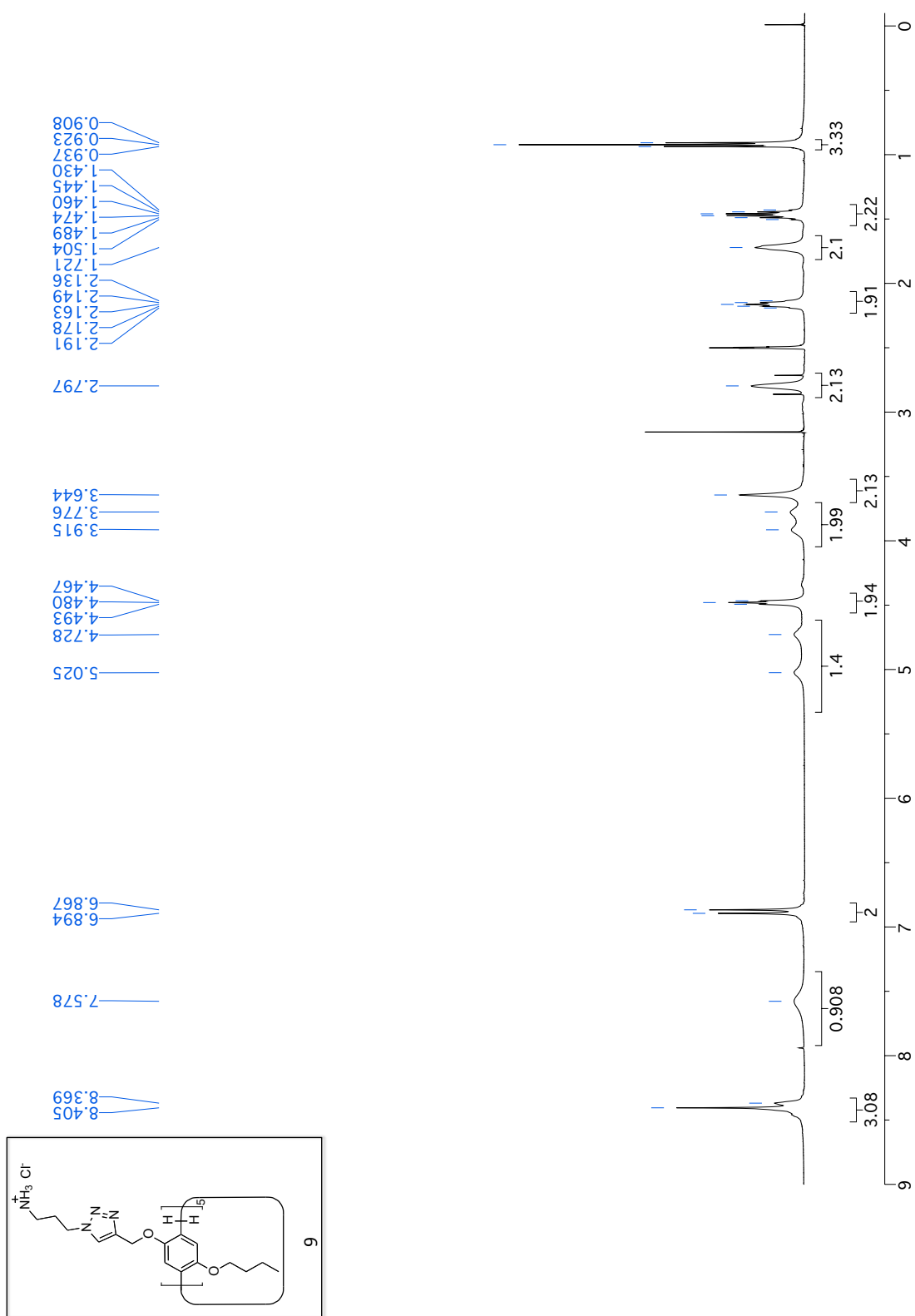
¹H-NMR spectrum of **8**



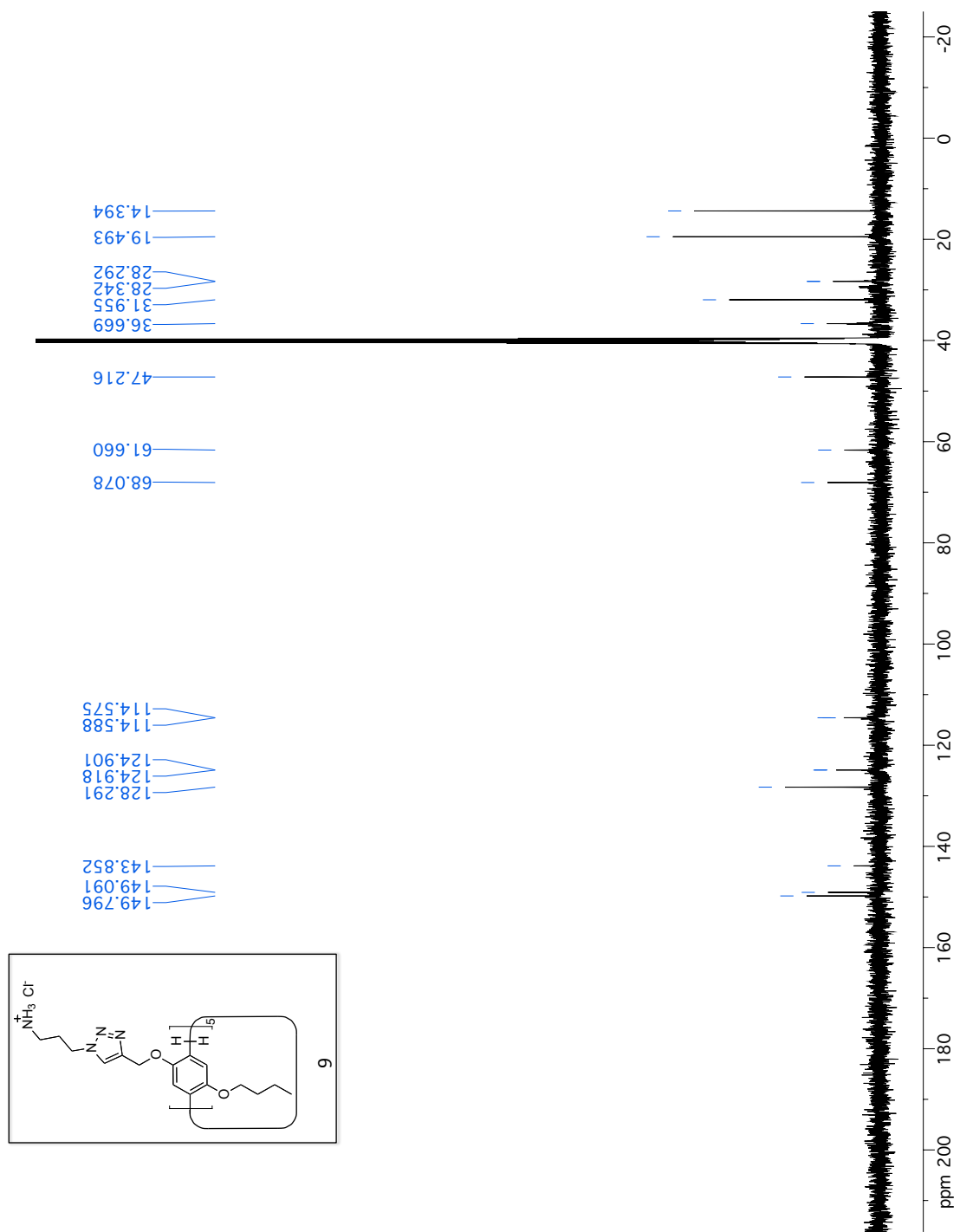
^{13}C -NMR spectrum of **8**



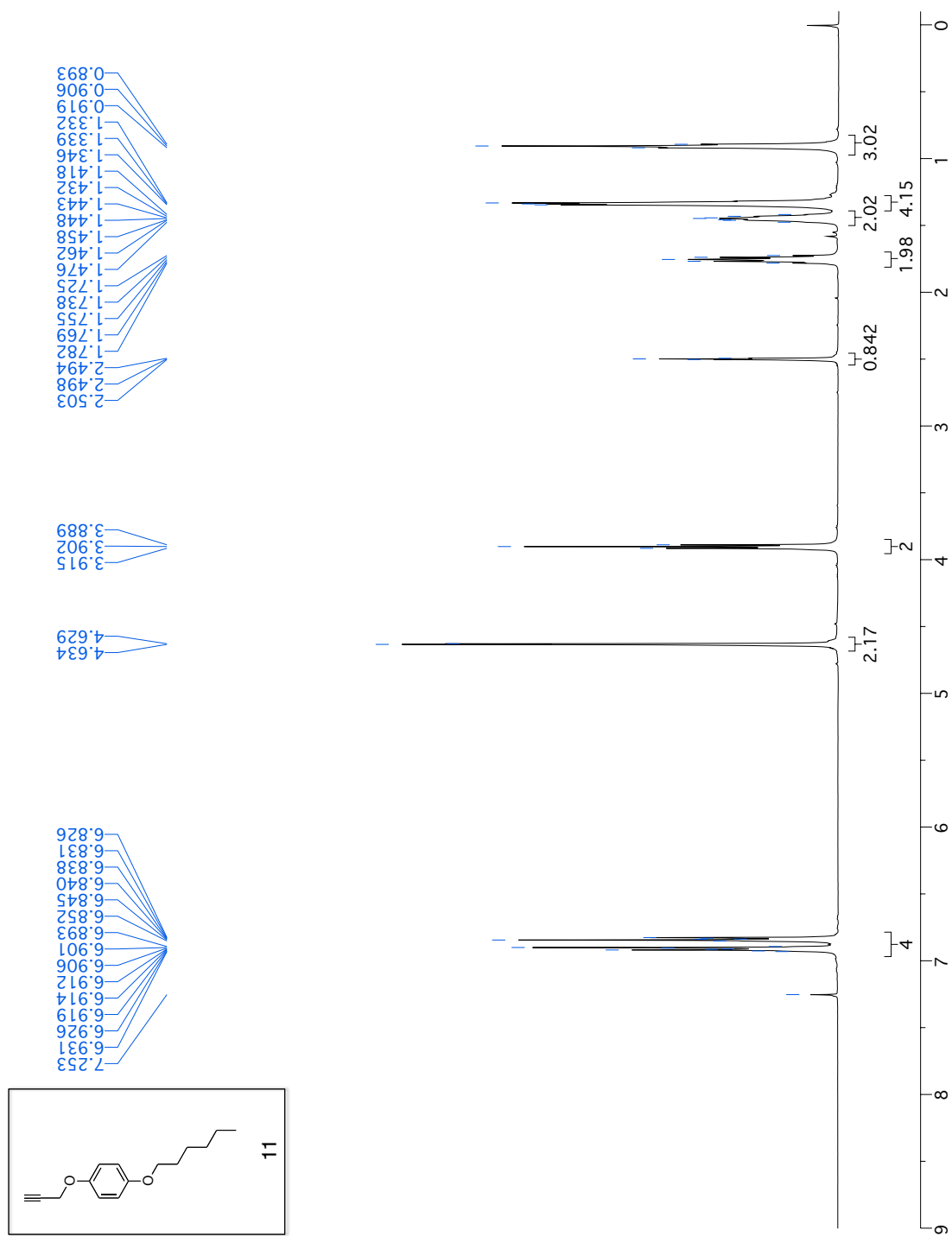
¹H-NMR spectrum of **9**



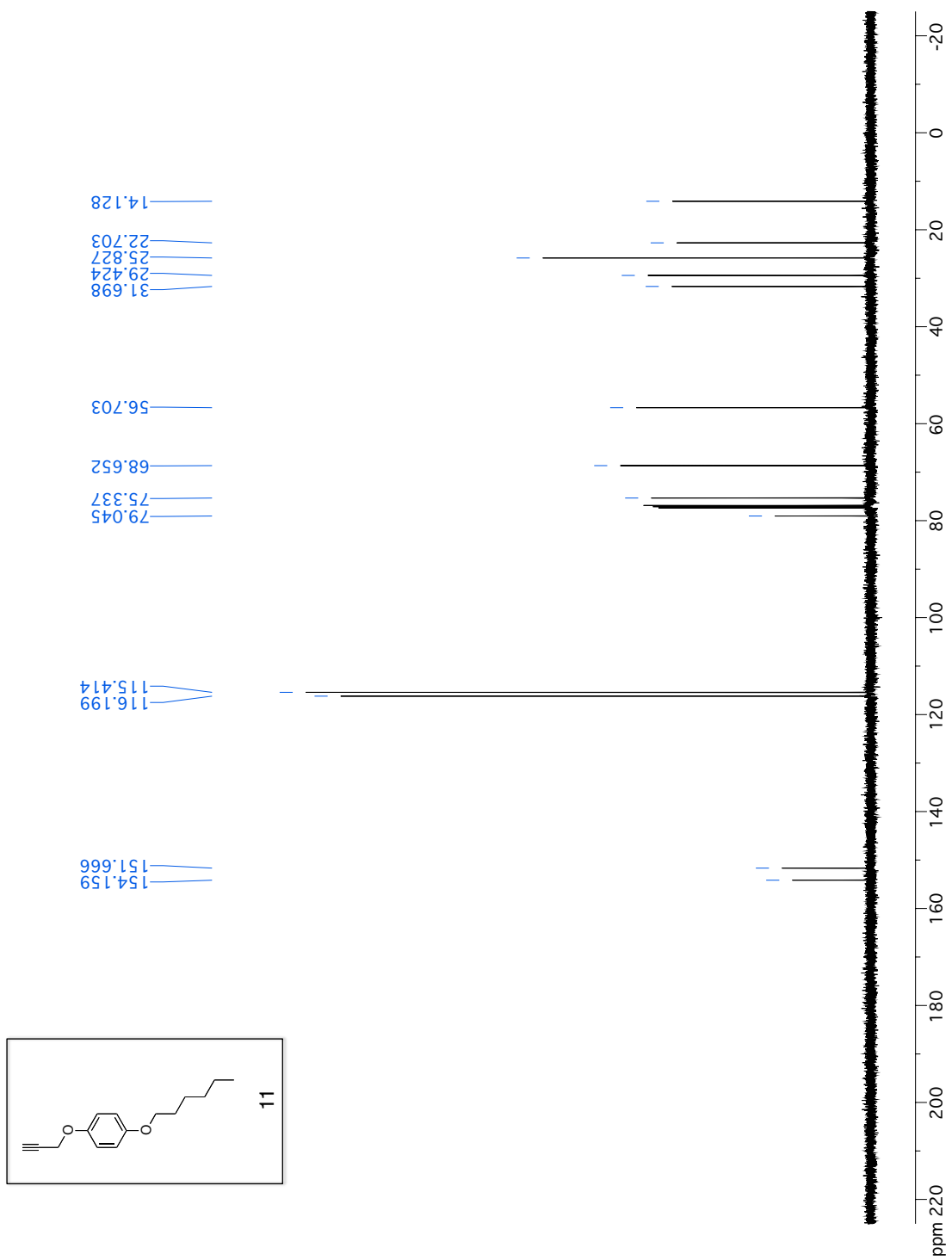
^{13}C -NMR spectrum of **9**



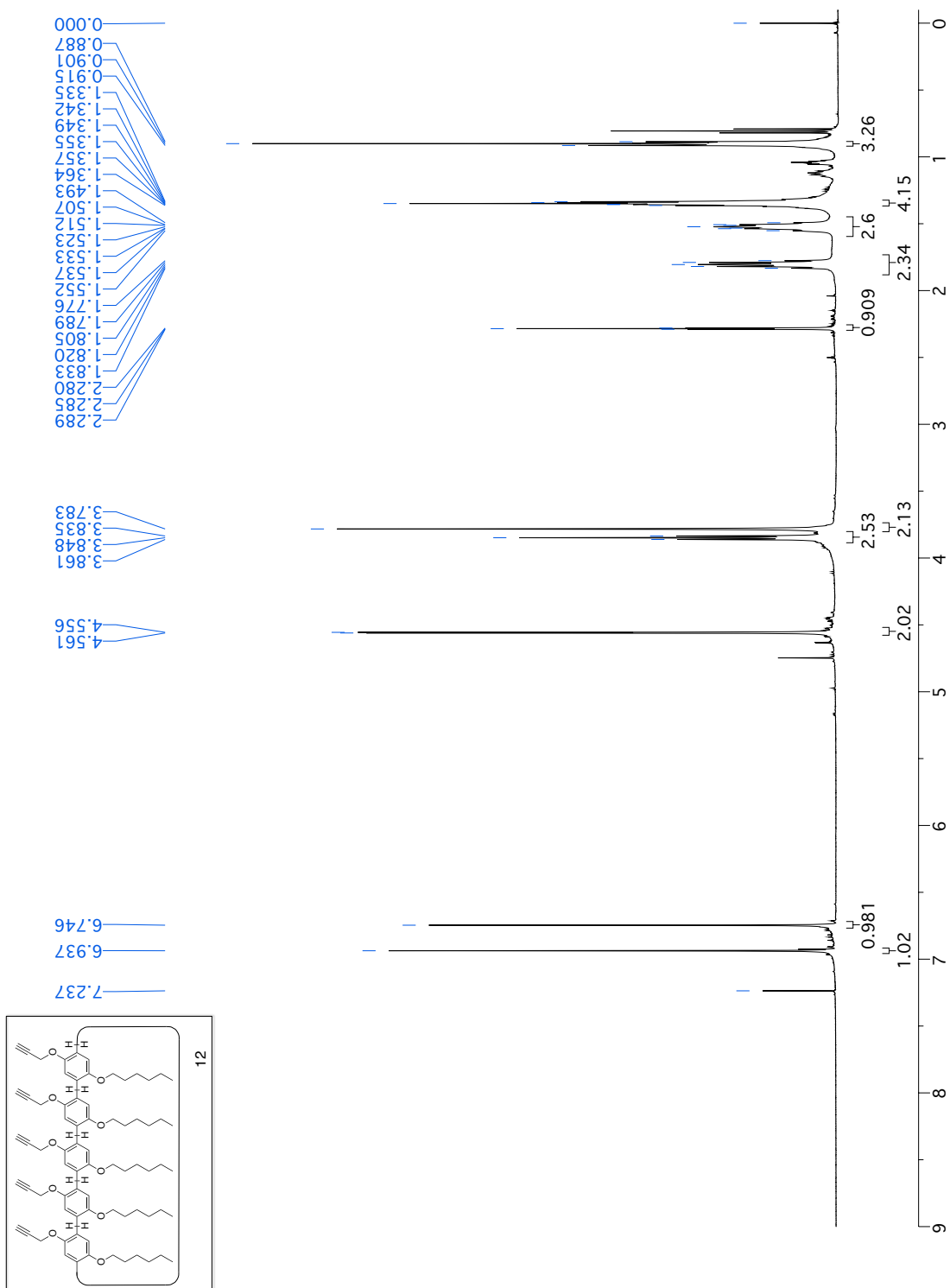
¹H-NMR spectrum of 11



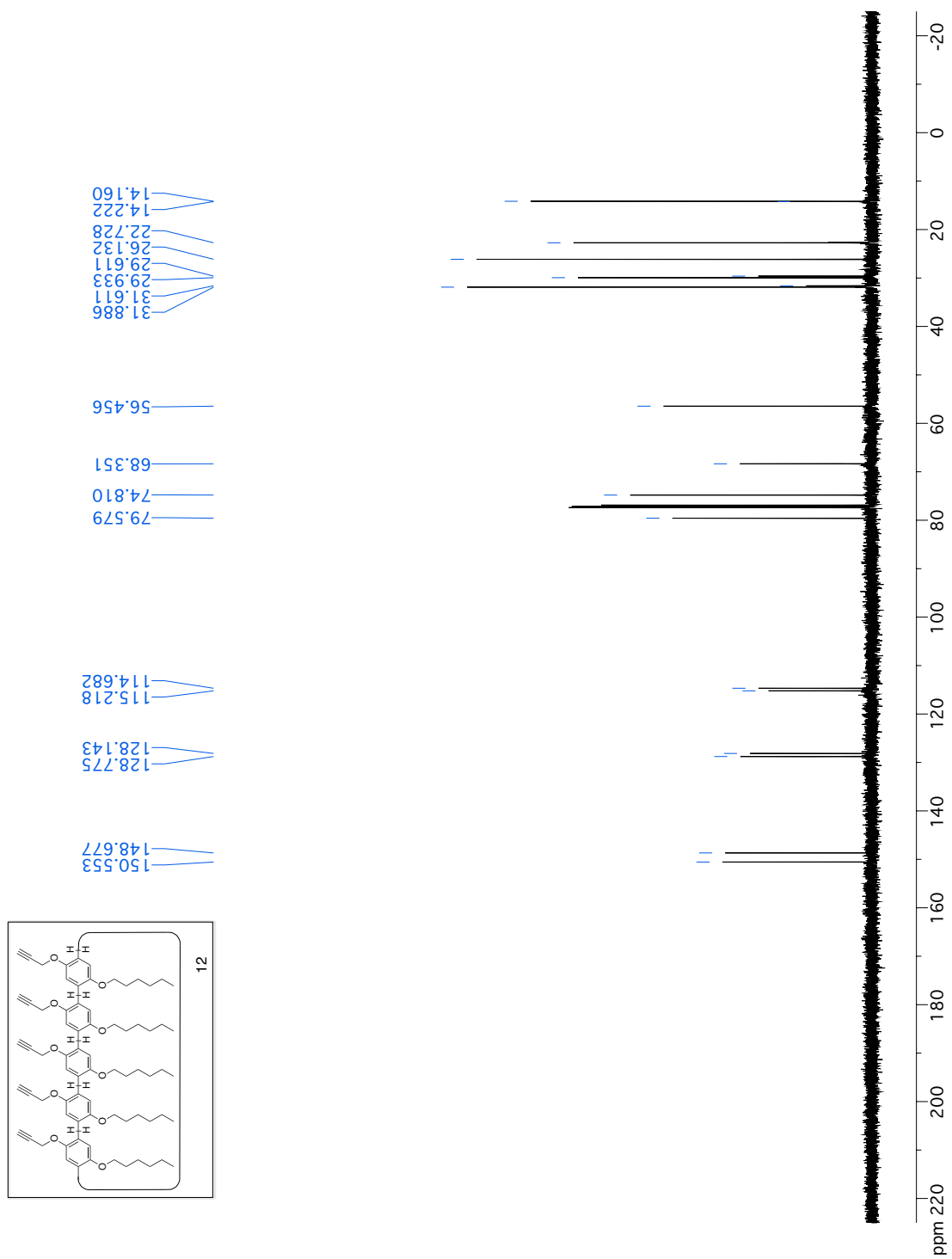
^{13}C -NMR spectrum of 11



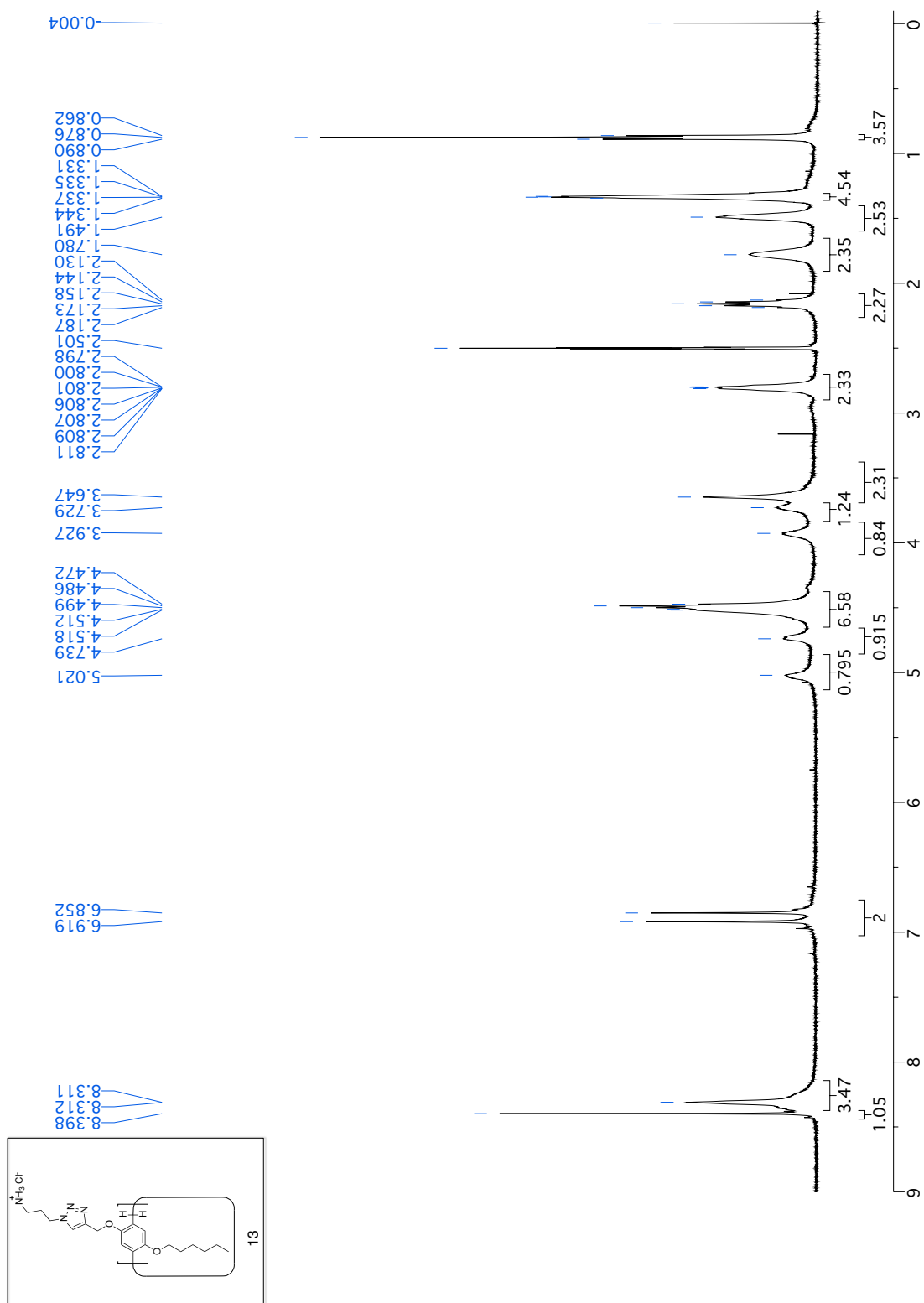
¹H-NMR spectrum of 12



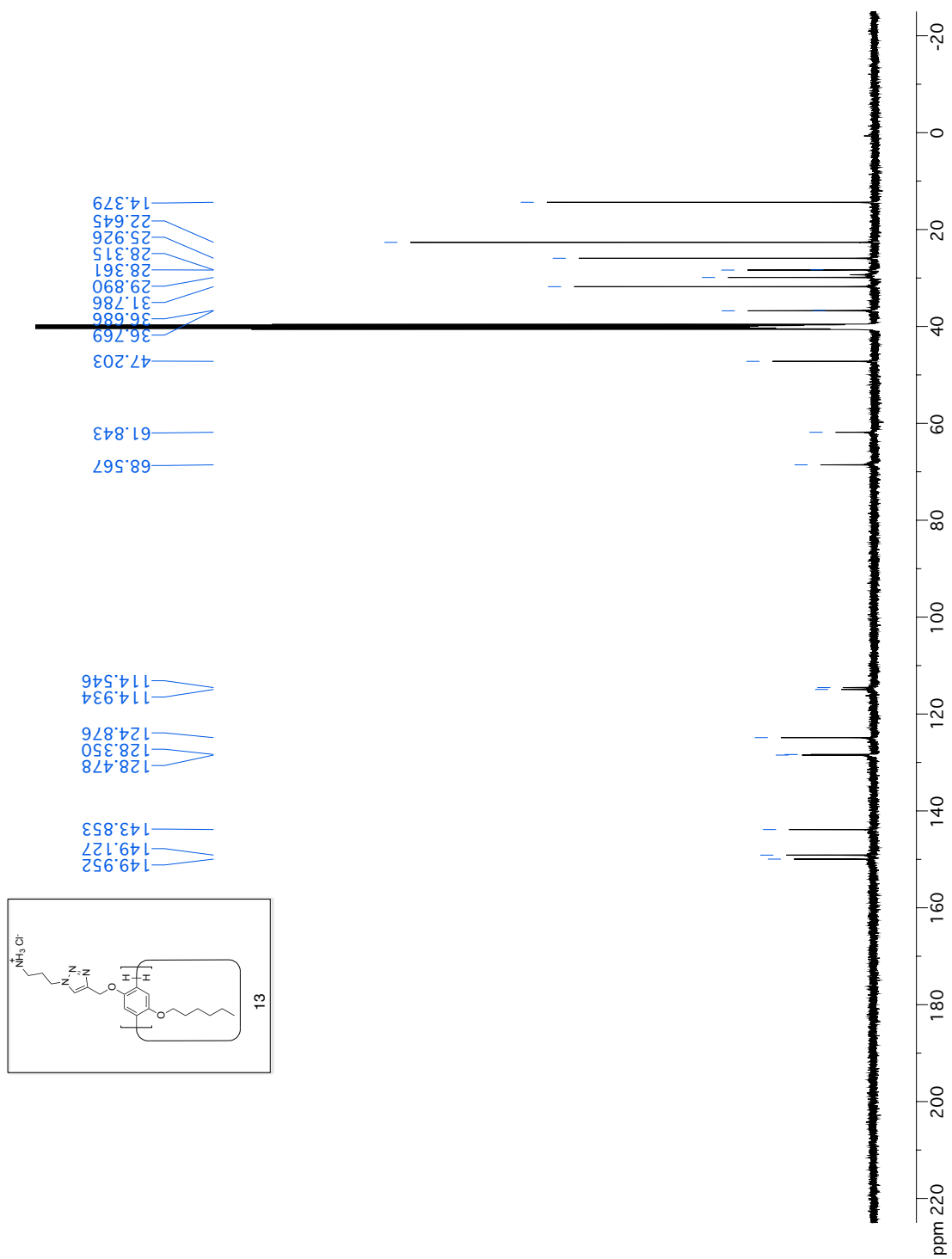
^{13}C -NMR spectrum of 12



¹H-NMR spectrum of 13



^{13}C -NMR spectrum of 13



Characterizations

SAXS measurements

SAXS measurements were performed at BL40B2 of SPring-8, Japan. A 30 cm × 30 cm imaging plate (Rigaku R-Axis VII) detector was placed at 0.7 or 1.8 m away from the sample. The wavelength of the incident beam (λ) was 1.0 Å. The 0.7 and 1.8 m set-ups provided a q range of 0.2–12 nm⁻¹ and 0.07–4.0 nm⁻¹, respectively, where q is the magnitude of the scattering vector defined by $q = 4\pi \sin \theta / \lambda$ with the scattering angle of 2θ . A bespoke SAXS vacuum sample chamber was used and the X-ray transmittance of the samples was determined with an ion chamber located in front of the sample and a Si photodiode for X-ray (Hamamatsu Photonics S8193) after the sample.^[2] The measured SAXS intensities were corrected to an absolute scale using the absolute scattering intensities of water.^[3] In the low q region, the scattering follows the Guinier relationship, $I(q) = I(0)\exp(-q^2R_g^2/3)$, where $I(0)$ and R_g are the forward scattering amplitude and the radius of gyration, respectively. Apparent R_g and $I(0)$ values are dependent on concentration of the amphiphile, due to inter-particle interference. In order to obtain the value for R_g and $I(0)$ at zero concentration, the intensity function extrapolated to zero concentration was obtained from a series of scattering measurements made at three different concentrations ranging from 7 to 10 mg/mL (Figure S4).

Molar mass determination

The molecular weight of the scattering micelle can be calculated according to eq 1.

$$M = I(0)(N_A/c\Delta\rho_M^2) \quad (1)$$

M is the molecular weight, $I(0)$ (cm⁻¹) is the forward scattering intensity at $q = 0$, c (g/cm³) is concentration of the amphiphiles, N_A is the Avogadro number, and $\Delta\rho_M$ (cm/g) is the scattering length difference per mass:

$$\Delta\rho_{\text{sc}} = \Delta\rho\bar{v} \quad (2)$$

The scattering length difference $\Delta\rho$ (cm^{-2}) can be calculated with the known chemical composition of the amphiphiles and the solvent. \bar{v} (cm^3/g) is the specific volume of the aggregates of the amphiphiles in solution, which can be calculated via density measurement of the solvent and the solution (WBA-505P, kyoto electronics manufacturing, Japan) (Figure S8).

Atomic Force Microscopy and Transmission Electron Microscopy

AFM: The mica was freshly cleaved before every experiment using mending tape. 5 μL of the sample solution was drop-cast on the mica surface and dried under N_2 atmosphere. The morphology of the aggregates were observed by AFM (SII NanoTechnology Inc.) operating in tapping mode at room temperature using a silicon tip (SI-DF20(AL)).

TEM: 5 μL of the sample solution was placed on a copper grid coated with an elastic carbon film. The excess sample solution was sucked away by a filter paper. A droplet of 2 wt% phosphotungstic acid solution as the staining agent was added and removed again. The sample was lyophilized. The grid was placed in a JEOL JEM-3010 electron microscope operated at 200 kV.

Field flow fractionation – Multi-angle light scattering

FFF/MALS measurement was performed by using an Eclipse 3+ separation system (Wyatt Technology Europe, Dernbach, Germany) connected to a Dawn Heleos II multiangle light scattering (MALS) detector and Optilab rEX DSP differential refractive index (RI) detector with a channel flow rate of 1.0 ml/min and an isocratic cross-flow rate of 1.5 ml/min. A Wyatt channel (Eclipse 3 channel LC) was used, which has a tip-to-tip length of 17.4 cm and a nominal thickness of 250 μm , and a membrane (Polyether Sulfone membrane 1 kDa) was attached on the bottom of the channel. The angular dependence of scattered light intensities was analyzed using berry's plot to determine the weight averaged molar mass. The specific refractive index increment (dn/dc)

of the aggregates in aqueous solution was determined with a DRM-1021 differential refractometer (Otsuka Electronics, Japan) (see Figure S7).

Dynamic light scattering (DLS)

DLS measurements were carried out with Zetasizer Nano ZS (Malvern, U.K.) instrument at a wavelength of 633 nm from a 4.0 mW, solid-state He-Ne laser at a scattering angle of 173°. Number average diameters were calculated from the autocorrelation function using cumulant analysis.

Determination of critical micelle concentration (cmc)

All solutions were prepared by diluting a stock solution (5 mM of compound 1 solution) with distilled water containing 50 mM NaCl (pH = 3.0). The concentration of pyrene was fixed at 1.0×10^{-5} M. The fluorescence measurements were carried out with a fluorescence spectrophotometer (Hitachi F-4500), by exciting at 335 nm and recording the emission spectrum in the range 350–650 nm. The scan speed and the slit widths were 260 nm min⁻¹ and 5.0 nm, respectively.

Ab initio modelling

The maximum dimension (D_{max}) and the distance distribution function of the micelle was determined using the indirect Fourier transform program package GNOM.^[4] The program DAMMIN^[5] was used for ab initio shape determination. A sphere of diameter D_{max} is filled with densely packed small spheres (dummy atoms) with diameter $r_0 \ll D_{max}$. At the initial step of the minimisation each bead is assigned randomly either to the solvent or to the particle phase. A simulated annealing procedure is employed to find a bead configuration X that minimises the function $f(X) = \chi^2 + \alpha P(X)$. Here, χ^2 is the discrepancy:

$$\chi^2 = \frac{1}{N-1} \sum_j \left[\frac{I(q_j) - I_{exp}(q_j)}{\sigma(q_j)} \right]^2$$

where N is the number of experimental points, and $I(q)$, $I_{exp}(q)$, and $\sigma(q)$ denote the calculated intensity of the model, the experimental intensity and the experimental error, respectively. The penalty term $P(X)$ taken with a positive

weight $\alpha > 0$ ensures that the model has low resolution with respect to the packing radius r_0 and "loose" or very detailed shapes are discouraged. It is also possible to impose point symmetry conditions on the models.

Rigid body modelling

An atomic model of the pillararene ring was constructed with the GaussView program [6] and quickly optimised at the HF/STO-3G level with GAUSSIAN [7] in order to achieve its D5 symmetry. Butyl tails were attached to the oxygen of one side of the ring and amphiphile 1 headgroup atomic models were also constructed using GaussView. The SAXS amplitudes from the pillararene ring with the butyl tails and the headgroup were computed using the program CRY SOL. [8] The model of the amphiphile 1 was constructed with the help of the program SASREF. SASREF constructs models from subunits with known structure by rigid body movements and rotations. Starting from an arbitrary initial configuration, the program employs simulated annealing to construct a model without steric overlaps fitting the experimental SAXS data of the dimer (using an $f(X) = x^2 + aP(X)$ scoring function similar to DAMMIN). Distance restraints were introduced to keep the tips of the butyl tails of the two molecules in the vicinity of each other and the headgroups close to the pillararene oxygens. Since the program's main objective is to fit the SAXS data, the produced models are to be considered in geometrical rather than physicochemical terms.

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Figure S1

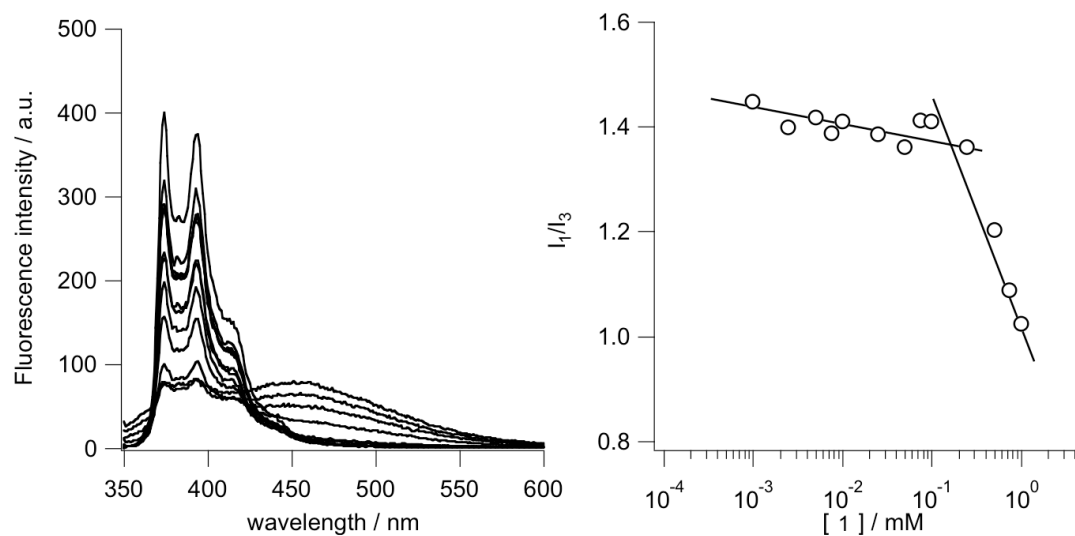


Figure S1(a) Fluorescence spectra of Pyrene in water (50mM NaCl, pH=3.0) at various concentration of Amphiphile 1. (b) the fluorescence intensity ratio (I_{374}/I_{383}) plotted against concentration of 1

Figure S2

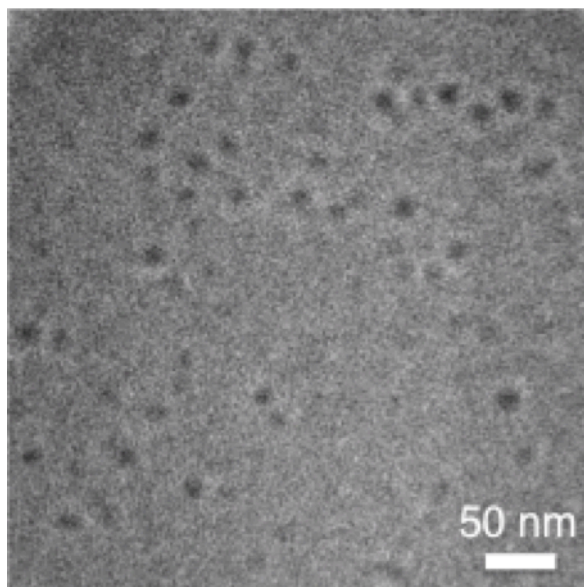


Figure S2 TEM image of self-assembled **1** in water (50mM NaCl, pH=3.0).

Figure S3

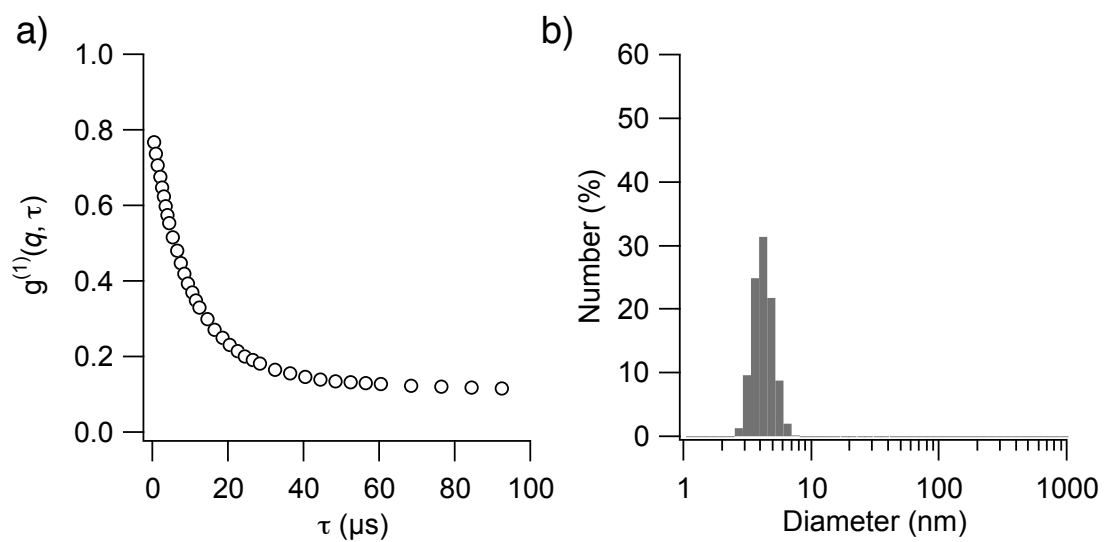


Figure S3 (a) A typical plot of $g^{(1)}(q, \tau)$ vs. time and (b) the size distribution determined with DLS.

Figure S4

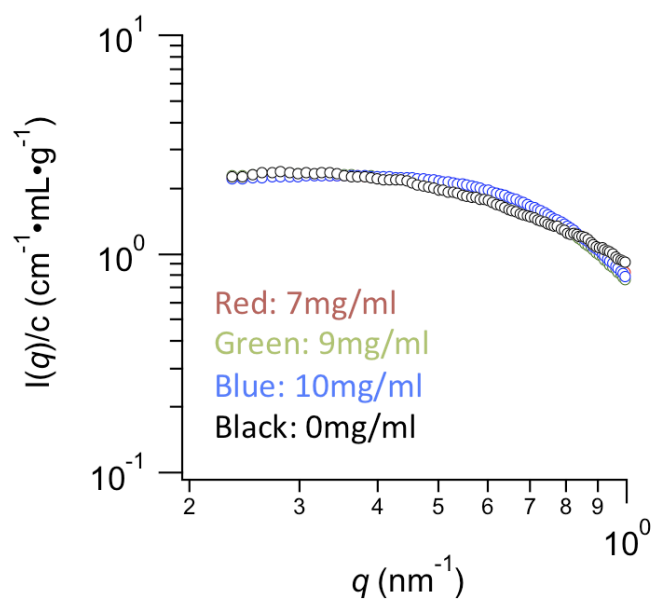


Figure S4 $I(q)/c$ vs q plots for different concentrations at $[\text{NaCl}] = 50 \text{ mM}$, including the extrapolated values at $c \rightarrow 0$ in the Guinier region

Figure S5

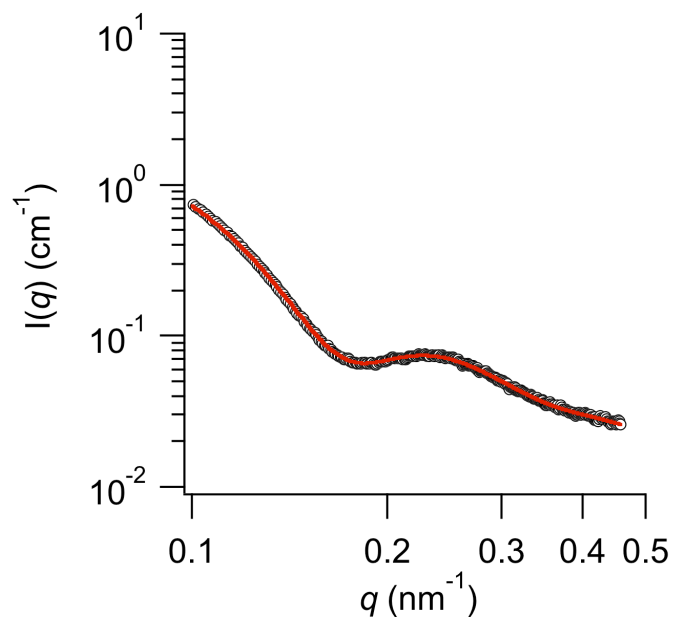


Figure S5 The profile of Dummy atoms model fitting.

Figure S6

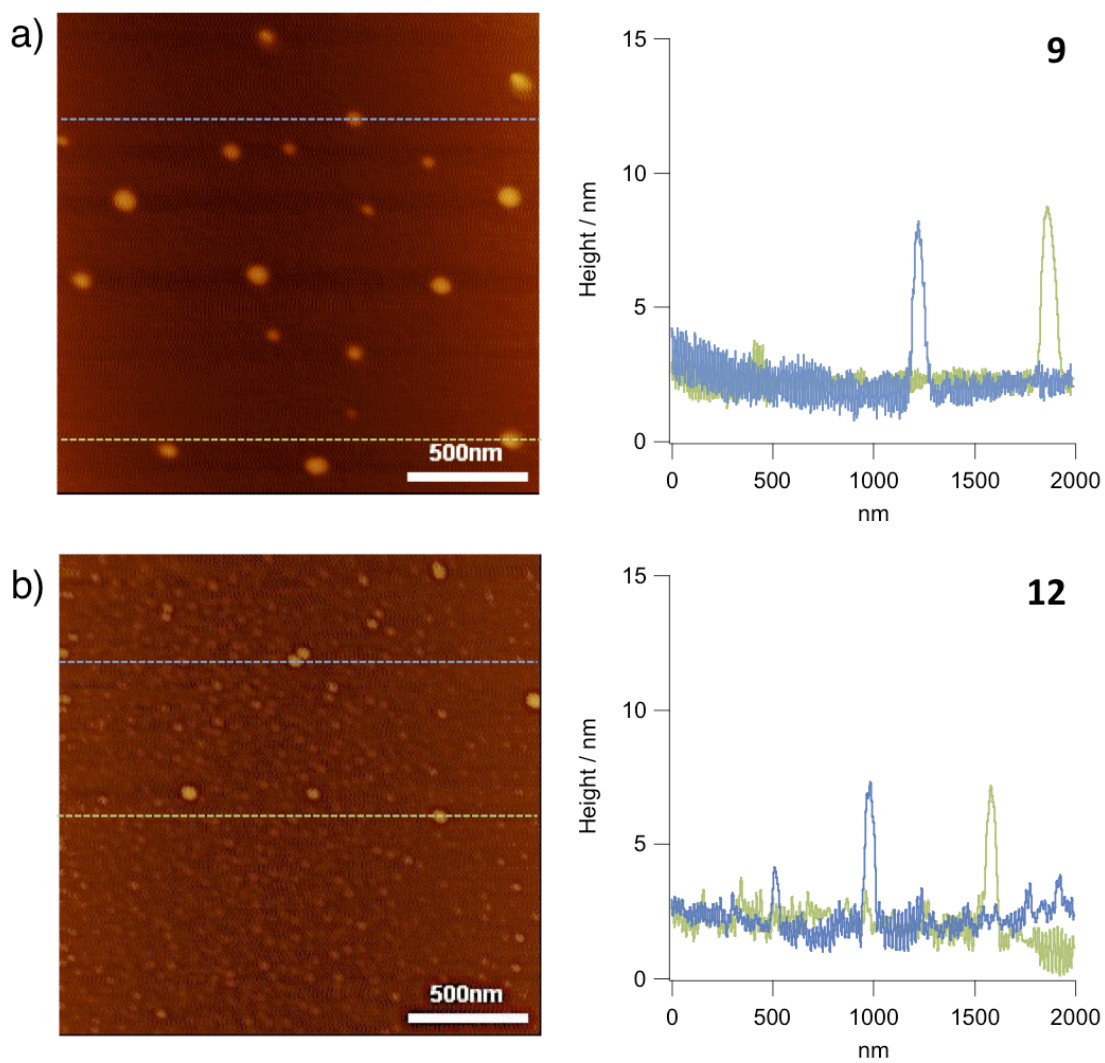


Figure S6 AFM tapping mode image (left) and height profiles along the lines indicated at each image (right) for a) self-assembled 9 and b) 12

Figure S7

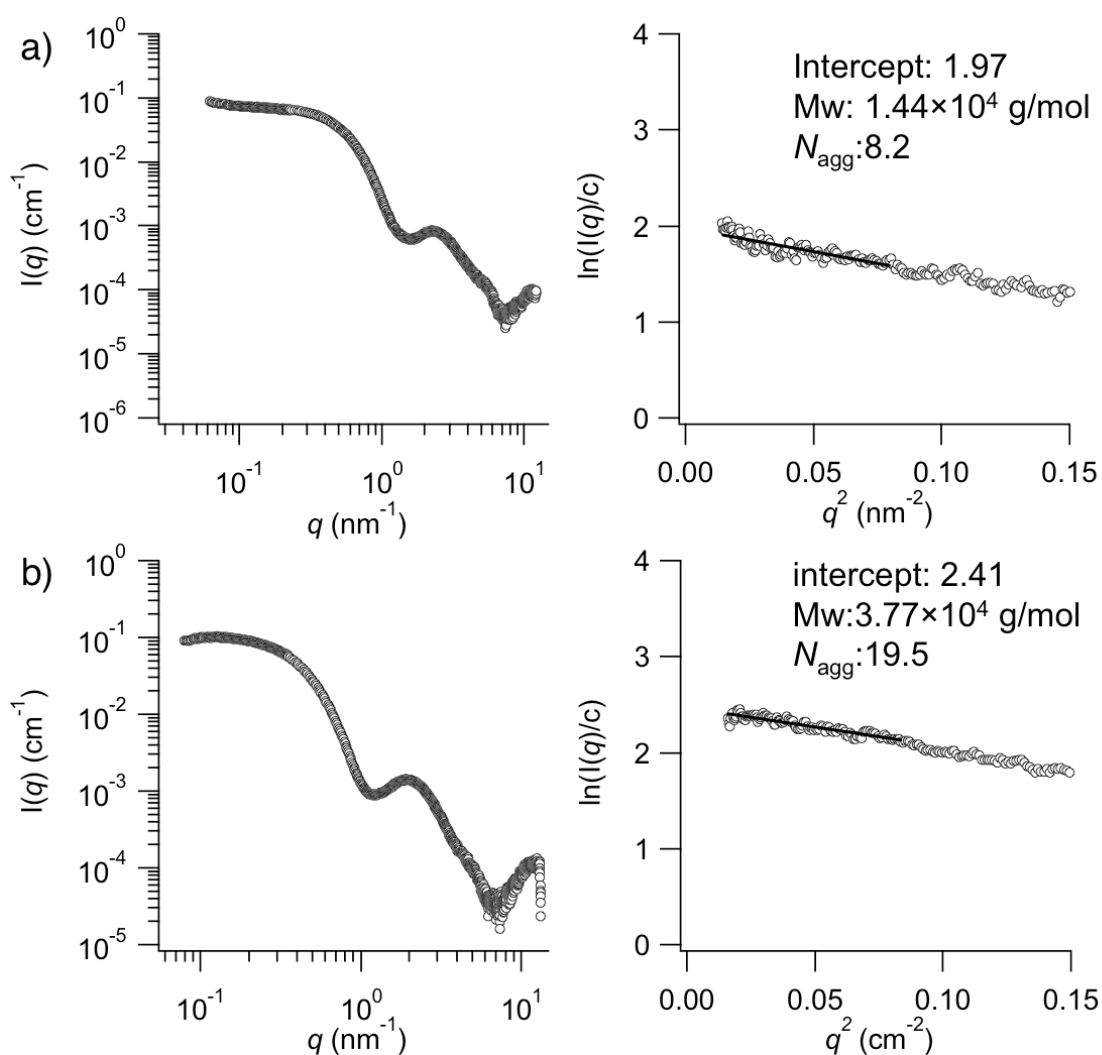


Figure S7 Absolute SAXS intensity plotted against q in water (50 mM NaCl, pH = 3.0) (left) and the Guinier plot at $c \rightarrow 0$ used to evaluate $I(0)/c$ by extrapolating $q \rightarrow 0$ (right) for a) 9 and b) 12

Figure S8

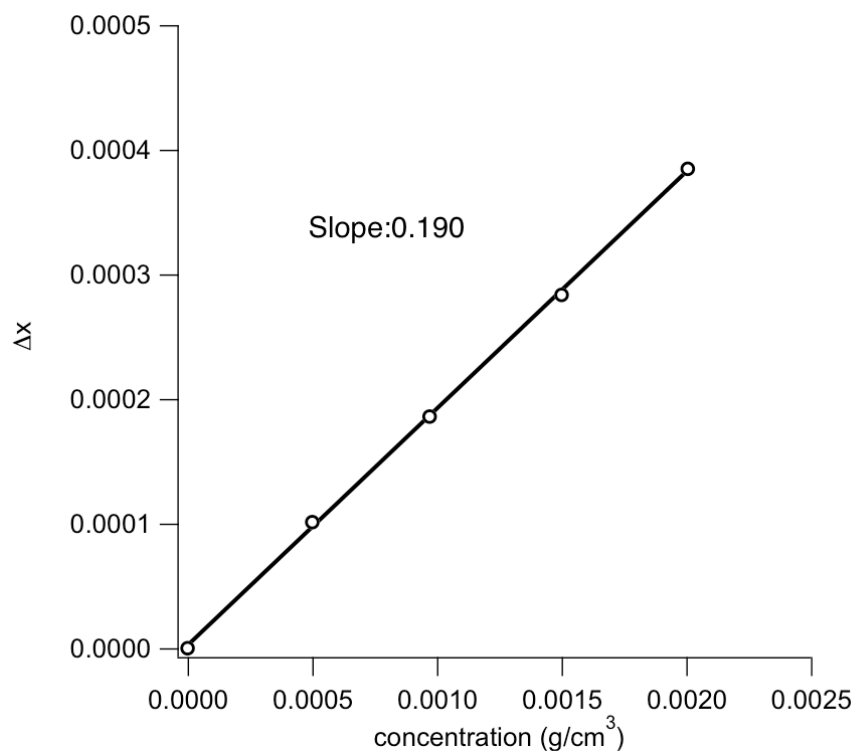


Figure S8 Concentration dependence of refractive index increment for 1

Figure S9

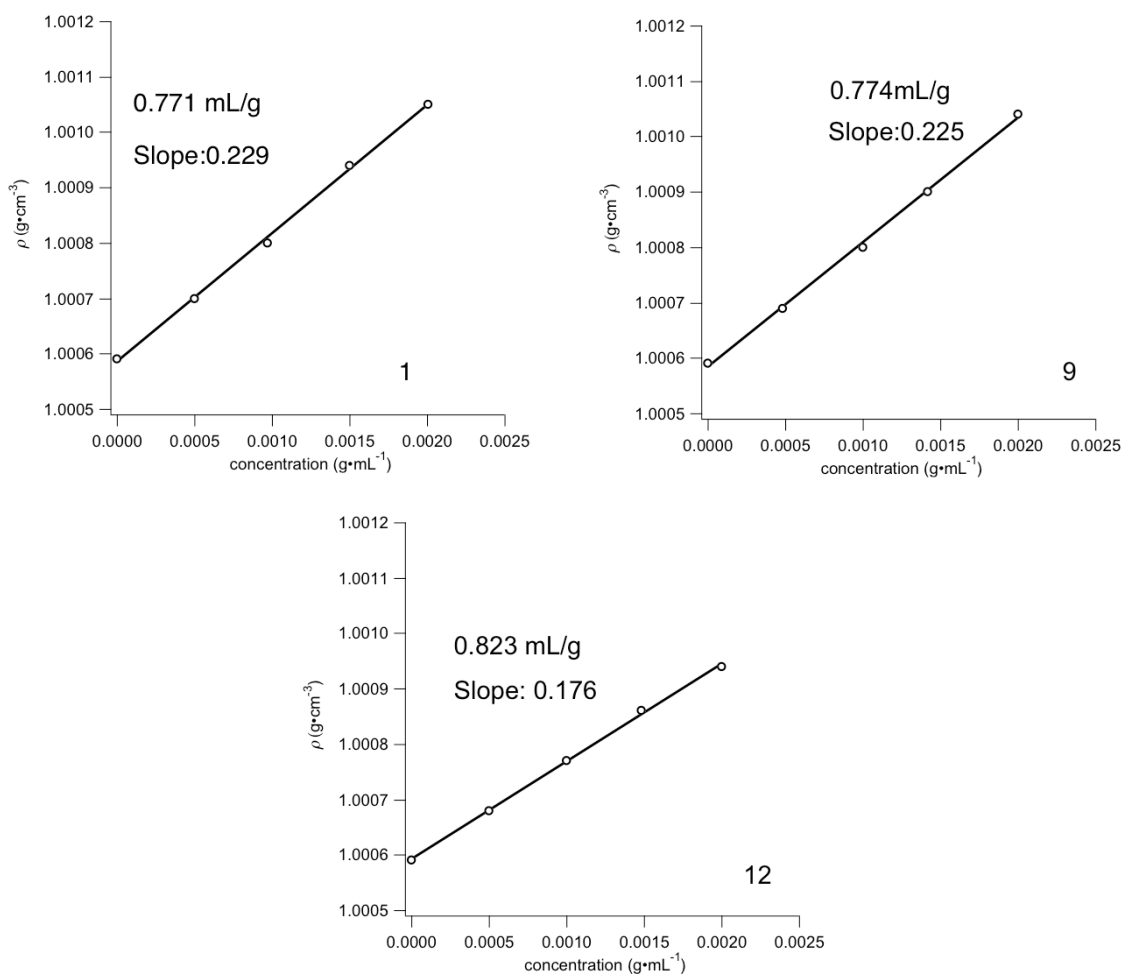


Figure S9 Concentration dependence of the density increment for 1, 9, and 12