

Supporting Information

Straightforward Synthesis of a Double-Lasso Macrocycle from a non-Symmetrical [c2]-Daisy Chain

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A. General methods

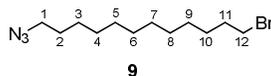
All reactions were achieved under an atmosphere of argon unless otherwise indicated. All reagents were purchased from Aldrich and were used as received without further purification. Dichloromethane was distilled over P₂O₅ and was degassed by bubbling Ar for 20 min. Analytical thin-layer chromatography (TLC) was performed on Merck silicagel 60 F254 plates. Compounds were visualized by dipping the plates in an ethanolic solution of ninhydrine or KMNO₄, followed by heating. ¹H NMR and ¹³C NMR spectra were obtained on a Bruker DRX-400 spectrometer (respectively at 400.13 MHz and 100.62 MHz). Chemical shifts of ¹H NMR and ¹³C NMR are given by using CHCl₃, CH₃CN or DMSO as references (7.27 ppm, 1.94 ppm and 2.50 ppm respectively for ¹H spectra and 77.00 ppm, 118.26 ppm and 39.52 ppm respectively for ¹³C spectra). Coupling constants (J) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s (singlet), br (broad), d (doublet), t (triplet), q (quartet), quint (quintuplet), m (multiplet).

Low and high-resolution ESI mass spectra were recorded on a Q-ToF I mass spectrometer (Waters, Milford, CA) fitted with an electrospray ion source. Data were acquired and processed with the Masslynx software. The mass spectrometer was calibrated in the positive ion mode using 1% phosphoric acid in water/acetonitrile solution (H₂O/CH₃CN, 50/50, v/v). Data were acquired by the ToF analyzer at 1 acquisition/s from *m/z* 100 to *m/z* 3000 with a resolution of 5000. Depending on the sample, 50 acquisitions were summed to produce the final spectrum. Samples were dissolved in a mixture H₂O/CH₃CN (50/50, v/v) and infused into the ESI source at a flow rate of 10 µl/min. Voltages were set at +3.0 kV for the capillary and adjusted for the sampling cone. The source was heated at 100°C. Nitrogen constituted both nebulizing and desolvation gas. The latter was heated at 120°C.

MALDI mass spectra were recorded on an Ultraflex III TOF/TOF instrument (Bruker Daltonics, Wissembourg, France). A pulsed Nd:YAG laser at a wavelength of 355 nm was operated at a frequency of 100 Hz with a delayed extraction time of 30 ns. The source was operated in the positive mode. Data were acquired with the Flex Control software and processed with the Flex Analysis software. A solution of the HCCA matrix in water/acetonitrile (50/50, v/v) at a concentration of 10 mg/ml was mixed with the sample in equal amount and 1 µl of this solution was deposited onto the MALDI target according to the dried droplet procedure. After evaporation of the solvent, the MALDI target was introduced into the mass spectrometer ion source. External calibration was performed with the commercial peptide mixture (Calibration peptide standard 2, Bruker Daltonics, Wissembourg, France). MS data were acquired under the following MS conditions. An acceleration voltage of 25.0 kV (IS1) was applied for a final acceleration of 21.85 kV (IS2). The reflectron mode was used for the ToF analyzer (voltages of 26.3 kV and 13.8 kV). Mass spectra were acquired from 500 laser shots, the laser fluence being adjusted for each studied sample. Ions were detected over a mass range from *m/z* 400 to 3000 or 4000.

B. Synthesis of the diazido pseudo [c2]Daisy chain 3

1) Preparation of the 1-azido-12-bromododecane 9



To a solution of 1,12-dibromododecane (3.07 g, 9.356 mmol, 1.5 equiv) in 15 mL of DMF at 60 °C, was added by portions NaN₃ (450 mg, 6.237 mmol, 1 equiv) during 30 min. The mixture was stirred for 4,5 hours at 60 °C. The solvent was then removed under *vacuo*, and Et₂O (30 mL) and NaOH 1M (30 mL) were added.

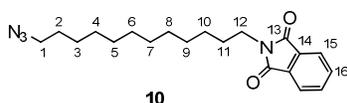
The two layers were stirred then separated and the aqueous layer was extracted with Et₂O (2 x 20 mL). The organic layers were combined, dried over MgSO₄ and concentrated. The crude was purified by chromatography on a silicagel column (solvent gradient elution: Petroleum ether, then Et₂O/Petroleum ether 3/97) to give the product (869 mg, 48%) as a yellow oil.

R_f (petroleum ether /AcOEt 9:1) 0.74

¹H NMR (CDCl₃, 400 MHz, 298K) : δ (ppm) = 3.42 (t, 2H, ³J_{H12-H11} = 7.0 Hz, H₁₂), 3.26 (t, 2H, ³J_{H1-H2} = 7.0 Hz, H₁), 1.86 (quint, 2H, ³J_{H11-H10} = ³J_{H11-H12} = 7.0 Hz, H₁₁), 1.65-1.55 (m, 2H, H₂), 1.49-1.23 (m, 16H, H₃ H₄ H₅ H₆ H₇ H₈ H₉ H₁₀).

JMOD ¹³C NMR (CDCl₃, 100 MHz, 298K) : δ (ppm) = 51.4 (C₁), 33.9 (C₁₂), 32.8 (C₁₁), 29.4 & 29.4 & 29.3 & 29.1 & 28.8 & 28.7 & 26.6 (C₂ C₃ C₄ C₅ C₆ C₇ C₈ C₉ C₁₀).

2) Preparation of the 1-phthalimido-12-azidododecane **10**



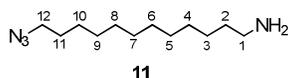
Potassium phthalimide (832 mg, 4.491 mmol, 1.5 equiv) was added to a solution of the 1-azido-12-bromododecane **9** (869 mg, 2.994 mmol, 1 equiv) in 20 mL of DMF. After stirring for 5 h at 70°C, the solvent was removed in *vacuo*. The solid residue was suspended in dichloromethane and filtered through a layer of silica gel. The filtrate was evaporated to give the desired product (965 mg) in 90% yield as a yellow solid.

¹H NMR (CDCl₃, 400 MHz, 298K) : δ (ppm) = 7.87-7.82 (m, 2H, H₁₅), 7.74-7.69 (m, 2H, H₁₆), 3.68 (t, 2H, ³J_{H12-H11} = 7.3 Hz, H₁₂), 3.26 (t, 2H, ³J_{H1-H2} = 7.0 Hz, H₁), 1.72-1.63 (m, 2H, H₁₁), 1.63-1.55 (m, 2H, H₂), 1.41-1.22 (m, 16H, H₃ H₄ H₅ H₆ H₇ H₈ H₉ H₁₀).

JMOD ¹³C NMR (CDCl₃, 100 MHz, 298K) : δ (ppm) = 167.8 (C₁₃), 133.4 (C₁₆), 131.8 (C₁₄), 122.6 (C₁₅), 51.0 (C₁), 37.6 (C₁₂), 29.1 & 29.1 & 29.1 & 28.8 & 28.8 & 28.5 & 28.2 & 26.5 & 26.3 (C₂ C₃ C₄ C₅ C₆ C₇ C₈ C₉ C₁₀ C₁₁).

MS (ESI): [M+H]⁺ calculated for [C₂₀H₂₉N₄O₂]⁺ : 357.2, found : 357.2

3) Preparation of the 12-azidododecan-1-amine **11**



Hydrazine monohydrate (474 mg, 9.475 mmol, 3.5 equiv) was added to a solution of the phthalimide **10** (965 mg, 2.707 mmol, 1 equiv) in 40 mL of ethanol. The mixture was stirred at reflux for 4 h, and then cooled to room temperature. An aqueous solution of KOH 1N (50 mL) was added and the solvent was removed in *vacuo*. The solution was extracted with dichloromethane (2x50 mL); then, the organic layers were combined, dried over MgSO₄ and concentrated to yield the desired product (563 mg, 92 %).

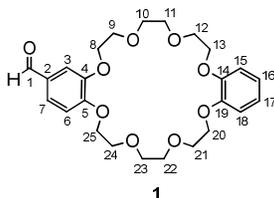
R_f (CH₂Cl₂ /CH₃OH 9:1) 0.1

¹H NMR (CDCl₃, 400 MHz, 298K) : δ (ppm) = 3.26 (t, 2H, ³J_{H12-H11} = 7.0 Hz, H₁₂), 2.68 (t, 2H, ³J_{H1-H2} = 7.0 Hz, H₁), 1.64-1.56 (m, 2H, H₁₁), 1.48-1.24 (m, 18H, H₂ H₃ H₄ H₅ H₆ H₇ H₈ H₉ H₁₀).

JMOD ¹³C NMR (CDCl₃, 100 MHz, 298K) : δ (ppm) = 50.6 (C₁₂), 41.5 (C₁), 33.1 (C₁₁), 28.9 & 28.8 & 28.8 & 28.7 & 28.4 & 28.1 & 26.2 & 26.0 (C₂ C₃ C₄ C₅ C₆ C₇ C₈ C₉ C₁₀).

MS (ESI): [M+H]⁺ calculated for [C₁₂H₂₇N₄]⁺ : 227.2, found : 227.2

4) Preparation of the crown ether **1**



This compound has been synthesized according to the procedure described by S. J. Cantrill, G. J. Youn, J. F. Stoddart.^[1]

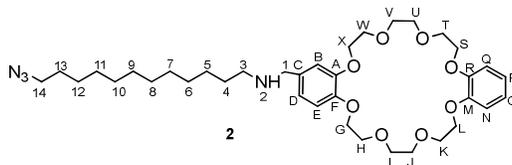
R_f (AcOEt) 0.3

¹H NMR (400 MHz, CDCl₃, 298K): δ (ppm) = 9.83 (s, 1H, H₁), 7.43 (dd, 1H, ³J_{H7-H6} = 8.2 Hz, ⁴J_{H7-H3} = 1.9 Hz, H₇), 7.38 (d, 1H, ⁴J_{H3-H7} = 1.9 Hz, H₃), 6.94 (d, 1H, ³J_{H6-H7} = 8.2 Hz, H₆), 6.90-6.86 (m, 4H, H₁₅ H₁₆ H₁₇ H₁₈), 4.24-4.20 (m, 4H, H₈ H₂₅), 4.17-4.15 (m, 4H, H₁₃ H₂₀), 3.98-3.92 (m, 8H, H₉ H₁₂ H₂₁ H₂₄), 3.86-3.84 (m, 8H, H₁₀ H₁₁ H₂₂ H₂₃).

JMOD ¹³C NMR (100 MHz, CDCl₃, 298K): δ (ppm) = 190.9 (C₁), 154.3 & 149.1 & 148.8 (C₄ C₅ C₁₄ C₁₉), 130.2 (C₂), 126.9 (C₇), 121.4 & 113.9 (C₁₅ C₁₆ C₁₇ C₁₈), 111.8 (C₆), 110.9 (C₃), 71.5 & 71.4 & 71.3 & 69.7 & 69.5 & 69.4 & 69.4 & 69.3 (CH₂O).

MS (ESI): [M+Na]⁺ calculated for C₂₅H₃₂O₉Na⁺: 499.52, found: 499.27

5) Preparation of the compound **2**



A solution of the crown ether aldehyde **1** (1.18 g, 2.49 mmol, 1 equiv) and the 12-azidododecan-1-amine **11** (563 mg, 2.49 mmol, 1 equiv) in 100 mL of toluene was heated under reflux for 30 h using a Dean-Stark apparatus. The solvent was then evaporated to give a yellow oil. The mixture was diluted with MeOH (70 mL), and then NaBH₄ (471 mg, 12.45 mmol, 5 equiv) was added portionwise at 5°C. Stirring was maintained at room temperature for a further 5 h. Then, an aqueous solution of HCl 5M (100 mL) was added to the reaction mixture. Methanol was evaporated, and the residue was diluted with dichloromethane (100 mL) and washed with an aqueous solution of NaOH 5M (120 mL). The two layers were separated and the aqueous layer was extracted with dichloromethane (3x100 mL). The organic layers were combined, dried over MgSO₄ and concentrated. The crude (1.78 g) was directly engaged in the following reaction.

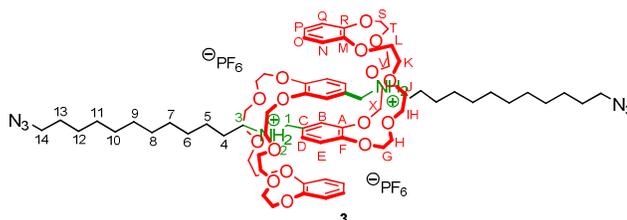
R_f (CH₂Cl₂ /CH₃OH 9:1) 0.1

¹H NMR (CDCl₃, 400 MHz, 298K): δ (ppm) = 6.93-6.83 (m, 6H, H_D H_E H_N H_O H_P H_Q), 6.82 (s, 1H, H_B), 4.20-4.10 (m, 8H, H_G H_L H_S H_X), 3.96-3.89 (m, 8H, H_H H_K H_T H_W), 3.84 (s, 8H, H_I H_J H_U H_V), 3.70 (s, 2H, H₁), 3.26 (t, 2H, ³J_{H14-H13} = 7.0 Hz, H₁₄), 2.60 (t, 2H, ³J_{H3-H4} = 7.3 Hz, H₃), 1.65-1.55 (m, 2H, H₁₃), 1.55-1.45 (m, 2H, H₄), 1.41-1.21 (m, 16H, H₅ H₆ H₇ H₈ H₉ H₁₀ H₁₁ H₁₂).

[¹] S. J. Cantrill, G. J. Youn, J. F. Stoddart, *J. Org. Chem.* **2001**, 66, 6857-6872.

JMOD ^{13}C NMR (CDCl₃, 100 MHz, 298K) : δ (ppm) = 148.7 & 148.6 & 147.6 (C_A C_F C_M C_R), 133.3 (C_C), 121.1 & 120.6 & 113.8 & 113.8 & 113.7 & 113.7 (C_B C_D C_E C_N C_O C_P C_Q), 71.1 & 69.6 & 69.1 (CH₂O_{DB24C8}), 53.4 (C_I), 51.2 (C₁₄), 49.1 (C₃), 29.7 & 29.3 & 29.3 & 29.3 & 29.2 & 29.2 (C₄ C₅ C₆ C₇ C₈ C₉ C₁₀ C₁₁ C₁₂ C₁₃).
MS (ESI): [M+H]⁺ calculated for [C₃₇H₅₉N₄O₈]⁺ : 687.4, found : 687.4

6) Preparation of the compound 3



A solution of HCl 2M in diethyl ether (12.5 mL, 25 mmol, 10 equiv) was added to the amine **2** (1.70 g, 2.49 mmol, 1 equiv). The mixture was stirred for 30 min, and then diethyl ether was evaporated to give a solid. To a solution of the previous solid in milliQ water (10 mL) was added NH₄PF₆ (1.22 g, 7.47 mmol, 3 equiv) and dichloromethane (10 mL). The biphasic solution was stirred vigorously for 30 min; then, the two layers were separated and the aqueous layer was extracted with dichloromethane (3x10 mL). The organic layers were then combined, dried over MgSO₄ and concentrated. The crude was purified by chromatography on a silicagel column (gradient solvent elution CH₂Cl₂/Acetone 1/0 to 9/1) to yield the compound **3** (1.45 g, 70% over the two steps).

R_f (CH₂Cl₂ /CH₃OH 9:1) 0.57

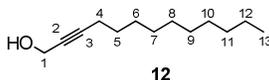
^1H NMR (CDCl₃, 400 MHz, 298K) : δ (ppm) = 6.92 (d, 2H, $^3J_{\text{HD-HE}}$ = 8.1 Hz, H_D), 6.87-6.69 (m, 10H, H_E H_N H_O H_P H_Q), 6.61 (s, 2H, H_B), 4.53-4.25 (m, 4H, H_I), 4.52-3.56 (m, 48H, CH₂O_{DB24C8}), 3.56-3.32 (m, 4H, H₃), 3.27 (t, 4H, $^3J_{\text{H14-H13}}$ = 7.0 Hz, H₁₄), 1.74-1.64 (m, 4H, H₄), 1.61 (tt, 4H, $^3J_{\text{H13-H12}}$ = $^3J_{\text{H13-H14}}$ = 7.0 Hz, H₁₃), 1.44-1.14 (m, 32H, H₅ H₆ H₇ H₈ H₉ H₁₀ H₁₁ H₁₂).

JMOD ^{13}C NMR (CDCl₃, 100 MHz, 298K) : δ (ppm) = 147.5 & 147.4 & 146.1 & 146.0 (C_A C_F C_M C_R), 124.7 (C_C), 122.8 (C_D), 120.9 & 120.8 & 112.6 & 112.6 & 111.6 & 111.6 (C_B C_E C_N C_O C_P C_Q), 72.1 & 71.7 & 70.1 & 70.7 & 70.6 & 70.5 & 70.2 & 70.1 (CH₂O_{DB24C8}), 52.0 (C_I), 51.3 (C₁₄), 48.8 (C₃), 29.3 & 29.3 & 29.3 & 29.3 & 29.0 & 28.9 & 28.7 & 26.6 (C₄ C₅ C₆ C₇ C₈ C₉ C₁₀ C₁₁ C₁₂ C₁₃).

MS (MALDI): [M-1H-2PF₆]⁺ calculated for [C₇₄H₁₁₇N₈O₁₆]⁺ : 1373.86, found : 1373.9

C. Synthesis of the dialkyne pseudo [c2]Daisy chain 5

1) Preparation of the tridec-2-yn-1-ol 12



To a stirred solution of 1-dodecyne (5g, 30.064 mmol, 1 equiv) in anhydrous THF at 5°C was added, under Argon, *n*-BuLi (20.7 mL, 33.077 mmol, 1.6 M in THF, 1.1 equiv). After 30 min at 5°C, paraformaldehyde (1.08 g, 36.077 mmol, 1.2 equiv) was added by portions. The solution was further stirred during 1h at 5°C, then during one night at room temperature. The reaction mixture was quenched with 120 mL of 1:1 water/saturated water with NH₄Cl. The biphasic solution was separated and the aqueous layer extracted twice

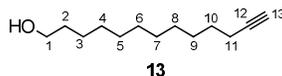
with 100 mL of ethyl acetate. The organic layers were then combined, dried over MgSO₄ and concentrated to afford compound **12** in a quantitative yield (5.90 g) as a yellow solid.

R_f (petroleum ether /AcOEt 9:1) 0.21

¹H NMR (CDCl₃, 400 MHz, 298K) : δ (ppm) = 4.25 (t, 2H, ⁵J_{H4-H1} = 2.0 Hz, H₁), 2.21 (tt, 2H, ⁵J_{H4-H1} = 2.0 Hz, ³J_{H4-H5} = 7.2 Hz, H₄), 1.55-1.46 (m, 2H, H₅), 1.42-1.33 (m, 2H, H₆), 1.33-1.20 (m, 12H, H₇ H₈ H₉ H₁₀ H₁₁ H₁₂), 0.89 (t, 3H, ³J_{H13-H12} = 6.9 Hz, H₁₃).

JMOD ¹³C NMR (CDCl₃, 100 MHz, 298K) : δ (ppm) = 86.6 & 78.2 (C₂ C₃), 51.4 (C₁), 31.9 & 29.6 & 29.5 & 29.3 & 29.1 & 28.9 & 28.6 & 22.7 (C₅ C₆ C₇ C₈ C₉ C₁₀ C₁₁ C₁₂), 18.7 (C₄), 14.1 (C₁₃).

2) Preparation of the tridec-12-yn-1-ol **13**



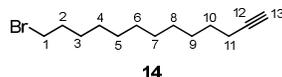
To dry ethylene-1,2-diamine (80 mL) at 0-5°C under argon was added NaH (11.90 g, 0.297 mol, 10 equiv, 60% in oil). The mixture was allowed to warm slowly at 60°C and stirred for 3h to give a deep blue mixture. Then, it was cooled to 45°C before adding portionwise the tridec-2-yn-1-ol **12** (5.84 g, 29.749 mmol, 1 equiv). The solution was stirred at 60°C for one night before being cooled to 0°C. 100 mL of diethyl ether and 100 mL of water were introduced slowly; then HCl 12M was added until pH 1. Aqueous layer was extracted with diethyl ether (4x100 mL). The organic layers were combined, dried and concentrated. The crude oil was purified by chromatography on a silicagel column (solvent elution: petroleum ether/AcOEt 1/1) to give the desired product (3.56 g, 61%) as a yellow solid.

R_f (petroleum ether /AcOEt 1:1) 0.71

¹H NMR (CDCl₃, 400 MHz, 298K) : δ (ppm) = 3.63 (t, 2H, ³J_{H1-H2} = 6.6 Hz, H₁), 2.18 (td, 2H, ³J_{H11-H10} = 7.1 Hz, ⁴J_{H11-H13} = 2.6 Hz, H₁₁), 1.94 (t, 1H, ⁴J_{H13-H11} = 2.6 Hz, H₁₃), 1.62-1.47 (m, 4H, H₂ H₁₀), 1.43-1.23 (m, 14H, H₃ H₄ H₅ H₆ H₇ H₈ H₉).

JMOD ¹³C NMR (CDCl₃, 100 MHz, 298K) : δ (ppm) = 84.4 (C₁₂), 68.0 (C₁₃), 62.2 (C₁), 32.4 (C₂) 29.4 & 29.3 & 29.3 & 29.2 & 28.9 & 28.5 & 28.2 (C₃ C₄ C₅ C₆ C₇ C₈ C₉ C₁₀), 25.6 (C₁₁).

3) Preparation of the 13-bromotridec-1-yne **14**



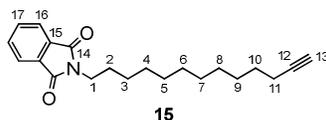
To a solution of the tridec-12-ynol **13** (2.40 g, 12.226 mmol, 1 equiv) in 40 mL of dry dichloromethane were added the tetrabromomethane (8.11 g, 24.451 mmol, 2 equiv) and the triphenylphosphine (6.41 g, 24.451 mmol, 2 equiv). The mixture was stirred at room temperature for 1h; then, the solvent was removed under reduced pressure. A solution of petroleum ether / ethyl acetate (9:1) was added and the resulted precipitate was filtered and washed abundantly. The filtrate was evaporated and the crude was purified by chromatography on a silicagel column (elution: petroleum ether/AcOEt 9/1) to give the brominated product **14** (3.07 g, 97%) as a yellow oil.

R_f (petroleum ether /AcOEt 97:3) 0.50

¹H NMR (CDCl₃, 400 MHz, 298K) : δ (ppm) = 3.42 (t, 2H, ³J_{H1-H2} = 6.9 Hz, H₁), 2.19 (td, 2H, ³J_{H11-H10} = 7.1 Hz, ⁴J_{H11-H13} = 2.7 Hz, H₁₁), 1.95 (t, 1H, ⁴J_{H13-H11} = 2.7 Hz, H₁₃), 1.90-1.81 (m, 2H, H₂), 1.57-1.48 (m, 2H, H₁₀), 1.48-1.23 (m, 14H, H₃ H₄ H₅ H₆ H₇ H₈ H₉).

JMOD ¹³C NMR (CDCl₃, 100 MHz, 298K) : δ (ppm) = 84.4 (C₁₂), 68.0 (C₁₃), 33.7 (C₁), 32.7 & 29.3 & 29.3 & 29.3 & 29.0 & 28.6 & 28.6 & 28.4 & 28.0 (C₂ C₃ C₄ C₅ C₆ C₇ C₈ C₉ C₁₀), 18.3 (C₁₁).

4) Preparation of the phthalimide 15



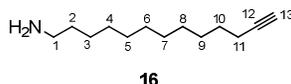
Potassium phthalimide (3.40 g, 18.34 mmol, 1.5 equiv) was added to a solution of the 13-bromotridec-1-yne **14** (3.17 g, 12.230 mmol, 1 equiv) in 60 mL of DMF. After stirring for 4 h at 70°C, the solvent was removed in *vacuo*. The solid residue was suspended in dichloromethane and filtered through a layer of silica gel. The filtrate was evaporated to give the desired product (3.98 g) in a quantitative yield as a yellow solid.

R_f (Petroleum ether/AcOEt 75/25) 0.50

¹H NMR (CDCl₃, 400 MHz, 298K) : δ (ppm) = 7.87-7.81 (m, 2H, H₁₆), 7.73-7.68 (m, 2H, H₁₇), 3.67 (t, 2H, ³J_{H1-H2} = 7.4 Hz, H₁), 2.17 (td, 2H, ³J_{H11-H10} = 7.8 Hz, ⁴J_{H11-H13} = 2.6 Hz, H₁₁), 1.94 (t, 1H, ⁴J_{H13-H11} = 2.6 Hz, H₁₃), 1.72-1.62 (m, 2H, H₂), 1.56-1.47 (m, 2H, H₁₀), 1.42-1.22 (m, 14H, H₃ H₄ H₅ H₆ H₇ H₈ H₉).

JMOD ¹³C NMR (CDCl₃, 100 MHz, 298K) : δ (ppm) = 168.0 (C₁₄), 133.5 (C₁₇), 131.9 (C₁₅), 122.8 (C₁₆), 84.4 (C₁₂), 68.0 (C₁₃), 37.7 (C₁), 29.2 & 29.2 & 28.9 & 28.8 & 28.5 & 28.3 & 28.2 & 26.6 (C₂ C₃ C₄ C₅ C₆ C₇ C₈ C₉ C₁₀), 18.1 (C₁₁).

5) Preparation of the tridec-12-yn-1-amine 16



Hydrazine monohydrate (2.14 g, 42.805 mmol, 3.5 equiv) was added to a solution of the phthalimide **15** (3.98 g, 12.230 mmol, 1 equiv) in 60 mL of ethanol. The mixture was stirred at reflux for 4 h, and then cooled to room temperature. An aqueous solution of KOH 1N (100 mL) was added and the solvent was removed in *vacuo*. The solution was extracted with dichloromethane (2x100 mL); then, the organic layers were combined, dried over MgSO₄ and concentrated to yield the desired product (2.10 g, 88 %) as a yellow solid.

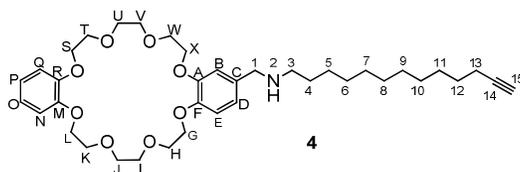
R_f (CH₂Cl₂/MeOH 9:1) 0

¹H NMR (CDCl₃, 400 MHz, 298K) : δ (ppm) = 2.67(t, 2H, ³J_{H1-H2} = 7.0 Hz, H₁), 2.18 (td, 2H, ³J_{H11-H10} = 7.2 Hz, ⁴J_{H11-H13} = 2.7 Hz, H₁₁), 1.93 (t, 1H, ⁴J_{H13-H11} = 2.7 Hz, H₁₃), 1.56-1.47 (m, 2H, H₁₀), 1.47-1.34 (m, 4H, H₂ H₉), 1.34-1.21 (m, 12H, H₃ H₄ H₅ H₆ H₇ H₈).

JMOD ¹³C NMR (CDCl₃, 100 MHz, 298K) : δ (ppm) = 84.6 (C₁₂), 67.9 (C₁₃), 42.0 (C₁), 33.6 (C₂), 29.4 & 29.4 & 29.3 & 28.9 & 26.7 (C₃ C₄ C₅ C₆ C₇ C₈ C₉ C₁₀), 18.2 (C₁₁).

MS (ESI): [M+H]⁺; calculated for [C₁₃H₂₆N]⁺: 196.2, found : 196.2

6) Preparation of the compound 4



A solution of the crown ether aldehyde **1** (5.78 g, 12.134 mmol, 1 equiv) and the tridec-12-yn-1-amine **16** (2.37 g, 12.134 mmol, 1 equiv) in 200 mL of toluene was heated under reflux for 30 h using a Dean-Stark apparatus. The solvent was then evaporated to give a yellow oil. The mixture was diluted with MeOH (150 mL), and then NaBH₄ (2.30 g, 60.670 mmol, 5 equiv) was added portionwise at 0-5°C. Stirring was maintained at room temperature for a further 5 h. Then, an aqueous solution of HCl 5M (100 mL) was added to the reaction mixture. Methanol was evaporated, and the residue was diluted with dichloromethane (100 mL) and washed with an aqueous solution of NaOH 5M (100 mL). The two layers were separated and the aqueous layer was extracted with dichloromethane (2x200 mL). The organic layers were combined, dried over MgSO₄ and concentrated. The crude (6.73 g) was directly engaged in the following reaction.

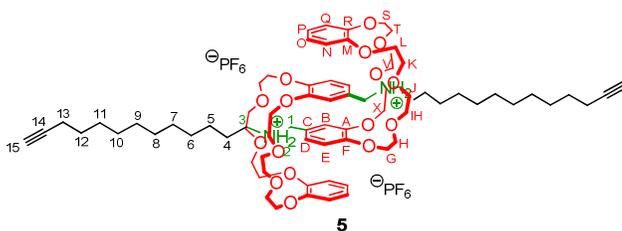
R_f (CH₂Cl₂/MeOH 9:1) 0.1

¹H NMR (CDCl₃, 400 MHz, 298K) : δ (ppm) = 6.90-6.80 (m, 7H, H_B H_D H_E H_N H_O H_P H_Q), 4.19-4.10 (m, 8H, H_G H_L H_S H_X), 3.95-3.89 (m, 8H, H_H H_K H_T H_W), 3.84 (s, 8H, H_I H_J H_U H_V), 3.70 (s, 2H, H₁), 2.60 (t, 2H, ³J_{H4-H3} = 7.3 Hz, H₃), 2.18 (td, 2H, ³J_{H13-H12} = 7.1 Hz, ⁴J_{H13-H15} = 2.7 Hz, H₁₃), 1.94 (t, 1H, ⁴J_{H15-H13} = 2.7 Hz, H₁₅), 1.57-1.45 (m, 4H, H₄ H₁₂), 1.44-1.34 (m, 2H, H₁₁), 1.33-1.23 (m, 12H, H₅ H₆ H₇ H₈ H₉ H₁₀).

JMOD ¹³C NMR (CDCl₃, 100 MHz, 298K) : δ (ppm) = 148.3 & 148.2 & 147.2 (C_A C_F C_M C_R), 132.8 (C_C), 120.7 & 120.2 & 113.4 & 113.4 & 113.3 (C_B C_D C_E C_N C_O C_P C_Q), 83.9 (C₁₄), 70.5 (C₁ C_J C_U C_V), 69.2 (C_H C_K C_T C_W), 68.6 (C_G C_L C_S C_X), 67.8 (C₁₅), 52.9 (C₁), 48.6 (C₃), 29.2 & 28.9 & 28.9 & 28.9 & 28.8 & 28.4 & 28.0 & 27.9 & 26.7 (C₄ C₅ C₆ C₇ C₈ C₉ C₁₀ C₁₁ C₁₂), 17.7 (C₁₃).

MS (ESI): [M+H]⁺; calculated for [C₃₈H₅₈NO₈]⁺: 656.4, found : 656.3

7) Preparation of the compound 5



A solution of HCl 2M in diethyl ether (20 mL, 0.2 mol, 19 equiv) was added to the amine **4** (6.73 g, 10.59 mmol, 1 equiv). The mixture was stirred for 30 min, and then diethyl ether was evaporated to give a solid. To a solution of the previous solid in milliQ water (50 mL) was added NH₄PF₆ (5.12 g, 31.77 mmol, 3 equiv) and dichloromethane (50 mL). The biphasic solution was stirred vigorously for 30 min; then, the two layers were separated and the aqueous layer was extracted with dichloromethane (3x30 mL). The organic layers were then combined, dried over MgSO₄ and concentrated. The crude was purified by chromatography on a silicagel column (solvent elution CH₂Cl₂/MeOH 98/2) to yield the compound **5** (8.40 g, 87% over the two steps) as a pale yellow solid.

R_f (CH₂Cl₂/MeOH 9:1) 0.54

¹H NMR (CDCl₃, 400 MHz, 298K) : δ (ppm) = 6.93 (dd, 1H, ⁴J_{HD-HB} = 1.5 Hz, ³J_{HD-HE} = 8.4 Hz, H_D), 6.87-6.72 (m, 5H, H_E H_N H_O H_P H_Q), 6.60 (d, 1H, ⁴J_{HB-HD} = 1.5 Hz, H_B), 4.52-4.28 (m, 2H, H_I), 4.52-3.59 (m, 24H, CH₂O_{DB24C8}), 3.58-3.30 (m, 2H, H₃), 2.19 (td, 2H, ³J_{H13-H12} = 7.1 Hz, ⁴J_{H13-H15} = 2.7 Hz, H₁₃), 1.96 (t, 1H, ⁴J_{H15-H13} = 2.7 Hz, H₁₅), 1.73-1.63 (m, 2H, H₄), 1.57-1.48 (m, 2H, H₁₂), 1.44-1.35 (m, 2H, H₁₁), 1.35-1.16 (m, 12H, H₅ H₆ H₇ H₈ H₉ H₁₀).

JMOD ¹³C NMR (CDCl₃, 100 MHz, 298K) : δ (ppm) = 147.6 & 147.5 & 146.2 & 146.0 (C_A C_F C_M C_R), 124.7 (C_C), 122.9 (C_D), 121.0 & 120.9 & 112.9 & 112.5 & 111.7 (C_B C_E C_N C_O C_P C_Q), 72.2 & 71.8 & 70.9 & 70.8 & 70.7 & 70.3 & 67.5 & 67.0 & 66.7 (CH₂O_{DB24C8}), 68.2 (C₁₅), 52.1 (C₁), 48.8 (C₃), 29.3 & 29.0 & 28.6 & 28.4 & 26.6 (C₄ C₅ C₆ C₇ C₈ C₉ C₁₀ C₁₁ C₁₂), 18.3 (C₁₃).

MS (MALDI): [M-1H-2PF₆]⁺ calculated for [C₇₆H₁₁₅N₂O₁₆]⁺ : 1311.82, found : 1311.8

D. Procedure for the protonation of a stoichiometric mixture of the amines 2 and 4 in order to obtain a statistical distribution of the pseudo rotaxane dimers 3, 5 and 6/6'

A suspension of the compound 4 (41 mg, 6.236.10⁻⁵ mol, 1 equiv) and the compound 2 (43 mg, 6.236.10⁻⁵ mol, 1 equiv) in 2.5 mL (2.5 mmol, 40 equiv) of HCl 1M in diethyl ether was stirred for 30 min. The mixture was then evaporated and washed with diethyl ether to give a solid. NH₄PF₆ (51 mg, 3.118.10⁻⁴ mol, 5 equiv) and 3 mL of dichloromethane were added to a suspension of the previous product in 3 mL of milliQ water. The resulted bilayer solution was vigorously stirred for 30 min. After separation, the aqueous layer was extracted twice with 3 mL of dichloromethane. The organic layers were combined, dried over MgSO₄ and concentrated to obtain the mixture of pseudo rotaxane dimers 3, 5 and 6/6' (100 mg, 98 %)

E. Kinetic study of exchange using matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry (MS) on a stoichiometric mixture of compounds 3 and 5

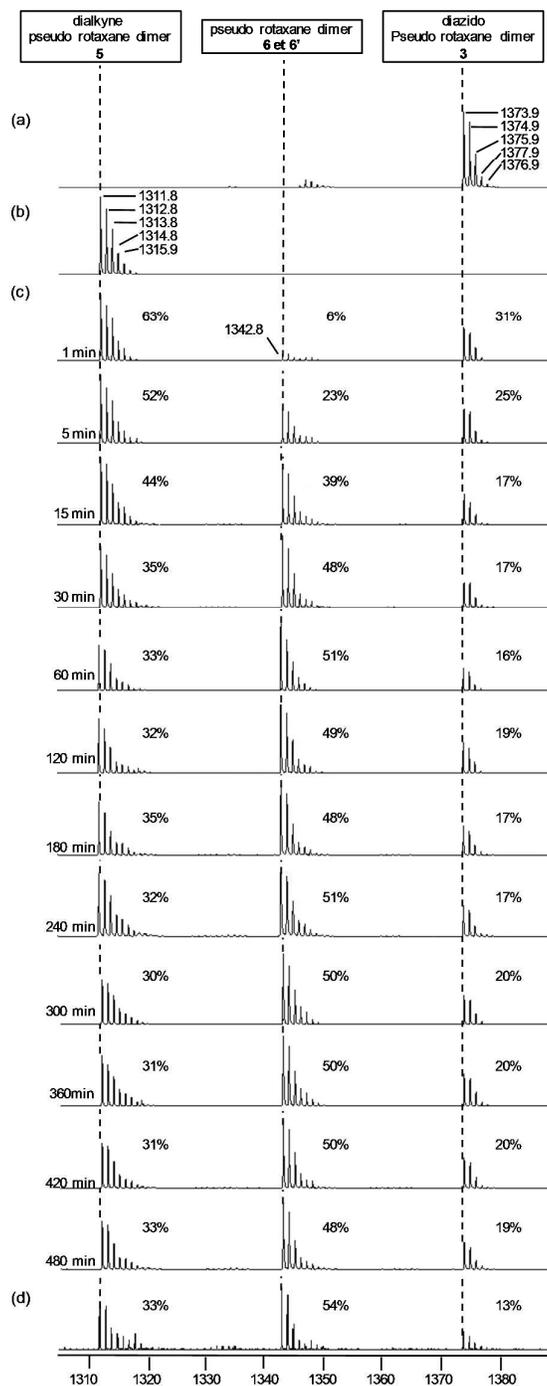
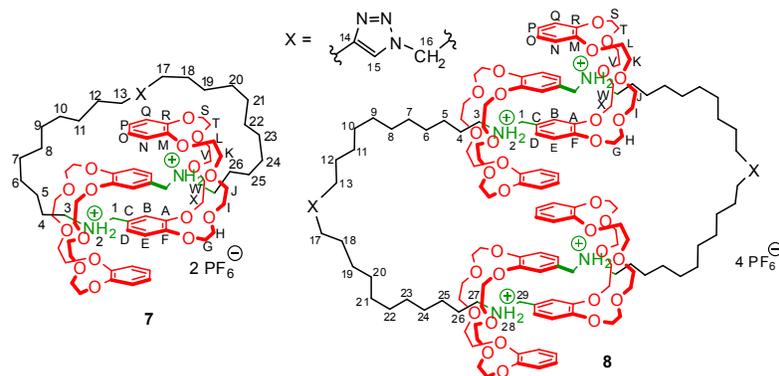


Figure 2. MALDI-TOF mass spectra of : (a) the diazido pseudo rotaxane dimer **3**, (b) the dialkyne pseudo rotaxane dimer **5**, (c) a stoichiometric mixture of pseudo rotaxane dimers **3** and **5** over time, (d) after protonation of a stoichiometric mixture of monomers **2** and **4**. The detected ions corresponds to $[M-2PF_6-1H]^+$.

F. Synthesis of the molecular lassoes 7



In a typical procedure, $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (67 mg, 0.180 mmol, 1 equiv) and 2,6-lutidine (2 mg, 0.018 mmol, 0.1 equiv) were added successively to a solution of the azido compound **3** (150 mg, 0.180 mmol, 1 equiv) and the alkyne compound **5** (144 mg, 0.180 mmol, 1 equiv) in 360 mL of dry dichloromethane (concentration 0.5 mM). The mixture was stirred for 4 days at room temperature, after which time the solvent was evaporated under *vacuo*. The crude was then directly purified by chromatography on a silicagel column (solvent gradient elution $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ 1/0 to 98/1) then on a LH20 sephadex column (eluent $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ 1/1) to afford the dilasso rotamacrocycle **7** (150 mg, 51%) accompanied by traces of tetralasso **8** which were only detected by mass spectrometry. Integration of the signals is given here for dilasso **7**.

^1H NMR (CD_3CN , 400 MHz, 298K) : δ (ppm) = 7.48 (s, 1H, H_{15}), 6.90-6.85 & 6.69-6.58 (2*br s, 4H, H_2 H_{28}), 6.84-6.70 (m, 12H, H_B H_D H_N H_O H_P H_Q), 6.43 (d, 2H, $^3J_{\text{HE-HD}} = 8.4$ Hz, H_E), 4.57-4.39 (m, 4H, H_1 H_{29}), 4.27 (t, 2H, $^3J_{\text{H16-H17}} = 7.3$ Hz, H_{16}), 4.33-3.62 (m, 48H, $\text{CH}_2\text{O}_{\text{DB24C8}}$), 3.47-3.35 (m, 4H, H_3 H_{27}), 2.64 (t, 2H, $^3J_{\text{H13-H12}} = 7.6$ Hz, H_{13}), 1.87-1.78 (m, 2H, H_{17}), 1.76-1.66 (m, 4H, H_4 H_{26}), 1.66-1.57 (m, 2H, H_{12}), 1.41-1.16 (m, 30H, H_5 H_6 H_7 H_8 H_9 H_{10} H_{11} H_{18} H_{19} H_{20} H_{21} H_{22} H_{23} H_{24} H_{25}).

JMOD ^{13}C NMR (CD_3CN , 100 MHz, 298K) : δ (ppm) = 148.7 & 147.7 & 147.0 (C_{14} C_A C_F C_M C_R), 126.2 (C_C), 122.3 (C_{15}), 123.5 & 121.6 & 114.1 & 113.0 & 112.7 & 112.7 (C_B C_D C_E C_N C_O C_P C_Q), 71.5 & 71.4 & 71.2 & 71.0 & 68.5 & 68.2 & 68.0 & 67.9 ($\text{CH}_2\text{O}_{\text{DB24C8}}$), 52.8 (C_1 C_{29}), 52.1 (C_{13}), 50.6 (C_3 C_{27}), 30.9 & 30.3 & 30.2 & 30.2 & 30.1 & 30.0 & 29.9 & 29.6 & 29.5 & 27.3 & 27.2 & 27.1 (C_4 C_5 C_6 C_7 C_8 C_9 C_{10} C_{11} C_{12} C_{17} C_{18} C_{19} C_{20} C_{21} C_{22} C_{23} C_{24} C_{25} C_{26}) 26.2 (C_{16}).

MS (MALDI): [M-1H-2PF₆] calculated for [$\text{C}_{75}\text{H}_{116}\text{N}_5\text{O}_{16}$]: 1342.84 found: 1342.8 (compound **7**); [M-3H-4PF₆] calculated for [$\text{C}_{150}\text{H}_{232}\text{N}_{10}\text{O}_{32}$]: 2685.68, found: 2684.7 (compound **8**).

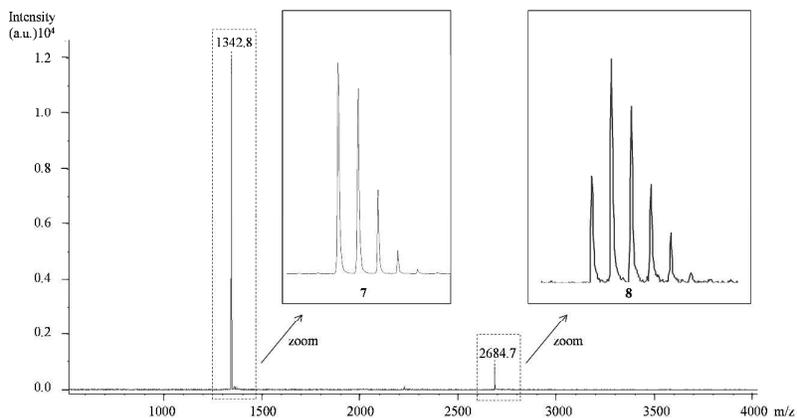
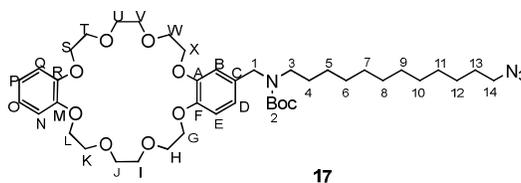


Figure 2. MALDI-TOF mass spectrum of lasso rotamacrocycle **7** and traces of **8** (with zoom of the isotopic clusters)

G. Synthesis of the uncomplexed compound 7u

1) Preparation of the compound 17



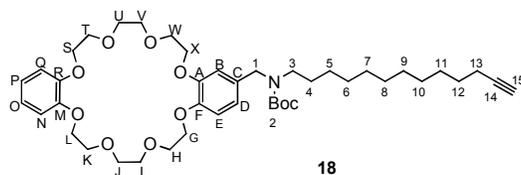
To a solution of the compound **2** (61 mg, 0.074 mmol, 1 equiv) in dichloromethane (6 mL) were added Boc₂O (48 mg, 0.221 mmol, 3 equiv) and DIEA (2.9 mg, 0.221 mmol, 3 equiv). The solution was stirred during 3 h at room temperature. The organic layer was washed successively with an aqueous solution of HCl 1M (2x10 mL), a saturated aqueous solution of NaHCO₃ (2x10 mL), then dried over MgSO₄ and concentrated under *vacuo*. The crude was purified by chromatography on a silicagel column (solvent elution CH₂Cl₂/MeOH 98/2) to yield the N-Boc protected compound **17** (56 mg, 97%) as a white solid.

¹H NMR (CDCl₃, 400 MHz, 298K) : δ (ppm) = 6.94-6.70 (m, 7H, H_B H_D H_E H_N H_O H_P H_Q), 4.37-4.28 (br s, 2H, H_I), 4.20-4.09 (m, 8H, H_G H_L H_S H_X), 3.96-3.87 (m, 8H, H_H H_K H_T H_W), 3.83 (s, 8H, H_I H_J H_U H_V), 3.26 (t, 2H, ³J_{H14-H13} = 7.0 Hz, H₁₄), 3.21-3.01 (m, 2H, H₃), 1.75-1.65 (br s, 2H, H₄), 1.64-1.55 (m, 2H, H₁₃), 1.53-1.18 (m, 25H, H₂ H₅ H₆ H₇ H₈ H₉ H₁₀ H₁₁ H₁₂).

JMOD ¹³C NMR (CDCl₃, 100 MHz, 298K) : δ (ppm) = 148.9 & 148.9 & 147.9 (C_A C_F C_M C_R, (CH₃)₃CCO), 131.9 (C_C), 121.4 & 114.1 & 113.8 (C_B C_D C_E C_N C_O C_P C_Q), 79.3 (CO_C(CH₃)₃), 71.1 (C₁ C_J C_U C_V), 69.8 (C_H C_K C_T C_W), 69.3 (C_G C_L C_S C_X), 51.4 (C₁₄), 49.3 (C₁), 46.1 (C₃), 29.5 & 29.4 & 29.4 & 29.43 & 29.3 & 29.1 & 28.8 & 26.8 & 26.6 (C₄ C₅ C₆ C₇ C₈ C₉ C₁₀ C₁₁ C₁₂ C₁₃), 28.4 ((CH₃)₃CCO).

MS (ESI): [M+H]⁺; calculated for [C₄₂H₆₇N₄O₁₀]⁺: 787.5, found : 787.5

2) Preparation of the compound 18



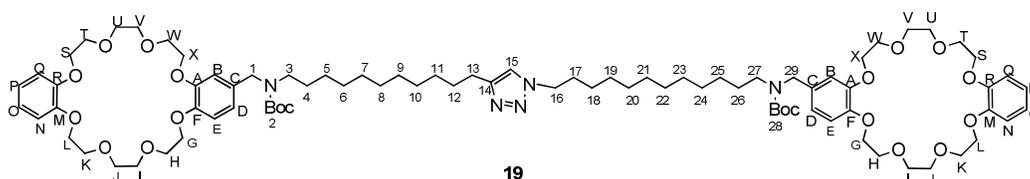
To a solution of the compound **4** (300 mg, 0.0374 mmol, 1 equiv) in dichloromethane (15 mL) were added Boc₂O (245 mg, 1.122 mmol, 3 equiv) and DIEA (0.145 mL, 1.122 mmol, 3 equiv). The solution was stirred during 3 h at room temperature. The organic layer was washed successively with an aqueous solution of HCl 1M (2x30 mL), a saturated aqueous solution of NaHCO₃ (2x30 mL), then dried over MgSO₄ and concentrated under *vacuo*. The crude was purified by chromatography on a silicagel column (solvent elution CH₂Cl₂/MeOH 98/2) to yield the N-Boc protected compound **18** (272 mg, 96%) as a white solid.

R_f (CH₂Cl₂/MeOH 9:1) 0.74

¹H NMR (CDCl₃, 400 MHz, 298K) : δ (ppm) = 6.94-6.70 (m, 7H, H_B H_D H_E H_N H_O H_P H_Q), 4.38-4.27 (br s, 2H, H_I), 4.21-4.09 (m, 8H, H_G H_L H_S H_X), 3.95-3.87 (m, 8H, H_H H_K H_T H_W), 3.83 (s, 8H, H_I H_J H_U H_V), 3.20-3.00 (m, 2H, H₃), 2.18 (td, 2H, ³J_{H13-H12} = 7.1 Hz, ⁴J_{H13-H15} = 2.7 Hz, H₁₃), 1.94 (t, 1H, ⁴J_{H15-H13} = 2.7 Hz, H₁₅), 1.57-1.18 (m, 18H, H₄ H₅ H₆ H₇ H₈ H₉ H₁₀ H₁₁ H₁₂), 1.45 (s, 9H, H₂).

JMOD ^{13}C NMR (CDCl_3 , 100 MHz, 298K) : δ (ppm) = 148.8 & 147.9 (C_A C_F C_M C_R), 131.9 (C_C), 121.4 & 114.6 & 113.8 (C_B C_D C_E C_N C_O C_P C_Q), 79.3 ($\text{CO}_2(\text{CH}_3)_3$), 71.1 (C_I C_J C_U C_V), 69.8 (C_H C_K C_T C_W), 69.3 (C_G C_L C_S C_X), 68.0 (C_{15}), 51.4 (C_1), 46.3(C_3), 29.5 & 29.4 & 29.4 & 29.3 & 29.0 & 28.7 & 26.8 (C_4 C_5 C_6 C_7 C_8 C_9 C_{10} C_{11} C_{12}), 28.4 ($(\text{CH}_3)_3\text{CCO}$), 18.4 (C_{13}).
MS (ESI): $[\text{M}+\text{H}]^+$; calculated for $[\text{C}_{43}\text{H}_{66}\text{NO}_{10}]^+$: 756.5, found : 756.5

3) Preparation of the compound 19

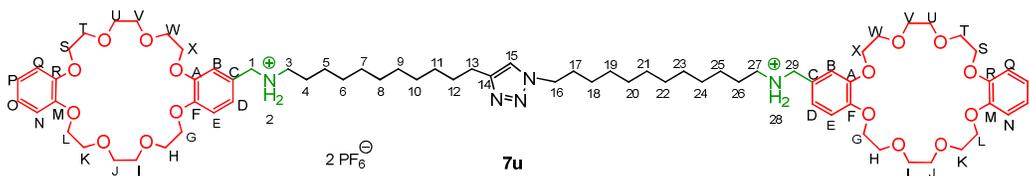


In a typical procedure, $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (22 mg, 0.060 mmol, 1 equiv) and 2,6-lutidine (0.6 mg, 0.006 mmol, 0.1 equiv) were added successively to a solution of the azido compound **17** (47 mg, 0.060 mmol, 1 equiv) and the alkyne compound **18** (45 mg, 0.060 mmol, 1 equiv) in 2 mL of dry dichloromethane. The mixture was stirred for 24 h at room temperature, after which time the solvent was evaporated under *vacuo*. The crude was then directly purified by chromatography on a silicagel column (solvent gradient elution CH_2Cl_2 / CH_3OH 1/0 to 98/2) to afford the compound **19** (48 mg, 52%).

^1H NMR (CD_3CN , 400 MHz, 298K) : δ (ppm) = 7.46 (s, 1H, H_{15}), 7.13-7.02 (m, 8H, H_E H_N H_O H_P H_Q), 7.00-6.97 (br s, 2H, H_B), 6.91 (dd, 2H, $^4J_{\text{HD-HB}} = 1.8$ Hz, $^3J_{\text{HD-HE}} = 8.3$ Hz, H_D), 4.34 (s, 4H, H_I H_{29}), 4.28-4.19 (m, 18H, H_G H_L H_S H_X H_{16}), 3.78-3.70 (m, 16H, H_H H_K H_T H_W), 3.60 & 3.60 (2*s, 16H, H_I H_J H_U H_V), 3.21-3.10 (br t, 4H, H_3 H_{27}), 2.63 (t, 2H, $^3J_{\text{H}_{13}-\text{H}_{12}} = 7.6$ Hz, H_{13}), 1.85-1.77 (m, 2H, H_{17}), 1.65-1.56 (m, 2H, H_{12}), 1.55-1.37 (m, 4H, H_4 H_{26}), 1.44 (s, 18H, H_2 H_{28}), 1.36-1.16 (m, 30H, H_5 H_6 H_7 H_8 H_9 H_{10} H_{11} H_{18} H_{19} H_{20} H_{21} H_{22} H_{23} H_{24} H_{25}).

JMOD ^{13}C NMR (CD_3CN , 100 MHz, 298K) : δ (ppm) = 149.2 & 149.1 & 149.1 & 148.1 (C_{14} C_A C_F C_M C_R), 135.4 (C_C), 124.1 & 124.0 & 122.8 & 117.5 & 117.4 & 117.3 & 116.5 (C_B C_D C_E C_N C_O C_P C_Q), 122.5 (C_{15}), 80.0 ($\text{CO}_2(\text{CH}_3)_3$), 69.7 & 69.6 & 69.4 & 68.7 & 68.6 & 68.6 & 68.2 & 68.1 & 68.0 ($\text{CH}_2\text{O}_{\text{DB}24\text{C}8}$), 50.6 (C_{16}), 50.2 (C_1 C_{29}), 47.6 (C_3 C_{27}), 30.9 & 30.2 & 30.2 & 30.2 & 30.1 & 30.1 & 30.1 & 30.0 & 29.8 & 29.6 & 27.5 & 27.0 (C_4 C_5 C_6 C_7 C_8 C_9 C_{10} C_{11} C_{12} C_{17} C_{18} C_{19} C_{20} C_{21} C_{22} C_{23} C_{24} C_{25} C_{26}), 28.6 ($(\text{CH}_3)_3\text{C}$), 26.2 (C_{13}).
MS (ESI): $[\text{M}+\text{H}]^+$; calculated for $[\text{C}_{85}\text{H}_{132}\text{N}_5\text{O}_{20}]^+$: 1543.9, found : 1543.9

4) Preparation of the uncomplexed compound 7u



A suspension of the N-Boc protected compound **19** (48 mg, 0.031 mmol, 1 equiv) in 1 mL of HCl 1M in diethyl ether was stirred for 1 hour. The mixture was then evaporated and washed with diethyl ether to give a solid. NH_4PF_6 (25 mg, 0.156 mmol, 5 equiv) and 3 mL of dichloromethane were added to a suspension of the previous product in 3 mL of milliQ water. The resulted bilayer solution was vigorously stirred for 30 min.

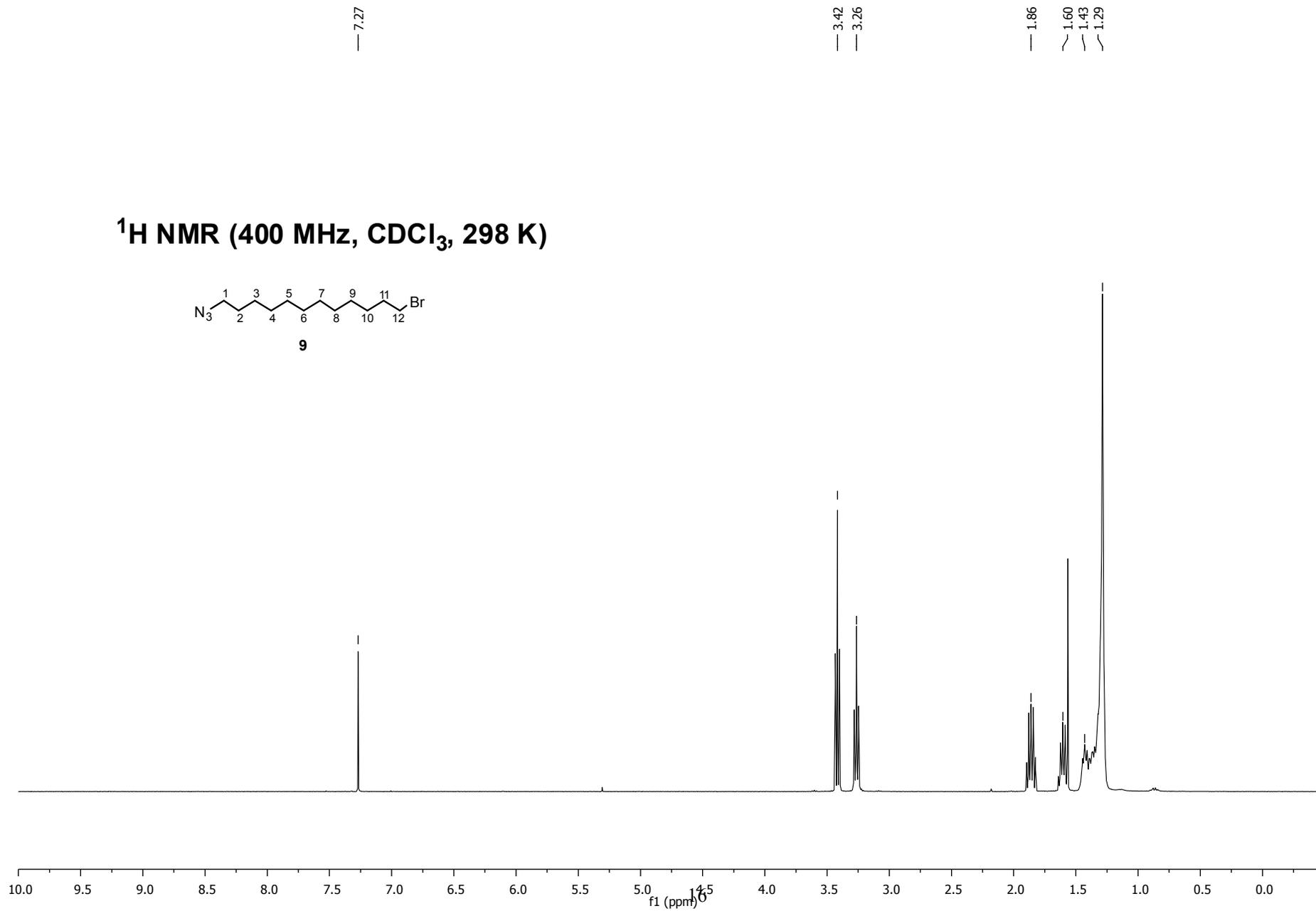
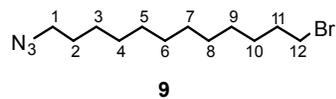
After separation, the aqueous layer was extracted twice with 3 mL of dichloromethane. The organic layers were combined, dried over MgSO₄ and concentrated to obtain the compound **7u** (40 mg, 78 %)

¹H NMR (CD₃CN, 400 MHz, 298K) : δ (ppm) = 7.50 (s, 1H, H₁₅), 7.21-7.02 (m, 14H, H_B H_D H_E H_N H_O H_P H_Q), 4.32-4.20 (m, 18H, H₁₆ H_G H_L H_S H_X), 4.10 & 4.10 (2*s, 4H, H₁ H₂₉), 3.82-3.70 (m, 16H, H_H H_K H_T H_W), 3.61 (s, 16H, H_I H_J H_U H_V), 3.07-2.96 (m, 4H, H₃ H₂₇), 2.61 (t, 2H, ³J_{H13-H12} = 7.5 Hz, H₁₃), 1.87-1.77 (m, 2H, H₁₇), 1.70-1.54 (m, 2H, H₄ H₁₂ H₂₆), 1.40-1.16 (m, 30H, H₅ H₆ H₇ H₈ H₉ H₁₀ H₁₁ H₁₈ H₁₉ H₂₀ H₂₁ H₂₂ H₂₃ H₂₄ H₂₅).

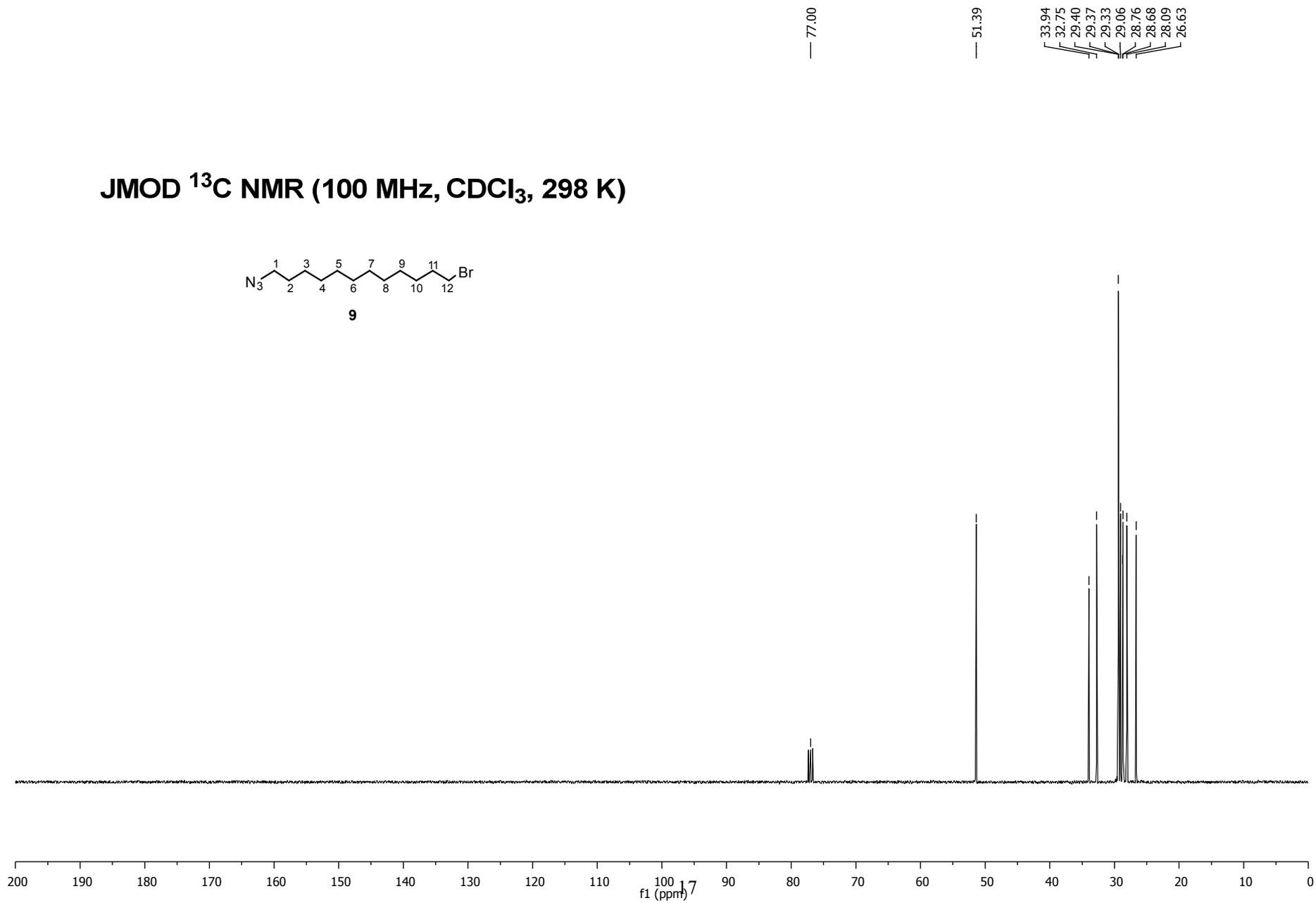
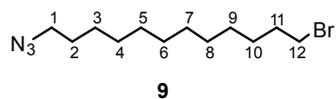
JMOD ¹³C NMR (CD₃CN, 100 MHz, 298K) : δ (ppm) = 150.2 & 149.2 & 149.0 & 148.9 & 148.6 (C₁₄ C_A C_F C_M C_R), 126.0 (C_C), 125.8 & 124.0 & 123.8 & 119.0 & 117.4 & 116.9 & 116.9 (C_B C_D C_E C_N C_O C_P C_Q), 122.2 (C₁₅), 69.8 & 69.7 & 69.1 & 69.0 & 68.9 & 68.8 & 68.6 & 68.3 & 68.2 & 68.1 (CH₂O_{DB24C8}), 51.9 (C₁ C₂₉), 50.6 (C₁₆), 48.7 (C₃ C₂₇), 30.7 & 30.2 & 30.0 & 29.9 & 29.9 & 29.8 & 29.8 & 29.8 & 29.7 & 29.7 & 29.5 & 29.4 & 29.3 & 26.8 & 26.8 & 26.8 & 26.5 & 26.5 (C₄ C₅ C₆ C₇ C₈ C₉ C₁₀ C₁₁ C₁₂ C₁₇ C₁₈ C₁₉ C₂₀ C₂₁ C₂₂ C₂₃ C₂₄ C₂₅ C₂₆), 26.0 (C₁₃).

NMR Spectra

^1H NMR (400 MHz, CDCl_3 , 298 K)



JMOD ^{13}C NMR (100 MHz, CDCl_3 , 298 K)

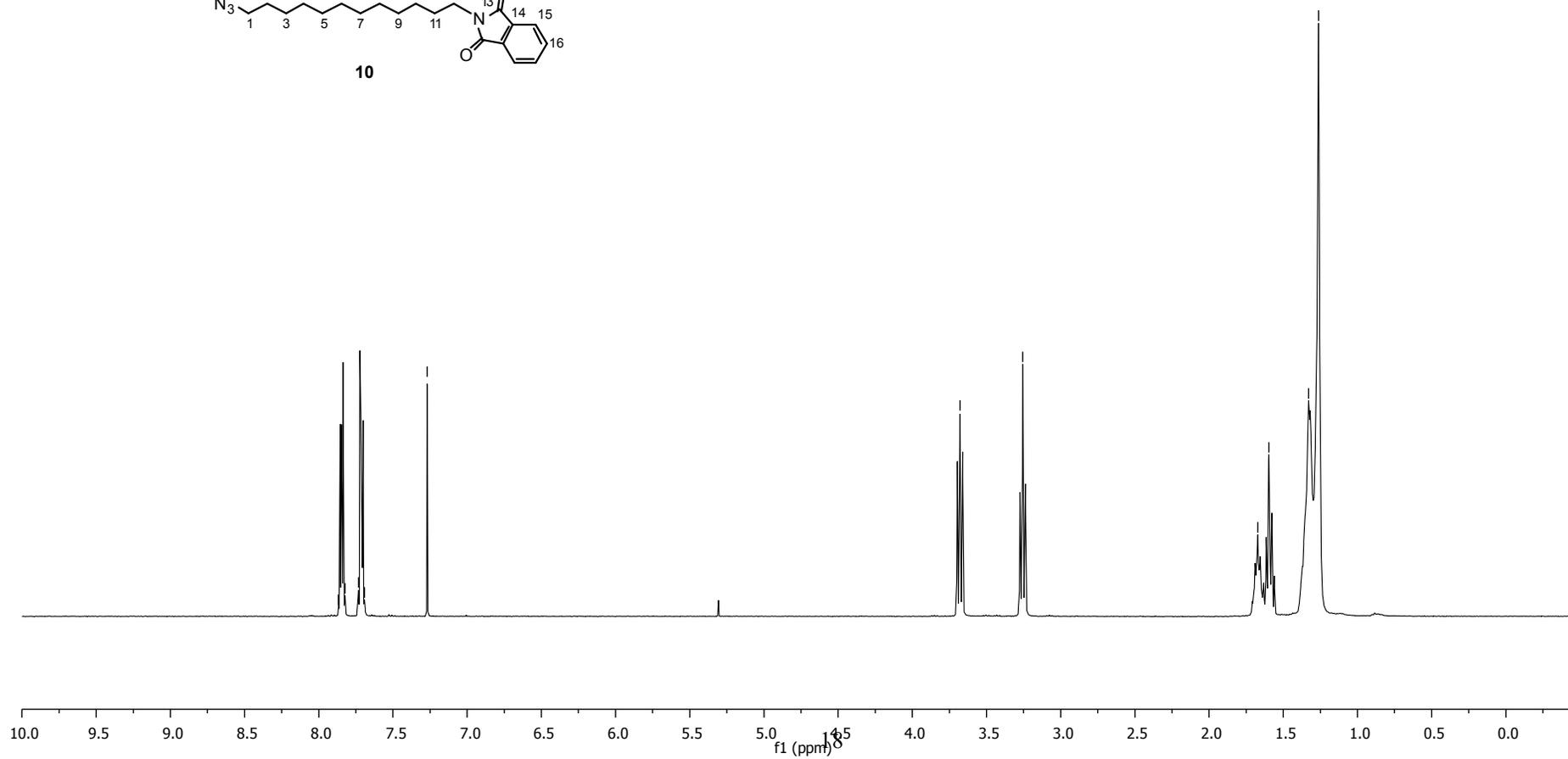
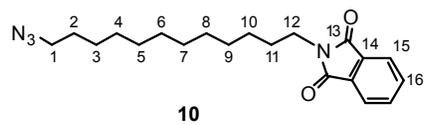


7.87
7.82
7.73
7.69
7.27

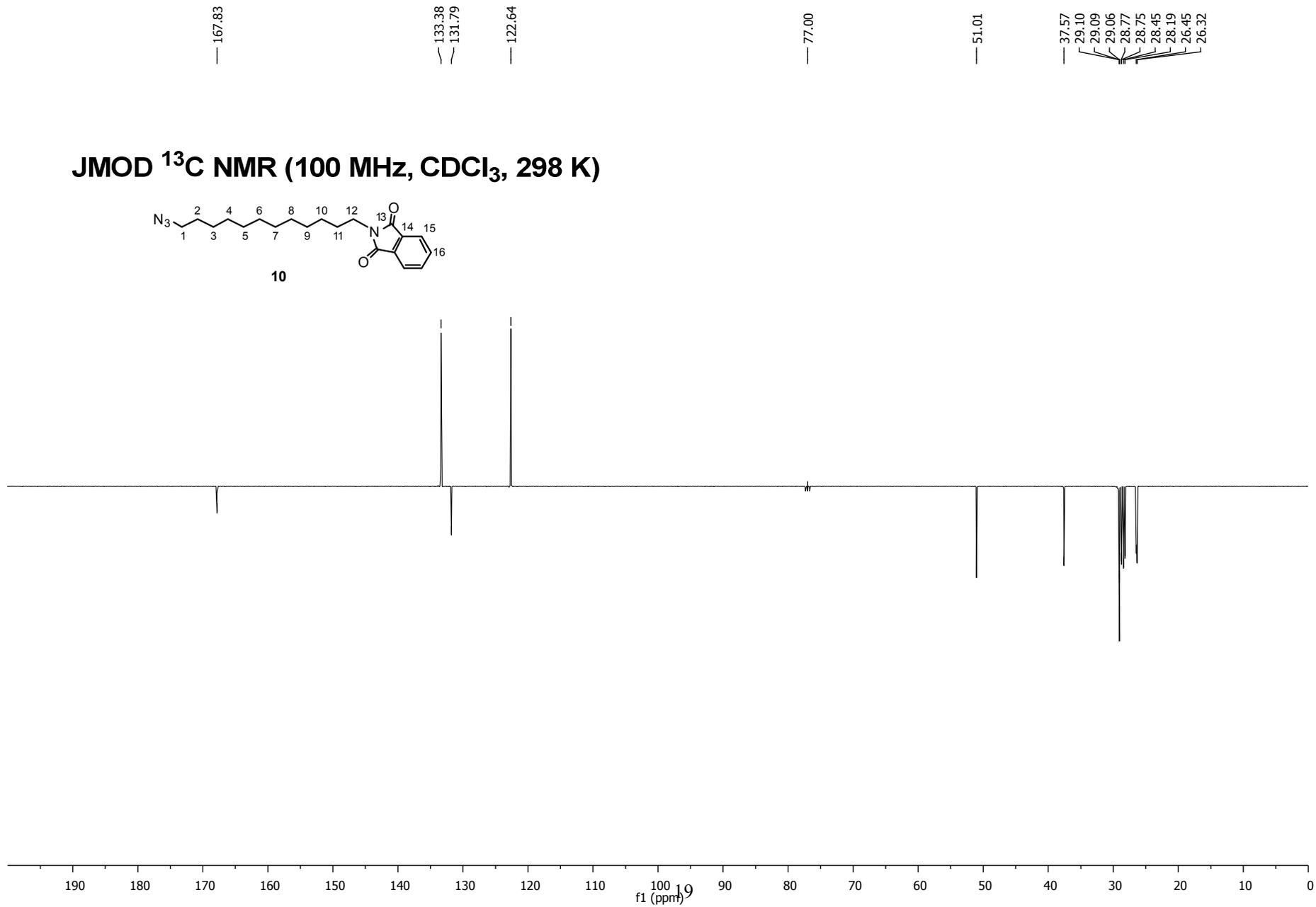
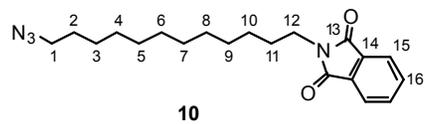
3.68
3.26

1.67
1.60
1.33
1.26

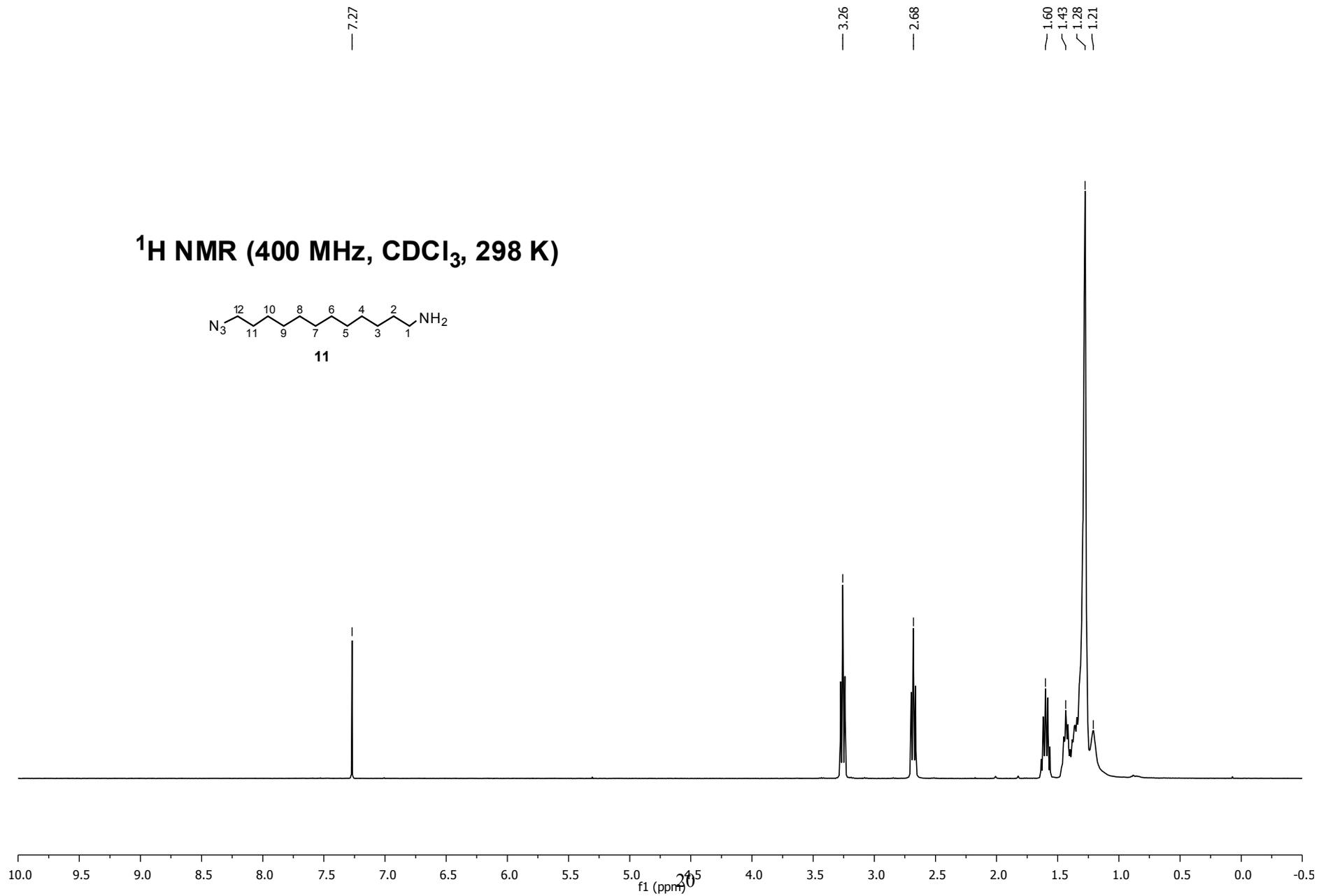
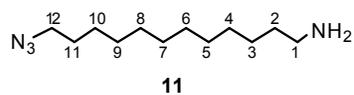
^1H NMR (400 MHz, CDCl_3 , 298 K)



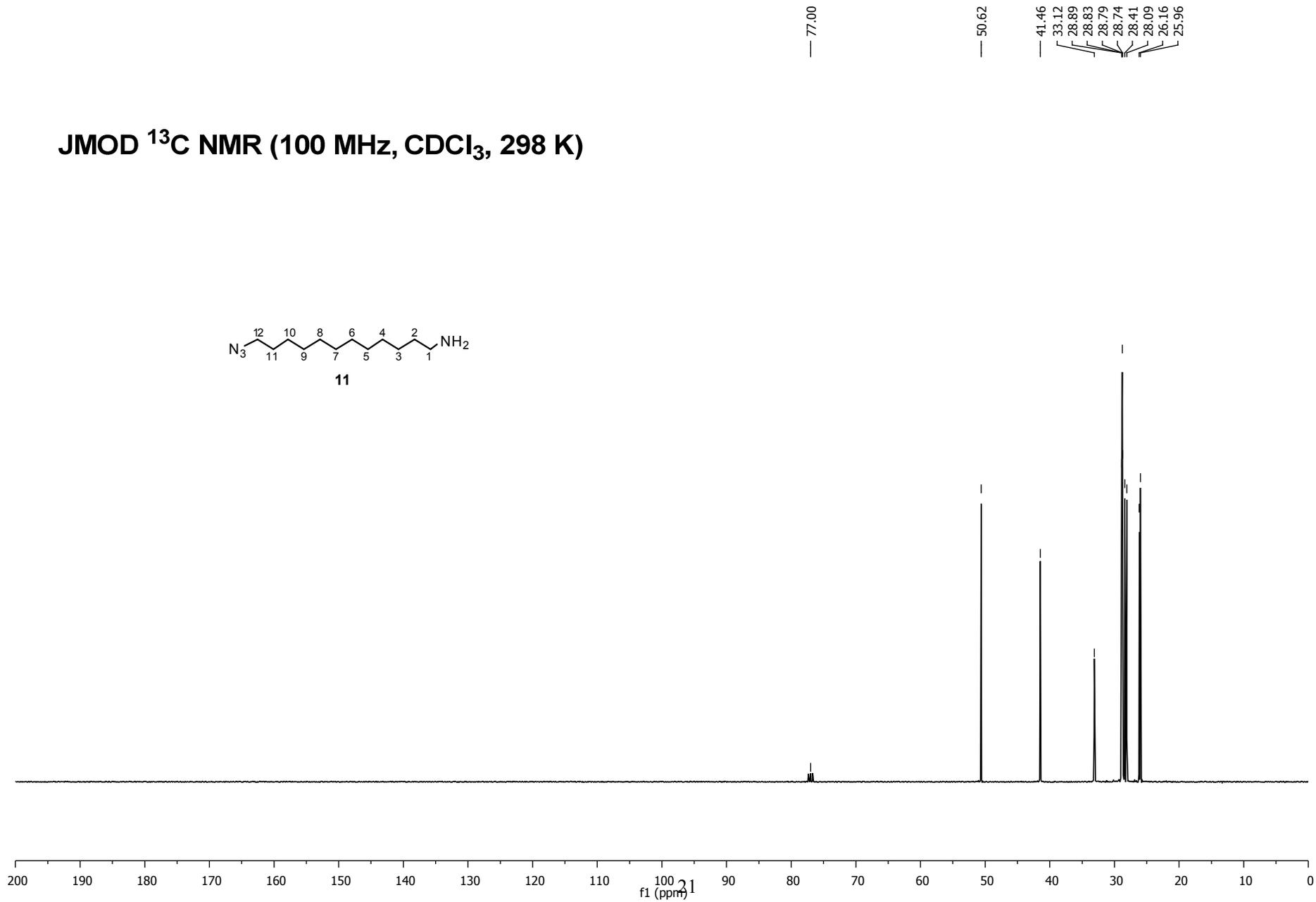
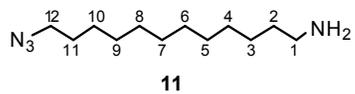
JMOD ¹³C NMR (100 MHz, CDCl₃, 298 K)



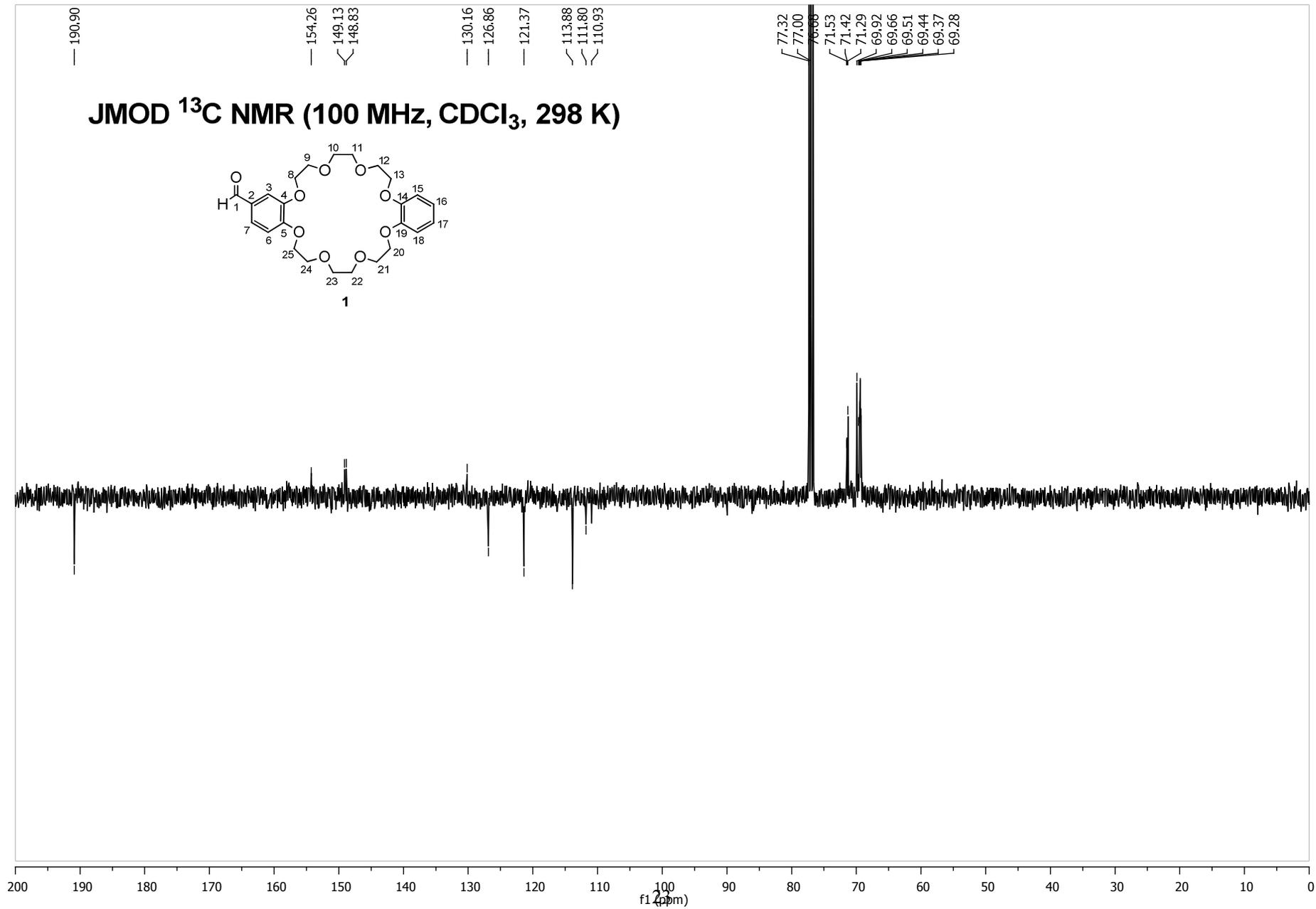
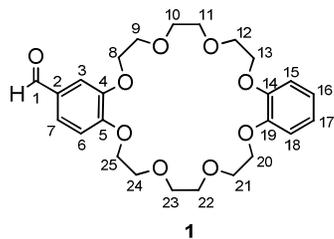
^1H NMR (400 MHz, CDCl_3 , 298 K)



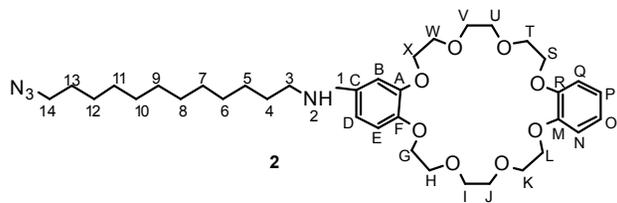
JMOD ^{13}C NMR (100 MHz, CDCl_3 , 298 K)



JMOD ¹³C NMR (100 MHz, CDCl₃, 298 K)



JMOD ^{13}C NMR (100 MHz, CDCl_3 , 298 K)



148.674
148.626
147.561

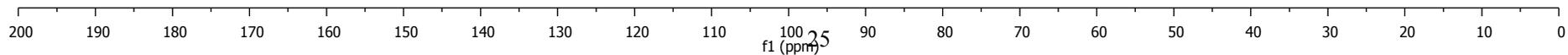
133.326

121.144
120.593
113.839
113.819
113.730
113.650

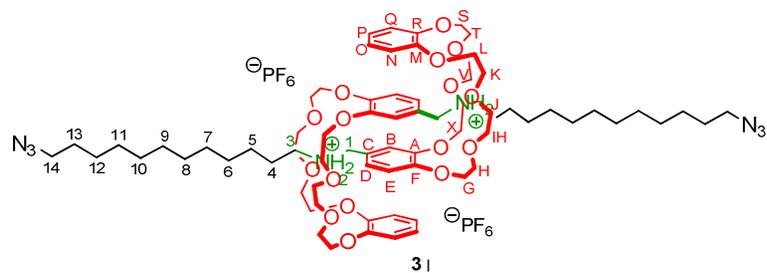
77.000
70.967
69.630
69.117

53.401
51.174
49.088

29.708
29.287
29.237
29.186
28.864
28.552
27.104
26.428



¹H NMR (400 MHz, CDCl₃, 298 K)

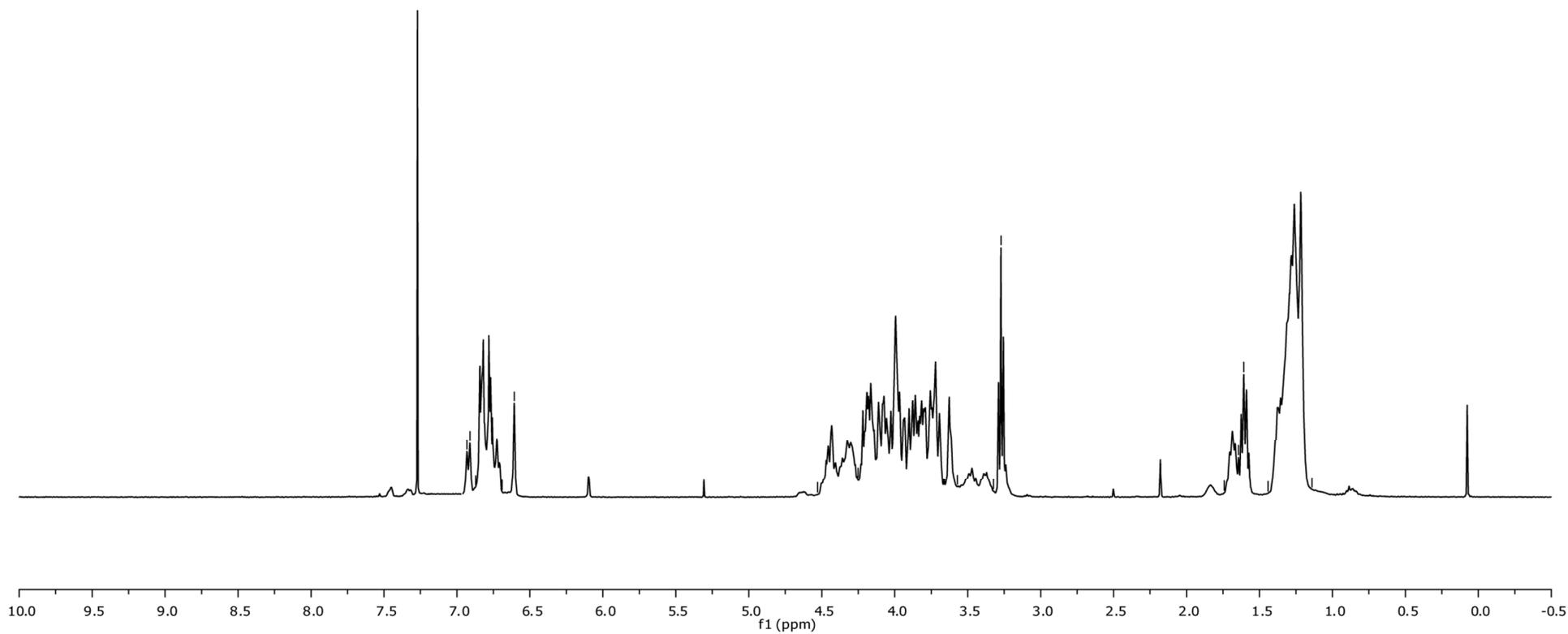


— 7.270
— 6.911
— 6.872
— 6.691
— 6.607

— 4.528
— 4.251

— 3.570
— 3.323
— 3.272

— 1.742
— 1.644
— 1.608
— 1.442
— 1.140



147.484
147.405
146.139
145.961

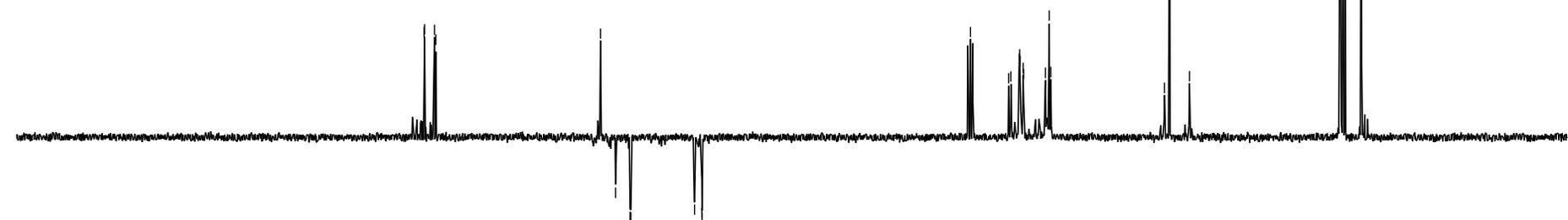
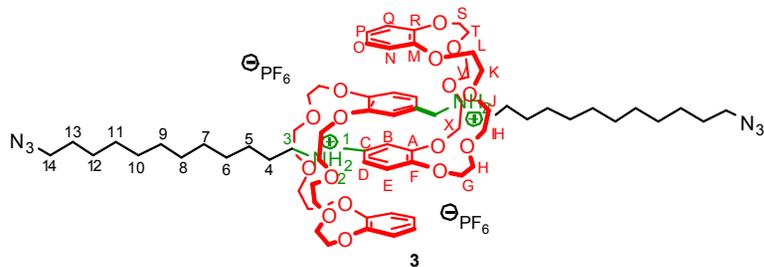
124.696
122.757
120.893
120.791
112.568
111.639
111.594

77.000
70.656
70.142
67.323
66.848
66.613

51.955
51.322
48.756

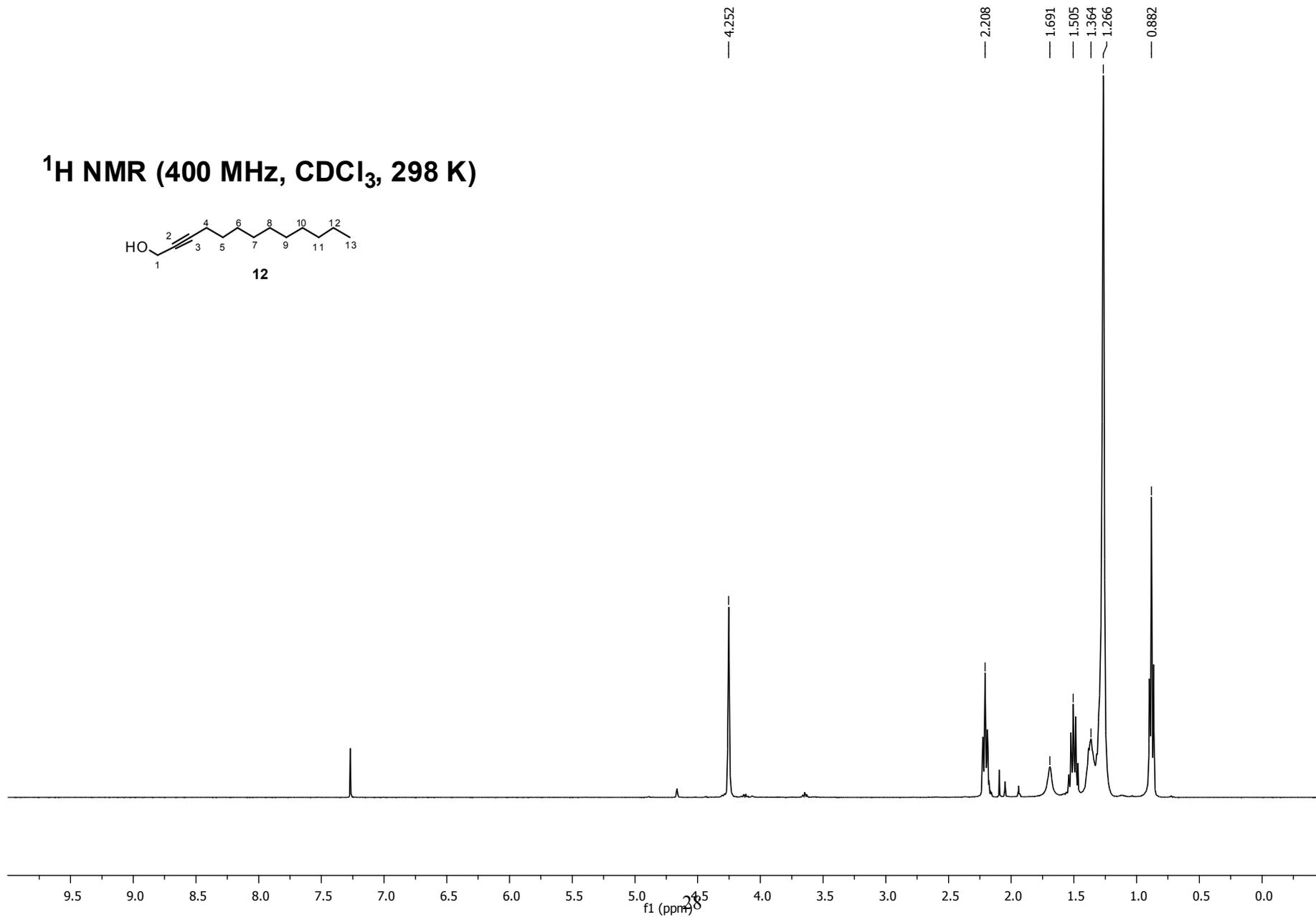
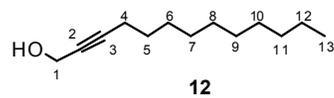
29.352
29.312
29.282
29.253
28.985
28.898
28.672
26.554

JMOD ^{13}C NMR (100 MHz, CDCl_3 , 298 K)

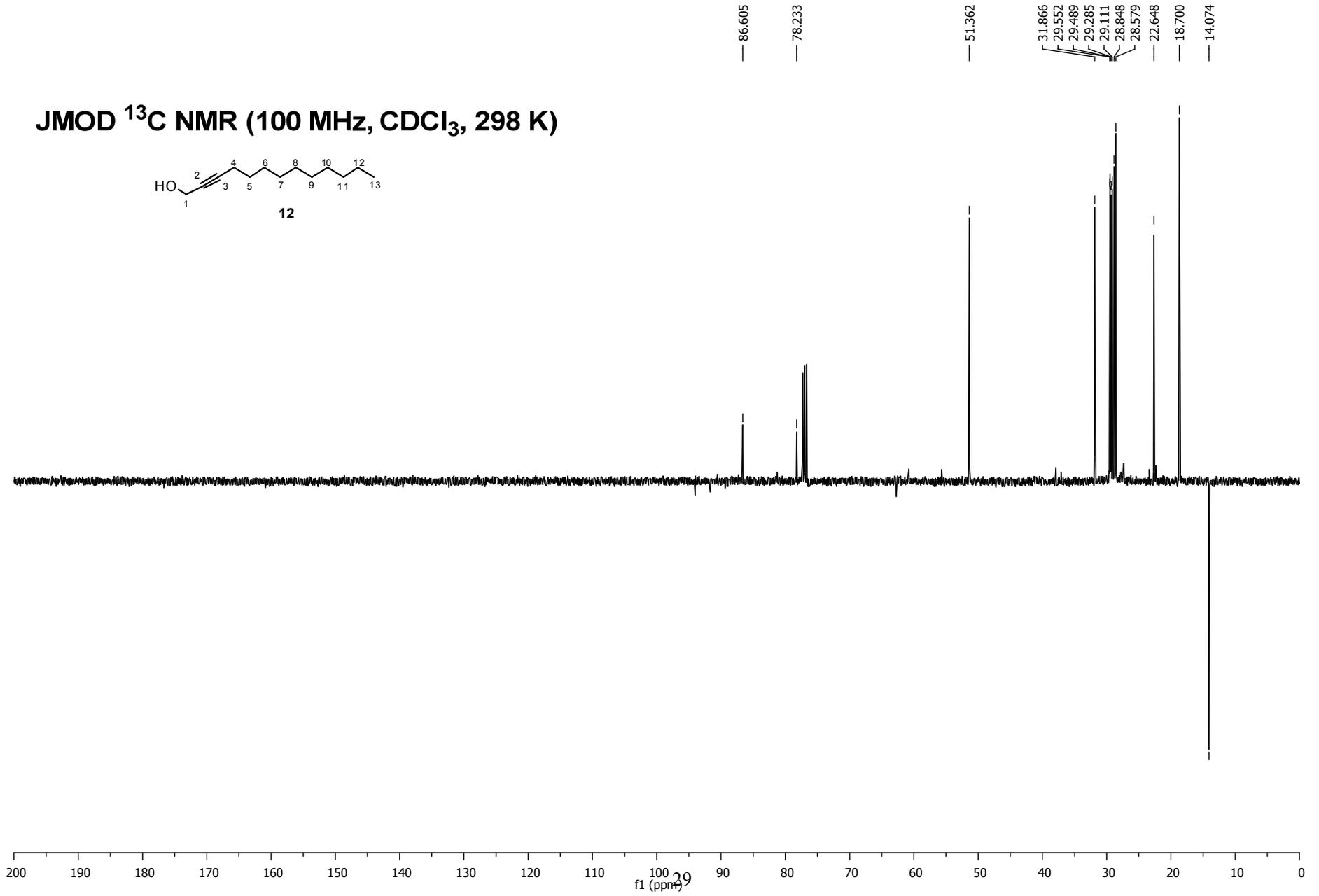
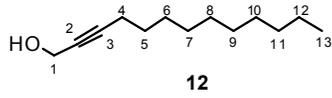


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

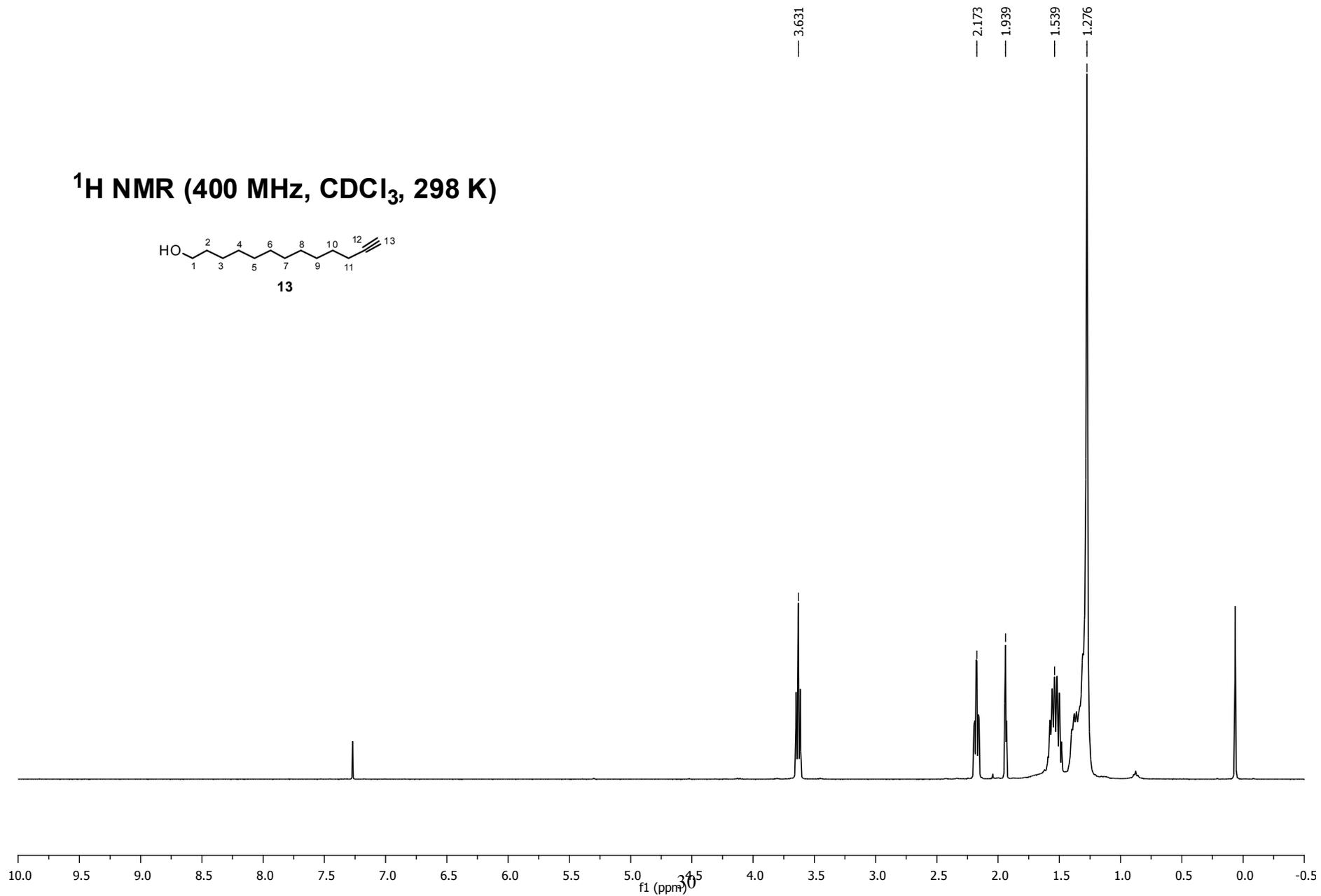
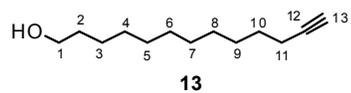
^1H NMR (400 MHz, CDCl_3 , 298 K)



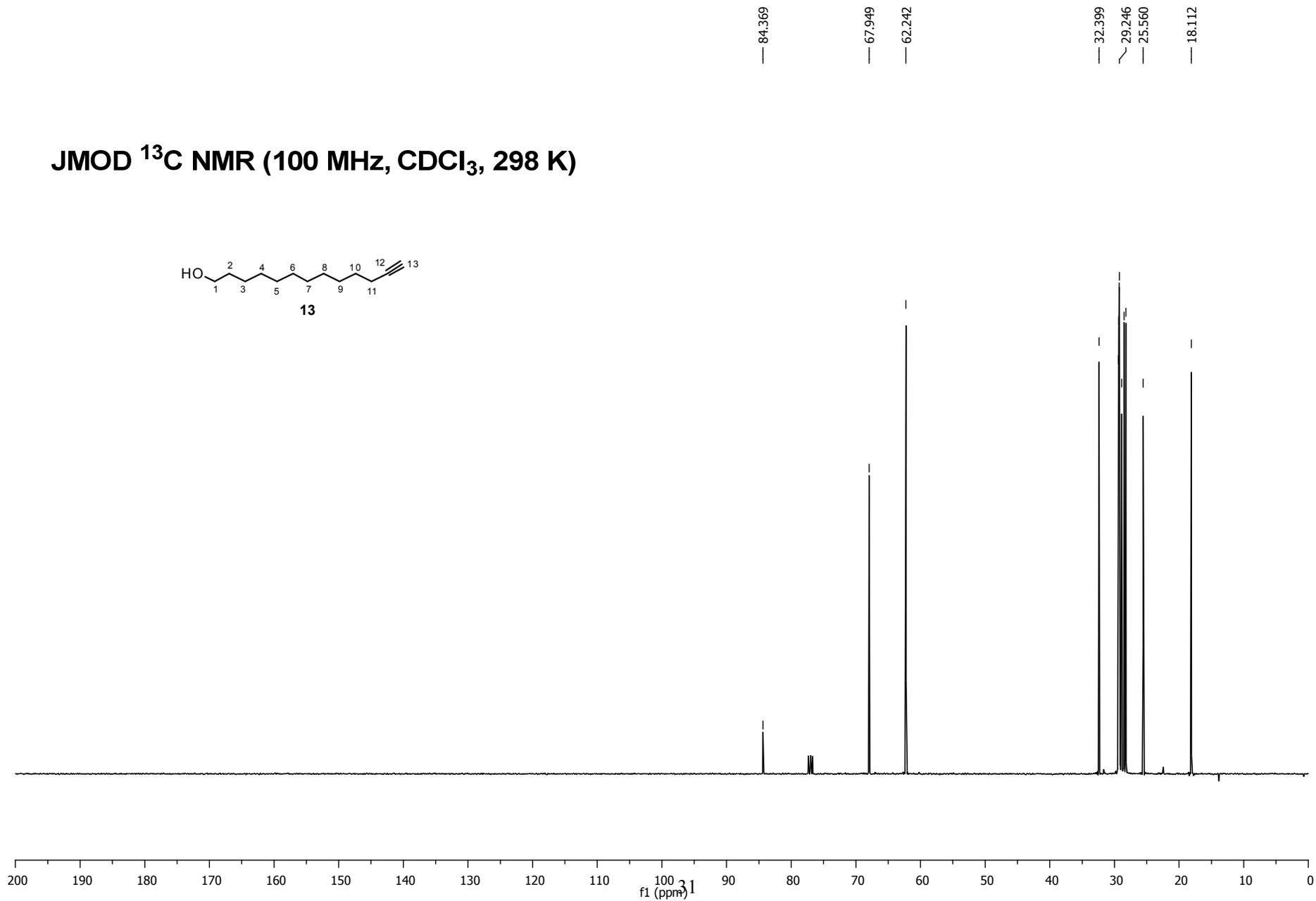
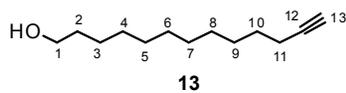
JMOD ^{13}C NMR (100 MHz, CDCl_3 , 298 K)



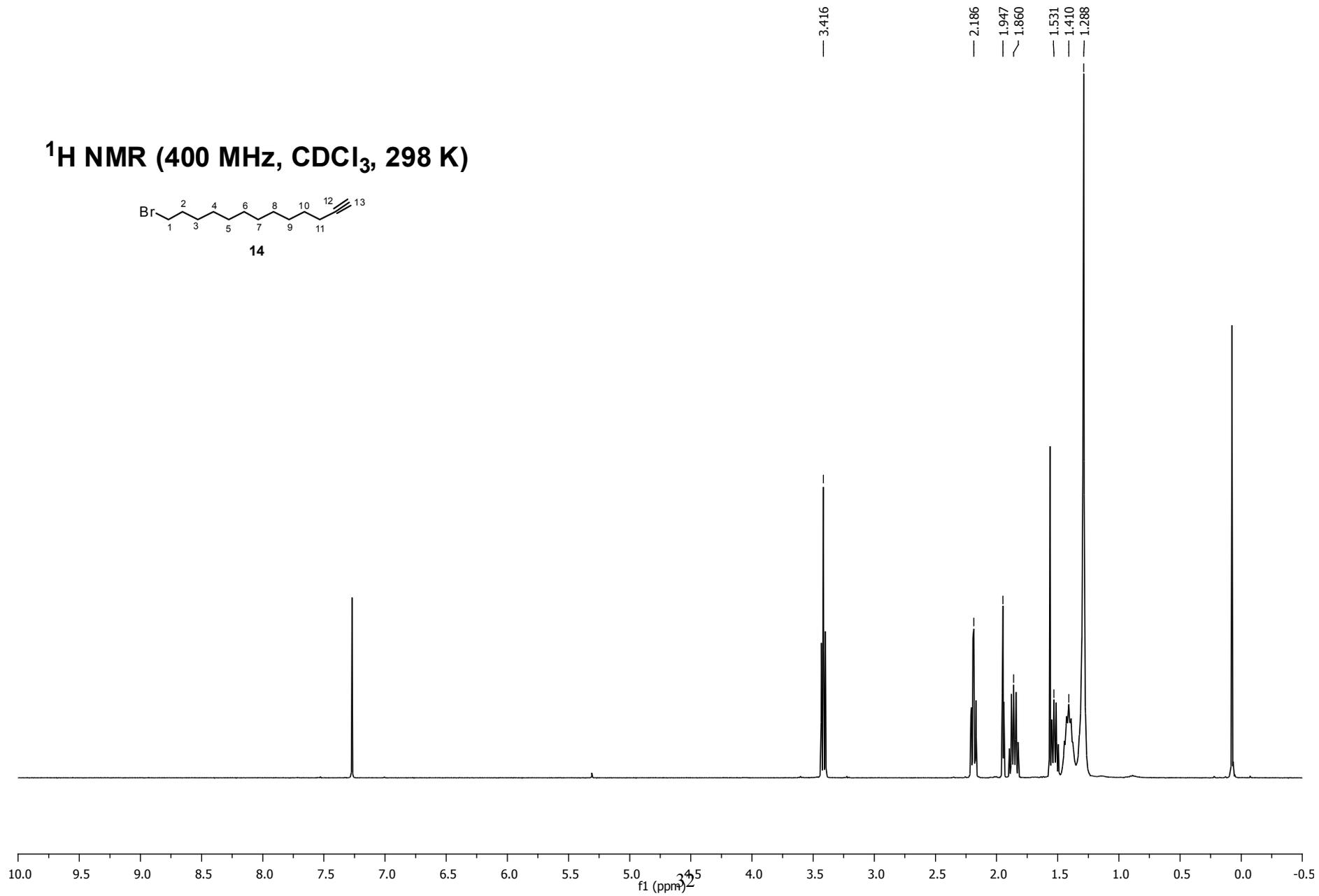
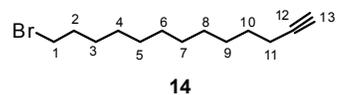
^1H NMR (400 MHz, CDCl_3 , 298 K)



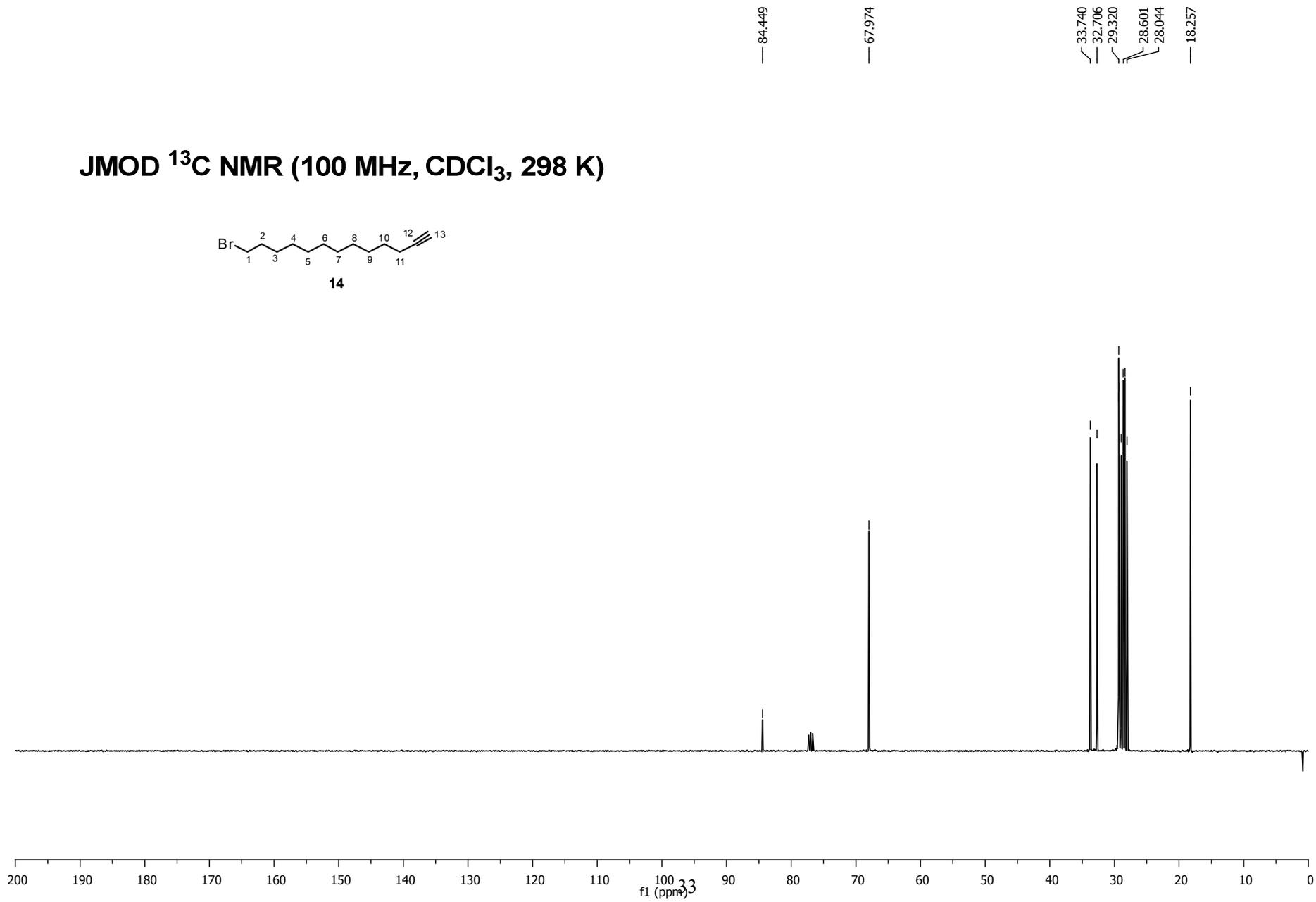
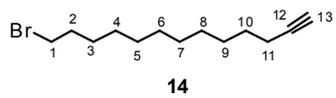
JMOD ^{13}C NMR (100 MHz, CDCl_3 , 298 K)



^1H NMR (400 MHz, CDCl_3 , 298 K)



JMOD ^{13}C NMR (100 MHz, CDCl_3 , 298 K)

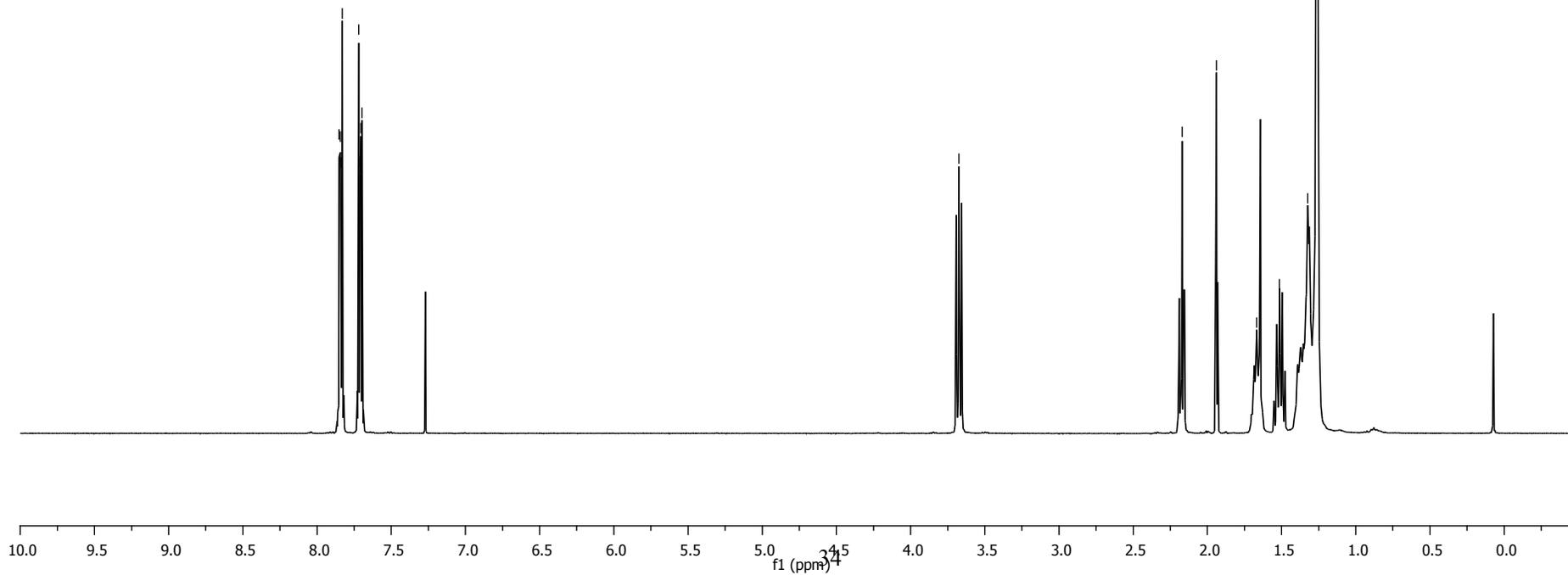


7.851
7.844
7.838
7.830
7.718
7.711
7.705
7.697

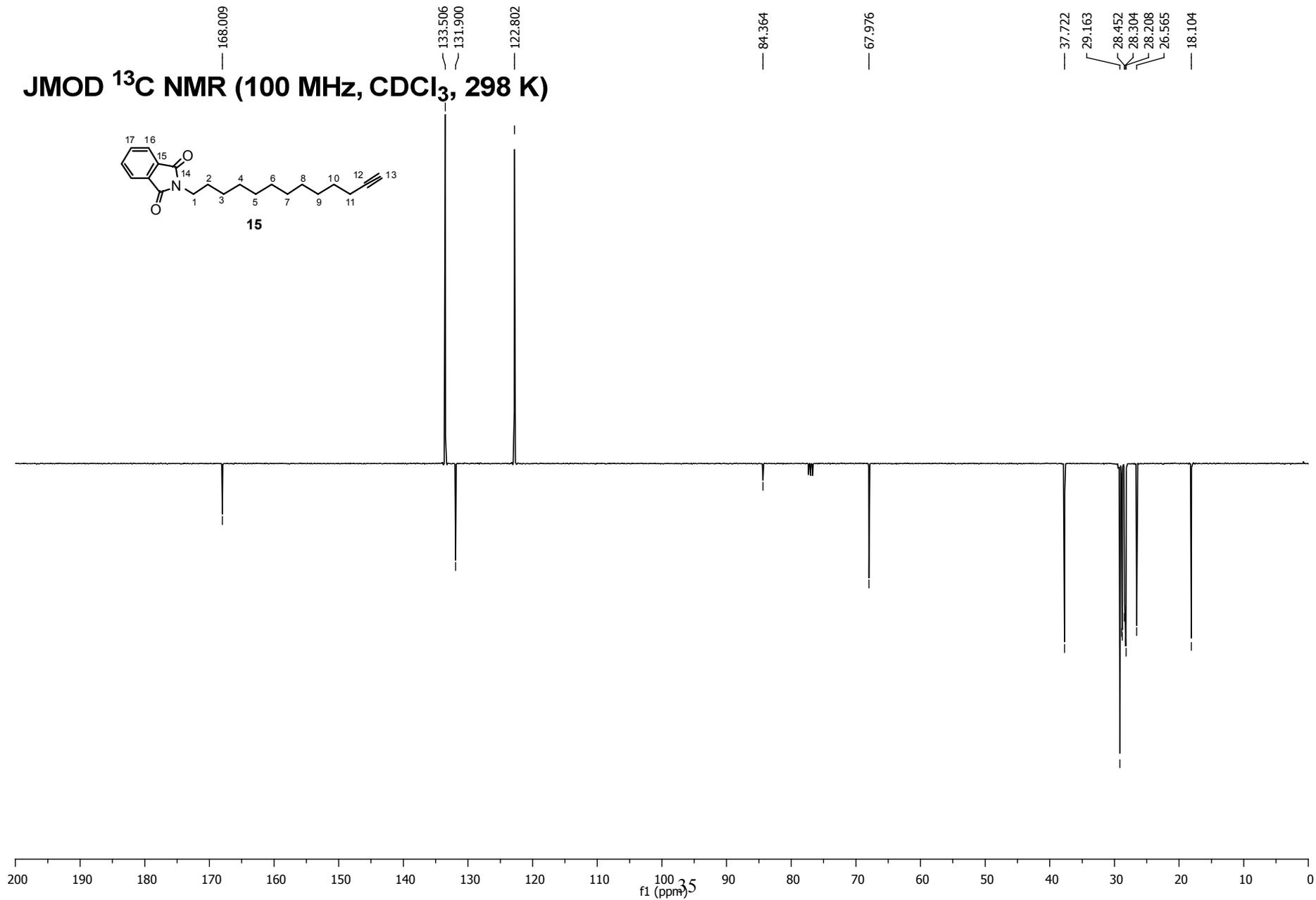
3.674

2.170
1.938
1.667
1.515
1.323
1.262

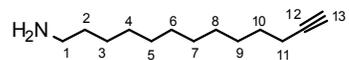
¹H NMR (400 MHz, CDCl₃, 298 K)



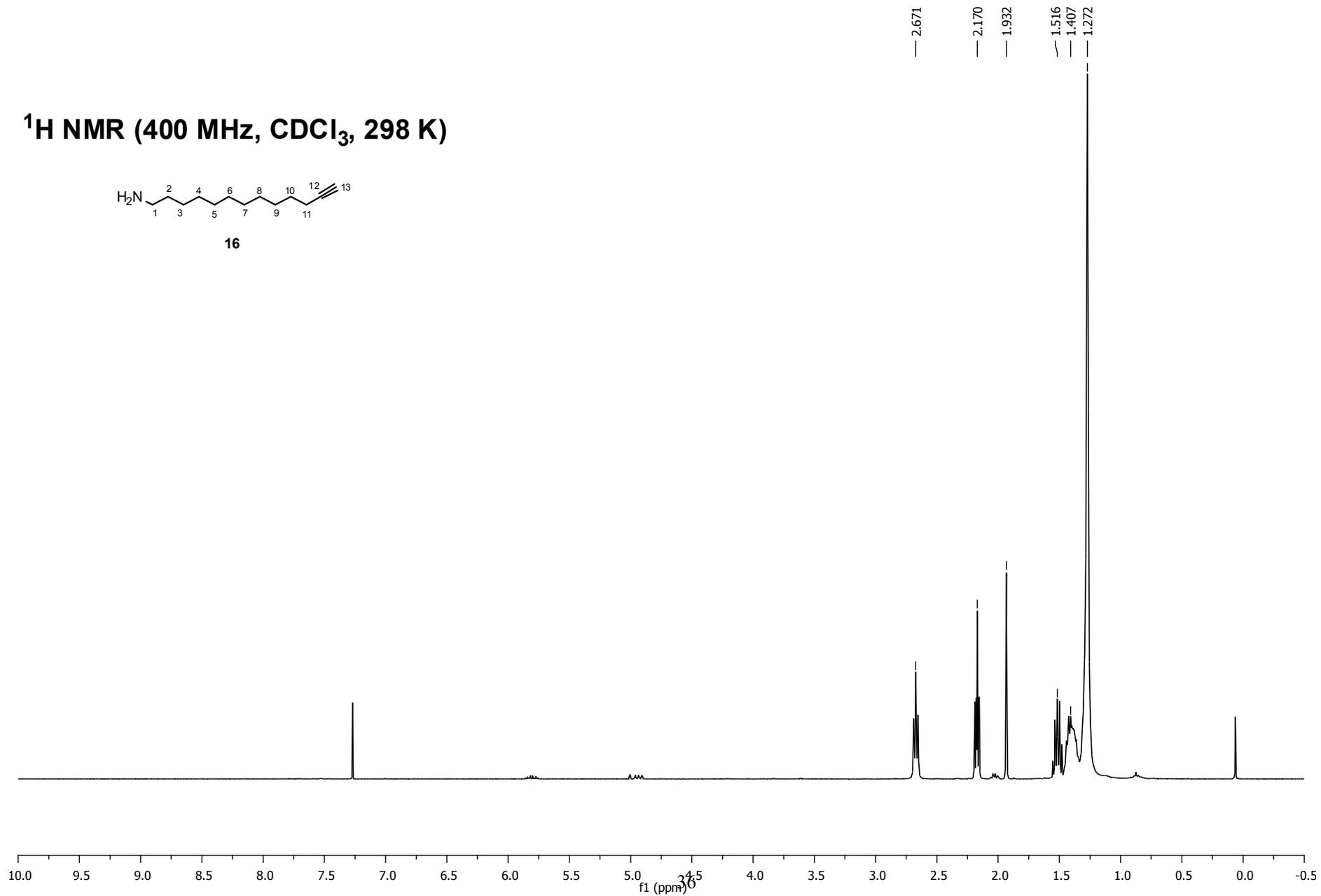
JMOD ¹³C NMR (100 MHz, CDCl₃, 298 K)



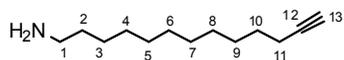
^1H NMR (400 MHz, CDCl_3 , 298 K)



16

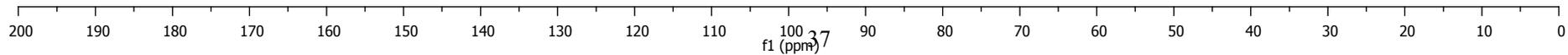


JMOD ¹³C NMR (100 MHz, CDCl₃, 298 K)

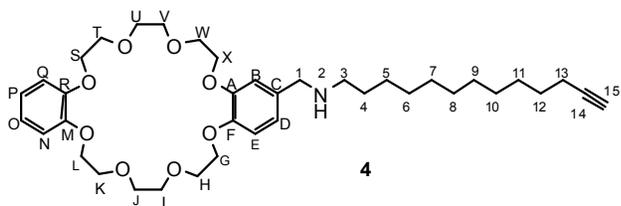


16

139.027
113.927
84.550
67.909
42.043
33.625
29.331
28.585
26.733
18.222



JMOD ^{13}C NMR (100 MHz, CDCl_3 , 298 K)



148.264
148.215
147.160

132.769

120.711
120.186

113.447
113.376
113.261

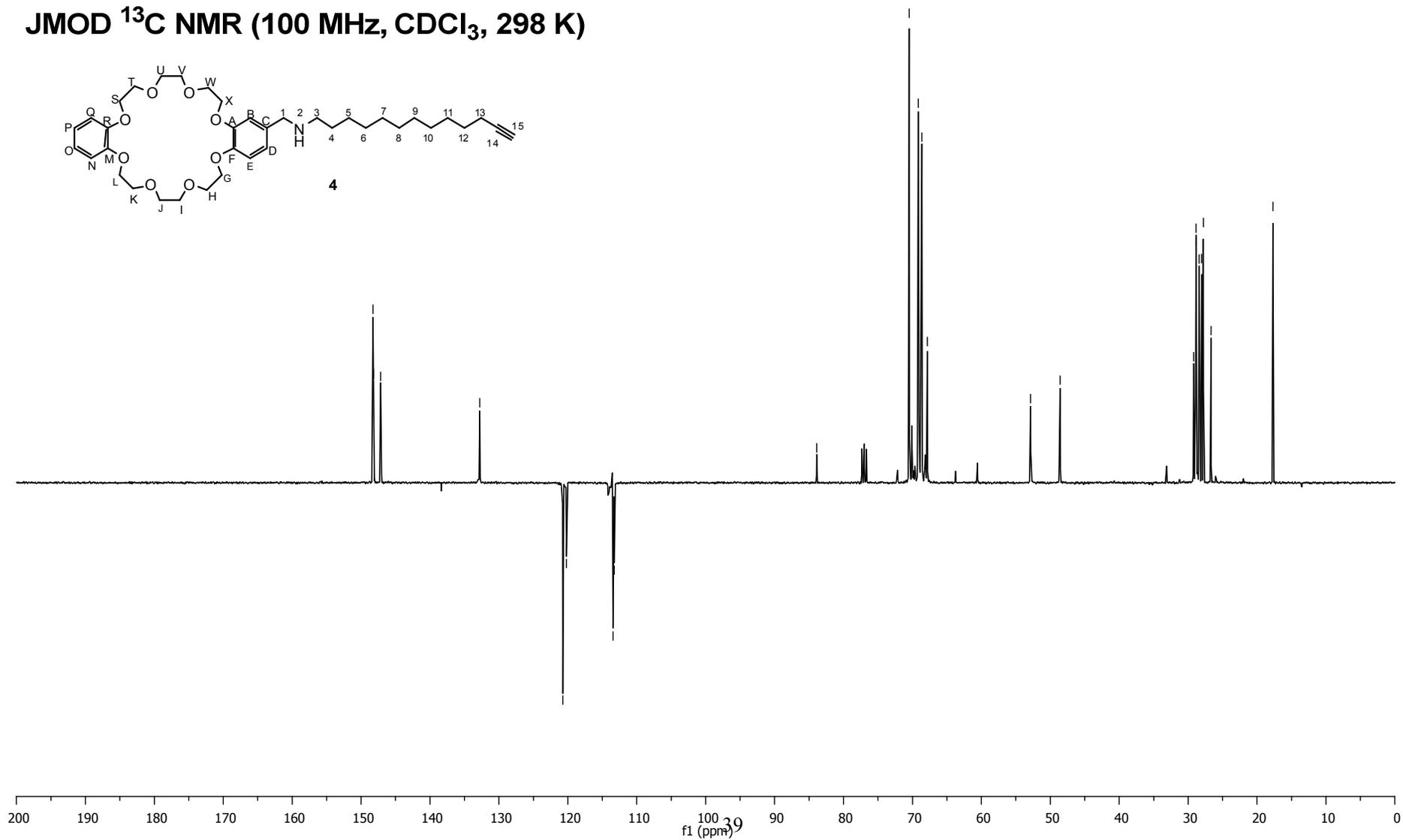
83.881

70.474
69.162
68.636
67.846

52.877
48.579

28.862
28.850
28.799
28.405
28.036
27.790
26.681

17.679



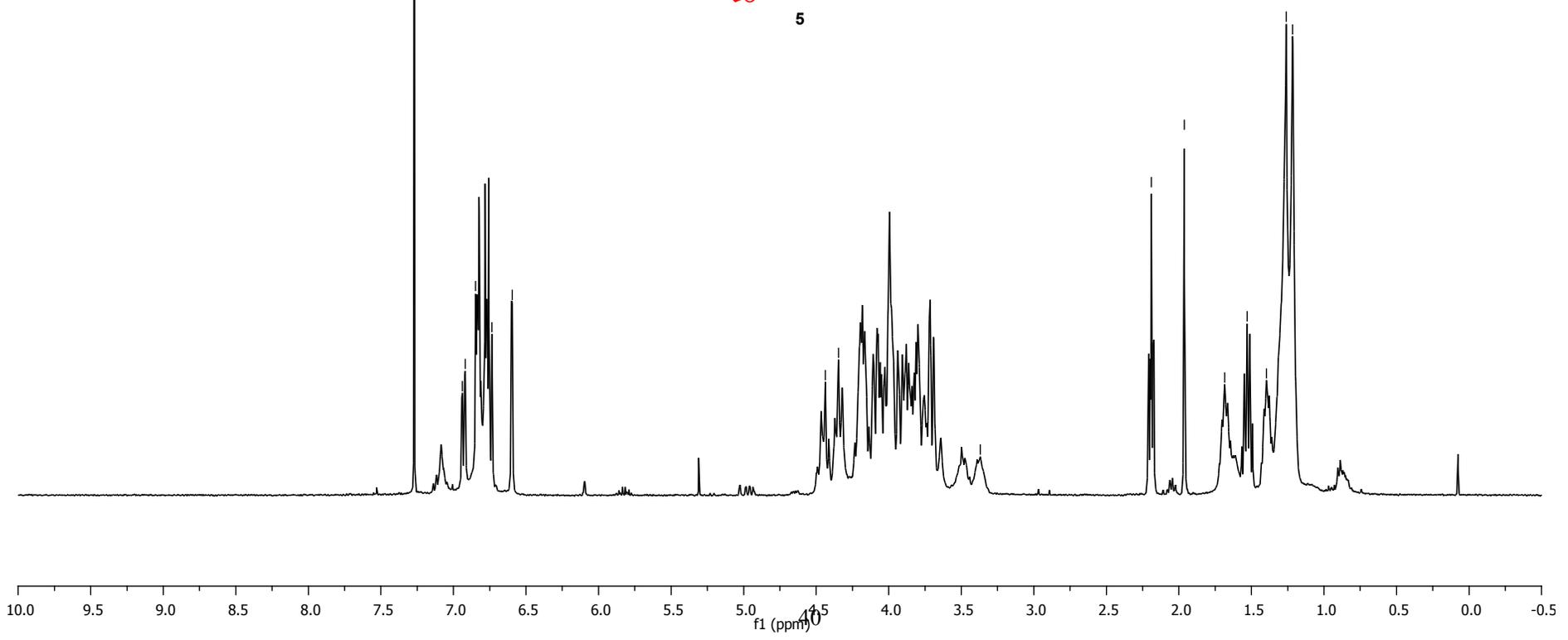
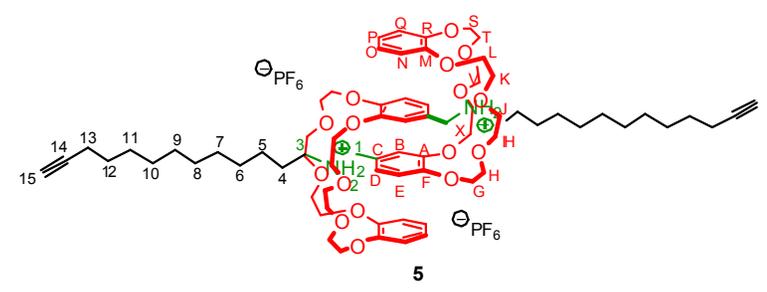
6.939
6.918
6.848
6.735
6.595

4.437
4.347

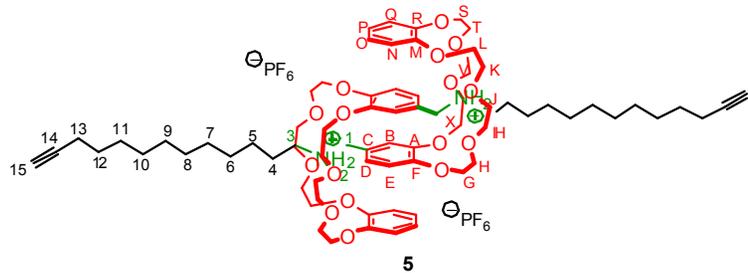
3.369

2.190
1.963
1.684
1.530
1.396
1.261
1.216

¹H NMR (400 MHz, CDCl₃, 298 K)



JMOD ¹³C NMR (100 MHz, CDCl₃, 298 K)



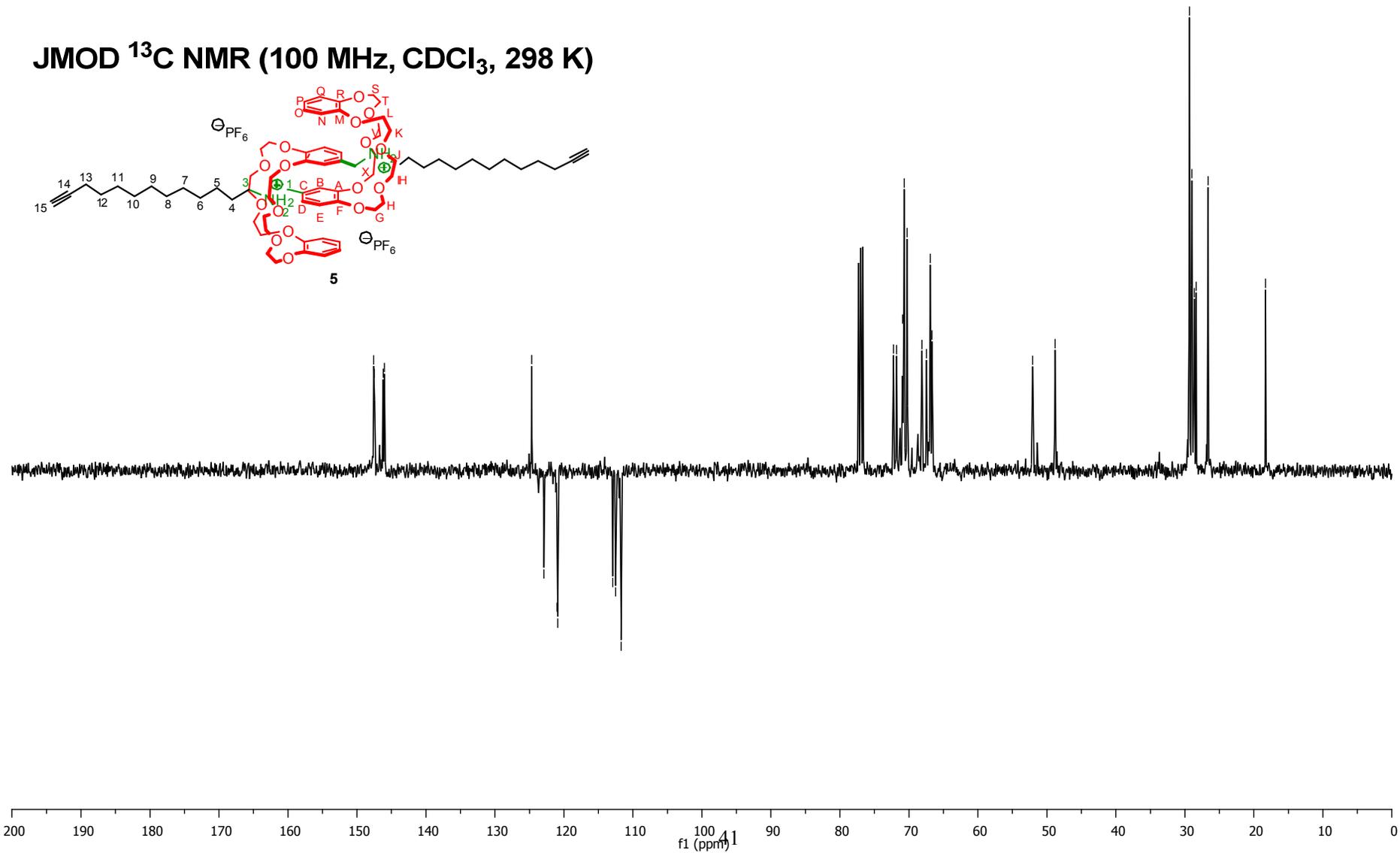
147.565
147.489
146.210
146.019

124.669
122.894
120.993
120.894
112.927
112.496
111.696

72.229
71.791
70.910
70.763
70.670
70.255
68.118
67.447
66.917
66.662

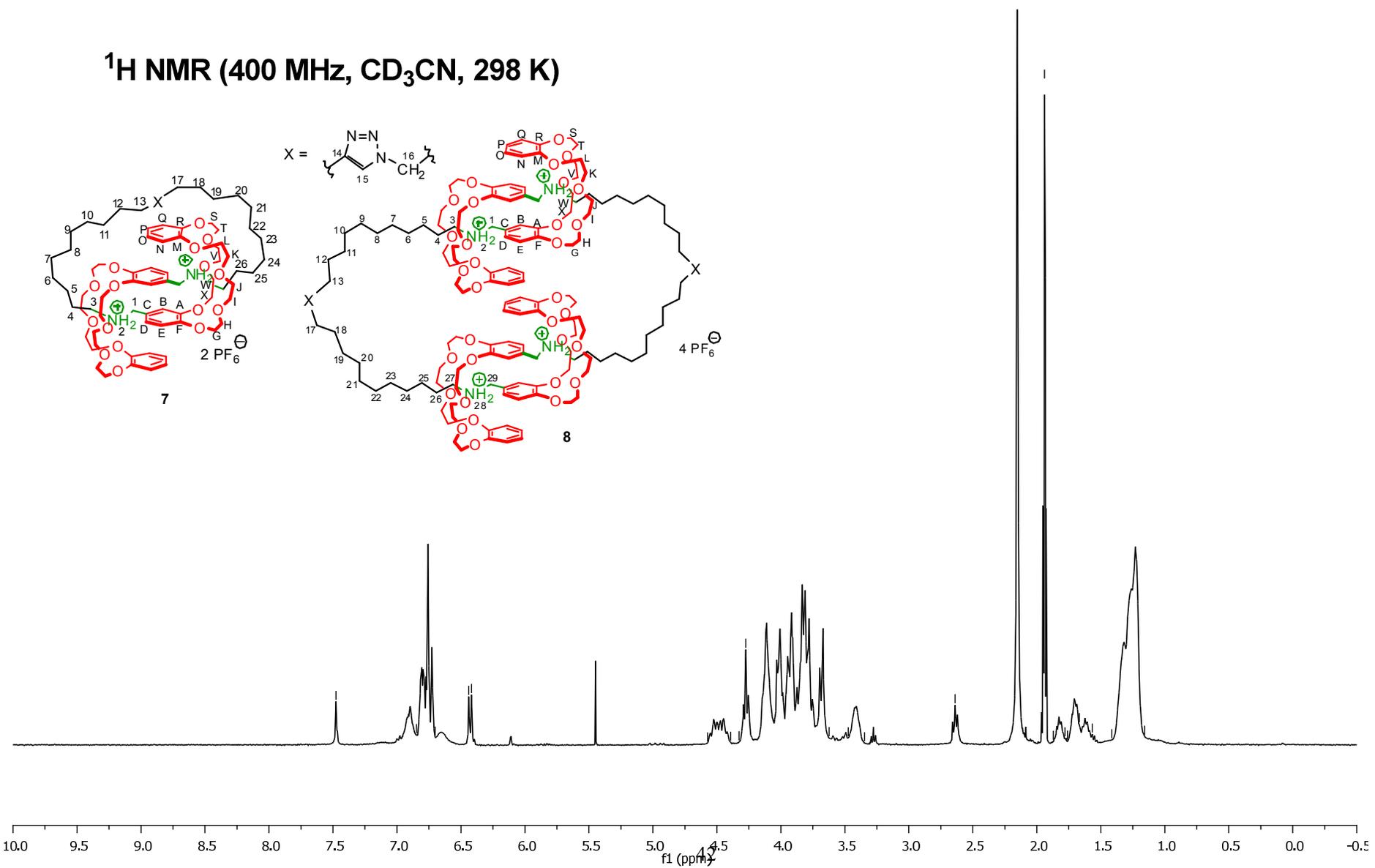
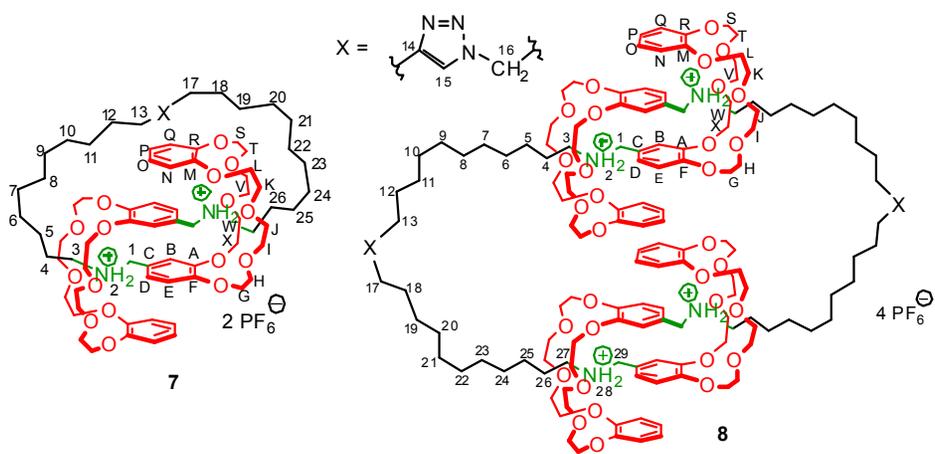
52.073
48.817

29.340
28.985
28.635
28.378
26.646
18.304



^1H NMR (400 MHz, CD_3CN , 298 K)

- 7.477
- 6.846
- 6.701
- 6.439
- 6.418
- 4.574
- 4.393
- 4.328
- 4.274
- 3.623
- 3.473
- 3.346
- 2.639
- 1.940
- 1.871
- 1.781
- 1.760
- 1.668
- 1.567
- 1.414
- 1.158



JMOD ^{13}C NMR (100 MHz, CD_3CN , 298 K)

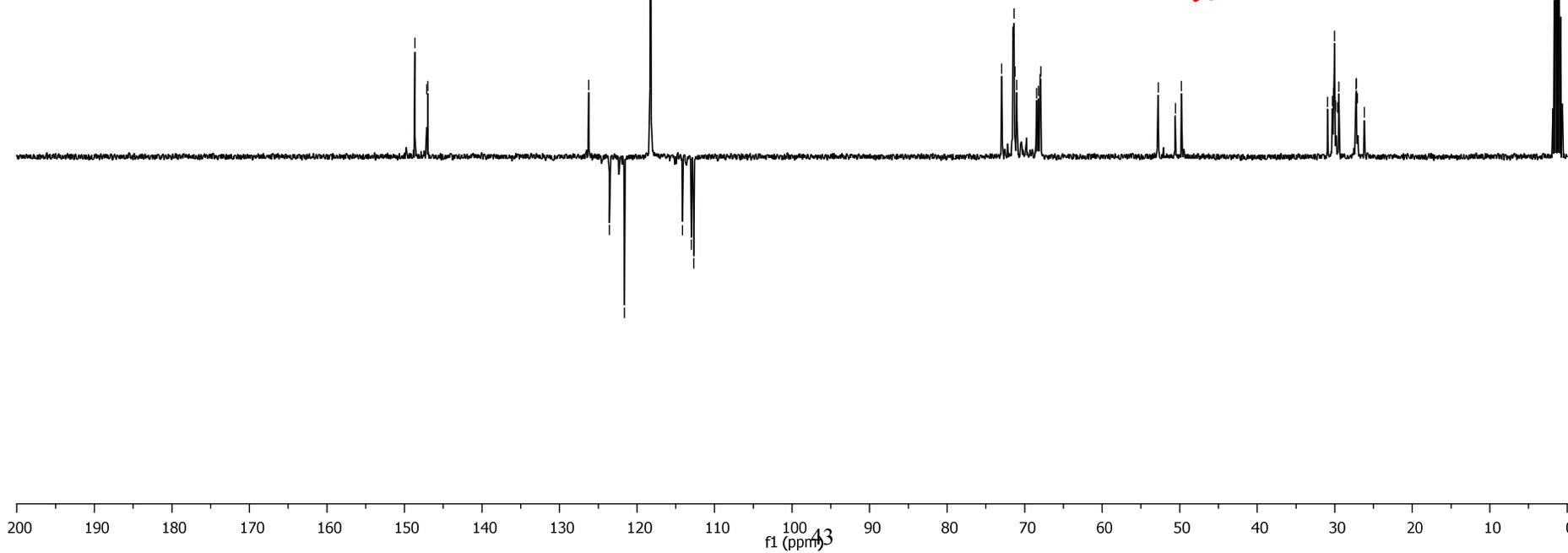
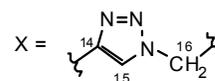
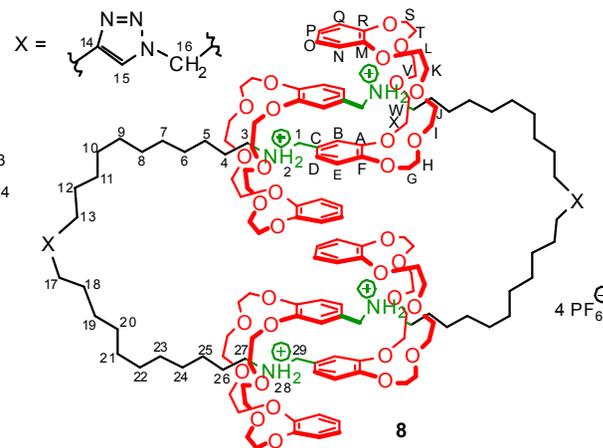
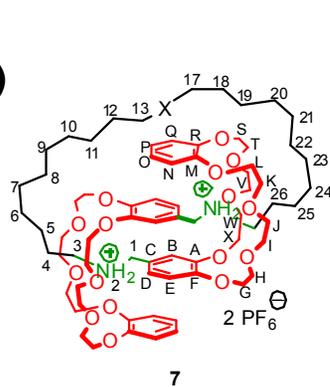
148.668
147.136
146.979

126.248
121.608
118.260
114.140
112.985
112.683

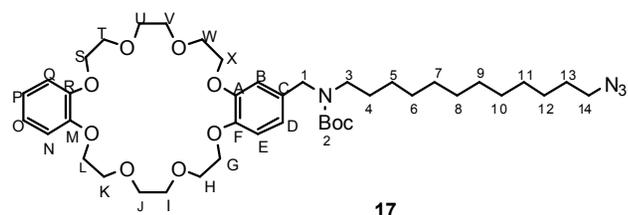
72.975
71.502
71.368
71.231
71.022
68.469
68.211
68.024
67.922

52.778
50.559
49.778

30.935
30.309
30.217
30.150
30.035
29.876
29.633
29.474
27.265
27.208
27.085
26.190



¹H NMR (400 MHz, CDCl₃, 298 K)



7.270

6.895

6.748

4.330

4.095

3.965

3.872

3.833

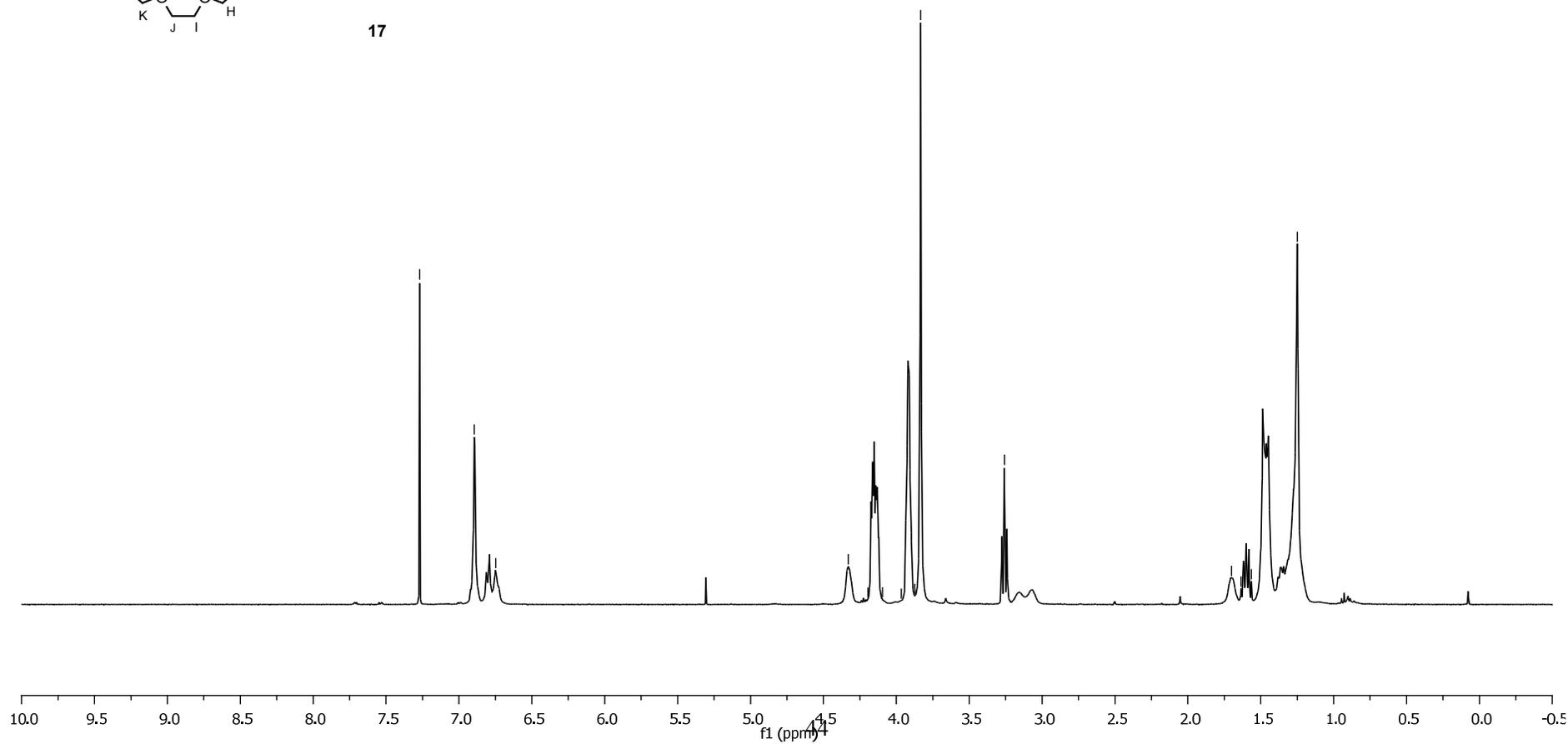
3.259

1.700

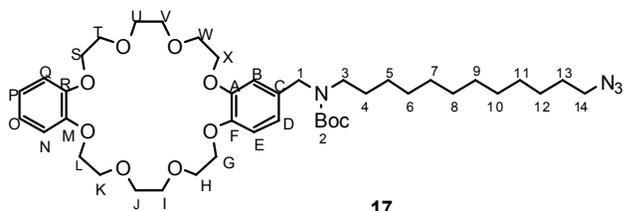
1.635

1.563

1.250



JMOD ¹³C NMR (100 MHz, CDCl₃, 298 K)



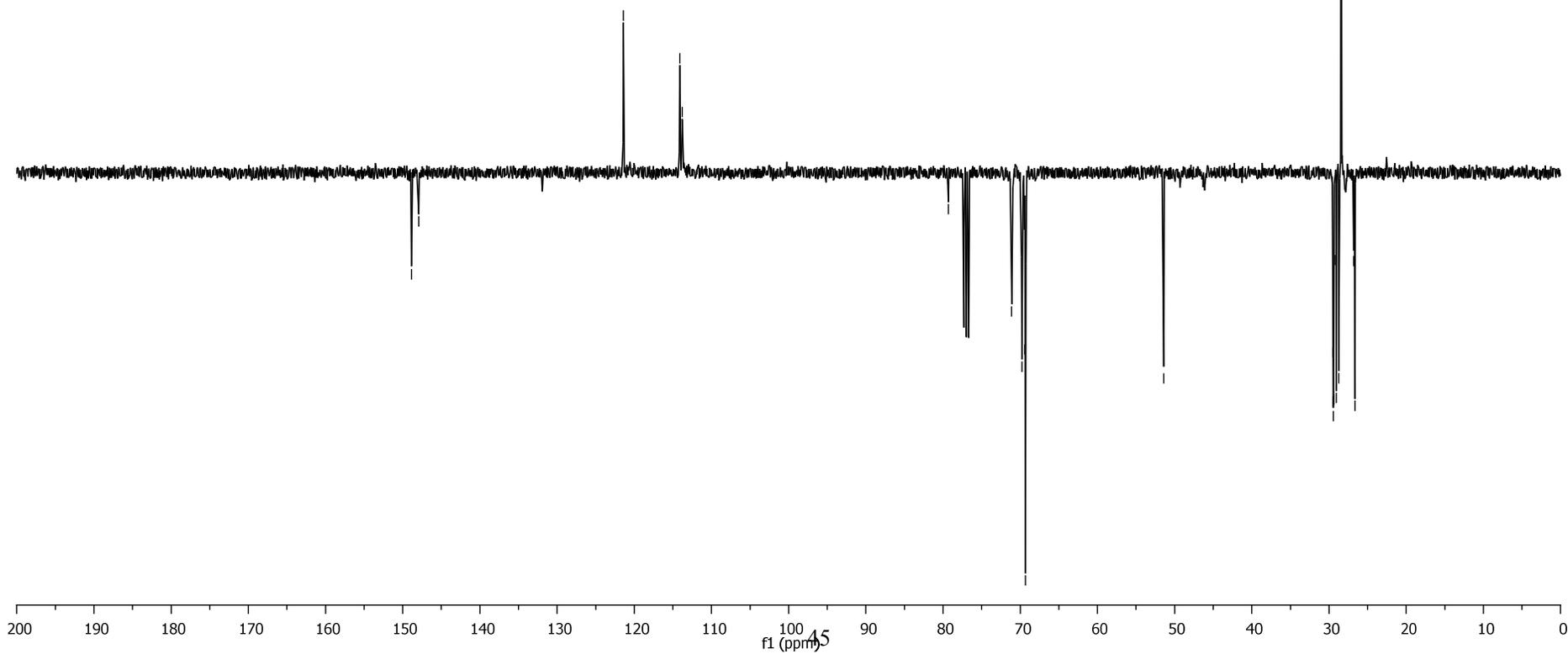
148.857
147.915

121.409
114.085
113.779

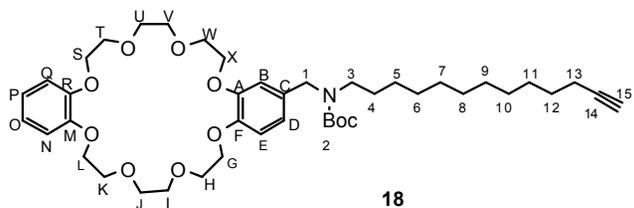
79.316
77.000
71.112
69.792
69.434
69.314

51.410

29.513
29.443
29.431
29.387
29.270
29.066
28.760
28.416
26.800
26.637



JMOD ^{13}C NMR (100 MHz, CDCl_3 , 298 K)



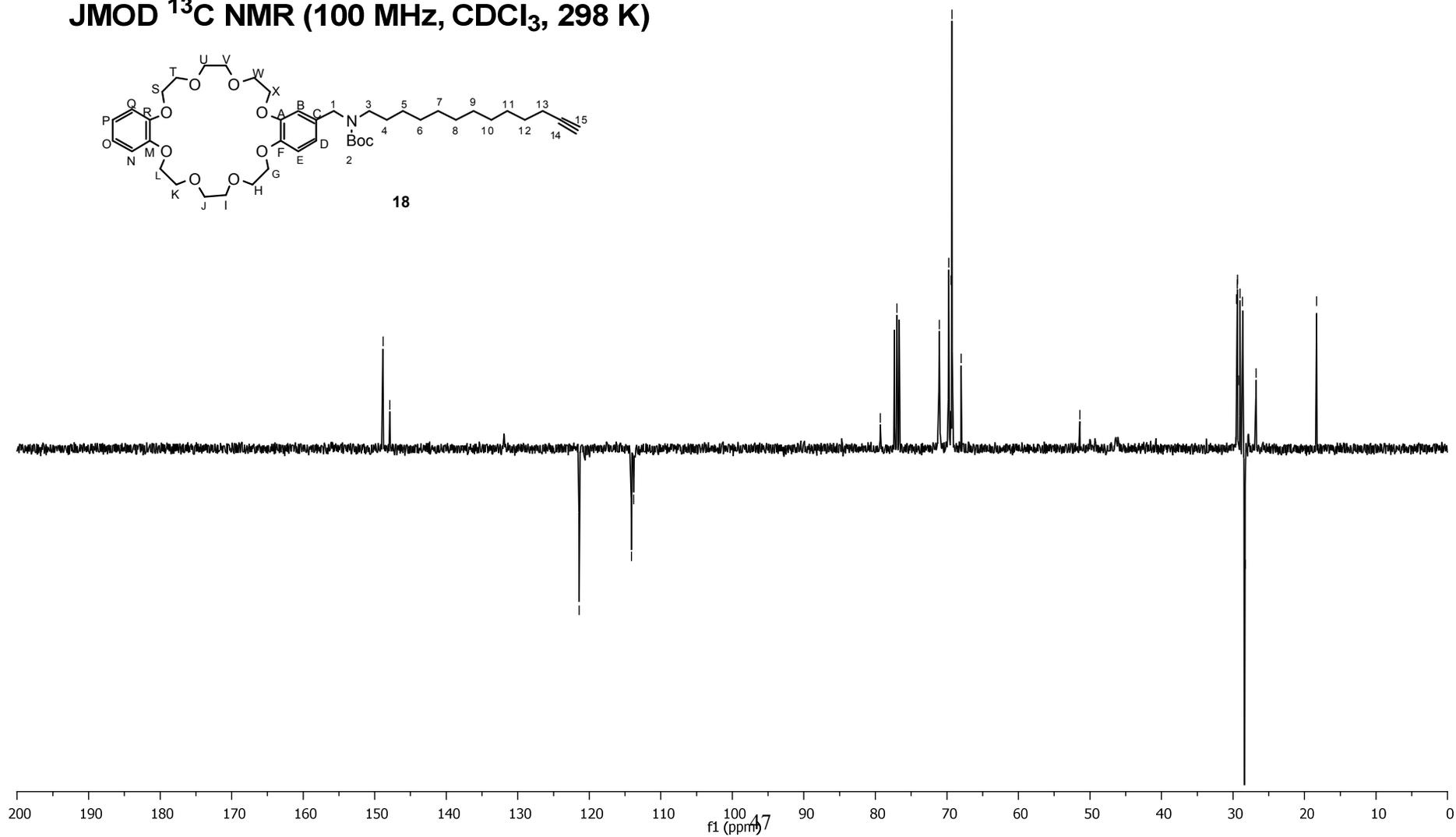
148.844
147.899

121.419
114.106
113.796

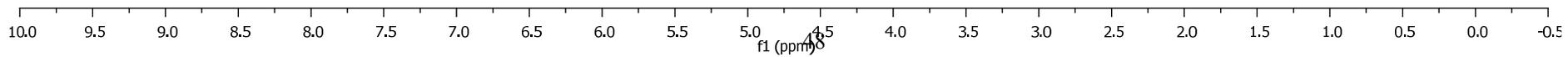
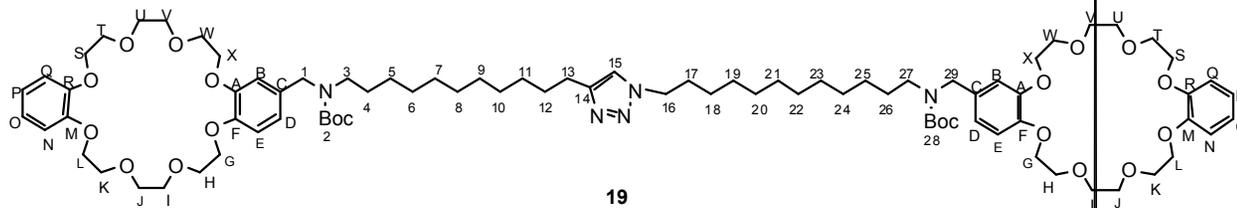
79.306
77.000
71.066
69.759
69.419
69.297
68.003

51.397

29.417
29.379
29.254
29.006
28.659
28.410
28.299
26.783
18.309



¹H NMR (400 MHz, CD₃CN, 298 K)



149.215
149.108
149.078
148.058

135.363

124.075
124.027
122.794

118.260
117.517
117.354
117.339
116.454

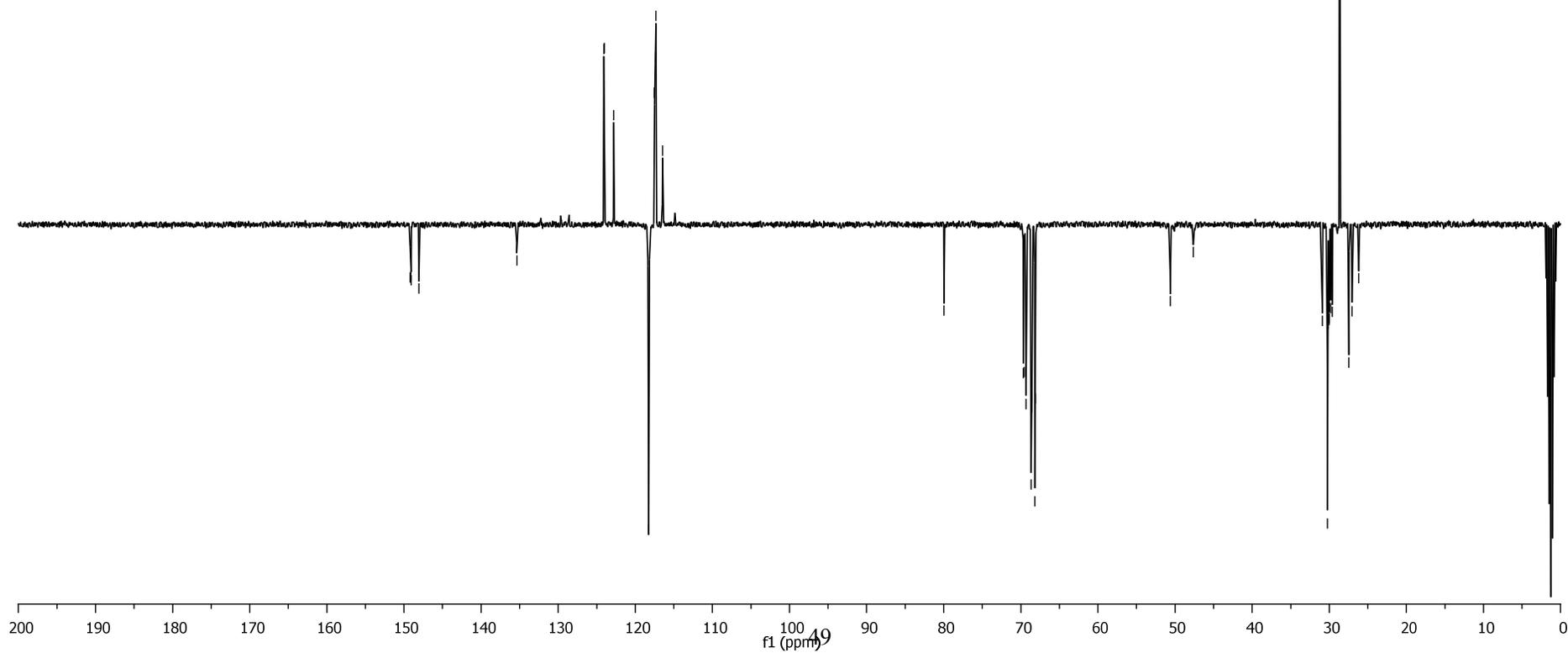
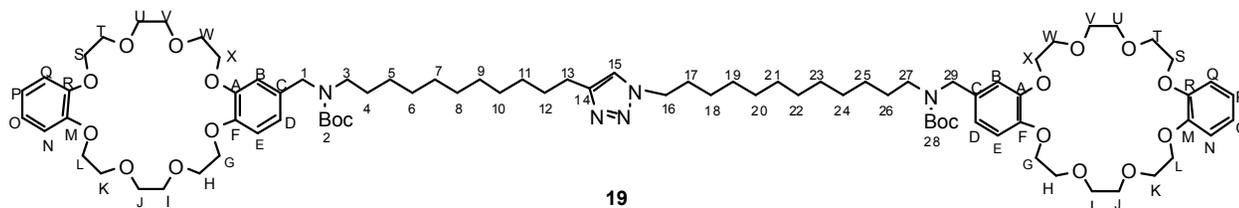
79.952

69.337
68.657
68.601
68.574
68.192
68.148
68.096

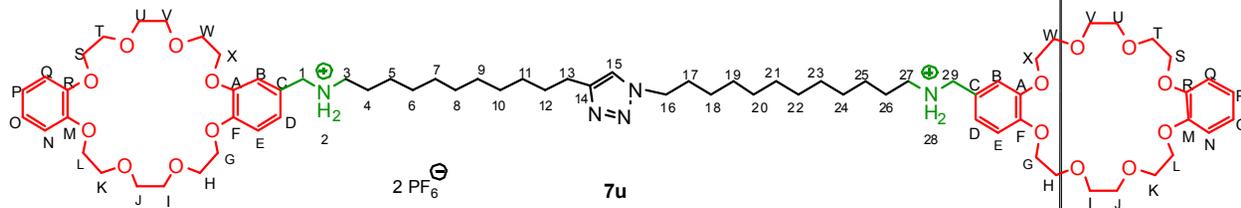
50.629
47.616

30.880
30.236
30.197
30.160
30.089
30.038
29.997
29.803
29.600
28.634
27.454
27.035
26.174

JMOD ^{13}C NMR (100 MHz, CD_3CN , 298 K)



¹H NMR (400 MHz, CD₃CN, 298 K)

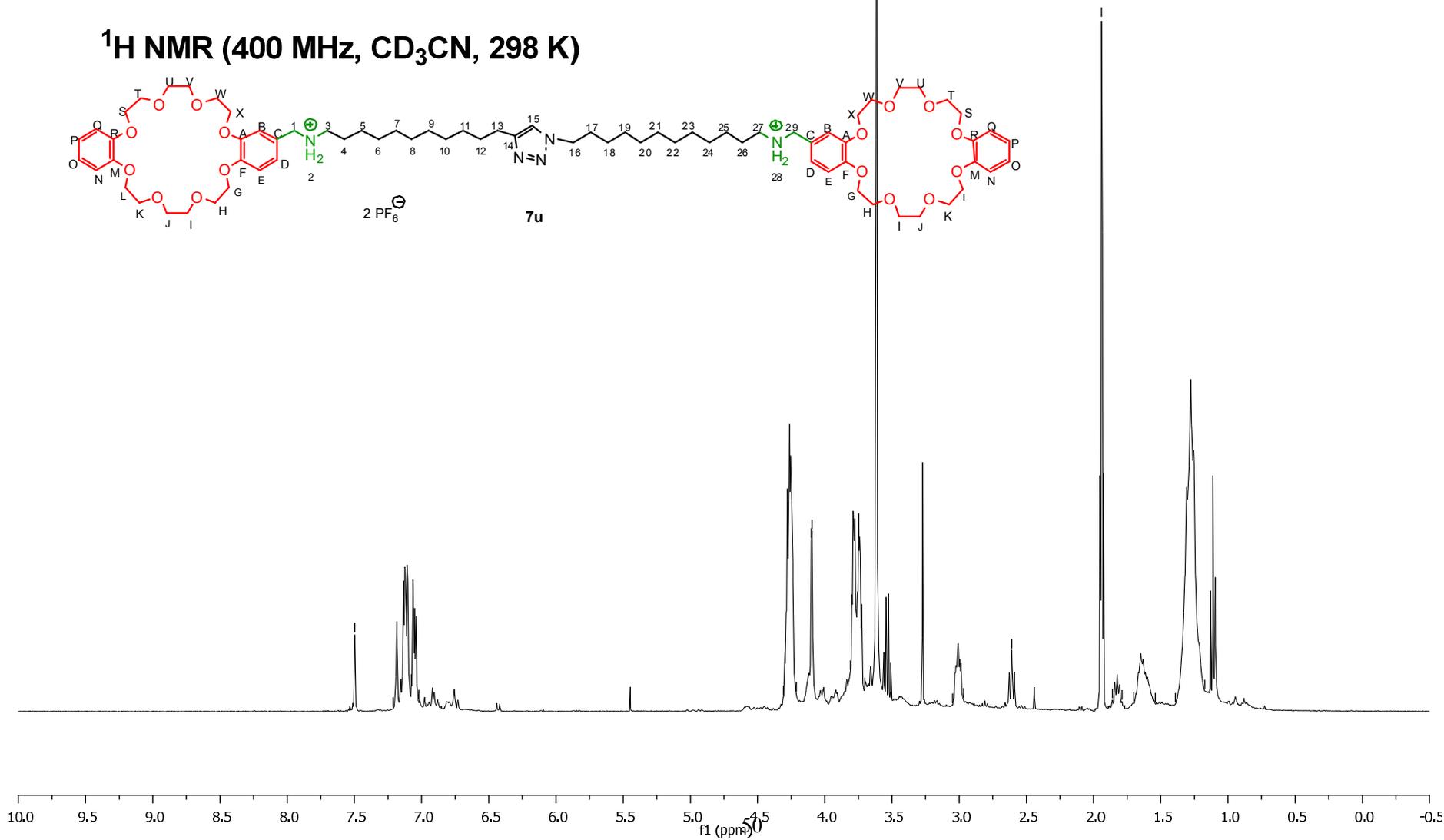


7.50
7.21
7.02

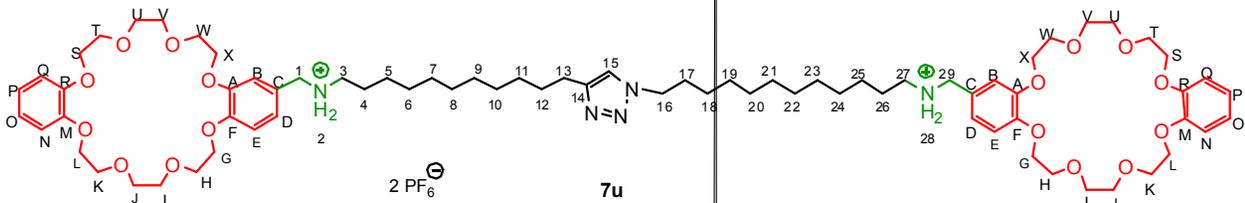
4.31
4.21
4.10
4.09
3.81
3.70
3.61

3.05
2.97
2.61

1.94
1.86
1.79
1.70
1.54
1.39
1.17



JMOD ¹³C NMR (100 MHz, CD₃CN, 298 K)



150.20
149.23
149.00
148.93
148.60

126.02
125.79
123.98
123.80
118.98
118.26
117.41
116.91
116.87

69.83
69.70
69.13
69.04
68.91
68.85
68.60
68.33
68.22
68.11

51.90
50.57
48.69

30.16
29.83
29.70
29.46
29.28
26.83
26.80
26.47
26.00

