Supplementary information

Tightening or Loosening a pH-Sensitive double-Lasso Molecular Machine Readily Synthesized from an Ends-Activated [c2]Daisy Chain

Camille Romuald[a], Ana Ardá Freire[b], Caroline Clavel[a], Jesús Jiménez-Barbero*[b] and Frédéric Coutrot*[a]

[a]*Institut des Biomolécules Max Mousseron (IBMM), UMR 5247 CNRS-Universités Montpellier 2 et 1, Bâtiment de Recherche Max Mousseron, Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France. Fax: +33 467-14-43-44; Tel: +33 467-14-72-97; E-mail: frederic.coutrot@univ-montp2.fr – http://www.glycorotaxane.fr*

[b] *Centro de Investigaciones Biológicas (CIB-CSIC), Ramiro de Maetzu, 9 – E28040 Madrid, Spain. E-mail: jjbarbero@cib.csic.es*

A. Synthesis of the stoppering azido precursor 1 3

1) Preparation of the anhydride **7** 3
2) Preparation of the 1,2,3,4-tetra-O-acetyl-β-D-glucuronic acid **8** 4
3) Preparation of the 1-azido-2,3,4-tri-O-acetyl-β-D-glucuronic acid **9** 4
4) Preparation of the pentafluorophenol 1-azido-2,3,4-tri-O-acetyl-β-D-glucuronic ester **1** 5

B. Synthesis of the alkyne pseudo [c2]Daisy chain 2 5

1) Preparation of the tridec-2-yn-1-ol **10** 5
2) Preparation of the tridec-12-yn-1-ol **11** 6
3) Preparation of the 13-bromotridec-1-yne **12** 6
4) Preparation of the phthalimide **13** 7
5) Preparation of the tridec-12-yn-1-amine **14** 7
6) Preparation of the crown ether **15** 8
7) Preparation of the compound **16** 8
8) Preparation of the compound **2** 9

C. Synthesis of the non-interlocked threads 5u and 6u 10

1) Preparation of the compound **17** 10
2) Preparation of the compound **18** 10
3) Preparation of the thread **19** 11

4) Preparation of the thread **20** 12
5) Preparation of the thread **5u** 13
6) Preparation of the thread **6u** 14

D. Synthesis of the double-lasso 15
1) Preparation of the activated rotaxane dimer **3** 15
2) Preparation of the double-lasso **4a-b** 16
3) Preparation of the double-lasso **5a-b** 17
4) Preparation of the double-lasso **6a-b** 18
5) Reprotonation procedure of **6a-b** 18

E. Molecular Modeling 18

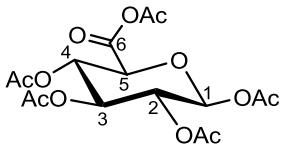
F. Stack plot ^{1}H NMR (400 MHz, 298K) of double-lasso 5 in different solvents 22

G. NMR Spectra 22

General Methods. All reactions were carried out under an atmosphere of argon unless otherwise indicated. All reagents were used as received without further purification. Dichloromethane was distilled over P_2O_5 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 10% sulphuric acid, ninhydrine or an aqueous solution of $KMNO_4$, followed by heating. ^{1}H NMR and ^{13}C NMR spectra were obtained on a spectrometer (respectively at 400.13 MHz and 100.62 MHz). Chemical shifts of ^{1}H NMR and ^{13}C NMR are given by using $CHCl_3$ CH_2Cl_2, CH_3OH, CH_3CN and DMSO as references (7.27 ppm, 5.32 ppm, 3.31 ppm, 1.94 ppm and 2.50 ppm respectively for ^{1}H spectrum, and 77.0 ppm, 54.0 ppm, 49.15 ppm, 118.26 ppm, and 39.51 ppm respectively for ^{13}C spectrum). ^{1}H assignments were deduced from 2D ^{1}H-^{1}H NMR COSY experiments. ^{13}C assignments were deduced from 2D ^{13}C-^{1}H NMR HMQC experiments. 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), m (multiplet). Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded respectively on a ZQ Micromass apparatus, a MALDI and a Q-TOF Micromass apparatus supplied with an ESI source (Waters, 2001).

A. Synthesis of the stoppering azido precursor 1

*1) Preparation of the anhydride **7***

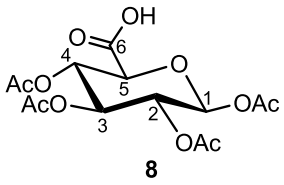


7

To a suspension of D-glucuronic acid (1.97 g, 10.15 mmol, 1 eq.) in 30 mL of acetic anhydride at 5°C was added slowly in portions iodine (260 mg, 1.015 mmol, 0.1 equiv). The suspension was stirred 1 h at 5°C and then 4 h at room temperature. The solution was co-evaporated with toluene and the solid residue was triturated with diethyl ether. A white powder was obtained (3.21g) with a yield of 78%.

^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ = 5.79 (d, 1H, $^3J_{H1\text{-}H2}$ = 8.3 Hz, H_1), 5.35 (t, 1H, $^3J_{H4\text{-}H3}$ = $^3J_{H4\text{-}H5}$ = 8.3 Hz, H_4), 5.27 (t, 1H, $^3J_{H3\text{-}H2}$ = $^3J_{H3\text{-}H4}$ = 8.3 Hz, H_3), 5.10 (t, 1H, $^3J_{H2\text{-}H1}$ = $^3J_{H2\text{-}H3}$ = 8.3 Hz, H_2), 4.31 (d, 1H, $^3J_{H5\text{-}H4}$ = 8.3 Hz, H_5), 2.25 (s, 3H, $COOCOCH_3$), 2.29 & 2.10 & 2.04 & 2.03 & 2.02 (5*s, 5*3H, CH_3CO).
^{13}C NMR JMOD (100 MHz, $CDCl_3$, 298K): δ = 169.7 & 169.3 & 169.1 & 168.6 ($\underline{C}OCH_3$), 164.7 & 162.5 ($\underline{C}OO\underline{C}OCH_3$), 91.3 ($C_1$), 72.9 ($C_5$), 71.2 ($C_3$), 70.0 ($C_2$), 67.9 ($C_4$), 22.0 ($COOCO\underline{C}H_3$), 20.6 & 20.4 & 20.4 ($\underline{C}H_3CO$).
MS (ESI): $[M+Na]^+$ calcd for $[C_{16}H_{20}O_{12}Na]^+$: 427.31, found: 427.14

2) Preparation of the 1,2,3,4-tetra-O-acetyl-β-D-glucuronic acid ***8***

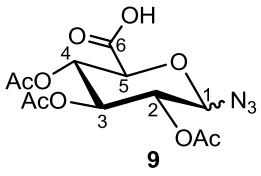


8

The anhydride **7** (1.40 g, 3.46 mmol) was stirred overnight at room temperature in 60 mL of a solution consisting of THF / water 2:1. The THF was then evaporated and the aqueous solution was extracted with dichloromethane (3 x 50 mL). The organic phase was dried over $MgSO_4$, filtered and evaporated to afford the acid compound **8** (1.23 g) in a quantitative yield.

R_f (AcOEt/éther de pétrole 4:1) 0.0
^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ = 5.81 (d, 1H, $^3J_{H1-H2}$ = 6.9 Hz, H_1), 5.39 (t, 1H, $^3J_{H3-H2}$ = $^3J_{H3-H4}$ = 8.7 Hz, H_3), 5.29 (t, 1H, $^3J_{H4-H3}$ = $^3J_{H4-H5}$ = 8.7 Hz, H_4), 5.13 (dd, 1H, $^3J_{H2-H1}$ = 6.9 Hz, $^3J_{H2-H3}$ = 8.7 Hz, H_2), 4.32 (d, 1H, $^3J_{H5-H4}$ = 8.7 Hz, H_5), 2.14 & 2.07 & 2.04 & 2.02 (4*s, 4*3H, CH_3CO).
^{13}C NMR JMOD (100 MHz, $CDCl_3$, 298K): δ = 170.0 & 169.7 & 169.6 & 169.3 & 168.9 (C_6 $\underline{C}OCH_3$), 91.2 (C_1), 72.4 (C_5), 71.8 (C_3), 70.0 (C_2), 68.5 (C_4), 20.7 & 20.5 & 20.5 & 20.4 ($\underline{C}H_3CO$).
MS (ESI): $[M+Na]^+$ calcd for $[C_{14}H_{18}O_{11}Na]^+$: 385.28, found: 385.10

3) Preparation of the 1-azido-2,3,4-tri-O-acetyl-β-D-glucuronic acid ***9***

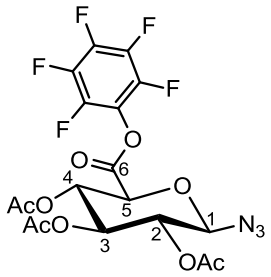


9

To a solution of the 1,2,3,4-tetra-*O*-acetyl-β-D-glucuronic acid **8** (3.93 g, 10.847 mmol, 1 equiv) in 25 mL of dichloromethane at 5°C were added trimethylsilylazide (3.57 mL, 27.117 mmol, 2.5 equiv) and tin(IV) chloride (5.4 mL, 5.423 mmol, 1M in CH_2Cl_2, 0.5 equiv). The reaction was allowed to stir overnight at 5°C. A saturated aqueous solution of $NaHCO_3$ was then added and the reaction mixture was stirred 20 min before separating the two layers. After a second wash with saturated $NaHCO_3$, the combined aqueous layers were acidified with hydrochloric acid 12M and extracted with dichloromethane (3 x 30 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated to yield the compound **9** (2.85 g, 75%, ratio α/β : 17/83) as a colorless solid.

β isomer : **^{1}H NMR (400 MHz, $CDCl_3$, 298K):** δ = 5.30 (t, 1H, $^3J_{H3-H2}$ = $^3J_{H3-H4}$ = 9.2 Hz, H_3), 5.26 (t, 1H, $^3J_{H4-H3}$ = $^3J_{H4-H5}$ = 9.2 Hz, H_4), 4.96 (t, 1H, $^3J_{H2-H1}$ = $^3J_{H2-H3}$ = 9.2 Hz, H_2), 4.76 (d, 1H, $^3J_{H1-H2}$ = 9.2 Hz, H_1), 4.18 (d, 1H, $^3J_{H5-H4}$ = 9.2 Hz, H_5), 2.07 & 2.04 & 2.02 (3*s, 3*3H, CH_3CO).
^{13}C NMR JMOD (100 MHz, $CDCl_3$, 298K): δ = 170.2 & 170.0 & 169.4 & 168.3 (C_6 $\underline{C}OCH_3$), 87.7 (C_1), 73.5 (C_5), 71.9 (C_3), 70.3 (C_2), 68.8 (C_4), 20.4 & 20.4 ($\underline{C}H_3CO$).
MS (ESI): $[M+Na]^+$ calcd for $[C_{12}H_{15}N_3O_9Na]^+$: 368.25, found: 368.00

*4) Preparation of the pentafluorophenol 1-azido-2,3,4-tri-O-acetyl-β-D-glucuronic ester **1***



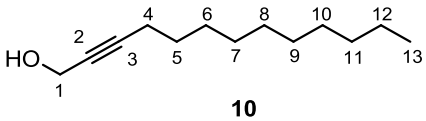
1

To a cooled solution (0°C) of the 1-azido-2,3,4-tri-*O*-acetyl-D-glucuronic acid **9** (2.84 g, 8.224 mmol, 1 equiv) in 30 mL of dichloromethane was added oxalyl chloride (1.44 mL, 16.449 mmol, 2 equiv). 3 mL of DMF was then slowly added to the stirring solution and evolution of gas was observed. The pale yellow solution was stirred for 30 min at 0°C and then for 2 h at room temperature. [1] The solution was evaporated to give a solid, which was diluted in 30 mL of dichloromethane and added by pentafluorophenol (1.82 g, 9.869 mmol, 1.2 equiv). The mixture was allowed to stir overnight at room temperature. The solution was washed with a saturated aqueous solution of $NaHCO_3$ (2 x 30 mL). After separation, the aqueous layer was extracted with dichloromethane (2 x 30mL). The organic layers were combined, dried over $MgSO_4$ and concentrated. The crude was purified by chromatography on silicagel column (gradient elution petroleum ether/AcOEt 9:1 to 1:1) to yield the compound **1** as a colorless solid (2.32 g, 56%) and as a unique β stereoisomer.

R_f (petroleum ether /AcOEt 1:1) 0.68
^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ = 5.44 (t, 1H, $^3J_{H3\text{-}H2} = {}^3J_{H3\text{-}H4}$ = 9.2 Hz, H_3), 5.32 (t, 1H, $^3J_{H4\text{-}H3} = {}^3J_{H4\text{-}H5}$ = 9.2 Hz, H_4), 5.05 (t, 1H, $^3J_{H2\text{-}H1} = {}^3J_{H2\text{-}H3}$ = 9.2 Hz, H_2), 4.83 (d, 1H, $^3J_{H1\text{-}H2}$ = 9.2 Hz, H_1), 4.54 (d, 1H, $^3J_{H5\text{-}H4}$ = 9.2 Hz, H_5), 2.11 & 2.06 & 2.05 (3*s, 3*3H, CH_3CO).
^{13}C NMR JMOD (100 MHz, $CDCl_3$, 298K): δ = 170.0 & 169.1 & 169.0 ($\underline{C}OCH_3$), 162.5 (C_6), 88.2 (C_1), 73.8 (C_5), 71.7 (C_3), 70.1 (C_2), 68.7 (C_4), 20.5 & 20.4 & 20.2 ($\underline{C}H_3CO$).

B. Synthesis of the alkyne pseudo [c2]Daisy chain 2

*1) Preparation of the tridec-2-yn-1-ol **10***



10

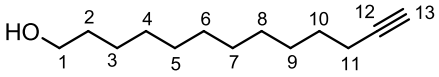
To a stirred solution of 1-dodecyne (5g, 30.064 mmol, 1 equiv) in anhydrous THF at 5°C was added, under Argon, *n*-BuLi (20.7 mL, 33.077 mmol, 1.6 M in THF, 1.1 equiv). After 30 min at 5°C, paraformaldehyde was added by portions. The solution was further stirred during 1h at 5°C, then during one night at room temperature. The reaction mixture was quenched with 120 mL of 1:1 water/saturated water with NH_4Cl. The biphasic solution was separated and the aqueous layer

[1] D. P. Temelkoff, M. Zeller, P. Norris, *Carbohydrate Research*, **2006**, 341, 1081-1090.

extracted twice with 100 mL of ethyl acetate. The organic layers were then combined, dried over $MgSO_4$ and concentrated to afford compound **10** in a quantitative yield (5.90 g) as a yellow oil.

R_f (petroleum ether /AcOEt 9:1) 0.21
^{1}H NMR ($CDCl_3$, 400 MHz, 298K) : δ (ppm) = 4.25 (t, 2H, $^5J_{H4\text{-}H1}$ = 2.0 Hz, H_1), 2.21 (tt, 2H, $^5J_{H4\text{-}H1}$ = 2.0 Hz, $^3J_{H4\text{-}H5}$ = 7.2 Hz, H_4), 1.55-1.46 (m, 2H, H_5), 1.42-1.33 (m, 2H, H_6), 1.33-1.20 (m, 12H, H_7 H_8 H_9 H_{10} H_{11} H_{12}), 0.89 (t, 3H, $^3J_{H13\text{-}H12}$ = 6.9 Hz, H_{13}).
^{13}C NMR JMOD ($CDCl_3$, 100 MHz, 298K) : δ (ppm) = 86.6 & 78.2 (C_2 C_3), 51.4 (C_1), 31.9 & 29.6 & 29.5 & 29.3 & 29.1 & 28.9 & 28.6 & 22.7 (C_5 C_6 C_7 C_8 C_9 C_{10} C_{11} C_{12}), 18.7 (C_4), 14.1 (C_{13}).

*2) Preparation of the tridec-12-yn-1-ol **11***

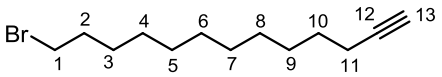


11

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 dropwise the tridec-2-yn-1-ol **10** (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 water and 100 mL of diethyl ether 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 oil.

R_f (petroleum ether /AcOEt 1:1) 0.71
^{1}H NMR ($CDCl_3$, 400 MHz, 298K) : δ (ppm) = 3.63 (t, 2H, $^3J_{H1\text{-}H2}$ = 6.6 Hz, H_1), 2.18 (td, 2H, $^3J_{H11\text{-}H10}$ = 7.1 Hz ,$^4J_{H11\text{-}H13}$ = 2.6 Hz, H_{11}), 1.94 (t, 1H, $^4J_{H13\text{-}H11}$ = 2.6 Hz, H_{13}), 1.62-1.47 (m, 4H, H_2 H_{10}), 1.43-1.23 (m, 14H, H_3 H_4 H_5 H_6 H_7 H_8 H_9).
^{13}C NMR ($CDCl_3$, 100 MHz, 298K) : δ (ppm) = 84.4 (C_{12}), 68.0 (C_{13}), 62.2 (C_1), 32.4 (C_2) 29.4 & 29.3 & 29.3 & 29.2 & 28.9 & 28.5 & 28.2 (C_3 C_4 C_5 C_6 C_7 C_8 C_9 C_{10}), 25.6 (C_{11}).

*3) Preparation of the 13-bromotridec-1-yne **12***



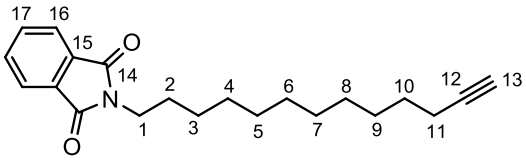
12

To a solution of the tridec-12-ynol **11** (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 **12** (3.07 g, 97%) as a yellow oil.

R_f (petroleum ether /AcOEt 97:3) 0.50

^{1}H NMR ($CDCl_3$, 400 MHz, 298K) : δ (ppm) = 3.42 (t, 2H, $^3J_{H1\text{-}H2}$ = 6.9 Hz, H_1), 2.19 (td, 2H, $^3J_{H11\text{-}H10}$ = 7.1 Hz ,$^4J_{H11\text{-}H13}$ = 2.7 Hz, H_{11}), 1.95 (t, 1H, $^4J_{H13\text{-}H11}$ = 2.7 Hz, H_{13}), 1.90-1.81 (m, 2H, H_2), 1.57-1.48 (m, 2H, H_{10}), 1.48-1.23 (m, 14H, H_3 H_4 H_5 H_6 H_7 H_8 H_9).
^{13}C NMR ($CDCl_3$, 100 MHz, 298K) : δ (ppm) = 84.4 (C_{12}), 68.0 (C_{13}), 33.7 (C_1), 32.7 & 29.3 & 29.3 & 29.3 & 29.0 & 28.6 & 28.6 & 28.4 & 28.0 (C_2 C_3 C_4 C_5 C_6 C_7 C_8 C_9 C_{10}), 18.3 (C_{11}).

*4) Preparation of the phthalimide **13***

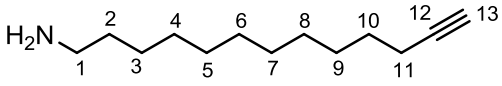


13

Potassium phthalimide (3.40 g, 18.34 mmol, 1.5 equiv) was added to a solution of the 13-bromotridec-1-yne **12** (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 oil.

R_f (Petroleum ether/AcOEt 75/25) 0.50
^{1}H NMR ($CDCl_3$, 400 MHz, 298K) : δ (ppm) = 7.87-7.81 (m, 2H, H_{16}), 7.73-7.68 (m, 2H, H_{17}), 3.67 (t, 2H, $^3J_{H1\text{-}H2}$ = 7.4 Hz, H_1), 2.17 (td, 2H, $^3J_{H11\text{-}H10}$ = 7.8 Hz ,$^4J_{H11\text{-}H13}$ = 2.6 Hz, H_{11}), 1.94 (t, 1H, $^4J_{H13\text{-}H11}$ = 2.6 Hz, H_{13}), 1.72-1.62 (m, 2H, H_2), 1.56-1.47 (m, 2H, H_{10}), 1.42-1.22 (m, 14H, H_3 H_4 H_5 H_6 H_7 H_8 H_9).
^{13}C NMR JMOD ($CDCl_3$, 100 MHz, 298K) : δ (ppm) = 168.0 (C_{14}), 133.5 (C_{17}), 131.9 (C_{15}), 122.8 (C_{16}), 84.4 (C_{12}), 68.0 (C_{13}), 37.7 (C_1), 29.2 & 29.2 & 28.9 & 28.8 & 28.5 & 28.3 & 28.2 & 26.6 (C_2 C_3 C_4 C_5 C_6 C_7 C_8 C_9 C_{10}), 18.1 (C_{11}).

*5) Preparation of the tridec-12-yn-1-amine **14***



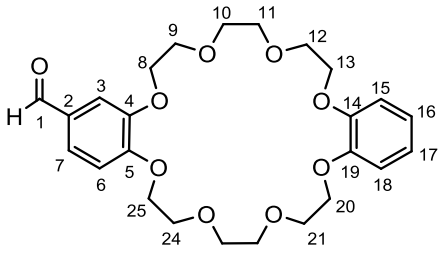
14

Hydrazine monohydrate (2.14 g, 42.805 mmol, 3.5 equiv) was added to a solution of the phthalimide **13** (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 $MgSO_4$ and concentrated to yield the desired product (2.10 g, 88 %) as a yellow solid.

R_f (CH_2Cl_2/MeOH 9:1) 0
^{1}H NMR ($CDCl_3$, 400 MHz, 298K) : δ (ppm) = 2.67 (t, 2H, $^3J_{H1\text{-}H2}$ = 7.0 Hz, H_1), 2.18 (td, 2H, $^3J_{H11\text{-}H10}$ = 7.2 Hz ,$^4J_{H11\text{-}H13}$ = 2.7 Hz, H_{11}), 1.93 (t, 1H, $^4J_{H13\text{-}H11}$ = 2.7 Hz, H_{13}), 1.56-1.47 (m, 2H, H_{10}), 1.47-1.34 (m, 4H, H_2 H_9), 1.34-1.21 (m, 12H, H_3 H_4 H_5 H_6 H_7 H_8).

^{13}C NMR ($CDCl_3$, 100 MHz, 298K) : δ (ppm) = 84.6 (C_{12}), 67.9 (C_{13}), 42.0 (C_1), 33.6 (C_2), 29.4 & 29.4 & 29.3 & 28.9 & 26.7 (C_3 C_4 C_5 C_6 C_7 C_8 C_9 C_{10}), 18.2 (C_{11}).
MS (ESI): $[M+H]^+$; calcd for $[C_{13}H_{26}N]^+$: 196.2, found : 196.2

*6) Preparation of the crown ether **15***



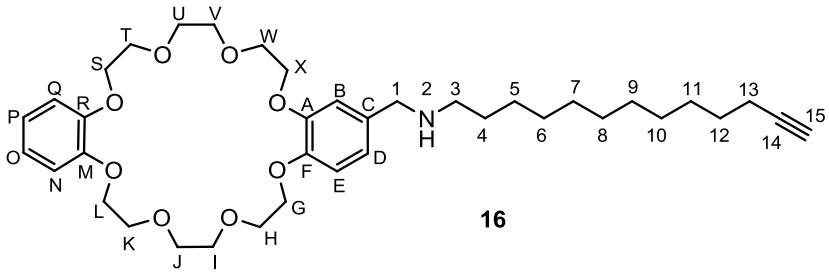
15

This compound has been synthesized according to the procedure described by S. J. Cantrill, G. J. Youn, J. F. Stoddart. [2]

R_f (AcOEt) 0.3
^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ (ppm) = 9.83 (s, 1H, H_1), 7.43 (dd, 1H, $^3J_{H7\text{-}H6}$ = 8.2 Hz, $^4J_{H7\text{-}H3}$ = 1.9 Hz, H_7), 7.38 (d, 1H, $^4J_{H3\text{-}H7}$ = 1.9 Hz, H_3), 6.94 (d, 1H, $^3J_{H6\text{-}H7}$ = 8.2 Hz, H_6), 6.90-6.86 (m, 4H, H_{15} H_{16} H_{17} H_{18}), 4.24-4.20 (m, 4H, H_8 H_{25}), 4.17-4.15 (m, 4H, H_{13} H_{20}), 3.98-3.92 (m, 8H, H_9 H_{12} H_{21} H_{24}), 3.86-3.84 (m, 8H, H_{10} H_{11} H_{22} H_{23}).

^{13}C NMR JMOD (100 MHz, $CDCl_3$, 298K): δ (ppm) = 190.9 (C_1), 154.3 & 149.1 & 148.8 (C_4 C_5 C_{14} C_{19}), 130.2 (C_2), 126.9 (C_7), 121.4 & 113.9 (C_{15} C_{16} C_{17} C_{18}), 111.8 (C_6), 110.9 (C_3), 71.5 & 71.4 & 71.3 & 69.7 & 69.5 & 69.4 & 69.4 & 69.3 ($\underline{C}H_2O$).
MS (ESI): $[M+Na]^+$ calcd for $C_{25}H_{42}O_9$: 499.52, found: 499.27

*7) Preparation of the compound **16***



16

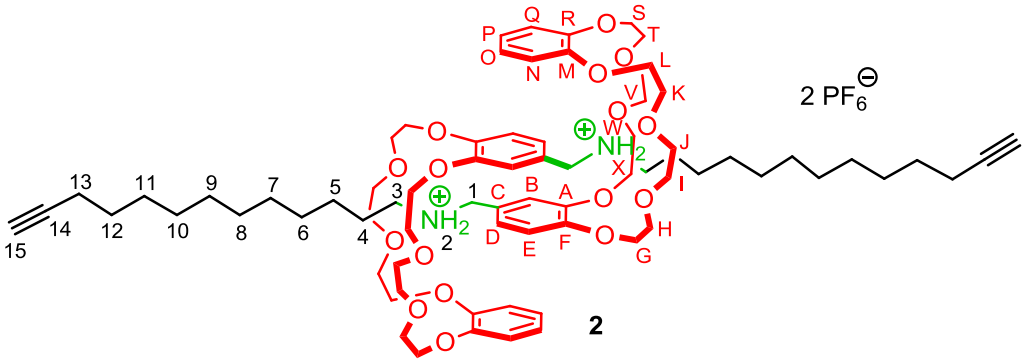
A solution of the crown ether aldehyde **15** (5.78 g, 12.134 mmol, 1 equiv) and the tridec-12-yn-1-amine **14** (2.37 g, 12.134 mmol, 1 equiv) in 200 mL of toluene was heated under reflux for 30 h using a Dean-Stark apparatus. The solvent was then evaporated to give a yellow oil. The mixture was diluted with MeOH (150 mL), and then $NaBH_4$ (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

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

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 $MgSO_4$ and concentrated. The crude (6.73 g) was directly engaged in the following reaction.

R_f (CH_2Cl_2/MeOH 9:1) 0.1
^{1}H NMR ($CDCl_3$, 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, H_1), 2.60 (t, 2H, $^3J_{H4\text{-}H3}$ = 7.3 Hz, H_3), 2.18 (td, 2H, $^3J_{H13\text{-}H12}$ = 7.1 Hz ,$^4J_{H13\text{-}H15}$ = 2.7 Hz, H_{13}), 1.94 (t, 1H, $^4J_{H15\text{-}H13}$ = 2.7 Hz, H_{15}), 1.57-1.45 (m, 4H, H_4 H_{12}), 1.44-1.34 (m, 2H, H_{11}), 1.33-1.23 (m, 12H, H_5 H_6 H_7 H_8 H_9 H_{10}).
^{13}C NMR ($CDCl_3$, 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 (C_{14}), 70.5 (C_I 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 (C_{15}), 52.9 (C_1), 48.6 (C_3), 29.2 & 28.9 & 28.9 & 28.9 & 28.8 & 28.4 & 28.0 & 27.9 & 26.7 (C_4 C_5 C_6 C_7 C_8 C_9 C_{10} C_{11} C_{12}), 17.7 (C_{13}).
MS (ESI): $[M+H]^+$; calcd for $[C_{38}H_{58}NO_8]^+$: 656.4, found : 656.3

*8) Preparation of the compound **2***



A solution of HCl 2M in diethyl ether (20 mL, 0.2 mol, 19 equiv) was added to the amine **16** (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 NH_4PF_6 (5.12 g, 31.77 mmol, 3 equiv) and dichloromethane (50 mL). The biphasic solution was stirred vigorously for 30 min; then, the two phases were separated and the aqueous layer was extracted with dichloromethane (3x30 mL). The organic layers were then combined, dried over $MgSO_4$ and concentrated. The crude was purified by chromatography on a silicagel column (solvent elution CH_2Cl_2/MeOH 98:2) to yield the compound **2** (8.40 g, 87% over the two steps) as a white solid.

R_f (CH_2Cl_2/MeOH 9:1) 0.54
^{1}H NMR ($CDCl_3$, 400 MHz, 298K) : δ (ppm) = 6.93 (dd, 1H, $^4J_{HD\text{-}HB}$ = 1.5 Hz, $^3J_{HD\text{-}HE}$ = 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, $^4J_{HB\text{-}HD}$ = 1.5 Hz, H_B), 4.52-4.28 (m, 2H, H_1), 4.52-3.59 (m, 24H, CH_2O_{DB24C8}), 3.58-3.30 (m, 2H, H_3), 2.19 (td, 2H, $^3J_{H13\text{-}H12}$ = 7.1 Hz ,$^4J_{H13\text{-}H15}$ = 2.7 Hz,

H_{13}), 1.96 (t, 1H, $^4J_{H15\text{-}H13}$ = 2.7 Hz, H_{15}), 1.73-1.63 (m, 2H, H_4), 1.57-1.48 (m, 2H, H_{12}), 1.44-1.35 (m, 2H, H_{11}), 1.35-1.16 (m, 12H, H_5 H_6 H_7 H_8 H_9 H_{10}).

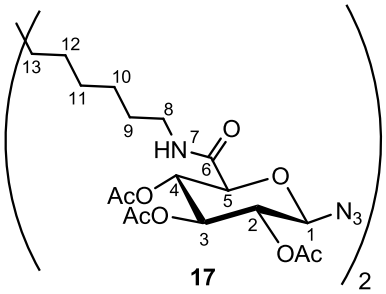
^{13}C NMR JMOD ($CDCl_3$, 100 MHz, 298K) : δ (ppm) = 147.6 & 147.5 & 146.2 & 146.0 (C_A C_F C_M C_R), 124.7 (C_C), 122.9 (C_D), 121.0 & 120.9 & 112.9 & 112.5 & 111.7 (C_B C_E C_N C_O C_P C_Q), 72.2 & 71.8 & 70.9 & 70.8 & 70.7 & 70.3 & 67.5 & 67.0 & 66.7 (CH_2O_{DB24C8}), 68.2 (C_{15}), 52.1 (C_1), 48.8 (C_3), 29.3 & 29.0 & 28.6 & 28.4 & 26.6 (C_4 C_5 C_6 C_7 C_8 C_9 C_{10} C_{11} C_{12}), 18.3 (C_{13}).

MS (ESI): $[M\text{-}2PF_6]^{2+}$; calcd for $[C_{76}H_{116}N_2O_{16}]^{2+}$: 656.42, found : 656.38

MS (MALDI): $[M\text{-}1H\text{-}2PF_6]^+$ calcd for $[C_{76}H_{115}N_2O_{16}]^+$: 1311.82, found : 1311.8

C. Synthesis of the non-interlocked threads 5u and 6u

*1) Preparation of the compound **17***



The compound **1** (200 mg, 0.391 mmol, 2 equiv) and the 1,12-diaminododecane (39 mg, 0.1955 mmol, 1 equiv) were stirred in 5 mL of dichloromethane at reflux for one night. The organic layer was washed successively with an aqueous solution of HCl 1M (2x5 mL), and with a saturated aqueous solution of NaCl (2x5 mL), then dried over $MgSO_4$ and concentrated under *vacuo* to afford the compound **17** (155 mg, 93%) as a white solid.

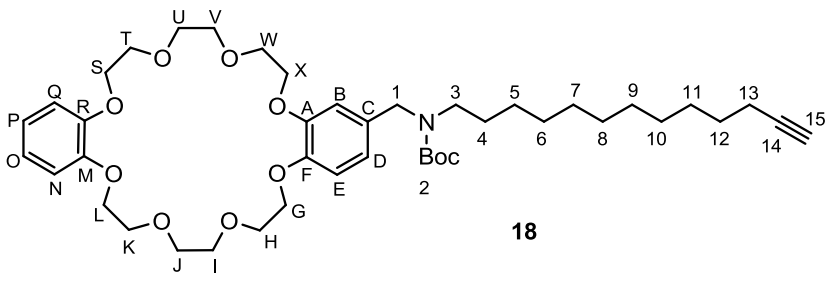
R_f (petroleum ether /AcOEt 1:1) 0.28

^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ = 6.49 (t, 2H, $^3J_{H7\text{-}H8}$ = 5.8 Hz, H_7), 5.24 (t, 2H, $^3J_{H3\text{-}H2}$ = $^3J_{H3\text{-}H4}$ = 9.3 Hz, H_3), 5.08 (t, 2H, $^3J_{H4\text{-}H3}$ = $^3J_{H4\text{-}H5}$ = 9.3 Hz, H_4), 4.87 (t, 2H, $^3J_{H2\text{-}H1}$ = $^3J_{H2\text{-}H3}$ = 9.3 Hz, H_2), 4.77 (d, 2H, $^3J_{H1\text{-}H2}$ = 9.3 Hz, H_1), 3.99 (d, 2H, $^3J_{H5\text{-}H4}$ = 9.3 Hz, H_5), 3.21-3.12 (m, 4H, H_8), 2.03 & 2.00 & 1.96 (3*s, 3*6H, CH_3CO), 1.50-1.40 (m, 4H, H_9), 1.29-1.15 (m, 16H, H_{10} H_{11} H_{12} H_{13}).

^{13}C NMR JMOD (100 MHz, $CDCl_3$, 298K): δ = 169.7 & 169.3 & 169.1 ($\underline{C}OCH_3$), 165.5 (C_6), 87.6 (C_1), 74.1 (C_5), 71.6 (C_3), 70.3 (C_2), 69.0 (C_4), 39.1 (C_8), 29.3 & 29.2 & 29.0 & 29.0 & 26.6 (C_9 C_{10} C_{11} C_{12} C_{13}), 20.4 & 20.3 & 20.3 ($\underline{C}H_3CO$).

MS (ESI): $[M+H]^+$; calcd for $[C_{36}H_{55}N_8O_{16}]^+$: 855.37, found : 855.46

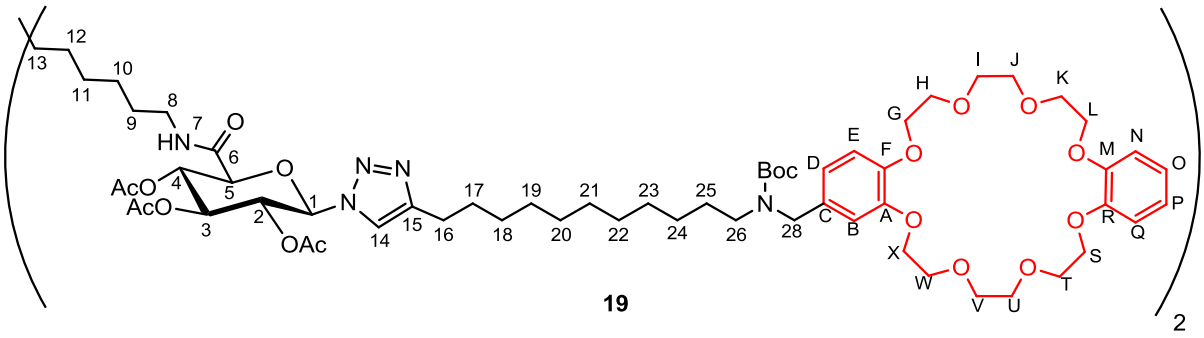
*2) Preparation of the compound **18***



To a solution of compound **2** (300 mg, 0.0374 mmol, 1 equiv) in dichloromethane (15 mL) were added Boc_2O (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 $NaHCO_3$ (2x30 mL), then dried over $MgSO_4$ and concentrated under *vacuo*. The crude was purified by chromatography on a silicagel column (solvent elution CH_2Cl_2/MeOH 98:2) to yield the N-Boc protected compound **18** (272 mg, 96%) as a white solid.

R_f (CH_2Cl_2/MeOH 9:1) 0.74
^{1}H NMR ($CDCl_3$, 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_1), 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, H_3), 2.18 (td, 2H, $^3J_{H13\text{-}H12}$ = 7.1 Hz ,$^4J_{H13\text{-}H15}$ = 2.7 Hz, H_{13}), 1.94 (t, 1H, $^4J_{H15\text{-}H13}$ = 2.7 Hz, H_{15}), 1.57-1.18 (m, 18H, H_4 H_5 H_6 H_7 H_8 H_9 H_{10} H_{11} H_{12}), 1.45 (s, 9H, H_2).
^{13}C NMR JMOD ($CDCl_3$, 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 ($CO\underline{C}(CH_3)_3$), 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 ($(\underline{C}H_3)_3CCO$), 18.4 (C_{13}).
MS (ESI): $[M+H]^+$; calcd for $[C_{43}H_{66}NO_{10}]^+$: 756.5, found : 756.5

*3) Preparation of the thread **19***



In a typical procedure, $Cu(CH_3CN)_4PF_6$ (36 mg, 0.0966 mmol, 1 equiv) and 2,6-lutidine (1 mg, 0.0097 mmol, 0.1 equiv) were added successively to a solution of the azido compound **17** (41 mg, 0.048 mmol, 0.5 equiv) and the alkyne compound **18** (73 mg, 0.0966 mmol, 1 equiv) in 4 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 /acetone 1:0 to 3:7) to afford the thread **19** (80 mg, 70%) as a yellow solid.

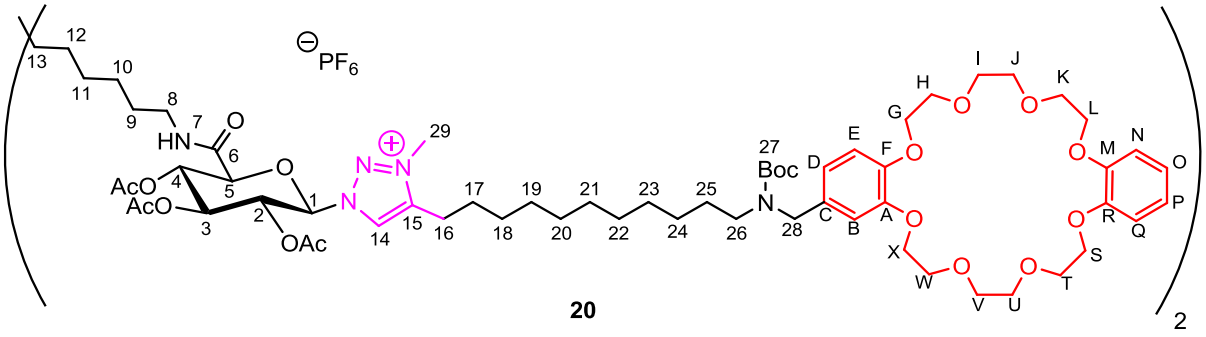
R_f (CH_2Cl_2/MeOH 9:1) 0.63
^{1}H NMR (CD_3CN, 400 MHz, 298K) : δ (ppm) = 7.79 (s, 2H, H_{14}), 7.17-7.05 (m, 10H, H_E H_N H_O H_P H_Q), 7.02 (br s, 2H, H_B), 6.94 (dd, 2H, $^4J_{HD\text{-}HB}$ = 1.4 Hz, $^3J_{HD\text{-}HE}$ = 8.3 Hz, H_D), 6.84 (t, 2H, $^3J_{H7\text{-}H8}$ = 5.7 Hz, H_7), 5.99 (d, 2H, $^3J_{H1\text{-}H2}$ = 9.5 Hz, H_1), 5.60 (t, 2H, $^3J_{H2\text{-}H1}$ = $^3J_{H2\text{-}H3}$ = 9.5 Hz, H_2), 5.50 (t, 2H, $^3J_{H3\text{-}H2}$ = $^3J_{H3\text{-}H4}$ = 9.5 Hz, H_3), 5.32 (t, 2H, $^3J_{H4\text{-}H3}$ = $^3J_{H4\text{-}H5}$ = 9.5 Hz, H_4), 4.34 (s, 4H, H_{28}), 4.30-4.22 (m, 18H, H_5 H_G H_L H_S H_X), 3.77-3.68 (m, 16H, H_H H_K H_T H_W), 3.59 (s, 16H, H_I H_J H_U H_V), 3.20-3.12 (br t, 4H, H_{26}), 3.11-3.04 (m, 4H, H_8), 2.66 (t, 4H, $^3J_{H16\text{-}H17}$ = 7.5 Hz, H_{16}), 1.99 & 1.97 & 1.78 (3*s, 3*6H,

CH_3CO), 1.66-1.56 (m, 4H, H_{17}), 1.51-1.34 (m, 8H, H_9 H_{25}), 1.45 (s, 18H, $C(CH_3)_3$), 1.33-1.19 (m, 44H, H_{10} H_{11} H_{12} H_{13} H_{18} H_{19} H_{20} H_{21} H_{22} H_{23} H_{24}).

^{13}C NMR JMOD (CD_3CN, 100 MHz, 298K) : δ (ppm) = 170.7 & 170.2 & 169.6 ($\underline{C}OCH_3$), 166.4 (C_6), 149.4 & 149.1 & 148.9 & 147.9 (C_{15} C_A C_F C_M C_R), 135.3 (C_C), 124.1 & 124.1 & 117.6 & 117.5 & 117.4 (C_E C_N C_O C_P C_Q), 122.8 (C_D), 121.5 (C_{14}), 116.5 (C_B), 85.4 (C_1), 79.9 ($\underline{C}(CH_3)_3$), 75.9 (C_5), 72.8 (C_3), 70.8 (C_2), 69.8 (C_4), 69.5 & 69.4 & 69.2 & 68.3 & 68.2 & 68.2 & 67.9 & 67.8 & 67.8 ($\underline{C}H_2O_{DB24C8}$), 50.0 ($C_{28}$), 47.5 ($C_{26}$), 39.7 ($C_8$), 30.2 & 30.1 & 30.1 & 29.9 & 29.9 & 29.8 & 29.8 & 29.6 & 27.4 (C_9 C_{10} C_{11} C_{12} C_{13} C_{17} C_{18} C_{19} C_{20} C_{21} C_{22} C_{23} C_{24} C_{25}), 28.5 ($(\underline{C}H_3)_3C$), 25.9 (C_{16}), 20.8 & 20.7 & 20.3 ($\underline{C}H_3CO$).

MS (ESI): $[M+H]^+$; calcd for $[C_{122}H_{185}N_{10}O_{36}]^+$: 2365.29, found : 2365.40

*4) Preparation of the thread **20***



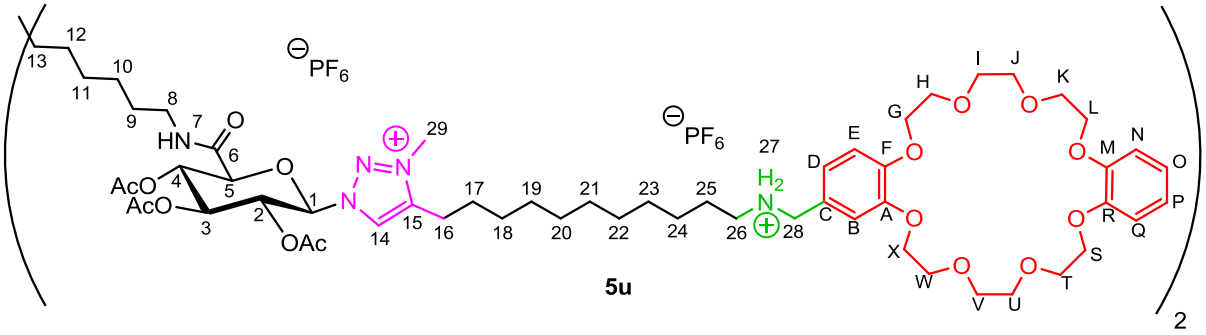
The thread **19** (75 mg, 0.0317 mmol, 1 equiv) was suspended in 2 mL of iodomethane and stirred for 4 days at room temperature. Then, iodomethane was evaporated under reduced pressure and the obtained solid was washed with diethyl ether to give a yellow solid. NH_4PF_6 (31 mg, 0.1901 mmol, 6 equiv) and 5 mL of dichloromethane were added to a suspension of the previous product in 5 mL of milliQ water. The resulted bilayer solution was vigorously stirred for 30 min. After separation, the aqueous layer was extracted twice with 5 mL of dichloromethane. The organic layers were combined, dried over $MgSO_4$ and concentrated to obtain the thread **20** (71 mg, 84%) as a yellow solid.

R_f (CH_2Cl_2/MeOH 9:1) 0.51

^{1}H NMR (CD_3CN, 400 MHz, 298K) : δ (ppm) = 8.53 (s, 2H, H_{14}), 7.01-6.85 (m, 14H, H_7 H_B H_E H_N H_O H_P H_Q), 6.81 (dd, 2H, $^4J_{HD\text{-}HB}$ = 1.4 Hz, $^3J_{HD\text{-}HE}$ = 8.1 Hz, H_D), 6.15-6.11 (m, 2H, H_1), 5.56-5.51 (m, 4H, H_2 H_3), 5.41-5.34 (m, 2H, H_4), 4.32 (d, 2H, $^3J_{H5\text{-}H4}$ = 10.0 Hz, H_5), 4.31 (s, 4H, H_{28}), 4.16-4.09 (m, 16H, H_G H_L H_S H_X), 4.14 (s, 6H, H_{29}), 3.80-3.75 (m, 16H, H_H H_K H_T H_W), 3.65 (s, 16H, H_I H_J H_U H_V), 3.18-3.07 (m, 8H, H_8 H_{26}), 2.79 (t, 4H, $^3J_{H16\text{-}H17}$ = 7.7 Hz, H_{16}), 1.99 & 1.99 & 1.91 (3*s, 3*6H, CH_3CO), 1.74-1.64 (m, 4H, H_{17}), 1.51-1.34 (m, 12H, H_9 H_{18} H_{25}), 1.44 (s, 18H, $C(CH_3)_3$), 1.33-1.17 (m, 40H, H_{10} H_{11} H_{12} H_{13} H_{19} H_{20} H_{21} H_{22} H_{23} H_{24}).

^{13}C NMR JMOD (CD_3CN, 100 MHz, 298K) : δ (ppm) = 170.6 & 170.1 & 170.0 ($\underline{C}OCH_3$), 165.4 (C_6), 149.4 & 149.4 & 149.3 & 148.4 & 146.9 (C_{15} C_A C_F C_M C_R), 133.9 (C_C), 127.8 (C_{14}), 122.8 & 121.6 & 115.7 & 115.6 & 115.5 & 114.8 (C_B C_D C_E C_N C_O C_P C_Q), 87.8 (C_1), 79.8 ($\underline{C}(CH_3)_3$), 76.2 (C_5), 72.1 (C_3), 70.7 (C_2), 69.2 (C_4), 70.4 & 69.7 & 69.6 & 69.5 & 69.4 ($\underline{C}H_2O_{DB24C8}$), 50.0 ($C_{28}$), 47.4 ($C_{26}$), 39.8 ($C_8$), 38.9 ($C_{29}$), 30.3 & 30.2 & 30.2 & 30.1 & 30.0 & 29.9 & 29.9 & 29.7 & 29.3 & 27.4 & 27.2 (C_9 C_{10} C_{11} C_{12} C_{13} C_{17} C_{18} C_{19} C_{20} C_{21} C_{22} C_{23} C_{24} C_{25}), 28.6 ($(\underline{C}H_3)_3C$), 23.8 (C_{16}), 20.8 & 20.7 & 20.5 ($\underline{C}H_3CO$).

*5) Preparation of the thread **5u***



A suspension of the N-Boc protected compound **20** (71 mg, 0.0281 mmol, 1 equiv) in 3 mL of HCl 2M 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 (27 mg, 0.1686 mmol, 6 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 5 mL of dichloromethane. The organic layers were combined, dried over $MgSO_4$ and concentrated to obtain the thread **5u** (68 mg, 78 %) as a pale yellow solid.

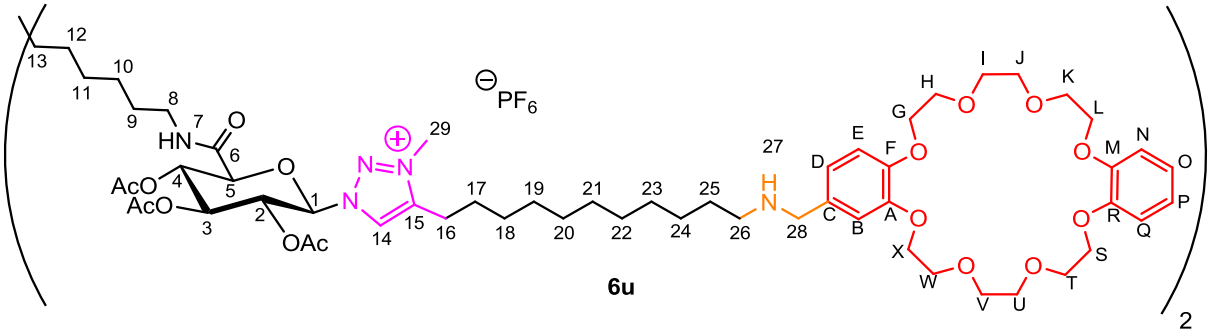
R_f (CH_2Cl_2/MeOH 9:1) 0.40

^{1}H NMR (CD_3CN, 400 MHz, 298K) : δ (ppm) = 8.52 (s, 2H, H_{14}), 7.07-6.91 (m, 14H, H_B H_D H_E H_N H_O H_P H_Q), 6.89 (t, 2H, $^3J_{H7\text{-}H8}$ = 5.9 Hz, H_7), 6.16-6.12 (m, 2H, H_1), 5.57-5.52 (m, 4H, H_2 H_3), 5.41-5.34 (m, 2H, H_4), 4.32 (d, 2H, $^3J_{H5\text{-}H4}$ = 10.0 Hz, H_5), 4.19-4.09 (m, 16H, H_G H_L H_S H_X), 4.14 (s, 6H, H_{29}), 4.04 (s, 4H, H_{28}), 3.84-3.75 (m, 16H, H_H H_K H_T H_W), 3.67 & 3.66 (2*s, 16H, H_I H_J H_U H_V), 3.14-3.07 (m, 4H, H_8), 2.94 (t, 4H, $^3J_{H26\text{-}H25}$ = 7.6 Hz, H_{26}), 2.80 (t, 4H, $^3J_{H16\text{-}H17}$ = 7.6 Hz, H_{16}), 1.99 & 1.99 & 1.91 (3*s, 3*6H, CH_3CO), 1.74-1.65 (m, 4H, H_{17}), 1.65-1.56 (m, 4H, H_{25}), 1.46-1.35 (m, 8H, H_9 H_{18}), 1.35-1.19 (m, 40H, H_{10} H_{11} H_{12} H_{13} H_{19} H_{20} H_{21} H_{22} H_{23} H_{24}).

^{13}C NMR JMOD (CD_3CN, 100 MHz, 298K) : δ (ppm) = 170.6 & 170.1 & 170.0 ($\underline{C}OCH_3$), 165.5 (C_6), 150.3 & 149.5 & 149.4 & 149.4 & 146.9 (C_{15} C_A C_F C_M C_R), 127.8 (C_{14}), 125.0 (C_C), 124.5 & 122.7 & 122.7 & 116.8 & 115.5 & 115.4 & 115.0 (C_B C_D C_E C_N C_O C_P C_Q), 87.8 (C_1), 76.2 (C_5), 72.1 (C_3), 70.7 (C_2), 69.2 (C_4), 70.7 & 70.6 & 70.6 & 69.8 & 69.8 & 69.7 & 69.6 & 69.5 & 69.4 ($\underline{C}H_2O_{DB24C8}$), 52.1 ($C_{28}$), 48.5 ($C_{26}$), 39.8 ($C_8$), 38.9 ($C_{29}$), 30.2 & 30.2 & 30.1 & 30.0 & 30.0 & 29.9 & 29.9 & 29.7 & 29.6 & 29.3 & 27.4 & 27.2 & 26.9 & 26.6 (C_9 C_{10} C_{11} C_{12} C_{13} C_{17} C_{18} C_{19} C_{20} C_{21} C_{22} C_{23} C_{24} C_{25}), 23.7 (C_{16}), 20.8 & 20.7 & 20.5 ($\underline{C}H_3CO$).

MS (ESI): $[M\text{-}3PF_6]^{3+}$; calcd for $[C_{114}H_{176}F_6N_{10}O_{32}]^{3+}$: 780.74, found : 781.08

*6) Preparation of the thread **6u***



A solution of the thread **5u** (68 mg, $2.447.10^{-5}$ mol) in 5 mL of dichoromethane was washed with 5 mL of an aqueous solution of NaOH 1M. After separation, the aqueous layer was extracted twice with 5 ml of dichlorométhane and the combined organic phases were dried over $MgSO_4$ and then evaporated to obtain product **6u** as a pale yellow solid (61 mg, quantitative).

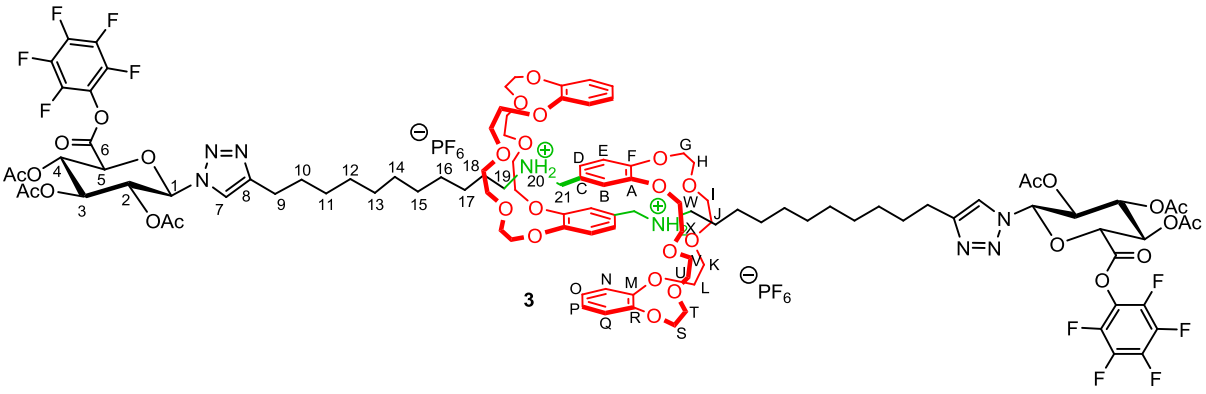
R_f (CH_2Cl_2/MeOH 9:1) 0.40

^{1}H NMR (CD_3CN, 400 MHz, 298K) : δ (ppm) = 8.54 (s, 2H, H_{14}), 7.02-6.82 (m, 16H, H_7 H_B H_D H_E H_N H_O H_P H_Q), 6.16-6.10 (m, 2H, H_1), 5.58-5.50 (m, 4H, H_2 H_3), 5.42-5.34 (m, 2H, H_4), 4.32 (d, 2H, $^3J_{H5\text{-}H4}$ = 9.9Hz, H_5), 4.17-4.07 (m, 16H, H_G H_L H_S H_X), 4.14 (s, 6H, H_{29}), 3.80-3.74 (m, 16H, H_H H_K H_T H_W), 3.65 & 3.65 (2*s, 16H, H_I H_J H_U H_V), 3.64 (s, 4H, H_{28}), 3.14-3.07 (m, 4H, H_8), 2.79 (t, 4H, $^3J_{H16\text{-}H17}$ = 7.7 Hz, H_{16}), 2.51 (t, 4H, $^3J_{H26\text{-}H25}$ = 7.0 Hz, H_{26}), 1.99 & 1.99 & 1.91 (3*s, 3*6H, CH_3CO), 1.74-1.64 (m, 4H, H_{17}), 1.50-1.34 (m, 12H, H_9 H_{18} H_{25}), 1.34-1.18 (m, 40H, H_{10} H_{11} H_{12} H_{13} H_{19} H_{20} H_{21} H_{22} H_{23} H_{24}).

^{13}C NMR JMOD (CD_3CN, 100 MHz, 298K) : δ (ppm) = 170.6 & 170.1 & 170.0 ($\underline{C}OCH_3$), 165.4 (C_6), 149.6 & 149.5 & 149.3 & 147.0 (C_{15} C_A C_F C_M C_R), 136.1 (C_C), 126.6 (C_{14}), 122.8 & 122.7 & 122.0 & 115.7 & 115.6 & 115.4 & 115.4 (C_B C_D C_E C_N C_O C_P C_Q), 87.9 (C_1), 76.2 (C_5), 72.1 (C_3), 70.8 (C_2), 69.2 (C_4), 70.6 & 69.8 & 69.7 & 69.7 & 69.6 & 69.5 & 69.5 ($\underline{C}H_2O_{DB24C8}$), 53.9 ($C_{28}$), 49.9 ($C_{26}$), 39.9 ($C_8$), 39.0 ($C_{29}$), 30.8 & 30.3 & 30.3 & 30.2 & 30.2 & 30.1 & 29.9 & 29.7 & 29.3 & 28.1 & 27.5 & 27.2 (C_9 C_{10} C_{11} C_{12} C_{13} C_{17} C_{18} C_{19} C_{20} C_{21} C_{22} C_{23} C_{24} C_{25}), 23.8 (C_{16}), 20.8 & 20.8 & 20.5 ($\underline{C}H_3CO$).

D. Synthesis of the double-lasso

*1) Preparation of the activated rotaxane dimer **3***



In a typical procedure, $Cu(CH_3CN)_4PF_6$ (73 mg, 0.1955 mmol, 1 equiv) and 2,6-lutidine (2 mg, 0.01955 mmol, 0.1 equiv) were added successively to a solution of the azido compound **1** (100 mg, 0.1955 mmol, 1 equiv) and the alkyne compound **2** (157 mg, 0.1955 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 /acetone 1:0 to 3:7) to afford the rotaxane dimer **3** (239 mg, 93%) as a yellow solid.

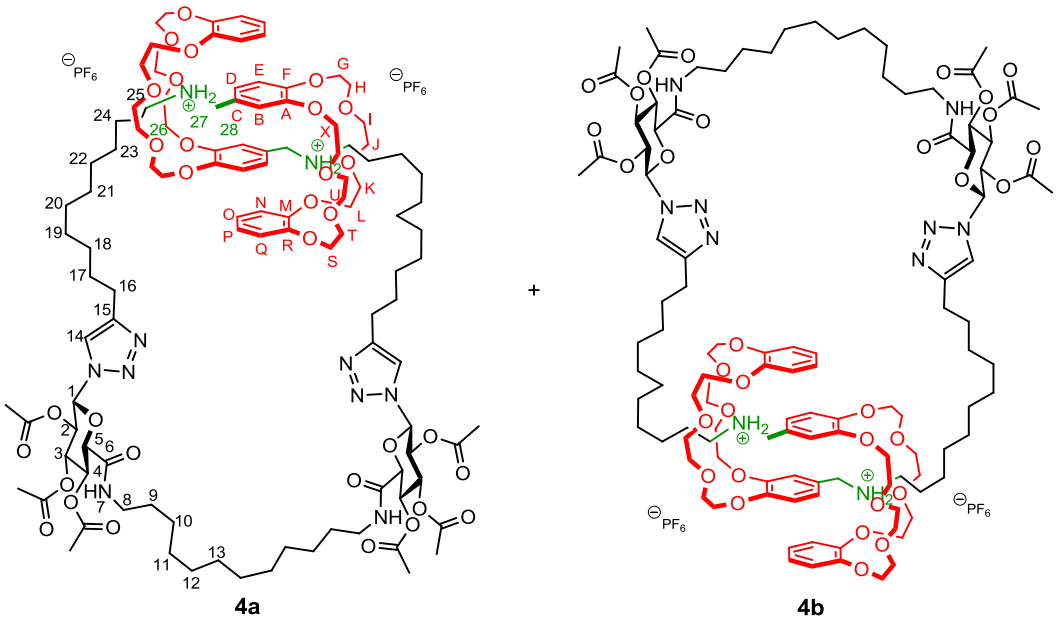
R_f (CH_2Cl_2/MeOH 9:1) 0.49

^{1}H NMR (CD_3CN, 400 MHz, 298K) : δ (ppm) = 7.82 (s, 2H, H_7), 6.95-6.85 & 6.69-6.56 (m, 4H, H_{20}), 6.85-6.71 (m, 12H, H_B H_D H_N H_O H_P H_Q), 6.42 (d, 2H, $^3J_{HE\text{-}HD}$ = 8.3 Hz, H_E), 6.11 (d, 2H, $^3J_{H1\text{-}H2}$ = 9.3 Hz, H_1), 5.77 (t, 2H, $^3J_{H2\text{-}H1}$ = $^3J_{H2\text{-}H3}$ = 9.3 Hz, H_2), 5.62 (t, 2H, $^3J_{H3\text{-}H2}$ = $^3J_{H3\text{-}H4}$ = 9.3 Hz, H_3), 5.56 (t, 2H, $^3J_{H4\text{-}H3}$ = $^3J_{H4\text{-}H5}$ = 9.3 Hz, H_4), 4.97 (d, 2H, $^3J_{H5\text{-}H4}$ = 9.3 Hz, H_5), 4.58-4.40 (m, 4H, H_{21}), 4.33-3.64 (m, 48H, CH_2O_{DB24C8}), 3.47-3.34 (m, 4H, H_{19}), 2.68 (t, 4H, $^3J_{H9\text{-}H10}$ = 7.3 Hz, H_9), 2.05 & 2.00 & 1.81 (3*s, 3*6H, CH_3CO), 1.75-1.67 (m, 4H, H_{18}), 1.67-1.58 (m, 4H, H_{10}), 1.40-1.18 (m, 28H, H_{11} H_{12} H_{13} H_{14} H_{15} H_{16} H_{17}).

^{13}C NMR JMOD (CD_3CN, 100 MHz, 298K) : δ (ppm) = 170.6 & 170.3 & 169.6 & 164.0 ($\underline{C}OCH_3$), 164.0 (C_6), 148.6 & 147.0 & 146.9 (C_8 C_A C_F C_M C_R), 126.2 (C_C), 123.5 & 122.9 & 120.5 & 114.0 & 112.9 & 112.6 & 112.6 (C_B C_D C_E C_N C_O C_P C_Q), 121.5 (C_7), 85.6 (C_1), 74.5 (C_5), 72.7 (C_3), 70.3 (C_2), 69.3 (C_4), 73.0 & 72.9 & 72.9 & 72.1 & 71.4 & 71.3 & 71.2 & 70.9 & 70.9 & 69.9 & 69.2 & 68.3 & 68.3 & 68.1 & 67.9 & 67.8 ($\underline{C}H_2O_{DB24C8}$), 52.7 ($C_{21}$), 49.7 ($C_{19}$), 30.1 & 30.0 & 29.9 & 29.8 & 29.6 & 29.4 & 27.2 & 27.1 (C_{10} C_{11} C_{12} C_{13} C_{14} C_{15} C_{16} C_{17} C_{18}), 25.9 (C_9), 20.7 & 20.6 & 20.3 ($\underline{C}H_3CO$).

HRMS (ESI): $[M\text{-}2PF_6]^{2+}$; calcd for $[C_{112}H_{144}F_{10}N_8O_{34}]^{2+}$: 1167.4813, found : 1167.5016

2) Preparation of the double-lasso ***4a-b***



To a stirred solution of the rotaxane dimer **3** (104 mg, 0.0396 mmol, 1 equiv) in 80 mL of dichloromethane (C = 5.10^{-4} M) was added the dodecane-1,12-diamine (7.92 mg, 0.0396 mmol, 1equiv). The solution was stirred for 4 days at room temperature, then evaporated and the crude was purified by chromatography on siligagel column (solvent gradient elution CH_2Cl_2 to CH_2Cl_2/acetone 3:7) to give the double-lasso **4a-b** (32 mg) as a yellow solid in 33% yield.

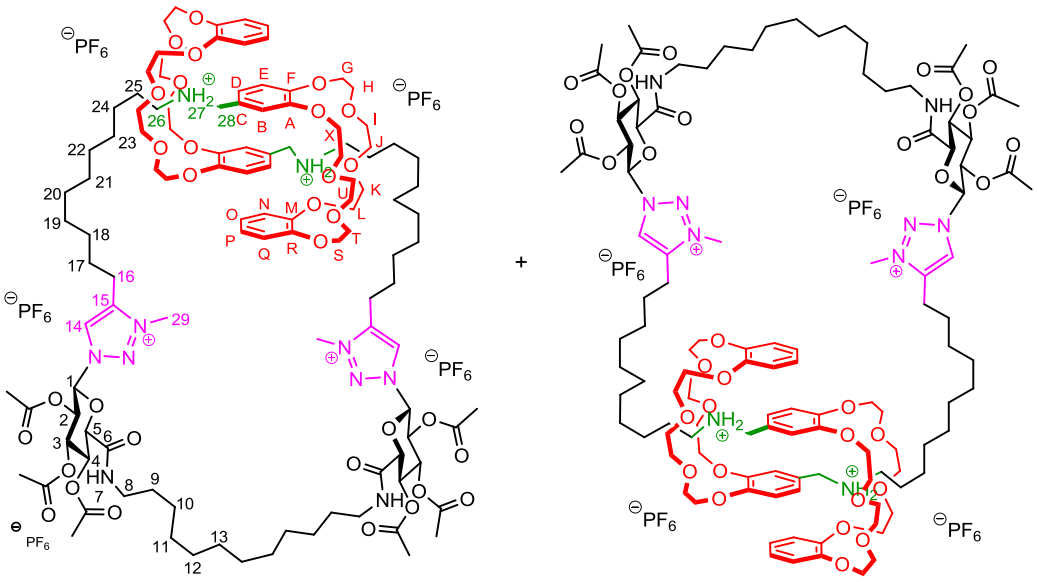
R_f (CH_2Cl_2/MeOH 9:1) 0.48

^{1}H NMR (CD_3CN, 400 MHz, 298K) : δ (ppm) = 7.78 (s, 2H, H_{14}), 7.04-6.85 & 6.70-6.54 (m, 4H, H_{27}), 6.84-6.70 (m, 16H, H_7 H_B H_D H_N H_O H_P H_Q), 6.44 & 6.43 (2*d, 2H, $^3J_{HE\text{-}HD}$ = 8.3 Hz, H_E), 5.99 & 5.99 (2*d, 2H, $^3J_{H1\text{-}H2}$ = 9.5 Hz, H_1), 5.61 & 5.60 (2*t, 2H, $^3J_{H2\text{-}H1}$ = $^3J_{H2\text{-}H3}$ = 9.5 Hz, H_2), 5.49 (t, 4H, $^3J_{H3\text{-}H2}$ = $^3J_{H3\text{-}H4}$ = 9.5 Hz, H_3), 5.32 & 5.32 (2*t, 2H, $^3J_{H4\text{-}H3}$ = $^3J_{H4\text{-}H5}$ = 9.5 Hz, H_4), 4.58-4.39 (m, 4H, H_{28}), 4.23 & 4.22 (2*d, 2H, $^3J_{H5\text{-}H4}$ = 9.5 Hz, H_5), 4.34-3.61 (m, 48H, CH_2O_{DB24C8}), 3.49-3.34 (m, 4H, H_{26}), 3.09-2.96 (m, 4H, H_8), 2.65 (t, 4H, $^3J_{H16\text{-}H17}$ = 7.4 Hz, H_{16}), 1.98 & 1.97 & 1.79 & 1.79 (4*s, 18H, CH_3CO), 1.76-1.66 (m, 4H, H_{25}), 1.66-1.55 (m, 4H, H_{17}), 1.41-1.14 (m, 48H, H_9 H_{10} H_{11} H_{12} H_{13} H_{18} H_{19} H_{20} H_{21} H_{22} H_{23} H_{24}).

^{13}C NMR JMOD (CD_3CN, 100 MHz, 298K) : δ (ppm) = 170.7 & 170.1 & 169.7 ($\underline{C}OCH_3$), 166.2 (C_6), 149.4 & 148.6 & 147.1 & 146.9 (C_{15} C_A C_F C_M C_R), 126.2 (C_C), 121.5 (C_{14}),123.5 & 123.5 & 121.6 & 114.1 & 113.0 & 112.9 & 112.7 & 112.6 (C_B C_D C_E C_N C_O C_P C_Q), 85.5 (C_1), 76.0 (C_5), 72.9 (C_3), 70.8 (C_2), 69.8 (C_4), 72.9 & 71.5 & 71.3 & 71.3 & 71.2 & 71.0 & 68.4 & 68.2 & 67.9 & 67.9 ($\underline{C}H_2O_{DB24C8}$), 52.7 ($C_{28}$), 49.7 ($C_{26}$), 39.7 ($C_8$), 30.3 & 30.3 & 29.9 & 29.8 & 29.8 & 29.5 & 29.5 & 29.4 & 29.1 & 27.5 & 27.0 & 26.9 (C_9 C_{10} C_{11} C_{12} C_{13} C_{17} C_{18} C_{19} C_{20} C_{21} C_{22} C_{23} C_{24} C_{25}), 25.9 (C_{16}), 20.8 & 20.8 & 20.4 ($\underline{C}H_3CO$).

HRMS (ESI): $[M\text{-}2PF_6]^{2+}$; calcd for $[C_{112}H_{170}F_{10}O_{32}]^{2+}$: 1083.5991, found : 1083.5991

*3) Preparation of the double-lasso **5a-b***



5a **5b**

The double-lasso **4a-b** (28 mg, 0.0114 mmol) was suspended in 3 mL of iodomethane and stirred for four days at room temperature. Then, iodomethane was evaporated under reduced pressure and the obtained solid was washed with diethyl ether to give a yellow solid. NH_4PF_6 (11 mg, 0.0683 mmol, 6 equiv) and 5 mL of dichloromethane were added to a suspension of the previous product in 5 mL of milliQ water. The resulted bilayer solution was vigorously stirred for 30 min. After separation, the aqueous layer was extracted twice with 5 mL of dichloromethane. The organic layers were combined, dried over $MgSO_4$ and concentrated to afford the double-lasso **5a-b** (32 mg) in a quantitative yield as a yellow solid.

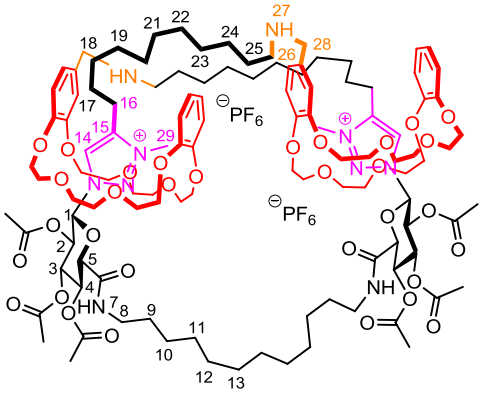
R_f (CH_2Cl_2/MeOH 9:1) 0.43

^{1}H NMR (CD_3CN, 400 MHz, 298K) : δ (ppm) = 8.50 (s, 2H, H_{14}), 7.00-6.88 & 6.71-6.57 (m, 4H, H_{27}), 6.84 (t, 2H, $^3J_{H7\text{-}H8}$ = 6.0 Hz, H_7), 6.88-6.71 (m, 12H, H_B H_D H_N H_O H_P H_Q), 6.42 (d, 2H, $^3J_{HE\text{-}HD}$ = 8.4 Hz, H_E), 6.15 (d, 2H, $^3J_{H1\text{-}H2}$ = 9.4 Hz, H_1), 5.59-5.49 (m, 4H, H_2 H_3), 5.37 & 5.36 (2*t, 2H, $^3J_{H4\text{-}H3}$ = $^3J_{H4\text{-}H5}$ = 9.4 Hz, H_4), 4.58-4.40 (m, 4H, H_{28}), 4.31 (d, 2H, $^3J_{H5\text{-}H4}$ = 9.4 Hz, H_5), 4.36-3.63 (m, 48H, CH_2O_{DB24C8}), 4.13 (s, 6H, H_{29}), 3.48-3.35 (m, 4H, H_{26}), 3.11-3.02 (m, 4H, H_8), 2.78 (t, 4H, $^3J_{H16\text{-}H17}$ = 7.6 Hz, H_{16}), 1.99 & 1.99 & 1.98 & 1.91 (4*s, 18H, CH_3CO), 1.78-1.63 (m, 8H, H_{17} H_{25}), 1.46-1.33 (m, 12H, H_9 H_{18} H_{24}), 1.33-1.13 (m, 36H, H_{10} H_{11} H_{12} H_{13} H_{19} H_{20} H_{21} H_{22} H_{23}).

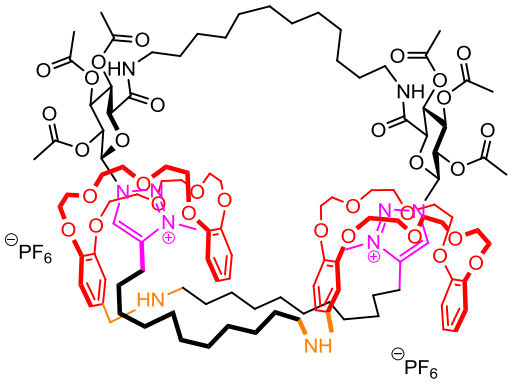
^{13}C NMR JMOD (CD_3CN, 100 MHz, 298K) : δ (ppm) = 170.6 & 170.1 & 170.0 ($\underline{C}OCH_3$), 165.4 (C_6), 148.6 & 148.6 & 147.1 & 147.0 & 146.9 (C_{15} C_A C_F C_M C_R), 127.6 (C_{14}), 126.2 (C_C), 123.5 & 121.6 & 114.1 & 112.9 & 112.7 & 112.6 (C_B C_D C_E C_N C_O C_P C_Q), 87.9 (C_1), 76.2 (C_5), 72.1 (C_3), 70.7 (C_2), 69.2 (C_4), 72.9 & 72.9 & 71.5 & 71.5 & 71.3 & 71.2 & 71.0 & 68.4 & 68.2 & 68.0 & 67.9 ($\underline{C}H_2O_{DB24C8}$), 52.7 ($C_{28}$), 49.7 ($C_{26}$), 39.9 ($C_8$), 38.9 ($C_{29}$), 30.4 & 30.4 & 30.0 & 30.0 & 29.9 & 29.8 & 29.7 & 29.3 & 29.3 & 27.5 & 27.1 & 27.0 (C_9 C_{10} C_{11} C_{12} C_{13} C_{17} C_{18} C_{19} C_{20} C_{21} C_{22} C_{23} C_{24} C_{25}), 23.8 (C_{16}), 20.8 & 20.7 & 20.5 ($\underline{C}H_3CO$).

HRMS (ESI): $[M\text{-}3PF_6]^{3+}$; calcd for $[C_{114}H_{176}F_6N_{10}O_{32}P]^{3+}$: 780.7365, found : 780.7440

*4) Preparation of the double-lasso **6a-b***



6a



6b

A solution of the double-lasso **5a-b** (22 mg, $7.917.10^{-6}$ mol) in 5 mL of dichoromethane was washed with 5 mL of an aqueous solution of NaOH 1M. After separation, the aqueous layer was extracted twice with 5 ml of dichlorométhane and the combined organic phases were dried over $MgSO_4$ and then evaporated to obtain product **6a-b** as a yellow solid (20 mg, quantitative).

R_f (CH_2Cl_2/MeOH 9:1) 0.46
^{1}H NMR (CD_3CN, 400 MHz, 298K) : δ (ppm) = 9.54 & 9.51 (2*s, 2H, H_{14}), 7.04 & 7.00 (2*t, 2H, $^3J_{H7\text{-}H8}$ = 6.0 & 5.7 Hz, H_7), 6.96-6.71 (m, 14H, H_B H_D H_E H_N H_O H_P H_Q), 6.19 & 6.16 (2*d, 2H, $^3J_{H1\text{-}H2}$ = 9.2 Hz, H_1), 5.58-5.50 (m, 2H, H_4), 5.44-5.29 (m, 4H, H_2 H_3), 4.40 & 4.39 (2*d, 2H, $^3J_{H5\text{-}H4}$ = 9.2 Hz, H_5), 4.36 & 4.36 (2*s, 6H, H_{29}), 4.28-3.10 (m, 48H, CH_2O_{DB24C8}), 3.74-3.56 (m, 4H, H_{28}), 3.24-3.10 (m, 4H, H_{26}), 3.08-2.95 & 2.73-2.63 (2*m, 4H, H_8), 2.53-2.42 (m, 4H, H_{16}), 2.00 & 1.99 (2*s, 18H, CH_3CO), 1.76-1.49 (m, 8 H, H_{17} H_{25}), 1.49-0.57 (m, 48H, H_9 H_{10} H_{11} H_{12} H_{13} H_{18} H_{19} H_{20} H_{21} H_{22} H_{23} H_{24}).

*5) Reprotonation procedure of **6a-b***

The double-lasso **6a-b** (20 mg, $7.917.10^{-6}$ mol) was suspended in 2 mL of a solution of HCl 2M in diethyl ether and stirred for 30 min at room temperature. After evaporation, the solid was washed with diethyl ether. Then, NH_4PF_6 (6.4 mg, $3.959.10^{-5}$ mol, 5 equiv) and 2 mL of dichloromethane were added to a suspension of the previous product in 2 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 $MgSO_4$ and concentrated to obtain the double-lasso **5a-b** (20 mg, 89%) as a yellow solid.

E. Molecular Modeling

NMR: NMR spectra were acquired on a Bruker Avance spectrometer operating at 500MHz. For DOSY experiments the standard Bruker sequence with double stimulated echoes and 3 spoil gradients for convection compensation was employed. Pulse field gradients were incremented in 64 steps from 2% to 95% of the maximum gradient strength. 48 scans were

used for each increment with a gradients length of 1.8 ms and a diffusion time of 200 ms. The spectra were processed by using Bruker´s Topspin2.0 software, and the diffusion coefficients were obtained directly from the spectra. Different solvents ($CDCl_3$, CD_3CN and DMSO-d6) and temperatures (from 298 to 278K) were employed. In DMSO and $CDCl_3$, diffusion coefficient between the protonated and non-protonated species does not change (see for example figures 1, 2 and 3). However, a significant variation was observed in CD_3CN at 278K (figure 4).

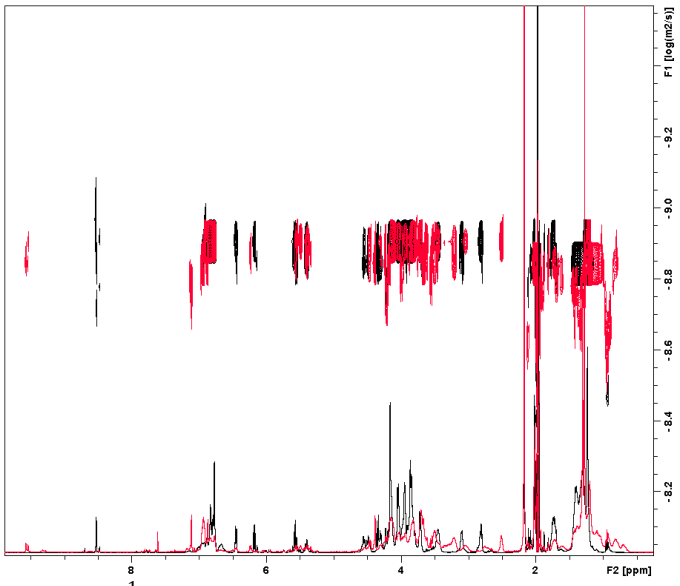


Figure 1. ^1H and DOSY spectra (500 MHz, **CD_3CN at 295K**). In black: spectra corresponding to the protonated species and, in red, spectra corresponding to the non protonated species. The diffusion coefficients of both compounds under these conditions is 1.23×10(-9) (from value in the abscise axe -8.907).

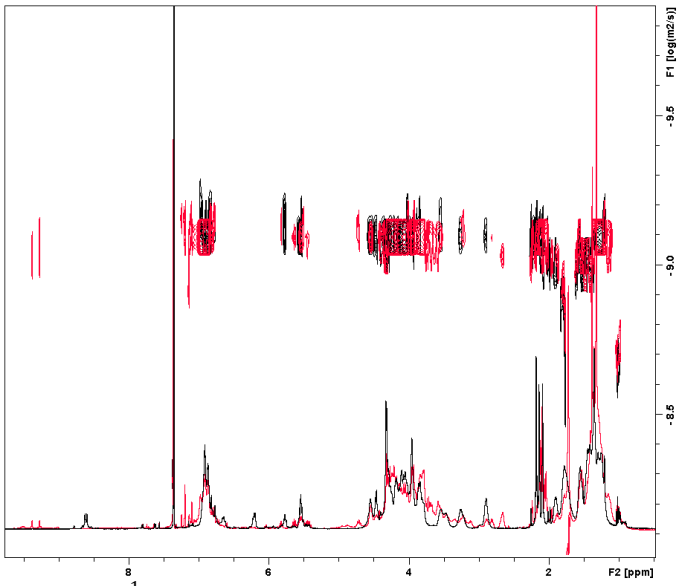


Figure 2. ^1H and DOSY spectra (500 MHz, **$CDCl_3$ at 295K**). In black: spectra corresponding to the protonated species and, in red, spectra corresponding to the non protonated species. The diffusion coefficients of both compounds under these conditions is 8.00×10(-10) (from value in the abscise axe -9.097).

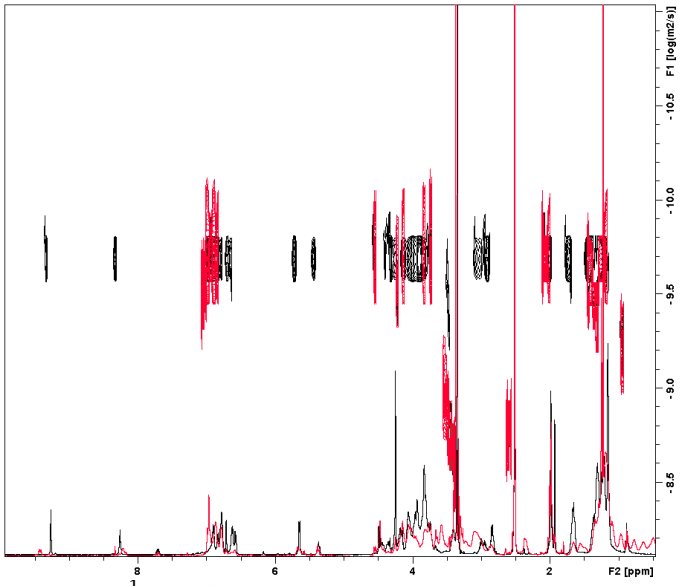


Figure 3. ^{1}H and DOSY spectra (500 MHz, **DMSO at 295K**). In black: spectra corresponding to the protonated species and, in red, spectra corresponding to the non protonated species. The diffusion coefficients of both compounds under these conditions is 2.05×10(-10) (from value in the abscise axe -9.688).

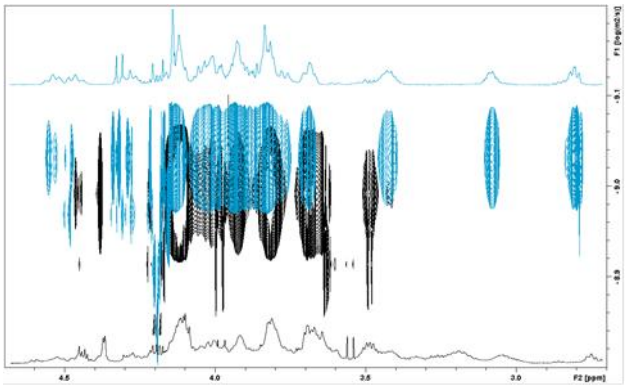


Figure 4. Partial DOSY spectra (500 MHz, **CD_3CN, 278 K**) of the protonated double-lasso macrocycle **5 (**in blue) and the deprotonated double-lasso macrocycle **6** (in black) The diffusion coefficients of protonated compound **5** and deprotonated compound **6** are respectively 8.93x10(-10) and 9.66x10(-10) under these conditions.

Modeling: The structures of compounds **5a**, **5b**, **6a** and **6b** were built in Maestro. As a starting point for the two interlocked DB24C8 units (in **5a** and **5b**), we took the crystallographic structure of a dibenzo-24-crown-8-ether deposited in the Cambridge crystallographic Data Centre (CCDC) with the TEVBEB CCDC code. The structures were submitted to minimization by use of conjugate gradients and/or Monte Carlo Torsional Sampling Conformational Search (MCMM) with the OPLS2005 force field with electrostatic treatment for acetonitrile, and 1500 minimum number of steps. The modeling of compounds **5** and **6** was carried out in using a continuum solvent model: (Generalized-Born/Surface Area, GB/SA). The actual counterions were not included in the calculations, given the lack of proper parameters of the force field for $PF6^-$. However, we performed several calculations

employing other simple counterions, such as phosphate (Figure 5). None effect in the results was observed.

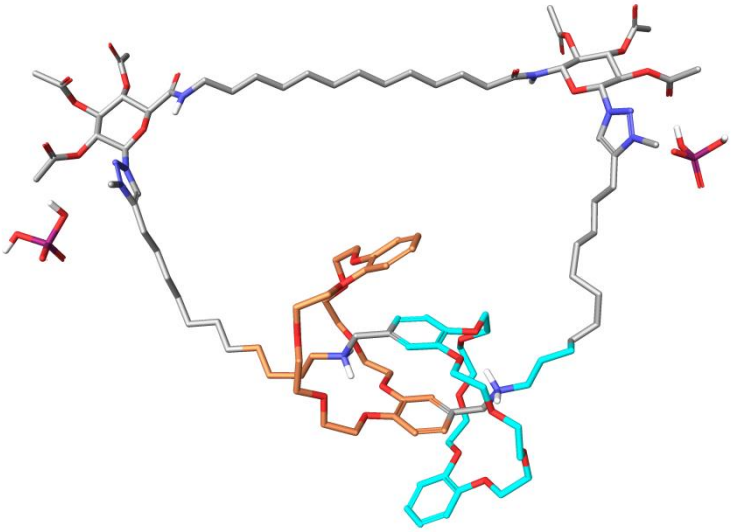
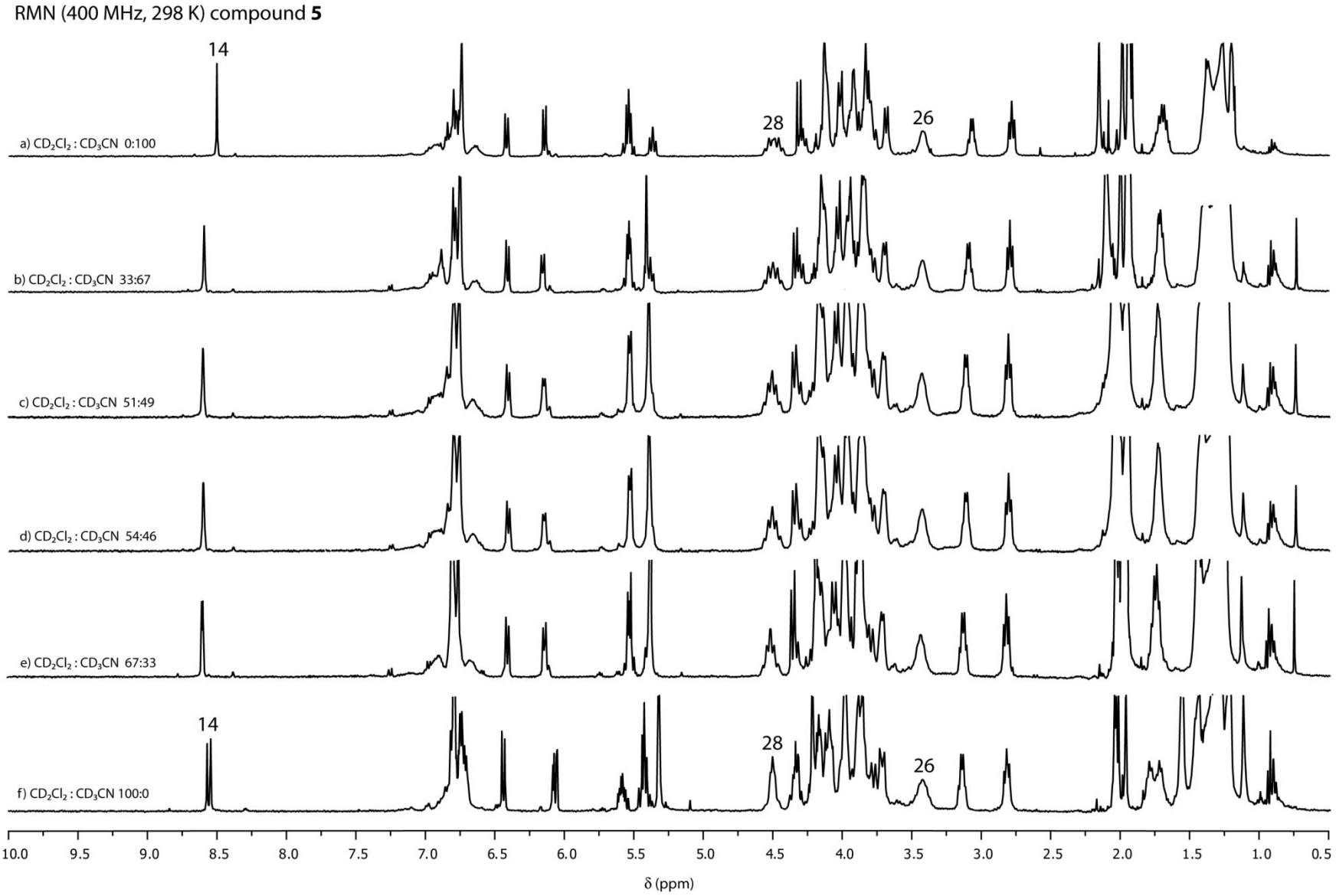
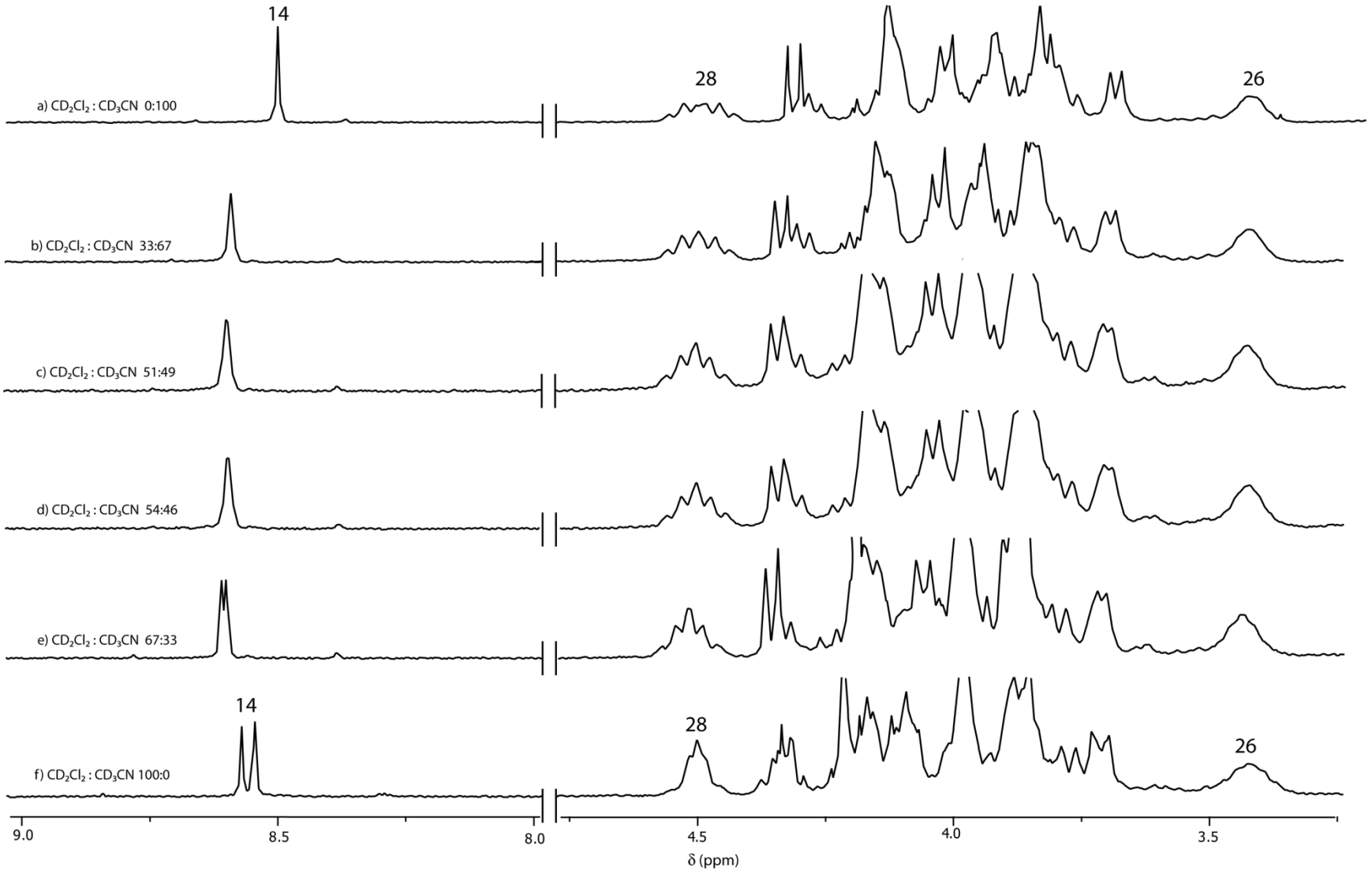


Figure 5. OPLS2005 minimised structure of compound **5b** with $H_2PO_4^-$ counterions on the triazolium.

F. Stack plot and partial zoomed stack plot ^{1}H NMR (400 MHz, 298K) of double-lasso 5 in different solvents

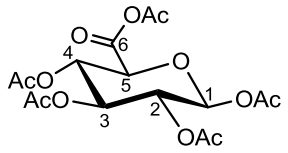


RMN (400 MHz, 298 K) compound **5**

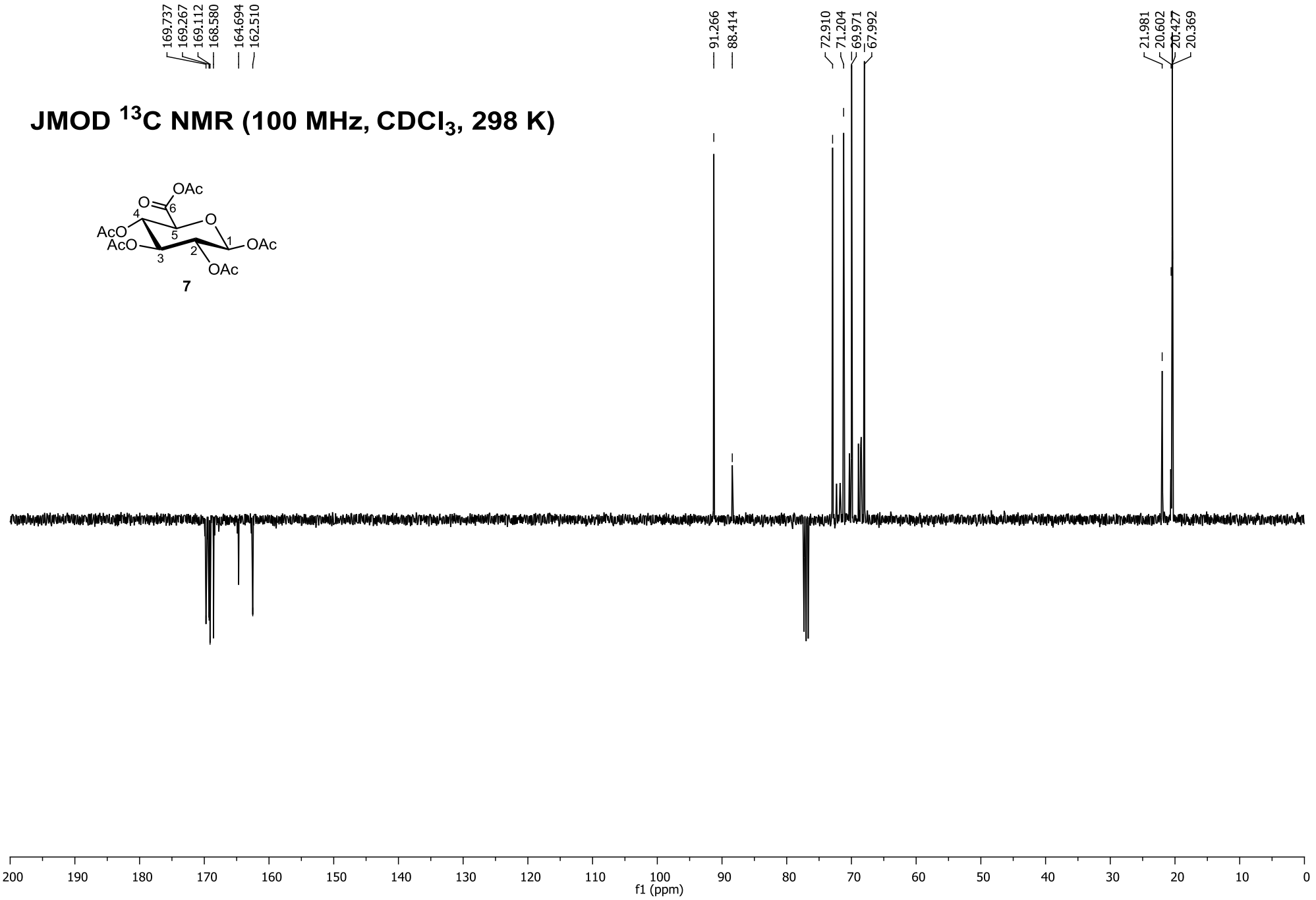


NMR Spectra

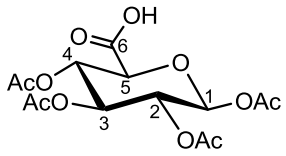
^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



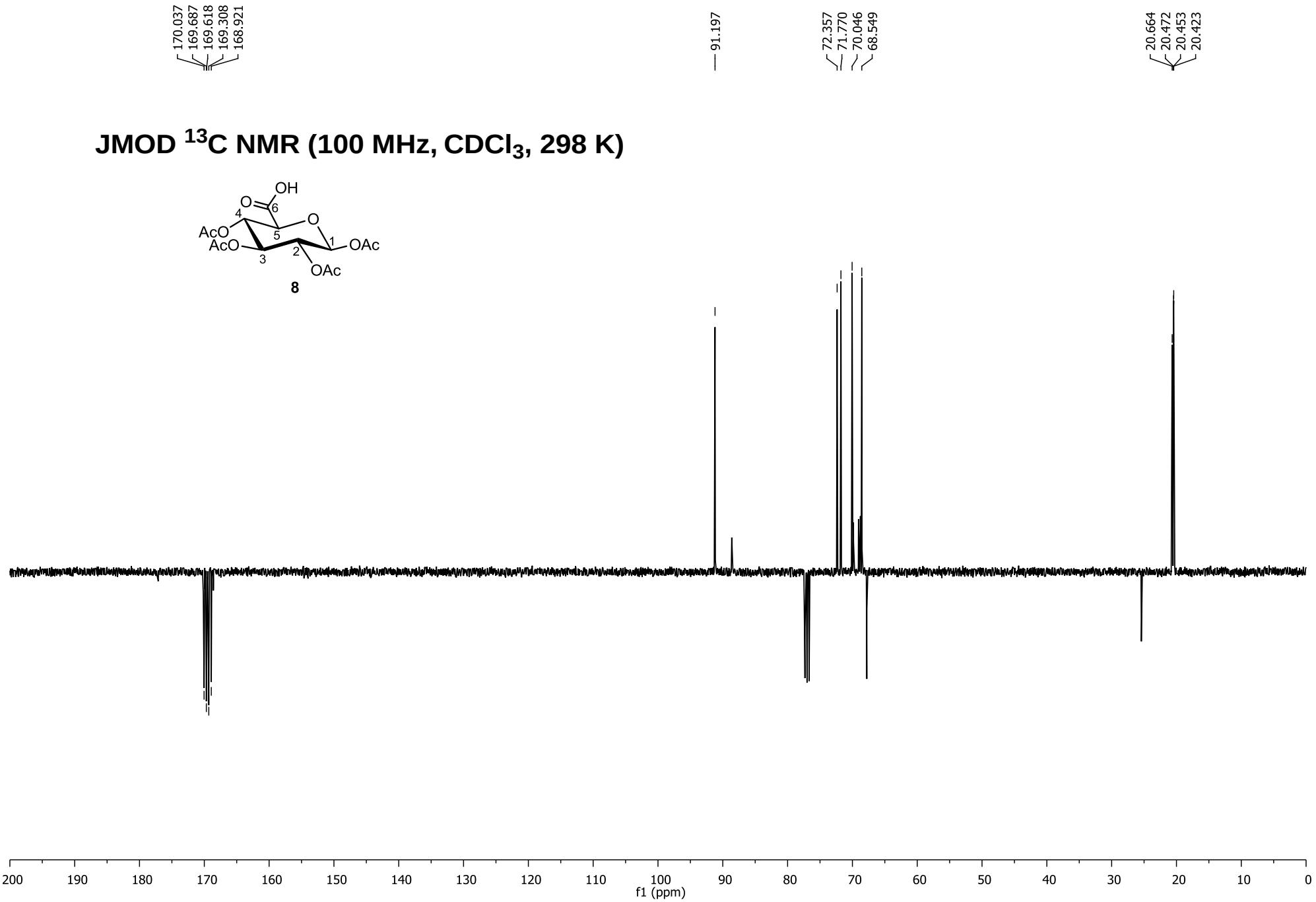
7

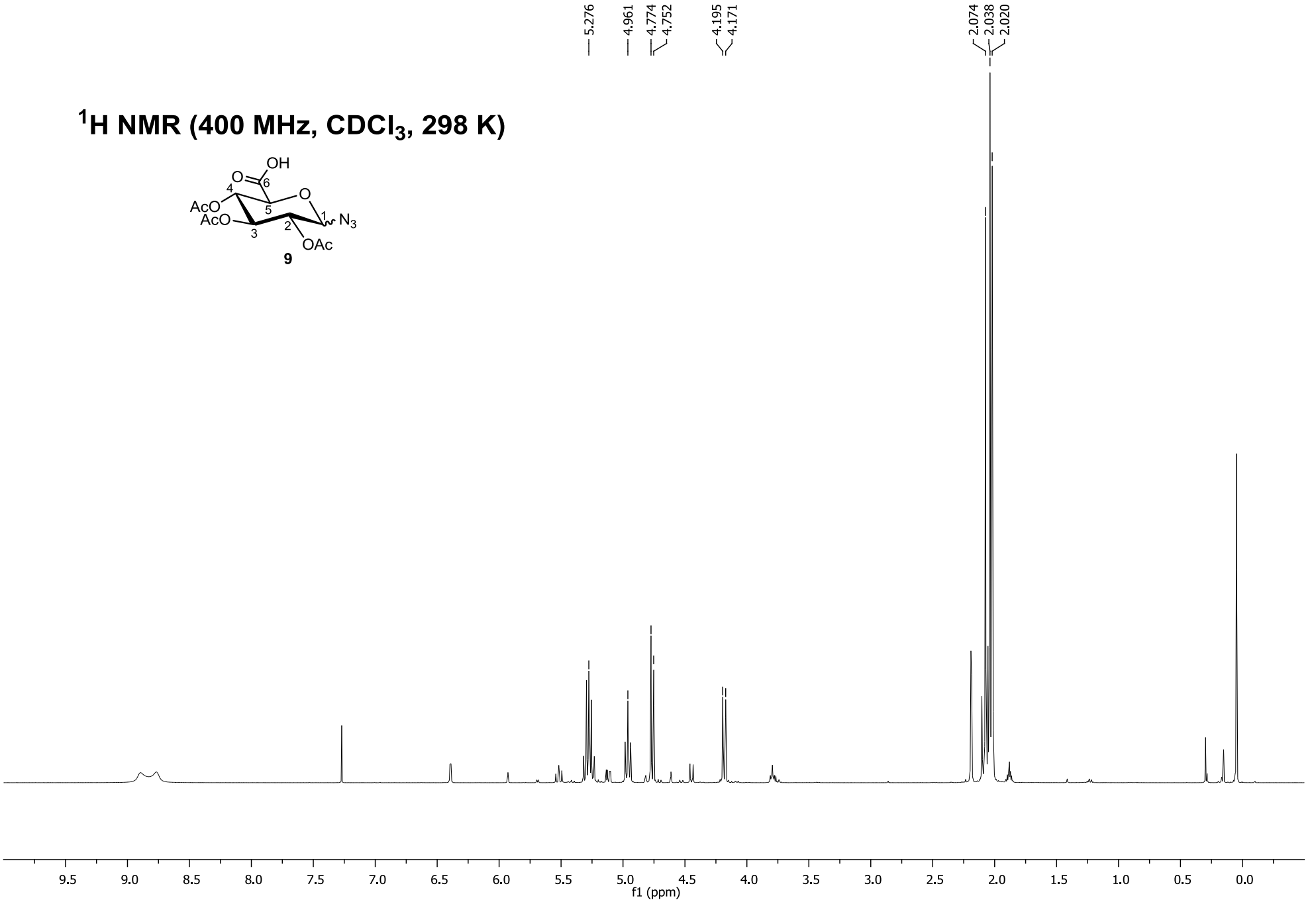


^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



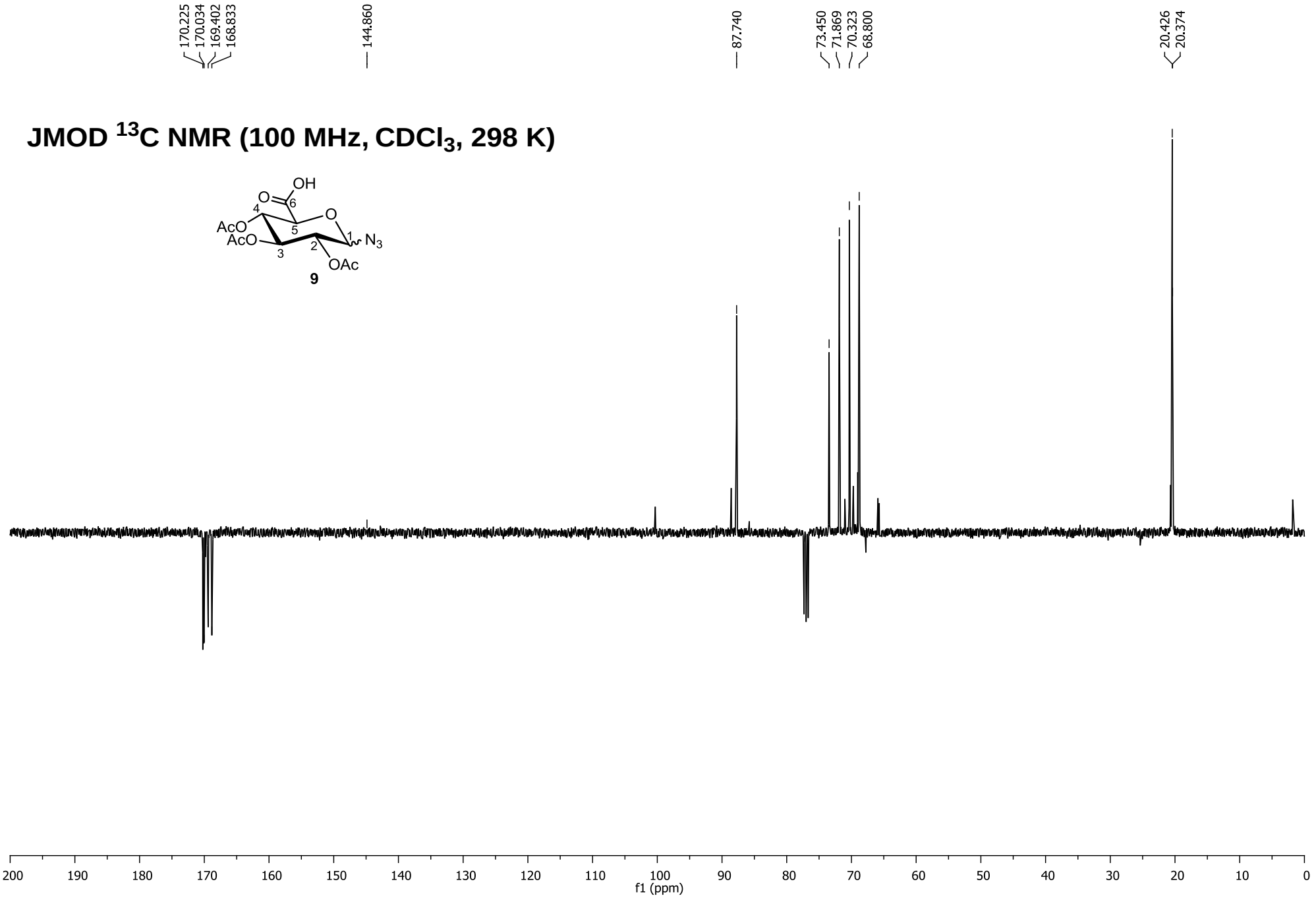
8



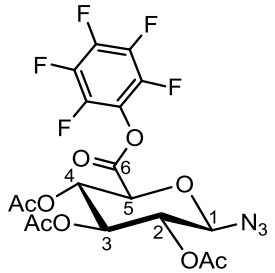


^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

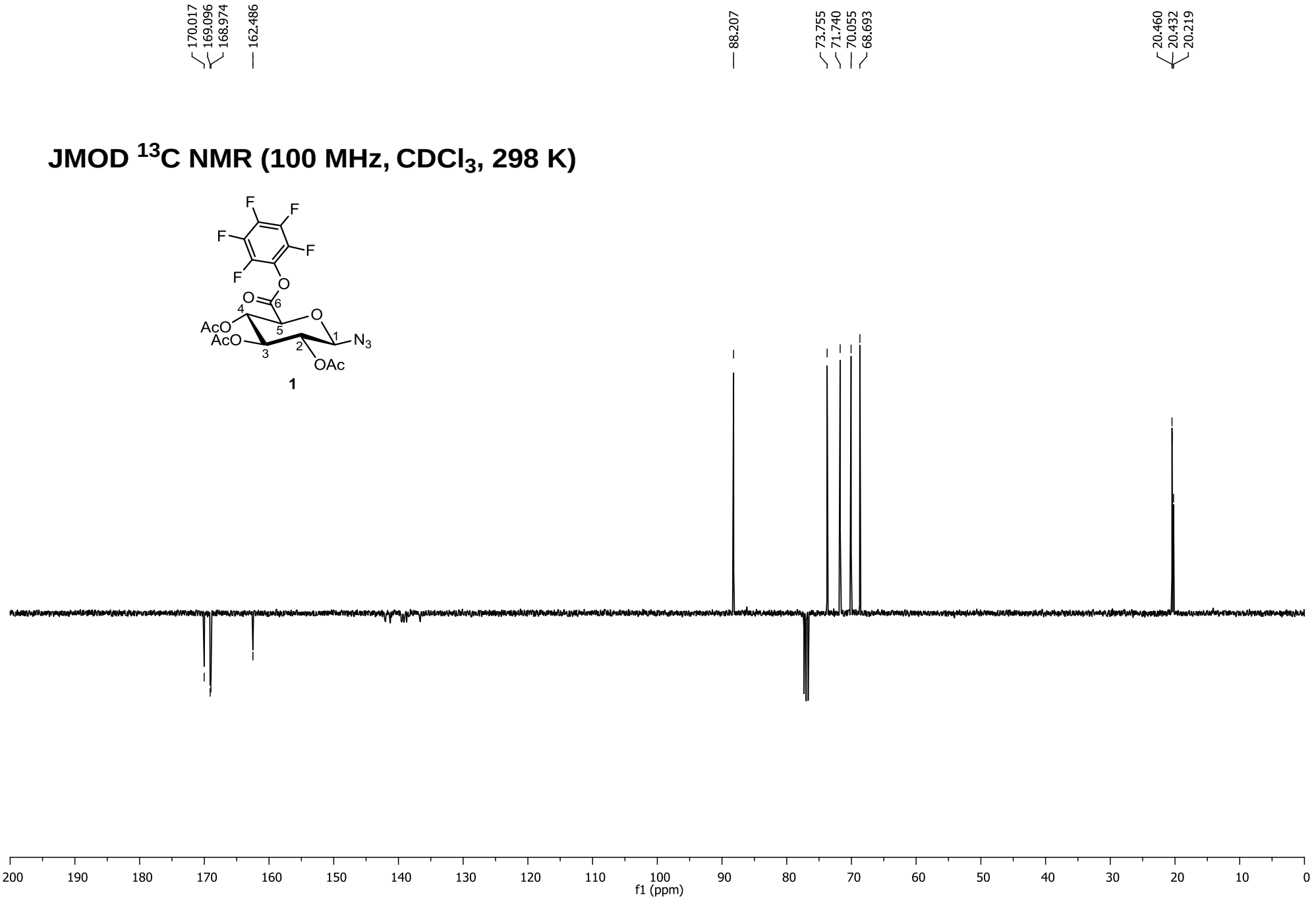
9


170.225
170.034
169.402
168.833
144.860
87.740
73.450
71.869
70.323
68.800
20.426
20.374
JMOD 13C NMR (100 MHz, CDCl3, 298 K)
OH
O
6
4
O
AcO
5
1
N3
AcO
3
2
OAc
9
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

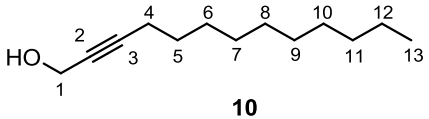
^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



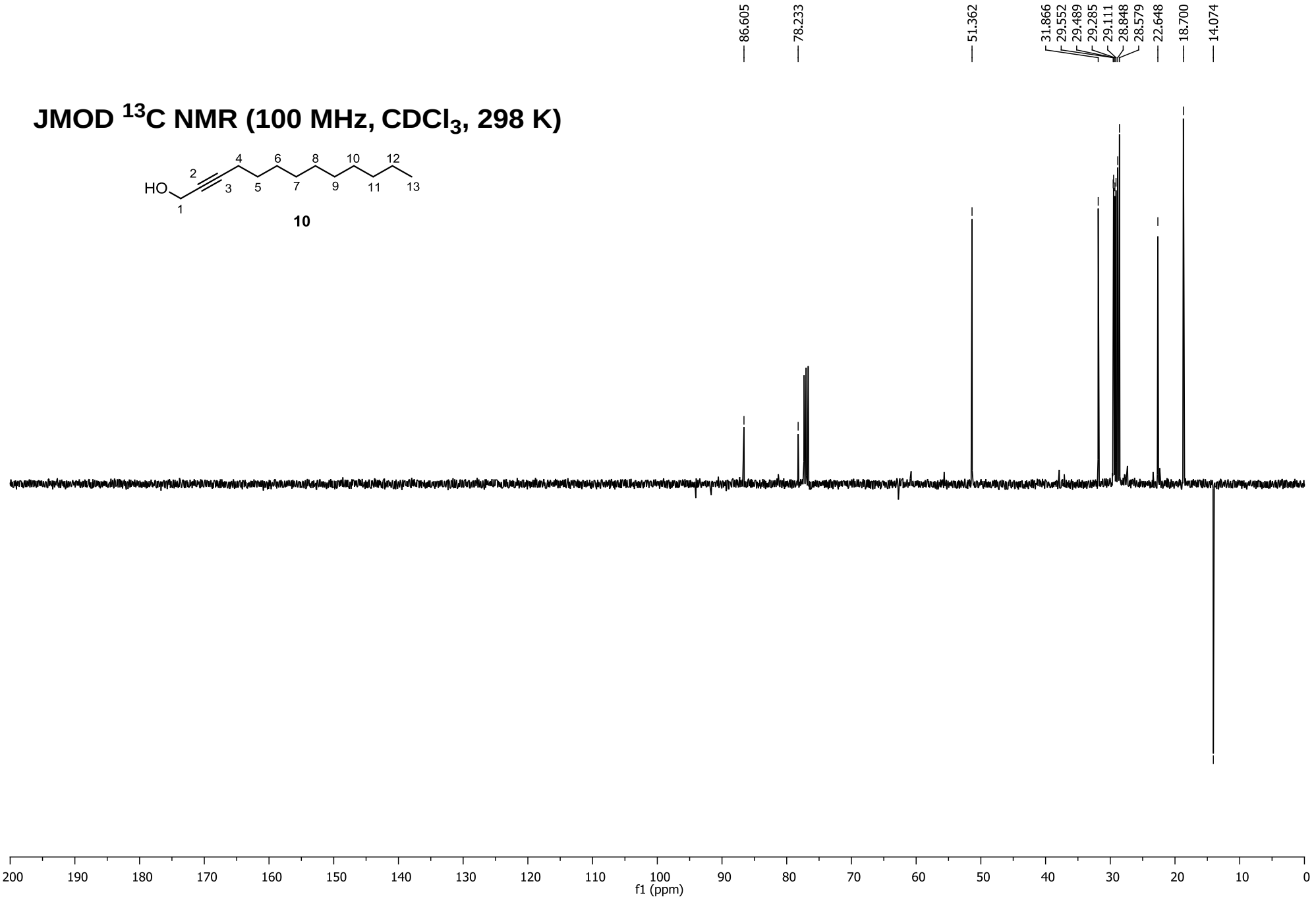
1



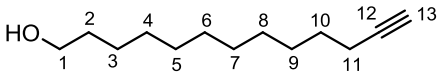
^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



10

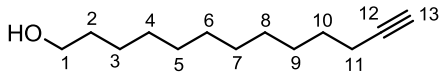


^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



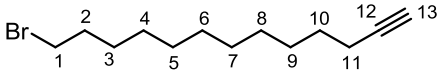
11

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



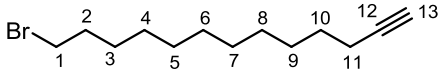
11

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



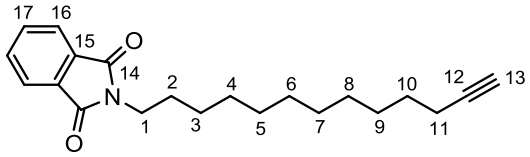
12

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

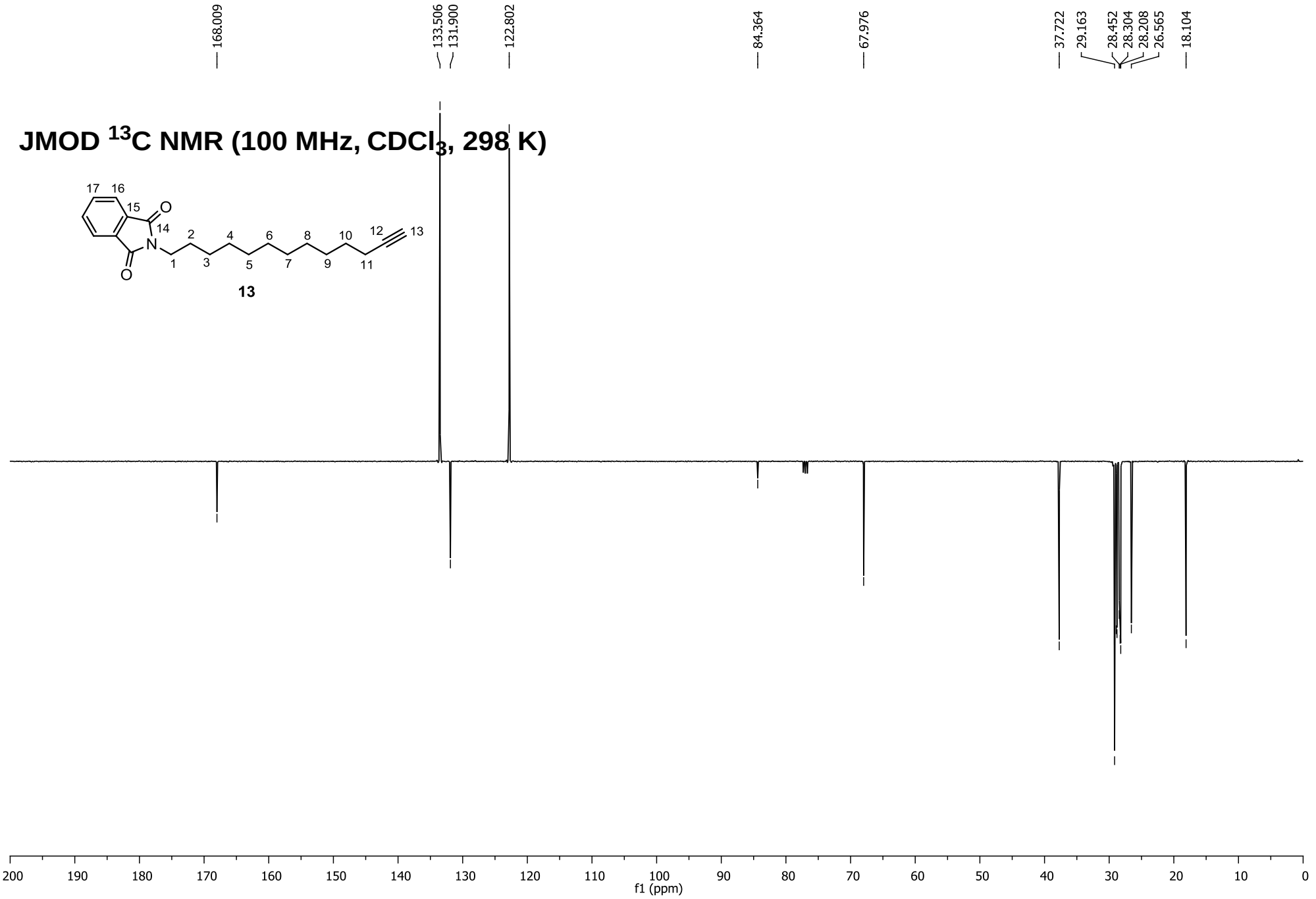


12

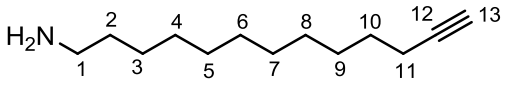
^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



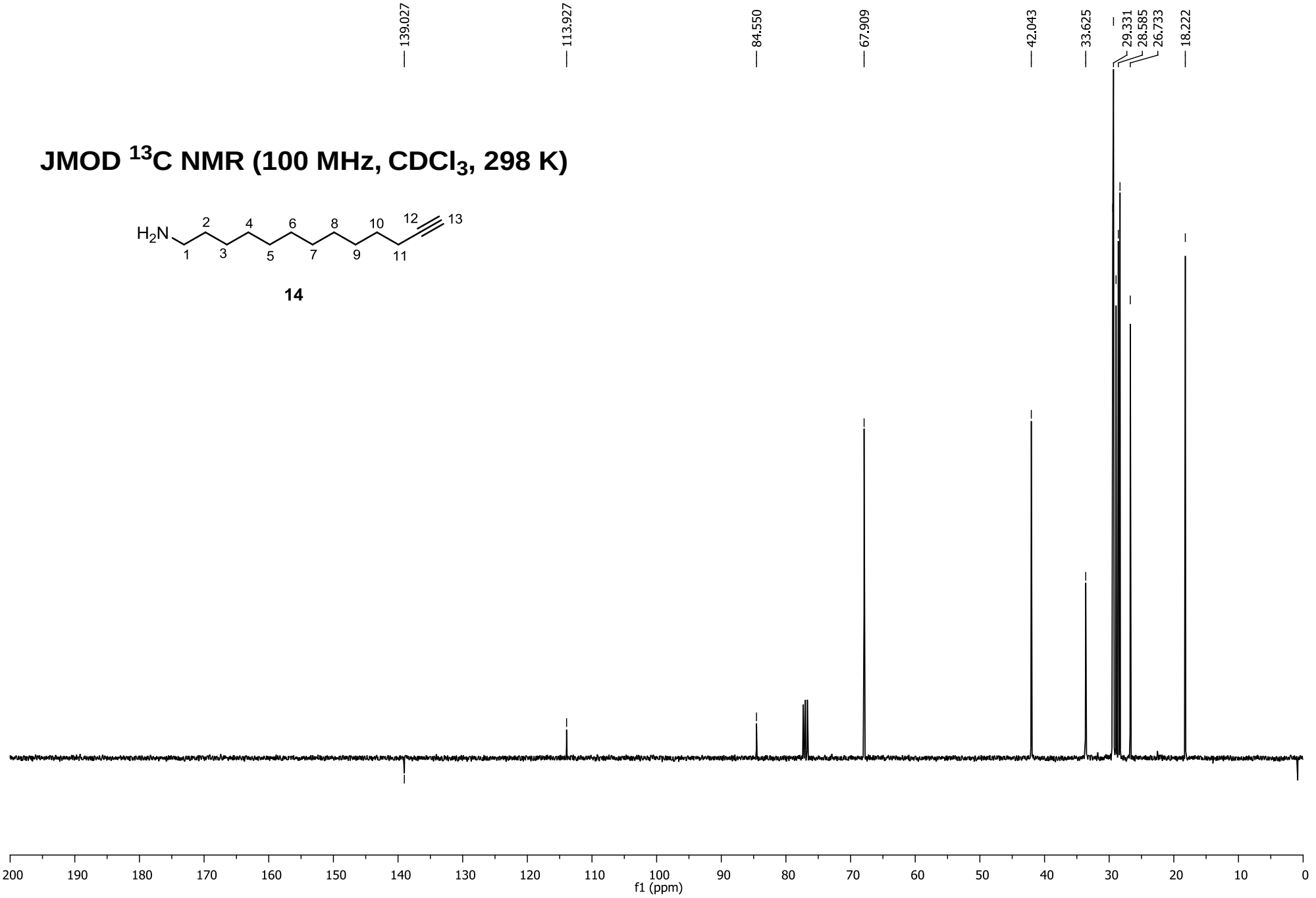
13

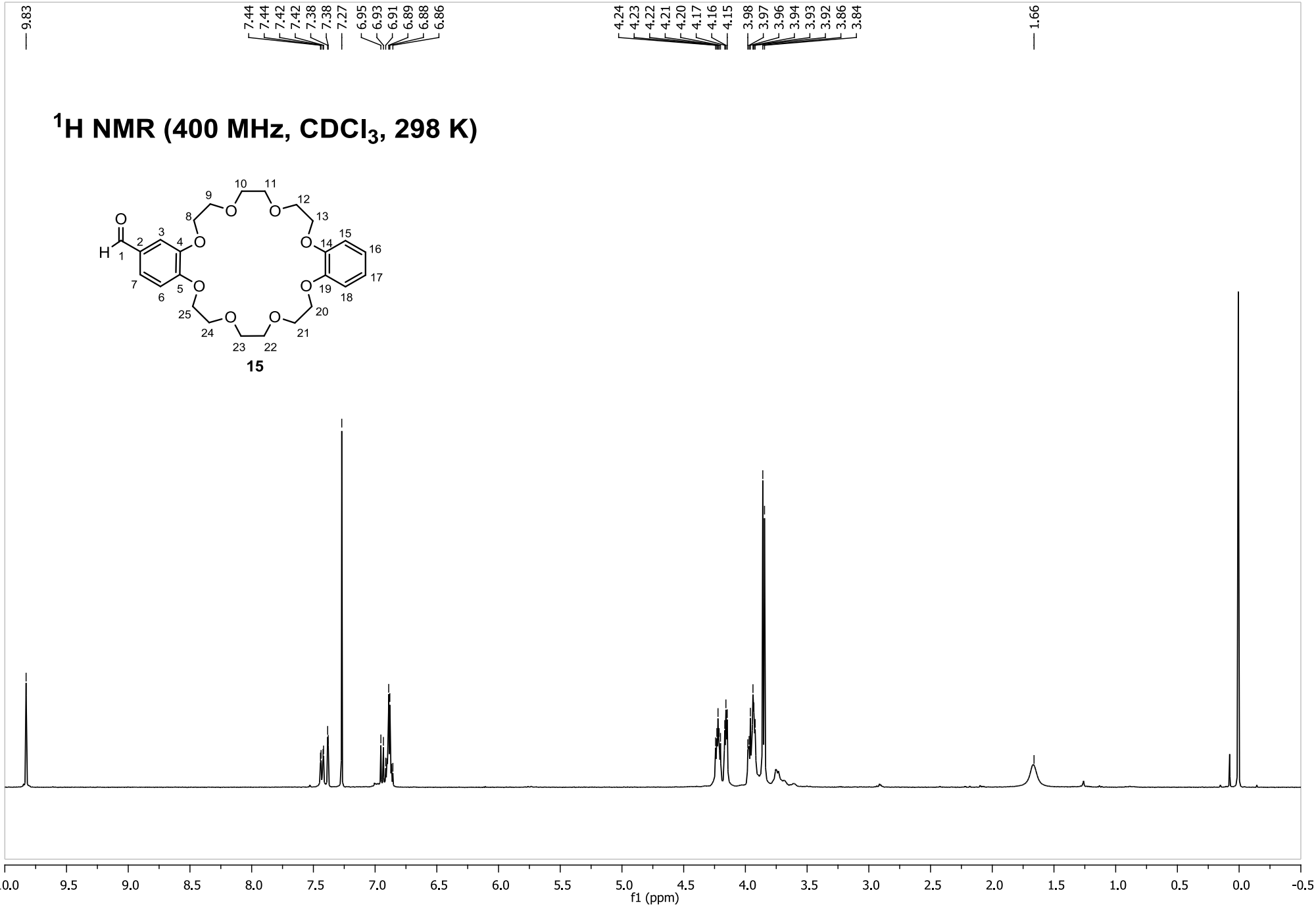


^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



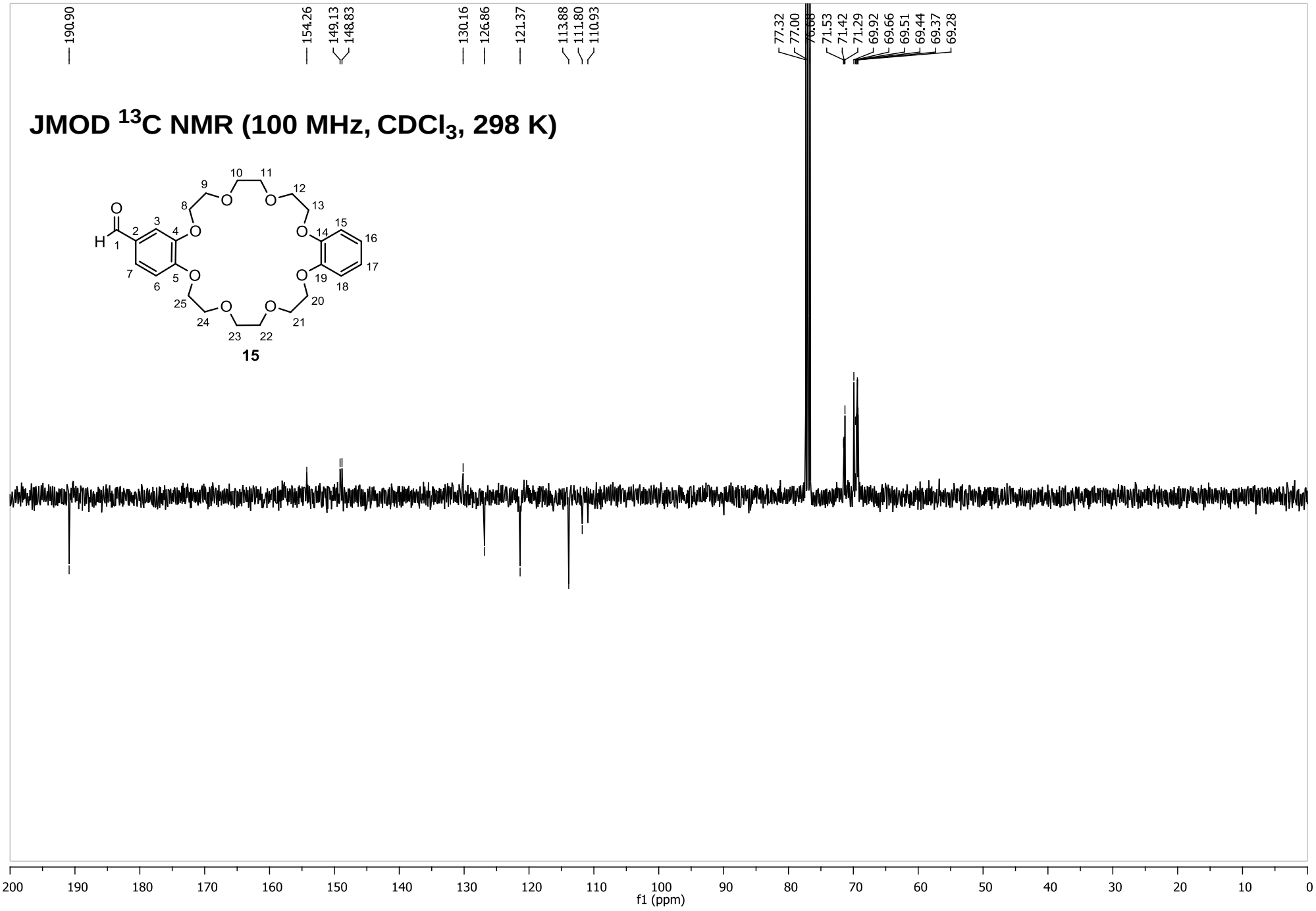
14



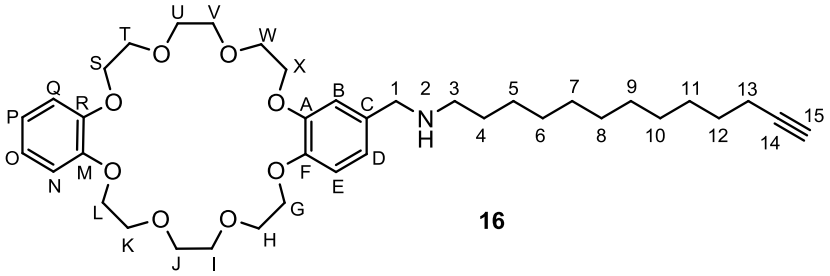


^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

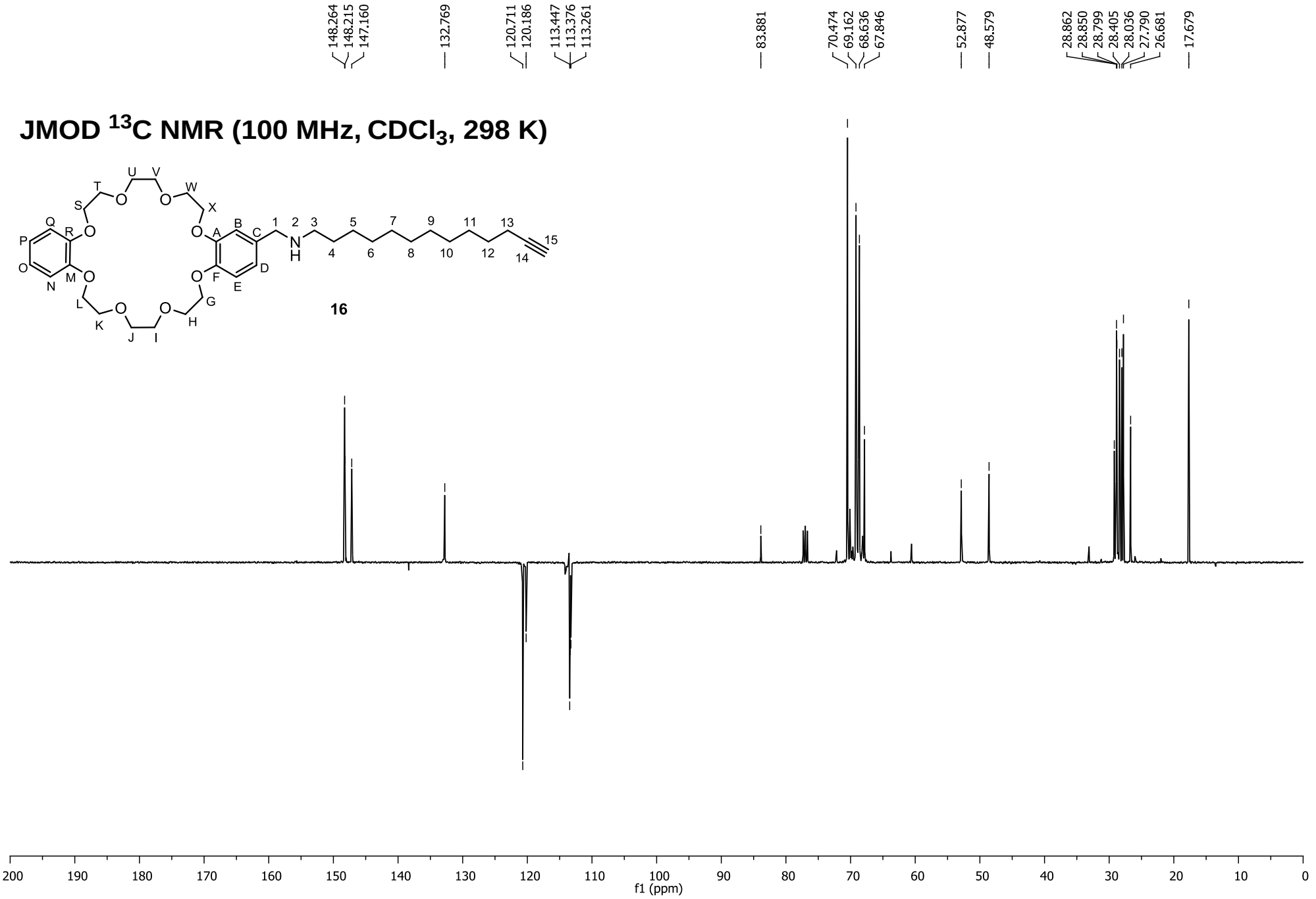
15

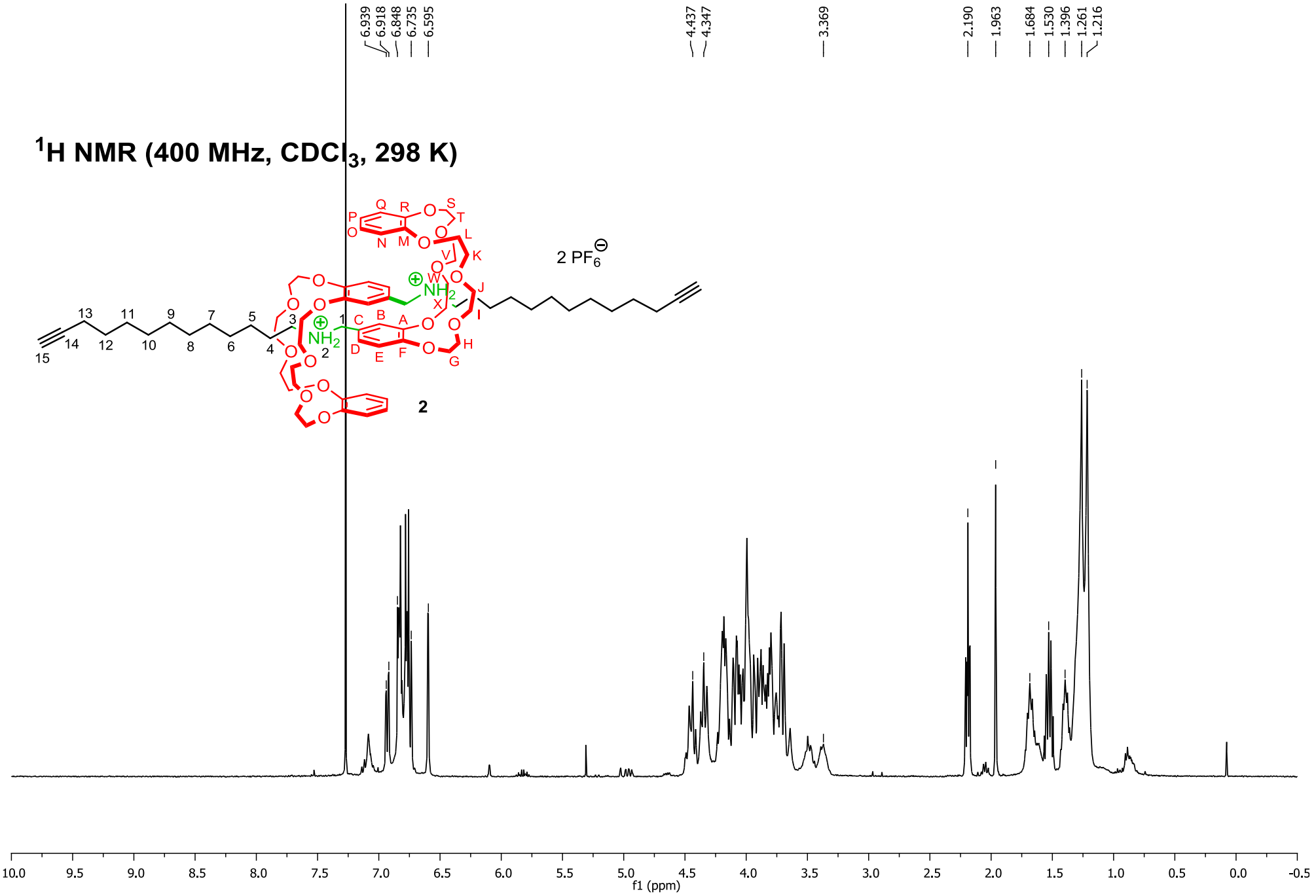


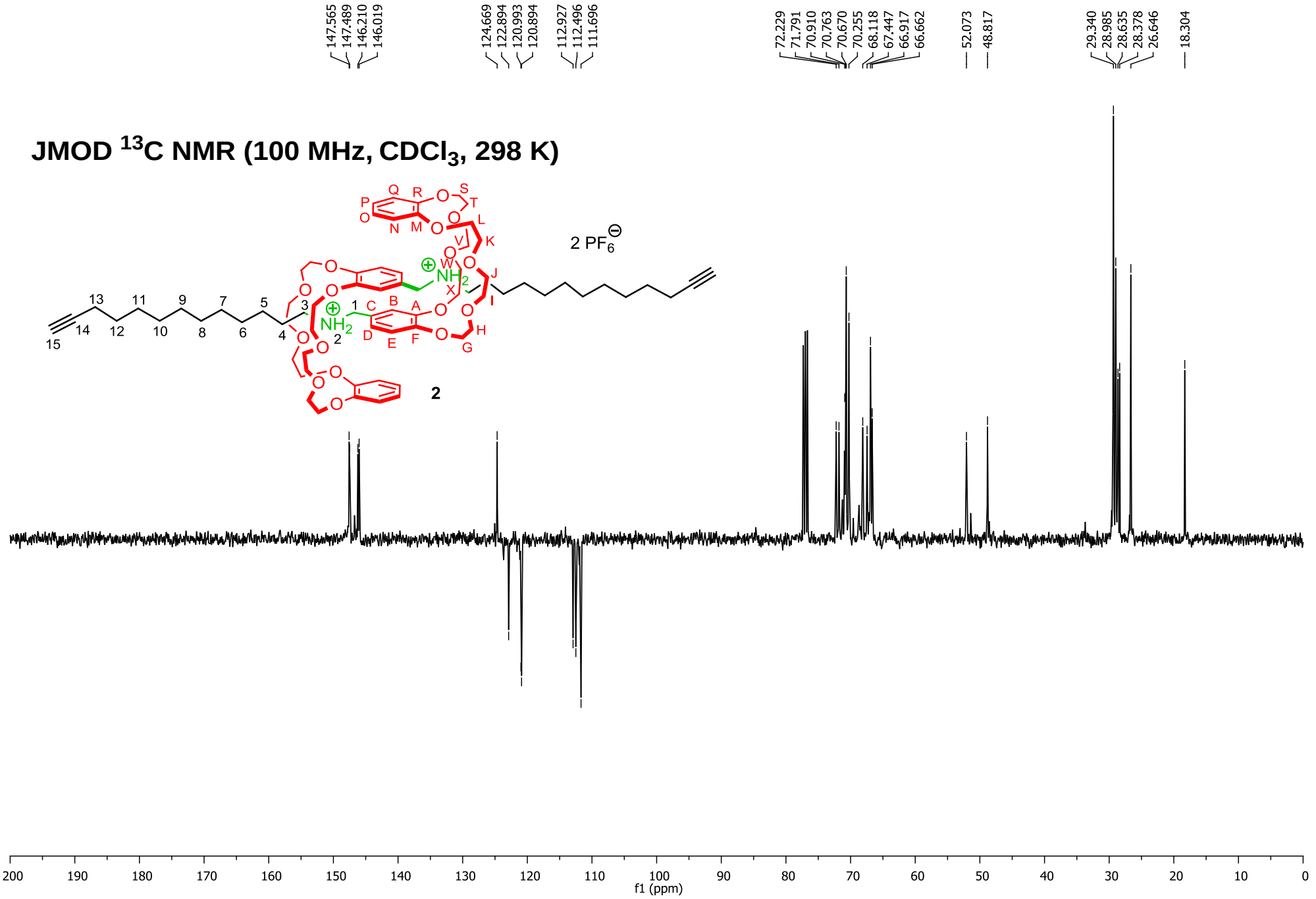
^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



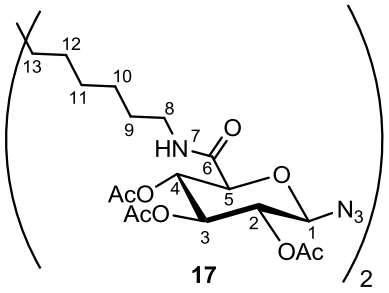
16



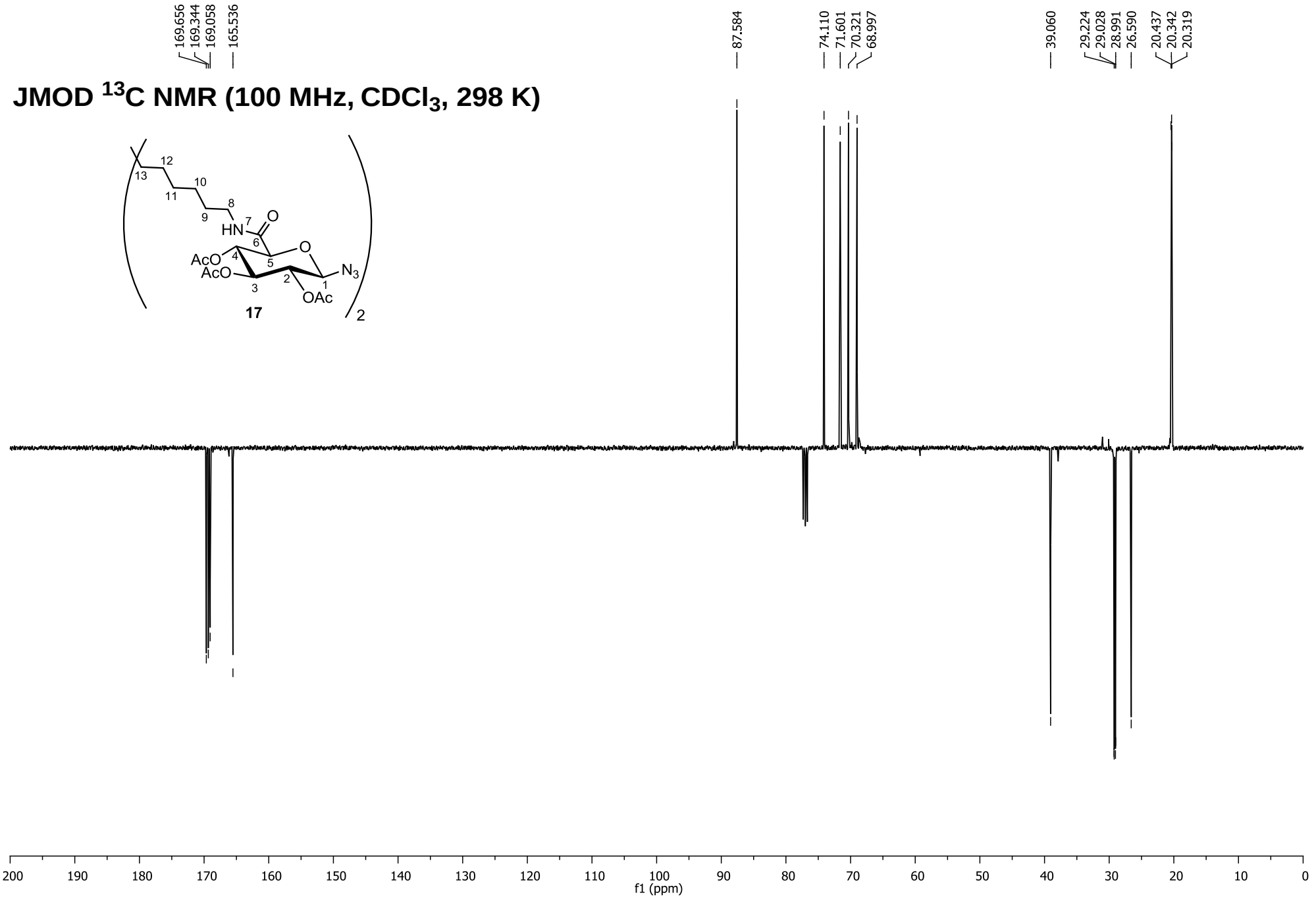


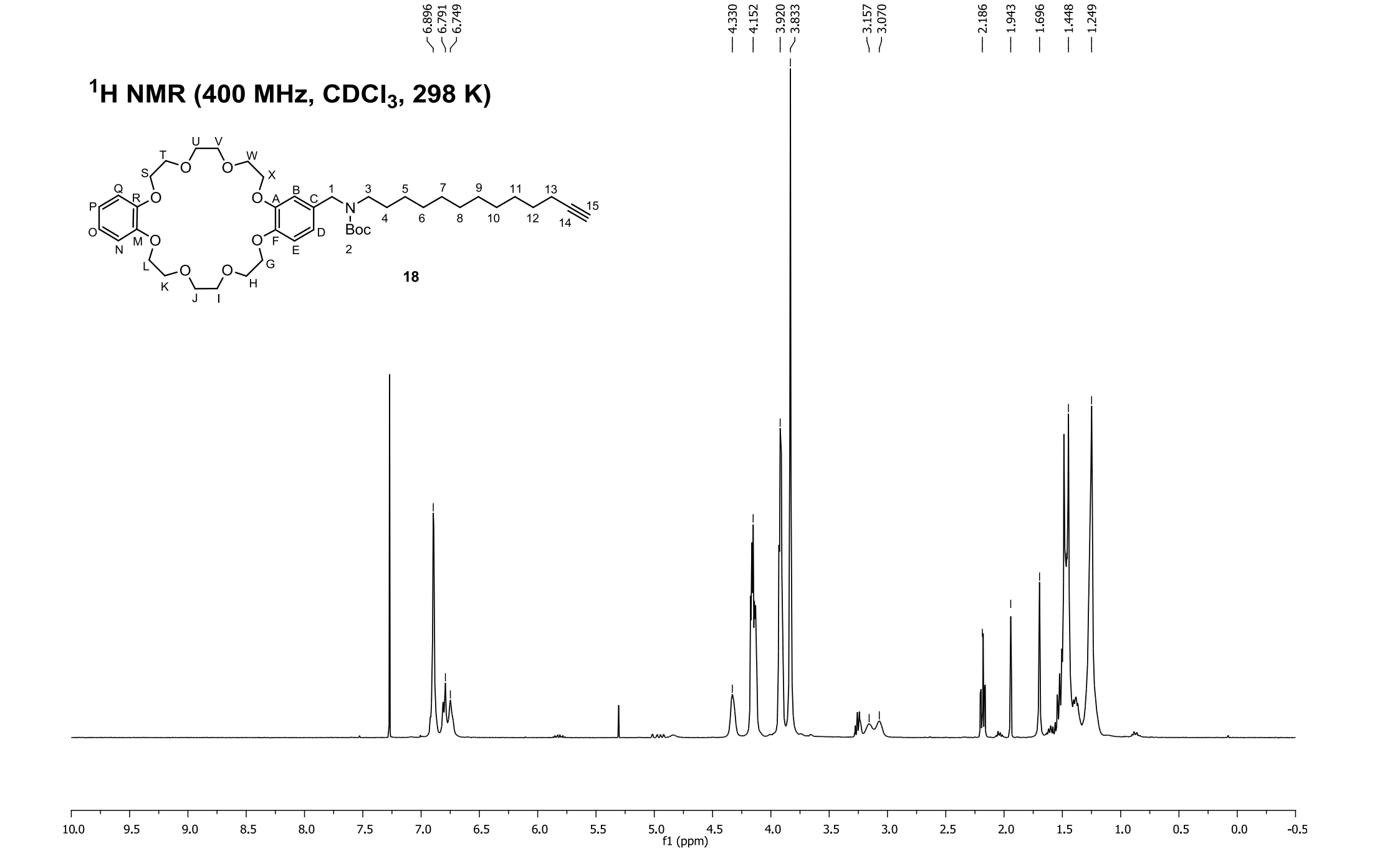


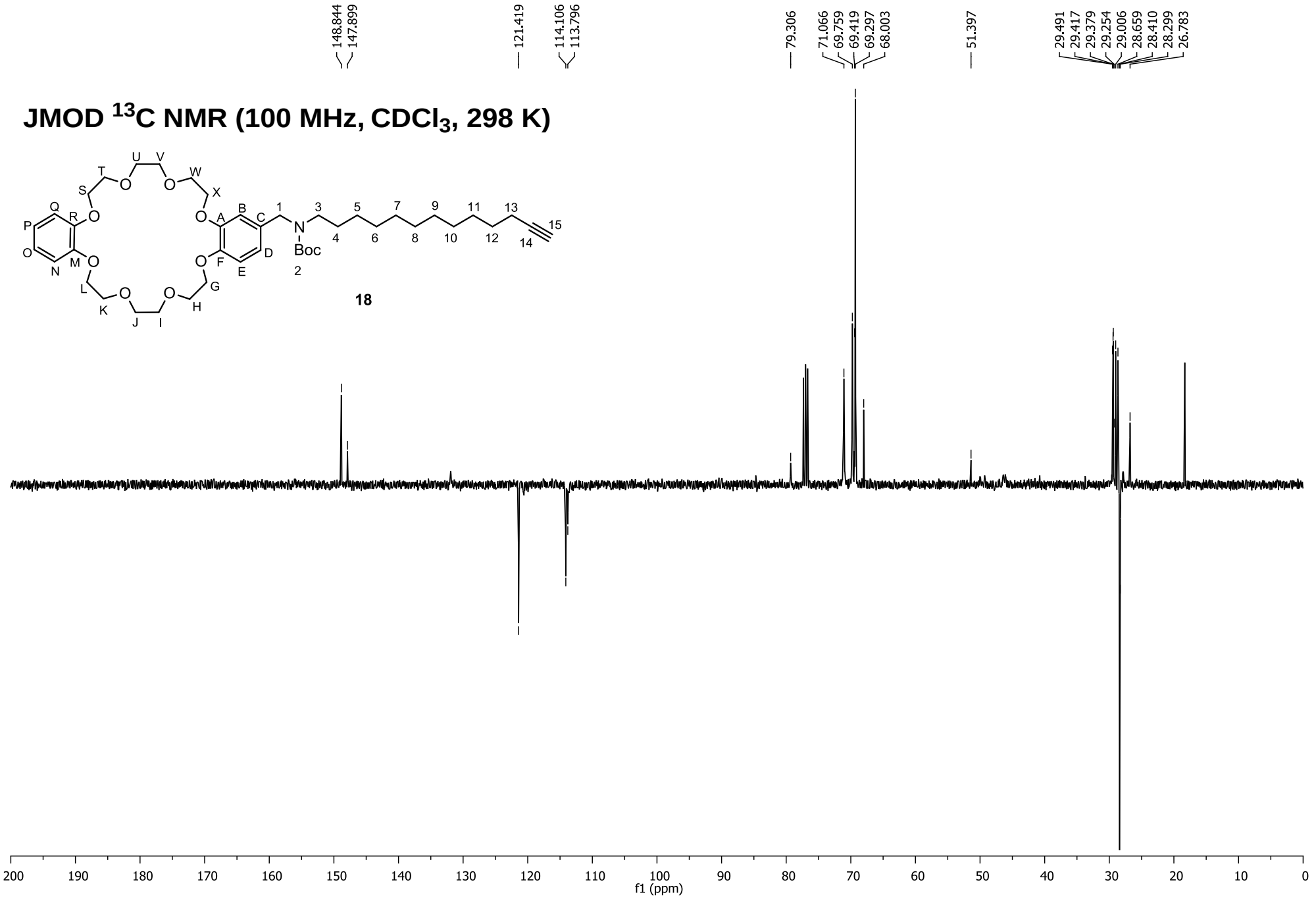
^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

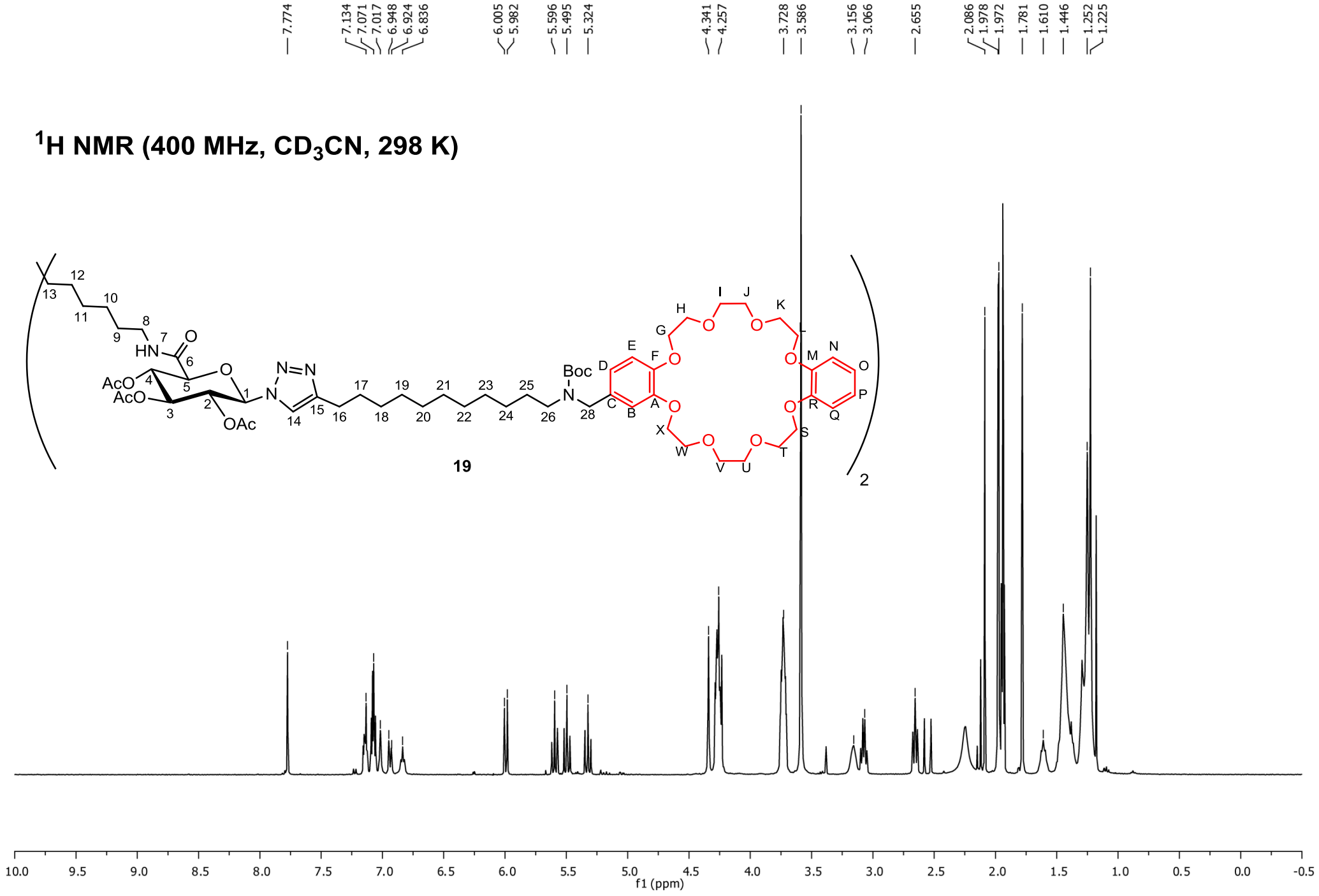


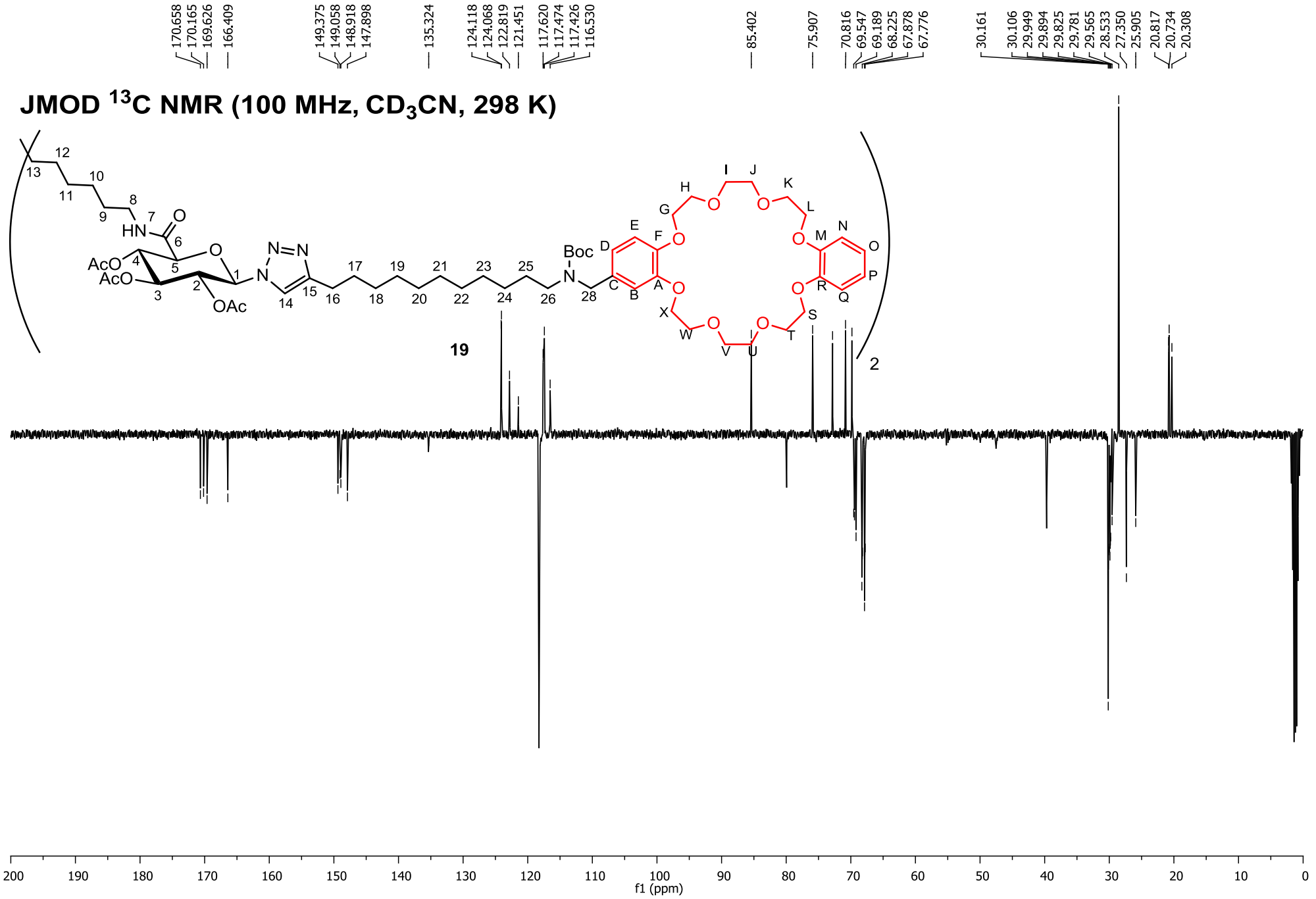
17

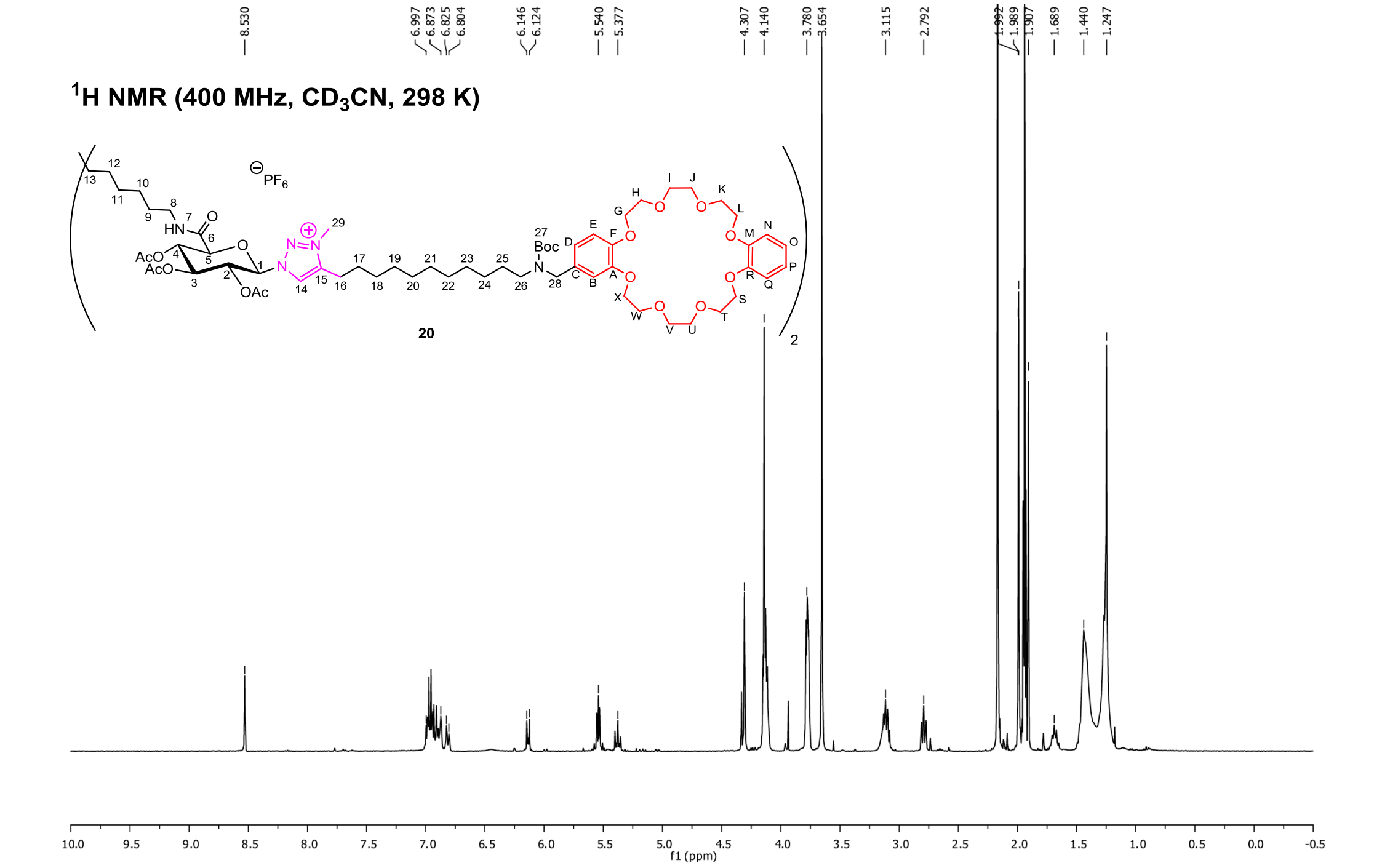


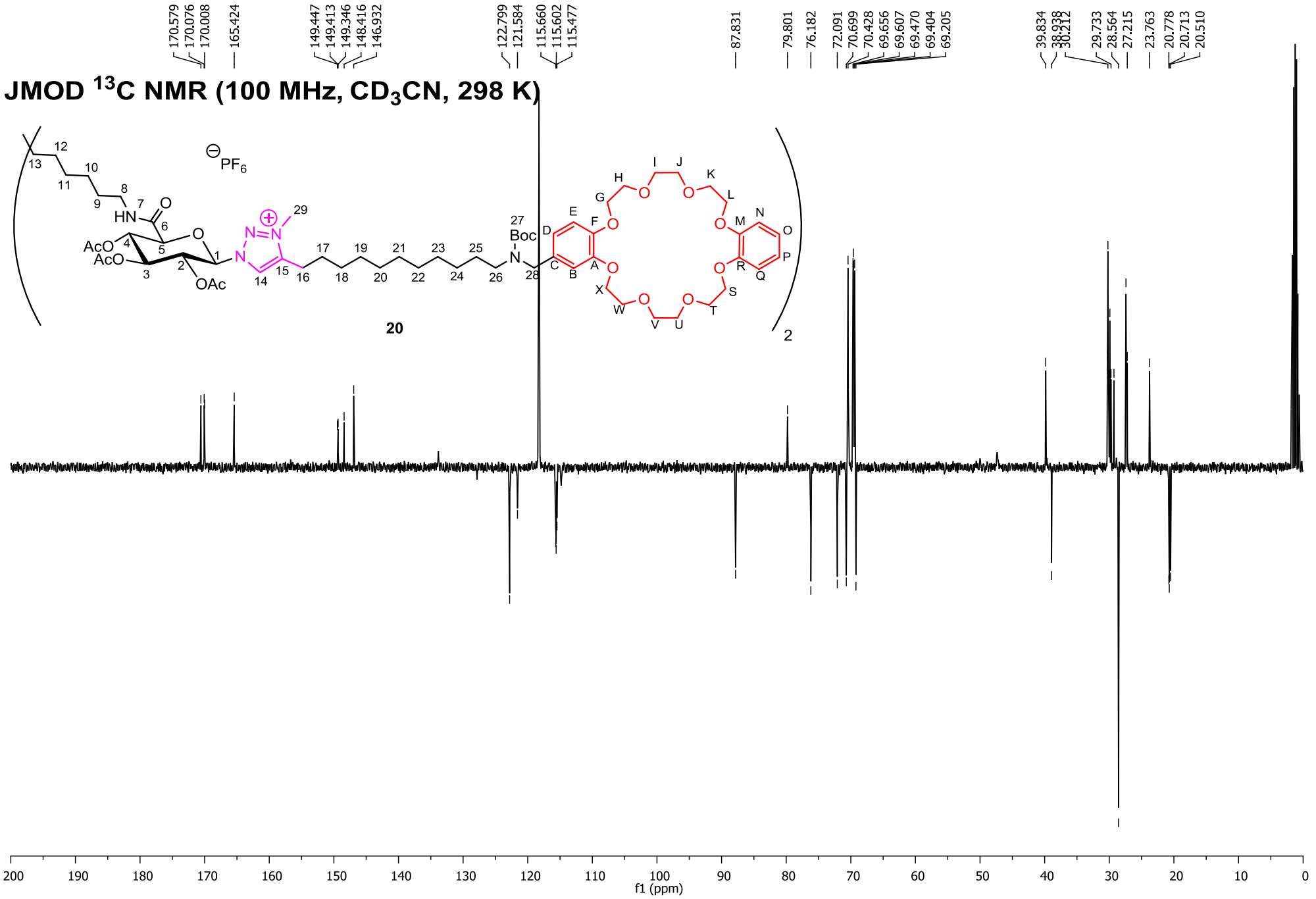


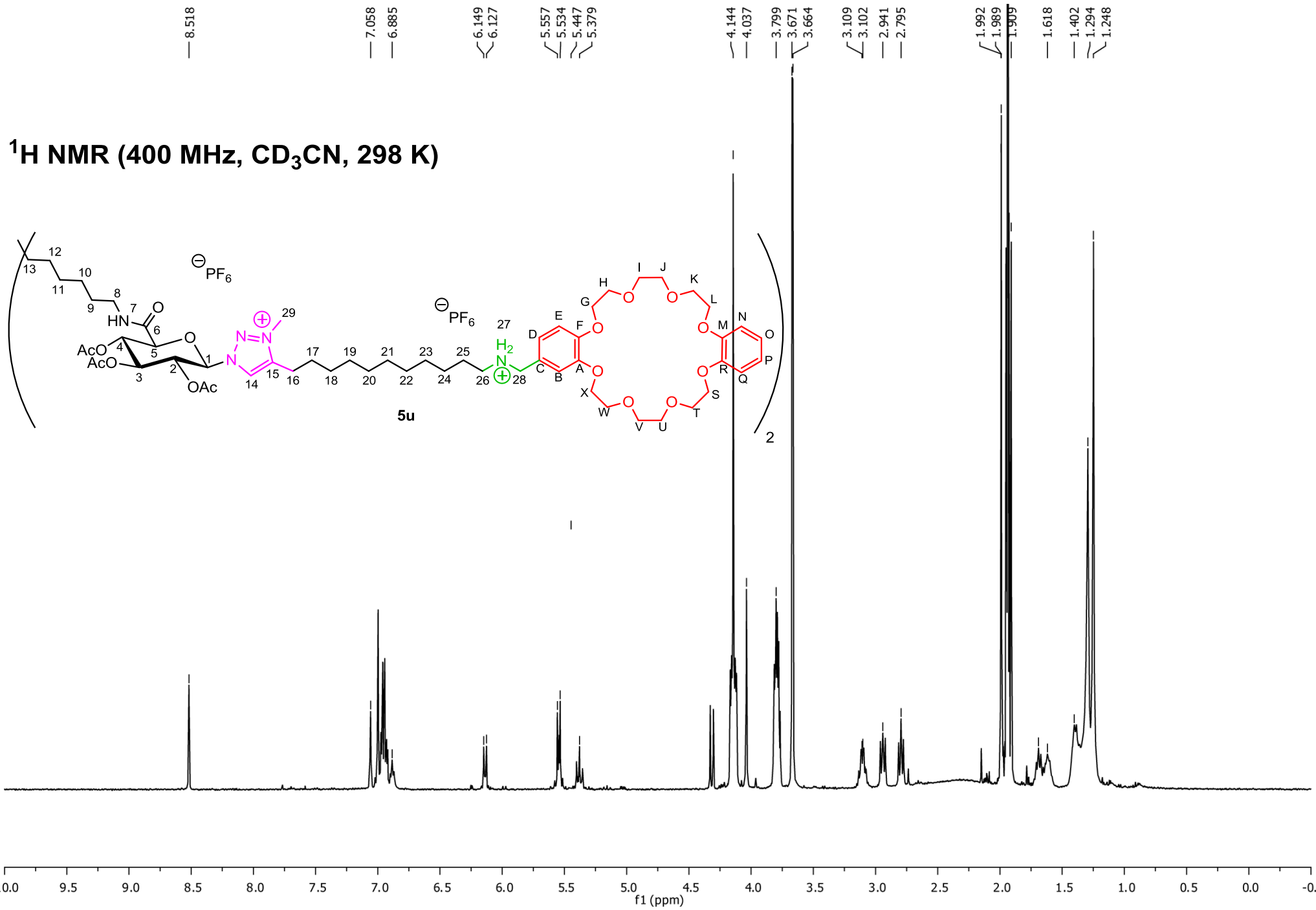


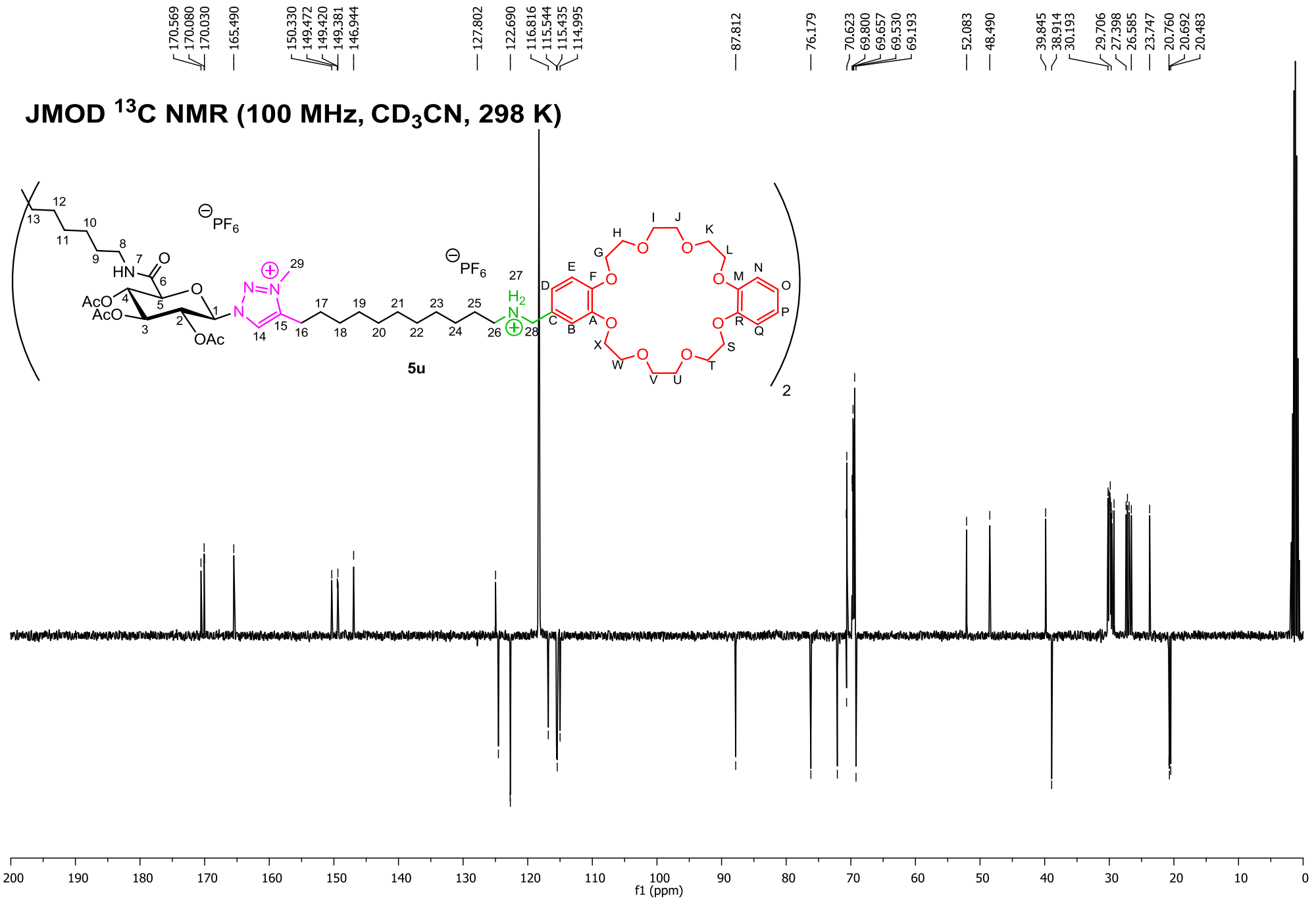

7.774
7.134
7.071
7.017
6.948
6.924
6.836
6.005
5.982
5.596
5.495
5.324
4.341
4.257
3.728
3.586
3.156
3.066
2.655
2.086
1.978
1.972
1.781
1.610
1.446
1.252
1.225
1H NMR (400 MHz, CD3CN, 298 K)
19
2
f1 (ppm)

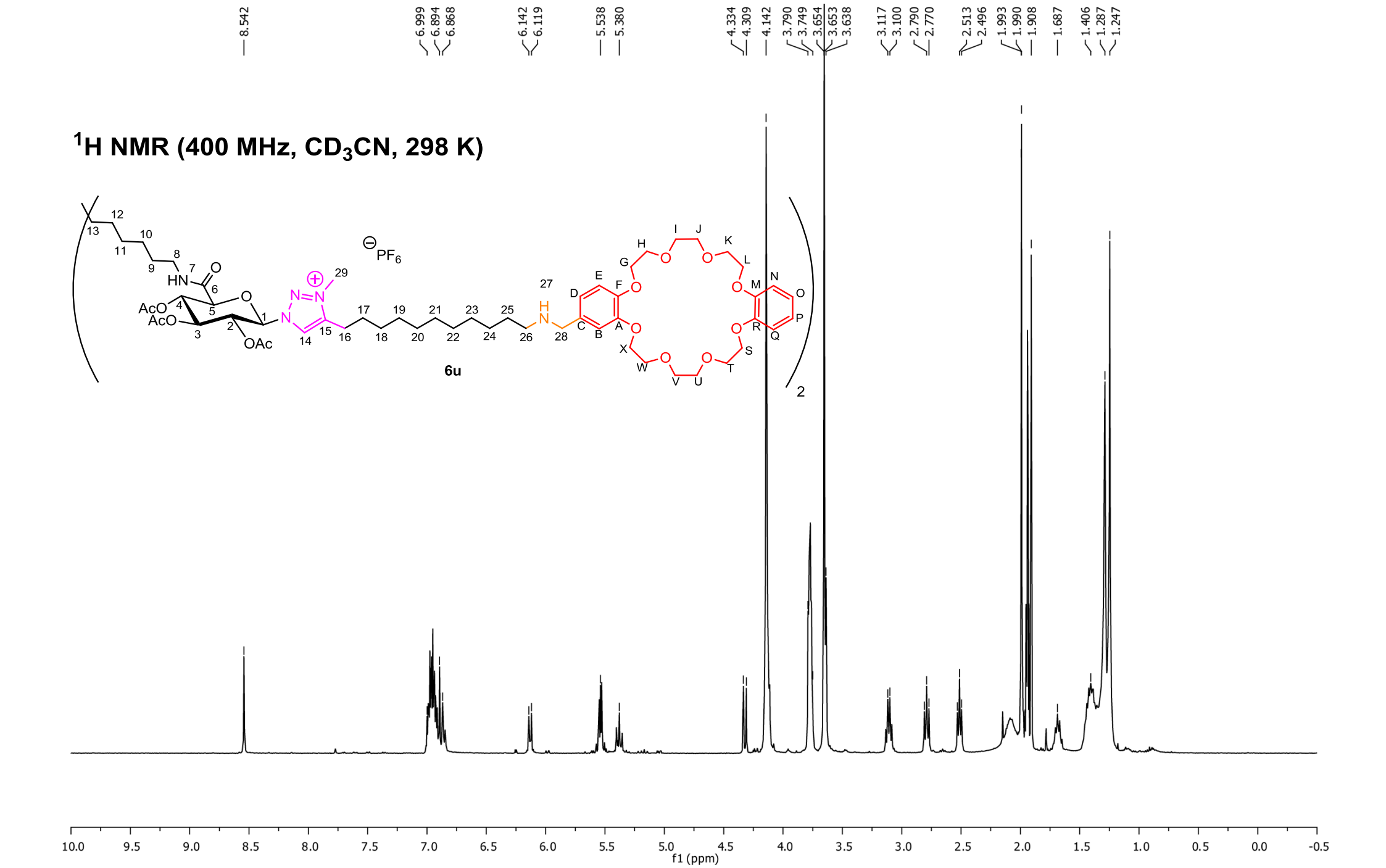


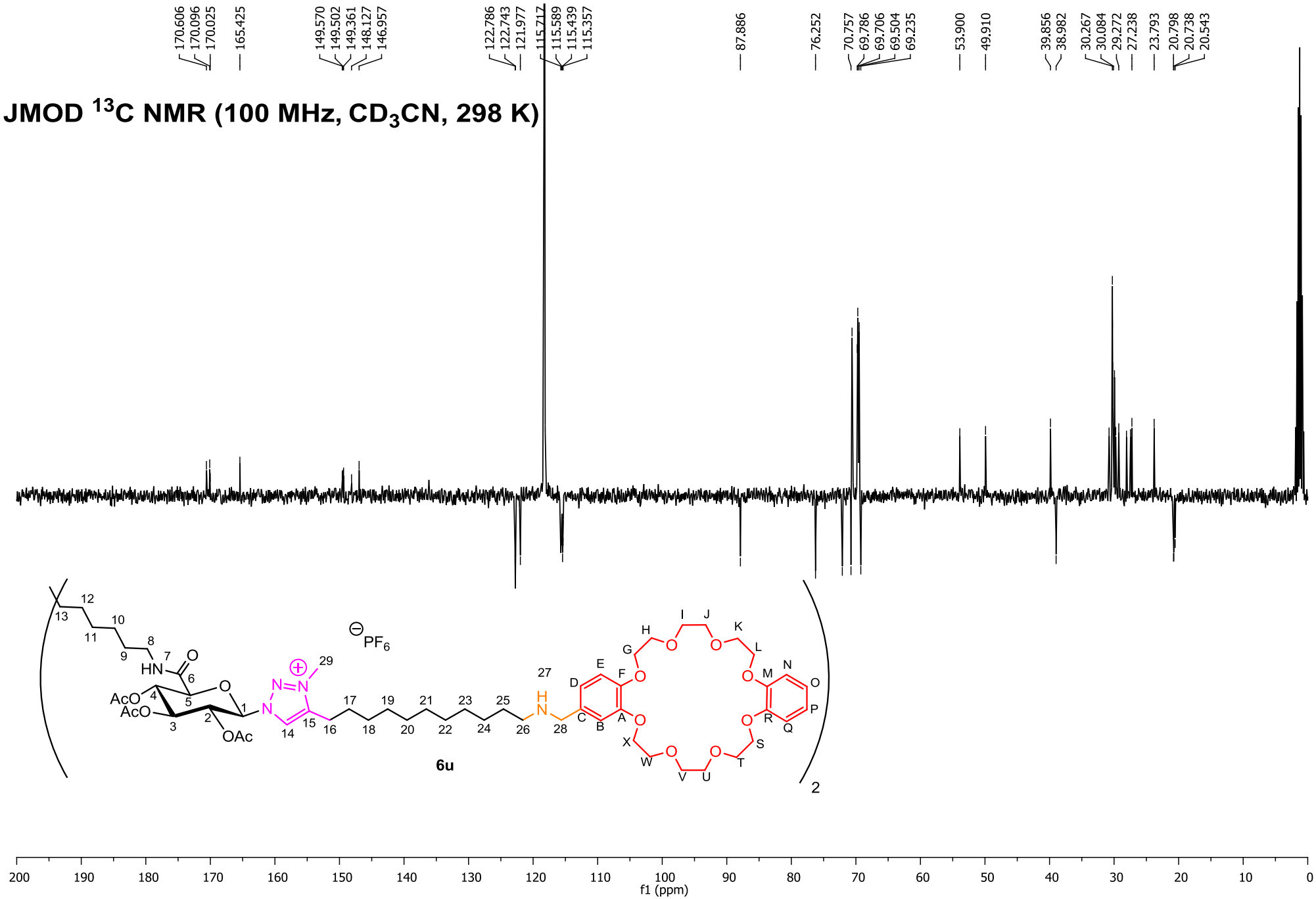


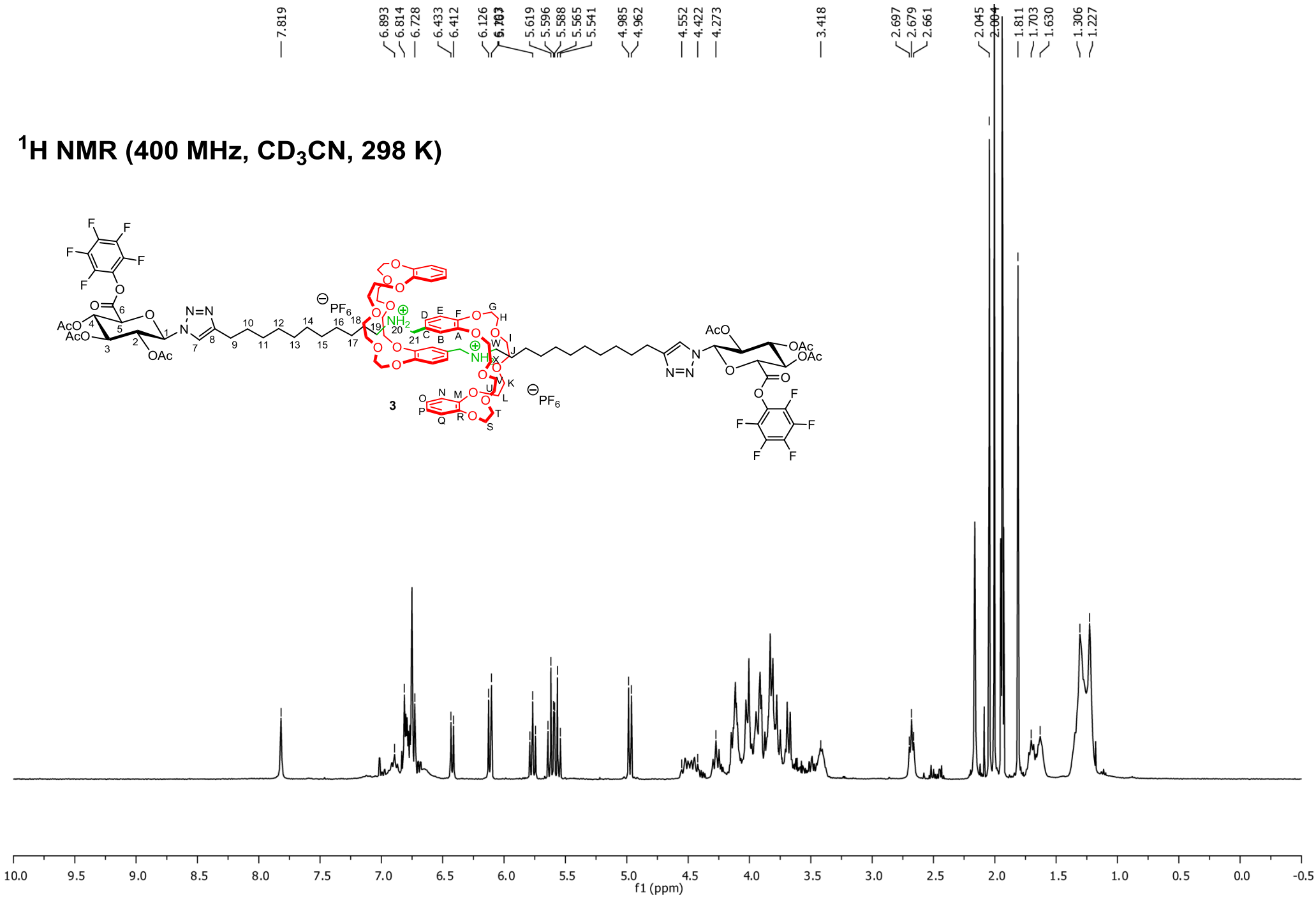

JMOD ^{13}C NMR (100 MHz, CD_3CN, 298 K)
170.579
170.076
170.008
165.424
149.447
149.413
149.346
148.416
146.932
122.799
121.584
115.660
115.602
115.477
87.831
79.801
76.182
72.091
70.699
70.428
69.656
69.607
69.470
69.404
69.205
39.834
38.938
30.212
29.733
28.564
27.215
23.763
20.778
20.713
20.510
$\ominus PF_6$
Boc
AcO
AcO
OAc
HN
20
2
f1 (ppm)

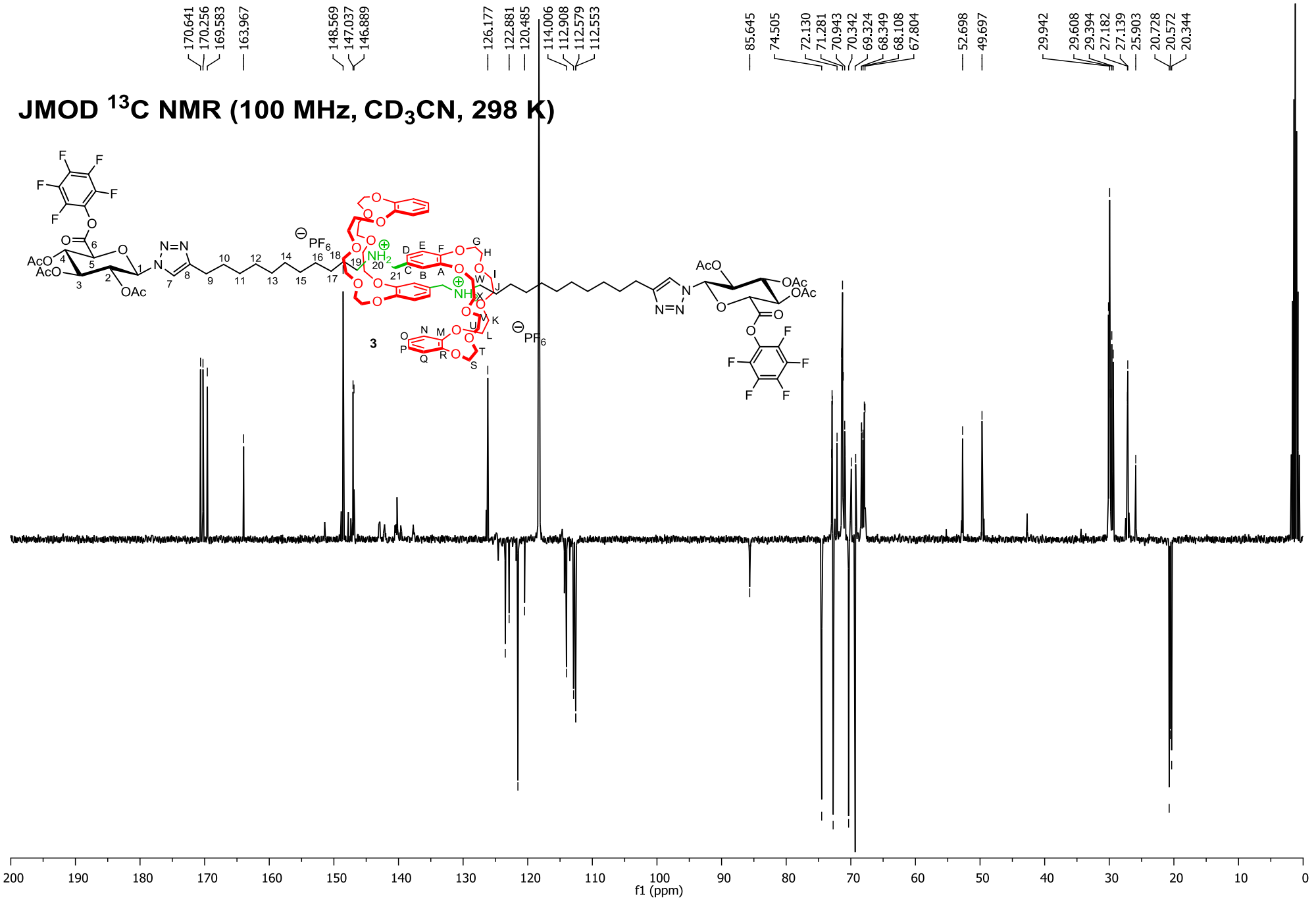

8.518
7.058
6.885
6.149
6.127
5.557
5.534
5.447
5.379
4.144
4.037
3.799
3.671
3.664
3.109
3.102
2.941
2.795
1.992
1.989
1.909
1.618
1.402
1.294
1.248
1H NMR (400 MHz, CD3CN, 298 K)
PF6
PF6
AcO
AcO
OAc
HN
O
N
N
H2
5u
2
f1 (ppm)

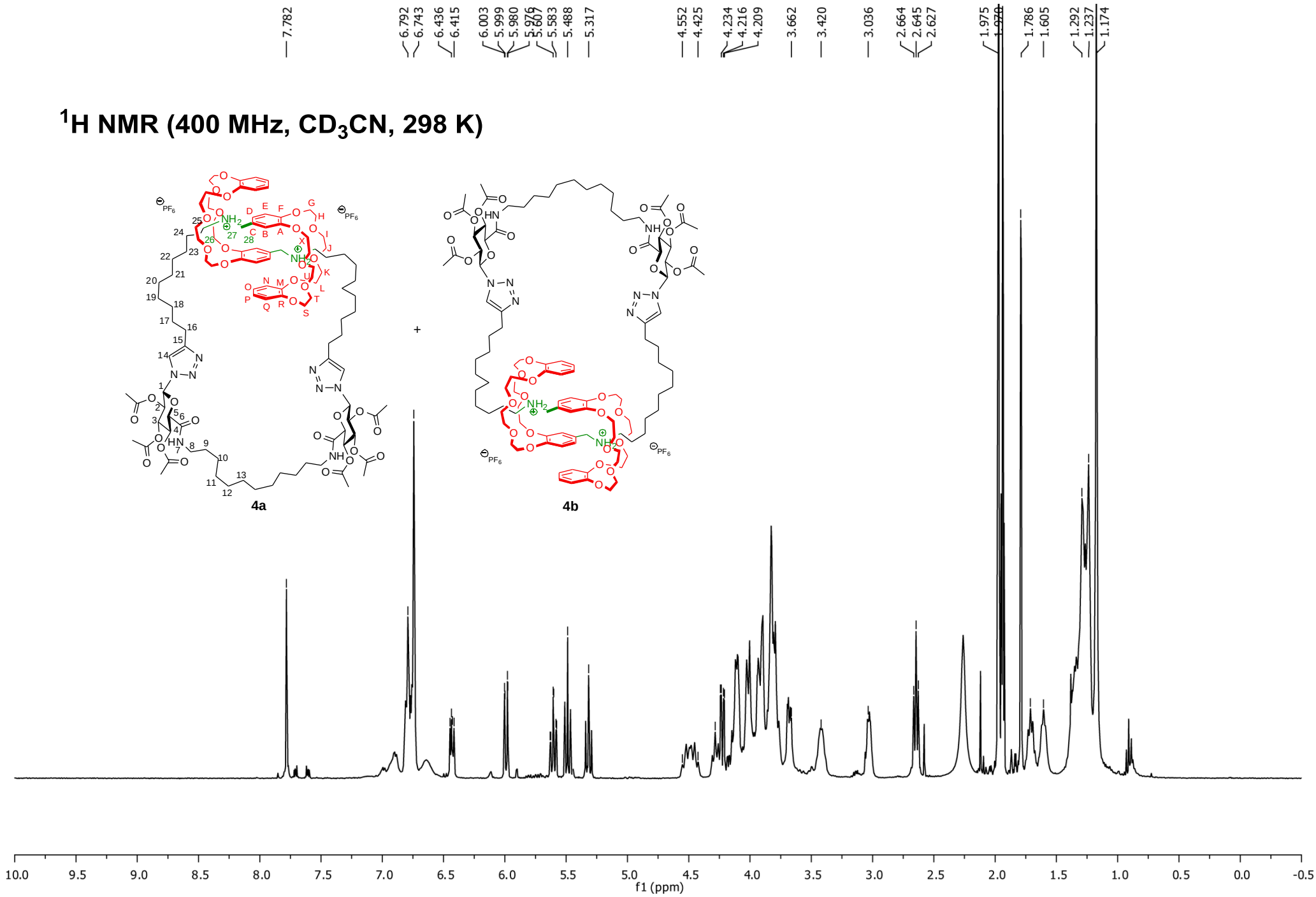


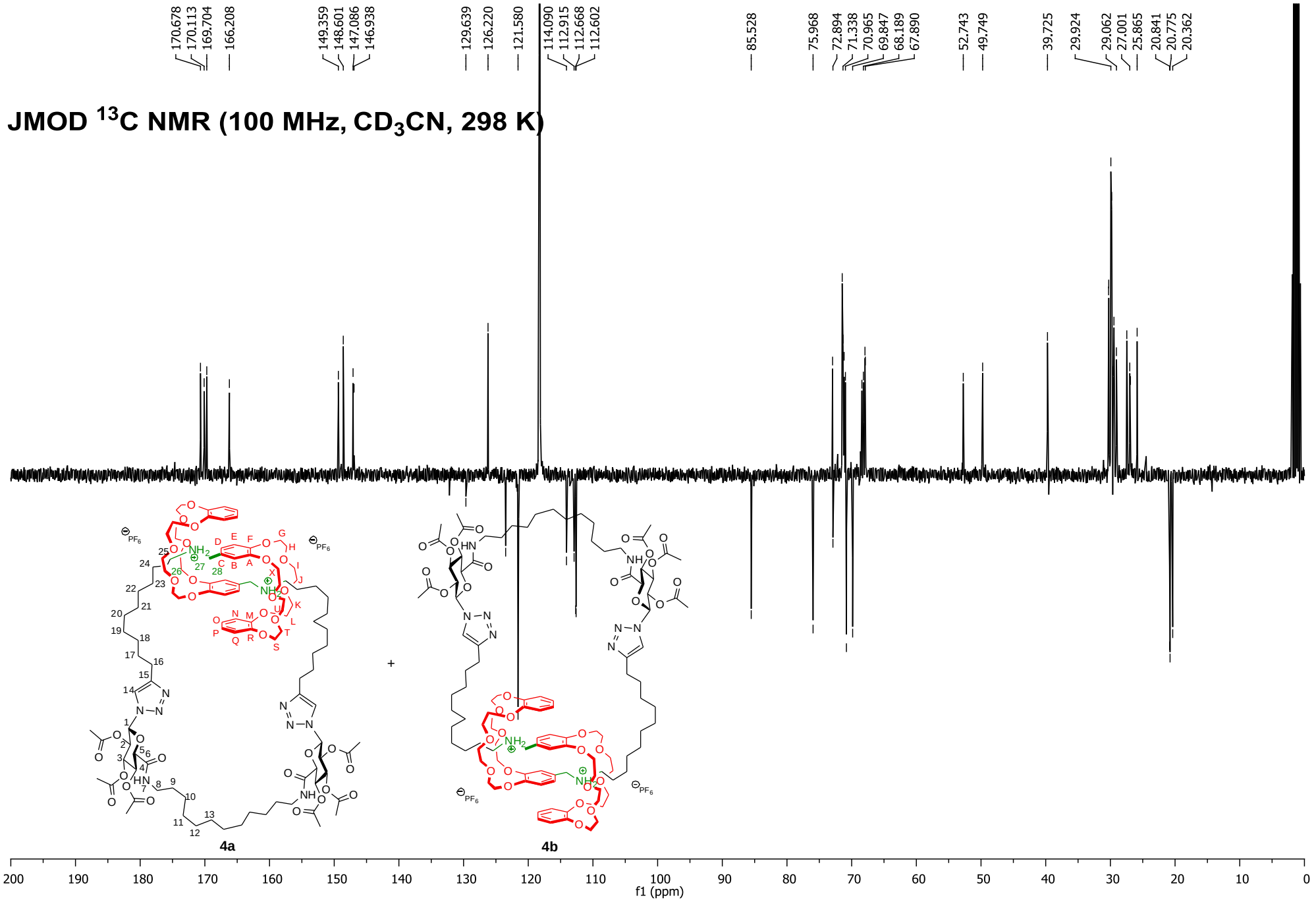

8.542
6.999
6.894
6.868
6.142
6.119
5.538
5.380
4.334
4.309
4.142
3.790
3.749
3.654
3.653
3.638
3.117
3.100
2.790
2.770
2.513
2.496
1.993
1.990
1.908
1.687
1.406
1.287
1.247
1H NMR (400 MHz, CD3CN, 298 K)
PF6
6u
2
f1 (ppm)

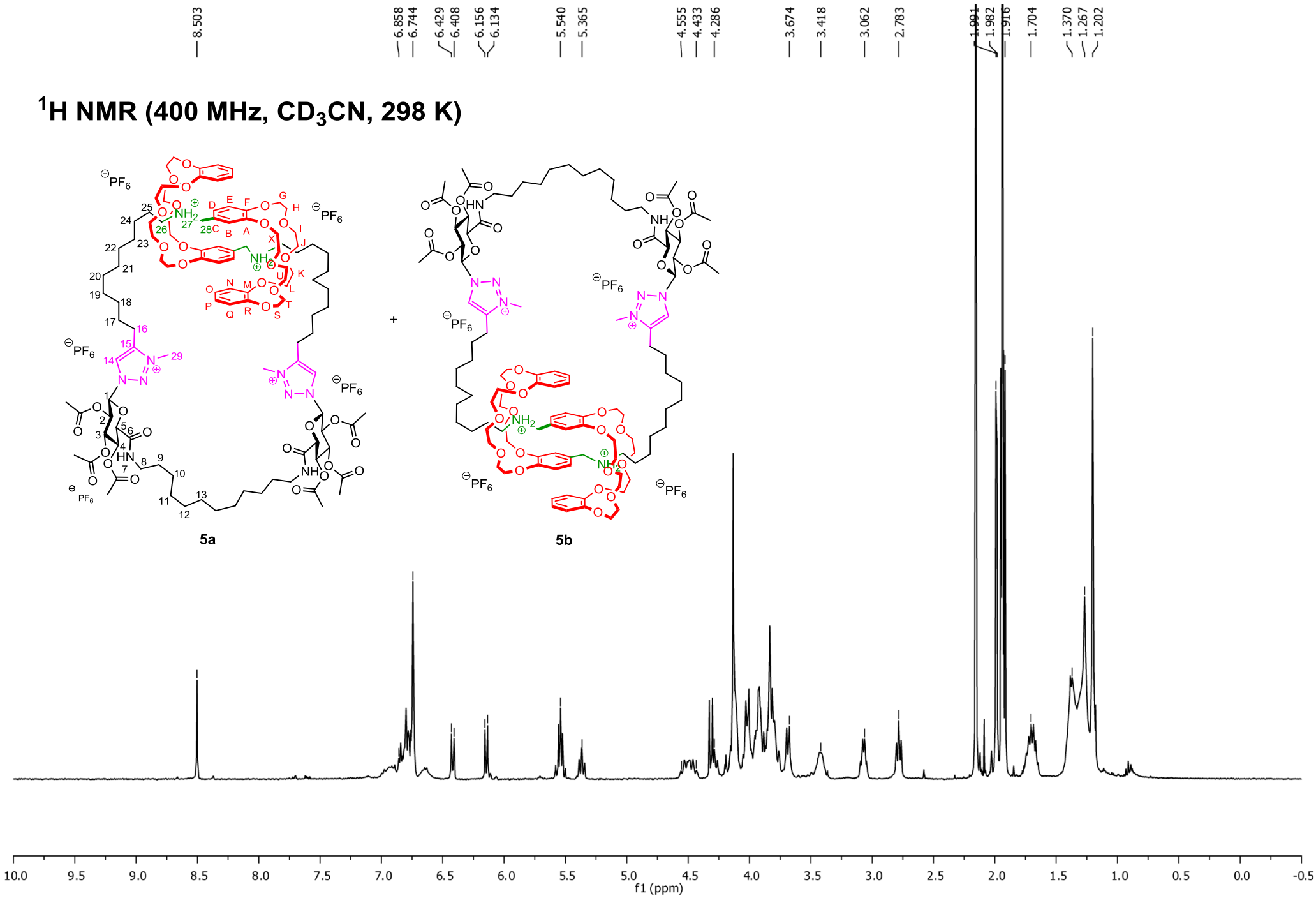

JMOD ^{13}C NMR (100 MHz, CD_3CN, 298 K)
170.606
170.096
170.025
165.425
149.570
149.502
149.361
148.127
146.957
122.786
122.743
121.977
115.712
115.589
115.439
115.357
87.886
76.252
70.757
69.786
69.706
69.504
69.235
53.900
49.910
39.856
38.982
30.267
30.084
29.272
27.238
23.793
20.798
20.738
20.543
6u
2
f1 (ppm)

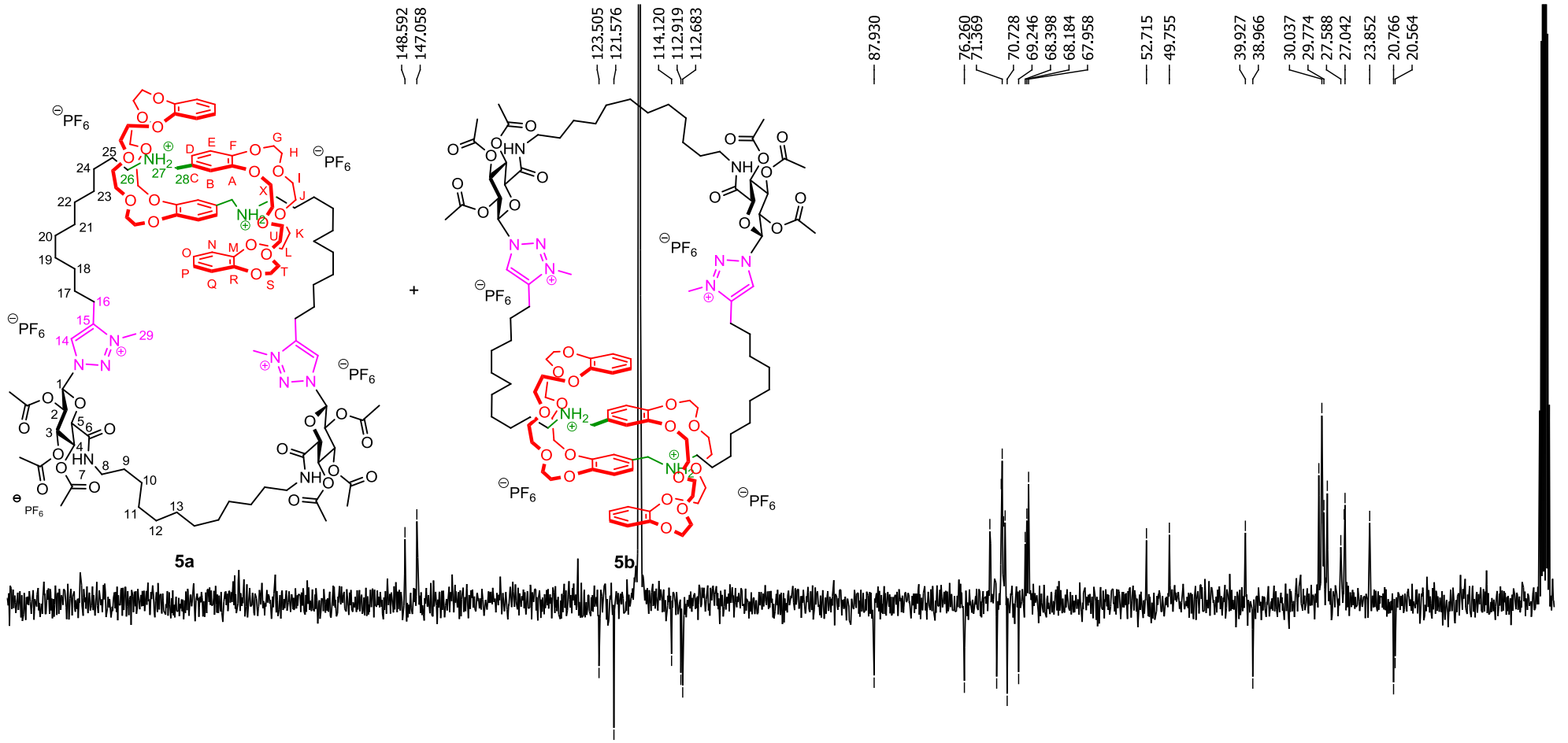



170.641
170.256
169.583
163.967
148.569
147.037
146.889
126.177
122.881
120.485
114.006
112.908
112.579
112.553
85.645
74.505
72.130
71.281
70.943
70.342
69.324
68.349
68.108
67.804
52.698
49.697
29.942
29.608
29.394
27.182
27.139
25.903
20.728
20.572
20.344
JMOD 13C NMR (100 MHz, CD3CN, 298 K)
3
f1 (ppm)

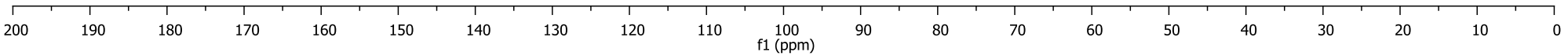



170.678
170.113
169.704
166.208
149.359
148.601
147.086
146.938
129.639
126.220
121.580
114.090
112.915
112.668
112.602
85.528
75.968
72.894
71.338
70.965
69.847
68.189
67.890
52.743
49.749
39.725
29.924
29.062
27.001
25.865
20.841
20.775
20.362
JMOD ^{13}C NMR (100 MHz, CD_3CN, 298 K)
4a
4b
f1 (ppm)

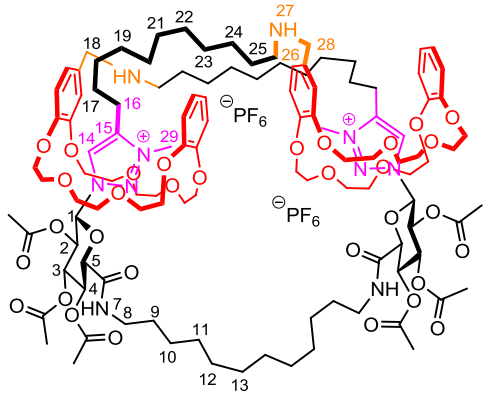




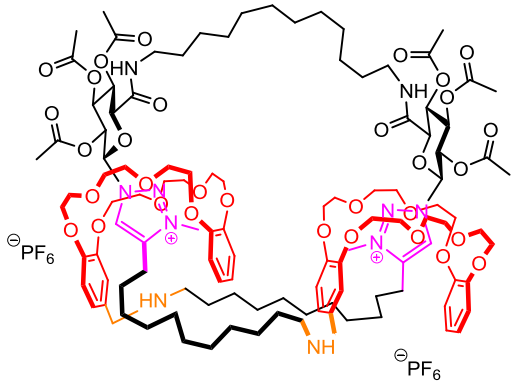
JMOD ^{13}C NMR (100 MHz, CD_3CN, 298 K)



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



6a



6b