# Synthesis of Triazolium-Based Mono- and Tris-branched [1]Rotaxanes Using a Molecular Transporter of Dibenzo-24-Crown-8

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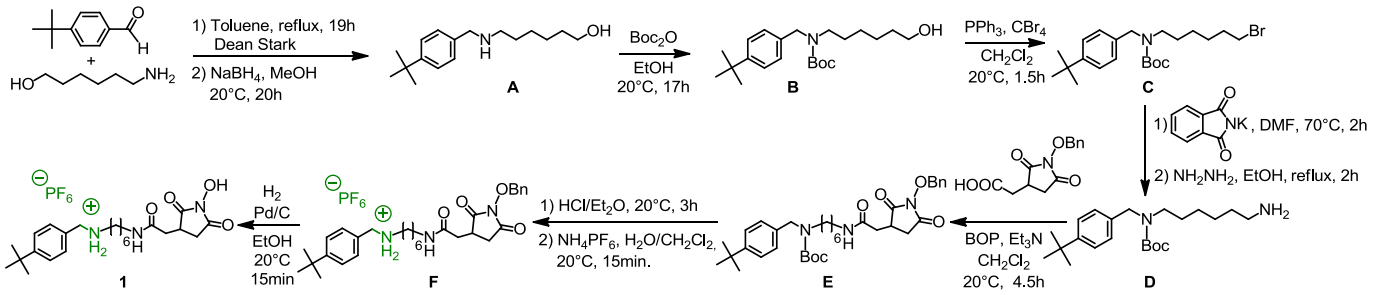
# 1. General methods

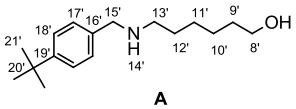
All reactions were carried out under an atmosphere of argon unless otherwise indicated. All reagents were used as received without further purification. Dichloromethane was distilled over $P_2O_5$ and was degassed by bubbling Ar for 20 min. Analytical thin-layer chromatography (TLC) was performed on silica gel 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. $^1H$ NMR and $^{13}C$ NMR spectra were obtained on a spectrometer (respectively at 600.27 or 400.13 MHz and 150.94 or 100.62 MHz). Chemical shifts of $^1H$ NMR and $^{13}C$ NMR are given by using $CHCl_3$, $CH_2Cl_2$ and $CH_3CN$ as references (7.27 ppm, 5.32 ppm, and 1.94 ppm respectively for $^1H$ spectrum, and 77.0 ppm, 54.0 ppm, and 118.26 ppm respectively for $^{13}C$ spectrum). $^1H$ assignments were deduced from 2D $^1H$-$^1H$ NMR COSY experiments. $^{13}C$ assignments were deduced from 2D $^{13}C$-$^1H$ NMR HSQC 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), quint (quintuplet), m (multiplet). Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded respectively on a ZQ Micromass apparatus and a Q-TOF Micro apparatus.

# 2. Synthesis of the molecular transporter 1

## 2.1. General synthetic pathway




## 2.2. Synthesis of the alcohol A *via* reductive amination



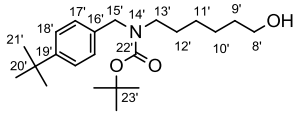

*Imine formation*

A solution of *tert*-butylbenzaldehyde (8.1 mL, 48 mmol, 1.2 equiv.) and 6-aminohexanol (4.688 g, 40 mmol, 1 equiv.) in toluene (100 mL) was stirred for 19h under reflux, using a Dean-Stark apparatus. At the end of the coupling reaction, the solution was cooled to room temperature, and then concentrated to give a yellow-orange oil which was directly engaged in the following reduction.

*Reduction*

The crude was dissolved in methanol (100 mL) and cooled to 0°C. Sodium borohydride (4.54 g, 120 mmol, 3 equiv.) was added slowly in small portions over 20 min. The reaction mixture was stirred for 20h at room temperature. 100 mL of an aqueous solution of HCl 5M was then added to the mixture. Methanol was evaporated under *vacuum*, before adding very slowly and under stirring 100 mL of an aqueous solution of NaOH 5M. The aqueous layer was extracted with $CH_2Cl_2$ (3x100 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. The crude yellow oil obtained was used for the next step without purification.

## 2.3. Synthesis of the *N*-carbamoylated alcohol compound B



**B**

The crude **A** (0.040 mol, 1 equiv.) was dissolved in ethanol (100 mL). $Boc_2O$ (14.07 g, 0.064 mol, 1.6 equiv.) was added and the reaction mixture was stirred for 17h at room temperature. At the end of the reaction, the ethanol was evaporated and the residue was diluted with $CH_2Cl_2$ (100 mL). The organic layer was washed with an aqueous solution of HCl 1M (100 mL). The acidic aqueous solution was then extracted with $CH_2Cl_2$ (3x100 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. The obtained crude was purified by chromatography on a silicagel column (PE/AcOEt 90:10 to 70:30) to give pure **B** (11.03 g, 76% over 3 steps) as a light yellow oil.

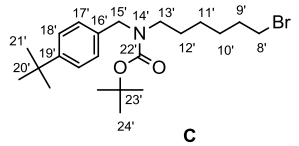
**$R_f$:** 0.52 (PE/AcOEt 6/4).

**$^1$H NMR (400 MHz, $CDCl_3$, 298K):** δ ppm = 7.34 (d, 2H, $^3J_{H18'-H17'}$ = 7.9Hz, $H_{18'}$), 7.19-7.12 (m, 2H, $H_{17'}$), 4.44-4.34 (m, 2H, $H_{15'}$), 3.60 (t, 2H, $^3J_{H8'-H9'}$ = 6.4Hz, $H_{8'}$), 3.24-3.06 (m, 2H, $H_{13'}$), 2.09 (br s, 1H, OH), 1.58-1.41 (m, 13H, $H_{24'}$ $H_{9'}$ $H_{12'}$), 1.40-1.21 (m, 4H, $H_{10'}$ $H_{11'}$), 1.31 (s, 9H, $H_{21'}$).

**$^{13}$C NMR (100 MHz, $CDCl_3$, 298K):** δ ppm = 155.7 ($C_{22'}$), 149.9 ($C_{19'}$), 135.4 ($C_{16'}$), 127.3 & 126.9 ($C_{17'}$), 125.2 ($C_{18'}$), 79.5 ($C_{23'}$), 62.6 & 62.4 ($C_{8'}$), 49.7 & 49.2 ($C_{15'}$), 46.1 & 45.8 ($C_{13'}$), 34.4 ($C_{20'}$), 31.3 ($C_{21'}$), 28.4 ($C_{24'}$), 32.5 & 28.0 & 27.5 & 26.6 & 26.2 & 25.4 & 25.1 ($C_{9'}$ $C_{10'}$ $C_{11'}$ $C_{12'}$).

**HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{22}H_{37}NO_3Na^+$: 386.2671, found: 386.2679.

## 2.4. Synthesis of the *N*-carbamoylated bromo compound C



**C**

To a solution of the alcohol **B** (11.03 g, 29.6 mmol, 1 equiv.) in $CH_2Cl_2$ (150 mL) was added successively $PPh_3$ (15.5 g, 59 mmol, 2 equiv.) and $CBr_4$ (19.6 g, 59 mmol, 2 equiv.). The light brown solution was stirred for 1h30 at room temperature before being concentrated and added by a solution of PE/AcOEt 95:5. The precipitate was filtered off and the filtrate concentrated. The obtained residue was purified by chromatography using a silicagel column (PE/AcOEt 100:0 to 75:35) to give the pure brominated compound **C** (11.56 g, 89%) as a pale yellow oil.

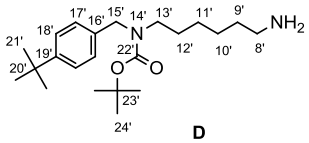
**$R_f$:** 0.70 (PE/AcOEt 6/4).

**$^1$H NMR (400 MHz, $CDCl_3$, 298K):** δ ppm = 7.35 (d, 2H, $^3J_{H18'-H17'}$ = 7.9Hz, $H_{18'}$), 7.21-7.14 (m, 2H, $H_{17'}$), 4.45-4.36 (m, 2H, $H_{15'}$), 3.39 (t, 2H, $^3J_{H8'-H9'}$ = 6.6Hz, $H_{8'}$), 3.24-3.08 (m, 2H, $H_{13'}$), 1.88-1.78 (m, 2H, $H_{9'}$), 1.56-1.37 (m, 13H, $H_{24'}$ $H_{10'}$ $H_{12'}$), 1.33 (s, 9H, $H_{21'}$), 1.33-1.23 (m, 2H, $H_{11'}$).

**$^{13}$C NMR (100 MHz, $CDCl_3$, 298K):** δ ppm = 155.6 ($C_{22'}$), 149.9 ($C_{19'}$), 135.3 ($C_{16'}$), 127.3 & 126.9 ($C_{17'}$), 125.3 ($C_{18'}$), 79.4 ($C_{23'}$), 49.9 & 49.3 ($C_{15'}$), 46.1 ($C_{13'}$), 34.4 ($C_{20'}$), 33.7 ($C_{8'}$), 32.6 ($C_{9'}$), 31.3 ($C_{21'}$), 28.4 ($C_{24'}$), 27.8 & 27.5 & 25.9 ($C_{10'}$ $C_{11'}$ $C_{12'}$).

**HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{22}H_{36}NO_2BrNa^+$: 448.1827, found: 448.1824.

## 2.5. Synthesis of the primary amino compound D



**D**

To a solution of the brominated compound **C** (6.11 g, 14 mmol, 1 equiv.) in dry DMF (78 mL) was added potassium phthalimide (3.91 g, 21 mmol, 1.5 equiv.). The solution was stirred for 2h at 70°C, then cooled to room temperature, and partially concentrated. The resulting mixture was filtered through a celite pad. After abundant washing of the celite pad with $CH_2Cl_2$, the filtrate was concentrated to a pale orange oil, which was used for the next step without further purification.

The obtained oil was diluted in ethanol (140 mL) and added by hydrazine (2.47 g, 49 mmol, 3.5 equiv.). The reaction mixture was vigorously stirred for 2h at reflux. At the end of the reaction, an aqueous solution of KOH 1M (140 mL) was added and the ethanol was evaporated. The aqueous layer was then extracted three times with $CH_2Cl_2$ (3x70 mL). The combined organic layers were dried over $MgSO_4$ and concentrated to give **D** (5.097 g, 99%) as a pale yellow oil.

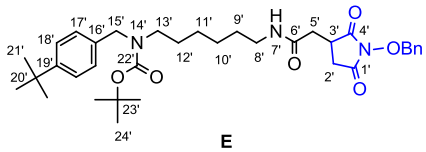
**$R_f$:** 0.11 (PE/AcOEt 2/8)

**$^1$H NMR (400 MHz, $CDCl_3$, 298K):** δ ppm = 7.34 (d, 2H, $^3J_{H18'-H17'}$ = 7.5Hz, $H_{18'}$), 7.19-7.11 (m, 2H, $H_{17'}$), 4.44-4.32 (m, 2H, $H_{15'}$), 3.22-3.05 (m, 2H, $H_{13'}$), 2.68 (t, 2H, $^3J_{H8'-H9'}$ = 6.7Hz, $H_{8'}$), 1.74 (br s, $NH_2$), 1.54-1.35 (m, 13H, $H_{24'}$ $H_{9'}$ $H_{12'}$), 1.34-1.21 (m, 4H, $H_{10'}$ $H_{11'}$), 1.30 (s, 9H, $H_{21'}$).

**$^{13}$C NMR (100 MHz, $CDCl_3$, 298K):** δ ppm = 155.9 ($C_{22'}$), 149.9 ($C_{19'}$), 135.4 ($C_{16'}$), 127.3 & 126.9 ($C_{17'}$), 125.2 ($C_{18'}$), 79.3 ($C_{23'}$), 49.8 & 49.2 ($C_{15'}$), 46.1 ($C_{13'}$), 42.0 ($C_{8'}$), 34.4 ($C_{20'}$), 31.3 ($C_{21'}$), 28.4 ($C_{24'}$), 33.6 & 28.0 & 27.6 & 26.6 & 26.5 ($C_{9'}$ $C_{10'}$ $C_{11'}$ $C_{12'}$).

**HRMS (ESI)**: $[M+H]^+$ calcd for $C_{22}H_{39}N_2O_2^+$: 363.3012, found: 363.3011.

## 2.6. Synthesis of compound E




**E**

The primary amine **D** (1.124g, 3.1 mmol, 1 equiv.) and the *O*-benzyl-*N*-hydroxysuccinimide derivative (818 mg, 3.1 mmol, 1 equiv.) were dissolved in $CH_2Cl_2$ (57 mL). To this solution was added successively BOP (1.790 g, 4.0 mmol, 1.3 equiv.) and $Et_3N$ (960 µL, 6.8 mmol, 2.2 equiv.). After checking the basicity of the solution, the mixture was stirred for 4h30 at RT. Then, an aqueous solution of HCl 1M was added until pH 1. The aqueous layer was extracted three times with $CH_2Cl_2$ (3x30 mL). The resulting organic layers were washed twice with a saturated aqueous $NaHCO_3$ solution (2x50 mL), then with brine (50 mL), dried over $MgSO_4$ and concentrated. The obtained crude was purified by chromatography on a silicagel column (PE/AcOEt 60:40 to 40:60) to give the pure compound **E** (1.647 g, 87%) as a white solid.

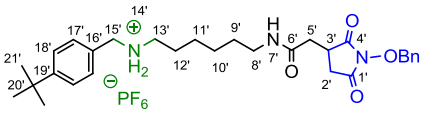
**$R_f$:** 0.46 (PE/AcOEt 2/8)

**$^1$H NMR (400 MHz, $CD_3Cl$, 298K):** δ ppm = 7.53-7.47 (m, 2H, $H_{OBn}$), 7.39-7.35 (m, 3H, $H_{OBn}$), 7.34 (d, 2H, $^3J_{H18'-H17'}$ = 7.9 Hz, $H_{18'}$), 7.15 (d, 2H, $^3J_{H17'-H18'}$ = 7.9 Hz, $H_{17'}$), 6.29 & 5.77 (2 br s, 1H, $H_{7'}$), 5.13 (s, 2H, $CH_{2\,OBn}$), 4.42-4.34 (m, 2H, $H_{15'}$), 3.24-3.06 (m, 4H, $H_{8'}$ $H_{13'}$), 3.05-2.96 (m, 1H, $H_{3'}$), 2.84 (dd, 1H, $^2J_{H2'b-H2'a}$ = 17.9 Hz, $^3J_{H2'b-H3'}$ = 9.1 Hz, $H_{2'b}$), 2.69-2.59 (m, 2H, $H_{5'}$), 2.50 (dd, 1H, $^2J_{H2'a-H2'b}$ = 17.9Hz, $^3J_{H2'a-H3'}$ = 4.6Hz, $H_{2'a}$), 1.55-1.39 (m, 4H, $H_{9'}$ $H_{12'}$), 1.45 (sl, 9H, $H_{24'}$), 1.35-1.20 (m, 4H, $H_{10'}$ $H_{11'}$), 1.31 (s, 9H, $H_{21'}$).

**$^{13}$C NMR (100 MHz, $CDCl_3$, 298K):** δ ppm = 173.8 ($C_{6'}$), 170.7 & 169.1 ($C_{1'}$ $C_{4'}$), 156.0 & 155.8 ($C_{22'}$), 150.0 ($C_{19'}$), 135.2 ($C_{IV\,OBn}$), 133.4 ($C_{16'}$), 129.8 & 129.2 & 128.4 ($CH_{OBn}$), 127.1 & 126.9 ($C_{17'}$), 125.3 ($C_{18'}$), 79.6 ($C_{23'}$), 78.5 ($CH_{2\,OBn}$), 49.6 & 49.1 ($C_{15'}$), 46.1 & 45.2 ($C_{13'}$), 39.5 & 38.8 ($C_{8'}$), 35.4 ($C_{5'}$), 34.4 ($C_{20'}$), 33.6 ($C_{3'}$), 31.7 ($C_{2'}$), 31.3 ($C_{21'}$), 28.4 ($C_{24'}$), 28.8 & 27.2 & 25.6 & 25.4 ($C_{9'}$ $C_{10'}$ $C_{11'}$ $C_{12'}$).

**HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{35}H_{49}N_3O_6Na^+$: 630.3519, found: 630.3523.

## 2.7. Synthesis of compound F



**F**

To the *N*-carbamoylated compound **E** (1.752 g, 2.88 mmol, 1 equiv.) was added a 0.9M solution of HCl in $Et_2O$ (40 mL, 36 mmol, 12.5 equiv.). After stirring for 3h at 0°C, the mixture was concentrated before being dissolved in a small volume of $Et_2O$ and concentrated three times. The resulting crude was diluted in $CH_2Cl_2$ (20 mL), milli-Q water (20 mL) and $NH_4PF_6$ (1.400 g, 8.6 mmol, 3 equiv.) were added. The biphasic mixture was vigorously stirred at room temperature for 15 min. The aqueous layer was extracted three times with $CH_2Cl_2$ (3x15mL). The combined organic layers were dried over $MgSO_4$ and concentrated. The resulting white solid was purified by chromatography on a silicagel column ($CH_2Cl_2$ /MeOH 98:2 to 94:6) to give the pure ammonium-containing product **F** (1.628 g, 86%) as a white solid.

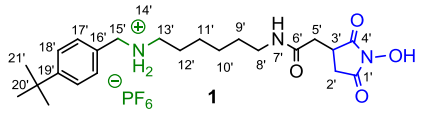
**$R_f$:** 0.53 ($CH_2Cl_2$/MeOH 9/1)

**$^1$H NMR (400 MHz, $CD_3CN$, 298K):** δ ppm = δ ppm = 7.52-7.46 (m, 2H, $H_{OBn}$), 7.50 (d, 2H, $^3J_{H18'-H17'}$ = 8.4 Hz, $H_{18'}$), 7.42-7.36 (m, 3H, $H_{OBn}$), 7.37 (d, 2H, $^3J_{H17'-H18'}$ = 8.4 Hz, $H_{17'}$), 7.06-6.46 (br s, 2H, $H_{14'}$), 6.52 (br t, 1H, $H_{7'}$), 5.02 (s, 2H, $CH_{2\,OBn}$), 4.10 (s, 2H, $H_{15'}$), 3.11 (q, 2H, $^3J_{H8'-H9'}$ = $^3J_{H8'-H7'}$ = 6.6 Hz, $H_{8'}$), 3.03-2.95 (m, 3H, $H_{3'}$ $H_{13'}$), 2.77 (dd, 1H, $^2J_{H2'a-H2'b}$ = 17.8Hz, $^3J_{H2'a-H3'}$ = 9.2 Hz, $H_{2'a}$), 2.66 (dd, 1H, $^2J_{H5'a-H5'b}$ = 16.3Hz, $^3J_{H5'a-H3'}$ = 5.9 Hz, $H_{5'a}$), 2.57 (dd, 1H, $^2J_{H5'b-H5'a}$ = 16.3Hz, $^3J_{H5'b-H3'}$ = 4.6 Hz, $H_{5'b}$), 2.34 (dd, 1H, $^2J_{H2'b-H2'a}$ = 17.8Hz, $^3J_{H2'b-H3'}$ = 4.4 Hz, $H_{2'b}$), 1.63 (quint, 2H, $^3J_{H12'-H11'}$ = $^3J_{H12'-H13'}$ = 7.5 Hz, $H_{12'}$), 1.43 (quint, 2H, $^3J_{H9'-H8'}$ = $^3J_{H9'-10'}$ = 6.9 Hz, 2H, $H_{9'}$), 1.38-1.25 (m, 4H, $H_{11'}$ $H_{10'}$), 1.31 (s, 9H, $H_{21'}$).

**$^{13}$C NMR (100 MHz, $CD_3CN$, 298K):** δ ppm = 175.3 & 172.3 & 170.9 ($C_{1'}$ $C_{4'}$ $C_{6'}$), 153.7 ($C_{19'}$), 135.2 ($C_{IV\text{-}OBn}$), 130.7 ($C_{17'}$), 130.6 & 130.0 & 129.4 ($CH_{OBn}$), 128.6 ($C_{16'}$), 126.9 ($C_{18'}$), 79.0 ($CH_{2\text{-}OBn}$), 52.0 ($C_{15'}$), 48.5 ($C_{13'}$), 39.4 ($C_{8'}$), 35.8 ($C_{5'}$), 35.2 ($C_{20'}$), 34.4 ($C_{3'}$), 32.3 ($C_{2'}$), 31.3 ($C_{21'}$), 29.7 ($C_{9'}$), 26.3 & 26.2 & 26.1 ($C_{10'}$ $C_{11'}$ $C_{12'}$).

**HRMS (ESI)**: $[M\text{-}PF_6]^+$ calcd for $C_{30}H_{42}N_3O_4^+$: 508.3175, found: 508.3179.

## 2.8. Synthesis of the molecular transporter 1



**1**

To a solution of **F** (351 mg, 0.54 mmol, 1 equiv.) in EtOH (15 mL) was added 10%-Pd/C (300 mg). The solution was stirred 15 min under a hydrogen atmosphere before filtration through a celite pad. After abundant washing of the celite pad, the filtrate was concentrated to give the pure **1** (297 mg, 98%) without any further purification.

**$R_f$:** 0.23 ($CH_2Cl_2$/MeOH 9/1)

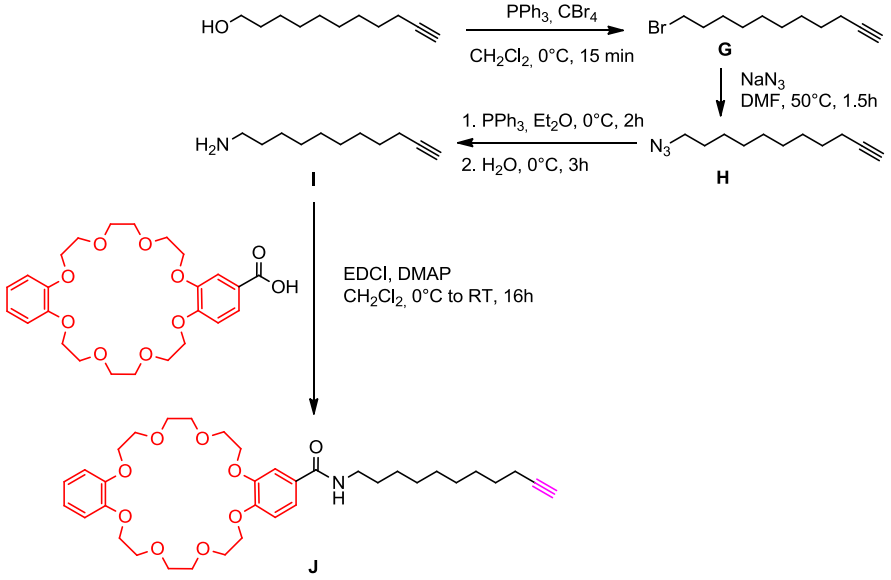
**$^1$H NMR (400 MHz, $CD_3CN$, 298K):** δ ppm = 7.50 (d, 2H, $^3J_{H18'-H17'}$ = 8.4 Hz, $H_{18'}$), 7.39 (d, 2H, $^3J_{H17'-H18'}$ = 8.4 Hz, $H_{17'}$), 6.57 (br t, 1H, $H_{7'}$), 4.13 (s, 2H, $H_{15'}$), 3.11 (q, 2H, $^3J_{H8'-H9'}$ = $^3J_{H8'-H7'}$ = 6.6 Hz, $H_{8'}$), 3.06-2.95 (m, 3H, $H_{3'}$ $H_{13'}$), 2.75 (dd, 1H, $^2J_{H2'a-H2'b}$ = 17.8 Hz, $^3J_{H2'a-H3'}$ = 9.0 Hz, $H_{2'a}$), 2.63 (dd, 1H, $^2J_{H5'a-H5'b}$ = 16.2 Hz, $^3J_{H5'a-H3'}$ = 6.0 Hz, $H_{5'a}$), 2.57 (dd, 1H, $^2J_{H5'b-H5'a}$ = 16.2 Hz, $^3J_{H5'b-H3'}$ = 4.9 Hz, $H_{5'b}$), 2.34 (dd, 1H, $^2J_{H2'b-H2'a}$ = 17.8 Hz, $^3J_{H2'b-H3'}$ = 4.4 Hz, $H_{2'b}$), 1.64 (quint, 2H, $^3J_{H12'-H11'}$ = $^3J_{H12'-H13'}$ = 7.5 Hz, $H_{12'}$), 1.43 (quint, 2H, $^3J_{H9'-H8'}$ = $^3J_{H9'-10'}$ = 6.9 Hz, 2H, $H_{9'}$), 1.38-1.23 (m, 4H, $H_{11'}$ $H_{10'}$), 1.31 (s, 9H, $H_{21'}$).

**$^{13}$C NMR (100 MHz, $CD_3CN$, 298K):** δ ppm = 175.7 & 172.8 & 171.3 ($C_1$ $C_4$ $C_6$), 153.6 ($C_{19}$), 130.6 ($C_{17}$), 128.6 ($C_{16}$), 126.8 ($C_{18}$), 52.0 ($C_{15}$), 48.5 ($C_{13}$), 39.5 ($C_8$), 35.7 ($C_5$), 35.2 ($C_{20}$), 34.4 ($C_3$), 32.1 ($C_2$), 31.3 ($C_{21}$), 29.5 ($C_9$), 26.3 & 26.2 & 26.0 ($C_{10}$ $C_{11}$ $C_{12}$).

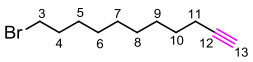
**HRMS (ESI)**: $[M\text{-}PF_6]^+$ calcd for $C_{23}H_{36}N_3O_4^+$: 418.2706, found: 418.2694.

# 3. Synthesis of the macrocycle

## 3.1. General synthetic pathway




## 3.2. Synthesis of the bromoalkyne compound G




**G**

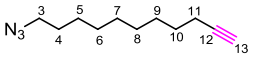
A solution of undec-10-ynol (1.546 g, 9.2 mmol, 1 equiv.) in $CH_2Cl_2$ (26 mL) was cooled at 0°C. To this solution was added $PPh_3$ (3.62 g, 13.8 mmol, 1.5 equiv.) and $CBr_4$ (4.57 g, 13.8 mmol, 1.5 equiv.). The light brown solution was stirred for 15 min at 0°C before being concentrated. To the resulting oil was added PE/AcOEt (95/5): the precipitate was filtered off and the filtrate concentrated. The crude was purified by chromatography on a silicagel column (PE/AcOEt 98:2 to 90:10) to afford the pure 11-bromoundec-1-yne **G** (1.93 g, 90%) as a colorless oil.

**$R_f$:** 0.88 (PE/AcOEt 98/2).

**$^1$H NMR (300 MHz, $CDCl_3$, 298K):** δ ppm = 3.42 (t, 2H, $^3J_{H3\text{-}H4}$ = 6.9Hz, $H_3$), 2.19 (td, 2H, $^3J_{H11\text{-}H10}$ = 7.0Hz, $^4J_{H11\text{-}H13}$ = 2.6Hz, $H_{11}$), 1.95 (t, 1H, $^4J_{H13\text{-}H11}$ = 2.6Hz, $H_{13}$), 1.86 (quint, 2H, $^3J_{H4\text{-}H3}$ = $^3J_{H4\text{-}H5}$ = 6.9Hz, $H_4$), 1.59-1.47 (m, 2H, $H_5$), 1.41-1.36 (m, 4H, $H_6$ $H_{10}$), 1.36-1.24 (m, 6H, $H_7$ $H_8$ $H_9$).

**$^{13}$C NMR (100 MHz, $CDCl_3$, 298K):** δ ppm = 84.6 ($C_{12}$), 68.0 ($C_{13}$), 33.9 ($C_3$), 32.7 ($C_4$), 29.2 & 28.9 & 28.6 & 28.4 & 28.1 ($C_5$ $C_6$ $C_7$ $C_8$ $C_9$ $C_{10}$), 18.3 ($C_{11}$).

## 3.3. Synthesis of the azidoalkyne H



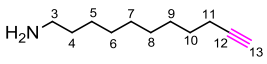

**H**

To a solution of the 11-bromoundec-1-yne **G** (2.38 g, 10.3 mmol, 1 equiv.) in DMF (26 mL) was added sodium azide (1.34 g, 20.6 mmol, 2 equiv.). The reaction mixture was heated at 50°C for 1.5h before being concentrated. The crude was then dissolved in $Et_2O$ (30 mL) and washed with water (2x10 mL). The combined aqueous layers were extracted with $Et_2O$ (2x10 mL) and the combined organic phases were dried over $MgSO_4$, filtered and concentrated to give the 11-azidoundec-1-yne **H** (1.923 g, 96%) as colorless oil, which was pure enough to be used without any further purification.

**$R_f$:** 0.30 (PE).

**$^1$H NMR (300 MHz, $CDCl_3$, 298K):** δ ppm = 3.26 (t, 2H, $^3J_{H3\text{-}H4}$ = 7.0Hz, $H_3$), 2.19 (td, 2H, $^3J_{H11\text{-}H10}$ = 7.0Hz, $^4J_{H11\text{-}H13}$ = 2.6Hz, $H_{11}$), 1.94 (t, 1H, $^4J_{H13\text{-}H11}$ = 2.6Hz, $H_{13}$), 1.60 (br quint, 2H, $H_4$), 1.53 (br quint, 2H, $H_{10}$), 1.66-1.25 (m, 10H, $H_5$ $H_6$ $H_7$ $H_8$ $H_9$).
**$^{13}$C NMR (100 MHz, $CDCl_3$, 298K):** δ ppm = 84.6 ($C_{12}$), 68.0 ($C_{13}$), 51.4 ($C_3$), 29.2 & 29.0 & 28.9 & 28.7 & 28.6 & 28.4 ($C_4$ $C_6$ $C_7$ $C_8$ $C_9$ $C_{10}$), 26.6 ($C_5$), 18.3 ($C_{11}$).
**HRMS (ESI)**: $[2M+H]^+$ calcd for $C_{22}H_{39}N_6^+$: 387.3236, found: 387.3230.

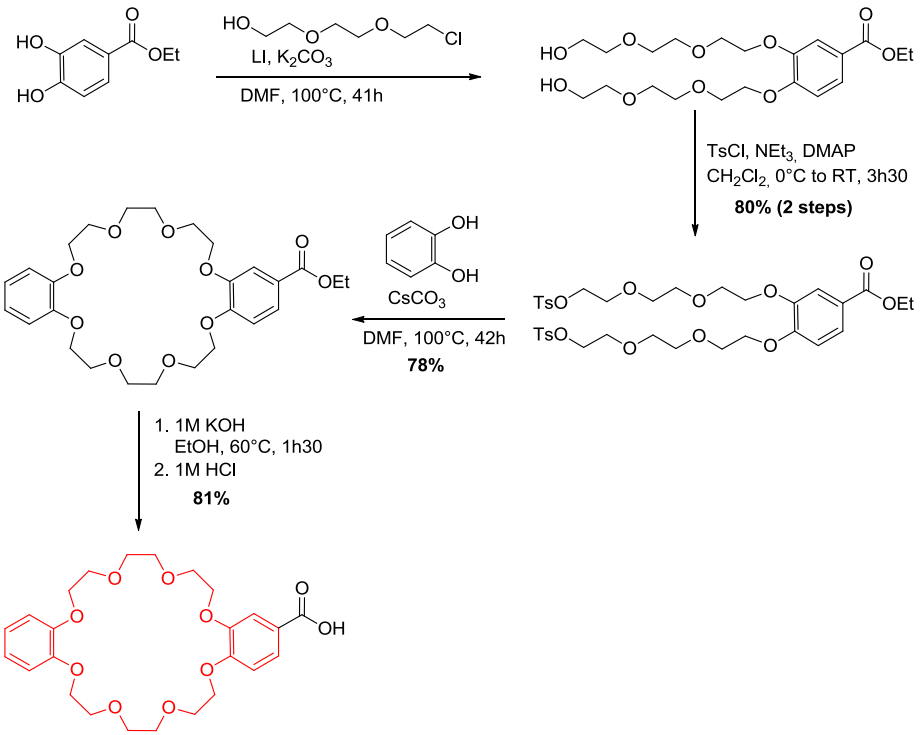
## 3.4. Synthesis of the aminoalkyne I




**I**

A solution of the 11-azidoundec-1-yne **H** (100 mg, 0.52 mmol, 1 equiv.) in $Et_2O$ (600 µL) was cooled to 0°C. To this solution was added $PPh_3$ (172 mg, 0.52 mmol, 1.2 equiv.). The mixture was stirred for 2h at 0°C. Then milli-Q water (600 µL) was added. The resulting mixture was stirred again for 3h at 0°C before being concentrated. The crude was purified by chromatography on a silicagel column ($CH_2Cl_2$, then $CH_2Cl_2$/MeOH 90:10, then $CH_2Cl_2$/MeOH/$NH_4OH$ 88:10:2) to give the pure undec-10-yn-1-amine **I** (76 mg, 88%) as a white solid.
**$R_f$:** 0.40 ($CH_2Cl_2$/MeOH/$NH_4OH$ 90/9/1).
**$^1$H NMR (600 MHz, $CD_3CN$, 298K):** δ ppm = 2.64 (br t, 2H, $H_3$), 2.13 (td, 2H, $^3J_{H11\text{-}H10}$ = 7.1Hz, $^4J_{H11\text{-}H13}$ = 2.6Hz, $H_{11}$), 1.89 (t, 1H, $^4J_{H13\text{-}H11}$ = 2.6Hz, $H_{13}$), 1.56 (br s, 2H, $NH_2$), 1.47 (quint, 2H, $^3J_{H4\text{-}H3}$ = $^3J_{H4\text{-}H5}$ = 7.2Hz, $H_4$), 1.40 (br quint, 2H, $H_5$), 1.34 (br quint, 2H, $H_{10}$), 1.30-1.21 (m, 8H, $H_6$ $H_7$ $H_8$ $H_9$).
**$^{13}$C NMR (150 MHz, $CD_3CN$, 298K):** δ ppm = 84.6 ($C_{12}$), 67.9 ($C_{13}$), 42.0 ($C_3$), 33.5 ($C_4$), 29.3 & 28.9 & 28.6 & 28.3 ($C_6$ $C_7$ $C_8$ $C_9$ $C_{10}$), 26.7 ($C_5$), 18.3 ($C_{11}$).
**HRMS (ESI)**: $[M+H]^+$ calcd for $C_{11}H_{22}N^+$: 168.1752, found: 168.1750.

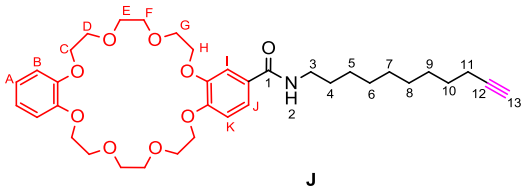
## 3.5. Synthesis of the DB24C8-ester derivative




The DB24C8-ester derivative was prepared according to the procedure described by Stoddart *et al.*[1] and for the saponification according to Li *et al.*[2]

[1] S. J. Cantrill, G. J. Youn, J. F. Stoddart, *J. Org. Chem.* 2001, **66**, 6857-6872.
[2] D. -J. Feng, X. -Q. Li, X. -Z. Wang, X. –K. Jiang, Z.-T. Li, *Tetrahedron* 2004, **60**, 6137–6144.

## 3.6. Synthesis of the DB24C8-alkyne derivative J



**J**

To a mixture of the previously synthesized carboxylic acid DB24C8 derivative (921 mg, 1.87 mmol, 1 equiv.) and undec-10-yn-1-amine **I** (313 mg, 1.87 mmol, 1 equiv.) in dry $CH_2Cl_2$ (70 mL) was added DMAP (297 mg, 2.43 mmol, 1.3 equiv.). The solution was cooled to 0°C, then added by EDCI (466 mg, 2.43 mmol, 1.3 equiv.) (by portions). The reaction mixture was allowed to warm up until room temperature and stirred overnight. The crude was successively washed with an aqueous solution of HCl 1M (2x50 mL), a saturated aqueous solution of $NaHCO_3$ (2x50 mL) and brine (50 mL). The organic layer was then dried over $MgSO_4$ and concentrated. The resulting solid was purified by chromatography on silicagel column ($CH_2Cl_2$ /$CH_3OH$ 100:0 to 90:10) to give the pure macrocycle **J** as a white powder (1.10 g, 96%).

**$R_f$:** 0.49 ($CH_2Cl_2$/$CH_3OH$ 90/10).

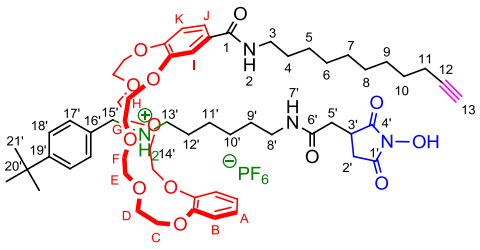
**$^1$H NMR (600 MHz, $CD_2Cl_2$, 298K):** δ ppm = 7.35 (d, 1H, $^4J_{HI\text{-}HJ}$ = 1.9Hz, $H_I$), 7.26 (dd, 1H, $^3J_{HJ\text{-}HK}$ = 8.3Hz, $^4J_{HJ\text{-}HI}$ = 1.9Hz, $H_J$), 6.91-6.85 (m, 4H, $H_A$ $H_B$), 6.87 (d, 1H, $^3J_{HK\text{-}HJ}$ = 8.3Hz, $H_K$), 6.13 (br t, 1H, $H_2$), 4.18-4.13 (m, 4H, $H_H$), 4.13-4.09 (m, 4H, $H_C$), 3.90-3.82 (m, 8H, $H_D$ $H_G$), 3.78-3.74 (m, 8H, $H_E$ $H_F$), 3.37 (q, 2H, $^3J_{H3\text{-}H4}$ = $^3J_{H3\text{-}NH}$ = 6.9Hz, $H_3$), 2.17 (td, 2H, $^3J_{H11\text{-}H10}$ = 7.2 Hz, $^4J_{H11\text{-}H13}$ = 2.6Hz, $H_{11}$), 1.96 (t, 1H, $^4J_{H13\text{-}H11}$ = 2.6Hz, $H_{13}$), 1.58 (quint, 2H, $^3J_{H4\text{-}H3}$ = $^3J_{H4\text{-}H5}$ = 6.9Hz, $H_4$), 1.50 (quint, 2H, $^3J_{H10\text{-}H11}$ = $^3J_{H10\text{-}H9}$ = 7.2Hz, $H_{10}$), 1.41-1.32 (m, 4H, $H_5$ $H_9$), 1.33-1.28 (m, 6H, $H_6$ $H_7$ $H_8$).

**$^{13}$C NMR (150 MHz, $CD_2Cl_2$, 298K):** δ (ppm) = 167.1 ($C_1$), 152.1 & 149.6 & 149.2 & 128.5 ($C_{IV\ arom\ DB24C8}$), 121.9 & 114.9 ($C_A$ $C_B$), 120.5 ($C_J$), 113.6 ($C_I$), 113.2 ($C_K$), 85.3 ($C_{12}$), 71.7 & 71.6 ($C_E$ $C_F$), 70.4 & 70.3 & 70.2 & 70.0 & 69.8 ($C_D$ $C_G$ $C_C$ $C_H$), 68.5 ($C_{13}$), 40.5 ($C_3$), 30.3 ($C_4$), 29.9 & 29.8 & 29.6 ($C_6$ $C_7$ $C_8$), 29.3 ($C_9$), 29.1 ($C_{10}$), 27.5 ($C_5$), 18.8 ($C_{11}$).

**HRMS (ESI)**: $[M+H]^+$ calcd for $C_{36}H_{52}NO_9^+$: 642.3642, found: 642.3640.

# 4. Synthesis of the rotaxanes

## 4.1. Synthesis of rotaxane 2



**2**

A 0.12 M solution of the transporter thread **1** (100 mg, 0.177 mmol, 1 equiv.) and the alkyne macrocycle **J** (342 mg, 0.532 mmol, 3 equiv.) in dry $CH_2Cl_2$ (1.5 mL) was stirred for 12h at room temperature before being concentrated. Addition of $CH_3CN$ allowed the removal of most of the excess of the insoluble alkyne macrocycle **J** by filtration. After concentration of the filtrate, the resulting solid was purified by chromatography on a lipophilic sephadex LH20 ($CH_2Cl_2$) to afford pure **2** (176.5 mg, 82%) as a white powder.

**$R_f$:** 0.42 ($CH_2Cl_2$/MeOH 9/1)

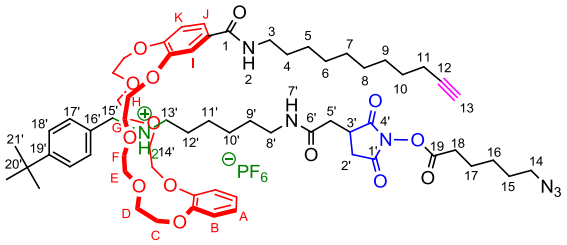
**$^1$H NMR (600 MHz, $CD_3CN$, 298K):** δ ppm = 7.36-7.33 (m, 2H, $H_I$ $H_J$), 7.30-7.27 (m, 2H, $H_{17'}$), 7.23-7.19 (m, 2H, $H_{18'}$), 7.15-7.04 (br s, 2H, $H_{14'}$), 7.06 (br t, 1H, $H_2$), 6.93 (d, 1H, $^3J_{HK\text{-}HJ}$ = 8.9Hz, $H_K$), 6.89 (s, 4H, $H_A$ $H_B$), 6.47 (br t, 1H, $H_{7'}$), 4.55-4.51 (m, 2H, $H_{15'}$), 4.29-4.23 & 4.17-4.03 (2m, 8H, $H_C$ $H_H$), 3.87-3.75 (m, 8H, $H_D$ $H_G$), 3.70-3.62 & 3.58-3.51 (2m, 2x4H, $H_E$ $H_F$), 3.33-3.28 (m, 2H, $H_3$), 3.30-3.23 (m, 2H, $H_{13'}$), 3.03-2.96 (m, 1H, $H_{3'}$), 2.95-2.89 (m, 2H, $H_{8'}$), 2.75 (dd, 1H, $^2J_{H2'a\text{-}H2'b}$ = 17.7Hz, $^3J_{H2'a\text{-}H3'}$ = 9.1Hz, $H_{2'a}$), 2.64-2.54 (m, 2H, $H_{5'}$), 2.36-2.33 (m, 1H, $H_{2'b}$), 2.18-2.11 (m, 2H, $H_{11}$ $H_{13}$), 1.58-1.52 (m, 2H,

$H_4$), 1.52-1.45 (m, 2H, $H_{10}$), 1.47-1.40 (m, 2H, $H_{12'}$), 1.40-1.35 (m, 2H, $H_9$), 1.35-1.32 (m, 2H, $H_5$), 1.32-1.27 (m, 6H, $H_6$ $H_7$ $H_8$), 1.22 (s, 9H, $H_{21'}$), 1.17-1.13 (m, 2H, $H_{9'}$), 1.04-0.96 (m, 4H, $H_{11'}$ $H_{10'}$).

**$^{13}$C NMR (150 MHz, $CD_3CN$, 298K):** δ ppm = 175.5 & 172.5 ($C_{1'}$ $C_{4'}$), 170.7 ($C_{6'}$), 167.4 ($C_1$), 153.1 ($C_{19'}$), 151.0 & 148.4 & 148.3 & 128.8 ($C_{IV\ arom\ macrocycle}$), 130.4 ($C_{16'}$ $C_{17'}$), 126.3 ($C_{18'}$), 122.4 & 113.6 ($C_A$ $C_B$), 121.5 ($C_J$), 112.8 ($C_K$), 112.4 ($C_I$), 85.6 ($C_{12}$), 71.7 & 71.6 ($C_E$ $C_F$), 71.0 & 70.9 ($C_D$ $C_G$), 69.6 & 69.3 & 69.0 ($C_C$ $C_H$ $C_{13}$), 52.8 ($C_{15'}$), 49.6 ($C_{13'}$), 40.6 ($C_3$), 39.7 ($C_{8'}$), 35.9 ($C_{5'}$), 35.1 ($C_{20'}$), 34.6 ($C_{3'}$), 32.4 ($C_{2'}$), 31.4 ($C_{21'}$), 30.3 ($C_4$), 30.1 & 30.0 & 29.7 & 27.7 ($C_5$ $C_6$ $C_7$ $C_8$ $C_{9'}$), 29.4 ($C_9$), 29.3 ($C_{10}$), 27.1 ($C_{12'}$), 26.7 & 26.6 ($C_{10'}$ $C_{11'}$), 18.7 ($C_{11}$).

**HRMS (ESI)**: $[M\text{-}PF_6]^+$ calcd for $C_{59}H_{87}N_4O_{13}^+$: 1059.6270, found: 1059.6267.

## 4.2. Synthesis of rotaxane 3



**3**

A solution of semi-rotaxane **2** (172 mg, 0.14 mmol, 1 equiv.) and 6-azidohexanoic acid (24.6 mg, 0.16 mmol, 1.1 equiv.) in dry $CH_2Cl_2$ (2 mL) was cooled at 0°C. To this solution was added DCC (62 mg, 0.30 mmol, 2.1 equiv.). The reaction mixture was allowed to warm up until room temperature and stirred overnight. At the end of the reaction, the DCU precipitate was filtered off and washed with $CH_2Cl_2$ (5 mL). The resulting solution was concentrated to give a solid which was purified by chromatography on a lipophilic sephadex LH20 ($CH_2Cl_2$) to afford the pure rotaxane **3** (167 mg, 87%) as a white powder.

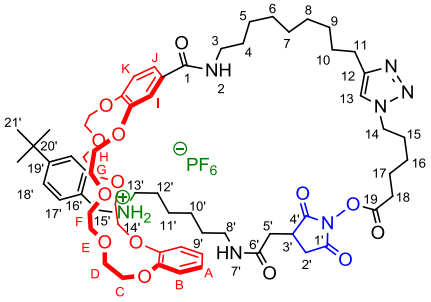
**$R_f$:** 0.50 ($CH_2Cl_2$/MeOH 9/1).

**$^1$H NMR (600 MHz, $CD_3CN$, 298K):** δ ppm = 7.38-7.36 (m, 2H, $H_I$ $H_J$), 7.28 (d, 2H, $^3J_{H17'\text{-}H18'}$ = 8.1Hz, $H_{17'}$), 7.20 (d, 2H, $^3J_{H18'\text{-}H17'}$ = 8.1Hz, $H_{18'}$), 7.15-7.04 (br s, 2H, $H_{14'}$), 7.03 (br s, 1H, $H_2$), 6.93 (d, 1H, $^3J_{HK\text{-}HJ}$ = 8.9Hz, $H_K$), 6.89 (s, 4H, $H_A$ $H_B$), 6.51 (br s, 1H, $H_{7'}$), 4.56-4.51 (m, 2H, $H_{15'}$), 4.27-4.20 & 4.17-4.02 (2m, 8H, $H_C$ $H_H$), 3.87-3.75 (m, 8H, $H_D$ $H_G$), 3.70-3.62 & 3.59-3.52 (2m, 2x4H, $H_E$ $H_F$), 3.34-3.24 (m, 6H, $H_{13'}$ $H_3$ $H_{14}$), 3.24-3.15 (m, 1H, $H_{3'}$), 2.98-2.90 (m, 3H, $H_{8'}$ $H_{2'a}$), 2.79-2.60 (m, 2H, $H_{5'}$), 2.62 (t, 2H, $^3J_{H18\text{-}H17}$ = 7.4Hz, $H_{18}$), 2.57-2.47 (m, 1H, $H_{2'b}$), 2.16 (dt, 2H, $^3J_{H11\text{-}H12}$ = 7.1Hz, $^4J_{H11\text{-}H13}$ = 2.7Hz, $H_{11}$), 2.13 (t, 1H, $^4J_{H13\text{-}H11}$ = 2.7Hz, $H_{13}$), 1.71 (quint, 2H, $^3J_{H17\text{-}H18}$ = $^3J_{H17\text{-}H16}$ = 7.4Hz, $H_{17}$), 1.60 (quint, 2H, $^3J_{H15\text{-}H16}$ = $^3J_{H15\text{-}H14}$ = 7.4Hz, $H_{15}$), 1.55 (quint, 2H, $^3J_{H4\text{-}H5}$ = $^3J_{H4\text{-}H3}$ = 7.0Hz, $H_4$), 1.51-1.41 (m, 6H, $H_{10}$ $H_{16}$ $H_{12'}$), 1.40-1.26 (m, 10H, $H_5$ $H_6$ $H_7$ $H_8$ $H_9$), 1.21 (s, 9H, $H_{21'}$), 1.15 (quint, 2H, $^3J_{H9'\text{-}H10'}$ = $^3J_{H9'\text{-}H8'}$ = 6.8Hz, $H_{9'}$), 1.07-0.97 (m, 4H, $H_{11'}$ $H_{10'}$).

**$^{13}$C NMR (150 MHz, $CD_3CN$, 298K):** δ ppm = 173.5 & 170.5 & 170.3 & 170.0 ($C_{1'}$ $C_{4'}$ $C_{6'}$ $C_{19}$), 167.0 ($C_1$), 153.0 ($C_{19'}$), 150.9 & 148.4 & 148.2 & 128.9 ($C_{IV\ arom\ macrocycle}$), 130.4 ($C_{16'}$ $C_{17'}$), 126.3 ($C_{18'}$), 122.3 & 113.5 ($C_A$ $C_B$), 121.4 ($C_J$), 112.7 ($C_K$), 112.3 ($C_I$), 85.5 ($C_{12}$), 71.6 ($C_E$ $C_F$), 71.1 & 70.9 ($C_D$ $C_G$), 69.6 & 69.2 & 69.0 ($C_C$ $C_H$ $C_{13}$), 52.7 ($C_{15'}$), 51.8 ($C_{14}$), 49.5 ($C_{13'}$), 40.5 ($C_3$), 39.7 ($C_{8'}$), 35.7 ($C_{5'}$), 35.1 ($C_{20'}$), 34.8 ($C_{3'}$), 32.6 ($C_{2'}$), 31.4 ($C_{21'}$), 31.3 ($C_{18}$), 30.3 & 30.1 & 30.0 & 29.7 & 29.4 & 29.2 & 27.6 & 27.1 & 26.6 & 26.5 ($C_4$ $C_5$ $C_6$ $C_7$ $C_8$ $C_9$ $C_{10}$ $C_{16}$ $C_{9'}$ $C_{10'}$ $C_{11'}$ $C_{12'}$), 28.9 ($C_{15}$), 24.9 ($C_{17}$), 18.7 ($C_{11}$).

**HRMS (ESI)**: $[M\text{-}PF_6]^+$ calcd for $C_{65}H_{96}N_7O_{14}^+$: 1198.7015, found: 1198.7010.

## 4.3. Cyclization reaction: synthesis of the triazole-containing loosened lasso



To a solution of the semi-rotaxane **3** (210 mg, 0.156 mmol, 1 equiv.) in dry $CH_2Cl_2$ (312 mL, $5.10^{-4}$M) were added successively $Cu(CH_3CN)_4PF_6$ (58 mg, 0.156 mmol, 1 equiv.) and 2,6-lutidine (2 µL, 0.016 mmol, 0.1 equiv.). The mixture was stirred for 48 h at room temperature before being concentrated. $CH_2Cl_2$ (20 mL) was added and this solution was washed with an aqueous solution of EDTA 0.1M (5x10 mL). The organic layer was dried over $MgSO_4$ and concentrated. The purification of the crude by chromatography on a lipophilic sephadex LH20 ($CH_2Cl_2$) affords the pure triazole containing [1]rotaxane (126 mg, 60%) as a white powder.

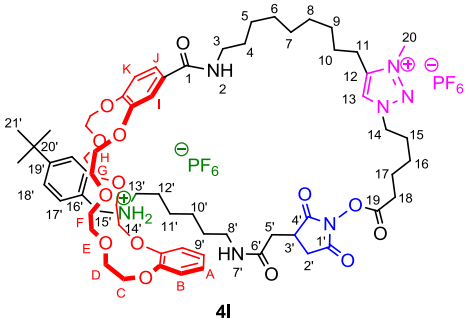
**$R_f$:** 0.48 ($CH_2Cl_2$/MeOH 9/1).

**$^1$H NMR (600 MHz, $CD_3CN$, 298K):** δ ppm = 7.54 (br s, 1H, $H_{13}$), 7.43-7.34 (m, 4H, $H_I$ $H_J$ $H_{17'}$), 7.34-7.29 (m, 2H, $H_{18'}$), 7.20-7.13 (m, 1H, $H_2$), 7.14-7.03 (br s, 2H, $H_{14'}$), 6.98 (d, 1H, $^3J_{HK-HJ}$ = 8.5Hz, $H_K$), 6.91 (s, 4H, $H_A$ $H_B$), 6.60 (br t, 1H, $H_{7'}$), 4.57-4.52 (m, 2H, $H_{15'}$), 4.32 (t, 2H, $^3J_{H14-H15}$ = 6.6Hz, $H_{14}$), 4.38-4.29 & 4.18-4.12 & 4.11-4.02 (3m, 8H, $H_C$ $H_H$), 3.91-3.83 & 3.83-3.73 (2m, 8H, $H_D$ $H_G$), 3.66-3.58 & 3.53-3.49 & 3.49-3.39 (3m, 8H, $H_E$ $H_F$), 3.32-3.26 (br q, 2H, $H_3$), 3.23-3.14 (m, 3H, $H_{3'}$ $H_{13'}$), 2.98-2.90 (m, 1H, $H_{2'a}$), 2.90-2.81 (m, 2H, $H_{8'}$), 2.77-2.61 (m, 2H, $H_{5'}$), 2.77-2.61 (m, 2H, $H_{11}$), 2.56 (t, 2H, $^3J_{H18-H17}$ = 7.3Hz, $H_{18}$), 2.59-2.47 (m, 1H, $H_{2'b}$), 1.86 (br quint, 2H, $H_{15}$), 1.70-1.60 (m, 4H, $H_{17}$ $H_{10}$), 1.53 (quint, 2H, $^3J_{H4-H5}$ = $^3J_{H4-H3}$ = 7.0Hz, $H_4$), 1.36-1.25 (m, 14H, $H_5$ $H_6$ $H_7$ $H_8$ $H_9$ $H_{16}$ $H_{12'}$), 1.26 (s, 9H, $H_{21'}$), 1.07-0.99 (m, 2H, $H_{9'}$), 0.90-0.81 (m, 4H, $H_{11'}$ $H_{10'}$).

**$^{13}$C NMR (150 MHz, $CD_3CN$, 298K):** δ ppm = 173.4 & 170.4 & 170.0 ($C_{1'}$ $C_{4'}$ $C_{6'}$ $C_{19}$), 167.4 ($C_1$), 153.3 ($C_{19'}$), 151.0 & 148.5 & 148.4 & 129.2 ($C_{IV\ arom\ macrocycle}$), 130.6 ($C_{16'}$ $C_{17'}$), 126.5 ($C_{18'}$), 122.5 & 113.7 ($C_A$ $C_B$), 121.6 ($C_J$), 112.9 ($C_K$), 112.7 ($C_I$), 71.7 & 71.5 ($C_E$ $C_F$), 71.0 & 70.8 ($C_D$ $C_G$), 69.4 & 69.2 & 69.1 ($C_C$ $C_H$), 52.8 ($C_{15'}$), 50.3 ($C_{14}$), 49.6 ($C_{13'}$), 40.5 ($C_3$), 39.8 ($C_{8'}$), 35.9 ($C_{5'}$), 35.2 ($C_{20'}$), 34.9 ($C_{3'}$), 32.6 ($C_{2'}$), 31.5 ($C_{21'}$), 31.3 ($C_{18}$), 30.3 & 30.2 & 30.1 & 30.0 & 29.8 & 29.7 & 29.3 & 27.5 & 27.0 & 26.5 ($C_4$ $C_5$ $C_6$ $C_7$ $C_8$ $C_9$ $C_{10}$ $C_{15}$ $C_{16}$ $C_{9'}$ $C_{10'}$ $C_{11'}$ $C_{12'}$), 26.1 ($C_{11}$), 24.7 ($C_{17}$).

**HRMS (ESI)**: $[M\text{-}PF_6]^+$ calcd for $C_{65}H_{96}N_7O_{14}^+$: 1198.7015, found: 1198.7032.

## 4.4. Synthesis of the [1]rotaxane 4l



**4l**

To the previously obtained triazole containing [1]rotaxane (120 mg, 0.089 mmol, 1 equiv.) was added $CH_2Cl_2$ (0.5 mL) and methyl iodide (3 mL). The mixture was stirred for 4 days at room temperature before being concentrated. The remaining solid was then diluted in $CH_2Cl_2$ (5 mL). To this solution was added $NH_4PF_6$ (36 mg, 0.22 mmol, 2.5 equiv.) and $H_2O$ milli-Q (0.5 mL); the biphasic solution was stirred vigorously for 30 min. The aqueous layer was extracted with $CH_2Cl_2$ (3×5 mL) and the combined organic layers were dried over $MgSO_4$ and concentrated under vacuum. The crude was purified by chromatography on a lipophilic sephadex LH20 ($CH_2Cl_2$) and provided the pure loosened triazolium-containing [1]rotaxane **4l** (120 mg, 90%) as a slightly yellow powder.

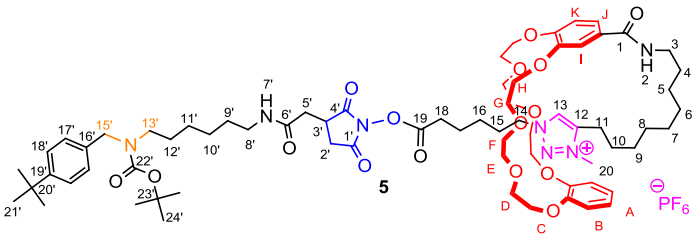
**$R_f$:** 0.50 ($CH_2Cl_2$/MeOH 9/1).

**$^1$H NMR (600 MHz, $CD_3CN$, 298K):** δ ppm = 8.18 (s, 1H, $H_{13}$), 7.44-7.40 (m, 3H, $H_I$ $H_{17'}$), 7.40-7.34 (m, 3H, $H_J$ $H_{18'}$), 7.24 (br s, 1H, $H_2$), 7.14-7.04 (br s, 2H, $H_{14'}$), 7.01 (d, 1H, $^3J_{HK\text{-}HJ}$ = 8.5Hz, $H_K$), 6.92 (s, 4H, $H_A$ $H_B$), 6.71 (br s, 1H, $H_{7'}$), 4.58-4.54 (m, 2H, $H_{15'}$), 4.52 (t, 2H, $^3J_{H14\text{-}H15}$ = 6.4Hz, $H_{14}$), 4.41-4.33 & 4.18-4.13 & 4.11-4.03 (3m, 8H, $H_C$ $H_H$), 4.09 (s, 3H, $H_{20}$), 3.93-3.85 & 3.81-3.76 & 3.76-3.71 (3m, 8H, $H_D$ $H_G$), 3.64-3.54 & 3.50-3.45 & 3.45-3.28 (3m, 8H, $H_E$ $H_F$), 3.31-3.26 (m, 2H, $H_3$), 3.23-3.16 (m, 1H, $H_{3'}$), 3.16-3.08 (m, 2H, $H_{13'}$), 2.98-2.91 (m, 1H, $H_{2'a}$), 2.88-2.79 (m, 2H, $H_{8'}$), 2.85-2.76 & 2.71-2.65 (m, 2H, $H_{5'}$), 2.78 (t, 2H, $^3J_{H11\text{-}H10}$ = 7.6Hz, $H_{11}$), 2.60 (t, 2H, $^3J_{H18\text{-}H17}$ = 6.8Hz, $H_{18}$), 2.55-2.44 (m, 1H, $H_{2'b}$), 2.00-1.94 (m, 2H, $H_{15}$), 1.76-1.66 (m, 4H, $H_{17}$ $H_{10}$), 1.55 (br quint, 2H, $H_4$), 1.41-1.27 (m, 14H, $H_5$ $H_6$ $H_7$ $H_8$ $H_9$ $H_{16}$ $H_{12'}$), 1.28 (s, 9H, $H_{21'}$), 1.04-0.95 (m, 2H, $H_{9'}$), 0.84-0.72 (m, 4H, $H_{11'}$ $H_{10'}$).

**$^{13}$C NMR (150 MHz, $CD_3CN$, 298K):** δ ppm = 173.6 & 170.5 & 170.3 & 169.9 ($C_{1'}$ $C_{4'}$ $C_{6'}$ $C_{19}$), 167.5 ($C_1$), 153.3 ($C_{19'}$), 151.0 & 148.5 & 148.4 & 129.1 ($C_{IV\ arom\ macrocycle}$), 145.9 ($C_{12}$), 130.6 ($C_{16'}$ $C_{17'}$), 128.7 ($C_{13}$), 126.5 ($C_{18'}$), 122.5 & 122.4 & 113.7 ($C_A$ $C_B$), 121.6 ($C_J$), 112.9 ($C_K$), 112.7 ($C_I$), 71.6 & 71.4 ($C_E$ $C_F$), 71.0 & 70.7 ($C_D$ $C_G$), 69.5 & 69.3 & 69.2 ($C_C$ $C_H$), 54.3 ($C_{14}$), 52.8 ($C_{15'}$), 49.6 ($C_{13'}$), 40.3 ($C_3$), 39.8 ($C_{8'}$), 38.2 ($C_{20}$), 35.7 ($C_{5'}$), 35.2 ($C_{20'}$), 34.9 ($C_{3'}$), 32.6 ($C_{2'}$), 31.4 ($C_{21'}$), 31.3 ($C_{18}$), 30.2 ($C_4$), 28.9 ($C_{15}$), 27.1 ($C_{10}$), 27.0 ($C_{12'}$), 26.6 ($C_{10'}$ $C_{11'}$), 29.7 & 29.6 & 29.5 & 29.0 & 27.3 & 25.2 ($C_5$ $C_6$ $C_7$ $C_8$ $C_9$ $C_{16}$ $C_{9'}$), 24.7 ($C_{17}$), 23.7 ($C_{11}$).

**HRMS (ESI)**: $[M\text{-}PF_6]^+$ calcd for $C_{66}H_{99}N_7O_{14}F_6P^+$: 1358.6892, found: 1358.6901.

## 4.5. Synthesis of the [1]rotaxane 5




To a solution of the rotaxane **4** (287 mg, 0.19 mmol, 1 equiv.) and $Boc_2O$ (208 mg, 0.95 mmol, 5 equiv.) in DMSO-*d*6 (5 mL) was added DIEA (1,67 mL, 9.5 mmol, 50 equiv.). The reaction mixture was stirred for 6h at room temperature. The DMSO was then lyophylisated. The resulting yellow oil was washed several times with $Et_2O$ (30 mL) in order to remove the excess of $Boc_2O$. The residue was then dissolved in $CH_2Cl_2$ (20 mL) and washed twice with an aqueous solution of HCl 1M (2x10 mL). The organic layer was then dried over $MgSO_4$ and concentrated. The resulting solid was purified by chromatography on a lipophilic sephadex LH20 ($CH_2Cl_2$) to afford the pure tightened lasso **5** (248 mg, 89%) as a beige powder.

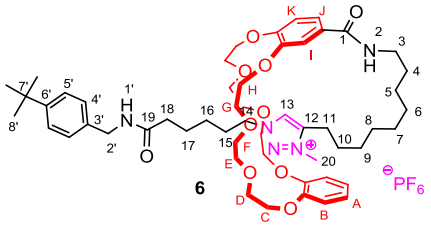
**$R_f$:** 0.62 ($CH_2Cl_2$/MeOH 9/1).

**$^1$H NMR (600 MHz, $CD_3CN$, 298K):** δ ppm = 8.38 (s, 1H, $H_{13}$), 7.37 (d, 2H, $^3J_{H18'\text{-}H17'}$ = 8.0Hz, $H_{18'}$), 7.33 (d, 1H, $^3J_{HJ\text{-}HK}$ = 8.2Hz, $H_J$), 7.22 (s, 1H, $H_I$), 7.16 (d, 2H, $^3J_{H17'\text{-}H18'}$ = 8.0Hz, $H_{17'}$), 6.92 (br t, 1H, $H_2$), 6.83-6.75 (m, 3H, $H_A$ $H_B$), 6.79 (d, 1H, $^3J_{HK\text{-}HJ}$ = 8.2Hz, $H_K$), 6.71 (d, 1H, $^3J$ = 7.8Hz, $H_A$ or $H_B$), 6.47 (br s, 1H, $H_{7'}$), 5.12 (dt, 1H, $^2J_{H14a\text{-}H14b}$ = 13.6Hz, $^3J_{H14a\text{-}H15}$ = 8.5Hz, $H_{14a}$), 4.99 (dt, 1H, $^2J_{H14b\text{-}H14a}$ = 13.6Hz, $^3J_{H14b\text{-}H15}$ = 8.9Hz, $H_{14b}$), 4.35 (s, 2H, $H_{15'}$), 4.27 (dd, 1H, $^2J$ = 11.2Hz, $^3J$ = 7.9Hz, $H_C$ or $H_H$), 4.15 (dd, 1H, $^2J$ = 11.5Hz, $^3J$ = 6.2Hz, $H_C$ or $H_H$), 4.10-3.99 & 3.96-3.90 (2m, 6H, $H_C$ $H_H$), 3.96-3.76 (m, 8H, $H_D$ $H_G$), 3.76-3.61 (m, 8H, $H_E$ $H_F$), 3.45-3.14 (m, 2H, $H_3$), 3.34 (s, 3H, $H_{20}$), 3.24-3.14 (m, 1H, $H_{3'}$), 3.16-3.09 (m, 2H, $H_{13'}$), 3.11-3.06 (m, 2H, $H_{8'}$), 2.94 (dd, 1H, $^2J_{H2'a\text{-}H2'b}$ = 17.9Hz, $^3J_{H2'a\text{-}H3'}$ = 9.1Hz, $H_{2'a}$), 2.78-2.60 (m, 2H, $H_{5'}$), 2.68 (t, 2H, $^3J_{H18\text{-}H17}$ = 7.4Hz, $H_{18}$), 2.59-2.48 (m, 1H, $H_{2'b}$), 2.36 (br quint, 2H, $H_{15}$), 1.90-1.82 (m, 3H, $H_{17}$ $H_{11a}$), 1.66-1.53 (m, 5H, $H_{16}$ $H_4$ $H_{11b}$), 1.50-1.14 (m, 25H, $H_5$ $H_6$ $H_7$ $H_8$ $H_{9'}$ $H_{10'}$ $H_{11'}$ $H_{12'}$ $H_{24'}$), 1.29 (s, 9H, $H_{21'}$), 1.28-1.08 (m, 4H, $H_9$ $H_{10}$).

**$^{13}$C NMR (150 MHz, $CD_3CN$, 298K):** δ ppm = 173.5 & 170.5 & 170.2 ($C_{1'}$ $C_{4'}$ $C_{6'}$ $C_{19}$), 166.8 ($C_1$), 156.7 ($C_{22'}$), 151.3 ($C_{19'}$), 150.9 & 148.8 & 148.4 & 148.0 & 128.4 ($C_{IV\ arom\ macrocycle}$), 142.4 ($C_{12}$), 137.1 ($C_{16'}$), 128.8 ($C_{13}$), 128.1 ($C_{17'}$), 126.3 ($C_{18'}$), 122.7 & 122.4 & 112.7 ($C_A$ $C_B$), 121.3 ($C_J$), 112.5 ($C_K$), 111.3 ($C_I$), 79.9 ($C_{23'}$), 71.9 & 71.8 & 71.7 ($C_E$ $C_F$), 70.9 & 70.7 & 70.6 ($C_D$ $C_G$), 70.1 & 69.4 & 69.0 & 68.8 ($C_C$ $C_H$), 54.3 ($C_{14}$), 50.5 & 50.2 ($C_{15'}$), 47.5 & 47.2 ($C_{13'}$), 39.8 ($C_{8'}$), 39.0 ($C_3$), 36.7 ($C_{20}$), 35.7 ($C_{5'}$), 35.1 ($C_{20'}$ $C_{3'}$), 32.6 ($C_{2'}$), 31.6 ($C_{21'}$), 31.4 ($C_{18}$), 28.7 ($C_{24'}$), 30.1 & 28.0 & 27.7 & 27.6 & 27.5 & 27.0 & 26.6 & 26.4 & 24.1 ($C_4$ $C_5$ $C_6$ $C_7$ $C_8$ $C_9$ $C_{10}$ $C_{15}$ $C_{16}$ $C_{9'}$ $C_{10'}$ $C_{11'}$ $C_{12'}$), 25.3 ($C_{17}$), 22.9 ($C_{11}$).

**HRMS (ESI)**: $[M\text{-}PF_6]^+$ calcd for $C_{71}H_{106}N_7O_{16}^+$: 1312.7696, found: 1312.7703.

## 4.6. Synthesis of the [1]rotaxane 6



6

To a solution of the rotaxane **5** (60 mg, 0.041 mmol, 1 equiv.) in dry $CH_3CN$ (2 mL) was added the 4-*tert*-butylbenzylamine in $CH_2Cl_2$ (15 µL, 0.082 mmol, 2 equiv.). The reaction mixture was stirred for 2h at room temperature before being concentrated. The resulting solid was purified by lipophilic sephadex LH20 ($CH_2Cl_2$) to give the rotaxane **6** (38 mg, 87%) as a white powder.

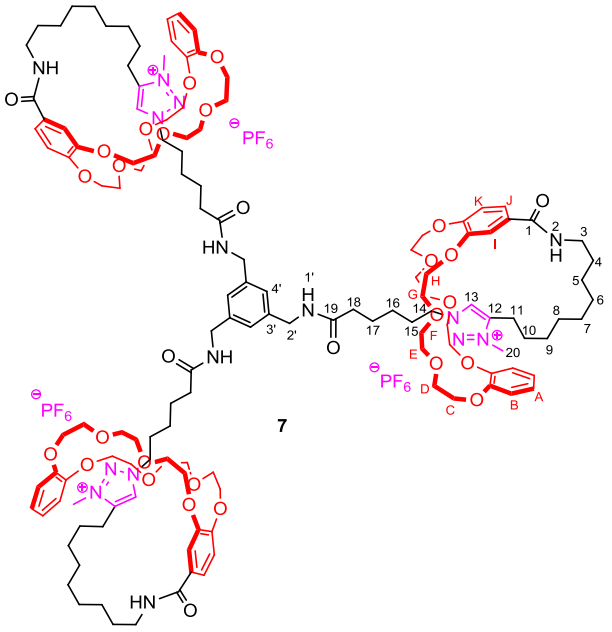
**$R_f$:** 0.60 ($CH_2Cl_2$/MeOH 9/1).

**$^1$H NMR (600 MHz, $CD_3CN$, 298K):** δ ppm = 8.38 (s, 1H, $H_{13}$), 7.36 (d, 2H, $^3J_{H5'-H4'}$ = 8.3Hz, $H_{5'}$), 7.33 (dd, 1H, $^3J_{HJ-HK}$ = 8.2Hz, $^4J_{HJ-HI}$ = 1.8Hz, $H_J$), 7.23-7.19 (m, 3H, $H_I$ $H_{4'}$), 6.91 (br t, 1H, $H_2$), 6.82-6.75 (m, 3H, $H_A$ $H_B$), 6.79 (d, 1H, $^3J_{HK-HJ}$ = 8.2Hz, $H_K$), 6.73 (br t, $H_{1'}$), 6.69 (d, 1H, $^3J_{HA-HB}$ = 7.4 Hz, $H_A$ or $H_B$), 5.14-5.05 & 5.02-4.94 (2m, 2H, $H_{14}$), 4.31 (d, 2H, $^3J_{H2'-H1'}$ = 6.0Hz, $H_{2'}$), 4.29-4.23 & 4.19-3.98 & 3.96-3.89 (3m, 8H, $H_C$ $H_H$), 3.96-3.60 (m, 8H, $H_D$ $H_G$), 3.74-3.60 (m, 8H, $H_E$ $H_F$), 3.46-3.39 & 3.40-3.34 (2m, 2H, $H_3$), 3.33 (s, 3H, $H_{20}$), 2.32 (br quint, 2H, $H_{15}$), 2.23 (t, 2H, $^3J_{H18-H17}$ = 7.5Hz, $H_{18}$), 1.90-1.82 (m, 1H, $H_{11a}$), 1.75 (br quint, 2H, $H_{17}$), 1.67-1.55 (m, 3H, $H_4$ $H_{11b}$), 1.56-1.48 (m, 2H, $H_{16}$), 1.42-1.27 (m, 8H, $H_5$ $H_6$ $H_7$ $H_8$), 1.29 (s, 9H, $H_{8'}$), 1.21-1.15 (m, 2H, $H_9$), 1.36-1.27 & 1.10-1.06 (2m, 2H, $H_{10}$).

**$^{13}$C NMR (150 MHz, $CD_3CN$, 298K):** δ ppm = 173.4 ($C_{19}$), 166.7 ($C_1$), 151.3 ($C_{6'}$), 150.8 & 148.7 & 148.4 & 147.9 & 128.3 ($C_{IV\ arom\ macrocycle}$), 142.3 ($C_{12}$), 137.7 ($C_{3'}$), 128.8 ($C_{13}$), 128.1 ($C_{4'}$), 126.3 ($C_{5'}$), 121.6 & 121.3 & 112.6 ($C_A$ $C_B$), 121.2 ($C_J$), 112.4 ($C_K$), 111.2 ($C_I$), 71.8 & 71.7 & 71.6 ($C_E$ $C_F$), 70.7 & 70.5 ($C_D$ $C_G$), 70.0 & 69.3 & 68.9 & 68.7 ($C_C$ $C_H$), 54.4 ($C_{14}$), 43.1 ($C_{2'}$), 38.9 ($C_3$), 36.9 ($C_{18}$), 36.7 ($C_{20}$), 35.0 ($C_{7'}$), 31.5 ($C_{8'}$), 28.6 & 27.9 & 27.8 & 27.7 & 27.5 & 27.0 & 26.9 & 24.0 ($C_4$ $C_5$ $C_6$ $C_7$ $C_8$ $C_9$ $C_{10}$ $C_{15}$ $C_{16}$), 26.5 ($C_{17}$), 22.9 ($C_{11}$).

**HRMS (ESI)**: $[M\text{-}PF_6]^+$ calcd for $C_{54}H_{80}N_5O_{10}^+$: 958.5905, found: 958.5914.

## 4.7. Synthesis of the tris-branched [1]rotaxane 7



7

The rotaxane **5** (60 mg, 0.041 mmol, 3.1 equiv.) was dissolved in dry $CH_3CN$ (2 mL). In another flask, 1 mL of a mother solution containing 1,3,5-tris(aminomethyl)benzene (21 mg, 0.13 mmol, 10 equiv.) and DIEA (140 µL, 2.4 mmol, 60 equiv.) in $CH_3CN$ (860 µL) was prepared. 100 µL of this solution were added to the solution containing the rotaxane **5**.

The reaction mixture was stirred during 18h at room temperature before being concentrated. The resulting crude was purified by successive chromatographies on a lipophilic sephadex LH20 ($CH_2Cl_2$), followed by a silica gel column chromatography ($CH_2Cl_2$/MeOH 100:0 to 85:15) to give one pure fraction of rotaxane **7** (5 mg, 13%).

**$R_f$:** 0.58 ($CH_2Cl_2$/MeOH 9/1).

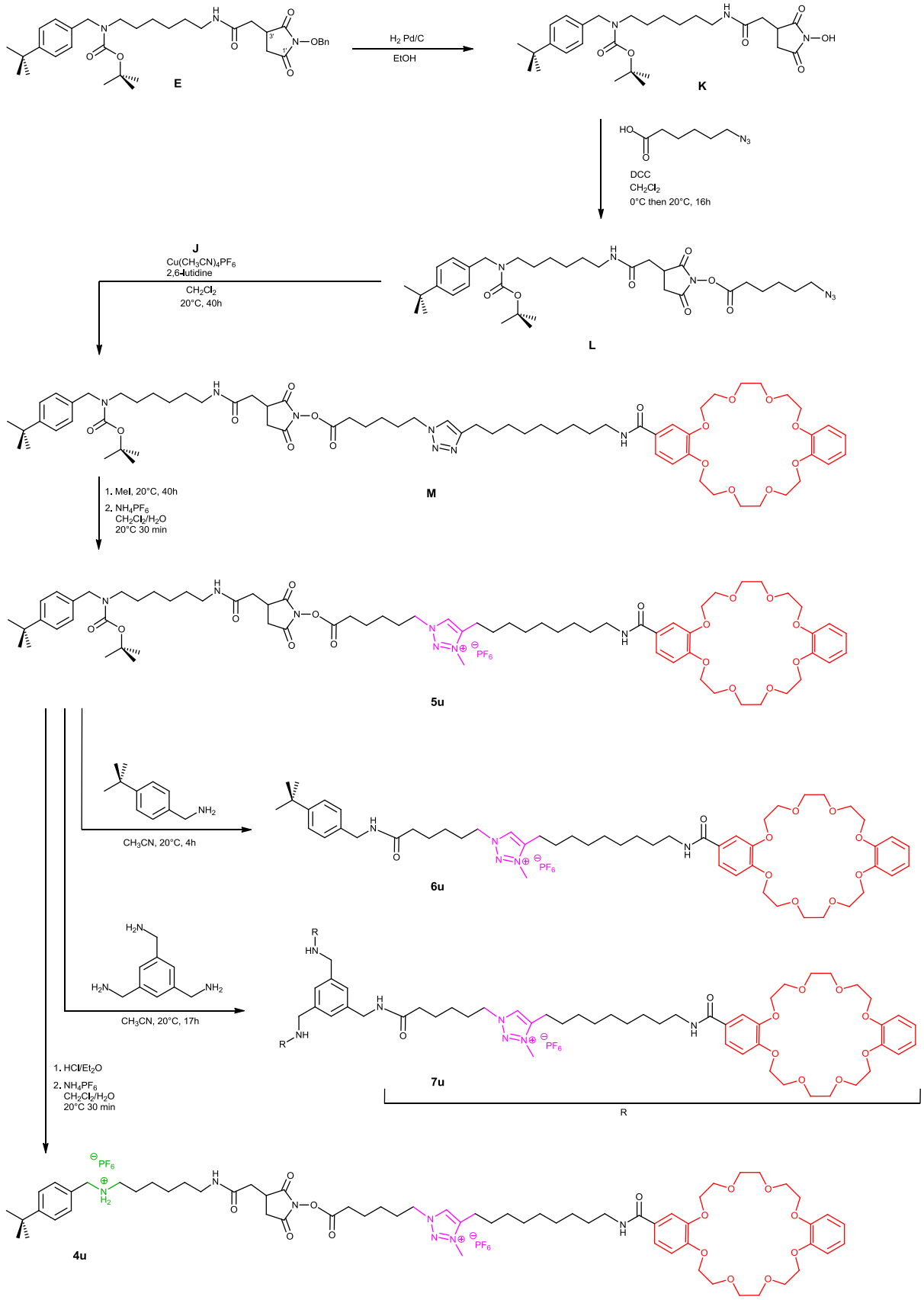
**$^1$H NMR (600 MHz, $CD_3CN$, 298K):** δ ppm = 8.34 (s, 3H, $H_{13}$), 7.31 (dd, 3H, $^3J_{HJ\text{-}HK}$ = 8.4Hz, $^4J_{HJ\text{-}HI}$ = 1.7Hz, $H_J$), 7.22 (d, 3H, $^4J_{HI\text{-}HJ}$ = 1.7Hz, $H_I$), 7.02 (s, 3H, $H_{4'}$), 6.98 (t, 3H, $^3J_{H2\text{-}H3}$ = 5.7Hz, $H_2$), 6.90 (br s, 3H, $H_{1'}$), 6.83-6.75 & 6.73-6.68 (2m, 12H, $H_A$ $H_B$), 6.77 (d, 3H, $^3J_{HK\text{-}HJ}$ = 8.4Hz, $H_K$), 5.06-4.97 & 4.95-4.86 (2m, 6H, $H_{14}$), 4.31 (d, 6H, $^3J_{H2'\text{-}H1'}$ = 5.0Hz, $H_{2'}$), 4.30-4.19 & 4.16-3.96 & 3.93-3.89 (3m, 24H, $H_C$ $H_H$), 3.93-3.58 (m, 24H, $H_D$ $H_G$), 3.70-3.58 (m, 24H, $H_E$ $H_F$), 3.42-3.36 (m, 6H, $H_3$), 3.38 (s, 9H, $H_{20}$), 2.29-2.22 (m, 6H, $H_{15}$), 2.26-2.20 (m, 6H, $H_{18}$), 1.95-1.89 (m, 3H, $H_{11a}$), 1.71 (br quint, 6H, $H_{17}$), 1.71-1.55 (m, 9H, $H_4$ $H_{11b}$), 1.50-1.42 (m, 6H, $H_{16}$), 1.42-1.21 (m, 24H, $H_5$ $H_6$ $H_7$ $H_8$), 1.25-1.12 (m, 6H, $H_9$), 1.29-1.23 & 1.14-1.07 (2m, 6H, $H_{10}$).

**$^{13}$C NMR (150 MHz, $CD_3CN$, 298K):** δ ppm = 173.8 ($C_{19}$), 166.8 ($C_1$), 151.2 & 148.8 & 148.4 & 148.0 & 128.8 ($C_{IV\ arom\ macrocycle}$), 142.6 ($C_{12}$), 140.9 ($C_{3'}$), 128.4 ($C_{13}$), 126.1 ($C_{4'}$), 121.7 & 121.4 & 112.7 ($C_A$ $C_B$), 121.2 ($C_J$), 112.4 ($C_K$), 111.3 ($C_I$), 71.9 & 71.7 & 71.6 ($C_E$ $C_F$), 70.8 & 70.7 & 70.6 & 70.5 ($C_D$ $C_G$), 70.0 & 69.3 & 69.0 & 68.7 ($C_C$ $C_H$), 54.4 ($C_{14}$), 43.6 ($C_{2'}$), 39.1 ($C_3$), 36.8 ($C_{18}$), 36.7 ($C_{20}$), 28.7 ($C_{10}$), 28.0 ($C_4$), 27.8 ($C_{15}$), 27.7 & 27.6 ($C_7$ $C_8$), 27.1 & 26.9 ($C_9$ $C_{16}$), 26.6 ($C_6$), 26.4 ($C_{17}$), 24.2 ($C_5$), 22.9 ($C_{11}$).

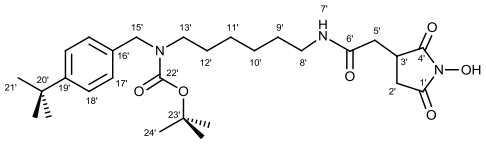
**HRMS (ESI)**: $[M\text{-}3PF_6]^{3+}$ calcd for $C_{138}H_{204}N_{15}O_{30}^+$: 850.4966, found: 850.4977.

# 5. Synthesis of the uncomplexed threads

## 5.1. General synthetic pathway



## 5.2. Synthesis of compound K



K

The compound **E** (600 mg, 0.99 mmol, 1 equiv.) was dissolved in EtOH (20 mL). 10%-Pd/C (500 mg) was added. The solution was stirred 15 min under an $H_2$ atmosphere, then filtered through a celite pad and concentrated. The resulting crude was purified by chromatography on a silicagel column ($CH_2Cl_2$/ MeOH 98:2 to 94:6) to give **K** (340 mg, 66%) as a pure white solid.

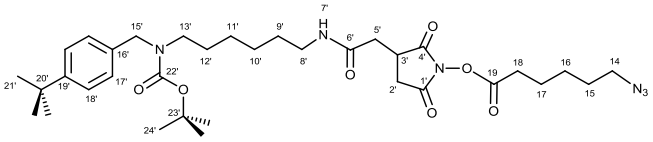
**$R_f$** 0.50 ($CH_2Cl_2$/MeOH 9/1)

**$^1$H NMR (400.13 MHz, $CD_3CN$, 298K):** δ ppm = 7.37 (d, 2H, $^3J_{H18'-H17'}$ = 8.3Hz, $H_{18'}$), 7.17 (d, 2H, $^3J_{H17'-H18'}$ = 8.3Hz, $H_{17'}$), 6.46 (br s, 1H, $H_{7'}$), 4.35 (s, 2H, $H_{15'}$), 3.13 (br t, 2H, $H_{13'}$), 3.08 (q, 2H, $^3J_{H8'-H7'}$ = $^3J_{H8'-H9'}$ = 6.0Hz, $H_{8'}$), 3.02-2.94 (m, 1H, $H_{3'}$), 2.75 (dd, 1H, $^2J_{H2'a-H2'b}$ = 17.7Hz, $^3J_{H2'a-H3'}$ = 9.1Hz, $H_{2'a}$), 2.64-2.52 (m, 2H, $H_{5'}$), 2.35 (dd, 1H, $^2J_{H2'b-H2'a}$ = 17.7Hz, $^3J_{H2'b-H3'}$ = 4.5Hz, $H_{2'b}$), 1.52-1.35 (m, 13H, $H_{9'}$ $H_{12'}$ $H_{24'}$), 1.29 (s, 9H, $H_{21'}$), 1.29-1.19 (m, 4H, $H_{10'}$ $H_{11'}$).

**$^{13}$C NMR (100 MHz, $CD_3CN$, 298K):** δ ppm = 175.6 & 172.7 & 170.9 ($C_{1'}$ $C_{4'}$ $C_{6'}$), 156.7 ($C_{22'}$), 150.8 ($C_{19'}$), 136.9 ($C_{16'}$), 128.0 ($C_{17'}$), 126.2 ($C_{18'}$), 80.0 ($C_{23'}$), 50.2 ($C_{15'}$), 47.4 ($C_{13'}$), 39.8 ($C_{8'}$), 35.9 ($C_{5'}$), 35.0 ($C_{20'}$), 34.5 ($C_{3'}$), 32.3 ($C_{2'}$), 31.6 ($C_{21'}$), 29.9 ($C_{9'}$), 28.6 ($C_{12'}$ $C_{24'}$), 27.1 & 27.0 ($C_{10'}$ $C_{11'}$).

**HRMS (ESI)**: $[M+H]^+$ calcd for $C_{23}H_{36}N_3O_4^+$: 418.2706, found: 418.2705.

## 5.3. Synthesis of compound L



L

A solution of **K** (350 mg, 0.63 mmol, 1 equiv.) and 6-azidohexanoic acid (103 mg, 0.66 mmol, 1.05 equiv.) in dry $CH_2Cl_2$ (5 mL) was cooled at 0°C before addition of DCC (273 mg, 1.323 mmol, 2.1 equiv.). The reaction mixture was allowed to warm until room temperature and stirred during 16h. At the end of the reaction, the DCU precipitate was filtered off and washed with $CH_2Cl_2$ (20 mL). The filtrate was successively washed with aqueous solutions of HCl 1M (15 mL), $NaHCO_3$ (15 mL) and brine (15 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated. The crude was successively purified by chromatography on a silicagel column (PE/AcOEt 70/30 to 50/50) and by chromatography on a lipophilic sephadex LH20 ($CH_2Cl_2$) to give pure **L** (265 mg, 60%) as a colorless oil.

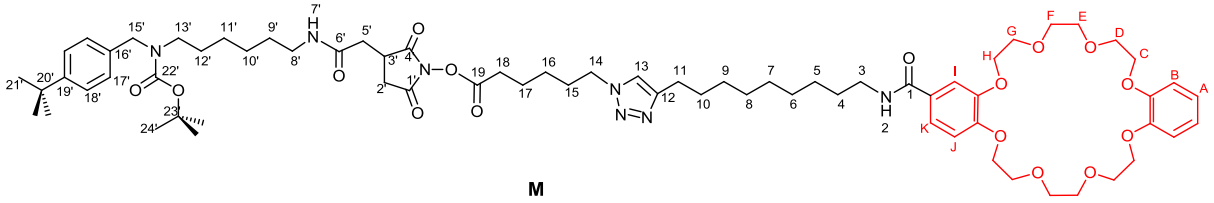
**$R_f$:** 0.63 (PE/AcOEt 40/60).

**$^1$H NMR (400.13 MHz, $CD_3CN$, 298K):** δ ppm = 7.37 (d, 2H, $^3J_{H18'-H17'}$ = 8.3Hz, $H_{18'}$), 7.17 (d, 2H, $^3J_{H17'-H18'}$ = 8.3Hz, $H_{17'}$), 6.49 (br s, 1H, $H_{7'}$), 4.35 (s, 2H, $H_{15'}$), 3.30 (t, 2H, $^3J_{H14-H15}$ = 6.8Hz, $H_{14}$), 3.22-3.14 (m, 1H, $H_{3'}$), 3.16 (br t, 2H, $H_{13'}$), 3.12 (q, 2H, $^3J_{H8'-H9'}$ = $^3J_{H8'-H7'}$ = 6.6Hz, $H_{8'}$), 2.93 (dd, 1H, $^2J_{H2'a-H2'b}$ = 17.9Hz, $^3J_{H2'a-H3'}$ = 9.1Hz, $H_{2'a}$), 2.67-2.60 (m, 2H, $H_{5'}$), 2.62 (t, 2H, $^3J_{H18-H17}$ = 7.3Hz, $H_{18}$), 2.58-2.47 (m, 1H, $H_{2'b}$), 1.72 (quint, 2H, $^3J_{H17-H18}$ = $^3J_{H17-H16}$ = 7.3Hz, $H_{17}$), 1.65-1.53 (m, 2H, $H_{15}$), 1.52-1.35 (m, 15H, $H_{16}$ $H_{9'}$ $H_{12'}$ $H_{24'}$), 1.29 (s, 9H, $H_{21'}$), 1.29-1.19 (m, 4H, $H_{10'}$ $H_{11'}$).

**$^{13}$C NMR (100 MHz, $CD_3CN$, 298K):** δ ppm = 175.1 & 173.4 & 170.4 & 170.0 ($C_{1'}$ $C_{4'}$ $C_{6'}$ $C_{19}$), 156.6 & 156.4 ($C_{22'}$), 150.9 ($C_{19'}$), 137.0 ($C_{16'}$), 128.1 ($C_{17'}$), 126.2 ($C_{18'}$), 79.9 ($C_{23'}$), 51.9 ($C_{14}$), 50.5 & 50.1 ($C_{15'}$), 47.4 & 47.1 ($C_{13'}$), 39.8 ($C_{8'}$), 35.8 ($C_{5'}$), 35.0 ($C_{20'}$), 34.1 ($C_{3'}$), 32.6 ($C_{2'}$), 31.6 ($C_{21'}$), 31.3 ($C_{18}$), 30.0 ($C_{9'}$), 28.9 ($C_{15}$), 28.6 ($C_{12'}$ $C_{24'}$), 27.1 & 27.0 ($C_{10'}$ $C_{11'}$), 26.5 ($C_{16}$), 24.9 ($C_{17}$).

**HRMS (ESI)**: $[M+H]^+$ calcd for $C_{29}H_{45}N_6O_5^+$: 557.3451, found: 557.3446.

## 5.4. Synthesis of compound M



**M**

To a solution of **L** (100 mg, 0.15 mmol, 1 equiv.) and the alkyne macrocycle **J** (98 mg, 0.15 mmol, 1 equiv.) in dry $CH_2Cl_2$ (725 µL) were successively added $Cu(CH_3CN)_4PF_6$ (57 mg, 0.15 mmol, 1 equiv.) and 2,6-lutidine (2 µL, 0.015 mmol, 0.1 equiv.). The reaction mixture was stirred for 40h at room temperature. Then, $CH_2Cl_2$ (20 mL) was added and this solution was washed with an aqueous solution of EDTA 0.1M (5x10 mL). The organic layer was dried over $MgSO_4$ and concentrated. A purification of the crude by chromatography on a lipophilic sephadex LH20 ($CH_2Cl_2$) gave the pure compound **M** (193 mg, 97%) as a colorless oil.

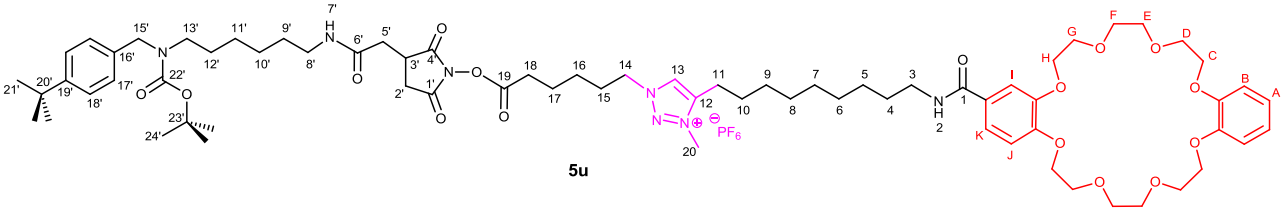
**$R_f$** 0.55 ($CH_2Cl_2$/MeOH 9:1)

**$^1$H NMR (400 MHz, $CD_3CN$, 298K):** δ ppm = 7.47 (s, 1H, $H_{13}$), 7.39-7.34 (m, 2H, $H_I$ $H_J$), 7.36 (d, 2H, $^3J_{H18'-H17'}$ = 8.2Hz, $H_{18'}$), 7.16 (d, 2H, $^3J_{H17'-H18'}$ = 8.2Hz, $H_{17'}$), 6.98 (br s, 1H, $H_2$), 6.95-6.86 (m, 5H, $H_A$ $H_B$ $H_K$), 6.54 (br s, 1H, $H_{7'}$), 4.35 (s, 2H, $H_{15'}$), 4.28 (t, 2H, $^3J_{H14-H15}$ = 7.0Hz, $H_{14}$), 4.17-4.12 & 4.11-4.06 (2m, 8H, $H_C$ $H_H$), 3.84-3.76 (m, 8H, $H_D$ $H_G$), 3.68 (s, 8H, $H_E$ $H_F$), 3.29 (br q, 2H, $H_3$), 3.19-3.11 (m, 1H, $H_{3'}$), 3.16-3.08 (m, 2H, $H_{13'}$), 3.12-3.05 (m, 2H, $H_{8'}$), 2.92 (dd, 1H, $^2J_{H2'a-H2'b}$ = 17.9Hz, $^3J_{H2'a-H3'}$ = 9.1Hz, $H_{2'a}$), 2.65-2.56 (m, 6H, $H_{5'}$ $H_{11}$ $H_{18}$), 2.56-2.47 (m, 1H, $H_{2'b}$), 1.89 (quint, 2H, $^3J_{H15-H16}$ = $^3J_{H15-H14}$ = 7.5Hz, $H_{15}$), 1.69 (quint, 2H, $^3J_{H17-H18}$ = $^3J_{H17-H16}$ = 7.6Hz, $H_{17}$), 1.60 (br quint, 2H, $H_{10}$), 1.54 (br quint, 2H, $H_4$), 1.50-1.27 (m, 25H, $H_5$ $H_6$ $H_7$ $H_8$ $H_9$ $H_{16}$ $H_{9'}$ $H_{12'}$ $H_{24'}$), 1.29 (s, 9H, $H_{21'}$), 1.27-1.16 (m, 4H, $H_{10'}$ $H_{11'}$).

**$^{13}$C NMR (100 MHz, $CD_3CN$, 298K):** δ ppm = 173.4 & 170.4 & 170.1 & 170.0 ($C_{1'}$ $C_{4'}$ $C_{6'}$ $C_{19}$), 167.1 ($C_1$), 156.7 ($C_{22'}$), 150.8 ($C_{19'}$), 152.1 & 149.7 & 149.1 & 148.6 & 128.7 ($C_{IV\ arom\ macrocycle}$), 137.1 ($C_{16'}$), 128.0 ($C_{17'}$), 126.2 ($C_{18'}$), 122.2 & 114.9 ($C_A$ $C_B$), 122.1 ($C_{13}$), 121.3 ($C_J$), 113.4 ($C_K$), 113.3 ($C_I$), 79.8 ($C_{23'}$), 71.6 ($C_E$ $C_F$), 70.5 & 70.4 & 70.2 ($C_D$ $C_G$), 69.8 & 69.7 ($C_C$ $C_H$), 50.2 ($C_{15'}$ $C_{14}$), 47.4 ($C_{13'}$), 40.4 ($C_3$), 39.8 ($C_{8'}$), 35.6 ($C_{5'}$), 35.0 ($C_{20'}$), 34.8 ($C_{3'}$), 32.5 ($C_{2'}$), 31.5 ($C_{21'}$), 31.2 ($C_{18}$), 30.4 & 30.3 & 30.2 & 30.1 & 30.0 & 29.9 & 29.7 & 27.6 ($C_4$ $C_5$ $C_6$ $C_7$ $C_8$ $C_9$ $C_{10}$ $C_{15}$ $C_{16}$ $C_{12'}$), 28.6 ($C_{24'}$), 27.1 & 27.0 ($C_{10'}$ $C_{11'}$), 26.2 & 26.1 ($C_{11}$ $C_{9'}$), 24.7 ($C_{17}$).

**HRMS (ESI)**: $[M+H]^+$ calcd for $C_{70}H_{104}N_7O_{16}^+$: 1298.7540, found: 1298.7540.

## 5.5. Synthesis of the *N*-carbamoylated thread 5u



**5u**

The compound **M** (147 mg, 0.11 mmol, 1 equiv.) was dissolved in MeI (2 mL) (completed with one drop of $CH_2Cl_2$ to help the dissolution). The reaction mixture was stirred for 40h at RT. At the end of the reaction, MeI and $CH_2Cl_2$ were removed in *vacuum* to give a slightly yellow oil (163 mg). This latter was then diluted in $CH_2Cl_2$ (3 mL) before adding milli-Q $H_2O$ (3 mL) and $NH_4PF_6$ (23 mg, 0.14 mmol, 3 equiv.). The biphasic solution was vigorously stirred for 20 min. Then, the aqueous layer was extracted with $CH_2Cl_2$ (3x5 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The resulting colorless oil **5u** (68 mg, quant.) was pure enough to be used without further purification.

**$R_f$** 0.60 ($CH_2Cl_2$/MeOH 9:1)

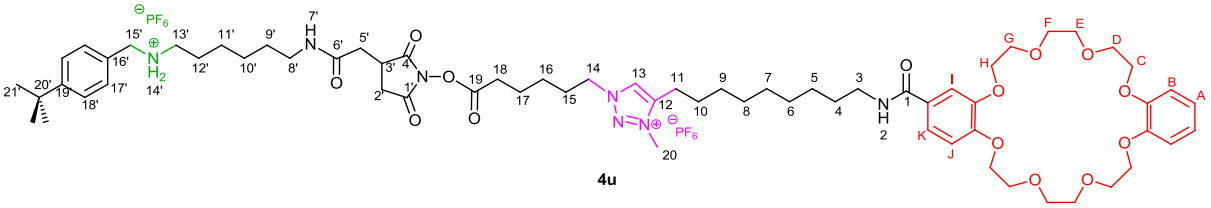
**$^1$H NMR (400 MHz, $CD_3CN$, 298K):** δ ppm = 8.12 (s, 1H, $H_{13}$), 7.40-7.33 (m, 2H, $H_I$ $H_J$), 7.37 (d, 2H, $^3J_{H18'-H17'}$ = 8.1Hz, $H_{18'}$), 7.16 (d, 2H, $^3J_{H17'-H18'}$ = 8.1Hz, $H_{17'}$), 6.97 (br s, 1H, $H_2$), 6.97-6.86 (m, 5H, $H_A$ $H_B$ $H_K$), 6.54 (br s, 1H, $H_{7'}$), 4.47 (t, 2H, $^3J_{H14-H15}$ = 6.9Hz, $H_{14}$), 4.35 (s, 2H, $H_{15'}$), 4.18-4.12 & 4.11-4.07 (2m, 8H, $H_C$ $H_H$), 4.07 (s, 3H, $H_{20}$), 3.84-3.76 (m, 8H, $H_D$ $H_G$), 3.68 (s, 8H, $H_E$ $H_F$), 3.31 (q, 2H, $^3J_{H3-H4}$ = $^3J_{H3-H2}$ = 6.5Hz, $H_3$), 3.19-3.10 (m, 1H, $H_{3'}$), 3.15-3.07 (m, 2H, $H_{13'}$), 3.11-3.03 (m, 2H, $H_{8'}$),

2.91 (dd, 1H, $^{2}J_{H2'a\text{-}H2'b}$ = 17.9Hz, $^{3}J_{H2'a\text{-}H3'}$ = 9.1Hz, $H_{2'a}$), 2.73-2.52 (m, 2H, $H_{5'}$), 2.77 (t, 2H, $^{3}J_{H11\text{-}H10}$ = 7.7Hz, $H_{11}$), 2.61 (t, 2H, $^{3}J_{H18\text{-}H17}$ = 7.1Hz, $H_{18}$), 2.56-2.44 (m, 1H, $H_{2'b}$), 1.95 (br quint, 2H, $H_{15}$), 1.73 (br quint, 2H, $H_{17}$), 1.66 (br quint, 2H, $H_{10}$), 1.56 (br quint, 2H, $H_4$), 1.51-1.25 (m, 25H, $H_5$ $H_6$ $H_7$ $H_8$ $H_9$ $H_{16}$ $H_{9'}$ $H_{12'}$ $H_{24'}$), 1.29 (s, 9H, $H_{21'}$), 1.26-1.18 (m, 4H, $H_{11'}$ $H_{10'}$).

**$^{13}$C NMR (100 MHz, $CD_3CN$, 298K):** δ ppm = 173.5 & 170.5 & 170.2 & 169.9 ($C_{1'}$ $C_{4'}$ $C_{6'}$ $C_{19}$), 167.1 ($C_1$), 156.7 & 156.3 ($C_{22'}$), 150.8 ($C_{19'}$), 152.1 & 149.7 & 149.1 & 128.7 ($C_{IV\ arom\ macrocycle}$), 145.7 ($C_{12}$), 137.0 ($C_{16'}$), 128.5 ($C_{13}$), 128.0 ($C_{17'}$), 126.2 ($C_{18'}$), 122.3 & 115.0 ($C_A$ $C_B$), 121.4 ($C_J$), 113.5 ($C_K$ $C_I$), 79.8 ($C_{23'}$), 71.4 ($C_E$ $C_F$), 70.3 & 70.2 & 70.1 ($C_D$ $C_G$), 69.8 & 69.7 & 69.6 ($C_C$ $C_H$), 54.1 ($C_{14}$), 50.5 & 50.1 ($C_{15'}$), 47.5 & 47.1 ($C_{13'}$), 40.3 ($C_3$), 39.8 ($C_{8'}$), 38.1 ($C_{20}$), 35.6 ($C_{5'}$), 35.0 ($C_{20'}$), 34.8 ($C_{3'}$), 35.2 ($C_{2'}$), 31.5 ($C_{21'}$), 31.2 ($C_{18}$), 30.2 & 30.0 & 29.9 & 29.8 & 29.6 & 29.3 & 29.1 & 27.5 & 27.4 & 27.1 & 27.0 & 25.4 ($C_4$ $C_5$ $C_6$ $C_7$ $C_8$ $C_9$ $C_{10}$ $C_{15}$ $C_{16}$ $C_{9'}$ $C_{10'}$ $C_{11'}$ $C_{12'}$), 28.6 ($C_{24'}$), 24.5 ($C_{17}$), 23.6 ($C_{11}$).

**HRMS (ESI)**: $[M\text{-}PF_6]^+$ calcd for $C_{71}H_{106}N_7O_{16}^+$: 1312.7696, found: 1312.7699.

## 5.6. Synthesis of the *N*-carbamoylated thread 4u



4u

To a solution of thread **5u** (95 mg, 0.066 mol, 1 equiv.) in $CH_2Cl_2$ (1 mL) was added HCl 2M in $Et_2O$. The reaction mixture was stirred for 1h30 at RT, then concentrated under *vacuum* to give a yellow oil. This oil was then dissolved in $CH_2Cl_2$ (3 mL). Milli-Q $H_2O$ (3 mL) and $NH_4PF_6$ were added (32 mg, 0.20 mmol, 3 equiv.). The biphasic solution was stirred for 20 min at RT. The aqueous layer was then extracted with $CH_2Cl_2$ (3x5 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. A purification of the crude by chromatography on a lipophilic sephadex LH20 ($CH_2Cl_2$) provided **4u** (81 mg, 81%) as a pure yellow oil.

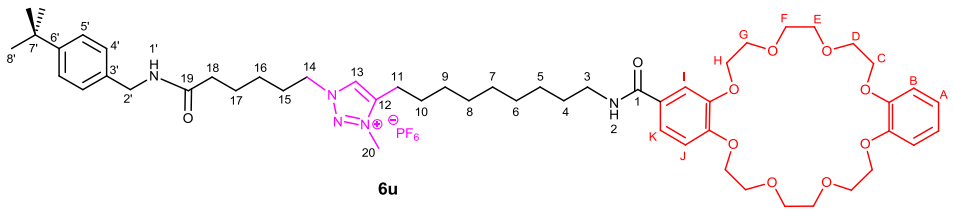
**$R_f$** 0.45 ($CH_2Cl_2$/MeOH 9:1)

**$^{1}$H NMR (400 MHz, $CD_3CN$, 298K):** δ ppm = 8.11 (s, 1H, $H_{13}$), 7.48 (d, 2H, $^{3}J_{H18'\text{-}H17'}$ = 8.4Hz, $H_{18'}$), 7.37 (d, 2H, $^{3}J_{H17'\text{-}H18'}$ = 8.4Hz, $H_{17'}$), 7.35-7.29 (m, 2H, $H_I$ $H_J$), 7.03 (br t, 1H, $H_2$), 6.97-6.86 (m, 5H, $H_A$ $H_B$ $H_K$), 6.58 (br t, 1H, $H_{7'}$), 4.48 (t, 2H, $^{3}J_{H14\text{-}H15}$ = 6.9Hz, $H_{14}$), 4.16-4.11 (m, 2H, $H_{15'}$), 4.17-4.05 (2m, 8H, $H_C$ $H_H$), 4.08 (s, 3H, $H_{20}$), 3.84-3.76 (m, 8H, $H_D$ $H_G$), 3.69 (s, 8H, $H_E$ $H_F$), 3.29 (q, 2H, $^{3}J_{H3\text{-}H4}$ = $^{3}J_{H3\text{-}H2}$ = 6.5Hz, $H_3$), 3.20-3.10 (m, 1H, $H_{3'}$), 3.13-3.02 (m, 2H, $H_{8'}$), 3.03-2.95 (m, 2H, $H_{13'}$), 2.92 (dd, 1H, $^{2}J_{H2'a\text{-}H2'b}$ = 17.9Hz, $^{3}J_{H2'a\text{-}H3'}$ = 9.1Hz, $H_{2'a}$), 2.67-2.58 (m, 2H, $H_{5'}$), 2.75 (t, 2H, $^{3}J_{H11\text{-}H10}$ = 7.7Hz, $H_{11}$), 2.61 (t, 2H, $^{3}J_{H18\text{-}H17}$ = 7.1Hz, $H_{18}$), 2.56-2.43 (m, 1H, $H_{2'b}$), 1.95 (br quint, 2H, $H_{15}$), 1.72 (br quint, 2H, $H_{17}$), 1.69-1.57 (m, 4H, $H_{10}$ $H_{12'}$), 1.55 (br quint, 2H, $H_4$), 1.43-1.22 (m, 18H, $H_5$ $H_6$ $H_7$ $H_8$ $H_9$ $H_{16}$ $H_{9'}$ $H_{10'}$ $H_{11'}$), 1.31 (s, 9H, $H_{21'}$).

**$^{13}$C NMR (100 MHz, $CD_3CN$, 298K):** δ ppm = 173.5 & 170.4 & 169.9 ($C_{1'}$ $C_{4'}$ $C_{6'}$ $C_{19}$), 167.5 ($C_1$), 153.7 ($C_{19'}$), 152.2 & 149.7 & 149.2 & 128.5 ($C_{IV\ arom\ macrocycle}$), 145.8 ($C_{12}$), 130.7 ($C_{16'}$ $C_{17'}$), 128.4 ($C_{13}$), 126.9 ($C_{18'}$), 122.2 & 114.9 ($C_A$ $C_B$), 121.4 ($C_J$), 113.4 ($C_K$), 113.3 ($C_I$), 71.6 ($C_E$ $C_F$), 70.5 & 70.4 & 70.2 ($C_D$ $C_G$), 69.9 & 69.7 ($C_C$ $C_H$), 54.2 ($C_{14}$), 52.0 ($C_{15'}$), 48.5 ($C_{13'}$), 40.3 ($C_3$), 39.5 ($C_{8'}$), 38.1 ($C_{20}$), 35.7 ($C_{5'}$), 35.3 ($C_{20'}$), 34.8 ($C_{3'}$), 35.2 ($C_{2'}$), 31.3 ($C_{21'}$), 31.1 ($C_{18}$), 30.2 ($C_4$), 29.9 & 29.8 & 29.6 & 29.3 & 27.5 & 26.3 & 25.4 ($C_5$ $C_6$ $C_7$ $C_8$ $C_9$ $C_{16}$ $C_{9'}$ $C_{10'}$ $C_{11'}$), 29.1 ($C_{15}$), 27.3 ($C_{10}$), 26.5 ($C_{12'}$), 24.5 ($C_{17}$), 23.6 ($C_{11}$).

**HRMS (ESI)**: $[M\text{-}2PF_6\text{+}H]^+$ calcd for $C_{66}H_{98}N_7O_{14}^+$: 1212.7172, found: 1212.7184.

## 5.7. Synthesis of the uncomplexed thread 6u



6u

To a solution of the thread **5u** (50 mg, 0.034 mmol, 1 equiv.) in dry $CH_3CN$ (2.5 mL) was added the 4-*tert*-butylbenzylamine (12 µL, 0.068 mmol, 2 equiv.). The reaction mixture was stirred for 4h at room temperature before being concentrated. The resulting solid was purified by chromatography on a lipophilic sephadex LH20 ($CH_2Cl_2$) to give the thread **6u** (36 mg, 95%) as a pure colorless oil.

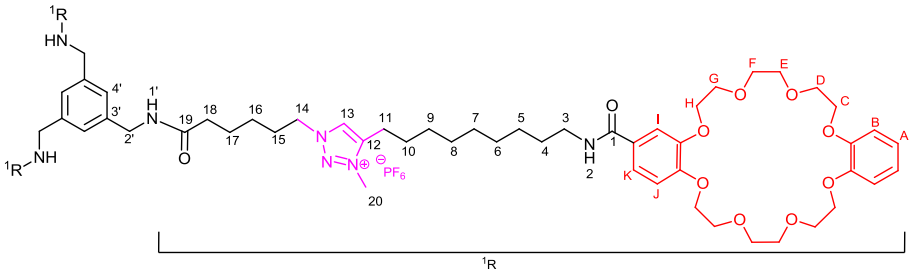
**$R_f$** 0.50 ($CH_2Cl_2$/MeOH 9:1)

**$^1$H NMR (600 MHz, $CD_3CN$, 298K):** δ ppm = 8.14 (s, 1H, $H_{13}$), 7.36 (d, 2H, $^3J_{H5'-H4'}$ = 8.2Hz, $H_{5'}$), 7.38-7.36 (m, 2H, $H_I$ $H_J$), 7.18 (d, 2H, $^3J_{H4'-H5'}$ = 8.2Hz, $H_{4'}$), 6.98-6.88 (m, 6H, $H_2$ $H_A$ $H_B$ $H_K$), 6.72 (br s, 1H, $H_{1'}$), 4.46 (t, 2H, $^3J_{H14-H15}$ = 7.1Hz, $H_{14}$), 4.28 (d, 2H, $^3J_{H2'-H1'}$ = 6.1Hz, $H_{2'}$), 4.17-4.14 & 4.12-4.06 (2m, 8H, $H_C$ $H_H$), 4.07 (s, 3H, $H_{20}$), 3.83-3.77 (m, 8H, $H_D$ $H_G$), 3.68 (s, 8H, $H_E$ $H_F$), 3.31 (q, 2H, $^3J_{H3-H4}$ = $^3J_{H3-H2}$ = 6.8Hz, $H_3$), 2.73 (t, 2H, $^3J_{H11-H10}$ = 7.7Hz, $H_{11}$), 2.16 (t, 2H, $^3J_{H18-H17}$ = 7.3Hz, $H_{18}$), 1.93 (br quint, 2H, $H_{15}$), 1.66 (br quint, 2H, $H_{10}$), 1.61 (br quint, 2H, $H_{17}$), 1.56 (br quint, 2H, $H_4$), 1.40-1.30 (m, 12H, $H_5$ $H_6$ $H_7$ $H_8$ $H_9$ $H_{16}$), 1.29 (s, 9H, $H_{8'}$).

**$^{13}$C NMR (150 MHz, $CD_3CN$, 298K):** δ ppm = 173.2 ($C_{19}$), 167.2 ($C_1$), 150.9 ($C_{6'}$), 152.2 & 149.8 & 149.2 & 129.0 ($C_{IV\ arom\ macrocycle}$), 145.7 ($C_{12}$), 137.6 ($C_{3'}$), 128.7 ($C_{13}$), 128.1 ($C_{4'}$), 126.3 ($C_{5'}$), 122.5 & 115.4 & 115.2 ($C_A$ $C_B$), 121.5 ($C_J$), 113.8 ($C_K$ $C_I$), 71.5 & 71.4 ($C_E$ $C_F$), 70.4 & 70.3 & 70.2 ($C_D$ $C_G$), 70.0 & 69.9 & 69.8 & 69.7 ($C_C$ $C_H$), 54.3 ($C_{14}$), 43.1 ($C_{2'}$), 40.4 ($C_3$), 38.2 ($C_{20}$), 36.2 ($C_{18}$), 35.0 ($C_{7'}$), 31.5 ($C_{8'}$), 30.3 ($C_4$), 29.9 & 29.8 & 29.6 & 29.5 & 29.3 & 27.4 & 26.1 ($C_5$ $C_6$ $C_7$ $C_8$ $C_9$ $C_{15}$ $C_{16}$), 27.6 ($C_{10}$), 25.3 ($C_{17}$), 23.7 ($C_{11}$).

**HRMS (ESI)**: $[M\text{-}PF_6]^+$ calcd for $C_{54}H_{80}N_5O_{10}^+$: 958.5905, found: 958.5908.

## 5.8. Synthesis of the uncomplexed thread 7u




**7u**

The thread **5u** (59 mg, 0.04 mmol, 3.1 equiv.) was dissolved in dry $CH_3CN$ (2 mL). In another flask, 1 mL of a mother solution containing 1,3,5-tris(aminomethyl)benzene (21 mg, 0.13 mmol, 10 equiv.) and DIEA (140 µL, 2.4 mmol, 60 equiv.) in $CH_3CN$ (860 µL) was prepared. 100 µL of this solution were added to the solution containing **5u**. The reaction mixture was stirred 17h at room temperature before being concentrated. The resulting crude was purified by chromatography on a lipophilic sephadex LH20 ($CH_2Cl_2$) to give **7u** (25 mg, 66%) as a pure colorless oil.

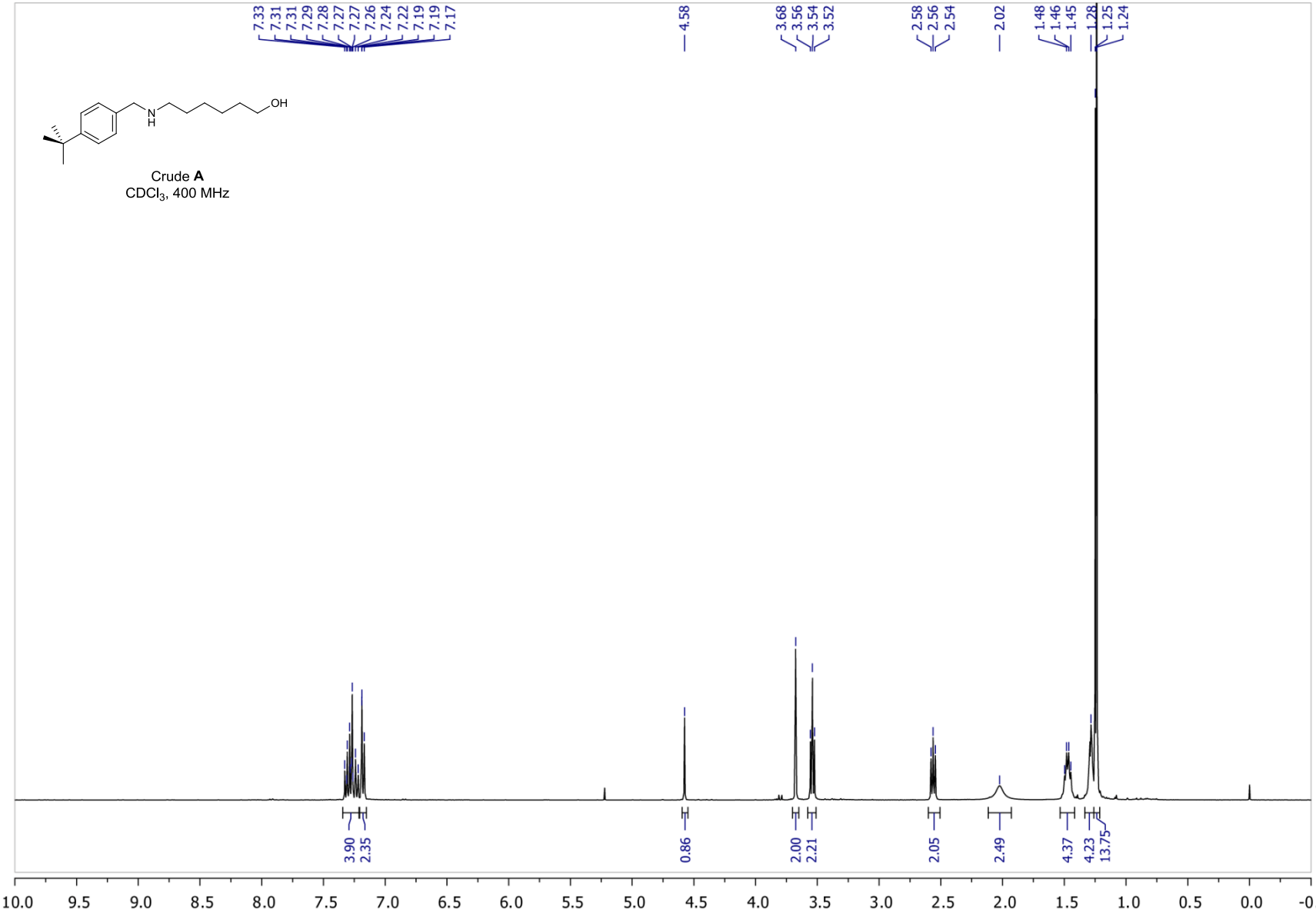
**$R_f$** 0.56 ($CH_2Cl_2$/MeOH 90:10)

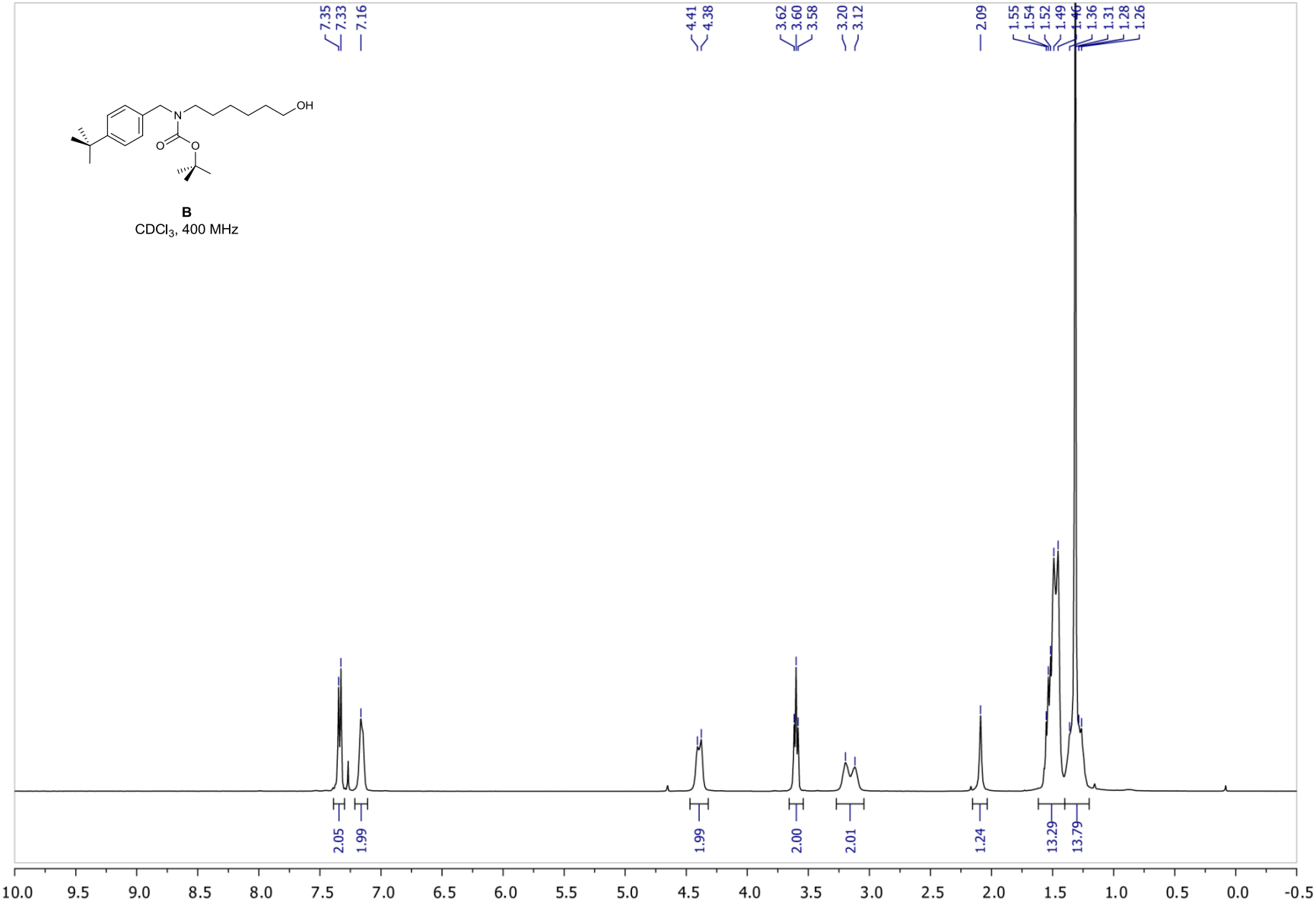
**$^1$H NMR (600 MHz, $CD_3CN$, 298K):** δ ppm = 8.21 (s, 3H, $H_{13}$), 7.38-7.33 (m, 6H, $H_I$ $H_J$), 7.08 (br t, 3H, $H_2$), 7.00 (s, 3H, $H_{4'}$), 6.98 (br t, 3H, $H_{1'}$), 6.94-6.86 (m, 15H, $H_A$ $H_B$ $H_K$), 4.45 (t, 6H, $^3J_{H14-H15}$ = 7.1Hz, $H_{14}$), 4.26 (d, 6H, $^3J_{H2'-H1'}$ = 6.0Hz, $H_{2'}$), 4.15-4.10 & 4.09-4.04 (2m, 24H, $H_C$ $H_H$), 4.07 (s, 9H, $H_{20}$), 3.83-3.76 (m, 24H, $H_D$ $H_G$), 3.68 (s, 24H, $H_E$ $H_F$), 3.28 (q, 6H, $^3J_{H3-H4}$ = $^3J_{H3-H2}$ = 6.8Hz, $H_3$), 2.72 (t, 6H, $^3J_{H11-H10}$ = 7.6Hz, $H_{11}$), 2.16 (t, 6H, $^3J_{H18-H17}$ = 7.3Hz, $H_{18}$), 1.93 (quint, 6H, $^3J_{H15-H16}$ = $^3J_{H15-H14}$ = 7.3Hz, $H_{15}$), 1.64 (br quint, 6H, $H_{10}$), 1.60 (br quint, 6H, $H_{17}$), 1.54 (br quint, 6H, $H_4$), 1.39-1.25 (m, 36H, $H_5$ $H_6$ $H_7$ $H_8$ $H_9$ $H_{16}$).

**$^{13}$C NMR (150 MHz, $CD_3CN$, 298K):** δ ppm = 173.4 ($C_{19}$), 167.3 ($C_1$), 152.2 & 149.8 & 149.2 & 129.0 ($C_{IV\ arom\ macrocycle}$), 145.7 ($C_{12}$), 141.0 ($C_{3'}$), 128.7 ($C_{13}$), 125.6 ($C_{4'}$), 122.3 & 115.0 ($C_A$ $C_B$), 121.4 ($C_J$), 113.5 ($C_K$ $C_I$), 71.7 & 71.6 ($C_E$ $C_F$), 70.5 & 70.4 & 70.3 ($C_D$ $C_G$), 70.0 & 69.8 ($C_C$ $C_H$), 54.2 ($C_{14}$), 43.3 ($C_{2'}$), 40.4 ($C_3$), 38.2 ($C_{20}$), 36.2 ($C_{18}$), 30.3 ($C_4$), 29.9 & 29.8 & 29.6 & 29.5 & 27.6 & 26.1 ($C_5$ $C_6$ $C_7$ $C_8$ $C_9$ $C_{16}$), 29.3 ($C_{15}$), 27.3 ($C_{10}$), 25.4 ($C_{17}$), 23.7 ($C_{11}$).

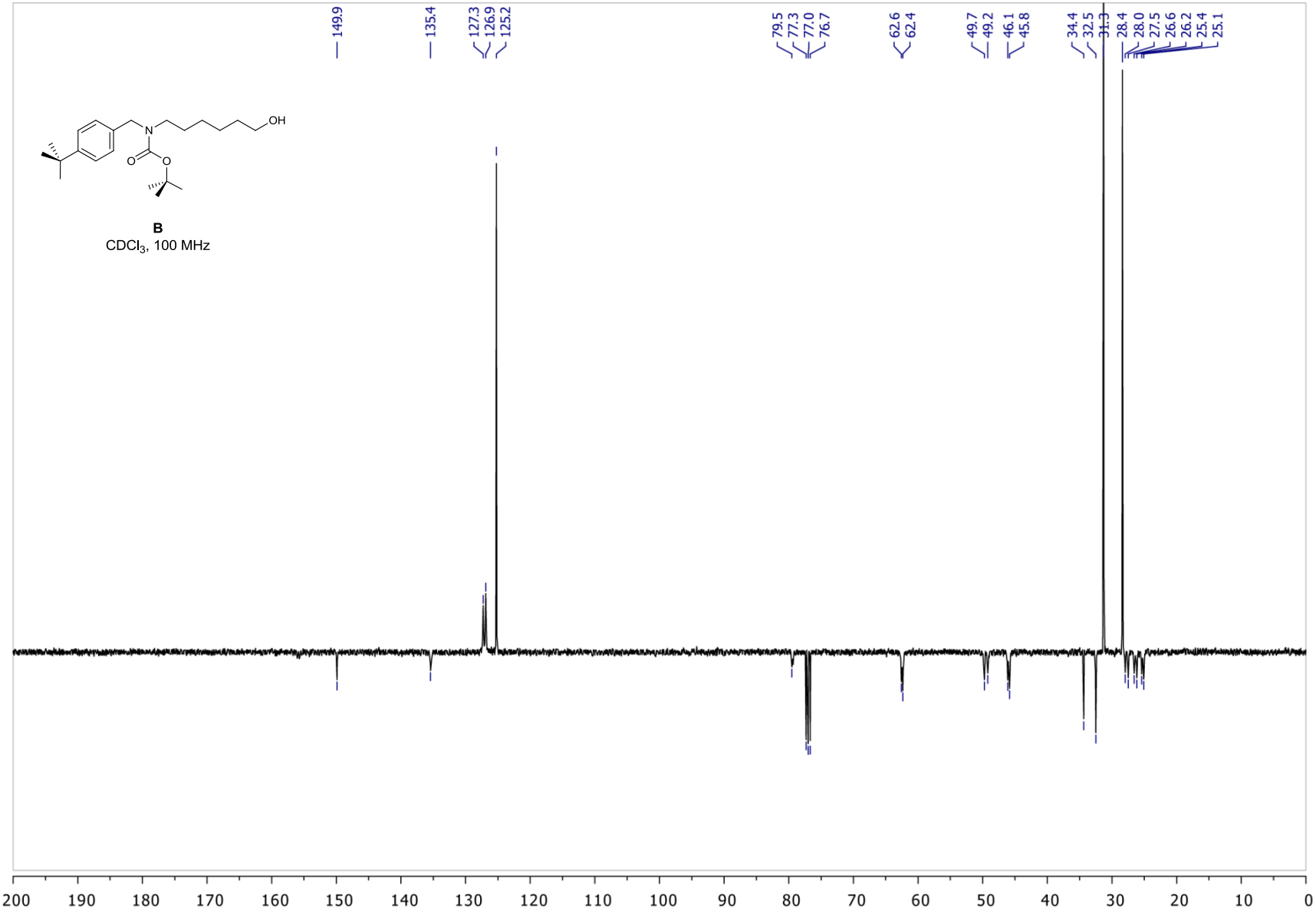
**HRMS (ESI)**: $[M\text{-}3PF_6]^{3+}$ calcd for $C_{138}H_{204}N_{15}O_{30}^+$: 850.4966, found: 850.4971.

# 6. NMR Spectra

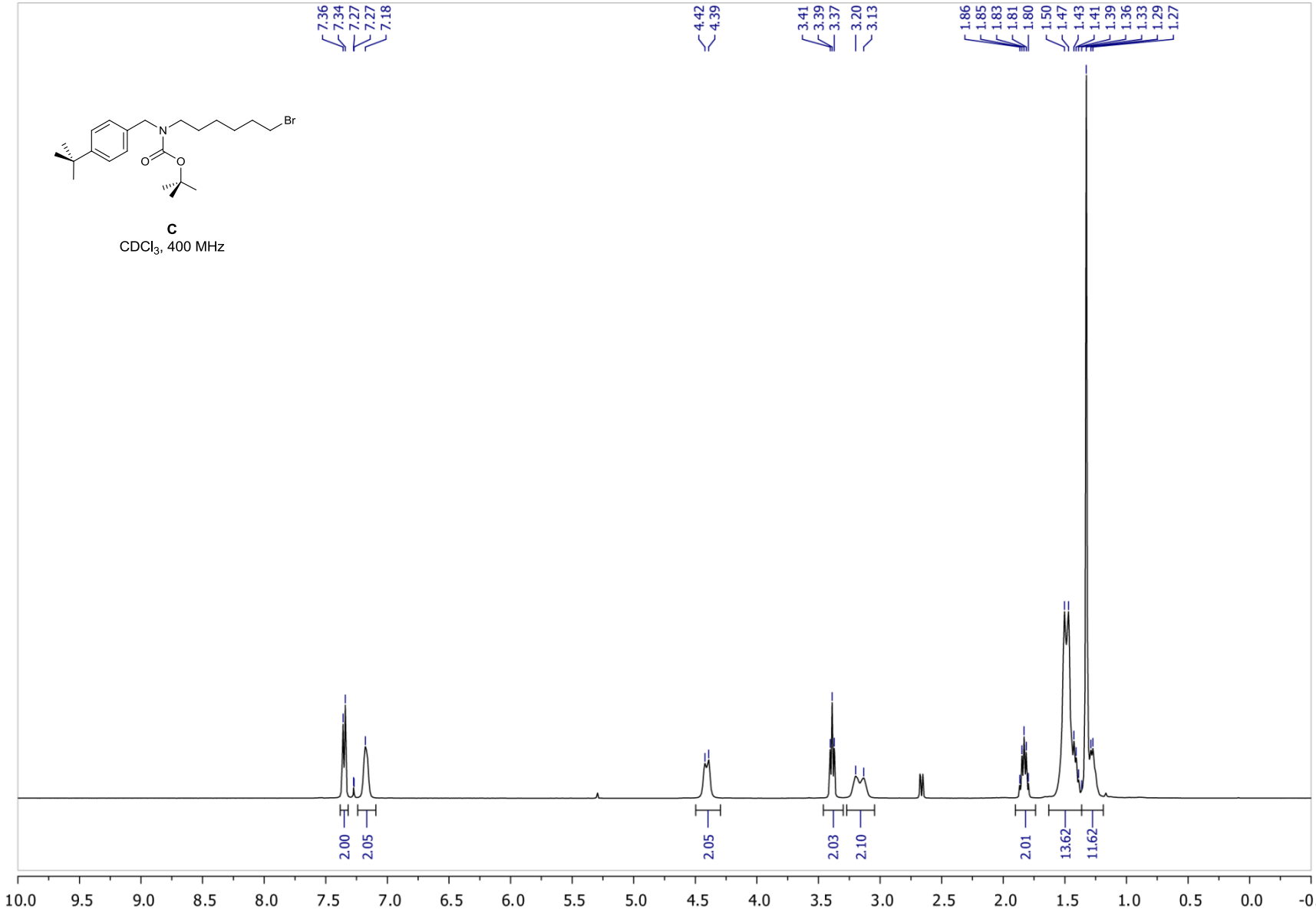

7.33
7.31
7.31
7.29
7.28
7.27
7.27
7.26
7.24
7.22
7.19
7.19
7.17
4.58
3.68
3.56
3.54
3.52
2.58
2.56
2.54
2.02
1.48
1.46
1.45
1.28
1.25
1.24
OH
N
H
Crude **A**
$CDCl_3$, 400 MHz
3.90
2.35
0.86
2.00
2.21
2.05
2.49
4.37
4.23
13.75
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5



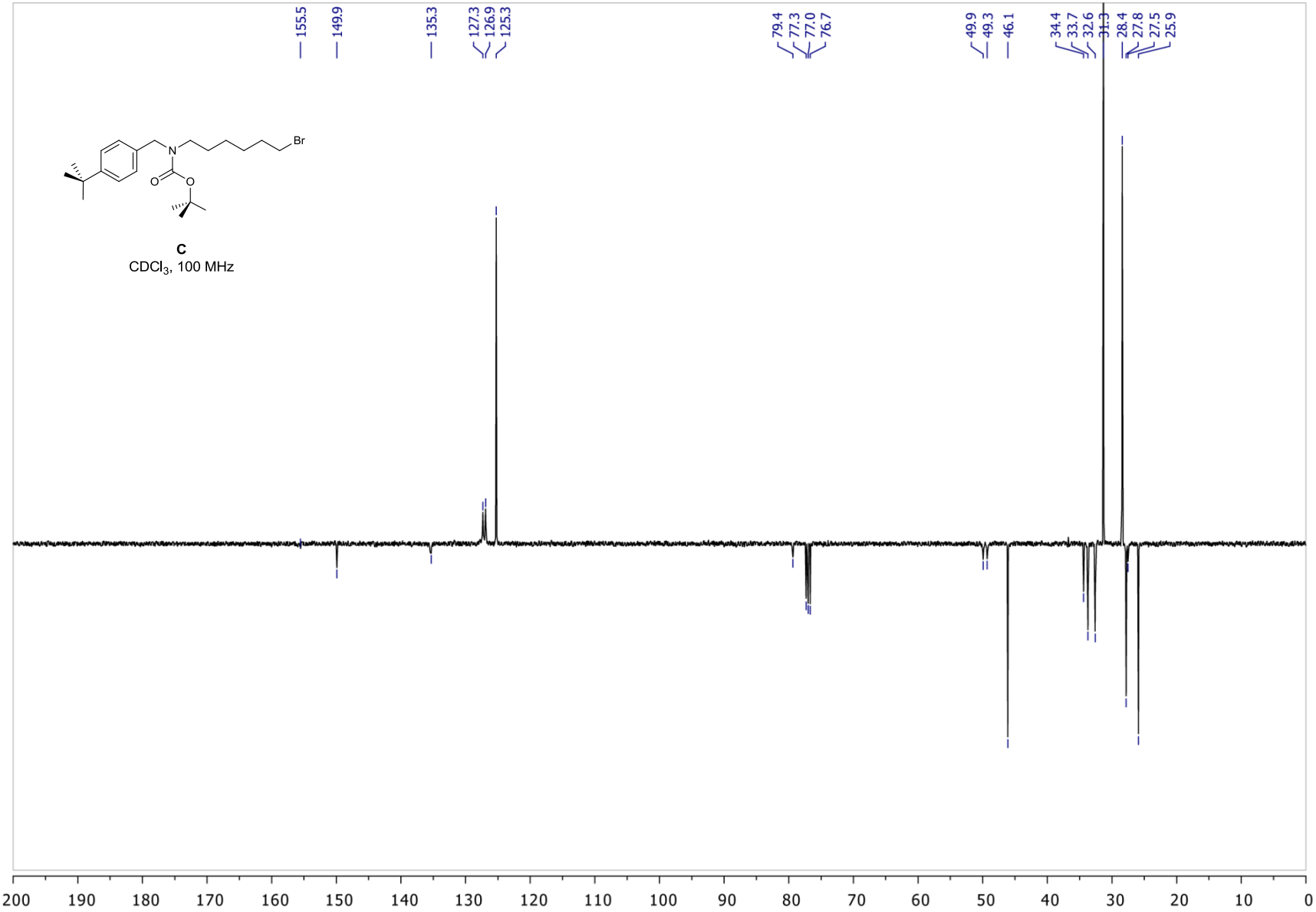

**B**
$CDCl_3$, 400 MHz




**B**
$CDCl_3$, 100 MHz

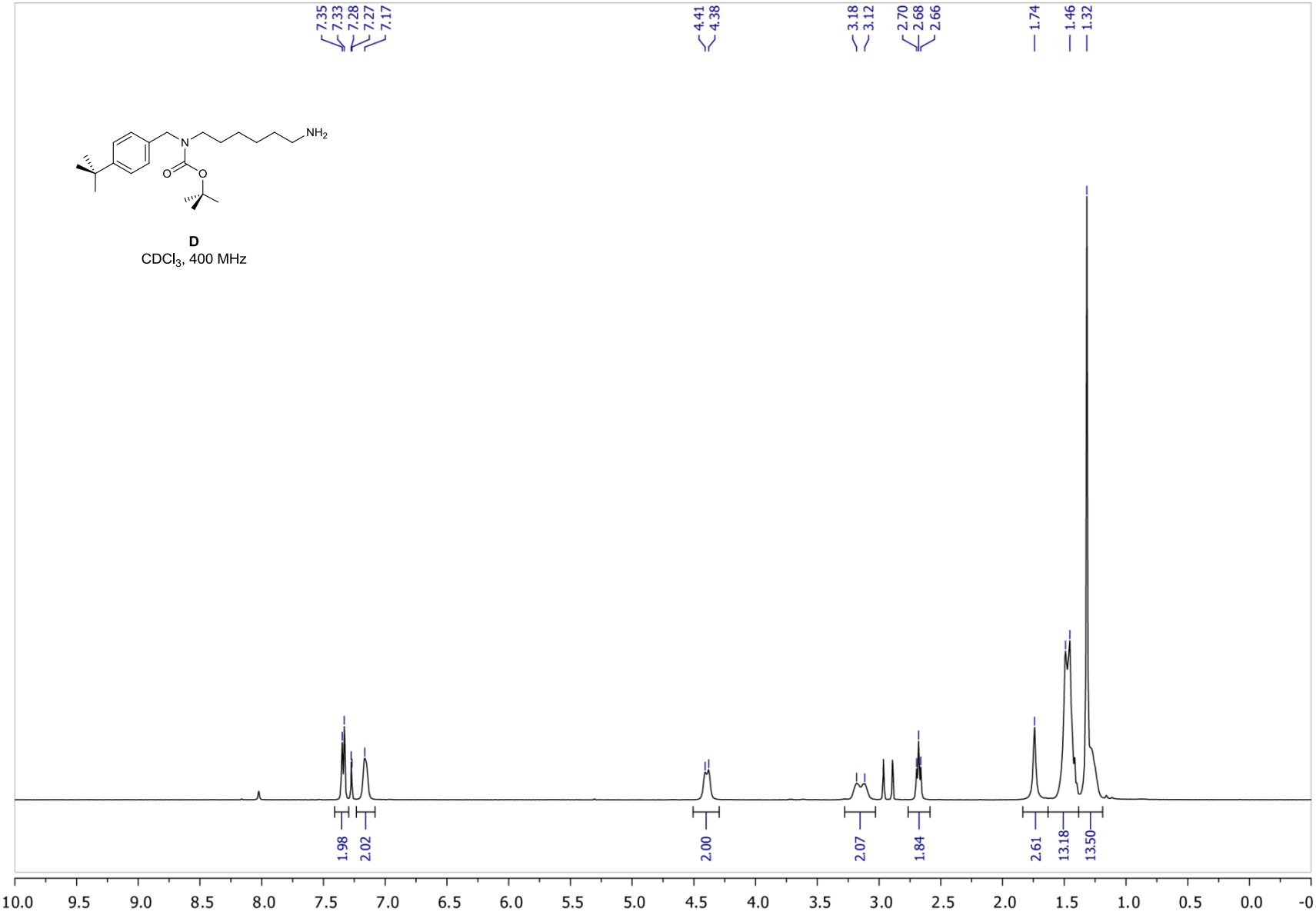



**C**
$CDCl_3$, 400 MHz



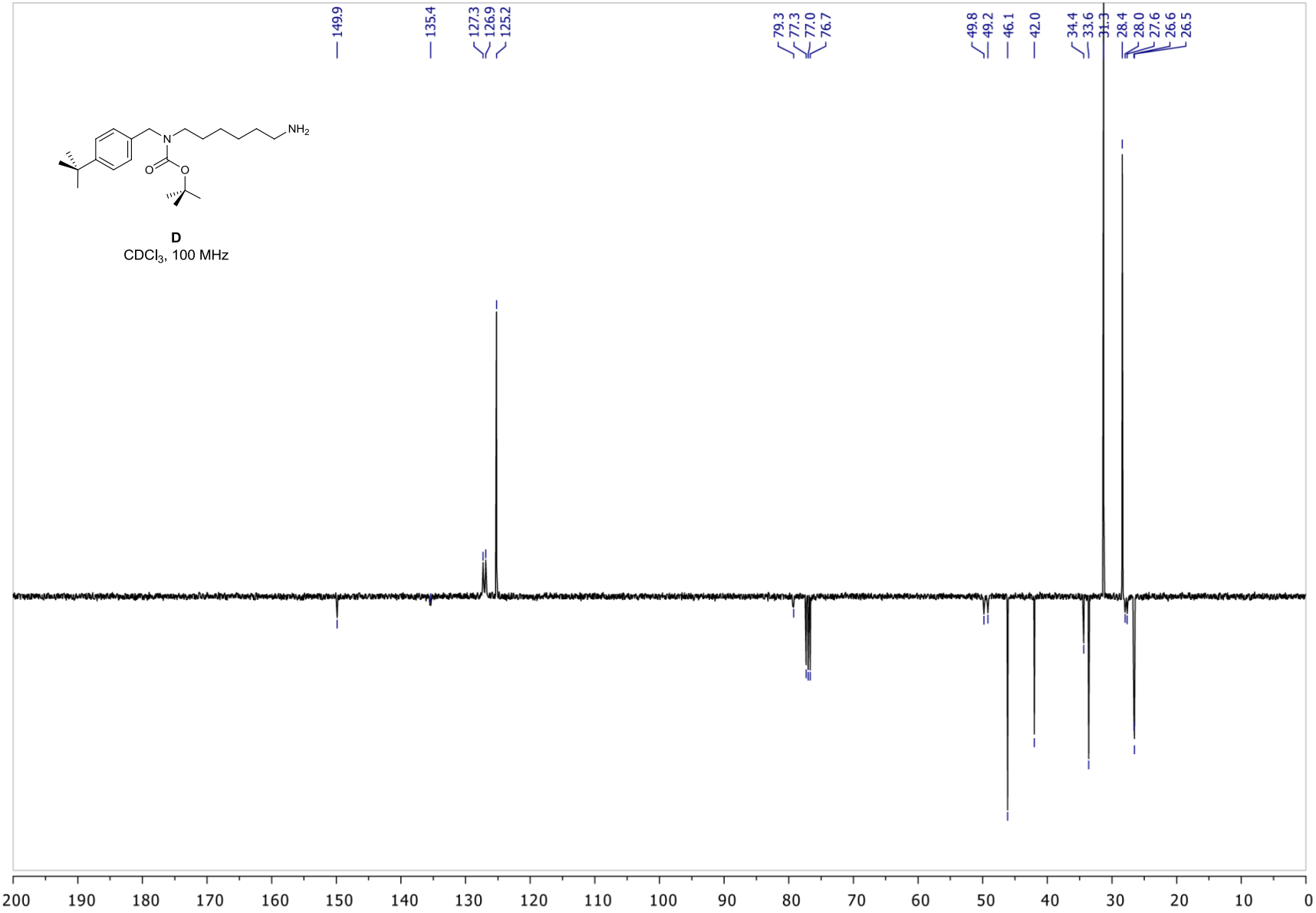

**C**

$CDCl_3$, 100 MHz

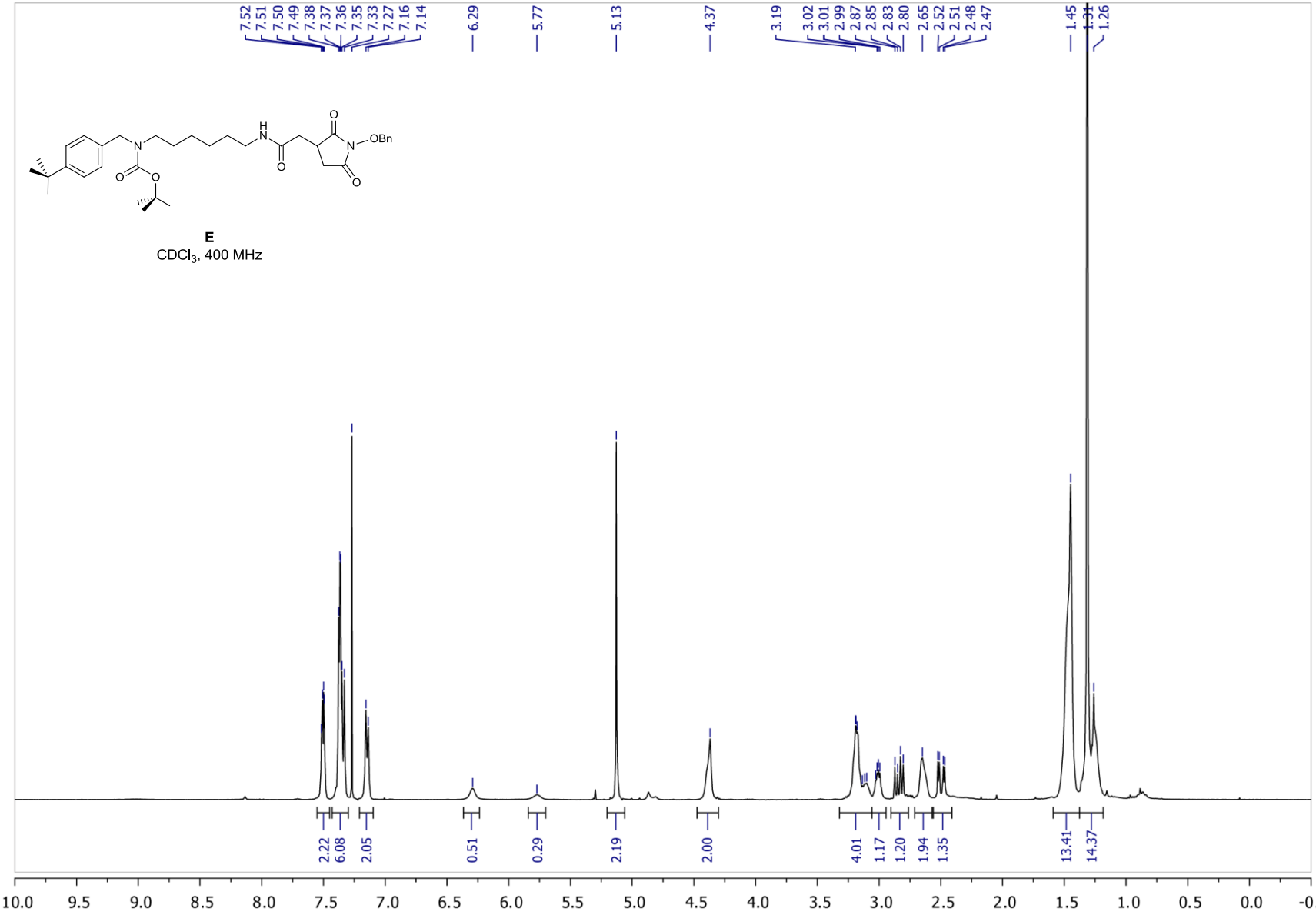



**D**

$CDCl_3$, 400 MHz

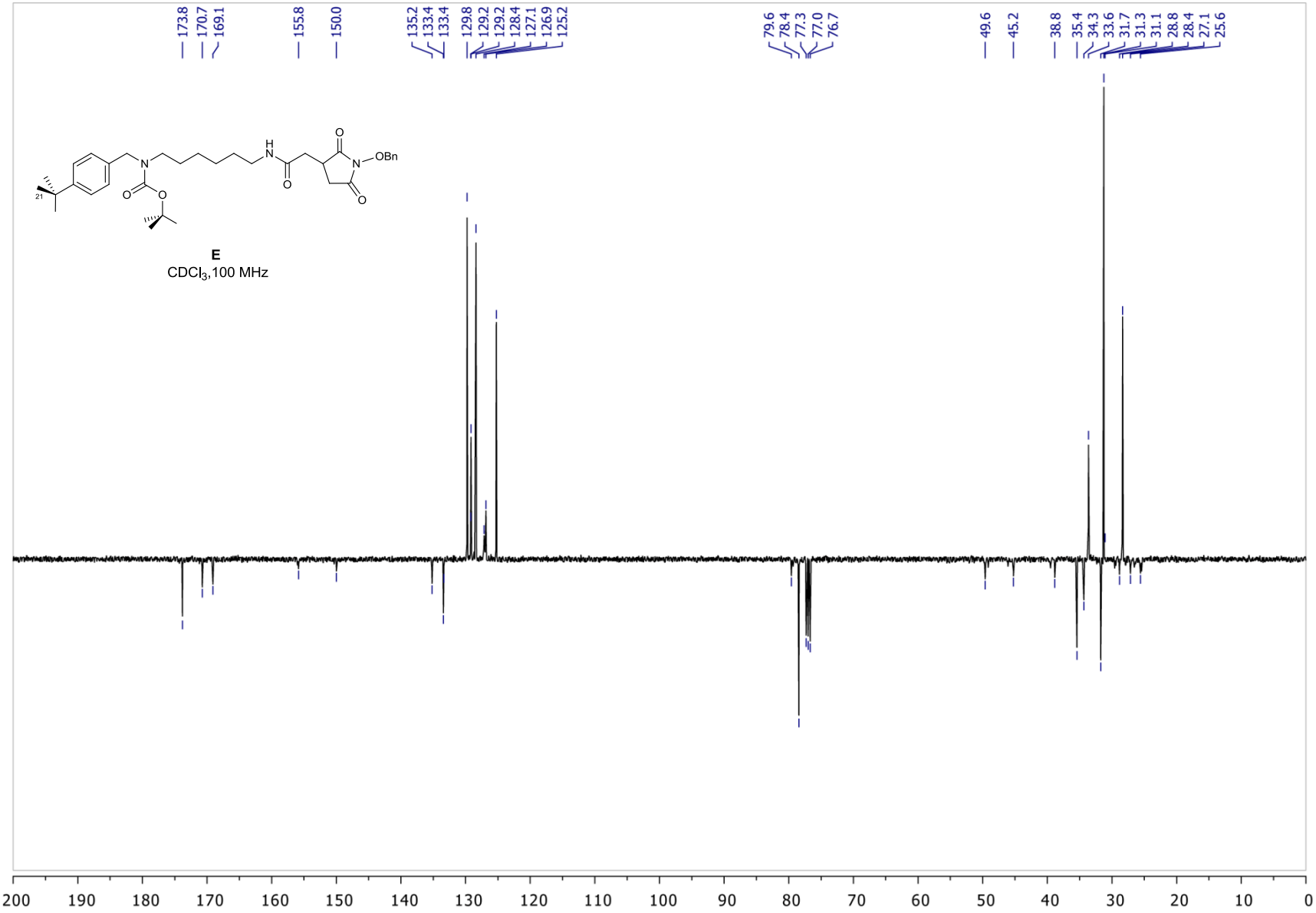


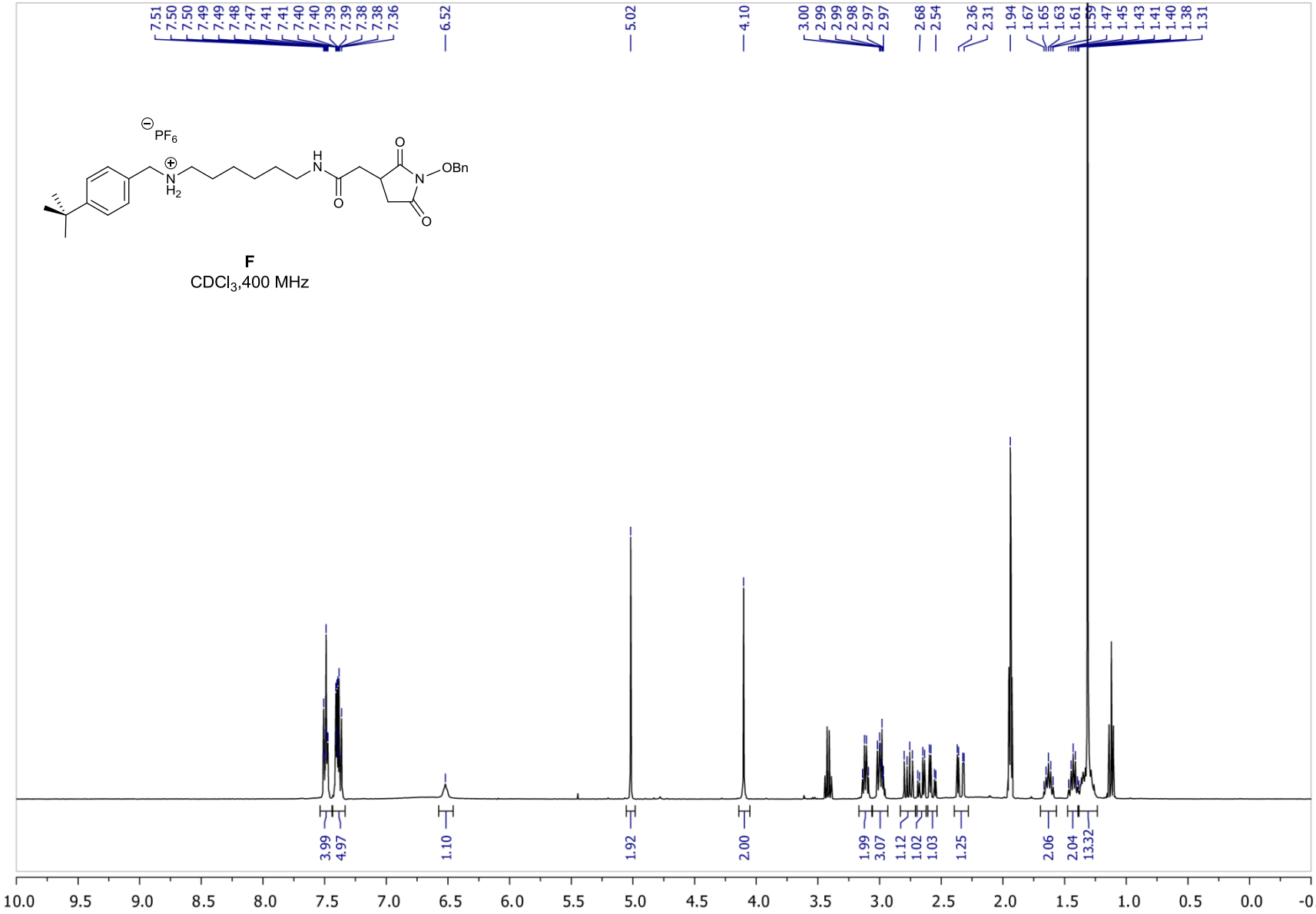

**D**
$CDCl_3$, 100 MHz




**E**

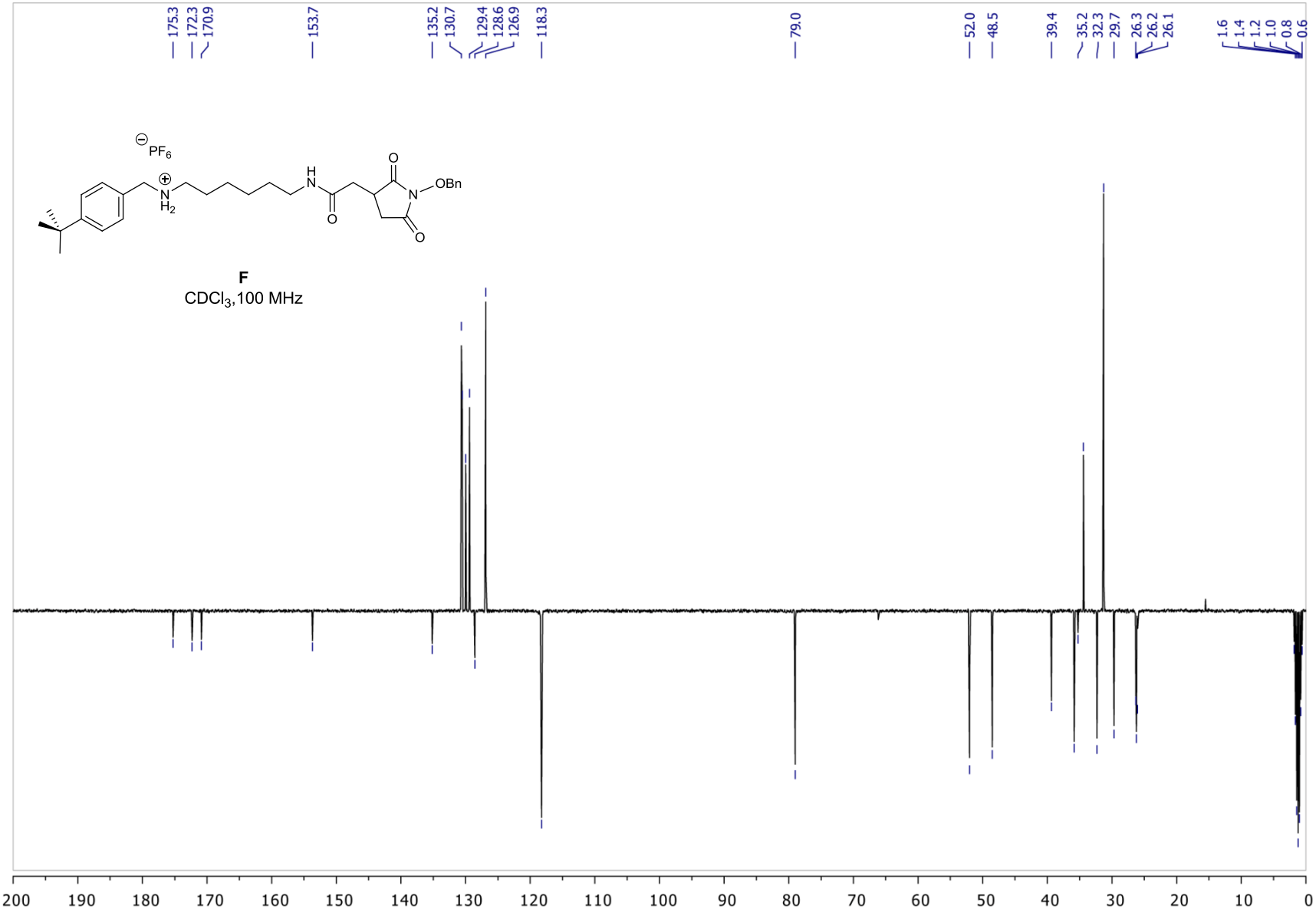
$CDCl_3$, 400 MHz

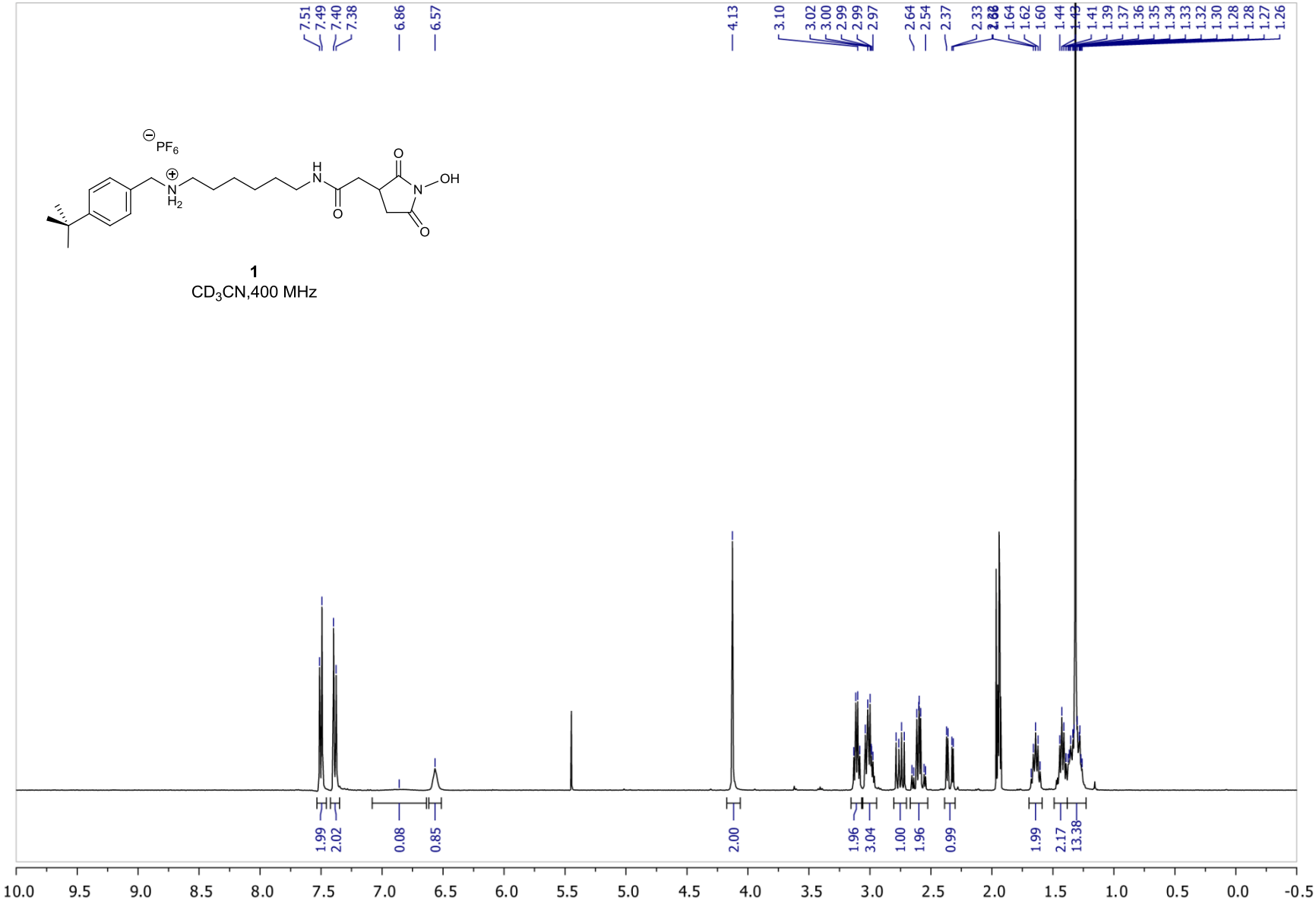

173.8
170.7
169.1
155.8
150.0
135.2
133.4
133.4
129.8
129.2
129.2
128.4
127.1
126.9
125.2
79.6
78.4
77.3
77.0
76.7
49.6
45.2
38.8
35.4
34.3
33.6
31.7
31.3
31.1
28.8
28.4
27.1
25.6
OBn
E
CDCl3,100 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0




**F**

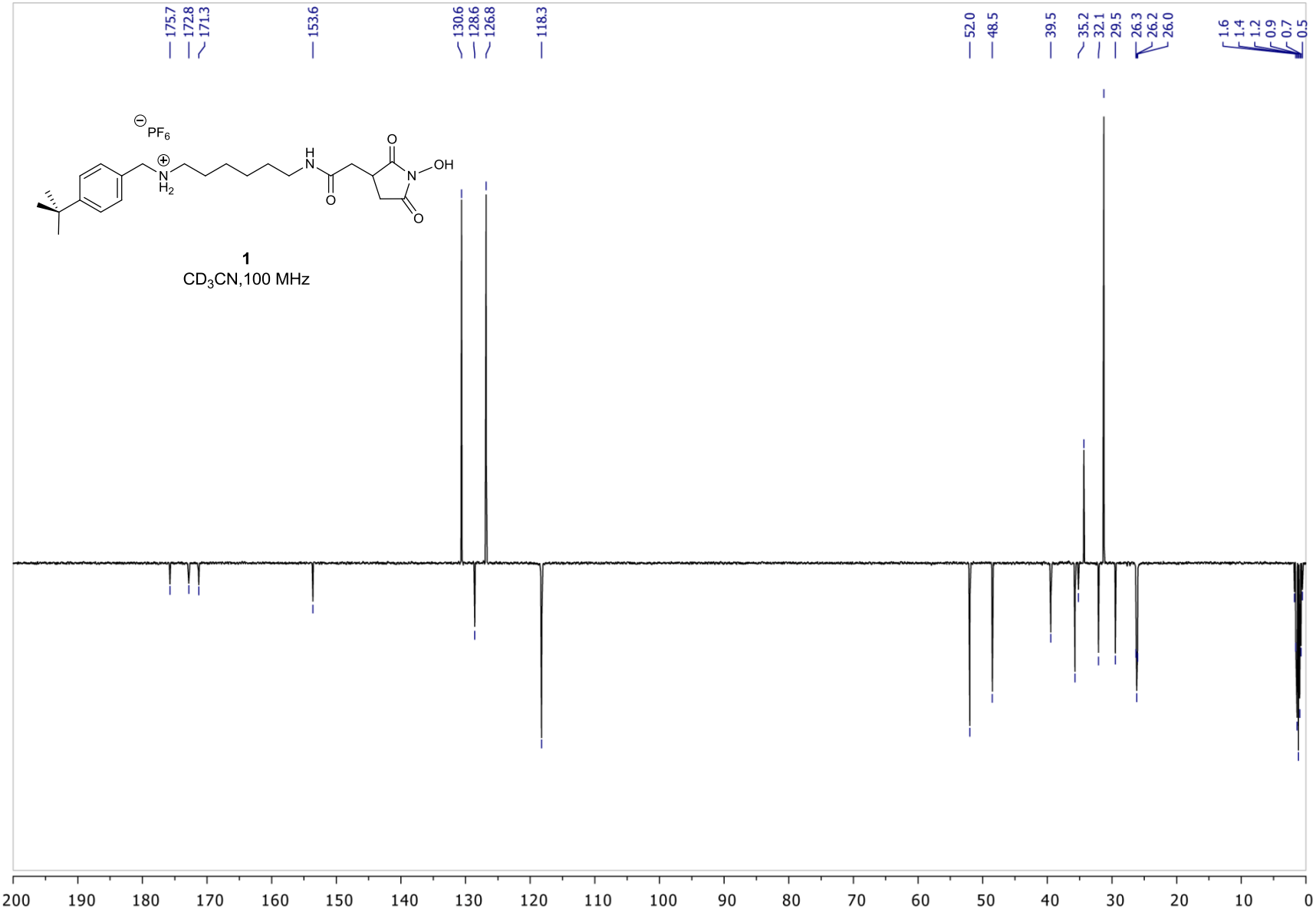
$CDCl_3$,400 MHz

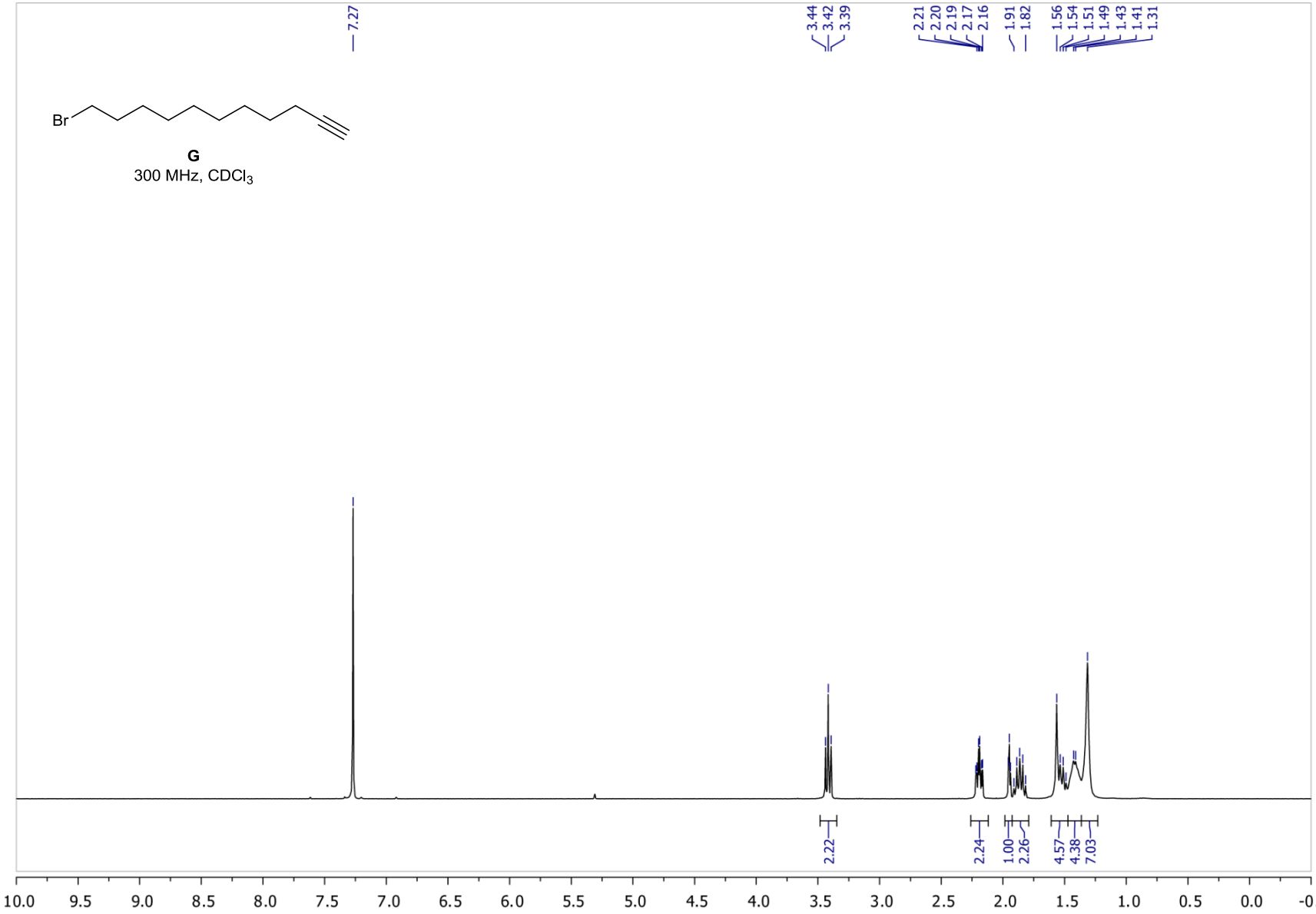

175.3
172.3
170.9
153.7
135.2
130.7
129.4
128.6
126.9
118.3
79.0
52.0
48.5
39.4
35.2
32.3
29.7
26.3
26.2
26.1
1.6
1.4
1.2
1.0
0.8
0.6
PF6
OBn
F
CDCl3,100 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

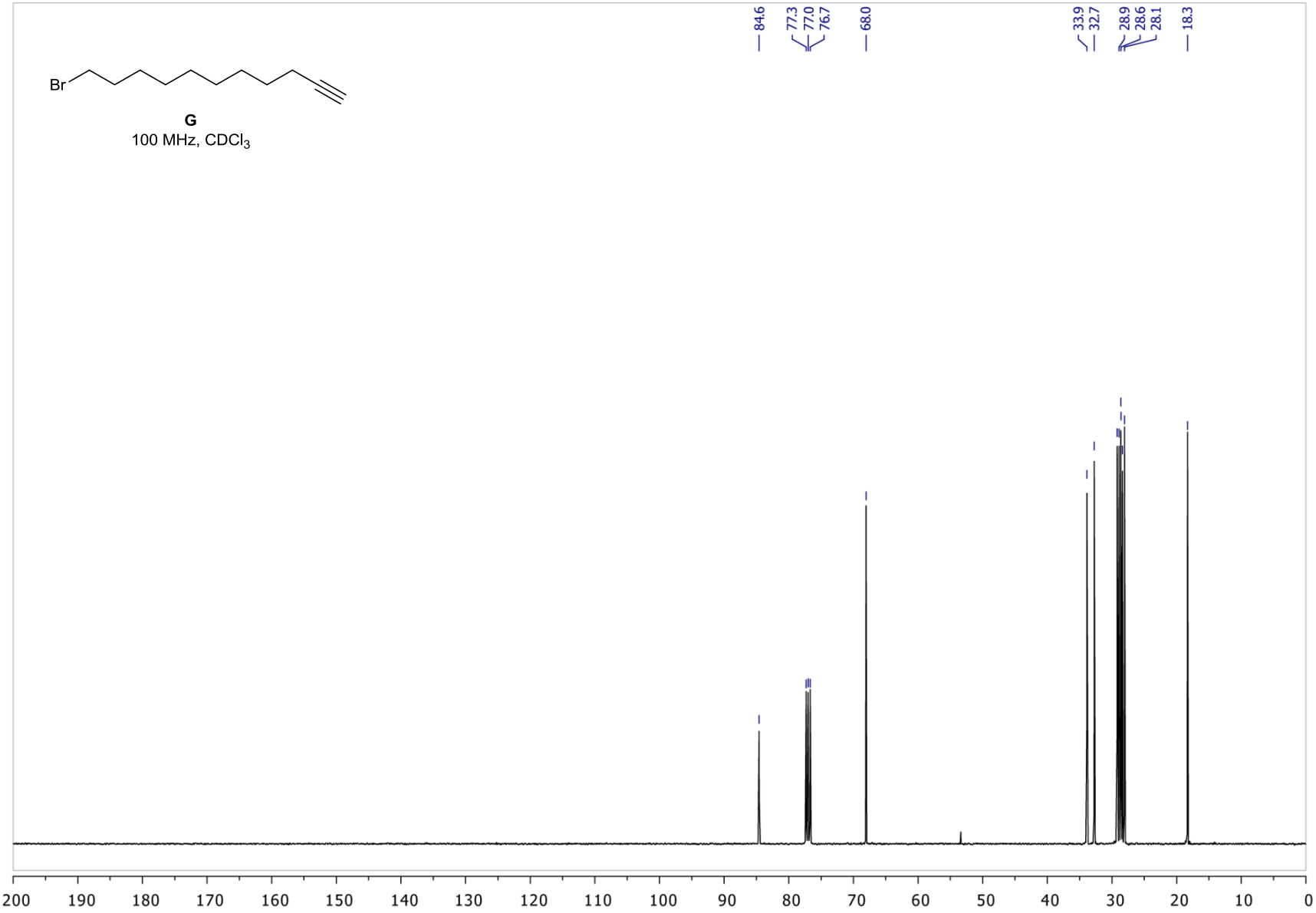


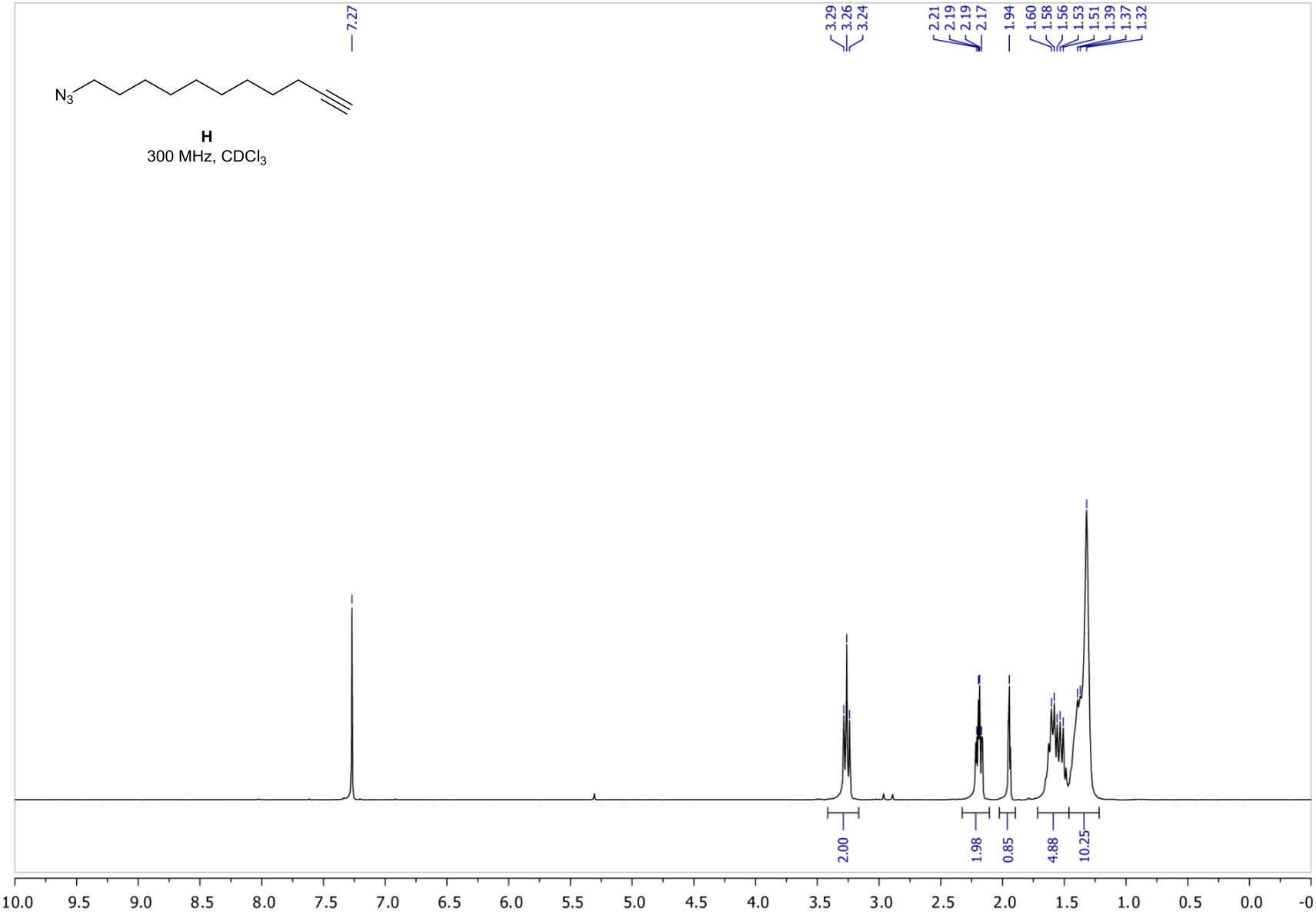

**1**

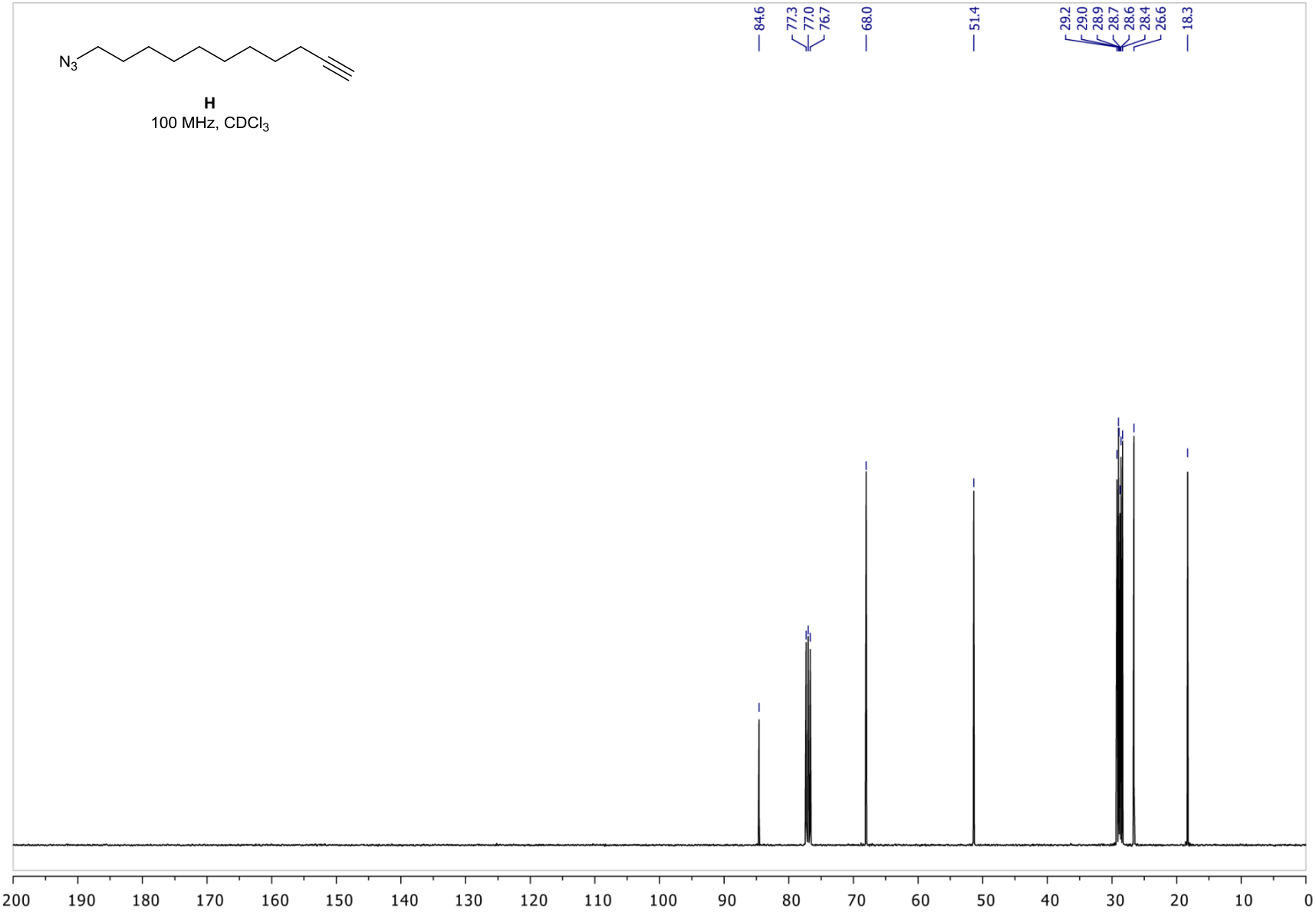
$CD_3CN$,400 MHz

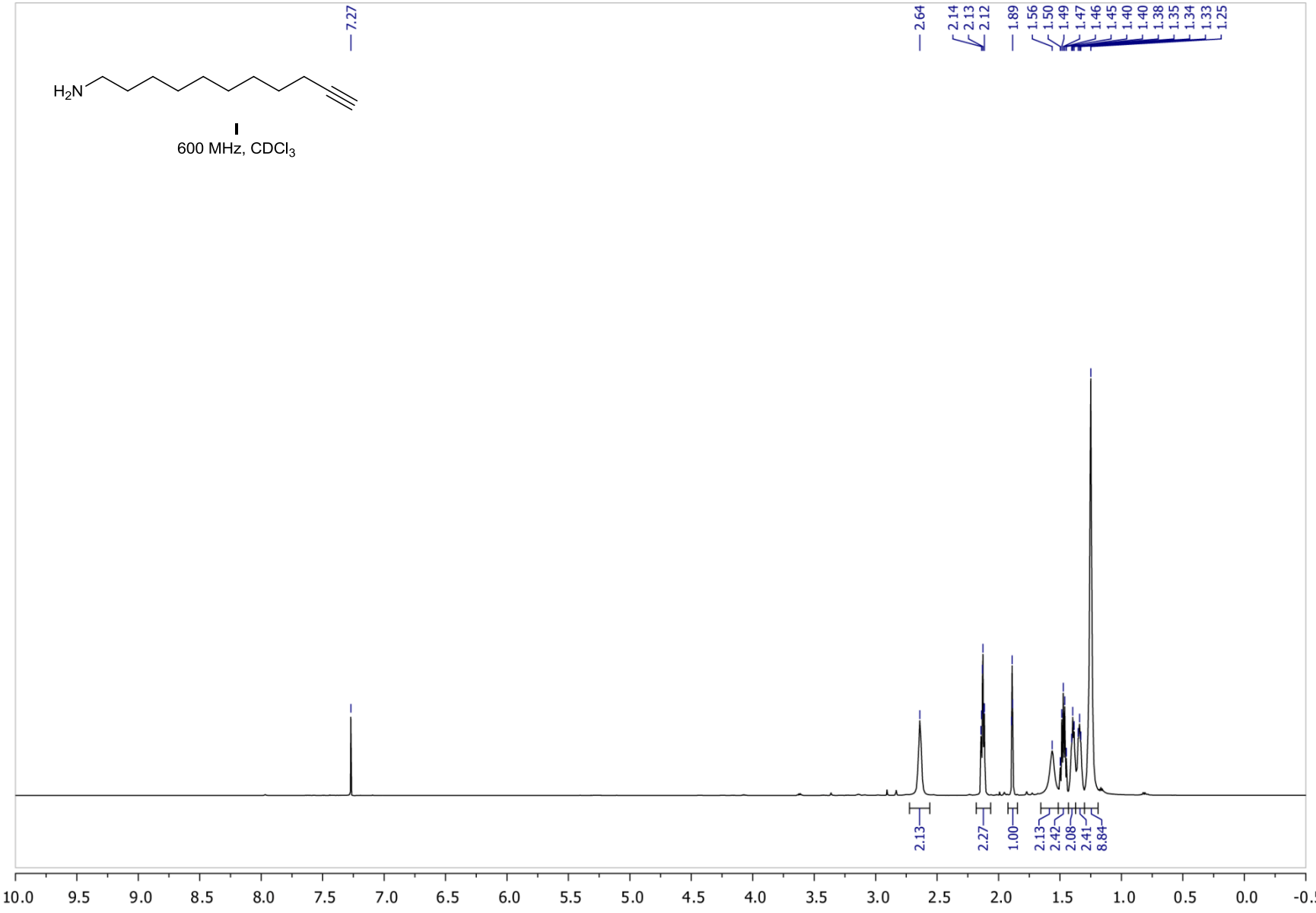

175.7
172.8
171.3
153.6
130.6
128.6
126.8
118.3
52.0
48.5
39.5
35.2
32.1
29.5
26.3
26.2
26.0
1.6
1.4
1.2
0.9
0.7
0.5
PF6
OH
1
CD3CN,100 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

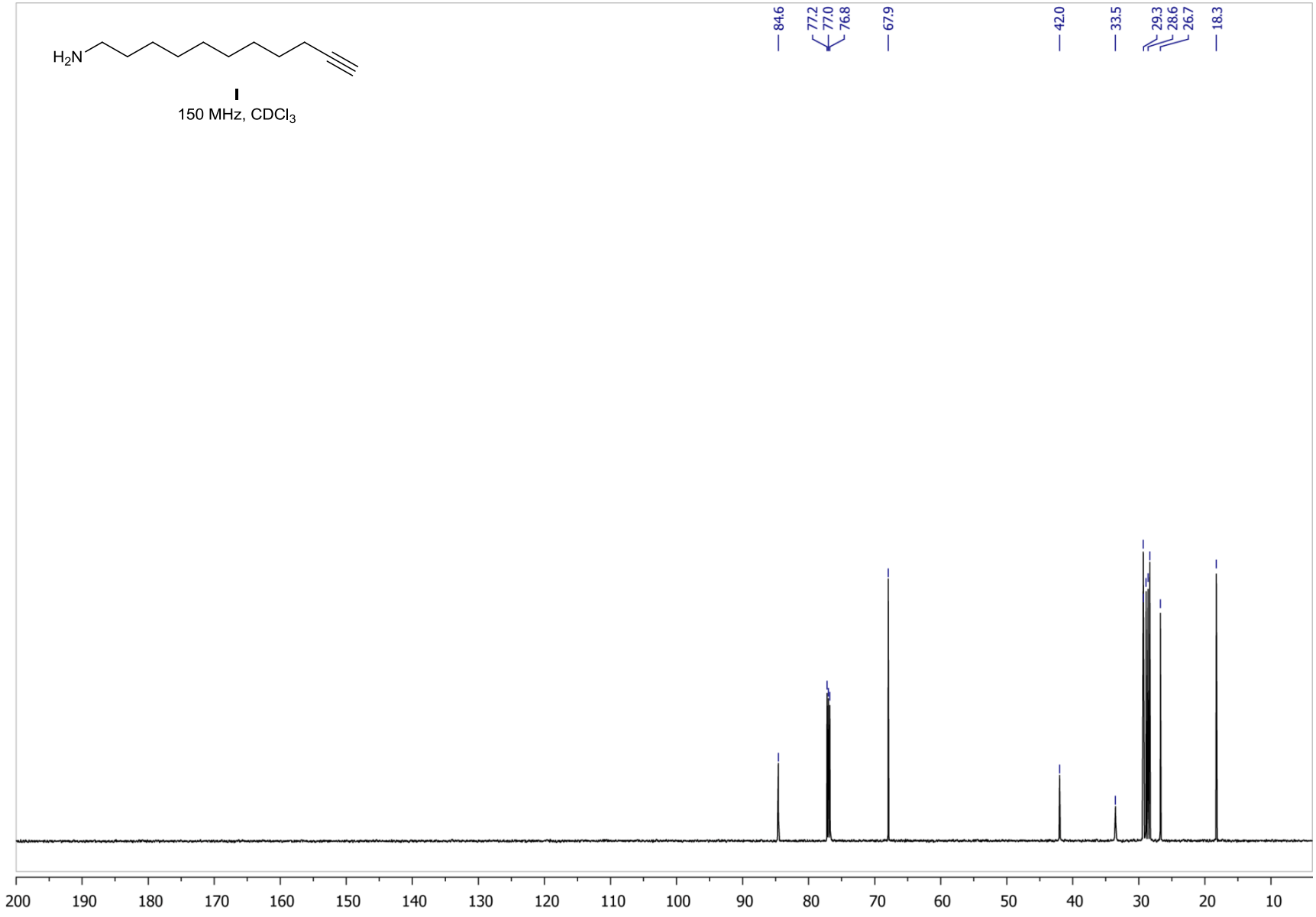

7.27
3.44
3.42
3.39
2.21
2.20
2.19
2.17
2.16
1.91
1.82
1.56
1.54
1.51
1.49
1.43
1.41
1.31
Br
G
300 MHz, CDCl3
2.22
2.24
1.00
2.26
4.57
4.38
7.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

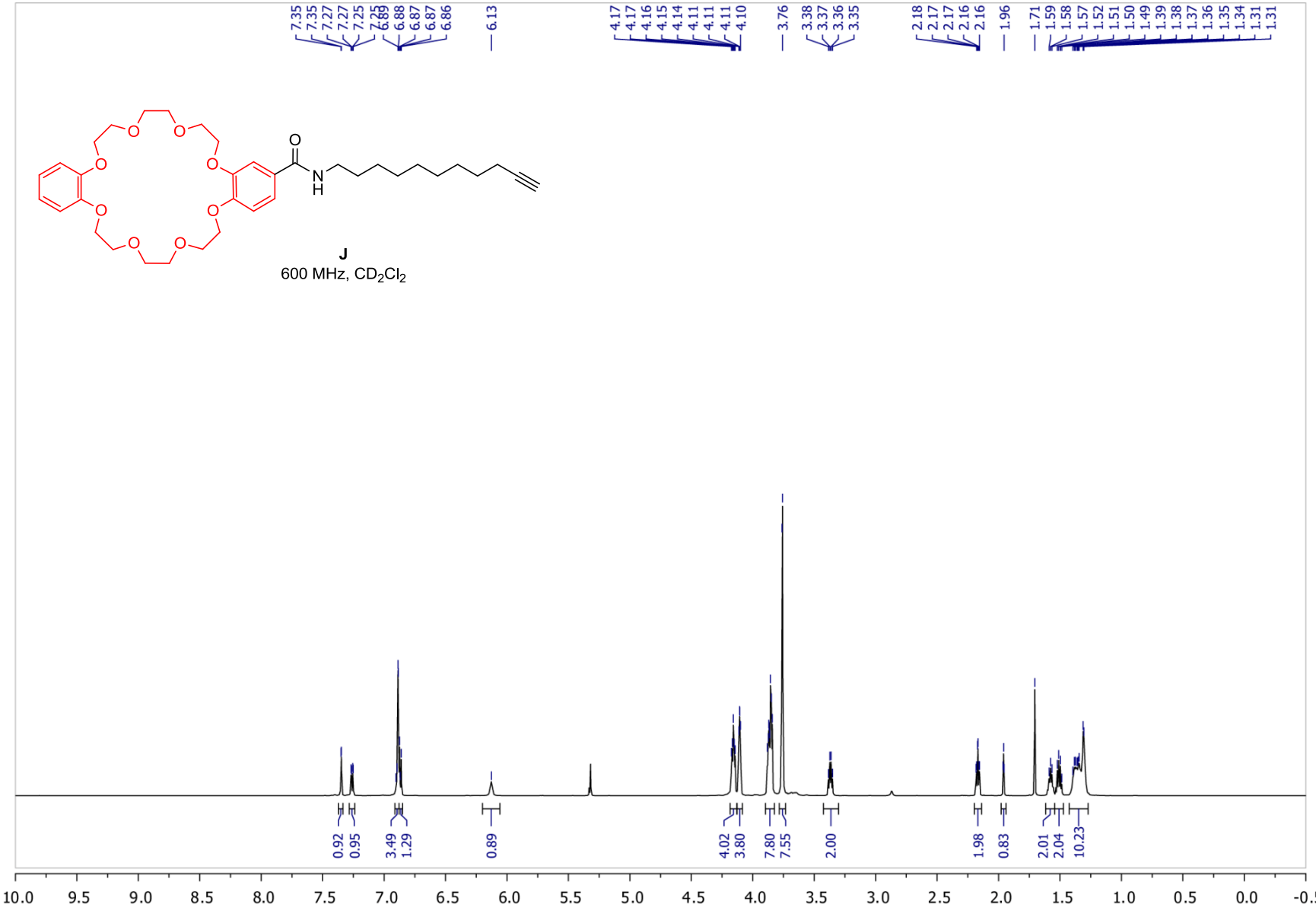

Br
G
100 MHz, CDCl3
84.6
77.3
77.0
76.7
68.0
33.9
32.7
28.9
28.6
28.1
18.3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.27
3.29
3.26
3.24
2.21
2.19
2.19
2.17
1.94
1.60
1.58
1.56
1.53
1.51
1.39
1.37
1.32
N3
H
300 MHz, CDCl3
2.00
1.98
0.85
4.88
10.25
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


N3
H
100 MHz, CDCl3
84.6
77.3
77.0
76.7
68.0
51.4
29.2
29.0
28.9
28.7
28.6
28.4
26.6
18.3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

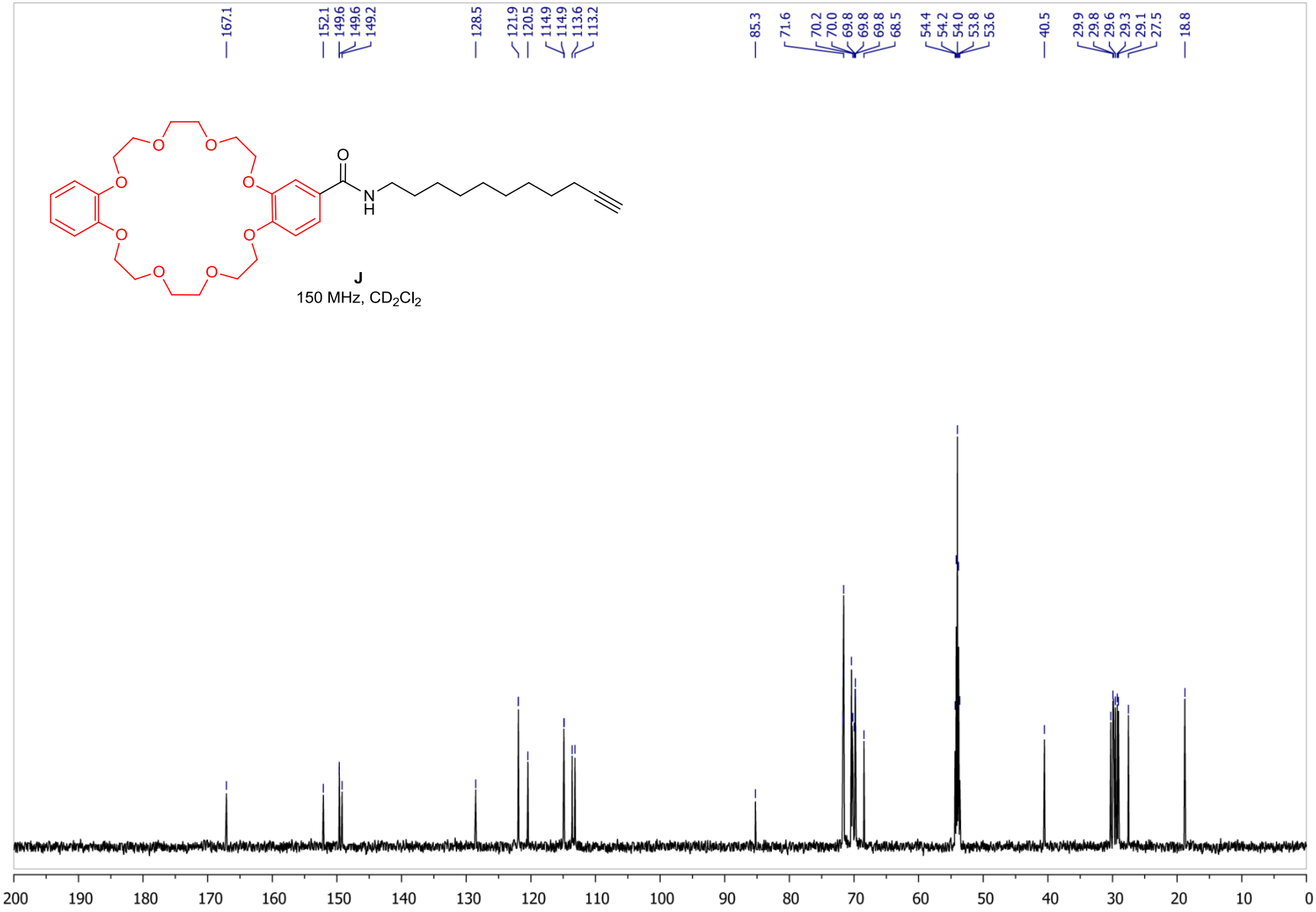

7.27
2.64
2.14
2.13
2.12
1.89
1.56
1.50
1.49
1.47
1.46
1.45
1.40
1.40
1.38
1.35
1.34
1.33
1.25
H2N
600 MHz, CDCl3
2.13
2.27
1.00
2.13
2.42
2.08
2.41
8.84
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

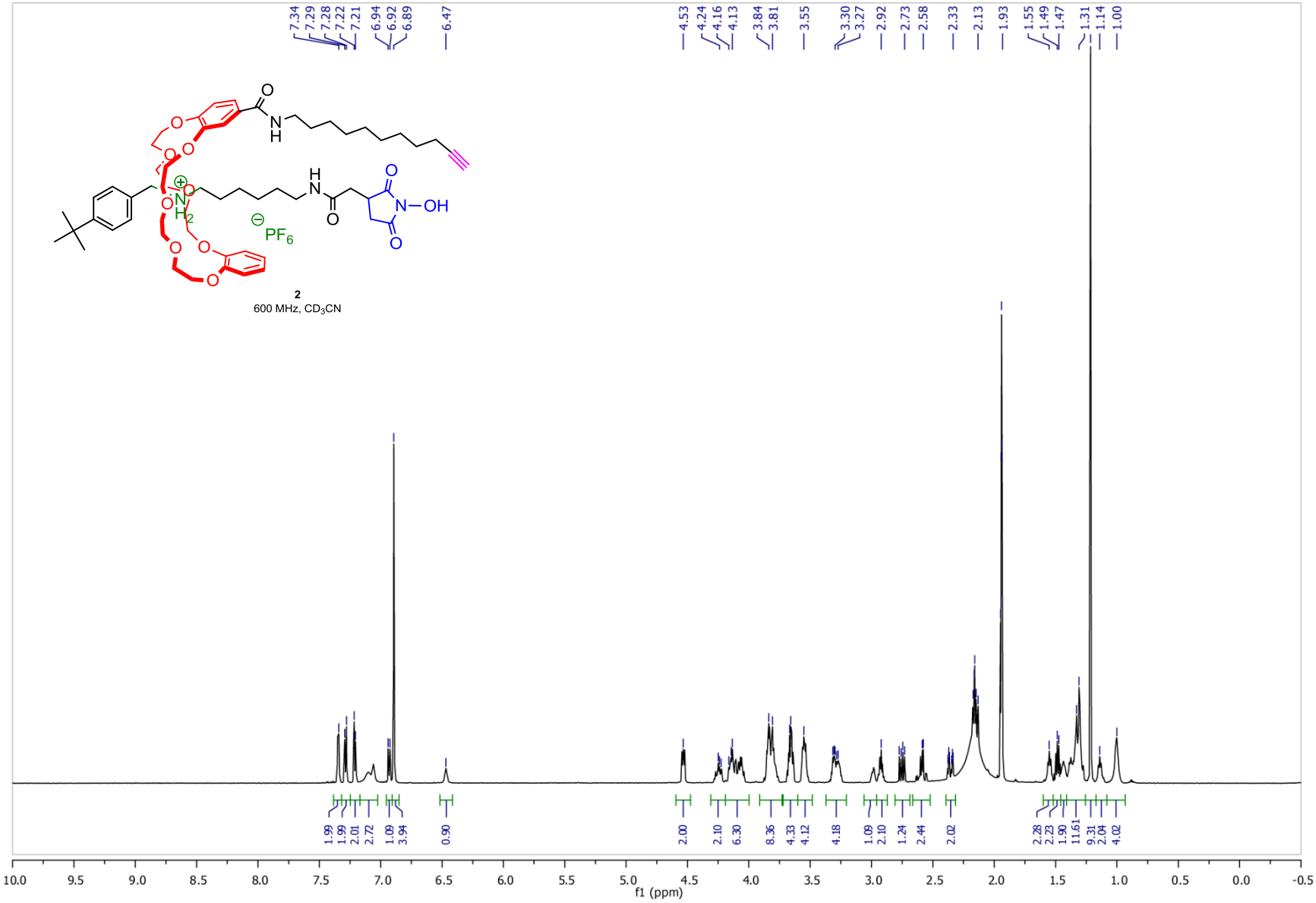

H2N
I
150 MHz, CDCl3
84.6
77.2
77.0
76.8
67.9
42.0
33.5
29.3
28.6
26.7
18.3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

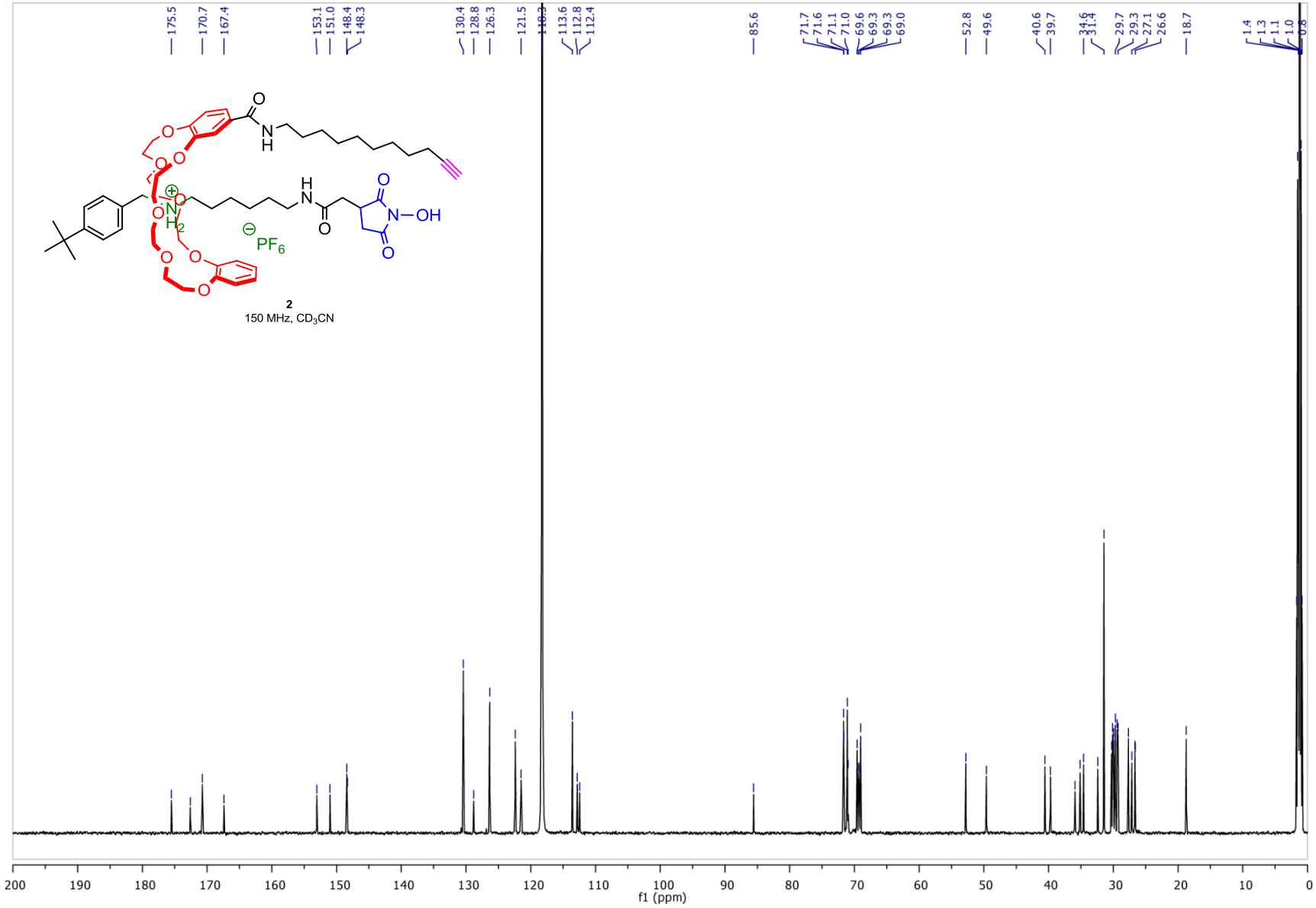


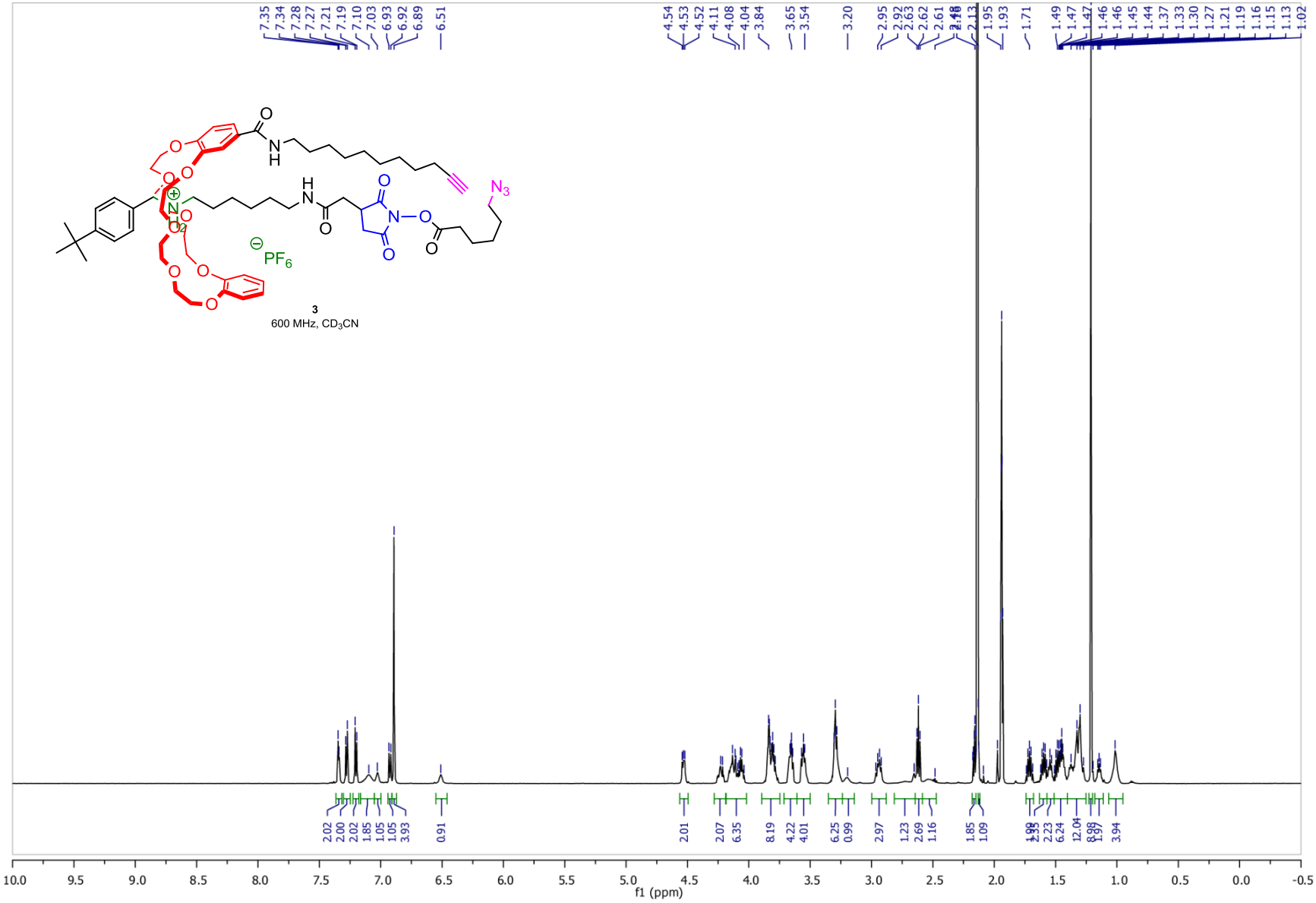

**J**

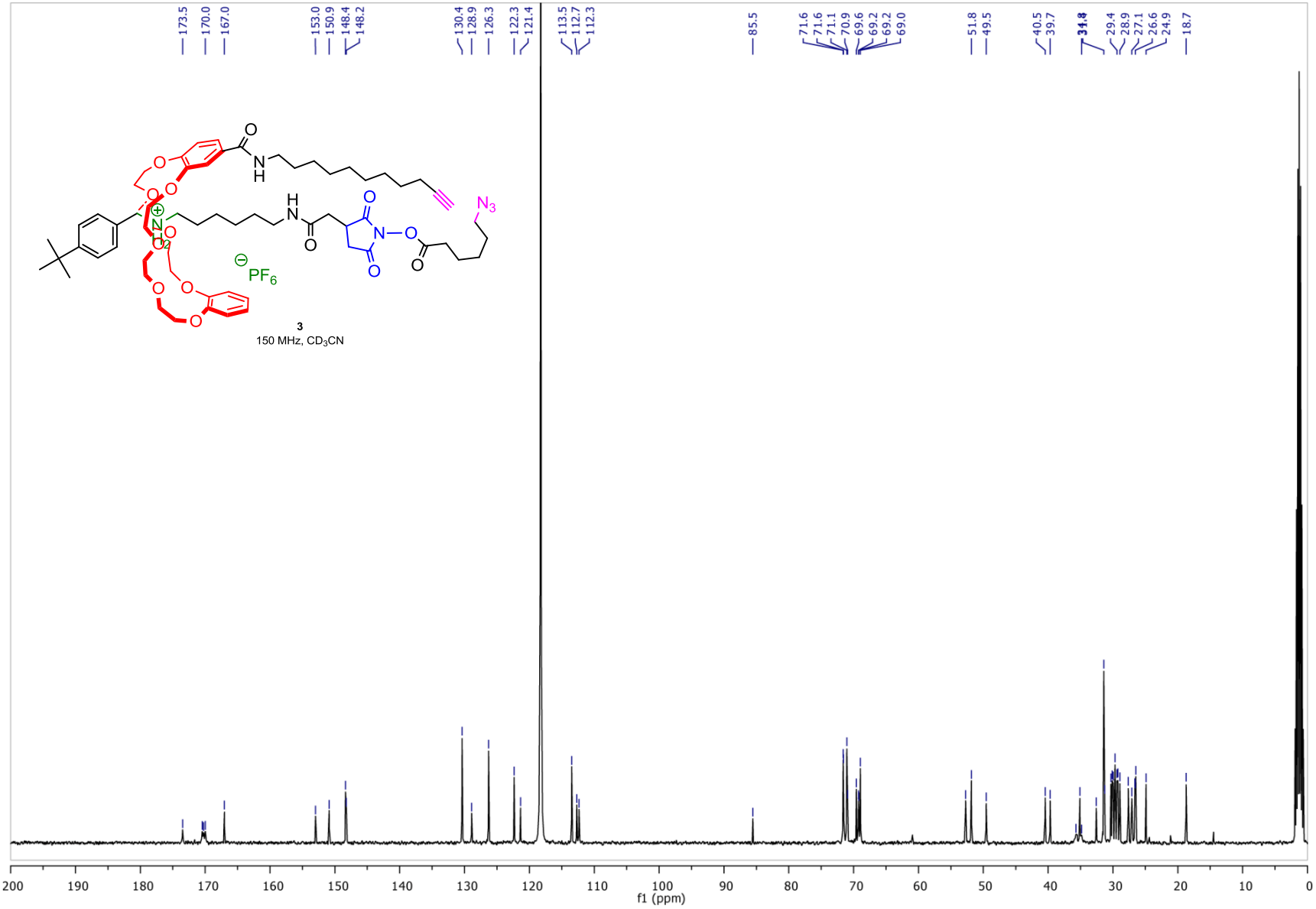
600 MHz, $CD_2Cl_2$

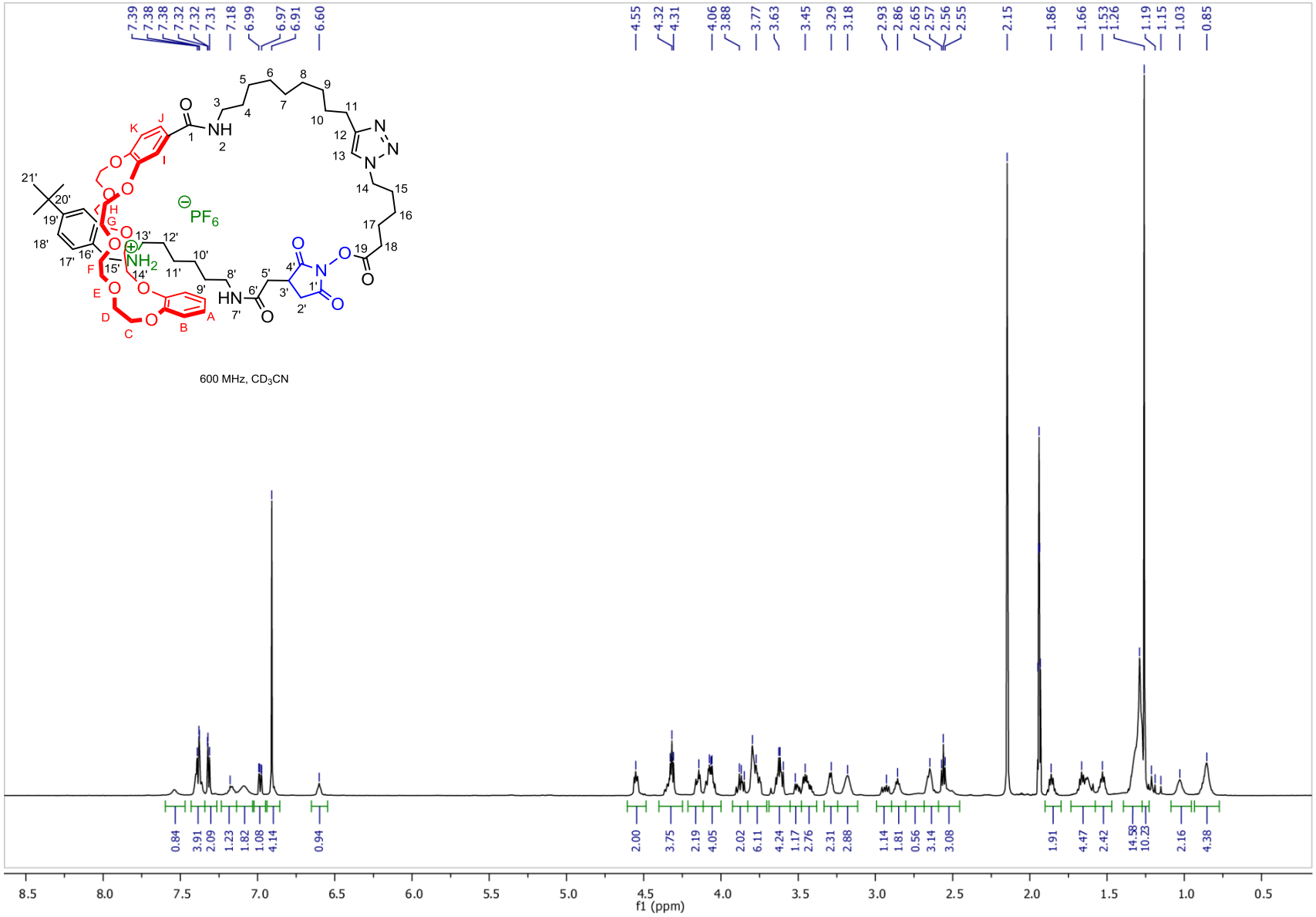

167.1
152.1
149.6
149.6
149.2
128.5
121.9
120.5
114.9
114.9
113.6
113.2
85.3
71.6
70.2
70.0
69.8
69.8
69.8
68.5
54.4
54.2
54.0
53.8
53.6
40.5
29.9
29.8
29.6
29.3
29.1
27.5
18.8
O
N
H
J
150 MHz, CD2Cl2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

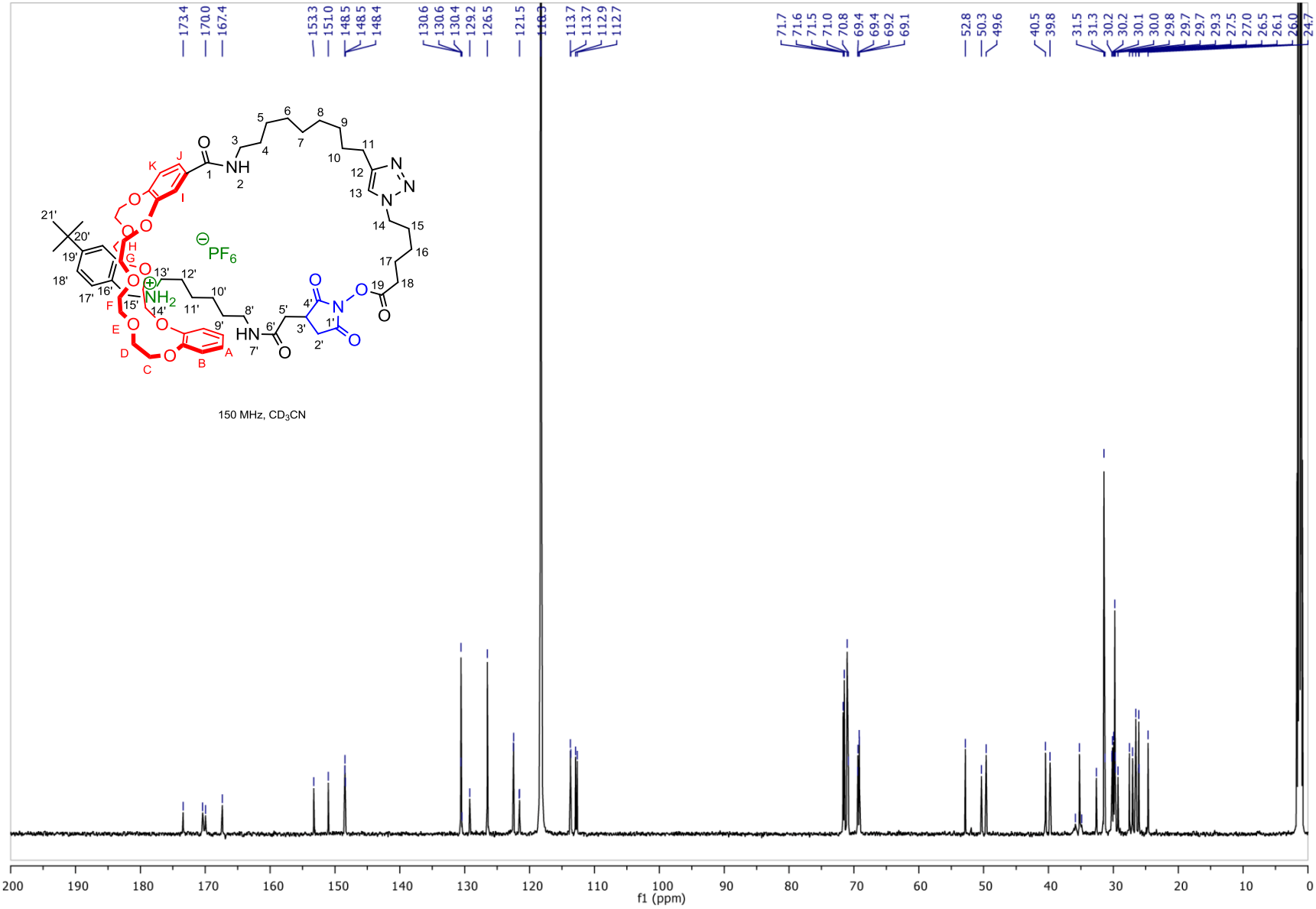

7.34
7.29
7.28
7.22
7.21
6.94
6.92
6.89
6.47
4.53
4.24
4.16
4.13
3.84
3.81
3.55
3.30
3.27
2.92
2.73
2.58
2.33
2.13
1.93
1.55
1.49
1.47
1.31
1.14
1.00
PF6
N–OH
2
600 MHz, CD3CN
1.99
1.99
2.01
2.72
1.09
3.94
0.90
2.00
2.10
6.30
8.36
4.33
4.12
4.18
1.09
2.10
1.24
2.44
2.02
2.28
2.23
1.90
11.61
9.31
2.04
4.02
f1 (ppm)

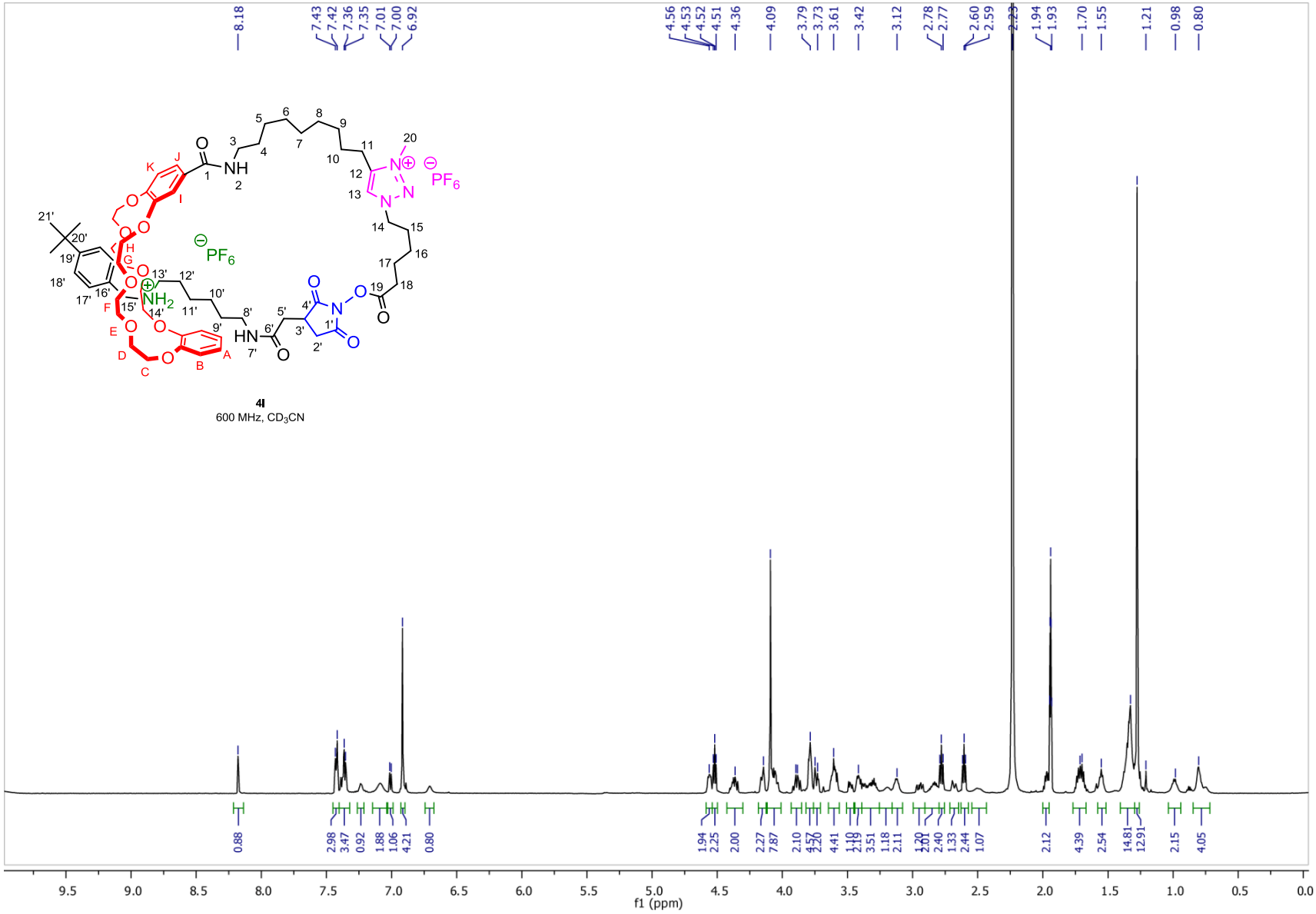

175.5
170.7
167.4
153.1
151.0
148.4
148.3
130.4
128.8
126.3
121.5
113.6
112.8
112.4
85.6
71.7
71.6
71.1
71.0
69.6
69.3
69.3
69.0
52.8
49.6
40.6
39.7
34.6
31.4
29.7
29.3
27.1
26.6
18.7
1.4
1.3
1.1
1.0
0.8
PF6
2
150 MHz, CD3CN
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.35
7.34
7.28
7.27
7.21
7.19
7.10
7.03
6.93
6.92
6.89
6.51
4.54
4.53
4.52
4.11
4.08
4.04
3.84
3.65
3.54
3.20
2.95
2.92
2.63
2.62
2.61
2.13
1.95
1.93
1.71
1.49
1.47
1.47
1.46
1.46
1.45
1.44
1.37
1.33
1.30
1.27
1.21
1.19
1.16
1.15
1.13
1.02
3
600 MHz, CD3CN
2.02
2.00
2.02
1.85
1.05
1.05
3.93
0.91
2.01
2.07
6.35
8.19
4.22
4.01
6.25
0.99
2.97
1.23
2.69
1.16
1.85
1.09
3.94
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

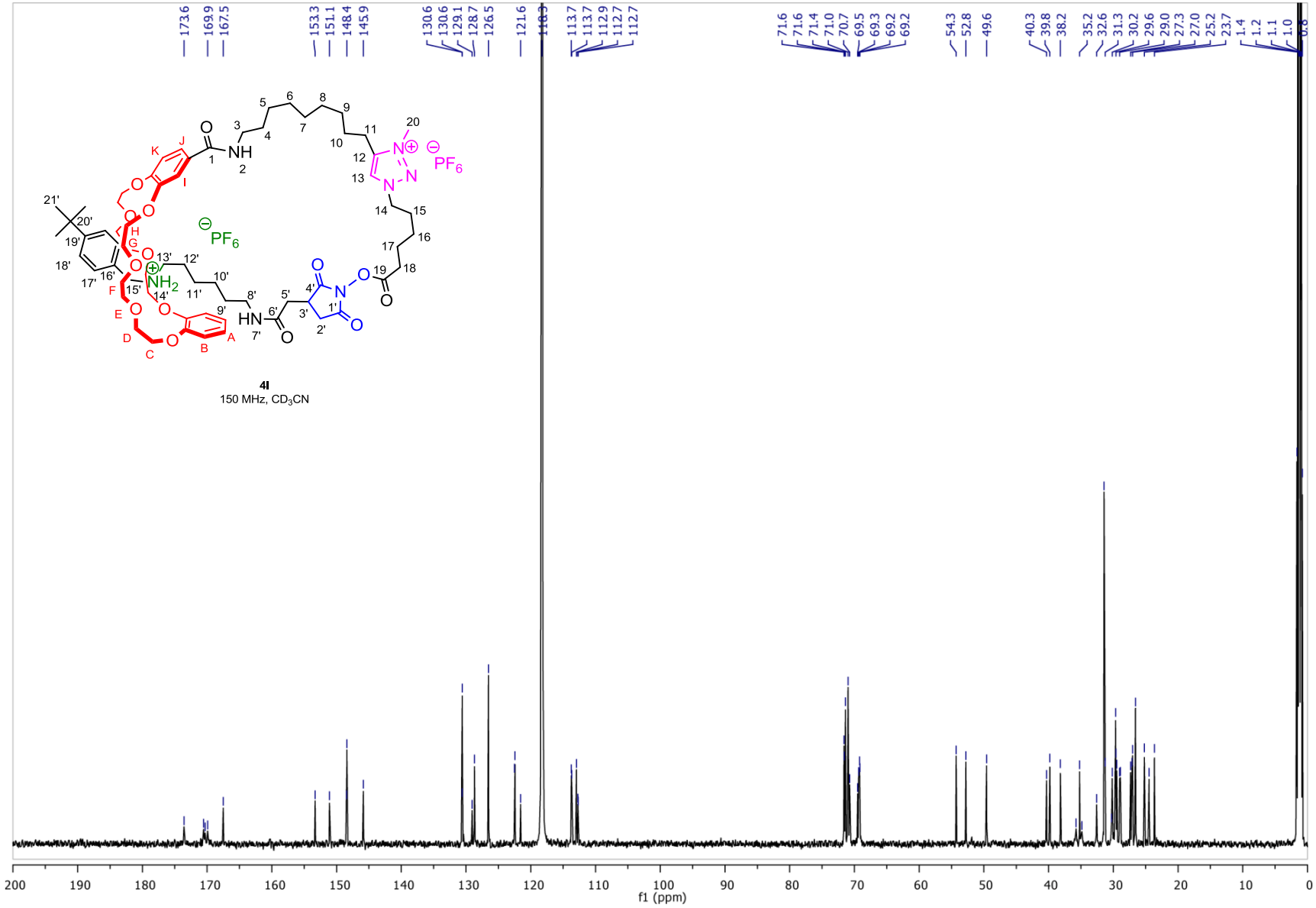

173.5
170.0
167.0
153.0
150.9
148.4
148.2
130.4
128.9
126.3
122.3
121.4
113.5
112.7
112.3
85.5
71.6
71.6
71.1
70.9
69.6
69.2
69.2
69.0
51.8
49.5
40.5
39.7
31.8
29.4
28.9
27.1
26.6
24.9
18.7
N3
PF6
3
150 MHz, CD3CN
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

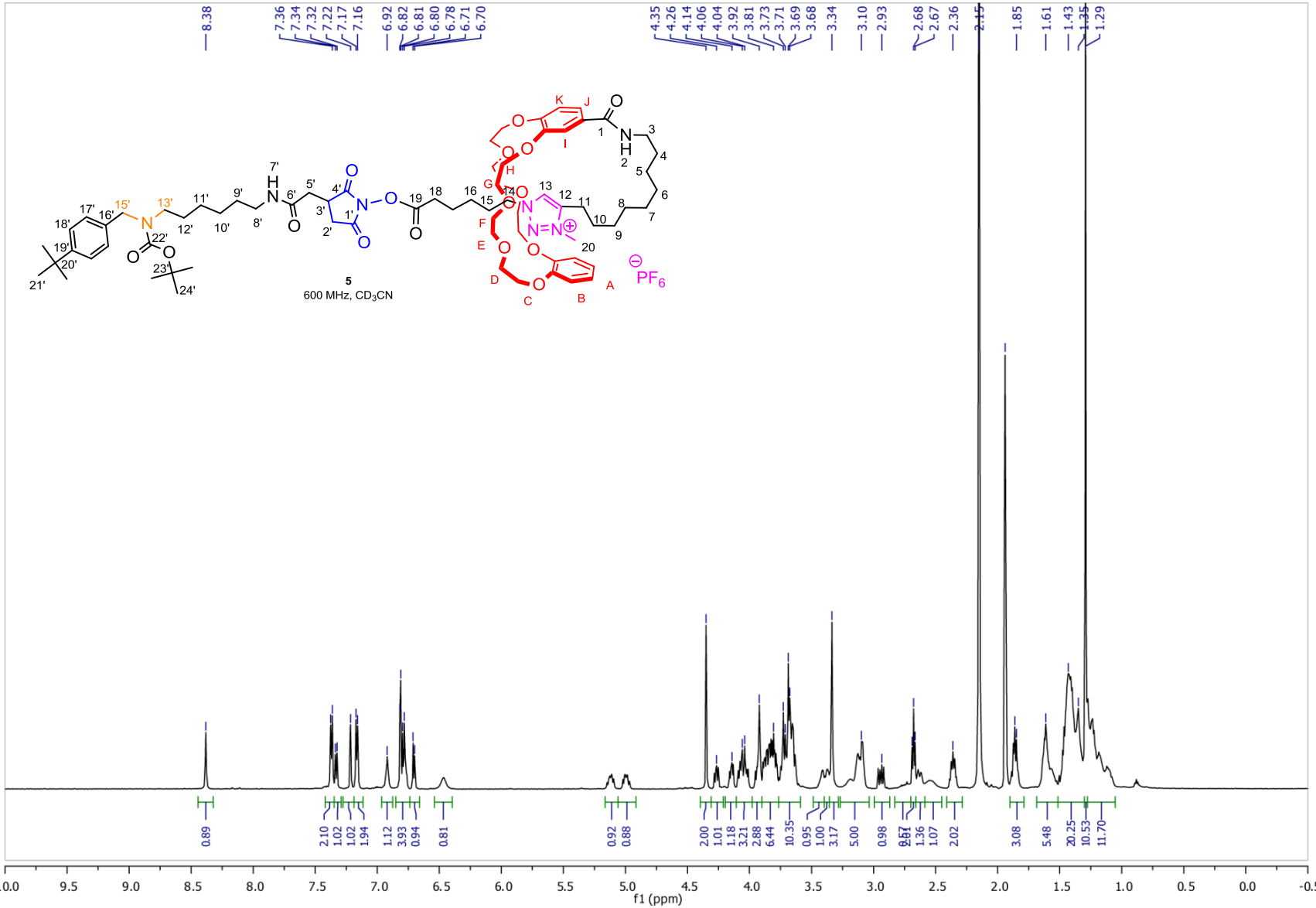

600 MHz, CD3CN
f1 (ppm)

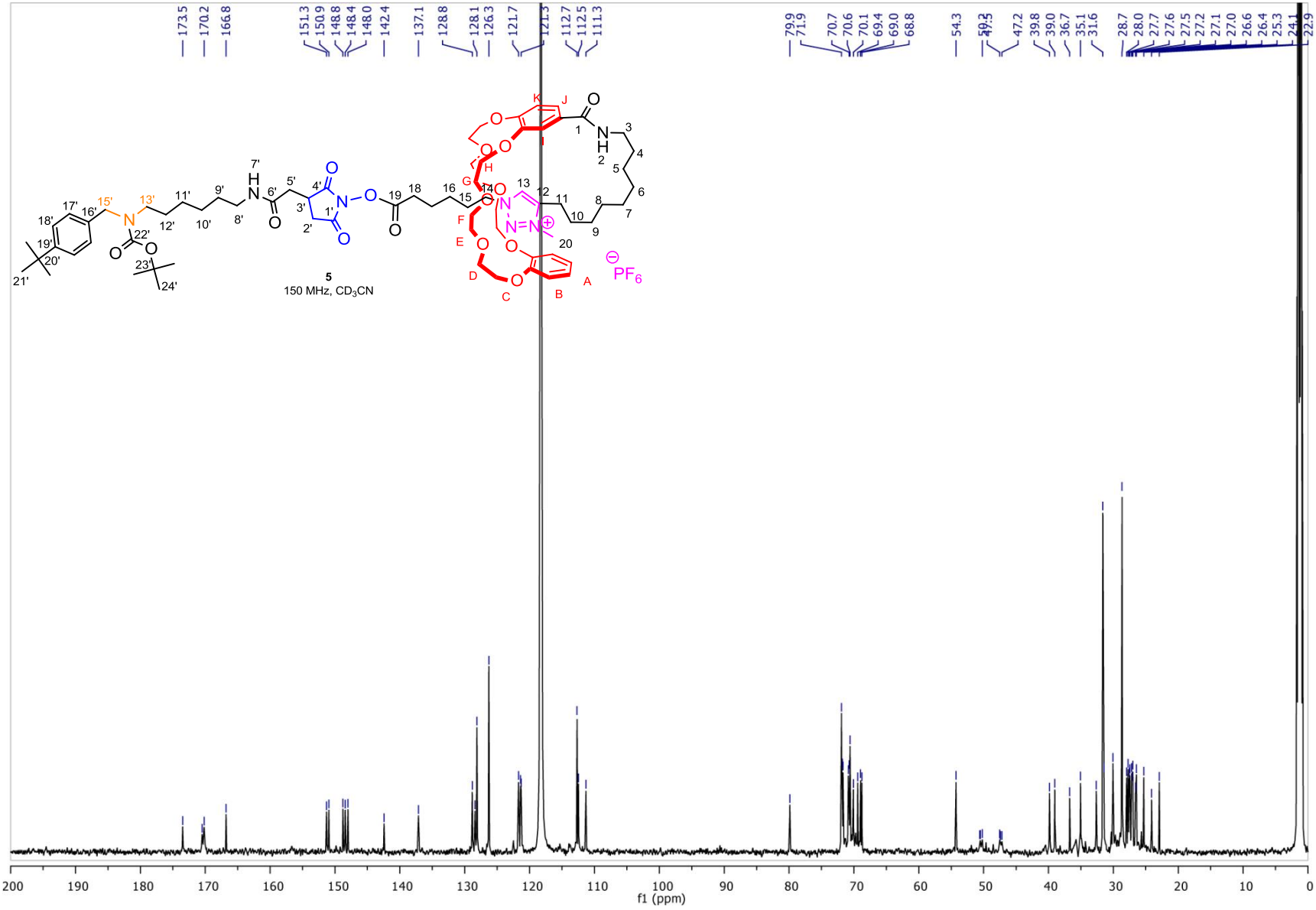

150 MHz, CD3CN
f1 (ppm)

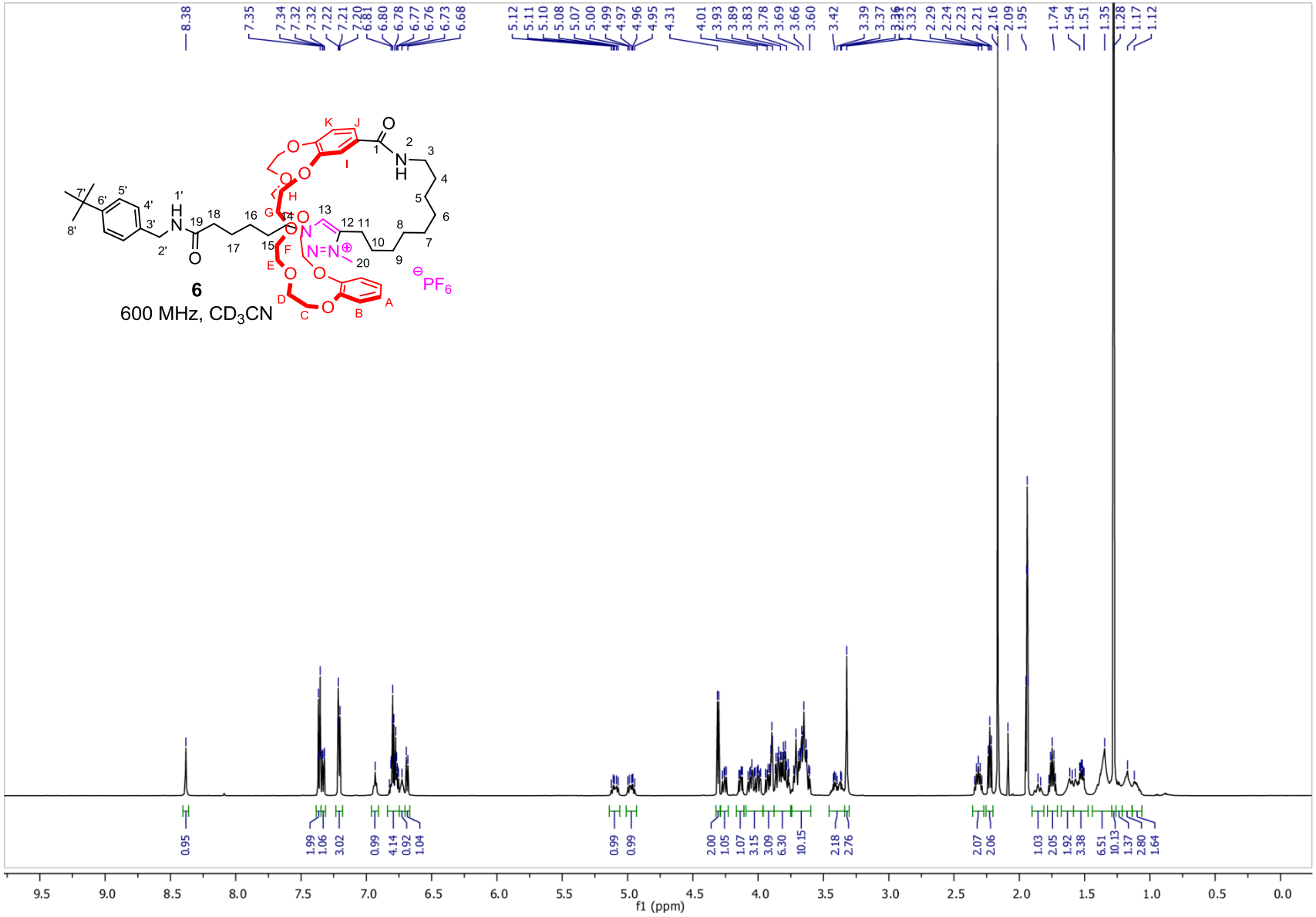


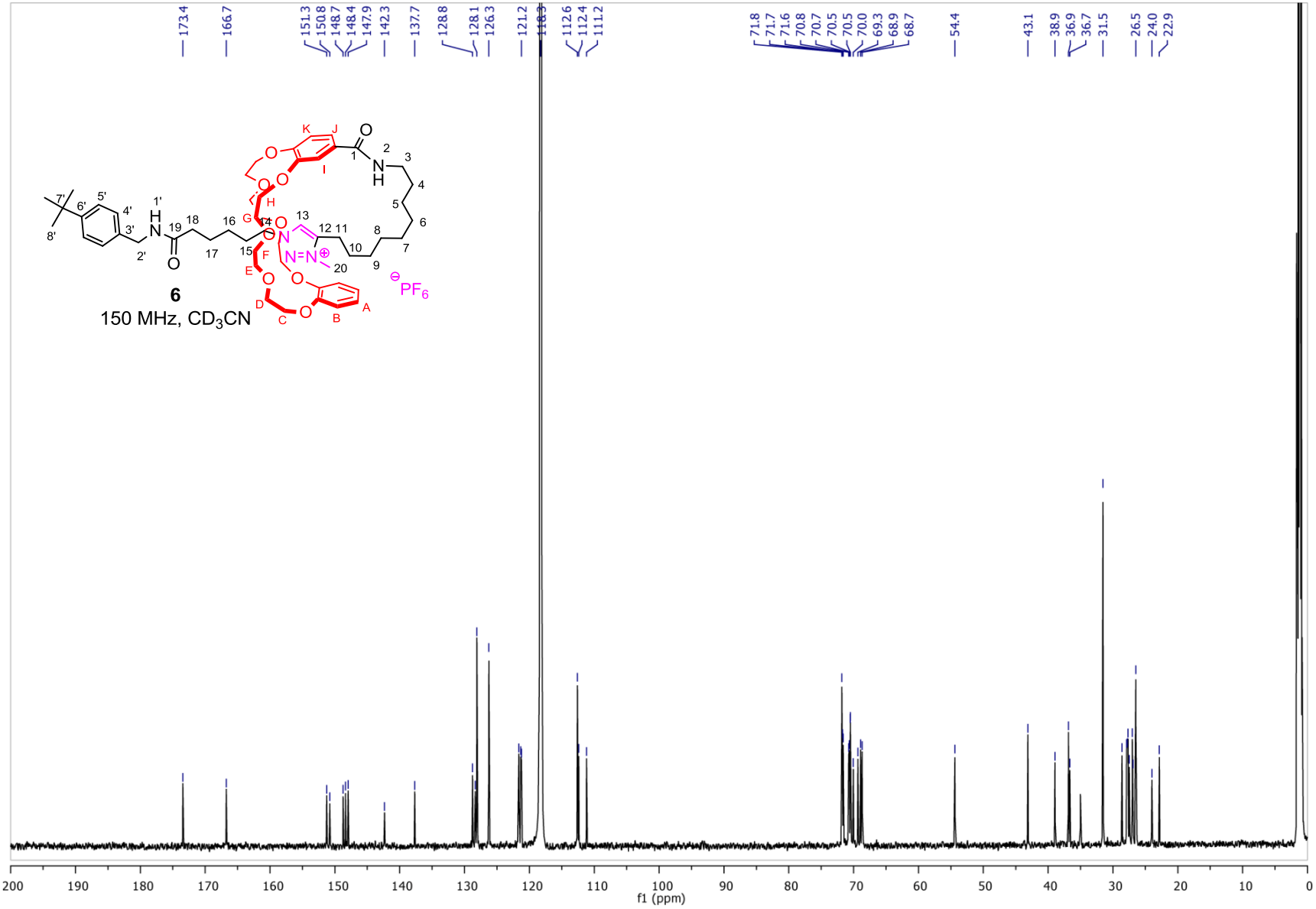

**4l**
600 MHz, $CD_3CN$

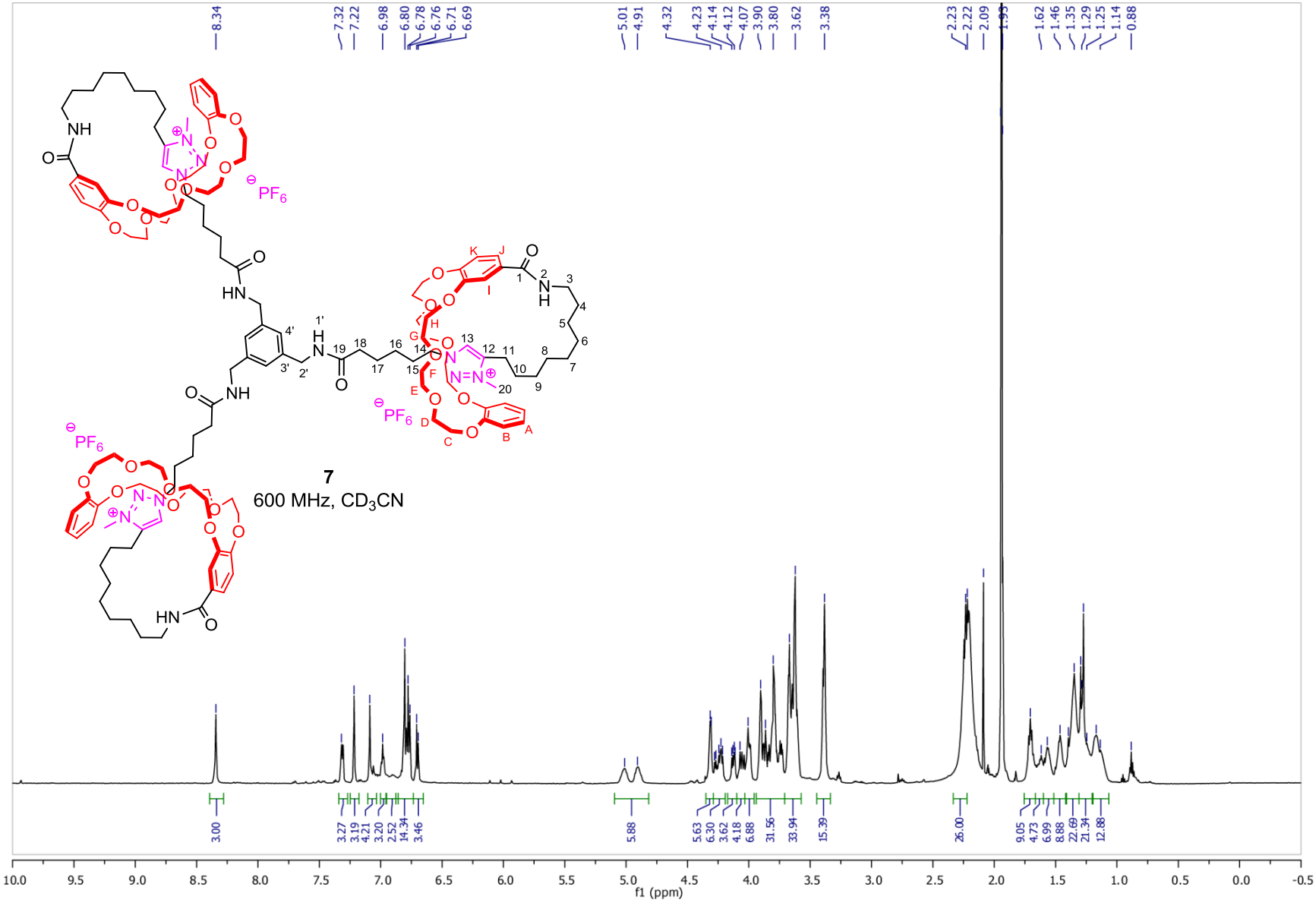

4l
150 MHz, CD3CN
f1 (ppm)

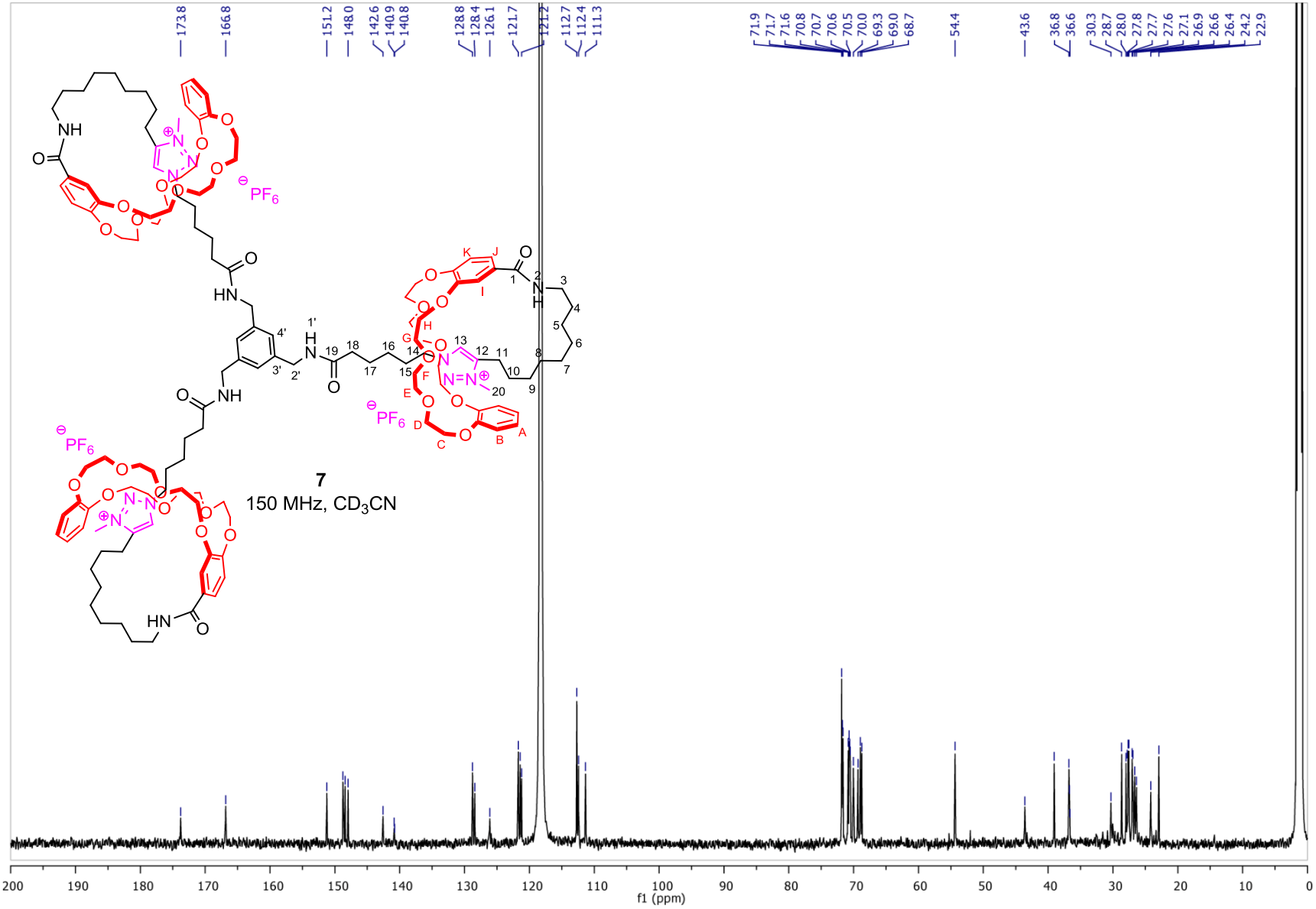

8.38
7.36
7.34
7.32
7.22
7.17
7.16
6.92
6.82
6.81
6.80
6.78
6.71
6.70
4.35
4.26
4.14
4.06
4.04
3.92
3.81
3.73
3.71
3.69
3.68
3.34
3.10
2.93
2.68
2.67
2.36
2.15
1.85
1.61
1.43
1.35
1.29
5
600 MHz, CD3CN
PF6
0.89
2.10
1.02
1.02
1.94
1.12
3.93
0.94
0.81
0.92
0.88
2.00
1.01
1.18
3.21
2.88
6.44
10.35
0.95
1.00
3.17
5.00
0.98
1.36
1.07
2.02
3.08
5.48
20.25
10.53
11.70
f1 (ppm)

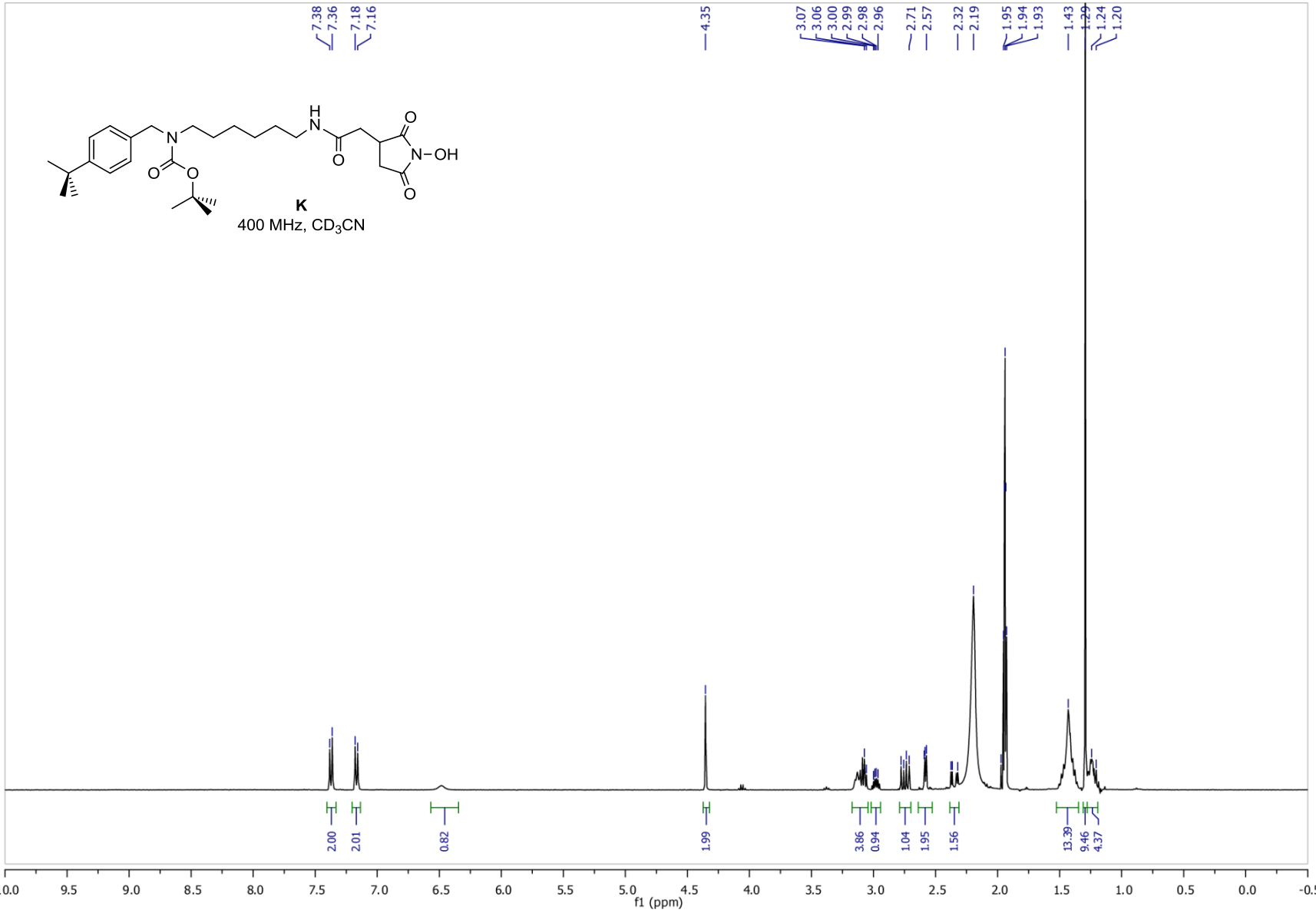

173.5
170.2
166.8
151.3
150.9
148.8
148.4
148.0
142.4
137.1
128.8
128.1
126.3
121.7
121.3
112.7
112.5
111.3
79.9
71.9
70.7
70.6
70.1
69.4
69.0
68.8
54.3
47.2
39.8
39.0
36.7
35.1
31.6
28.7
28.0
27.7
27.6
27.5
27.2
27.1
27.0
26.6
26.4
25.3
24.1
22.9
5
150 MHz, CD3CN
PF6
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

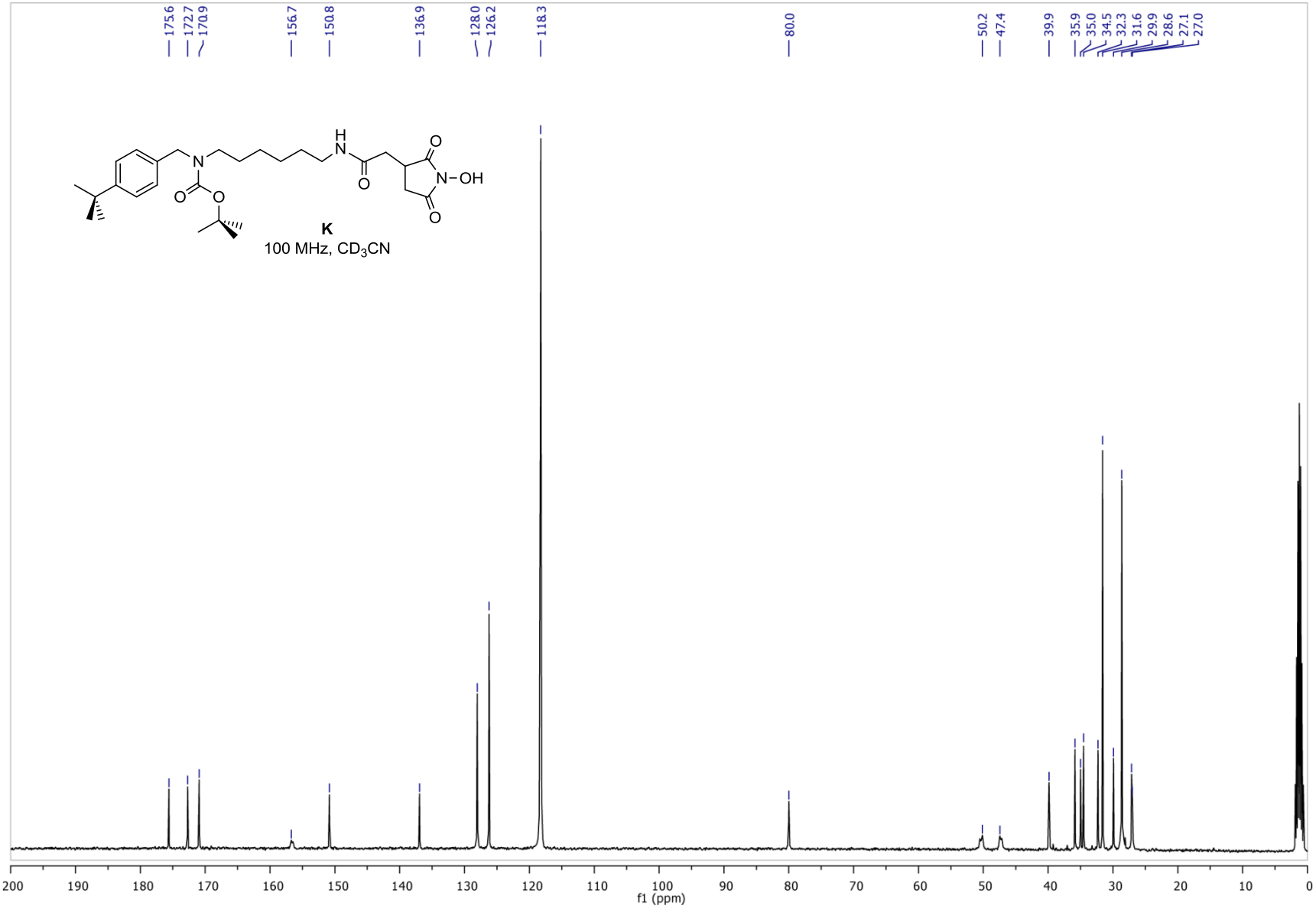

6
600 MHz, CD3CN
f1 (ppm)

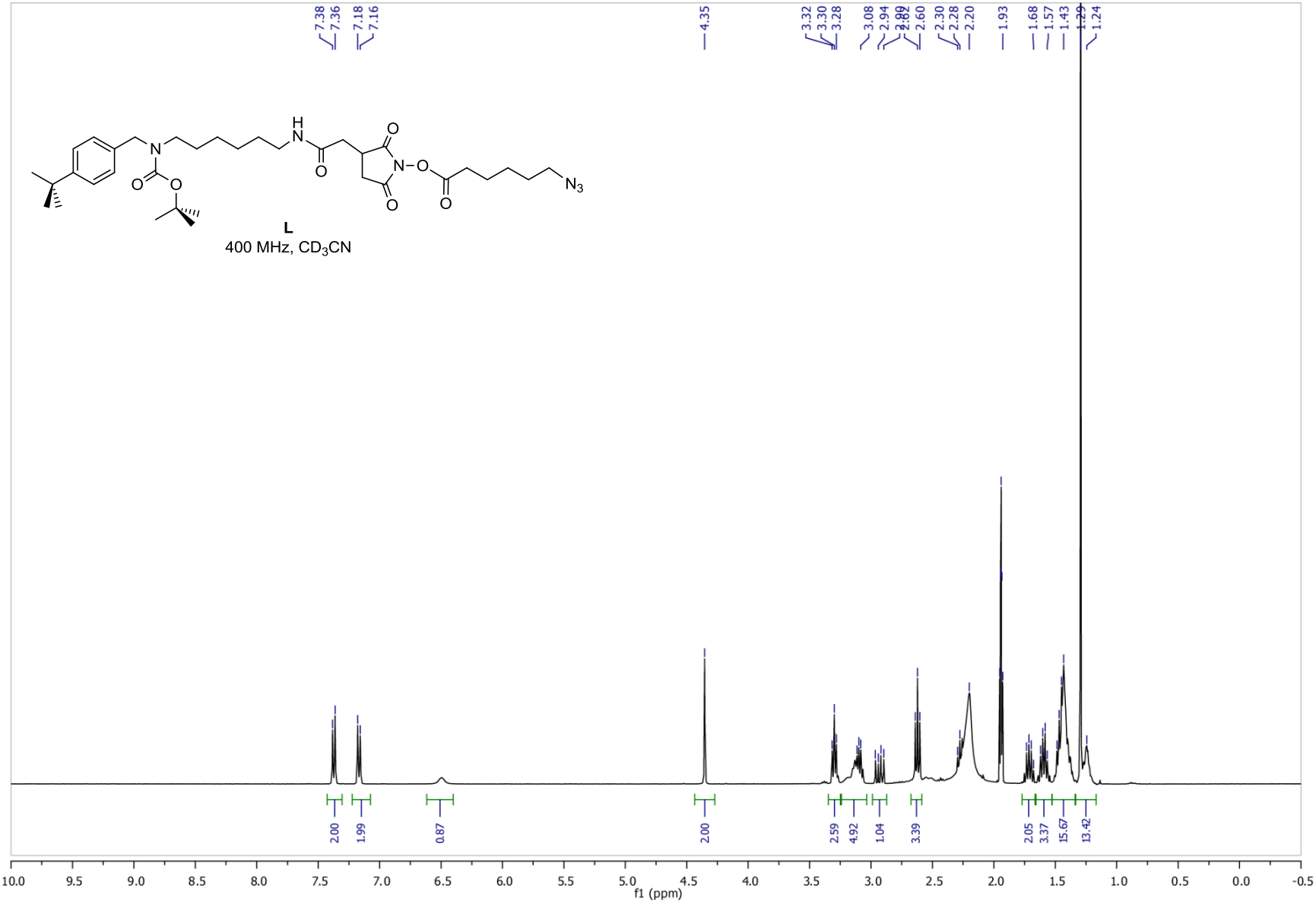

173.4
166.7
151.3
150.8
148.7
148.4
147.9
142.3
137.7
128.8
128.1
126.3
121.2
118.3
112.6
112.4
111.2
71.8
71.7
71.6
70.8
70.7
70.5
70.5
70.0
69.3
68.9
68.7
54.4
43.1
38.9
36.9
36.7
31.5
26.5
24.0
22.9
6
150 MHz, CD3CN
PF6
f1 (ppm)


7
600 MHz, CD3CN
f1 (ppm)


7
150 MHz, CD3CN
f1 (ppm)

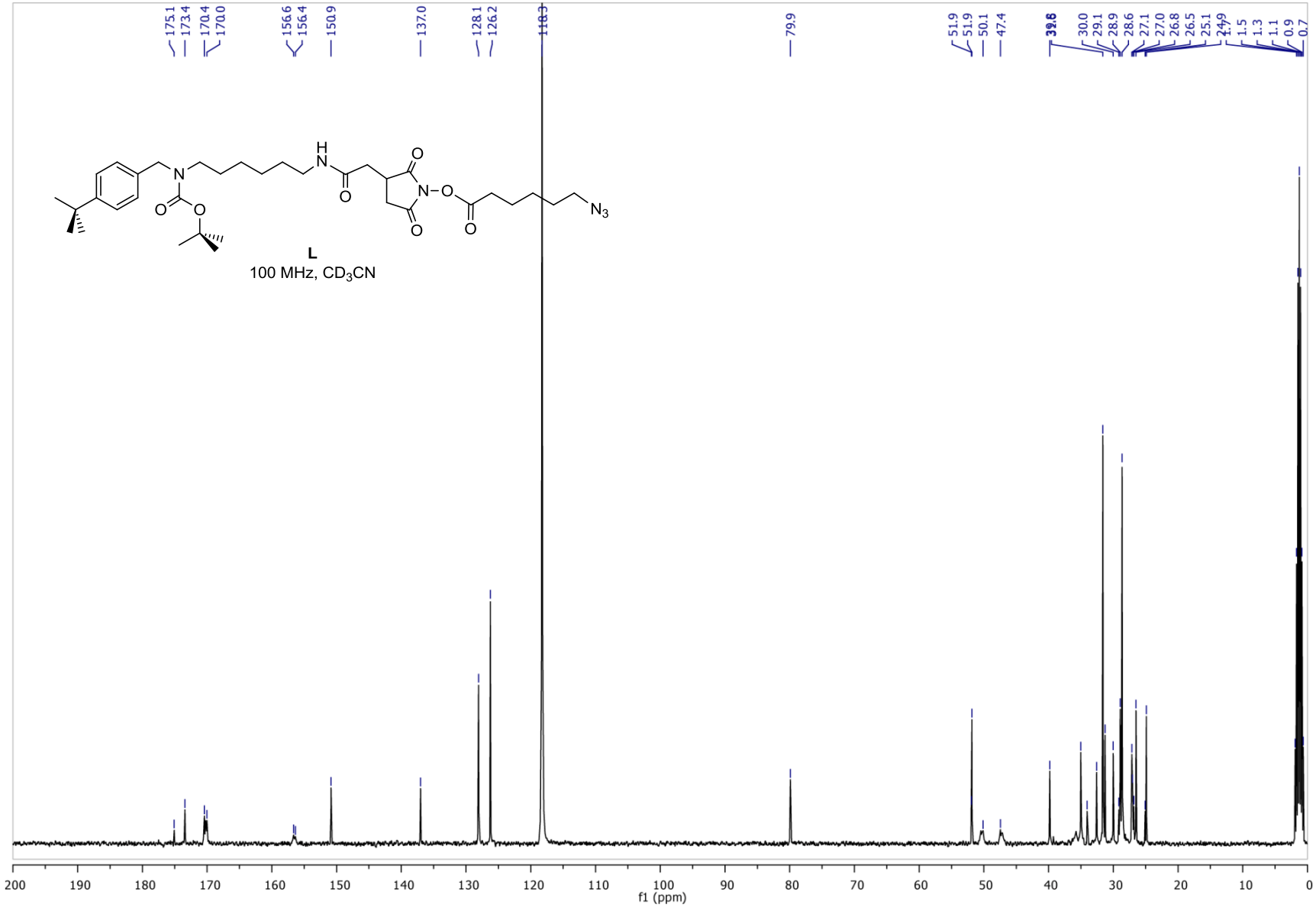

7.38
7.36
7.18
7.16
4.35
3.07
3.06
3.00
2.99
2.98
2.96
2.71
2.57
2.32
2.19
1.95
1.94
1.93
1.43
1.24
1.20
K
400 MHz, CD3CN
2.00
2.01
0.82
1.99
3.86
0.94
1.04
1.95
1.56
13.39
9.46
4.37
f1 (ppm)


175.6
172.7
170.9
156.7
150.8
136.9
128.0
126.2
118.3
80.0
50.2
47.4
39.9
35.9
35.0
34.5
32.3
31.6
29.9
28.6
27.1
27.0
H
N
N
O
O
O
O
N–OH
O
K
100 MHz, CD3CN
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



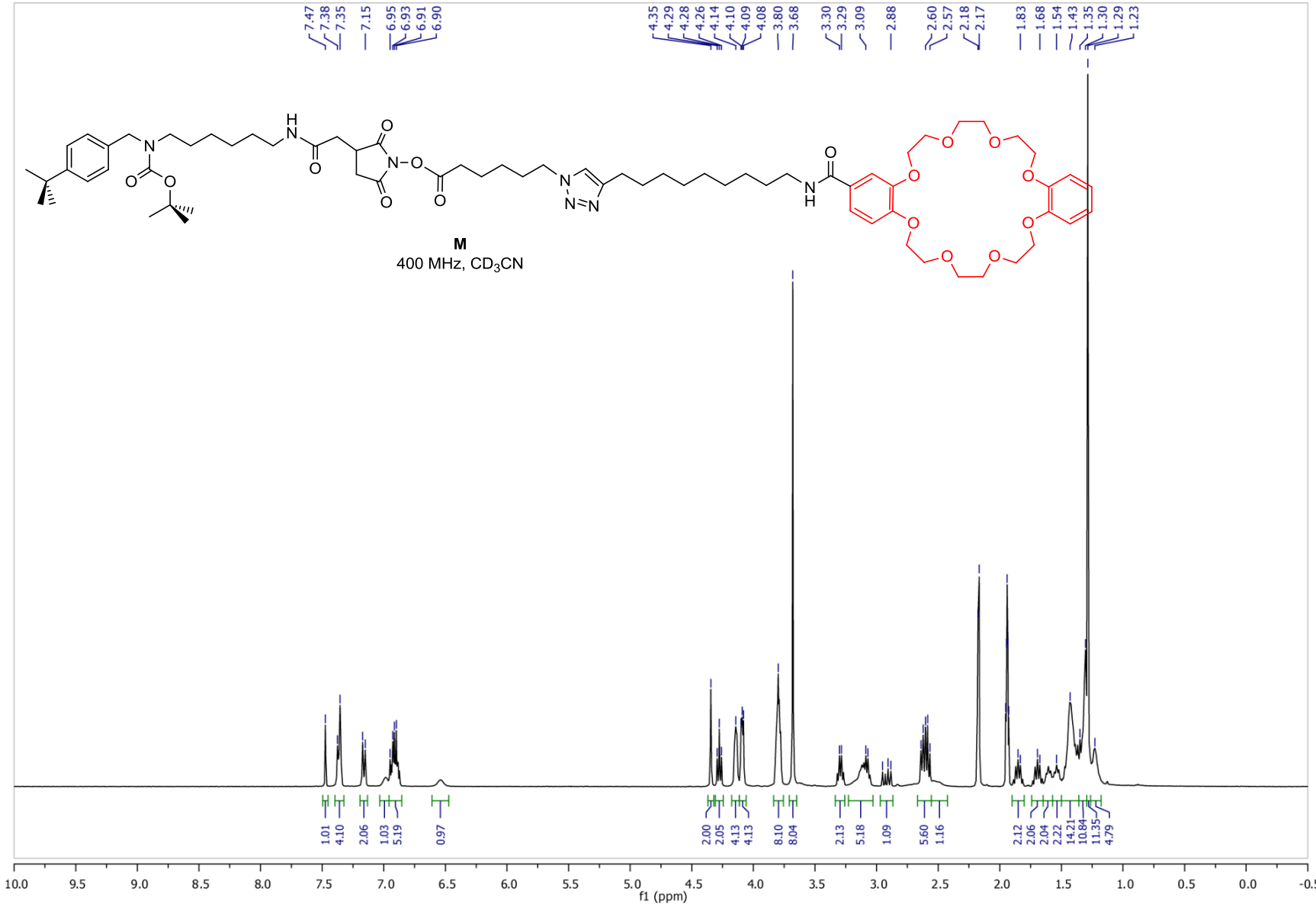

**L**

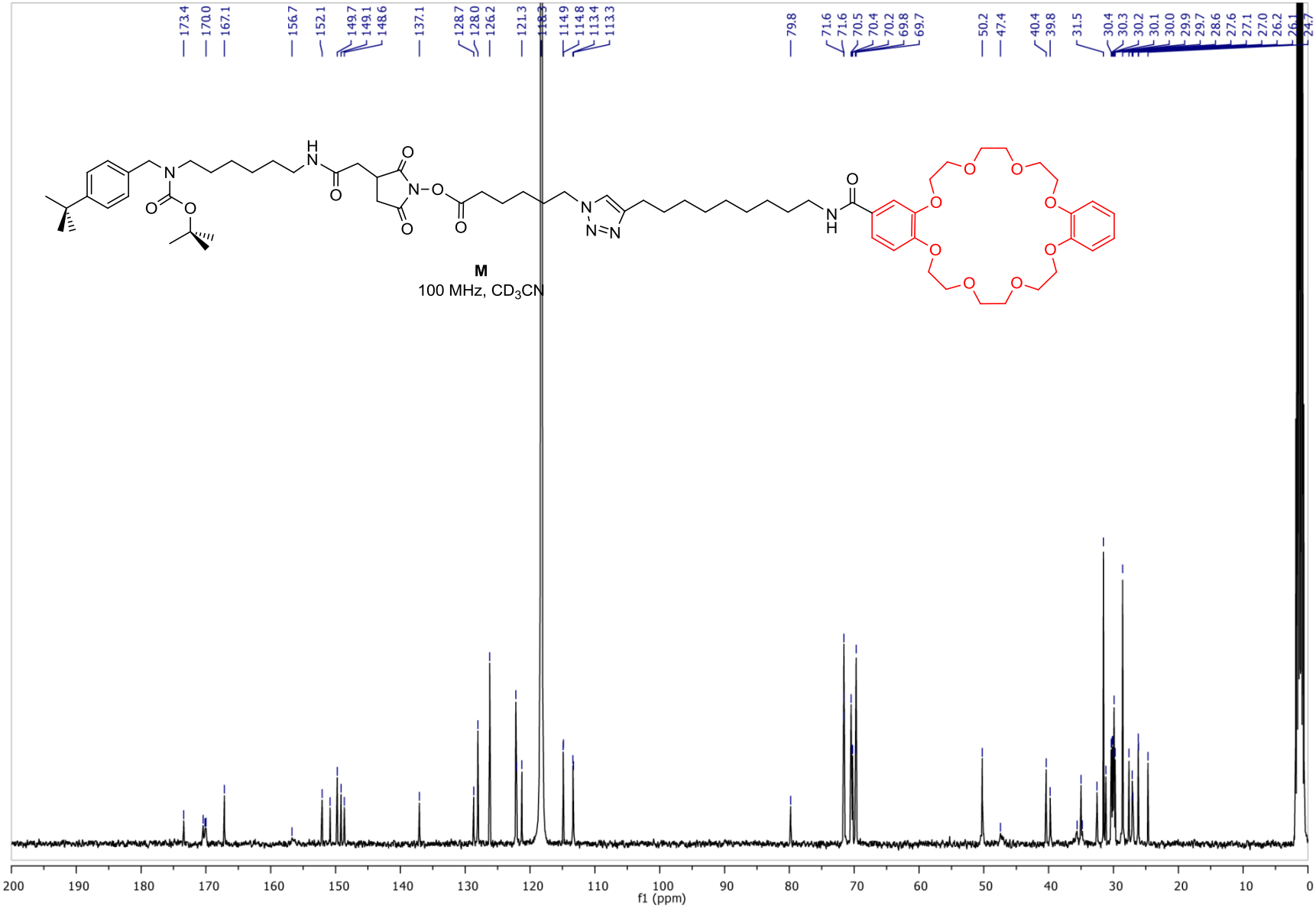
400 MHz, $CD_3CN$

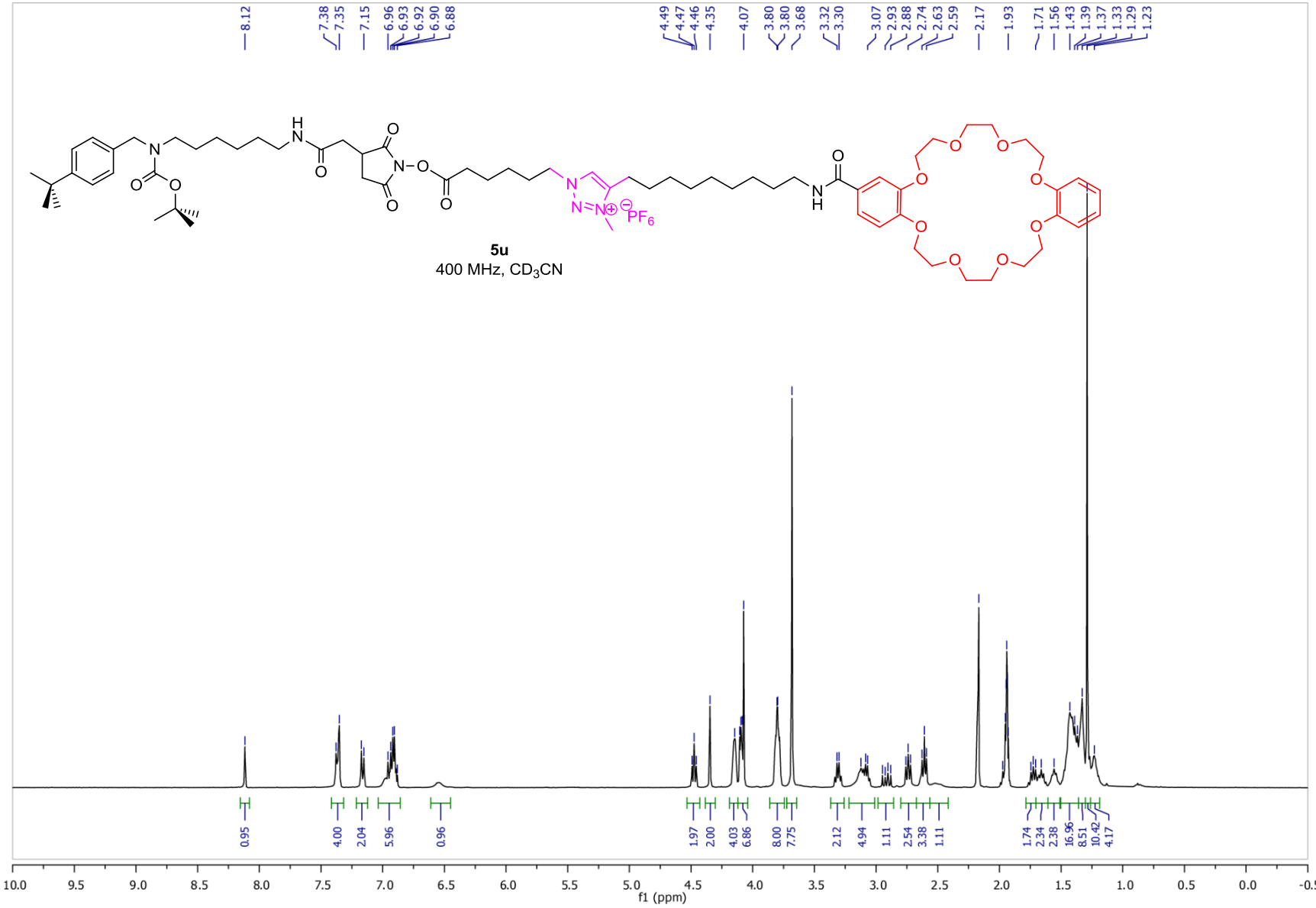


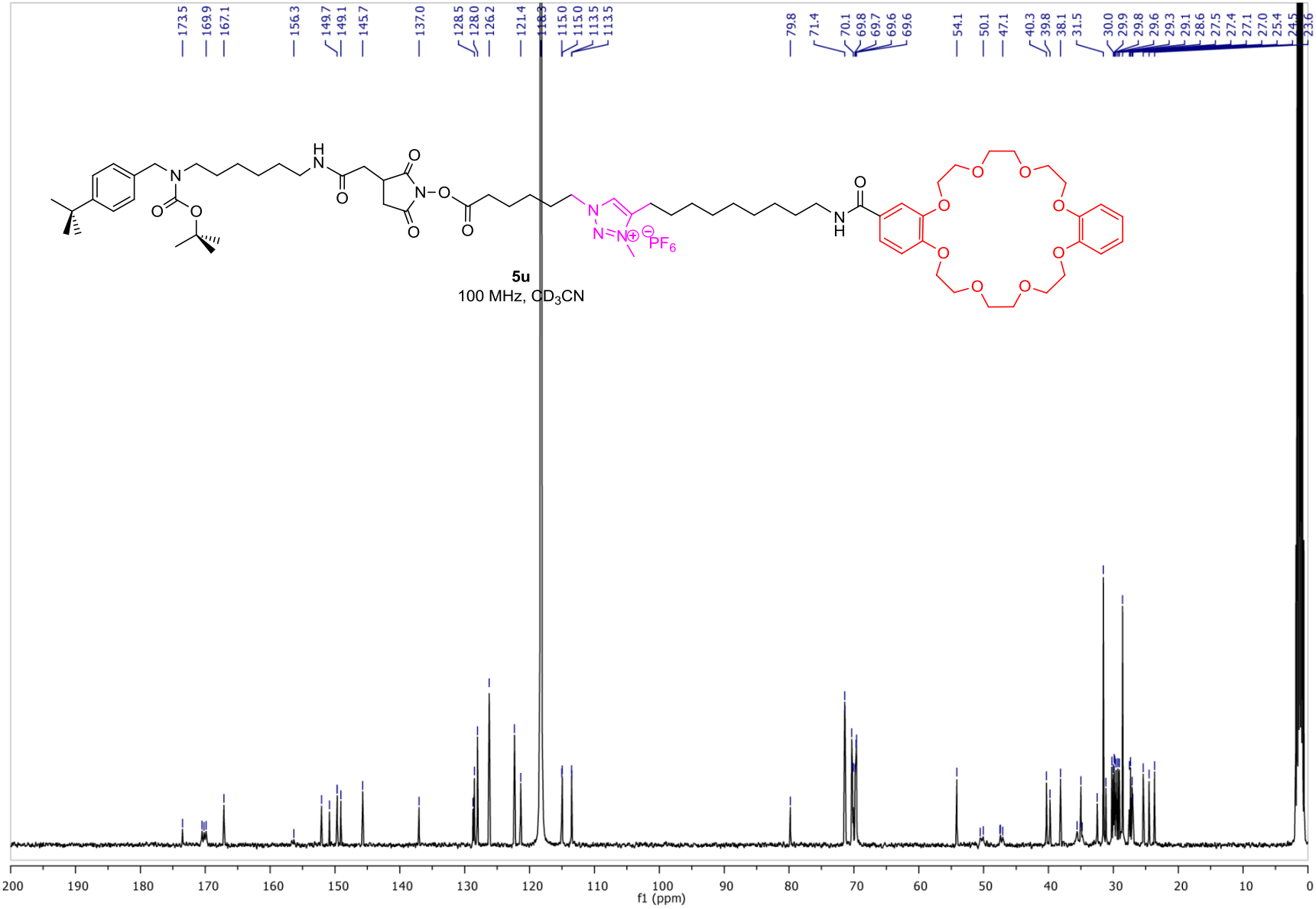

**L**

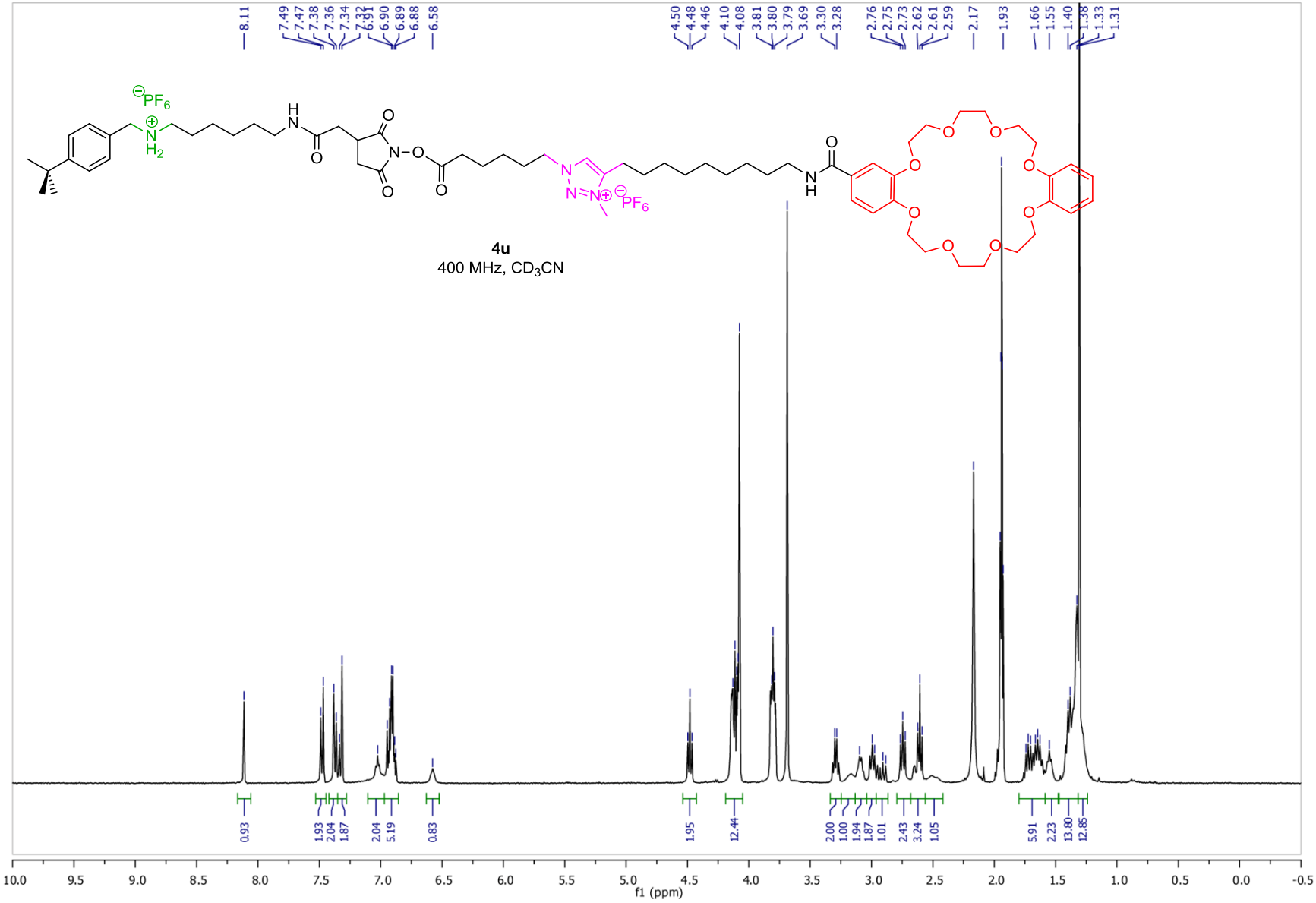
100 MHz, $CD_3CN$

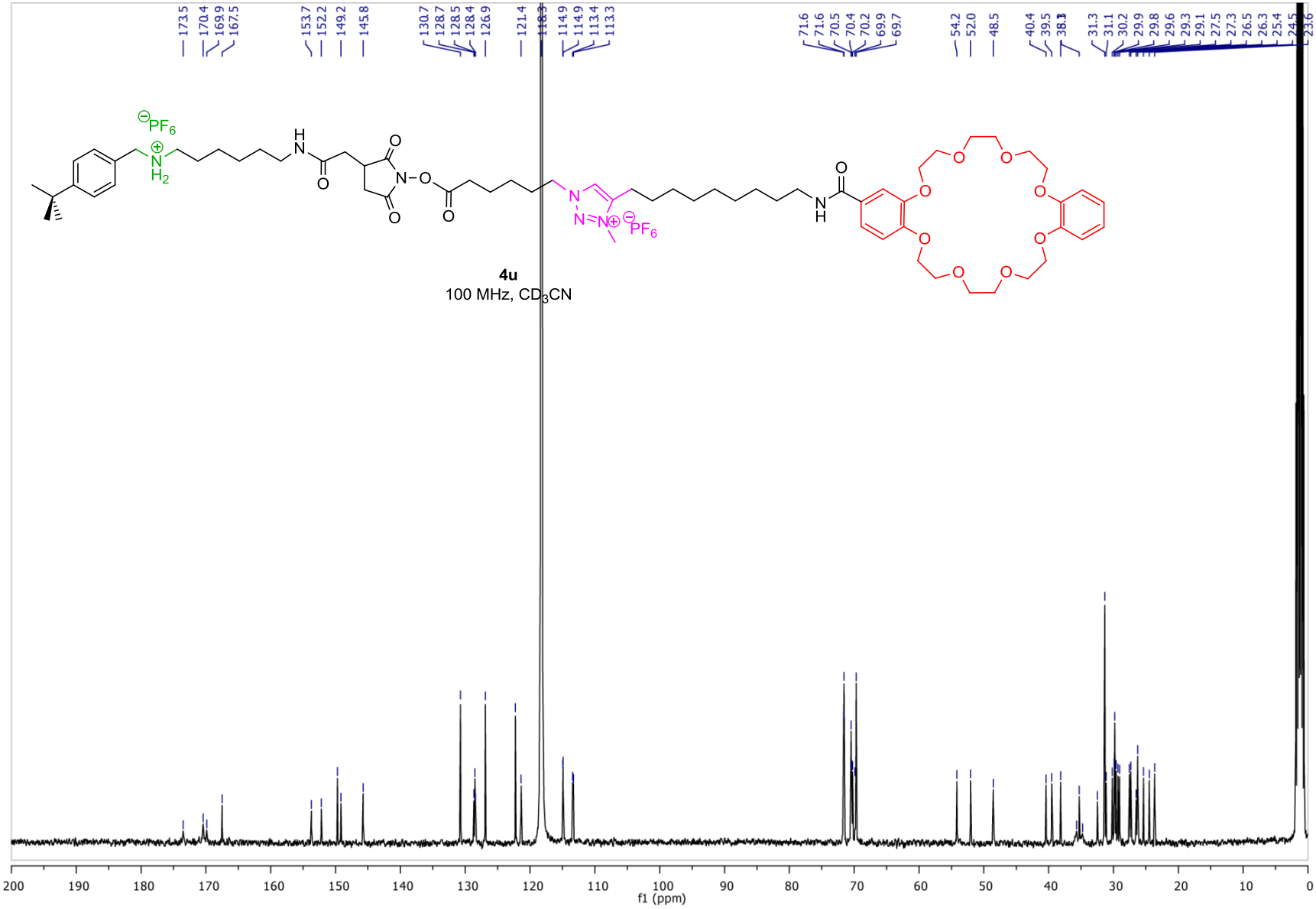

7.47
7.38
7.35
7.15
6.95
6.93
6.91
6.90
4.35
4.29
4.28
4.26
4.14
4.10
4.09
4.08
3.80
3.68
3.30
3.29
3.09
2.88
2.60
2.57
2.18
2.17
1.83
1.68
1.54
1.43
1.35
1.30
1.29
1.23
M
400 MHz, CD3CN
1.01
4.10
2.06
1.03
5.19
0.97
2.00
2.05
4.13
4.13
8.10
8.04
2.13
5.18
1.09
5.60
1.16
2.12
2.06
2.04
2.22
14.21
10.84
11.35
4.79
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

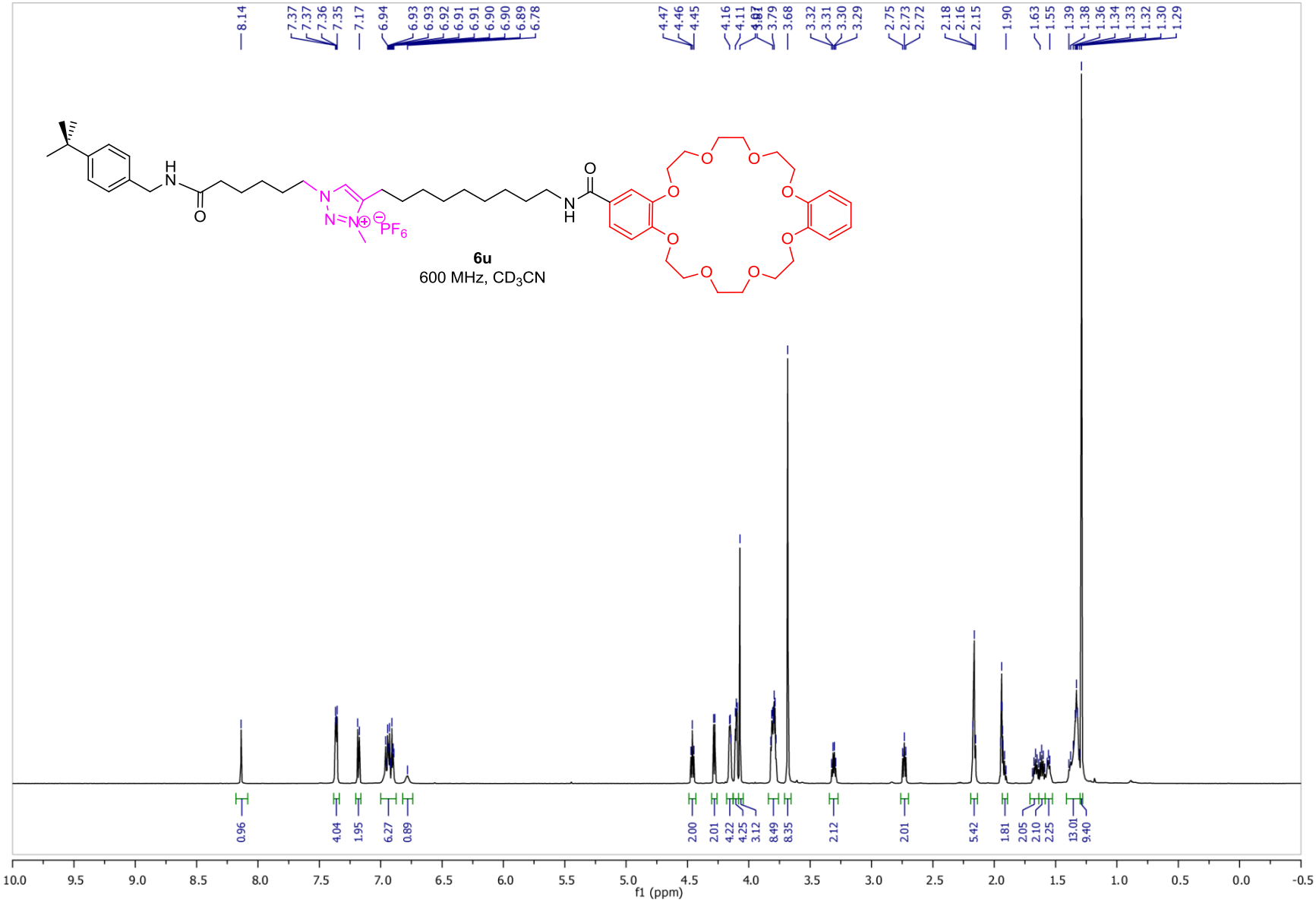

173.4
170.0
167.1
156.7
152.1
149.7
149.1
148.6
137.1
128.7
128.0
126.2
121.3
114.9
114.8
113.4
113.3
79.8
71.6
71.6
70.5
70.4
70.2
69.8
69.7
50.2
47.4
40.4
39.8
31.5
30.4
30.3
30.2
30.1
30.0
29.9
29.7
28.6
27.6
27.1
27.0
26.2
26.1
24.7
M
100 MHz, CD3CN
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

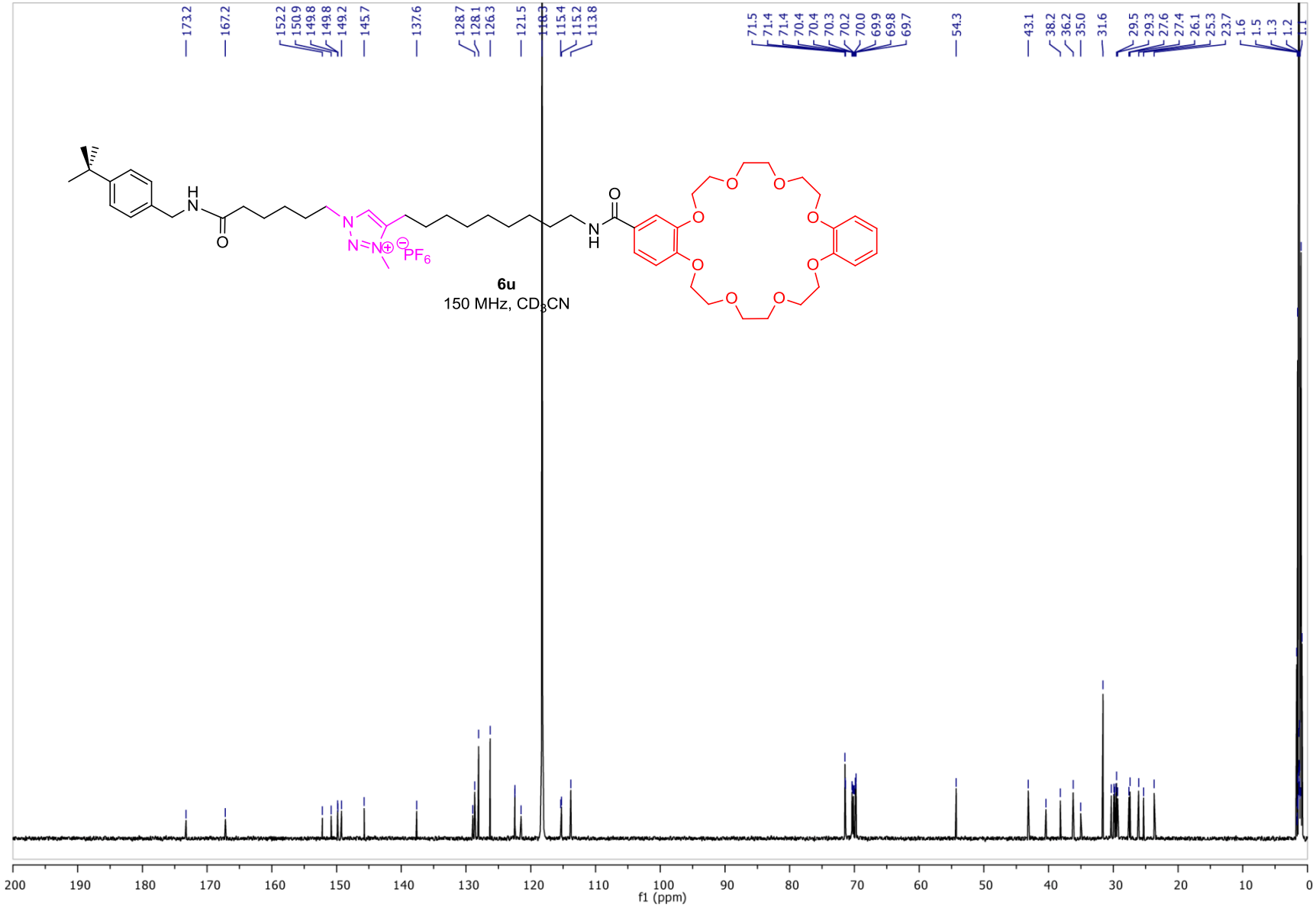

8.12
7.38
7.35
7.15
6.96
6.93
6.92
6.90
6.88
4.49
4.47
4.46
4.35
4.07
3.80
3.80
3.68
3.32
3.30
3.07
2.93
2.88
2.74
2.63
2.59
2.17
1.93
1.71
1.56
1.43
1.39
1.37
1.33
1.29
1.23
PF6
5u
400 MHz, CD3CN
0.95
4.00
2.04
5.96
0.96
1.97
2.00
4.03
6.86
8.00
7.75
2.12
4.94
1.11
2.54
3.38
1.11
1.74
2.34
2.38
16.96
8.51
10.42
4.17
f1 (ppm)

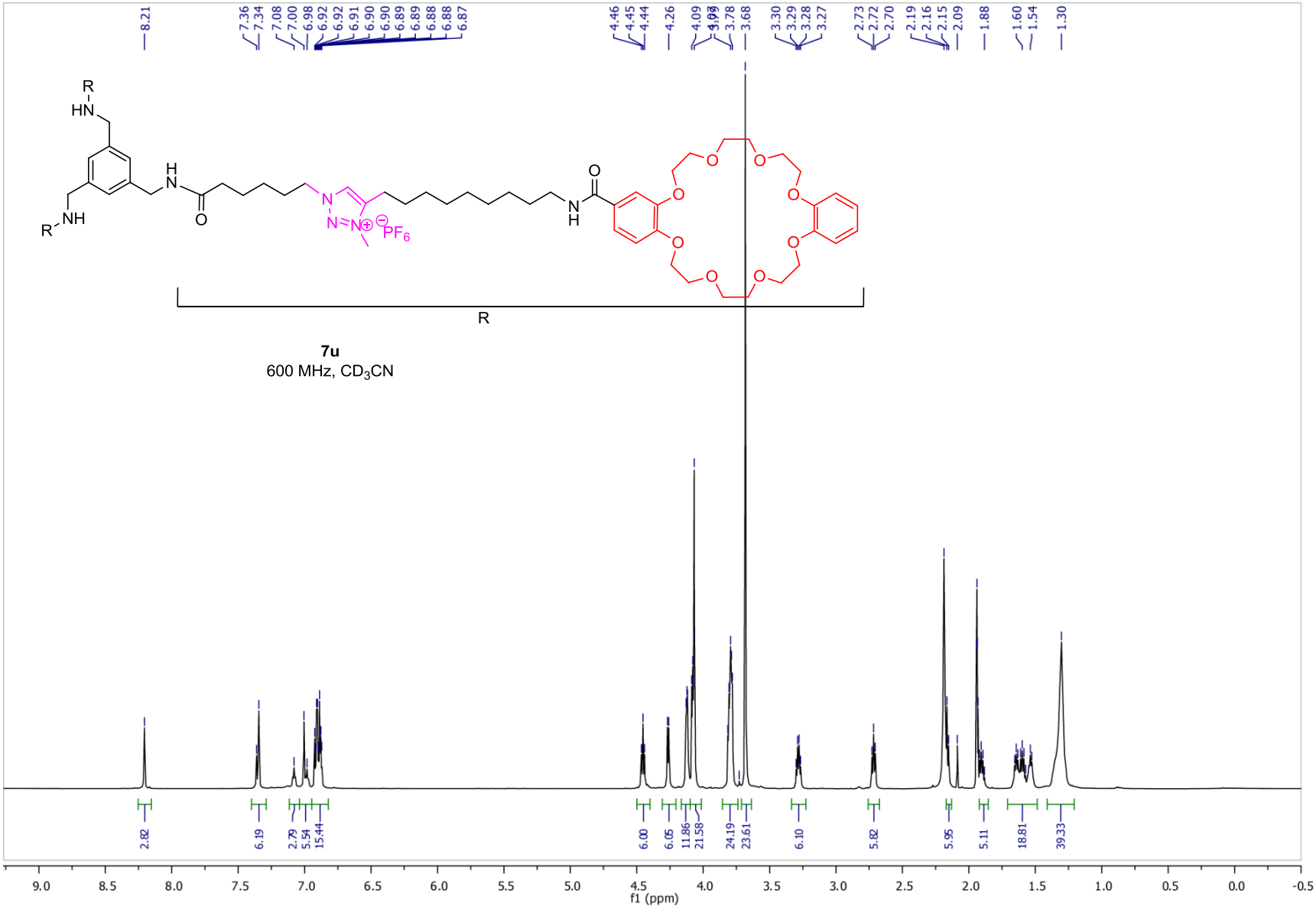

173.5
169.9
167.1
156.3
149.7
149.1
145.7
137.0
128.5
128.0
126.2
121.4
118.3
115.0
115.0
113.5
113.5
79.8
71.4
70.1
69.8
69.7
69.6
69.6
54.1
50.1
47.1
40.3
39.8
38.1
31.5
30.0
29.9
29.8
29.6
29.3
29.1
28.6
27.5
27.4
27.1
27.0
25.4
24.5
23.6
5u
100 MHz, CD3CN
PF6
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

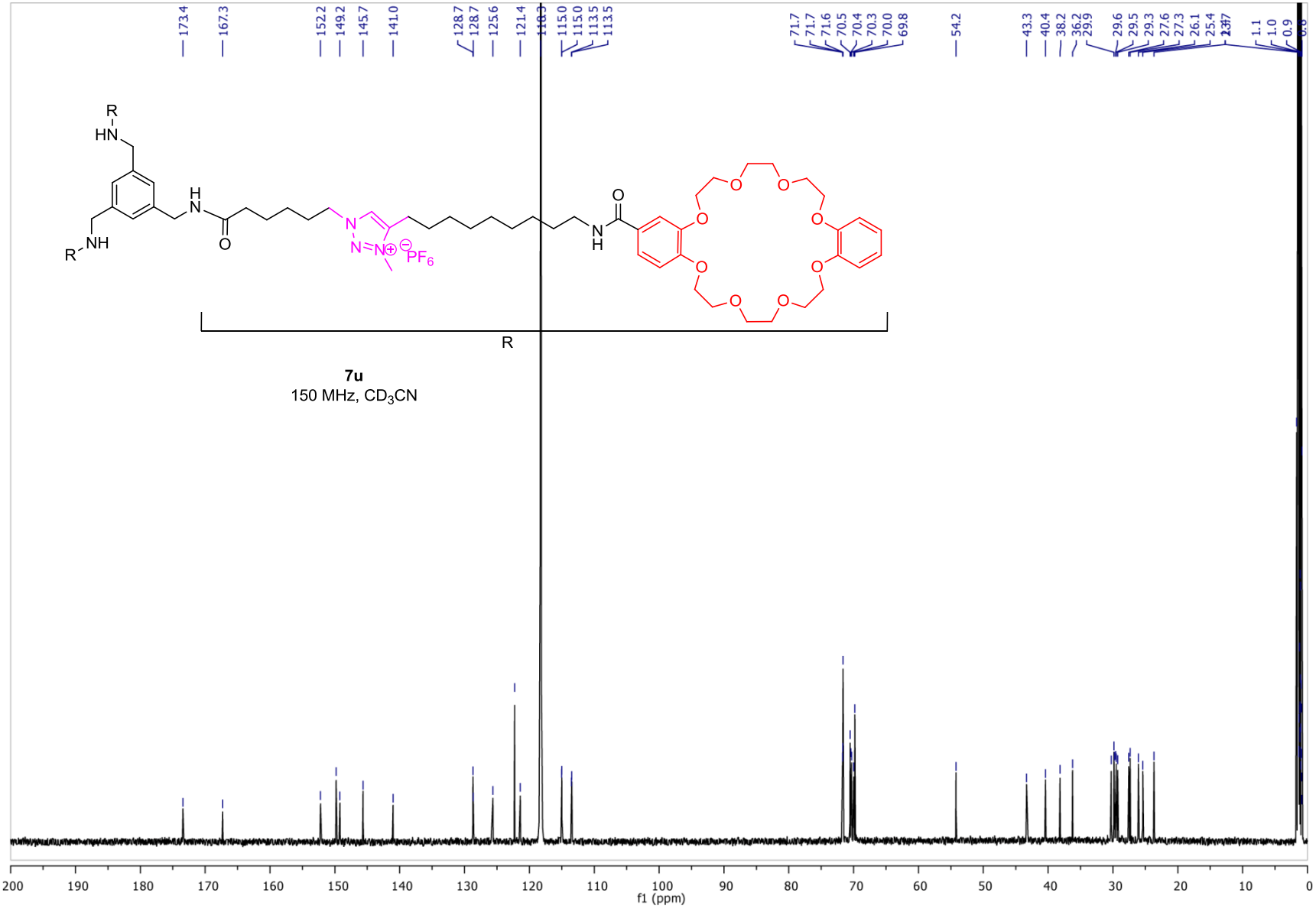

8.11
7.49
7.47
7.38
7.36
7.34
7.32
6.91
6.90
6.89
6.88
6.58
4.50
4.48
4.46
4.10
4.08
3.81
3.80
3.79
3.69
3.30
3.28
2.76
2.75
2.73
2.62
2.61
2.59
2.17
1.93
1.66
1.55
1.40
1.38
1.33
1.31
4u
400 MHz, CD3CN
0.93
1.93
2.04
1.87
2.04
5.19
0.83
1.95
12.44
2.00
1.00
1.94
1.87
1.01
2.43
3.24
1.05
5.91
2.23
13.80
12.85
f1 (ppm)


4u
100 MHz, CD3CN
f1 (ppm)


8.14
7.37
7.37
7.36
7.35
7.17
6.94
6.93
6.93
6.92
6.91
6.91
6.90
6.90
6.89
6.78
4.47
4.46
4.45
4.16
4.11
3.79
3.68
3.32
3.31
3.30
3.29
2.75
2.73
2.72
2.18
2.16
2.15
1.90
1.63
1.55
1.39
1.38
1.36
1.34
1.33
1.32
1.30
1.29
H
N
O
N
N=N⊕
⊖PF6
O
H
N
O
O
O
O
O
O
O
O
O
O
6u
600 MHz, CD3CN
0.96
4.04
1.95
6.27
0.89
2.00
2.01
4.22
4.25
3.12
8.49
8.35
2.12
2.01
5.42
1.81
2.05
2.10
2.25
13.01
9.40
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


173.2
167.2
152.2
150.9
149.8
149.8
149.2
145.7
137.6
128.7
128.1
126.3
121.5
118.3
115.4
115.2
113.8
71.5
71.4
71.4
70.4
70.4
70.3
70.2
70.0
69.9
69.8
69.7
54.3
43.1
38.2
36.2
35.0
31.6
29.5
29.3
27.6
27.4
26.1
25.3
23.7
1.6
1.5
1.3
1.2
1.1
6u
150 MHz, CD3CN
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.21
7.36
7.34
7.08
7.00
6.98
6.92
6.92
6.91
6.90
6.90
6.89
6.89
6.88
6.88
6.87
4.46
4.45
4.44
4.26
4.09
3.78
3.68
3.30
3.29
3.28
3.27
2.73
2.72
2.70
2.19
2.16
2.15
2.09
1.88
1.60
1.54
1.30
R
HN
NH
H
N
O
N
N
N
PF6
O
O
O
O
O
O
O
O
R
7u
600 MHz, CD3CN
2.82
6.19
2.79
5.54
15.44
6.00
6.05
11.86
21.58
24.19
23.61
6.10
5.82
5.95
5.11
18.81
39.33
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


173.4
167.3
152.2
149.2
145.7
141.0
128.7
128.7
125.6
121.4
115.0
115.0
113.5
113.5
71.7
71.7
71.6
70.5
70.4
70.3
70.0
69.8
54.2
43.3
40.4
38.2
36.2
29.9
29.6
29.5
29.3
27.6
27.3
26.1
25.4
1.1
1.0
0.9
R
HN
NH
H
N
O
N
N
N
PF6
O
O
O
O
O
O
O
O
O
O
R
7u
150 MHz, CD3CN
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)