Electronic Supplementary Material (ESI) for ChemComm.

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1. Materials and methods for NMR, mass spectrometry, X-ray crystallography and molecular modeling

1.1. Nuclear magnetic resonance spectroscopy and mass spectrometry

NMR spectra were recorded on 3 different NMR spectrometers: (1) an Avance II NMR spectrometer (Bruker Biospin) with a vertical 7.05 T narrow-bore / ultrashield magnet operating at 300 MHz for ^{1}H observation, 282 MHz for ^{19}F observation and 75 MHz for ^{13}C observation by means of a 5-mm direct BBO H / X probe with Z gradient capabilities; (2) an Avance 400 NMR spectrometer (Bruker Biospin) with a vertical 9.4 T narrow-bore / ultrashield magnet operating at 400 MHz for ^{1}H observation, 376 MHz for ^{19}F observation and 100 MHz for ^{13}C observation by means of a 5-mm direct QNP ^{1}H / ^{13}C / ^{31}P / ^{19}F probe with gradient capabilities; (3) an Avance III NMR spectrometer (Bruker Biospin) with a vertical 16.45 T narrow-bore / ultrashield magnet operating at 700 MHz for ^{1}H observation by means of a 5-mm TXI ^{1}H / ^{13}C / ^{15}N probe with Z gradient capabilities. Chemical shifts are reported in parts per million (δ, ppm) relative to the ^{1}H residual signal of the deuterated solvent used (respectively at 7.26 ppm, 1.94 ppm and 3.31 for $CHCl_3$, CH_3CN and CD_3OD for ^{1}H spectrum, and 77.16 ppm, 1.32 ppm and 49.00 for ^{13}C spectrum). ^{1}H NMR signal assignments were deduced from 2D ^{1}H-^{1}H NMR COSY while ^{13}C assignments were deduced from 2D ^{13}C-^{1}H NMR HSQC. ^{1}H NMR splitting patterns with observed first-order coupling are designated as singlet (s), doublet (d), triplet (t), quartet (q) or multiplet (m). Coupling constants (*J*) are reported in hertz (Hz). Data processing was performed with Topspin 4.0 and Mnova V.14 softwares. Samples were not degassed. $CDCl_3$ from Sigma-Aldrich was used after filtration through a basic alumina pad. High-resolution mass spectra (HRMS) were recorded respectively on a ZQ Micromass apparatus and a Q-TOF Micro apparatus (Physical Measurements Laboratory, Institute of Biomolecules Max Mousseron, UMR 5247, Montpellier, France) or on a Thermo Scientific Exactive Orbitrap spectrometer (Mass Spectrometry Laboratory, European Institute of Chemistry and Biology, UMS 3033, Pessac, France). The instrument is equipped with an ESI source and experiment were recorded in positive or negative mode. The spray voltage was maintained at 3 500 V and capillary temperature set at 220 °C. Sample were injected in the ESI source using a 250 µL hamilton syringe at 6 $\mu L.min^{-1}$.

1.2. X-ray crystallography

The diffraction data for compound **1⊃2** were collected at the IECB X-ray facility (CNRS UMS 3033 – INSERM US001, University of Bordeaux) with a Rigaku FRX rotating anode (2.9 kW) diffractometer using CuKα wavelength with a partial chi goniometer (AFC11). The X-ray source is equipped with high flux Osmic Varimax mirrors and a Pixel Hybrid Dectris Eiger1M detector. Data were processed with the Rigaku Oxford Diffraction CrysalisPro software (version1.171.41.118a).[1] The crystal structure was solved with the dual-space algorithm implemented into Shelxt[2] and refined by full-matrix least-squares method on F2 with Shelxl-2014[2] within Olex2.[3] Only non-H atoms of the backbones and side chains observable in the electron density maps were refined with anisotropic displacement parameters. H-atoms were refined in the riding-model approximation, with Uiso(H)=1.2Ueq (CH, CH2, NH). DFIX, AFIX, and RIGU restraints were apply to model geometry of the molecules and thermal motion parameters. Some residual electron density peaks observed in the difference Fourier maps could not be modelled. The PLATON/SQUEEZE[4] procedure was applied. A solvent mask was calculated and 6280 electrons were found in a volume of 26832 A3 in one void per unit cell. The solvent content was water, Chloroform and *n*-Hexane.

[1] CrysAlisPRO: CrysAlisPRO, Oxford Diffraction /Agilent Technologies UK Ltd, Yarnton, England.
[2] G. M. Sheldrick, *Acta Cryst*. **2015**, A71, 3–8.
[3] OLEX2: O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann. *J. Appl. Cryst.* **2009**, 42, 339–341.
[4] A. Spek, *Acta Cryst*. **2015**, C71, 9–18.

1.3. Molecular modelling

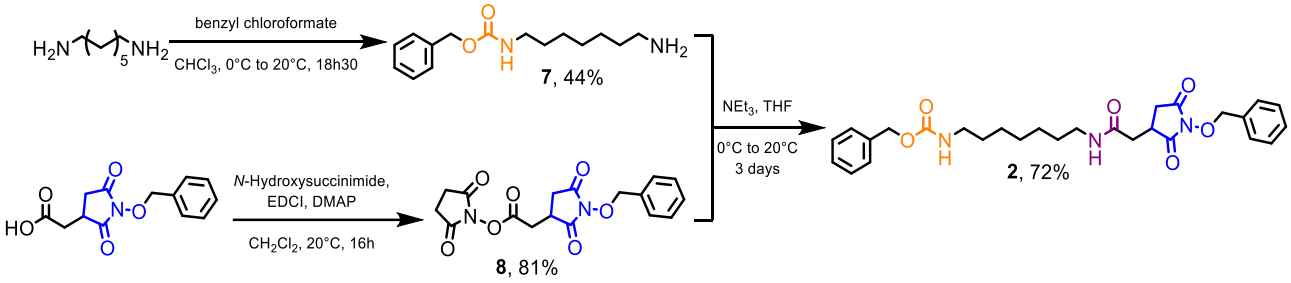
The X-ray crystal structure of the foldaxane **1⊃2** was used to build its energy minimized molecular model. After the appropriate modifications of this model **1⊃2**, the model of the foldarotaxane **1⊃3-Boc** was obtained by minimization using the Merck Molecular Force Field static (MMFFs) implemented in MacroModel version 8.6 *via* Maestro version 6.5 (Schrödinger). Molecular model of the contracted rotaxane **6** was built using the same method.

1.4. Methods for chemical synthesis

Reactions were carried out under a dry inert atmosphere unless otherwise specified. Commercial reagents were purchased from Sigma-Aldrich, Fisher Scientific or TCI Chemicals and were used without further purification. Chloroform ($CHCl_3$) and Dichloromethane (CH_2Cl_2) were distilled over P_2O_5 and was degassed by bubbling Ar for 20 min; Triethylamine (NEt_3) was distilled over calcium hydride (CaH_2). Tetrahydrofuran (THF) was refluxed with sodium alloy and benzophenone until the deep blue colour of the radical-anion was observed and collected in the distillate trap. Reactions were monitored by thin layer chromatography (TLC) on Merck silica gel 60-F254 plates and observed under UV light and by dipping the plates in ninhydrin, bromocresol or an aqueous solution of $KMnO_4$, followed by heating. Column chromatography purifications were carried out on Merck GEDURAN Si60 (40 - 63 µm). Preparative recycling Gel Permeation Chromatography (GPC) was performed on JAIGEL 20*600 mm columns (Japan Analytical Industry) at a flow rate of 7 mL.min^{-1} or 10 mL.min^{-1} with a mobile phase composed of 1 % (vol / vol) EtOH and 0.5 % (vol / vol) NEt_3 in $CHCl_3$, monitored by UV detector at 254 nm, 280 nm, 300 nm and 360 nm. RP-HPLC analyses were performed on an analytical system using a RP-18 column (4.6*100 mm, 5 µm). The mobile phase was composed of 0.1 % (vol/vol) TFA in H_2O (solvent A) and 0.1 % (vol/vol) TFA in CH_3CN (solvent B), monitored by UV detector (diode-array) at 214 nm, 254 nm and 300 nm The aromatic oligoamide foldamer **1** was prepared by following the reported synthetic protocols.[5]

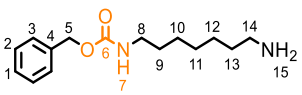
2. Synthesis of rod 2

2.1. General synthetic pathway



Scheme S1. Synthesis of rod **2**.

2.2. Synthesis of compound 7



To a solution of 1,7-diaminoheptane (3.0 g, 23.05 mmol, 3 equiv.) in $CHCl_3$ (150 mL) at 0°C, was added dropwise a solution of benzyl chloroformate (1.10 mL, 7.68 mmol, 1 equiv.) in $CHCl_3$ (30 mL). The reaction mixture was allowed to warm up to room temperature for 18h30, under argon atmosphere. The solvent was removed under

[5] Wang X., Gan Q., Wicher B., Ferrand Y. & Huc I., Directional Threading and Sliding of a Dissymmetrical Foldamer Helix on Dissymmetrical Axles, *Angew. Chem. Int. Ed.*, **2019**, *58*, 4205-4209.

vacuum and the obtained crude was purified by chromatography on silica gel (CH_2Cl_2/MeOH/NH_3 90:10:0 to 90:10:7) to give pure **7** (895 mg, 44%) as a colorless paste.

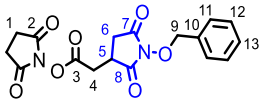
R_f: 0.47 (CH_2Cl_2/MeOH/NH_3 90/10/5)

^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ ppm = 7.38-7.28 (m, 5H, H_1, H_2, H_3), 5.09 (br s, 2H, H_5), 4.87 (br s, 1H, H_7), 3.17 (q, 2H, $^3J_{7\text{-}8}$ = 8 Hz, $^3J_{8\text{-}9}$ = 8 Hz, H_8), 2.67 (t, 2H, $^3J_{13\text{-}14}$ = 8 Hz, H_{14}), 1.57-1.46 (m, 2H, H_9), 1.45-1.38 (m, 2H, H_{13}), 1.36-1.25 (m, 6H, H_{10}, H_{11}, H_{12}).

^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ ppm = 156.5 (C_6), 136.8 (C_4), 128.6 & 128.2 (C_1, C_2 & C_3), 66.6 (C_5), 42.2 (C_{14}), 41.2 (C_8), 33.6 (C_{13}), 30.0 (C_9), 29.2 (C_{10}), 26.8 (C_{11} & C_{12}).

HRMS (ESI): $[M+H]^+$ calcd for $C_{15}H_{25}N_2O_2^+$: 265.1916, found: 265.1917.

2.3. Synthesis of compound 8



To a solution of *O*-benzyl-*N*-hydroxysuccinimide derivative (300 mg, 1.14 mmol, 1 equiv.), *N*-hydroxysuccinimide (131 mg, 1.14 mmol, 1 equiv.) and DMAP (279 mg, 2.28 mmol, 2 equiv.) in CH_2Cl_2 (10 mL) at 0°C, was added EDCI (328 mg, 1.71 mmol, 1.5 equiv.) and the reaction mixture was allowed to warm up to room temperature for 16h under argon atmosphere. The organic layer was washed successively with an aqueous solution of HCl 1M (3 x 5 mL) and a saturated aqueous solution of $NaHCO_3$ (2 x 5 mL). The organic layer was dried over $MgSO_4$ before being concentrated. The obtained crude was purified by flash chromatography (CH_2Cl_2/MeOH 100:0 to 90:10) to give pure **8** (331 mg, 81%) as a white powder.

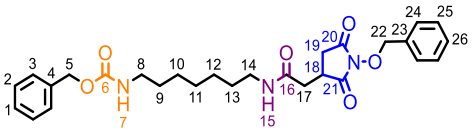
R_f: 0.74 (CH_2Cl_2/MeOH 90/10)

^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ ppm = 7.52-7.46 (m, 2H, H_{12}), 7.42-7.35 (m, 3H, H_{11}, H_{13}), 5.11 (s, 2H, H_9), 3.21-3.11 (m, 2H, H_4), 2.99-2.88 (m, 2H, H_5, H_6), 2.83 (br s, 4H, H_1), 2.51 (dd, 1H, $^2J_{6\text{-}6'}$ = 20 Hz, $^3J_{5\text{-}6'}$ = 4 Hz, $H_{6'}$).

^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ ppm = 171.6, 169.7, 168.7 & 166.4 (C_2, C_3, C_7 & C_8), 133.3 (C_{10}), 130.1 (C_{12}), 129.6 (C_{13}), 128.7 (C_{11}), 78.9 (C_9), 33.4 (C_4), 31.8 (C_5), 31.5 (C_6), 25.7 (C_1).

HRMS (ESI): $[M+H]^+$ calcd for $C_{17}H_{17}N_2O_7^+$: 361.1036, found: 361.1038.

2.4. Synthesis of rod 2



A solution of **7** (110 mg, 0.42 mmol, 1 equiv.), **8** (150 mg, 0.42 mmol, 1 equiv.) and few drops of dry NEt_3 in dry THF (5 mL) was stirred at 0°C, and the reaction mixture was allowed to warm up to room temperature for 3 days, under argon atmosphere. The solvent was removed under *vacuum* and the obtained crude was purified by flash chromatography (CH_2Cl_2/MeOH 100:0 to 90:10) to give pure the rod **2** (154 mg, 72%) as a white powder.

R_f: 0.50 (CH_2Cl_2/MeOH 90/10)

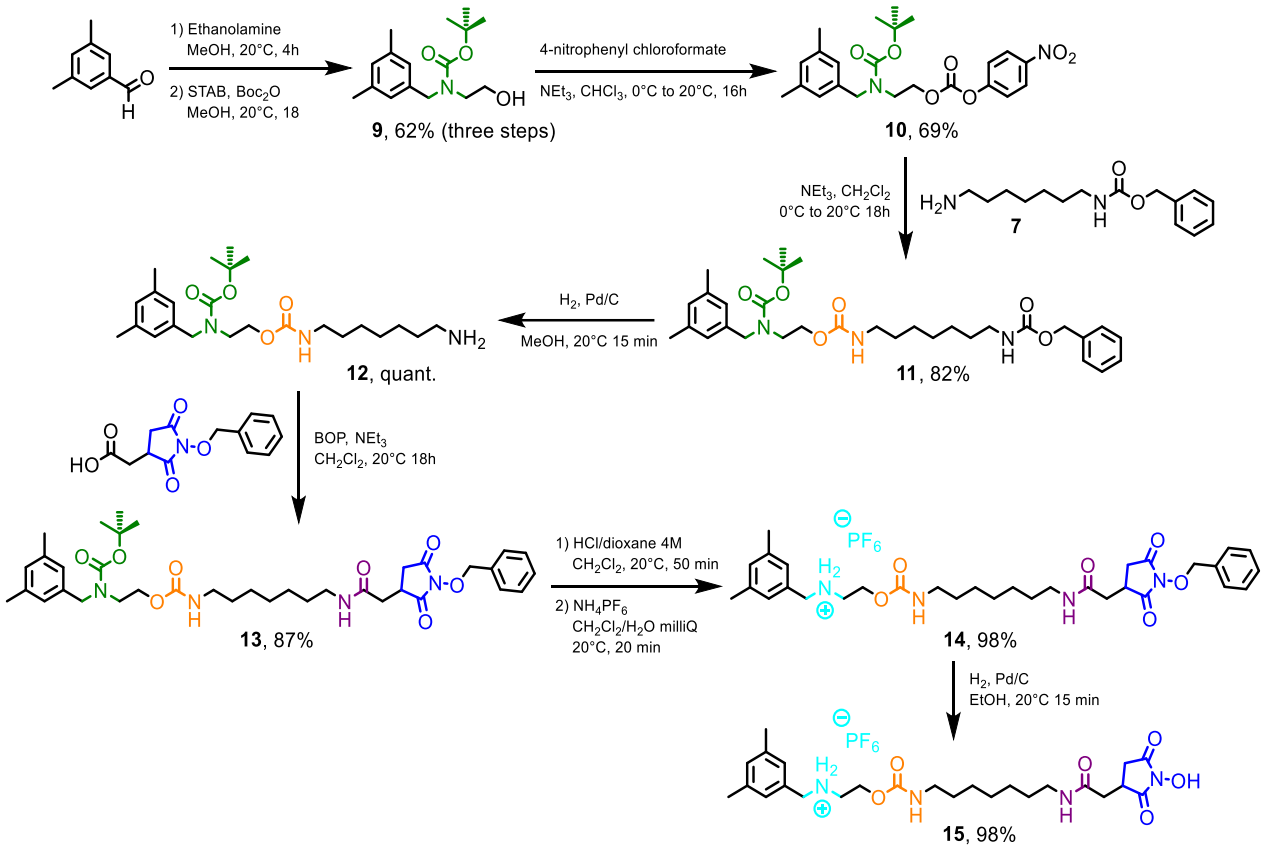
^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ ppm = 7.53-7.46 (m, 2H, H_1, H_{26}), 7.40-7.28 (m, 8H, H_2, H_3, H_{24}, H_{25}), 5.94 (br s, 1H, H_{15}), 5.11 & 5.07 (2br s, 4H, H_5, H_{22}), 4.96 (br s, 1H, H_7), 3.21-3.09 (m, 4H, H_8, H_{14}), 3.01-2.91 (m, 1H, H_{18}), 2.80 (dd, 1H, $^2J_{19\text{-}19'}$ = 20 Hz, $^3J_{18\text{-}19}$ = 8 Hz, H_{19}), 2.59 (d, 2H, $^3J_{17\text{-}18}$ = 8 Hz, H_{17}), 2.47 (dd, 1H, $^2J_{19\text{-}19'}$ = 20 Hz, $^3J_{18\text{-}19'}$ = 4 Hz, $H_{19'}$), 1.52-1.37 (m, 4H, H_9, H_{13}), 1.33-1.23 (m, 6H, H_{10}, H_{11}, H_{12}).

^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ ppm = 173.9, 170.9 & 169.2 (C_{16}, C_{20} & C_{21}), 156.6 (C_6), 136.7 (C_4), 133.6 (C_{23}), 129.9 & 129.4 (C_1 & C_{26}), 128.6, 128.2 & 128.1 (C_2, C_3, C_{24} & C_{25}), 78.6 (C_{22}), 66.6 (C_5), 41.0 & 39.6 (C_8 & C_{14}), 35.6 (C_{17}), 33.9 (C_{18}), 31.9 (C_{19}), 29.8 & 29.4 (C_9 & C_{13}), 28.7, 26.6 & 26.5 (C_{10}, C_{11} & C_{12}).

HRMS (ESI): $[M+H]^+$ calcd for $C_{28}H_{36}N_3O_6^+$: 510.2604, found: 510.2607.

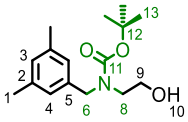
3. Synthesis of the molecular translocator 15

3.1. General synthetic pathway



Scheme S2. Synthesis of the molecular translocator **15**.

3.2. Synthesis of compound 9



Under argon atmosphere, a solution of 3,5-dimethylbenzaldehyde (2.40 mL, 17.9 mmol, 1 equiv.) and ethanolamine (1.29 mL, 21.48 mmol, 1.2 equiv.) in MeOH (30 mL), was stirred for 4h at room temperature. Sodium triacetoxyborohydride "STAB" (3.79 g, 17.9 mmol, 1 equiv.) and Boc_2O (3.91 g, 17.9 mmol, 1 equiv.) were then added and stirred for 18h at room temperature. The solvent was removed under *vacuum* and the obtained crude was dissolved in CH_2Cl_2 (30 mL). The organic layer was washed with an aqueous solution of HCl 1M (2 x 20 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were washed with brine (1 x 20 mL). The organic layer was dried over $MgSO_4$ before being concentrated. The obtained crude was purified by flash chromatography (PE/EtOAc 100/0 to 60/40) to give pure **9** (3.08 g, 62%) as a colorless oil.

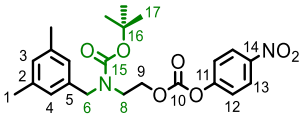
R_f: 0.43 (PE/EtOAc 60/40)

^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ ppm = 6.91 (s, 1H, H_3), 6.84 (s, 2H, H_4), 4.41 (br s, 2H, H_6), 3.76-3.63 (m, 2H, H_9), 3.44-3.26 (m, 2H, H_8), 2.31 (s, 6H, H_1), 1.49 (s, 9H, H_{13}).

^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ ppm = 157.6 (C_{11}), 138.3 (C_2 & C_5), 129.1 (C_3), 125.2 (C_4), 80.6 (C_{12}), 62.3 (C_9), 51.9 (C_6), 49.8 (C_8), 28.5 (C_{13}), 21.4 (C_1).

HRMS (ESI): $[M+H]^+$ calcd for $C_{16}H_{26}NO_3^+$: 280.1907, found: 280.1908.

3.3. Synthesis of compound 10



To a solution of 4-nitrophenyl chloroformate (1.83 g, 9.09 mmol, 1 equiv.) in dry $CHCl_3$ (20 mL) at 0°C, was added dropwise a solution of **9** (2.54 g, 9.09 mmol, 1 equiv.) and dry NEt_3 (3.78 mL, 27.27 mmol, 3 equiv.) in dry $CHCl_3$ (15 mL). The reaction mixture was allowed to warm-up to room temperature and stirred for 16h, under argon atmosphere. The organic layer was washed with an aqueous solution of HCl 1M (1 x 20 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ (3 x 20 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$ before being concentrated. The obtained crude was purified by flash chromatography (PE/EtOAc 100:0 to 92:8) to give pure **10** (2.80 g, 69%) as a yellow oil.

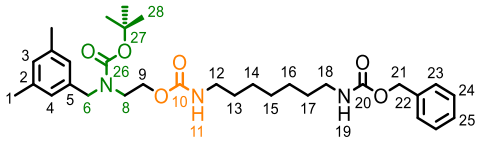
R_f: 0.66 (PE/EtOAc 80/20)

^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ ppm = 8.29 (d, 2H, $^3J_{12\text{-}13}$ = 8 Hz, H_{13}), 7.39 (d, 2H, $^3J_{12\text{-}13}$ = 8 Hz, H_{12}), 6.91 (s, 1H, H_3), 6.85 (br s, 2H, H_4), 4.52-4.43 (m, 2H, H_6), 4.40-4.31 (m, 2H, H_9), 3.64-3.45 (m, 2H, H_8), 2.30 (s, 6H, H_1), 1.56-1.45 (m, 9H, H_{17}).

^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ ppm = 158.0 (C_{15}), 155.8 (C_{10}), 152.5 (C_{11}), 145.5 (C_{14}), 138.3 (C_2 & C_5), 129.1 (C_3), 125.5 (C_4), 125.1 (C_{13}), 122.0 (C_{12}), 80.6 (C_{16}), 67.2 (C_9), 51.5 & 50.7 (C_6), 45.1 (C_8), 28.5 (C_{17}), 21.4 (C_1).

HRMS (ESI): $[M+H]^+$ calcd for $C_{23}H_{29}N_2O_7^+$: 445.1969, found: 445.1960.

3.4. Synthesis of compound 11



To a solution of **7** (1.17 g, 4.43 mmol, 1 equiv.) and NEt_3 (1.23 mL, 8.86 mmol, 2 equiv.) in CH_2Cl_2 (15 mL) at 0°C, was added dropwise a solution of **10** (1.97 g, 4.43 mmol, 1 equiv.) in CH_2Cl_2 (15 mL). The reaction mixture was allowed to warm up to room temperature for 18h, under argon atmosphere. The organic layer was washed successively with: an aqueous solution of NaOH 1M (3 x 20 mL), an aqueous solution of HCl 1M (2 x 20 mL) and brine (1 x 20 mL). The combined organic layers were dried over $MgSO_4$ before being concentrated. The obtained crude was purified by flash chromatography (PE/EtOAc 100:0 to 50:50) to give pure **11** (2.06 g, 82%) as a pale-yellow oil.

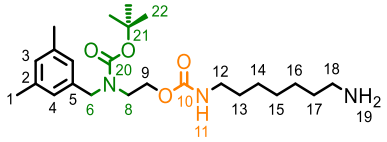
R_f: 0.64 (PE/EtOAc 50/50)

^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ ppm = 7.39-7.28 (m, 5H, H_{23}, H_{24}, H_{25}), 6.89 (s, 1H, H_3), 6.87-6.79 (m, 2H, H_4), 5.10 (br s, 2H, H_{21}), 4.83-4.70 (m, 1H, H_{19}), 4.64-4.49 (m, 1H, H_{11}), 4.48-4.36 (m, 2H, H_6), 4.23-4.07 (m, 2H, H_9), 3.52-3.30 (m, 2H, H_8), 3.23-3.08 (m, 4H, H_{12}, H_{18}), 2.30 (s, 6H, H_1), 1.54-1.43 (m, 13H, H_{13}, H_{17}, H_{28}), 1.35-1.27 (m, 6H, H_{14}, H_{15}, H_{16}).

^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ ppm = 156.5 (C_{10}, C_{20} & C_{26}), 138.1 & 136.8 (C_2, C_5 & C_{22}), 128.9 (C_3), 128.7 & 128.2 (C_{23}, C_{24} & C_{25}), 125.8 & 125.1 (C_4), 80.1 (C_{27}), 66.7 (C_{21}), 62.8 (C_9), 51.3 & 50.9 (C_6), 45.8 (C_8), 41.1 (C_{12} & C_{18}), 30.0 (C_{13} & C_{17}), 29.0 (C_{15}), 28.6 (C_{28}), 26.7 (C_{14} & C_{16}), 21.4 (C_1).

HRMS (ESI): $[M+H]^+$ calcd for $C_{32}H_{48}N_3O_6^+$: 570.3538, found: 570.3537.

3.5. Synthesis of compound 12



To a solution of **11** (860 mg, 1.51 mmol, 1 equiv.) in MeOH (40 mL) was added 40%-Pd/C (345 mg). The solution was stirred 15 min under a hydrogen atmosphere before filtration through a celite pad. After abundant washing of the celite pad with a solution of MeOH/NH_3 (90/10), the filtrate was concentrated to give pure **12** (662 mg, quant.) as a pale-yellow oil without any further purification.

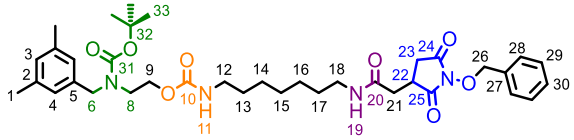
R_f: 0.68 (CH_2Cl_2/MeOH/NH_3 90/10/5)

^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ ppm = 6.89 (s, 1H, H_3), 6.87-6.80 (m, 2H, H_4), 4.67-4.50 (m, 1H, H_{11}), 4.48-4.37 (m, 2H, H_6), 4.20-4.07 (m, 2H, H_9), 3.48-3.32 (m, 2H, H_8), 3.18-3.08 (m, 2H, H_{12}), 2.68 (t, 2H, $^3J_{17\text{-}18}$ = 8 Hz, H_{18}), 2.29 (s, 6H, H_1), 1.54-1.38 (m, 15H, H_{13}, H_{17}, H_{19}, H_{22}), 1.35-1.28 (m, 6H, H_{14}, H_{15}, H_{16}).

^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ ppm = 156.4 & 155.9 (C_{10} & C_{20}), 138.1 (C_2 & C_5), 128.9 (C_3), 125.8 & 125.1 (C_4), 80.1 (C_{21}), 62.7 (C_9), 51.3 & 50.8 (C_6), 45.8 (C_8), 42.3 (C_{18}), 41.1 (C_{12}), 30.1, 29.3 & 29.2 (C_{13}, C_{15} & C_{17}), 28.5 (C_{22}), 26.9 (C_{14} & C_{16}), 21.4 (C_1).

HRMS (ESI): $[M+H]^+$ calcd for $C_{24}H_{42}N_3O_4^+$: 436.3170, found: 436.3188.

3.6. Synthesis of compound 13



To a solution of the amine **12** (1.46 g, 3.35 mmol, 1 equiv.) and the *O*-benzyl-NHS acid derivative (882 mg, 3.35 mmol, 1 equiv.) in CH_2Cl_2 (50 mL), was added BOP (1.93 g, 4.36 mmol, 1.3 equiv.) and NEt_3 (1.02 mL, 7.37 mmol, 2.2 equiv.). After checking the basicity of the solution, the mixture was stirred for 18h at room temperature, under argon atmosphere. The organic layer was washed with an aqueous solution of HCl 1M (2 x 20 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The organic layer was washed with a saturated aqueous solution of $NaHCO_3$ (3 x 20 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were dried over $MgSO_4$ before being concentrated. The obtained crude was purified by flash chromatography (PE/EtOAc 100:0 to 0:100) to give pure **13** (1.99 g, 87%) as a white solid.

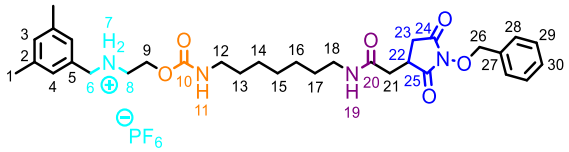
R_f: 0.49 (PE/EtOAc 15/85)

^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ ppm = 7.54-7.48 (m, 2H, H_{28}), 7.41-7.34 (m, 3H, H_{29}, H_{30}), 6.89 (s, 1H, H_3), 6.86-6.78 (m, 2H, H_4), 5.88-5.74 (m, 1H, H_{19}), 5.13 (s, 2H, H_{26}), 4.75-4.55 (m, 1H, H_{11}), 4.47-4.35 (m, 2H, H_6), 4.21-4.07 (m, 2H, H_9), 3.49-3.31 (m, 2H, H_8), 3.20 (q, 2H, $^3J_{17\text{-}18}$ = 8 Hz, $^3J_{18\text{-}19}$ = 8 Hz, H_{18}), 3.16-3.07 (m, 2H, H_{12}), 3.04-2.95 (m, 1H, H_{22}), 2.87-2.76 (m, 1H, H_{23}), 2.68-2.56 (m, 2H, H_{21}), 2.56-2.43 (m, 1H, $H_{23'}$), 2.29 (s, 6H, H_1), 1.54-1.40 (m, 13H, H_{13}, H_{17}, H_{33}), 1.34-1.25 (m, 6H, H_{14}, H_{15}, H_{16}).

^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ ppm = 173.9, 170.8 & 169.1 (C_{20}, C_{24} & C_{25}), 156.5 (C_{10} & C_{31}), 138.2 & 133.7 (C_2, C_5 & C_{27}), 130.0 (C_{28}), 129.4 (C_{30}), 128.9 (C_3), 128.6 (C_{29}), 125.7 & 125.1 (C_4), 80.2 (C_{32}), 78.7 (C_{26}), 62.5 (C_9), 51.2 & 50.8 (C_6), 45.8 (C_8), 41.0 (C_{12}), 39.7 (C_{18}), 35.8 (C_{21}), 34.0 (C_{22}), 32.1 (C_{23}), 29.9 & 29.5 (C_{13} & C_{17}), 28.8 (C_{15}), 28.5 (C_{33}), 26.7 & 26.5 (C_{14} & C_{16}), 21.4 (C_1).

HRMS (ESI): $[M+H]^+$ calcd for $C_{37}H_{53}N_4O_8^+$: 681.3858, found: 681.3870.

3.7. Synthesis of compound 14



To a solution of the carbamoylated thread **13** (513 mg, 0.75 mmol, 1 equiv.) in CH_2Cl_2 (2 mL) was added a 4M solution of chlorhydric acid in dioxane (6 mL, excess). The mixture was stirred at room temperature for 50 min. The mixture was evaporated to dryness and the residue was partitioned between CH_2Cl_2 (5 mL) and milliQ H_2O (2 mL). NH_4PF_6 (368 mg, 2.26 mmol, 3 equiv.) was added and the biphasic mixture was vigorously stirred for 20 min. The aqueous layer was extracted with CH_2Cl_2 (5 x 5 mL) and the combined organic layers were dried over $MgSO_4$ before being concentrated to afford the ammonium thread **14** (532 mg, 98%) as a white solid without any further purification.

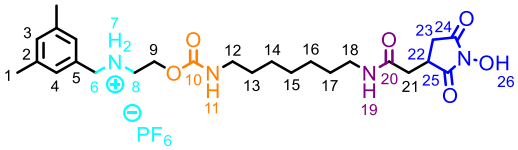
R_f: 0.49 (CH_2Cl_2/MeOH 90/10)

^{1}H NMR (400 MHz, CD_3CN, 298K): δ ppm = 7.52-7.47 (m, 2H, H_{28}), 7.44-7.38 (m, 3H, H_{29}, H_{30}), 7.11 (s, 1H, H_3), 7.05 (s, 2H, H_4), 6.52 (br t, 1H, H_{19}), 5.78 (br t, 1H, H_{11}), 5.02 (s, 2H, H_{26}), 4.28-4.19 (m, 2H, H_9), 4.11 (s, 2H, H_6), 3.28-3.22 (m, 2H, H_8), 3.13-3.02 (m, 4H, H_{12}, H_{18}), 3.01-2.94 (m, 1H, H_{22}), 2.76 (dd, 1H, $^2J_{23\text{-}23'}$ = 16 Hz, $^3J_{22\text{-}23}$ = 8 Hz, H_{23}), 2.69-2.51 (m, 2H, H_{21}), 2.37-2.29 (m, 7H, H_1, $H_{23'}$), 1.59-1.36 (m, 4H, H_{13}, H_{17}), 1.32-1.24 (m, 6H, H_{14}, H_{15}, H_{16}).

^{13}C NMR (100 MHz, CD_3CN, 298K): δ ppm = 175.4, 172.4 & 170.8 (C_{20}, C_{24} & C_{25}), 157.8 (C_{10}), 140.0, 135.4 & 131.4 (C_2, C_5 & C_{27}), 132.2 (C_3), 130.6 (C_{28}), 130.1 (C_{30}), 129.5 (C_{29}), 128.6 (C_4), 79.1 (C_{26}), 61.0 (C_9), 52.4 (C_6), 48.7 (C_8), 41.7 & 39.8 (C_{12} & C_{18}), 35.9 (C_{21}), 34.6 (C_{22}), 32.5 (C_{23}), 30.2 & 29.9 (C_{13} & C_{17}), 29.3 (C_{15}), 27.3 & 27.2 (C_{14} & C_{16}), 21.3 (C_1).

HRMS (ESI): $[M+H]^+$ calcd for $C_{32}H_{45}N_4O_6^+$: 581.3334, found: 581.3341.

3.8. Synthesis of the molecular translocator 15



To a solution of **14** (532 mg, 0.73 mmol, 1 equiv.) in MeOH (20 mL) was added 40%-Pd/C (213 mg). The solution was stirred 15 min under a hydrogen atmosphere before filtration through a cotton pad. After abundant washing of the cotton pad with MeOH, the filtrate was concentrated to give pure **15** (457 mg, 98%) as a white solid without any further purification.

R_f: 0.12 (CH_2Cl_2/MeOH 90/10)

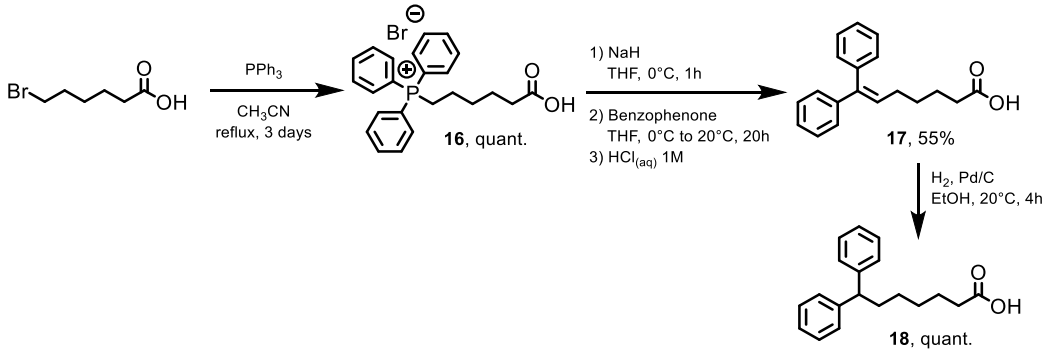
^{1}H NMR (400 MHz, CD_3CN, 298K): δ ppm = 7.92 (br s, 1H H_{26}), 7.37-7.14 (m, 2H, H_7), 7.12 (s, 1H, H_3), 7.05 (s, 2H, H_4), 6.64-6.44 (m, 1H, H_{19}), 5.83-5.74 (m, 1H, H_{11}), 4.30-4.18 (m, 2H, H_9), 4.17-4.08 (m, 2H, H_6), 3.28-3.22 (m, 2H, H_8), 3.08 (q, 4H, $^3J_{11\text{-}12}$ = $^3J_{18\text{-}19}$ = 8 Hz, $^3J_{12\text{-}13}$ = $^3J_{17\text{-}18}$ = 8 Hz, H_{12}, H_{18}), 3.03-2.95 (m, 1H, H_{22}), 2.81-2.73 (m, 1H, H_{23}), 2.59 (d, 2H, $^3J_{21\text{-}22}$ = 4 Hz, H_{21}), 2.36-2.31 (m, 7H, H_1, $H_{23'}$), 1.51-1.37 (m, 4H, H_{13}, H_{17}), 1.32-1.25 (m, 6H, H_{14}, H_{15}, H_{16}).

^{13}C NMR (100 MHz, CD_3CN, 298K): δ ppm = 176.1, 172.6 & 171.5 (C_{20}, C_{24} & C_{25}), 157.8 (C_{10}), 140.0 (C_2), 132.2 (C_3), 131.3 (C_5), 128.6 (C_4), 61.0 (C_9), 52.5 (C_6), 48.6 (C_8), 41.7 & 40.1 (C_{12} & C_{18}), 36.1 (C_{21}), 34.5 (C_{22}), 32.4 (C_{23}), 30.2 & 29.7 (C_{13} & C_{17}), 29.3 (C_{15}), 27.2 (C_{14} & C_{16}), 21.3 (C_1).

HRMS (ESI): $[M+H]^+$ calcd for $C_{25}H_{39}N_4O_6^+$: 491.2870, found: 491.2874.

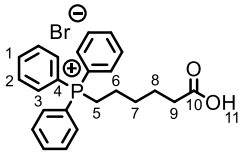
4. Synthesis of the extended axle 18

4.1. General synthetic pathway



Scheme S3. Synthesis of the extended axle **18**.

4.2. Synthesis of compound 16



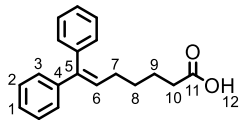
A solution 6-bromohexanoic acid (2.00 g, 10.25 mmol, 1 equiv.) and triphenylphosphine (2.83 g, 10.79 mmol, 1.05 equiv.) in dry CH_3CN (12 mL) was stirred for 3 days under reflux. The solvent was removed under *vacuum* and the crude was triturated with Et_2O (10 x 10 mL) to remove the excess of triphenylphosphine. The solvent was removed under *vacuum* to afford the pure phosphonium salt **16** (4.69 g, quant.) as a white powder without any further purification.

^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ ppm = 7.78-7.58 (m, 15H, H_1, H_2, H_3), 3.58-3.44 (m, 2H, H_5), 2.31-2.19 (m, 2H, H_9), 1.65-1.46 (m, 6H, H_6, H_7, H_8).

^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ ppm = 175.8 (C_{10}), 135.0, 133.4 & 130.5 (C_1, C_2 & C_3), 118.3 & 117.5 (C_4), 34.0 (C_9), 29.3 (C_6), 23.9 (C_8), 22.6 (C_5), 21.8 (C_7).

HRMS (ESI): $[M]^+$ calcd for $C_{24}H_{26}O_2P^+$: 377.1670, found: 377.1669.

4.3. Synthesis of compound 17



To a suspension of the phosphonium salt **16** (1.50 g, 3.28 mmol, 1 equiv.) in dry THF (20 mL) at 0°C, was added portionwise NaH (60% dispersion, 656 mg, 16.40 mmol, 5 equiv.). The reaction mixture was stirred at 0°C for 1h, under argon atmosphere. A solution of benzophenone (717 mg, 3.94 mmol, 1.2 equiv.) in dry THF (20 mL) was added dropwise at 0°C and the reaction mixture was heated at reflux for 20h, under argon atmosphere. The solution was cooled at 0°C and an aqueous solution of HCl 1M was added dropwise until the pH reached 1. The solvent was removed under *vacuum* and the aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were dried over $MgSO_4$ before being concentrated. The obtained crude was purified by flash chromatography (PE/EtOAc 100:0 to 75:25) to give pure **17** (509 mg, 55%) as a white solid.

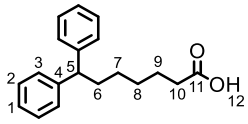
R_f: 0.65 (PE/EtOAc 60/40)

^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ ppm = 7.43-7.20 (m, 10H, H_1, H_2, H_3), 6.11 (t, 1H, $^3J_{6\text{-}7}$ = 8 Hz, H_6), 2.35 (t, 2H, $^3J_{9\text{-}10}$ = 8 Hz, H_{10}), 2.19 (q, 2H, $^3J_{6\text{-}7}$ = 8 Hz, $^3J_{7\text{-}8}$ = 8 Hz, H_7), 1.69 (quint, 2H, $^3J_{8\text{-}9}$ = 8 Hz, $^3J_{9\text{-}10}$ = 8 Hz, H_9), 1.55 (quint, 2H, $^3J_{7\text{-}8}$ = 8 Hz, $^3J_{8\text{-}9}$ = 8 Hz, H_8).

^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ ppm = 180.2 (C_{11}), 142.8, 142.2 & 140.3 (C_4, $C_{4'}$ & C_5), 130.0, 129.4, 128.3, 128.2, 127.3, 127.1 & 127.0 (C_1, $C_{1'}$, C_2, $C_{2'}$, C_3, $C_{3'}$ & C_6), 34.0 (C_{10}), 29.4 (C_7 & C_8), 24.3 (C_9).

HRMS (ESI): $[M\text{-}H]^-$ calcd for $C_{19}H_{19}O_2^-$: 279.1385, found: 279.1387.

4.4. Synthesis of the extended axle 18



To a solution of **17** (508 mg, 1.81 mmol, 1 equiv.) in MeOH (10 mL) was added 50%-Pd/C (250 mg). The solution was stirred 1h under a hydrogen atmosphere before filtration through a celite pad. After abundant washing of the celite pad with MeOH, the filtrate was concentrated to give pure **18** (512 mg, quant.) as a white powder without any further purification.

R_f: 0.65 (PE/EtOAc 60/40)

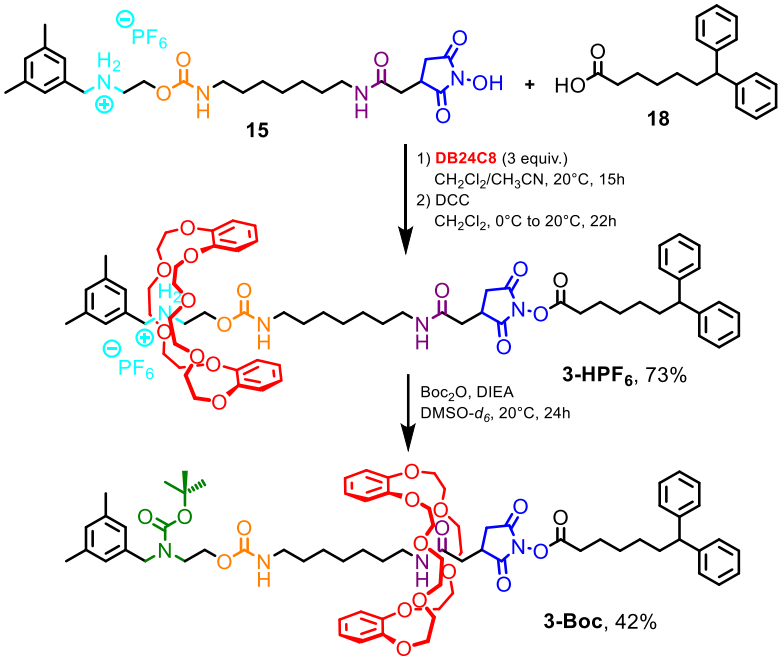
^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ ppm = 11.22 (br s, 1H, H_{12}), 7.30-7.16 (2m, 10H, H_1, H_2, H_3), 3.89 (t, 1H, $^3J_{5\text{-}6}$ = 8 Hz, H_5), 2.33 (t, 2H, $^3J_{9\text{-}10}$ = 8 Hz, H_{10}), 2.06 (q, 2H, $^3J_{5\text{-}6}$ = 8 Hz, $^3J_{6\text{-}7}$ = 8 Hz, H_6), 1.62 (quint, 2H, $^3J_{8\text{-}9}$ = 8 Hz, $^3J_{9\text{-}10}$ = 8 Hz, H_9), 1.39 (quint, 2H, $^3J_{7\text{-}8}$ = 8 Hz, $^3J_{8\text{-}9}$ = 8 Hz, H_8), 1.29 (quint, 2H, $^3J_{6\text{-}7}$ = 8 Hz, $^3J_{7\text{-}8}$ = 8 Hz, H_7).

^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ ppm = 180.0 (C_{11}), 145.2 (C_4), 128.5, 127.9 & 126.2 (C_1, C_2 & C_3), 51.4 (C_5), 35.6 (C_6), 34.1 (C_{10}), 29.1 (C_8), 27.7 (C_7), 24.6 (C_9).

HRMS (ESI): $[M\text{-}H]^-$ calcd for $C_{19}H_{21}O_2^-$: 281.1547, found: 281.1561.

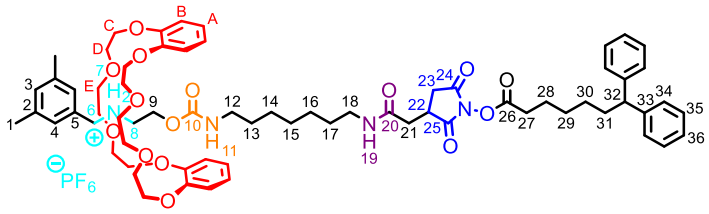
5. Synthesis of the [2]rotaxanes 3-HPF_6 and 3-Boc

5.1. General synthetic pathway



Scheme S4. Synthesis of the protonated rotaxane **3-HPF_6** and the *N*-Boc-protected rotaxane **3-Boc**.

5.2. Synthesis of the protonated [2]rotaxane 3-HPF$_6$



To a solution of the ammonium thread **15** (840 mg, 1.32 mmol, 1 equiv.) and DB24C8 (1.77 g, 3.95 mmol, 3 equiv.) in a mixture of CH_2Cl_2/CH_3CN (1.6 mL/0.4 mL, [**11**] = 0.66M) was stirred at room temperature for 15h under argon atmosphere. The solvent was removed under *vacuum* and the obtained crude was diluted in CH_2Cl_2 (5 mL). The carboxylic acid **18** (373 mg, 1.32 mmol, 1 equiv.) was added and the reaction mixture was cooled to 0°C. DCC (626 mg, 3.04 mmol, 2.3 equiv.) was added and the reaction mixture was allowed to warm-up to room temperature for 22h under argon atmosphere. The mixture was filtered to remove the DCU and the solvent was evaporated to dryness. The obtained crude was triturated with toluene (10 x 7 mL). The residue was heated at reflux of toluene (20 mL), and directly filtered. The precipitate was washed with toluene and dissolved in CH_2Cl_2. The filtrate was evaporated to dryness, to afford the ammonium [2]rotaxane **3-HPF$_6$** (1.30 g, 73%) as a white solid.

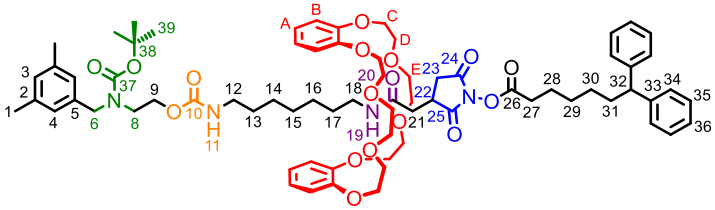
R_f: 0.73 (CH_2Cl_2/Acetone 60/40)

^{1}H NMR (600 MHz, CD_3CN, 298K): δ ppm = 7.43-7.32 (m, 2H, H_7), 7.30-7.24 (m, 8H, H_{34}, H_{35}), 7.18-7.13 (m, 2H, H_{36}), 6.92-6.84 (m, 8H, H_A, H_B), 6.78 (s, 2H, H_4), 6.73 (s, 1H, H_3), 6.44-6.37 (m, 1H, H_{19}), 5.21-5.16 (m, 1H, H_{11}), 4.45-4.39 (m, 2H, H_6), 4.26-4.20 (m, 2H, H_9), 4.14-4.05 (m, 8H, H_C, $H_{C'}$), 3.93 (t, 1H, $^3J_{31\text{-}32}$ = 8 Hz, H_{32}), 3.90-3.85 (m, 4H, H_D), 3.80-3.74 (m, 6H, H_8, $H_{D'}$), 3.72-3.68 (m, 4H, H_E), 3.68-3.61 (m, 4H, $H_{E'}$), 3.23-3.13 (m, 1H, H_{22}), 3.06 (q, 2H, $^3J_{17\text{-}18}$ = 8 Hz, $^3J_{18\text{-}19}$ = 8 Hz, H_{18}), 2.96 (q, 2H, $^3J_{11\text{-}12}$ = 8 Hz, $^3J_{12\text{-}13}$ = 8 Hz, H_{12}), 2.94-2.88 (m, 1H, H_{23}), 2.71-2.58 (m, 2H, H_{21}), 2.55 (t, 2H, $^3J_{27\text{-}28}$ = 8 Hz, H_{27}), 2.53-2.45 (m, 1H, $H_{23'}$), 2.09-2.01 (m, 8H, H_1, H_{31}), 1.64 (quint, 2H, $^3J_{27\text{-}28}$ = 8 Hz, $^3J_{28\text{-}29}$ = 8 Hz, H_{28}), 1.42 (quint, 2H, $^3J_{28\text{-}29}$ = 8 Hz, $^3J_{29\text{-}30}$ = 8 Hz, H_{29}), 1.34-1.24 (m, 6H, H_{13}, H_{17}, H_{30}), 1.20-1.06 (m, 6H, H_{14}, H_{15}, H_{16}).

^{13}C NMR (150 MHz, CD_3CN, 298K): δ ppm = 173.5 (C_{26}), 170.1 (C_{20}, C_{24} & C_{25}), 156.5 (C_{10}), 148.6 ($C_{IV\ arom.\ DB24C8}$), 146.6 (C_2), 139.0 (C_5), 132.4 (C_{33}), 131.1 (C_3), 129.4 & 128.6 (C_{34} & C_{35}), 128.3 (C_4), 127.0 (C_{36}), 122.3 (C_A), 113.4 (C_B), 71.6 (C_E), 71.2 (C_D), 69.0 (C_C), 61.2 (C_9), 53.5 (C_6), 51.9 (C_{32}), 49.0 (C_8), 41.4 (C_{12}), 39.8 (C_{18}), 35.7 (C_{21} & C_{31}), 34.9 (C_{22}), 32.6 (C_{23}), 31.4 (C_{27}), 30.4, 30.1, 29.4, 29.1, 28.2, 27.3 & 27.2 (C_{13}, C_{14}, C_{15}, C_{16}, C_{17}, C_{29} & C_{30}), 25.2 (C_{28}), 21.2 (C_1).

HRMS (ESI): $[M\text{-}PF_6]^+$ calcd for $C_{68}H_{91}N_4O_{15}^+$: 1203.6481, found: 1203.6492.

5.3. Synthesis of the *N*-carbamoylated [2]rotaxane 3-Boc



To a solution of protonated [2]rotaxane **3-HPF$_6$** (50 mg, 0.037 mmol, 1 equiv.) in DMSO-d_6 (0.6 mL) was added Boc_2O (202 mg, 0.925 mmol, 25 equiv.) and DIEA (315 µL, 1.850 mmol, 50 equiv.). The mixture was stirred at room temperature for 24h under argon atmosphere. H_2O milliQ (3 mL) was added and the aqueous layer was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were dried over $MgSO_4$ before being concentrated. The obtained crude was purified by chromatography on lipophilic Sephadex LH20 column (CH_2Cl_2) to afford the *N*-carbamoylated [2]rotaxane **3-Boc** (20 mg, 42%) as a pale orange paste.

R_f: 0.42 (CH_2Cl_2/MeOH 95/5)

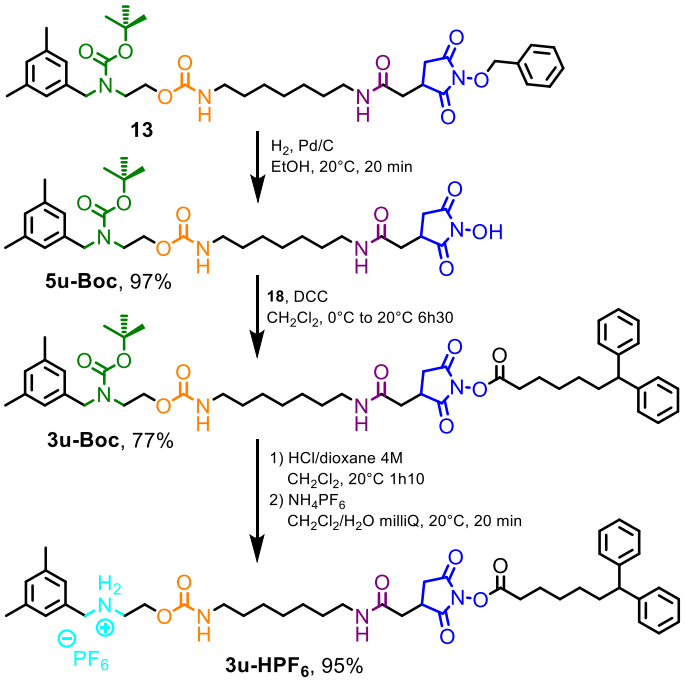
^{1}H NMR (600 MHz, CD_3CN, 298K): δ ppm = 7.30-7.24 (m, 8H, H_{34}, H_{35}), 7.17-7.12 (m, 2H, H_{36}), 6.91-6.82 (m, 10H, H_4, H_A, H_B), 6.78-6.74 (m, 2H, H_3, H_{19}), 5.64, 5.48 & 5.36 (3br s, 1H, H_{11}), 4.37 (br s, 2H, H_6), 4.13-4.03 (m, 10H, H_9, H_C), 3.93 (t, 1H, $^{3}J_{31\text{-}32}$ = 8 Hz, H_{32}), 3.82-3.71 (m, 8H, H_D), 3.63-3.56 (m, 8H, H_E), 3.49-3.22 (m, 5H, H_8, H_{18}, H_{21}), 3.16-2.87 (m, 4H, H_{12}, $H_{21'}$, H_{22}), 2.82-2.73 (m, 1H, H_{23}), 2.55 (t, 2H, $^{3}J_{27\text{-}28}$ = 8 Hz, H_{27}), 2.52-2.46 (m, 1H, $H_{23'}$), 2.26 & 2.24 (2s, 6H, H_1), 2.05 (q, 2H, $^{3}J_{30\text{-}31}$ = 8 Hz, $^{3}J_{31\text{-}32}$ = 8 Hz, H_{31}), 1.64 (quint, 2H, $^{3}J_{27\text{-}28}$ = 8 Hz, $^{3}J_{28\text{-}29}$ = 8 Hz, H_{28}), 1.47-1.37 (m, 11H, H_{29}, H_{39}), 1.35-1.30 (m, 2H, H_{17}), 1.29-1.20 (m, 4H, H_{13}, H_{30}), 1.04-0.85 (m, 6H, H_{14}, H_{15}, H_{16}).

^{13}C NMR (150 MHz, CD_3CN, 298K): δ ppm = 173.8 (C_{26}), 170.8, 170.2 & 169.1 (C_{20}, C_{24} & C_{25}), 157.1 & 156.5 (C_{10} & C_{37}), 149.3 ($C_{IV\ arom.\ DB24C8}$), 146.6, 139.7 & 139.0 (C_2, C_5 & C_{33}), 129.4, 128.8 & 128.7 (C_4, C_{34} & C_{35}), 127.0 (C_{36}), 126.0 (C_3), 121.7 (C_A), 113.3 (C_B), 80.3 (C_{38}), 71.6 (C_E), 70.6 (C_D), 69.2 (C_C), 63.2 (C_9), 51.9 (C_{32}), 51.2 (C_6), 46.8 (C_8), 43.2 (C_{21}), 41.7 (C_{12}), 40.4 (C_{18}), 35.7 (C_{31}), 34.9 (C_{22}), 32.5 (C_{23}), 31.5 (C_{27}), 30.2, 30.0, 29.3, 29.2, 28.6, 28.2, 27.4 & 27.3 (C_{13}, C_{14}, C_{15}, C_{16}, C_{17}, C_{29}, C_{30} & C_{39}), 25.3 (C_{28}), 21.4 (C_1).

HRMS (ESI): $[M+H]^+$ calcd for $C_{73}H_{99}N_4O_{17}^+$: 1303.7005, found: 1303.6976.

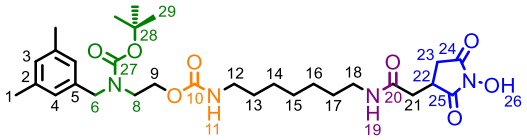
6. Synthesis of the uncomplexed rods 3u-HPF$_6$, 3u-Boc and 5u-Boc

6.1. General synthetic pathway



Scheme S5. Synthesis of the protonated uncomplexed rod **3u-HPF$_6$** and the *N*-Boc-protected uncomplexed rod **3u-Boc**.

6.2. Synthesis of compound 5u-Boc



To a solution of **13** (326 mg, 0.479 mmol, 1 equiv.) in EtOH (15 mL) was added 40%-Pd/C (130 mg). The solution was stirred 20 min under a hydrogen atmosphere before filtration through a cotton pad. After abundant washing of the cotton pad with EtOH, the filtrate was concentrated to give pure **5u-Boc** (275 mg, 97%) as a white solid without any further purification.

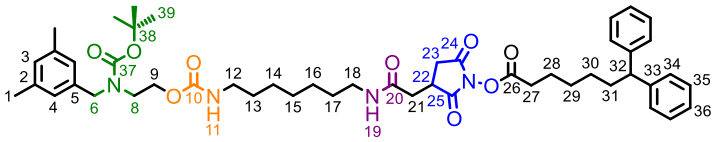
R_f: 0.44 (CH_2Cl_2/MeOH 90/10)

^{1}H NMR (400 MHz, CD_3CN, 298K): δ ppm = 6.91 (s, 1H, H_3), 6.84 (s, 2H, H_4), 6.46 (br s, 1H, H_{19}), 5.50 (br s, 1H, H_{11}), 4.38 (br s, 2H, H_6), 4.06 (t, 2H, $^3J_{8\text{-}9}$ = 5 Hz, H_9), 3.42-3.27 (m, 2H, H_8), 3.09 (q, 2H, $^3J_{17\text{-}18}$ = 6.6 Hz, $^3J_{18\text{-}19}$ = 6.6 Hz, H_{18}), 3.05 (q, 2H, $^3J_{11\text{-}12}$ = 6.6 Hz, $^3J_{12\text{-}13}$ = 6.6 Hz, H_{12}), 3.01-2.94 (m, 1H, H_{22}), 2.74 (dd, 1H, $^2J_{23\text{-}23'}$ = 17.6 Hz, $^3J_{22\text{-}23}$ = 8.9 Hz, H_{23}), 2.65-2.50 (m, 2H, H_{21}), 2.35 (dd, 1H, $^2J_{23\text{-}23'}$ = 17.6 Hz, $^3J_{22\text{-}23'}$ = 4.6 Hz, $H_{23'}$), 2.27 (s, 6H, H_1), 1.50-1.36 (m, 13H, H_{13}, H_{17}, H_{29}), 1.33-1.24 (m, 6H, H_{14}, H_{15}, H_{16}).

^{13}C NMR (100 MHz, CD_3CN, 298K): δ ppm = 175.5, 172.6 & 170.7 (C_{20}, C_{24} & C_{25}), 157.3 & 156.4 (C_{10} & C_{27}), 139.6 & 139.0 (C_2 & C_5), 129.5 (C_3), 126.0 (C_4), 80.4 (C_{28}), 63.2 (C_9), 51.9 & 51.0 (C_6), 46.7 (C_8), 41.5 (C_{12}), 39.8 (C_{18}), 35.8 (C_{21}), 34.6 (C_{22}), 32.3 (C_{23}), 30.5, 30.0, 29.5, 27.3 & 27.3 (C_{13}, C_{14}, C_{15}, C_{16} & C_{17}), 28.5 (C_{29}), 21.3 (C_1).

HRMS (ESI): $[M+H]^+$ calcd for $C_{30}H_{47}N_4O_8^+$: 591.3388, found: 591.3410.

6.3. Synthesis of the *N*-carbamoylated uncomplexed rod 3u-Boc



To a solution of carbamoylated rod **5u-Boc** (128 mg, 0.217 mmol, 1 equiv.) and carboxylic acid **18** (61 mg, 0.217 mmol, 1 equiv.) in CH_2Cl_2 (3.5 mL) at 0°C, was added DCC (103 mg, 0.499 mmol, 2.3 equiv.). The reaction mixture was allowed to warm-up to room temperature for 6h30 under argon atmosphere. The mixture was filtered to remove DCU and the filtrate was evaporated. The obtained crude was purified by flash chromatography (PE/EtOAC 100:0 to 10:90) to afford the carbamoylated uncomplexed rod **3u-Boc** (142 mg, 77%) as a white solid.

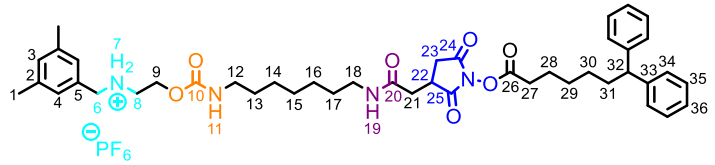
R_f: 0.70 (PE/EtOAc 10/90)

^{1}H NMR (400 MHz, CD_3CN, 298K): δ ppm = 7.33-7.24 (m, 8H, H_{34}, H_{35}), 7.21-7.11 (m, 2H, H_{36}), 6.91 (s, 1H, H_3), 6.85 (s, 2H, H_4), 6.57 (br t, 1H, H_{19}), 5.57 (br t, 1H, H_{11}), 4.39 (br s, 2H, H_6), 4.07 (br t, 2H, H_9), 3.93 (t, 1H, $^3J_{31\text{-}32}$ = 8 Hz, H_{32}), 3.44-3.30 (m, 2H, H_8), 3.26-3.16 (m, 1H, H_{22}), 3.11 (q, 2H, $^3J_{17\text{-}18}$ = 6.6 Hz, $^3J_{18\text{-}19}$ = 6.6 Hz, H_{18}), 3.06 (q, 2H, $^3J_{11\text{-}12}$ = 6.6 Hz, $^3J_{12\text{-}13}$ = 6.6 Hz, H_{12}), 2.92 (dd, 1H, $^2J_{23\text{-}23'}$ = 17.4 Hz, $^3J_{22\text{-}23}$ = 8.7 Hz, H_{23}), 2.77-2.42 (m, 5H, H_{21}, $H_{23'}$, H_{27}), 2.27 (s, 6H, H_1), 2.05 (q, 2H, $^3J_{30\text{-}31}$ = 8 Hz, $^3J_{31\text{-}32}$ = 8 Hz, H_{31}), 1.64 (quint, 2H, $^3J_{27\text{-}28}$ = 7.5 Hz, $^3J_{28\text{-}29}$ = 7.5 Hz, H_{28}), 1.51-1.38 (m, 15H, H_{13}, H_{17}, H_{29}, H_{39}), 1.32-1.23 (m, 8H, H_{14}, H_{15}, H_{16}, H_{30}).

^{13}C NMR (100 MHz, CD_3CN, 298K): δ ppm = 173.5 (C_{26}), 170.5, 170.3 & 170.2 (C_{20}, C_{24} & C_{25}), 157.3 & 156.5 (C_{10} & C_{37}), 146.6 (C_{33}), 139.6 & 139.0 (C_2 & C_5), 129.5 (C_3), 129.4 & 128.7 (C_{34} & C_{35}), 127.0 (C_{36}), 126.1 (C_4), 80.4 (C_{38}), 63.3 (C_9), 51.9 (C_{32}), 51.1 (C_6), 46.7 (C_8), 41.5 (C_{12}), 39.9 (C_{18}), 35.7 (C_{21} & C_{31}), 35.0 (C_{22}), 32.6 (C_{23}), 31.4 (C_{27}), 30.5, 30.1, 29.6, 29.2, 28.2, 27.4 & 27.4 (C_{13}, C_{14}, C_{15}, C_{16}, C_{17}, C_{29} & C_{30}), 28.6 (C_{39}), 25.3 (C_{28}), 21.5 (C_1).

HRMS (ESI): $[M+H]^+$ calcd for $C_{49}H_{67}N_4O_9^+$: 855.4903, found: 855.4913.

6.4. Synthesis of the protonated uncomplexed rod 3u-HPF_6



To a solution of the carbamoylated rod **3u-Boc** (62 mg, 0.073 mmol, 1 equiv.) in CH_2Cl_2 (2 mL) was added a 4M solution of chlorhydric acid in dioxane (3 mL, excess). The mixture was stirred at room temperature for 1h10. The mixture was evaporated to dryness and the residue was partitioned between CH_2Cl_2 (4 mL) and milliQ H_2O (2 mL). NH_4PF_6 (35 mg, 0.218 mmol, 3 equiv.) was added and the biphasic mixture was vigorously stirred for 20 min. The aqueous layer was extracted with CH_2Cl_2 (3 x 5 mL) and the combined organic layers were dried over

$MgSO_4$ before being concentrated to afford the ammonium rod **3u-HPF$_6$** (63 mg, 95%) as a white solid without any further purification.

R_f: 0.46 (CH_2Cl_2/MeOH 90/10)

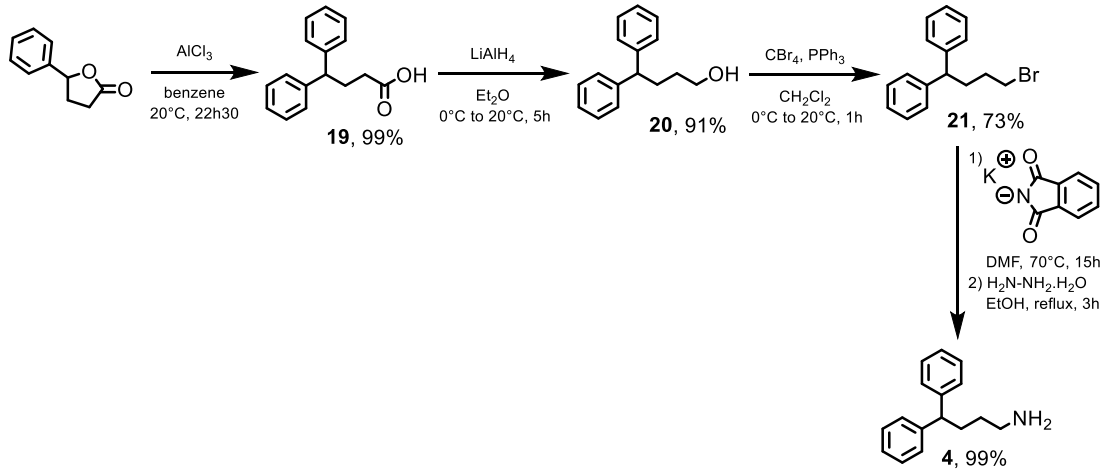
^{1}H NMR (400 MHz, CD_3CN, 298K): δ ppm = 7.32-7.24 (m, 8H, H_{34}, H_{35}), 7.19-7.13 (m, 2H, H_{36}), 7.11 (s, 1H, H_3), 7.06 (s, 2H, H_4), 6.52 (br t, 1H, H_{19}), 5.78 (br t, 1H, H_{11}), 4.29-4.21 (m, 2H, H_9), 4.12 (s, 2H, H_6), 3.93 (t, 1H, $^3J_{31\text{-}32}$ = 8 Hz, H_{32}), 3.27-3.22 (m, 2H, H_8), 3.22-3.14 (m, 1H, H_{22}), 3.08 (2q, 4H, $^3J_{11\text{-}12}$ = 6.6 Hz, $^3J_{12\text{-}13}$ = 6.6 Hz, $^3J_{17\text{-}18}$ = 6.6 Hz, $^3J_{18\text{-}19}$ = 6.6 Hz, H_{12}, H_{18}), 2.92 (dd, 1H, $^2J_{23\text{-}23'}$ = 17.4 Hz, $^3J_{22\text{-}23}$ = 8.7 Hz, H_{23}), 2.69-2.45 (m, 5H, H_{21}, $H_{23'}$, H_{27}), 2.32 (s, 6H, H_1), 2.05 (q, 2H, $^3J_{30\text{-}31}$ = 8 Hz, $^3J_{31\text{-}32}$ = 8 Hz, H_{31}), 1.64 (quint, 2H, $^3J_{27\text{-}28}$ = 7.5 Hz, $^3J_{28\text{-}29}$ = 7.5 Hz, H_{28}), 1.49-1.38 (m, 6H, H_{13}, H_{17}, H_{29}), 1.31-1.24 (m, 8H, H_{14}, H_{15}, H_{16}, H_{30}).

^{13}C NMR (100 MHz, CD_3CN, 298K): δ ppm = 173.5 (C_{26}), 170.5 & 170.2 (C_{20}, C_{24} & C_{25}), 157.8 (C_{10}), 146.6 (C_{33}), 140.0 (C_2), 132.2 (C_3), 131.4 (C_5), 129.5 & 128.7 (C_{34} & C_{35}), 128.6 (C_4), 127.1 (C_{36}), 61.1 (C_9), 52.4 (C_6), 51.9 (C_{32}), 48.7 (C_8), 41.7 (C_{12}), 39.9 (C_{18}), 35.7 (C_{21} & C_{31}), 34.4 (C_{22}), 32.6 (C_{23}), 31.4 (C_{27}), 30.2, 29.9, 29.3, 29.2, 28.2, 27.3 & 27.2 (C_{13}, C_{14}, C_{15}, C_{16}, C_{17}, C_{29} & C_{30}), 25.3 (C_{28}), 21.3 (C_1).

HRMS (ESI): $[M]^+$ calcd for $C_{44}H_{59}N_4O_7^+$: 755.4378, found: 755.4382.

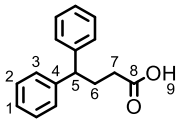
7. Synthesis of the amine stopper 4

7.1. General synthetic pathway



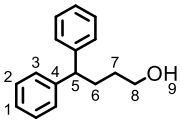
Scheme S6. Synthesis of the amine stopper **4**.

7.2. Synthesis of compound 19



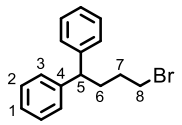
This compound has been synthesized in one step from the *γ*-phenyl-*γ*-butyrolactone according to the procedure described by: Q. Gan, Y. Ferrand, C. Bao, B. Kauffman, A. Grélard, H. Jiang, I. Huc, *Science*, **2011**, 331, 1172-1175.

7.3. Synthesis of compound 20



This compound has been synthesized in one step from the compound **19** according to the procedure described by: Q. Gan, Y. Ferrand, C. Bao, B. Kauffman, A. Grélard, H. Jiang, I. Huc, *Science*, **2011**, 331, 1172-1175.

7.4. Synthesis of compound 21



To a solution of **20** (1.12 g, 4.95 mmol, 1 equiv.) and CBr_4 (1.97 g, 5.94 mmol, 1.2 equiv.) in CH_2Cl_2 (20 mL) at 0°C, was added portionwise PPh_3 (1.56 g, 5.94 mmol, 1.2 equiv.). The reaction was allowed to warm-up to room temperature for 1h under argon atmosphere. The solvent was removed under *vacuum* and the obtained crude was purified by flash chromatography (PE/EtOAc 100:0 to 90:10) to give the pure **21** (1.04 g, 73%) as a colorless oil.

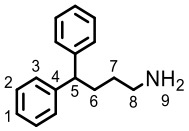
R_f: 0.57 (PE/EtOAc 60/40)

^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ ppm = 7.35-7.23 (m, 8H, H_2, H_3), 7.23-7.17 (m, 2H, H_1), 3.94 (t, 1H, $^3J_{5-6}$ = 8 Hz, H_5), 3.42 (t, 2H, $^3J_{7-8}$ = 8 Hz, H_8), 2.23 (q, 2H, $^3J_{5-6}$ = 8 Hz, $^3J_{6-7}$ = 8 Hz, H_6), 1.85 (quint, 2H, $^3J_{6-7}$ = 8 Hz, $^3J_{7-8}$ = 8 Hz, H_7).

^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ ppm = 144.6 (C_4), 128.7 & 127.9 (C_2 & C_3), 126.4 (C_1), 50.7 (C_5), 34.2 (C_6), 33.9 (C_8), 31.3 (C_7).

HRMS (ESI): compound **21** was not ionisable.

7.5. Synthesis of the amine stopper 4



A solution of **21** (714 mg, 2.47 mmol, 1 equiv.) and Potassium Phtalimide (685 mg, 3.70 mmol, 1.5 equiv.) in DMF (20 mL), was heated at 70°C for 15h, under argon atmosphere. The solvent was removed under *vacuum*. CH_2Cl_2 was added to the obtained crude and the formed precipitate was filtered. The precipitate was washed with CH_2Cl_2. The filtrate was evaporated. The obtained crude was dissolved in EtOH (20 mL) and hydrazine monohydrate was added. The reaction mixture was stirred for 3h under reflux. 20 mL of an aqueous solution of NaOH 1M was added and the mixture was concentrated. The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were dried over $MgSO_4$ before being concentrated to afford the amine **4** (551 mg, 99%) as a pale-yellow oil without any further purification.

R_f: 0.18 (CH_2Cl_2/MeOH 90/10)

^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ ppm = 7.33-7.24 (m, 8H, H_2, H_3), 7.22-7.16 (m, 2H, H_1), 3.91 (t, 1H, $^3J_{5-6}$ = 8 Hz, H_5), 2.72 (t, 2H, $^3J_{7-8}$ = 8 Hz, H_8), 2.10 (q, 2H, $^3J_{5-6}$ = 8 Hz, $^3J_{6-7}$ = 8 Hz, H_6), 1.43 (quint, 2H, $^3J_{6-7}$ = 8 Hz, $^3J_{7-8}$ = 8 Hz, H_7), 1.29 (br s, 2H, H_9).

^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ ppm = 145.1 (C_4), 128.5 & 127.9 (C_2 & C_3), 126.2 (C_1), 51.4 (C_5), 42.3 (C_8), 33.1 (C_6), 32.5 (C_7).

HRMS (ESI): $[M+H]^+$ calcd for $C_{16}H_{20}N^+$: 226.1590, found: 226.1601.

8. ^{1}H NMR characterization for the [2]rotaxanes 3-HPF$_6$ and 3-Boc

8.1. ^{1}H NMR characterization for the protonated [2]rotaxane 3-HPF$_6$

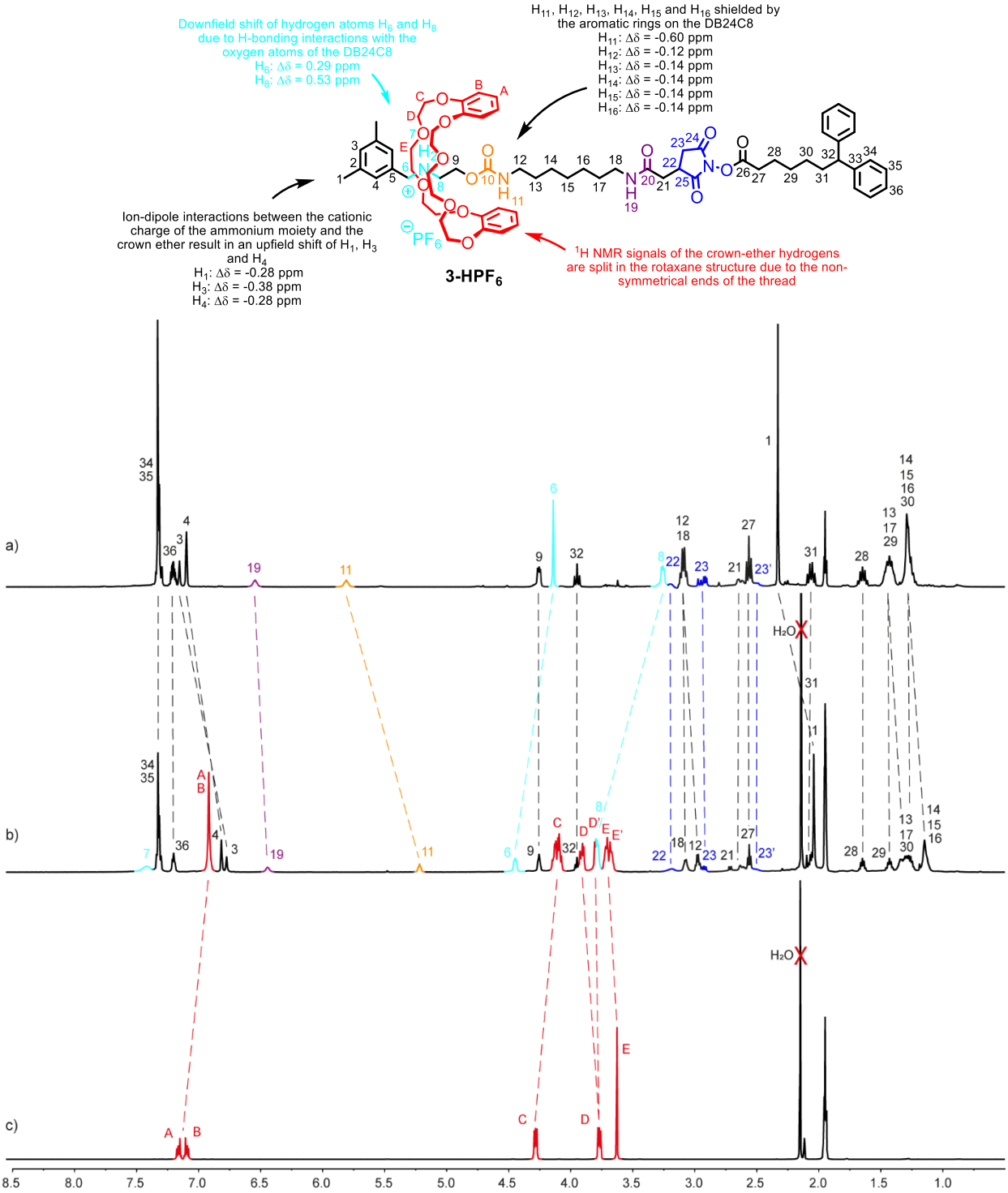


Figure S1. ^{1}H NMR spectra (400 MHz, CD_3CN, 298K) of: a) the protonated uncomplexed rod **3u-HPF$_6$**, b) the protonated [2]rotaxane **3-HPF$_6$** and c) the free DB24C8.

8.2. ^{1}H NMR characterization for the *N*-carbamoylated [2]rotaxane 3-Boc

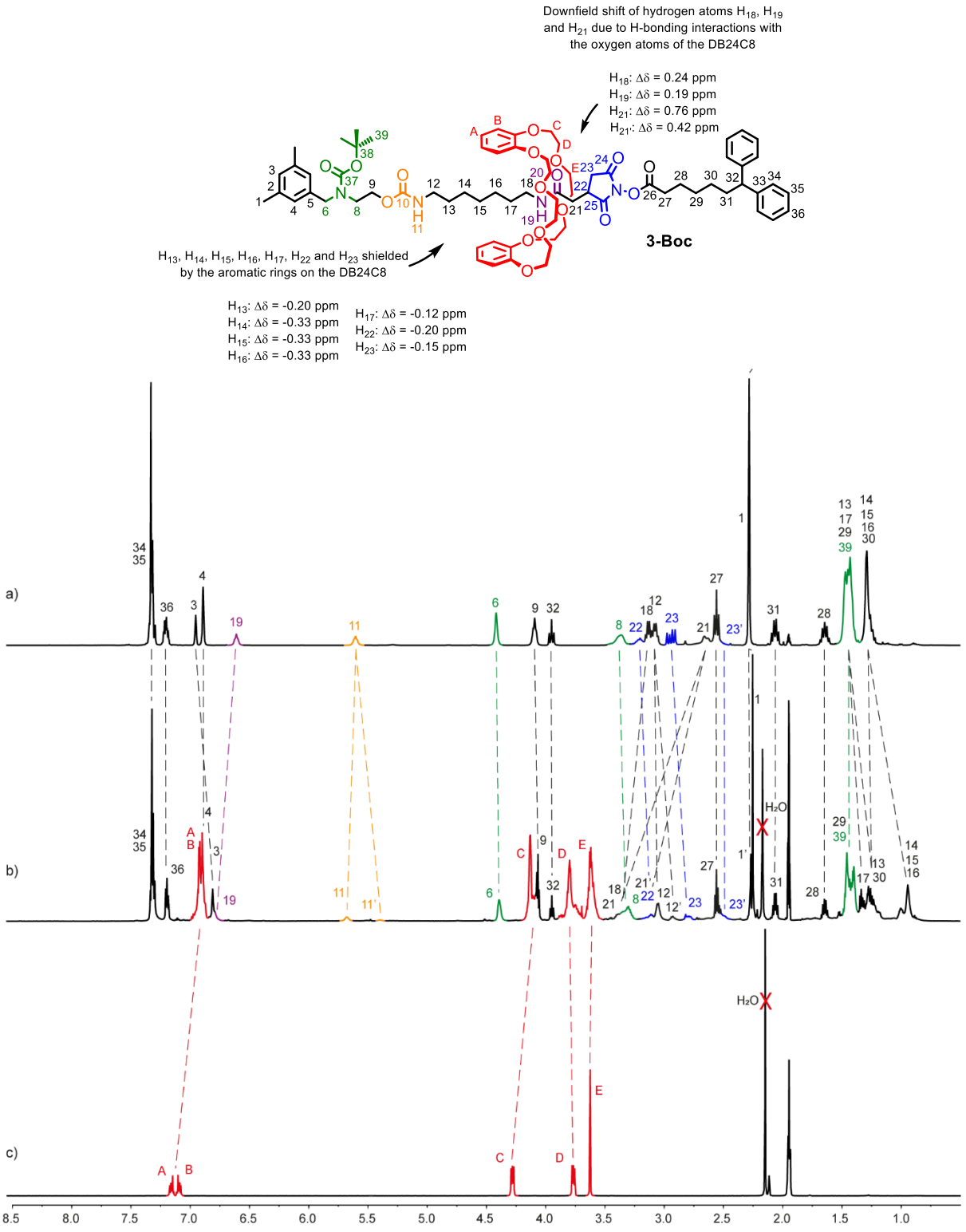


Figure S2. ^{1}H NMR spectra (400 MHz, CD_3CN, 298K) of: a) the *N*-carbamoylated uncomplexed rod **3u-Boc**, b) the *N*-carbamoylated [2]rotaxane **3-Boc** and c) the free DB24C8.

8.3. ^{1}H NMR characterization of the molecular machinery

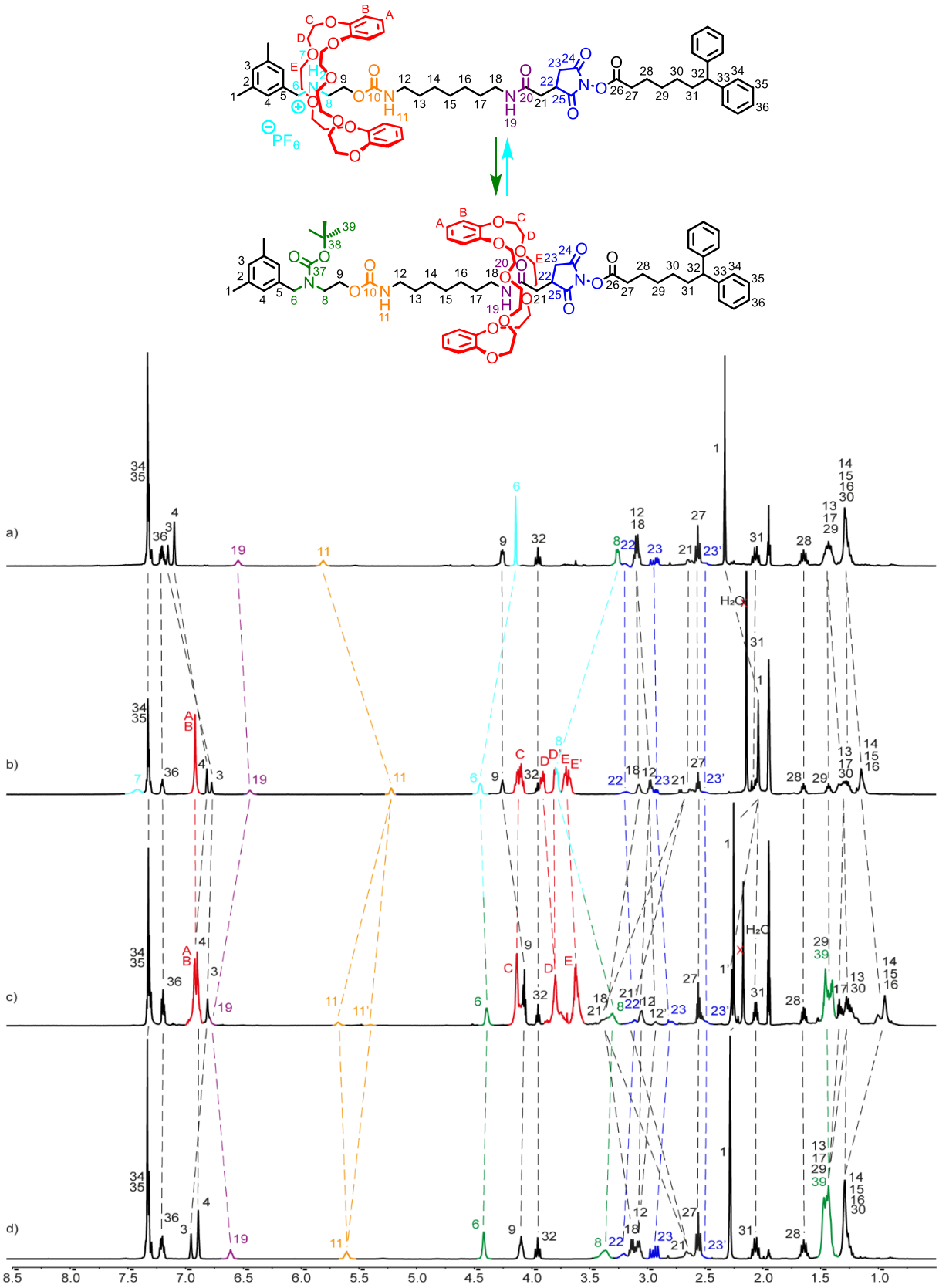


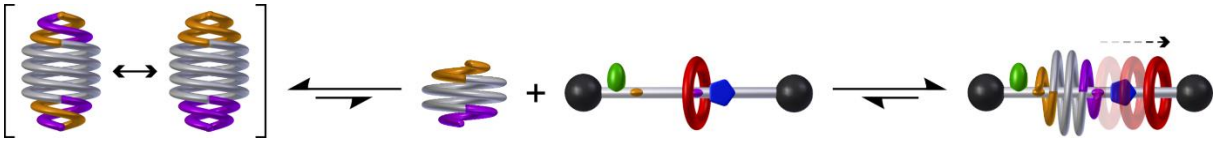
Figure S3. ^{1}H NMR spectra (400 MHz, CD_3CN, 298K) of: a) the protonated uncomplexed rod **3u-HPF$_6$**, b) the protonated [2]rotaxane **3-HPF$_6$**, c) the *N*-carbamoylated [2]rotaxane **3-Boc** and d) the *N*-carbamoylated uncomplexed rod **3u-Boc**.

Molecular shuttling was evidenced by the direct comparisons between the ^{1}H NMR spectra in CD_3CN of the [2]rotaxanes **3-HPF$_6$** and **3-Boc** with their non-interlocked analogues **3u-HPF$_6$** and **3u-Boc** (**Figure S3.**). Comparison between the ^{1}H NMR spectrum of the protonated [2]rotaxane **3-HPF$_6$** and that of its non-interlocked analogue **3u-HPF$_6$** demonstrated the localization of the crown ether around the ammonium station (**Figure S3.a-b**). Briefly, in the protonated [2]rotaxane **3-HPF$_6$**, hydrogen atoms H_6 and H_8 are shifted downfield ($\Delta\delta$ = 0.29 ppm and 0.53 ppm, respectively) due to their hydrogen bonding interactions with the oxygen atoms of the DB24C8, while hydrogen atoms $H_{11\text{-}16}$ are shifted upfield ($\Delta\delta$ = from -0.12 to -0.60 ppm) because they experience the shielding effect of the aromatic rings of the crown ether. Moreover, the electron withdrawal effect of the ammonium group decreases when in interaction with the DB24C8, slightly shifting upfield the chemical shifts of the hydrogen atoms $H_{1,3,4}$ belonging to the neighbouring dimethylaryl stopper ($\Delta\delta$ = -0.28 ppm, -0.38 ppm and -0.28 ppm, respectively). Due to the dissymmetry of the thread, the hydrogen atoms of the DB24C8 $H_{C\text{-}E}$ are split in the [2]rotaxane **3-HPF$_6$**.

Deprotonation-then-carbamoylation of the rotaxane **3-HPF$_6$** triggered the shuttling of the DB24C8 around the amide site (**Figure S3.b-c**). The new position of the DB24C8 was confirmed by the comparison between ^{1}H NMR spectra of the *N*-carbamoylated [2]rotaxane **3-Boc** and its non-interlocked rod **3u-Boc** (**Figure S3.c-d**). In [2]rotaxane **3-Boc**, with respect to **3u-Boc**, hydrogen atoms $H_{18\text{-}21}$ are shifted downfield ($\Delta\delta$ = from 0.19 to 0.75 ppm), due to their hydrogen bonding interactions with the DB24C8. On contrary, the hydrogen atoms located on the two edges of this molecular station, respectively $H_{13\text{-}17}$ and $H_{22\text{-}23}$ are all shielded by the aromatic rings of the DB24C8 ($\Delta\delta$ = from -0.12 to -0.33 ppm).

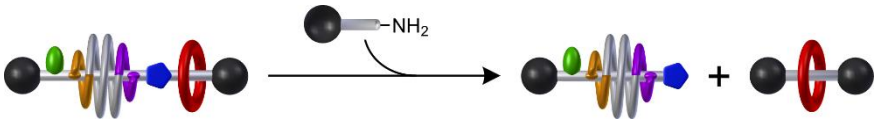
9. Formation and cleavage of the foldarotaxane

9.1 Methods for the formation and the cleavage of the foldarotaxane 1⊃3-Boc



Self-assembly of the foldarotaxane 1⊃3-Boc and compartmentalization of the macrocycle:

The formation of the foldarotaxane **1⊃3-Boc** was performed in a NMR tube (5 mm diameter) by mixing the foldamer helix **1** (6 mM) and the *N*-Boc protected rotaxane **3-Boc** (15 mM) in $CDCl_3$ (500 µL). After homogenization, the NMR sample was evaporated using a high vacuum line and then 125 µL of $CDCl_3$ was added to the NMR tube in the purpose to increase concentrations (24 mM of the foldamer **1** and 60 mM of the *N*-Boc protected rotaxane **3-Boc**). High concentration enhance the kinetic of binding *via* unfolding-refolding mechanism of the helix around the rotaxane guest. Finally, the sample was heated to 328 K and the self-assembly of the target foldarotaxane **1⊃3-Boc** was followed by ^{1}H NMR spectroscopy using a 700 MHz spectrometer at 298 K after the prior addition of 330 µL of $CDCl_3$ (NMR acquisition in 500 µL of $CDCl_3$ with 6 mM of the foldamer helix **1** and 15 mM of the *N*-Boc protected rotaxane **3-Boc**). The thermodynamic equilibrium and the quantitative self-assembly of the foldarotaxane **1⊃3-Boc** is reach after 6 days at high concentrations (24 mM of the foldamer **1** and 60 mM of the *N*-Boc protected rotaxane **3-Boc**) and 328 K.



Cleavage of the foldarotaxane 1⊃3-Boc and characterization of the rotaxane 6:

Firstly, the NMR tube containing the previously formed foldarotaxane **1⊃3-Boc** was evaporated using a high vacuum line and then 500 µL of a solution of the bulky amine **4** in $CDCl_3$ (16.5 mM) was added. The cleavage of the NHS moiety of the foldarotaxane **1⊃3-Boc** was monitored over time by ^{1}H NMR spectroscopy using a 700 MHz spectrometer at 298 K. The emergence of a new set of signals is distinguishable on the resulting ^{1}H NMR spectra, corresponding to the foldaxane by-product **1⊃5-Boc**, in slow exchange at the NMR time scale with the initial foldarotaxane **1⊃3-Boc**. The cleavage is quantitative after 18 h and the resulting mixture was evaporated using a high vacuum line. Later, the crude mixture was injected on a preparative recycling Gel Permeation Chromatography (GPC) composed of JAIGEL 20*600 mm columns (from the Japan Analytical Industry) at a flow rate of 10 mL.min^{-1} with a mobile phase composed of 1 % (vol / vol) EtOH and 0.5 % (vol / vol) NEt_3 in $CHCl_3$, monitored by a UV detector (254 nm, 280 nm, 300 nm and 360 nm) in the purpose to remove the foldaxane by-product **1⊃5-Boc**. Finally, the target rotaxane **6** was isolated by flash chromatography (SiO_2) eluting with CH_2Cl_2 / MeOH (100:0 to 80:20).

9.2 ^{1}H NMR titration of the foldamer helix 1 with the rod 2

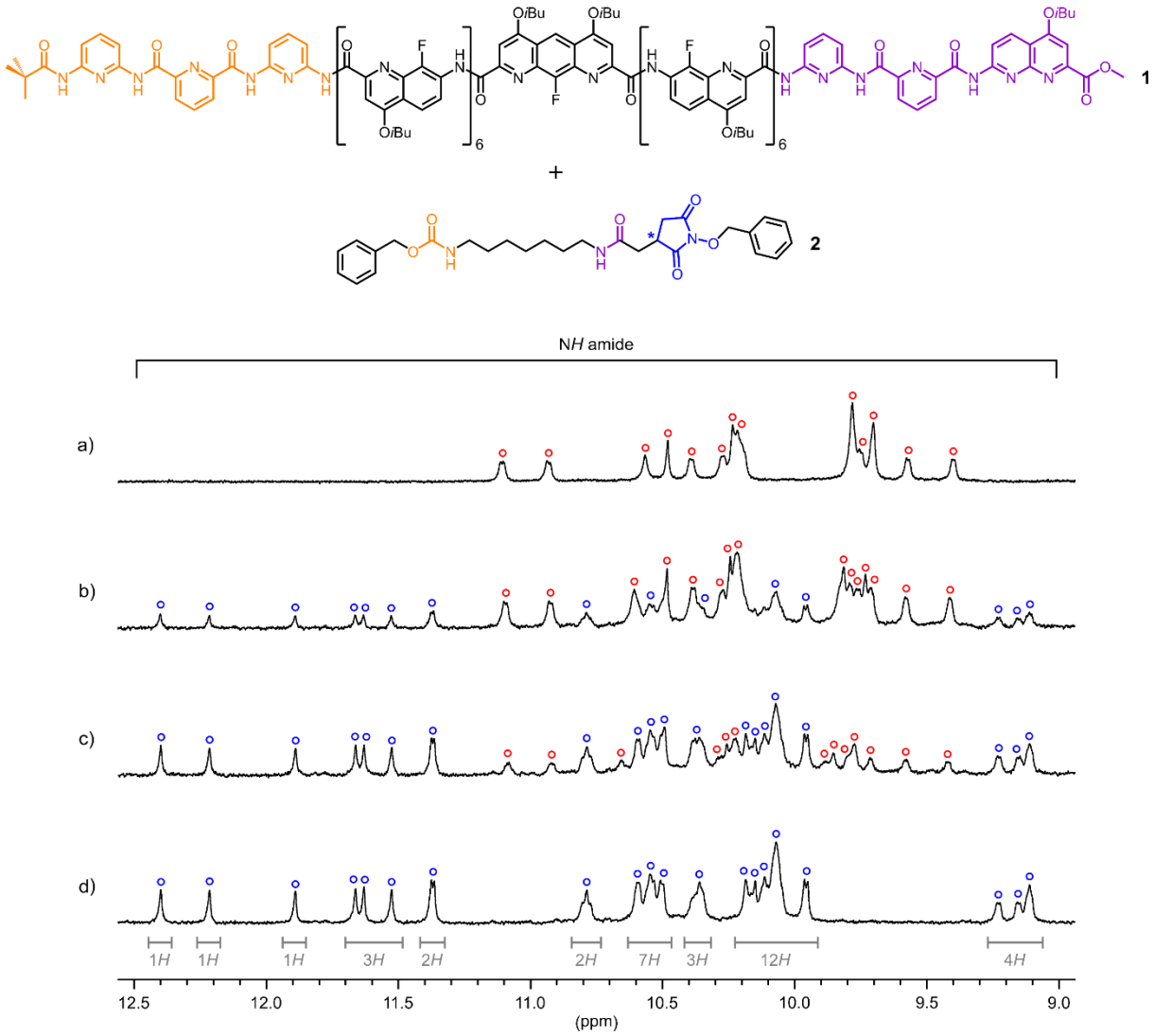


Figure S4. Part of the ^{1}H NMR spectra (300 MHz) of the amide region in $CDCl_3$ at 298 K of the foldamer **1** (1 mM) in the presence of a) 0 equiv., b) 0.5 equiv., c) 1 equiv. and d) 2 equiv. of the rod **2**. Amide signals of the single helix **1** and the foldaxane **1⊃2** are marked with red and blue circles, respectively. Numbers below the last spectrum represent the integration values of the proton resonances of interest. Two diastereomers of the foldaxane **1⊃2** (36 N*H* amides) are present due to an absence of chiral communication between the foldamer helix **1** (axial chirality, P or M) and the chiral rod **2** (racemic mixture, stereocenter marked with a blue star). The apparent association constant K_a, between the foldamer helix **1** and the rod **2**, was measured to be 8 500 (± 300) L.mol^{-1} in $CDCl_3$, based on the integration of amide resonances.

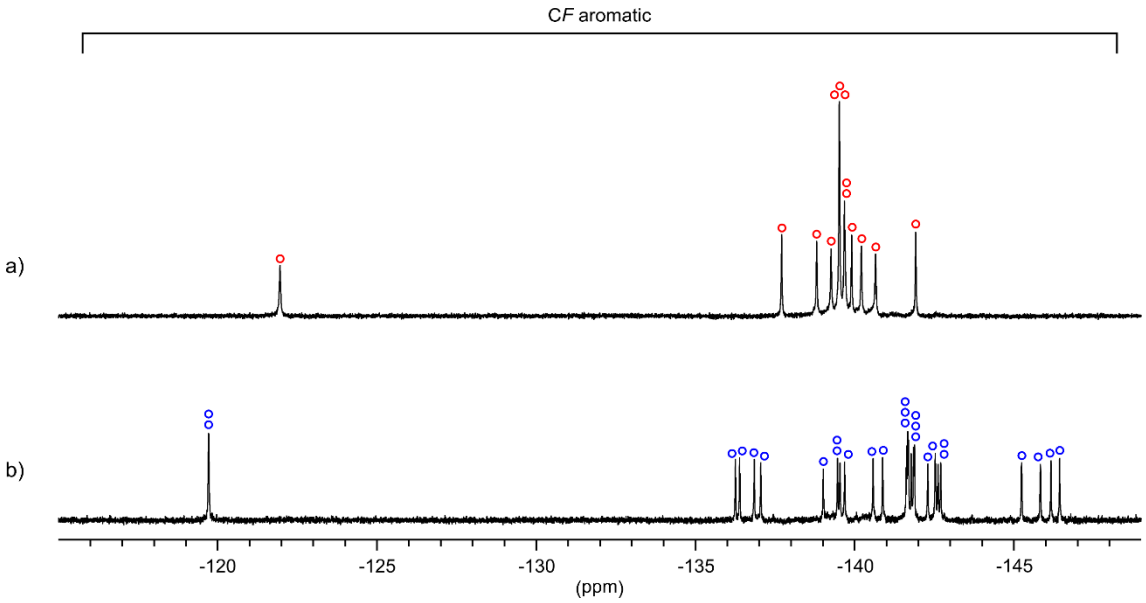


Figure S5. Part of the ^{19}F NMR spectra (282 MHz) of the C*F* aromatic region in $CDCl_3$ at 298 K of a) the foldamer **1** (1 mM) and b) the foldaxane **1⊃2** (1 mM). Fluorine signals of the single helix **1** and the foldaxane **1⊃2** are marked with red and blue circles, respectively. Two diastereomers of the foldaxane **1⊃2** (26 fluorine signals) are present due to an absence of chiral communication between the foldamer helix **1** (axial chirality, P or M) and the chiral rod **2** (racemic mixture). Spectra were calibrated with 2,2,2-trifluoroethanol (external NMR standard, insert tube).

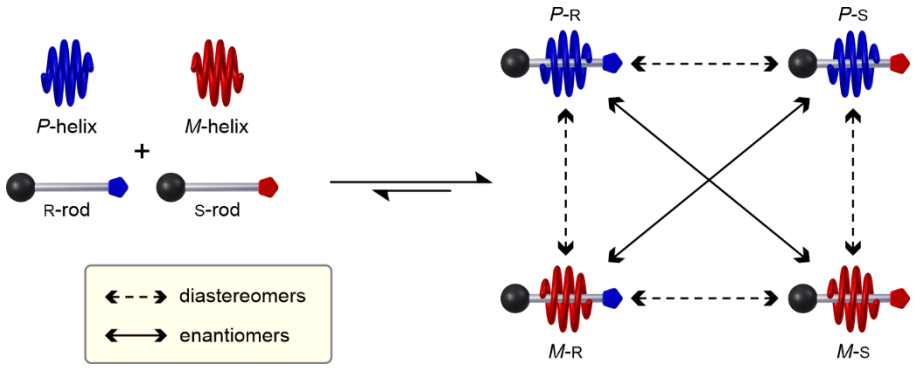


Figure S6. Schematic representation of the winding of a racemic helical foldamer (P and M handedness are denoted in blue and red, respectively) around a racemic mixture of a guest rod (R and S chiral moities are represented in blue and red, respectively). Foldaxane self-assembly proceeds to give both the matching (blue around blue or red around red) and the mismatching (blue around red or red around blue) complexes.

9.3 Self-assembly of the foldarotaxane 1⊃3-Boc

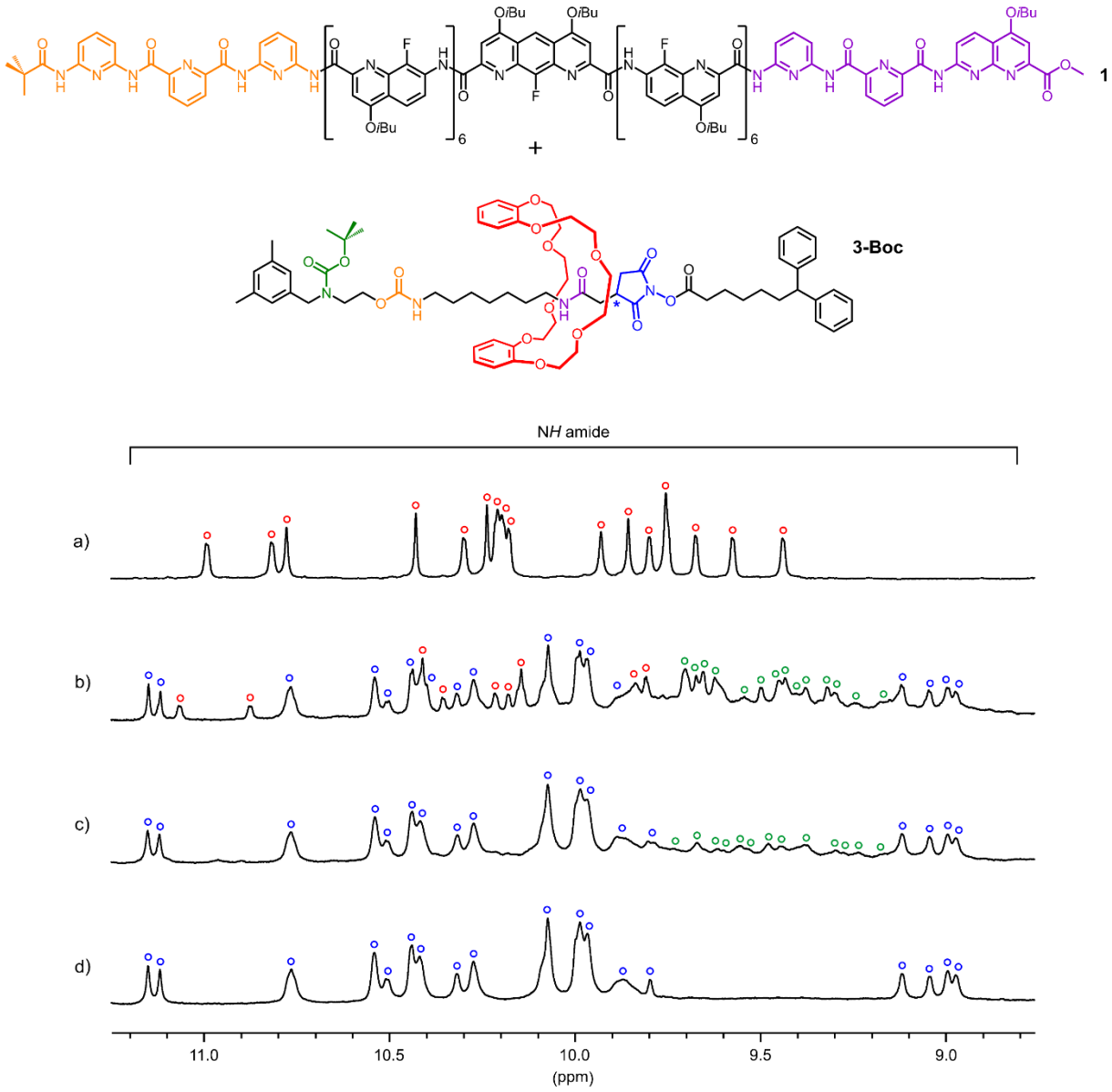


Figure S7. Part of the ^{1}H NMR spectra (700 MHz) of the amide region in $CDCl_3$ at 298 K of a) the foldamer **1** alone (6 mM) and in the presence of the *N*-Boc protected rotaxane **3-Boc** (15 mM) after b) 18 h, c) 3 days and d) 6 days (thermodynamic equilibrium) at high concentrations (24 mM of the foldamer **1** and 60 mM of the *N*-Boc protected rotaxane **3-Boc**) and 328 K. Amide signals of the single helix **1**, the double helix **(1)$_2$** (which can be parallel or anti-parallel) and the foldarotaxane **1⊃3-Boc** are marked with red, green and blue circles, respectively. Two diastereomers of the foldarotaxane **1⊃3-Boc** (36 N*H* amides) are present due to an absence of chiral communication between the foldamer helix **1** (axial chirality, P or M) and the chiral rotaxane **3-Boc** (racemic mixture, stereocenter marked with a blue star). The association constant was not measured due to a complex equilibrium.

9.4 Aminolysis of the foldarotaxane 1⊃3-Boc

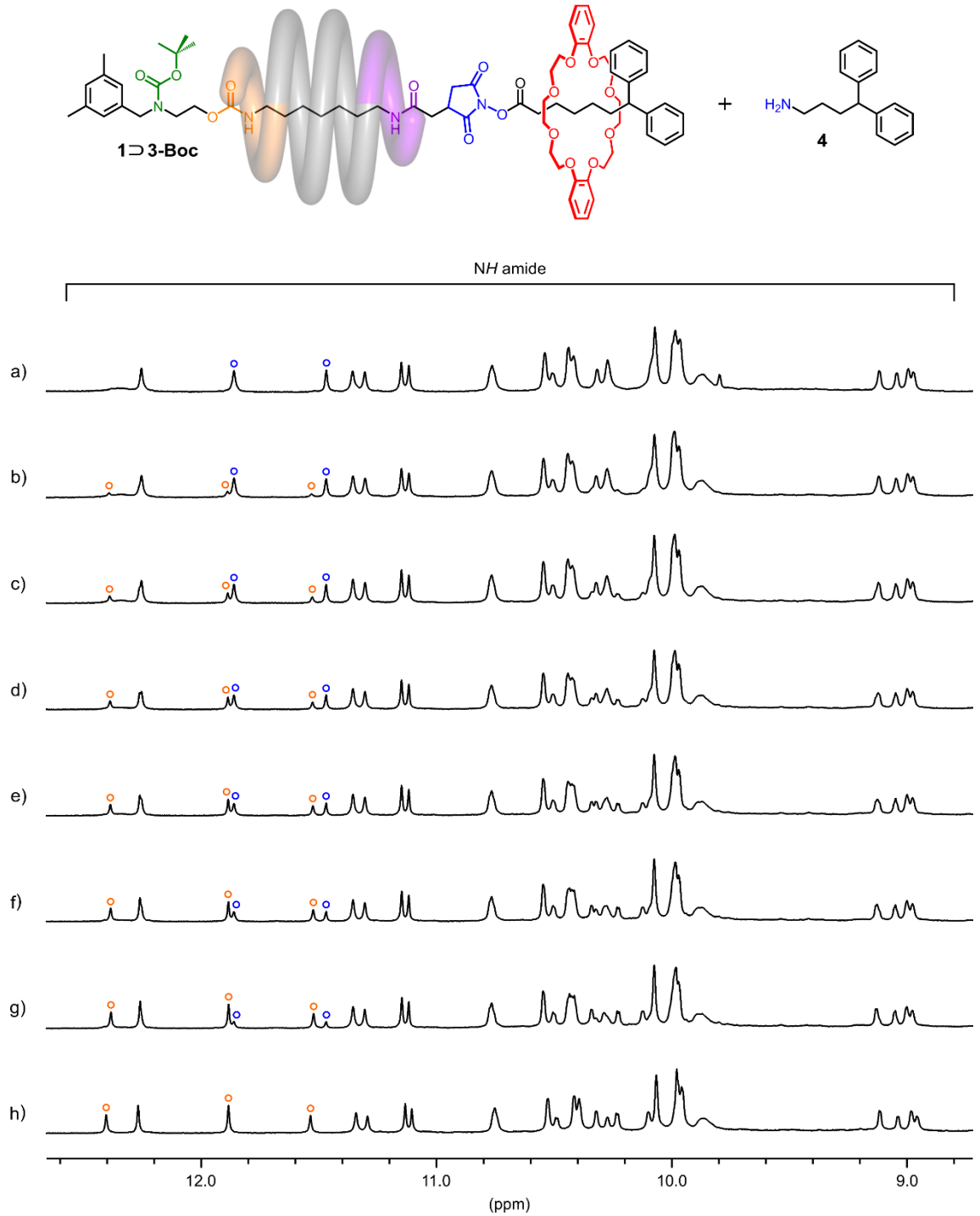


Figure S8. Part of the ^{1}H NMR spectra (700 MHz) of the amide region in $CDCl_3$ at 298 K of a) the foldarotaxane **1⊃3-Boc** (6 mM) in the presence of the amine stopper **4** (16.5 mM) after b) 30 min, c) 1 h, d) 2 h, e) 3 h 30 min, f) 5 h, g) 10 h and h) 18 h. Amide signals of the foldarotaxane **1⊃3-Boc** and the foldaxane **1⊃5-Boc** are marked with blue and orange circles, respectively. For both complexes (**1⊃3-Boc** and **1⊃5-Boc**), two diastereomers (36 N*H* amides) are present due to an absence of chiral communication between the foldamer helix and the chiral guest.

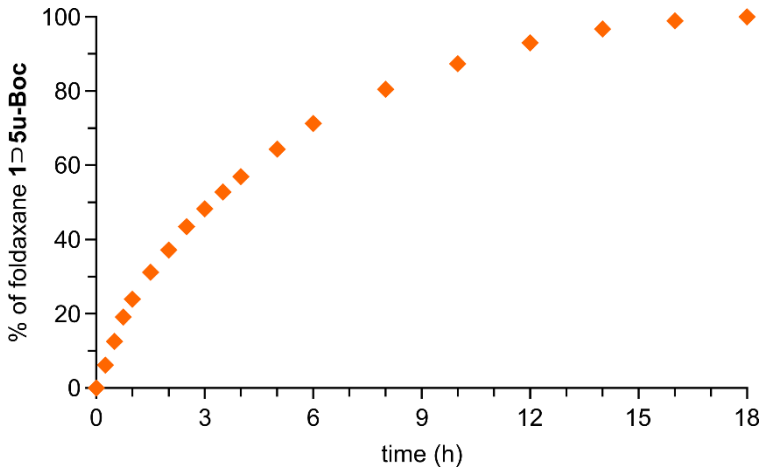


Figure S9. Time trace of the formation of the foldaxane by-product **1⊃5u-Boc** after the addition of the amine stopper **4** (16.5 mM) to a solution of the foldarotaxane **1⊃3-Boc** in $CDCl_3$ (6 mM), monitored by ^1H NMR spectroscopy (700 MHz, 298 K). The aminolysis of the complex **1⊃3-Boc** is quantitative after 18 h at 298 K.

9.5 Purification and characterizations of the contracted rotaxane 6

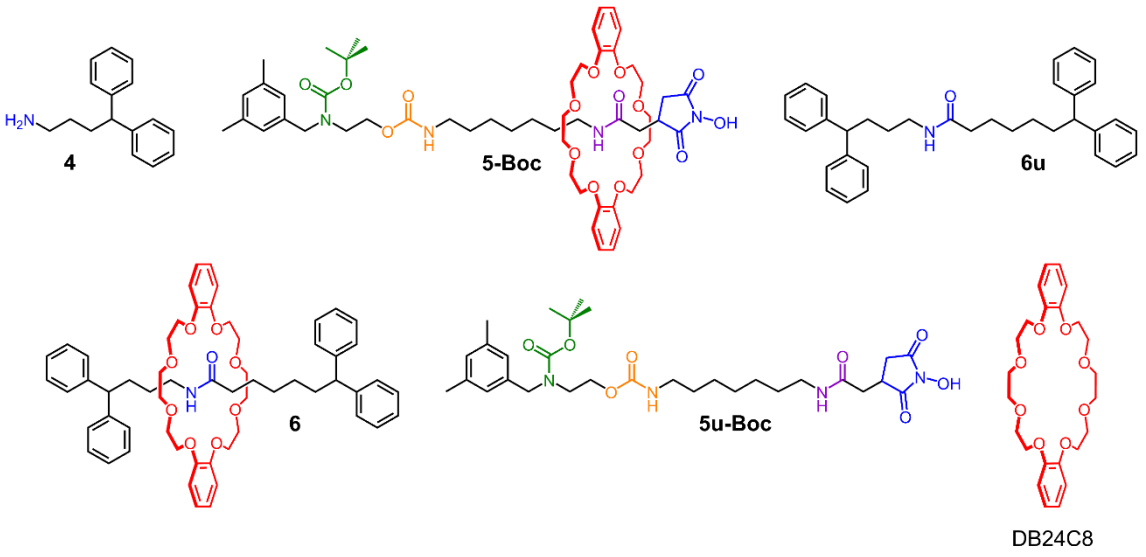


Figure S10. Formulas of expected components after the aminolysis of the foldarotaxane **1⊃3-Boc** at the exception of the foldaxane **1⊃5u-Boc**: the excess of the amine stopper **4**, the pseudorotaxane **5-Boc** and the dumbbell rod **6u** from the aminolysis of the excess of the rotaxane **3-Boc**, the target contracted rotaxane **6** and the unthreaded axle **5u-Boc** and the free macrocycle DB24C8 from the possible dissociation of the pseudorotaxane **5-Boc**.

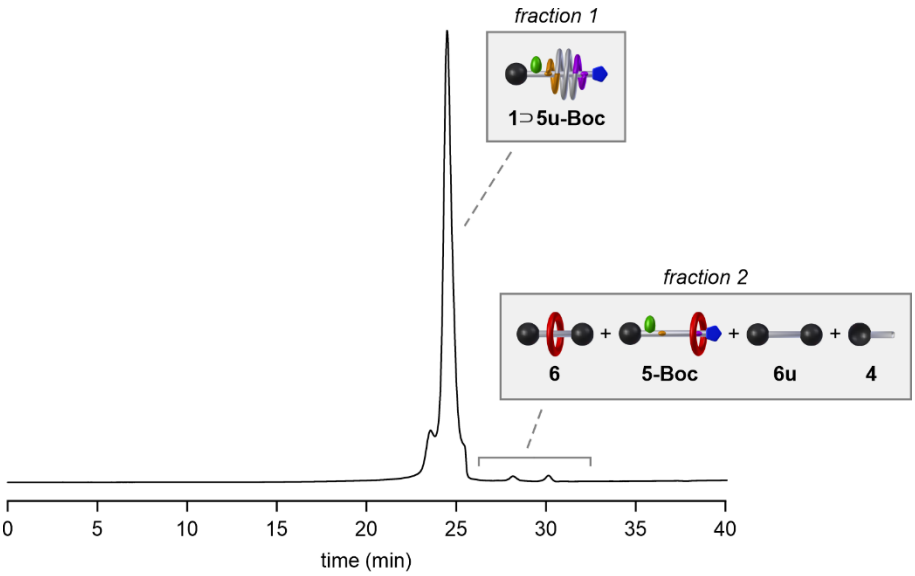


Figure S11. Preparative recycling Gel Permeation Chromatography (GPC) profil of the mixture after the cleavage of the foldarotaxane **1⊃3-Boc** performed in the purpose to remove the foldaxane by-product **1⊃5u-Boc**. Conditions for the GPC: JAIGEL 20*600 mm columns with a mobile phase composed of 1 % (vol / vol) EtOH and 0.5 % (vol / vol) NEt_3 in $CHCl_3$ at a flow rate of 10 $mL.min^{-1}$, monitored by UV detector at 254 nm.

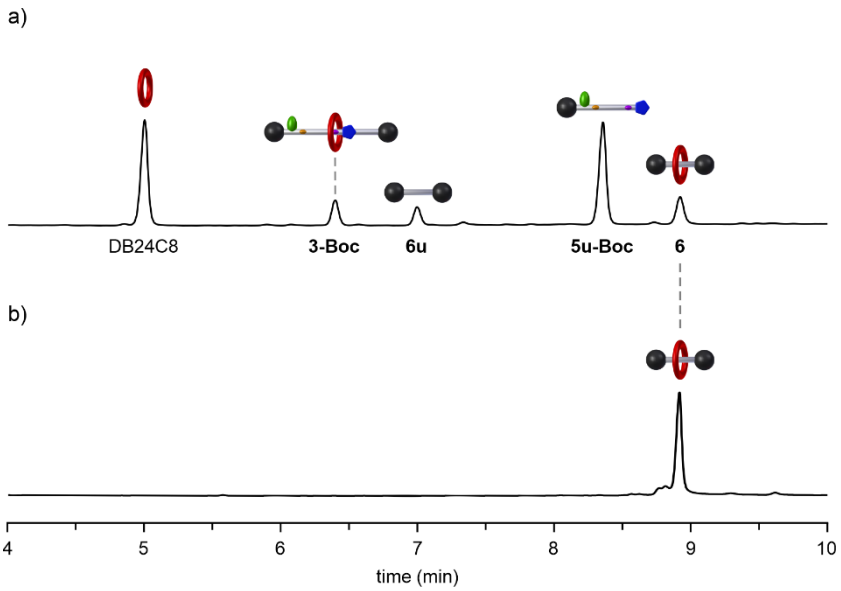


Figure S12. HPLC chromatograms of a) the fraction 2 collected from the GPC and b) the pure contracted rotaxane **6** obtained after silica gel chromatography. The target rotaxane **6** was isolated with 87 % yield and 93 % purity. Conditions for the HPLC: C8 column, H_2O + 0.1 % TFA / MeCN + 0.1 % TFA - 60:40 to 0:100, 293 K, 254 nm.

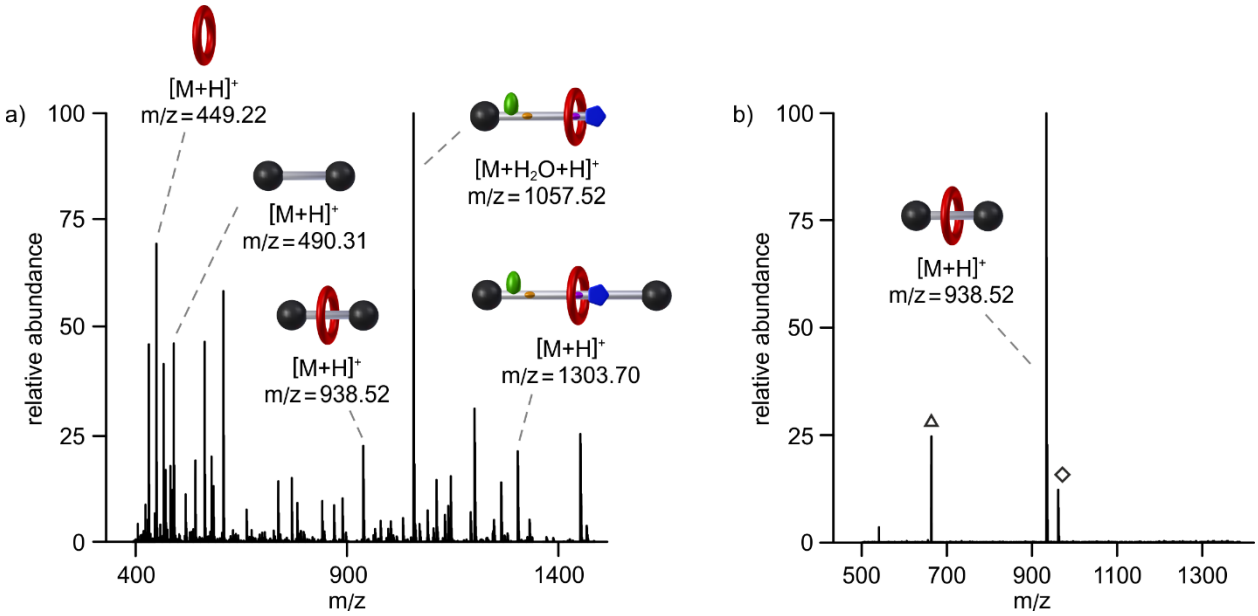


Figure S13. Electrospray ionization mass spectra (ESI-MS) of a) the fraction 2 collected from the GPC and b) the pure contracted rotaxane **6** obtained after silica gel chromatography. The triangle and the diamond denote an artefact of the mass spectrometer and an undetermined m/z value of [**6** + 28], respectively.

10. Solid state studies and molecular modeling

10.1 Mode of binding P_3⊃carbamate and P_2N⊃amide

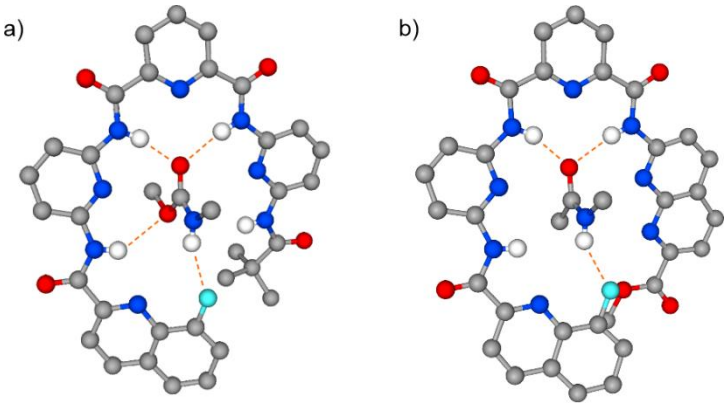


Figure S14. Parts of the crystal structure of the foldaxane **1⊃2** showing the mode of binding between a) the P_3 trimer of the helix **1** and the carbamate function of the rod **2** and b) the P_2N trimer of the helix **1** and the amide function of the rod **2**. Intermolecular hydrogen bonds are denoted with orange dashed lines.

10.2 Crystal structure of the foldaxane 1⊃2

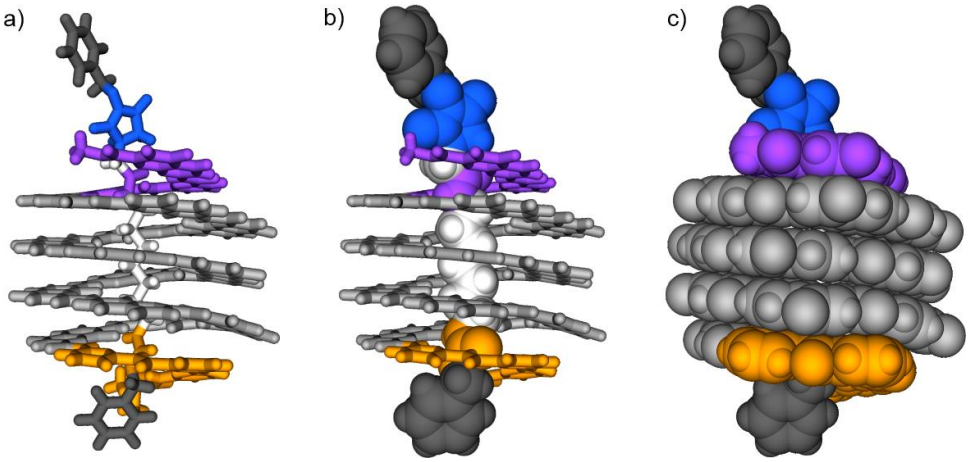


Figure S15. Crystal structure of the foldaxane **1⊃2** a) in stick representation, b) with the rod in CPK representation and the foldamer helix in stick representation and c) in CPK representation. Binding motifs P_3⊃carbamate, P_2N⊃amide and the NHS moiety are colored in orange, purple and blue, respectively. Isobutoxy side chains of the helix and included solvent molecules have been removed for clarity.

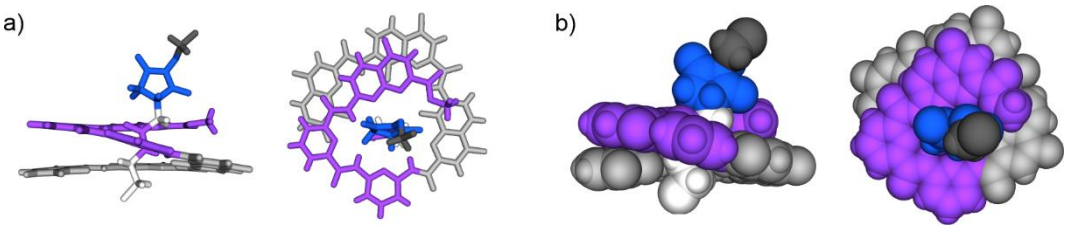


Figure S16. Part of the crystal structure of the foldaxane **1⊃2** showing the side view (left) and the top view (right) of a zoom around the NHS moiety of the complex **1⊃2** a) in stick representation and b) in CPK representation.

10.3 Optimized structure of the foldarotaxane 1⊃3-Boc

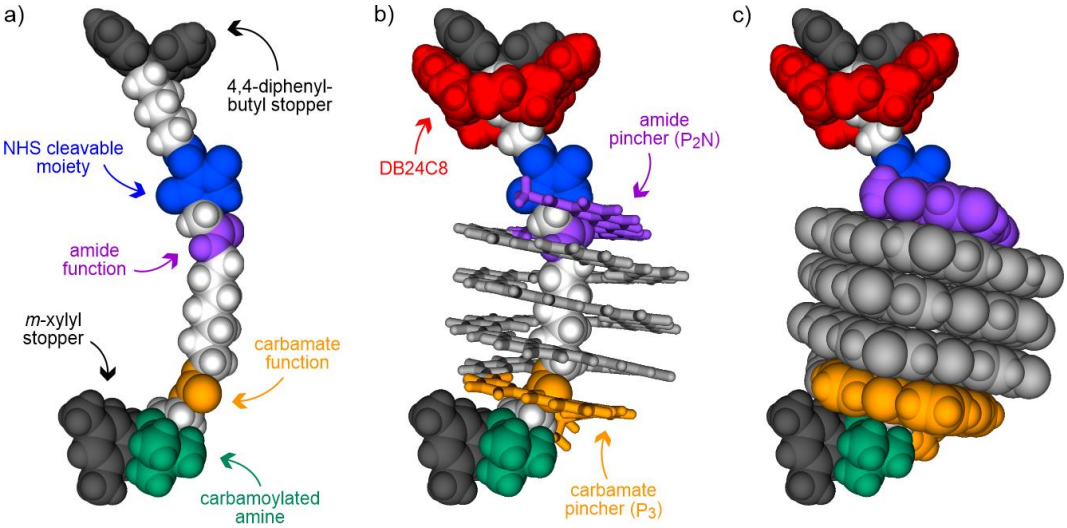


Figure S17. Optimized structure (MMFFs) of a) the molecular axle of the foldarotaxane **1⊃3-Boc** in CPK representation and the foldarotaxane **1⊃3-Boc** b) with the molecular axle in CPK representation and the foldamer helix in stick representation and c) in CPK representation. Isobutoxy side chains of the helix have been removed for clarity.

10.4 Optimized structure of the contracted rotaxane 6

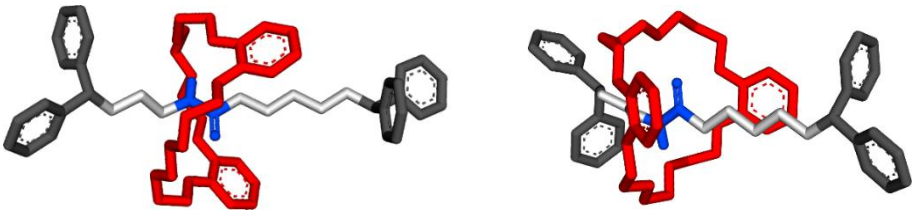


Figure S18. Different views of the optimized structure (MMFFs) of the contracted rotaxane **6** in stick representation. The amide fonction of the rod is represented in blue and non-polar hydrogen atoms have been removed for clarity.

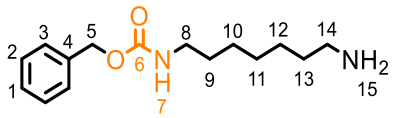
10.5 X-ray data of the foldaxane 1⊃2

Table 1: Crystal data and structure refinement for **1⊃2**.

CCDC	2175298
Empirical formula	$C_{267}H_{259}F_{13}N_{42}O_{42}$
Formula weight	4975.15
Temperature/K	135
Crystal system	orthorhombic
Space group	Pbca
a/Å	28.3005(4)
b/Å	47.5333(10)
c/Å	51.9586(7)
α/°	90.0
β/°	90.0
γ/°	90.0
Volume/Å^3	69896(2)
Z	8
ρcalcg/cm^3	0.946
μ/mm^{-1}	0.580
F(000)	20864.0
Crystal size/mm^3	0.08 × 0.05 × 0.05
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	4.012 to 102.76
Index ranges	$-26 \leq h \leq 28$, $-48 \leq k \leq 46$, $-47 \leq l \leq 52$
Reflections collected	160074
Independent reflections	37609 [R_{int} = 0.0503, R_{sigma} = 0.0463]
Data/restraints/parameters	37609/198/3320
Goodness-of-fit on F^2	1.159
Final R indexes [I>=2σ (I)]	R1 = 0.0953, wR2 = 0.2948
Final R indexes [all data]	R1 = 0.1333, wR2 = 0.3297

11. NMR Spectra

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



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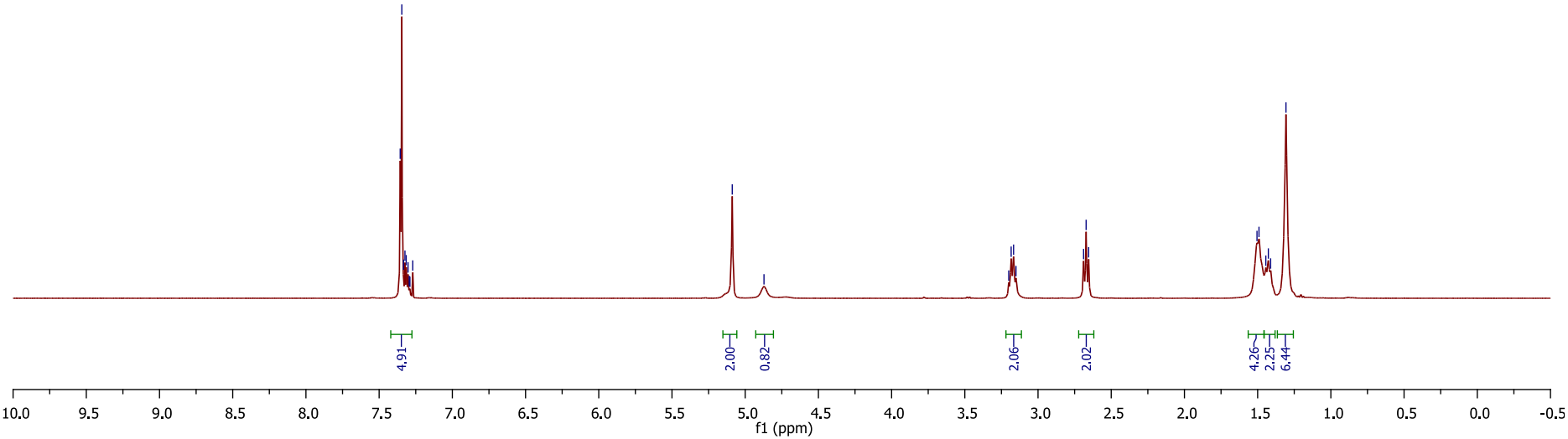
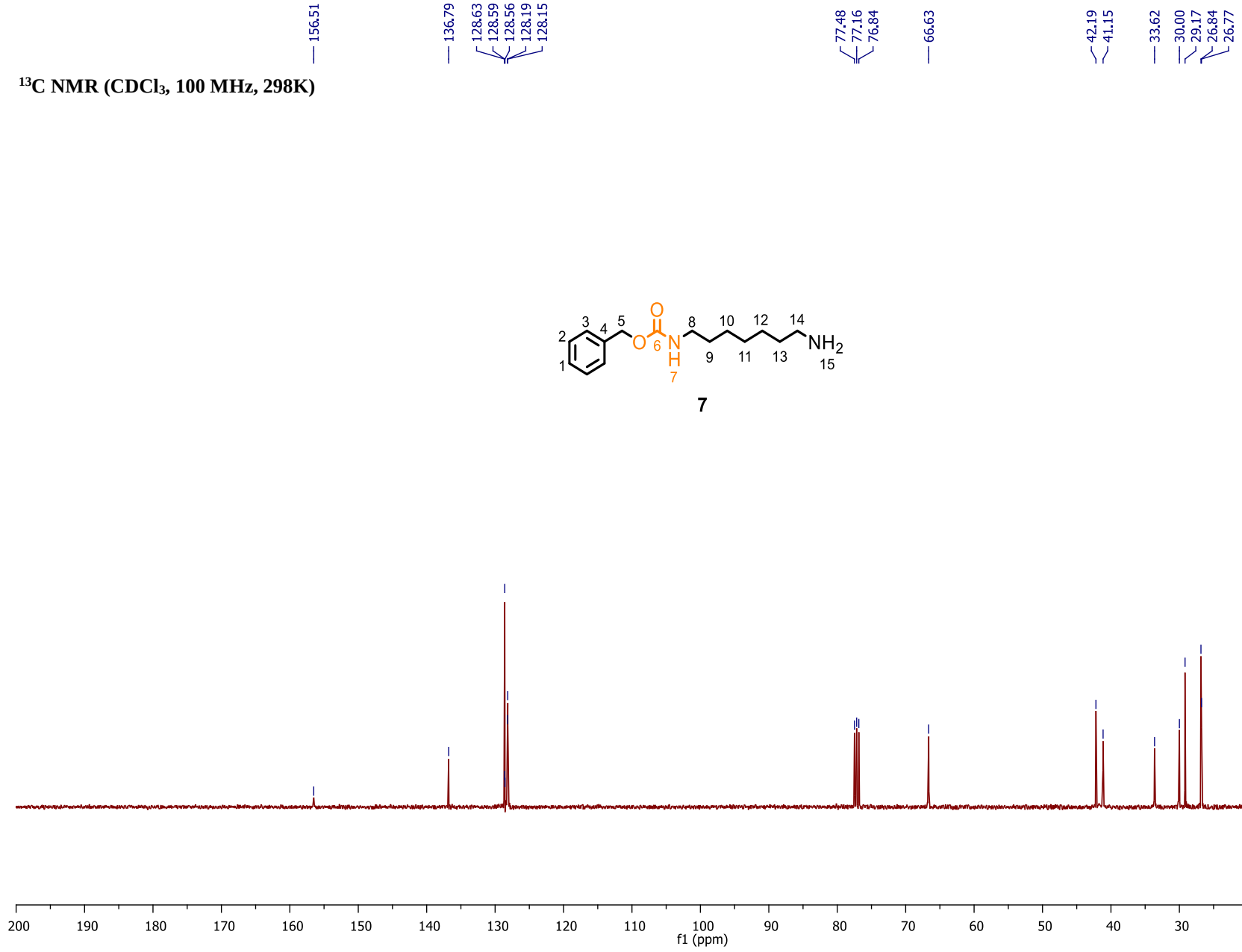


^{13}C NMR ($CDCl_3$, 100 MHz, 298K)



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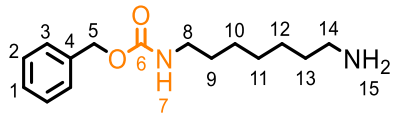
2D-COSY ^{1}H NMR ($CDCl_3$, 400 MHz, 298K)



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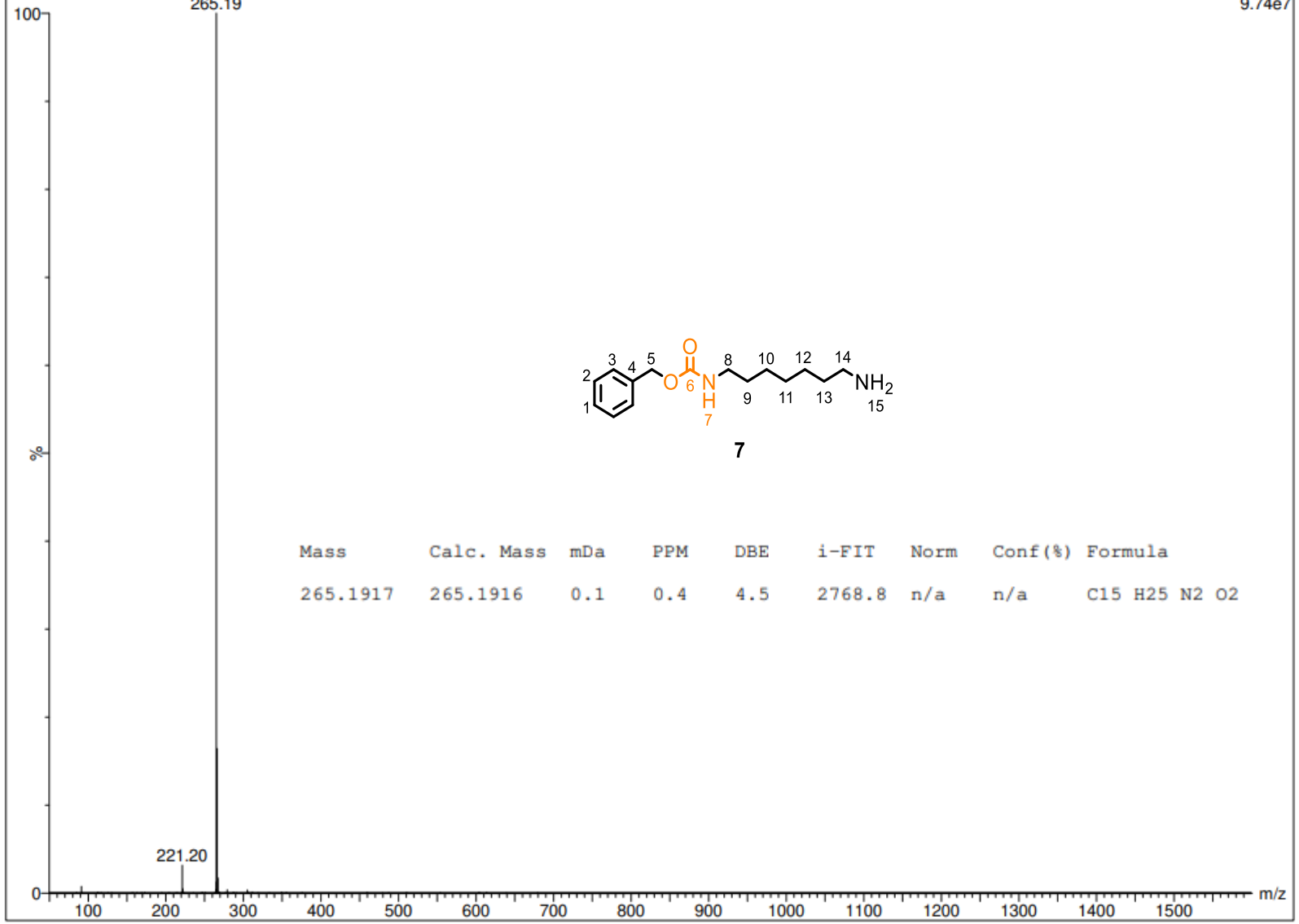
2D-HSQC ^{13}C NMR ($CDCl_3$, 400 MHz, 298K)

SYNAPT G2-S#UEB205 MXG-ANR-42 11-Apr-2019

Y-SMART19041102 5 (0.228) Cm (5:7) 1: TOF MS ES+

9.74e7



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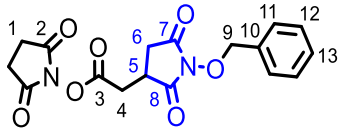
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
265.1917	265.1916	0.1	0.4	4.5	2768.8	n/a	n/a	C15 H25 N2 O2

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



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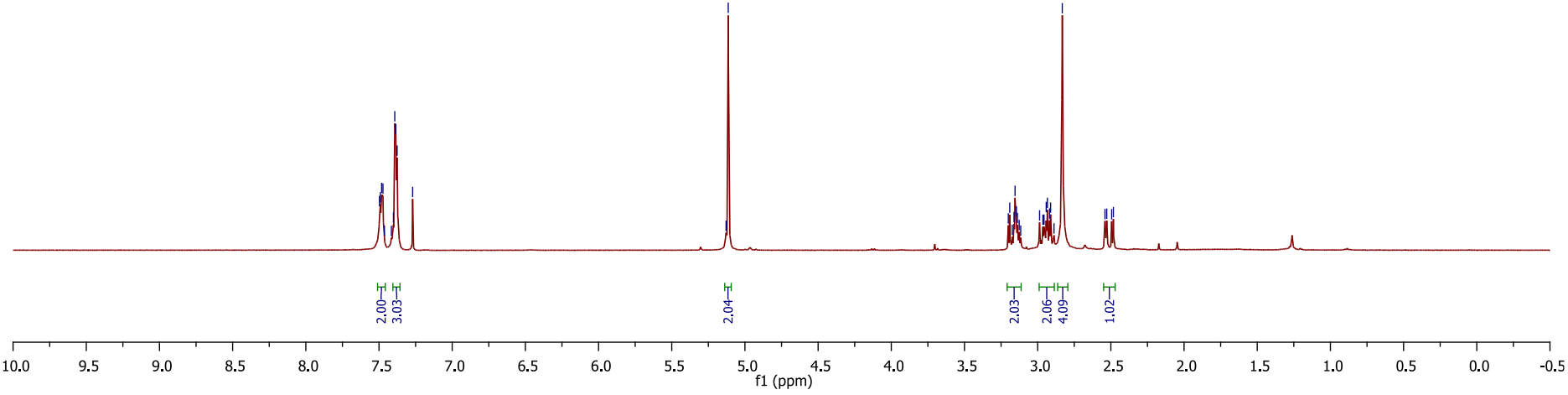
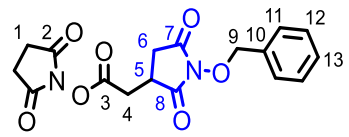


171.64
169.67
168.71
166.38
133.30
130.12
129.63
128.69
78.87
77.48
77.16
76.84
33.40
31.82
31.47
25.66

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



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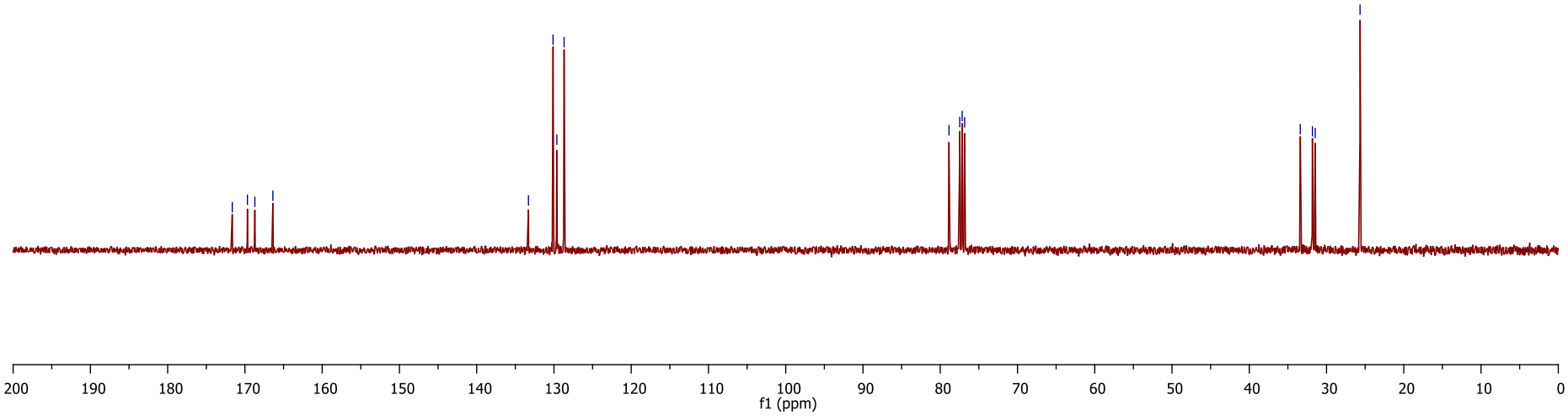

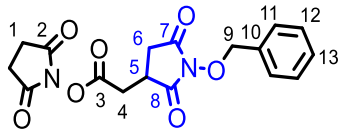

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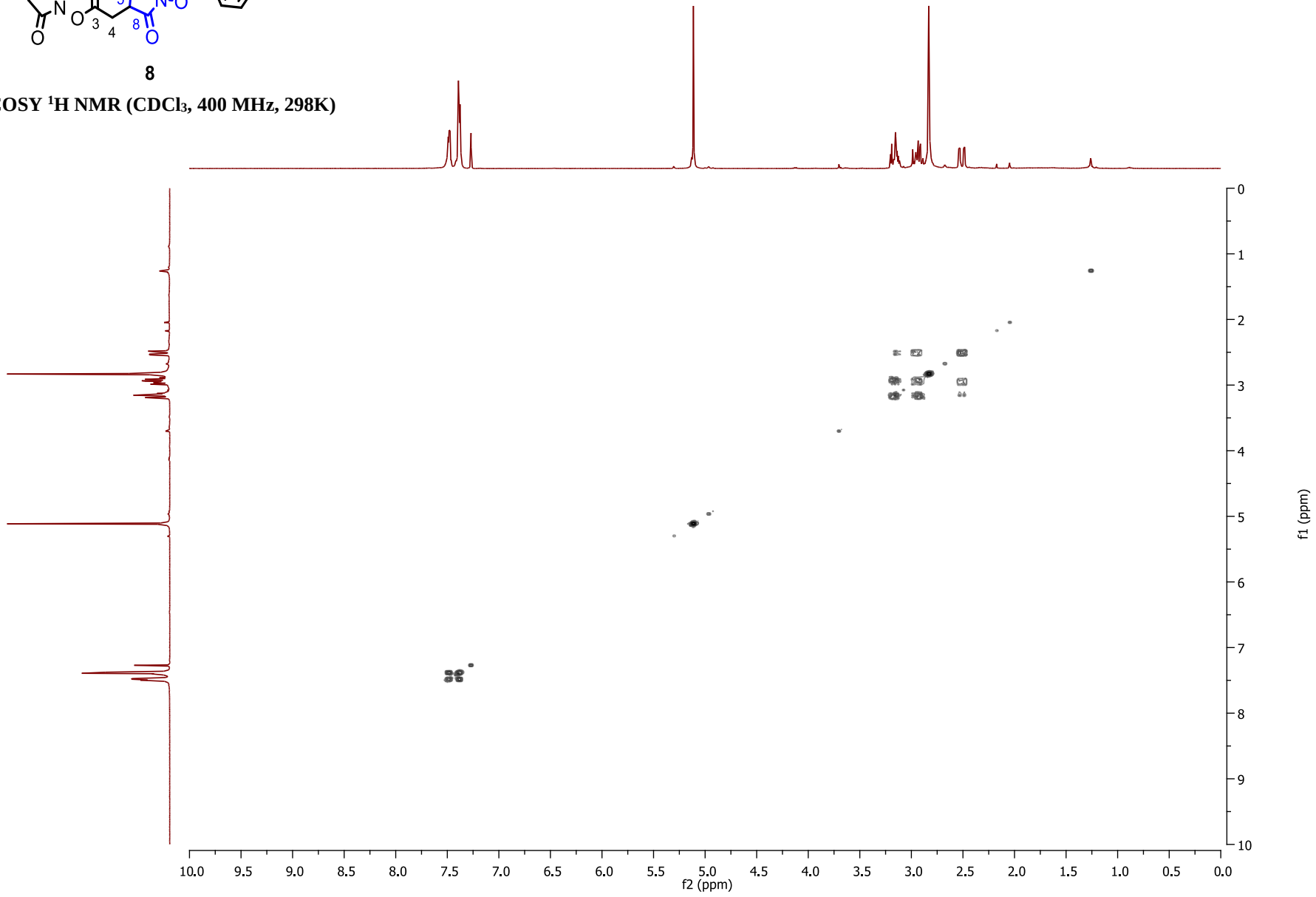
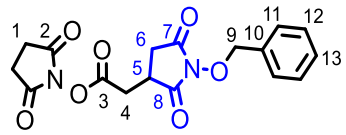
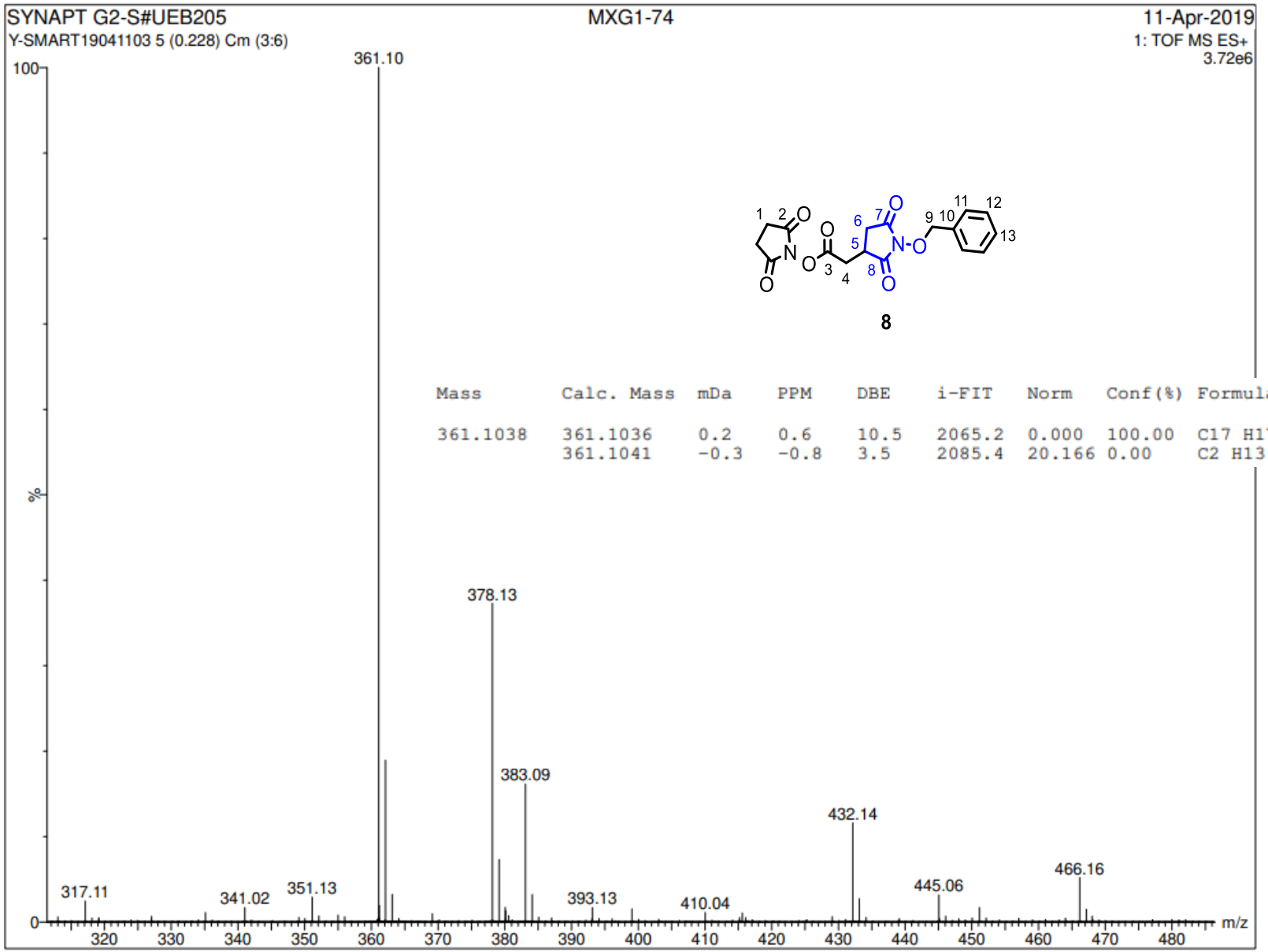
2D-COSY ^{1}H NMR ($CDCl_3$, 400 MHz, 298K)





8

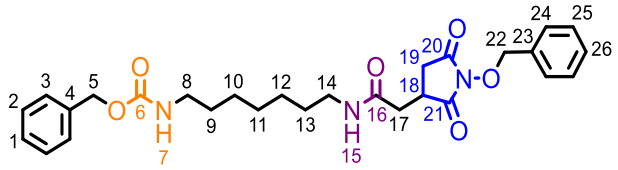
2D-HSQC ^{13}C NMR ($CDCl_3$, 400 MHz, 298K)



8

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
361.1038	361.1036	0.2	0.6	10.5	2065.2	0.000	100.00	C17 H17 N2 O7
	361.1041	-0.3	-0.8	3.5	2085.4	20.166	0.00	C2 H13 N14 O8

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



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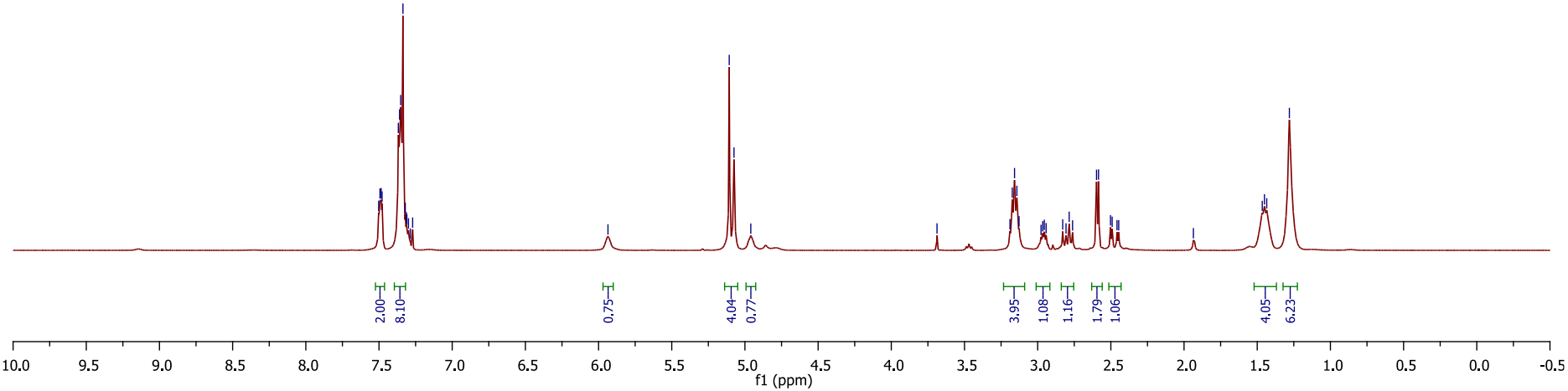
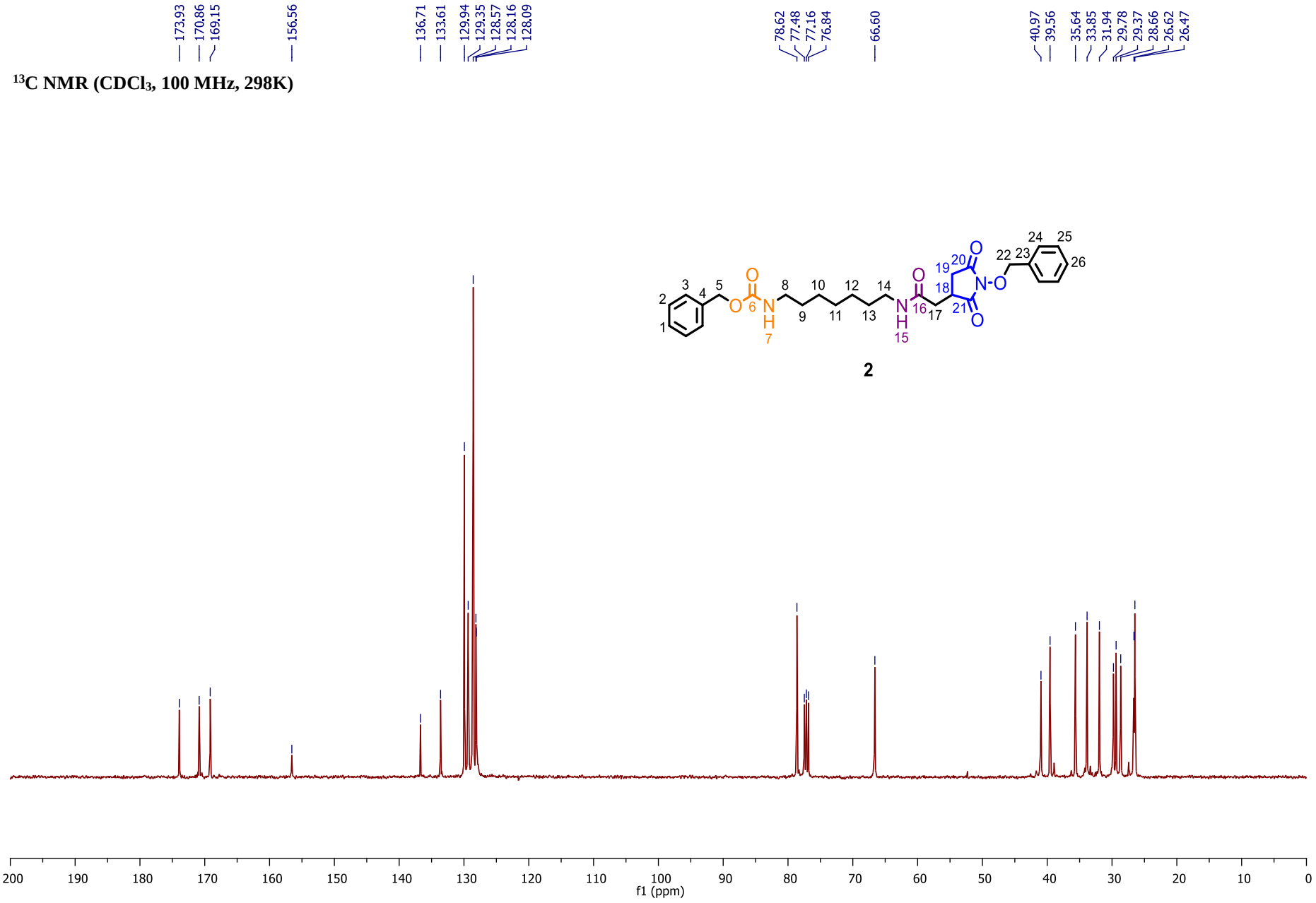
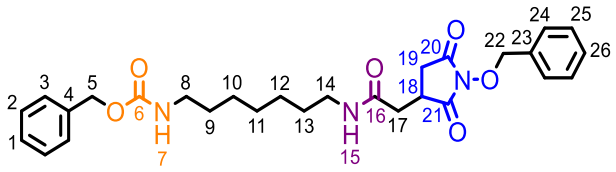


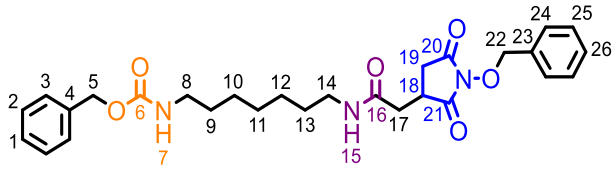
^{13}C NMR ($CDCl_3$, 100 MHz, 298K)





2

2D-COSY ^{1}H NMR ($CDCl_3$, 400 MHz, 298K)



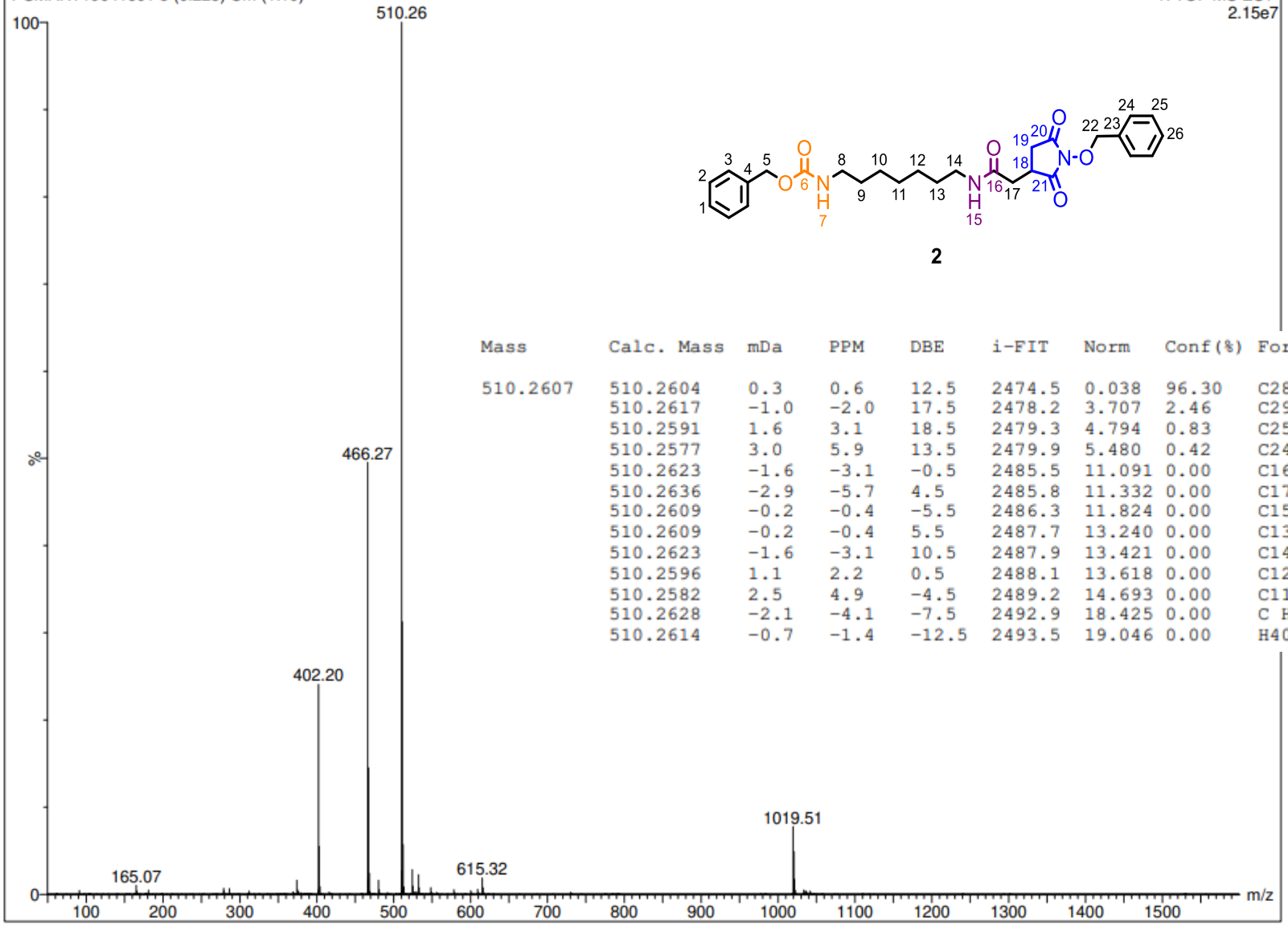
2

2D-HSQC ^{13}C NMR ($CDCl_3$, 400 MHz, 298K)

SYNAPT G2-S#UEB205 MXG-ANR-45 16-Apr-2019

Y-SMART19041601 5 (0.228) Cm (1:10) 1: TOF MS ES+

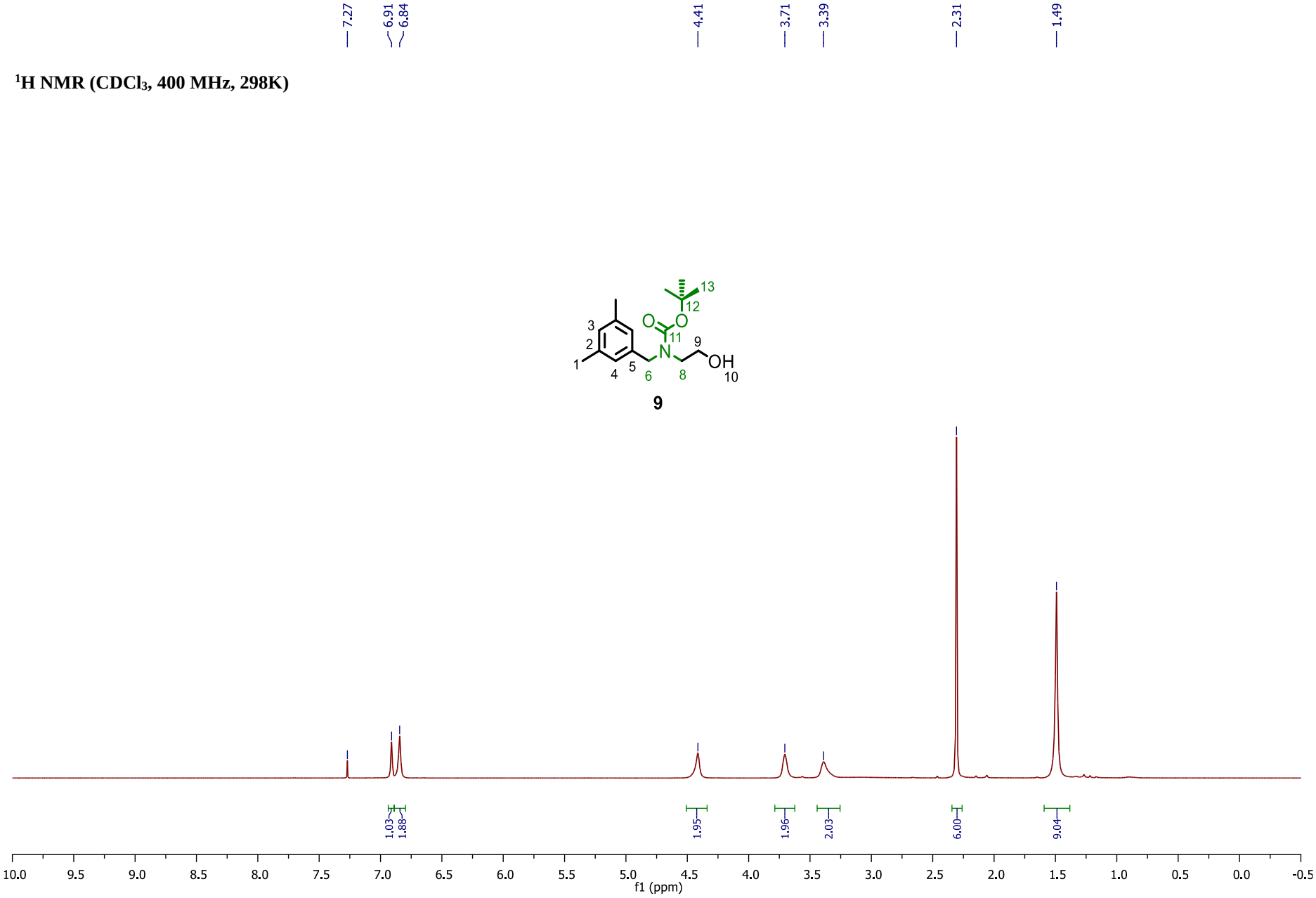
2.15e7



2

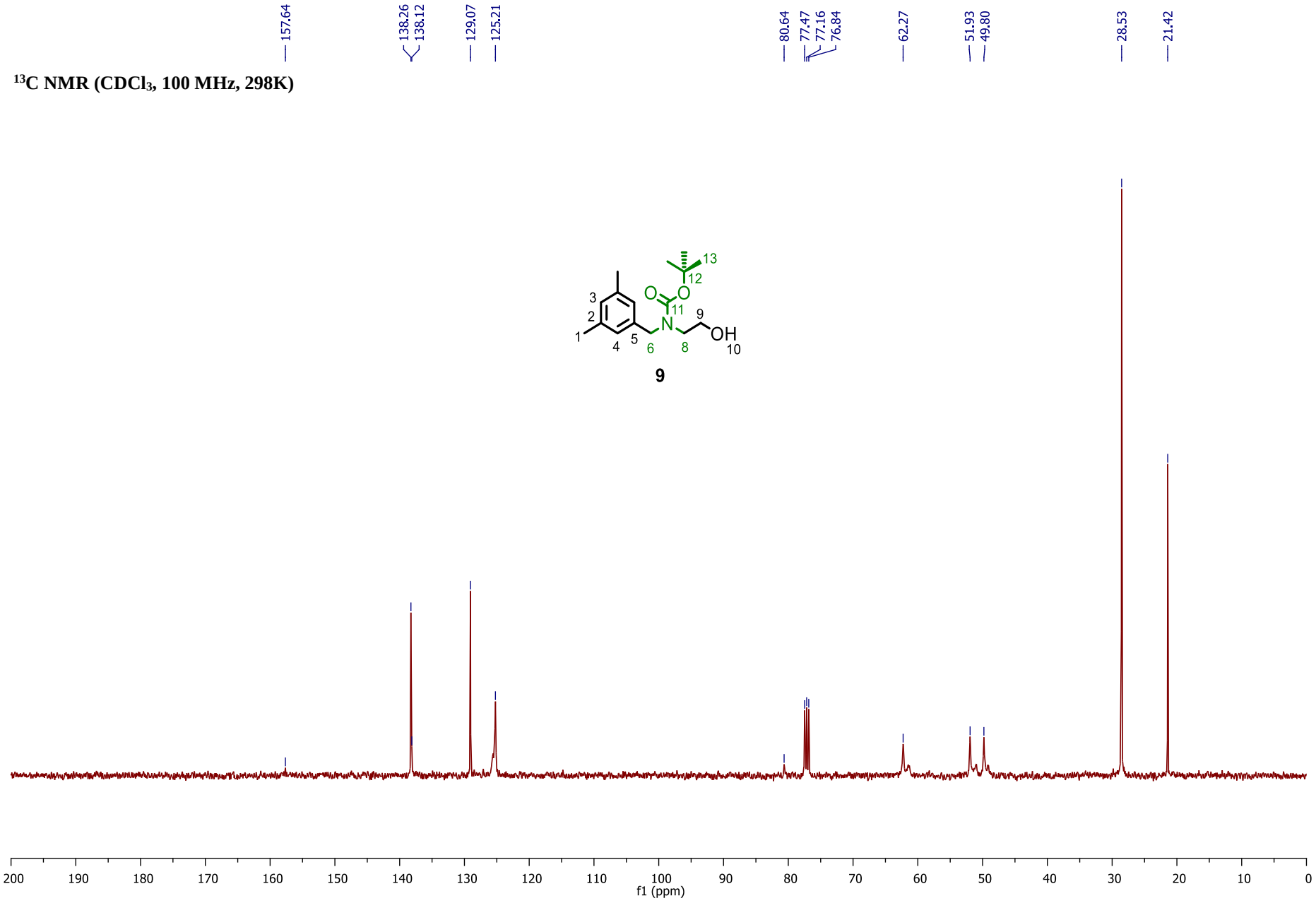
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
510.2607	510.2604	0.3	0.6	12.5	2474.5	0.038	96.30	C28 H36 N3 O6
	510.2617	-1.0	-2.0	17.5	2478.2	3.707	2.46	C29 H32 N7 O2
	510.2591	1.6	3.1	18.5	2479.3	4.794	0.83	C25 H28 N13
	510.2577	3.0	5.9	13.5	2479.9	5.480	0.42	C24 H32 N9 O4
	510.2623	-1.6	-3.1	-0.5	2485.5	11.091	0.00	C16 H40 N5 O13
	510.2636	-2.9	-5.7	4.5	2485.8	11.332	0.00	C17 H36 N9 O9
	510.2609	-0.2	-0.4	-5.5	2486.3	11.824	0.00	C15 H44 N O17
	510.2609	-0.2	-0.4	5.5	2487.7	13.240	0.00	C13 H32 N15 O7
	510.2623	-1.6	-3.1	10.5	2487.9	13.421	0.00	C14 H28 N19 O3
	510.2596	1.1	2.2	0.5	2488.1	13.618	0.00	C12 H36 N11 O11
	510.2582	2.5	4.9	-4.5	2489.2	14.693	0.00	C11 H40 N7 O15
	510.2628	-2.1	-4.1	-7.5	2492.9	18.425	0.00	C H36 N17 O14
	510.2614	-0.7	-1.4	-12.5	2493.5	19.046	0.00	H40 N13 O18

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

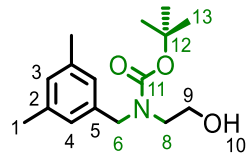


9

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

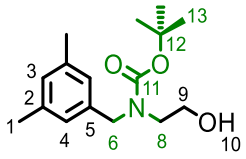


9



9

2D-COSY ^{1}H NMR ($CDCl_3$, 400 MHz, 298K)



9

2D-HSQC ^{13}C NMR ($CDCl_3$, 400 MHz, 298K)

Analysis Info

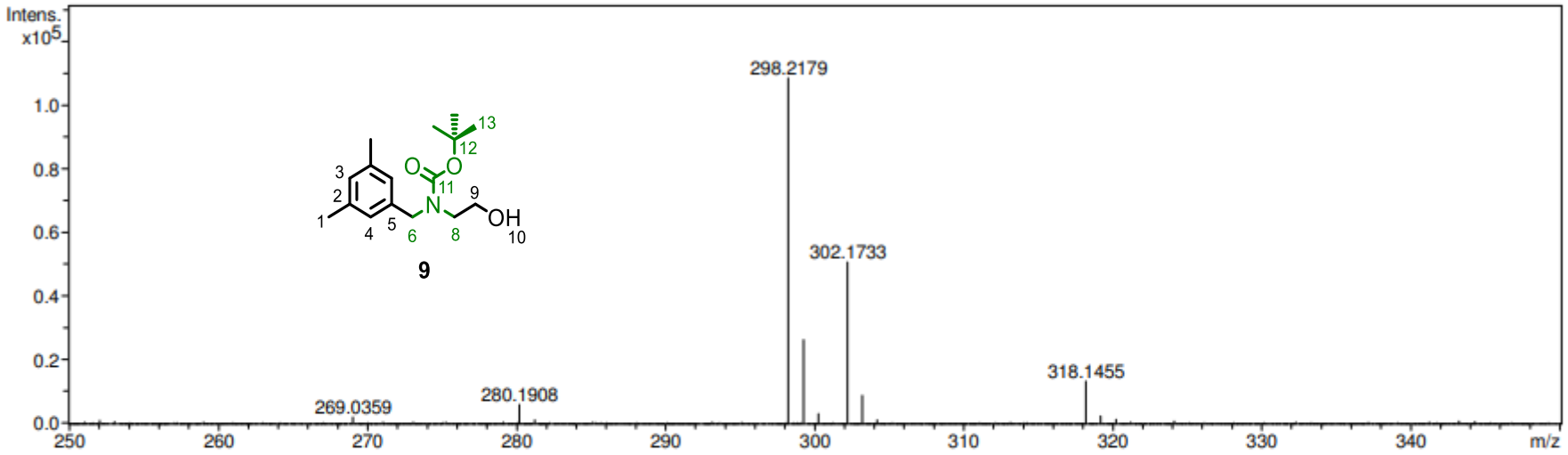
Sample Name **MXG-ANR-87**

Acquisition Date 7/11/2019 1:45:44 PM

Instrument / Ser# micrOTOF-Q II 10300

Acquisition Parameter

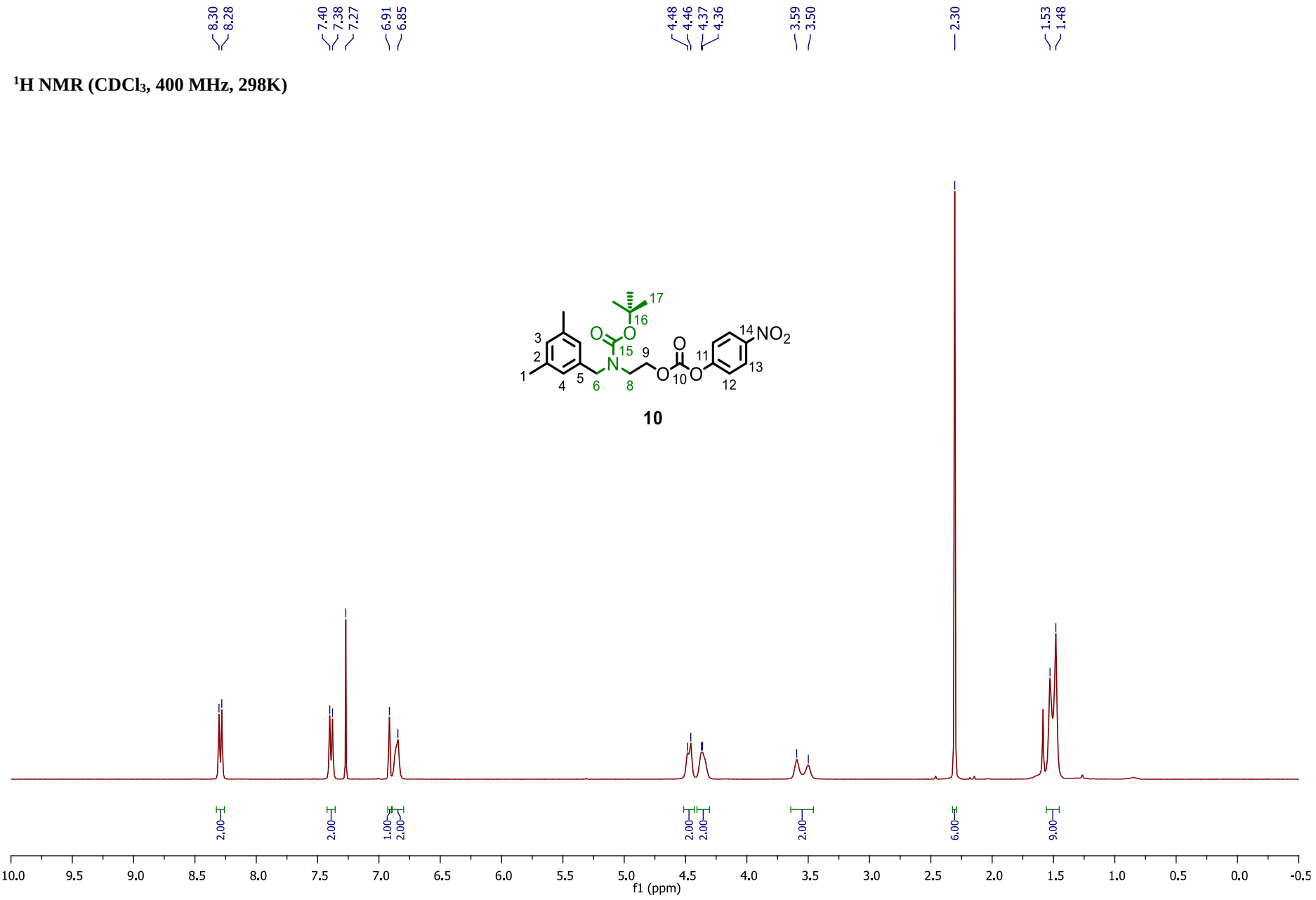
Source Type ESI | Ion Polarity Positive | Scan Begin 50 m/z | Scan End 2200 m/z



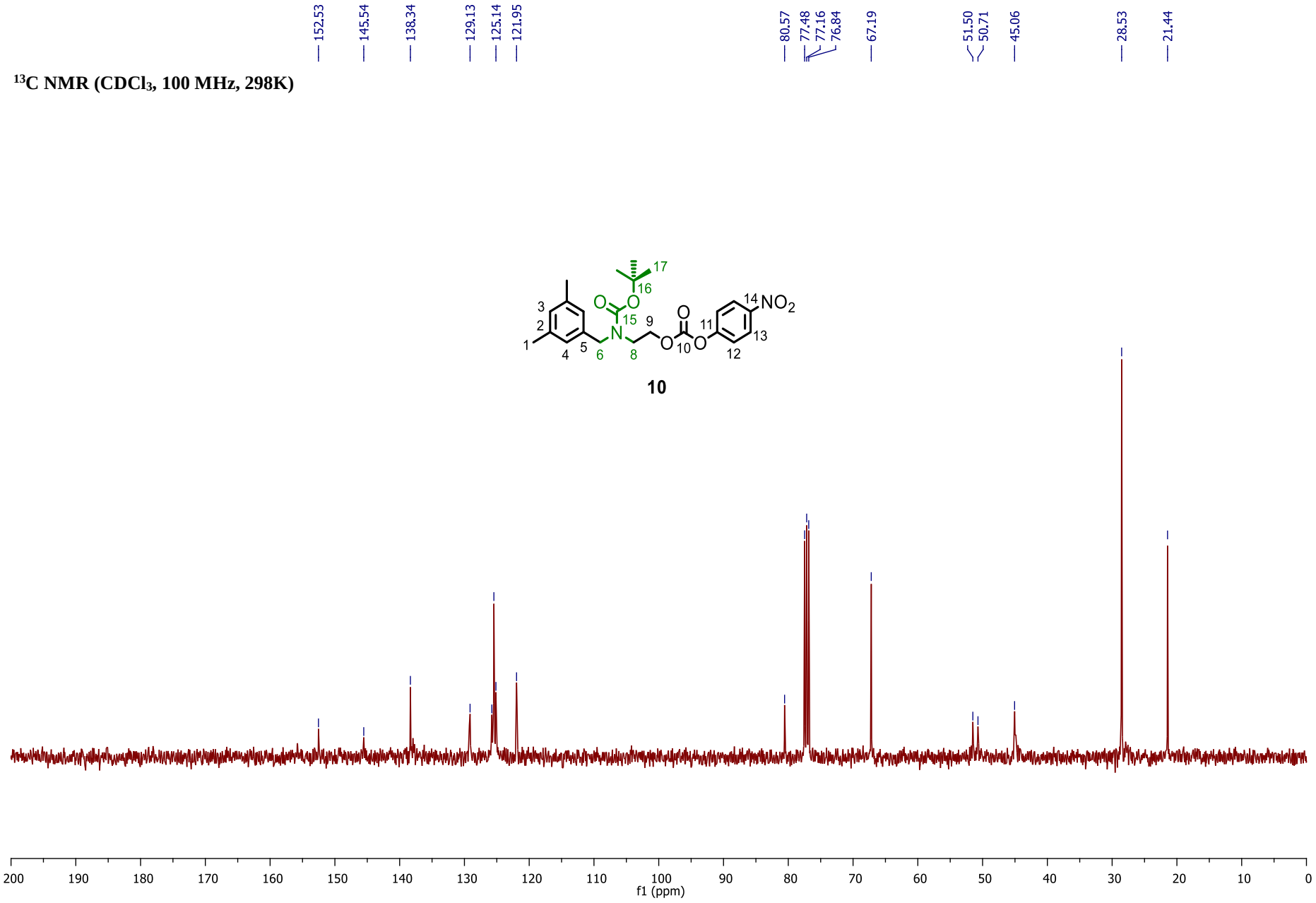
9

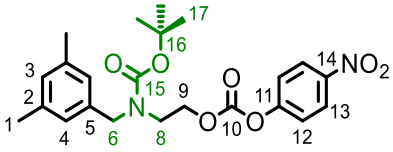
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	rdb	e⁻ Conf	N-Rule
280.1908	1	C 16 H 26 N O 3	100.00	280.1907	-0.0	-0.1	4.5	even	ok
302.1733	1	C 16 H 25 N Na O 3	100.00	302.1727	-0.6	-2.1	4.5	even	ok

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



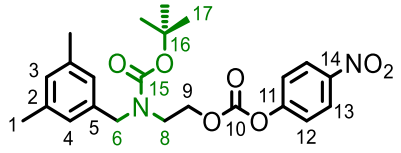
^{13}C NMR ($CDCl_3$, 100 MHz, 298K)





10

2D-COSY ^{1}H NMR ($CDCl_3$, 400 MHz, 298K)



10

2D-HSQC ^{13}C NMR ($CDCl_3$, 400 MHz, 298K)

Analysis Info

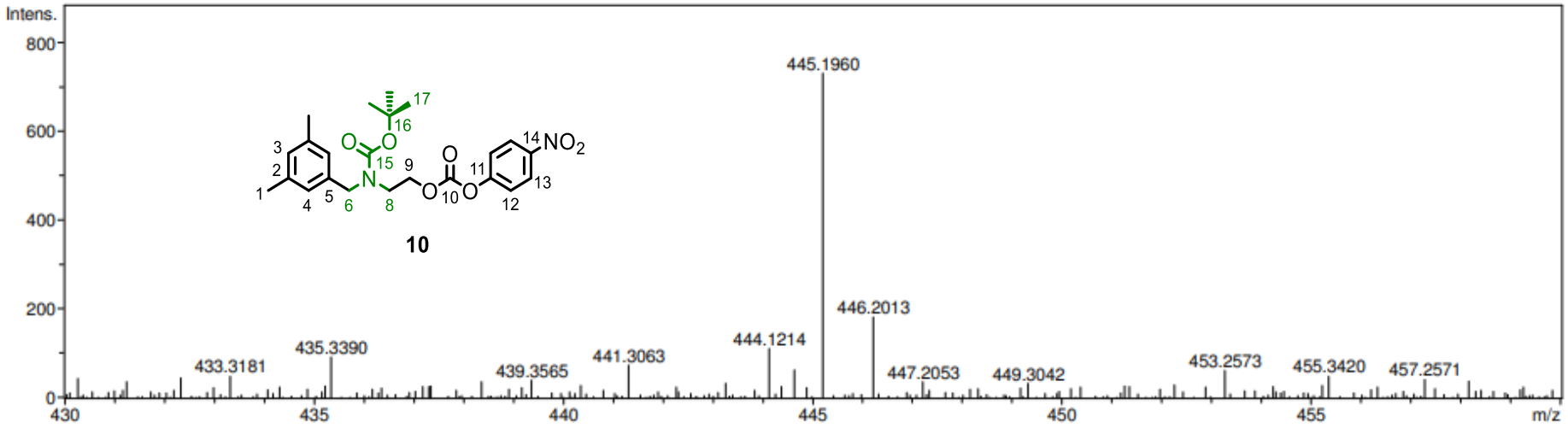
Sample Name **MXG-ANR-90**

Acquisition Date 7/18/2019 3:05:45 PM

Instrument / Ser# micrOTOF-Q II 10300

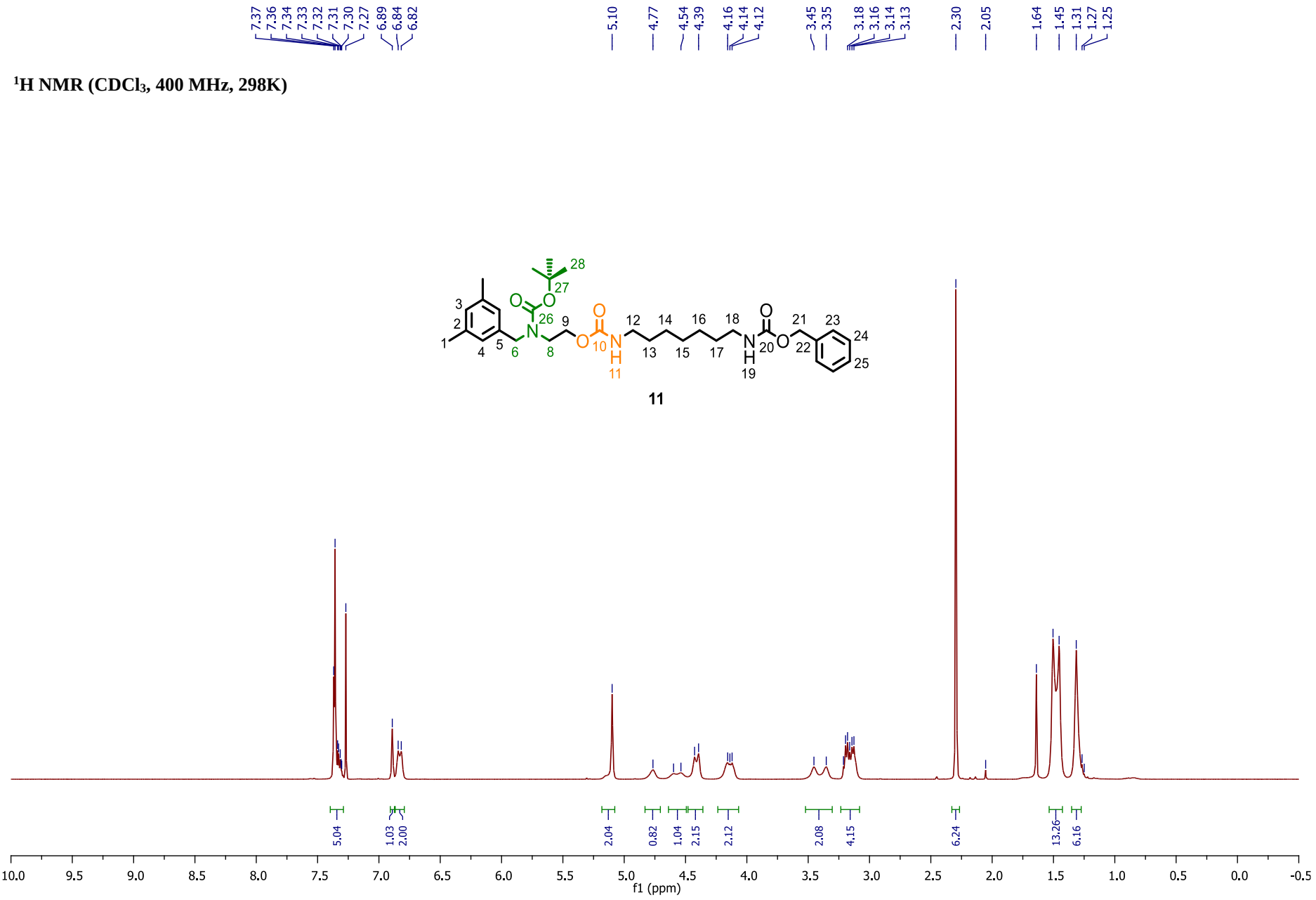
Acquisition Parameter

Source Type ESI | Ion Polarity Positive | Scan Begin 50 m/z | Scan End 2200 m/z

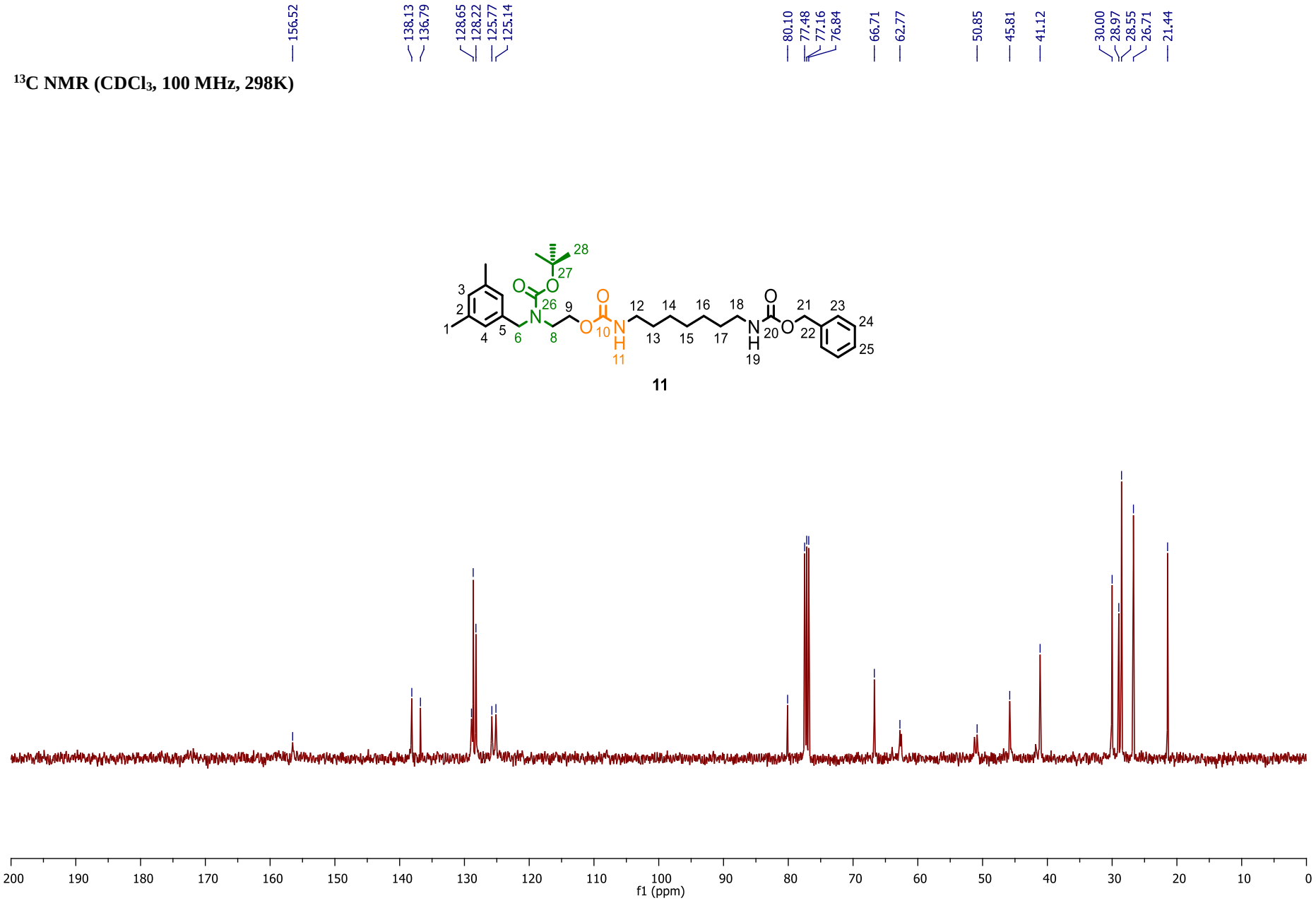


Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	rdb	e⁻ Conf	N-Rule
445.1960	1	C 23 H 29 N 2 O 7	88.22	445.1969	0.9	2.1	10.5	even	ok
	2	C 19 H 25 N 8 O 5	46.54	445.1942	-1.8	-3.9	11.5	even	ok
	3	C 20 H 21 N 12 O	100.00	445.1956	-0.4	-0.9	16.5	even	ok
	4	C 35 H 25	18.19	445.1951	-0.9	-2.1	23.5	even	ok

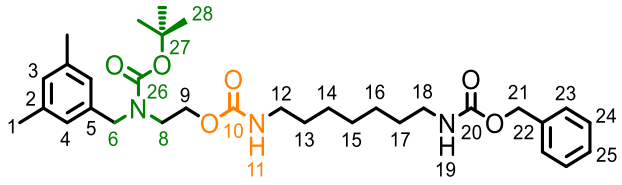
^{1}H NMR ($CDCl_3$, 400 MHz, 298K)



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

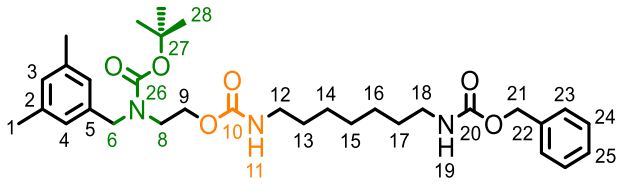


11



11

2D-COSY ^{1}H NMR ($CDCl_3$, 400 MHz, 298K)



11

2D-HSQC ^{13}C NMR ($CDCl_3$, 400 MHz, 298K)

Analysis Info

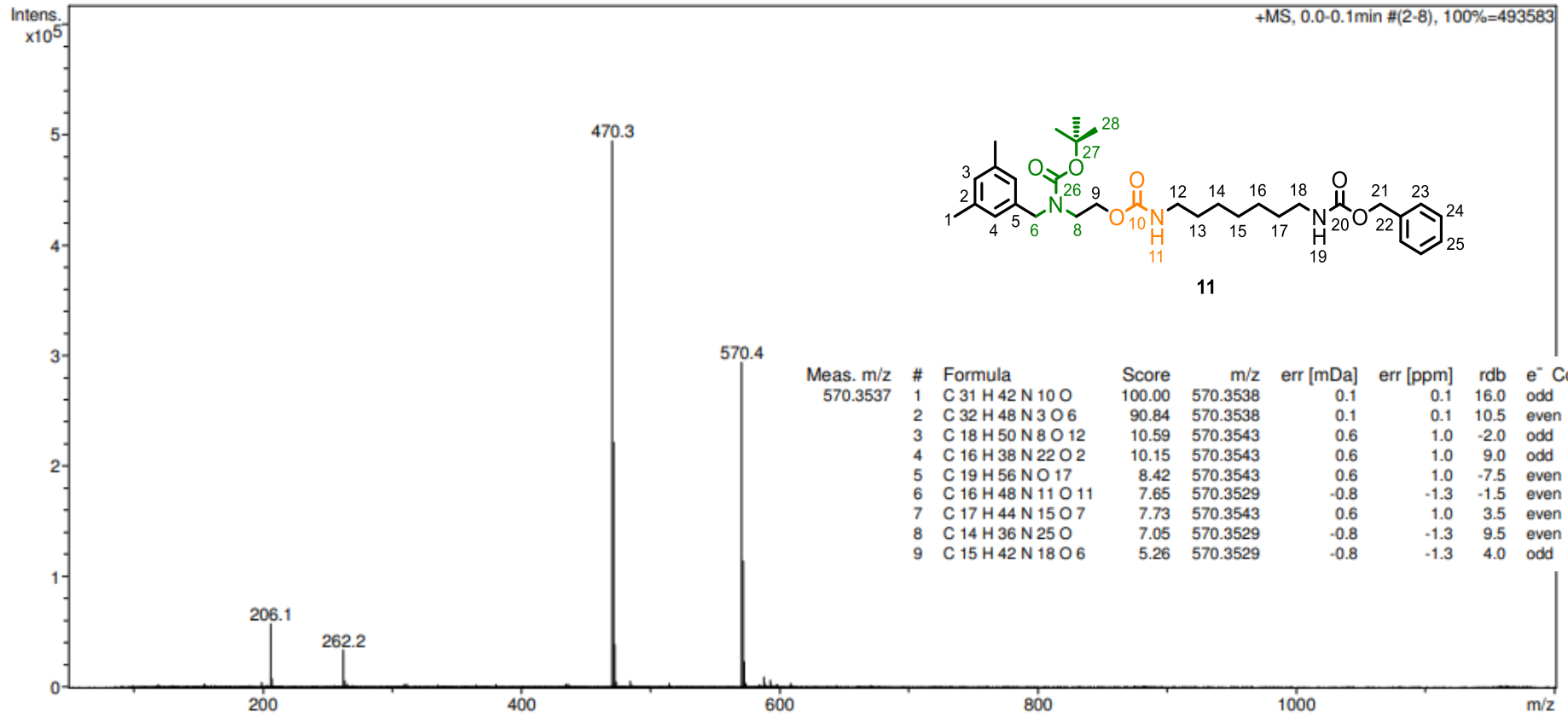
Sample Name **MXG-ANR-99**

Acquisition Date 7/22/2019 6:50:33 PM

Instrument / Ser# micrOTOF-Q II 10300

Acquisition Parameter

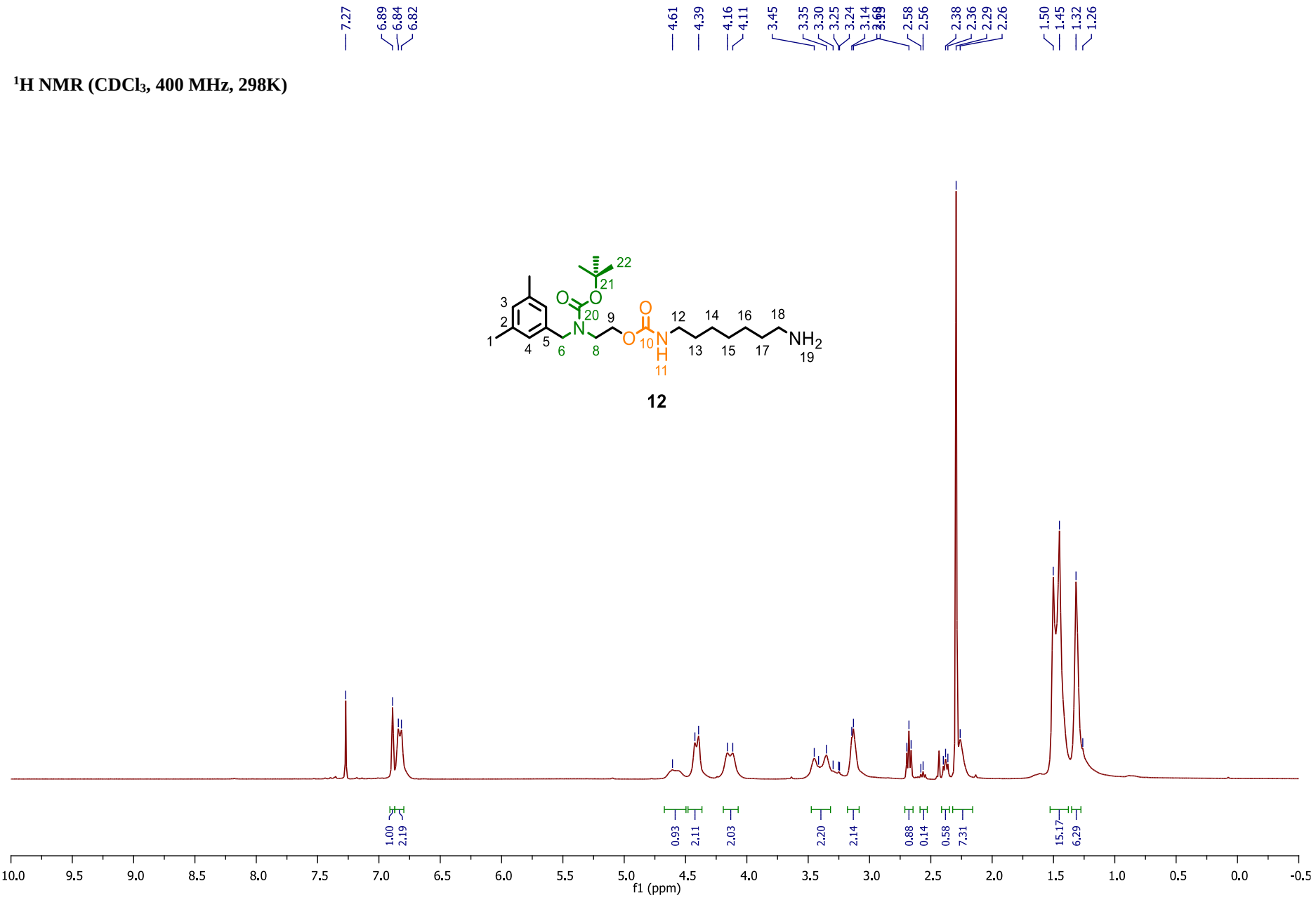
Source Type ESI | Ion Polarity Positive | Scan Begin 50 m/z | Scan End 2200 m/z



11

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	rdb	e⁻ Conf	N-Rule
570.3537	1	C 31 H 42 N 10 O	100.00	570.3538	0.1	0.1	16.0	odd	ok
	2	C 32 H 48 N 3 O 6	90.84	570.3538	0.1	0.1	10.5	even	ok
	3	C 18 H 50 N 8 O 12	10.59	570.3543	0.6	1.0	-2.0	odd	ok
	4	C 16 H 38 N 22 O 2	10.15	570.3543	0.6	1.0	9.0	odd	ok
	5	C 19 H 56 N O 17	8.42	570.3543	0.6	1.0	-7.5	even	ok
	6	C 16 H 48 N 11 O 11	7.65	570.3529	-0.8	-1.3	-1.5	even	ok
	7	C 17 H 44 N 15 O 7	7.73	570.3543	0.6	1.0	3.5	even	ok
	8	C 14 H 36 N 25 O	7.05	570.3529	-0.8	-1.3	9.5	even	ok
	9	C 15 H 42 N 18 O 6	5.26	570.3529	-0.8	-1.3	4.0	odd	ok

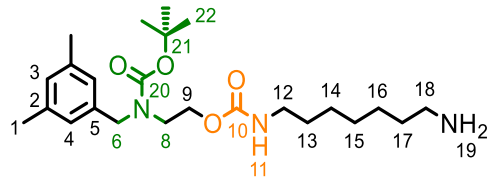
^{1}H NMR ($CDCl_3$, 400 MHz, 298K)



12

156.40
155.92
138.11
128.93
125.77
125.12
80.08
77.48
77.16
76.84
74.85
62.74
52.91
51.25
50.80
45.81
42.26
41.13
33.70
30.06
27.68
26.87
21.43

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



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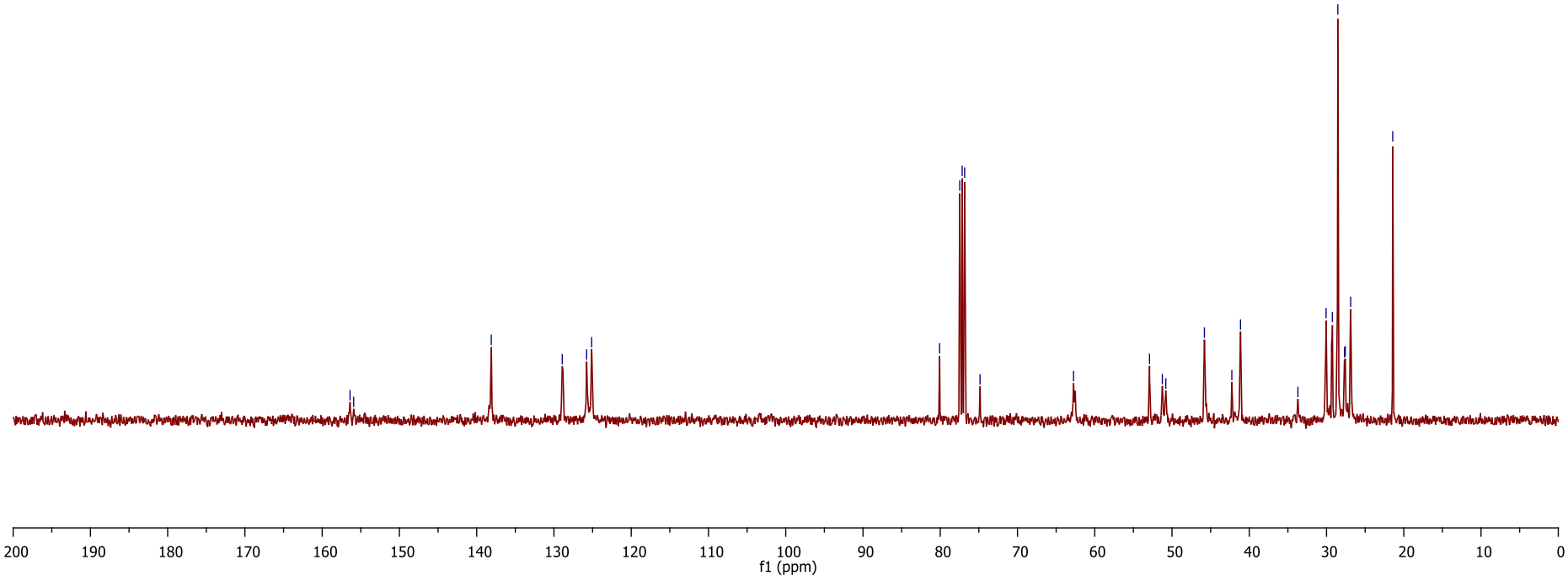
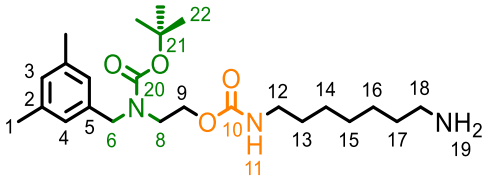
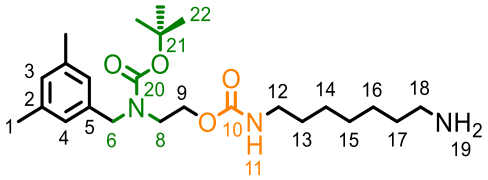




12

2D-COSY ^{1}H NMR ($CDCl_3$, 400 MHz, 298K)



12

2D-HSQC ^{13}C NMR ($CDCl_3$, 400 MHz, 298K)

Analysis Info

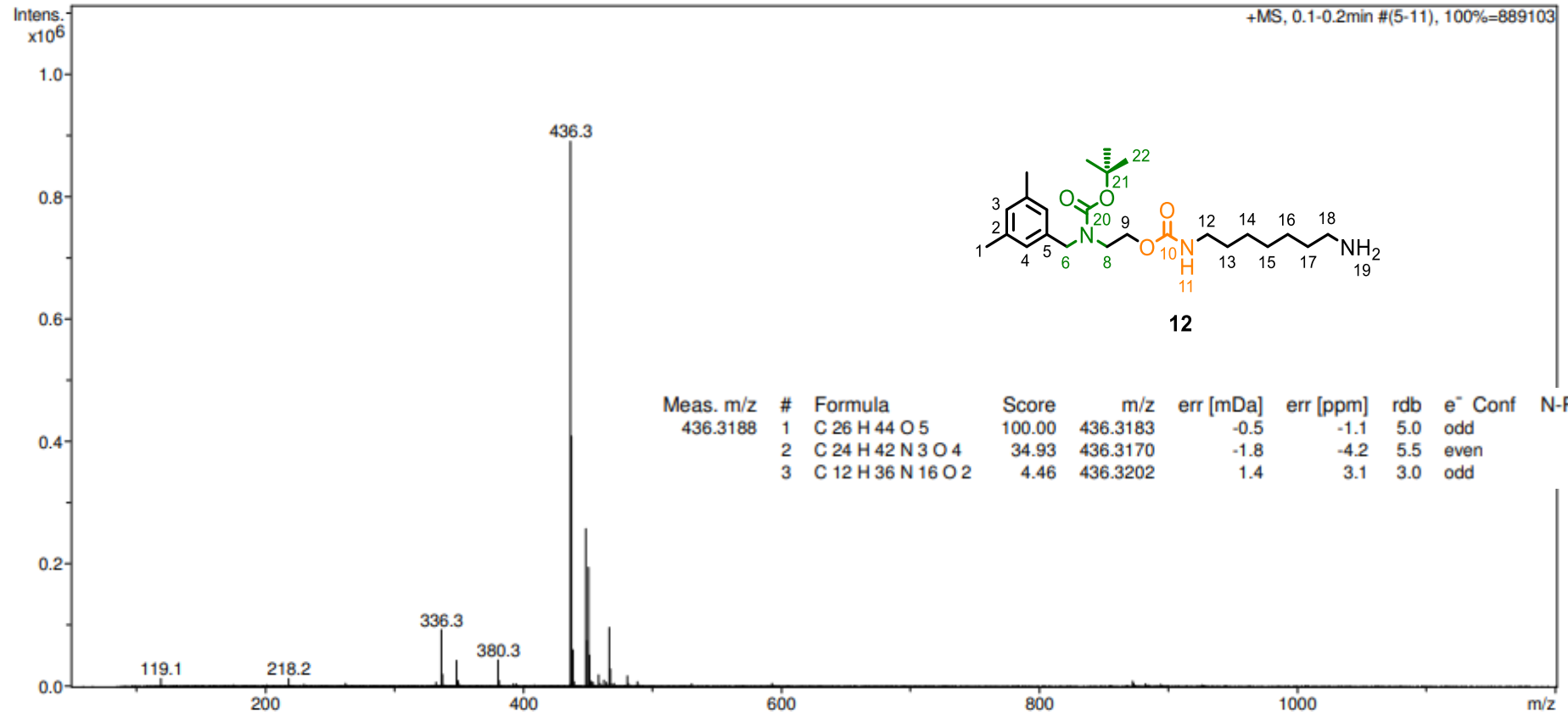
Sample Name **MXG-ANR-101**

Acquisition Date 7/22/2019 6:52:36 PM

Instrument / Ser# micrOTOF-Q II 10300

Acquisition Parameter

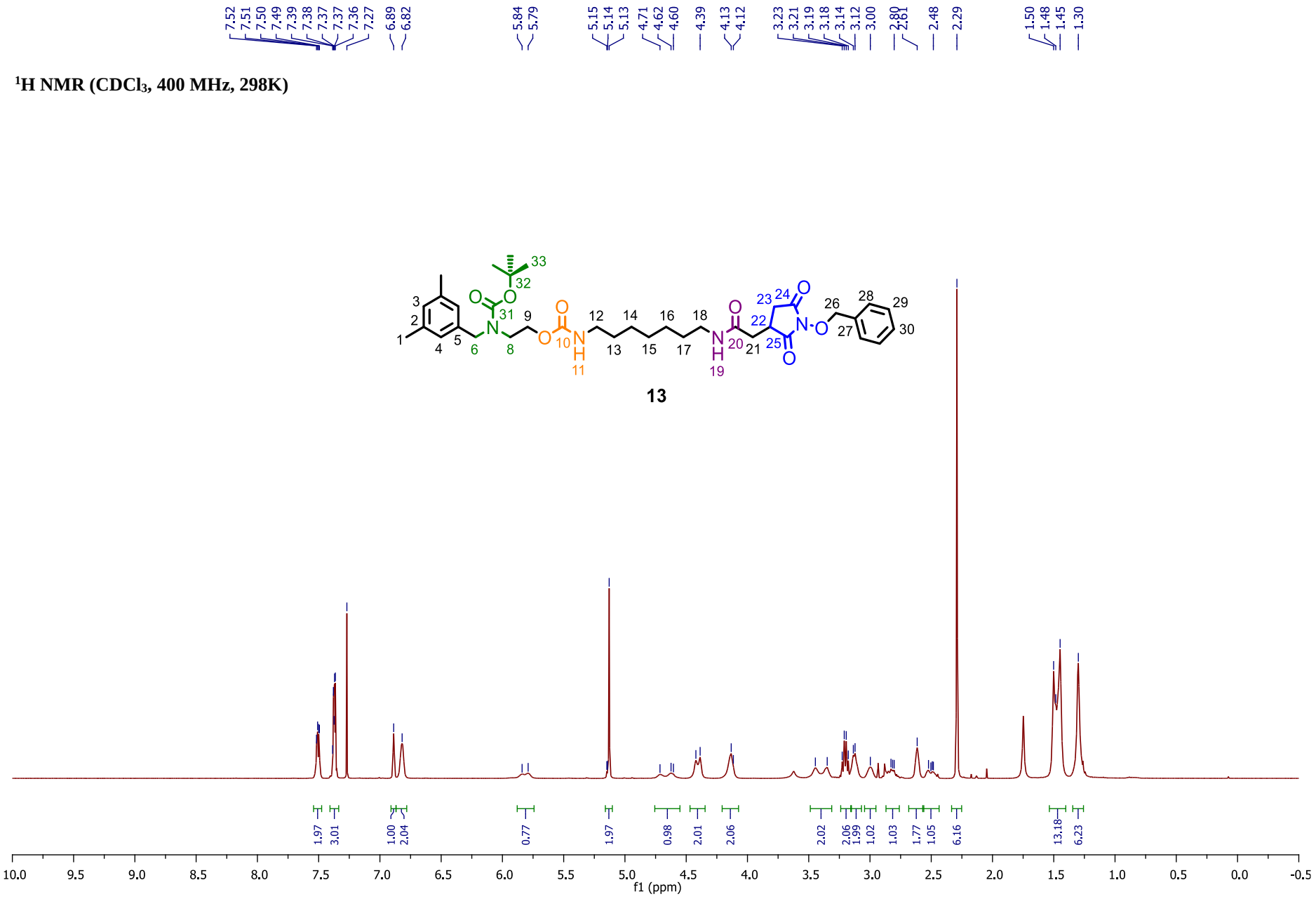
Source Type ESI | Ion Polarity Positive | Scan Begin 50 m/z | Scan End 2200 m/z



12

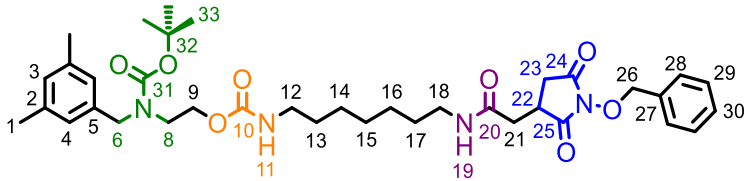
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	rdb	e⁻ Conf	N-Rule
436.3188	1	C 26 H 44 O 5	100.00	436.3183	-0.5	-1.1	5.0	odd	ok
	2	C 24 H 42 N 3 O 4	34.93	436.3170	-1.8	-4.2	5.5	even	ok
	3	C 12 H 36 N 16 O 2	4.46	436.3202	1.4	3.1	3.0	odd	ok

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

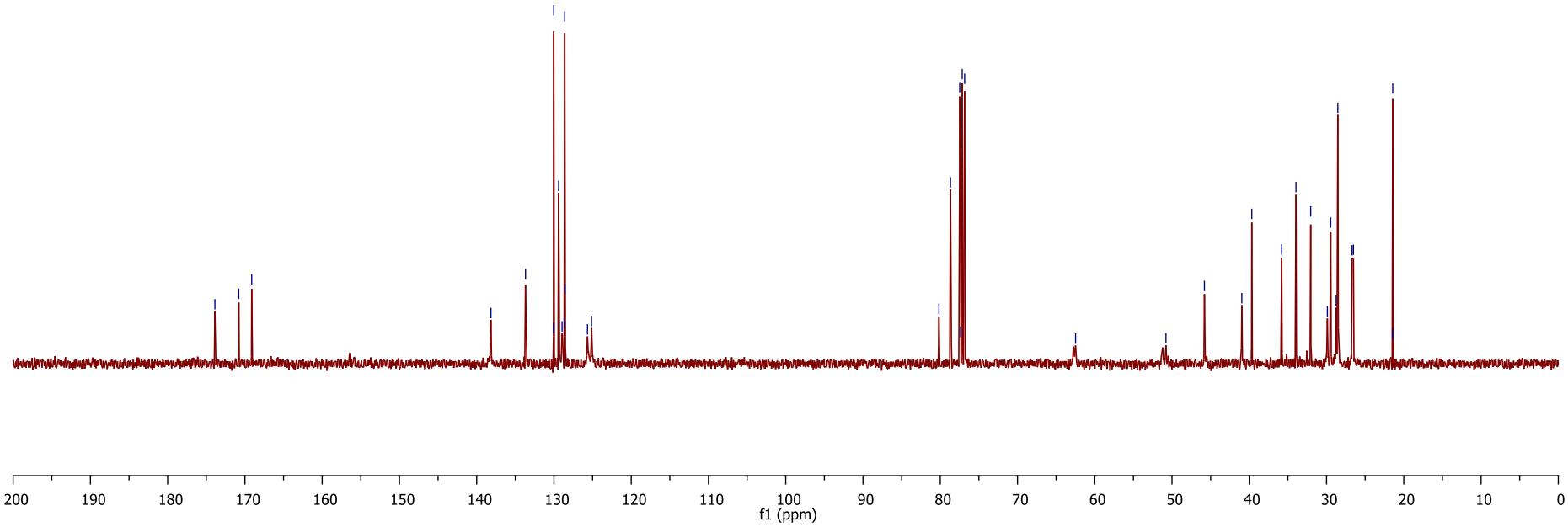


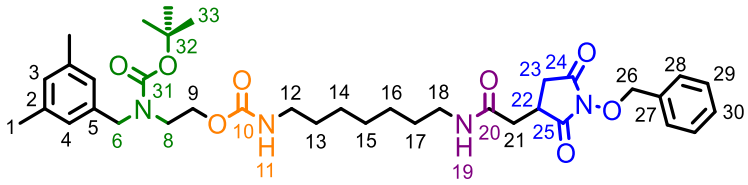
173.89
170.80
169.12
138.15
133.68
128.58
125.66
125.13
80.17
78.68
77.48
77.36
77.16
76.84
62.48
50.78
45.80
40.96
39.67
32.05
29.45
28.54
26.52
21.46
21.43

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



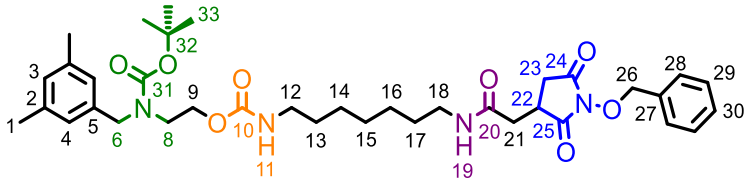
13





13

2D-COSY ^{1}H NMR ($CDCl_3$, 400 MHz, 298K)



13

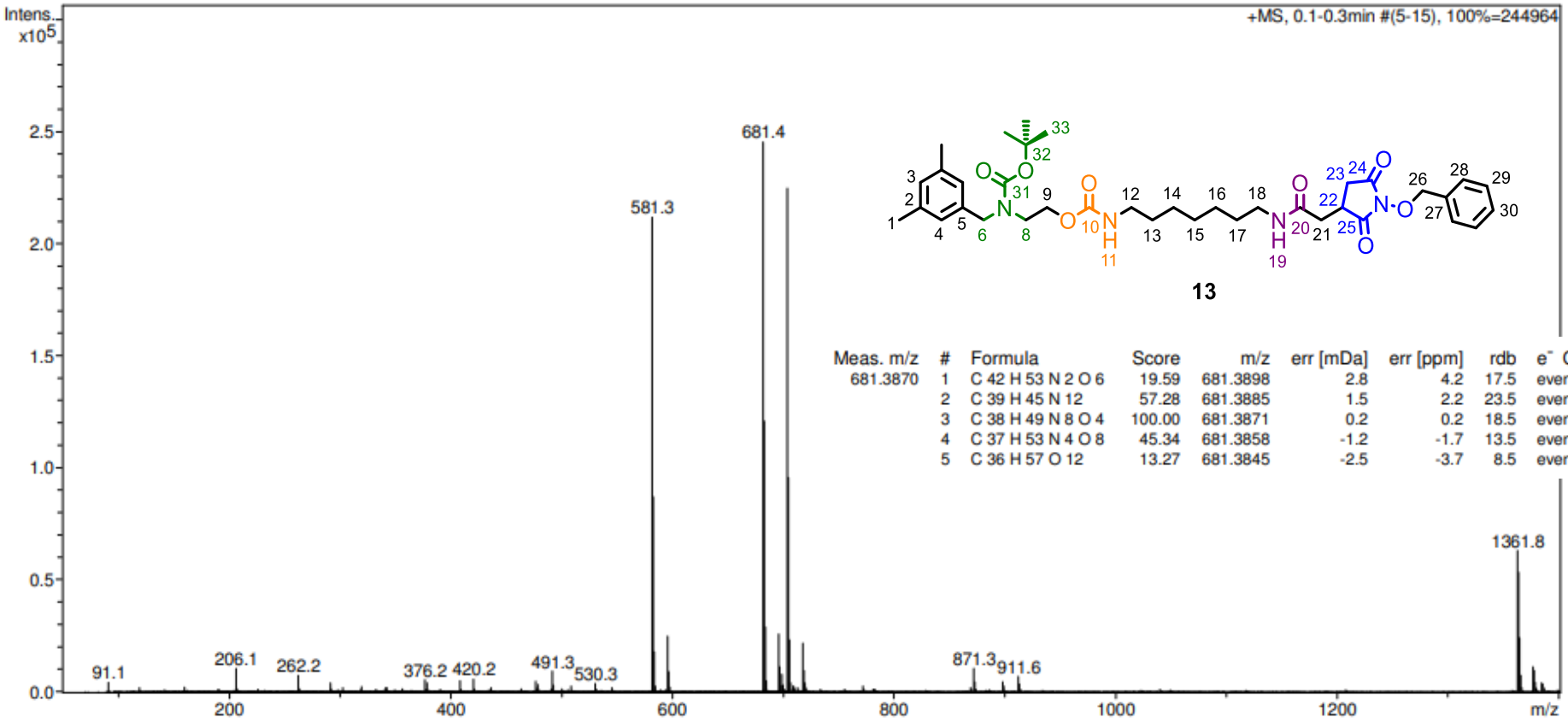
2D-HSQC ^{13}C NMR ($CDCl_3$, 400 MHz, 298K)

Analysis Info

Sample Name	**MXG-ANR-102**	Acquisition Date	7/24/2019 6:39:24 PM
		Instrument / Ser#	micrOTOF-Q II 10300

Acquisition Parameter

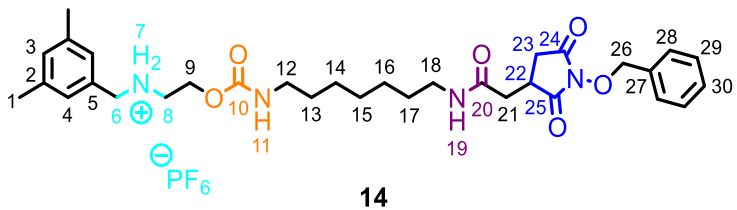
Source Type	ESI	Ion Polarity	Positive	Scan Begin	50 m/z	Scan End	2200 m/z



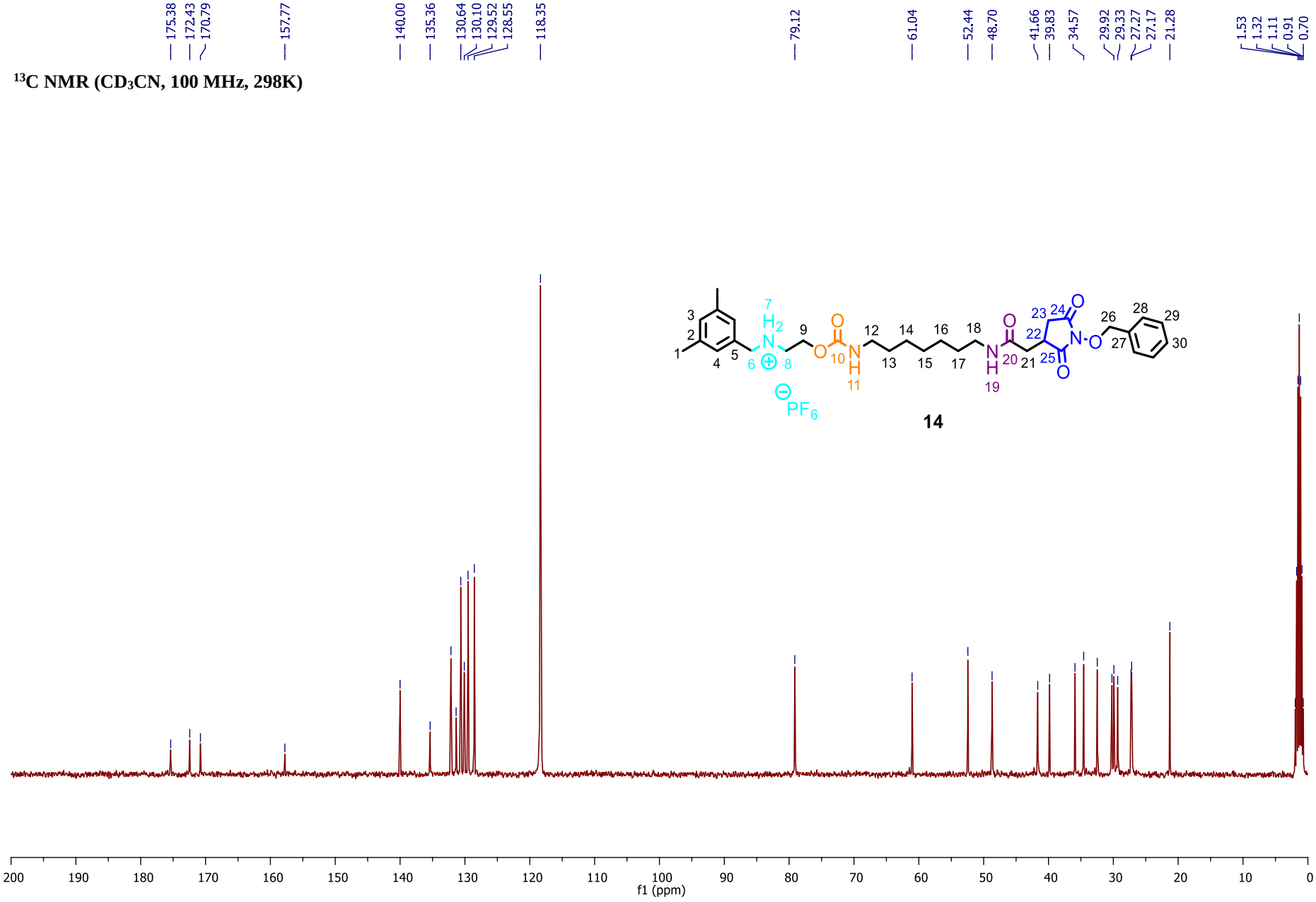
13

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	rdb	e⁻ Conf	N-Rule
681.3870	1	C 42 H 53 N 2 O 6	19.59	681.3898	2.8	4.2	17.5	even	ok
	2	C 39 H 45 N 12	57.28	681.3885	1.5	2.2	23.5	even	ok
	3	C 38 H 49 N 8 O 4	100.00	681.3871	0.2	0.2	18.5	even	ok
	4	C 37 H 53 N 4 O 8	45.34	681.3858	-1.2	-1.7	13.5	even	ok
	5	C 36 H 57 O 12	13.27	681.3845	-2.5	-3.7	8.5	even	ok

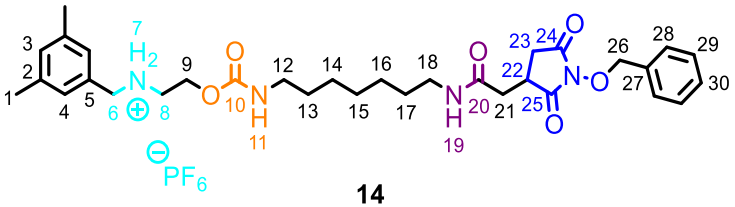
^{1}H NMR (CD_3CN, 400 MHz, 298K)



14

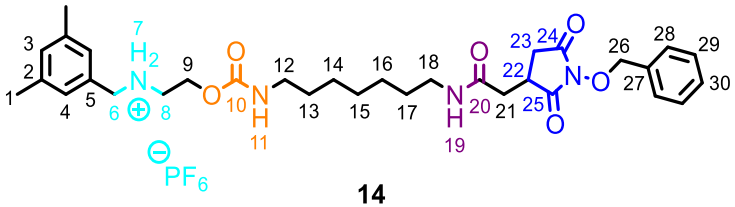


^{13}C NMR (CD_3CN, 100 MHz, 298K)



14

2D-COSY ^{1}H NMR (CD_3CN, 400 MHz, 298K)



14

2D-HSQC ^{13}C NMR (CD_3CN, 400 MHz, 298K)

Analysis Info

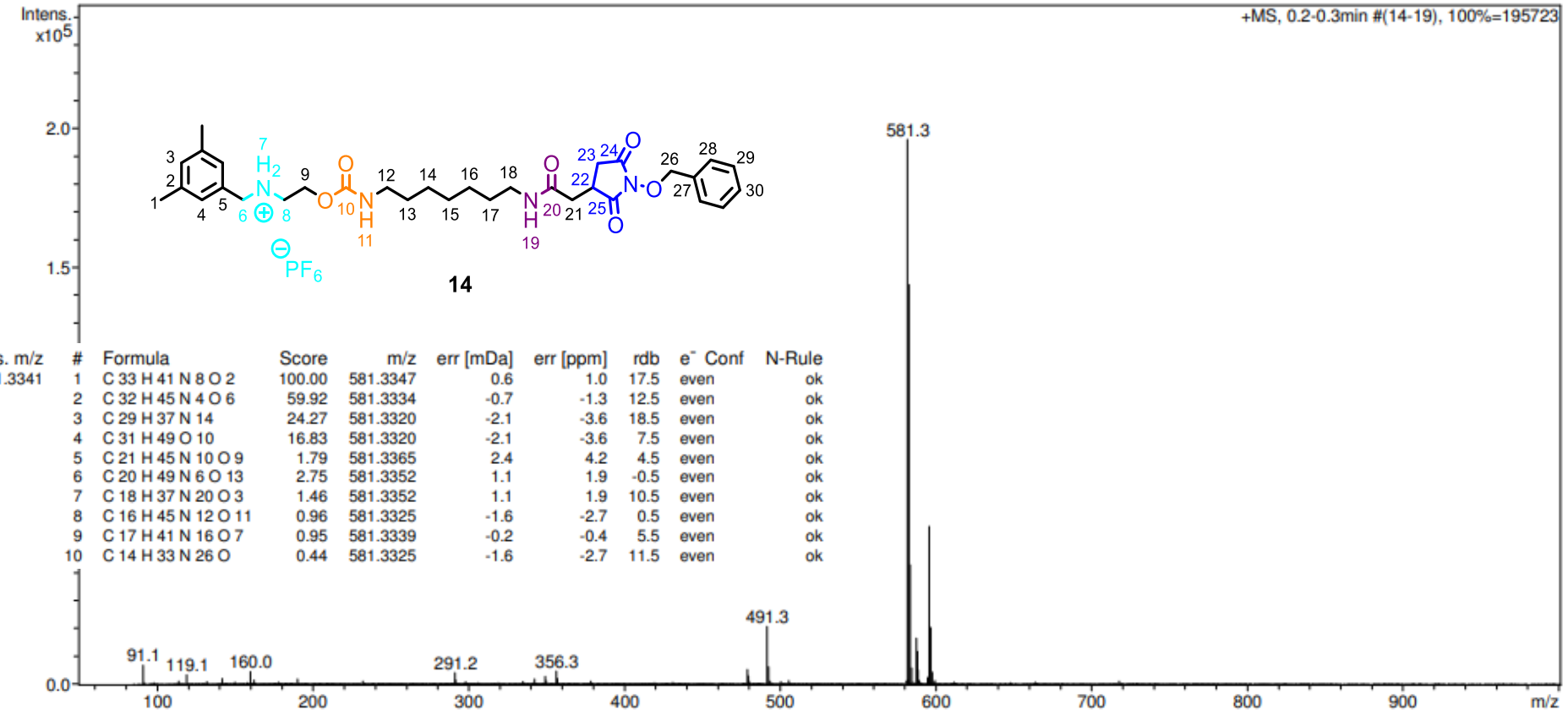
Sample Name **MXG-ANR-104**

Acquisition Date 7/24/2019 6:37:16 PM

Instrument / Ser# micrOTOF-Q II 10300

Acquisition Parameter

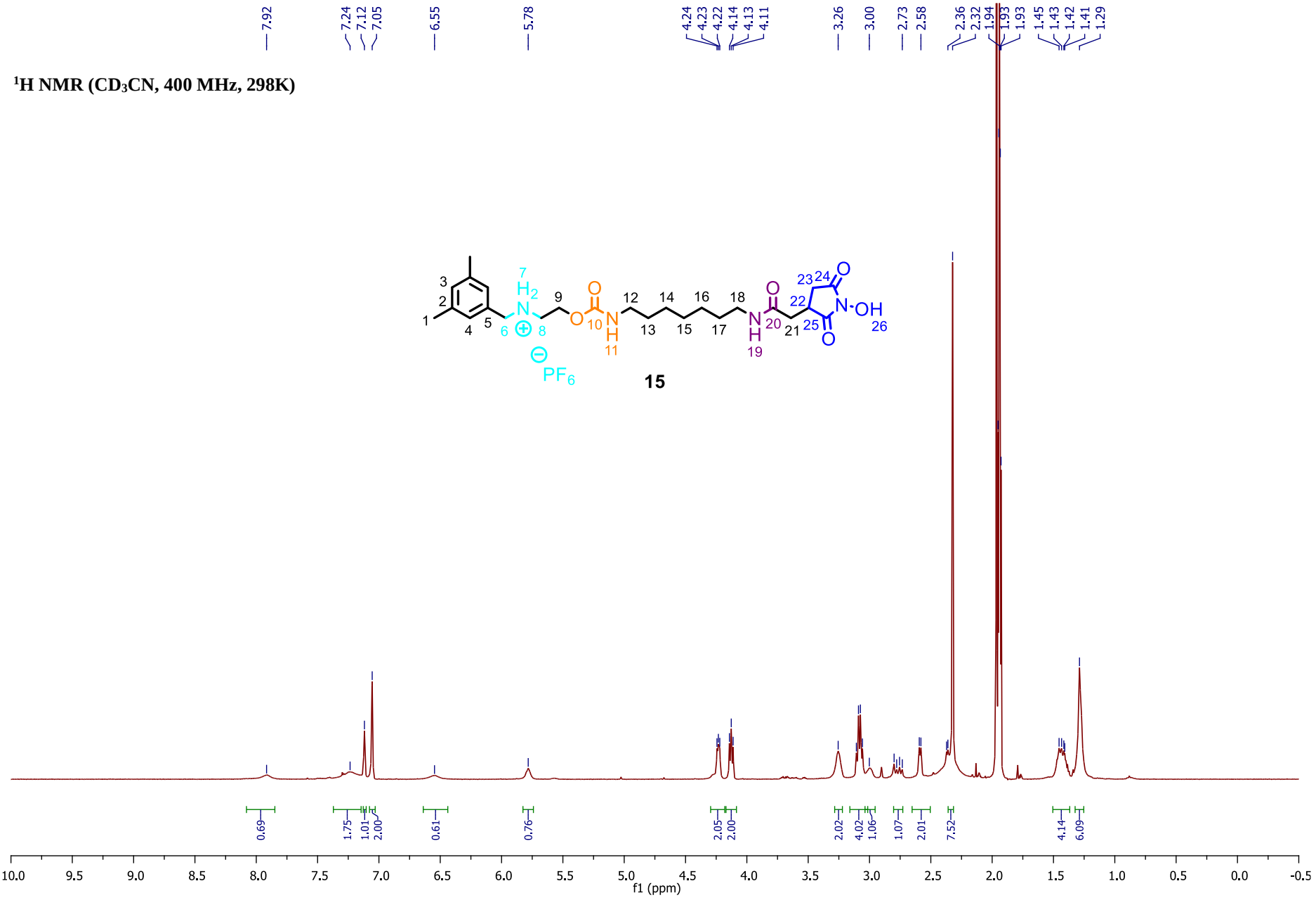
Source Type ESI | Ion Polarity Positive | Scan Begin 50 m/z | Scan End 2200 m/z



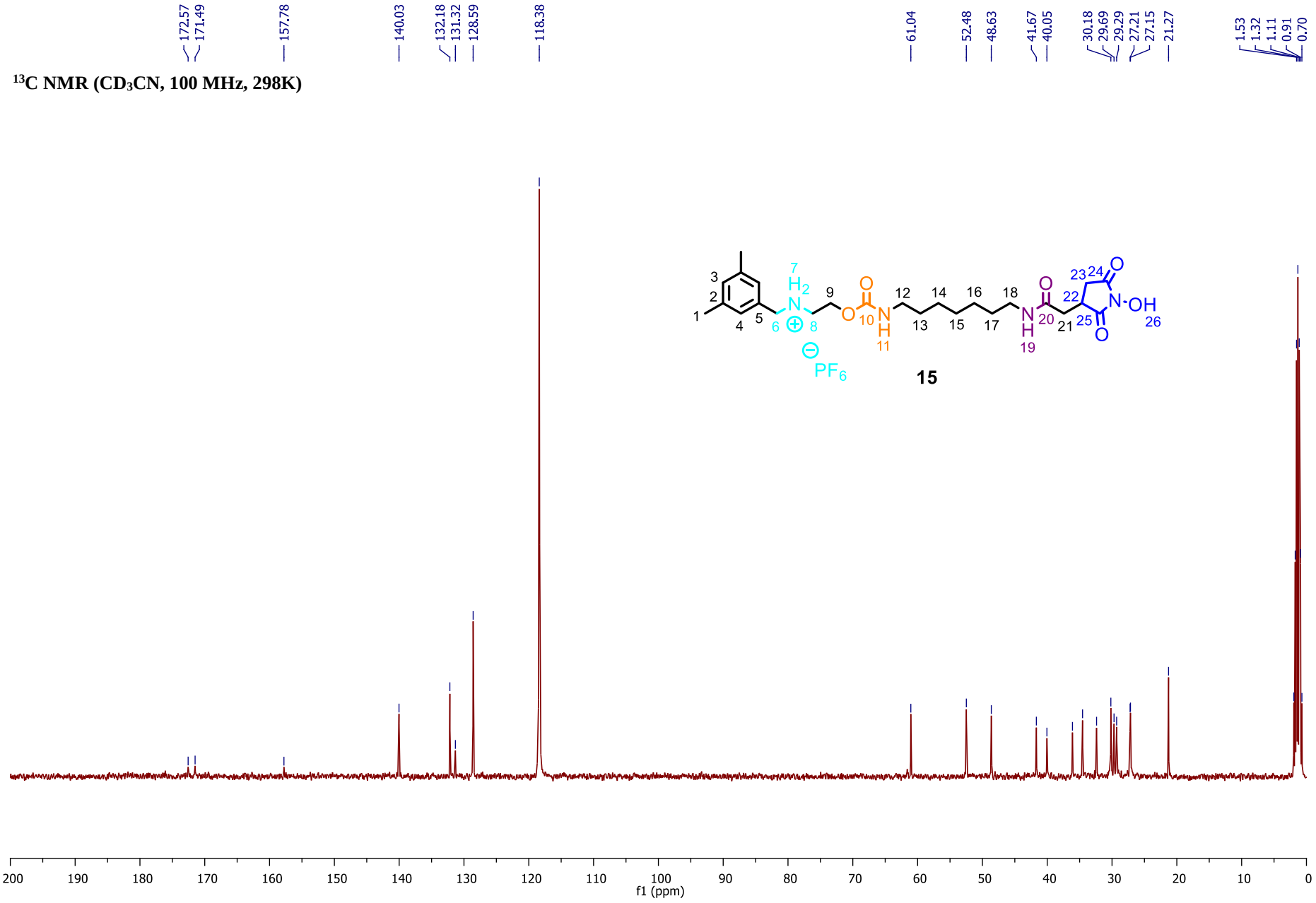
14

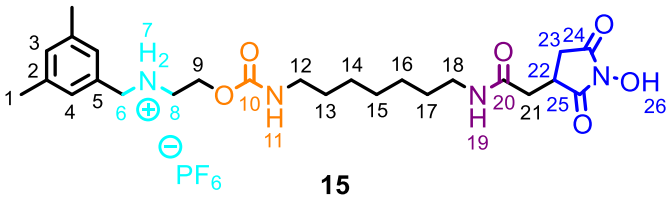
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	rdb	e⁻ Conf	N-Rule
581.3341	1	C 33 H 41 N 8 O 2	100.00	581.3347	0.6	1.0	17.5	even	ok
	2	C 32 H 45 N 4 O 6	59.92	581.3334	-0.7	-1.3	12.5	even	ok
	3	C 29 H 37 N 14	24.27	581.3320	-2.1	-3.6	18.5	even	ok
	4	C 31 H 49 O 10	16.83	581.3320	-2.1	-3.6	7.5	even	ok
	5	C 21 H 45 N 10 O 9	1.79	581.3365	2.4	4.2	4.5	even	ok
	6	C 20 H 49 N 6 O 13	2.75	581.3352	1.1	1.9	-0.5	even	ok
	7	C 18 H 37 N 20 O 3	1.46	581.3352	1.1	1.9	10.5	even	ok
	8	C 16 H 45 N 12 O 11	0.96	581.3325	-1.6	-2.7	0.5	even	ok
	9	C 17 H 41 N 16 O 7	0.95	581.3339	-0.2	-0.4	5.5	even	ok
	10	C 14 H 33 N 26 O	0.44	581.3325	-1.6	-2.7	11.5	even	ok

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



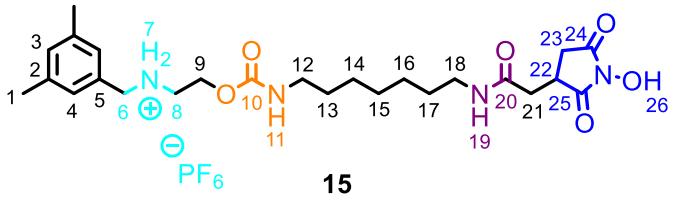
^{13}C NMR (CD_3CN, 100 MHz, 298K)





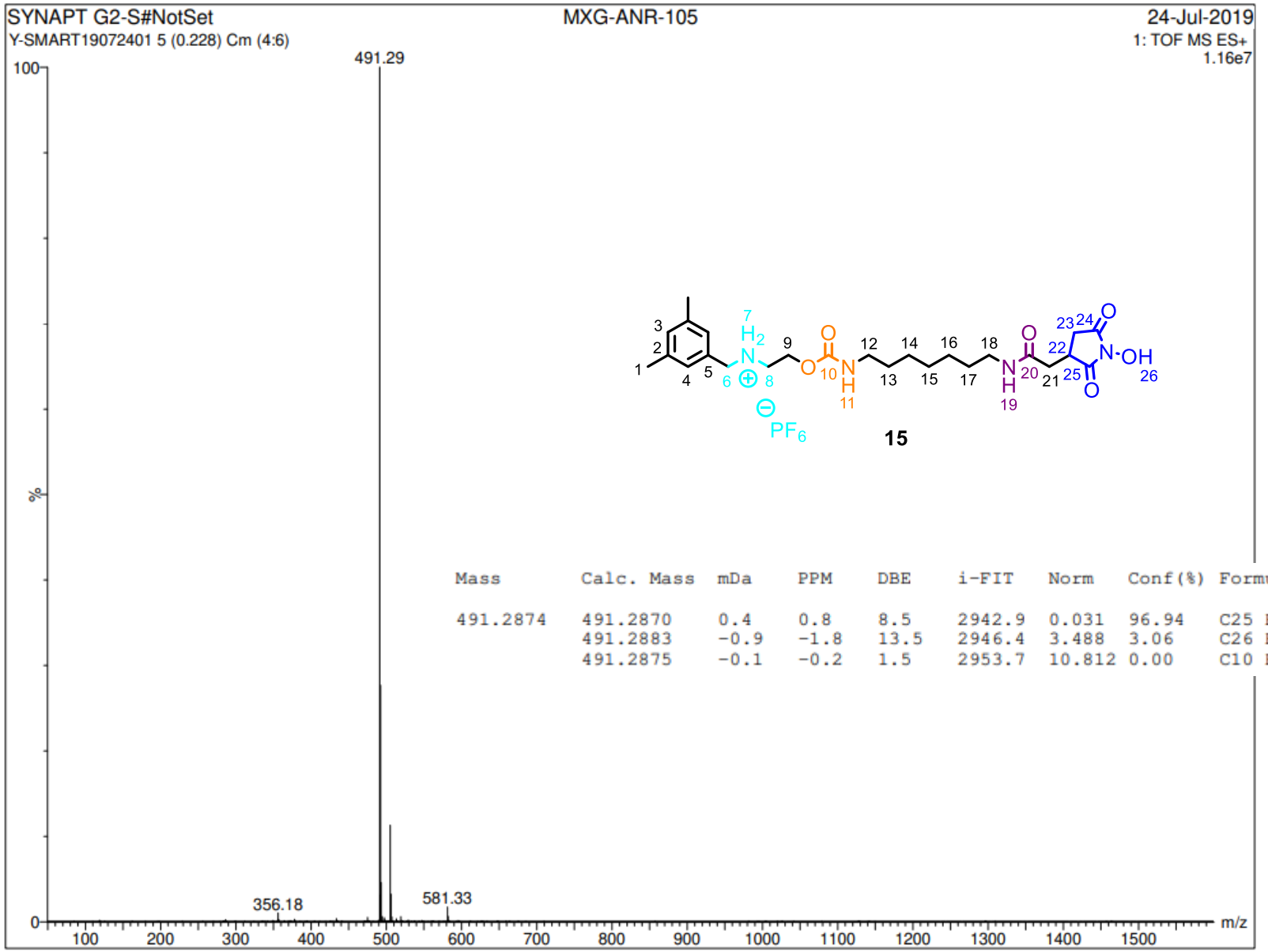
15

2D-COSY ^{1}H NMR (CD_3CN, 400 MHz, 298K)



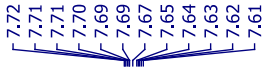
15

2D-HSQC ^{13}C NMR (CD_3CN, 400 MHz, 298K)

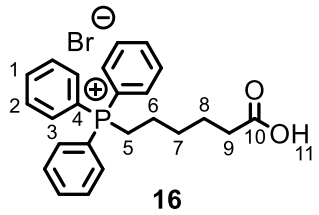


15

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
491.2874	491.2870	0.4	0.8	8.5	2942.9	0.031	96.94	C25 H39 N4 O6
	491.2883	-0.9	-1.8	13.5	2946.4	3.488	3.06	C26 H35 N8 O2
	491.2875	-0.1	-0.2	1.5	2953.7	10.812	0.00	C10 H35 N16 O7



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



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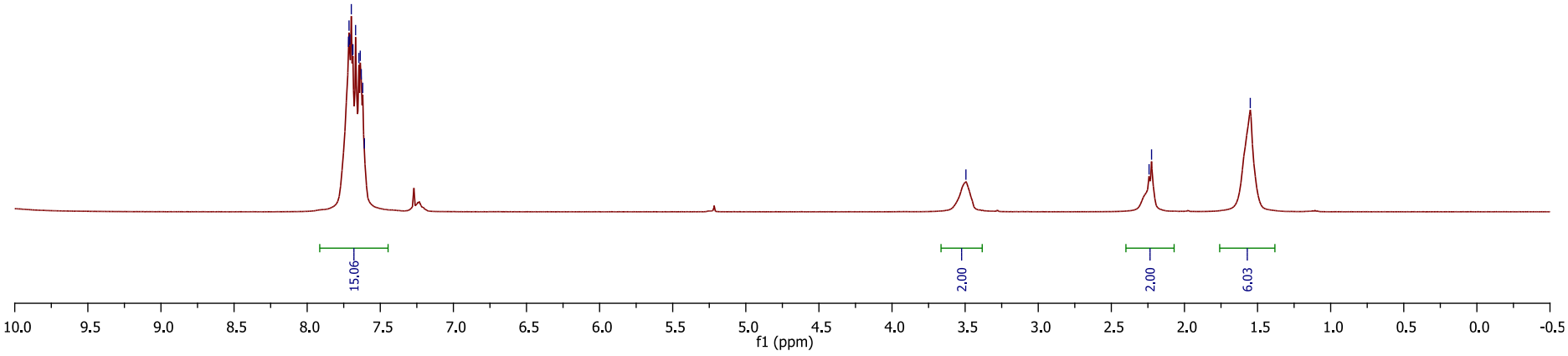
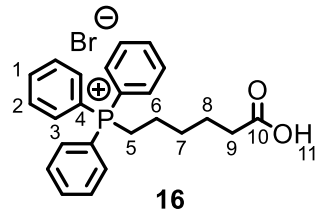


^{13}C NMR ($CDCl_3$, 100 MHz, 298K)



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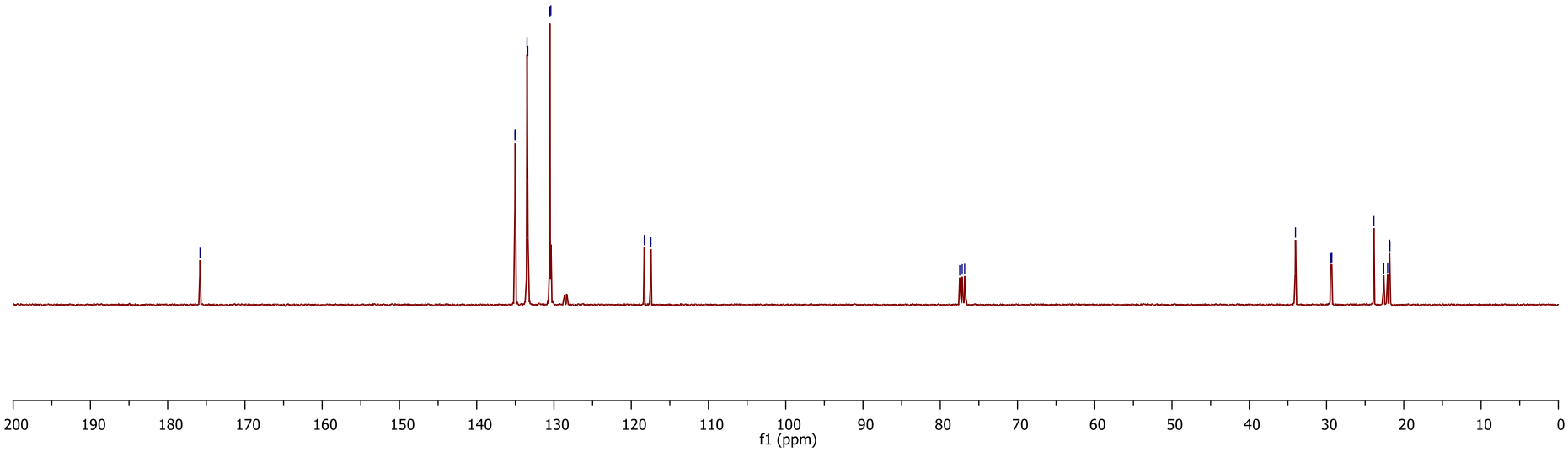
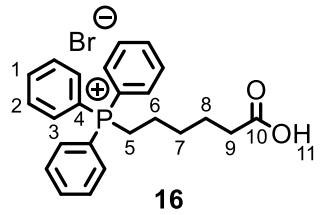
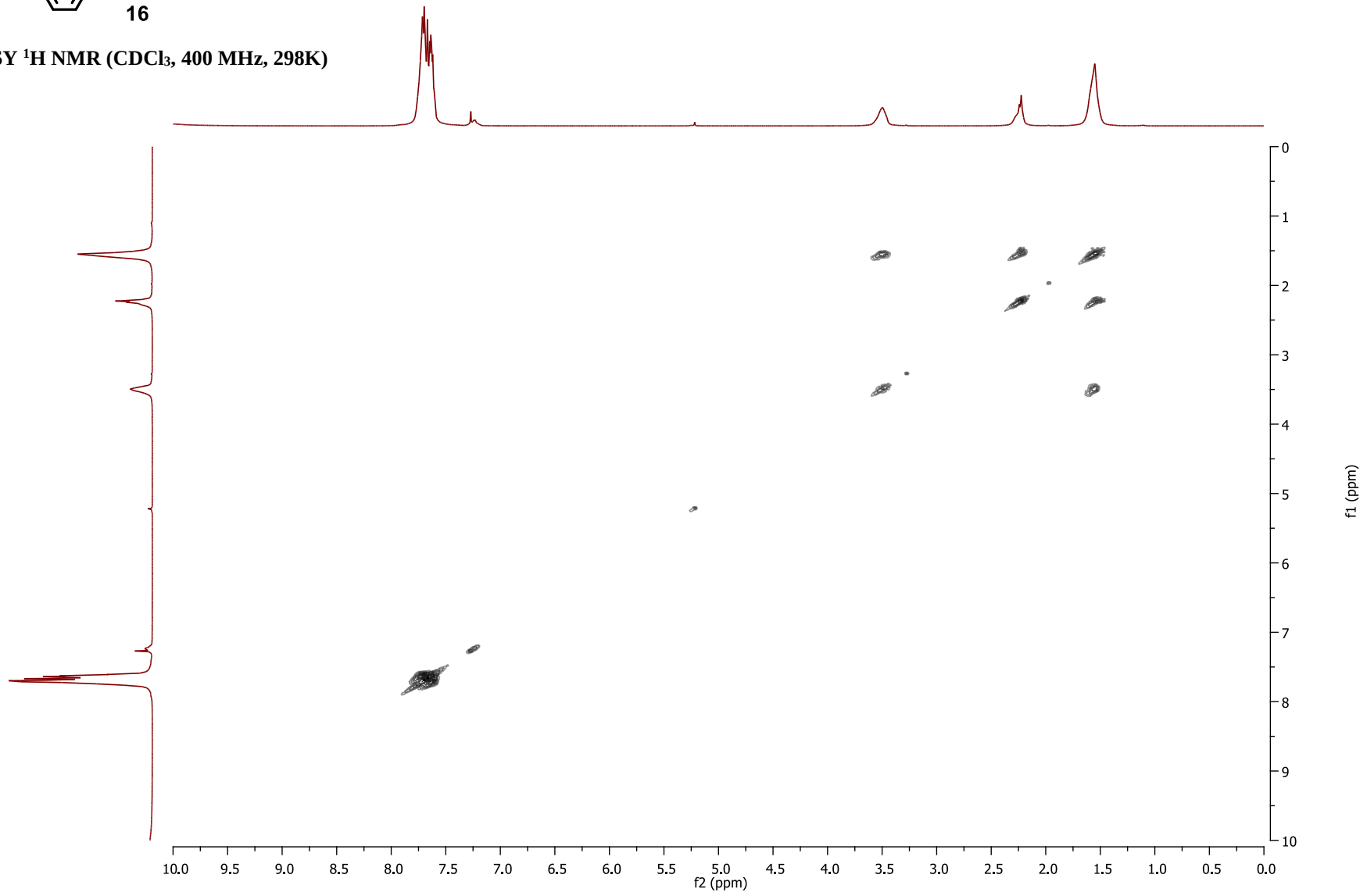
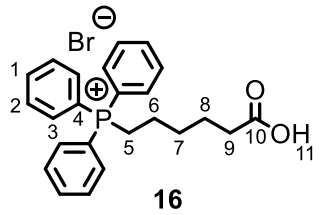




16

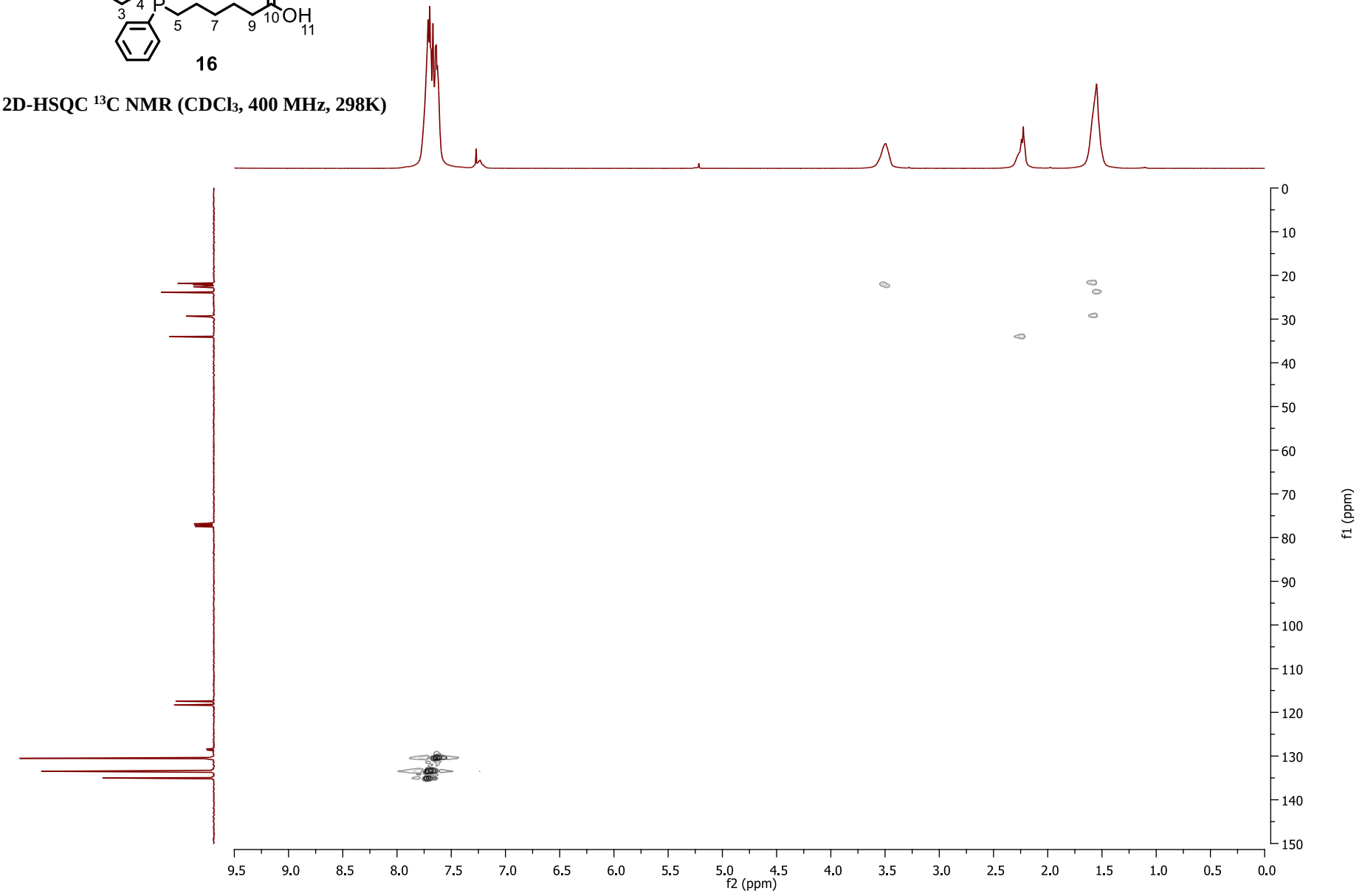
2D-COSY ^{1}H NMR ($CDCl_3$, 400 MHz, 298K)





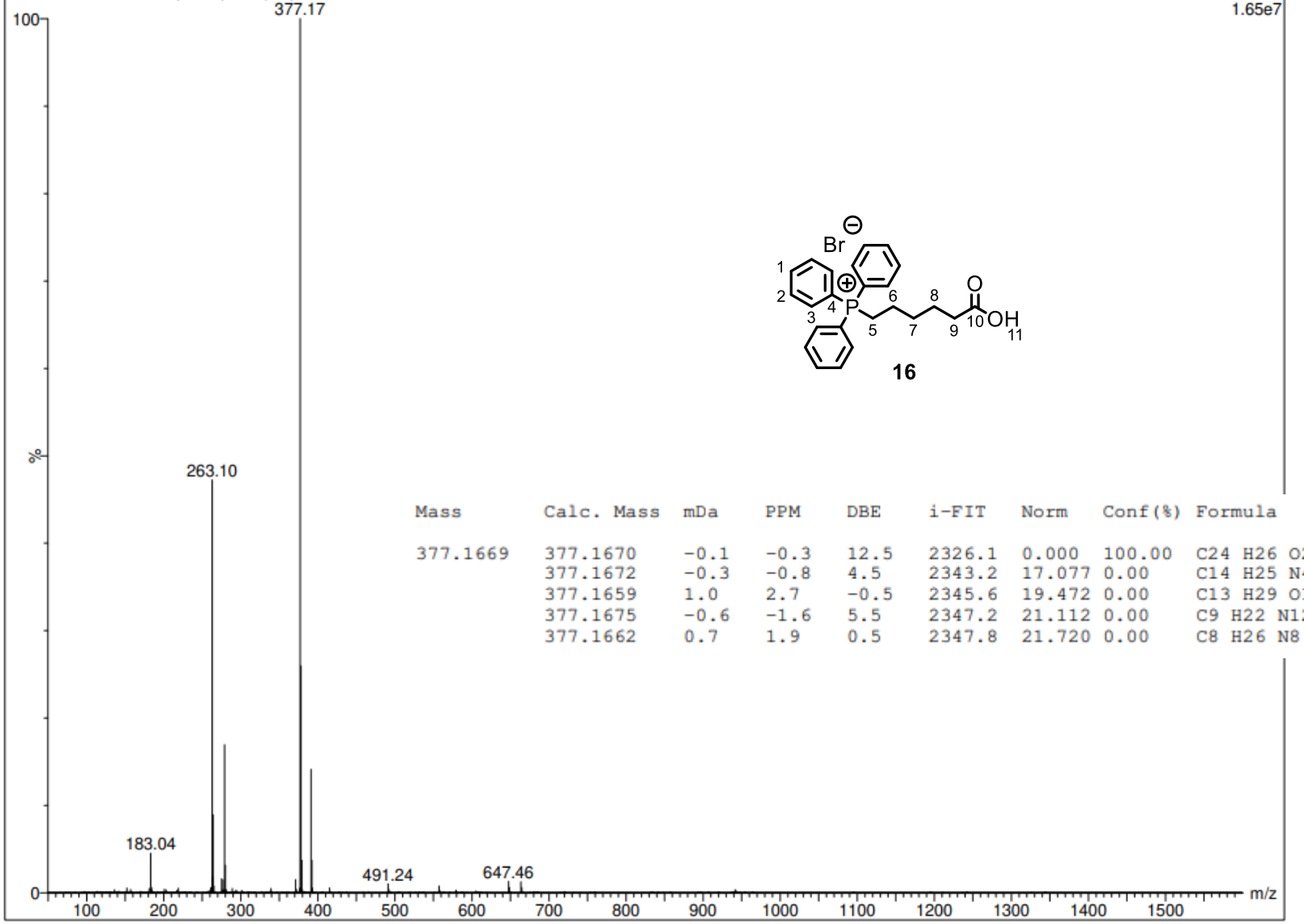
16

2D-HSQC ^{13}C NMR ($CDCl_3$, 400 MHz, 298K)



SYNAPT G2-S#UEB205 MXG1-101 06-May-2019

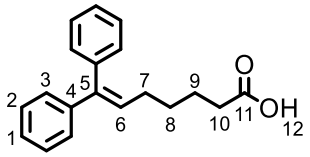
Y-SMART19050603 6 (0.262) Cm (3:9) 1: TOF MS ES+ 1.65e7



16

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
377.1669	377.1670	-0.1	-0.3	12.5	2326.1	0.000	100.00	C24 H26 O2 P
	377.1672	-0.3	-0.8	4.5	2343.2	17.077	0.00	C14 H25 N4 O8
	377.1659	1.0	2.7	-0.5	2345.6	19.472	0.00	C13 H29 O12
	377.1675	-0.6	-1.6	5.5	2347.2	21.112	0.00	C9 H22 N12 O3 P
	377.1662	0.7	1.9	0.5	2347.8	21.720	0.00	C8 H26 N8 O7 P

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



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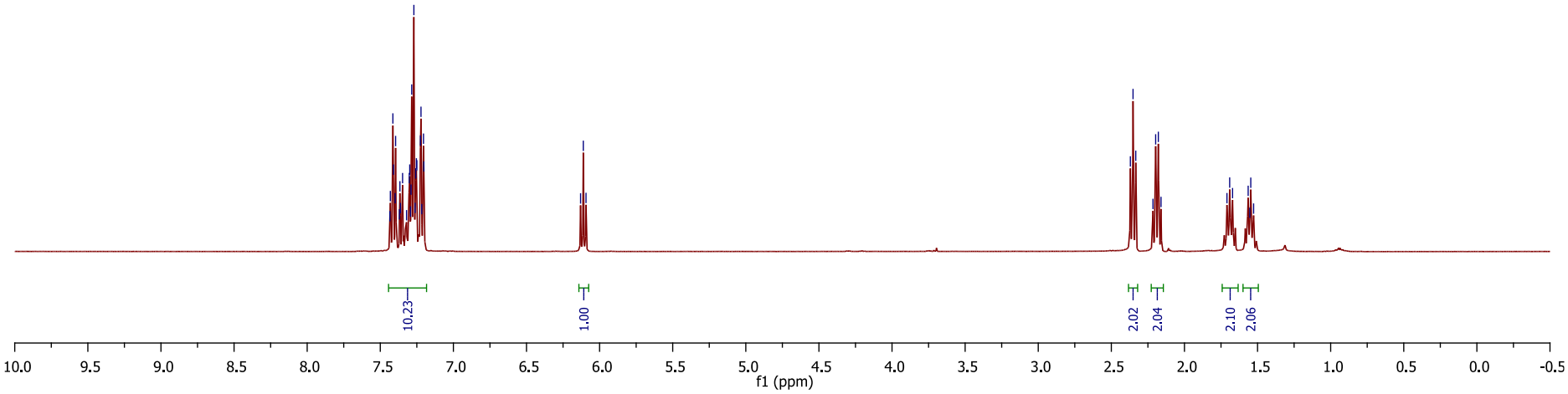
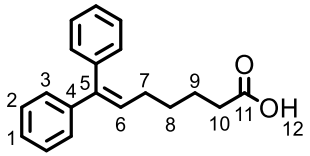


^{13}C NMR ($CDCl_3$, 100 MHz, 298K)



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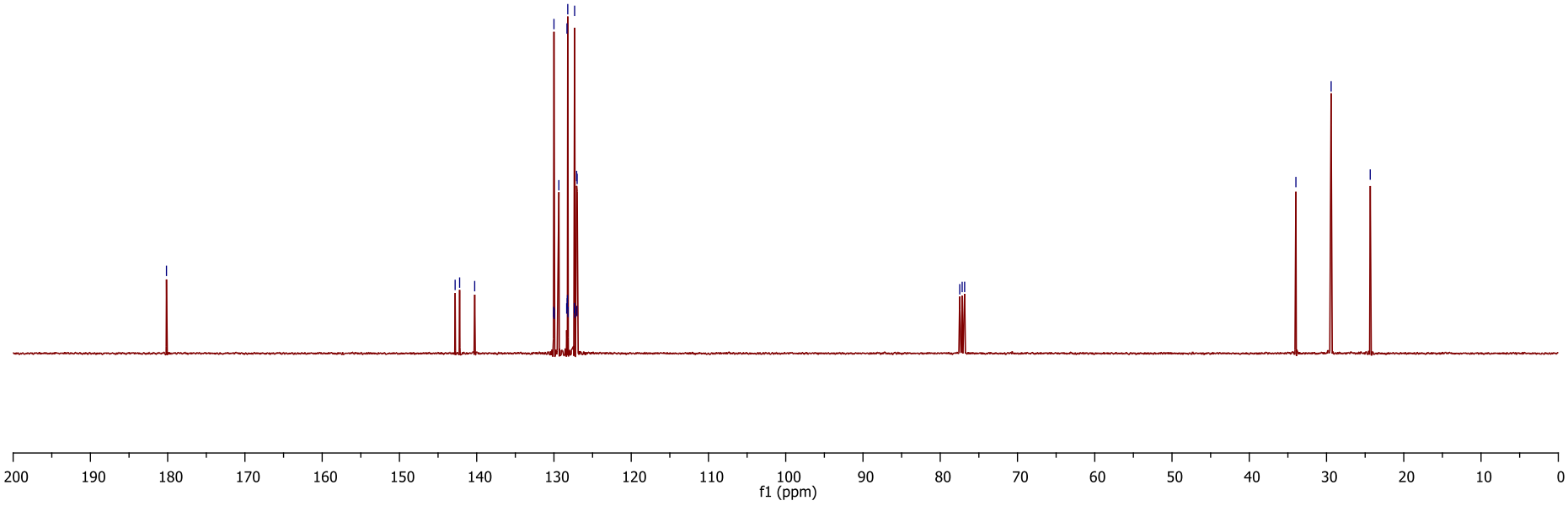
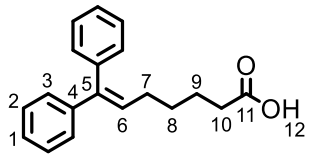
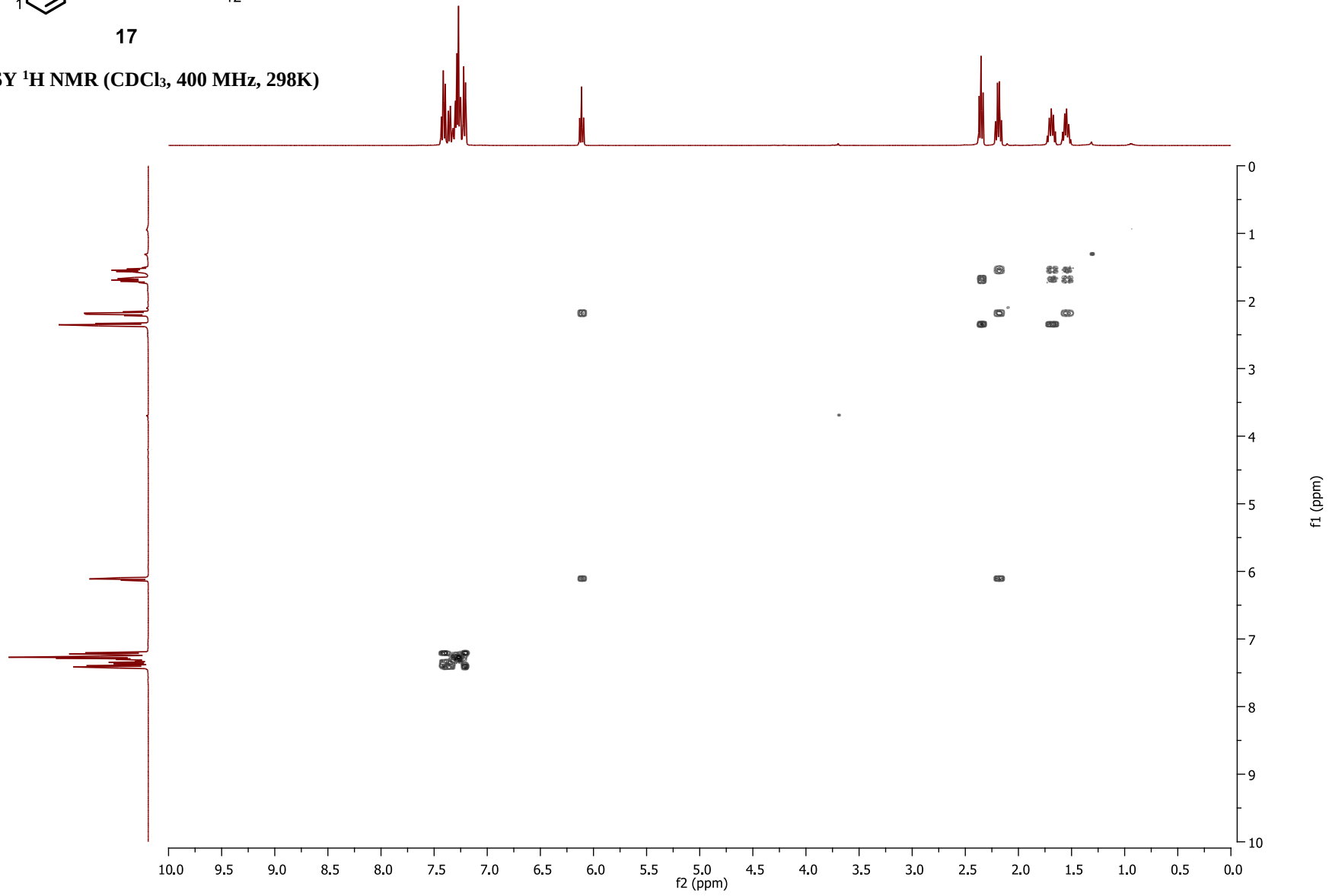
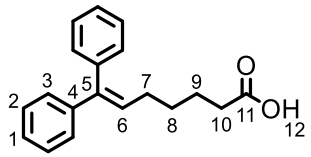




17

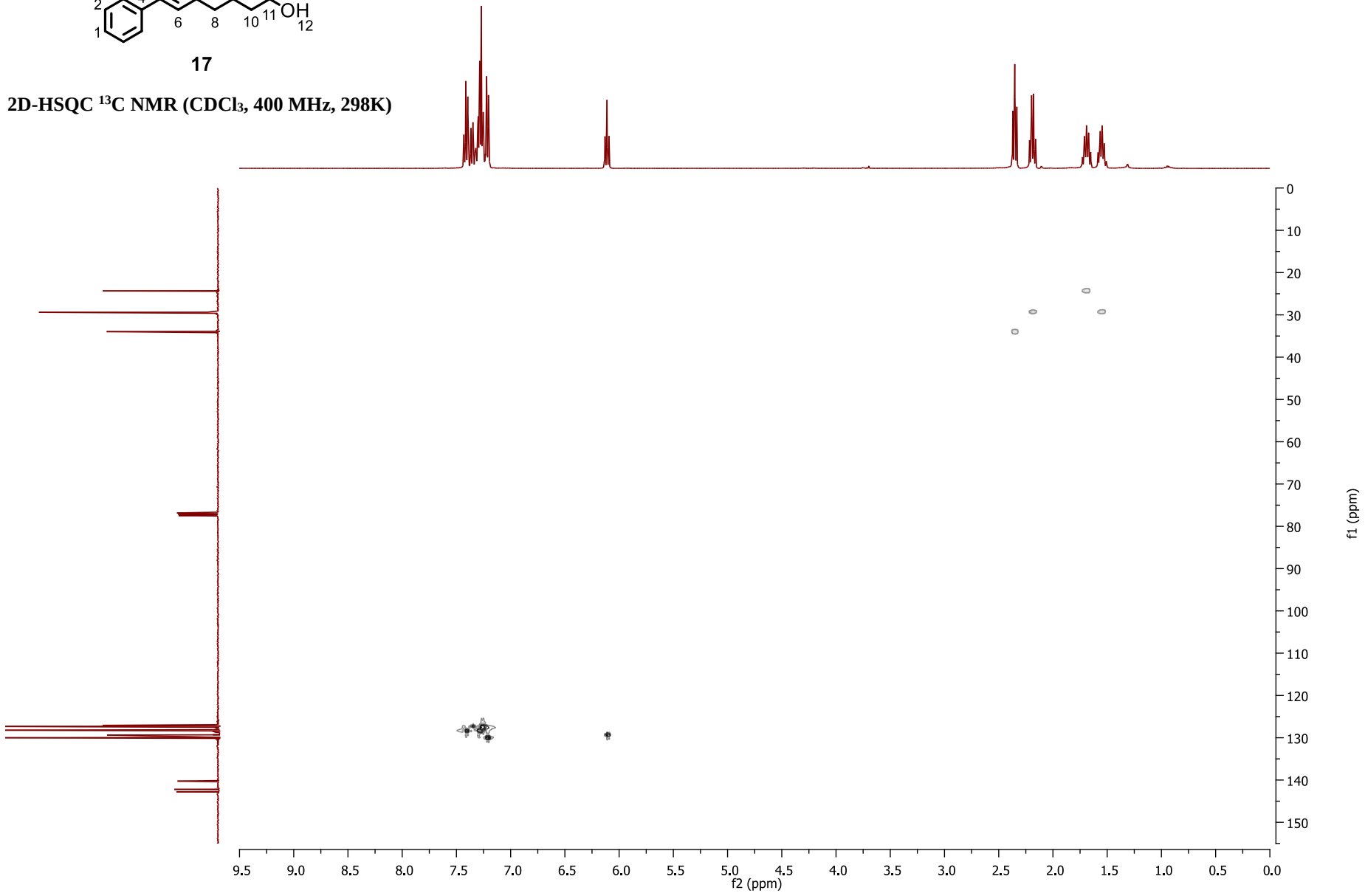
2D-COSY ^{1}H NMR ($CDCl_3$, 400 MHz, 298K)





17

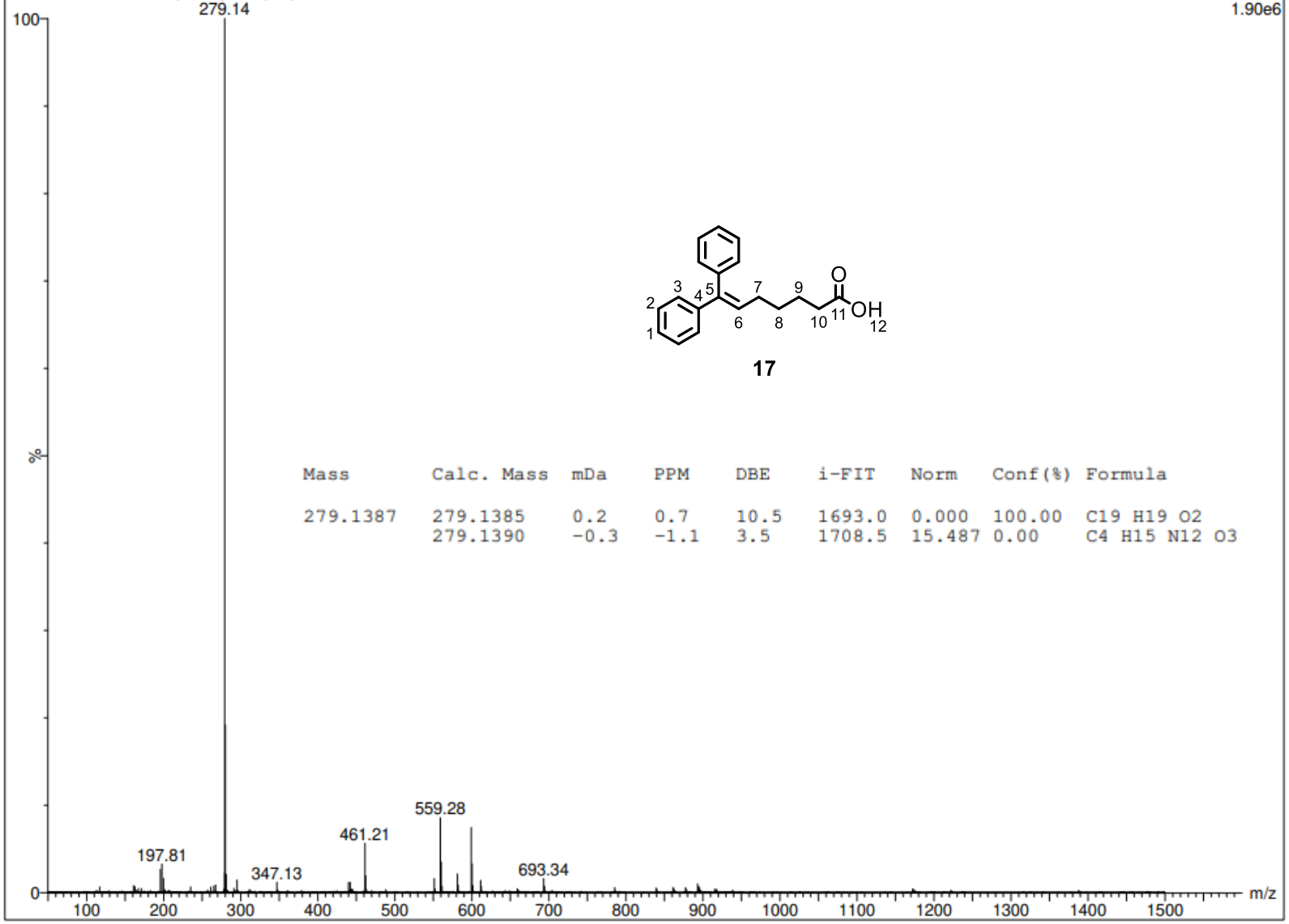
2D-HSQC ^{13}C NMR ($CDCl_3$, 400 MHz, 298K)



SYNAPT G2-S#UEB205 MXG1-102 06-May-2019

Y-SMART19050604 4 (0.214) Cm (3:6) 1: TOF MS ES-

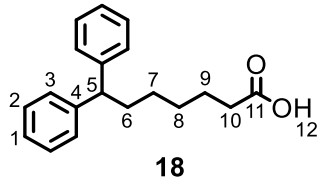
1.90e6



17

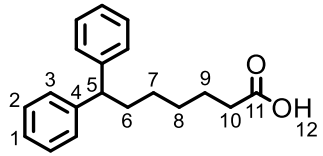
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
279.1387	279.1385	0.2	0.7	10.5	1693.0	0.000	100.00	C19 H19 O2
	279.1390	-0.3	-1.1	3.5	1708.5	15.487	0.00	C4 H15 N12 O3

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



18

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



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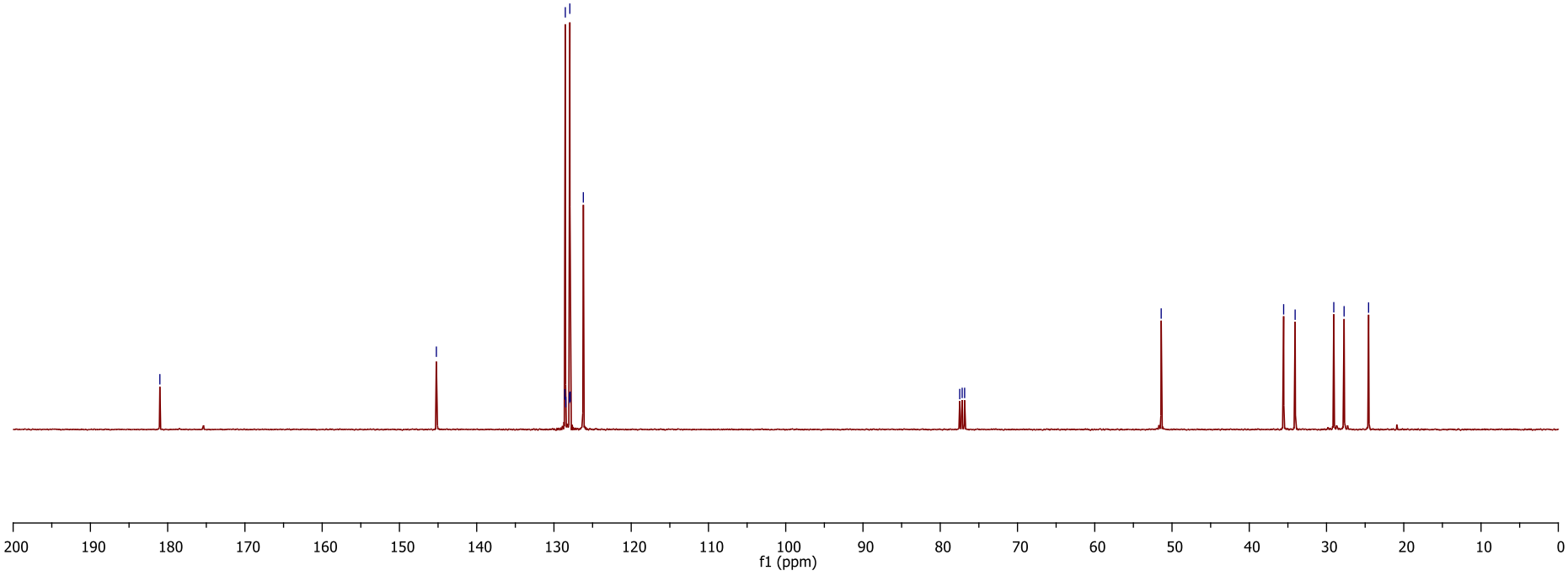
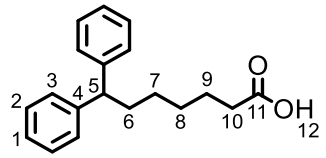
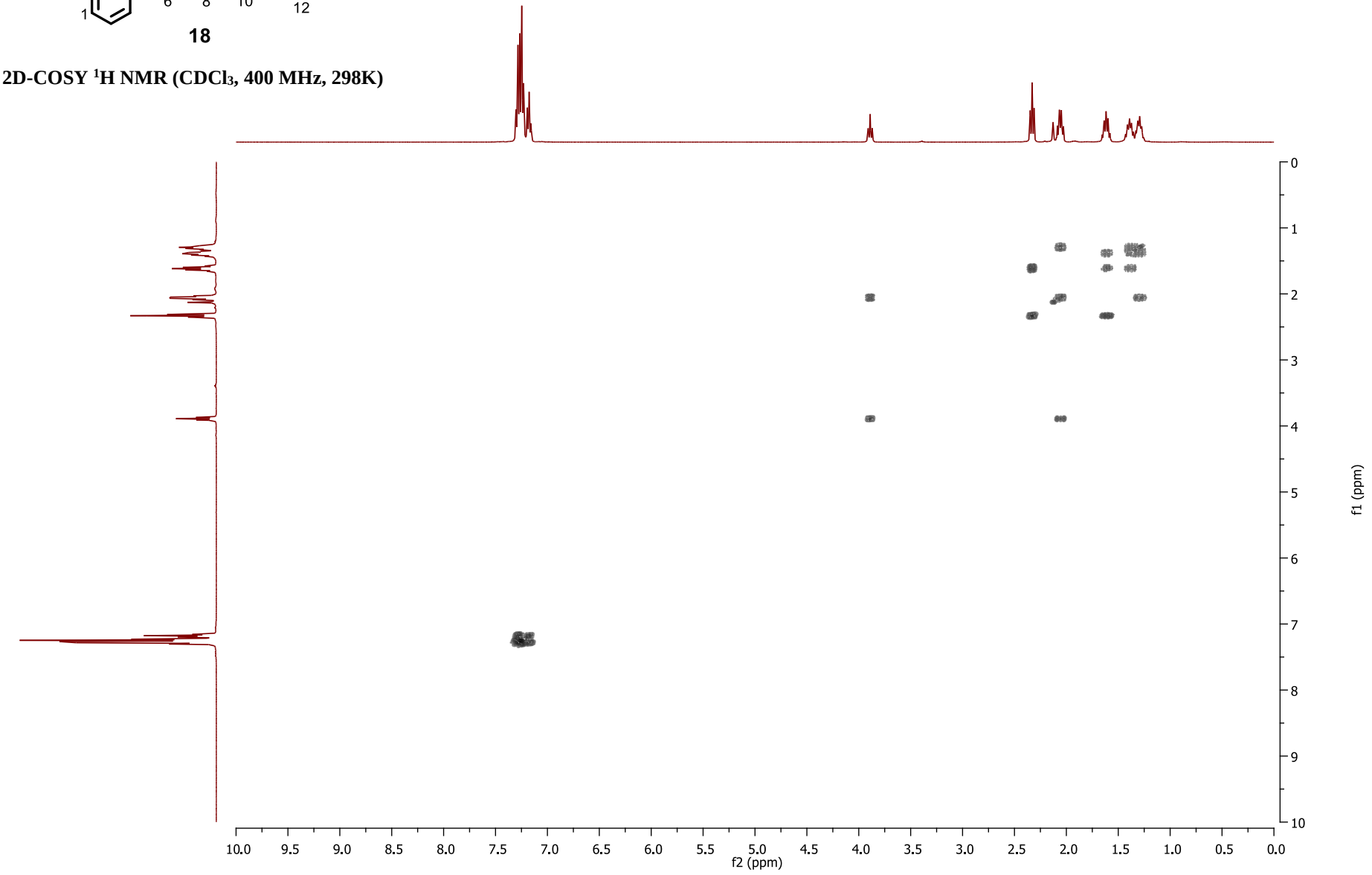
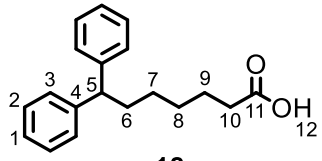




18

2D-COSY ^{1}H NMR ($CDCl_3$, 400 MHz, 298K)





18

2D-HSQC ^{13}C NMR ($CDCl_3$, 400 MHz, 298K)

Analysis Info

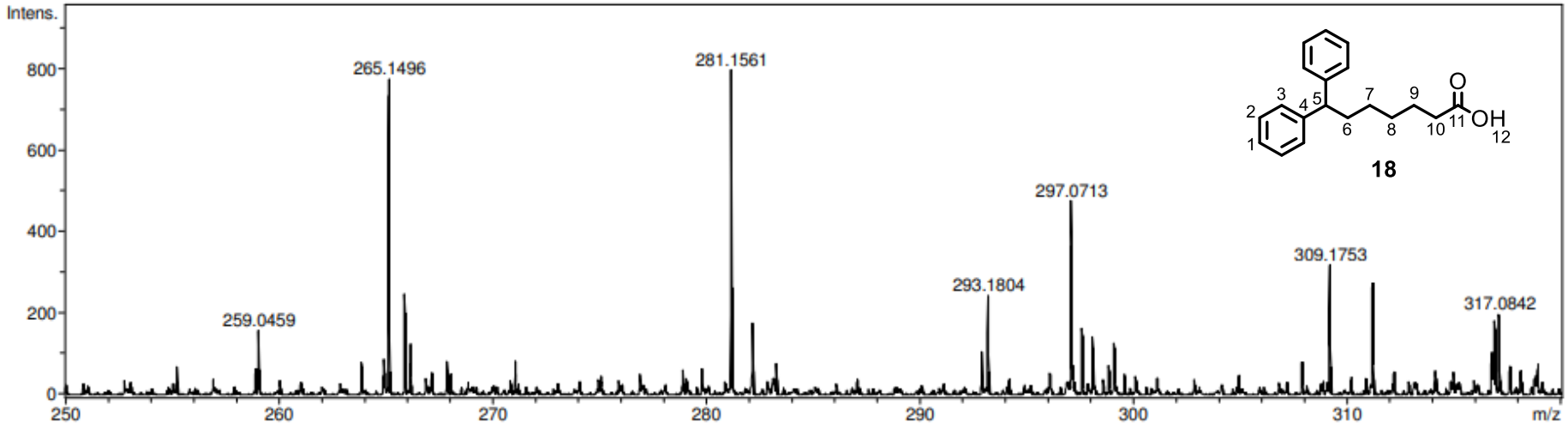
Sample Name **PWX78**

Acquisition Date 4/16/2019 12:03:59 PM

Instrument / Ser# micrOTOF-Q II 10300

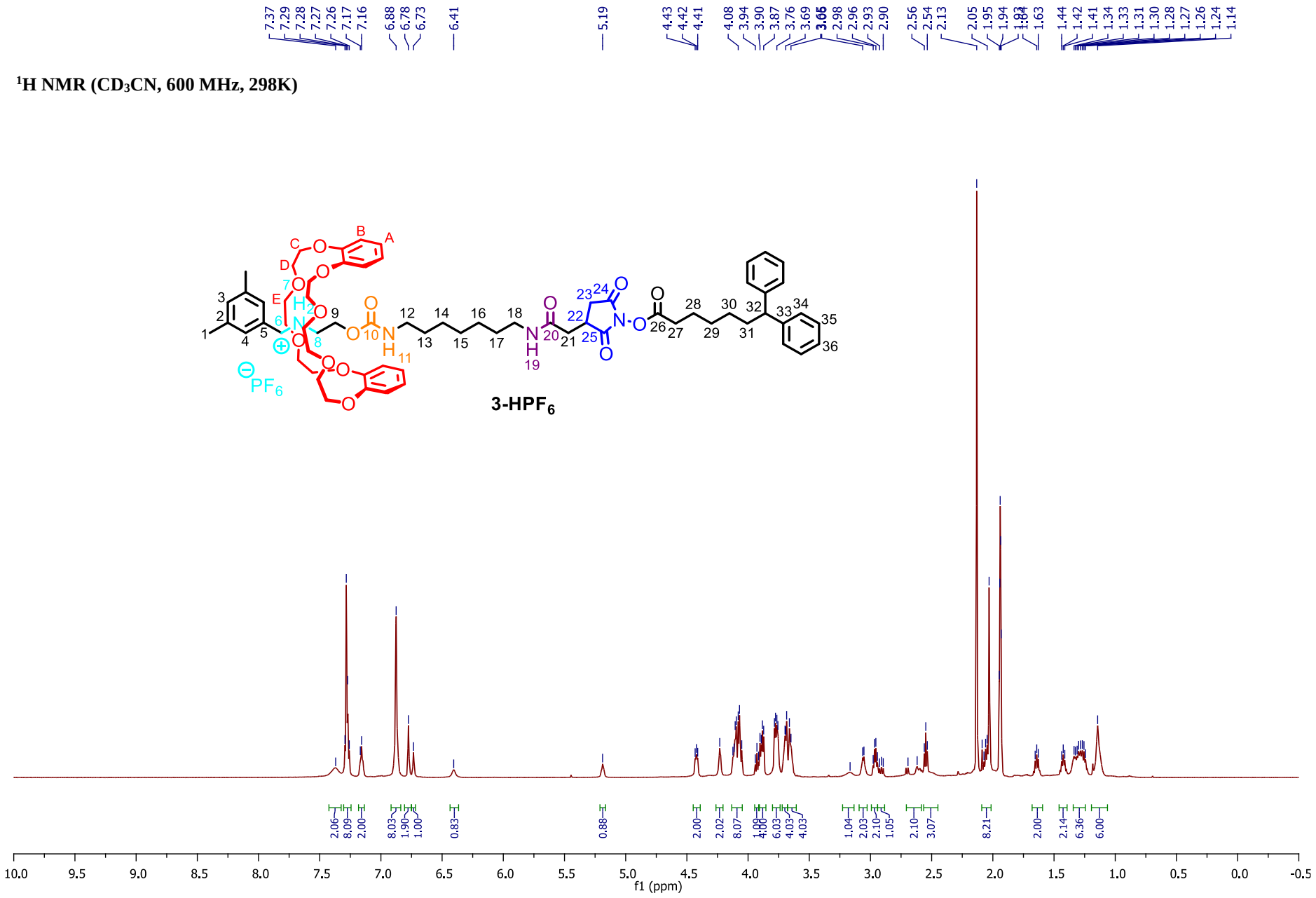
Acquisition Parameter

Source Type ESI | Ion Polarity Negative | Scan Begin 50 m/z | Scan End 1600 m/z

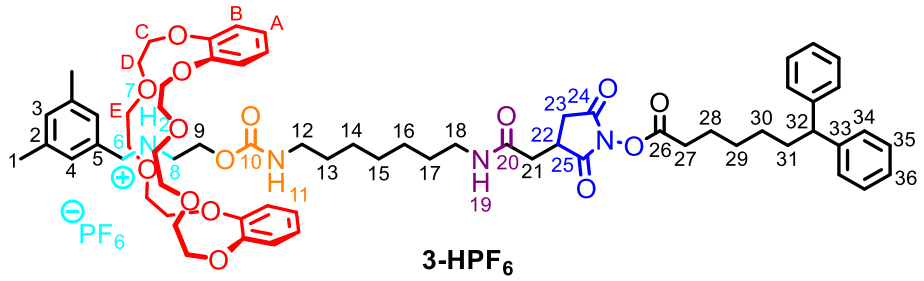


Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	rdb	e⁻ Conf	N-Rule
281.1561	1	C 19 H 21 O 2	100.00	281.1547	-1.4	-5.0	9.5	even	ok
	2	C 15 H 17 N 6	7.34	281.1520	-4.1	-14.5	10.5	even	ok

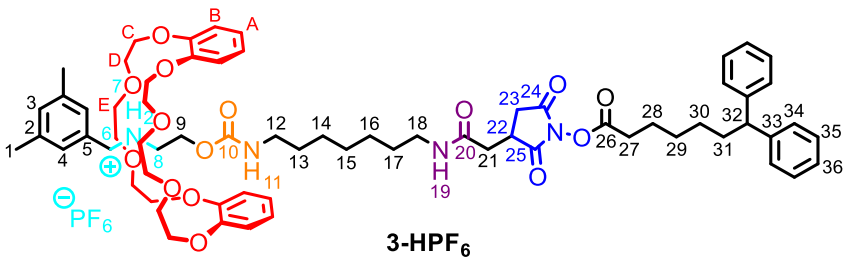
^{1}H NMR (CD_3CN, 600 MHz, 298K)



^{13}C NMR (CD_3CN, 150 MHz, 298K)

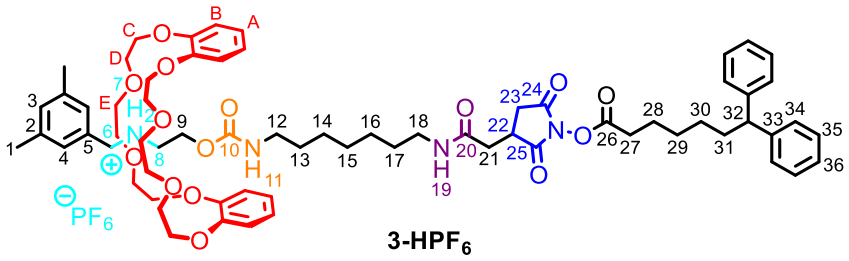


3-HPF_6



3-HPF$_6$

2D-COSY ^{1}H NMR (CD$_3$CN, 600 MHz, 298K)



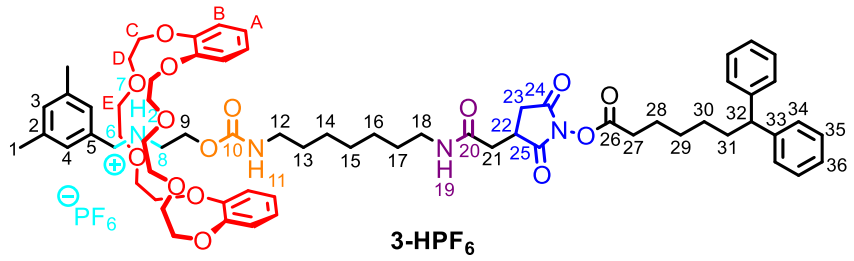
3-HPF$_6$

2D-HSQC ^{13}C NMR (CD$_3$CN, 600 MHz, 298K)

SYNAPT G2-S#NotSet MXG-ANR-109 30-Jul-2019

Y-SMART19073001 5 (0.228) Cm (5:6) 1: TOF MS ES+

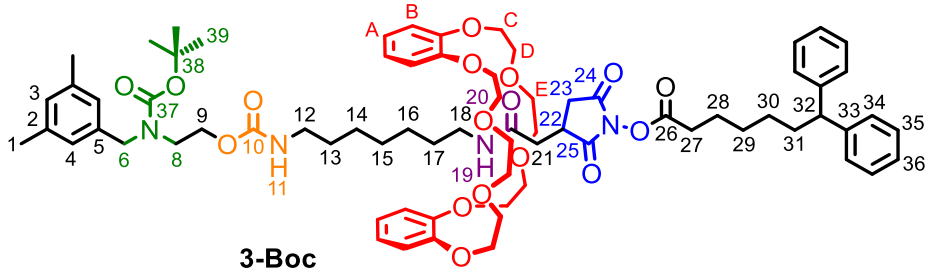
5.64e7



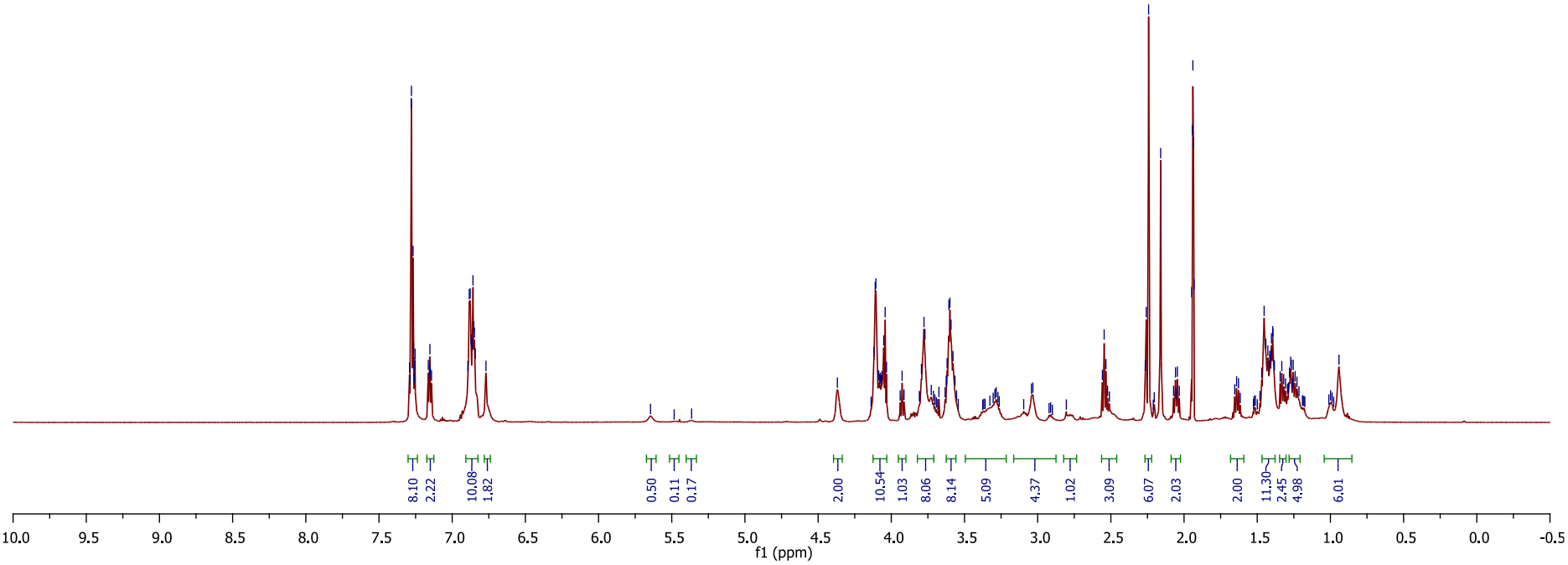
3-HPF$_6$

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
1203.6492	1203.6481	1.1	0.9	25.5	1128.9	0.691	50.09	C68 H91 N4 O15
	1203.6481	1.1	0.9	36.5	1129.3	1.134	32.16	C66 H79 N18 O5
	1203.6494	-0.2	-0.2	30.5	1130.0	1.791	16.67	C69 H87 N8 O11
	1203.6499	-0.7	-0.6	23.5	1133.1	4.939	0.72	C54 H83 N20 O12
	1203.6486	0.6	0.5	18.5	1134.1	5.961	0.26	C53 H87 N16 O16
	1203.6489	0.3	0.2	48.5	1135.4	7.265	0.07	C82 H79 N10
	1203.6503	-1.1	-0.9	42.5	1136.4	8.254	0.03	C85 H87 O6

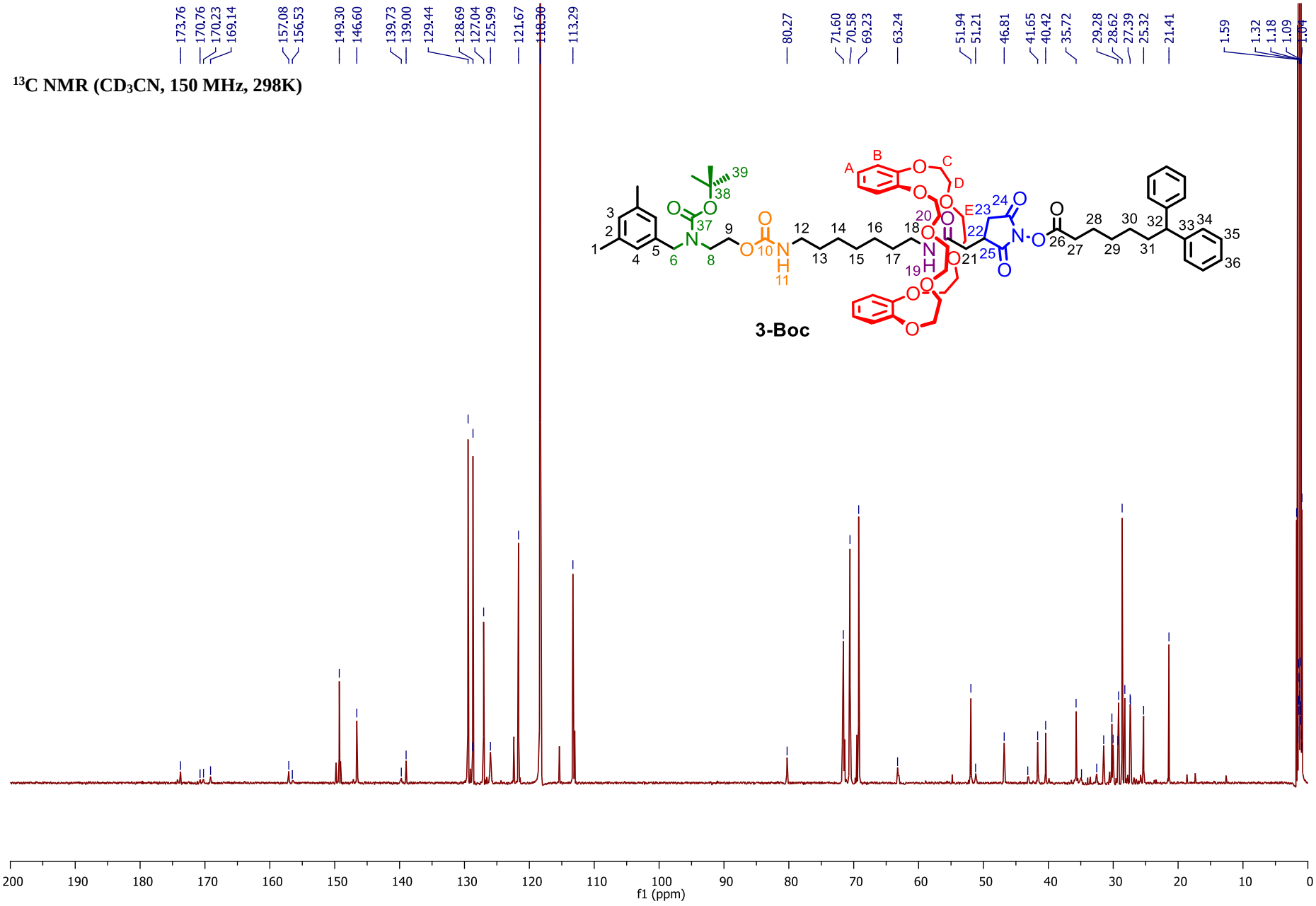
^{1}H NMR (CD_3CN, 600 MHz, 298K)

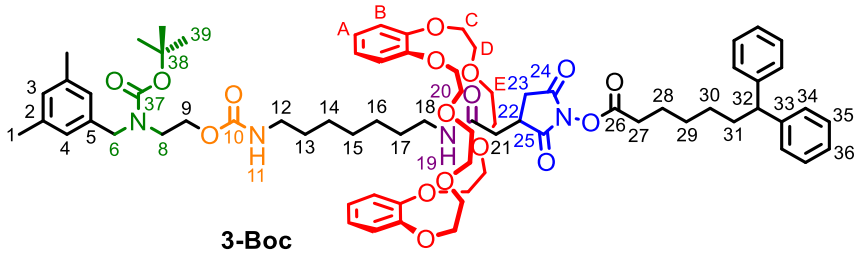


3-Boc



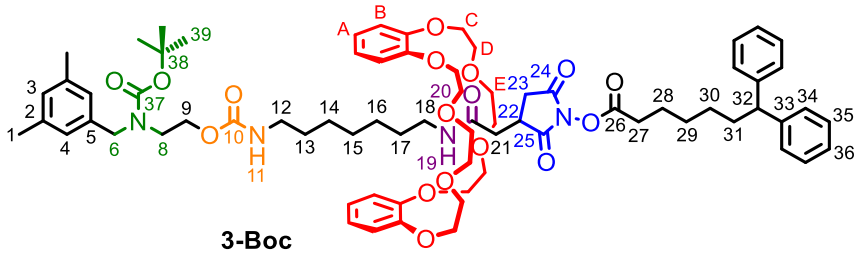
^{13}C NMR (CD_3CN, 150 MHz, 298K)





3-Boc

2D-COSY ^{1}H NMR (CD_3CN, 600 MHz, 298K)

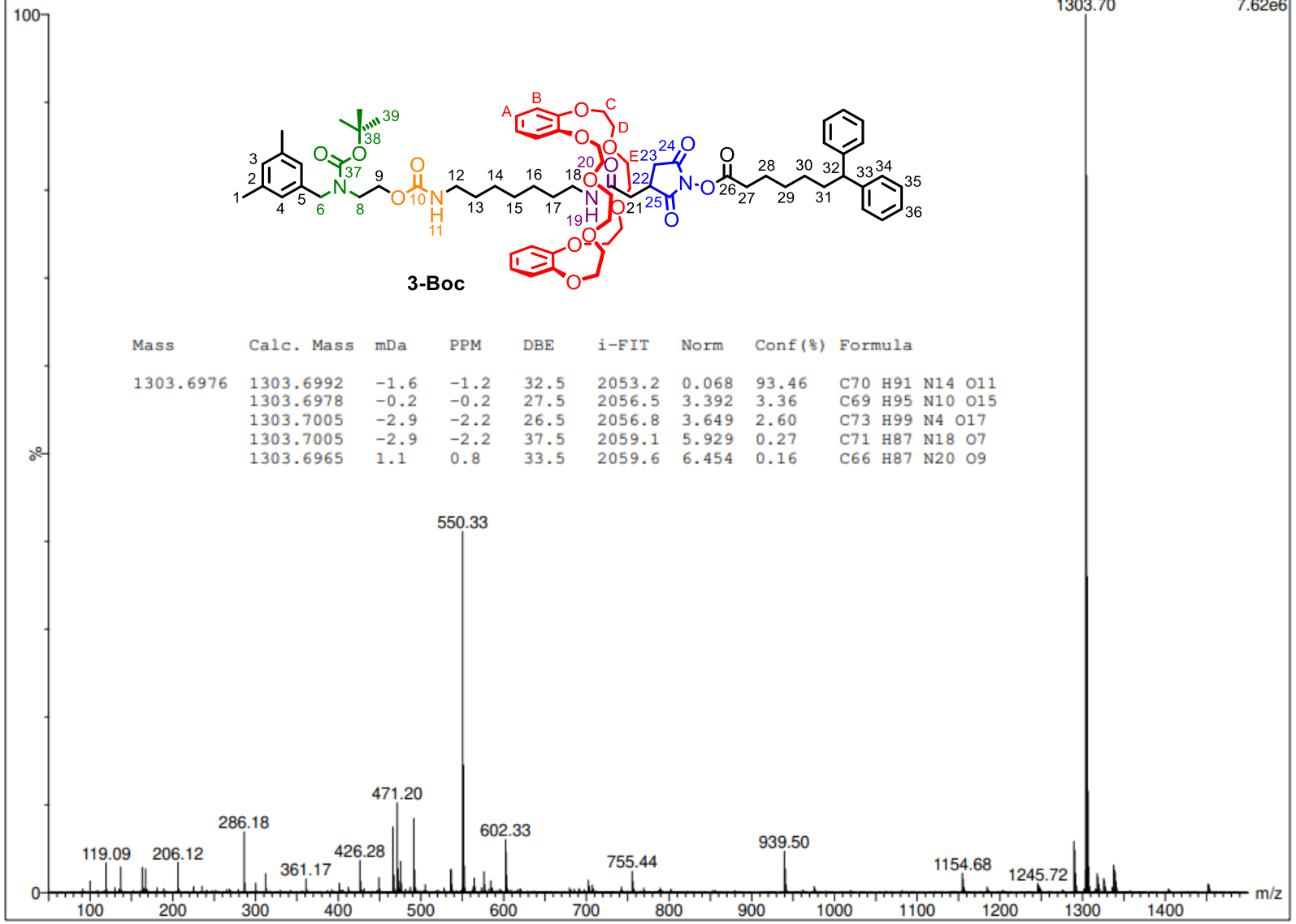


3-Boc

2D-HSQC ^{13}C NMR (CD_3CN, 600 MHz, 298K)

SYNAPT G2-S#NotSet MXG1-139 07-Oct-2019

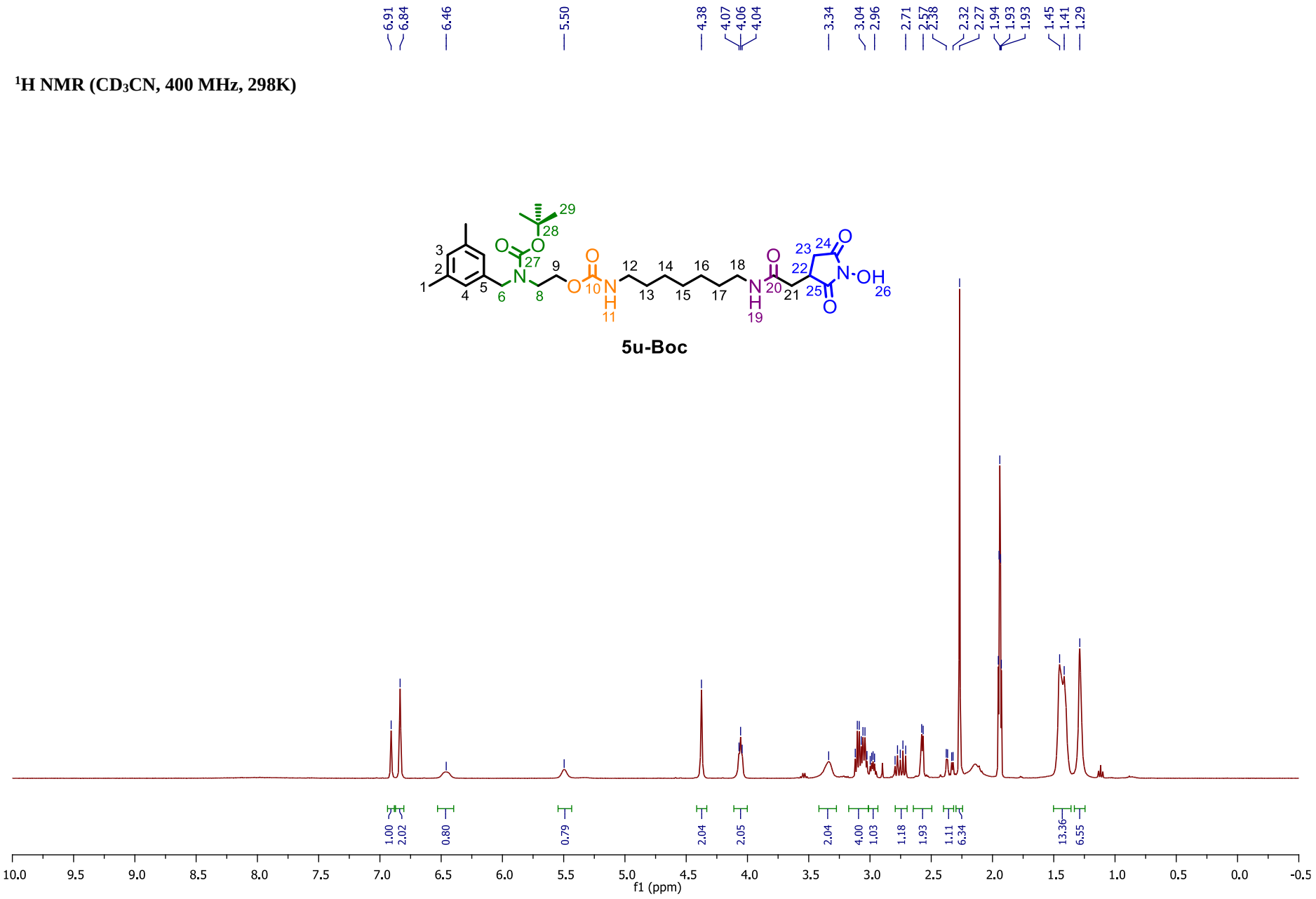
Y-SMART19100701 5 (0.228) Cm (5:8) 1: TOF MS ES+ 7.62e6



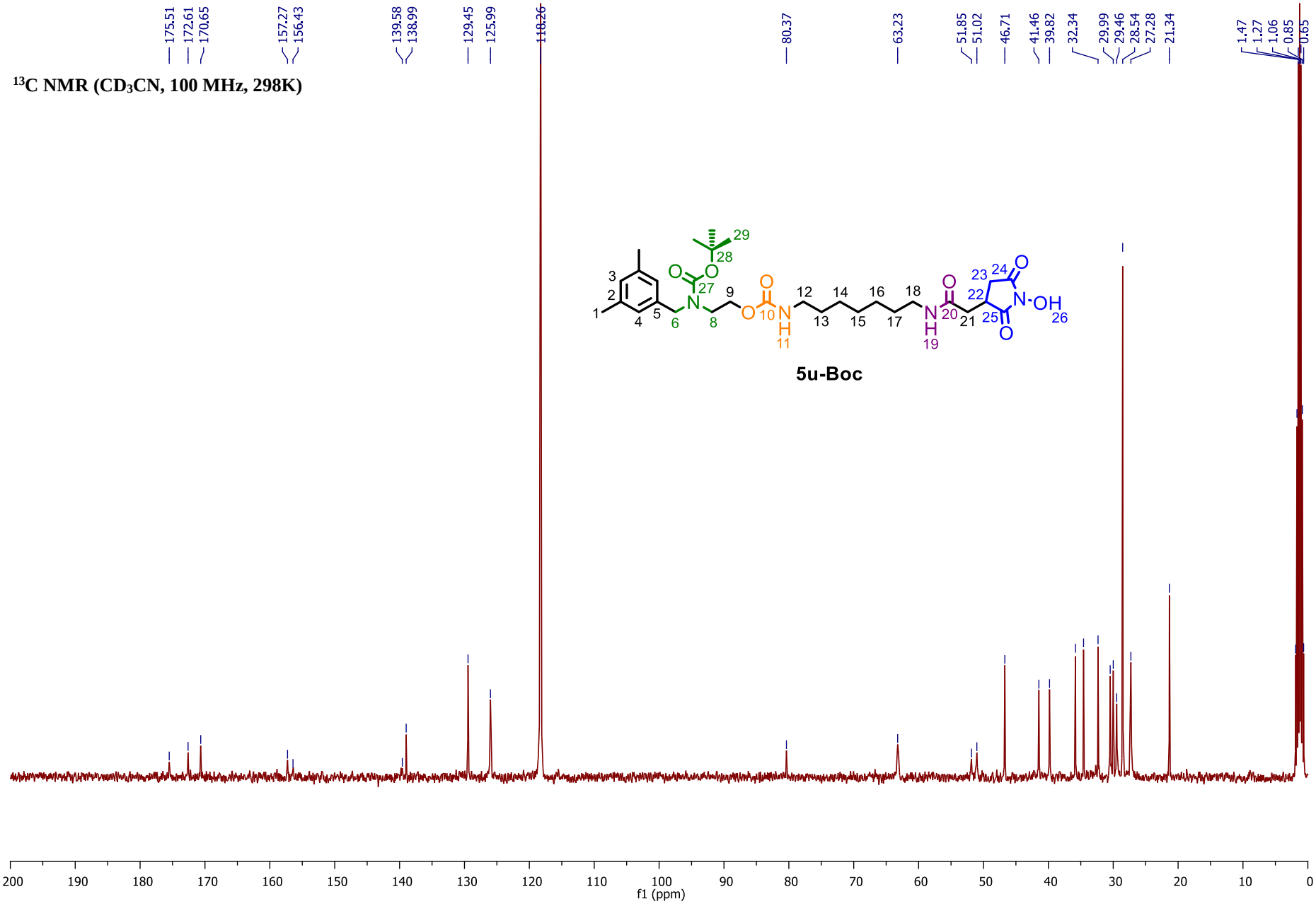
3-Boc

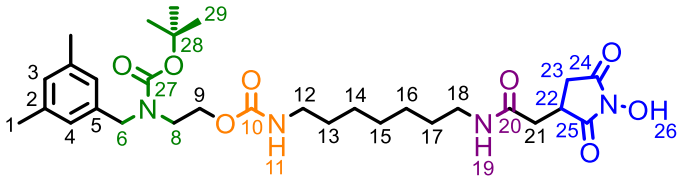
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
1303.6976	1303.6992	-1.6	-1.2	32.5	2053.2	0.068	93.46	C70 H91 N14 O11
	1303.6978	-0.2	-0.2	27.5	2056.5	3.392	3.36	C69 H95 N10 O15
	1303.7005	-2.9	-2.2	26.5	2056.8	3.649	2.60	C73 H99 N4 O17
	1303.7005	-2.9	-2.2	37.5	2059.1	5.929	0.27	C71 H87 N18 O7
	1303.6965	1.1	0.8	33.5	2059.6	6.454	0.16	C66 H87 N20 O9

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



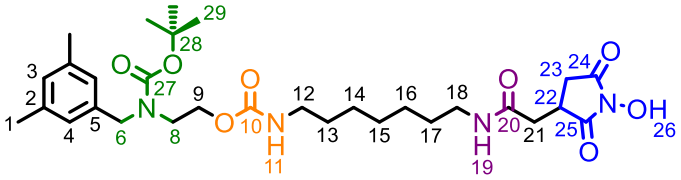
^{13}C NMR (CD_3CN, 100 MHz, 298K)





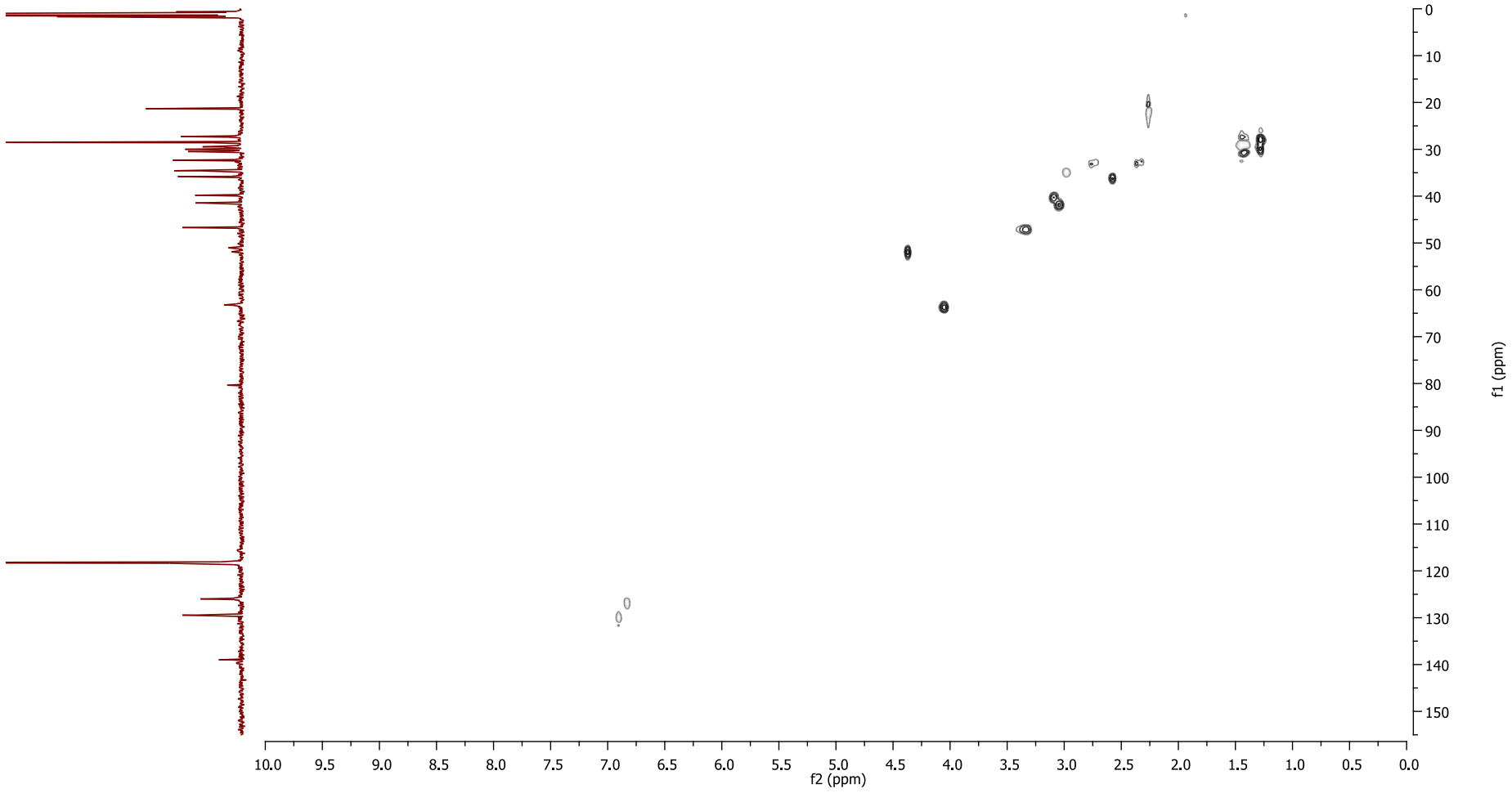
5u-Boc

2D-COSY ^{1}H NMR (CD_3CN, 400 MHz, 298K)



5u-Boc

2D-HSQC ^{13}C NMR (CD_3CN, 400 MHz, 298K)



Analysis Info

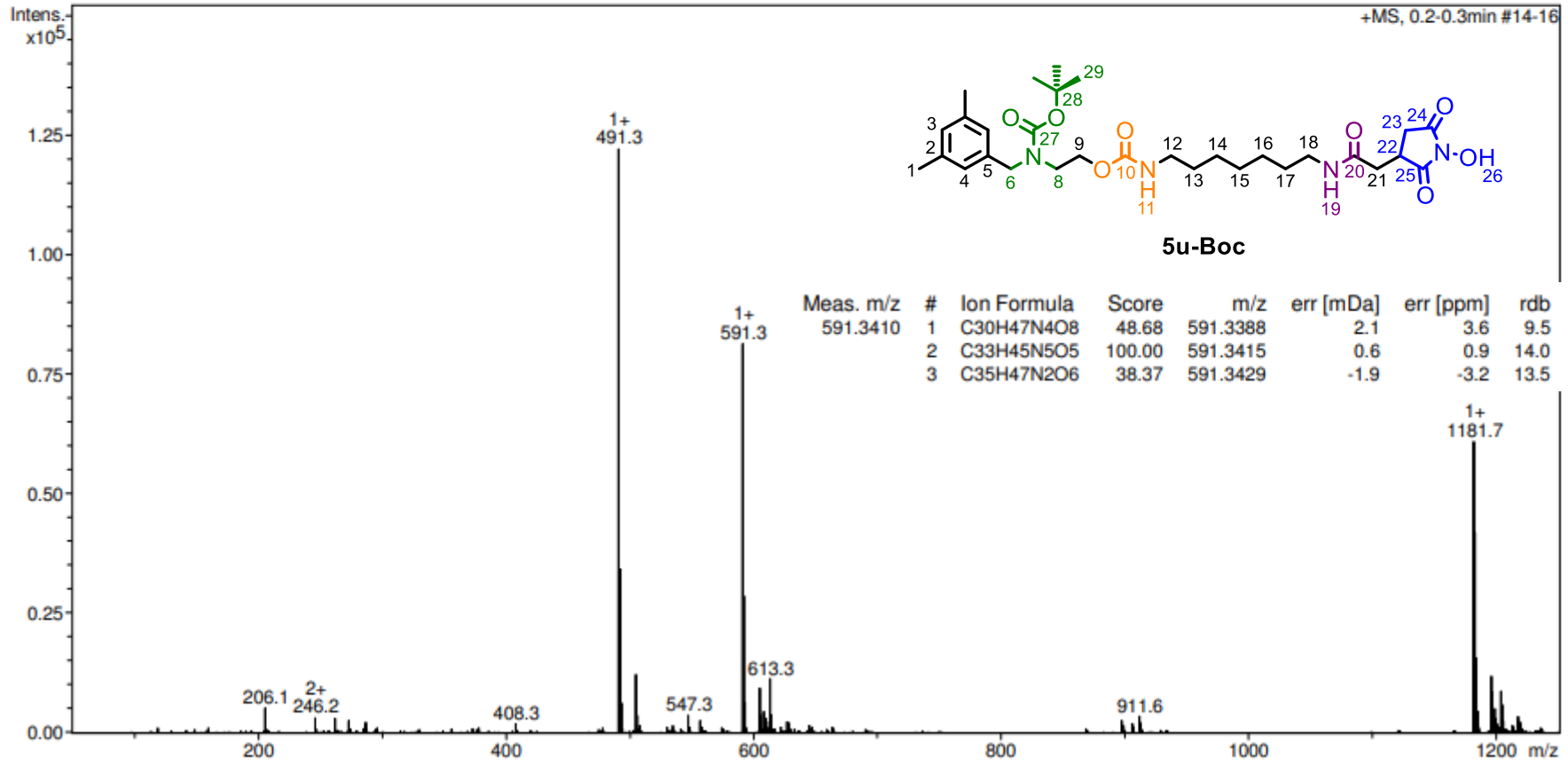
Sample Name **MXG2-14**

Acquisition Date 12/6/2019 2:43:05 PM

Instrument / Ser# micrOTOF-Q 228888.10300

Acquisition Parameter

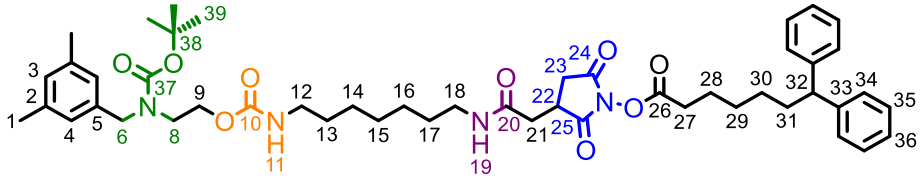
Source Type ESI | Ion Polarity Positive | Scan Begin 50 m/z | Scan End 2200 m/z



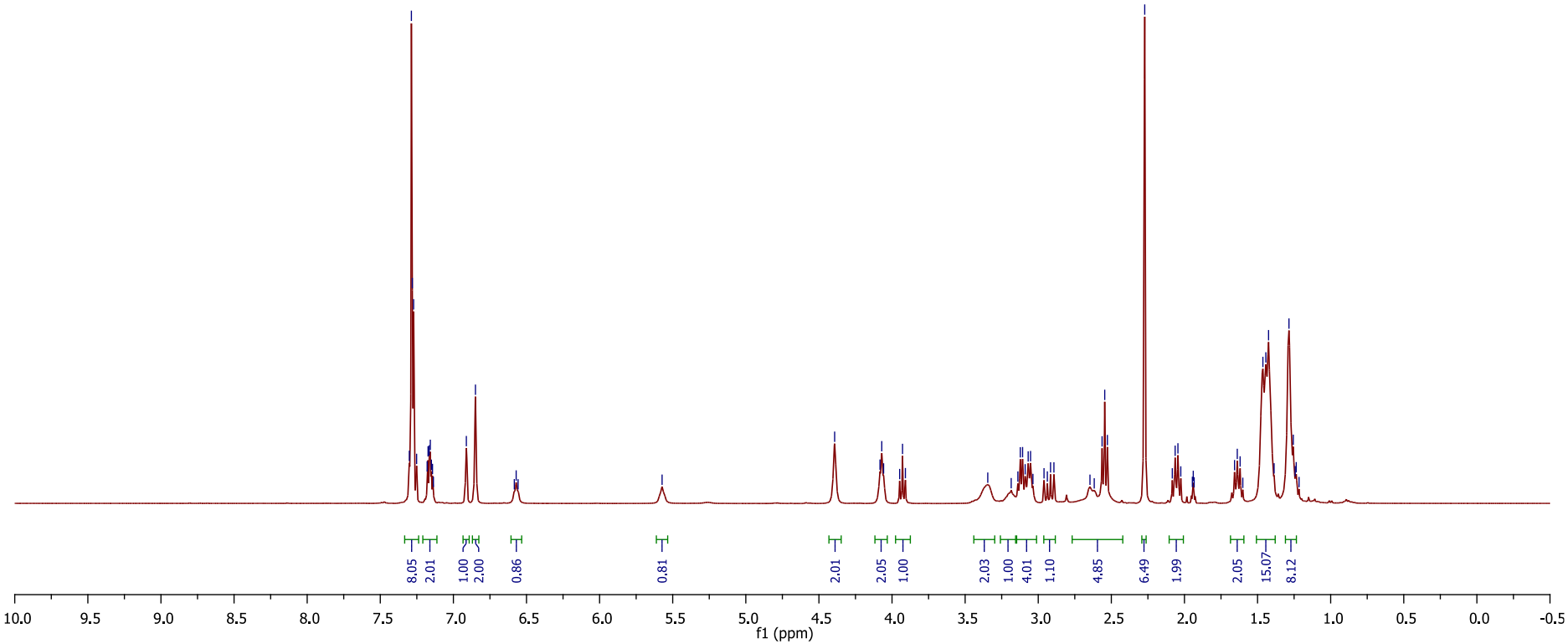
5u-Boc

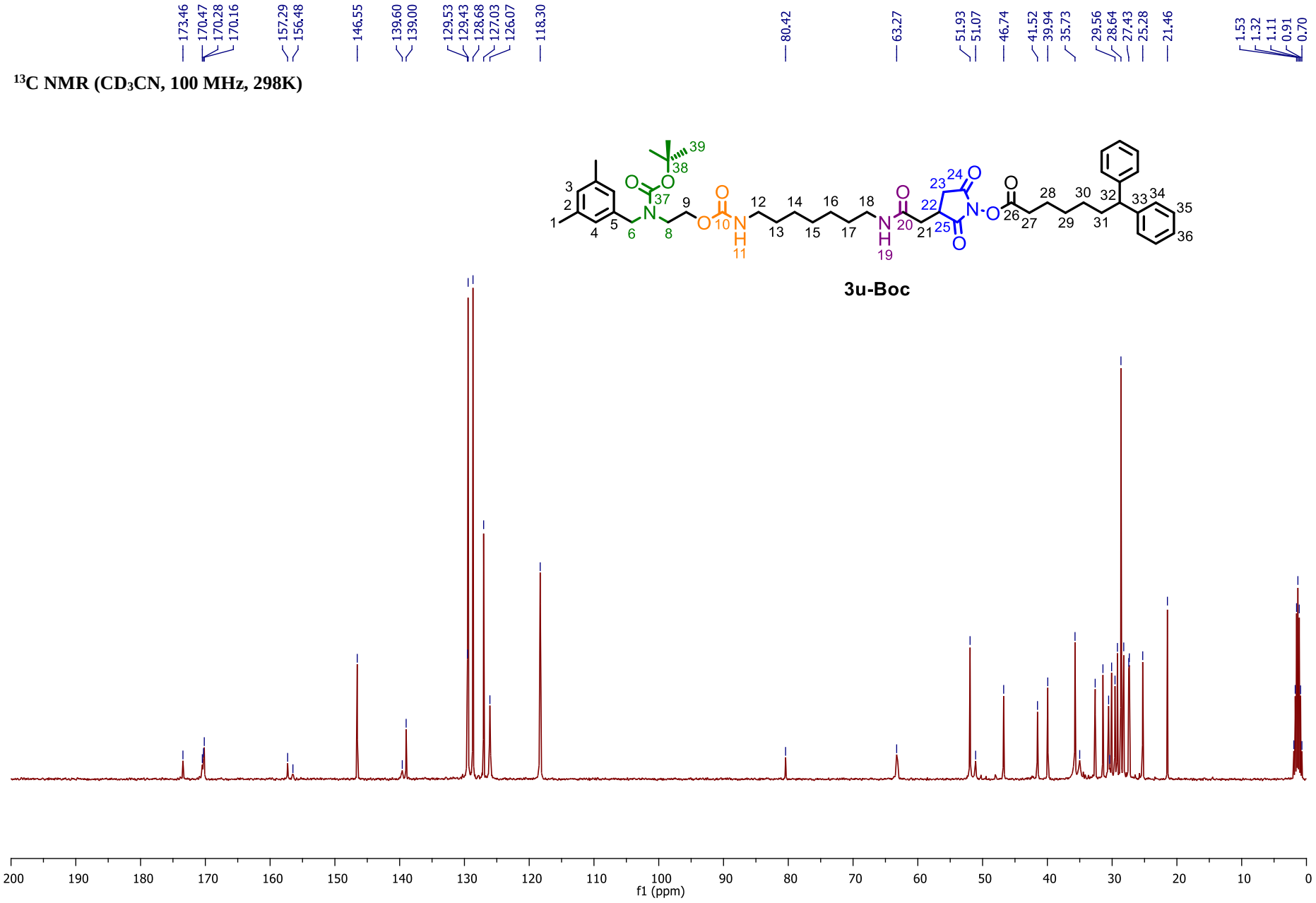
Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	rdb	e⁻ Conf	N-Rule
591.3410	1	C30H47N4O8	48.68	591.3388	2.1	3.6	9.5	even	ok
	2	C33H45N5O5	100.00	591.3415	0.6	0.9	14.0	odd	ok
	3	C35H47N2O6	38.37	591.3429	-1.9	-3.2	13.5	even	ok

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

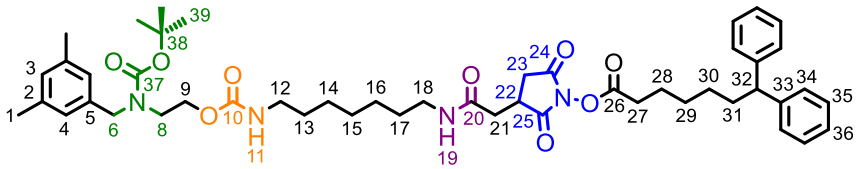


3u-Boc



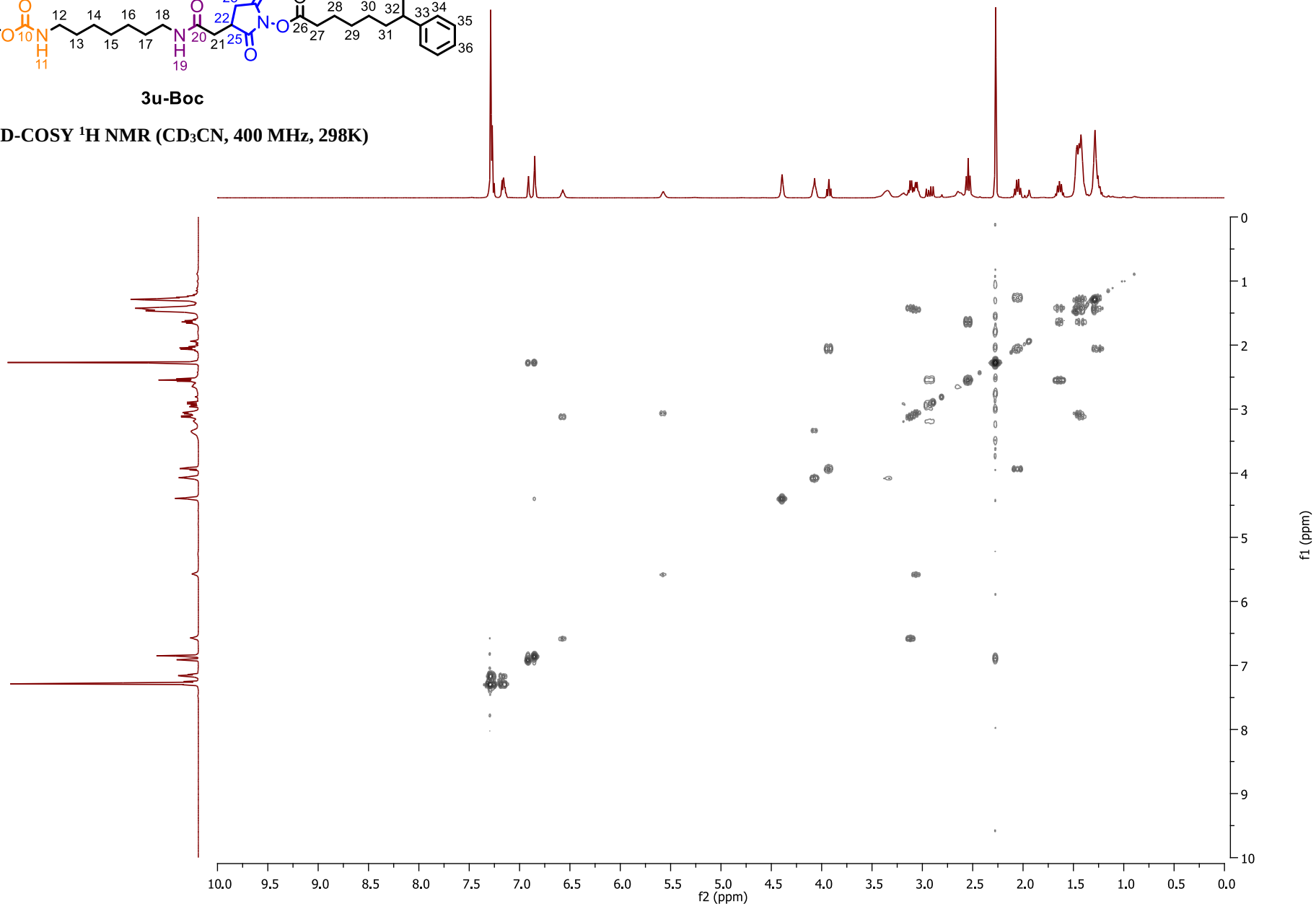


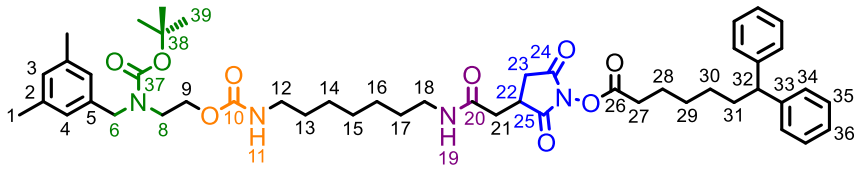
^{13}C NMR (CD_3CN, 100 MHz, 298K)



3u-Boc

2D-COSY ^{1}H NMR (CD_3CN, 400 MHz, 298K)





3u-Boc

2D-HSQC ^{13}C NMR (CD_3CN, 400 MHz, 298K)

Analysis Info

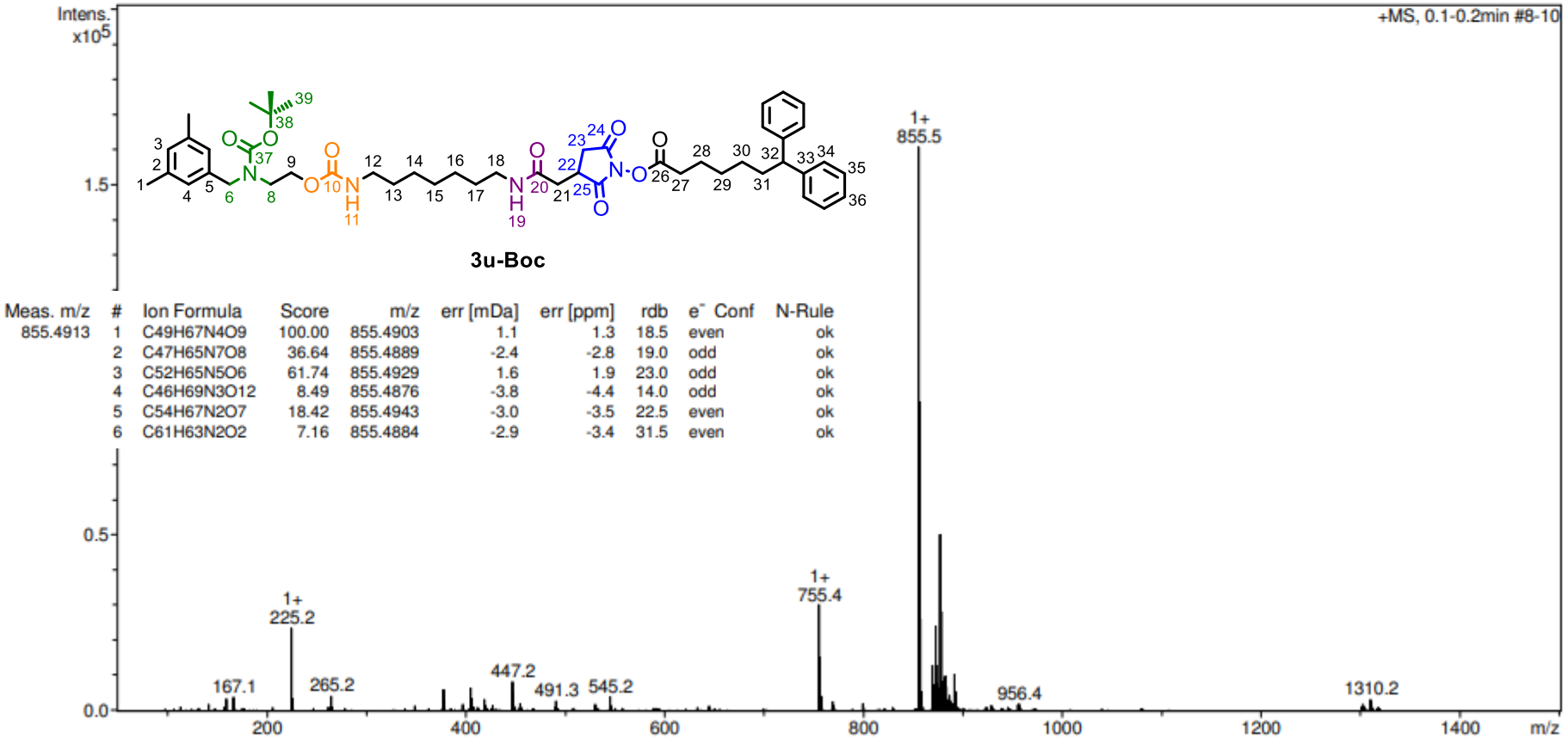
Sample Name **MGX2-16**

Acquisition Date 12/10/2019 5:34:11 PM

Instrument / Ser# micrOTOF-Q 228888.10300

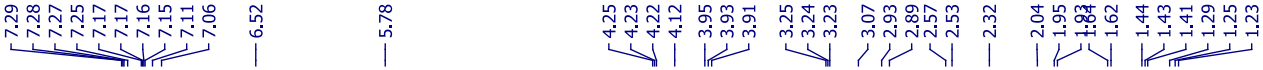
Acquisition Parameter

Source Type ESI | Ion Polarity Positive | Scan Begin 50 m/z | Scan End 2200 m/z

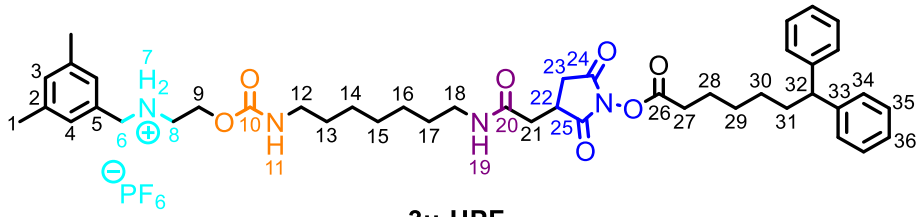


3u-Boc

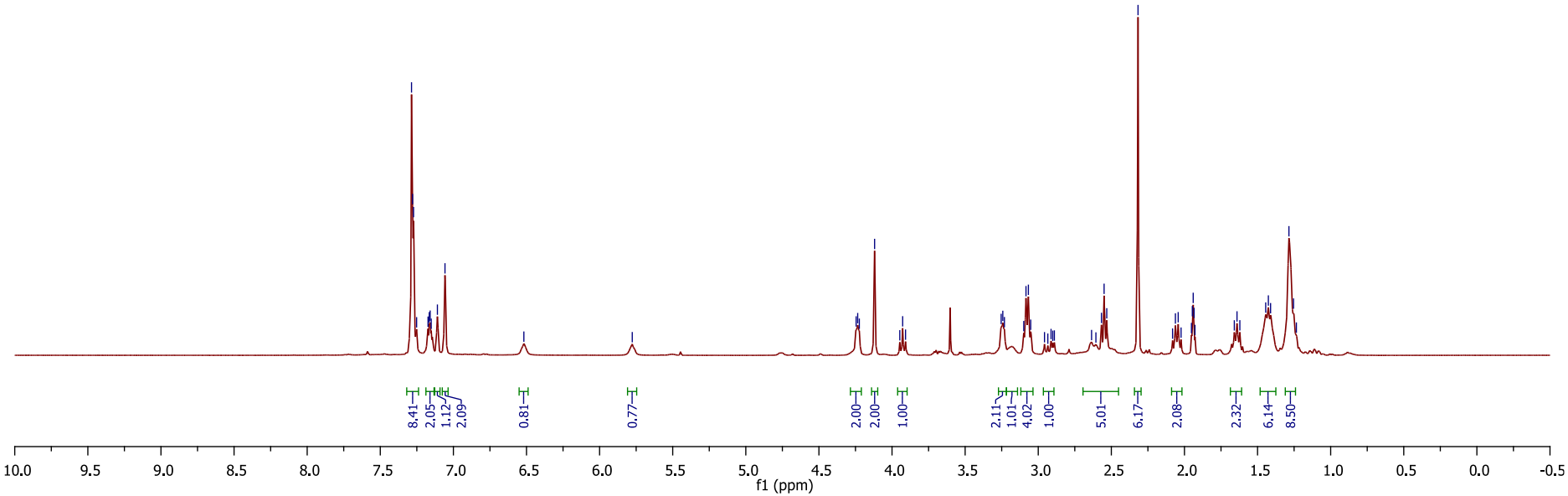
Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	rdb	e⁻ Conf	N-Rule
855.4913	1	C49H67N4O9	100.00	855.4903	1.1	1.3	18.5	even	ok
	2	C47H65N7O8	36.64	855.4889	-2.4	-2.8	19.0	odd	ok
	3	C52H65N5O6	61.74	855.4929	1.6	1.9	23.0	odd	ok
	4	C46H69N3O12	8.49	855.4876	-3.8	-4.4	14.0	odd	ok
	5	C54H67N2O7	18.42	855.4943	-3.0	-3.5	22.5	even	ok
	6	C61H63N2O2	7.16	855.4884	-2.9	-3.4	31.5	even	ok



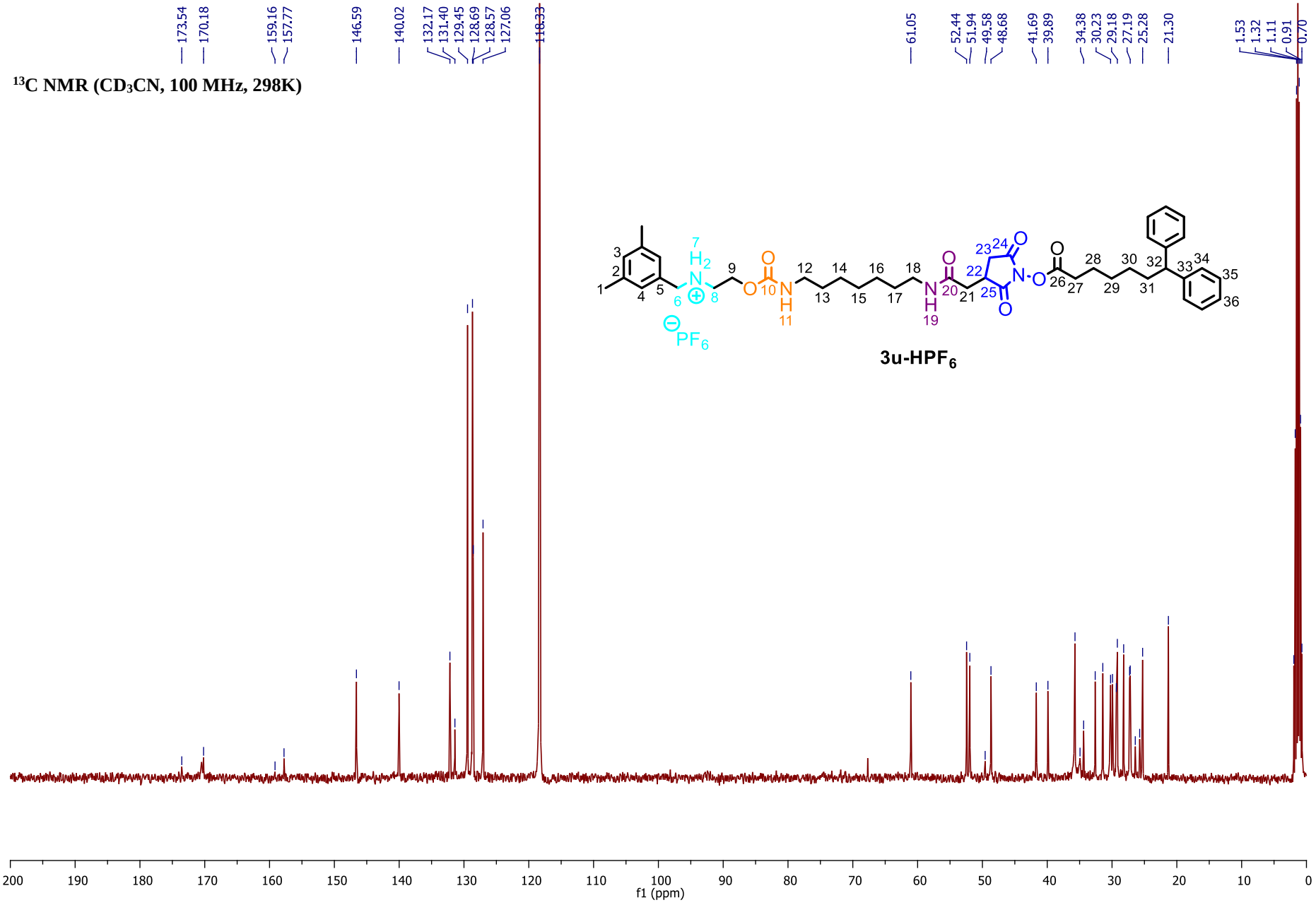
^{1}H NMR (CD_3CN, 400 MHz, 298K)



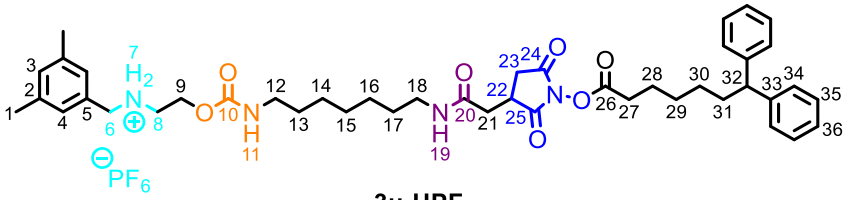
3u-HPF_6



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

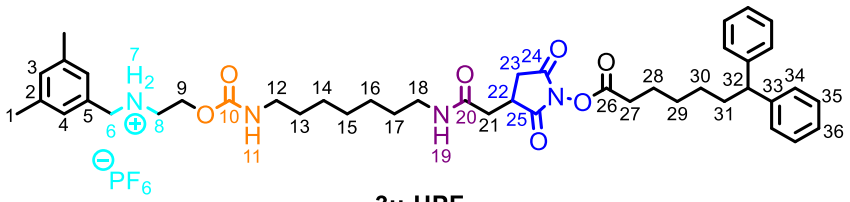


3u-HPF$_6$



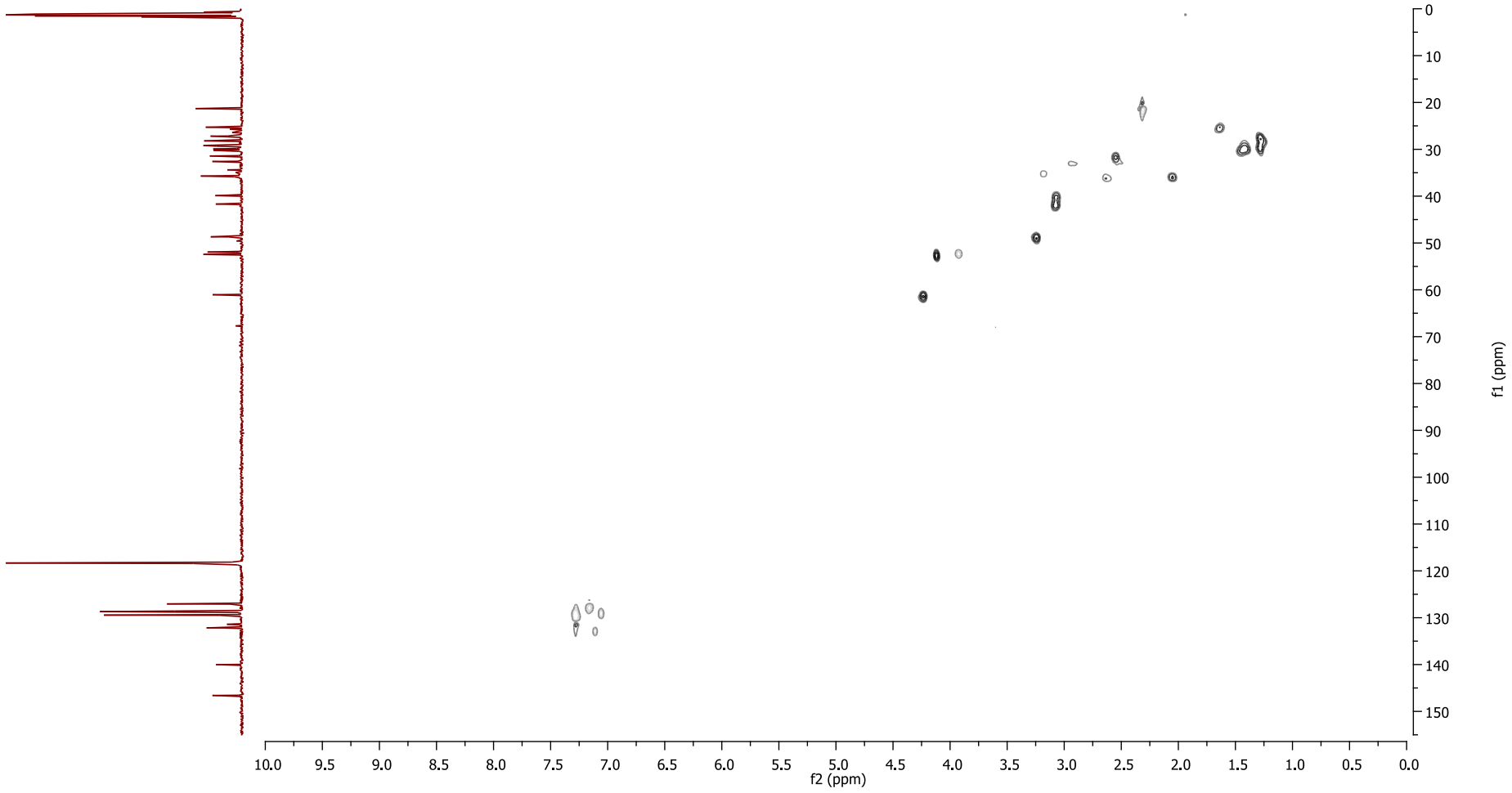
3u-HPF$_6$

2D-COSY ^{1}H NMR (CD$_3$CN, 400 MHz, 298K)



3u-HPF$_6$

2D-HSQC ^{13}C NMR (CD$_3$CN, 400 MHz, 298K)



Analysis Info

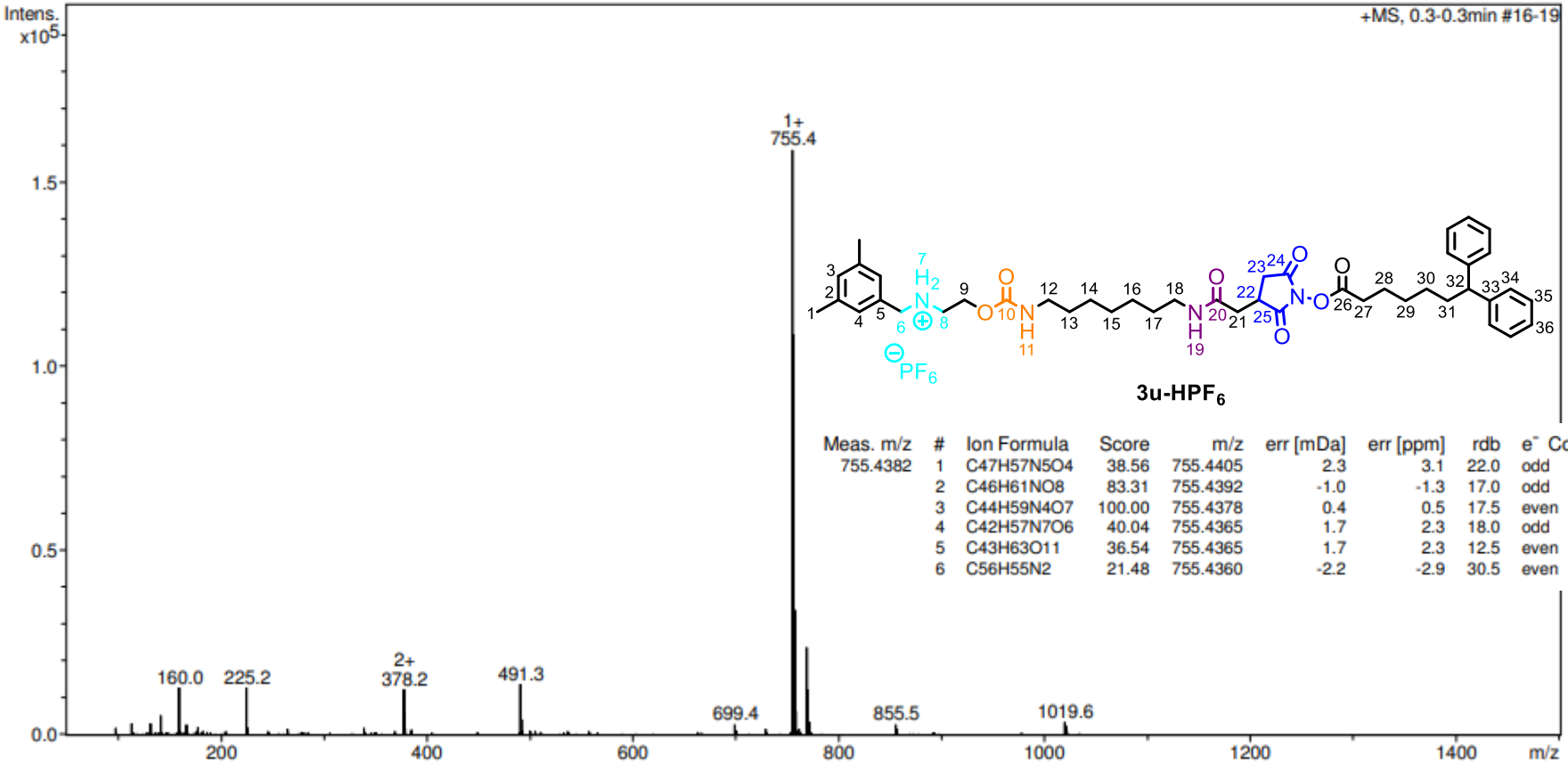
Sample Name **MGX2-18**

Acquisition Date 12/10/2019 11:44:28 AM

Instrument / Ser# micrOTOF-Q 228888.10300

Acquisition Parameter

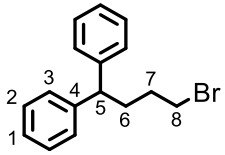
Source Type ESI | Ion Polarity Positive | Scan Begin 50 m/z | Scan End 2200 m/z



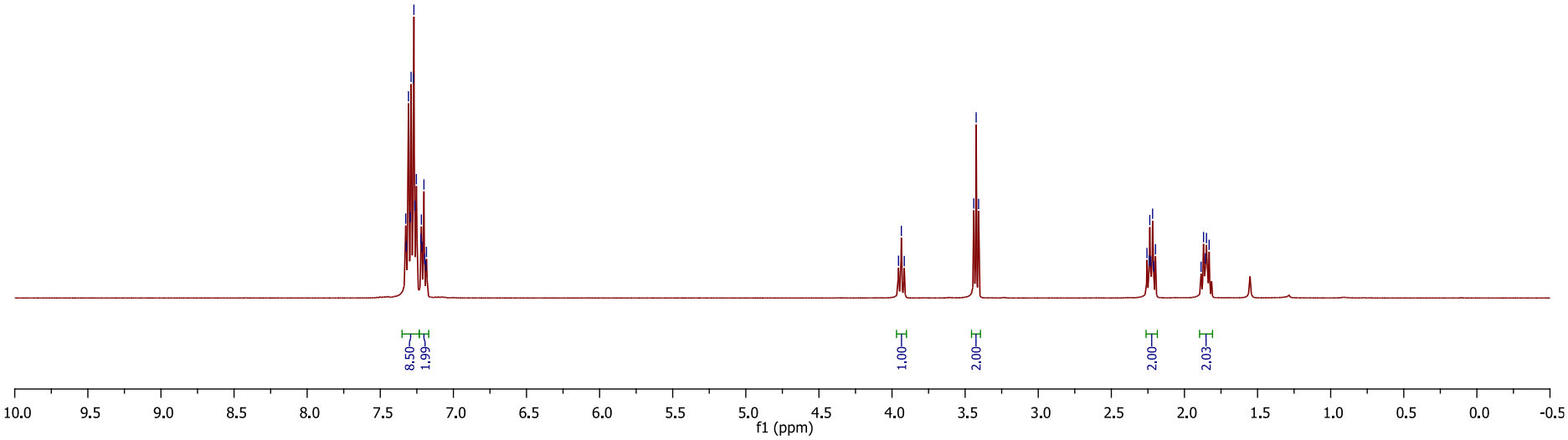
3u-HPF$_6$

Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	rdb	e⁻ Conf	N-Rule
755.4382	1	C47H57N5O4	38.56	755.4405	2.3	3.1	22.0	odd	ok
	2	C46H61NO8	83.31	755.4392	-1.0	-1.3	17.0	odd	ok
	3	C44H59N4O7	100.00	755.4378	0.4	0.5	17.5	even	ok
	4	C42H57N7O6	40.04	755.4365	1.7	2.3	18.0	odd	ok
	5	C43H63O11	36.54	755.4365	1.7	2.3	12.5	even	ok
	6	C56H55N2	21.48	755.4360	-2.2	-2.9	30.5	even	ok

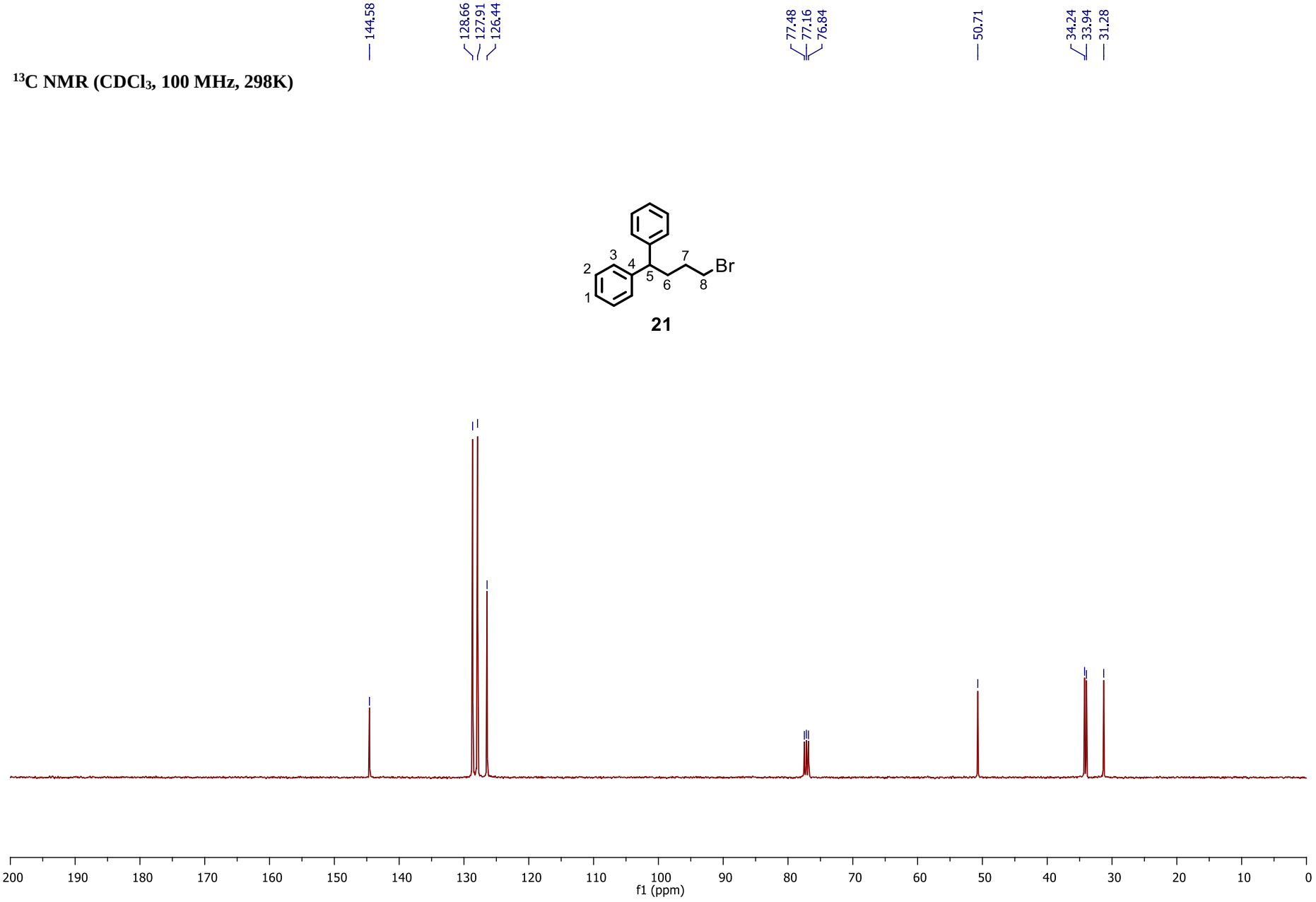
^{1}H NMR ($CDCl_3$, 400 MHz, 298K)

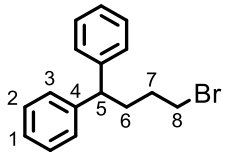


21



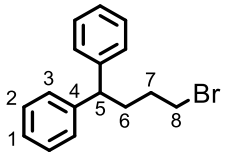
^{13}C NMR ($CDCl_3$, 100 MHz, 298K)





21

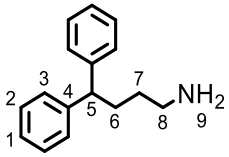
2D-COSY ^{1}H NMR ($CDCl_3$, 400 MHz, 298K)



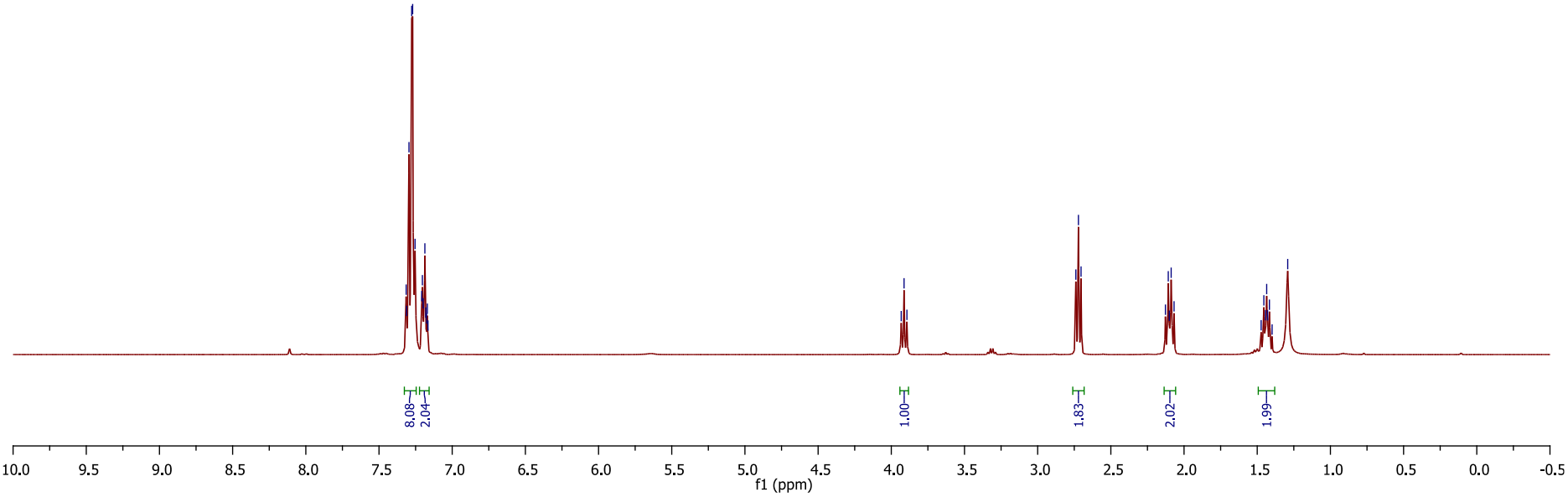
21

2D-HSQC ^{13}C NMR ($CDCl_3$, 400 MHz, 298K)

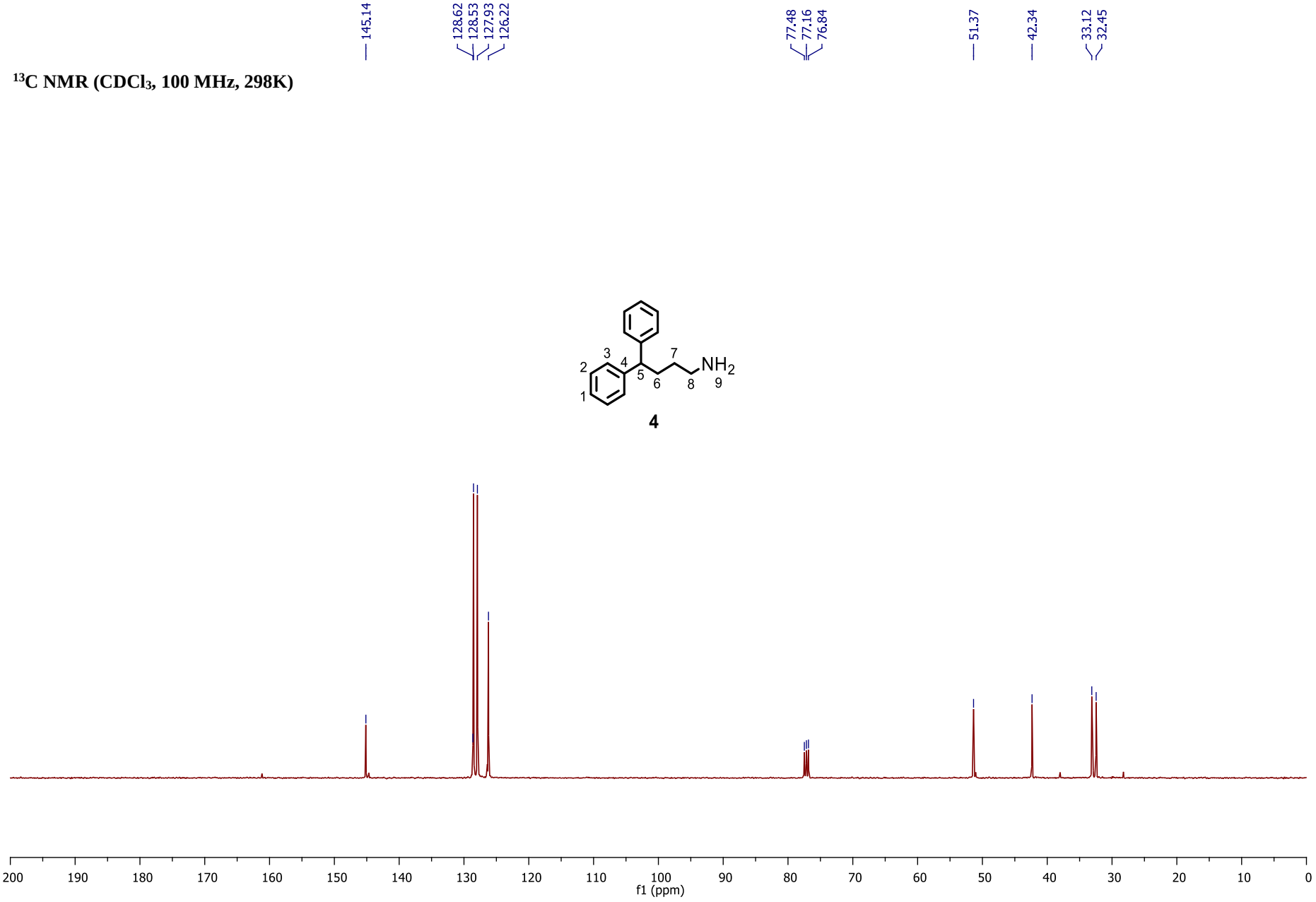
^{1}H NMR ($CDCl_3$, 400 MHz, 298K)

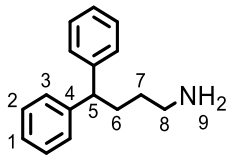


4



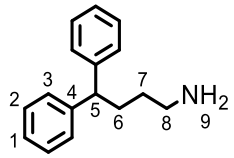
^{13}C NMR ($CDCl_3$, 100 MHz, 298K)





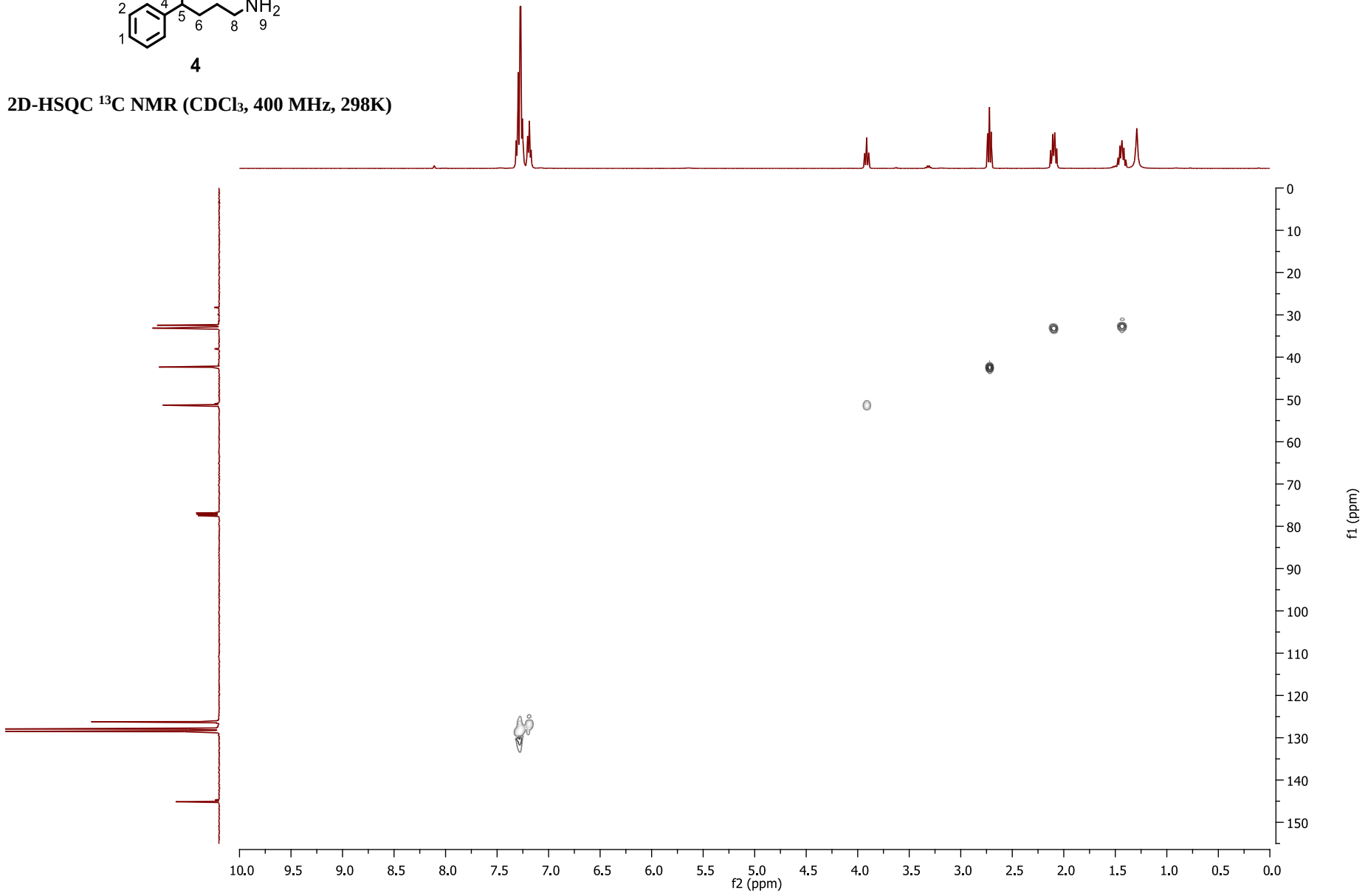
4

2D-COSY ^{1}H NMR ($CDCl_3$, 400 MHz, 298K)



4

2D-HSQC ^{13}C NMR ($CDCl_3$, 400 MHz, 298K)



Analysis Info

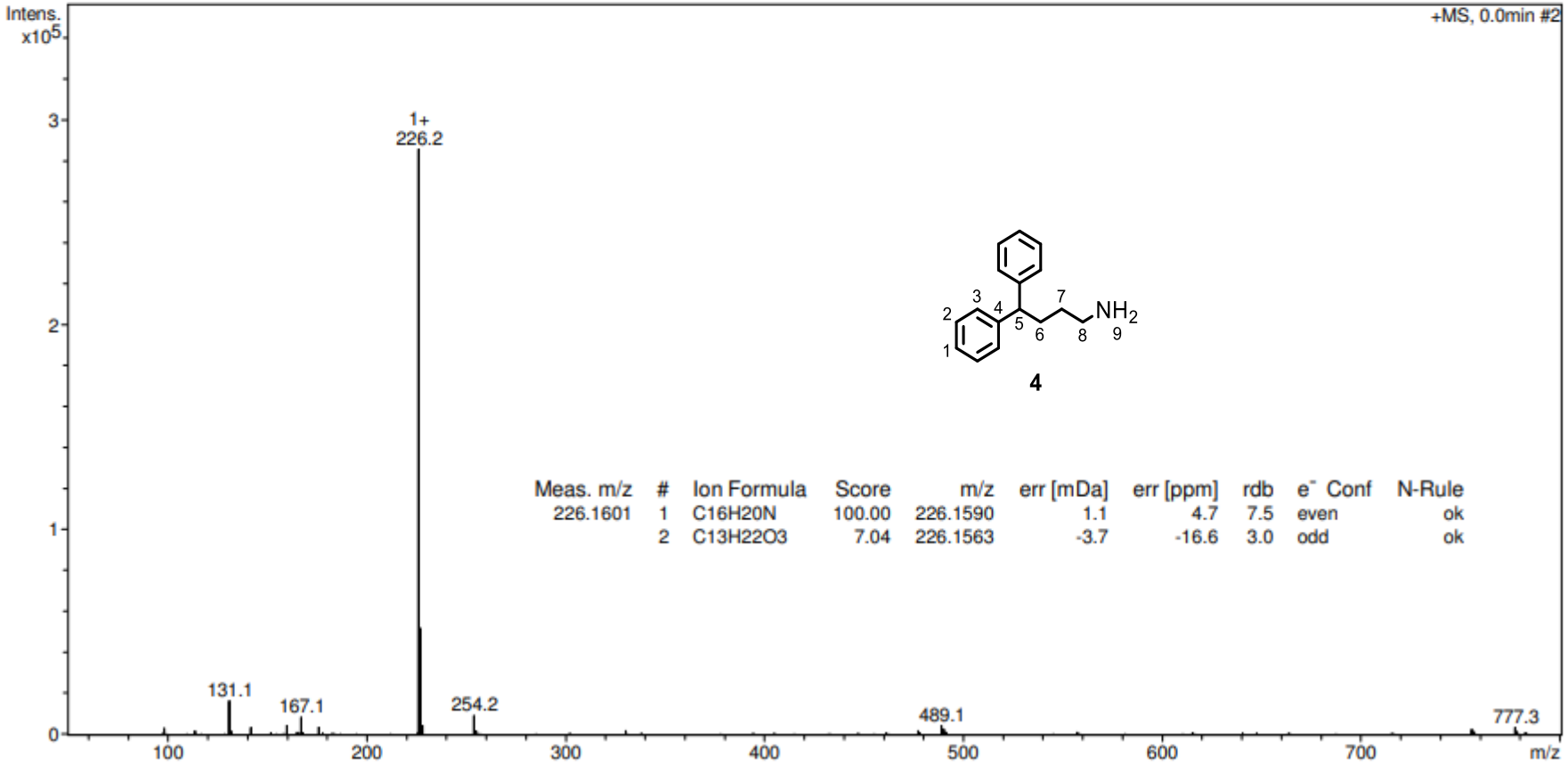
Sample Name **MXG1-194**

Acquisition Date 12/11/2019 9:31:04 AM

Instrument / Ser# micrOTOF-Q 228888.10300

Acquisition Parameter

Source Type ESI | Ion Polarity Positive | Scan Begin 50 m/z | Scan End 2200 m/z



4

Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	rdb	e⁻ Conf	N-Rule
226.1601	1	C16H20N	100.00	226.1590	1.1	4.7	7.5	even	ok
	2	C13H22O3	7.04	226.1563	-3.7	-16.6	3.0	odd	ok