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Supporting Information

Interplay between a Foldamer Helix and a Macrocycle in a Foldarotaxane Architecture

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Other Supplementary Materials for this manuscript includes the following:

Crystallographic information files for (**1**)$_2$ (CIF 2050780), **1⊃2-HPF$_6$** (CIF 2050779).

1. Methods for NMR, X-ray crystallography and molecular modeling

1.1 Nuclear magnetic resonance spectroscopy

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 and 1.94 ppm for $CHCl_3$ and CH_3CN for ^{1}H spectrum, and 77.16 ppm and 1.32 ppm 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.

1.2 Nuclear magnetic resonance titrations

Titrations were performed in an NMR tube (5 mm diameter) by adding aliquots of the guest stock solutions in $CDCl_3$ (rotaxane or rod) by means of a microsyringe (25 µL) to a 500 µL solution of the foldamer **1** in $CDCl_3$ (0.1 mM). After homogenization, the volume was reduced to 50 µL to reach a concentration of 1 mM. High concentration enhance the kinetic of binding *via* unfolding - refolding mechanism of the helix around the guest. Finally, the sample was heated to 318 K until the thermondynamic equilibrium was reached and after dilution to 0.1 mM and equilibration, NMR spectra were recorded using a 700 MHz spectrometer (298 K).

1.3 X-ray crystallography

The diffraction data for compounds **(1)$_2$**, **1⊃2-HPF$_6$** 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. The X-ray source is equipped with high flux Osmic Varimax mirrors and a Dectris Pilatus 300K detector. Data were processed with the Rigaku Oxford Diffraction CrysalisPro software (version1.171.40.69a).[1] Structures were solved with Shelxt and refined by full-matrix least-squares method on F^2 with Shelxl-2014[2] within Olex2.[3] Only non-H atoms were refined with anisotropic displacement parameters. H atoms were positioned geometrically and constrained depending on their environment. Those H-atoms were refined in the riding-

[1] CrysalisPro (Rigaku Oxford Diffraction, 2020).

[2] G.M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3.

[3] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339.

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 mainly for isobutoxy side chains. For the structure of **1⊃2-HPF$_6$** the modelling strategy adopted was to build the foldarotaxane with RESI restraints on every monomer units. Due to the large disorder solvent content the SQUEEZE[4] procedure was used to flattened the electron density map. For search and analysis of solvent accessible voids in the structures default parameters were applied: grid 0.20 Å, probe radius 1.2 Å and NStep 6. Calculated total potential solvent accessible void volumes and electron counts per unit cell are given in the CIF files. The final CIF files were checked using IUCR's checkcif algorithm. Due to the characteristics of the crystals, i.e. large volume fractions of disordered solvent molecules, weak diffraction intensity, incompleteness of the data and moderate resolution, a number of A - level and B - level alerts remain in the check CIF files. These alerts are inherent to the data and refinement procedures and do not reflect errors. The refinement statistics and CCDC numbers are given in the cif files and tables below.

1.4 Molecular modeling

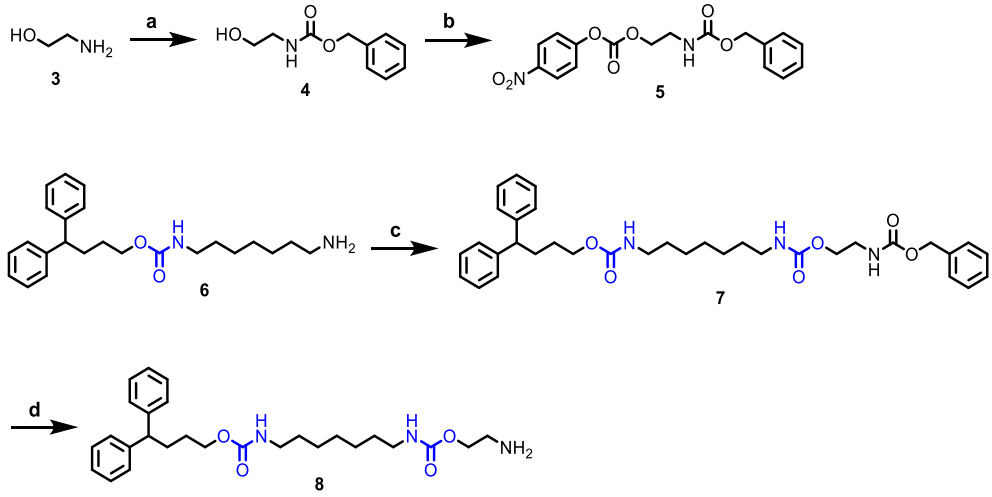
The X-ray structure of **1⊃2-HPF$_6$** was used to build its energy minimized model. After the appropriate modifications of the model of **1⊃2-HPF$_6$**, the molecular models of **1⊃2** and **1⊃2-Boc** were obatined by minimization using the Merck Molecular Force Field static (MMFFs) implemented in MacroModel version 8.6 via Maestro version 6.5 (Schrödinger).

2. Methods for chemical synthesis

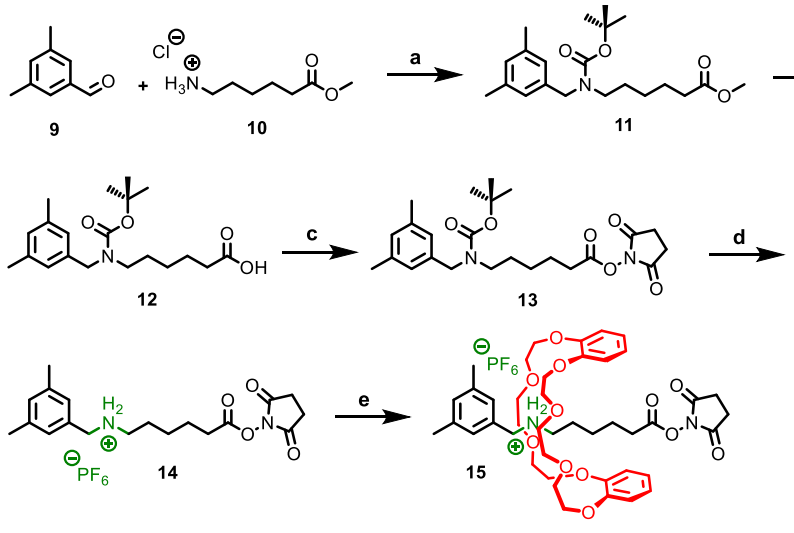
Reactions were carried out under a dry inert atmosphere unless otherwise specified. Commercial reagents were purchased from Sigma-Aldrich, Fisher Scientific or TCI Chemicals and were used without further purification. Dichloromethane (CH_2Cl_2) were dried over alumina columns (MBRAUN SPS-800 solvent purification system); chloroform ($CHCl_3$) was dried over oven dried potassium carbonate (K_2CO_3) then filtered and distilled from phosphorus pentoxide (P_2O_5); triethylamine (NEt_3) was distilled over calcium hydride (CaH_2). Reactions were monitored by thin layer chromatography (TLC) on Merck silica gel 60-F254 plates and observed under UV light. 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. ESI mass spectra were obtained from the Mass Spectrometry Laboratory at the European Institute of Chemistry and Biology (UMS 3033 & US01 – IECB, Pessac, France) and from the Analysis Laboratory at the Institut des Biomolécules Max Mousseron of the university of Montpellier (UMR CNRS 5247, Montpellier, France). High-resolution mass spectra (HRMS) were recorded respectively on a ZQ Micromass apparatus and a Q-TOF Micro apparatus. Oligomer **1** and compound **6** were prepared according to the litterature.[4]

[4] Q. Gan, X. Wang, B. Kauffmann, F. Rosu, Y. Ferrand, I. Huc, *Nature Nanotech.* **2017**, *12*, 447.

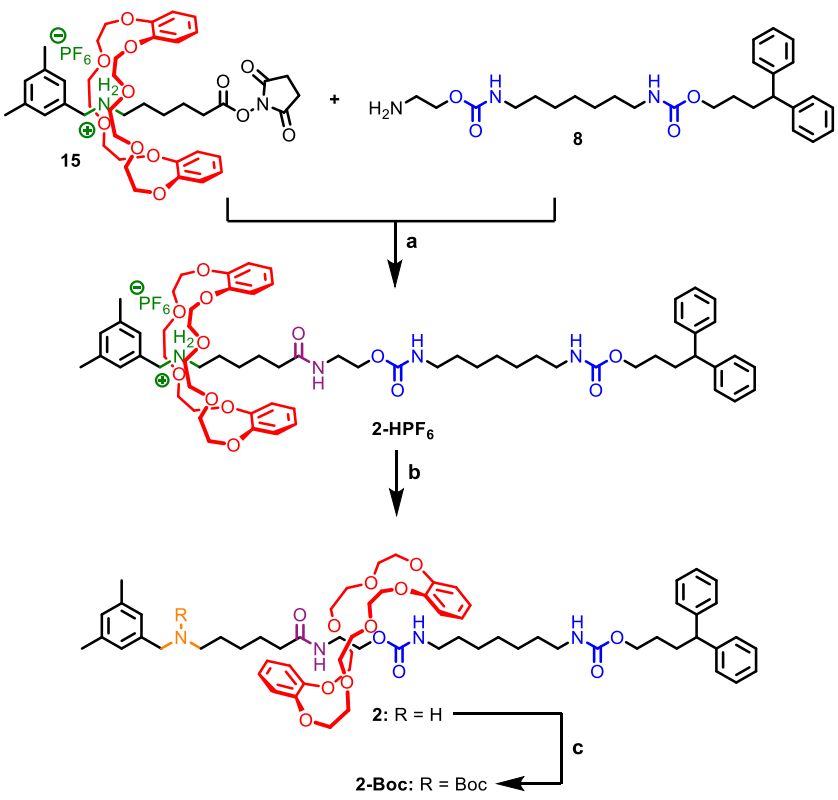
2.1 Synthesis of rotaxanes 2-HPF$_6$, 2 and 2-Boc



Scheme S1. Synthesis of the helix station **8**: a) benzyl chloroformate, NEt_3, CH_2Cl_2, room temperature, overnight, 61 % yield. b) 4-nitrophenyl chloroformate, NEt_3, CH_2Cl_2, room temperature, overnight, 77 % yield. c) **5**, NEt_3, CH_2Cl_2, room temperature, overnight, 69 % yield. d) H_2, Pd/C, MeOH, room temperature, 24 h, 93 % yield.

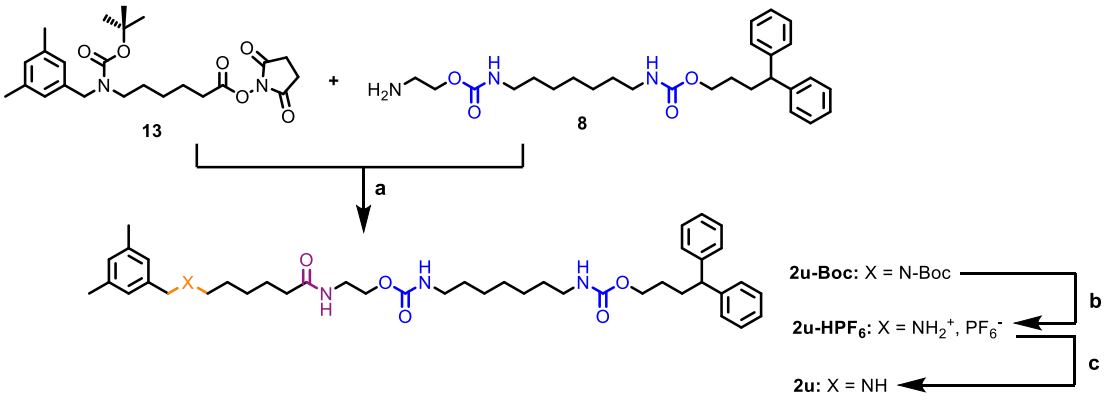


Scheme S2. Synthesis of the activated-rotaxane **15**: a) NEt_3, MeOH, room temperature, 2 h then Boc_2O, STAB, MeOH, room temperature, overnight, overall yield 64 %. b) KOH, MeOH, reflux, 30 min then HCl, CH_2Cl_2, overall yield 93 %. c) *N*-hydroxysuccinimide, EDC, DMAP, CH_2Cl_2, room temperature, 2 days, 97 % yield. d) HCl in dioxane, room temperature, 30 min then NH_4PF_6, CH_2Cl_2 / milliQ H_2O, room temperature, 30 min, overall yield 86 %. e) DB24C8, CH_3CN, 60 °C, 3 days, 69 % yield.



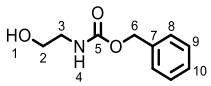
Scheme S3. Synthesis of the protonated rotaxane **2-HPF$_6$**, the deprotonated rotaxane **2** and the *N*-Boc-protected rotaxane **2-Boc**: a) CH_2Cl_2, room temperature, overnight, quantitative. b) NaOH 1 M, CH_2Cl_2, quantitative. c) Boc_2O, CH_2Cl_2, room temperature, 16 h, 58 % yield.

2.2 Synthesis of rods 2u-HPF$_6$, 2u and 2u-Boc

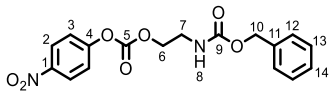


Scheme S4. Synthesis of the protonated rod **2u-HPF$_6$**, the deprotonated rod **2u** and the *N*-Boc-protected rod **2u-Boc**: a) CH_2Cl_2, room temperature, 18 h, 63 % yield. b) CH_2Cl_2, HCl in dioxane, room temperature, 1 h then NH_4PF_6, CH_2Cl_2 / milliQ H_2O, room temperature, 30 min, quantitative. c) NaOH 1 M, CH_2Cl_2, quantitative.

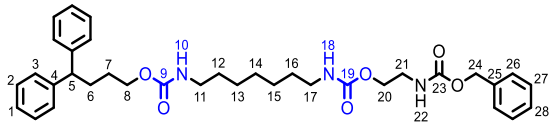
2.3 Experimental procedures



Compound 4. To ethanolamine (2 g, 32.7 mmol) and distilled NEt_3 (9.1 mL, 65.4 mmol) in dry CH_2Cl_2 (20 mL) at 0°C was added dropwise a solution of benzyl chloroformate (5.6 mL, 39.2 mmol) in dry CH_2Cl_2 (5 mL). Then the reaction mixture was allowed to come back at room temperature and was stirred overnight. The solution was evaporated and the residue was purified by flash chromatography (SiO_2) eluting with CH_2Cl_2 / MeOH (100:0 to 97:3) to give the product **4** as a white solid (3.9 g, 61 %). ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) = 7.42-7.26 (m, 5H, H_8, H_9, H_{10}), 7.18 (br t, 1H, H_4), 5.00 (s, 2H, H_6), 4.63 (t, 1H, $^3J(H_1, H_2)$ = 5.5 Hz, H_1), 3.43-3.34 (m, 2H, H_2), 3.10-3.01 (m, 2H, H_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) = 156.3 (C_5), 137.3 (C_7), 128.4 & 127.8 (C_8, C_9, C_{10}), 65.2 (C_6), 60.0 (C_2), 43.1 (C_3). HRMS (ESI): *m/z* calcd for $C_{10}H_{14}NO_3^+$ $[M+H]^+$ 196.0968 found 196.0993.

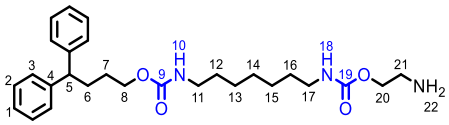


Compound 5. To a solution of 4-nitrophenyl chloroformate (3.8 g, 19.1 mmol) in dry CH_2Cl_2 (40 mL) was added dropwise a mixture of the compound **4** (3.1 g, 15.9 mmol) and distilled NEt_3 (6.6 mL, 47.7 mmol) in CH_2Cl_2 (30 mL) at 0°C. Then the reaction mixture was allowed to proceed at room temperature overnight. The solution was evaporated and the residue was purified by flash chromatography (SiO_2) eluting with cyclohexane / ethyl acetate (80:20) to obtain the product **5** as a white solid (4.4 g, 77 %). ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) = 8.36-8.28 (m, 2H, H_2), 7.59-7.50 (m, 3H, H_3, H_8), 7.41-7.26 (m, 5H, H_{12}, H_{13}, H_{14}), 5.05 (s, 2H, H_{10}), 4.26 (t, 2H, $^3J(H_6, H_7)$ = 5.3 Hz, H_6), 3.42-3.34 (m, 2H, H_7). ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) = 156.4 (C_9), 155.3 (C_1), 152.0 (C_5), 145.1 (C_4), 137.0 (C_{11}), 128.3 & 127.8 (C_{12}, C_{13}, C_{14}), 125.4 (C_2), 122.5 (C_3), 67.8 (C_6), 65.4 (C_{10}), 39.1 (C_7). HRMS (ESI): *m/z* calcd for $C_{17}H_{17}N_2O_7^+$ $[M+H]^+$ 361.1030 found 361.1073.

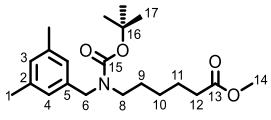


Compound 7. To a solution of the compound **5** (700 mg, 1.94 mmol) in dry CH_2Cl_2 (5 mL) was added dropwise a mixture of the free amine **6** (815 mg, 2.13 mmol) and distilled NEt_3 (1.1 mL, 7.76 mmol) in dry CH_2Cl_2 (5 mL) at 0°C. Then the reaction mixture was allowed to proceed at room temperature overnight. The solution was washed with an aqueous solution of NaOH 1 M several times and dried over $MgSO_4$. After filtration and concentration, the residue was purified by flash chromatography (SiO_2) eluting with cyclohexane / ethyl acetate (70:30 to 50:50) to obtain the product **7** as a colorless oil (810 mg, 69 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.43-7.16 (m, 15H, H_1, H_2, H_3, H_{26}, H_{27}, H_{28}), 5.31 (br t, 1H, H_{22}), 5.14 (s, 2H, H_{24}), 4.91 & 4.79 (2br t, 2H, H_{10}, H_{18}), 4.16 (t, 2H, $^3J(H_{20}, H_{21})$ = 4 Hz, H_{20}), 4.09 (t, 2H, $^3J(H_7, H_8)$ = 8 Hz, H_8), 3.94 (t, 1H, $^3J(H_5, H_6)$ = 8 Hz, H_5), 3.51-3.40 (m, 2H, H_{21}), 3.21-.3.11 (m, 4H,

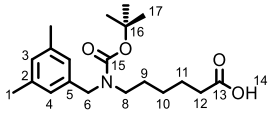
H_{11}, H_{17}), 2.20-2.08 (m, 2H, H_6), 1.67-1.55 (m, 2H, H_7), 1.54-1.42 (m, 4H, H_{12}, H_{16}), 1.37-1.28 (m, 6H, H_{13}, H_{14}, H_{15}). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 156.8 (C_9, C_{19}), 156.4 (C_{23}), 144.8 (C_4), 136.5 (C_{25}), 128.6 & 128.2 (C_{26}, C_{27}, C_{28}), 128.5 (C_2), 127.8 (C_3), 126.2 (C_1), 66.8 (C_{24}), 64.6 (C_8), 63.6 (C_{20}), 51.0 (C_5), 41.0 (C_{21}), 40.9 & 40.8 (C_{11}, C_{17}), 31.9 (C_6), 29.9 & 29.8 (C_{12}, C_{16}), 28.8 (C_{13}, C_{15}), 27.7 (C_7), 26.6 (C_{14}). HRMS (ESI): *m/z* calcd for $C_{35}H_{46}N_3O_6^+$ $[M+H]^+$ 604.3381 found 604.3437.



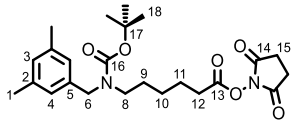
Compound 8. Compound **7** (950 mg, 1.57 mmol) was dissolved in MeOH (100 mL) and 20 % activated Pd/C (190 mg) was added. The reaction mixture was stirred for 24 hours under hydrogen at atmospheric pressure. Then the reaction mixture was filtered through celite, eluted with CH_2Cl_2 / MeOH (80:20) and evaporated to offered the compound **8** as a colorless oil (700 mg, 93 %) which was used directly without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.35-7.15 (m, 10H, H_1, H_2, H_3), 4.93 & 4.80 (2br t, 2H, H_{10}, H_{18}), 4.15-4.03 (m, 4H, H_8, H_{20}), 3.93 (t, 1H, ^3J(H_5, H_6) = 8 Hz, H_5), 3.23-3.10 (m, 4H, H_{11} H_{17}), 2.97-2.88 (m, 2H, H_{21}), 2.20-2.06 (m, 2H, H_6), 1.71-1.56 (m, 4H, H_7, H_{22}), 1.54-1.44 (m, 4H, H_{12}, H_{16}), 1.39-1.26 (m, 6H, H_{13}, H_{14}, H_{15}). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 156.8 & 156.6 (C_9, C_{19}), 144.8 (C_4), 128.5 (C_2), 127.8 (C_3), 126.2 (C_1), 66.9 (C_{20}), 64.6 (C_8), 51.0 (C_5), 41.4 (C_{21}), 40.9 (C_{11}, C_{17}), 31.9 (C_6), 29.9 (C_{12}, C_{16}), 28.9 (C_{13}, C_{15}), 27.7 (C_7), 26.6 (C_{14}). HRMS (ESI): *m/z* calcd for $C_{27}H_{40}N_3O_4^+$ $[M+H]^+$ 470.3013 found 470.3049.



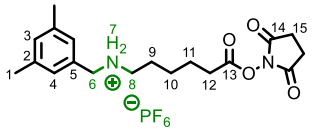
Compound 11. Under argon atmosphere, a solution of 3,5-dimethylbenzaldehyde **9** (1.24 g, 9.21 mmol), methyl 6-amino-hexanoate hydrochloride **10** (1.68 g, 9.21 mmol) and distilled NEt_3 (1.93 mL, 13.8 mmol) in dry MeOH (15 mL) was stirred for 2 hours at room temperature. Sodium triacetoxyborohydride "STAB" (2.34 g, 11.1 mmol), Boc_2O (2.42 g, 11.1 mmol) and dry MeOH (15 mL) were then added and stirred overnight at room temperature. The solvent was removed under vacuum and the obtained crude was diluted in CH_2Cl_2 (40 mL). The resulting organic layer was washed successively with an aqueous solution of HCl 1 M (1 x 40 mL) and a saturated aqueous solution of $NaHCO_3$ (1 x 40 mL). The combined organic layers were dried over $MgSO_4$ before being concentrated. The obtained crude was purified by flash chromatography (SiO_2) eluting with petroleum ether / EtOAc (100:0 to 96:4) to give the product **11** as a colorless oil (2.17 g, 64 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.88 (s, 1H, H_3), 6.82 (s, 2H, H_4), 4.34 (br s, 2H, H_6), 3.65 (s, 3H, H_{14}), 3.24-3.05 (m, 2H, H_8), 2.32-2.25 (m, 8H, H_1, H_{12}), 1.61 (quint, 2H, ^3J(H_{10}, H_{11}) = 8 Hz, ^3J(H_{11}, H_{12}) = 8 Hz, H_{11}), 1.54-1.41 (m, 11H, H_9, H_{17}), 1.27 (quint, 2H, ^3J(H_9, H_{10}) = 8 Hz, ^3J(H_{10}, H_{11}) = 8 Hz, H_{10}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 174.2 (C_{13}), 156.2 (C_{15}), 138.1 (C_2, C_5), 128.8 (C_3), 125.6 & 125.0 (C_4), 79.6 (C_{16}), 51.6 (C_{14}), 50.3 & 49.7 (C_6), 46.3 & 46.1 (C_8), 34.1 (C_{12}), 28.6 (C_{17}), 27.8 & 27.6 (C_9), 26.5 (C_{10}), 24.8 (C_{11}), 21.4 (C_1). HRMS (ESI): *m/z* calcd for $C_{21}H_{34}NO_4^+$ $[M+H]^+$ 364.2482 found 364.2483.



Compound 12. To a solution of methyl ester **11** (2.76 g, 7.59 mmol) in MeOH (100 mL) was added an aqueous solution of KOH 1 M (46 mL, 46.0 mmol) and the mixture was stirred for 30 minutes under reflux. MeOH was removed under vacuum. The obtained crude was diluted in CH_2Cl_2 (50 mL) and an aqueous solution of HCl 1 M was added until the pH reached 4. The aqueous layer was extracted with CH_2Cl_2 (3 x 50 mL) and the combined organic layers were dried over $MgSO_4$ before being concentrated to afford the carboxylic acid **12** as a colorless oil (2.47 g, 93 %) which was used directly without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.88 (s, 1H, H_3), 6.82 (s, 2H, H_4), 4.34 (br s, 2H, H_6), 3.25-3.04 (m, 2H, H_8), 2.36-2.26 (m, 8H, H_1, H_{12}), 1.62 (quint, 2H, ^3J(H_{10}, H_{11}) = 8 Hz, ^3J(H_{11}, H_{12}) = 8 Hz, H_{11}), 1.56-1.39 (m, 11H, H_9, H_{17}), 1.29 (quint, 2H, ^3J(H_9, H_{10}) = 8 Hz, ^3J(H_{10}, H_{11}) = 8 Hz, H_{10}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 179.6 (C_{13}), 156.1 (C_{15}), 138.1 (C_2 & C_5), 128.9 (C_3), 125.7 & 125.1 (C_4), 79.8 (C_{16}), 50.5 & 49.9 (C_6), 46.5 & 46.3 (C_8), 34.2 (C_{12}), 28.7 (C_{17}), 27.9 & 27.7 (C_9), 26.5 (C_{10}), 24.7 (C_{11}), 21.6 (C_1). HRMS (ESI): *m/z* calcd for $C_{20}H_{30}NO_4^-$ $[M-H]^-$ 348.2180 found 348.2185.

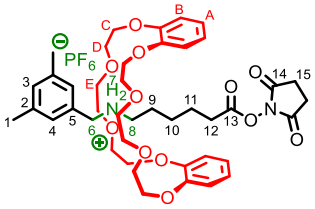


Compound 13. To a solution of carboxylic acid **12** (2.27 g, 6.50 mmol) and *N*-hydroxysuccinimide (748 mg, 6.50 mmol) in CH_2Cl_2 (45 mL) at 0°C, was added EDC (1.87 g, 9.75 mmol) and DMAP (1.59 g, 13.0 mmol). The reaction mixture was allowed to warm-up to room temperature and stirred for 2 days under argon atmosphere. An aqueous solution of HCl 1 M was added until the pH reached 1. The aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The organic layer was washed with a saturated aqueous solution of $NaHCO_3$ (2 x 10 mL). The combined organic layers were dried over $MgSO_4$ before being concentrated to afford the NHS ester **13** as a white solid (2.81 g, 97 %), which was used directly without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.88 (s, 1H, H_3), 6.82 (s, 2H, H_4), 4.34 (br s, 2H, H_6), 3.25-3.05 (m, 2H, H_8), 2.89-2.75 (m, 4H, H_{15}), 2.57 (t, 2H, ^3J(H_{11}, H_{12}) = 8 Hz, H_{12}), 2.29 (s, 6H, H_1), 1.73 (quint, 2H, ^3J(H_{10}, H_{11}) = 8 Hz, ^3J(H_{11}, H_{12}) = 8 Hz, H_{11}), 1.56-1.41 (m, 11H, H_9, H_{18}), 1.35 (quint, 2H, ^3J(H_9, H_{10}) = 8 Hz, ^3J(H_{10}, H_{11}) = 8 Hz, H_{10}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 172.5 (C_{16}), 169.3 & 168.7 (C_{13}, C_{14}), 138.1 (C_2, C_5), 128.9 (C_3), 125.7 & 125.1 (C_4), 79.8 (C_{17}), 50.4 & 49.8 (C_6), 46.3 & 46.2 (C_8), 31.0 (C_{12}), 28.6 (C_{18}), 27.7 & 27.5 (C_9), 26.2 (C_{10}), 25.7 (C_{15}), 24.5 (C_{11}), 21.5 (C_1). HRMS (ESI): *m/z* calcd for $C_{24}H_{35}N_2O_6^+$ $[M+H]^+$ 447.2490 found 447.2493.

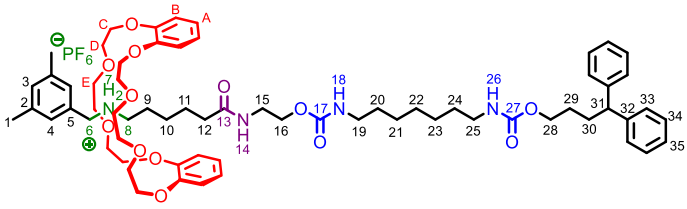


Compound 14. To a solution of *N*-carbamoylated thread **13** (1.59 g, 3.56 mmol) was added a 4 M solution of chlorhydric acid in dioxane (15 mL) and the mixture was stirred at room temperature until TLC analysis revealed no trace of starting material (30 minutes). The mixture was evaporated to dryness and the residue was partitioned between CH_2Cl_2 (20 mL) and milliQ H_2O (10 mL). NH_4PF_6 (1.73 g, 10.6 mmol) was added and the biphasic mixture was vigorously stirred for 30 minutes. The aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL) and the combined organic layers were dried over

$MgSO_4$ before being concentrated to afford the ammonium thread **14** as a white solid (1.45 g, 86 %) which was used directly without further purification. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) = 7.11 (s, 1H, H_3), 7.06 (s, 2H, H_4), 6.74 (br quint, 2H, H_7), 4.07 (t, 2H, $^3J(H_6, H_7)$ = 8 Hz, H_6), 3.02 (quint, 2H, $^3J(H_7, H_8)$ = 8 Hz, $^3J(H_8, H_9)$ = 8 Hz, H_8), 2.80-2.73 (m, 4H, H_{15}), 2.64 (t, 2H, $^3J(H_{11}, H_{12})$ = 8 Hz, H_{12}), 2.32 (s, 6H, H_1), 1.78-1.64 (m, 4H, H_9, H_{11}), 1.45 (quint, 2H, $^3J(H_9, H_{10})$ = 8 Hz, $^3J(H_{10}, H_{11})$ = 8 Hz, H_{10}). ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) = 171.2 & 170.0 (C_{13}, C_{14}), 139.9 (C_2), 132.1 (C_3), 131.4 (C_5), 128.6 (C_4), 52.5 (C_6), 48.5 (C_8), 31.1 (C_{12}), 26.4 & 25.9 (C_9, C_{10}, C_{15}), 24.6 (C_{11}), 21.3 (C_1). HRMS (ESI): *m/z* calcd for $C_{19}H_{27}N_2O_4^+$ $[M+H]^+$ 347.1965 found 347.1975.

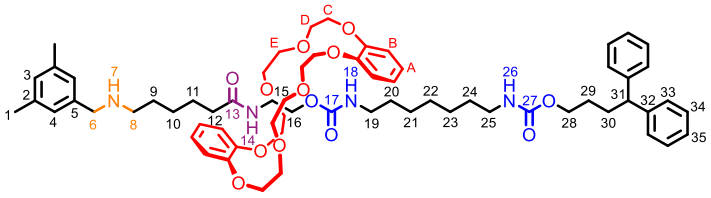


Compound 15. A solution of ammonium thread **19** (524 mg, 1.06 mmol) and DB24C8 (1.43 g, 3.18 mmol) in CH_3CN (1 mL) was stirred at 60 °C for 3 days, under argon atmosphere. The solvent was removed under vacuum and the obtained crude was triturated with toluene at 50°C (5 x 10 mL) to remove the DB24C8 excess and to afford the pure rotaxane **20** as a white solid (690 mg, 69 %) which was used directly without further purification. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) = 7.13 (br quint, 2H, H_7), 6.94-6.87 (m, 10H, H_4, H_A, H_B), 6.78 (s, 1H, H_3), 4.52-4.45 (m, 2H, H_6), 4.19-4.11 (m, 4H, H_C), 4.11-4.03 (m, 4H, $H_{C'}$), 3.90-3.75 (m, 8H, H_D, $H_{D'}$), 3.71-3.63 (m, 4H, H_E), 3.61-3.53 (m, 4H, $H_{E'}$), 3.38-3.27 (m, 2H, H_8), 2.80-2.73 (m, 4H, H_{15}), 2.38 (t, 2H, $^3J(H_{11}, H_{12})$ = 8 Hz, H_{12}), 2.09 (s, 6H, H_1), 1.55 (quint, 2H, $^3J(H_8, H_9)$ = 8 Hz, $^3J(H_9, H_{10})$ = 8 Hz, H_9), 1.49 (quint, 2H, $^3J(H_{10}, H_{11})$ = 8 Hz, $^3J(H_{11}, H_{12})$ = 8 Hz, H_{11}), 1.21 (quint, 2H, $^3J(H_9, H_{10})$ = 8 Hz, $^3J(H_{10}, H_{11})$ = 8 Hz, H_{10}). ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) = 171.1 & 169.8 (C_{13}, C_{14}), 148.5 ($C_{IV\ arom.\ DB24C8}$), 139.2 (C_2), 133.3 (C_5), 131.1 (C_3), 128.2 (C_4), 122.4 (C_A), 113.5 (C_B), 71.7 (C_E), 71.2 (C_D), 68.9 (C_C), 53.1 (C_6), 49.4 (C_8), 31.0 (C_{12}), 26.7, 26.4 & 26.1 (C_9, C_{10}, C_{15}), 24.6 (C_{11}), 21.2 (C_1). HRMS (ESI): *m/z* calcd for $C_{43}H_{59}N_2O_{12}^+$ $[M-PF_6]^+$ 795.4063 found 795. 4059.

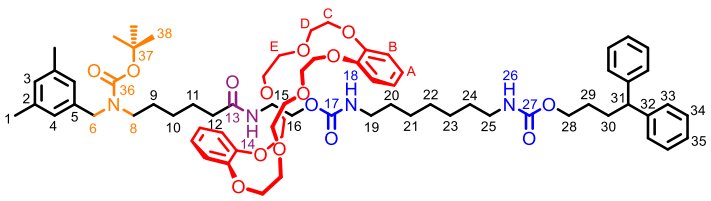


Compound 2-HPF$_6$. A solution of the activated-rotaxane **15** (46 mg, 0.049 mmol) and the compound **8** (46 mg, 0.098 mmol) in dry CH_2Cl_2 (2 mL) was stirred overnight, under argon atmosphere, at room temperature. The solvent was removed under vacuum and the crude was purified by flash chromatography (SiO_2) eluting with CH_2Cl_2 / MeOH (100:0 to 97:3) to afford the pure protonated [2]rotaxane **2-HPF$_6$** as a white powder (66 mg, quantitative). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.31-7.21 (m, 8H, H_{33}, H_{34}), 7.20-7.13 (m, 2H, H_{35}), 7.11 (br quint, 2H, H_7), 7.00 (s, 2H, H_4), 6.97-6.91 (m, 4H, H_A), 6.91-6.86 (m, 5H, H_3, H_B), 6.56 (t, 1H, $^3J(H_{14}, H_{15})$ = 4 Hz, H_{14}), 5.38 & 4.71 (2t, 2H, $^3J(H_{18}, H_{19})$ = $^3J(H_{25}, H_{26})$ = 4 Hz, H_{18}, H_{26}), 4.56-4.48 (m, 2H, H_6), 4.32-4.21 (m, 4H, H_C), 4.14-3.99 (m, 8H, H_{16}, H_{28}, $H_{C'}$), 3.91 (t, 1H, $^3J(H_{30}, H_{31})$ = 8 Hz, H_{31}), 3.87-3.76 (m, 8H, H_D, $H_{D'}$), 3.69-3.59 (m, 4H, H_E), 3.45 (q, 2H, $^3J(H_{14}, H_{15})$ = 4 Hz, $^3J(H_{15}, H_{16})$ = 4 Hz, H_{15}), 3.42-3.33 (m, 4H, $H_{E'}$), 3.17-3.09 (m, 4H, H_{19}, H_{25}), 3.09-3.02 (m, 2H, H_8), 2.20 (s, 6H, H_1), 2.15-2.02

(m, 4H, H_{12}, H_{30}), 1.58 (quint, 2H, $^3J(H_{28}, H_{29})$ = 8 Hz, $^3J(H_{29}, H_{30})$ = 8 Hz, H_{29}), 1.53-1.44 (m, 4H, H_{20}, H_{24}), 1.44-1.36 (m, 4H, H_9, H_{11}), 1.33-1.26 (m, 6H, H_{21}, H_{22}, H_{23}), 1.04 (quint, 2H, $^3J(H_9, H_{10})$ = 8 Hz, $^3J(H_{10}, H_{11})$ = 8 Hz, H_{10}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 173.3 (C_{13}), 156.9 (C_{17}, C_{27}), 147.6 ($C_{IV\ arom.\ DB24C8}$), 144.9 (C_{32}), 138.2 (C_2), 132.6 (C_5), 130.6 (C_3), 128.5 & 127.9 (C_{33}, C_{34}), 127.6 (C_4), 126.3 (C_{35}), 122.0 (C_A), 112.9 (C_B), 70.8 (C_E), 70.3 (C_D), 68.4 (C_C), 64.6 (C_{28}), 63.7 (C_{16}), 52.4 (C_6), 51.0 (C_{31}), 49.2 (C_8), 41.0 (C_{19}, C_{25}), 38.7 (C_{15}), 35.7 (C_{12}), 32.0 (C_{30}), 29.9 & 29.7 (C_{20}, C_{24}), 28.9 (C_{22}), 27.7 (C_{29}), 26.7 & 26.6 (C_{21}, C_{23}), 26.4 (C_9), 26.1 (C_{10}), 25.0 (C_{11}), 21.3 (C_1). HRMS (ESI): *m/z* calcd for $C_{66}H_{93}N_4O_{13}^+$ $[M\text{-}PF_6]^+$ 1149.6734 found 1149.6741.

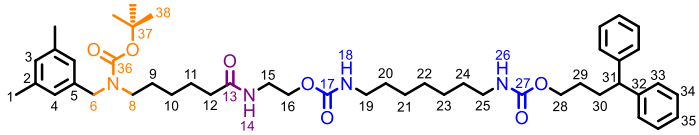


Compound 2. A solution of the protonated [2]rotaxane **2-HPF$_6$** (33 mg, 0.025 mmol) in CH_2Cl_2 (5 mL) was stirred during 10 minutes with an aqueous solution of NaOH 1 M (10 mL). Then the aqueous layer was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were dried over $MgSO_4$ before being concentrated to afford the deprotonated [2]rotaxane **2** as a colorless paste (29 mg, quantitative) which was used directly without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.29-7.21 (m, 8H, H_{33}, H_{34}), 7.19-7.14 (m, 2H, H_{35}), 7.03-6.97 (m, 1H, H_{14}), 6.92 (s, 2H, H_4), 6.89 (s, 1H, H_3), 6.87-6.82 (m, 4H, H_A), 6.82-6.77 (m, 4H, H_B), 5.52 & 4.68 (2t, 2H, $^3J(H_{18}, H_{19})$ = $^3J(H_{25}, H_{26})$ = 4 Hz, H_{18}, H_{26}), 4.40 (t, 2H, $^3J(H_{15}, H_{16})$ = 4 Hz, H_{16}), 4.18-4.10 (m, 8H, H_C), 4.05 (t, 2H, $^3J(H_{28}, H_{29})$ = 8 Hz, H_{28}), 3.89 (t, 1H, $^3J(H_{30}, H_{31})$ = 8 Hz, H_{31}), 3.89-3.79 (m, 8H, H_D), 3.71-3.59 (m, 12H, H_6, H_{15}, H_E), 3.06 (t, 2H, $^3J(H_{24}, H_{25})$ = 8 Hz, H_{25}), 2.99 (t, 2H, $^3J(H_{19}, H_{20})$ = 8 Hz, H_{19}), 2.51 (t, 2H, $^3J(H_8, H_9)$ = 8 Hz, H_8), 2.30 (s, 6H, H_1), 2.10 (q, 2H, $^3J(H_{29}, H_{30})$ = 8 Hz, $^3J(H_{30}, H_{31})$ = 8 Hz, H_{30}), 1.93 (t, 2H, $^3J(H_{11}, H_{12})$ = 8 Hz, H_{12}), 1.57 (quint, 2H, $^3J(H_{28}, H_{29})$ = 8 Hz, $^3J(H_{29}, H_{30})$ = 8 Hz, H_{29}), 1.46 (quint, 2H, $^3J(H_{10}, H_{11})$ = 8 Hz, $^3J(H_{11}, H_{12})$ = 8 Hz, H_{11}), 1.40-1.28 (m, 4H, H_9, H_{24}), 1.27-1.18 (m, 2H, H_{20}), 1.16-1.02 (m, 8H, H_{10}, H_{21}, H_{22}, H_{23}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 172.7 (C_{13}), 157.2 & 156.7 (C_{17}, C_{27}), 148.4 ($C_{IV\ arom.\ DB24C8}$), 144.8 (C_{32}), 140.5 (C_5), 137.9 (C_2), 128.5 & 127.9 (C_3, C_{33}, C_{34}), 126.3 & 126.0 (C_4, C_{35}), 120.9 (C_A), 112.4 (C_B), 70.8 (C_E), 69.9 (C_D), 68.4 (C_C), 64.5 (C_{28}), 63.4 (C_{16}), 54.1 (C_6), 51.0 (C_{31}), 49.5 (C_8), 40.8 (C_{25}), 40.5 (C_{19}), 39.0 (C_{15}), 36.3 (C_{12}), 31.9 (C_{30}), 29.9, 29.8 & 29.7 (C_9, C_{20}, C_{24}), 29.0 (C_{22}), 27.7 (C_{29}), 27.4 (C_{10}), 26.6 (C_{21}, C_{23}), 25.7 (C_{11}), 21.4 (C_1). HRMS (ESI): *m/z* calcd for $C_{66}H_{93}N_4O_{13}^+$ $[M+H]^+$ 1149.6734 found 1149.6741.

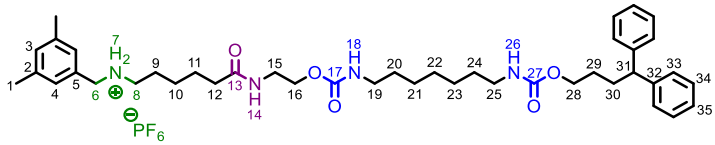


Compound 2-Boc. To a solution of the [2]rotaxane **2** (73 mg, 0.064 mmol) in CH_2Cl_2 (1 mL) was added Boc_2O (17 mg, 0.076 mmol). The reaction mixture was stirred for 16 h, under argon atmosphere, at room temperature. The solvent was removed under vacuum and the obtained crude was purified by flash chromatography (SiO_2) eluting with CH_2Cl_2 / acetone (100:0 to 50:50) to afford the *N*-Boc-protected [2]rotaxane **2-Boc** as a colorless paste (46 mg, 58 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.33-7.24 (m, 8H, H_{33}, H_{34}), 7.23-7.17 (m, 2H, H_{35}), 7.04-6.98 (m, 1H, H_{14}), 6.94-6.78 (m, 11H,

H_3, H_4, H_A, H_B), 5.56-5.48 (m, 1H, H_{18}), 4.73-4.66 (m, 1H, H_{26}), 4.44 (t, 2H, $^3J(H_{15}, H_{16})$ = 4 Hz, H_{16}), 4.38-4.30 (m, 2H, H_6), 4.26-4.13 (m, 8H, H_C), 4.09 (t, 2H, $^3J(H_{28}, H_{29})$ = 8 Hz, H_{28}), 3.93 (t, 1H, $^3J(H_{30}, H_{31})$ = 8 Hz, H_{31}), 3.91-3.78 (m, 8H, H_D), 3.76-3.56 (m, 10H, H_{15}, H_E), 3.22-3.07 (m, 4H, H_8, H_{25}), 3.03 (q, 2H, $^3J(H_{19}, H_{20})$ = 8 Hz, H_{19}), 2.33 (s, 6H, H_1), 2.14 (q, 2H, $^3J(H_{29}, H_{30})$ = 8 Hz, $^3J(H_{30}, H_{31})$ = 8 Hz, H_{30}), 1.96 (t, 2H, $^3J(H_{11}, H_{12})$ = 8 Hz, H_{12}), 1.61 (quint, 2H, $^3J(H_{28}, H_{29})$ = 8 Hz, $^3J(H_{29}, H_{30})$ = 8 Hz, H_{29}), 1.55-1.44 (m, 11H, H_{11}, H_{38}), 1.42-1.32 (m, 4H, H_9, H_{24}), 1.31-1.25 (m, 2H, H_{20}), 1.22-0.96 (m, 8H, H_{10}, H_{21}, H_{22}, H_{23}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 172.7 (C_{13}), 157.3 & 156.8 (C_{17}, C_{27}, C_{36}), 148.5 ($C_{IV\ arom.\ DB24C8}$), 144.8 (C_{32}), 138.0 (C_2), 128.7, 128.6 & 127.9 (C_3, C_5, C_{33}, C_{34}), 126.3 (C_{35}), 125.5 & 125.0 (C_4), 121.0 (C_A), 112.5 (C_B), 79.5 (C_{37}), 70.9 (C_E), 70.0 (C_D), 68.4 (C_C), 64.6 (C_{28}), 63.5 (C_{16}), 51.0 (C_{31}), 50.2 & 49.7 (C_6), 46.5 (C_8), 41.0 (C_{25}), 40.7 (C_{19}), 39.2 (C_{15}), 36.4 (C_{12}), 32.0 (C_{30}), 29.8 & 29.0 (C_{20}, C_{24}), 28.6 (C_{38}), 27.8 (C_9, C_{29}), 27.0 (C_{10}), 26.6 (C_{21}, C_{22}, C_{23}), 25.6 (C_{11}), 21.4 (C_1). HRMS (ESI): *m/z* calcd for $C_{71}H_{101}N_4O_{15}^+$ $[M+H]^+$ 1249.7258 found 1249.7264.

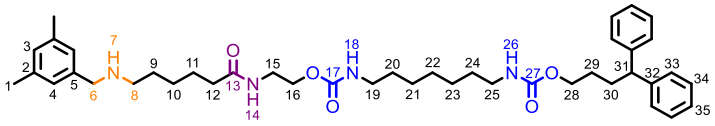


Compound 2u-Boc. A solution of the compound **13** (86 mg, 0.19 mmol) and the compound **8** (90 mg, 0.19 mmol) in dry CH_2Cl_2 (1 mL) was stirred for 18 hours, under argon atmosphere, at room temperature. The solvent was removed under vacuum and the obtained crude was purified by flash chromatography (SiO_2) eluting with CH_2Cl_2 / MeOH (100:0 to 90:10) followed by chromatography on lipophilic Sephadex LH-20 column (CH_2Cl_2) to give the pure compound **2u-Boc** as a colorless oil (97 mg, 63 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.31-7.22 (m, 8H, H_{33}, H_{34}), 7.21-7.15 (m, 2H, H_{35}), 6.89 (s, 1H, H_3), 6.83 (s, 2H, H_4), 6.03 (br t, 1H, H_{14}), 4.92 & 4.70 (2br t, 2H, H_{18}, H_{26}), 4.34 (br s, 2H, H_6), 4.15 (t, 2H, $^3J(H_{15}, H_{16})$ = 4 Hz, H_{16}), 4.06 (t, 2H, $^3J(H_{28}, H_{29})$ = 8 Hz, H_{28}), 3.91 (t, 1H, $^3J(H_{30}, H_{31})$ = 8 Hz, H_{31}), 3.48 (q, 2H, $^3J(H_{14}, H_{15})$ = 4 Hz, $^3J(H_{15}, H_{16})$ = 4 Hz, H_{15}), 3.22-3.07 (m, 6H, H_8, H_{19}, H_{25}), 2.30 (s, 6H, H_1), 2.19-2.06 (m, 4H, H_{12}, H_{30}), 1.68-1.55 (m, 4H, H_{11}, H_{29}), 1.54-1.41 (m, 15H, H_9, H_{20}, H_{24}, H_{38}), 1.35-1.25 (m, 8H, H_{10}, H_{21}, H_{22}, H_{23}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 173.2 (C_{13}), 156.8 (C_{17}, C_{27}, C_{36}), 144.8 (C_{32}), 138.1 (C_2, C_5), 128.8 (C_3), 128.6 & 127.9 (C_{33}, C_{34}), 126.3 (C_{35}), 125.1 (C_4), 79.6 (C_{37}), 64.7 (C_{28}), 63.6 (C_{16}), 51.1 (C_{31}), 50.2 (C_6), 46.3 (C_8), 41.1 & 41.0 (C_{19}, C_{25}), 39.6 (C_{15}), 36.6 (C_{12}), 32.0 (C_{30}), 30.0 & 29.9 (C_{20}, C_{24}), 28.9 (C_{21}, C_{23}), 28.6 (C_{38}), 27.7 (C_9, C_{29}), 26.7 (C_{10}, C_{22}), 25.5 (C_{11}), 21.4 (C_1). HRMS (ESI): *m/z* calcd for $C_{47}H_{69}N_4O_7^+$ $[M+H]^+$ 801.5161 found 801.5169.



Compound 2u-HPF$_6$. To a solution of the carbamoylated thread **2u-Boc** (97 mg, 0.12 mmol) in CH_2Cl_2 (1 mL) was added a 4 M solution of chlorhydric acid in dioxane (3 mL). The mixture was stirred at room temperature for 1 hour. The mixture was evaporated to dryness and the residue was partitioned between CH_2Cl_2 (3 mL) and milliQ H_2O (1 mL). NH_4PF_6 (59 mg, 0.36 mmol) was added and the biphasic mixture was vigorously stirred for 30 minutes. 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 **2u-HPF$_6$** as a white solid (102 mg, quantitative) which was used directly without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.86 (br quint, 2H, H_7), 7.39-7.27 (m, 8H, H_{33}, H_{34}),

7.27-7.20 (m, 2H, H_{35}), 7.11 (s, 2H, H_4), 7.08 (s, 1H, H_3), 6.73 (t, 1H, $^3J(H_{14}, H_{15})$ = 4 Hz, H_{14}), 5.32 & 4.84 (2t, 2H, $^3J(H_{18}, H_{19})$ = $^3J(H_{25}, H_{26})$ = 4 Hz, H_{18}, H_{26}), 4.17 (s, 2H, H_6), 4.13-4.02 (m, 4H, H_{16}, H_{28}), 3.96 (t, 1H, $^3J(H_{30}, H_{31})$ = 8 Hz, H_{31}), 3.47-3.35 (m, 2H, H_{15}), 3.21-3.03 (m, 6H, H_8, H_{19}, H_{25}), 2.36 (s, 6H, H_1), 2.23 (t, 2H, $^3J(H_{11}, H_{12})$ = 8 Hz, H_{12}), 2.16 (q, 2H, $^3J(H_{29}, H_{30})$ = 8 Hz, $^3J(H_{30}, H_{31})$ = 8 Hz, H_{30}), 1.84-1.74 (m, 2H, H_9), 1.69-1.56 (m, 4H, H_{11}, H_{29}), 1.56-1.46 (m, 4H, H_{20}, H_{24}), 1.42 (quint, 2H, $^3J(H_9, H_{10})$ = 8 Hz, $^3J(H_{10}, H_{11})$ = 8 Hz, H_{10}), 1.37-1.29 (m, 6H, H_{21}, H_{22}, H_{23}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 174.4 (C_{13}), 157.0 (C_{17}, C_{27}), 144.8 (C_{32}), 139.0 (C_2), 131.4 (C_3), 130.0 (C_5), 128.6 & 127.9 (C_{33}, C_{34}), 127.6 (C_4), 126.3 (C_{35}), 64.7 (C_{28}), 63.0 (C_{16}), 52.2 (C_6), 51.0 (C_{31}), 47.6 (C_8), 41.0 (C_{19}, C_{25}), 39.0 (C_{15}), 35.4 (C_{12}), 32.0 (C_{30}), 29.8 & 29.6 (C_{20}, C_{24}), 28.8 (C_{21}, C_{23}), 27.7 (C_{29}), 26.6 (C_{22}), 25.3 (C_9, C_{10}), 24.3 (C_{11}), 21.1 (C_1). HRMS (ESI): *m/z* calcd for $C_{42}H_{61}N_4O_5^+$ $[M\text{-}PF_6]^+$ 701.4642 found 701.4645.



Compound 2u. A solution of ammonium-containing thread **2u-HPF$_6$** (40 mg, 0.047 mmol) in CH_2Cl_2 (5 mL) was stirred during 10 minutes with an aqueous solution of NaOH 1 M (10 mL). Then 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 to afford the amine thread **2u** as a yellow paste (33 mg, quantitative) which was used directly without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.31-7.21 (m, 8H, H_{33}, H_{34}), 7.20-7.15 (m, 2H, H_{35}), 6.92 (s, 2H, H_4), 6.89 (s, 1H, H_3), 6.11 (br t, 1H, H_{14}), 5.02 & 4.77 (2br , 2H, H_{18}, H_{26}), 4.14 (t, 2H, $^3J(H_{15}, H_{16})$ = 4 Hz, H_{16}), 4.06 (t, 2H, $^3J(H_{28}, H_{29})$ = 8 Hz, H_{28}), 3.91 (t, 1H, $^3J(H_{30}, H_{31})$ = 8 Hz, H_{31}), 3.69 (s, 2H, H_6), 3.52-3.43 (m, 2H, H_{15}), 3.19-3.07 (m, 4H, H_{19}, H_{25}), 2.62 (t, 2H, $^3J(H_8, H_9)$ = 8 Hz, H_8), 2.31 (s, 6H, H_1), 2.17 (t, 2H, $^3J(H_{11}, H_{12})$ = 8 Hz, H_{12}), 2.11 (q, 2H, $^3J(H_{29}, H_{30})$ = 8 Hz, $^3J(H_{30}, H_{31})$ = 8 Hz, H_{30}), 1.64 (quint, 2H, $^3J(H_{10}, H_{11})$ = 8 Hz, $^3J(H_{11}, H_{12})$ = 8 Hz, H_{11}), 1.61-1.50 (m, 4H, H_9, H_{29}), 1.50-1.42 (m, 4H, H_{20}, H_{24}), 1.36 (quint, 2H, $^3J(H_9, H_{10})$ = 8 Hz, $^3J(H_{10}, H_{11})$ = 8 Hz, H_{10}), 1.33-1.25 (m, 6H, H_{21}, H_{22}, H_{23}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 173.2 (C_{13}), 156.8 (C_{17}, C_{27}), 144.8 (C_{32}), 140.3 (C_5), 138.0 (C_2), 128.6 (C_3), 128.6 & 127.9 (C_{33}, C_{34}), 126.3 (C_{35}), 126.0 (C_4), 64.6 (C_{28}), 63.5 (C_{16}), 54.0 (C_6), 51.0 (C_{31}), 49.3 (C_8), 40.9 & 40.8 (C_{19}, C_{25}), 39.4 (C_{15}), 36.6 (C_{12}), 32.0 (C_{30}), 29.9 & 29.8 (C_{20}, C_{24}), 29.8 (C_9), 28.9 (C_{21}, C_{23}), 27.7 (C_{29}), 27.0 (C_{10}), 26.6 (C_{22}), 25.6 (C_{11}), 21.3 (C_1). HRMS (ESI): *m/z* calcd for $C_{42}H_{61}N_4O_5^+$ $[M+H]^+$ 701.4642 found 701.4645.

3. Host-guest complex

3.1 Folding principles of the helix

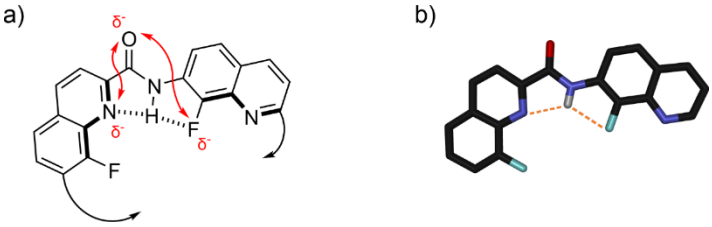


Figure S1. a) Folding patterns of fluoroquinoline foldamers. Conjugation, hydrogen bonds (dashed lines) and electrostatic repulsions (red arrows) concur to stabilize a preferred conformation of each aryl-amide linkages, resulting in a bent conformation that gives rise to a helix. Intramolecular aromatic staking comes as an additional, solvent dependent, force stabilizing the helix. b) Slice of the crystal structure **1⊃2-HPF$_6$** confirming the expected pattern.

3.2 Binding mode of the helix with the rotaxane

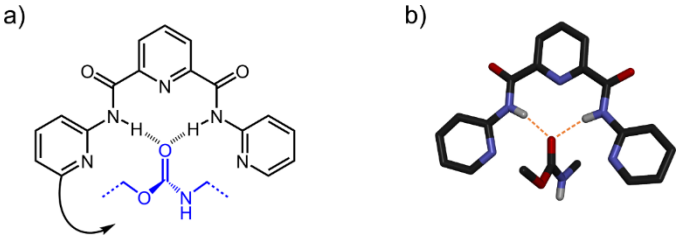
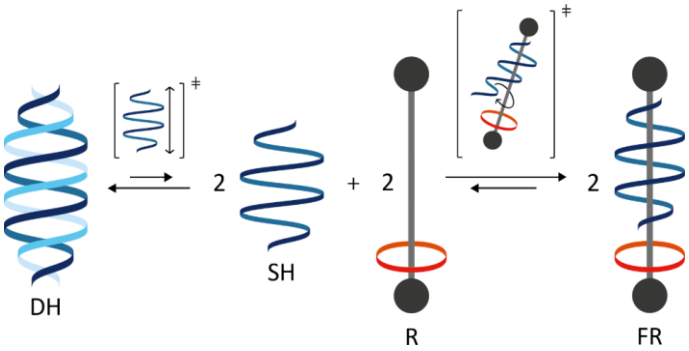


Figure S2. a) Binding mode showing that the pyridine trimers of the helical foldamer (hydrogen bonds donors) act as a carbamate cleft and hydrogen bond (dashed lines) the carbamates functions (hydrogen bonds acceptors) of the rotaxane. b) Slice of the crystal structure **1⊃2-HPF$_6$** confirming the expected pattern.

3.3 Host-guest complex formation

a)



b)

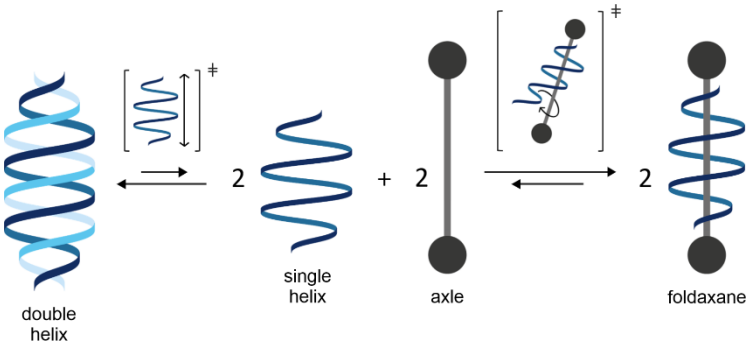


Figure S3. Schematic representation showing the equilibrium between a single helix (**SH**) and a guest (rotaxane or axle) that can form either a foldarotaxane (or foldaxane) or reassemble as a double helix (DH). The formation of the foldarotaxane or the foldaxane with an axle equipped with stoppers requires the unfolding and refolding of the helix around the dicarbamate station of the molecular axle.

For the equilibrium shown in equation (1), the dimerization constant K_{dim} of the foldamer **1** is given by the equation (2). And for the equilibrium shown in equation (3), the association constant K_a between the foldamer **1** and the dicarbamate station of the guest (rotaxane or axle) is given by the equation (4):

(1) $2\ SH \rightleftarrows DH$

(2) $K_{dim} = \dfrac{[DH]}{[SH]^2}$

(3) $SH + G \rightleftarrows HG$

(4) $K_a = \sqrt{\dfrac{[HG]^2 \times K_{dim}}{[DH] \times [G]^2}}$

Where : SH: foldamer **1** as a single helix

DH: foldamer **1** as a double helix

G: guest (rotaxane or axle)

HG: host-guest complex (foldarotaxane or foldaxane)

[SH] = concentration of the single helix (mol.L^{-1})

[DH] = concentration of the double helix (mol.L^{-1})

[HG] = concentration of the host-guest complex (mol.L^{-1})

[G] = concentration of the free guest (mol.L^{-1})

Table S1. Titration of the foldamer **1** with the different rotaxanes (**2-HPF$_6$**, **2** and **2-Boc**) and the different rods (**2u-HPF$_6$**, **2u** and **2u-Boc**) monitored by ^{1}H NMR (700 MHz) in $CDCl_3$ at 298 K.

Guest	K_a (10^3 L.mol^{-1})					
	2-HPF$_6$	**2**	**2-Boc**	**2u-HPF$_6$**	**2u**	**2u-Boc**
1	207 (± 1.9 %)	9.1 (± 2.2 %)	3.8 (± 2.6 %)	375 (± 2.1 %)	397 (± 2.0 %)	317 (± 2.5 %)

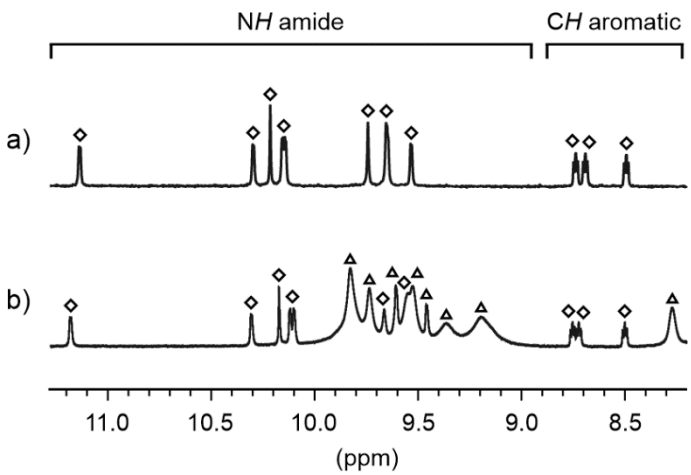


Figure S4. Part of the ^{1}H NMR spectra of the amide region (700 MHz) at 298 K of **1** (0.1 mM) in $CDCl_3$ at a) t = 0 and b) t = 72 h (thermodynamic equilibrium). Amides signals of the free single helix **1** and the double helix $\mathbf{(1)_2}$ are marked with diamonds and triangles, respectively. Some aromatic resonances of the single helix **1** and the double helix $\mathbf{(1)_2}$ are denoted with diamonds and triangles, respectively. The dimerization constant K_{dim} was mesured to be 2.5 10^3 L.mol^{-1} in $CDCl_3$ at 298 K, based on the integration of the amides resonances.

4. Solution state studies

4.1 ^{1}H NMR characterizations of rotaxanes 2-HPF$_6$, 2 and 2-Boc

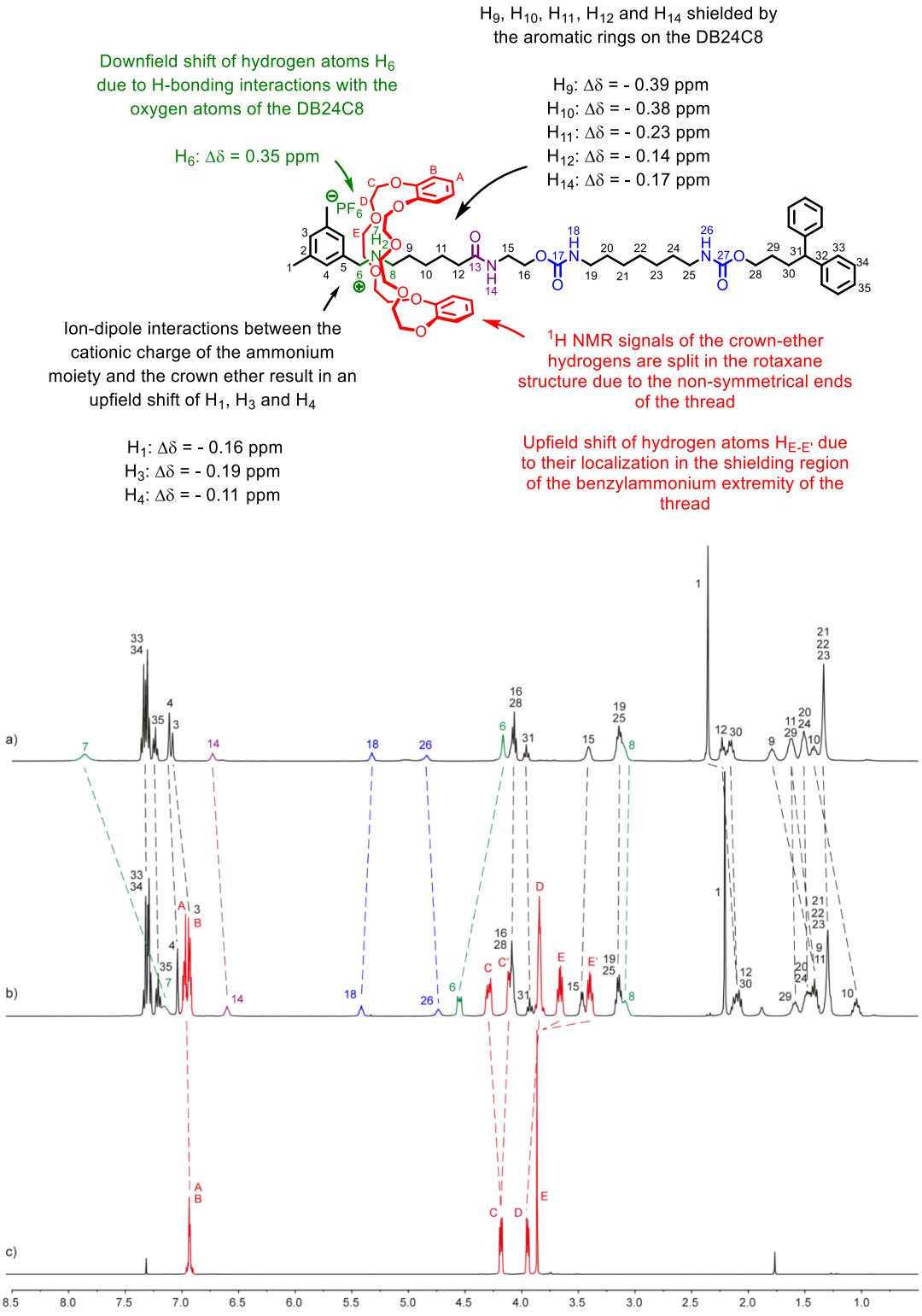


Figure S5. Characterization of the protonated rotaxane **2-HPF$_6$**. ^{1}H NMR spectra (400 MHz) at 298 K in $CDCl_3$ of a) the protonated rod **2u-HPF$_6$**, b) the protonated rotaxane **2-HPF$_6$** and c) the free macrocycle DB24C8.

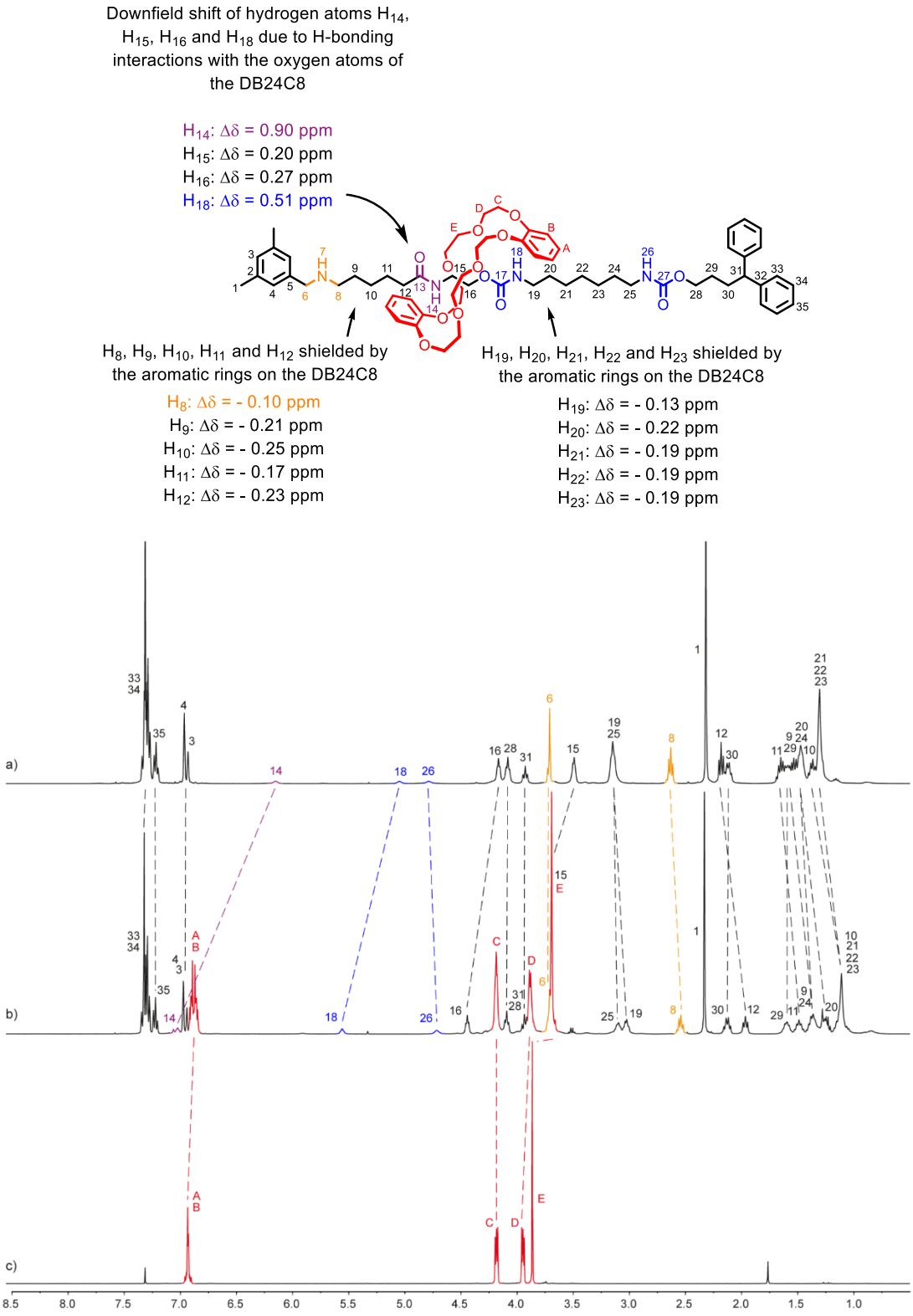


Figure S6. Characterization of the deprotonated rotaxane **2**. ^{1}H NMR spectra (400 MHz) at 298 K in $CDCl_3$ of a) the deprotonated rod **2u**, b) the deprotonated rotaxane **2** and c) the free macrocycle DB24C8.

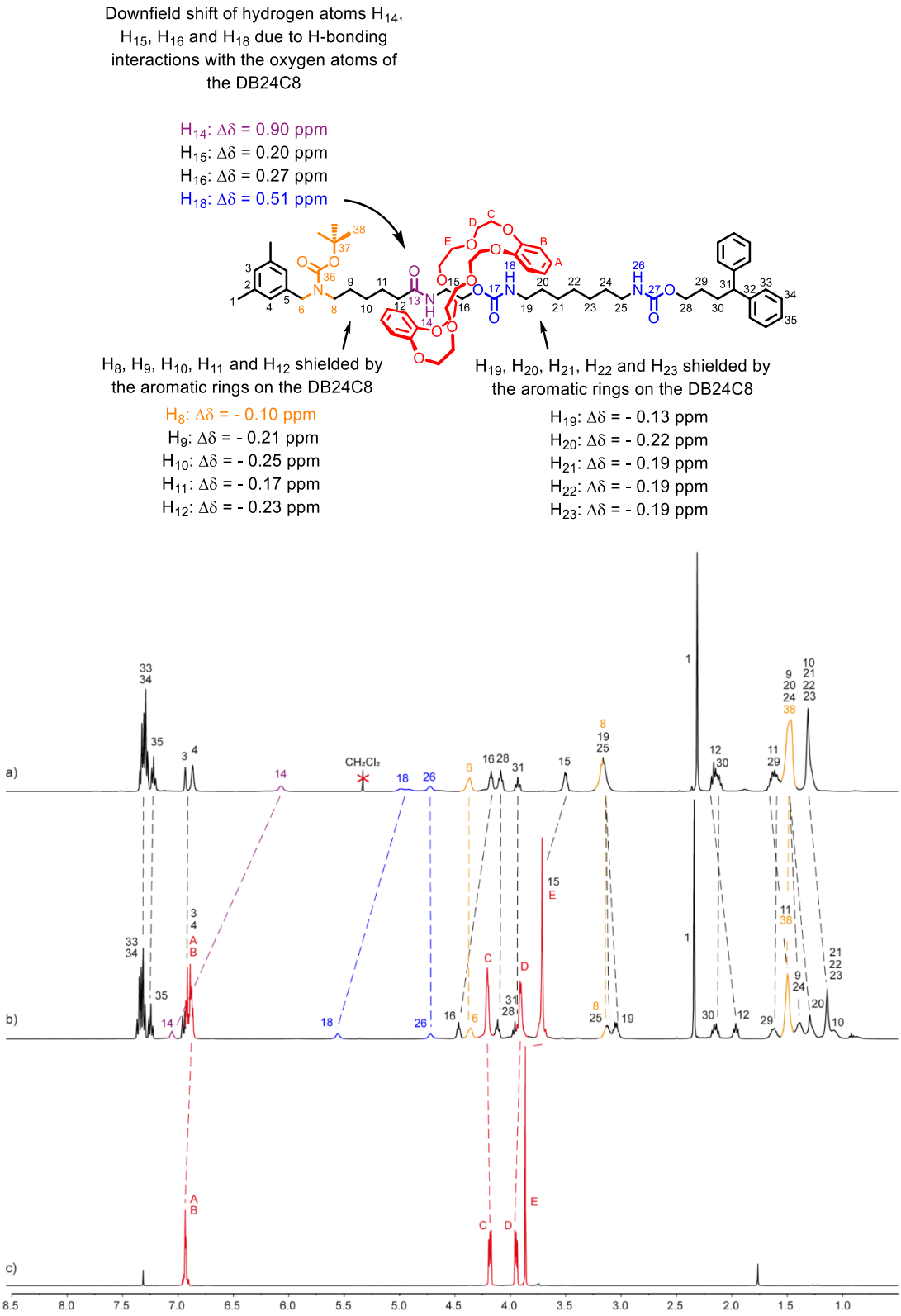


Figure S7. Characterization of the *N*-Boc-protected rotaxane **2-Boc**. ^{1}H NMR spectra (400 MHz) at 298 K in $CDCl_3$ of a) the *N*-Boc-protected rod **2u-Boc**, b) the *N*-Boc-protected rotaxane **2-Boc** and c) the free macrocycle DB24C8.

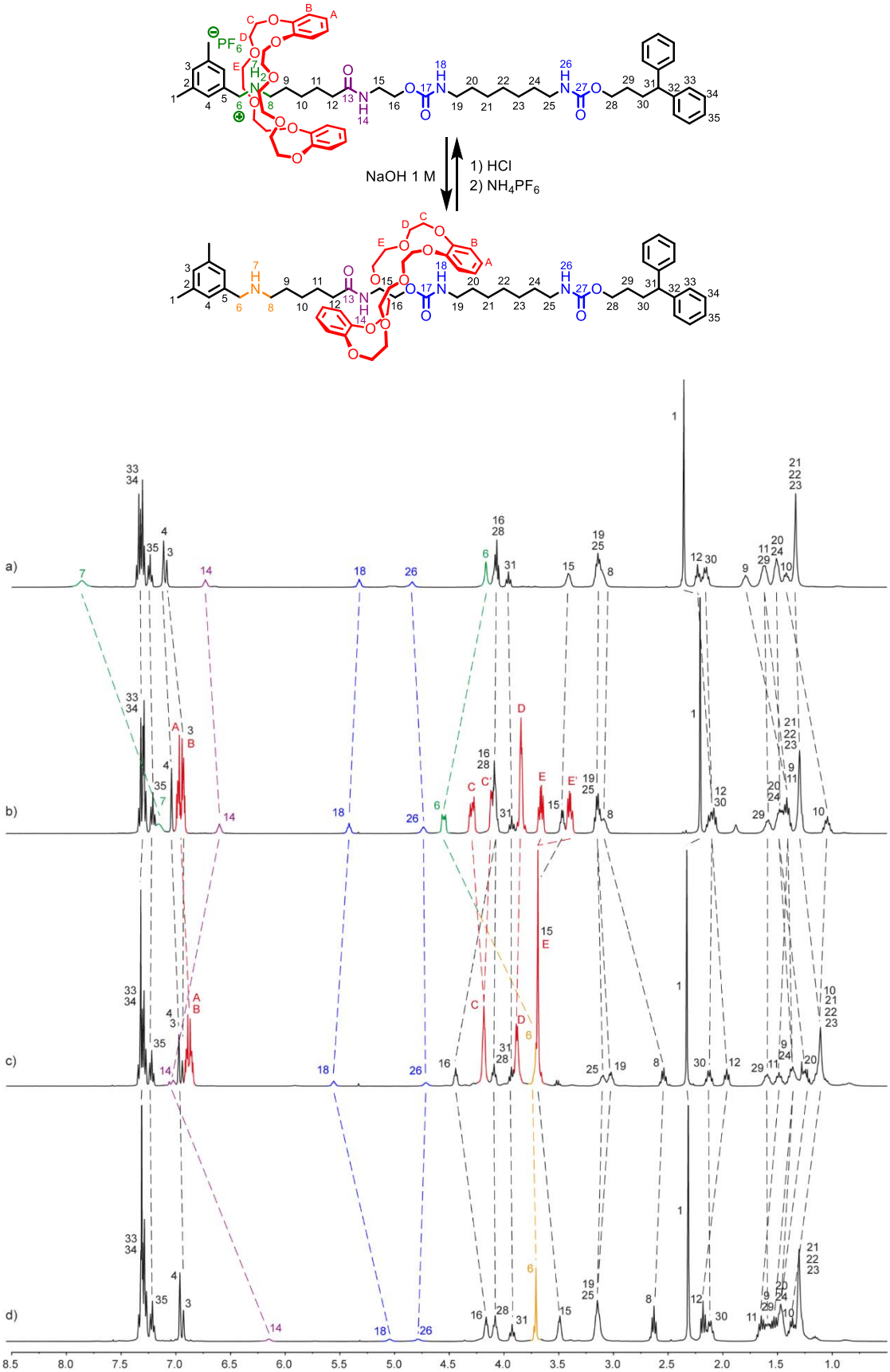


Figure S8. Characterization of the molecular machinery. ^{1}H NMR spectra (400 MHz) at 298 K in $CDCl_3$ of a) the protonated rod **2u-HPF$_6$**, b) the protonated rotaxane **2-HPF$_6$**, c) the deprotonated rotaxane **2** and d) the deprotonated rod **2u**.

Evidences of the molecular machinery were deduced from the ^{1}H NMR comparison of spectra of both the protonated and deprotonated rotaxanes **2-HPF$_6$** and **2** with their respective non-interlocked thread analogues **2u-HPF$_6$** and **2u**. The direct comparison between spectra of **2u-HPF$_6$** and **2-HPF$_6$** demonstrated the localization of the DB24C8 around the ammonium in **2u-HPF$_6$** (Figure S8.a-b). Briefly, in the protonated [2]rotaxane **2-HPF$_6$**, hydrogen atoms H_6 are shifted downfield ($\Delta\delta$ = 0.35 ppm) due to their hydrogen bonding interactions with the oxygen atoms of the DB24C8, while hydrogen atoms $H_{9\text{-}14}$ are shifted upfield ($\Delta\delta$ = -0.39 to -0.17 ppm) because they experience the shielding effect of the aromatic rings of the DB24C8. 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 neighboring dimethylaryl stopper ($\Delta\delta$ = -0.19 to -0.11 ppm). Due to the dissymmetry of the thread, the hydrogen atoms of the DB24C8 $H_{A\text{-}E}$ are all split in the rotaxane **2-HPF$_6$**, while H_E are shifted upfield because they are located in the shielding region of the dimethylaryl stoppering boundaries. Deprotonation of the rotaxane **2-HPF$_6$** triggered the shuttling of the DB24C8 around the amide site and the next carbamate moiety. This might be quickly deduced from the upfield shift of H_6 and the downfield shift of $H_{14,15,16,18}$ in **2** (Figure S8.b-c). The new position of the DB24C8 was confirmed by the comparison between ^{1}H NMR spectra of the deprotonated rotaxane **2** and its non-interlocked thread **2u** (Figure S8.c-d). In rotaxane **2**, with respect to **2u**, hydrogen atoms $H_{14\text{-}16,18}$ of the amide-carbamate station are shifted downfield, due to their hydrogen bonding interactions with the DB24C8 ($\Delta\delta$ = 0.90, 0.20, 0.27, 0.51 ppm, respectively). On contrary, the hydrogen atoms located on the two edges of this molecular station, respectively $H_{8\text{-}12}$ and $H_{19\text{-}23}$ are all shielded by the aromatic rings of the D24C8 ($\Delta\delta$ = from -0.25 to -0.10 ppm). Identical localization of the DB24C8 around the amide-carbamate site was observed in **2-Boc**.

4.2 ^{1}H NMR titrations of foldamer 1 with rotaxanes 2-HPF$_6$, 2 and 2-Boc

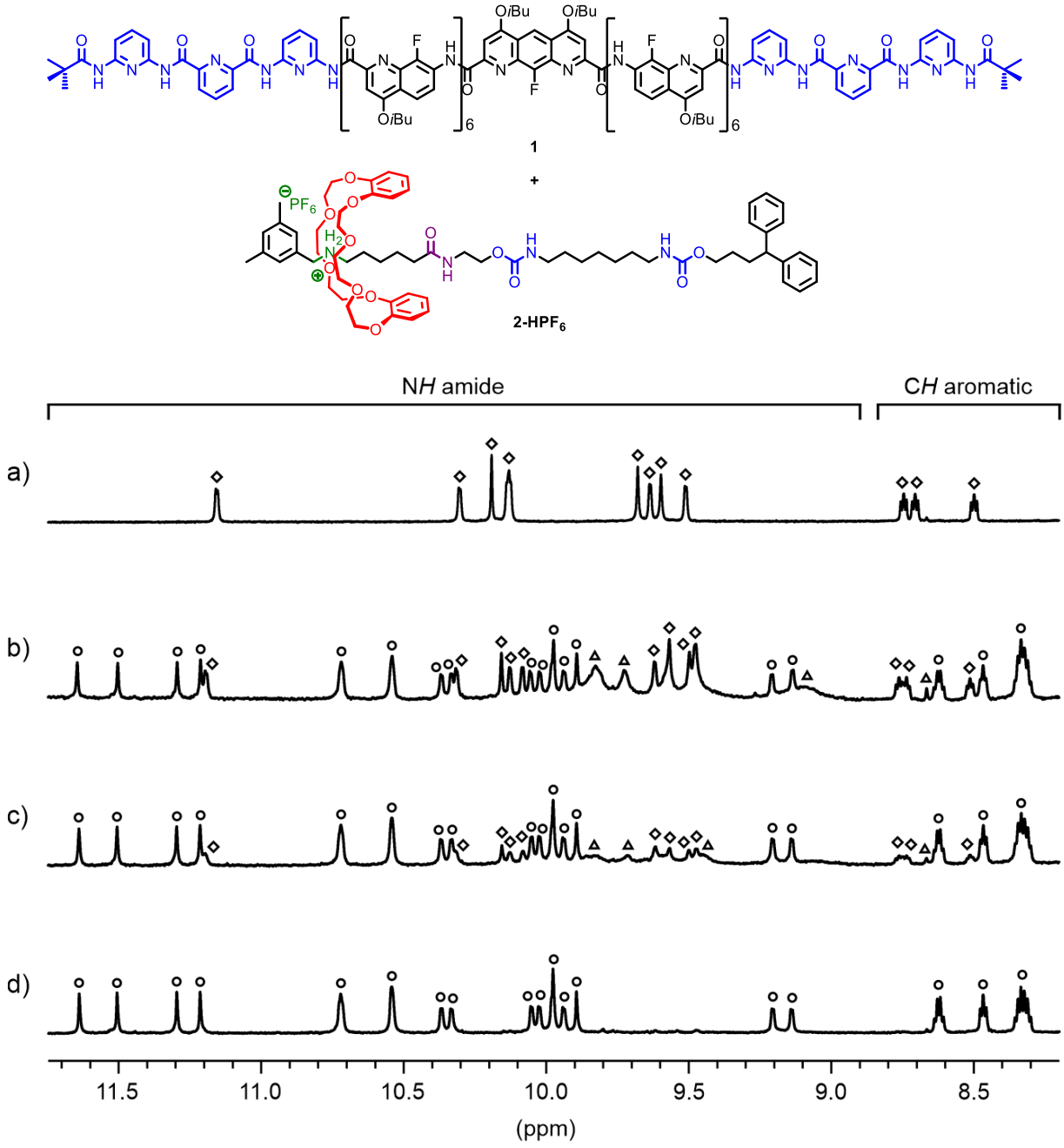


Figure S9. Part of the ^{1}H NMR spectra of the amide region (700 MHz) at 298 K of **1** (0.1 mM) in $CDCl_3$ in the presence of a) 0 equiv., b) 0.5 equiv., c) 1 equiv. and d) 2 equiv. of the protonated rotaxane **2-HPF$_6$**. Amides signals of the free single helix **1** and the double helix **(1)$_2$** are marked with diamonds and triangles, respectively. Whereas amides signals of the protonated foldarotaxane **1⊃2-HPF$_6$** are marked with circles. Some aromatic resonances of the single helix **1**, the double helix **(1)$_2$** and the complex **1⊃2-HPF$_6$** are denoted with diamonds, triangles and circles, respectively. The association constant K_a, between the single helix **1** and the carbamate / carbamate station of the protonated rotaxane **2-HPF$_6$**, was mesured to be 207 000 L.mol^{-1} in $CDCl_3$, based on the integration of the amides resonances.

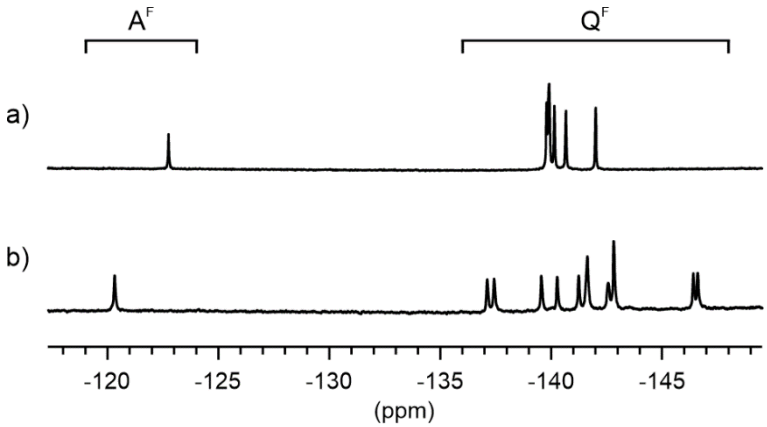


Figure S10. Part of the ^{19}F NMR spectra (282 MHz) at 298 K in $CDCl_3$ of a) the free single helix **1** and b) the protonated foldarotaxane **1⊃2-HPF$_6$**. A^F and Q^F designate fluoro-anthracene (1,8-diaza-9-fluoro-2,7-anthracene-dicaboxylic acid) and fluoro-quinoline (7-amino-8-fluoro-2-quinolinecarboxylic acid), respectively.

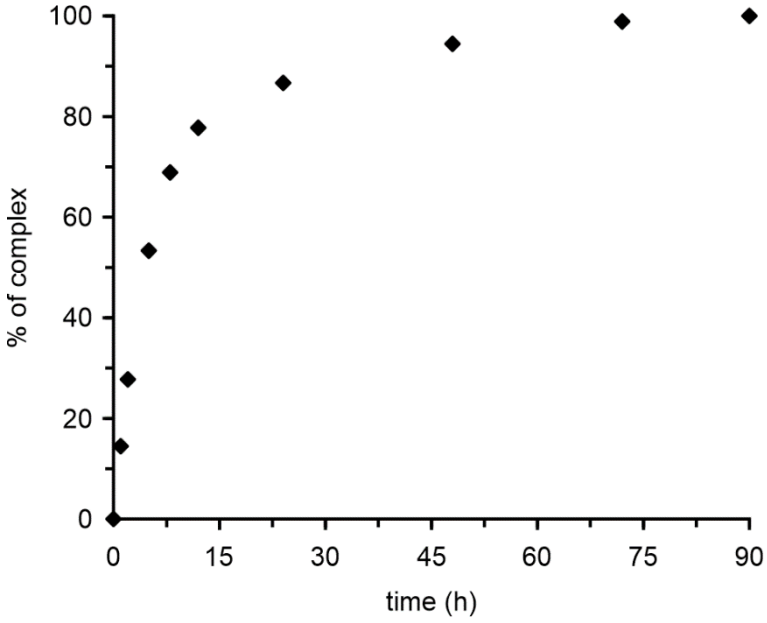


Figure S11. Time trace of the formation of the protonated foldarotaxane **1⊃2-HPF$_6$** from the foldamer **1** (1 mM) and the protonated rotaxane **2-HPF$_6$** (2 mM) in $CDCl_3$ monitored by ^1H NMR (300 MHz) at 298 K.

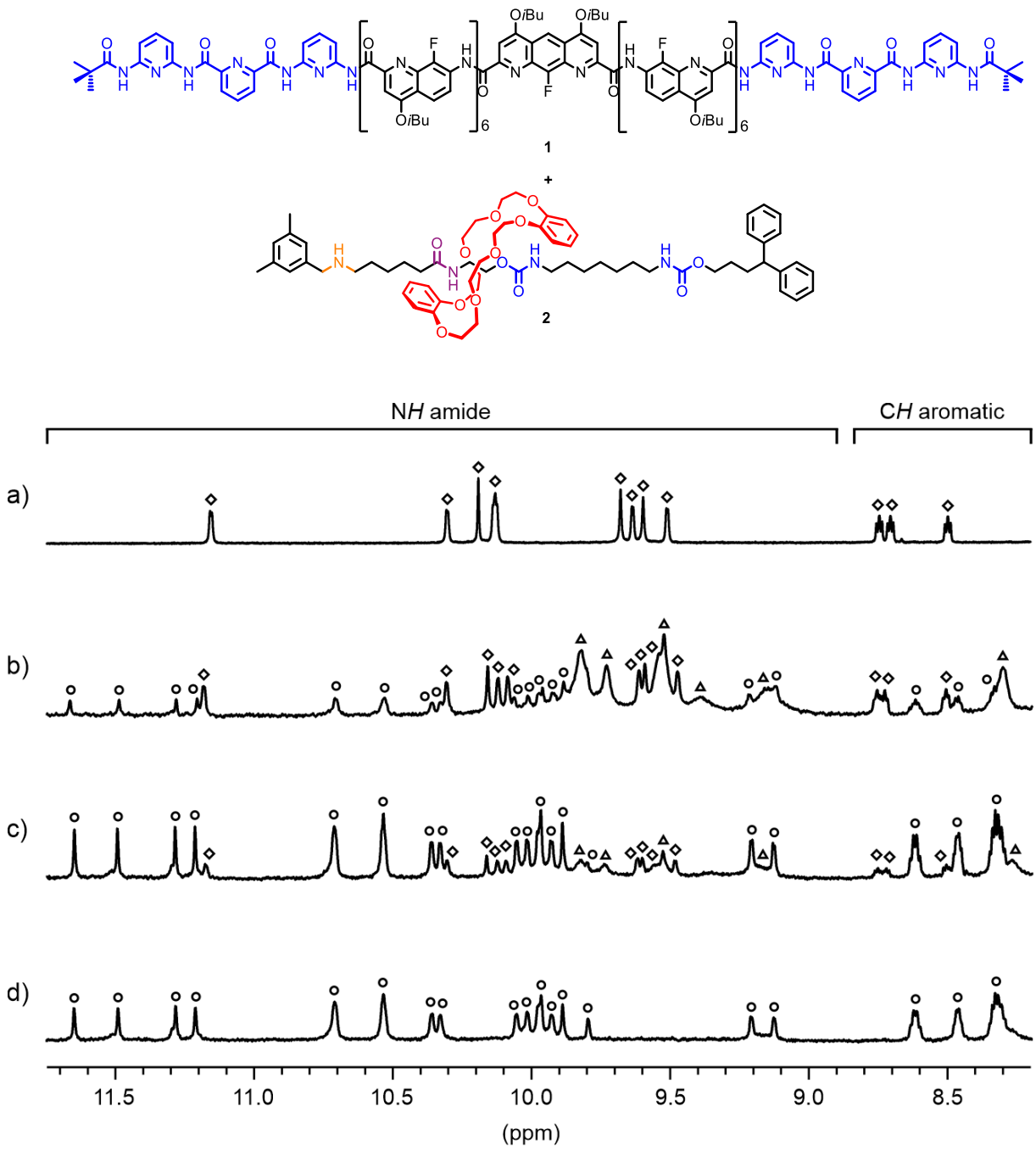


Figure S12. Part of the ^{1}H NMR spectra of the amide region (700 MHz) at 298 K of **1** (0.1 mM) in $CDCl_3$ in the presence of a) 0 equiv., b) 0.5 equiv., c) 2.5 equiv. and d) 4 equiv. of the deprotonated rotaxane **2**. Amides signals of the free single helix **1** and the double helix **(1)**$_2$ are marked with diamonds and triangles, respectively. Whereas amides signals of the deprotonated foldarotaxane **1⊃2** are marked with circles. Some aromatic resonances of the single helix **1**, the double helix **(1)**$_2$ and the complex **1⊃2** are denoted with diamonds, triangles and circles, respectively. The association constant K_a, between the single helix **1** and the carbamate / carbamate station of the deprotonated rotaxane **2**, was mesured to be 9 100 L.mol^{-1} in $CDCl_3$, based on the integration of the amides resonances.

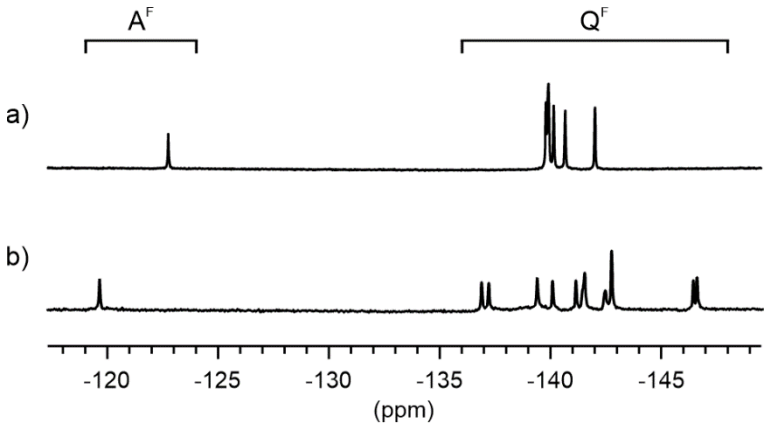


Figure S13. Part of the ^{19}F NMR spectra (282 MHz) at 298 K in $CDCl_3$ of a) the free single helix **1** and b) the deprotonated foldarotaxane **1⊃2**. A^F and Q^F designate fluoro-anthracene (1,8-diaza-9-fluoro-2,7-anthracene-dicaboxylic acid) and fluoro-quinoline (7-amino-8-fluoro-2-quinolinecarboxylic acid), respectively.

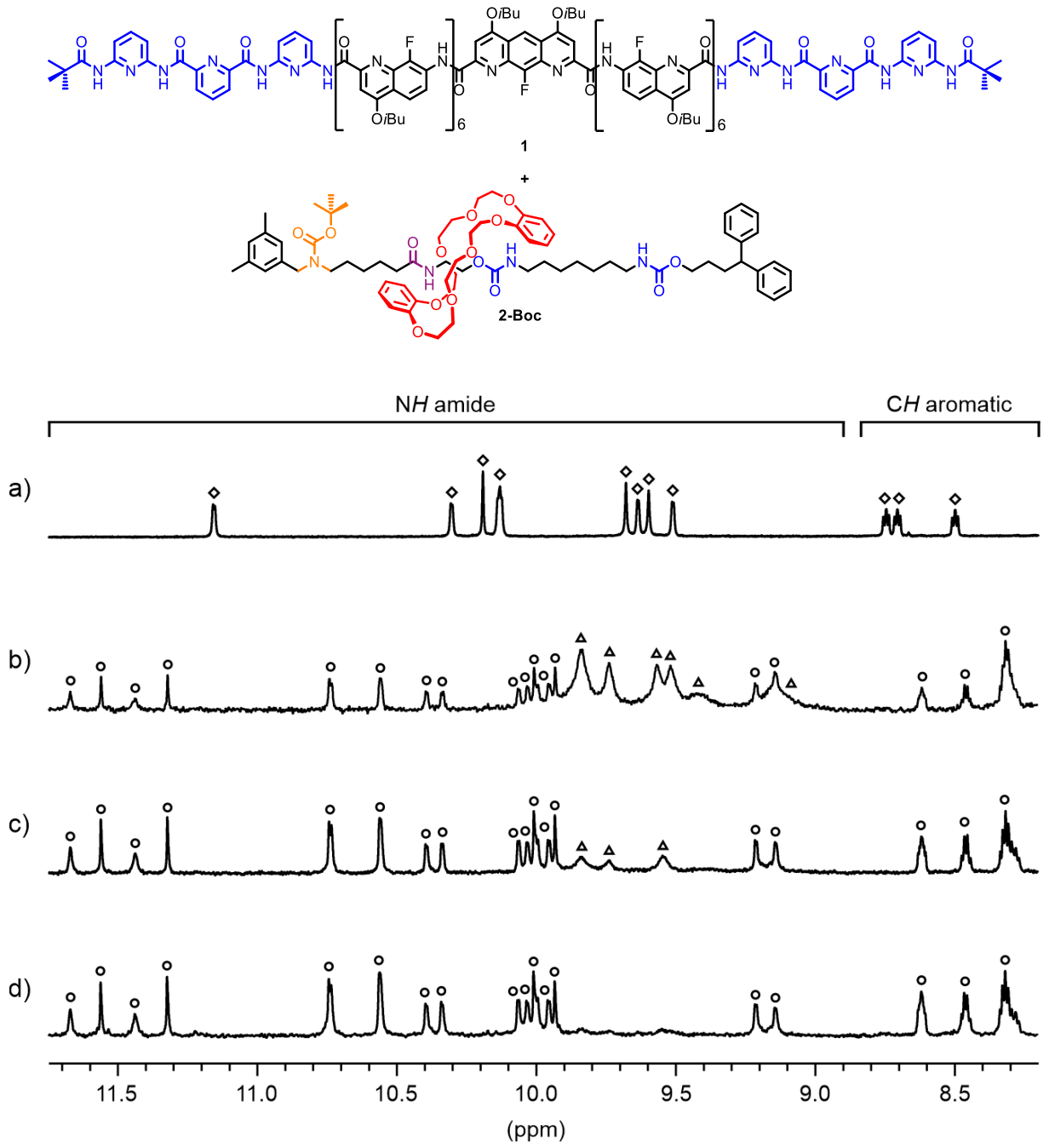


Figure S14. Part of the ^{1}H NMR spectra of the amide region (700 MHz) at 298 K of **1** (0.1 mM) in $CDCl_3$ in the presence of a) 0 equiv., b) 0.5 equiv., c) 3 equiv. and d) 7 equiv. of the *N*-Boc-protected rotaxane **2-Boc**. Amides signals of the free single helix **1** and the double helix **(1)**$_2$ are marked with diamonds and triangles, respectively. Whereas amides signals of the *N*-Boc-protected foldarotaxane **1⊃2-Boc** are marked with circles. Some aromatic resonances of the single helix **1** and the complex **1⊃2-Boc** are denoted with diamonds and circles, respectively. The association constant K_a, between the single helix **1** and the carbamate / carbamate station of the *N*-Boc-protected rotaxane **2-Boc**, was mesured to be 3 800 L.mol^{-1} in $CDCl_3$, based on the integration of the amides resonances.

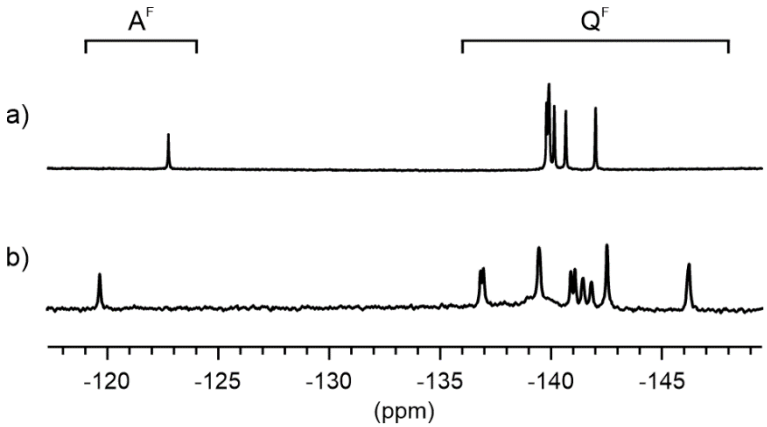


Figure S15. Part of the ^{19}F NMR spectra (282 MHz) at 298 K in $CDCl_3$ of a) the free single helix **1** and b) the *N*-Boc-protected foldarotaxane **1⊃2-Boc**. A^F and Q^F designate fluoro-anthracene (1,8-diaza-9-fluoro-2,7-anthracene-dicaboxylic acid) and fluoro-quinoline (7-amino-8-fluoro-2-quinolinecarboxylic acid), respectively.

4.3 ^{1}H NMR titrations of foldamer 1 with rods 2u-HPF$_6$, 2u and 2u-Boc

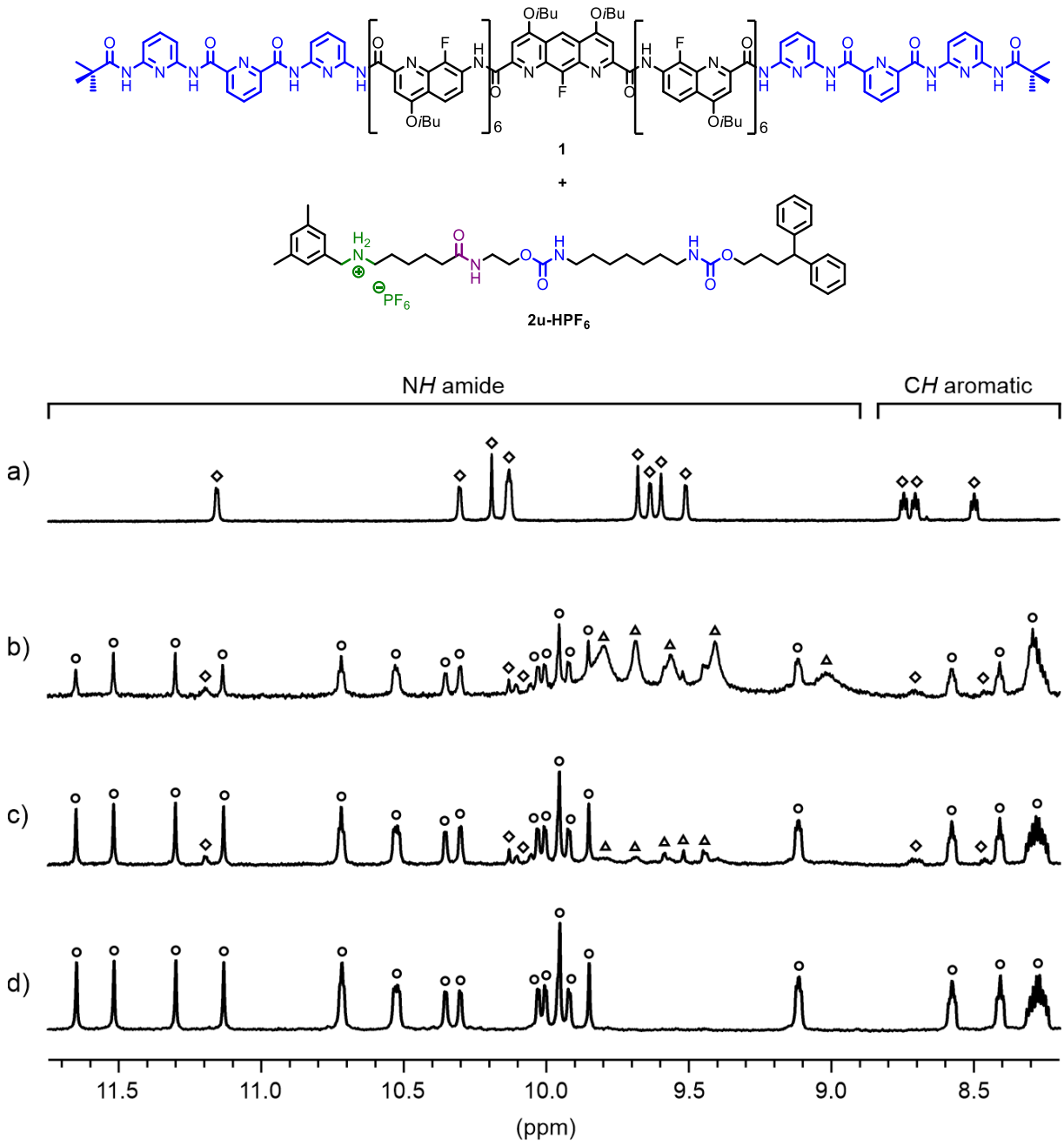


Figure S16. Part of the ^{1}H NMR spectra of the amide region (700 MHz) at 298 K of **1** (0.1 mM) in $CDCl_3$ in the presence of a) 0 equiv., b) 0.5 equiv., c) 1.5 equiv. and d) 2.5 equiv. of the protonated rod **2u-HPF$_6$**. Amides signals of the free single helix **1** and the double helix **(1)$_2$** are marked with diamonds and triangles, respectively. Whereas amides signals of the protonated foldaxane **1⊃2u-HPF$_6$** are marked with circles. Some aromatic resonances of the single helix **1** and the complex **1⊃2u-HPF$_6$** are denoted with diamonds and circles, respectively. The association constant K_a, between the single helix **1** and the carbamate / carbamate station of the protonated rod **2u-HPF$_6$**, was mesured to be 375 000 L.mol^{-1} in $CDCl_3$, based on the integration of the amides resonances.

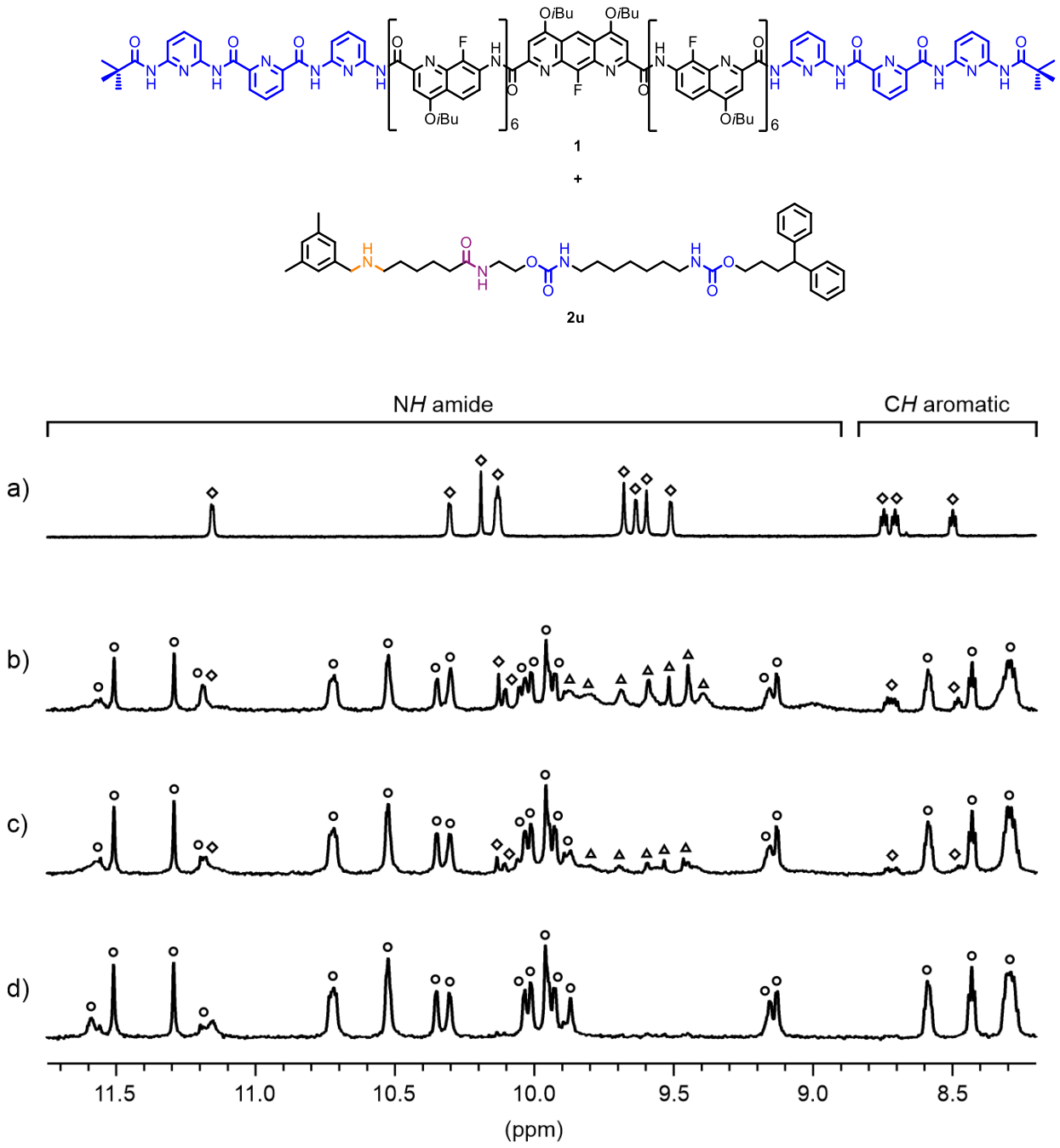


Figure S17. Part of the ^{1}H NMR spectra of the amide region (700 MHz) at 298 K of **1** (0.1 mM) in $CDCl_3$ in the presence of a) 0 equiv., b) 1 equiv., c) 1.5 equiv. and d) 3 equiv. of the deprotonated rod **2u**. Amides signals of the free single helix **1** and the double helix **(1)**$_2$ are marked with diamonds and triangles, respectively. Whereas amides signals of the deprotonated foldaxane **1⊃2u** are marked with circles. Some aromatic resonances of the single helix **1** and the complex **1⊃2u** are denoted with diamonds and circles, respectively. The association constant K_a, between the single helix **1** and the carbamate / carbamate station of the deprotonated rod **2u**, was mesured to be 397 000 L.mol^{-1} in $CDCl_3$, based on the integration of the amides resonances.

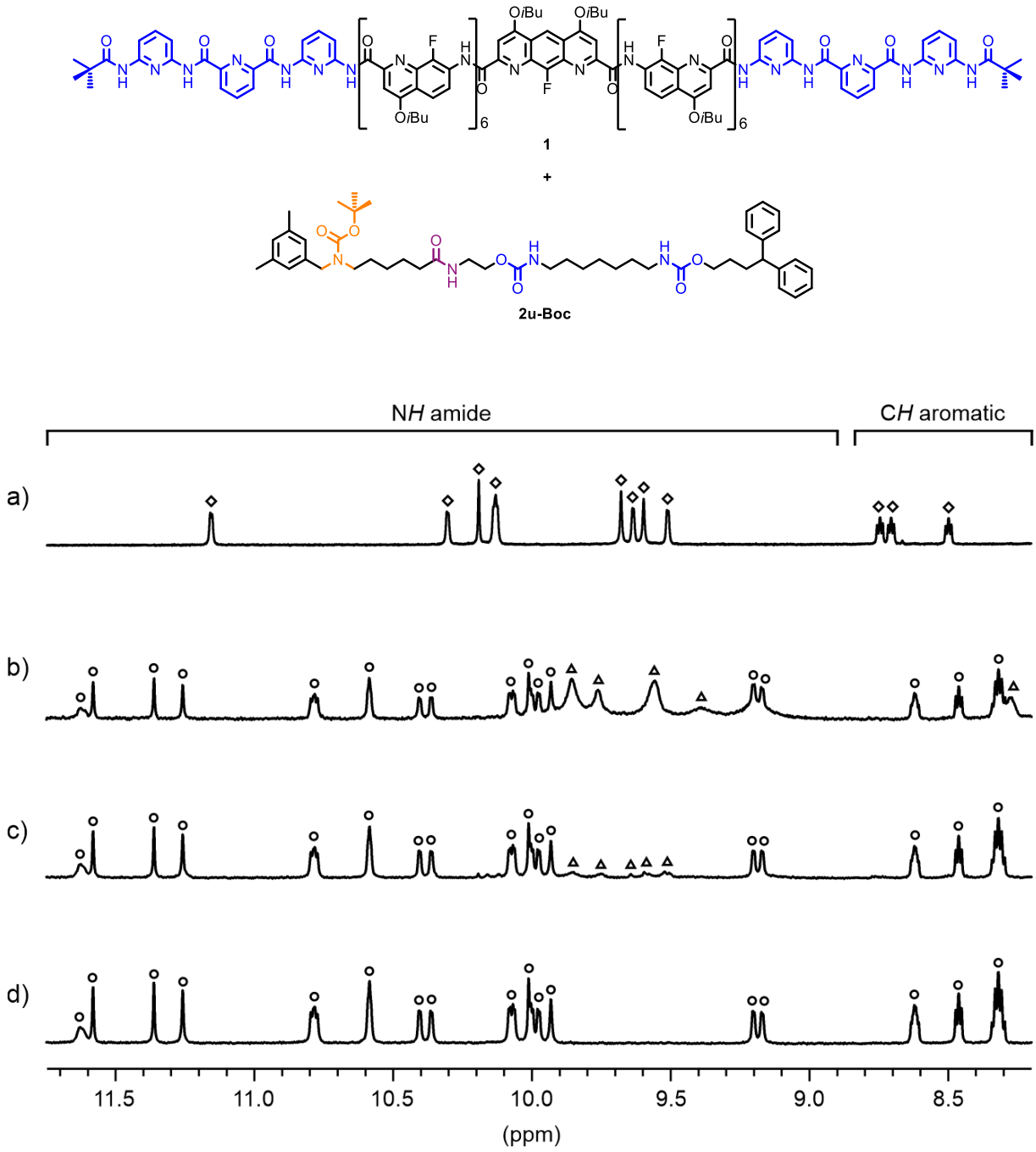
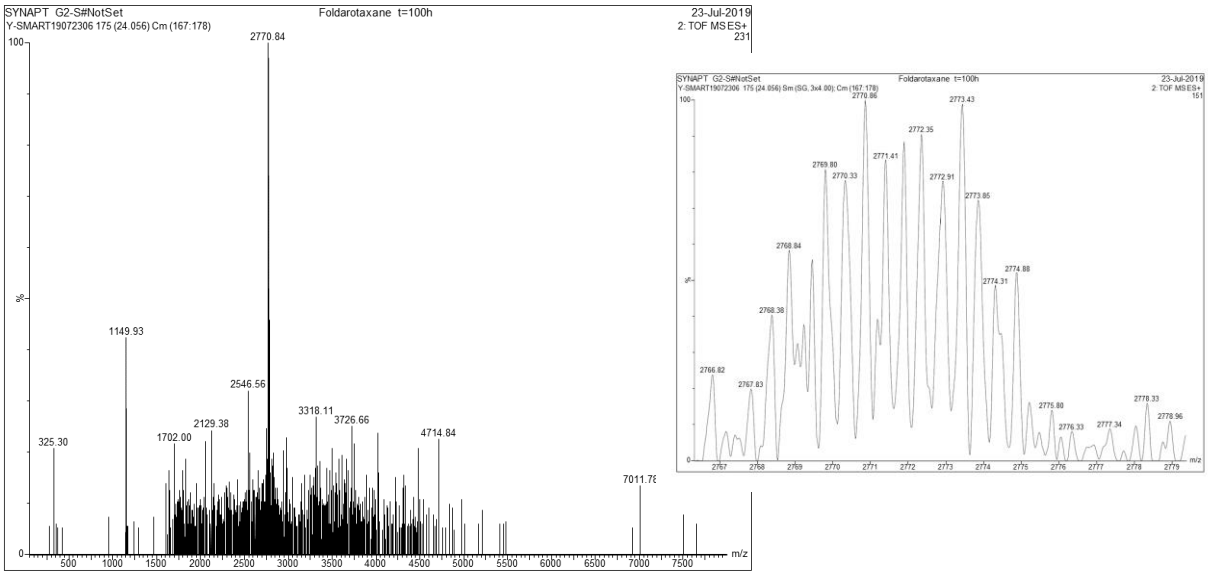


Figure S18. Part of the ^{1}H NMR spectra of the amide region (700 MHz) at 298 K of **1** (0.1 mM) in $CDCl_3$ in the presence of a) 0 equiv., b) 0.5 equiv., c) 2 equiv. and d) 3 equiv. of the *N*-Boc-protected rod **2u-Boc**. Amides signals of the free single helix **1** and the double helix **(1)$_2$** are marked with diamonds and triangles, respectively. Whereas amides signals of the *N*-Boc-protected foldaxane **1⊃2u-Boc** are marked with circles. Some aromatic resonances of the single helix **1**, the double helix **(1)$_2$** and the complex **1⊃2u-Boc** are denoted with diamonds, triangles and circles, respectively. The association constant K_a, between the single helix **1** and the carbamate / carbamate station of the *N*-Boc-protected rod **2u-Boc**, was mesured to be 317 000 L.mol^{-1} in $CDCl_3$, based on the integration of the amides resonances.

4.4 Mass spectrometry of the protonated foldarotaxane 1⊃2-HPF$_6$



MS (ESI): *m/z* calcd for $C_{300}H_{316}F_{13}N_{44}O_{47}$ $[M+H-PF_6]^{2+}$ 2766.67 ; found 2766.82

5. Solid state studies: X-ray crystallography

5.1 Crystal structure and X-ray data for the double helix $(1)_2$

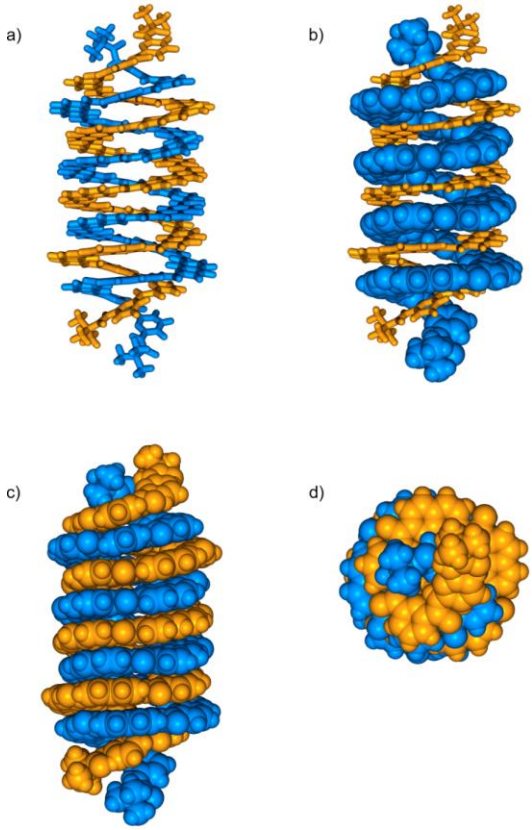


Figure S19. a-c) Side views of the double helix $\mathbf{(1)_2}$ a) in tube representation, b) with a strand in tube representation and the other in CPK representation and c) in CPK representation. d) Top view of the double helix $\mathbf{(1)_2}$ in CPK representation. Isobutyl side chains have been removed for clarity.

Table S2. Crystal data and structure refinement for the double helix **(1)**$_2$ (CCDC number 2050780).

Formula	$C_{238}\ H_{230}\ Cl_4\ F_{13}\ N_{40}\ O_{34}$
M	4582.41
Crystal system	Monoclinic
Space group	C2/c
a / Å	50.7910(17)
b / Å	24.6964(4)
c / Å	50.4864(15)
α / o	90
β / o	114.623(4)
γ / o	90
U / Å^3	57570(3)
T / K	130
Z	8
ρ / g.cm^{-1}	1.058
Size (mm)	0.1x0.1x0.05
λ / Å	1.54178
μ / mm^{-1}	0.976
Unique data	33641
Parameters / restraints	2996/154
R1, wR2	0.1582, 0.4450
Goodness of fit	1.772

5.2 Crystal structure and X-ray data for the protonated foldarotaxane 1⊃2-HPF$_6$

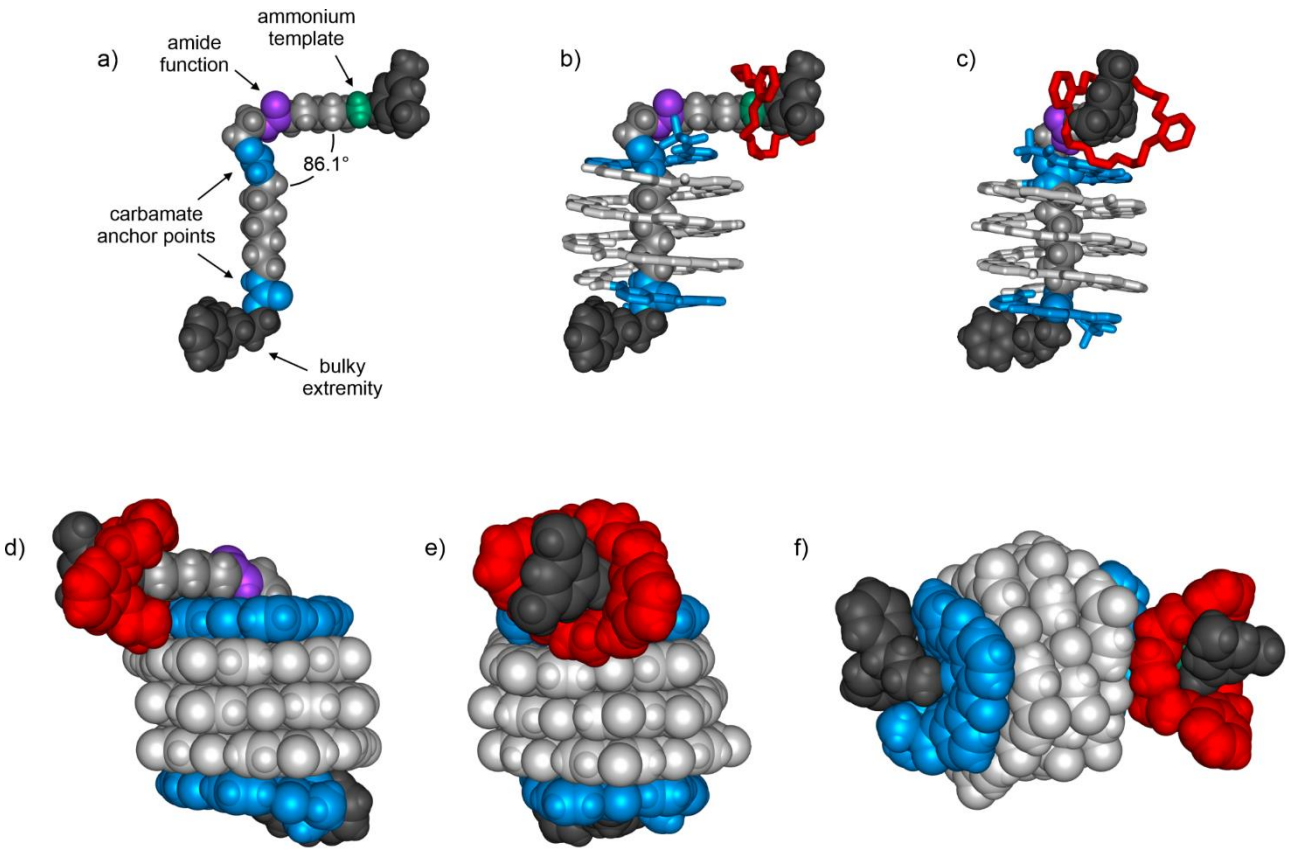


Figure S20. a) Structure of the dumbbell rod in CPK representation, as it exists in the structure of the protonated foldarotaxane **1⊃2-HPF$_6$**, showing a kink due to a hydrogen bond between the amide function (hydrogen bond donor) and the central carbamate function (hydrogen bond acceptor). b,c) Different views of the protonated foldarotaxane **1⊃2-HPF$_6$** structure with the rod in CPK representation and the helix and the macrocycle in tube representation. Isobutyl side chains of the helix and hydrogen atoms of the helix and the macrocycle have been removed for clarity. d-f) Different views of the protonated foldarotaxane **1⊃2-HPF$_6$** structure in CPK representation. Isobutyl side chains of the helix have been removed for clarity.

Table S3. Crystal data and structure refinement for the protonated foldarotaxane **1⊃2-HPF$_6$** (CCDC number 2050779).

Formula	C_{312} H_{324} Cl_2 F_{13} N_{44} O_{47}
M	5760.03
Crystal system	Triclinic
Space group	P-1
a / Å	18.0431(4)
b / Å	28.0019(6)
c / Å	35.1727(8)
α / o	98.272(2)
β / o	98.635(2)
γ / o	91.043(2)
U / Å^3	17372.1(7)
T / K	130
Z	2
ρ / g.cm^{-1}	1.101
Size (mm)	0.1x0.05x0.05
λ / Å	1.54178
μ / mm^{-1}	0.923
Unique data	40737
Parameters / restraints	3799/21547
R1, wR2	0.0955, 0.2846
Goodness of fit	1.234

6. Molecular modeling

6.1 Optimized structure of the *N*-Boc-protected rotaxane 2-Boc

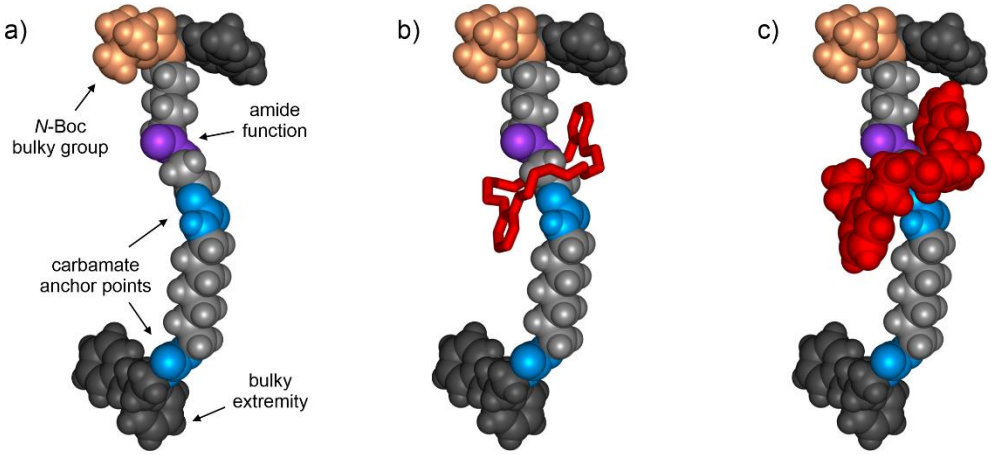


Figure S21. Minimized structure (MMFFs) of: a) the *N*-Boc-protected dumbbell rod as it exists in the molecular modeling of the *N*-Boc-protected rotaxane **2-Boc** in CPK representation, b) the *N*-Boc-protected rotaxane **2-Boc** with the rod in CPK representation and the macrocycle in tube representation (hydrogen atoms of the macrocycle have been removed for clarity) and c) the *N*-Boc-protected rotaxane **2-Boc** in CPK representation.

6.2 Optimized structure of the deprotonated foldarotaxane 1⊃2

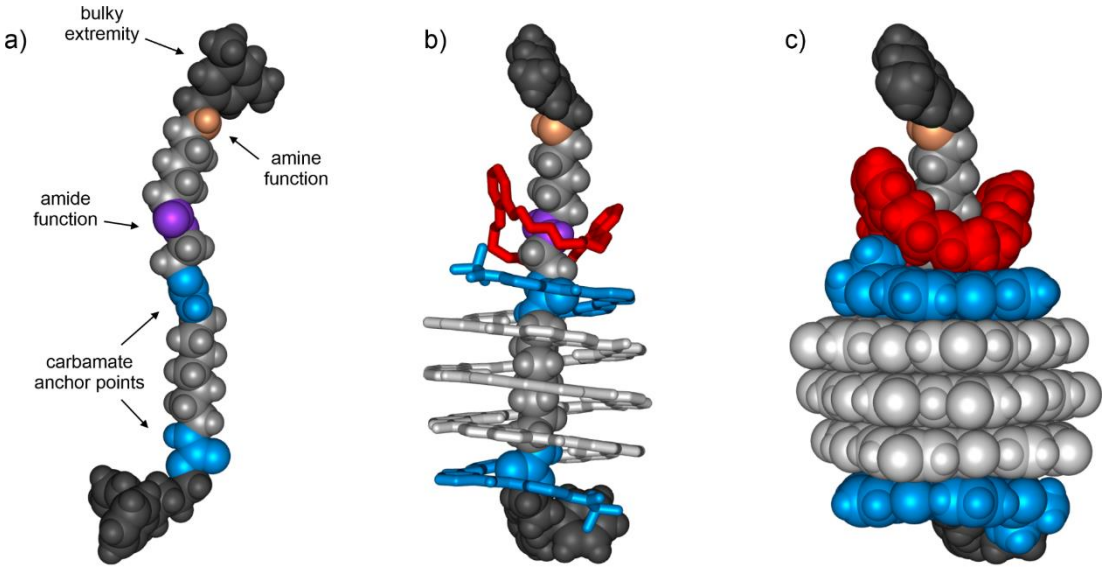


Figure S22. Optimized structure of a) the deprotonated dumbbell rod as it exists in the molecular modeling of the deprotonated foldarotaxane **1⊃2** in CPK representation, b) the deprotonated foldarotaxane **1⊃2** with the rod in CPK representation and the helix and the macrocycle in tube representation (hydrogen atoms of the helix and the macrocycle and isobutyl side chains of the helix have been removed for clarity) and c) the deprotonated foldarotaxane **1⊃2** in CPK representation (isobutyl side chains of the helix have been removed for clarity).

6.3 Optimized structure of the deprotonated foldarotaxane 1⊃2-Boc

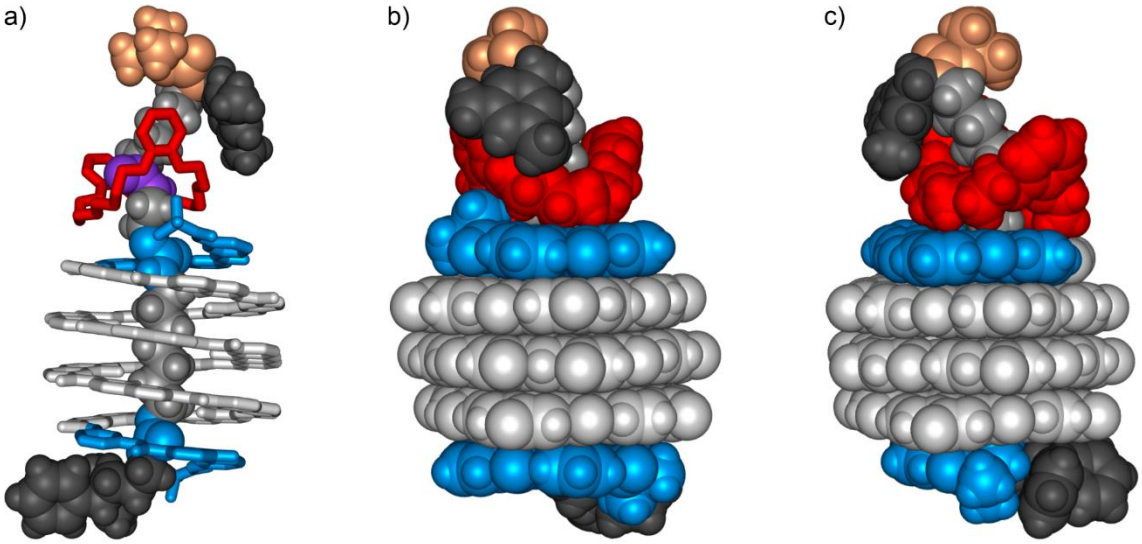
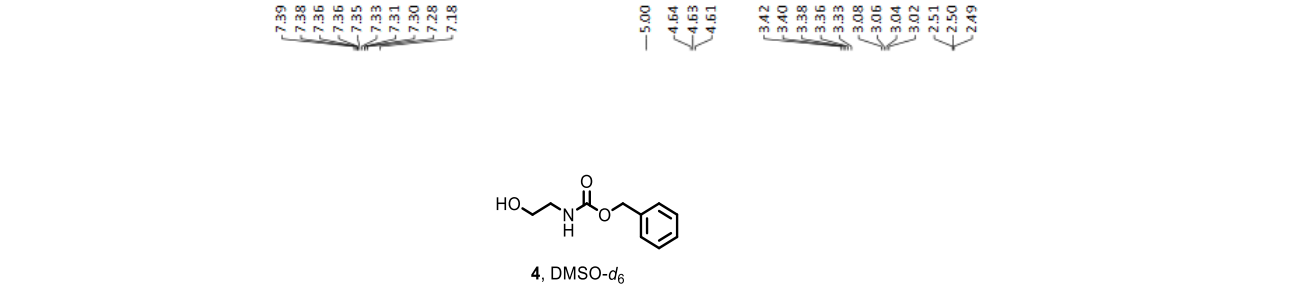


Figure S23. Optimized structure of the *N*-Boc-protected foldarotaxane **1⊃2-Boc** a) with the rod in CPK representation and the helix and the macrocycle in tube representation (hydrogen atoms of the helix and the macrocycle and isobutyl side chains of the helix have been removed for clarity) and b,c) in CPK representation (isobutyl side chains of the helix have been removed for clarity).

7. ^{1}H and ^{13}C NMR spectra of new synthetic compounds



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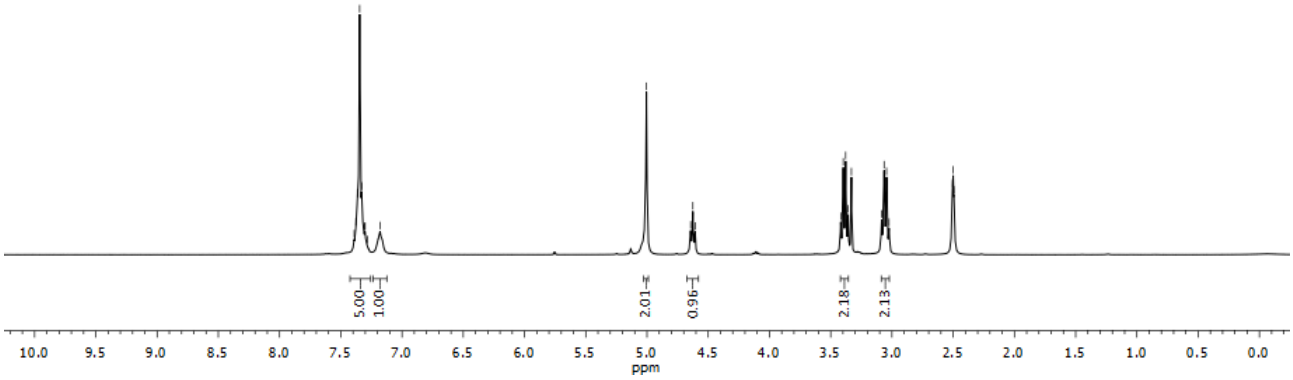

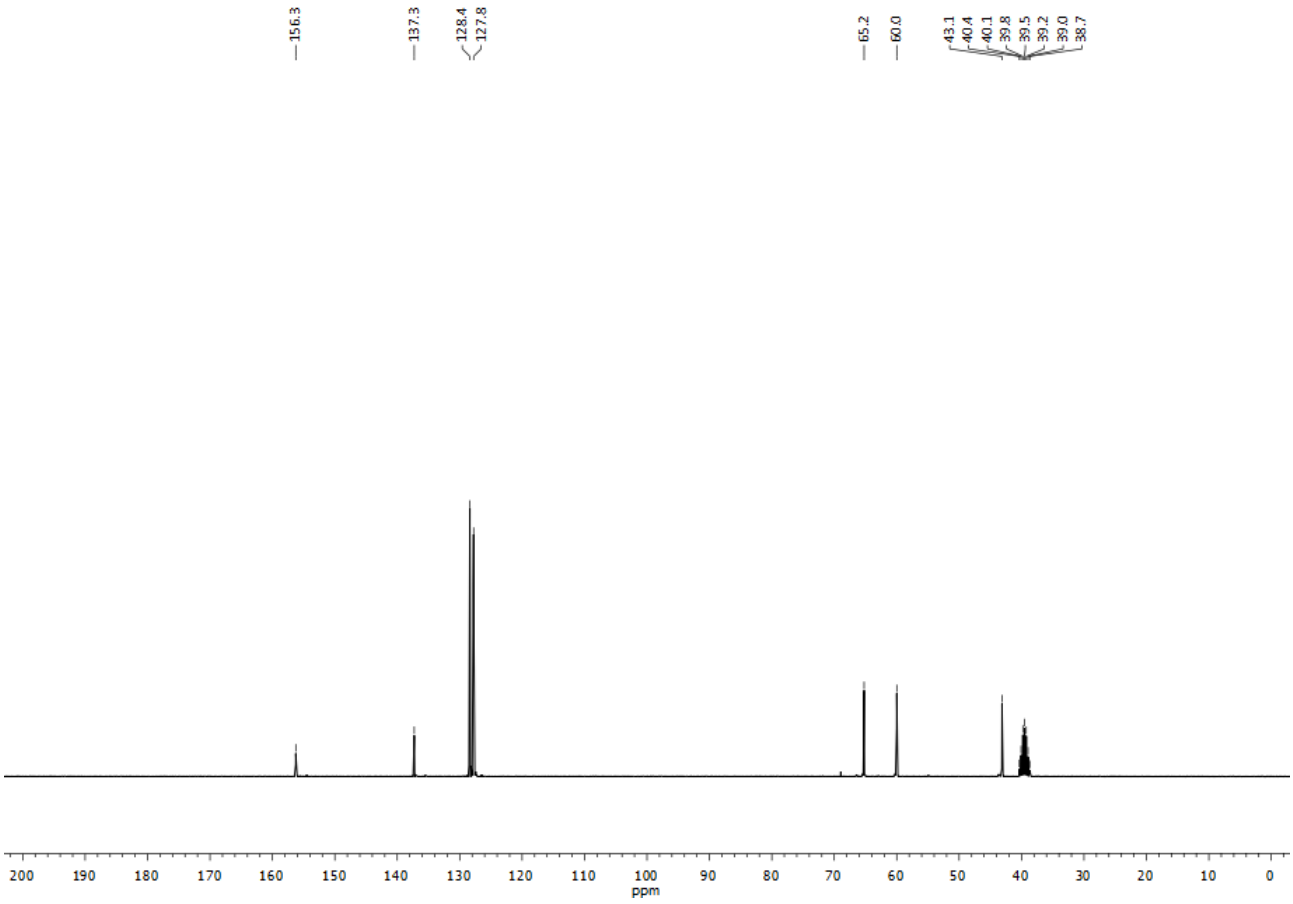


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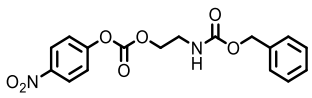
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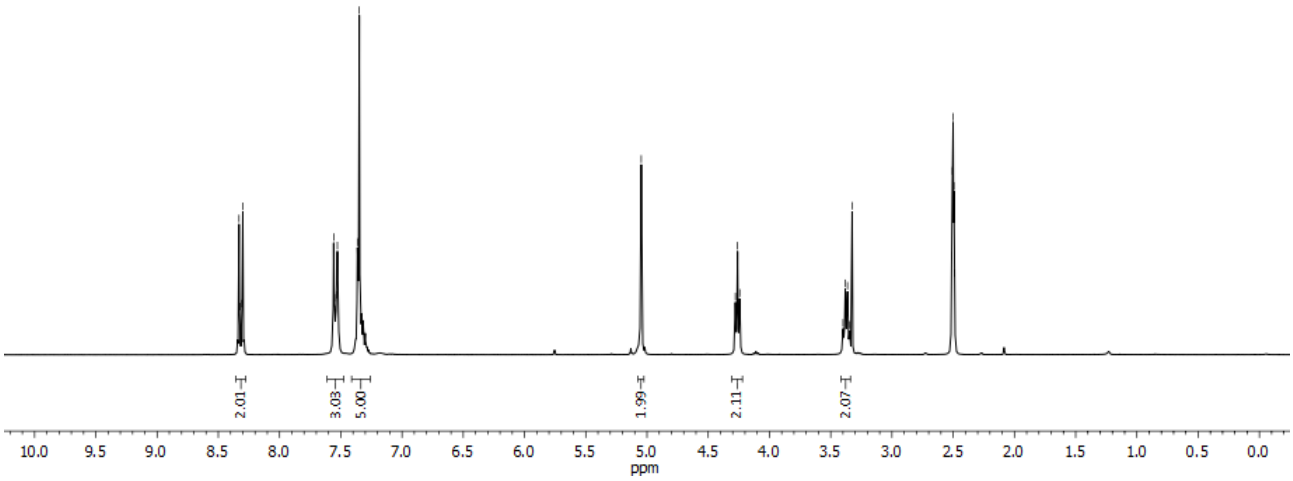
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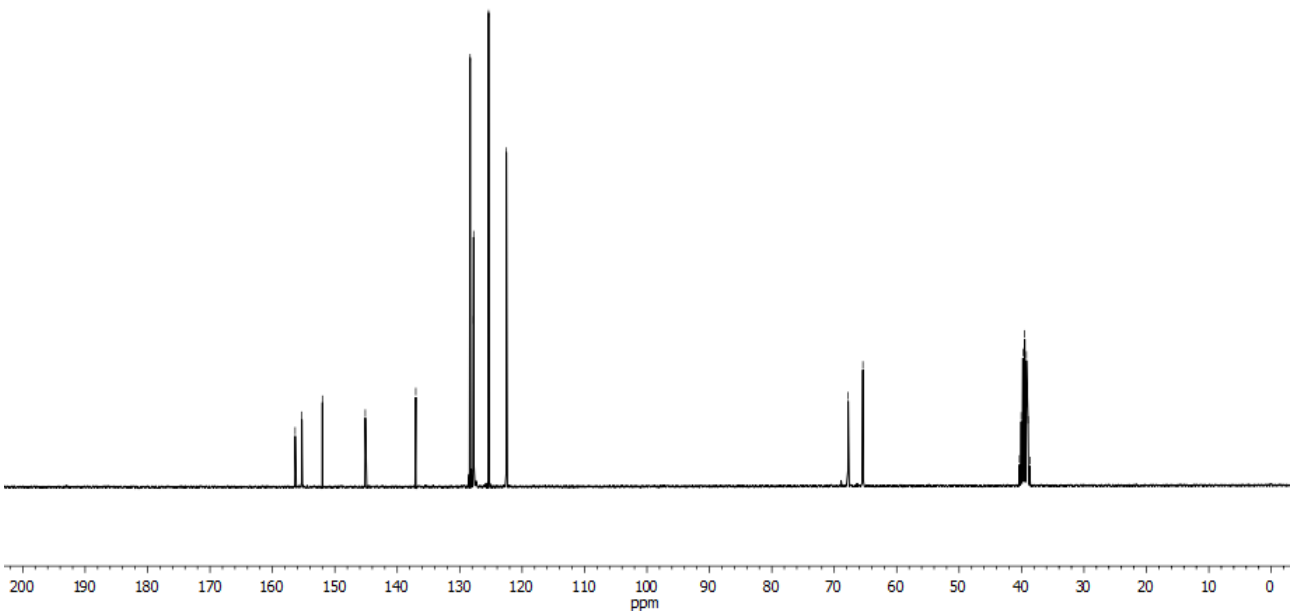
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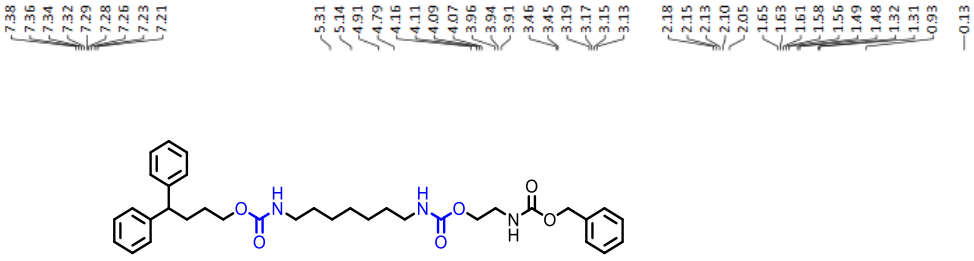

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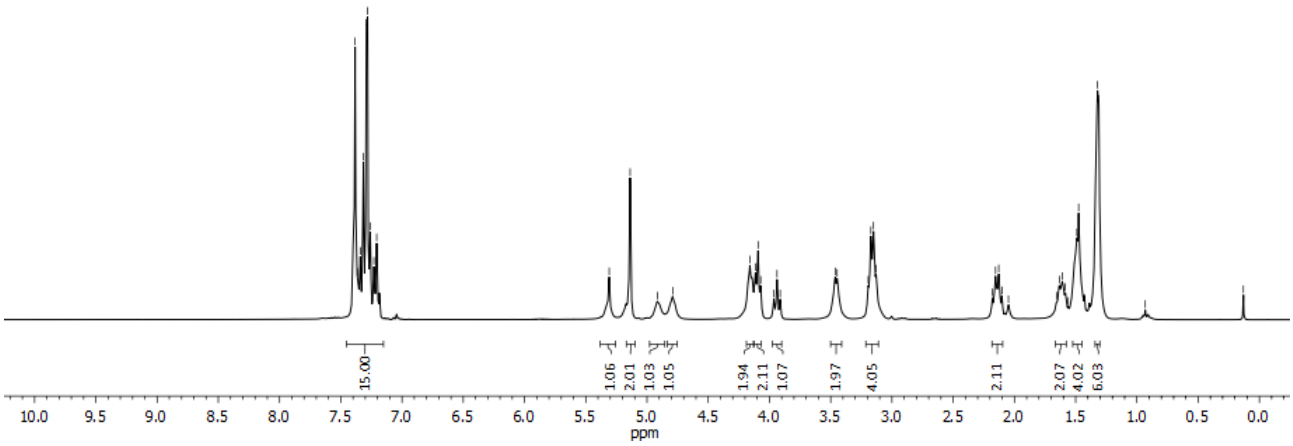

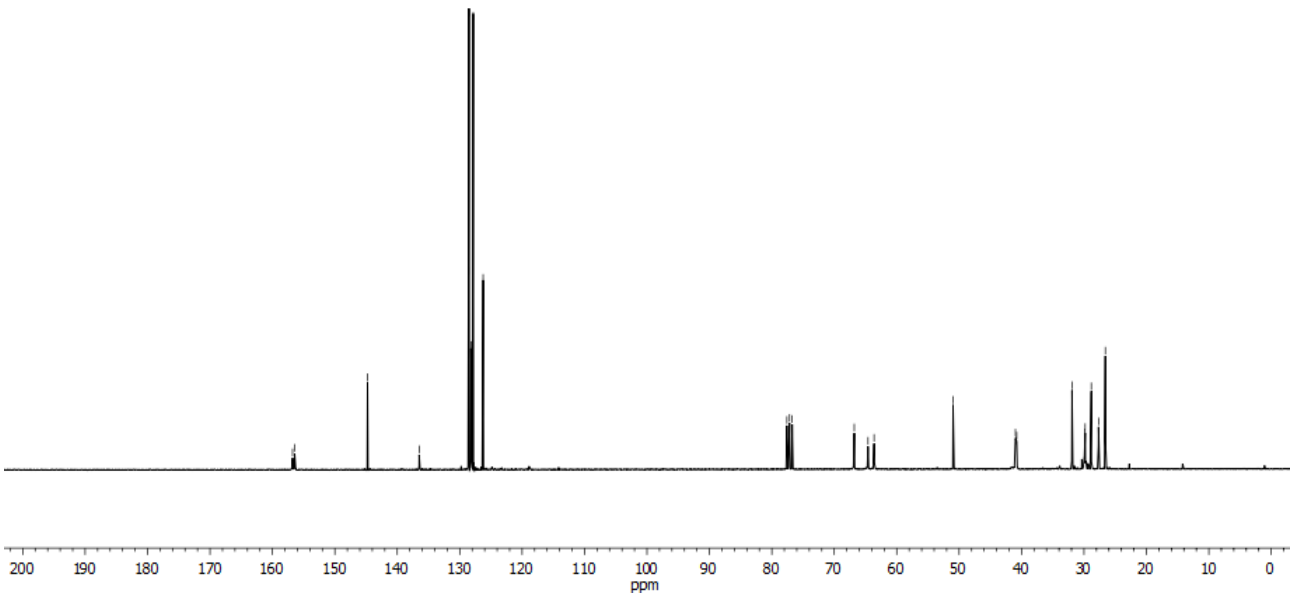

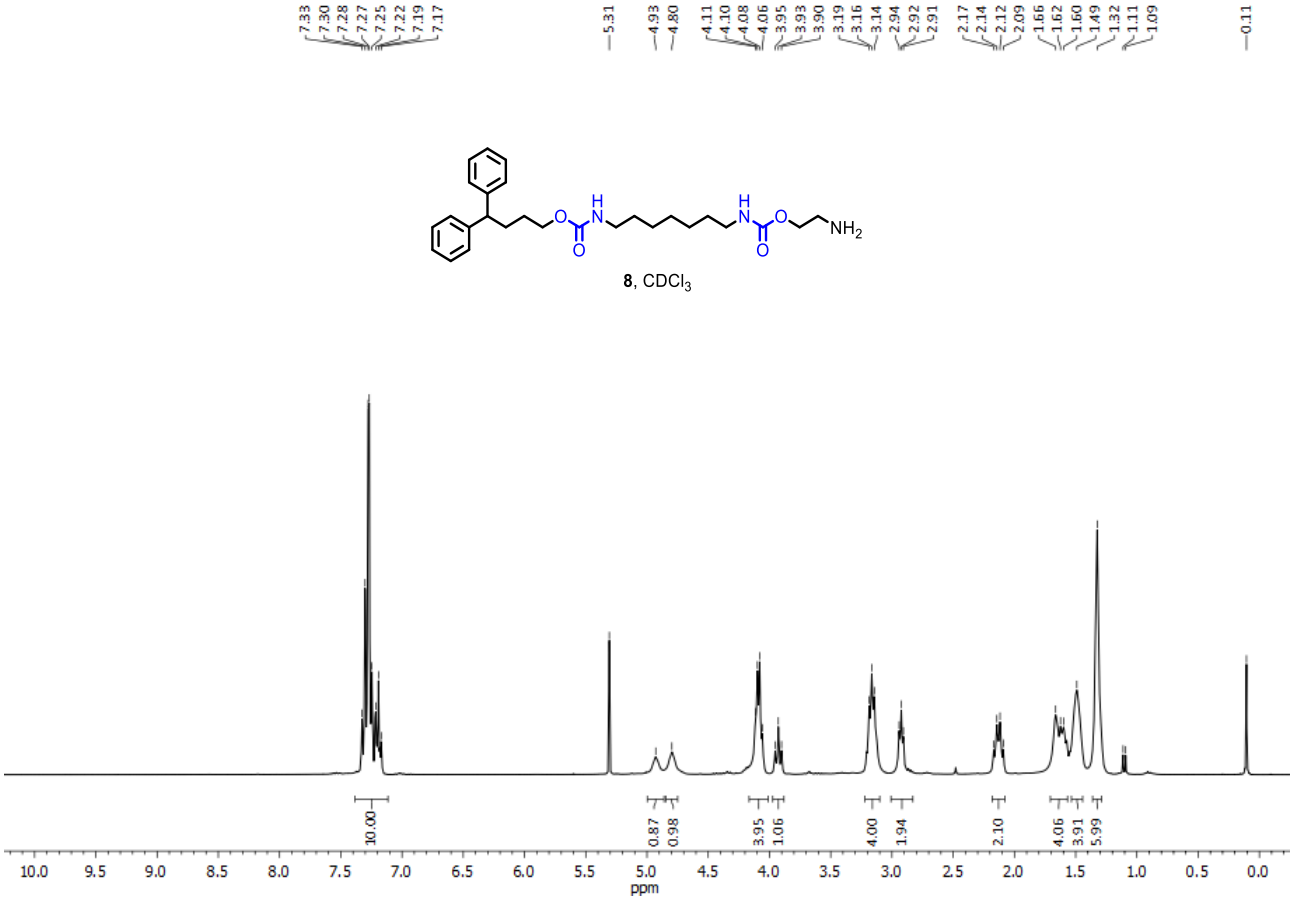
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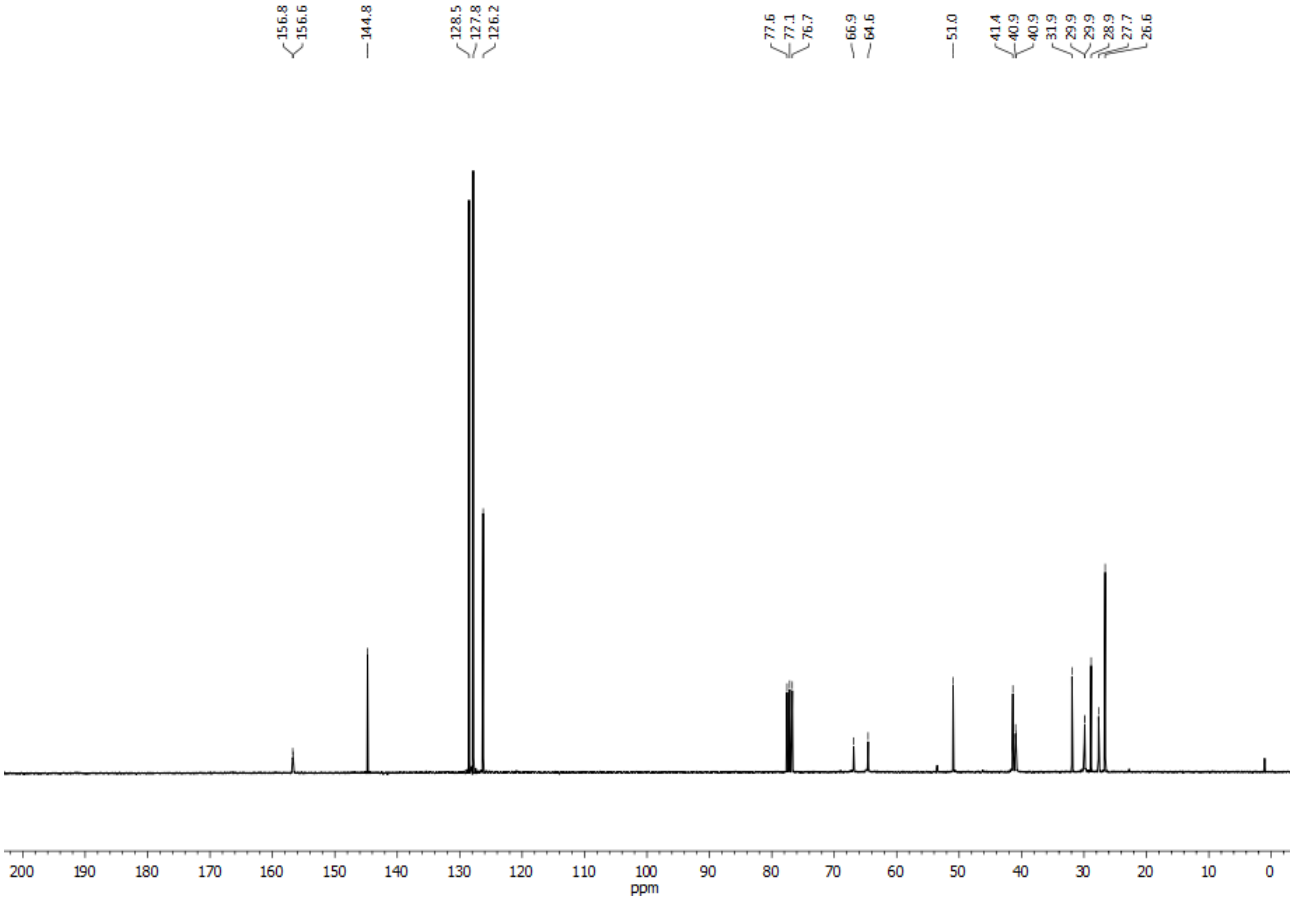
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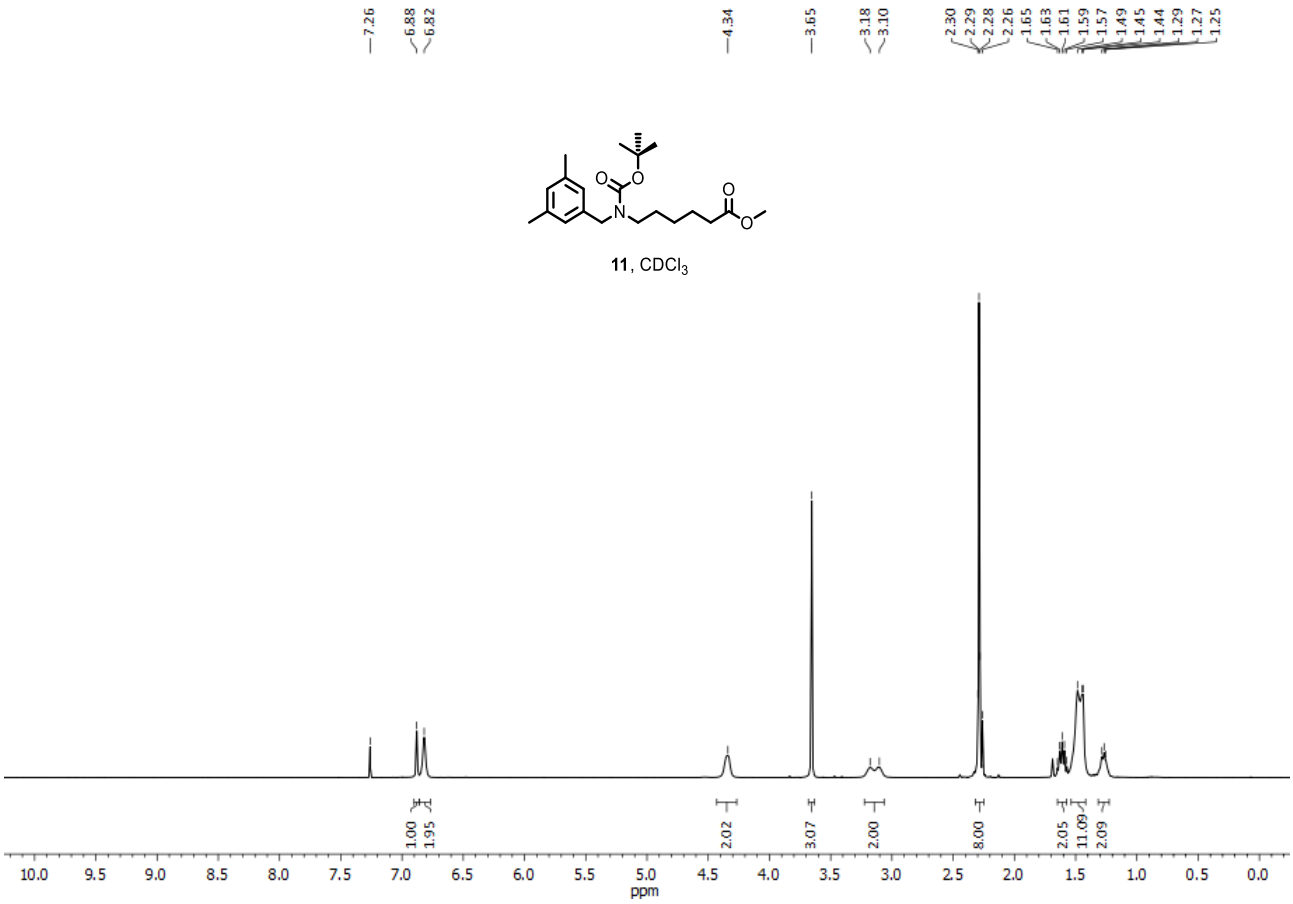
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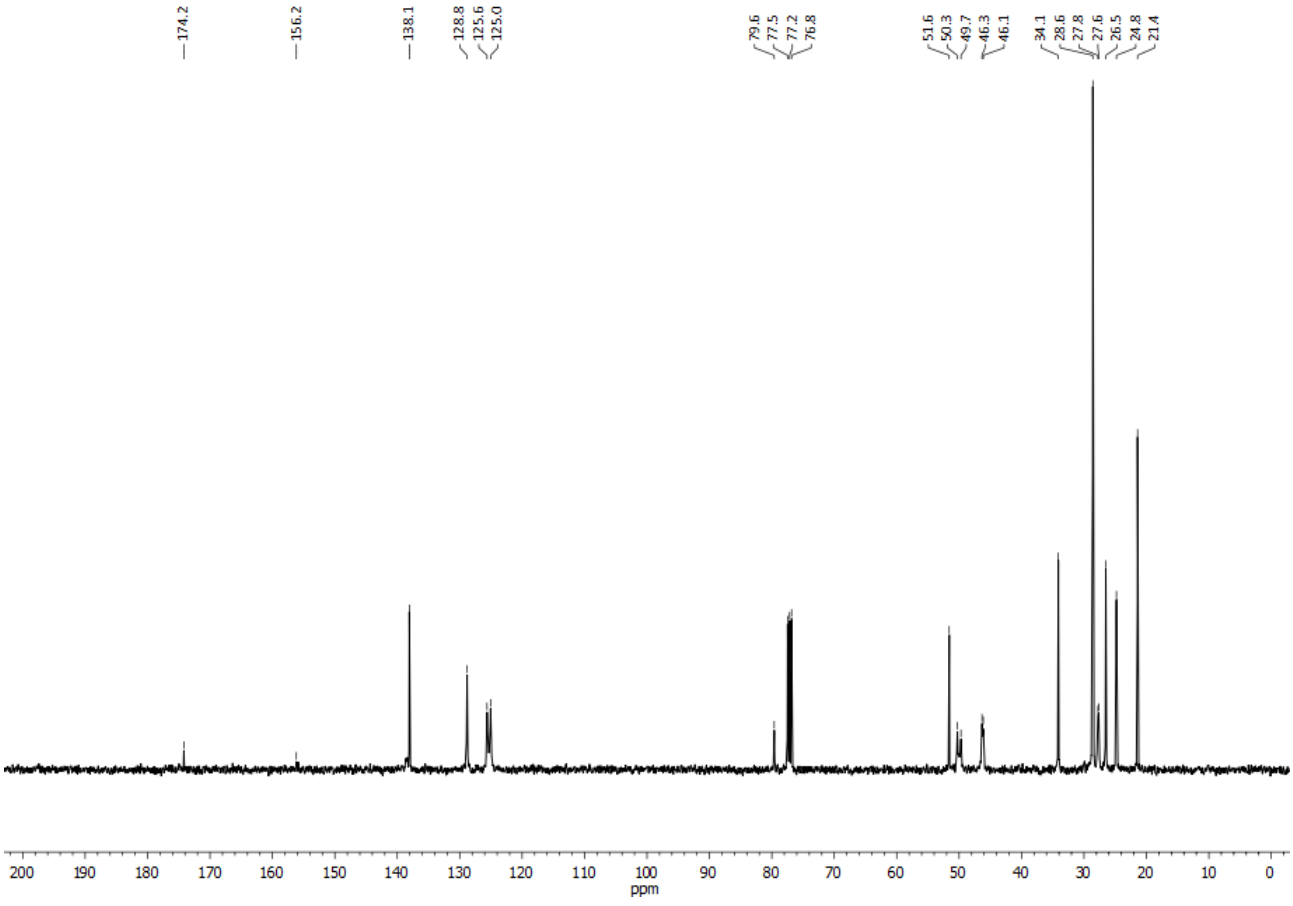
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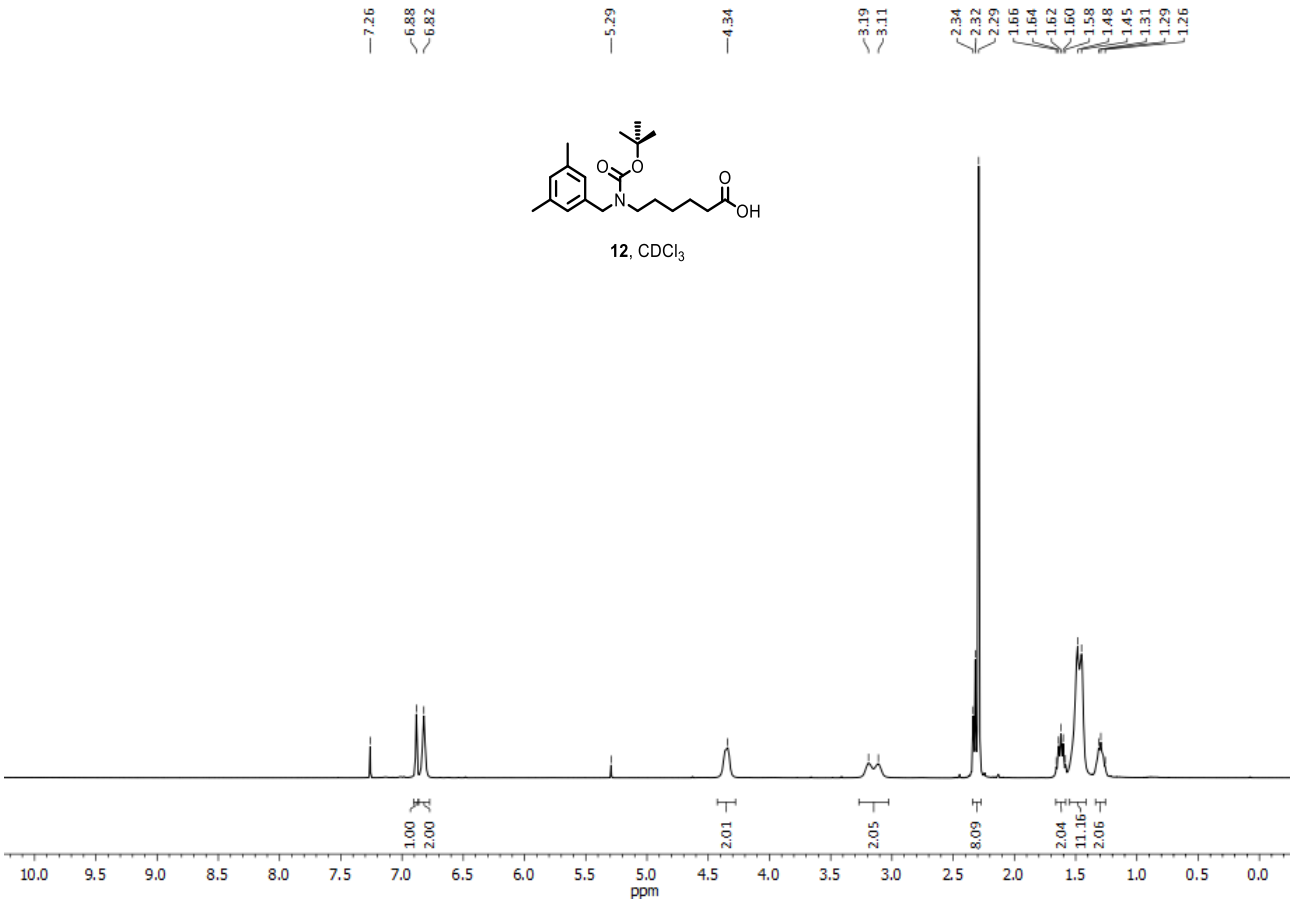
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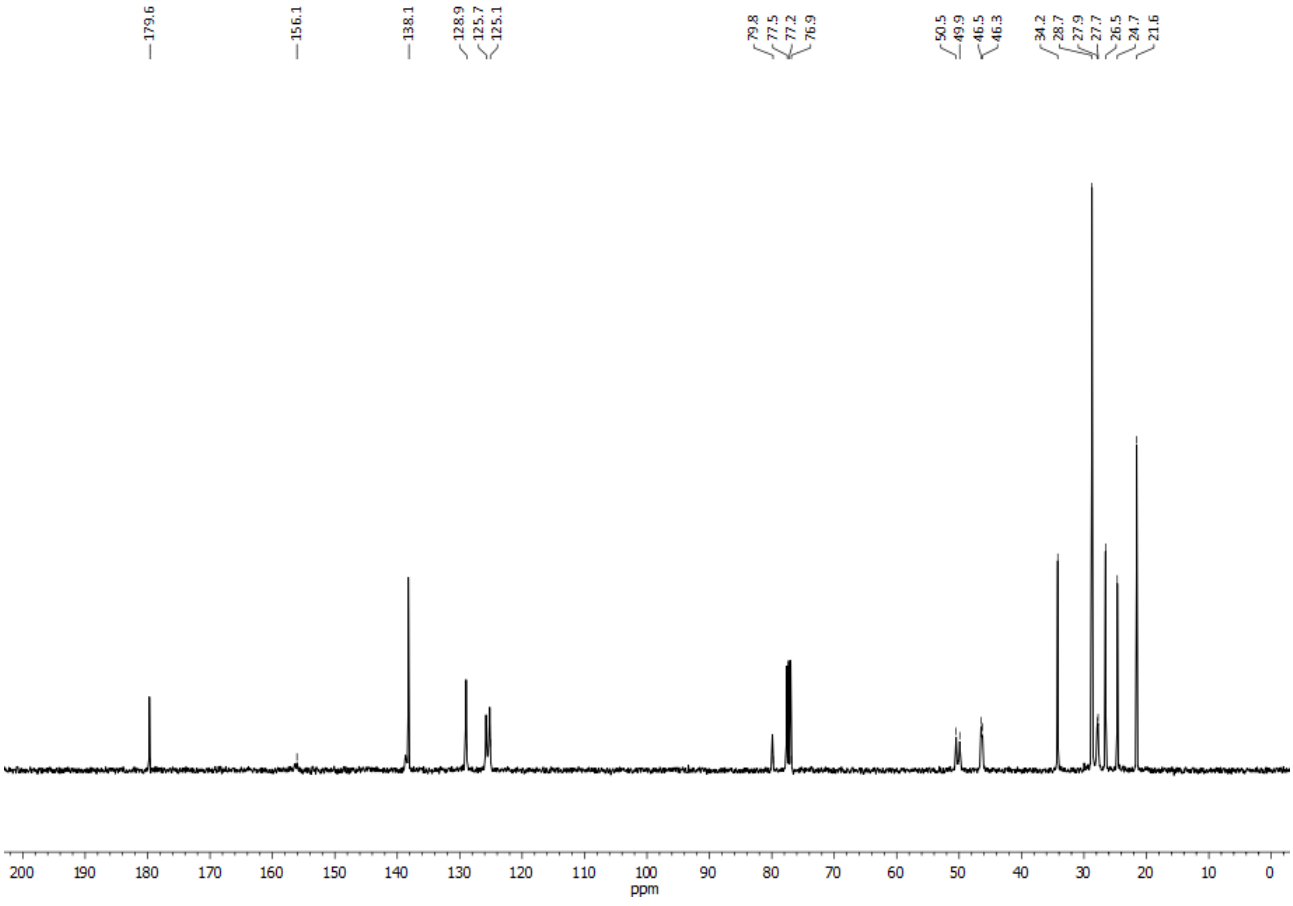
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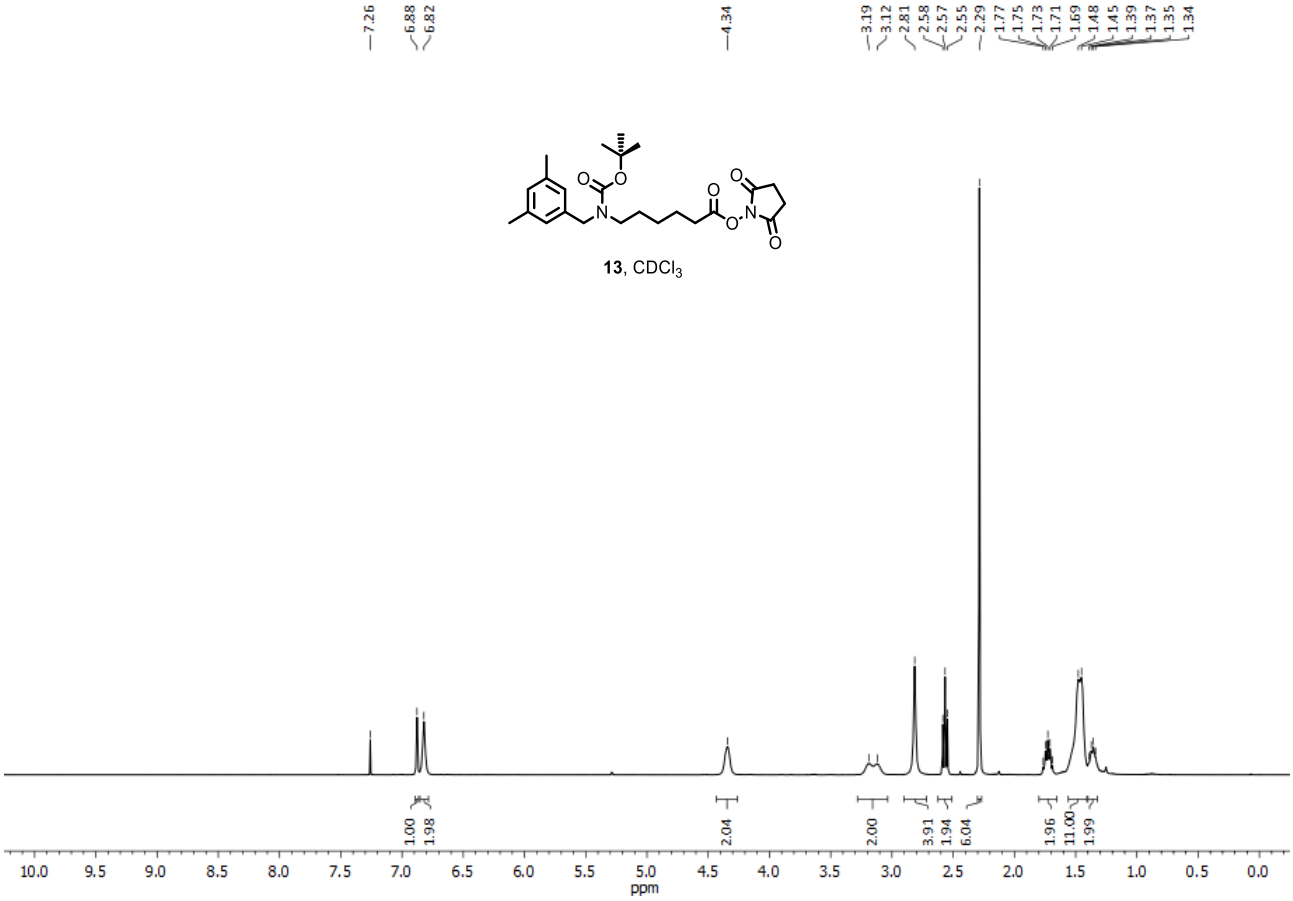
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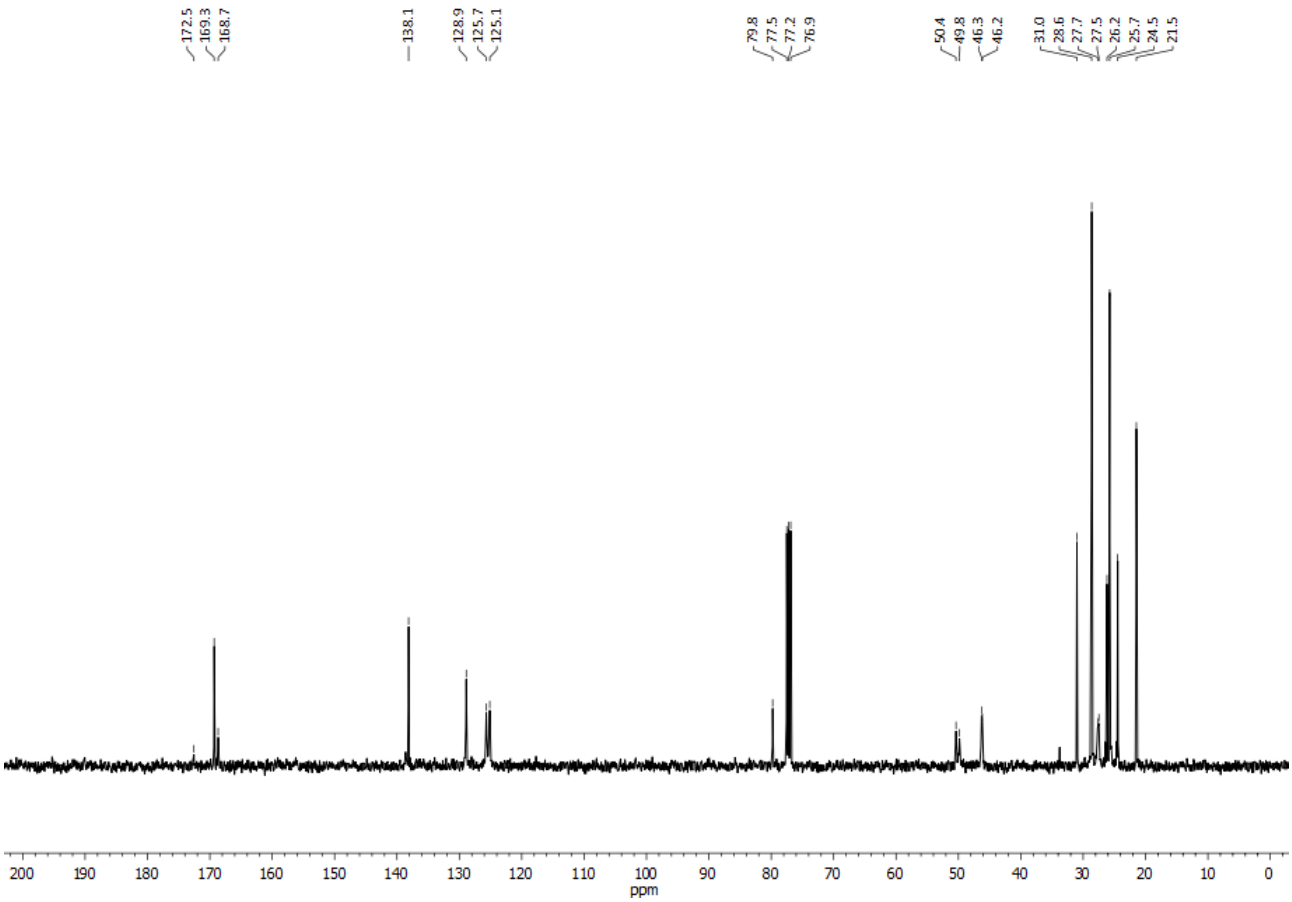
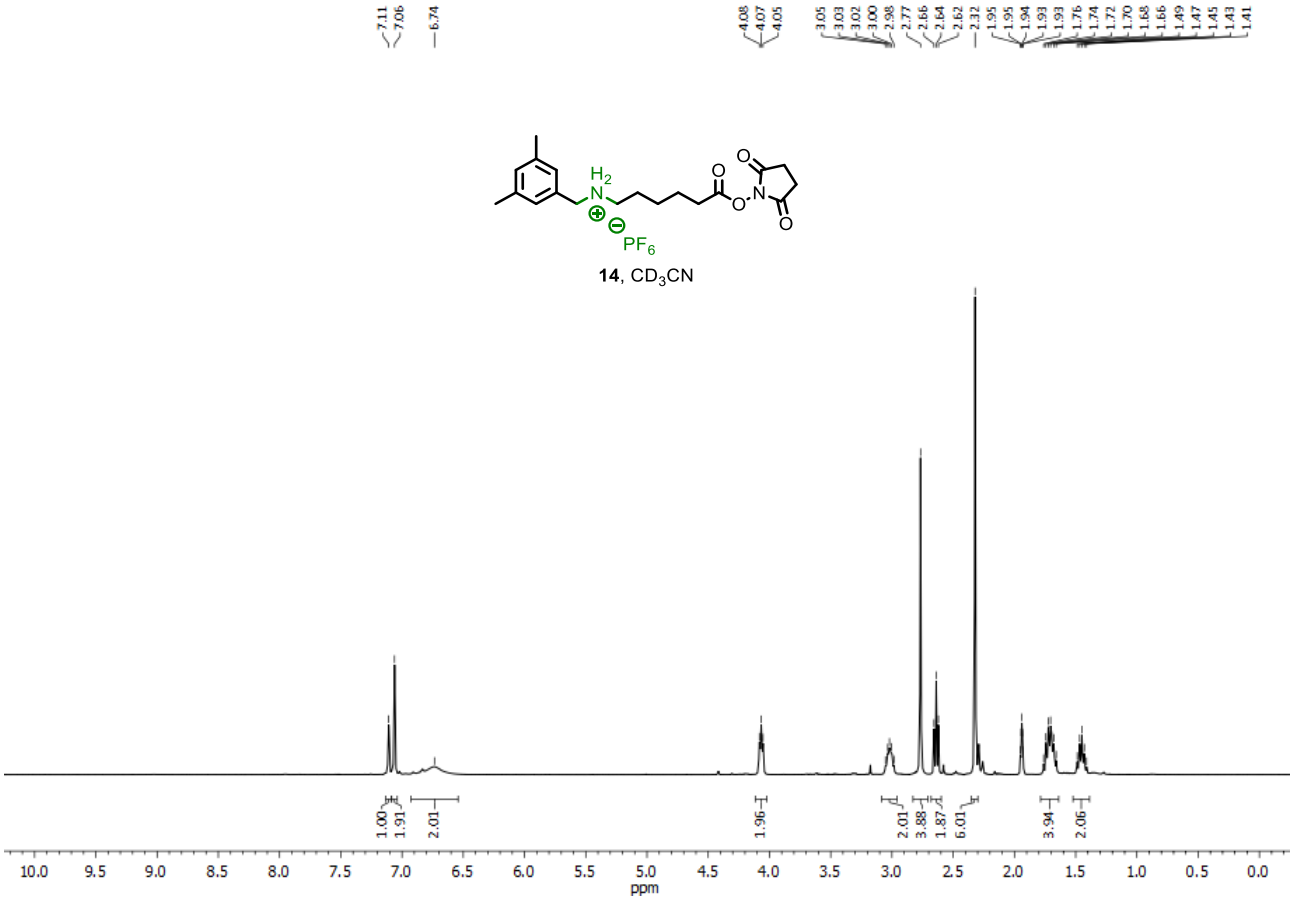
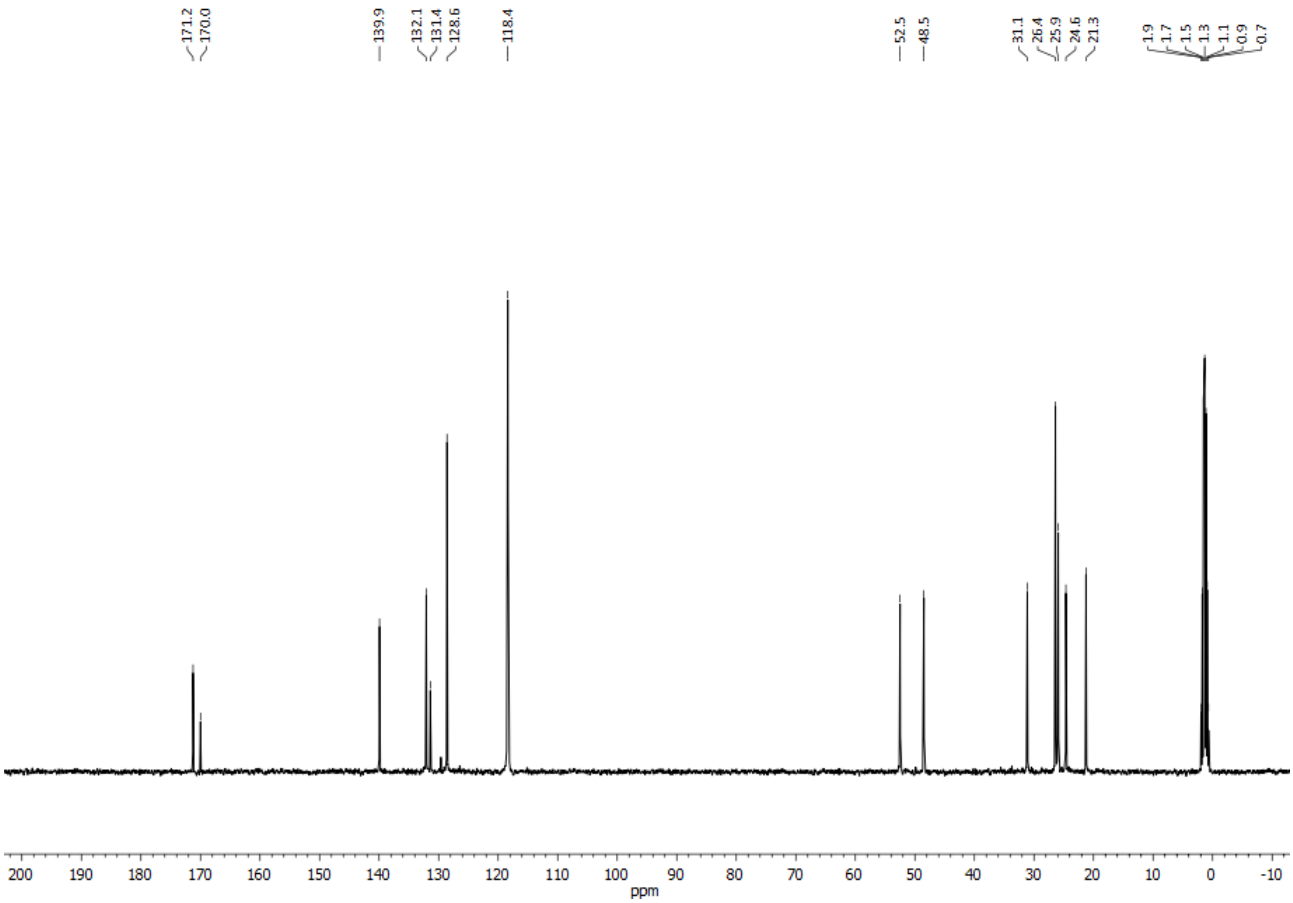
ppm

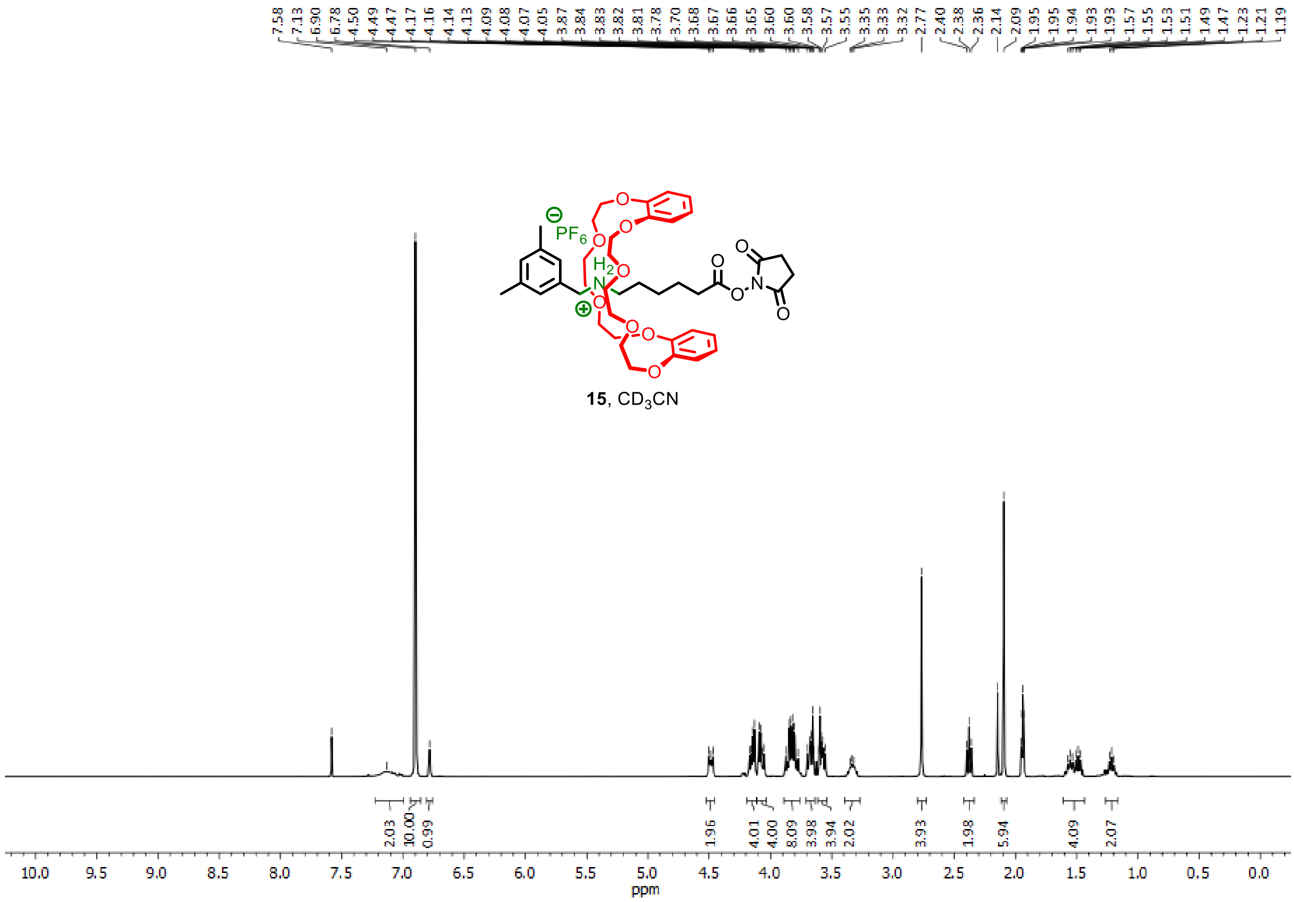
13, $CDCl_3$

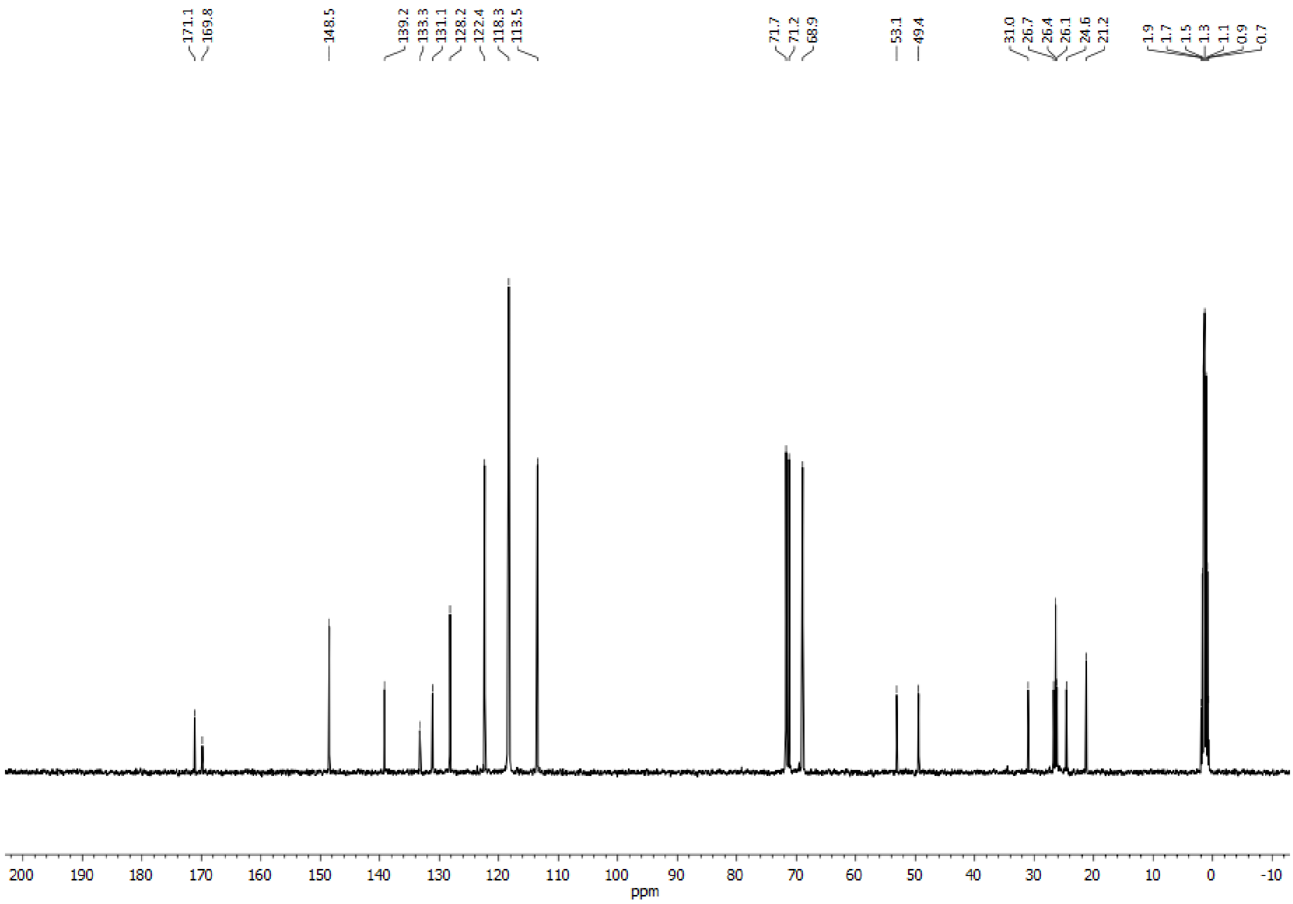

172.5
169.3
168.7
138.1
128.9
125.7
125.1
79.8
77.5
77.2
76.9
50.4
49.8
46.3
46.2
31.0
28.6
27.7
27.5
26.2
25.7
24.5
21.5
ppm

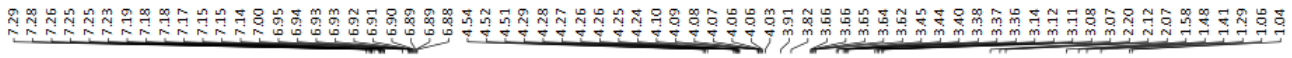

7.11
7.06
6.74
4.08
4.07
4.05
3.05
3.03
3.02
3.00
2.98
2.77
2.66
2.64
2.62
2.32
1.95
1.94
1.93
1.93
1.76
1.74
1.72
1.70
1.68
1.66
1.49
1.47
1.45
1.43
1.41
H2
N
O
O
O
N
O
PF6
1.00
1.91
2.01
1.96
2.01
3.88
1.87
6.01
3.94
2.06
ppm

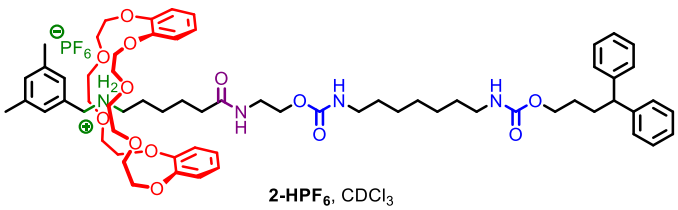
14, CD_3CN


171.2
170.0
139.9
132.1
131.4
128.6
118.4
52.5
48.5
31.1
26.4
25.9
24.6
21.3
1.9
1.7
1.5
1.3
1.1
0.9
0.7
ppm

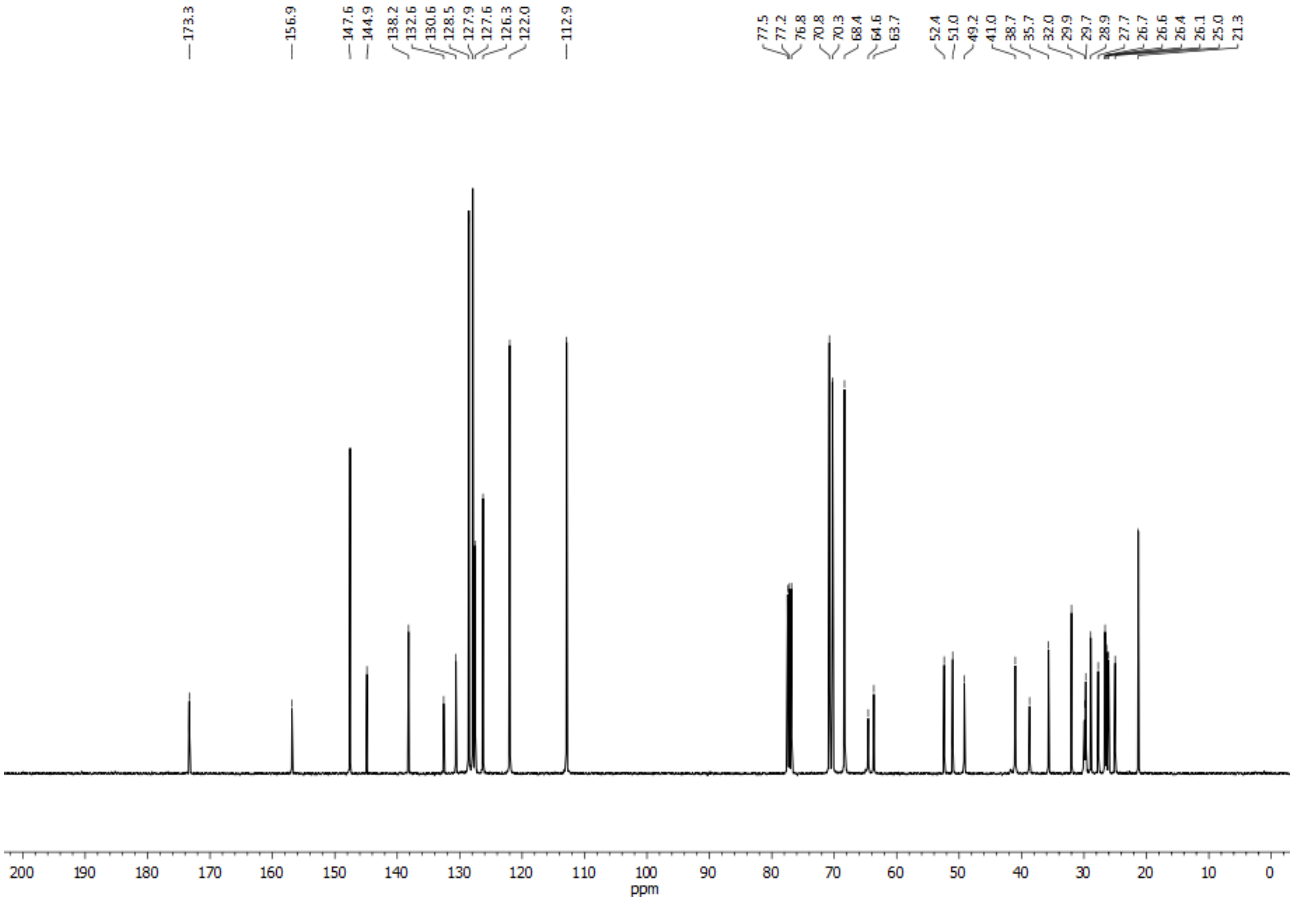

7.58 7.13 6.90 6.78 4.50 4.49 4.47 4.17 4.16 4.14 4.13 4.09 4.08 4.07 4.05 3.87 3.84 3.83 3.82 3.81 3.78 3.70 3.68 3.67 3.66 3.65 3.60 3.60 3.58 3.57 3.55 3.35 3.33 3.32 2.77 2.40 2.38 2.36 2.14 2.09 1.95 1.95 1.94 1.93 1.93 1.57 1.55 1.53 1.51 1.49 1.47 1.23 1.21 1.19
PF6
H2
N
15, CD3CN
2.03 10.00 0.99 1.96 4.01 4.00 8.09 3.98 3.94 2.02 3.93 1.98 5.94 4.09 2.07
ppm

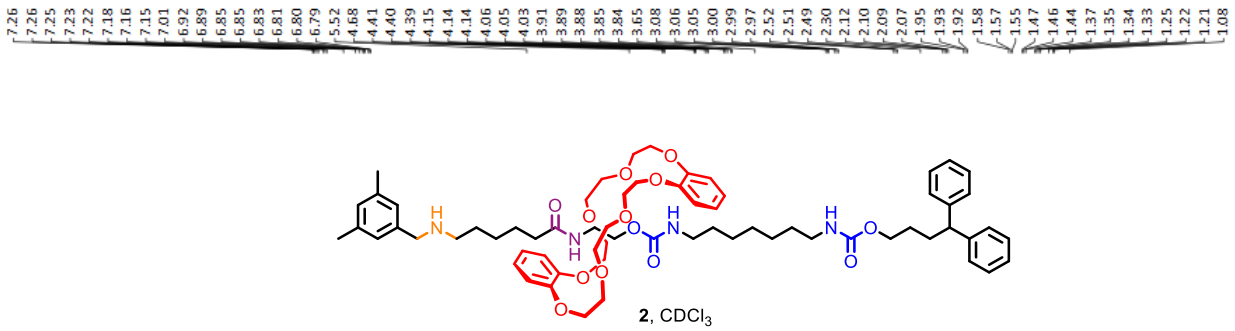

171.1 169.8 148.5 139.2 133.3 131.1 128.2 122.4 118.3 113.5 71.7 71.2 68.9 53.1 49.4 31.0 26.7 26.4 26.1 24.6 21.2 1.9 1.7 1.5 1.3 1.1 0.9 0.7
ppm



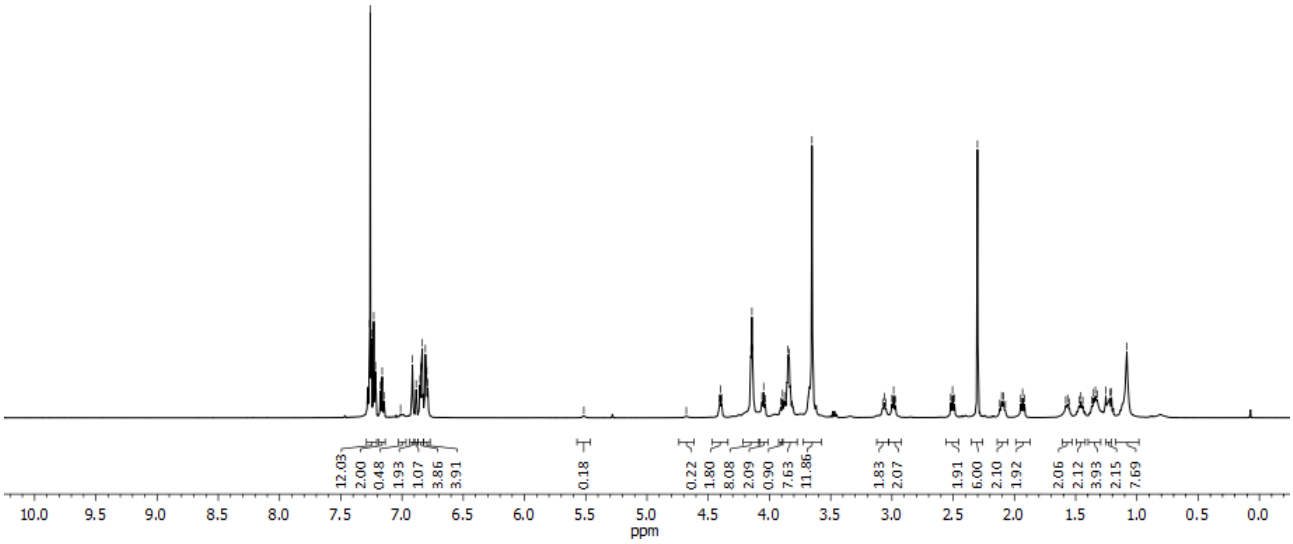


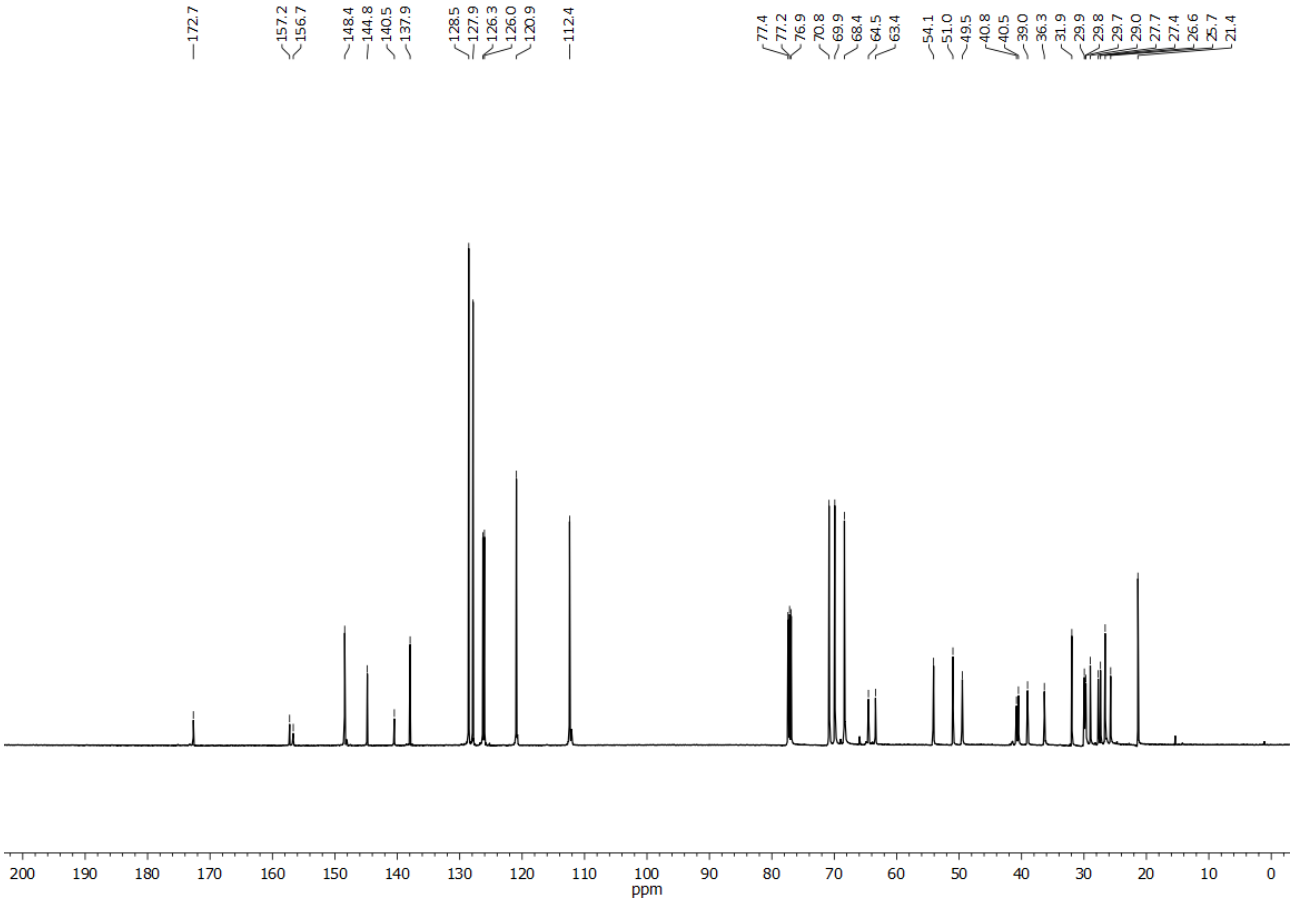
2-HPF$_6$, $CDCl_3$

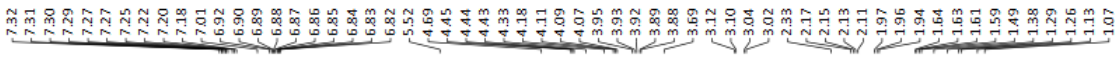


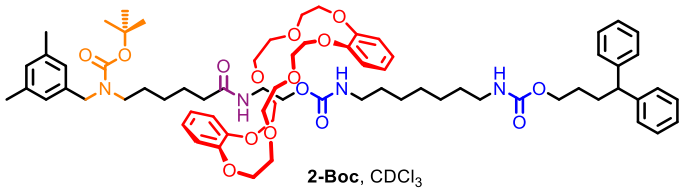


2, $CDCl_3$

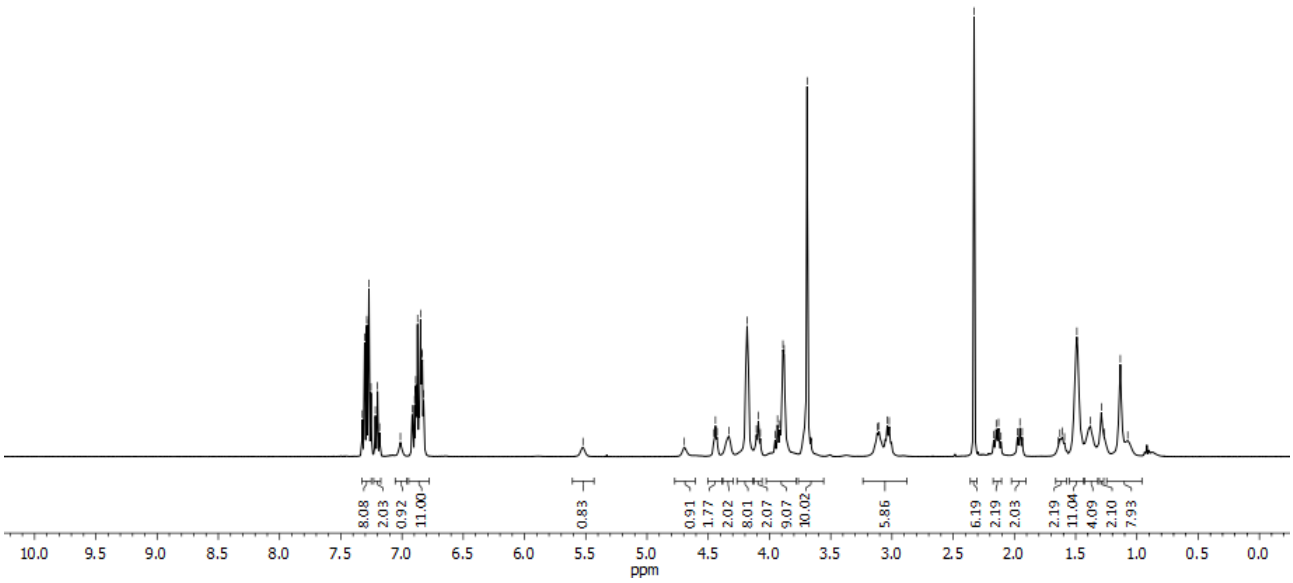


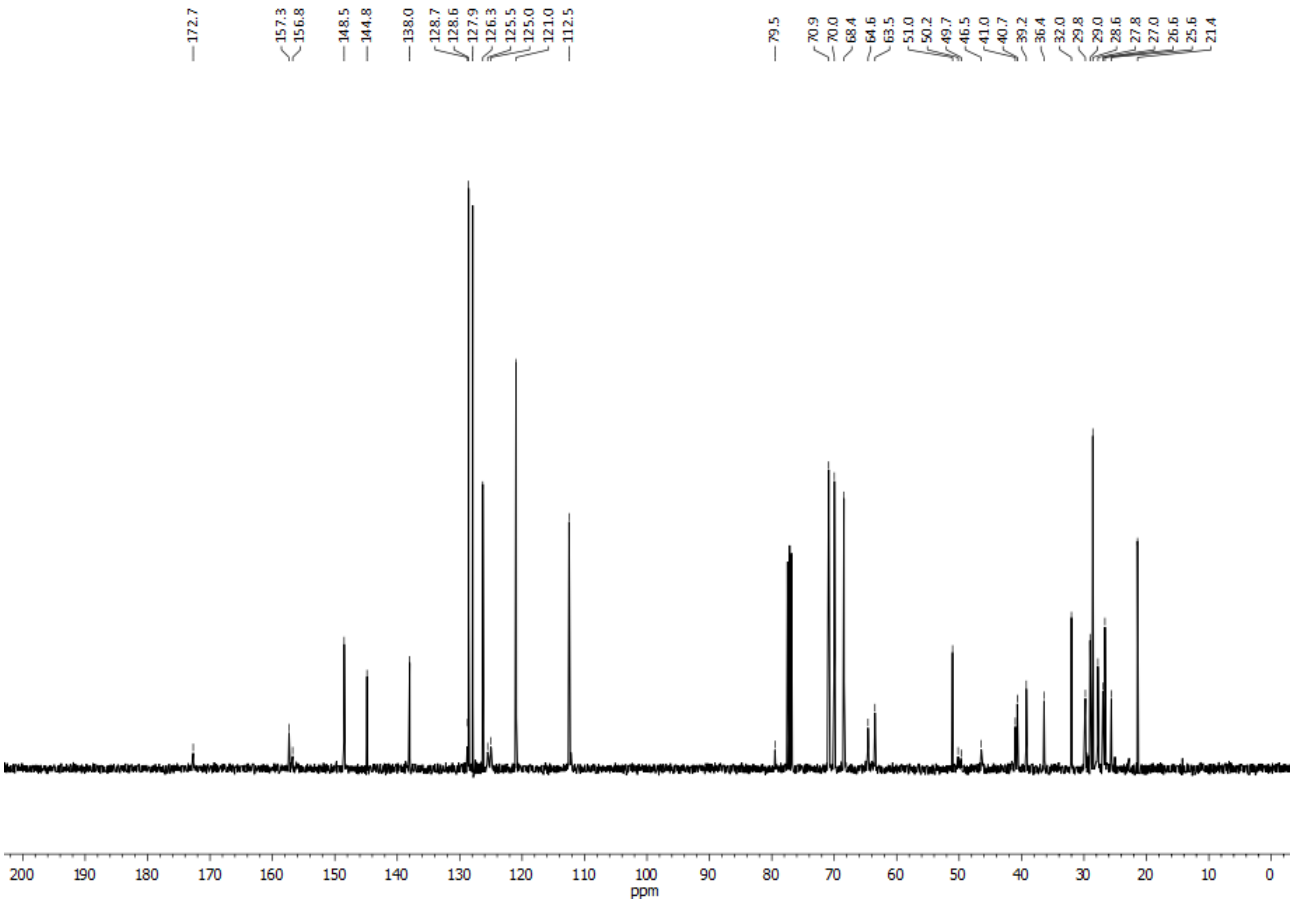


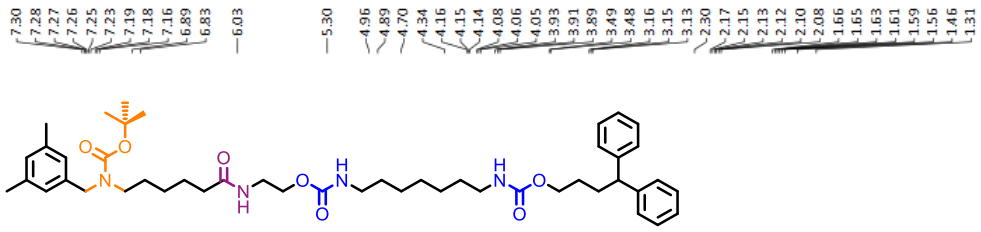




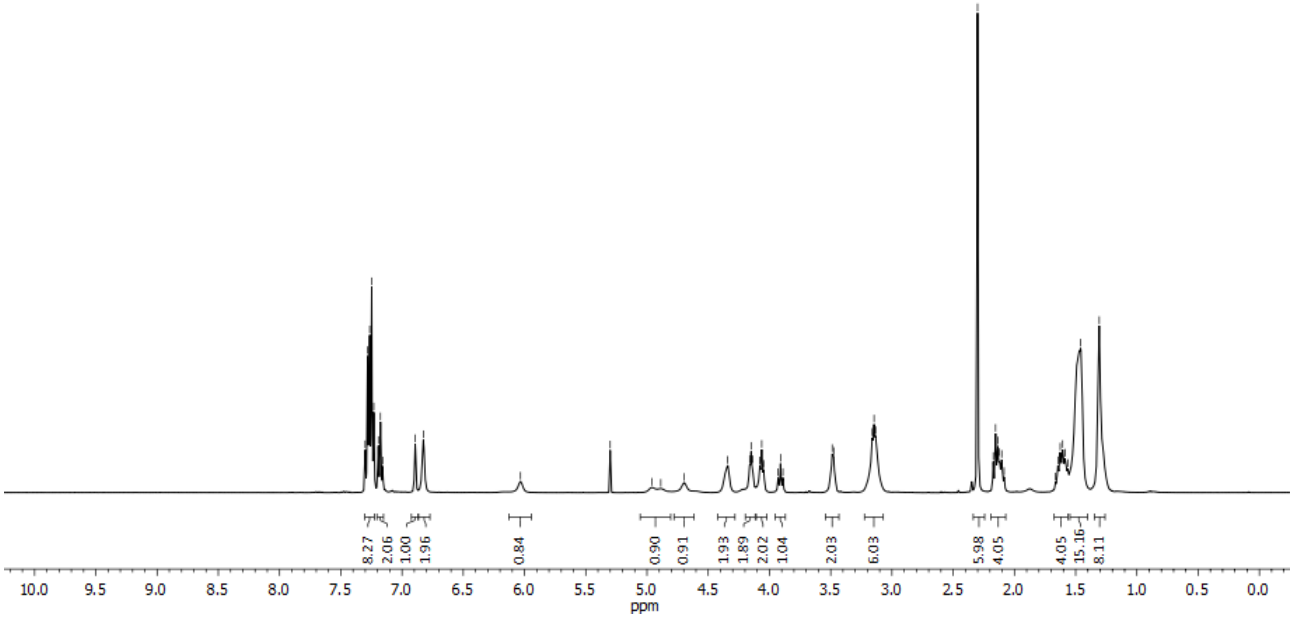
2-Boc, $CDCl_3$

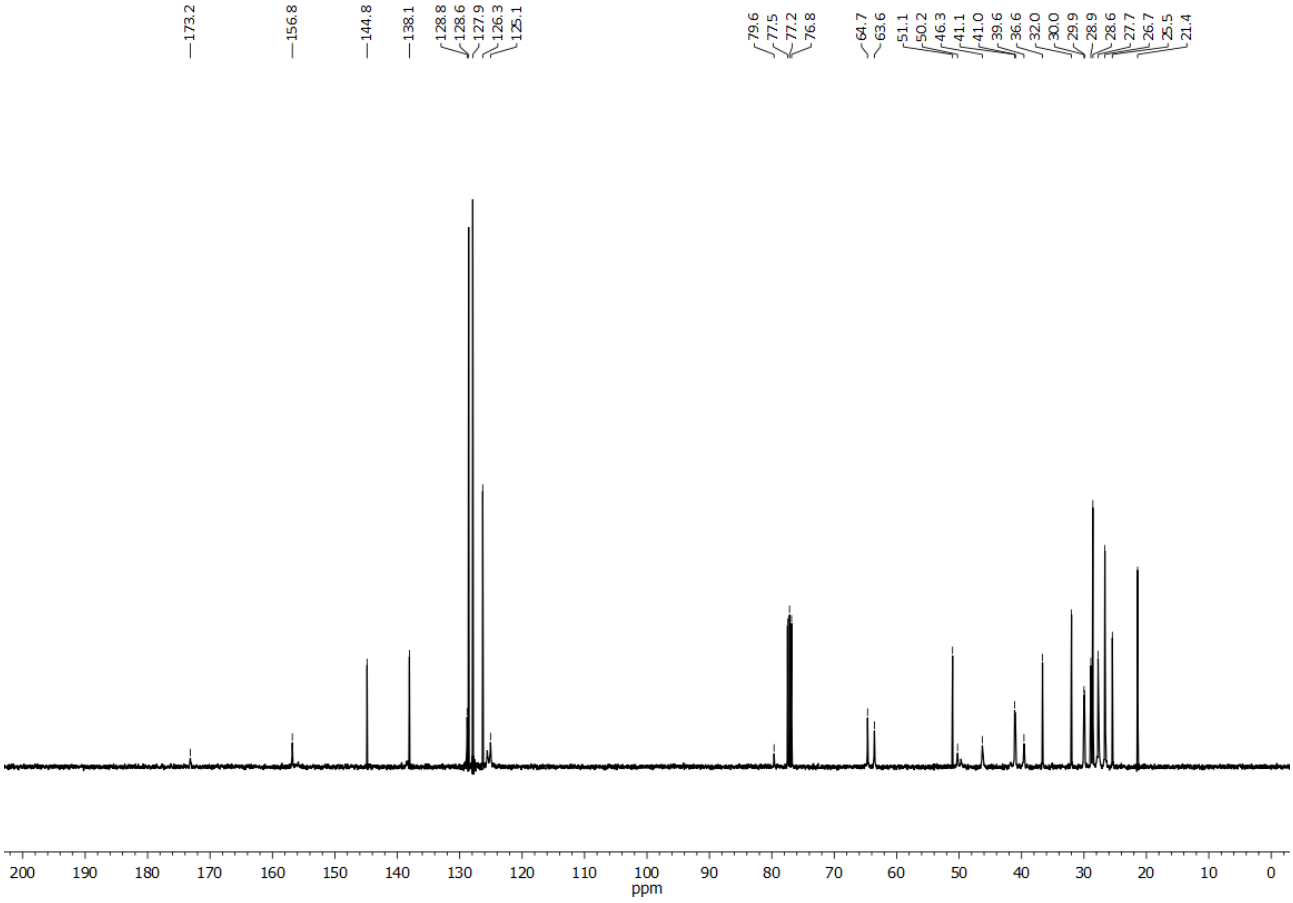


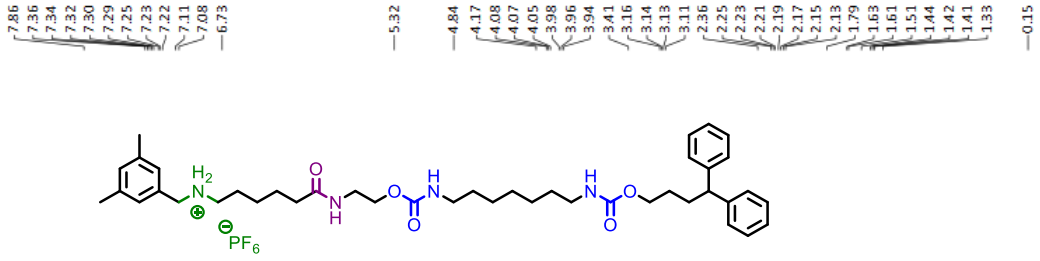




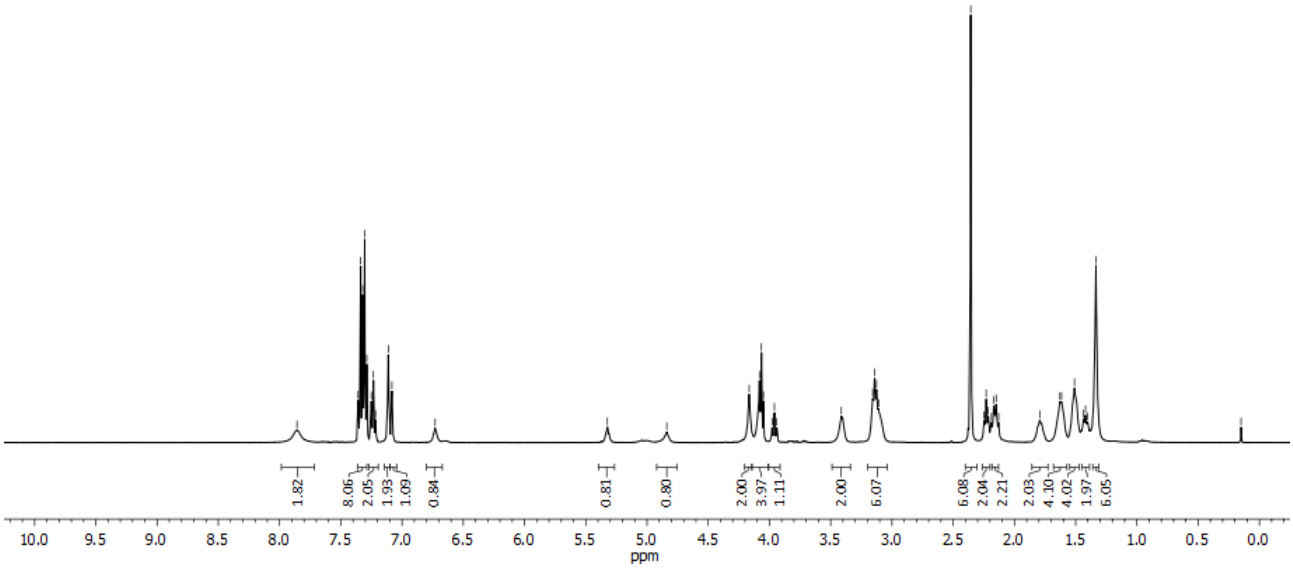
2u-Boc, $CDCl_3$

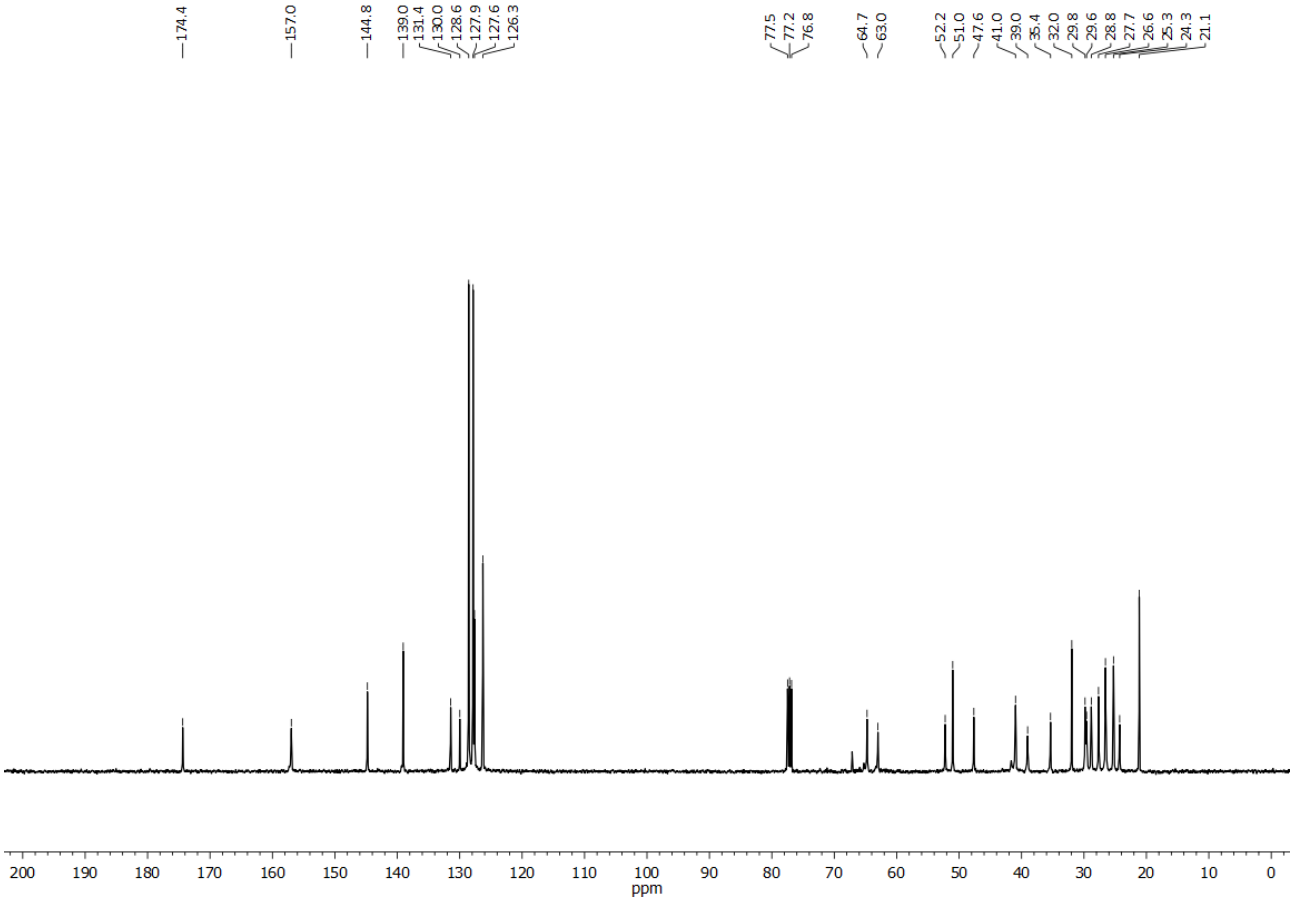


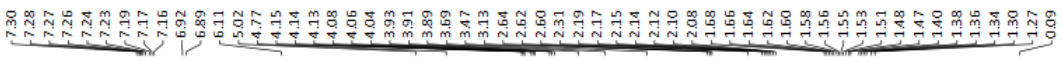


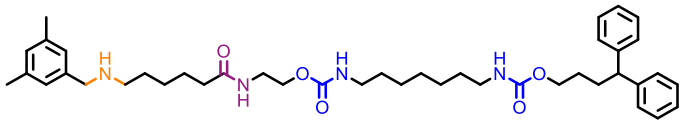


2u-HPF$_6$, $CDCl_3$









2u, $CDCl_3$