Supporting Information

Synthesis of Linear [5]Catenanes via Olefin Metathesis Dimerization of Pseudorotaxanes Composed of a [2]Catenane and a Secondary Ammonium Salt

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General Information

Reactions were conducted in oven- or flame-dried glassware under an atmosphere of nitrogen or argon, unless otherwise noted. All solvents were reagent grade. All chemicals were purchased from commercial vendors, unless otherwise referenced. Dichloromethane was freshly distilled over P_2O_5. Tetrahydrofuran (99.5%, anhydrous, inhibitor free) was purchased from Kanto Chemical Co. Reactions were magnetically stirred unless otherwise stated. Analytical thin-layer chromatography (TLC) was performed on aluminium sheets, precoated with silica gel 60-F254 (Merck 5554). Column chromatography was performed using Silica gel 60N, spherical neutral from Kanto Chemical Co. GPC was performed using a JAI LC-9201 equipped with JAIGEL 1H-40/2H-40 columns. Proton and carbon NMR spectra were recorded on a Varian System 700, and a Varian-Mercury 300 NMR spectrometer at 700, and 300 MHz (^{1}H NMR) and with a Varian System 700, a JEOL-ECA 600, and a Varian-Mercury 300 NMR spectrometer at 176, 151, and 75 MHz (^{13}C NMR). Chemical shifts are reported relative to chloroform (δ 7.26) for ^{1}H-NMR and chloroform (δ 77.16) for ^{13}C-NMR. Infrared spectra were recorded on a Jasco Model FT/IR-420 infrared spectrometer. High-resolution mass spectra (HRMS) were measured on an Exactive Orbitrap mass spectrometer (Thermo Fisher Scientific).

Experimental Sections

Synthesis of [2]catenane 2

[2]Catenane 2. To a stirred solution of BPP34C10 **3** (3.22 g, 6 mmol) and **4a** (408 mg, 0.6 mmol) in CH_2Cl_2 (degassed, 300 ml) was added Grubbs catalyst 1st generation (47 mg, 0.057 mmol). After being stirred at 0 °C for 2 days, to the mixture was added Grubbs 1st catalyst (25 mg, 0.03 mmol) again and it was stirred for 1 day. The mixture was evaporated *in vacuo* to give a residue for the next step without further purification. To a solution of the residue in THF (150 ml) was added Wilkinson's catalyst (56 mg, 0.06 mmol). After being stirred at 35 °C under 1 atm of H_2 for 3 days, the solvent was removed. The residue was purified by column chromatography on silica gel with 1% methanol in $CHCl_3$ to yield **2** (373 mg, 52%) as a white amorphous solid. ^{1}H-NMR (700 MHz, $CDCl_3$) δ = 7.71 (br, 2H), 7.40 (d, J = 6 Hz, 4H), 7.32 (d, J = 6 Hz, 4H), 6.78 (s, 8H), 4.51 (s, 4H), 4.01 (br, 8H), 3.98 (br, 4H), 3.77 (m, 8H), 3.45 (t, J = 6 Hz, 4H), 3.42 (br, 8H), 1.59 (dd, 4H), 1.33 (dd, J = 8, 6 Hz, 4H), 1.16-2.26 (m, 24H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 152.83, 141.18, 130.06, 129.43, 128.29, 115.69, 72.26, 70.80, 70.66, 70.61, 70.24, 68.01, 52.22, 29.91, 29.73, 29.67, 29.57, 29.41, 29.37, 29.28, 26.49; IR (KBr): 2925, 2854, 1733, 1590, 1508, 1456, 1359, 1289, 1229, 1107, 955, 841; HRMS (ESI) m/z calcd for $C_{62}H_{94}NO_{12}^+$ $[M–PF_6^–]^+$ 1044.6771, found 1044.6746.

Synthesis of [5]catenane 1

[5]Catenane 6. To a stirred solution of [2]catenane **2** (353.6 mg, 0.30 mmol) and **4b** (168.6 mg, 0.30 mmol) in CH_2Cl_2 (degassed, 15 ml) was added Grubbs catalyst 1st generation (23.1 mg, 28.1 μmol). After being refluxed for 22.5 h, the solvent was removed *in vacuo*. The residue was purified on a silica gel chromatography (methanol/$CHCl_3$ = 20%). Further purification by GPC (eluted with $CHCl_3$) gave [5]catenane **6** (62.0 mg, 12%) as a white amorphous powder. ^{1}H-NMR (700 MHz, $CDCl_3$) δ = 7.52 (br s, 4H), 7.42 (br s, 4H), 7.17 (m, 16H), 7.10 (m, 16H), 6.91 (s, 8H), 6.90 (s, 8H), 5.39 (m, 4H), 4.41 (s, 16H), 4.09 (s, 8H), 4.04 (s, 8H), 3.95 (br, 16H), 3.60 (br, 16H), 3.42 (m, 16H), 3.31 (br, 16H), 3.17 (br, 16H), 1.99 (8H, m), 1.58 (m, 16H), 1.42 (16H, m), 1.25 (m, 48H); ^{13}C-NMR (176 MHz, $CDCl_3$): 152.2, 152.0, 140.7, 140.7, 130.4, 129.9, 129.8, 129.6, 115.6, 72.1, 72.0, 70.7, 70.6, 70.5, 70.5, 70.4, 70.2, 70.1, 67.1, 67.0, 52.4, 52.3, 32.4, 29.9, 29.8, 29.8, 29.6, 29.6, 29.5, 29.3, 29.3, 29.2, 29.2; IR (KBr): 2929, 1720, 1585, 1507, 1456, 1358, 1288, 1243, 1090, 957, 852; HRMS (ESI) m/z calcd for $C_{176}H_{260}N_4O_{28}^{4+}$ $[M–4PF_6^–]^{4+}$ 719.4756, found 719.4745.

[5]Catenane 1. To a solution of [5]catenane **6** (102.9 mg, 29.7 μmol) in THF (5.0 ml) was added Wilkinson's catalyst (5.0 mg, 5.4 μmol). After being stirred at 35 °C under 1 atm of H_2 for 17 h, the

solvent was removed. The residue was purified by silica gel column chromatography (methanol/$CHCl_3$ = 1:19) to give [5]catenane **1** (86.1 mg, 84%) as a white amorphous powder. ^{1}H-NMR (700 MHz, $CDCl_3$) δ = 7.51 (s, 4H), 7.40 (s, 4H), 7.21-7.03 (m, 32H), 6.95-6.82 (m, 16H), 4.40 (d, J = 8 Hz, 16H), 4.08 (m, 8H), 4.04 (m, 8H), 3.95 (m, 16H), 3.59 (m, 16H), 3.46-3.34 (m, 16H), 3.31 (m, 16H), 3.17 (m, 16H), 1.62-1.53 (m, 16H), 1.39-1.08 (m, 90H); ^{13}C-NMR (176 MHz, $CDCl_3$): δ = 152.26, 152.04, 140.71, 129.84, 129.80, 129.66, 127.98, 127.67, 115.66, 72.19, 72.07, 70.80, 70.74, 70.50, 70.46, 70.40, 70.18, 67.13, 67.02, 52.40, 29.87, 29.78, 29.66, 29.63, 29.57, 29.50, 29.38, 29.31, 29.25, 26.46, 26.30;; IR (KBr): 2929, 2856, 1586, 1508, 1456, 1358, 1291, 1090, 957, 849; HRMS (ESI) m/z calcd for $C_{176}H_{264}N_4O_{28}^{4+}$ $[M–PF_6^-]^{4+}$ 720.4834, found 720.4810.

Synthesis of [5]catenane 10

[2]Catenane 8. To a solution of 2-(pyren-1-yl)acetic acid (181.5 mg, 0.70 mmol), EDCI•HCl (182.4 mg, 0.95 mmol), and DMAP (78.7 mg, 0.64 mmol) in CH_2Cl_2 (10 mL) was added [2]catenane **2** (412.7 mg, 0.35 mmol) under nitrogen atmosphere at room temperature. After stirring for 2 days, the reaction mixture was quenched with 1M HCl, and extracted with CH_2Cl_2. The organic layer was washed with saturated aqueous $NaHCO_3$, brine, and dried over anhydrous Na_2SO_4. After removing Na_2SO_4 by filtration, the solvent was concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (30% ethyl acetate in CH_2Cl_2) to give [2]catenane **8** (435.7 mg, 98%) as a pale yellow liquid. ^{1}H NMR (700MHz, $CDCl_3$): δ = 8.17 (d, J = 8 Hz, 1H), 8.16 (d, J = 8 Hz, 1H), 8.15 (d, J = 9 Hz, 1H), 8.11 (d, J = 8 Hz, 1H), 8.09 (d, J = 9 Hz, 1H), 8.04–8.02 (m, 2H), 7.99 (dd, J = 8, 8 Hz, 1H), 7.91 (d, J = 8 Hz, 1H), 7.18 (d, J = 8 Hz, 2H), 7.17 (d, J = 8 Hz, 2H), 7.10 (d, J = 8 Hz, 2H), 6.96 (d, J = 8 Hz, 2H), 6.54 (s, 8H), 4.54 (s, 2H), 4.43 (s, 2H), 4.39 (s, 2H), 4.38 (s, 2H), 4.34 (s, 2H), 3.91–3.83 (m, 8H), 3.67–3.64 (m, 8H), 3.59–3.53 (m, 16H), 3.41–3.34 (m, 4H), 1.57–1.46 (m, 4H), 1.27 (m, 4H), 1.20–1.01 (m, 24H); ^{13}C NMR (75MHz, $CDCl_3$) : δ = 171.81, 152.78, 138.18, 138.03, 136.30, 135.48, 131.36, 130.87, 130.56, 129.39, 129.37, 128.61, 128.14, 127.87, 127.74, 127.47, 127.43, 127.15, 126.49, 125.98, 125.22, 125.09, 124.98, 124.82, 123.25, 115.49, 72.49, 72.43, 70.80, 70.73, 70.68, 70.39, 70.34, 69.55, 68.00, 49.65, 47.81, 38.83, 30.14, 29.96, 29.84, 29.77, 29.70, 29.62, 29.41, 26.56, 26.48; IR (neat): 3044, 2924, 2853, 1650, 1507, 1455, 1413, 1353, 1231, 1105, 844 cm^{-1}; HRMS (ESI): m/z calcd for $C_{80}H_{104}NO_{13}^+$ $[M+H^+]$ 1286.7502, found 1286.7462.

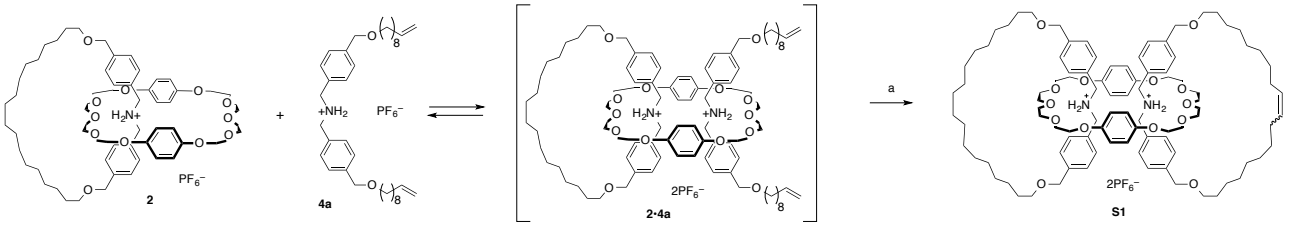
[5]Catenane 9. To a stirred solution of **8** (190 mg, 0.15mmol) and **4b** (84 mg, 0.15 mmol) in CH_2Cl_2 (degassed, 7.5 ml) was added Grubbs 1st catalyst (12.3 mg, 10 mol%). After being refluxed for 22.5 h, the solvent was removed *in vacuo*. The residue was purified by silica gel chromatography (methanol/$CHCl_3$ = 20%). Further purification by GPC (eluted with $CHCl_3$) gave

[5]catenane **9** (20 mg, 7%) as a pale yellow liquid. ^{1}H NMR (700 MHz, $CDCl_3$) δ = 8.16 (d, *J* = 8 Hz, 4H), 8.11 (d, *J* = 9 Hz, 2H), 8.09 (d, *J* = 7 Hz, 2H), 8.07 (d, *J* = 9 Hz, 2H), 8.03–7.96 (m, 6H), 7.89 (d, *J* = 8 Hz, 2H), 7.80 (br, 4H), 7.47 (d, *J* = 8 Hz, 4H), 7.43 (d, *J* = 8 Hz, 4H), 7.41 (d, *J* = 8 Hz, 4H), 7.38 (d, *J* = 8 Hz, 4H), 7.20 (d, *J* = 8 Hz, 4H), 7.11 (d, *J* = 8 Hz, 4H), 7.01 (d, *J* = 8 Hz, 4H), 6.97 (d, *J* = 8 Hz, 4H), 6.70 (d, *J* = 9 Hz, 8H), 6.59 (d, *J* = 9 Hz, 8H), 5.48–5.29 (m, 4H), 4.54 (s, 4H), 4.53 (s, 4H), 4.49 (s, 4H), 4.45 (s, 4H), 4.40 (s, 4H), 4.37 (s, 4H), 4.34 (s, 4H), 4.01–3.91 (m, 8H), 3.86–3.77 (m, 8H), 3.77–3.69 (m, 8H), 3.64 (m, 16H), 3.55–3.44 (m, 24H), 3.37–3.29 (m, 8H), 3.29–3.20 (m, 8H), 2.91–2.81 (m, 8H), 2.10–1.96 (m, 8H), 1.49–1.31 (m, 16H), 1.28–0.81 (m, 60H); ^{13}C NMR (176 MHz, $CDCl_3$) δ = 171.97, 154.21, 151.89, 141.46, 141.41, 138.43, 138.17, 136.21, 135.58, 131.39, 130.86, 130.66, 130.47, 130.00, 129.92, 129.83, 129.45, 129.20, 128.98, 128.58, 128.45, 128.06, 128.01, 127.88, 127.55, 127.50, 127.31, 126.59, 126.14, 125.39, 125.21, 125.12, 125.01, 124.81, 123.22, 116.12, 115.67, 72.50, 72.05, 70.95, 70.91, 70.76, 70.64, 70.59, 70.45, 69.90, 69.54, 69.07, 67.64, 52.75, 50.00, 48.13, 38.95, 32.44, 32.22, 30.10, 29.93, 29.86, 29.73, 29.71, 29.63, 29.51, 29.50, 29.48, 29.36, 29.24, 27.11, 26.72, 26.52, 26.47, 26.40, 26.29; IR ($CHCl_3$): 2928, 2857, 1641, 1508, 1455, 1357, 1236, 1102, 957, 846 cm^{-1}; HRMS (ESI): m/z calcd for $C_{212}H_{278}N_4O_{30}{}^{2+}$ $[M–2PF_6{}^-]^{2+}$ 1680.0170, found 1680.0154.

[5]Catenane 10. To a solution of [5]catenane **9** (54.9 mg, 15.0 μmol) in THF (5.0 ml) was added Wilkinson's catalyst (4.8 mg, 5.2 μmol). After being stirred at 35 °C under 1 atm of H_2 for 8 h, the solvent was removed. The residue was purified by silica gel column chromatography (methanol/$CHCl_3$ = 1:19) to give **12** (51.2 mg, 93%) as a pale yellow liquid. ^{1}H-NMR (700 MHz, $CDCl_3$) *δ* = 8.17 (d, *J* = 8 Hz, 2H), 8.16 (d, *J* = 8 Hz, 2H), 8.13 (d, *J* = 9 Hz, 2H), 8.09 (d, *J* = 8 Hz, 2H), 8.07 (d, *J* = 9 Hz, 2H), 8.03 (d, *J* = 9 Hz, 2H), 8.00 (d, *J* = 9 Hz, 2H), 8.00 (dd, *J*= 8, 8 Hz, 2H), 7.89 (d, *J* = 8 Hz, 2H), 7.80 (br, 4H), 7.47 (d, *J* = 8 Hz, 4H), 7.43 (d, *J* = 8 Hz, 4H), 7.41 (d, *J* = 8 Hz, 4H), 7.37 (d, *J* = 8 Hz, 4H), 7.18 (d, *J* = 8 Hz, 4H), 7.10 (d, *J* = 8 Hz, 4H), 7.00 (d, *J* = 8 Hz, 4H), 6.95 (d, *J* = 8 Hz, 4H), 6.70 (d, *J* = 9 Hz, 8H), 6.59 (d, *J* = 9 Hz, 8H), 4.55 (s, 4H), 4.54 (s, 4H), 4.50 (s, 4H), 4.46 (s, 4H), 4.39 (s, 4H), 4.37 (s, 4H), 4.34 (s, 4H), 3.99–3.91 (m, 8H), 3.85–3.78 (m, 8H), 3.77–3.71 (m, 8H), 3.69–3.64 (m, 8H), 3.64–3.59 (m, 8H), 3.53–3.44 (m, 24H), 3.36–3.30 (m, 8H), 3.30–3.23 (m, 8H), 2.94–2.85 (m, 8H), 1.63 (tt, *J* = 7.1, 7.1 Hz, 8H), 1.44–1.25 (m, 16H), 1.22–0.86 (m, 72H); ^{13}C-NMR (176 MHz, $CDCl_3$): δ = 171.87, 154.28, 151.95, 141.58, 141.53, 138.47, 138.21, 136.29, 135.68, 131.46, 130.92, 130.70, 129.92, 129.82, 129.48, 129.25, 129.01, 128.66, 128.42, 128.08, 128.04, 128.00, 127.86, 127.54, 127.51, 127.33, 126.63, 126.15, 125.41, 125.22, 125.19, 125.03, 124.88, 123.26, 116.18, 115.76, 72.53, 72.08, 70.98, 70.68, 70.64, 70.50, 69.96, 69.59, 69.13, 67.70, 52.81, 50.03, 48.12, 39.03, 30.13, 29.96, 29.88, 29.77, 29.67, 29.51, 29.44, 26.55, 26.51, 26.25; IR ($CHCl_3$): 2929, 2856, 1641, 1508, 1455, 1358, 1289, 1177, 1099,

957, 848; HRMS (ESI) m/z calcd for $C_{212}H_{282}N_4O_{30}^{2+}$ $[M–2PF_6^-]^{2+}$ 1682.0326, found 1682.0309.

Synthesis of [3]catenane S1



Scheme S1. Reagents and conditions: (a) [2]=[4a]=0.05M, CH_2Cl_2, Grubbs 1st. cat., CH_2Cl_2,14%.

[3]Catenane S1. To a stirred solution of [2]catenane **2** (60 mg, 0.05 mmol) and **4a** (34 mg, 0.05 mmol) in CH_2Cl_2 (degassed, 2.5 ml) was added Grubbs catalyst 1st generation (8.2 mg, 10.0 μmol). After being refluxed for 22.5 h, the solvent was removed *in vacuo*. The residue was purified by silica gel chromatography (methanol/$CHCl_3$ = 20%). Further purification by GPC (eluted with $CHCl_3$) gave [3]catenane **S1** (13 mg, 14%) as a white amorphous powder. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.42 (s, 4H), 7.19 (d, J = 8 Hz, 8H), 7.12 (d, J = 8 Hz, 8H), 6.95 (s, 8H), 5.4–5.2 (m, 2H), 4.42 (s, 8H), 4.09 (m, 8H), 3.99 (m, 8H), 3.60 (m, 8H), 3.41 (m, 8H), 3.32 (m, 8H), 3.15 (m, 8H), 2.0–1.8 (m, 4H), 1.7–1.5 (m, 8H), 1.4–1.1 (m, 48H); ^{13}C-NMR (75 MHz, $CDCl_3$): 152.17, 140.77, 130.48, 129.88, 128.11, 127.95, 115.72, 77.58, 77.16, 76.74, 72.19, 70.75, 70.52, 67.03, 52.42, 32.46, 29.89, 29.67, 29.54, 29.40, 29.34, 29.26, 28.68, 26.48; HRMS (ESI) m/z calcd for $C_{96}H_{146}N_2O_{14}^{2+}$ $[M–2PF_6^-]^{2+}$ 775.5382, found 775.5357.

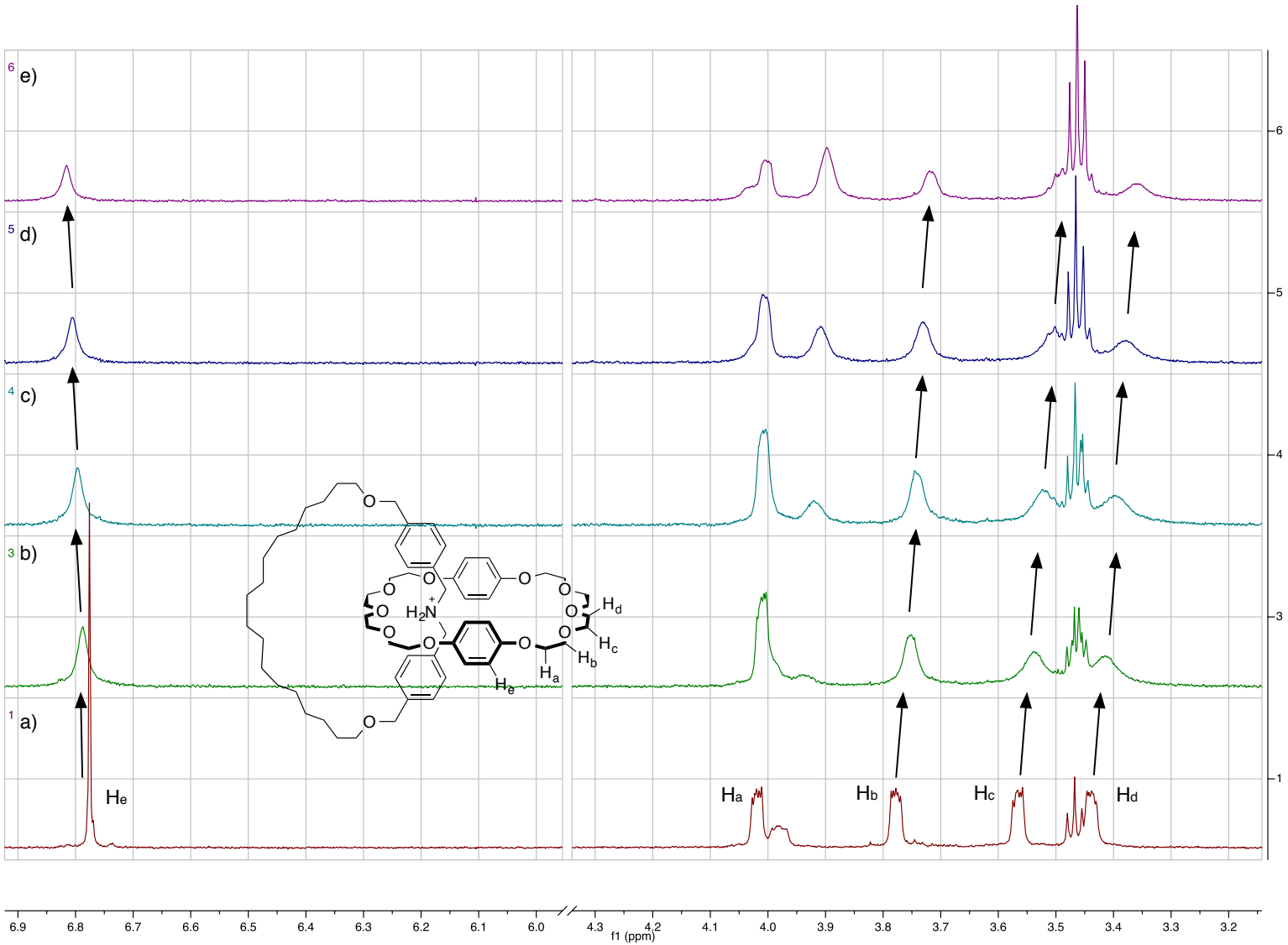


Figure S1. ^{1}H-NMR spectra (500 MHz, $CDCl_3$, 297 K) of [2]catenane **2** (1 mM) upon the addition of **4b** (a, 0.0; b, 0.5; c, 1.0; d, 2.0; e, 4.0 mM).

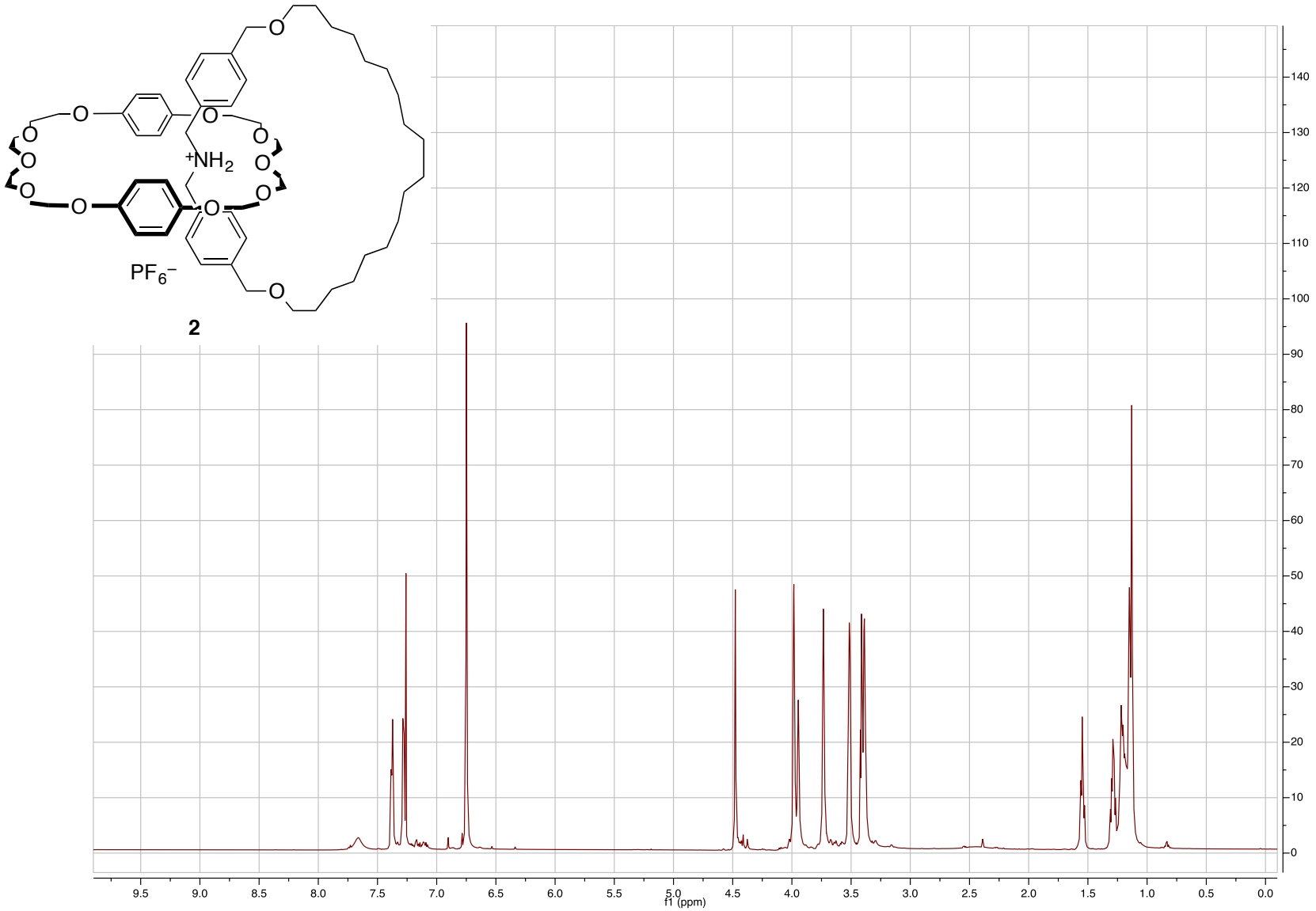


Figure S2. ^{1}H-NMR spectrum (700 MHz, $CDCl_3$) of [2]catenane **2**.

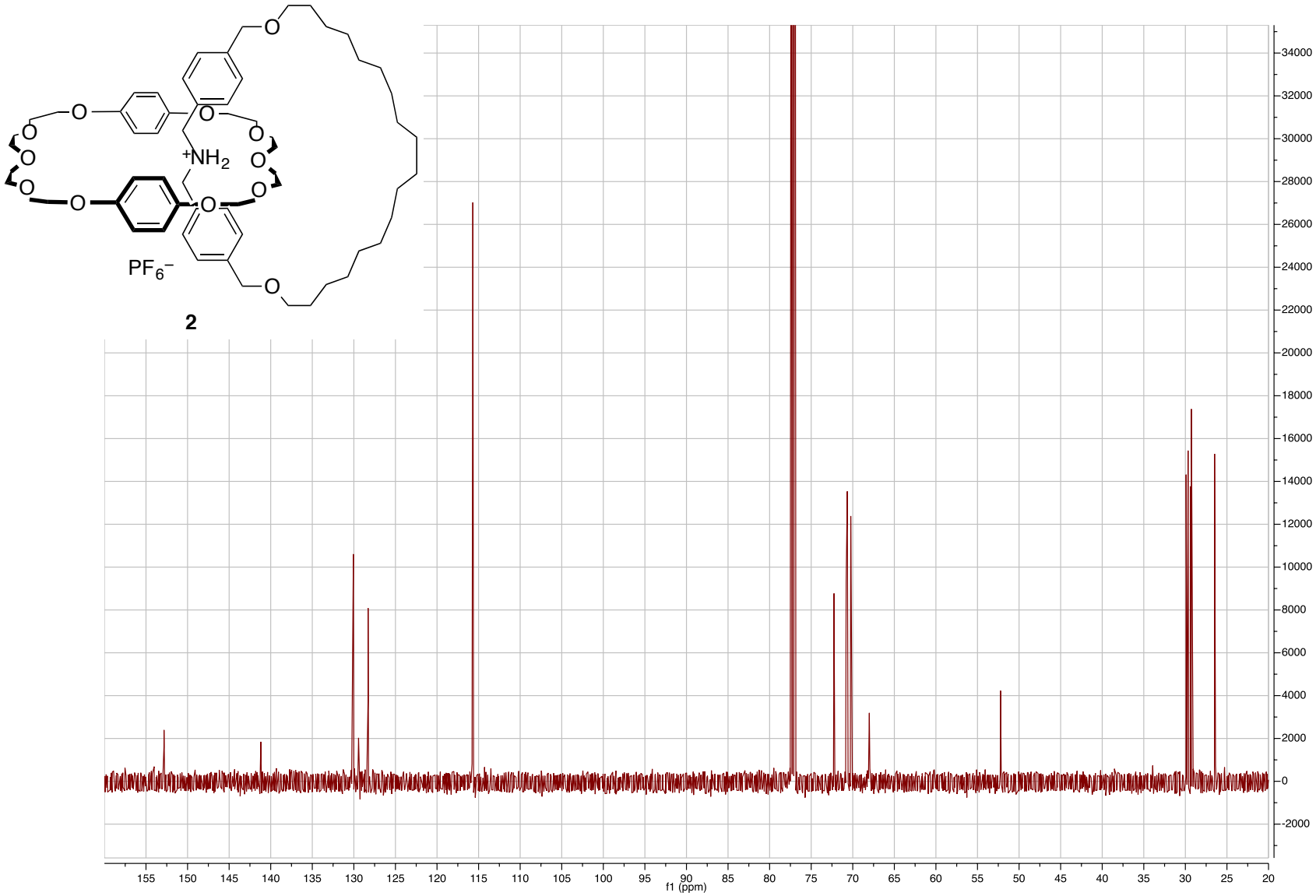


Figure S3. ^{13}C-NMR spectrum (151 MHz, $CDCl_3$) of [2]catenane **2**.

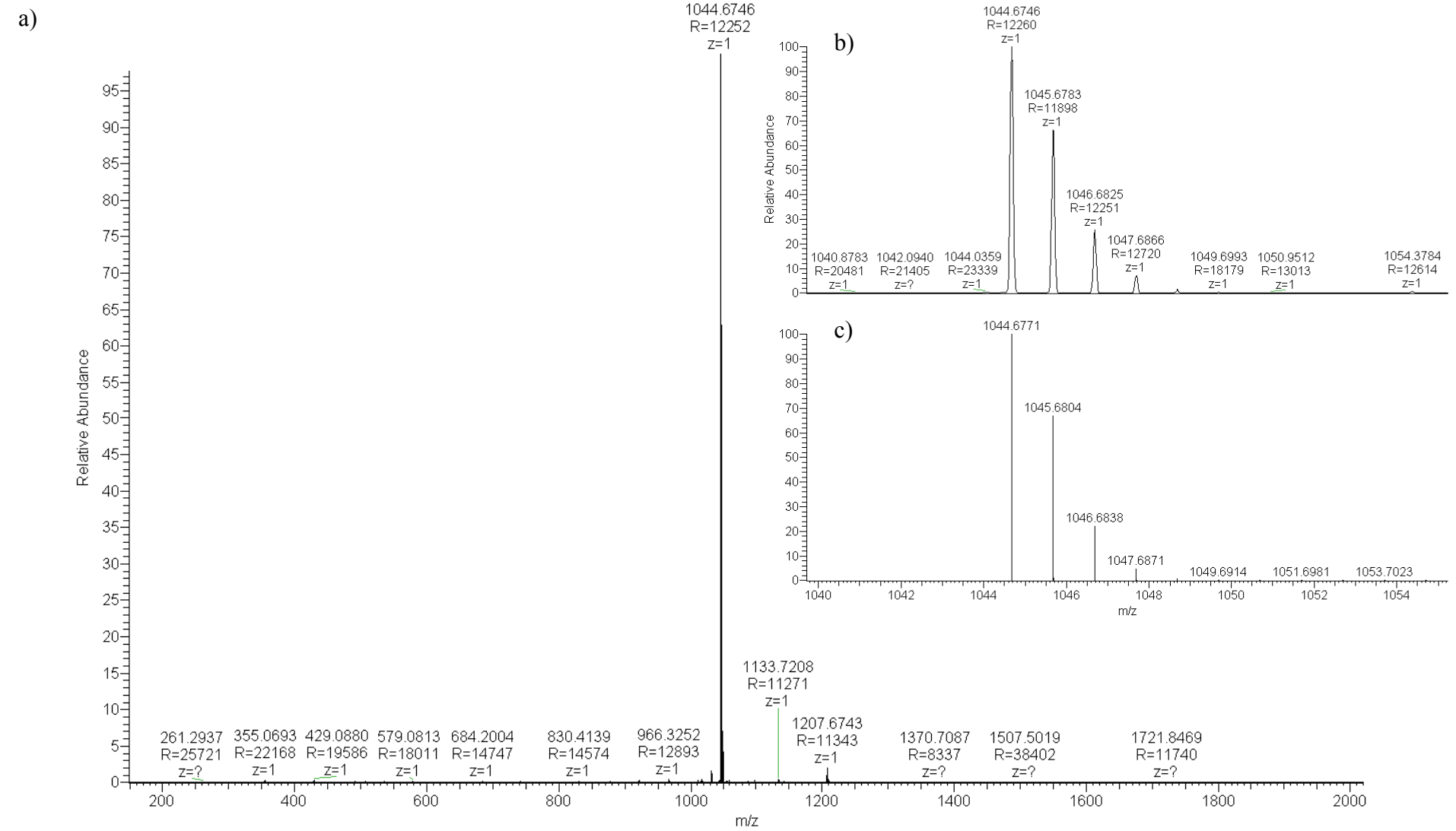


Figure S4. a) High resolution (ESI^+) mass spectrum of [2]catenane **2**; b) experimental spectrum and c) calculated isotopic distribution of $C_{62}H_{94}NO_{12}^+$ $[M–PF_6^-]^+$.

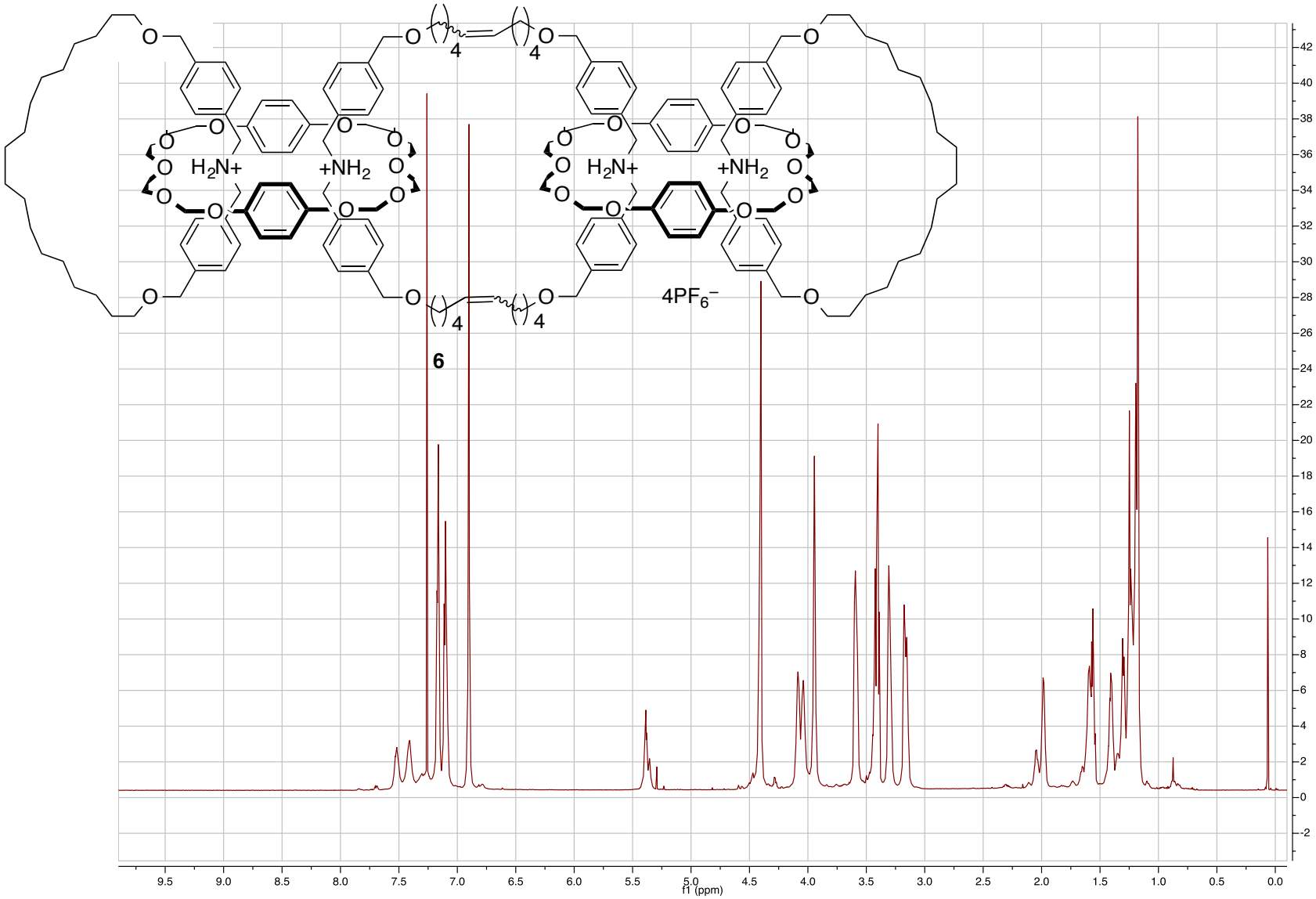


Figure S5. ^{1}H-NMR spectrum (700 MHz, $CDCl_3$) of [5]catenane **6**.

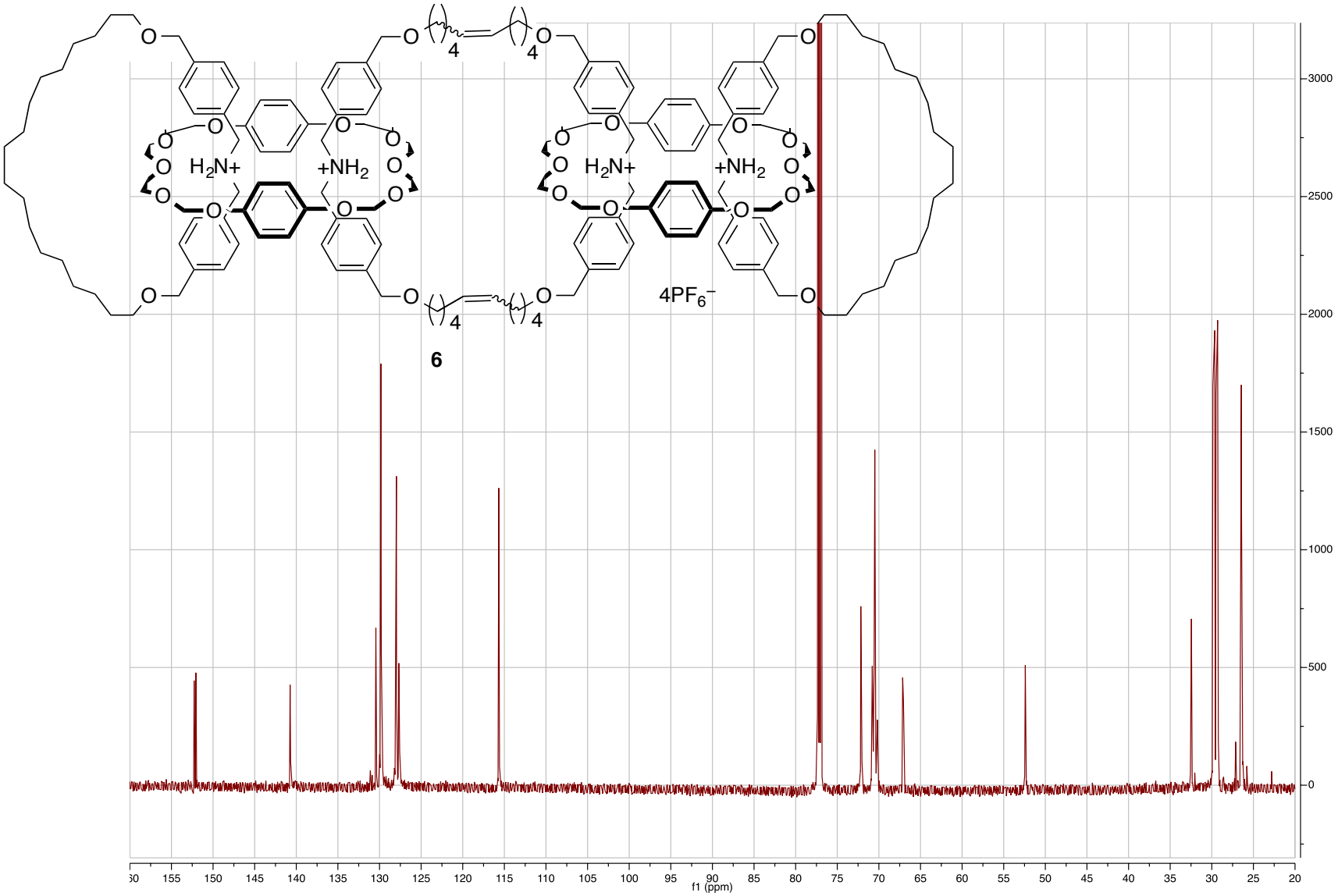


Figure S6. ^{13}C-NMR spectrum (176 MHz, $CDCl_3$) of [5]catenane **6**.

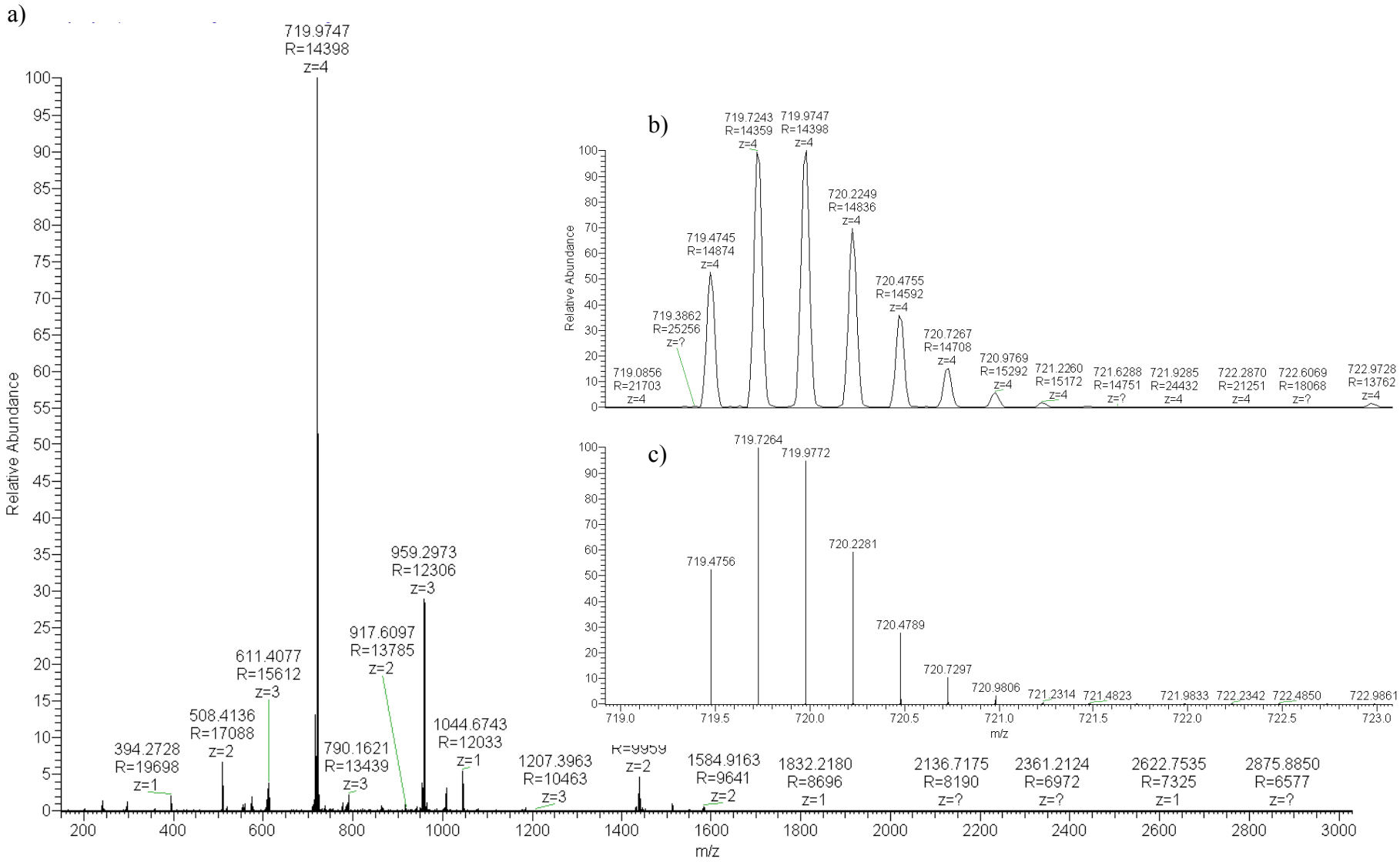


Figure S7. a) High resolution (ESI^+) mass spectrum of [5]catenane **6**; b) experimental spectrum and c) calculated isotopic distribution of $C_{176}H_{260}N_4O_{28}{}^{4+}$ $[M–4PF_6{}^-]^{4+}$.

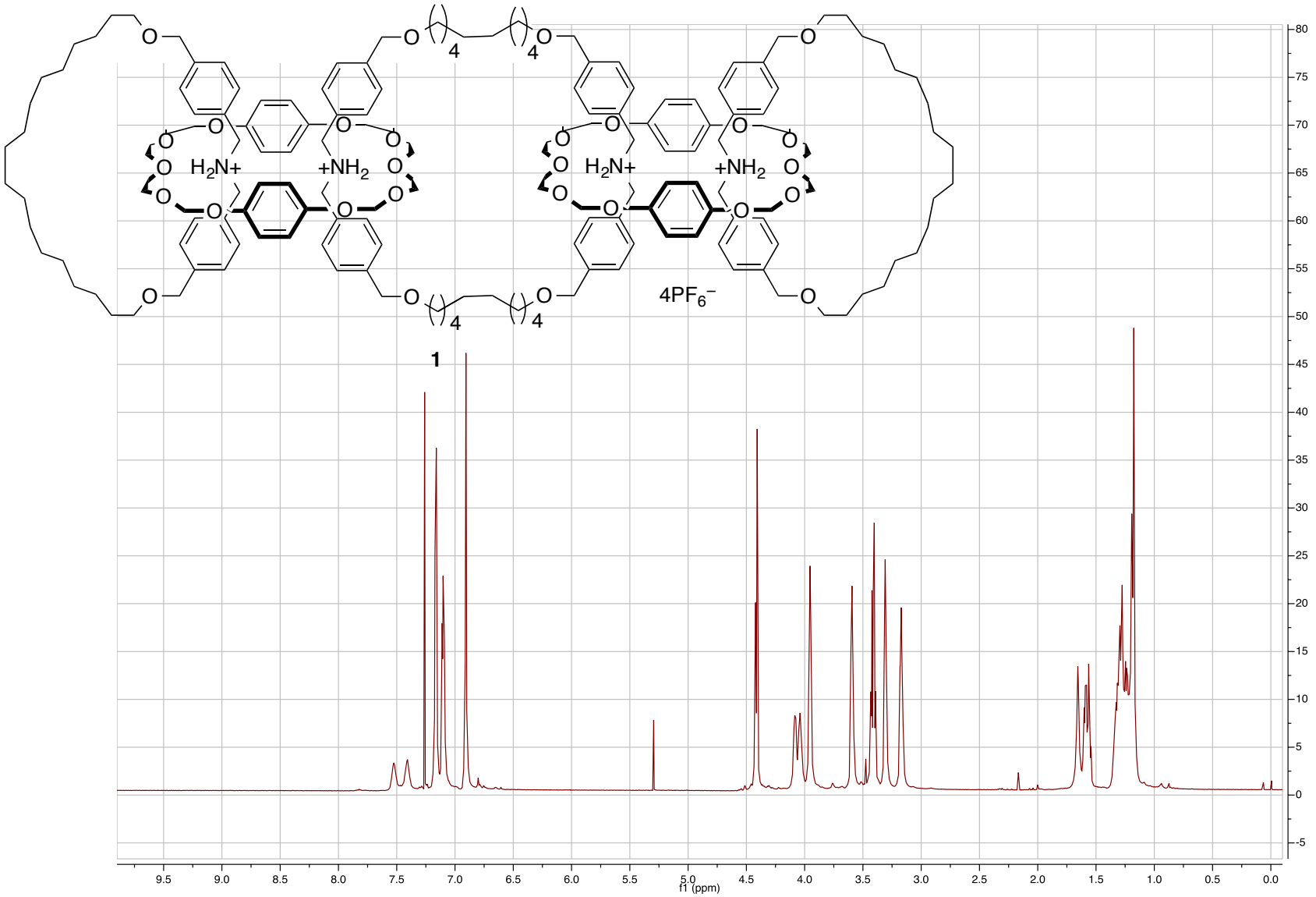


Figure S8. ^{1}H-NMR spectrum (700 MHz, $CDCl_3$) of [5]catenane **1**.

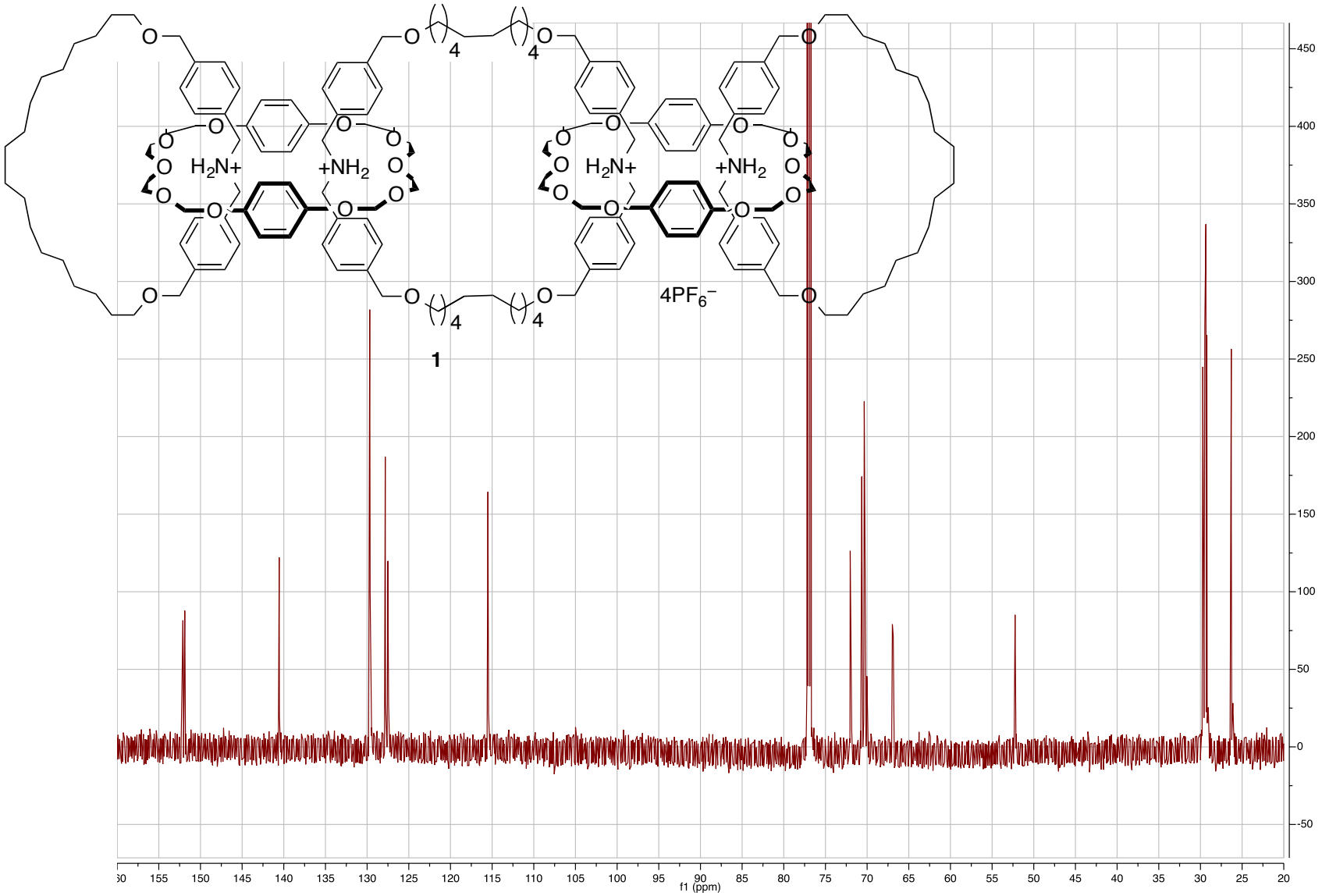


Figure S9. ^{13}C-NMR spectrum (176 MHz, $CDCl_3$) of [5]catenane **1**.

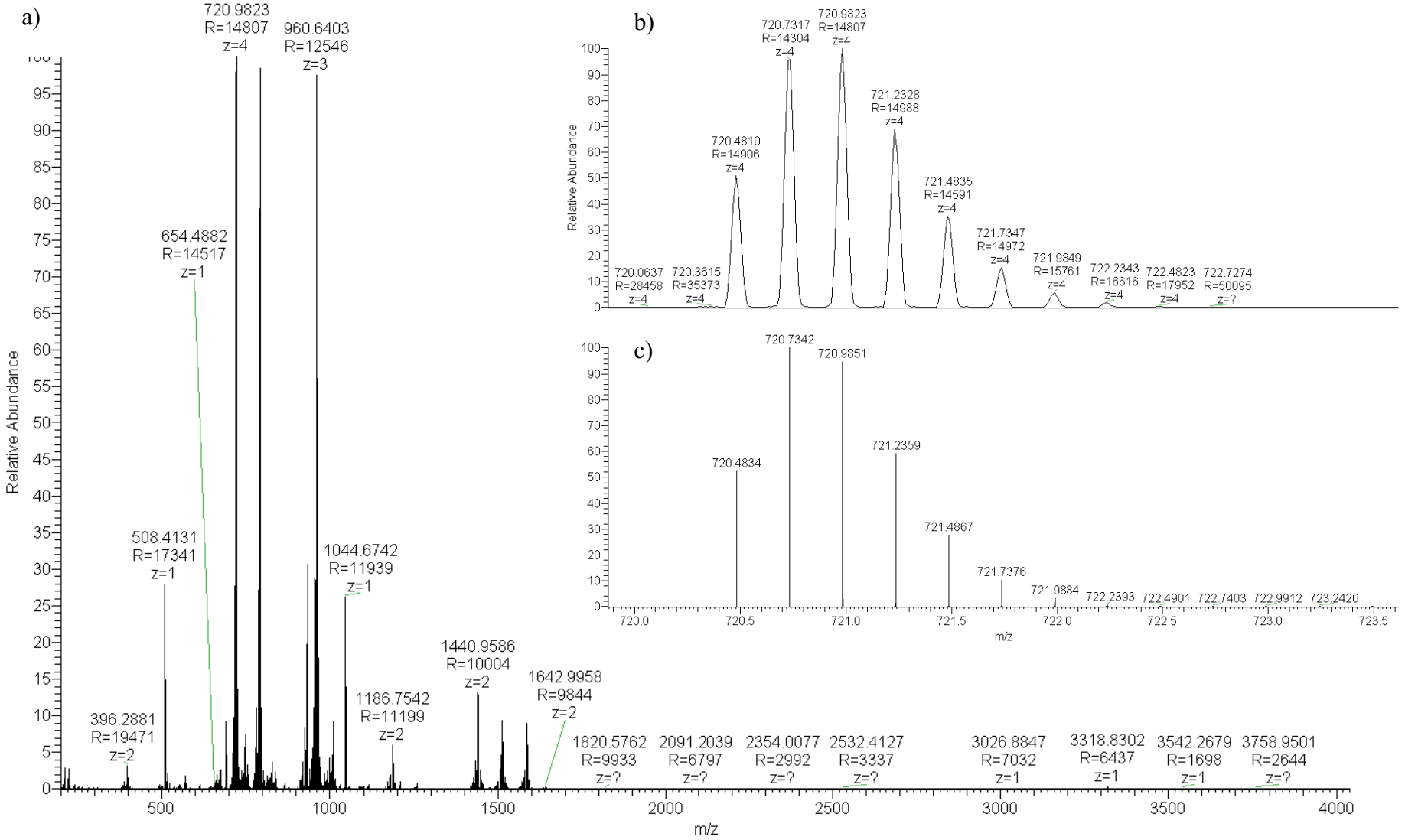


Figure S10. a) High resolution (ESI^+) mass spectrum of [5]catenane **1**; b) experimental spectrum and c) calculated isotopic distribution of $C_{176}H_{264}N_4O_{28}{}^{4+}$ $[M–4PF_6^-]^{4+}$.

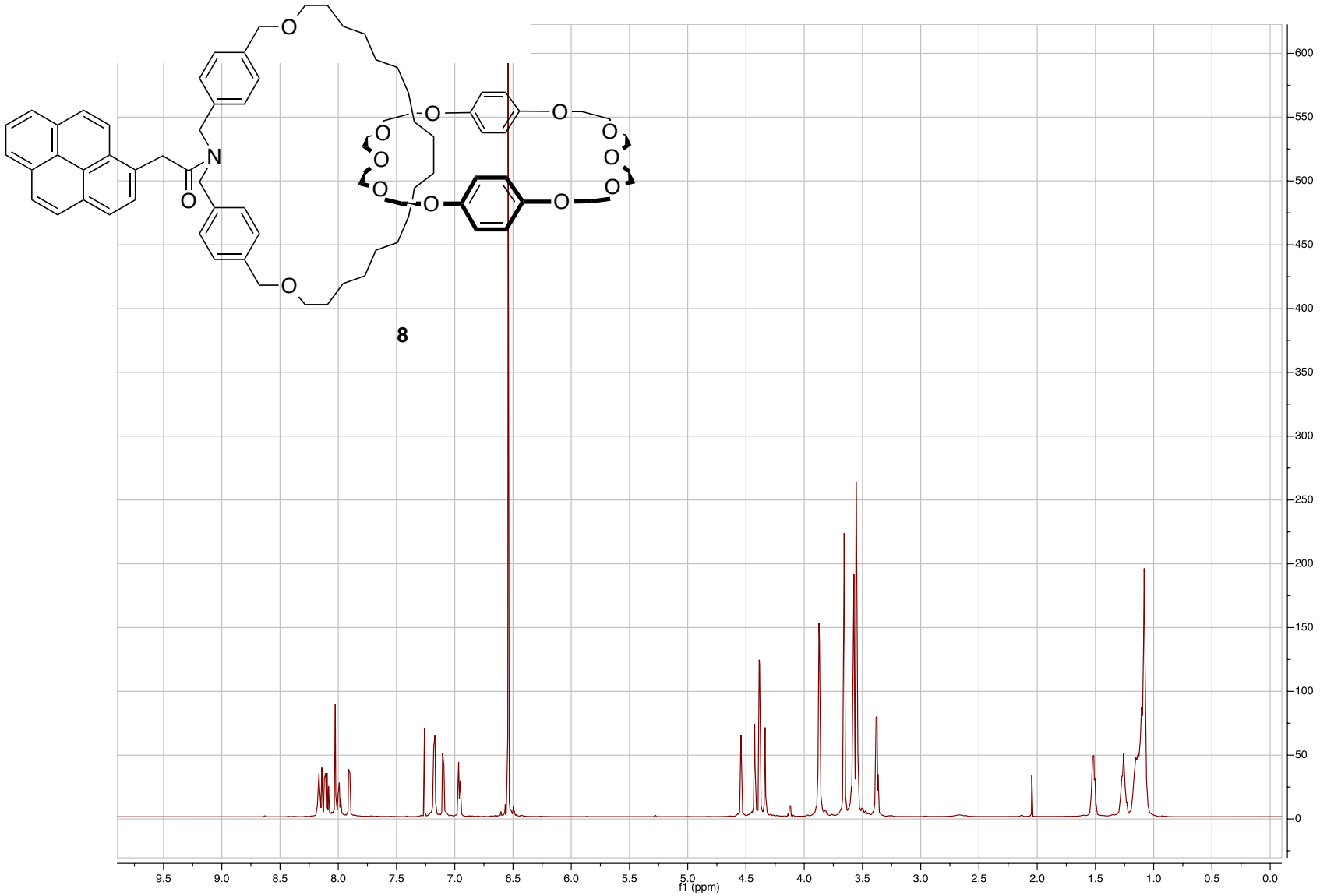


Figure S11. ^{1}H-NMR spectrum (700 MHz, $CDCl_3$) of [2]catenane **8**.

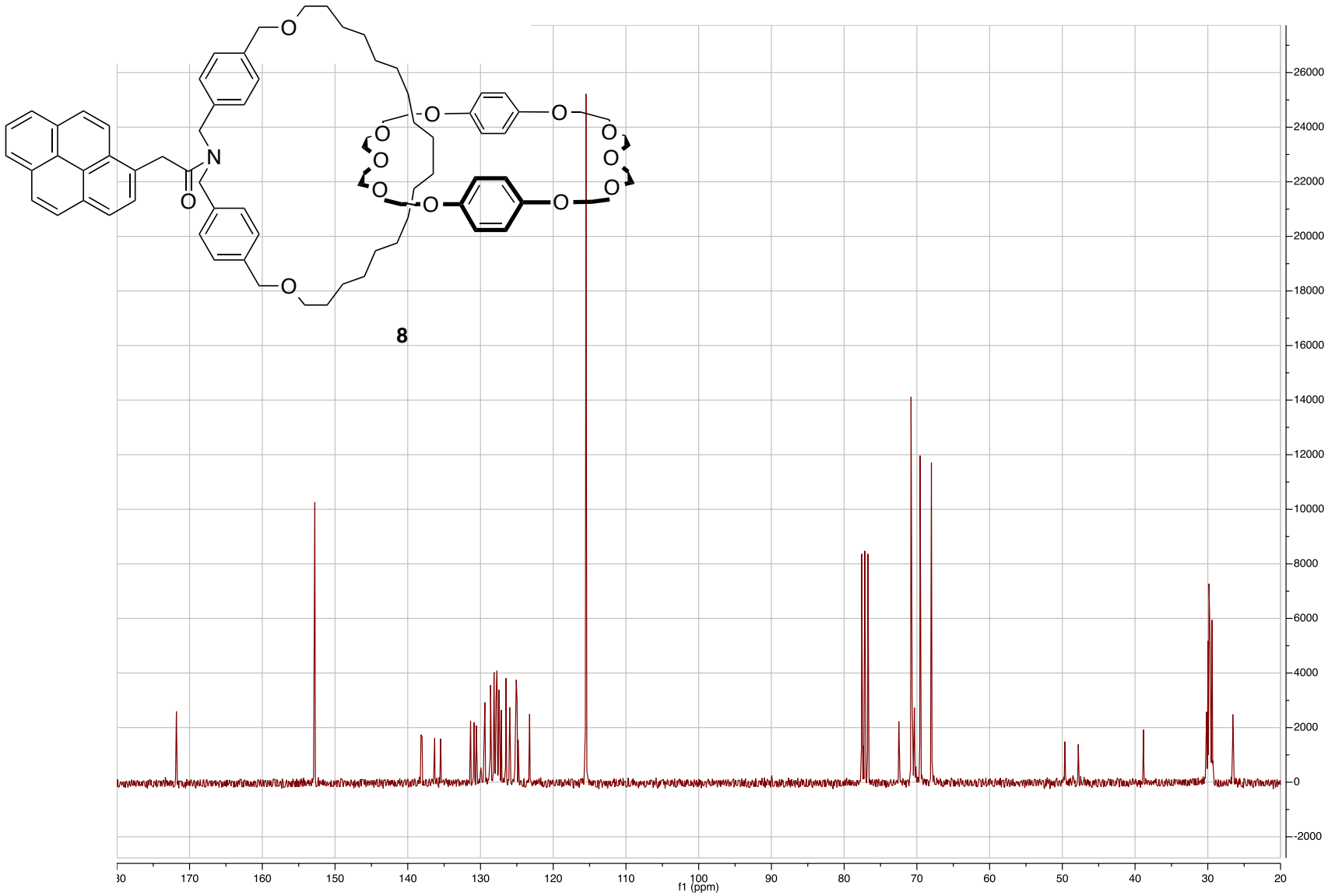


Figure S12. ^{13}C-NMR spectrum (75 MHz, $CDCl_3$) of [2]catenane **8**.

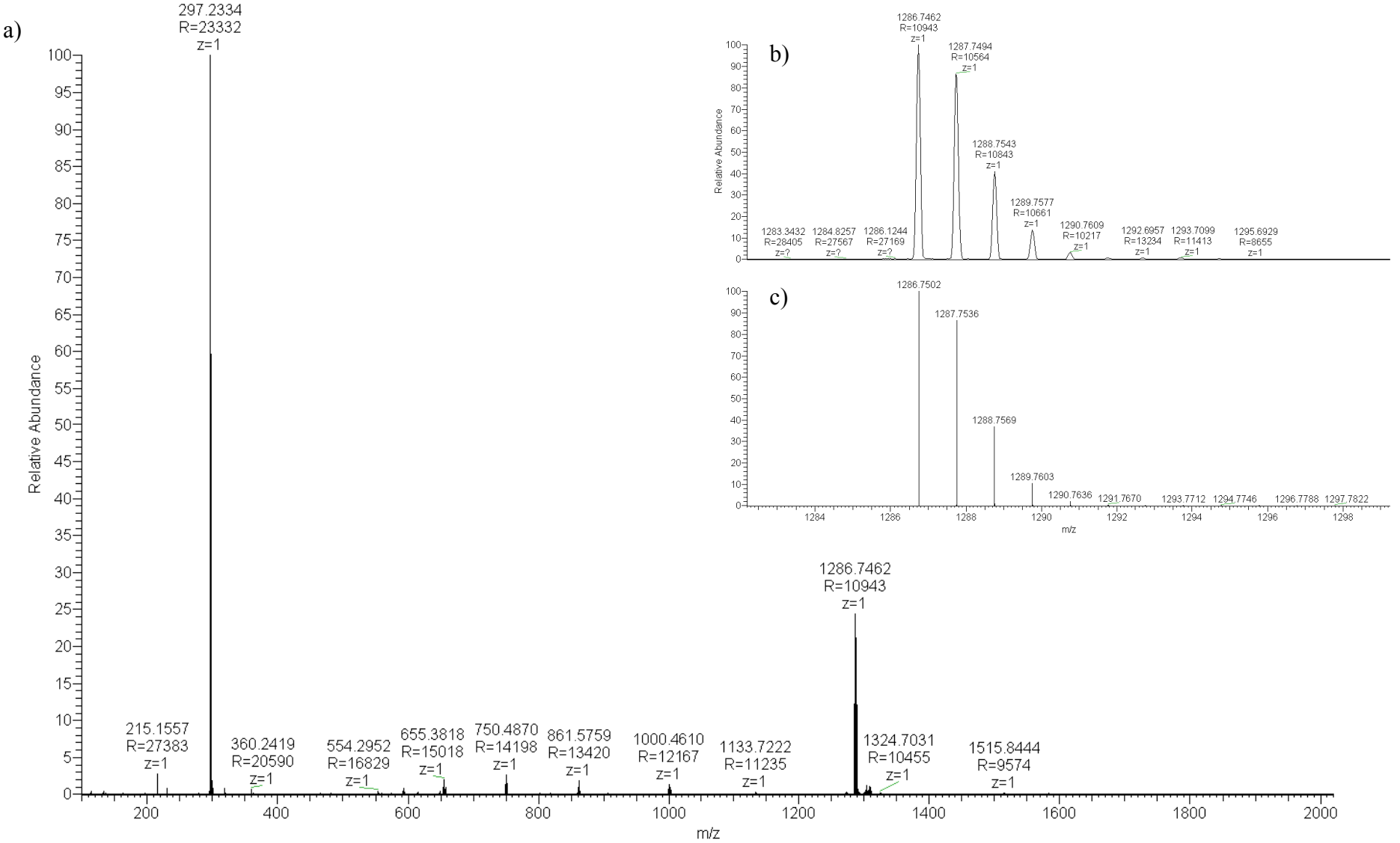


Figure S13. a) High resolution (ESI^+) mass spectrum of [2]catenane **8**; b) experimental spectrum and c) calculated isotopic distribution of $C_{80}H_{104}NO_{13}^+$ [$M+H^+$].

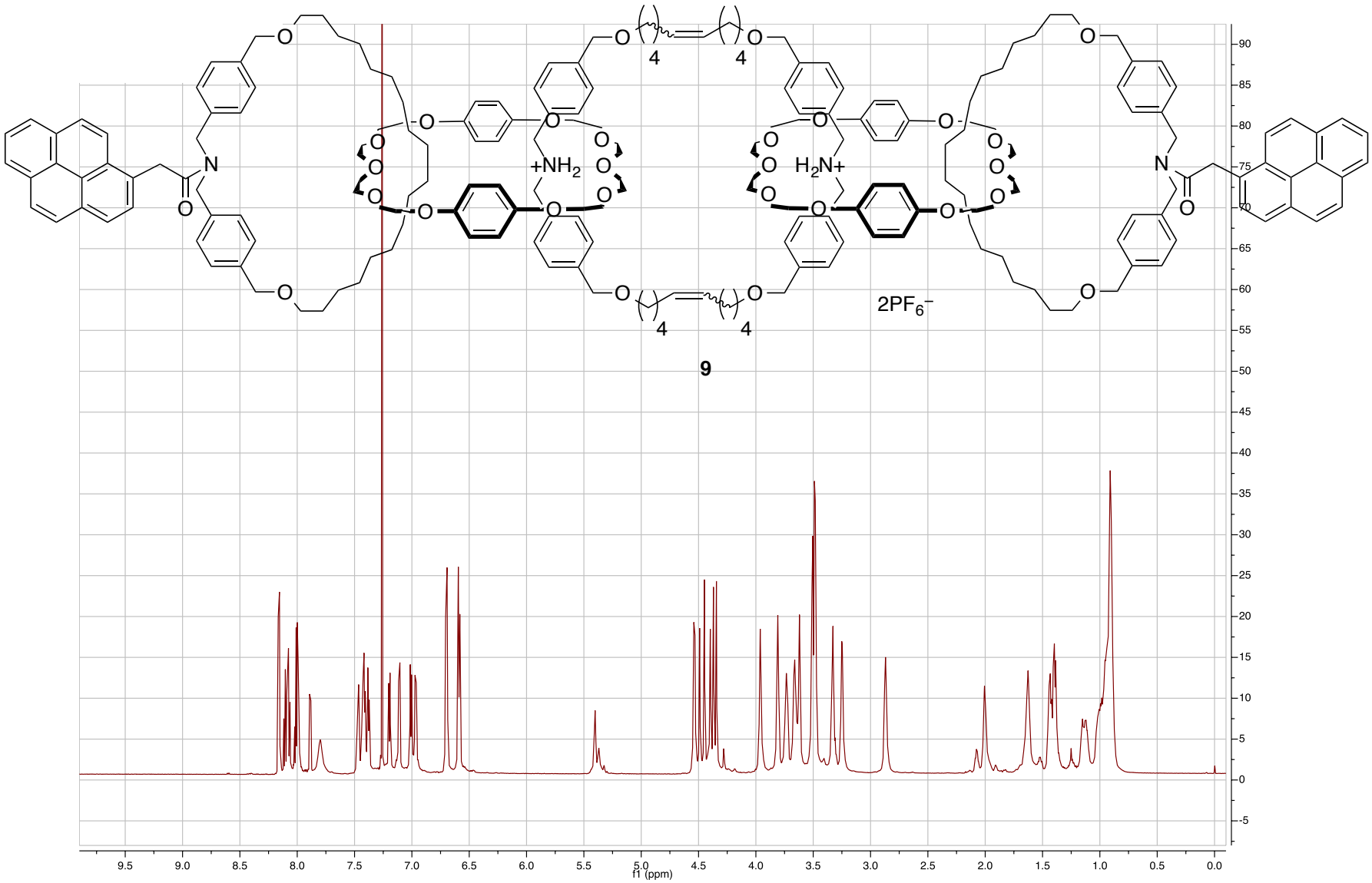


Figure S14. ^{1}H-NMR spectrum (700 MHz, $CDCl_3$) of [5]catenane **9**.

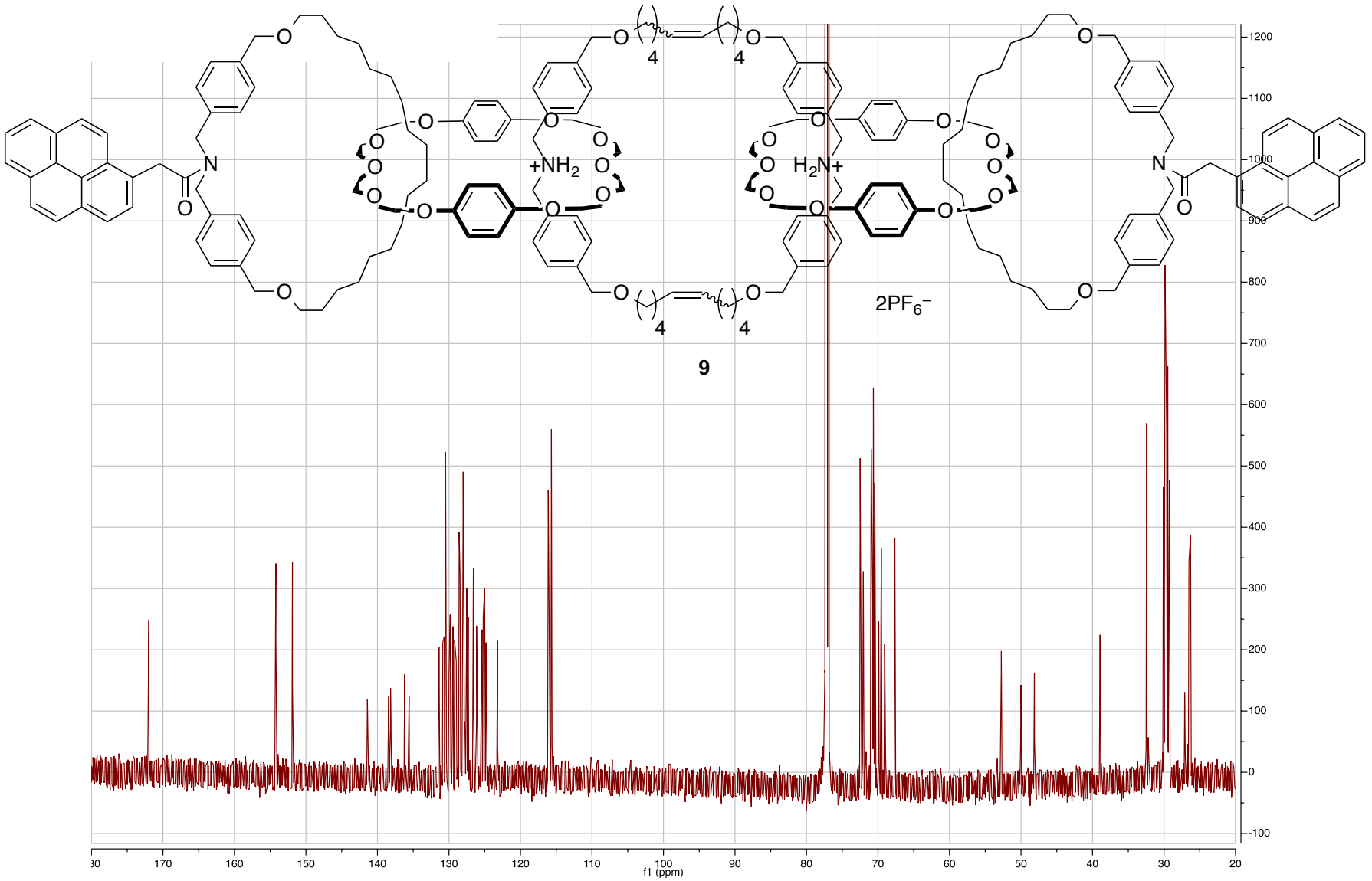


Figure S15. ^{13}C-NMR spectrum (176 MHz, $CDCl_3$) of [5]catenane **9**.

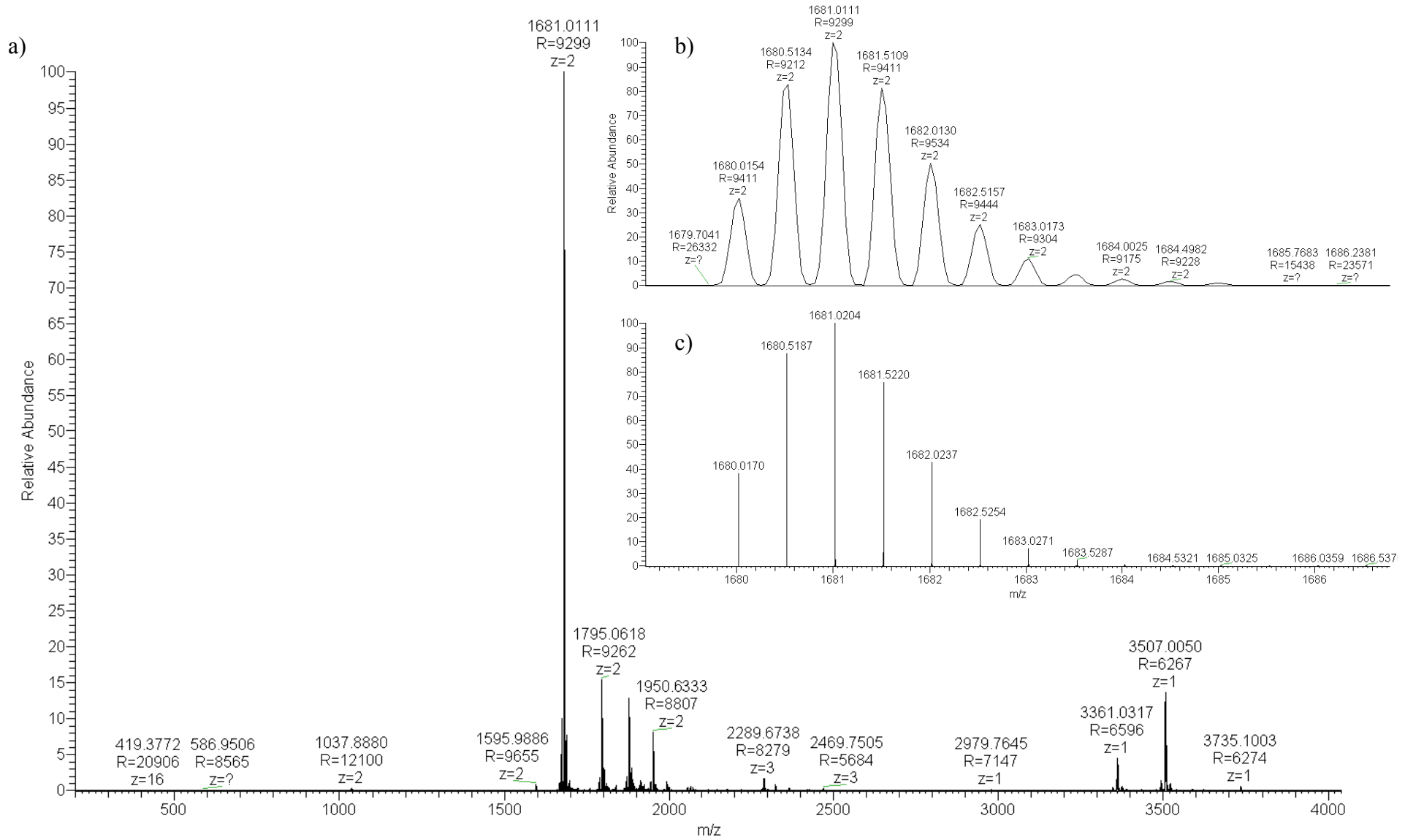


Figure S16. a) High resolution (ESI^+) mass spectrum of [5]catenane **9**; b) experimental spectrum and c) calculated isotopic distribution of $C_{212}H_{278}N_4O_{30}{}^{2+}$ $[M–2PF_6{}^-]^{2+}$.

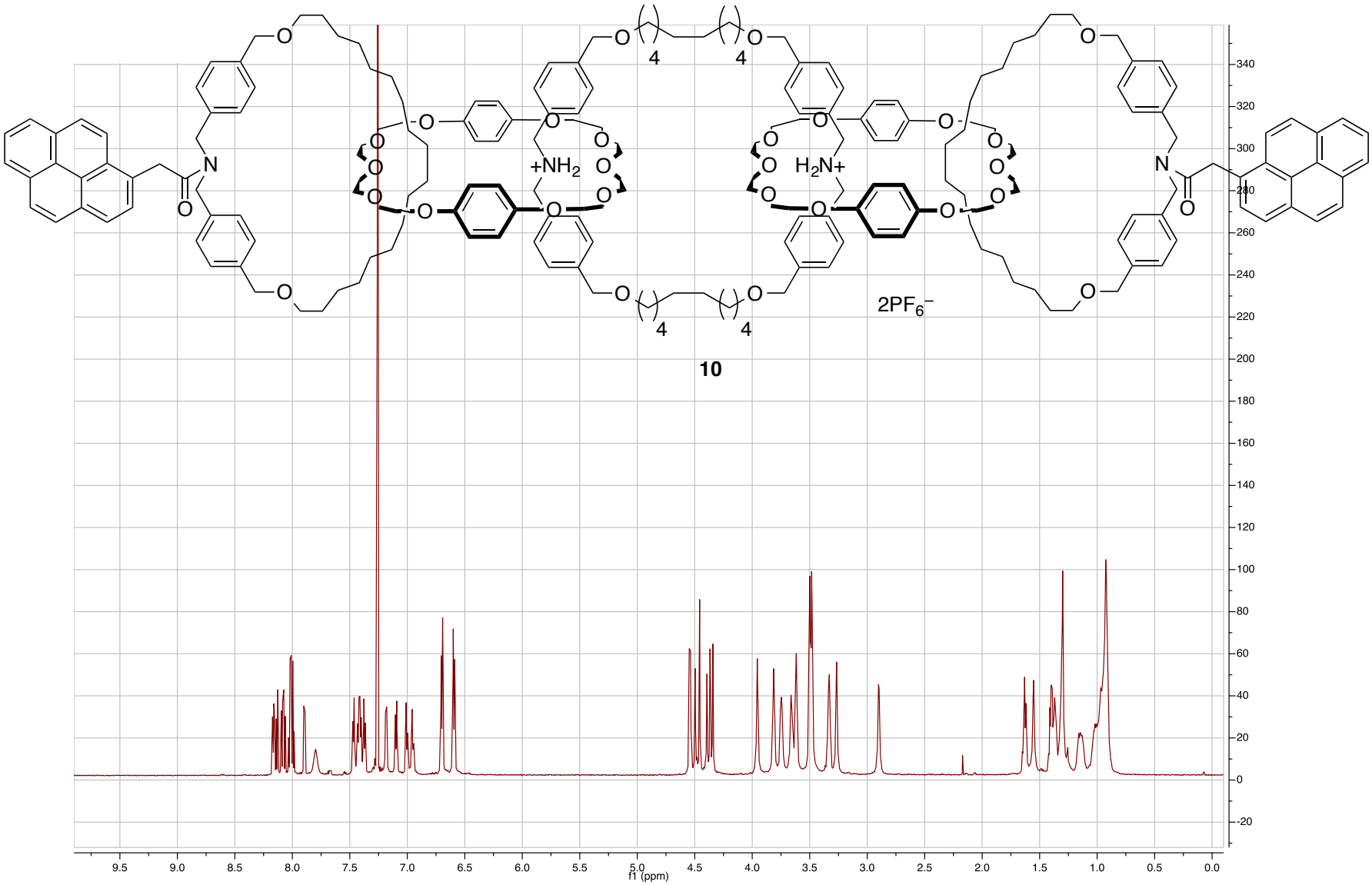


Figure S17. ^{1}H-NMR spectrum (700 MHz, $CDCl_3$) of [5]catenane **10**.

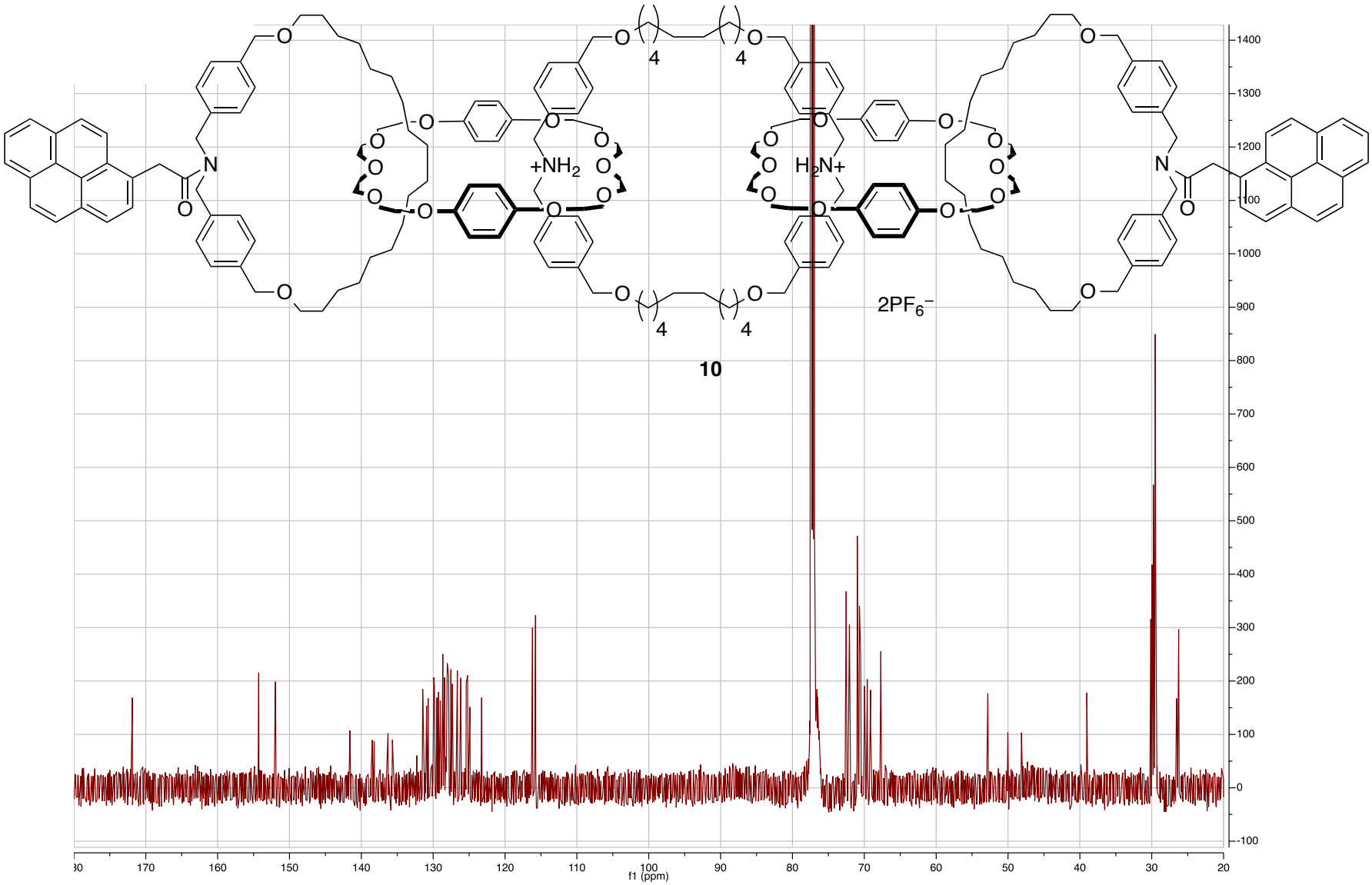


Figure S18. ^{13}C-NMR spectrum (176 MHz, $CDCl_3$) of [5]catenane **10**.

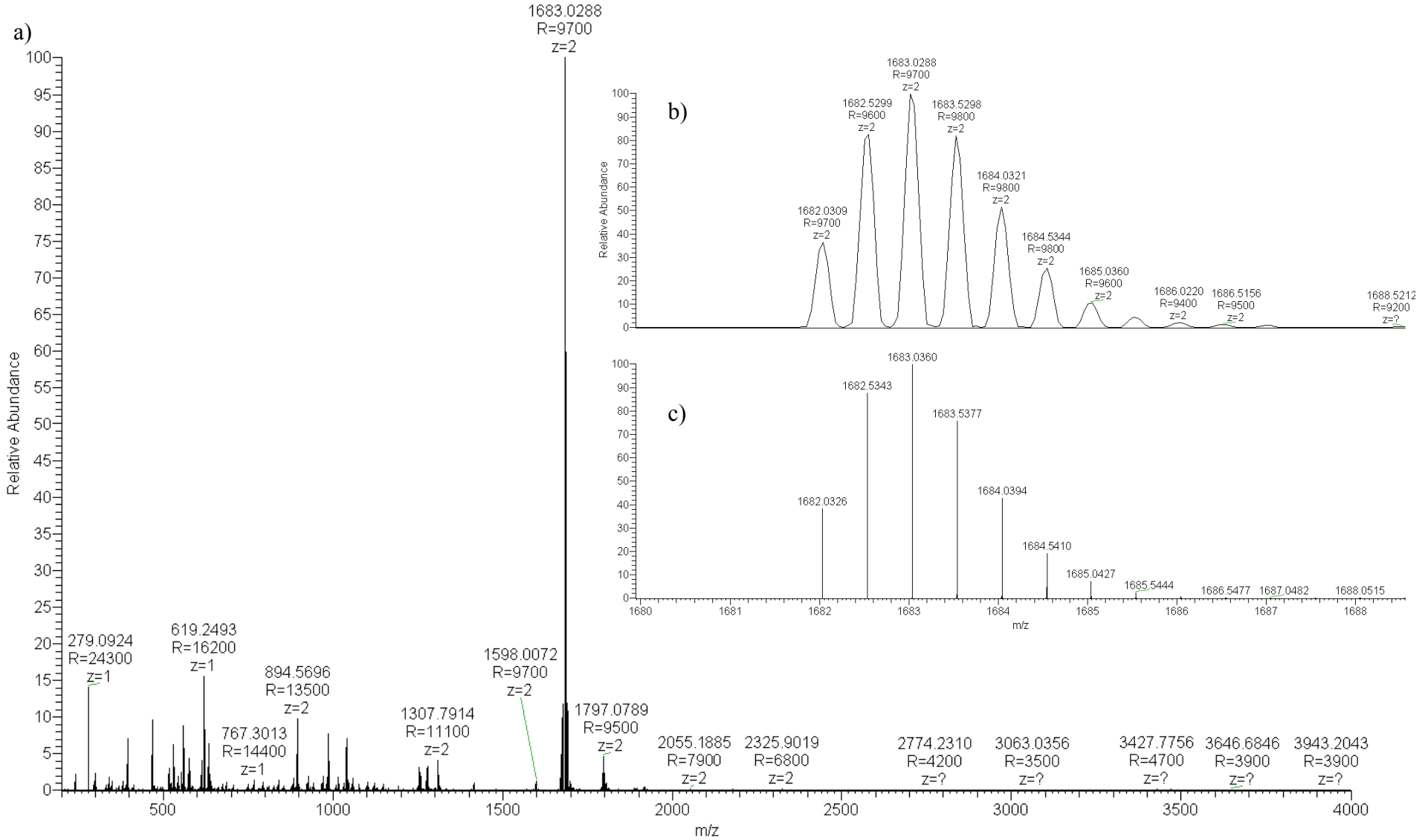


Figure S19. a) High resolution (ESI^+) mass spectrum of [5]catenane **10**; b) experimental spectrum and c) calculated isotopic distribution of $C_{212}H_{282}N_4O_{30}{}^{2+}$ $[M–2PF_6{}^-]^{2+}$.

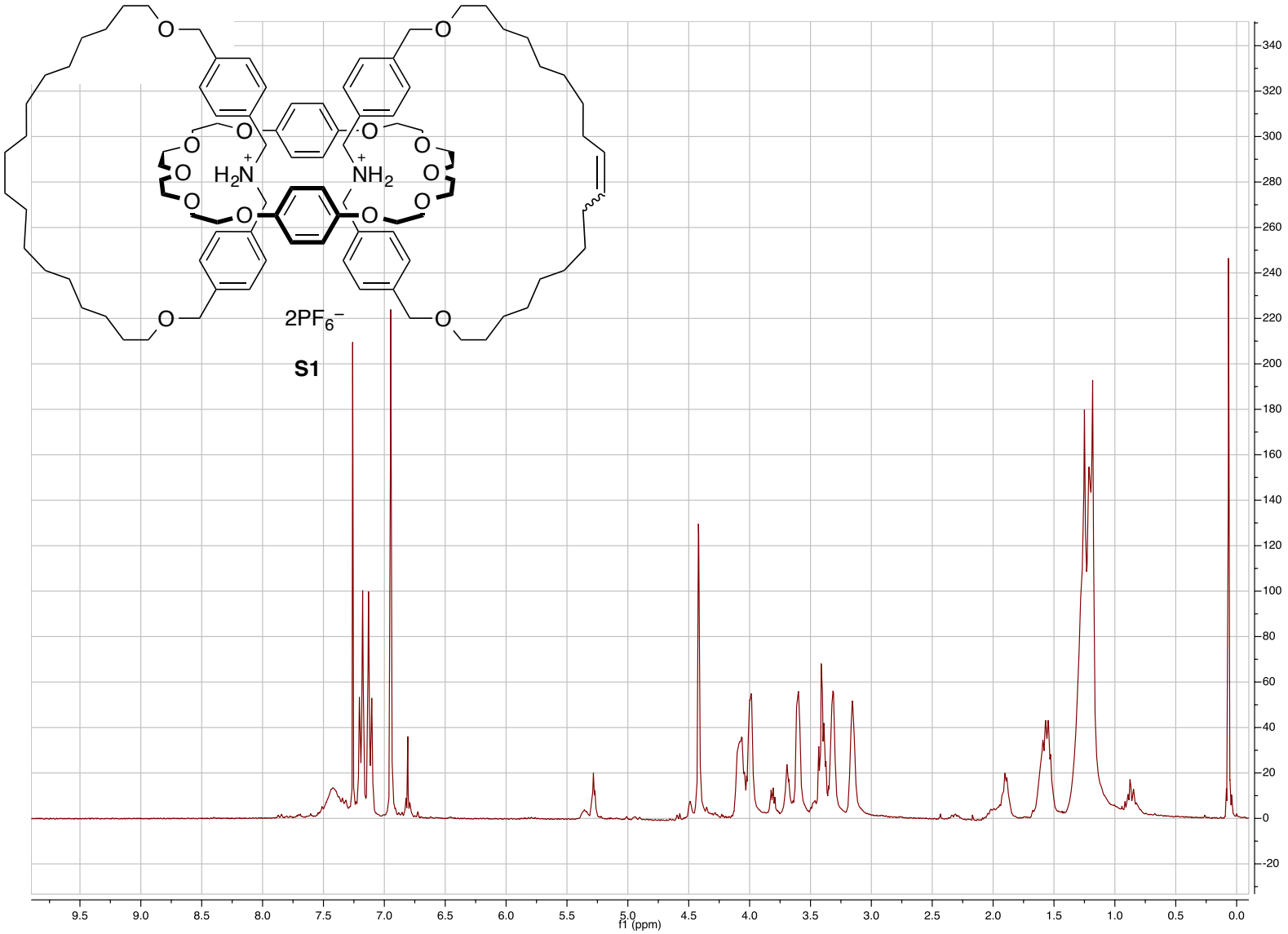


Figure S20. ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of [3]catenane **S1**.

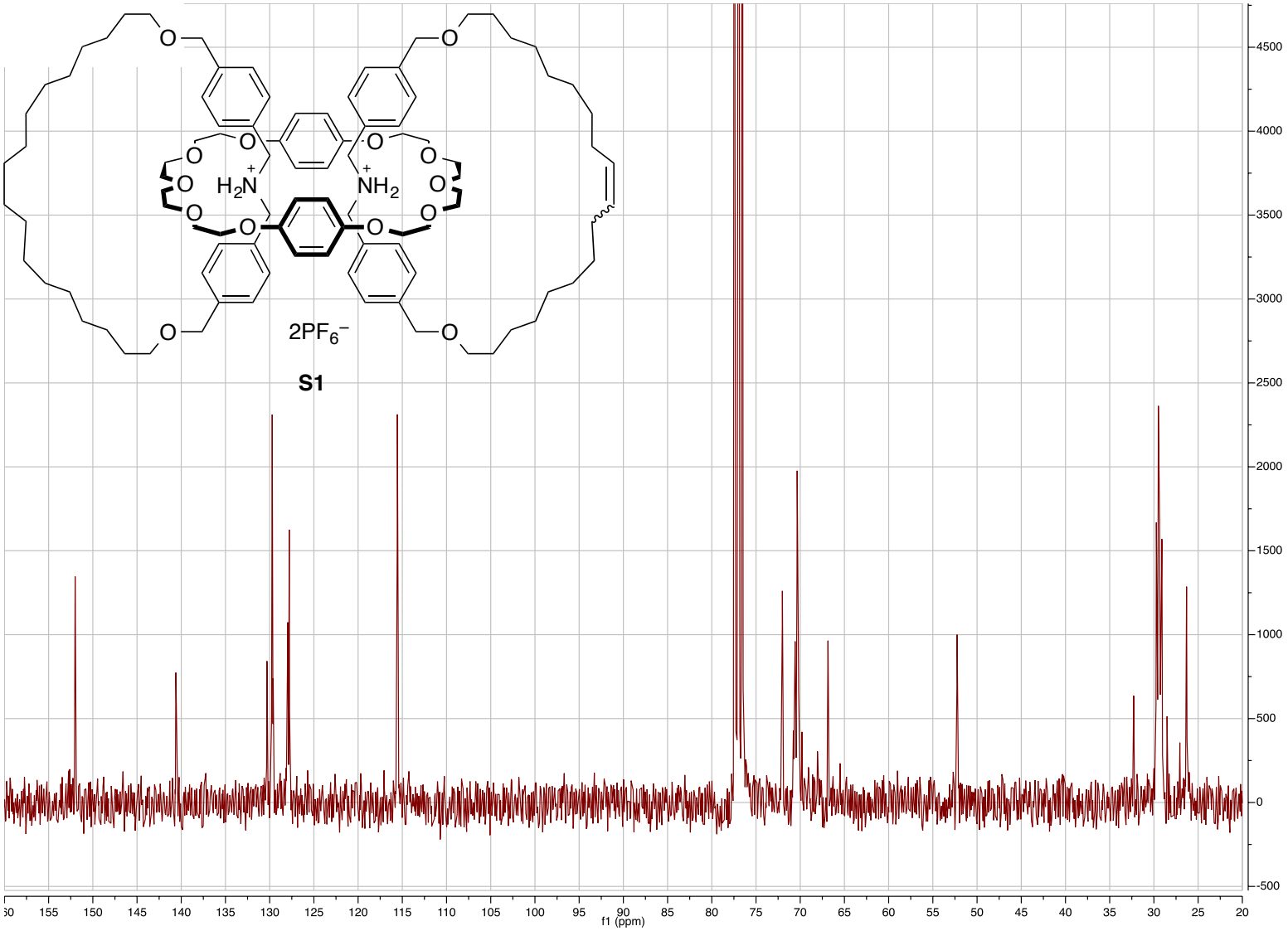


Figure S21. ^{13}C-NMR spectrum (75 MHz, $CDCl_3$) of [3]catenane **S1**.

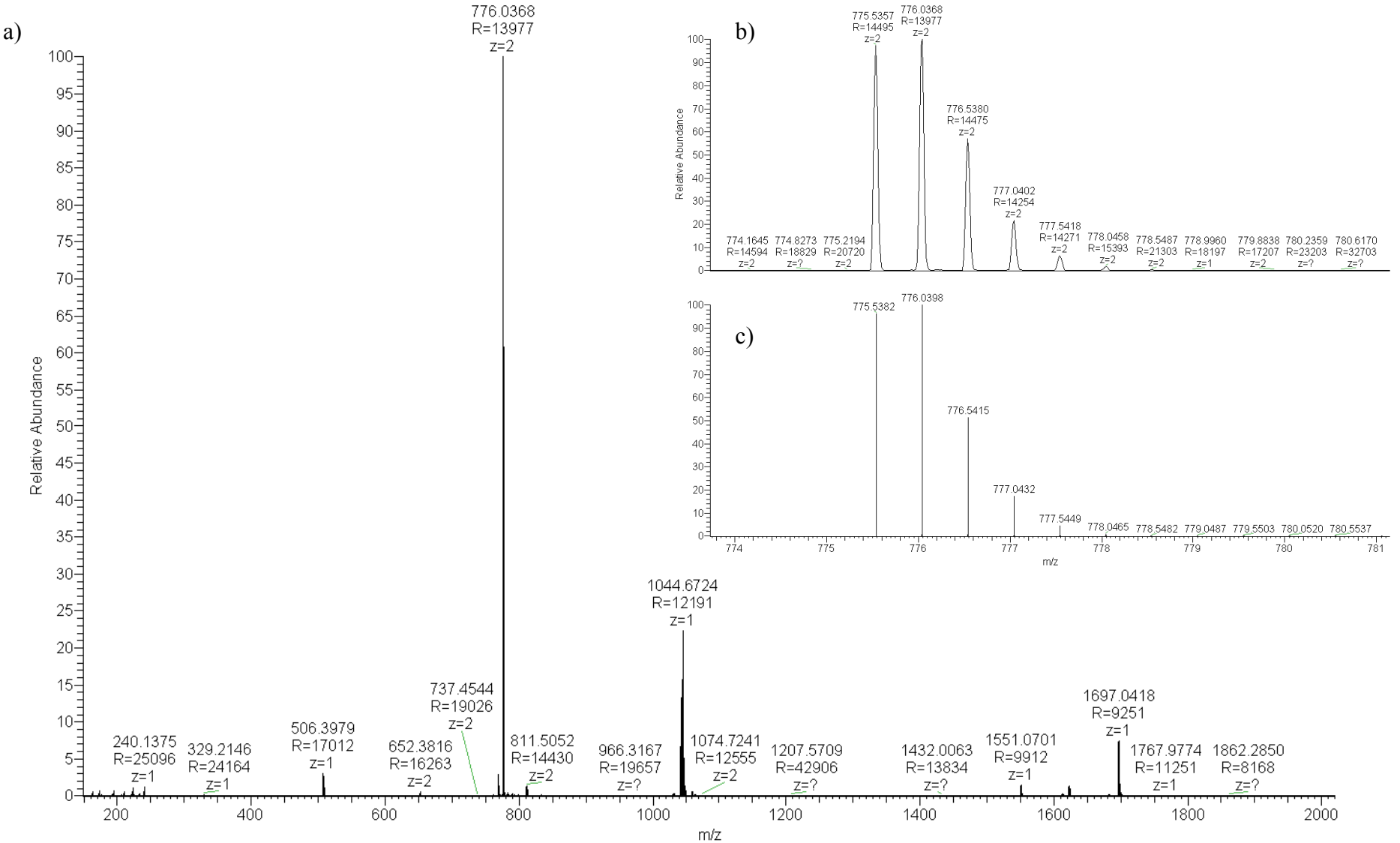


Figure S22. a) High resolution (ESI^+) mass spectrum of [3]catenane **S1**; b) experimental spectrum and c) calculated isotopic distribution of $C_{96}H_{146}N_2O_{14}^{2+}$ $[M–2PF_6^-]^{2+}$.