Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Electronic Supporting Information

Self-templated Synthesis of Amide Catenanes and Formation of a Catenane Coordination Polymer

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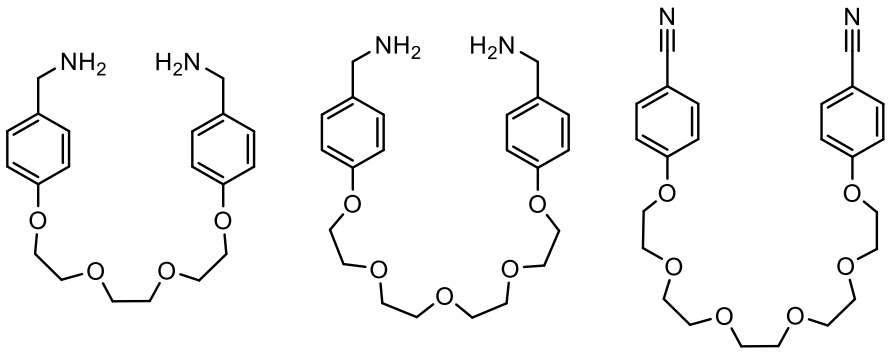
General Experimental

Synthesis: Unless otherwise stated, all reagents, including anhydrous solvents, were purchased from commercial sources and used without further purification. Triethylamine and $CDCl_3$ were stored over 4 Å molecular sieves prior to use. All reactions were carried out under an atmosphere of N_2 using anhydrous solvents unless otherwise stated. Petrol refers to the fraction of petroleum ether boiling in the range 40-60 °C. Analytical TLC was performed on pre-coated silica gel plates (0.25 mm thick, 60F254, Merck, Germany) and observed under UV light or visualised with an aqueous $KMnO_4$ stain.

Analysis: NMR spectra were recorded on Bruker AV400 or AV500 instrument, at a constant temperature of 300 K. Chemical shifts are reported in parts per million from low to high field and referenced to residual solvent. Standard abbreviations indicating multiplicity were used as follows: m = multiplet, quint = quintet, q = quartet, t = triplet, d = doublet, s = singlet, app. = apparent, br. = broad. Signal assignment was carried out using 2D NMR methods (HSQC, HMBC, COSY, NOESY) where necessary. In the case of some signals absolute assignment was not possible. Here indicative either/or assignments (e.g. H_A/H_B for H_A or H_B) are provided. All melting points were determined using a hot stage apparatus and are uncorrected. Mass spectrometry was carried out by the Imperial College London, Department of Chemistry Mass Spectroscopy Service using Waters LCT Premier for HR-ESI-MS and Thermo Scientific Q-Exactive for tandem MS.



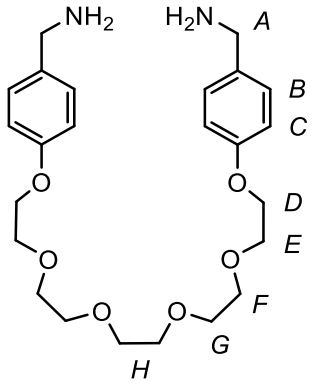
2a **2b** **S1**

The following compounds were synthesised according to literature procedures: **2a**,[1] **2b**[2] and **S1**.[3]

N.B. 2a-2d were all dried on high vacuum prior to use.

Synthesis and Characterisation of Macrocycle Precursors

2c



A solution of **S1** (0.881 g, 2.0 mmol, 1 eq.) in THF (dry, 10 mL) was added to a suspension of $LiAlH_4$ (0.493 g, 16 mmol, 8 eq.) in THF (dry, 10 mL) under N_2 before stirring at reflux for 17 h. H_2O (10 mL) was added carefully to the cooled reaction before filtering through celite, washing through with THF. The solvent was removed *in vacuo* and the resultant residue taken up in CH_2Cl_2 (50 mL) and washed with brine (25 mL). The aqueous phase was extracted with CH_2Cl_2 (10 mL), the combined organic phases dried ($MgSO_4$) and the solvent removed *in vacuo* to give **2c** (0.569 g, 63%) as a cream solid. M.p. 56-58 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.20 (d, J = 8.7 Hz, 4H, H_B), 6.87 (d, J = 8.7 Hz, 4H, H_C), 4.12-4.09 (m, 4H, H_D), 3.85-3.82 (m, 4H, H_E), 3.79 (s, 4H, H_A), 3.73-3.70 (m, 4H, H_F/H_G), 3.68-3.65 (m, 4H, H_F/H_G), 3.65 (s, 4H, H_H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.9, 135.8, 128.4 (C_B), 114.9 (C_C), 71.0 (C_F/C_G/C_H), 70.8 (×2; 2 of C_F/C_G/C_H), 69.9 (C_E), 67.7 (C_D), 46.0 (C_A), 30.5. HR-ESI-MS *m/z* = 449.2660 $[M+H]^+$ calc. 449.2652.

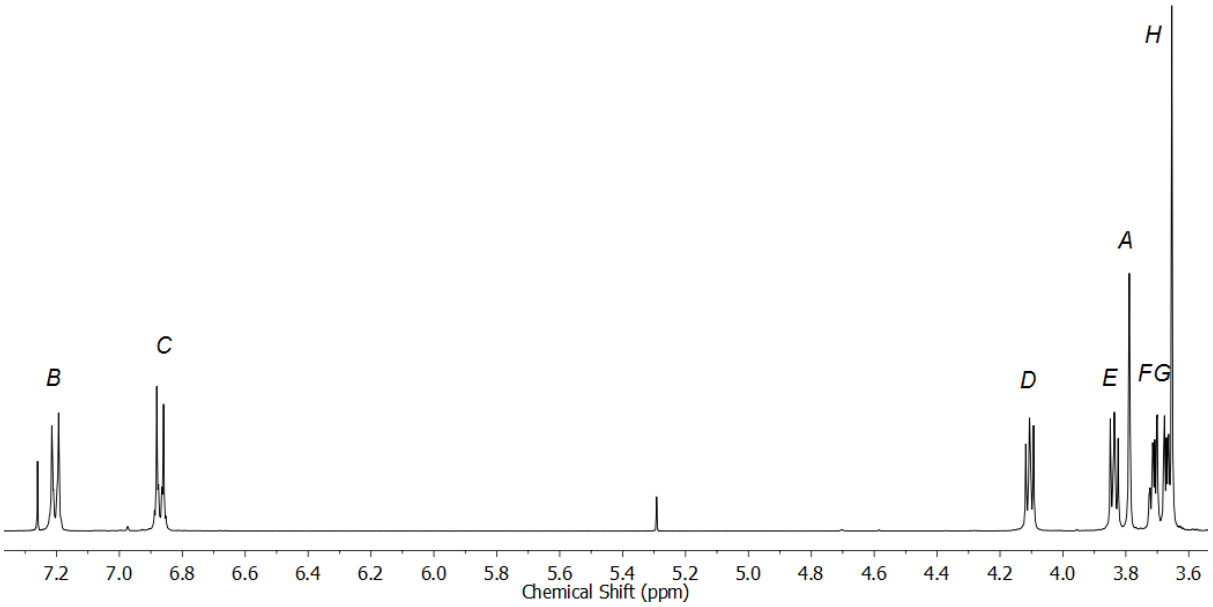


Figure S1 ^{1}H NMR ($CDCl_3$, 400 MHz) of **2c**.

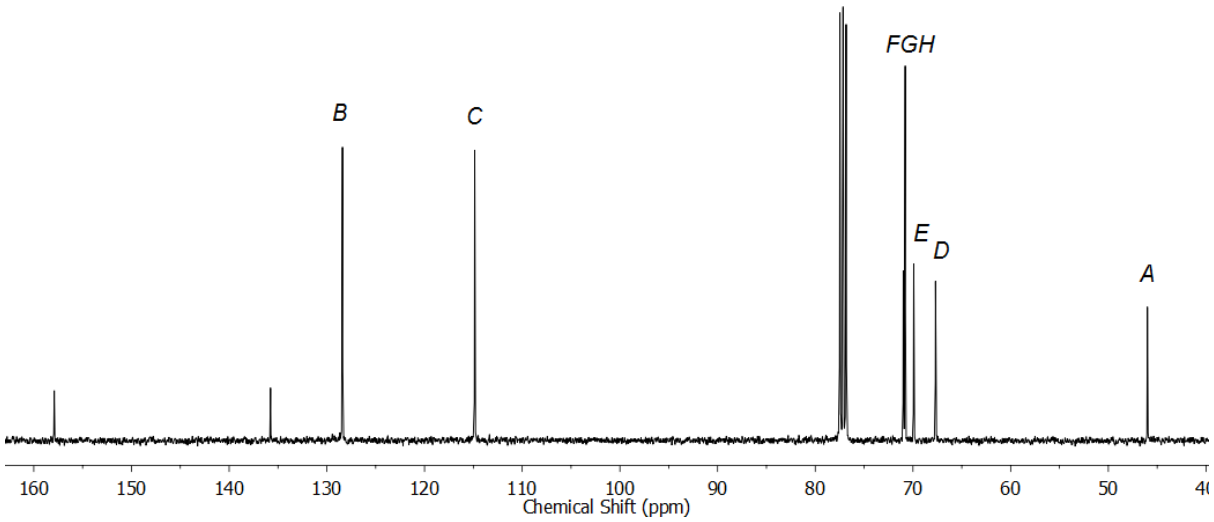


Figure S2 ^{13}C NMR ($CDCl_3$, 101 MHz) of **2c**.

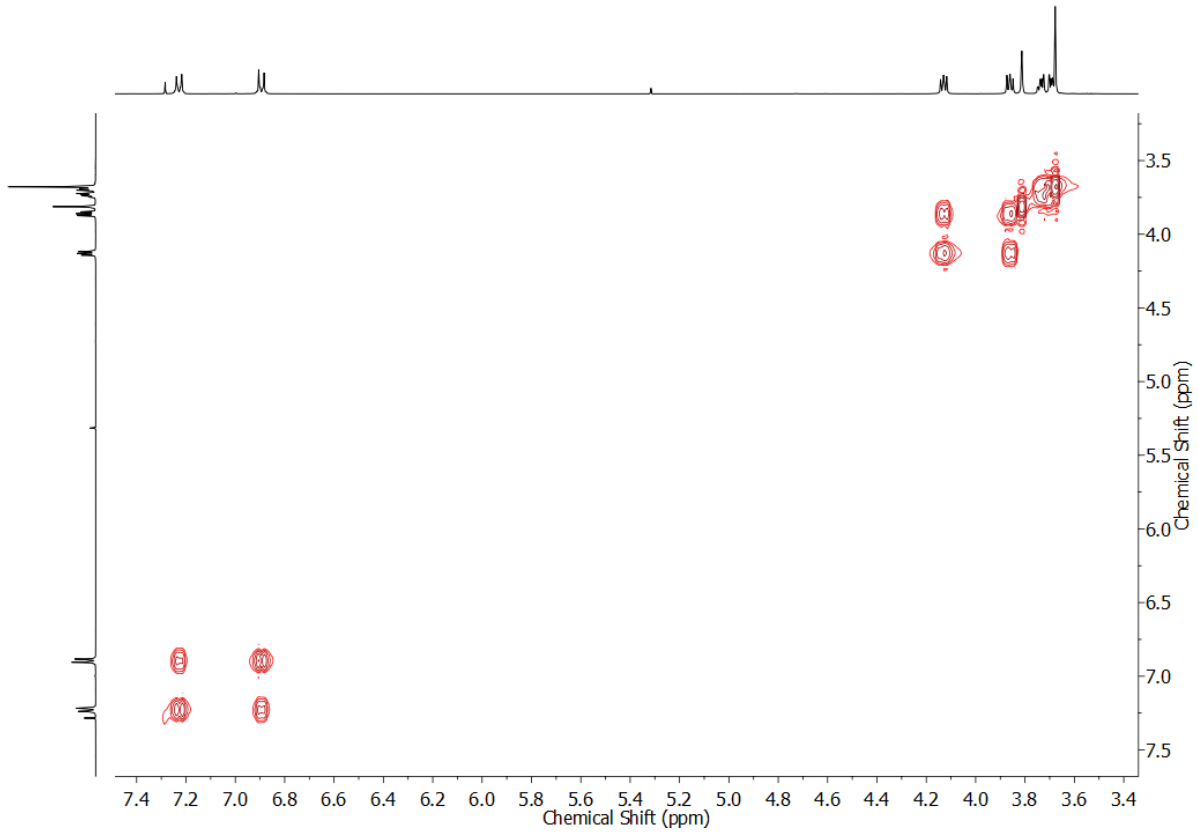


Figure S3 COSY NMR ($CDCl_3$) of **2c**.

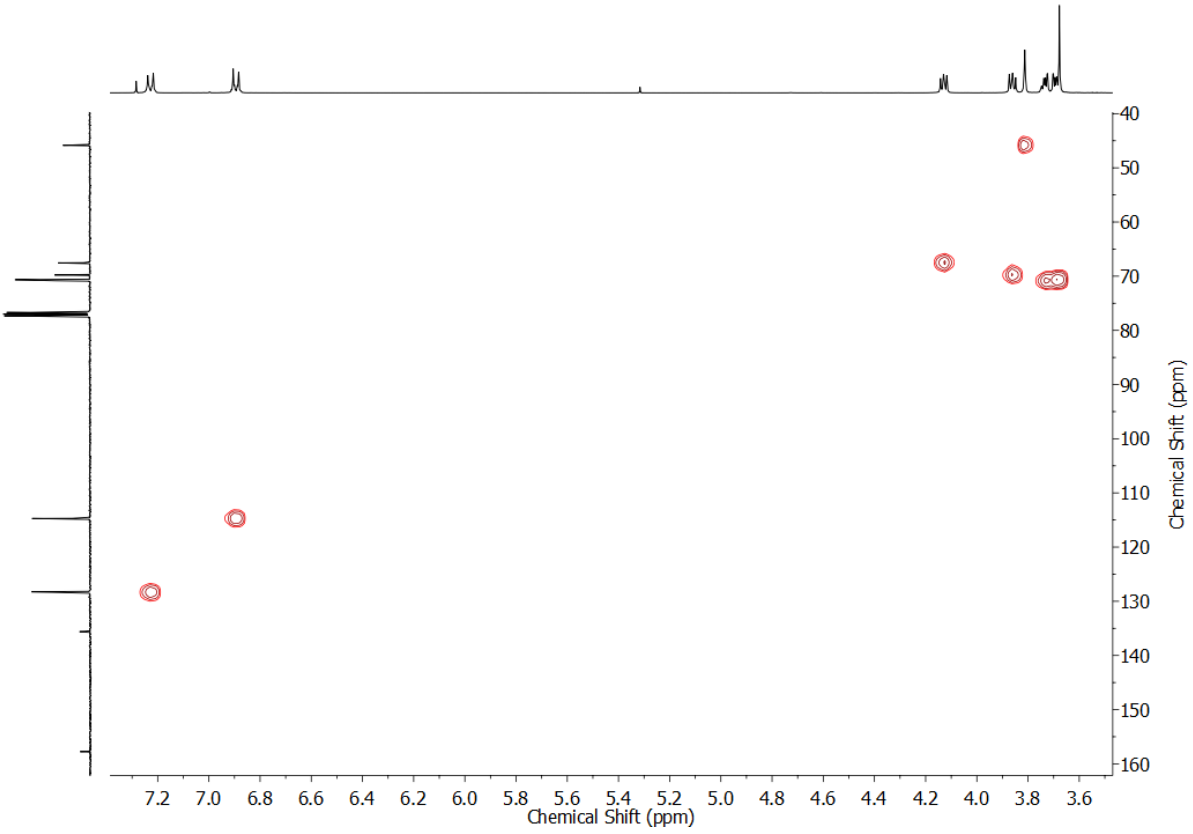


Figure S4 HSQC NMR ($CDCl_3$) of **2c**.

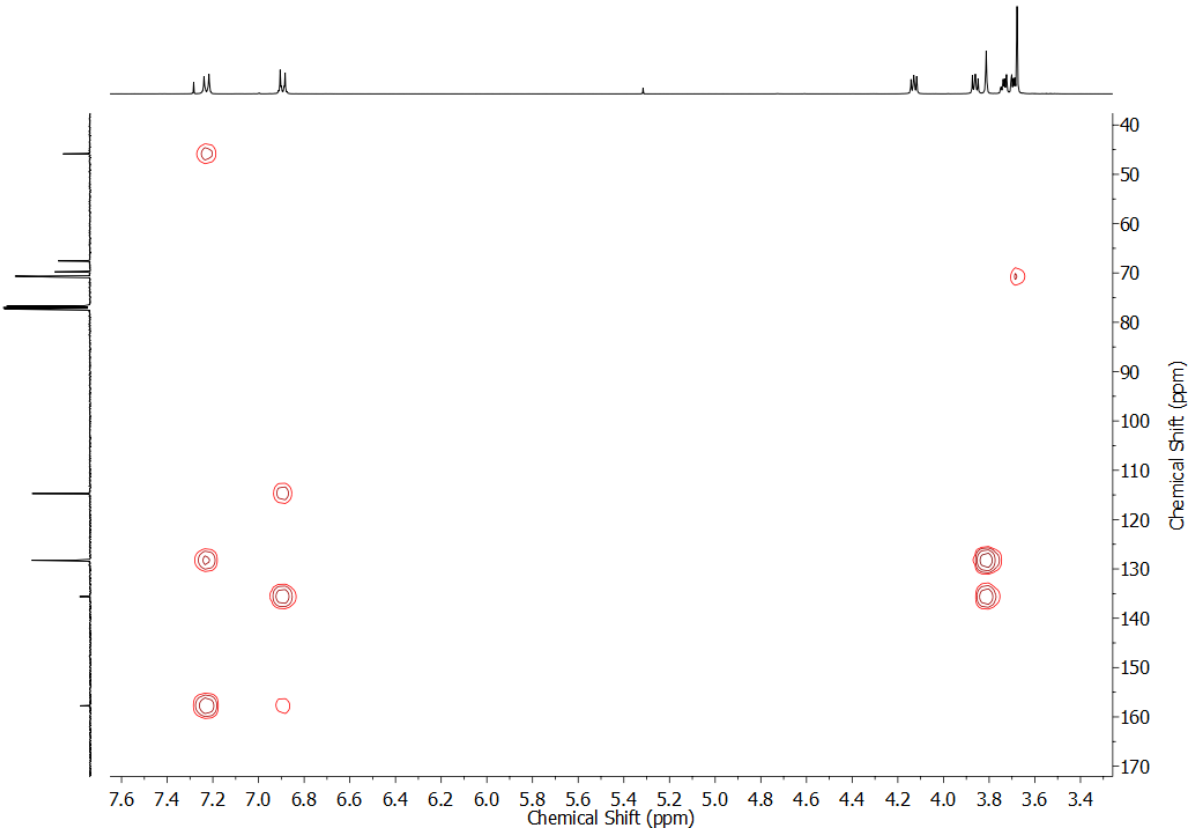
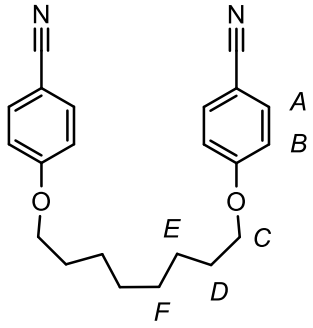


Figure S5 HMBC NMR ($CDCl_3$) of **2c**.

S2



1,8-Dibromooctane (1.36 g, 5.0 mmol, 1 eq.), 4-hydroxybenzonitrile (1.49 g, 12.5 mmol, 2.5 eq.) and K_2CO_3 (5.53 g, 40 mmol, 8 eq.) were stirred at 80 °C in MeCN (50 mL) for 17 h. The cooled reaction mixture was filtered through celite, washing through with CH_2Cl_2. After removal of the solvent *in vacuo* the crude product was purified by column chromatography on silica, eluting with 1:1 petrol/CH_2Cl_2 followed by neat CH_2Cl_2 to give **S2** as a white solid (1.42 g, 82%). M.p. 116-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (d, *J* = 8.9 Hz, 4H, H_A/H_B), 6.93 (d, *J* = 8.8 Hz, 4H, H_A/H_B), 4.00 (t, *J*, = 6.5 Hz, 4H, H_C), 1.84-1.77 (m, 4H, H_D), 1.51-1.38 (m, 8H, H_E, H_F). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.6, 134.1 (C_A/C_B), 119.4, 115.3 (C_A/C_B), 103.9, 68.5 (C_C), 29.4 (C_E/C_F), 29.1 (C_D), 26.0 (C_E/C_F). HR-ESI-MS *m/z* = 371.1718 $[M+Na]^+$ calc. 371.1735.

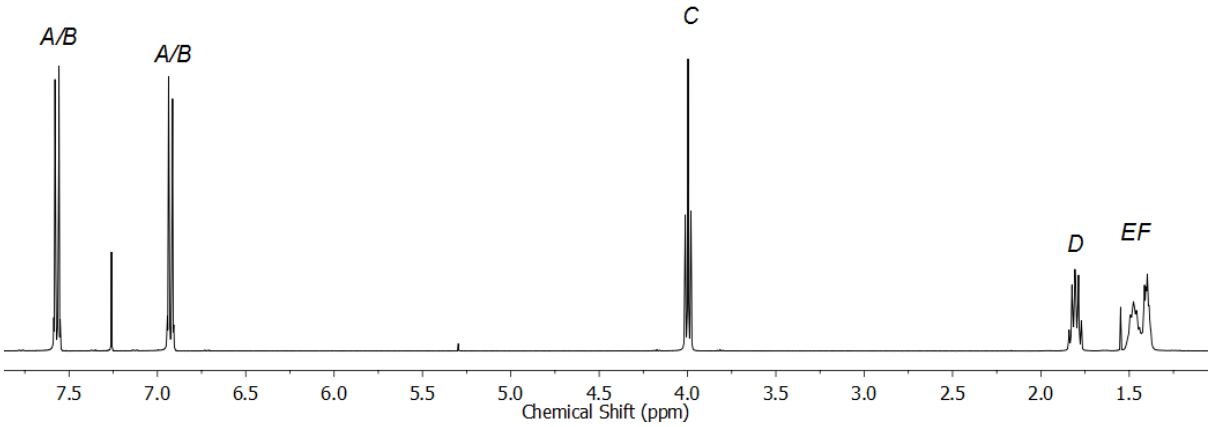


Figure S6 ^{1}H NMR ($CDCl_3$, 400 MHz) of **S2**.

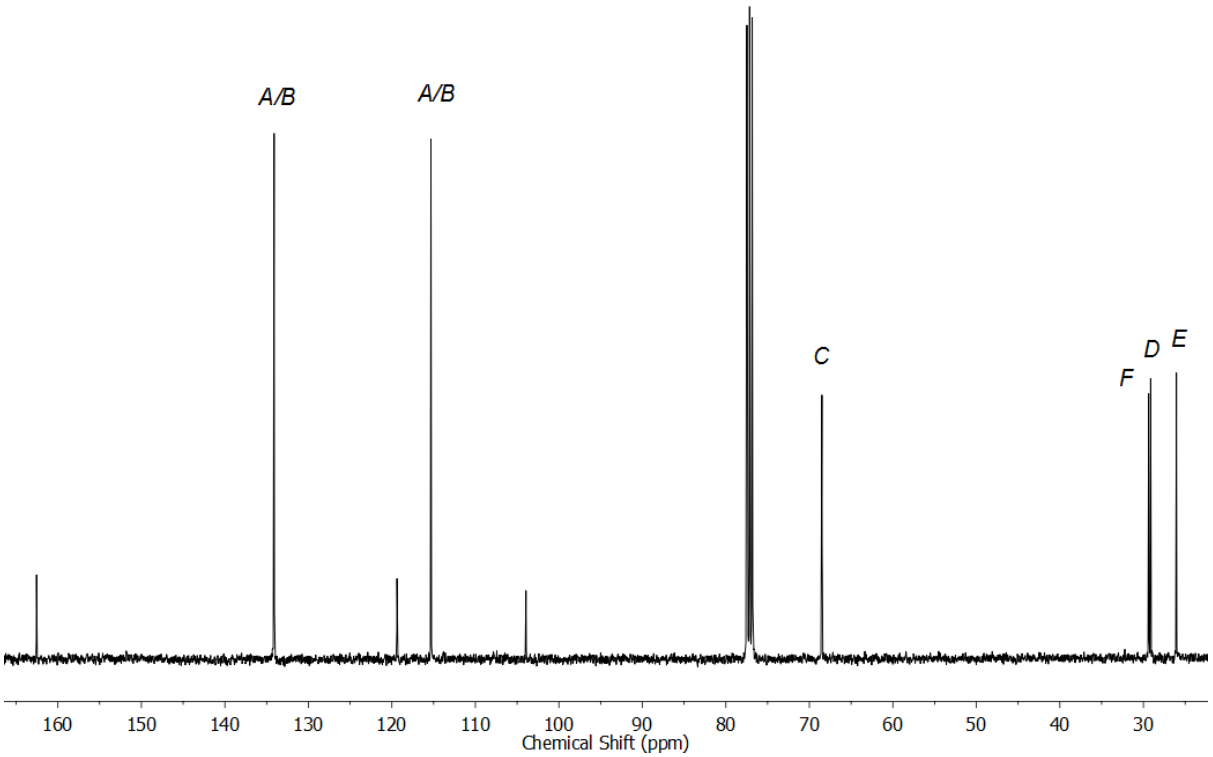


Figure S7 ^{13}C NMR ($CDCl_3$, 101 MHz) of **S2**.

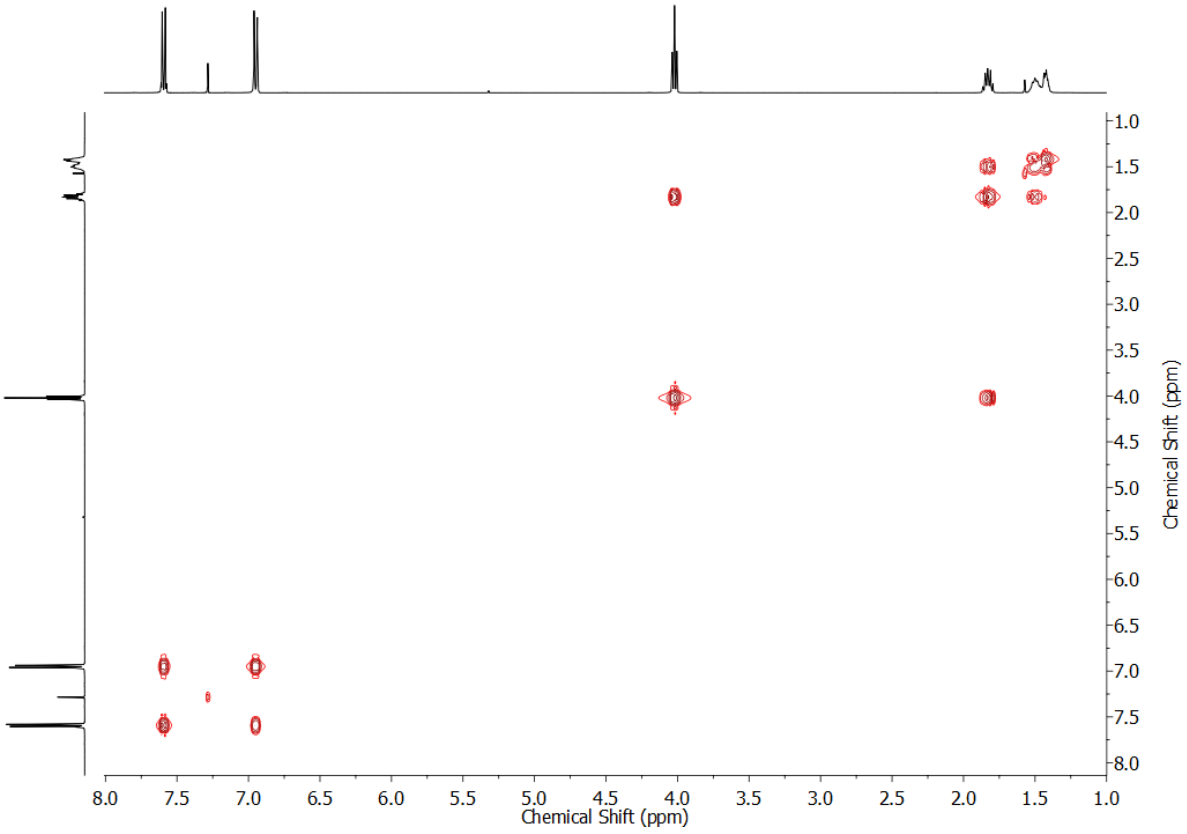


Figure S8 COSY NMR ($CDCl_3$) of **S2**.

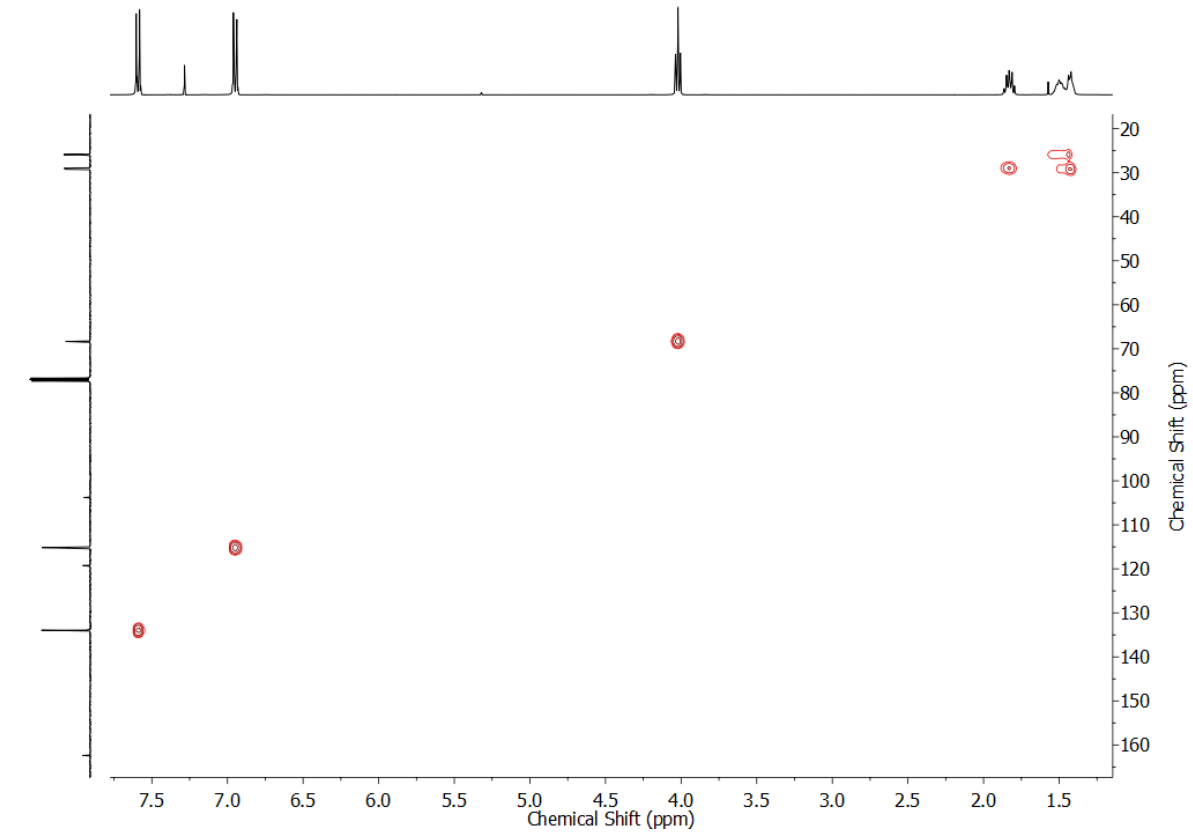


Figure S9 HSQC NMR ($CDCl_3$) of **S2**.

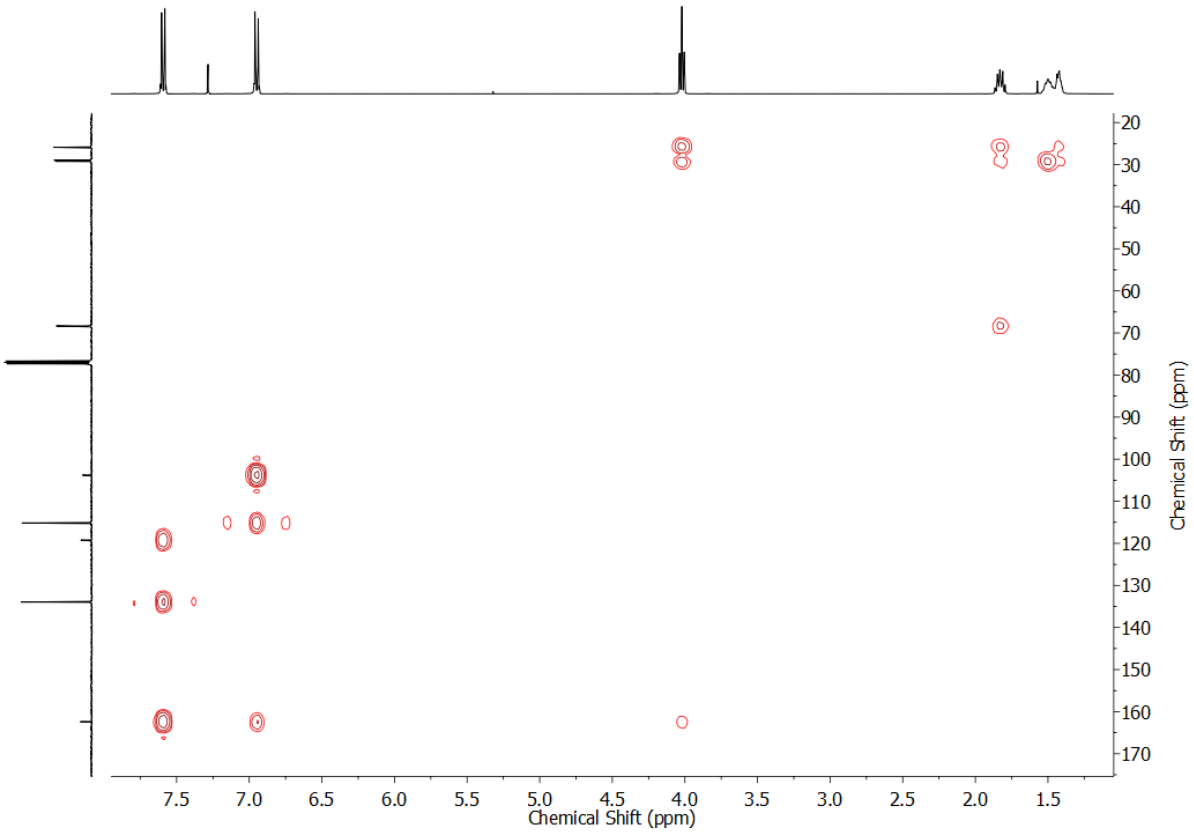
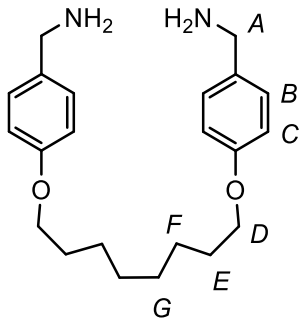


Figure S10 HMBC NMR ($CDCl_3$) of **S2**.

2d



To a stirring suspension of $LiAlH_4$ (0.759 g, 20 mmol, 8 eq.) in THF (dry, 30 mL) under N_2 was added **S2** (0.871 g, 2.5 mmol, 1 eq.) as a solid. The reaction was stirred at reflux for 4 h. H_2O (10 mL) was added carefully to the cooled reaction before filtering through celite, washing through with THF. The solvent was removed *in vacuo* and the resultant residue taken up in CH_2Cl_2 (50 mL) and washed with brine (25 mL). The organic phase was dried (MgSO4) and the solvent removed *in vacuo* to give **2d** as an off-white solid (0.422 g, 47%). M.p. 92-94 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.21 (d, J = 8.8 Hz, 4H, H_B), 6.86 (d, J = 8.6 Hz, 4H, H_C), 3.94 (t, J = 6.6 Hz, 4H, H_D), 3.80 (s, 4H, H_A), 1.80-1.75 (m, 4H, H_E), 1.47 (br. m, 4H, H_F), 1.40-1.37 (m, 4H, H_G). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 158.2, 135.6, 128.4 (C_B), 114.7 (C_C), 68.1 (C_A), 46.1 (C_D), 29.5 (C_E/C_G), 29.4 (C_E/C_G), 26.1 (C_F). HR-ESI-MS m/z = 357.2552 $[M+H]^+$ calc. 357.2542.

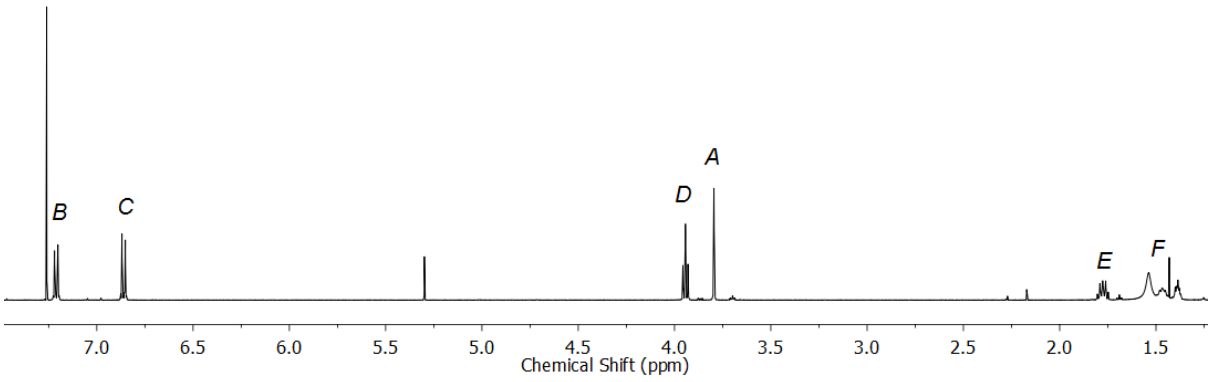


Figure S11 ^{1}H NMR ($CDCl_3$, 500 MHz) of **2d**.

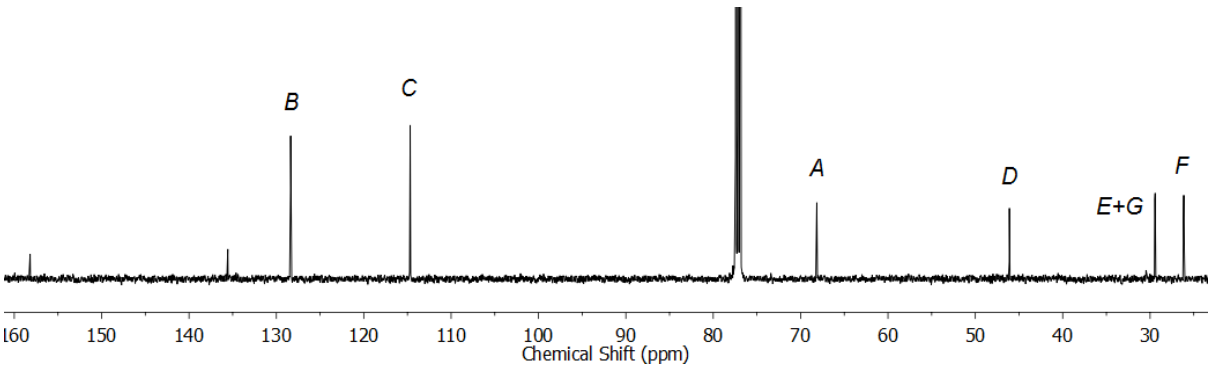


Figure S12 ^{13}C NMR ($CDCl_3$, 126 MHz) of **2d**.

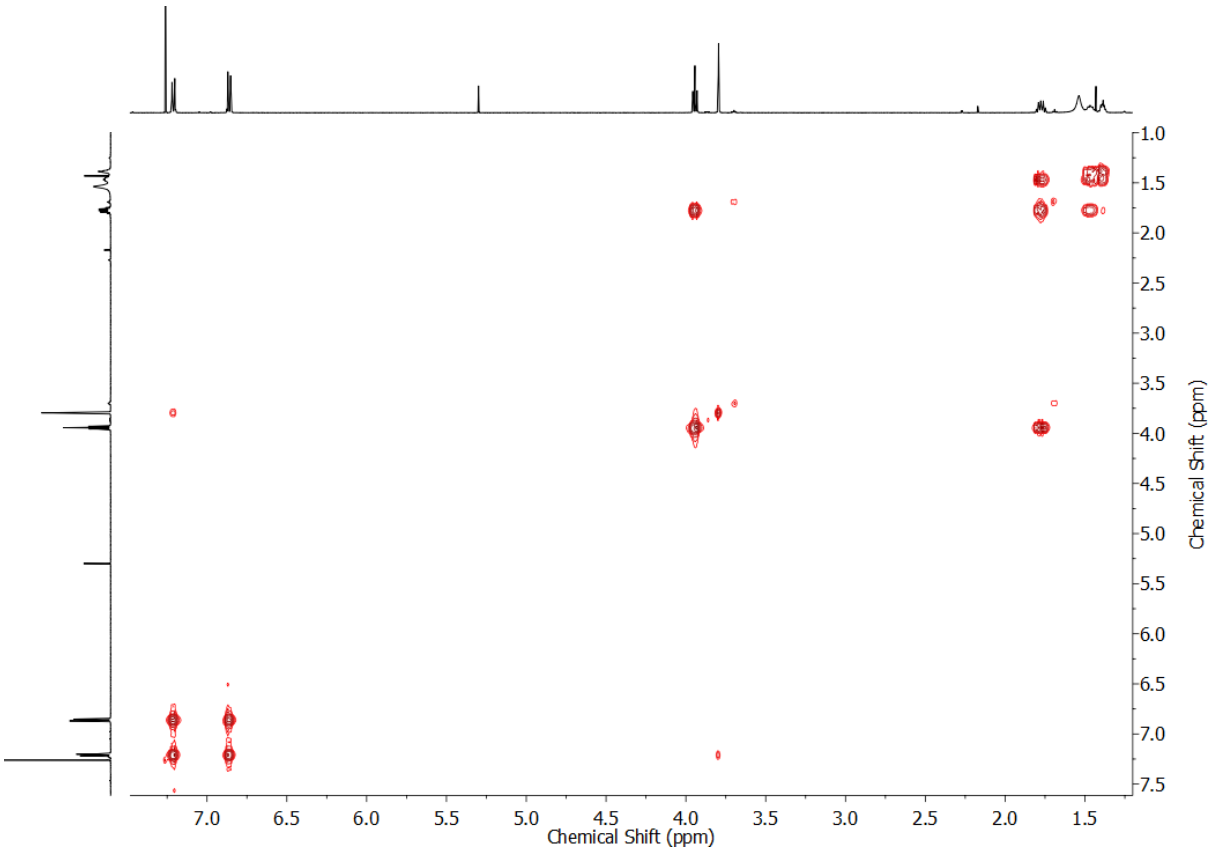


Figure S13 COSY NMR ($CDCl_3$) of **2d**.

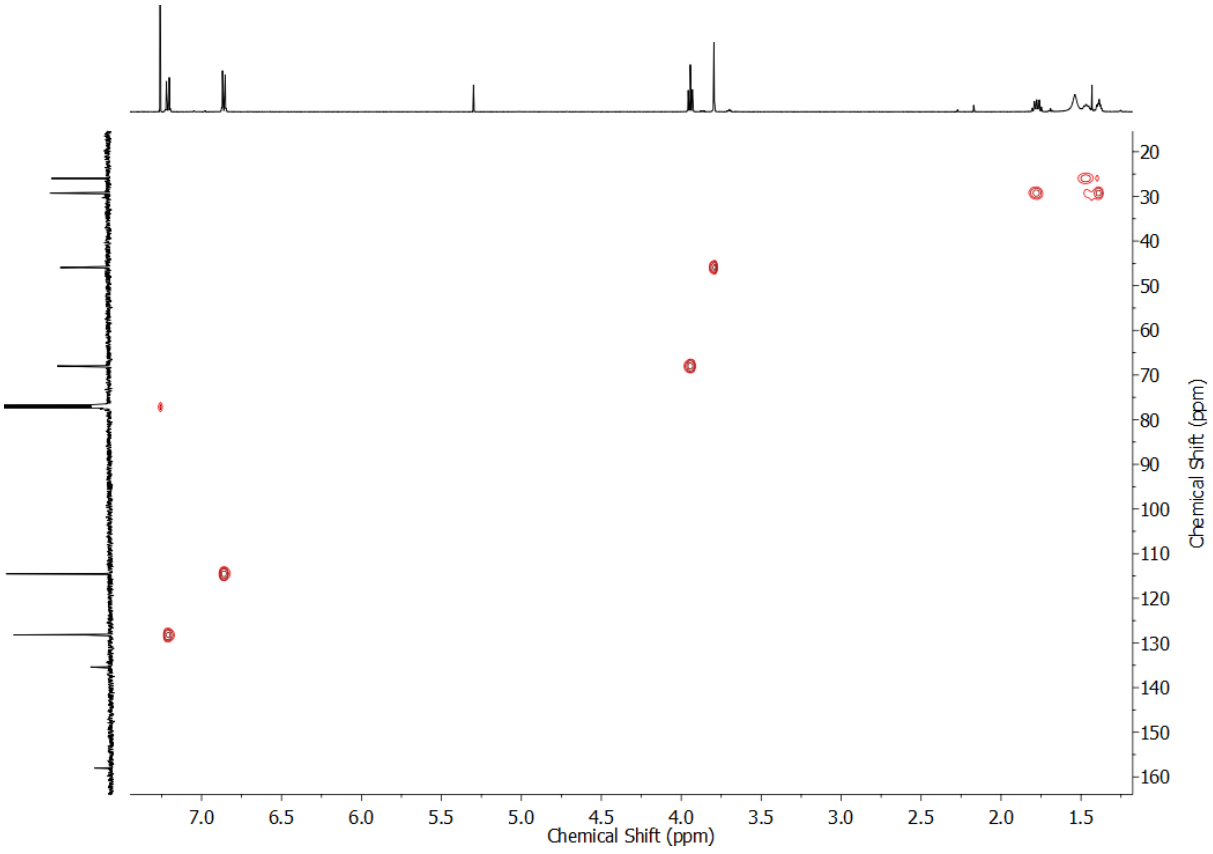


Figure S14 HSQC NMR ($CDCl_3$) of **2d**.

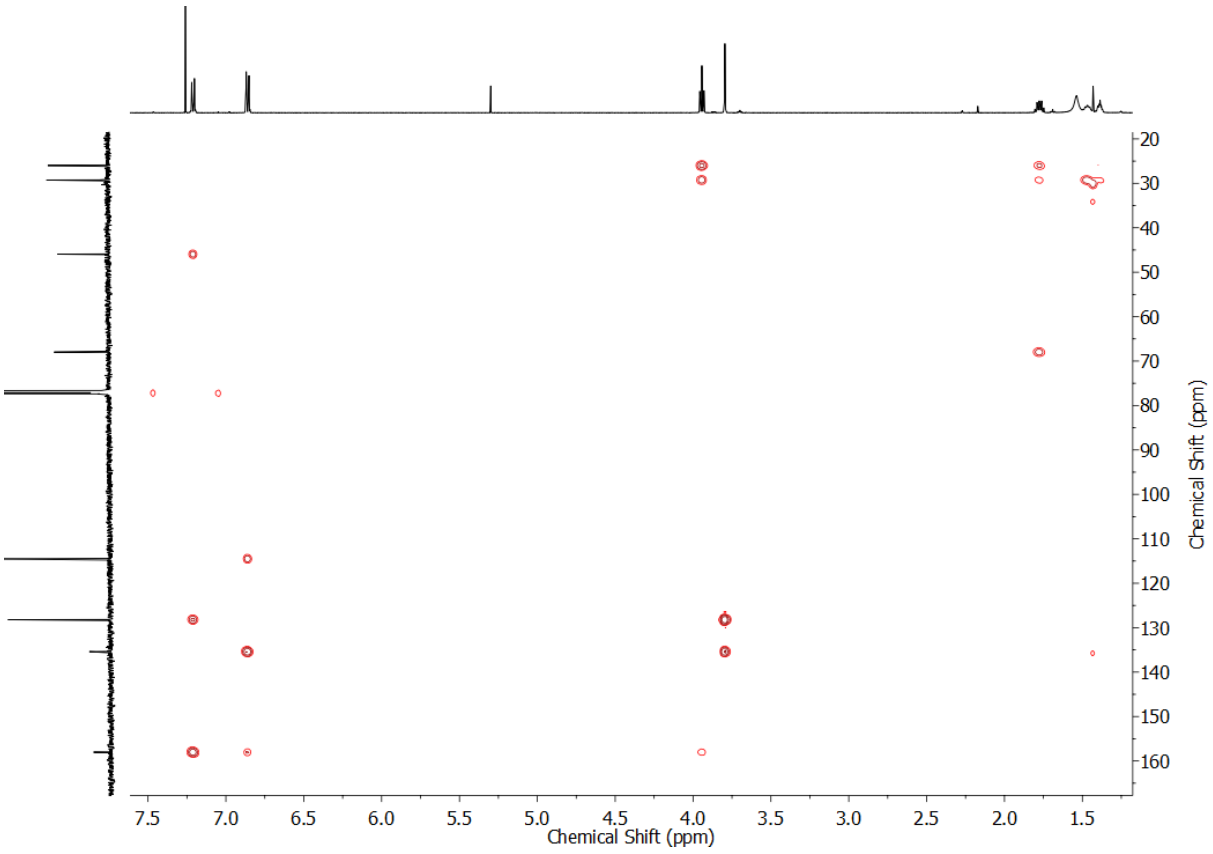


Figure S15 HMBC NMR ($CDCl_3$) of **2d**.

Synthesis and Characterisation of Macrocycles and [2]Catenanes

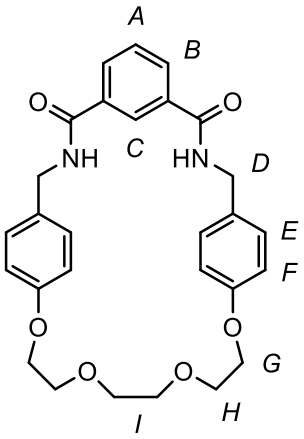
General Procedure

1/**5**/**6** (0.102 g, 0.50 mmol, 1 eq.) in $CHCl_3$ (dry, 40 mL) and **2** (0.50 mmol, 1 eq.) in $CHCl_3$ (dry, 40 mL) were added simultaneously via syringe pump to NEt_3 (0.35 mL, 2.5 mmol, 5 eq.) in $CHCl_3$ (dry, 40 mL) over 2 h at rt under N_2 before stirring for an additional 16 h. The reaction mixture was washed with 1 M $HCl_{(aq)}$ (50 mL), 1 M $KOH_{(aq)}$ (50 mL) and brine (50 mL), dried ($MgSO_4$) and the solvent removed *in vacuo*. The products were purified by column chromatography on silica eluting with CH_2Cl_2 with a step gradient in 10% increments of acetone up to 50% acetone/CH_2Cl_2.

Macrocycle 3a and [2]Catenane 4a

Using the general procedure with **1** and **2a** (0.180 g, 0.5 mmol) gave **3a** (0.104 g, 42%) as a white solid and **4a** (0.053 g, 22%) as a white solid.

Macrocycle 3a



M.p. 202-204 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.06 (dd, *J* = 7.8, 1.7 Hz, 2H, H_B), 7.60 (br. t, *J* = 1.7 Hz, 1H, H_C), 7.54 (t, *J* = 7.8 Hz, 1H, H_A), 7.24 (d, *J* = 8.6 Hz, 4H, H_E), 6.87 (d, *J* = 8.6 Hz, 4H, H_F), 6.23 (br. m, 2H, H_{NH}), 4.50 (d, *J* = 5.1, 4H, H_D), 4.13-4.11 (m, 4H, H_G), 3.86-3.84 (m, 4H, H_H), 3.71 (s, 4H, H_I). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 166.6, 158.8, 134.8, 131.4 (C_B), 130.1 (C_E), 129.8, 129.8 (C_A), 122.9 (C_C), 115.1 (C_F), 70.9 (C_I), 69.8 (C_H), 67.6 (C_G), 44.4 (C_D). HR-ESI-MS *m/z* = 491.2190 $[M+H]^+$ calc. 491.2182.

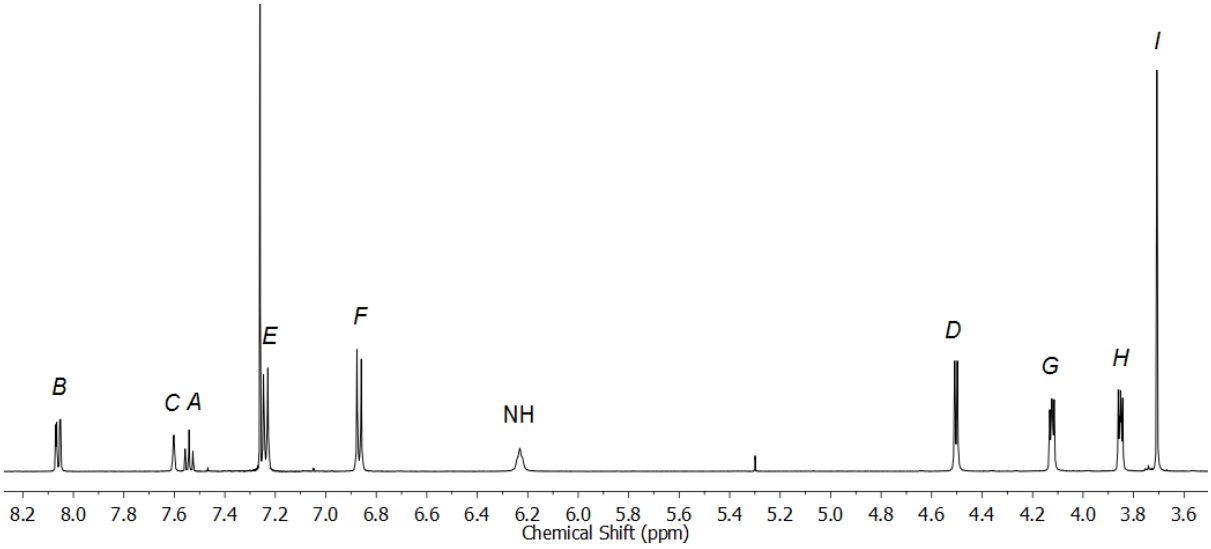


Figure S16 ^{1}H NMR ($CDCl_3$, 500 MHz) of **3a**.

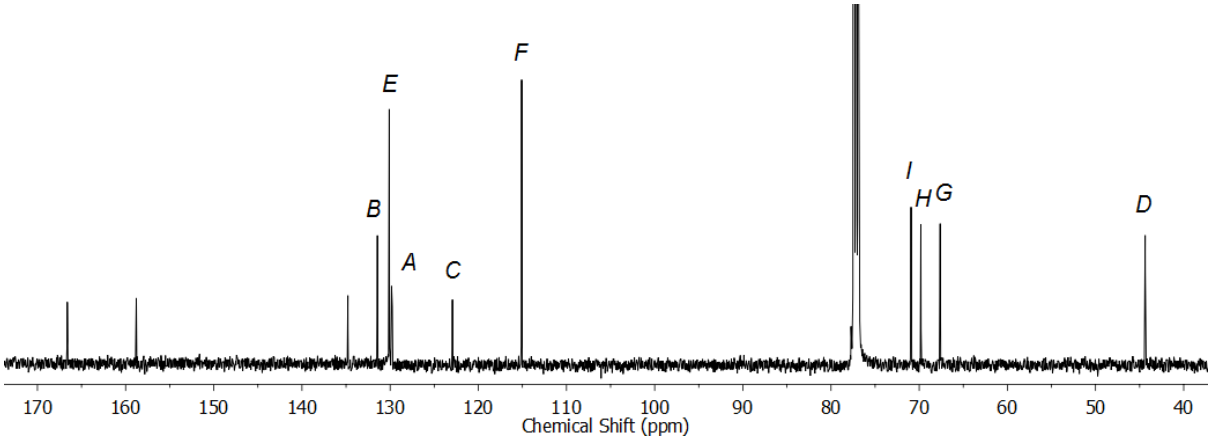


Figure S17 ^{13}C NMR ($CDCl_3$, 126 MHz) of **3a**.

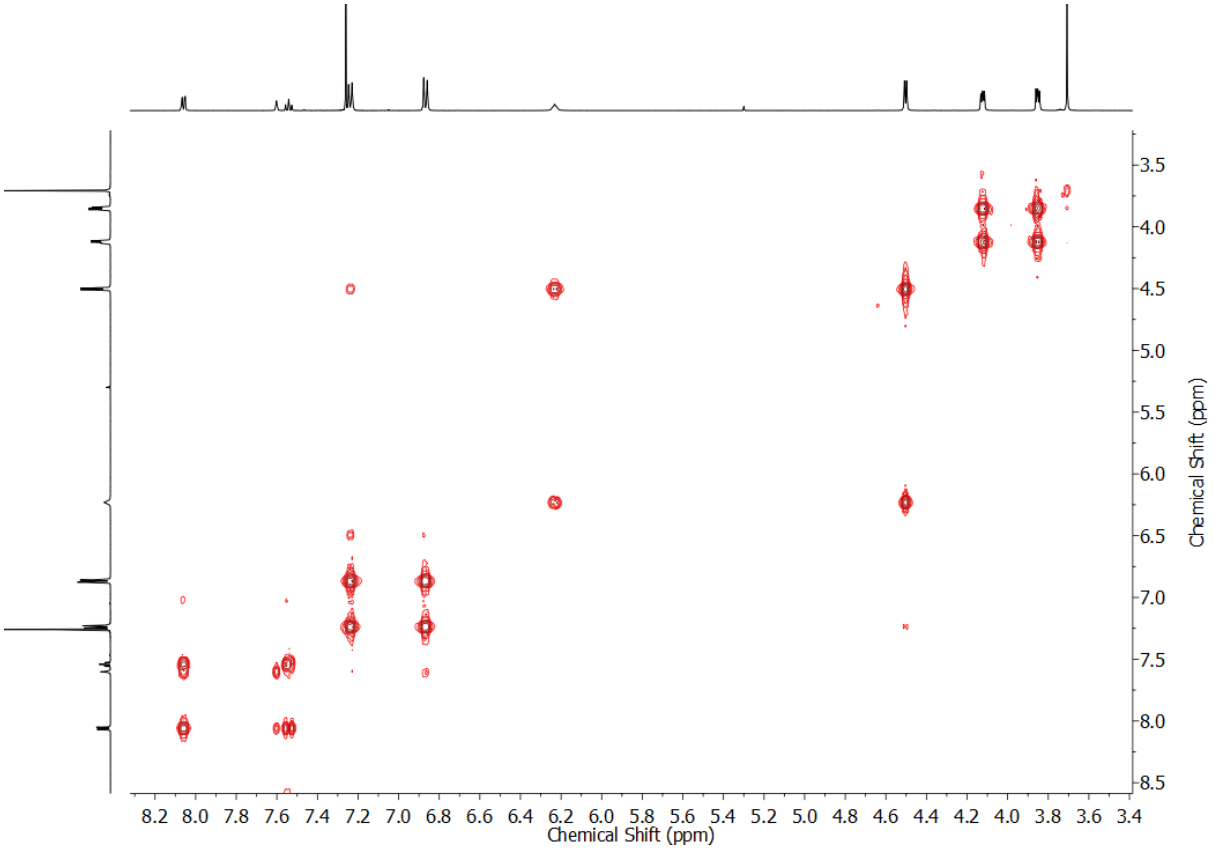


Figure S18 COSY NMR ($CDCl_3$) of **3a**.

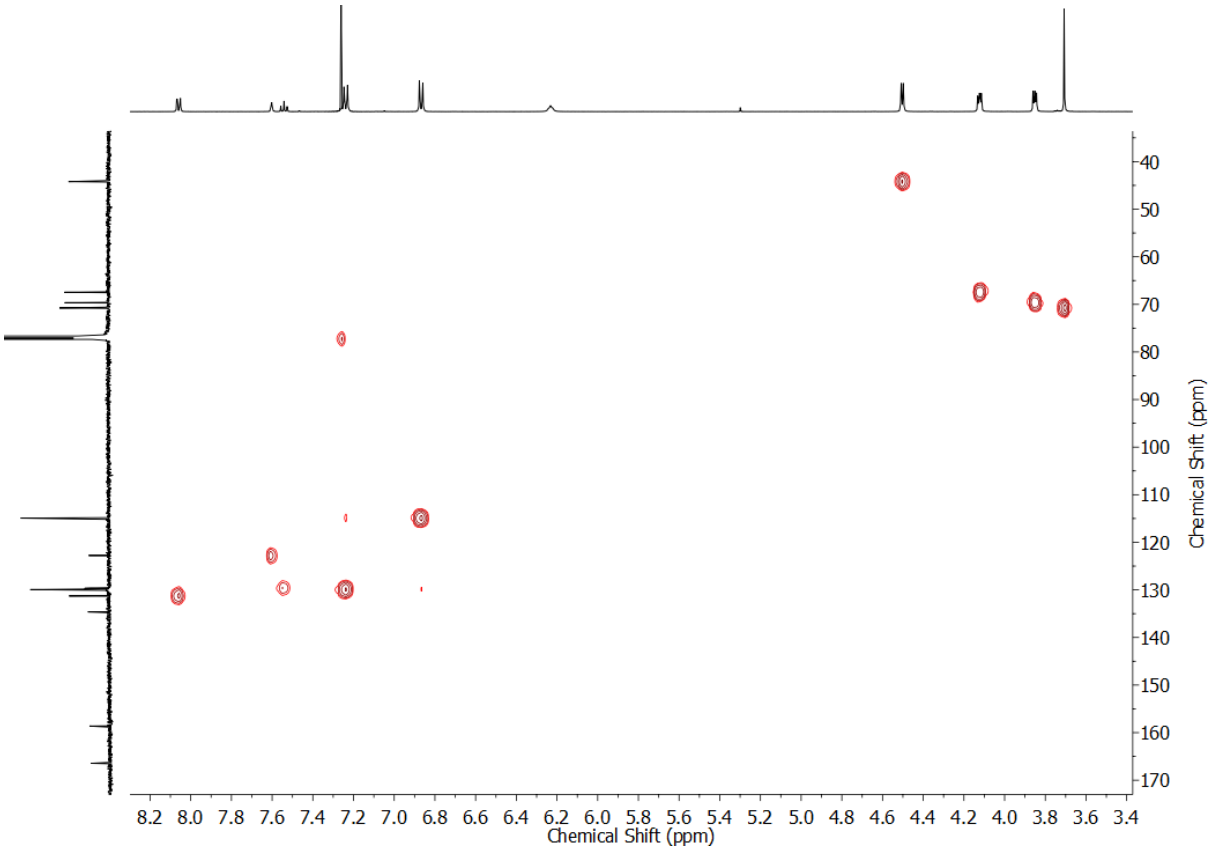


Figure S19 HSQC NMR ($CDCl_3$) of **3a**.

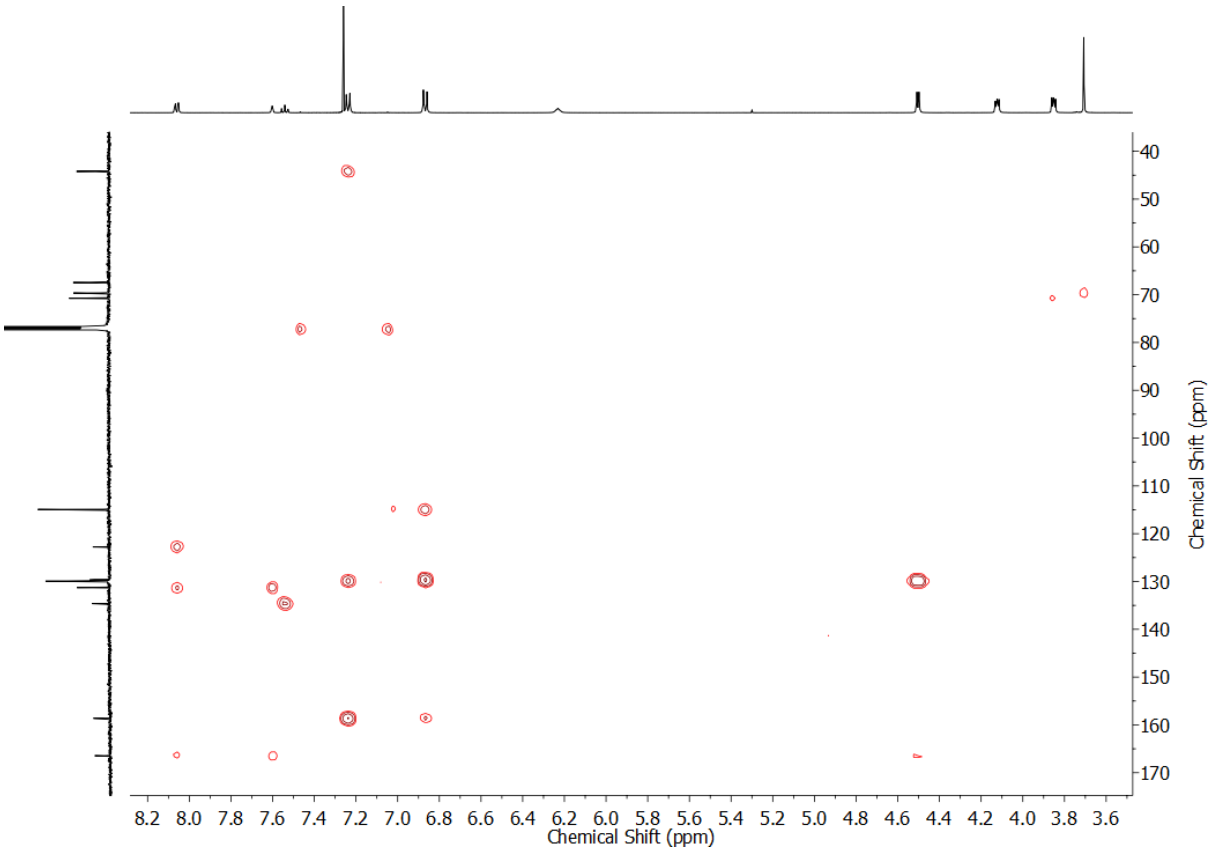
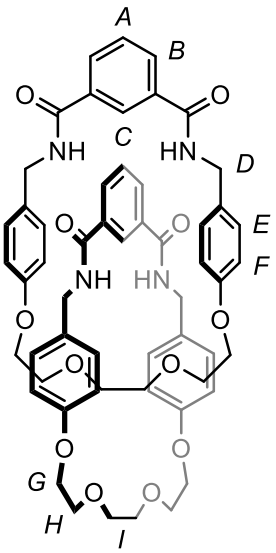


Figure S20 HMBC NMR ($CDCl_3$) of **3a**.

[2]Catenane 4a



M.p. 206-208 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.14 (dd, *J* = 7.8, 1.6 Hz, 4H, H_B), 8.04 (br. s, 2H, H_C), 7.53 (t, *J* = 7.8 Hz, 2H, H_A), 7.05 (d, *J* = 8.6 Hz, 8H, H_E), 7.01 (br. m, 4H, H_{NH}), 6.51 (d, *J* = 8.3 Hz, 8H, H_F), 4.31 (d, *J* = 4.3 Hz, 8H, H_D), 3.79 (br. m, 8H, H_G), 3.44 (br. m, 8H, H_H), 3.28 (s, 8H, H_I). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 166.0, 157.9, 133.5, 132.2 (C_B), 130.5 (C_E), 129.3, 129.0 (C_A), 123.3 (C_C), 114.3 (C_F), 70.7 (C_I), 69.5 (C_H), 67.4 (C_G), 44.8 (C_D). HR-ESI-MS *m/z* = 981.4290 $[M+H]^+$ calc. 981.4286.

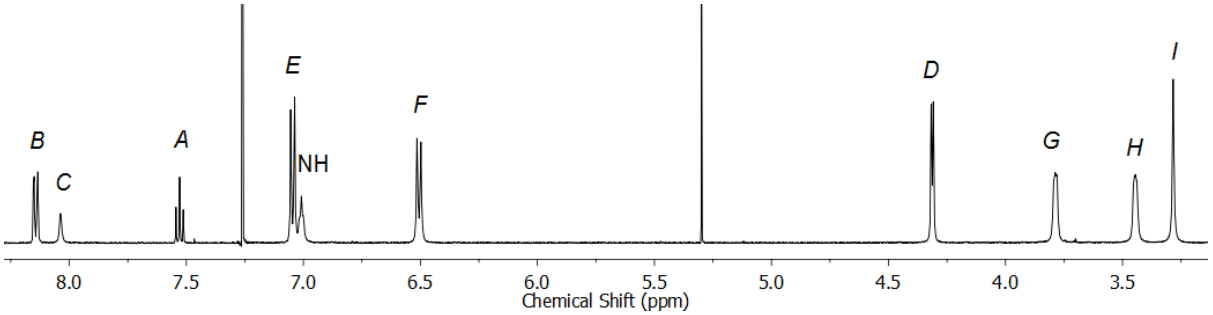


Figure S21 ^{1}H NMR ($CDCl_3$, 500 MHz) of **4a**.

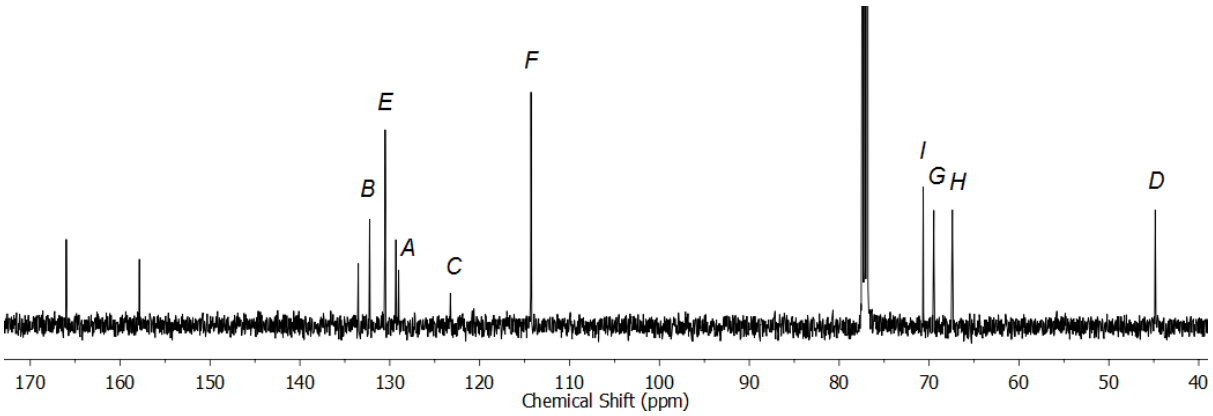


Figure S22 ^{13}C NMR ($CDCl_3$, 126 MHz) of **4a**.

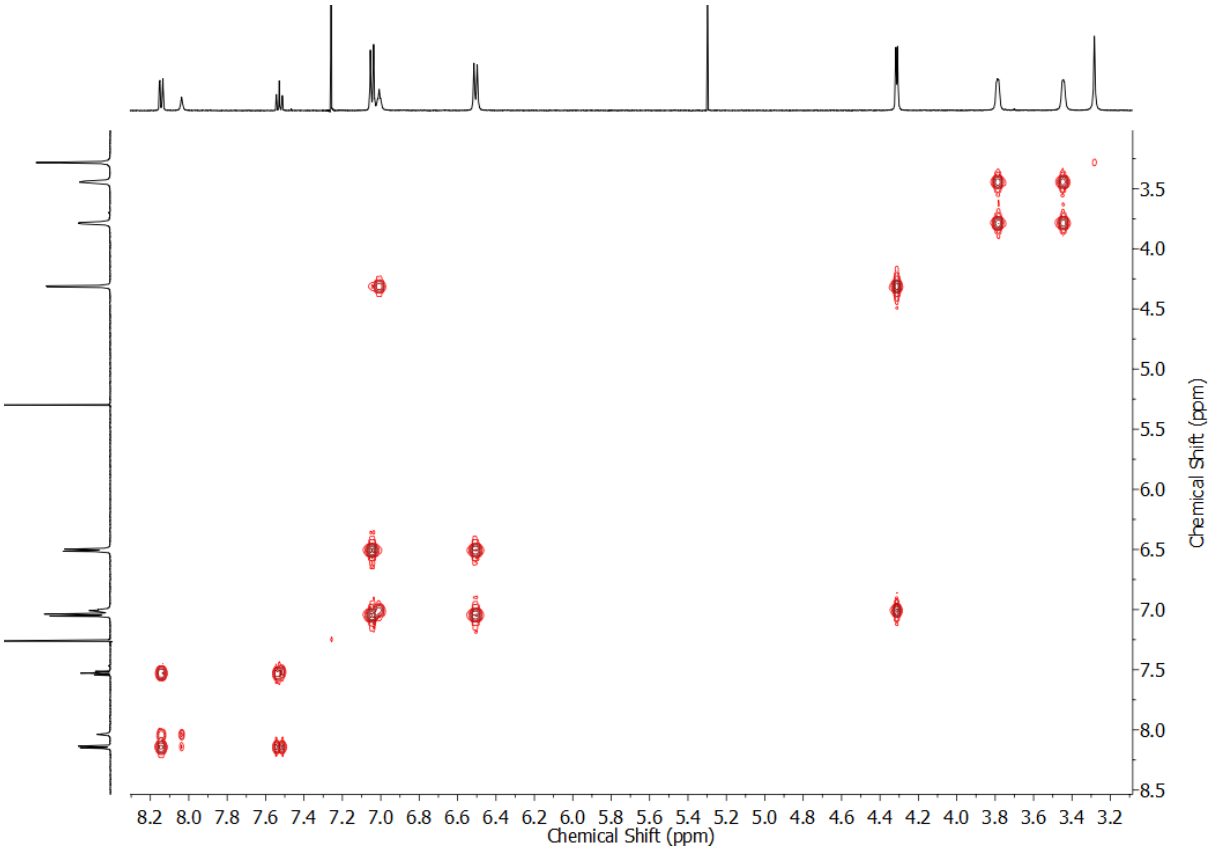


Figure S23 COSY NMR ($CDCl_3$) of **4a**.

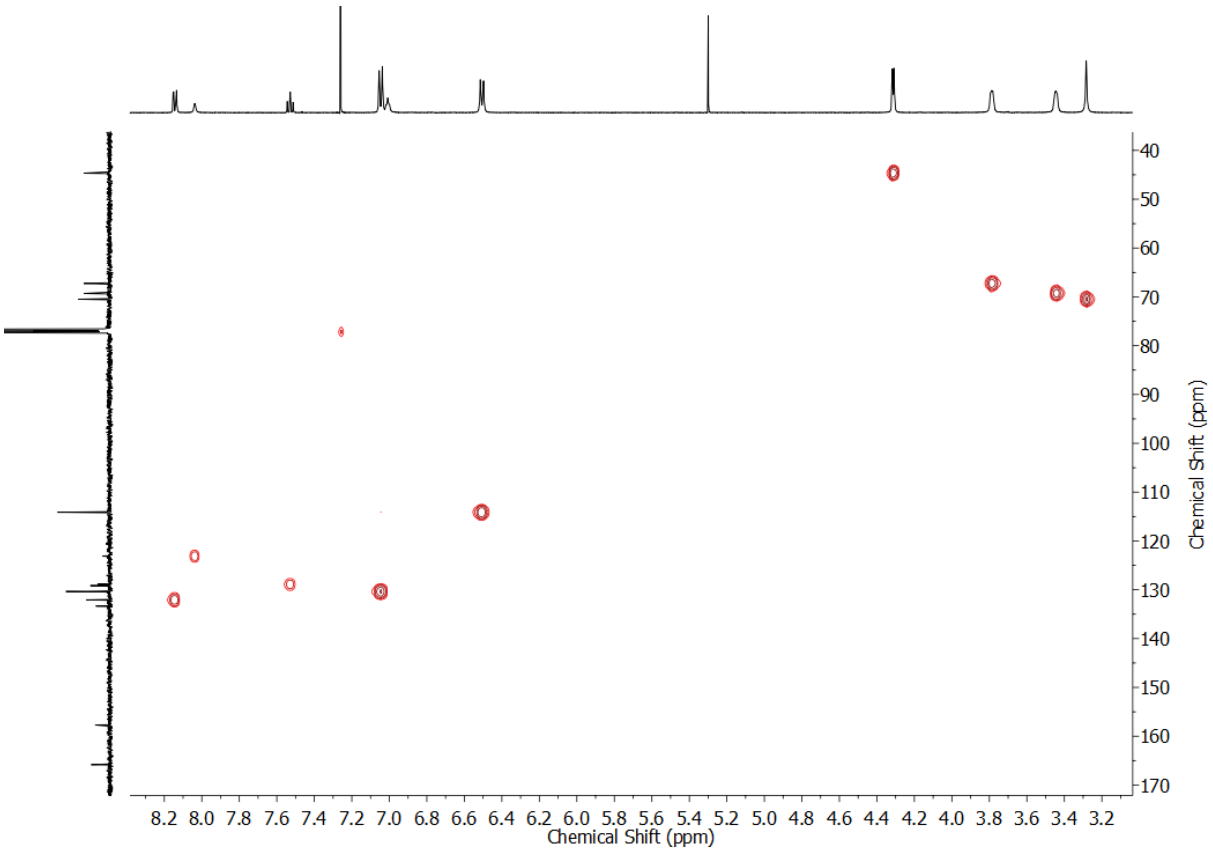


Figure S24 HSQC NMR ($CDCl_3$) of **4a**.

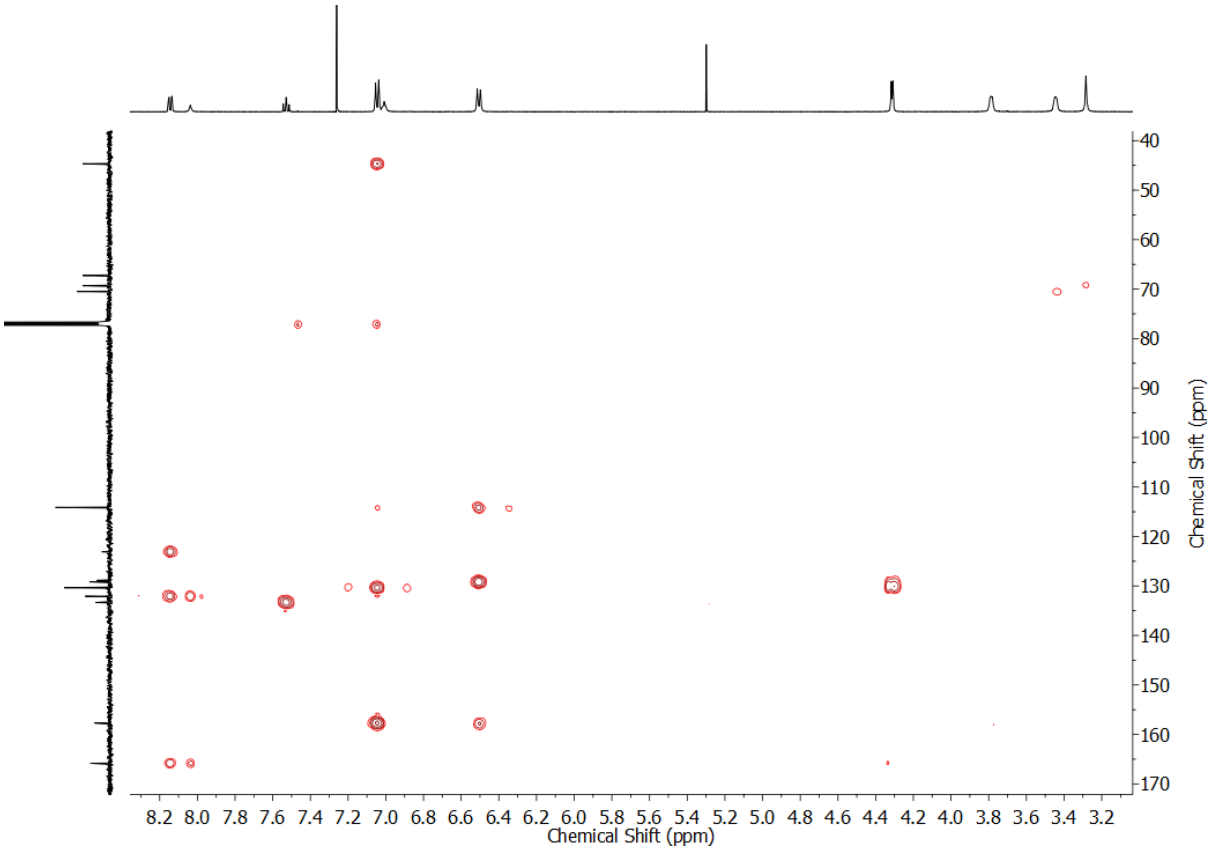


Figure S25 HMBC NMR ($CDCl_3$) of **4a**.

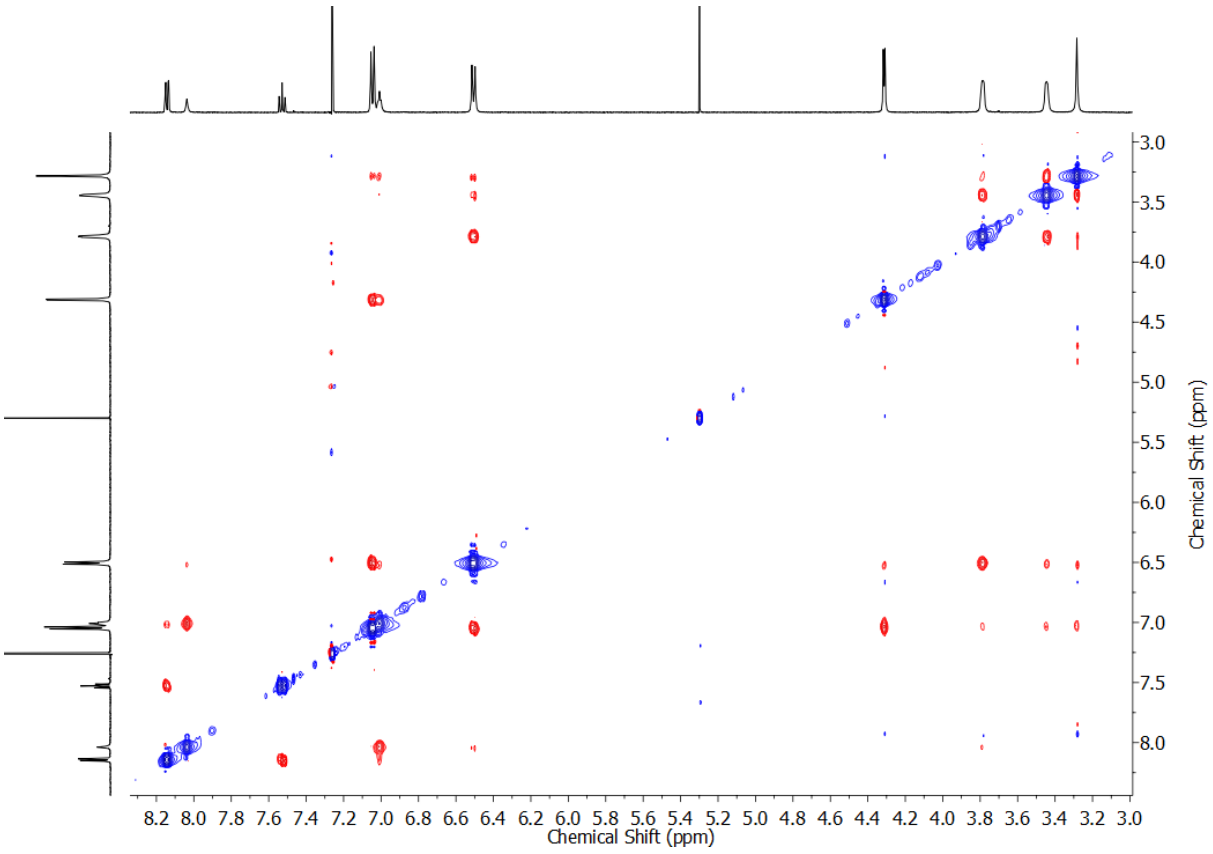


Figure S26 NOESY NMR ($CDCl_3$) of **4a**.

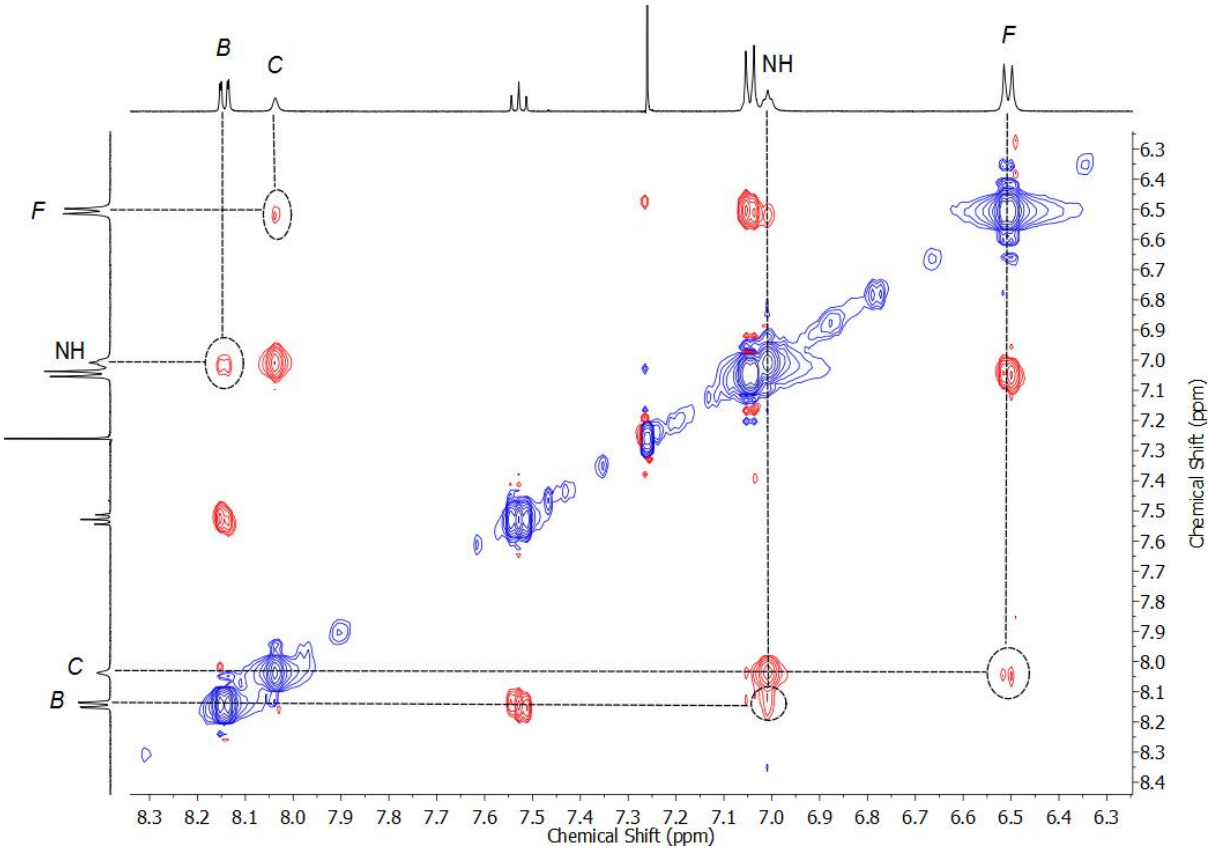


Figure S27 Partial NOESY NMR ($CDCl_3$) of **4a**. Cross peaks indicative of catenane structure are highlighted.

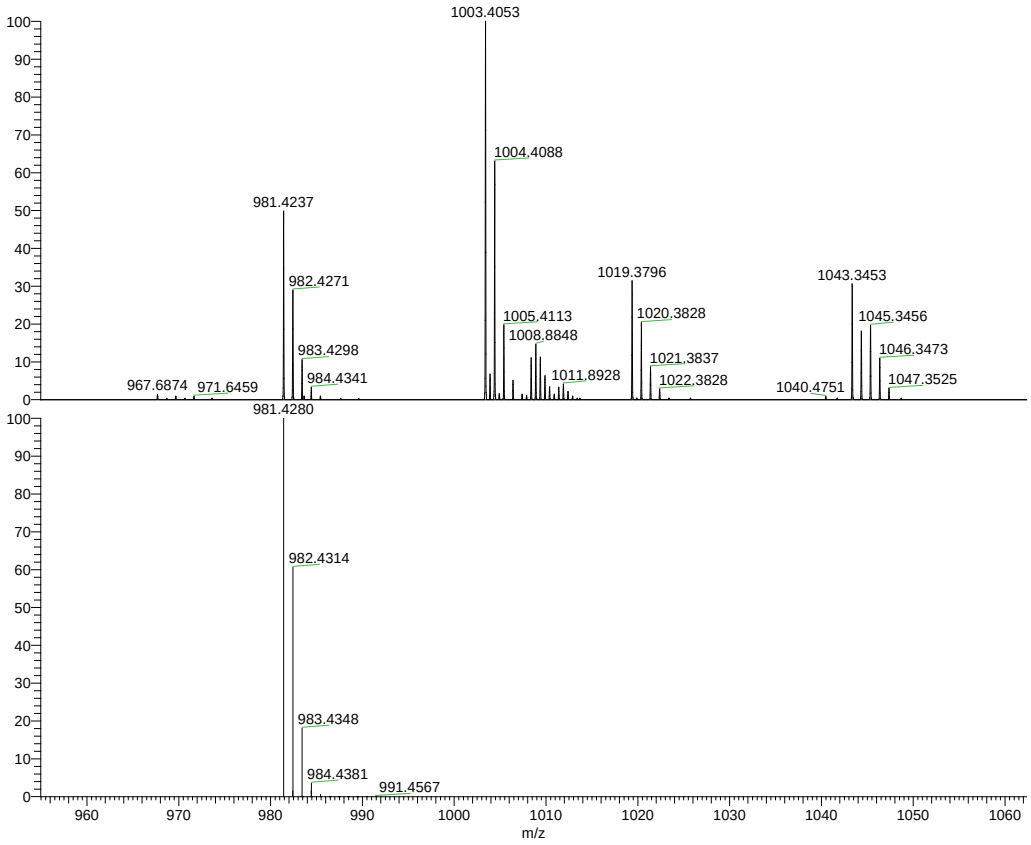


Figure S28 Partial HR-ESI-MS of **4a** (top) and calculated isotopic pattern for [**4a**+H]$^+$ (bottom).

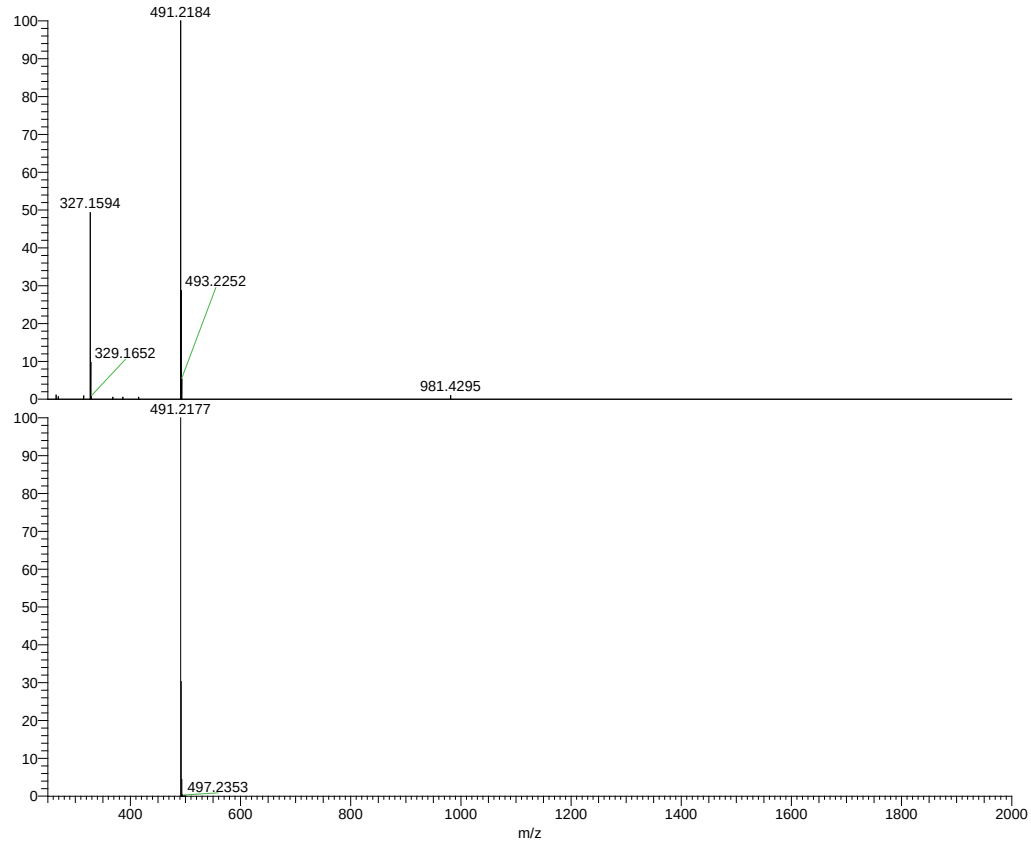
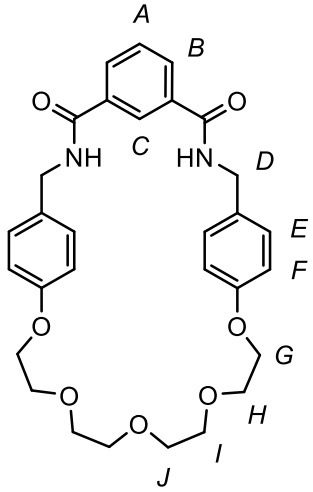


Figure S29 HR-ESI-MSMS of *m/z* = 981 peak (top) and calculated isotopic pattern for [**3a**+H]$^+$ (bottom).

Macrocycle 3b and [2]Catenane 4b

Using the general procedure with **1** and **2b** (0.202 g, 0.5 mmol) gave **3b** (0.082 g, 31%) as a white solid and **4b** (0.137 g, 51%) as a white foam.



Macrocycle 3b

M.p. 209-211 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (br. s, 1H, H_C), 7.95 (dd, J = 7.8, 1.5 Hz, 2H, H_B), 7.42 (t, J = 7.7 Hz, 1H, H_A), 7.14 (d, J = 8.6 Hz, 4H, H_E), 6.89 (t, J = 5.3 Hz, 2H, H_{NH}), 6.69 (d, J = 8.6 Hz, 4H, H_F), 4.47 (d, J = 5.3 Hz, 4H, H_D), 3.97-3.95 (m, 4H, H_G), 3.80-3.78 (m, 4H, H_H), 3.70 (s, 8H, H_I, H_J). ^{13}C NMR (400 MHz, $CDCl_3$) δ: 166.6, 158.2, 134.1, 131.3 (C_B), 130.2, 129.6 (C_E), 129.3 (C_A), 123.8 (C_C), 114.8 (C_F), 71.0 (C_I/C_J), 70.9 (C_I/C_J), 69.7 (C_H), 67.5 (C_G), 44.1 (C_D). HR-ESI-MS m/z = 535.2441 $[M+H]^+$ calc. 535.2444.

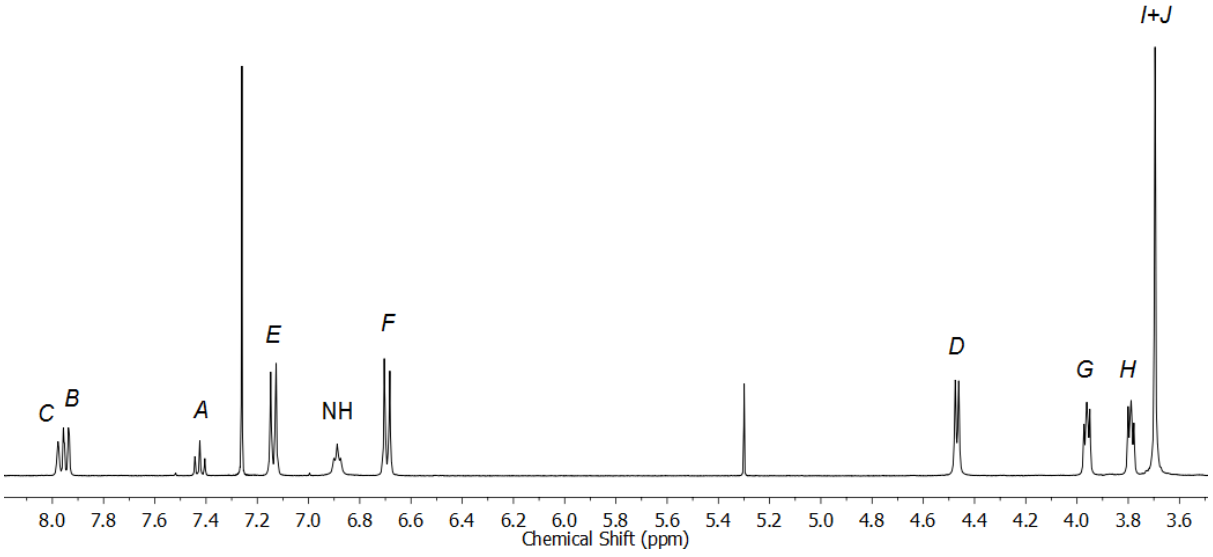


Figure S30 ^{1}H NMR ($CDCl_3$, 400 MHz) of **3b**.

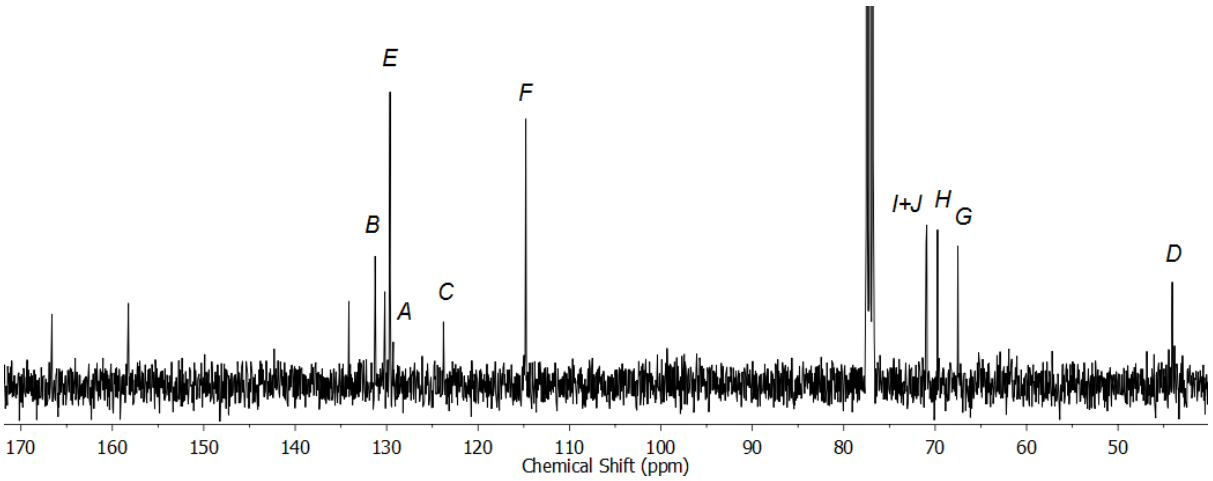


Figure S31 ^{13}C NMR ($CDCl_3$, 101 MHz) of **3b**.

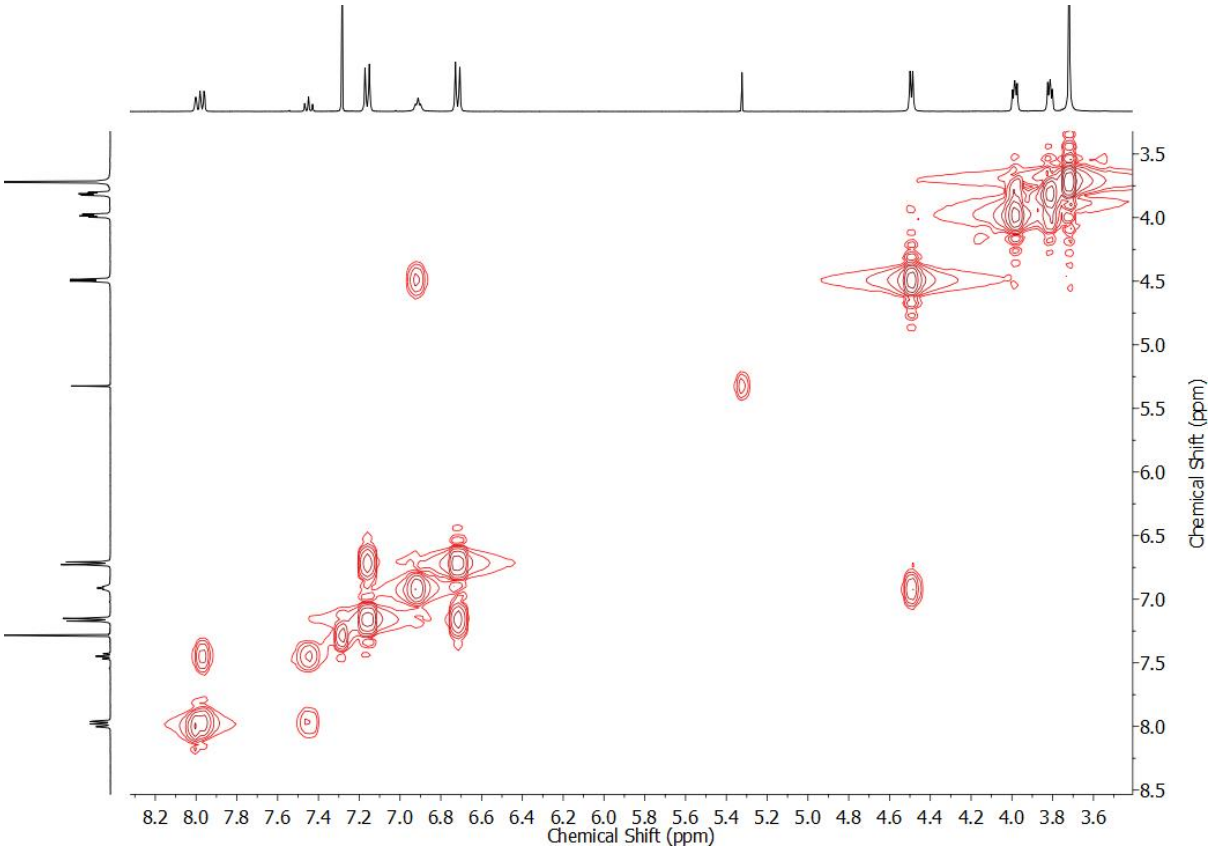


Figure S32 COSY NMR ($CDCl_3$) of **3b**.

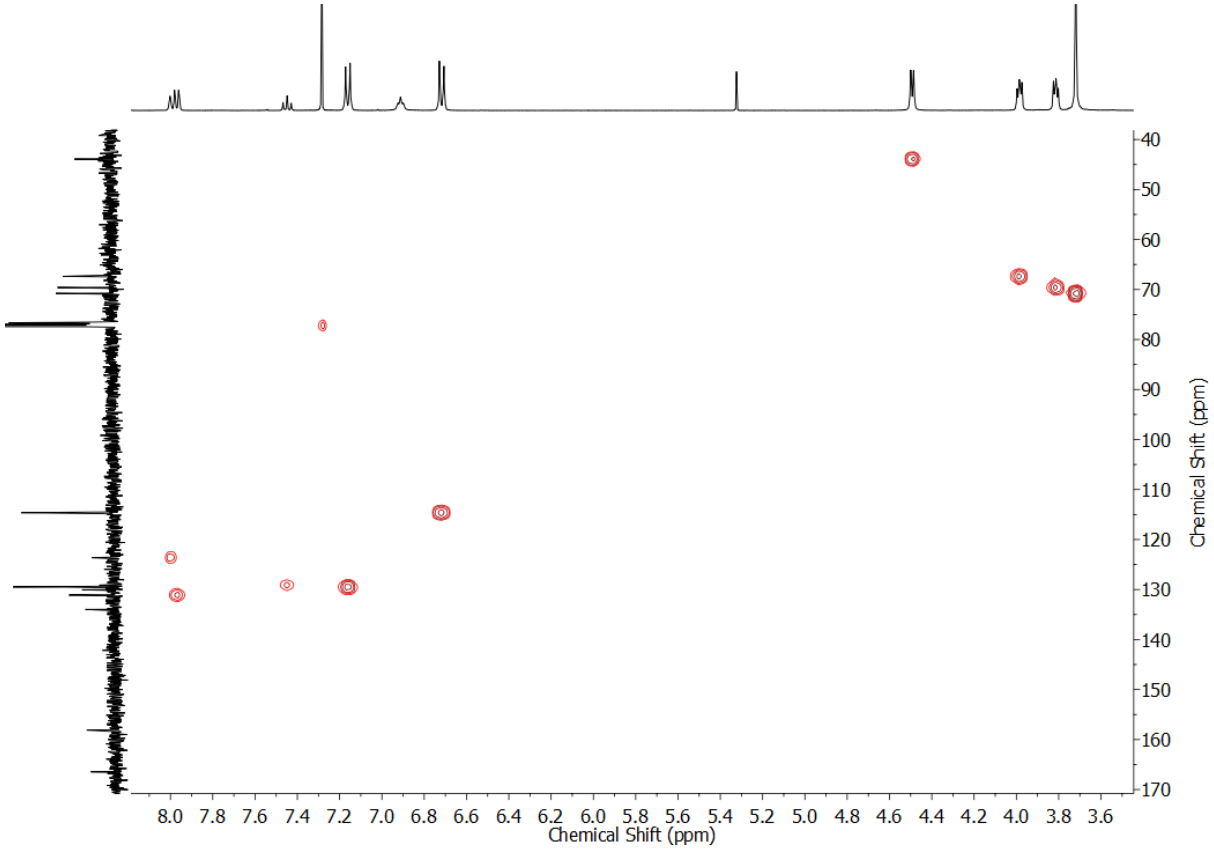


Figure S33 HSQC NMR ($CDCl_3$) of **3b**.

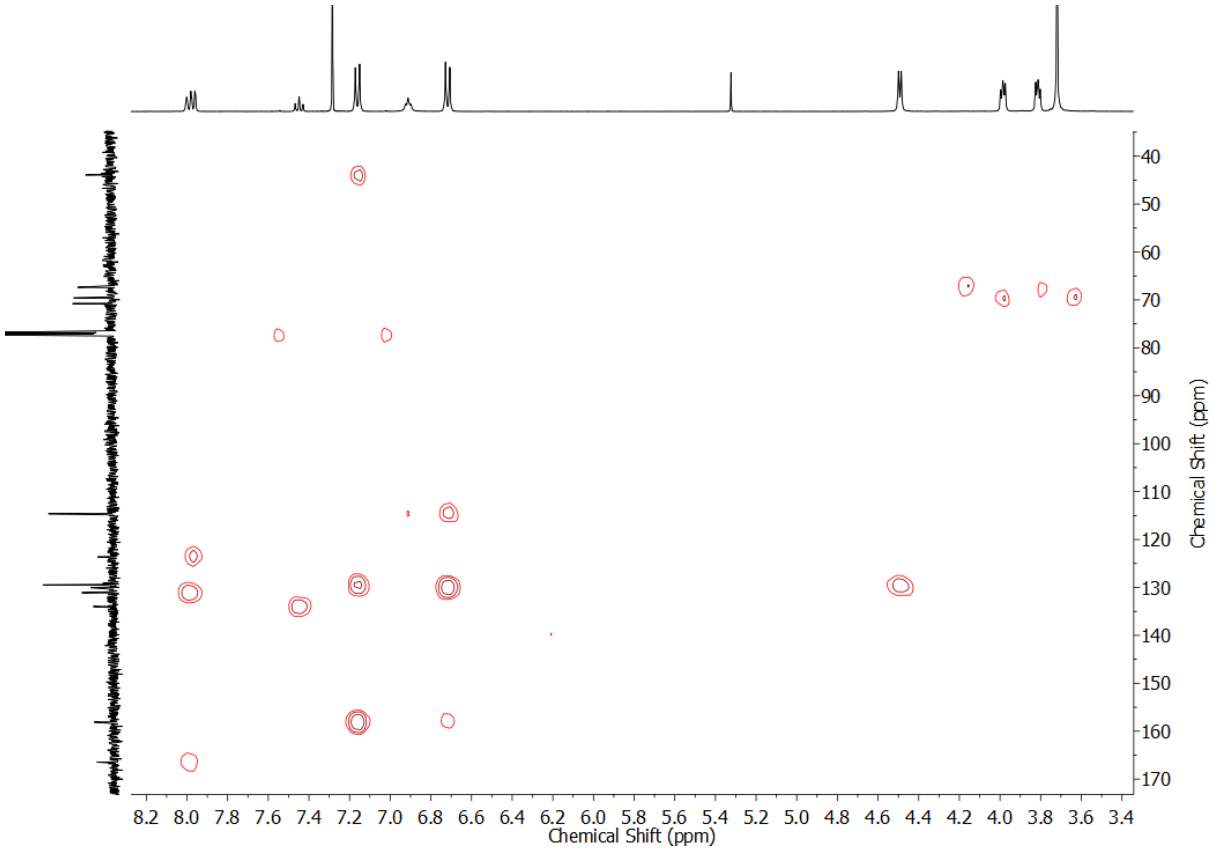
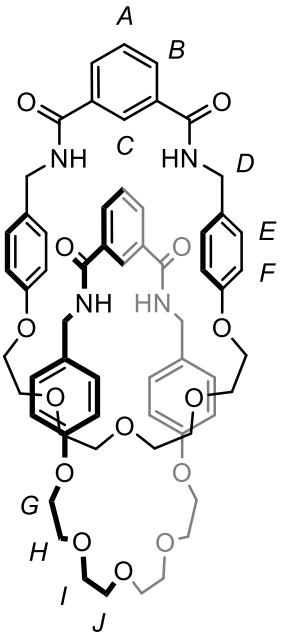


Figure S34 HMBC NMR ($CDCl_3$) of **3b**.



[2]Catenane 4b

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.34 (br. s, 2H, H_C), 8.26 (dd, *J* = 7.8, 1.4 Hz, 4H, H_B), 7.61 (t, *J* = 7.8 Hz, 2H, H_A), 7.33 (br. t, *J* = 4.6 Hz, 4H, H_{NH}), 6.84 (d, *J* = 8.5 Hz, 8H, H_E), 6.19 (d, *J* = 8.6 Hz, 8H, H_F), 4.39 (d, *J* = 4.8 Hz, 8H, H_D), 3.74-3.70 (m, 16H, 2 of H_G/H_H/H_I/H_J), 3.53-3.45 (m, 16H, 2 of H_G/H_H/H_I/H_J). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.9, 157.3, 134.0, 132.1 (C_B), 129.6 (C_E), 129.4 (C_A), 123.0 (C_C), 113.8 (C_F), 70.7 (C_G/C_H/C_I/C_J), 70.5 (C_G/C_H/C_I/C_J), 69.7 (C_G/C_H/C_I/C_J), 67.1 (C_G/C_H/C_I/C_J), 44.1 (C_D). HR-ESI-MS *m/z* = 1069.4807 $[M+H]^+$ calc. 1069.4810.

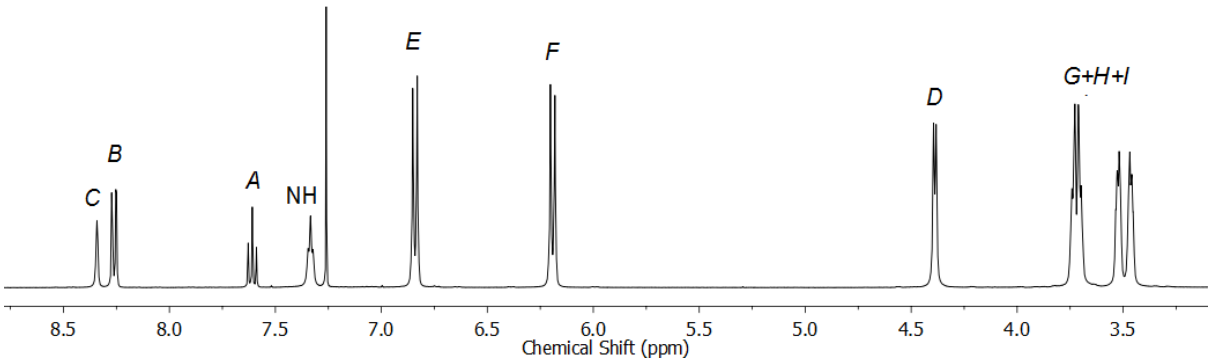


Figure S35 ^{1}H NMR ($CDCl_3$, 400 MHz) of **4b**.

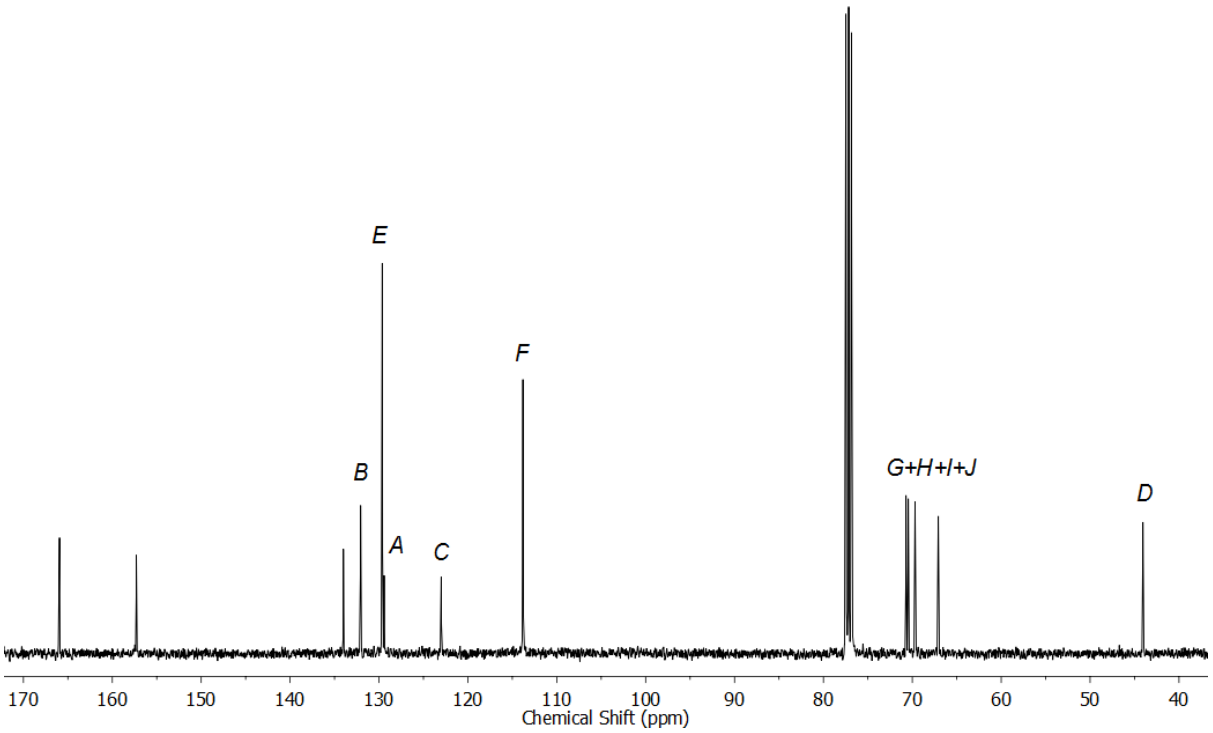


Figure S36 ^{13}C NMR ($CDCl_3$, 101 MHz) of **4b**.

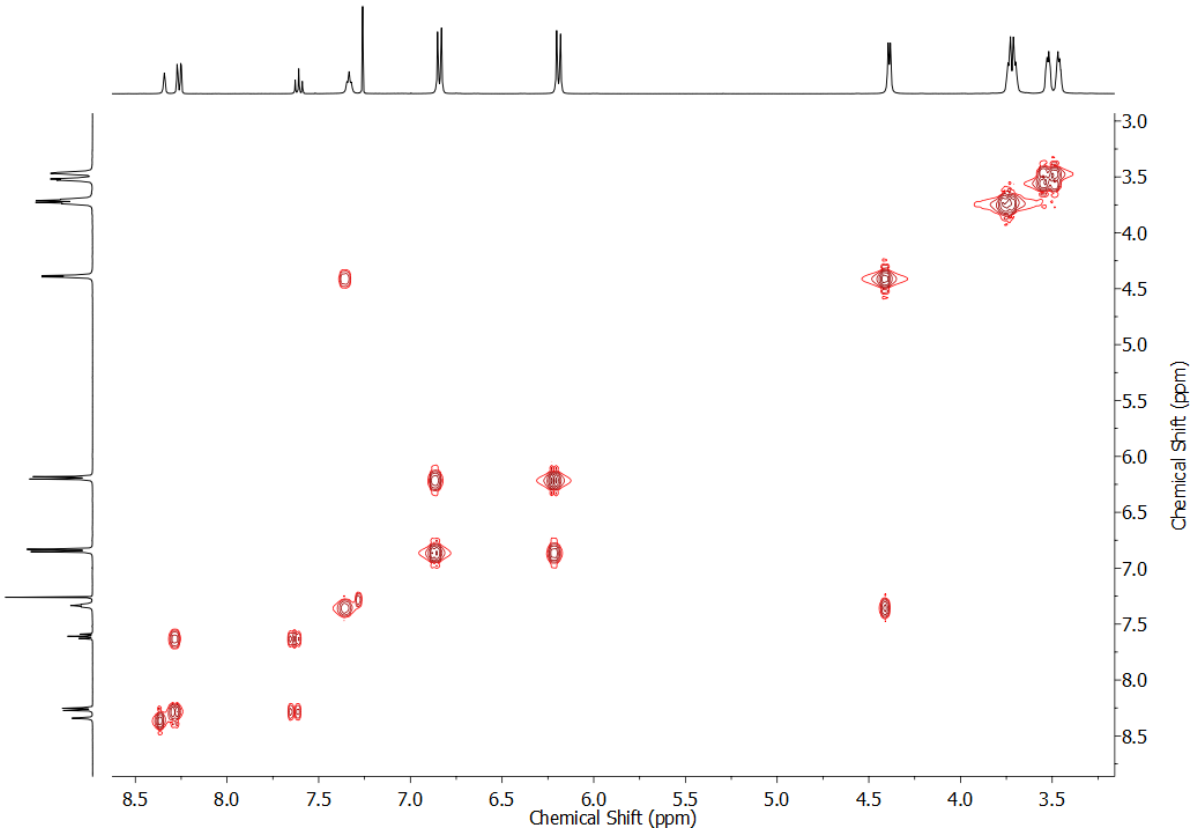


Figure S37 COSY NMR ($CDCl_3$) of **4b**.

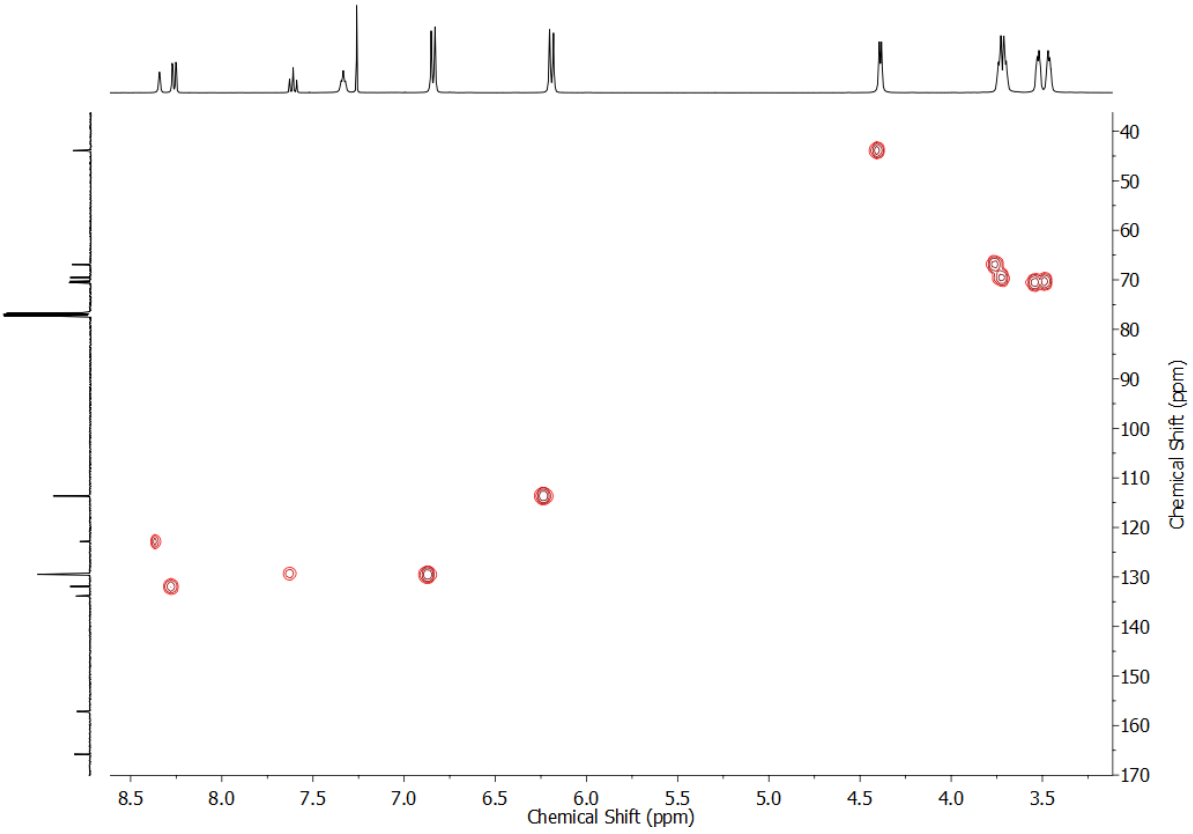


Figure S38 HSQC NMR ($CDCl_3$) of **4b**.

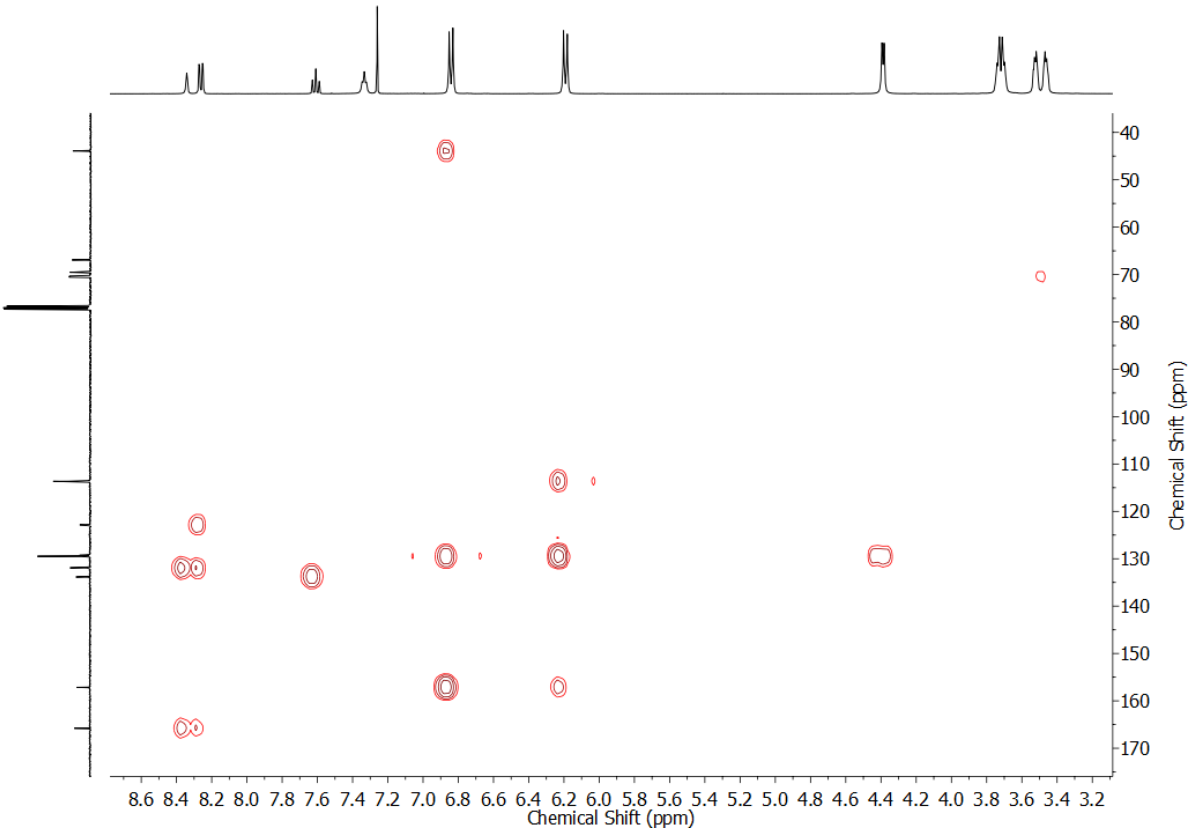


Figure S39 HMBC NMR ($CDCl_3$) of **4b**.

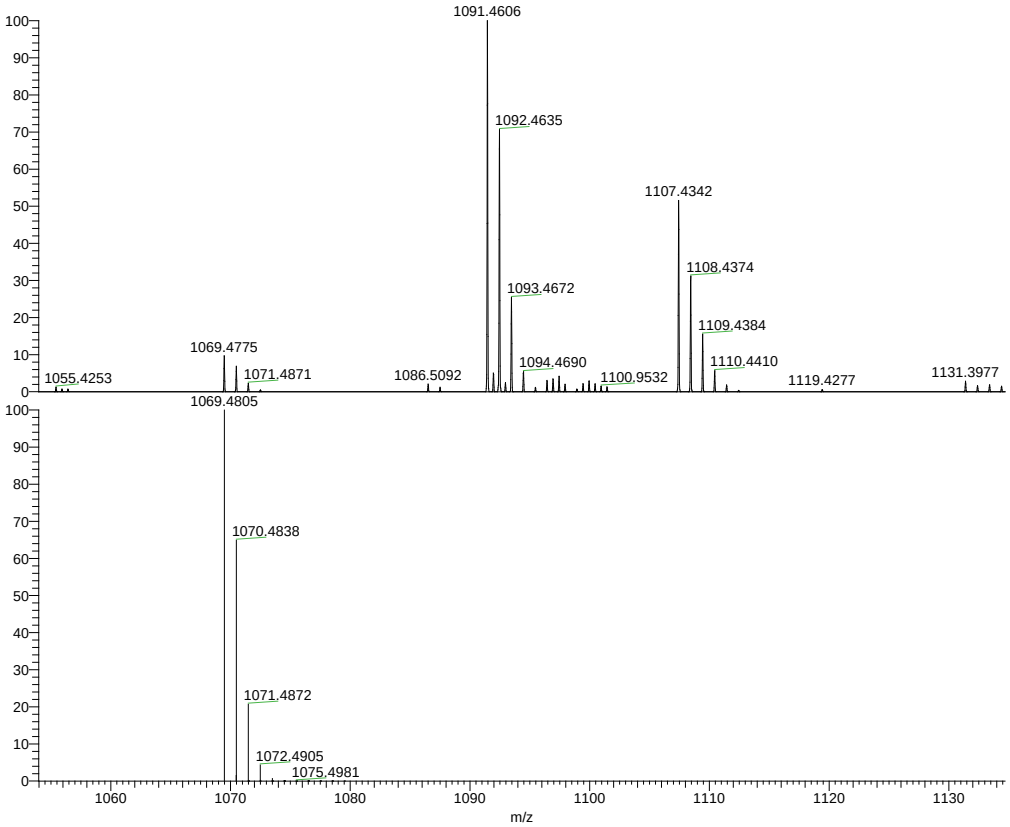


Figure S40 Partial HR-ESI-MS of **4b** (top) and calculated isotopic pattern for [**4b**+H]$^+$ (bottom).

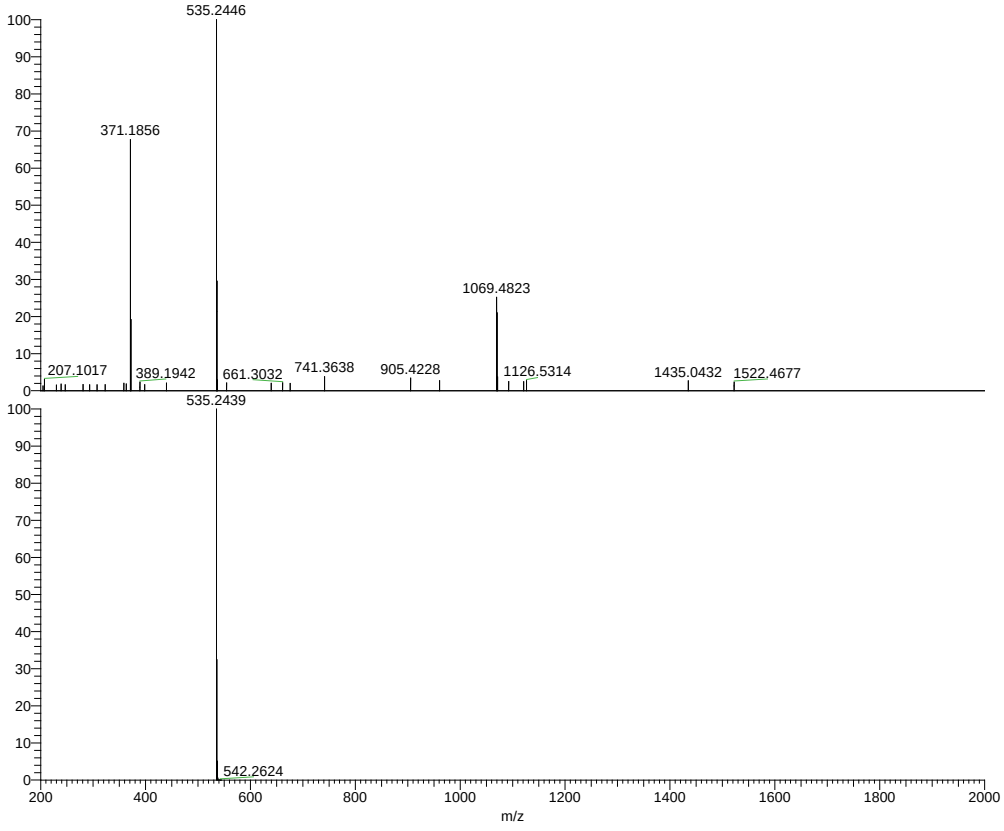
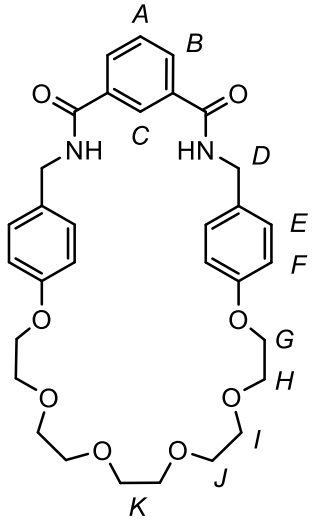


Figure S41 HR-ESI-MSMS of *m/z* = 1069 peak (top) and calculated isotopic pattern for [**3b**+H]$^+$ (bottom).

Macrocycle 3c and [2]Catenane 4c

Using the general procedure with **1** and **2c** (0.224 g, 0.5 mmol) gave **3c** (0.121 g, 42%) as a white solid and **4c** (0.026 g, 9%) as a colourless glass.



Macrocycle 3c

M.p. 183-185 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.07 (t, *J* = 1.8 Hz, 1H, H_C), 7.94 (dd, *J* = 7.8, 1.7 Hz, 2H, H_B), 7.43 (t, *J* = 7.8 Hz, 1H, H_A), 7.14 (d, *J* = 8.6 Hz, 4H, H_E), 7.00 (t, *J* = 5.5 Hz, 2H, H_{NH}), 6.70 (d, *J* = 8.7 Hz, 4H, H_F), 4.46 (d, *J* = 5.5 Hz, 4H, H_D), 3.95-3.93 (m, 4H, H_G), 3.76-3.74 (m, 4H, H_H), 3.68-3.67 (m, 12H, H_I, H_J, H_K). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 166.6, 158.2, 134.2, 131.0 (C_B), 130.3, 129.4 (C_E), 129.2 (C_A), 124.2 (C_C), 114.9 (C_F), 71.1 (C_I/C_J/C_K), 71.0 (C_I/C_J/C_K), 70.9 (C_I/C_J/C_K), 69.7 (C_H), 67.5 (C_G), 43.9 (C_D). HR-ESI-MS *m/z* = 579.2700 $[M+H]^+$ calc. 579.2706.

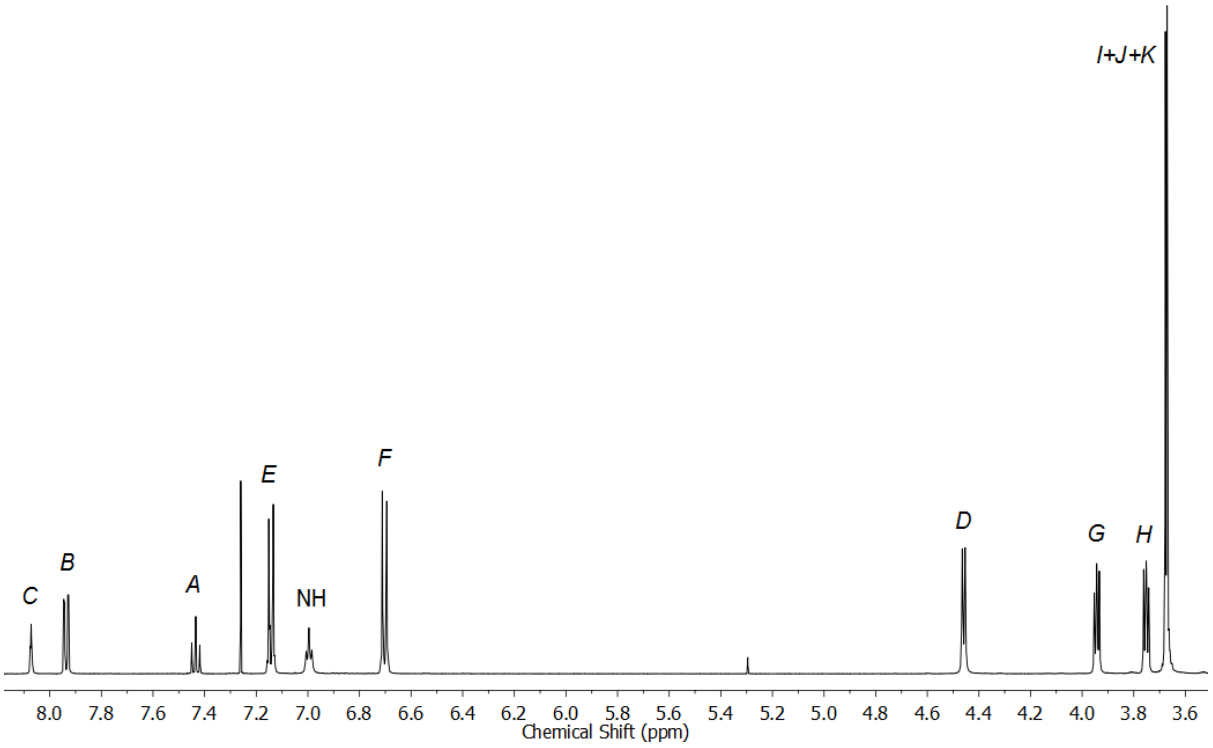


Figure S42 ^{1}H NMR ($CDCl_3$, 500 MHz) of **3c**.

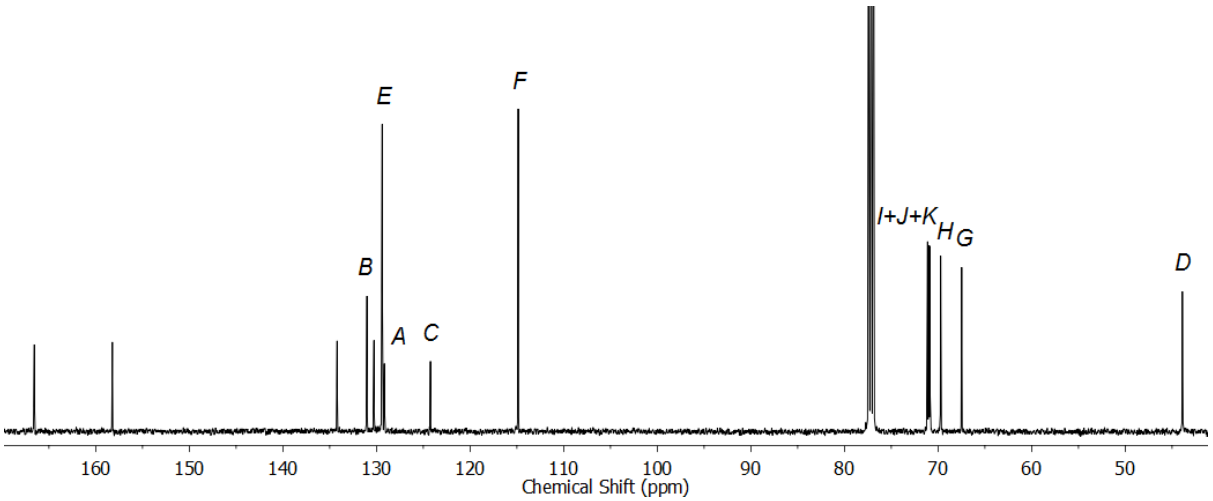


Figure S43 ^{13}C NMR ($CDCl_3$, 126 MHz) of **3c**.

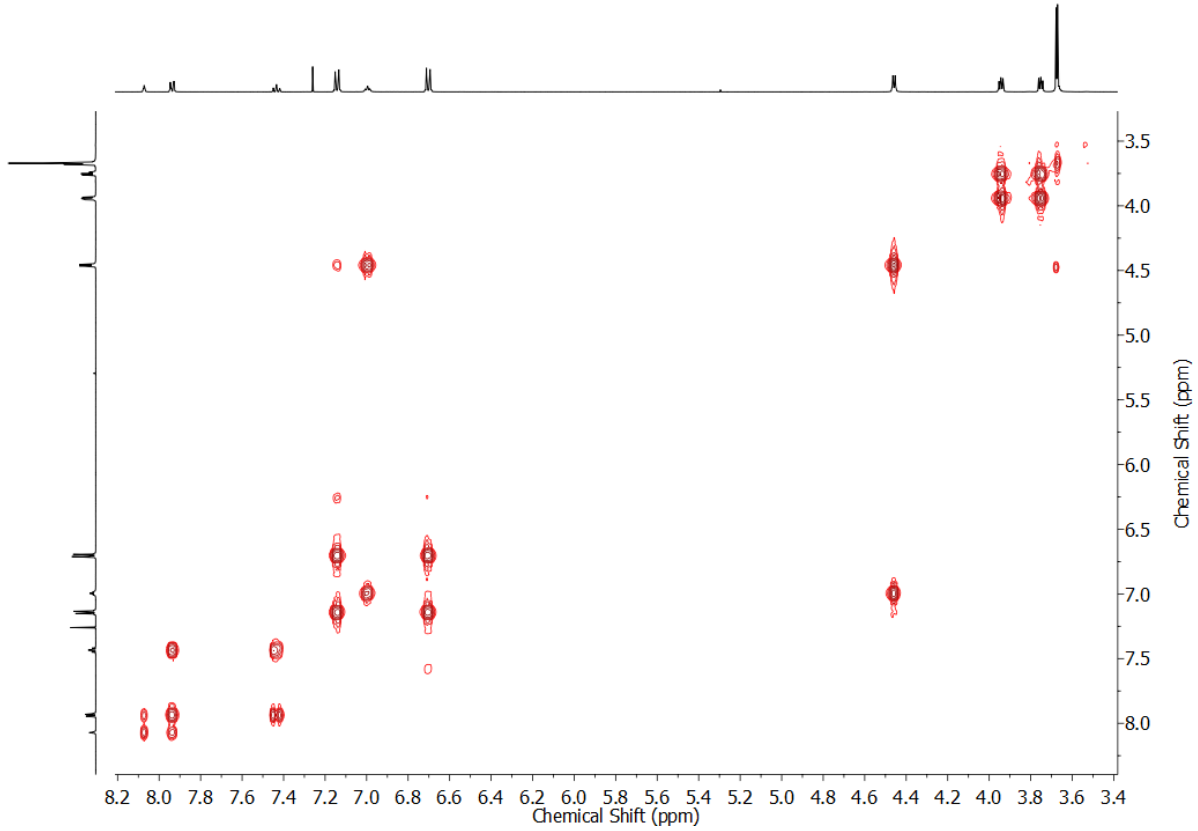


Figure S44 COSY NMR ($CDCl_3$) of **3c**.

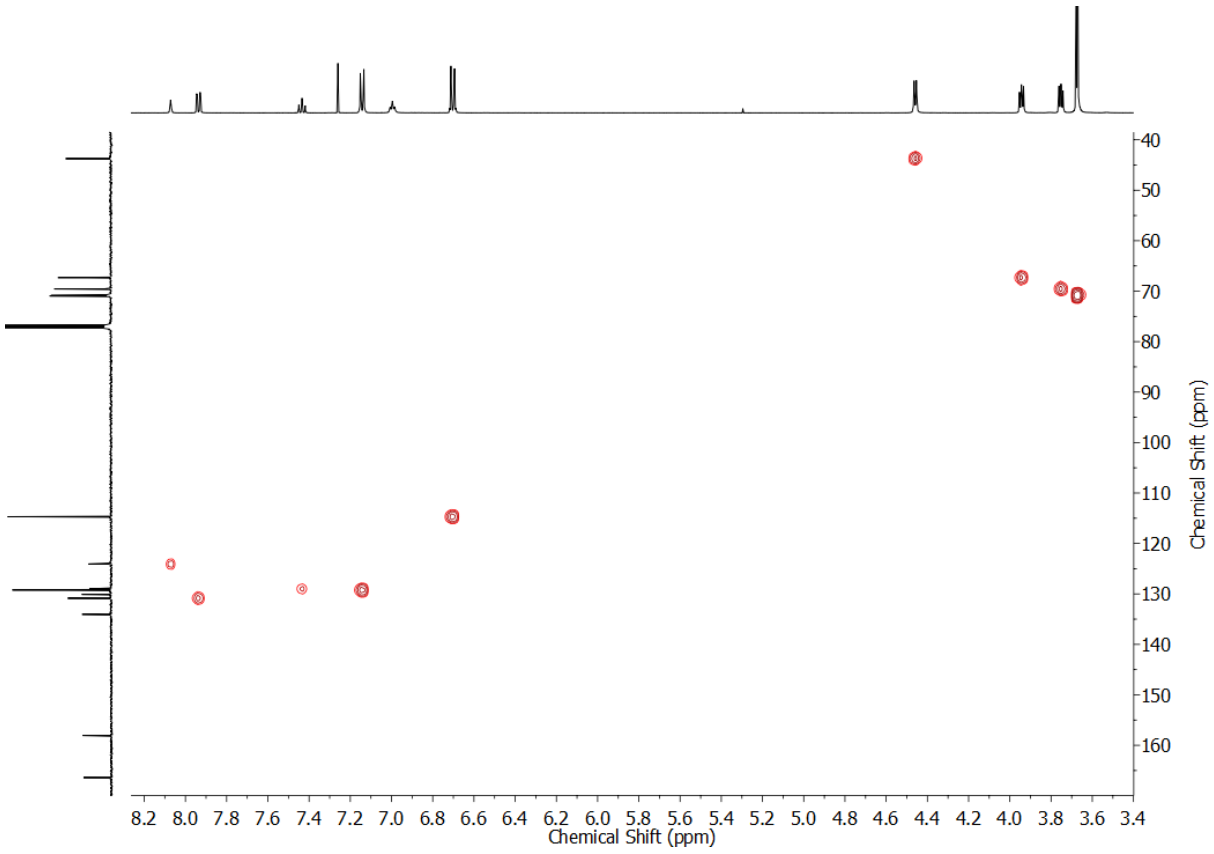


Figure S45 HSQC NMR ($CDCl_3$) of **3c**.

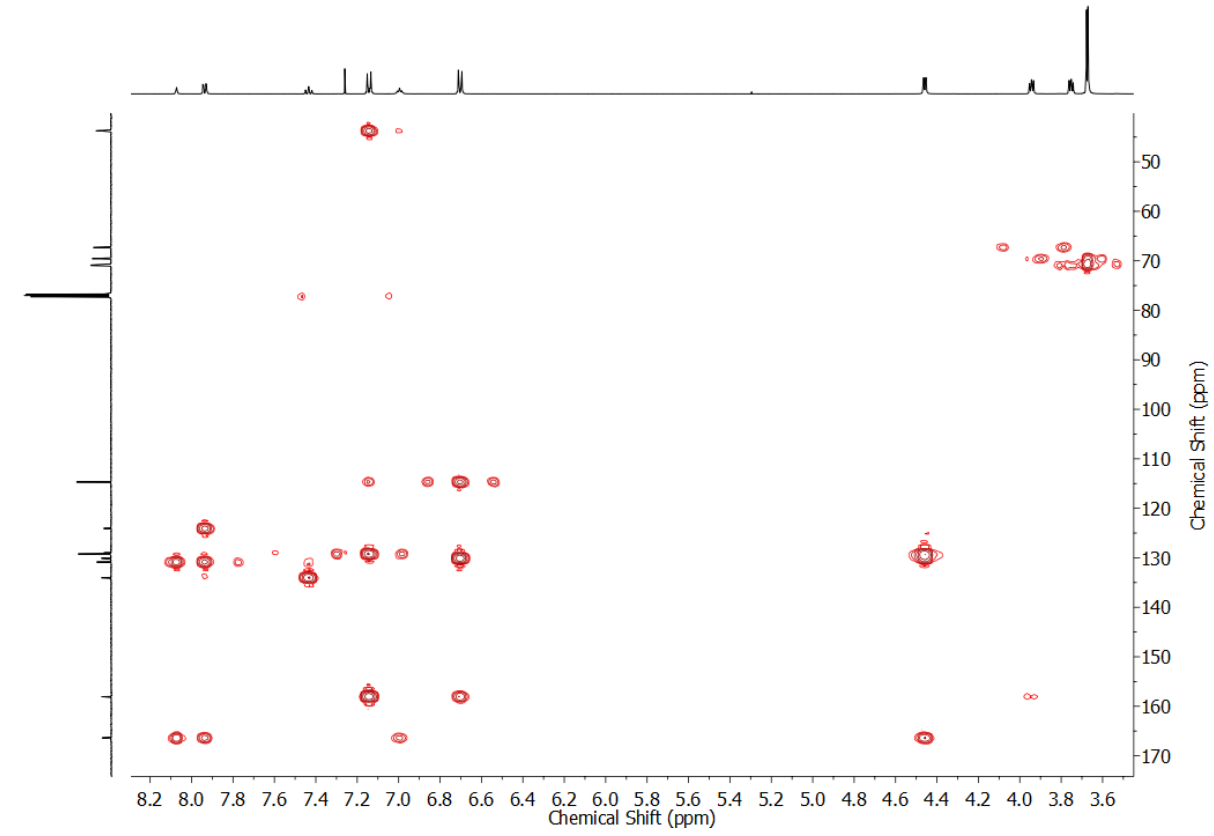
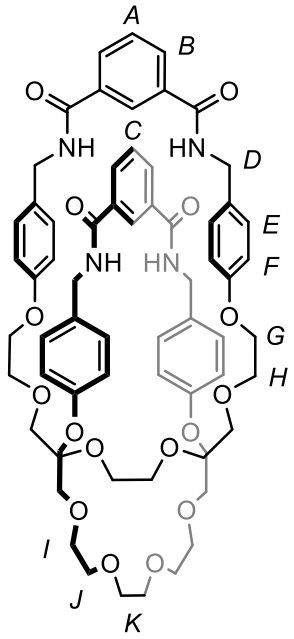


Figure S46 HMBC NMR ($CDCl_3$) of **3c**.



[2]Catenane 4c

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (s, 2H, H_C), 8.15 (dd, *J* = 7.8, 1.5 Hz, 4H, H_B), 7.61 (br. m, 4H, H_{NH}), 7.55 (t, *J* = 7.8 Hz, 2H, H_A), 6.96 (d, *J* = 8.6 Hz, 8H, H_E), 6.49 (d, *J* = 8.6 Hz, 8H, H_F), 4.34 (d, *J* = 5.1 Hz, 8H, H_D), 3.85-3.83 (m, 8H, H_G), 3.66-3.64 (m, 8H, H_H), 3.53-3.51 (m, 8H, H_I), 3.45-3.43 (m, 16H, H_J, H_K). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.3, 157.8, 134.0, 131.8 (C_B), 130.3, 129.6 (C_E), 129.1 (C_A), 123.9 (C_C), 114.5 (C_F), 70.9 (C_I/C_J/C_K), 70.6 (C_I/C_J/C_K), 70.5 (C_I/C_J/C_K), 69.7 (C_H), 67.4 (C_G), 43.8 (C_D). HR-ESI-MS *m/z* = 1157.5369 $[M+H]^+$ calc. 1157.5335.

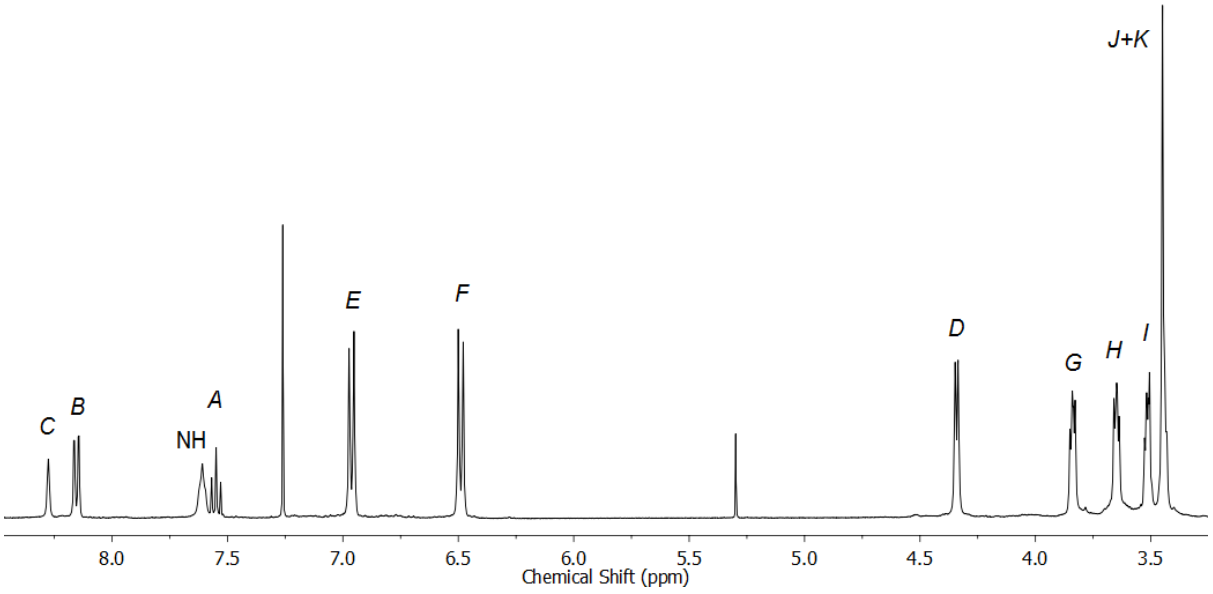


Figure S47 ^{1}H NMR ($CDCl_3$, 400 MHz) of **4c**.

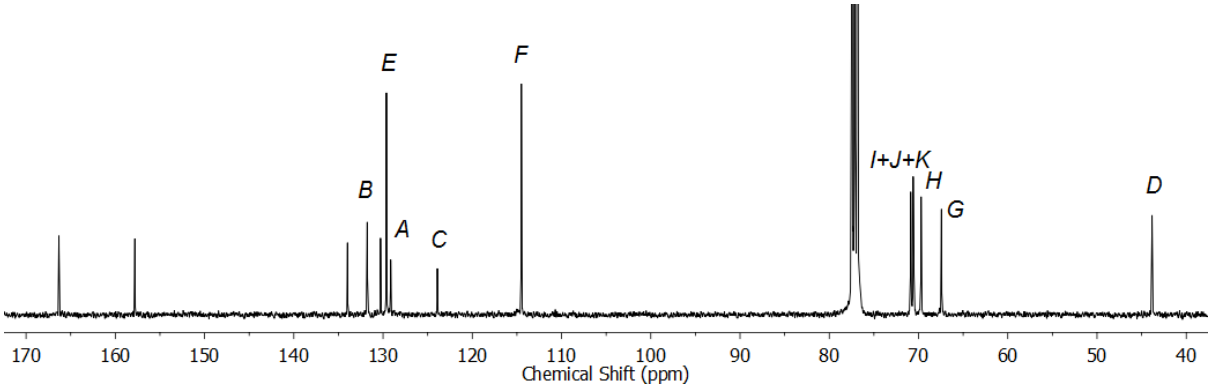


Figure S48 ^{13}C NMR ($CDCl_3$, 101 MHz) of **4c**.

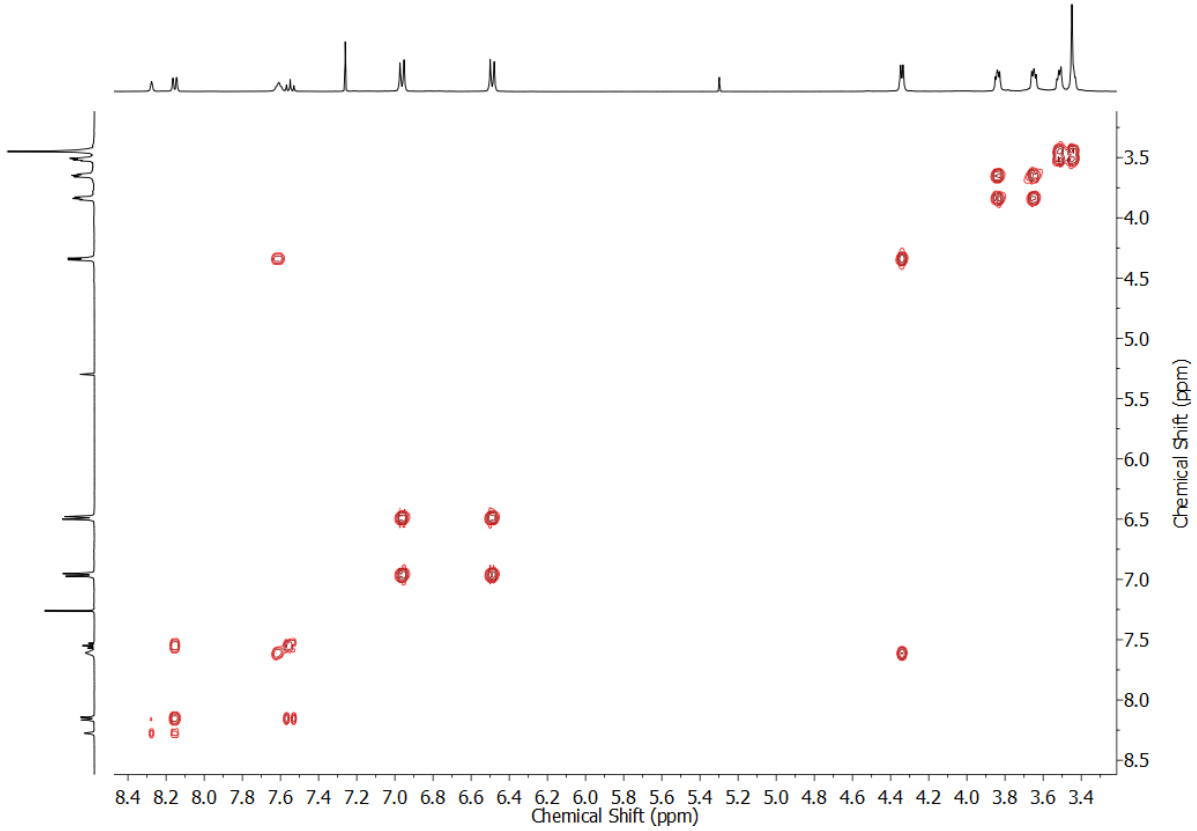


Figure S49 COSY NMR ($CDCl_3$) of **4c**.

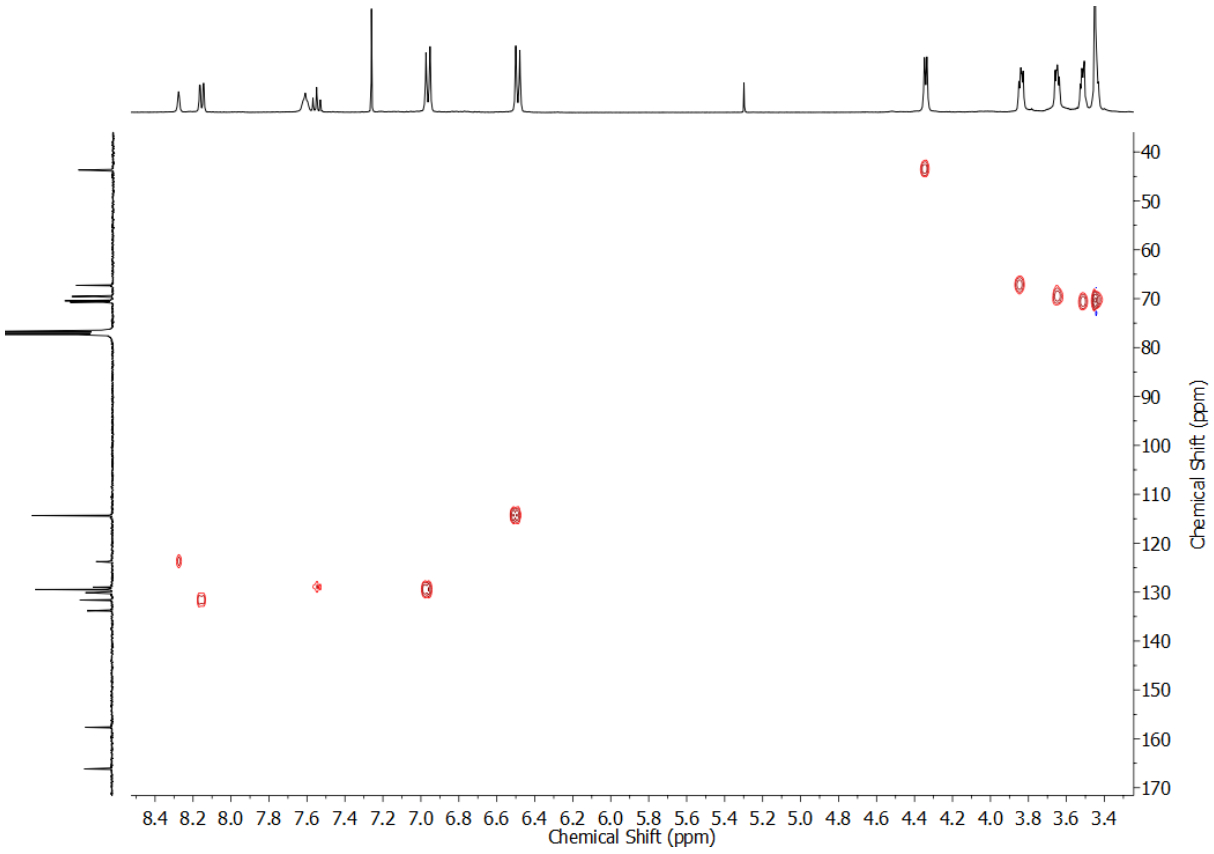


Figure S50 HSQC NMR ($CDCl_3$) of **4c**.

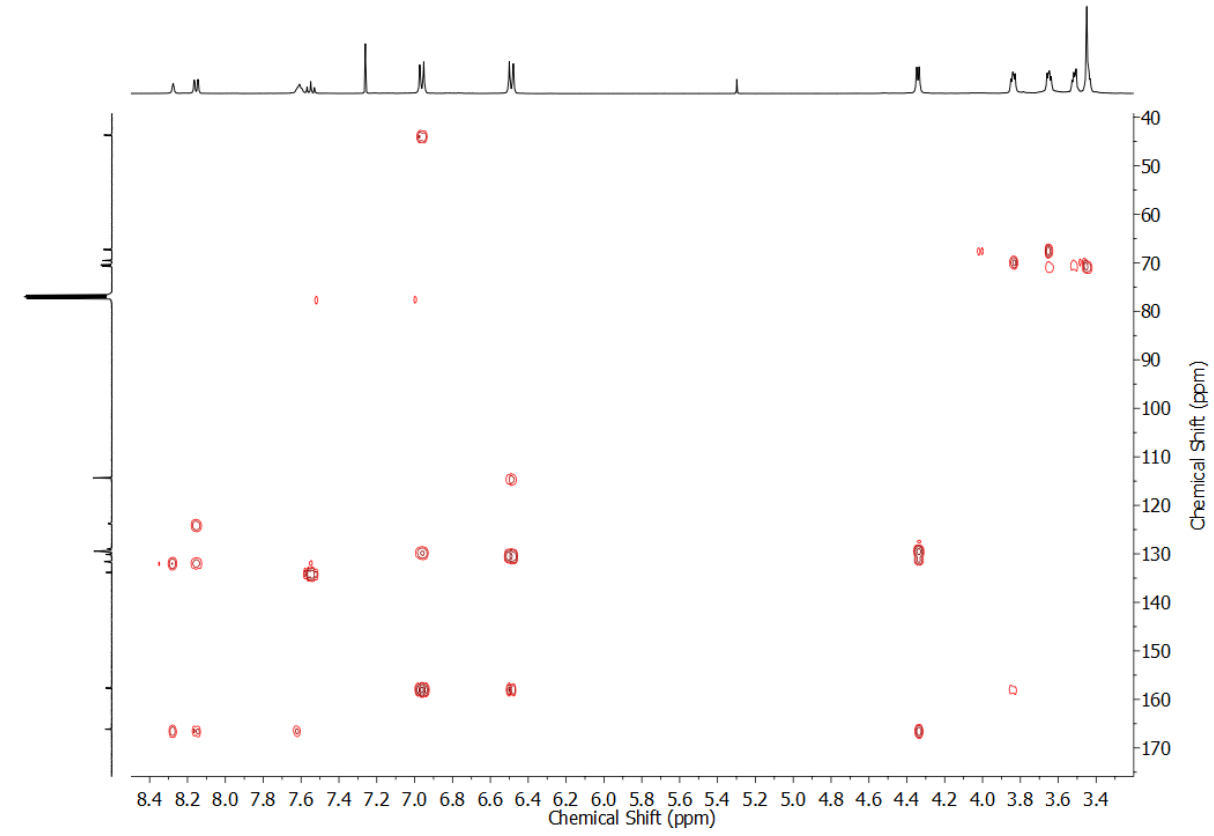


Figure S51 HMBC NMR ($CDCl_3$) of **4c**.

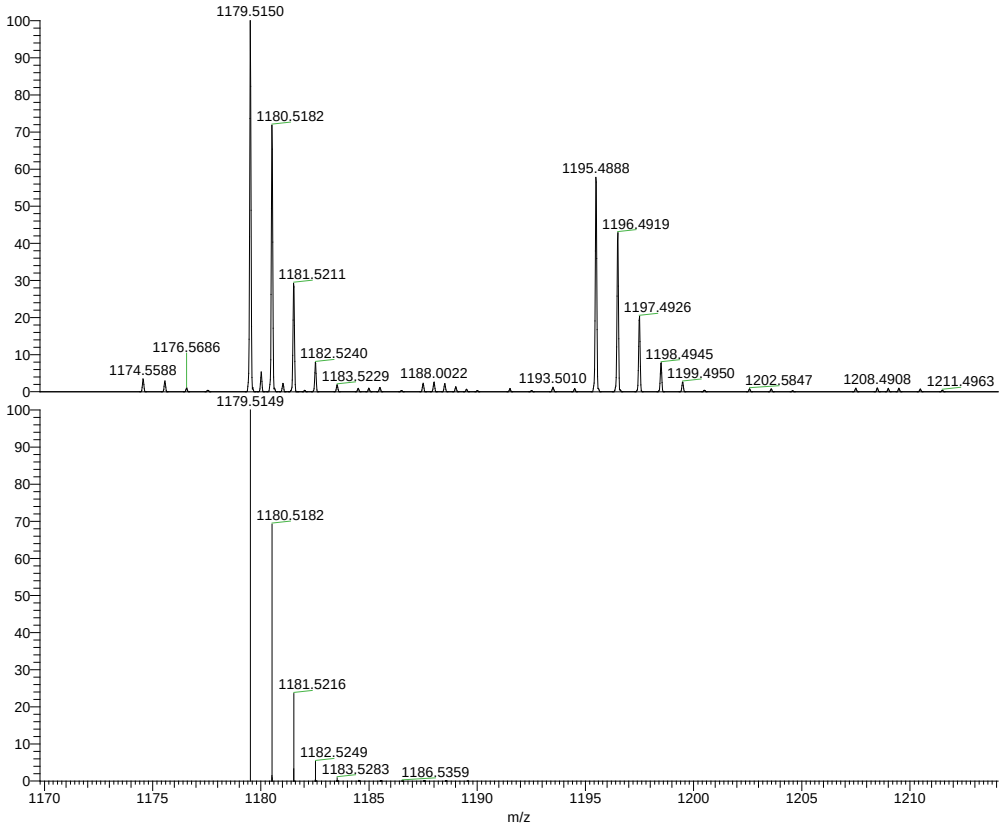


Figure S52 Partial HR-ESI-MS of **4c** (top) and calculated isotopic pattern for [**4c**+Na]$^+$ (bottom).

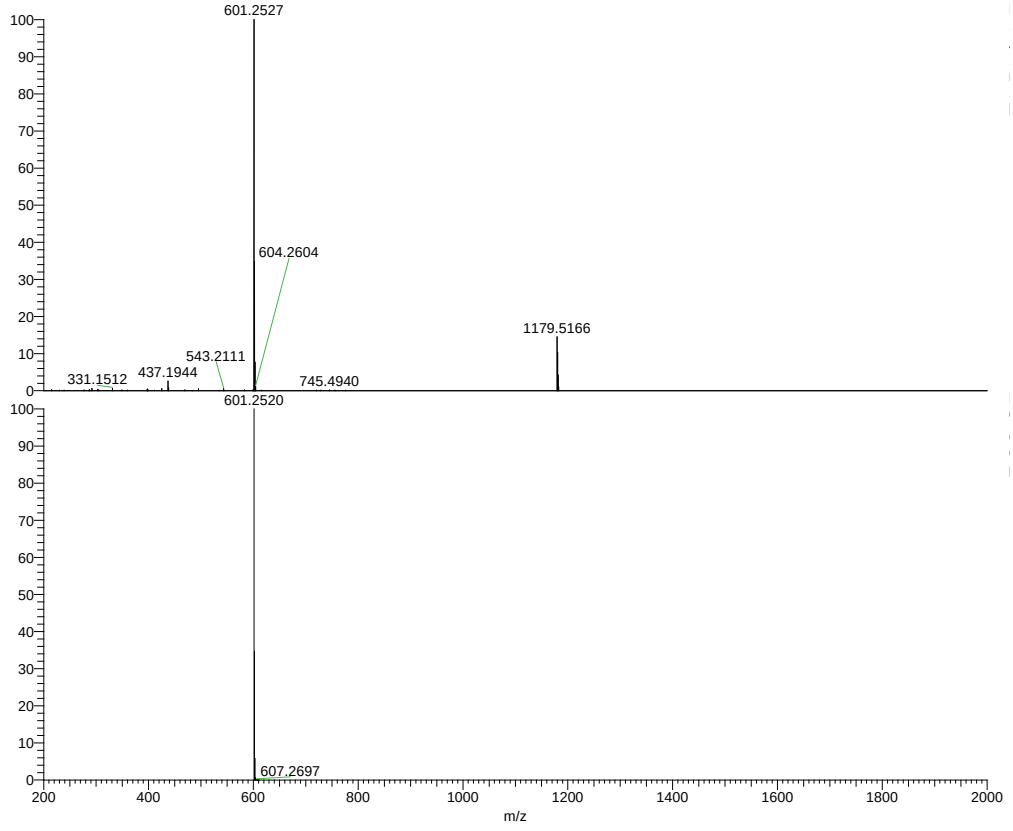
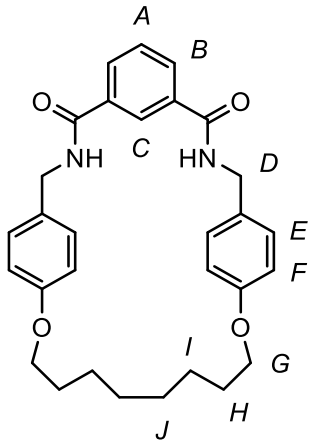


Figure S53 HR-ESI-MSMS of *m/z* = 1179 peak (top) and calculated isotopic pattern for [**3c**+Na]$^+$ (bottom).

Macrocycle 3d



Using the general procedure with **1** and **2d** (0.178 g, 0.5 mmol) gave **3d** (0.112 g, 46%) as a white solid. M.p. 214-216 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (dd, *J* = 7.7, 1.7 Hz, 2H, H_B), 7.65 (t, *J* = 1.5 Hz, 1H, H_C), 7.53 (t, *J* = 7.8 Hz, 1H, H_A), 7.23 (d, *J* = 8.6, 4H, H_E), 6.84 (d, *J* = 8.6 Hz, 4H, H_F), 6.34 (t, *J* = 4.9 Hz, 2H, H_{NH}), 4.48 (d, *J* = 5.3 Hz, 4H, H_D), 3.98 (t, *J* = 6.1 Hz, 4H, H_G), 1.74 (quint, *J* = 6.5 Hz, 4H, H_H), 1.44 (br. m, 4H, H_I), 1.31-1.27 (m, 4H, H_J). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.6, 158.9, 134.9, 131.2 (C_B), 130.0 (C_E), 129.6 (C_A), 123.3 (C_C), 115.1 (C_F), 67.2 (C_G), 44.3 (C_D), 28.9 (C_J), 28.6 (C_H), 25.6 (C_I). HR-ESI-MS *m/z* = 487.2610 $[M+H]^+$ calc. 487.2597.

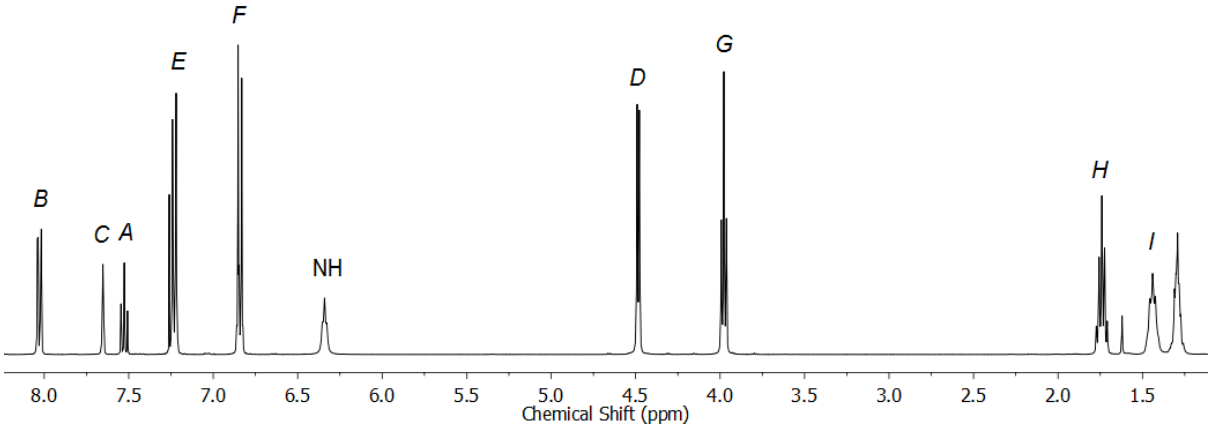


Figure S54 ^{1}H NMR ($CDCl_3$, 400 MHz) of **3d.**

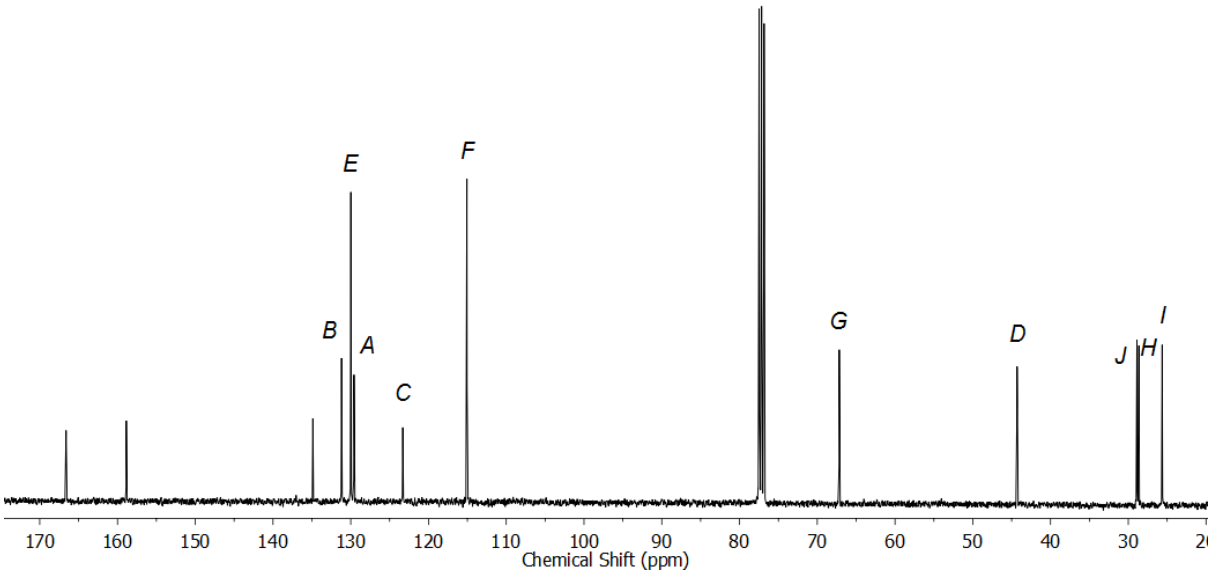


Figure S55 ^{13}C NMR ($CDCl_3$, 101 MHz) of **3d.**

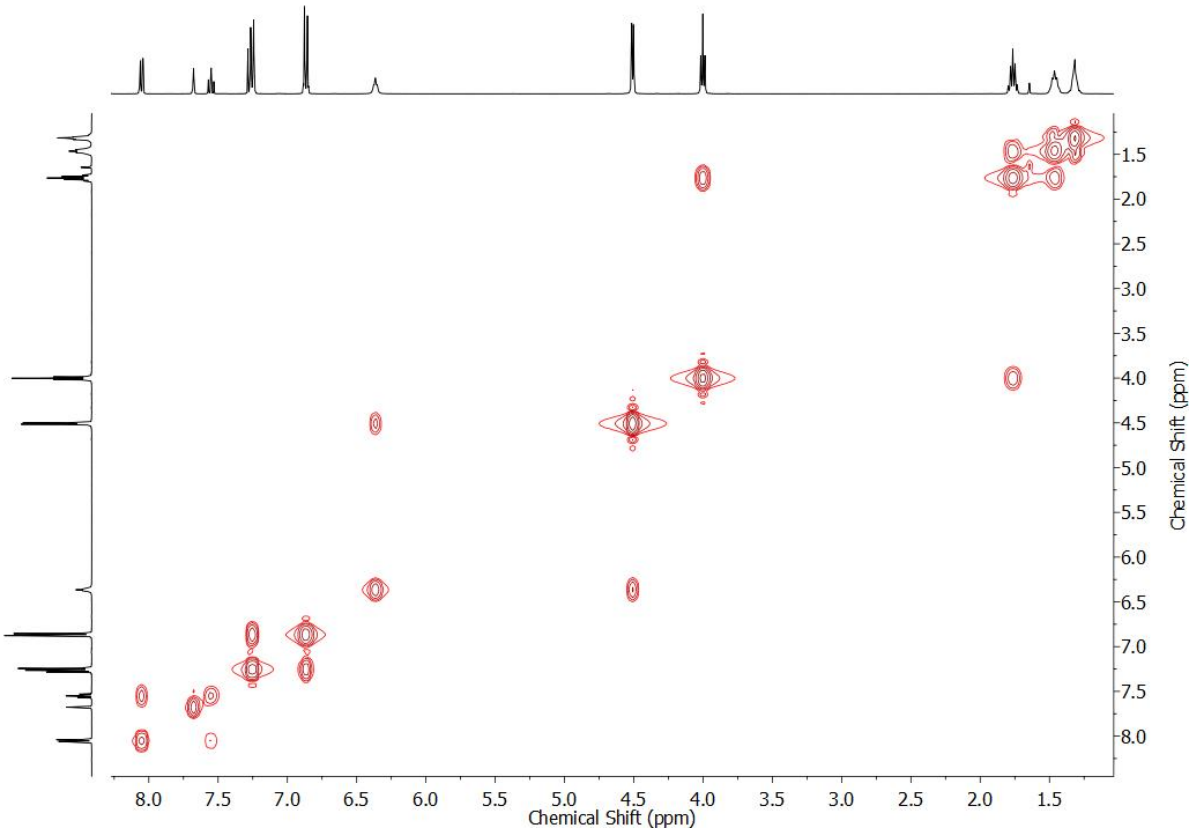


Figure S56 COSY NMR ($CDCl_3$) of **3d**.

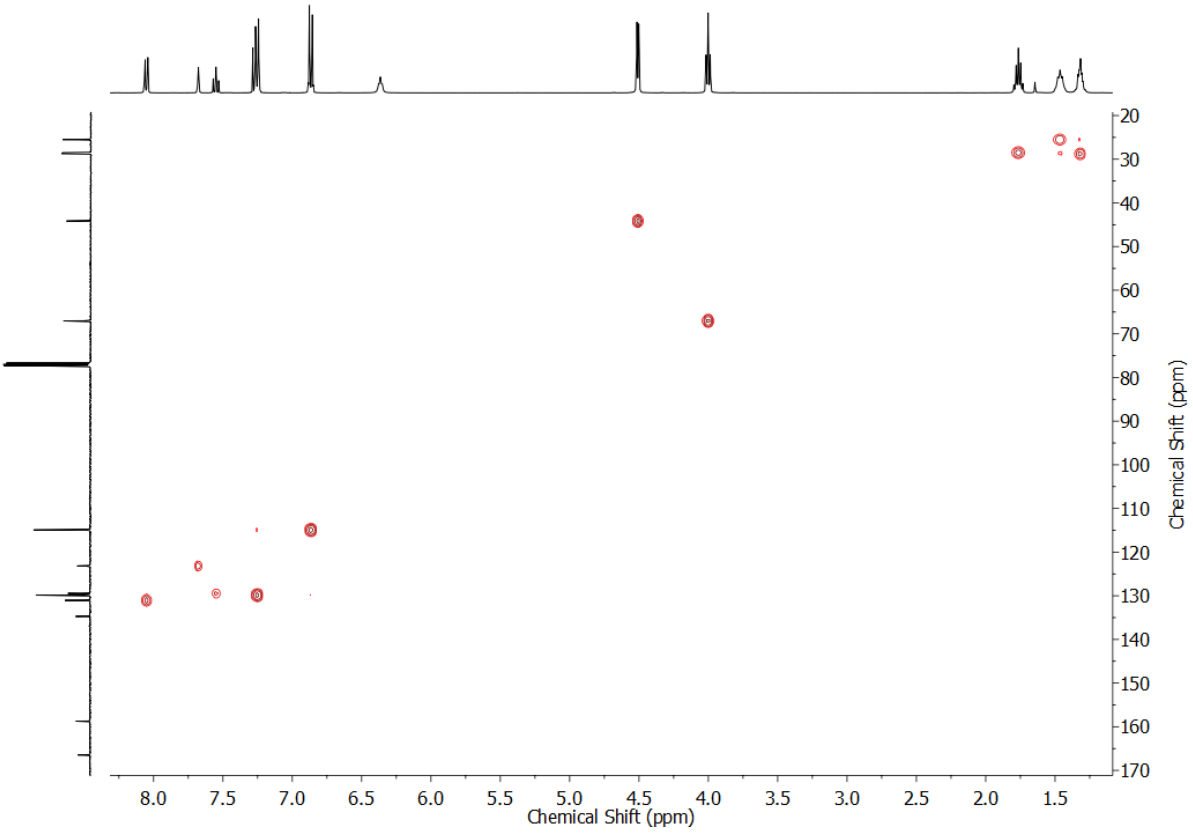


Figure S57 HSQC NMR ($CDCl_3$) of **3d**.

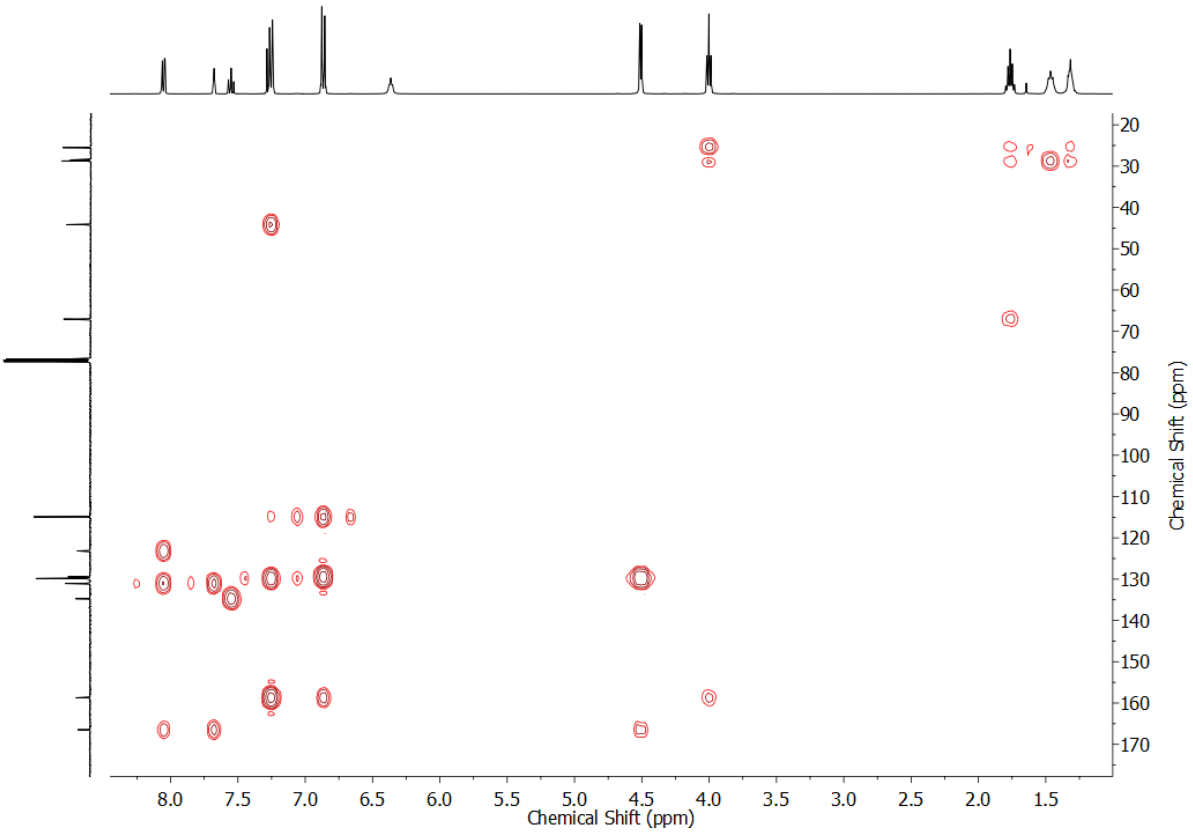
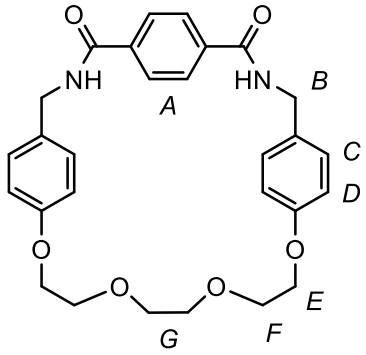


Figure S58 HMBC NMR ($CDCl_3$) of **3d**.

Macrocycle 3e



Using the general procedure with **5** and **2a** (0.180 g, 0.5 mmol) gave **3e** (0.060 g, 24%) as a white solid. M.p. 179-181 °C. ^{1}H NMR (400 MHz, d_6-DMSO) δ: 8.54 (br. s, 2H, H_{NH}), 7.79 (br. s, 4H, H_A), 7.15 (br. d, J = 7.6 Hz, 4H, H_C), 6.77 (br. d, J = 7.2 Hz, 4H, H_D), 4.33 (br. d, J = 4.4 Hz, 4H, H_B), 4.03 (br. app. s, 4H, H_E), 3.58 (br. app. s, 4H, H_F), 3.45 (br. s, 4H, H_G). ^{13}C NMR (101 MHz, d_6-DMSO) δ: 165.5, 157.4, 136.9, 132.6, 129.3 (C_C), 127.2 (C_A), 114.5 (C_D), 69.6 (C_G), 68.6 (C_F), 66.8 (C_E), 42.6 (C_B). HR-ESI-MS m/z = 491.2192 $[M+H]^+$ calc. 491.2182.

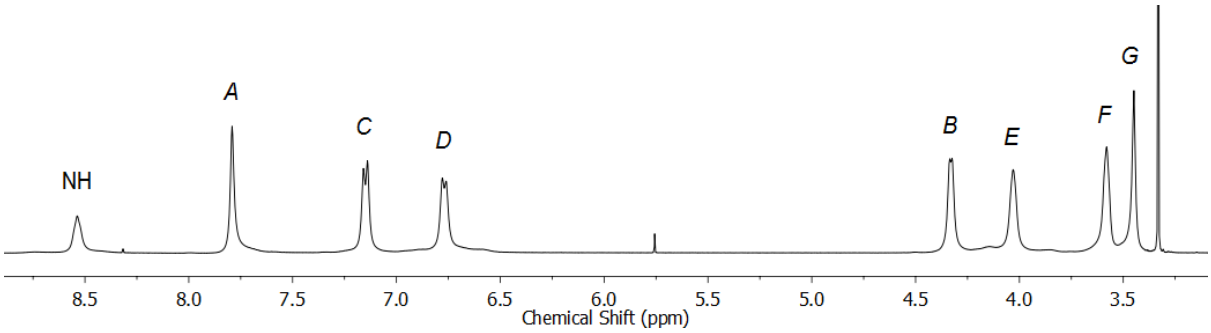


Figure S59 ^{1}H NMR (d_6-DMSO, 400 MHz) of **3e**.

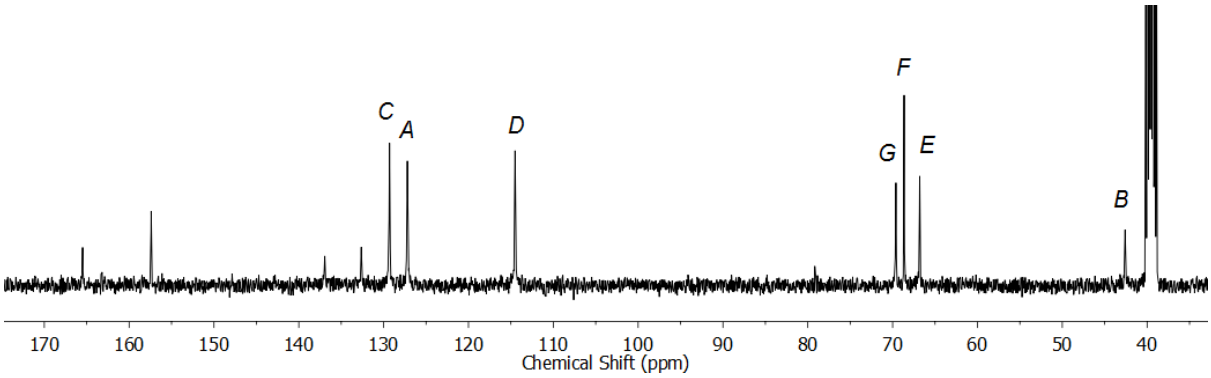


Figure S60 ^{13}C NMR (d_6-DMSO, 101 MHz) of **3e**.

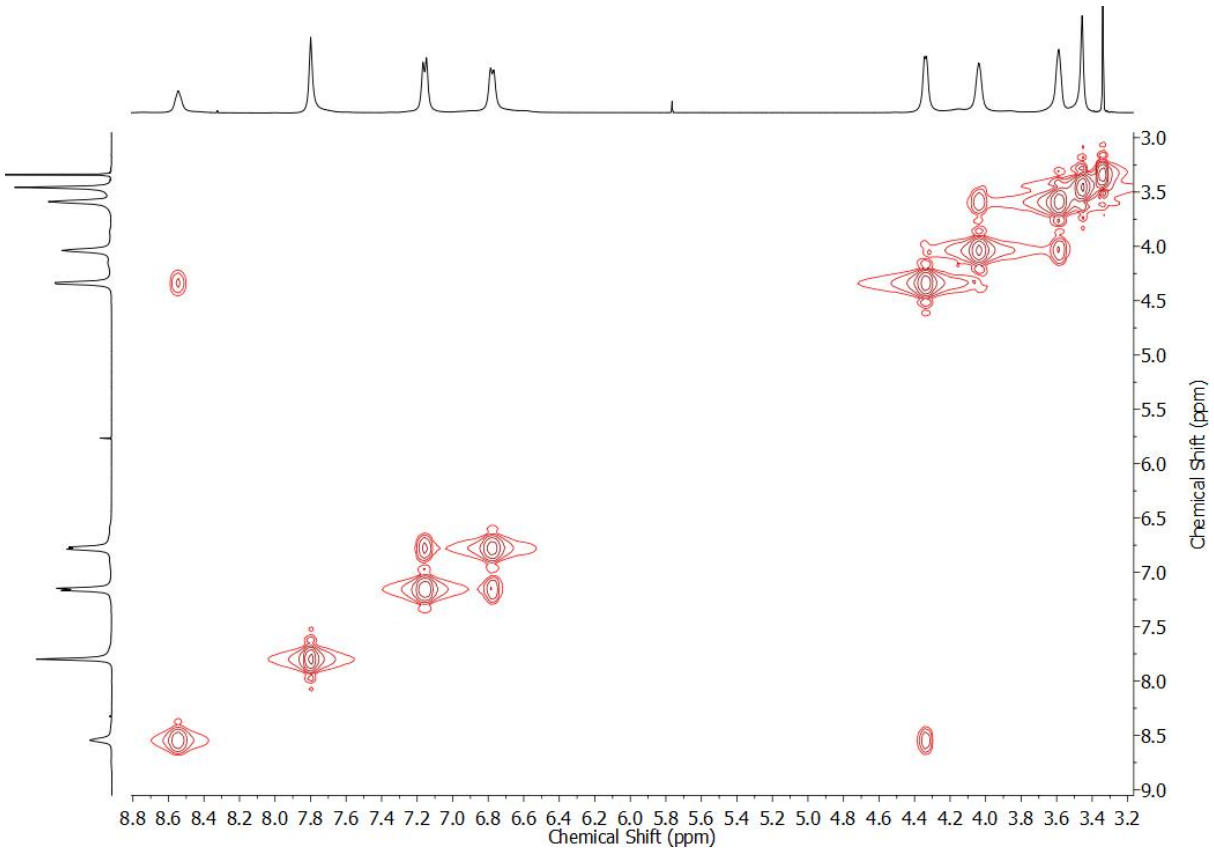


Figure S61 COSY NMR (d_6-DMSO) of **3e**.

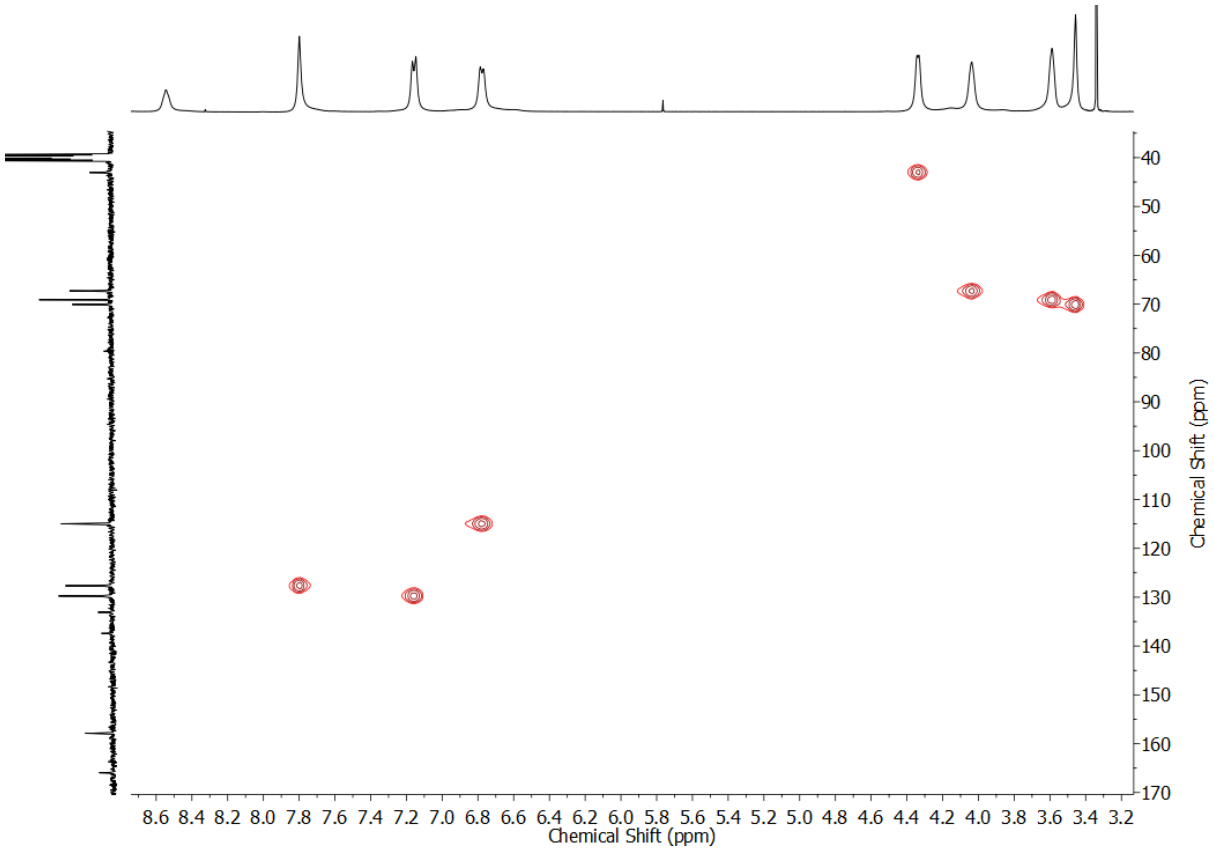


Figure S62 HSQC NMR (d_6-DMSO) of **3e**.

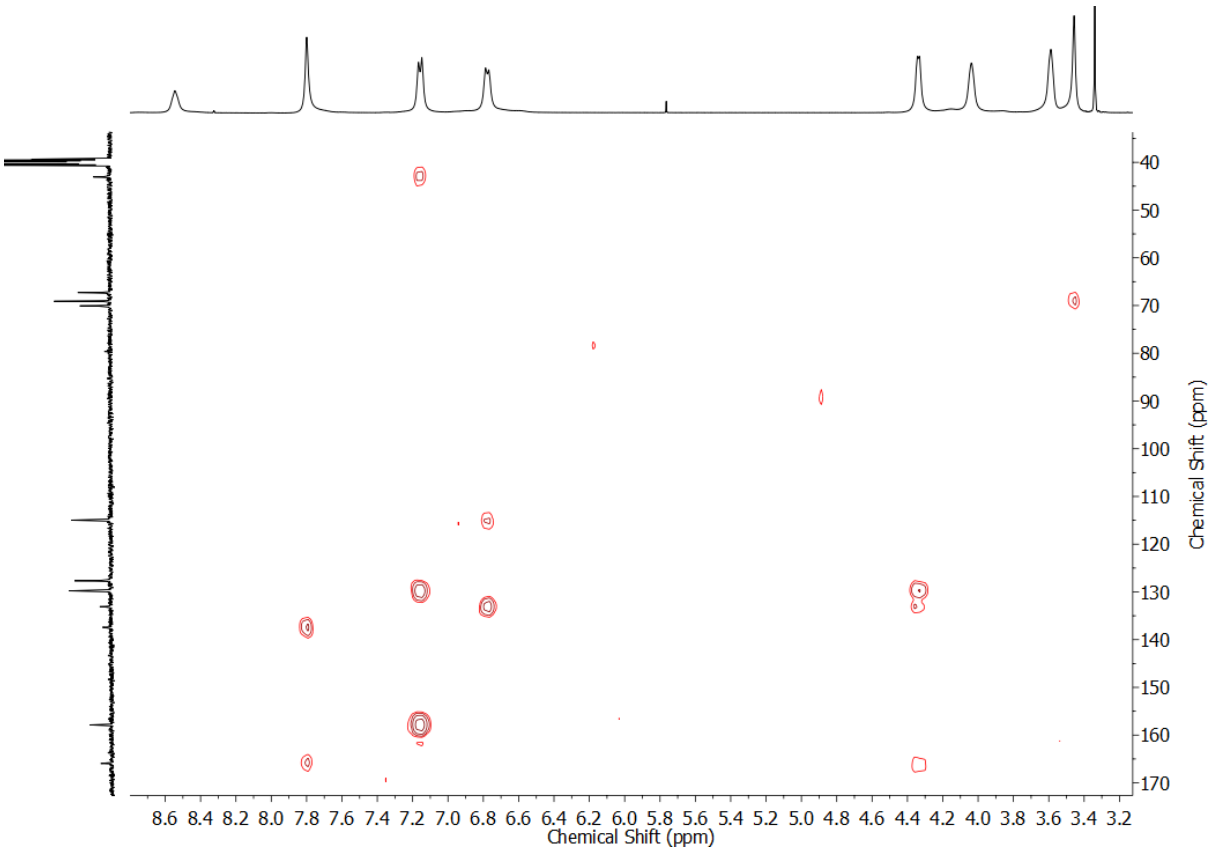
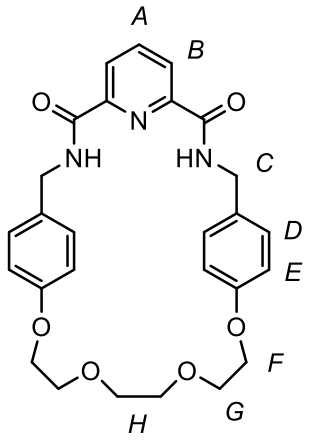


Figure S63 HMBC NMR (d_6-DMSO) of **3e**.

Macrocycle 3f



Using the general procedure with **6** and **2a** (0.180 g, 0.5 mmol) gave **3f** (0.074 g, 30%) as a white solid. Spectra were consistent with those previously reported.[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.26 (d, *J* = 7.8 Hz, 2H, H_B), 8.00 (t, *J* = 7.8 Hz, 1H, H_A), 7.87 (br. t, *J* = 5.0 Hz, 2H, H_{NH}), 7.14 (d, *J* = 8.6 Hz, 4H, H_D), 6.80 (d, *J* = 8.7 Hz, 4H, H_E), 4.56 (d, *J* = 5.3 Hz, 4H, H_C), 4.12-4.10 (m, 4H, H_F), 3.92-3.89 (m, 4H, H_G), 3.77 (s, 4H, H_H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.3, 158.7, 148.8, 139.4 (C_A), 129.7, 128.8 (C_D), 125.1 (C_B), 115.2 (C_E), 71.2 (C_H), 69.9 (C_G), 67.8 (C_F), 43.3 (C_C).

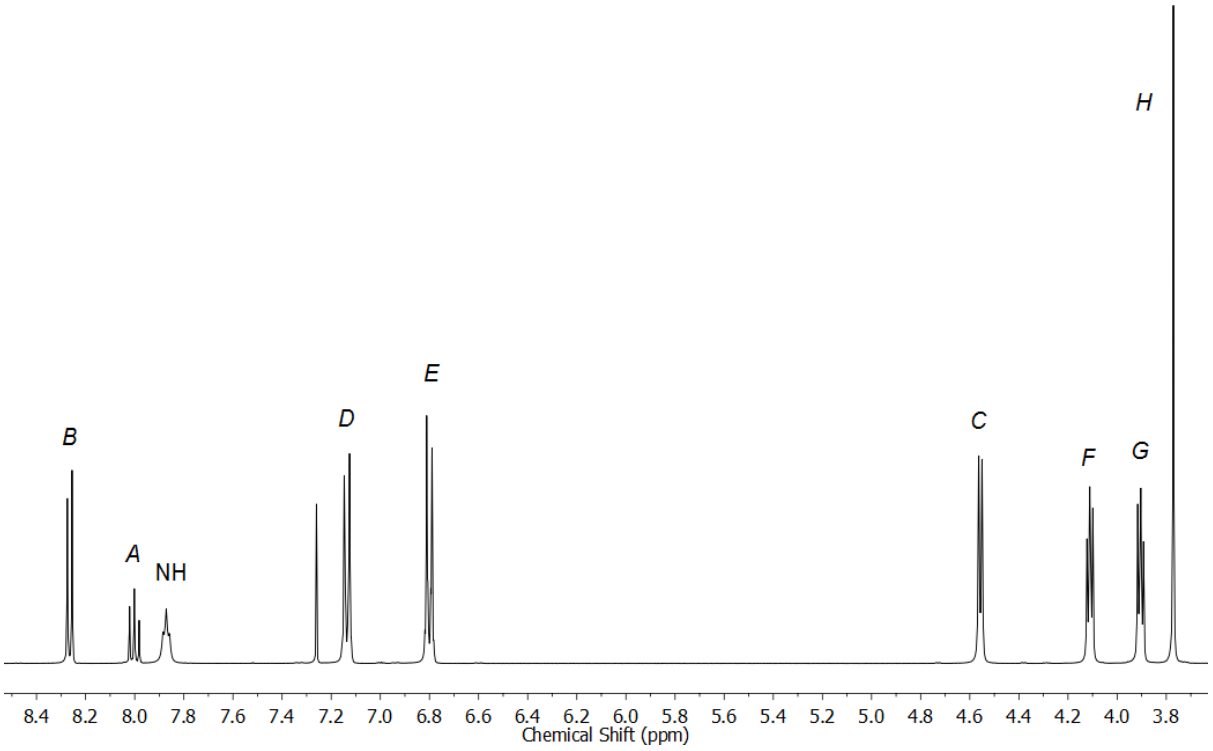


Figure S64 ^{1}H NMR ($CDCl_3$, 400 MHz) of **3f**.

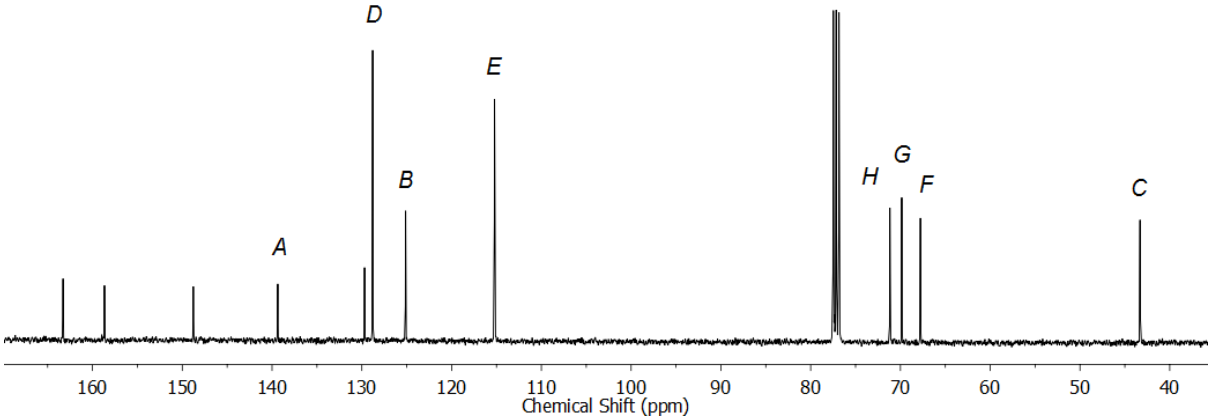


Figure S65 ^{13}C NMR ($CDCl_3$, 101 MHz) of **3f**.

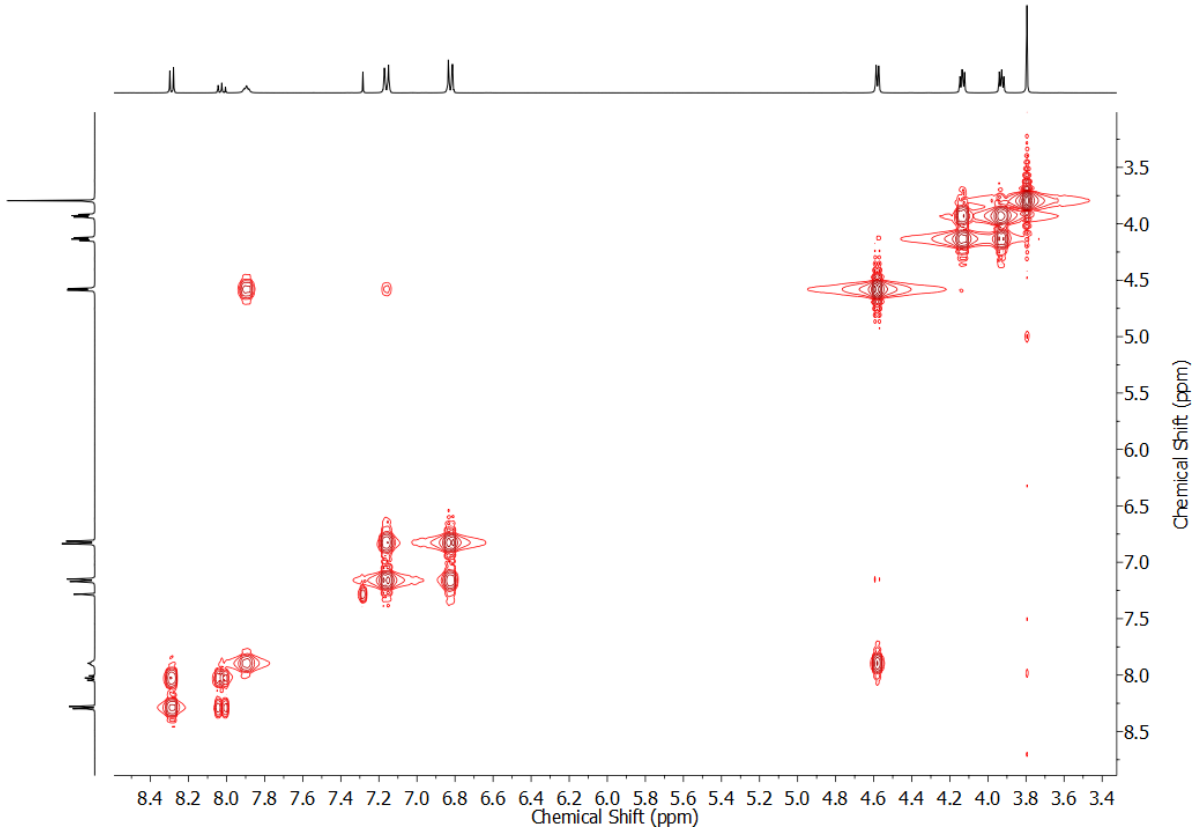


Figure S66 COSY NMR ($CDCl_3$) of **3f**.

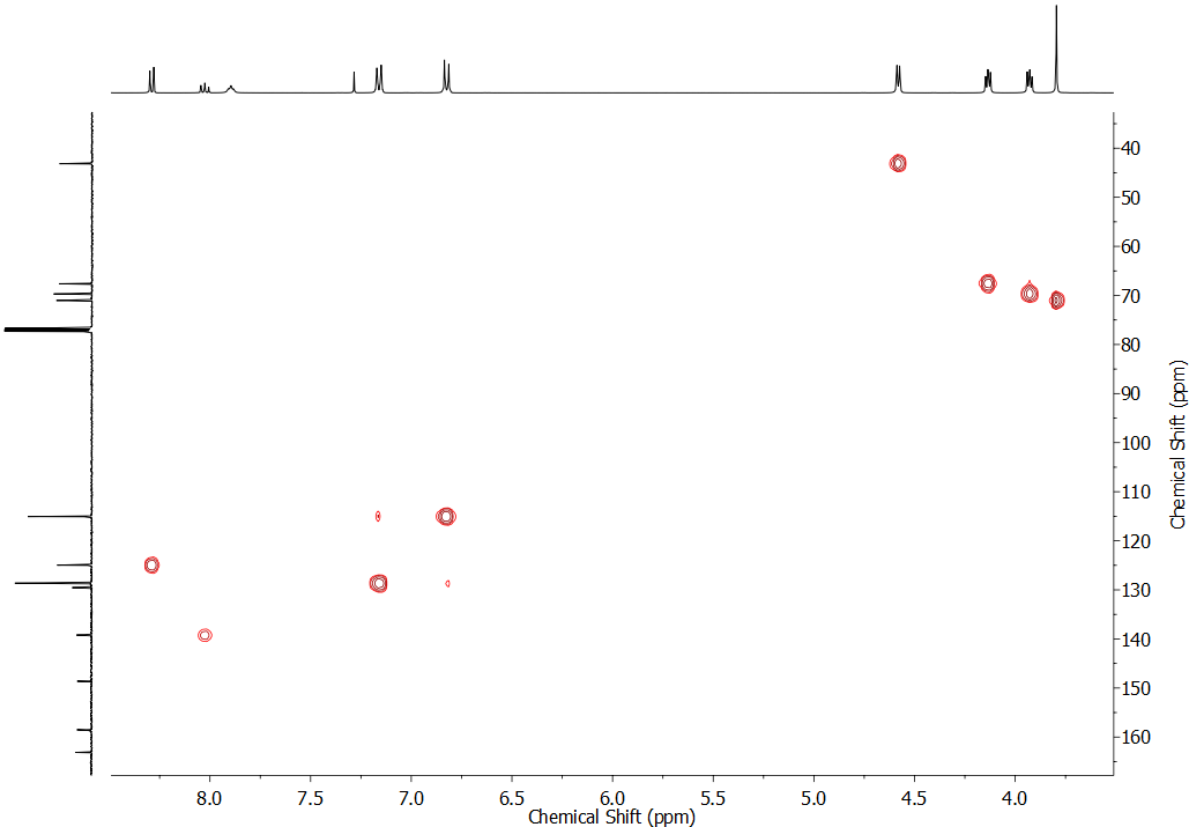


Figure S67 HSQC NMR ($CDCl_3$) of **3f**.

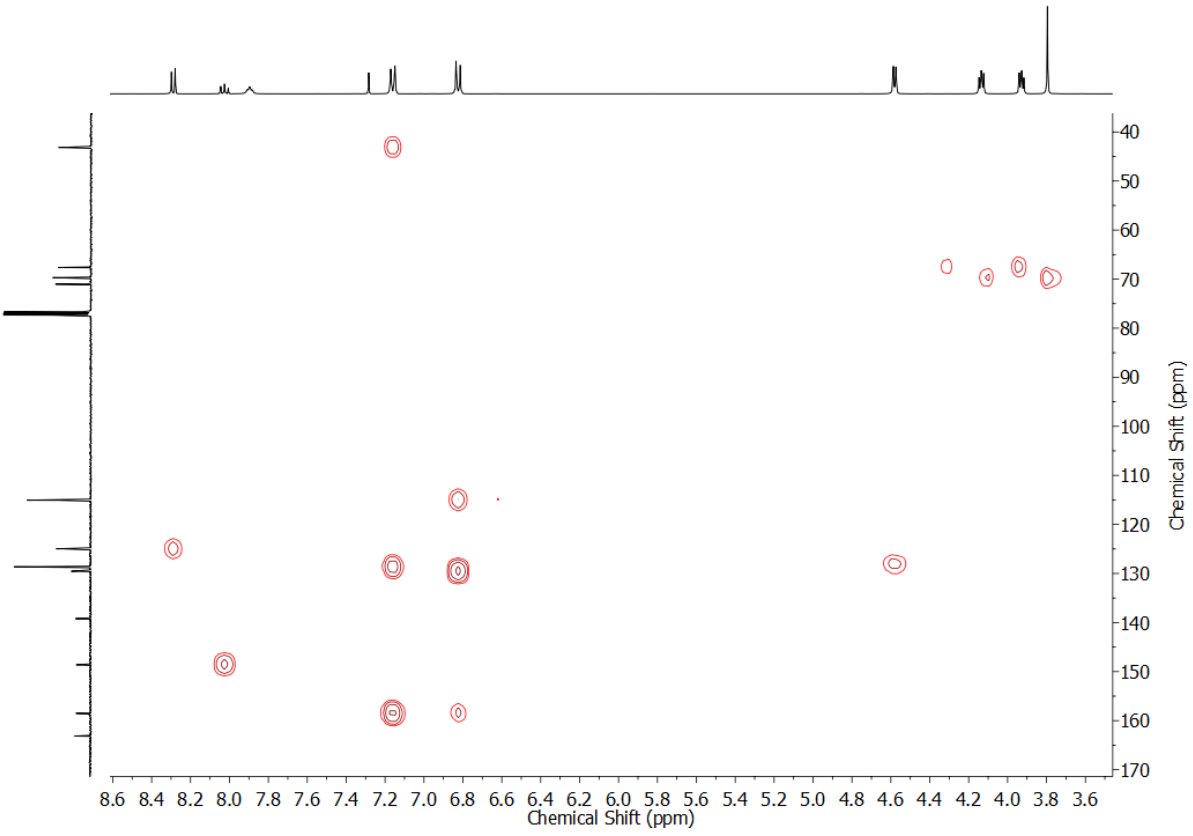
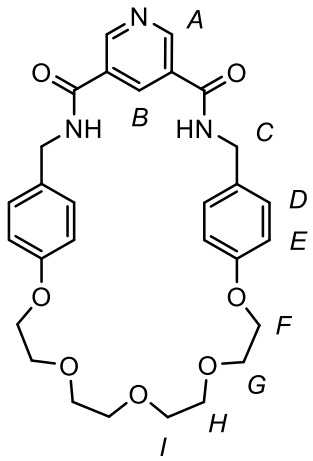


Figure S68 HMBC NMR ($CDCl_3$) of **3f**.

Macrocycle 3g and [2]Catenane 4g

7 (0.102 g, 0.50 mmol, 1 eq.) in CH_2Cl_2 (dry, 40 mL) and **2b** (0.202 g, 0.50 mmol, 1 eq.) in CH_2Cl_2 (dry, 40 mL) were added simultaneously via syringe pump to NEt_3 (0.35 mL, 2.5 mmol, 5 eq.) in CH_2Cl_2 (dry, 40 mL) over 2 h at rt under N_2 before stirring for an additional 16 h. The reaction mixture was washed with 1 M $HCl_{(aq)}$ (50 mL), 1 M $KOH_{(aq)}$ (50 mL) and brine (50 mL), dried ($MgSO_4$) and the solvent removed *in vacuo*. Purification by column chromatography on silica eluting with CH_2Cl_2 with a step gradient in 10% increments of acetone up to 50% acetone/CH_2Cl_2 to elute **3g** followed by 1:9 MeOH/CH_2Cl_2 to elute **4g**, gave **3g** (0.065 g, 24%) as a white solid, and **4g** (0.101 g, 38%) as an off-white foam.



Macrocycle 3g

^{1}H NMR (400 MHz, d_6-DMSO) δ: 9.30 (d, J = 2.1 Hz, 2H, H_A), 8.99 (t, J = 5.6 Hz, 2H, H_{NH}), 8.40 (t, J = 2.1 Hz, 1H, H_B), 7.25 (d, J = 8.7 Hz, 4H, H_D), 6.68 (d, J = 8.6 Hz, 4H, H_E), 4.39 (d, J = 5.5 Hz, 4H, H_C), 4.08-4.02 (m, 4H, H_F), 3.71-3.66 (m, 4H, H_G), 3.56-3.48 (m, 8H, H_H, H_I). ^{13}C NMR (101 MHz, d_6-DMSO) δ: 164.5, 157.6, 150.5 (C_A), 133.3 (C_B), 130.8, 129.7, 129.4 (C_D), 114.3 (C_E), 69.9 (C_H/C_I), 69.9 (C_H/C_I), 68.8 (C_G), 67.2 (C_F), 42.5 (C_C). HR-ESI-MS m/z = 536.2394 $[M+H]^+$ calc. 536.2397.

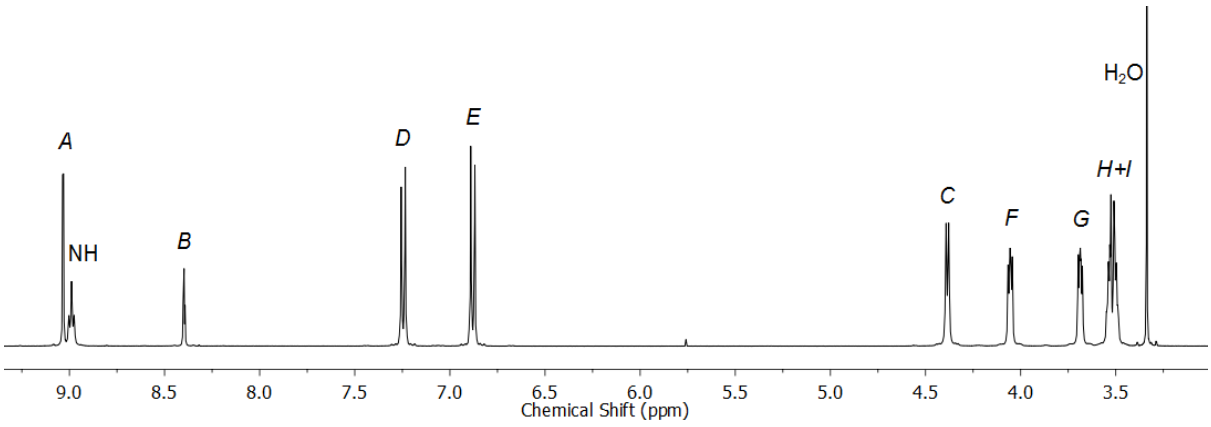


Figure S69 ^{1}H NMR (d_6-DMSO, 400 MHz) of **3g**.

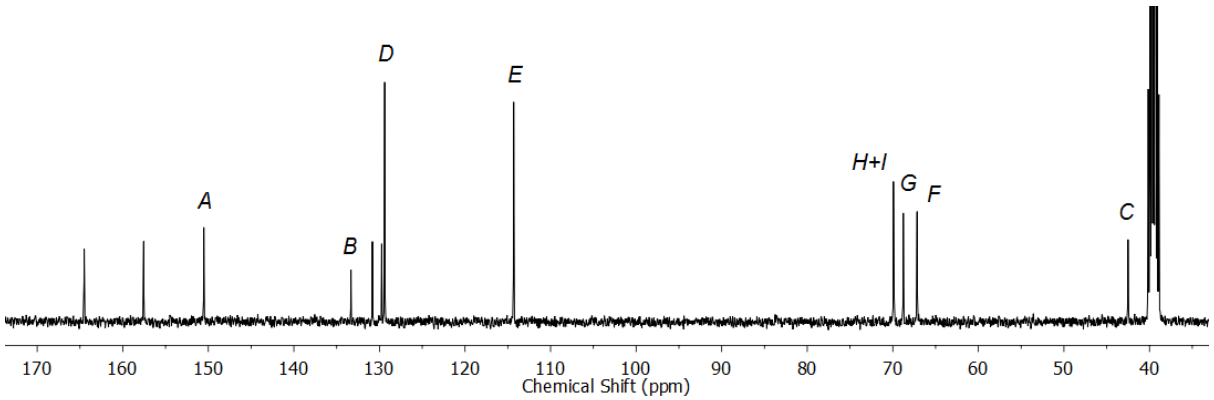


Figure S70 ^{13}C NMR (d_6-DMSO, 101 MHz) of **3g**.

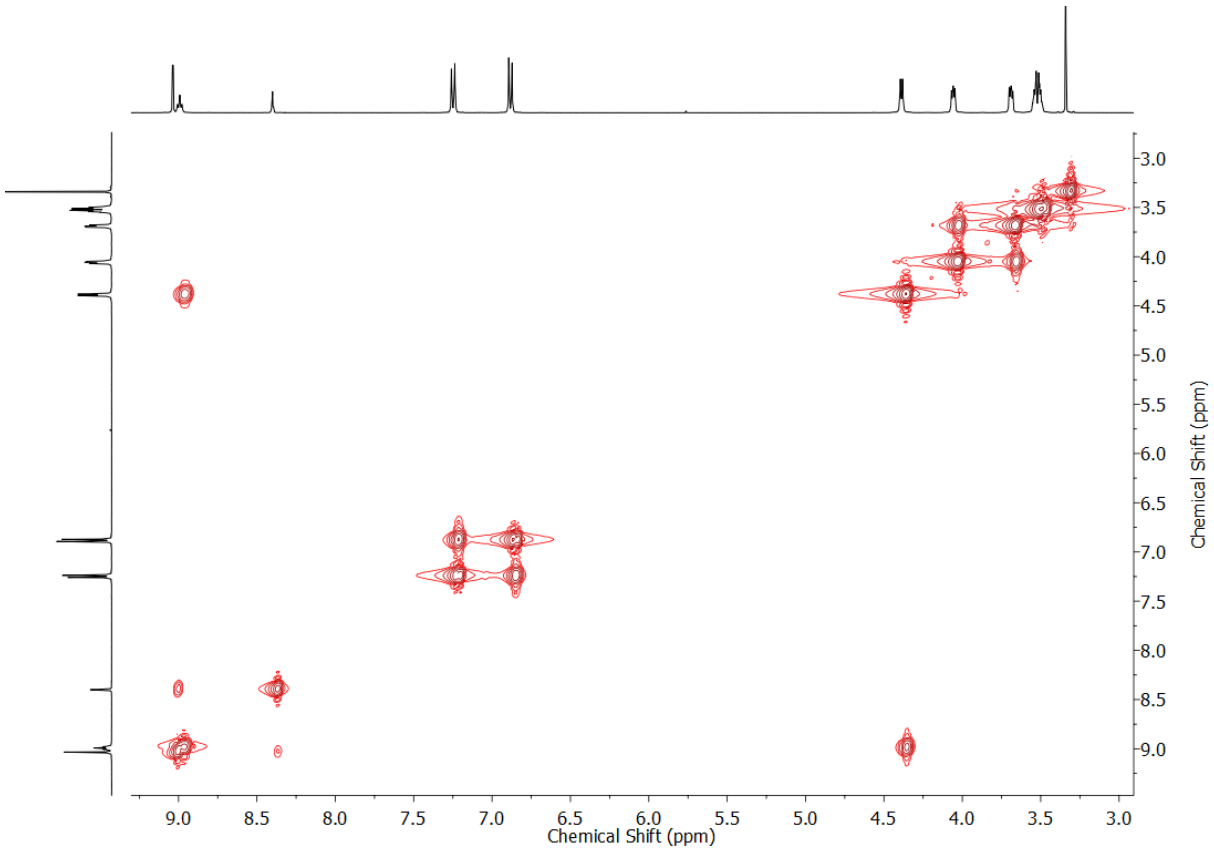


Figure S71 COSY NMR (d_6-DMSO) of **3g**.

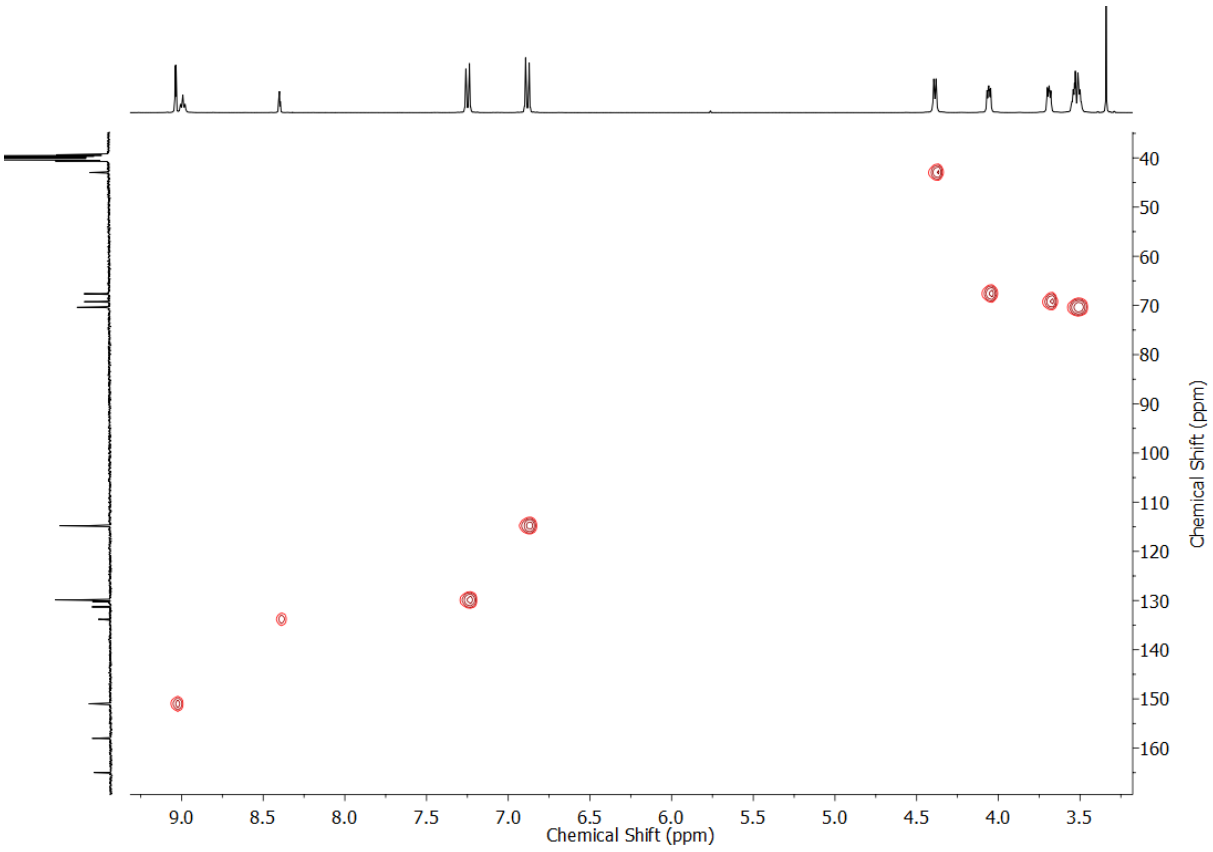


Figure S72 HSQC NMR (d_6-DMSO) of **3g**.

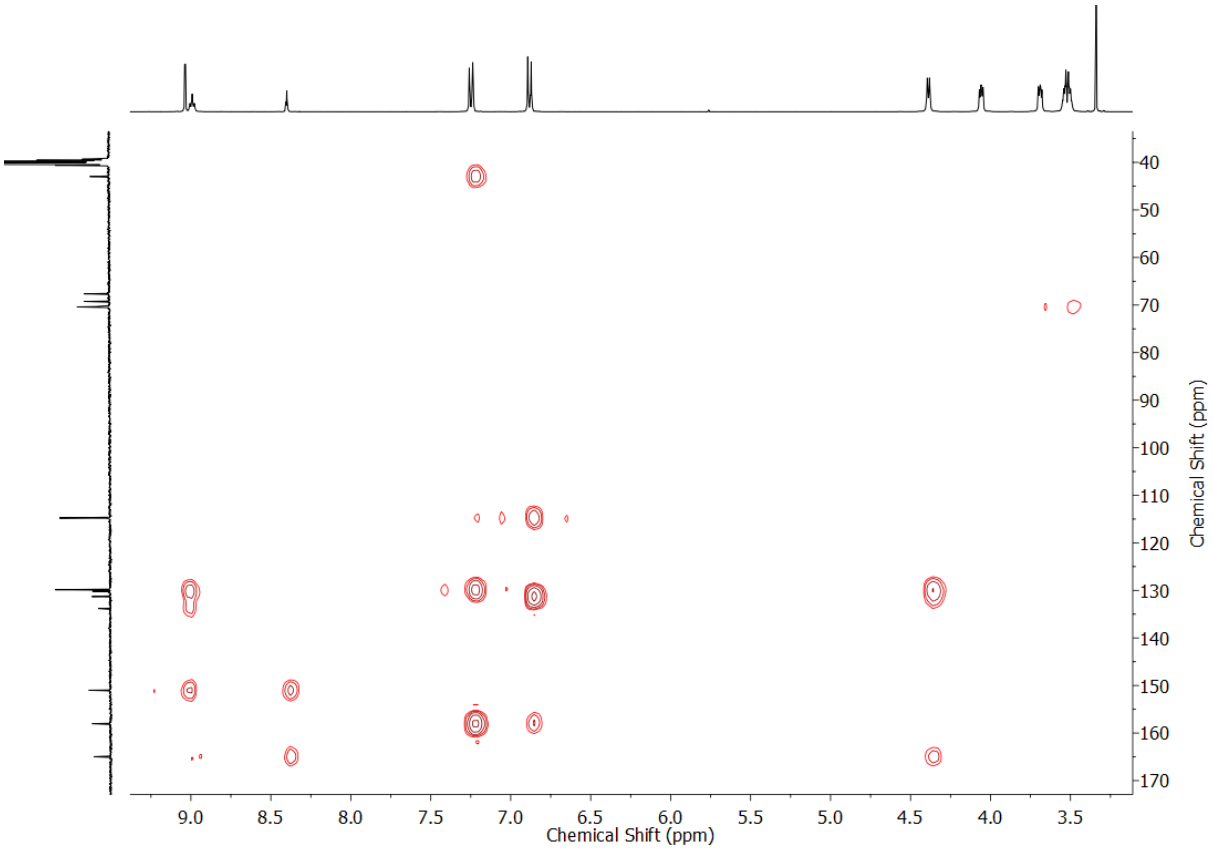
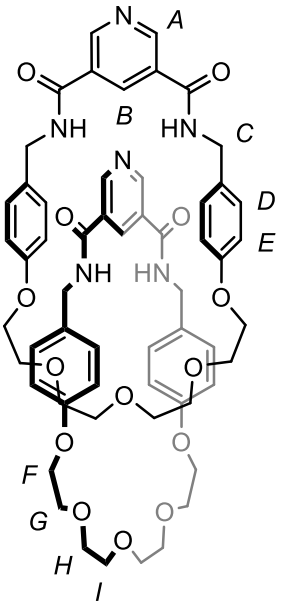


Figure S73 HMBC NMR (d_6-DMSO) of **3g**.



[2]Catenane 4g

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.12 (d, *J* = 2.0 Hz, 4H, H_A), 8.54 (t, *J* = 2.1 Hz, 2H, H_B), 7.59 (t, *J* = 5.0 Hz, 4H, H_{NH}), 6.98 (d, *J* = 8.6 Hz, 8H, H_D), 6.44 (d, *J* = 8.6 Hz, 8H, H_E), 4.32 (d, *J* = 4.8 Hz, 8H, H_C), 3.84-3.79 (m, 8H, H_F), 3.66-3.61 (m, 8H, H_G), 3.49 (s, 16H, H_H, H_I). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.4, 157.7, 152.2 (C_A), 131.6 (C_B), 130.1 (C_D), 129.7, 128.7, 114.1 (C_E), 70.7 (C_H/C_I), 70.6 (C_H/C_I), 69.7 (C_G), 67.3 (C_F), 44.1 (C_C). HR-ESI-MS *m/z* = 1071.4700 $[M+H]^+$ calc. 1071.4715.

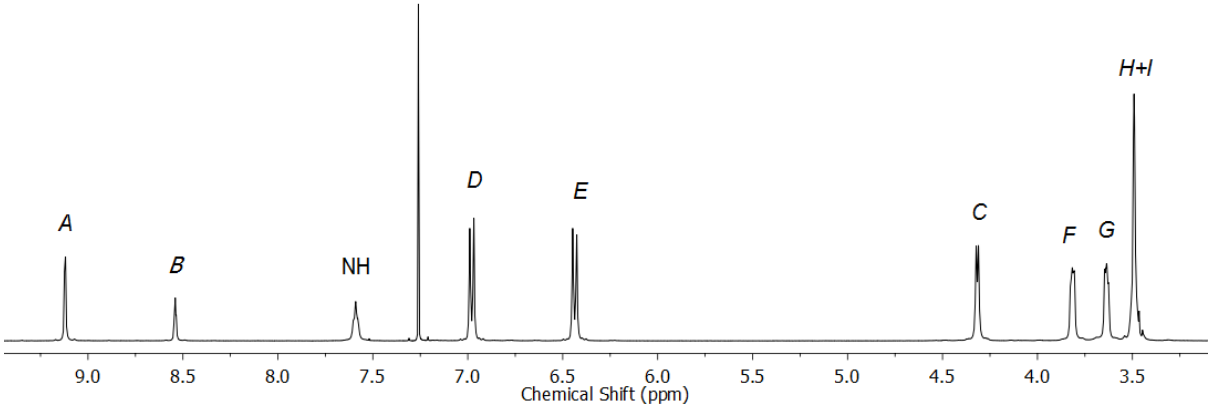


Figure S74 ^{1}H NMR ($CDCl_3$, 400 MHz) of **4g**.

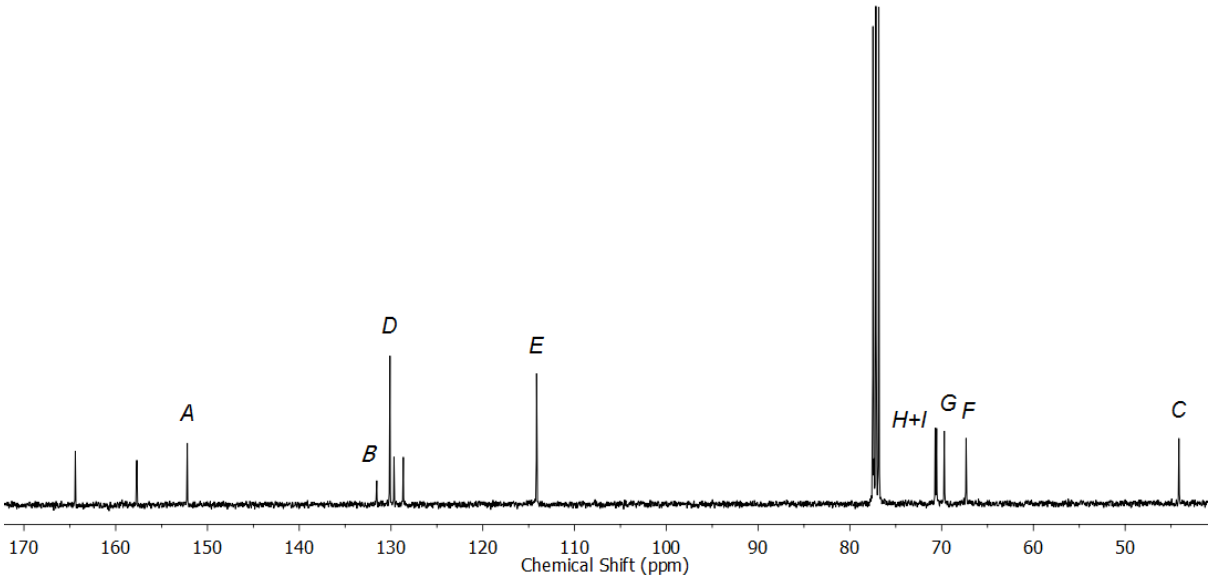


Figure S75 ^{13}C NMR ($CDCl_3$, 101 MHz) of **4g**.

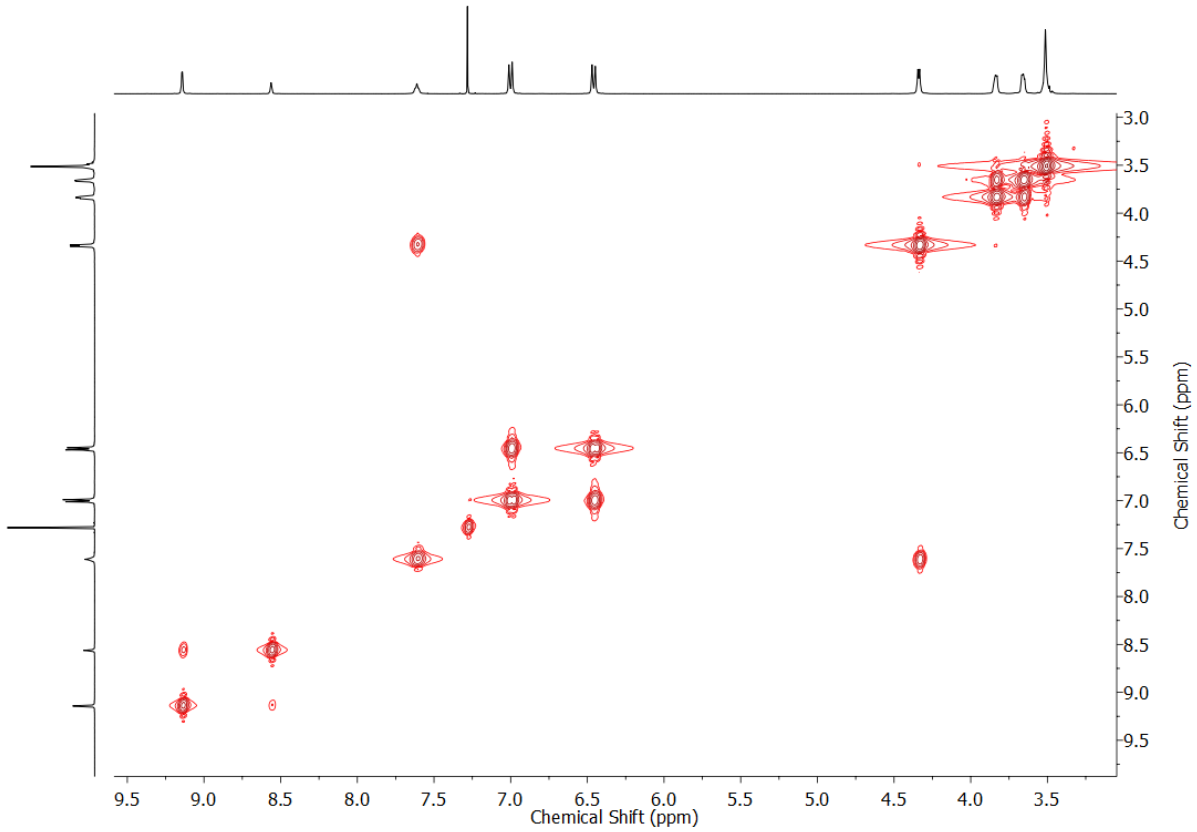


Figure S76 COSY NMR ($CDCl_3$) of **4g**.

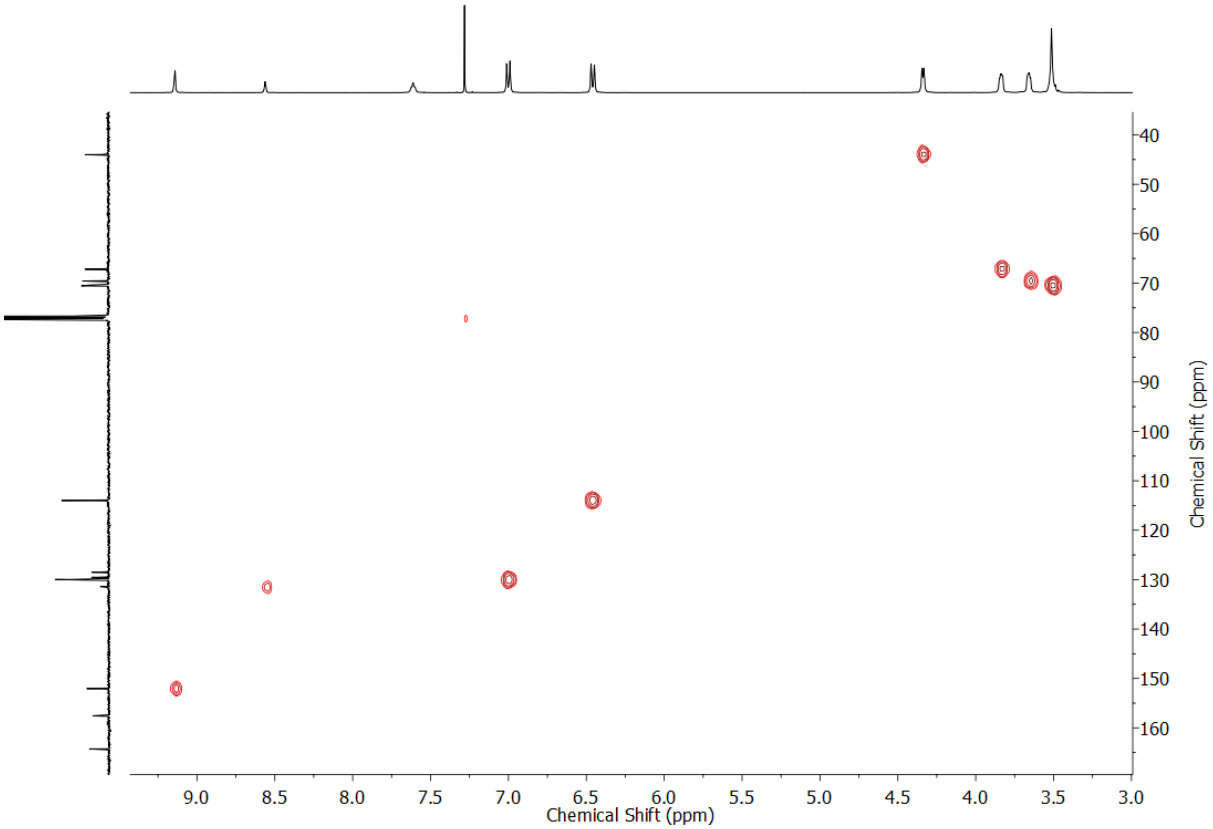


Figure S77 HSQC NMR ($CDCl_3$) of **4g**.

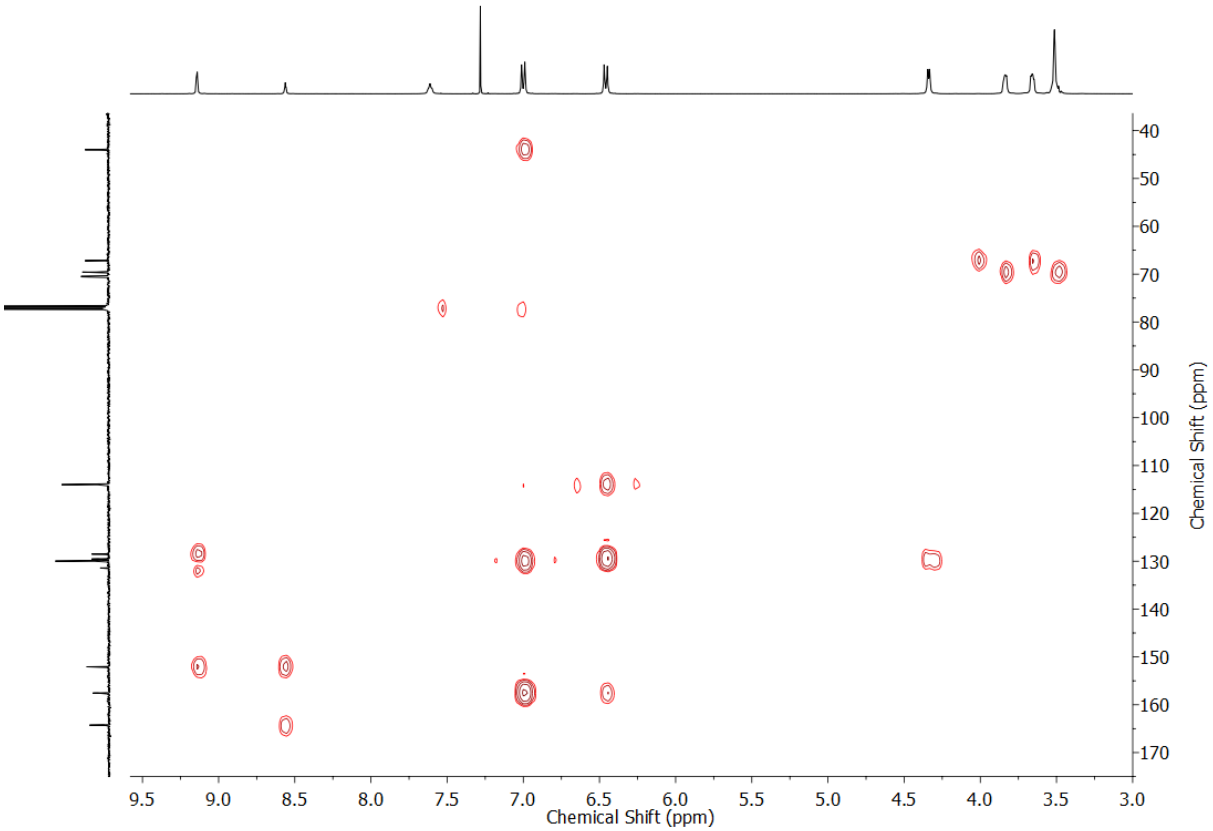


Figure S78 HMBC NMR ($CDCl_3$) of **4g**.

Crude Reaction ^{1}H NMR Spectra

0.05 mmol Catenane Reactions

1 (10.2 mg, 0.050 mmol, 1 eq.) in $CHCl_3$ (dry, 4 mL) and **2** (0.050 mmol, 1 eq.) in $CHCl_3$ (dry, 4 mL) were added simultaneously via syringe pump to NEt_3 (0.04 mL, 0.25 mmol, 5 eq.) in $CHCl_3$ (dry, 4 mL) over 2 h at rt under N_2 before stirring for an additional 16 h. To the crude reaction mixture was added a 0.05 M solution of 1,3,5-trimethoxybenzene in $CHCl_3$ (1.0 mL, 0.05 mmol, 1 eq.). The solvent was removed *in vacuo* and the mixture analysed by ^{1}H NMR.

	NMR Yield[a]	
2	**(1+1) Macrocycle 3**	**(1+1+1+1) Catenane 4**
2a	48%	24-25%
2b	35-39%	44-47%
2c	43%	14-19%

[a]Where multiple signals for the species could be reliably identified and integrated, the range of values determined is given.

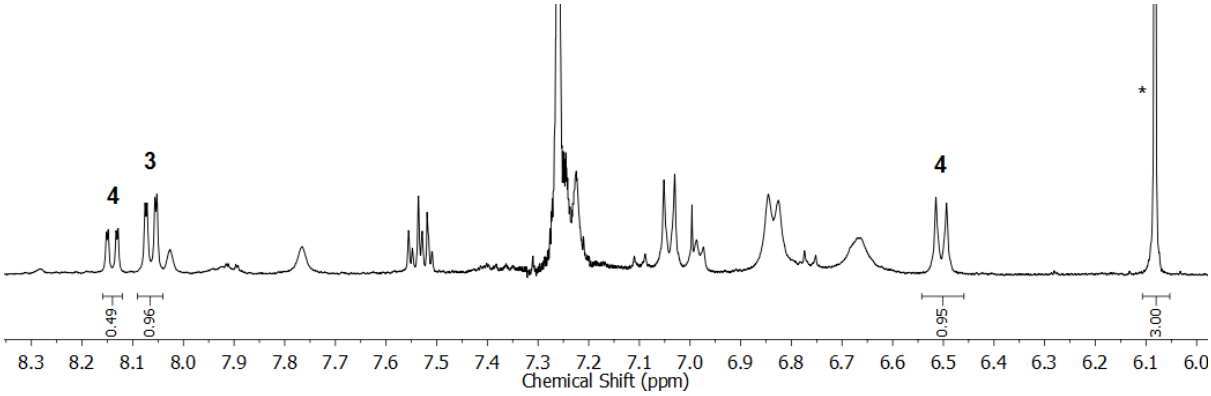


Figure S79 Partial ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of the crude **3a**/**4a** reaction mixture. * = 1,3,5-trimethoxybenzene reference signal.

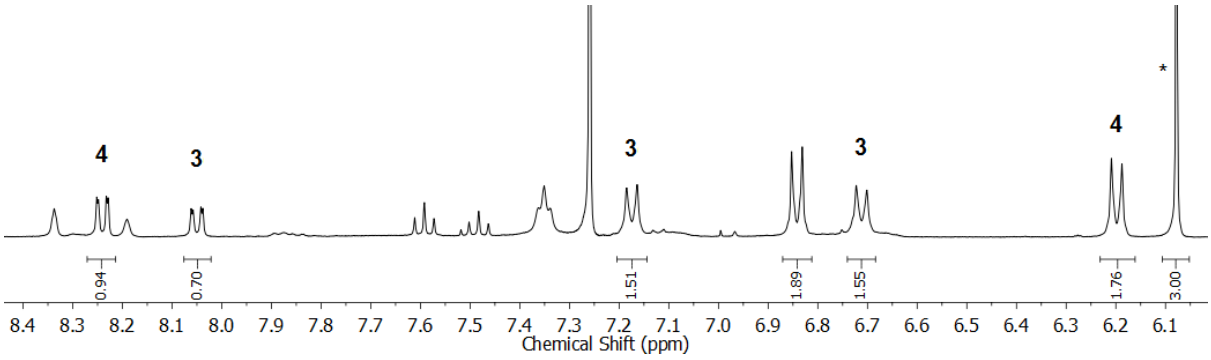


Figure S80 Partial ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of the crude **3b**/**4b** reaction mixture. * = 1,3,5-trimethoxybenzene reference signal.

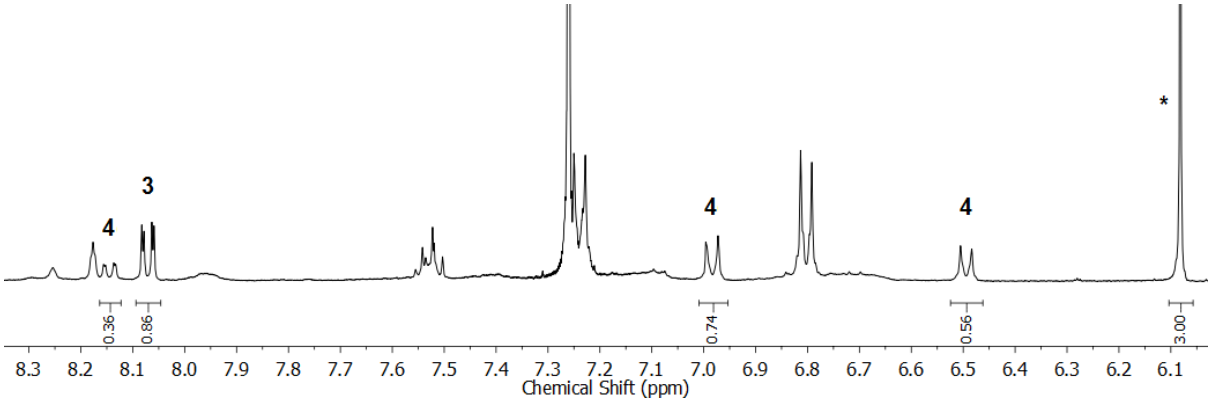


Figure S81 Partial ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of the crude **3c**/**4c** reaction mixture. * = 1,3,5-trimethoxybenzene reference signal.

Additional Crude Reaction NMR Spectra

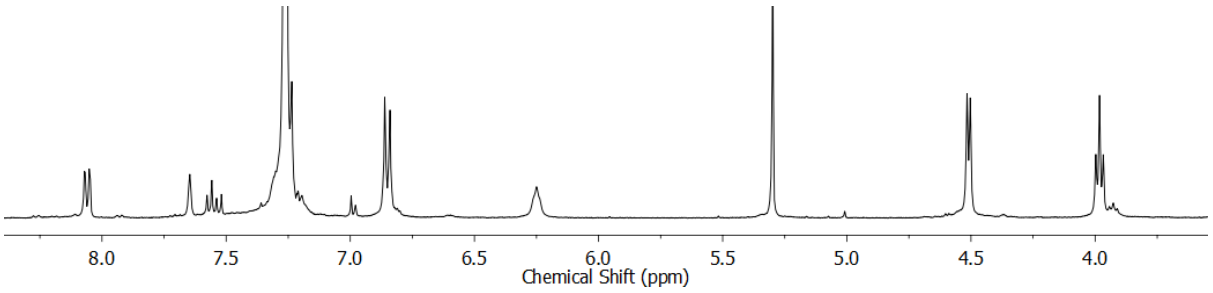


Figure S82 Partial ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of crude **3d** reaction mixture.

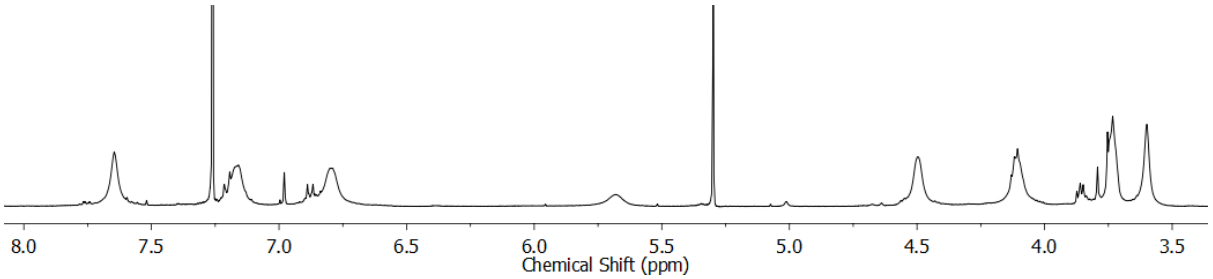


Figure S83 Partial ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of crude **3e** reaction mixture.

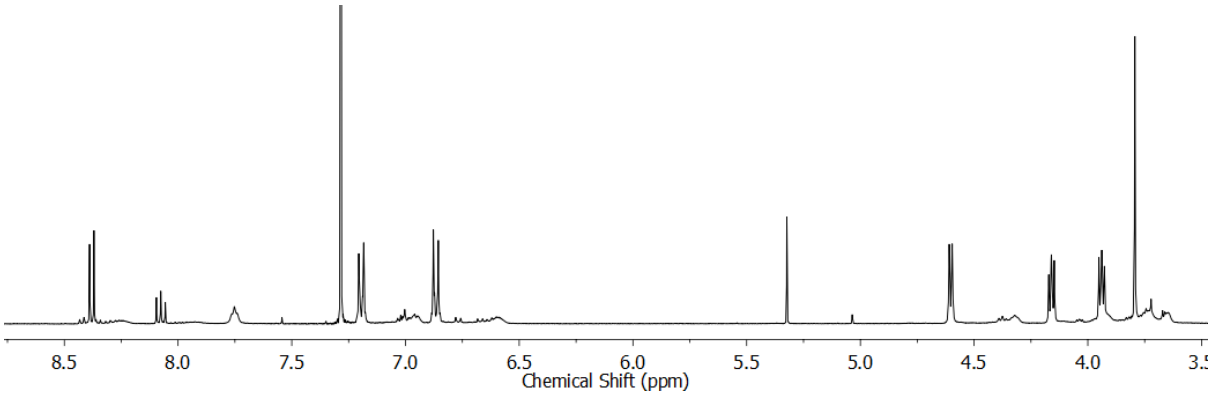


Figure S84 Partial ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of crude **3f** reaction mixture.

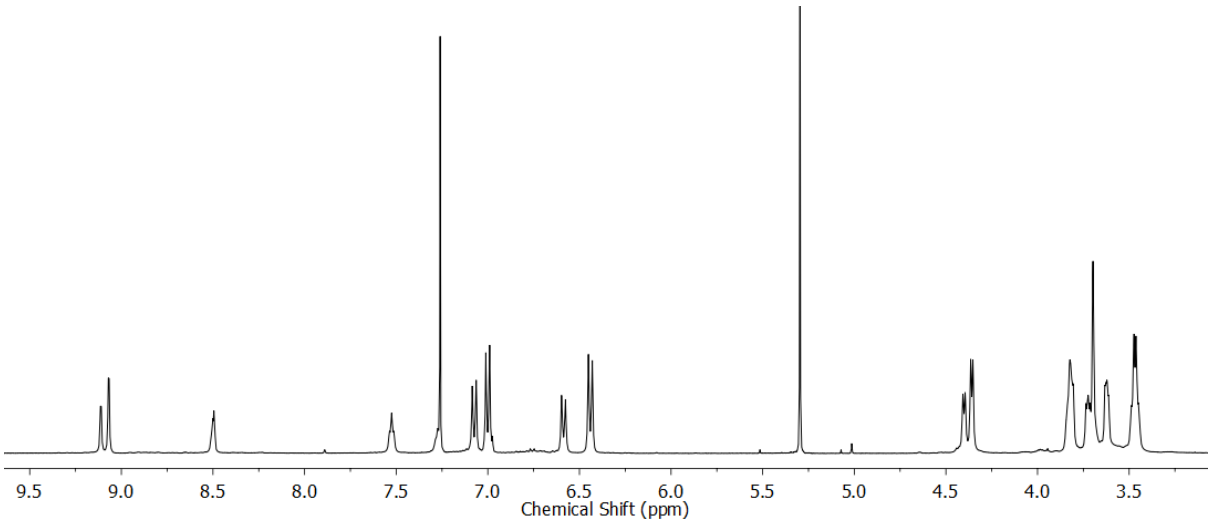


Figure S85 Partial ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of crude **4g** reaction mixture.

^{1}H NMR N-benzyl-/phenyl-benzamide Binding Studies

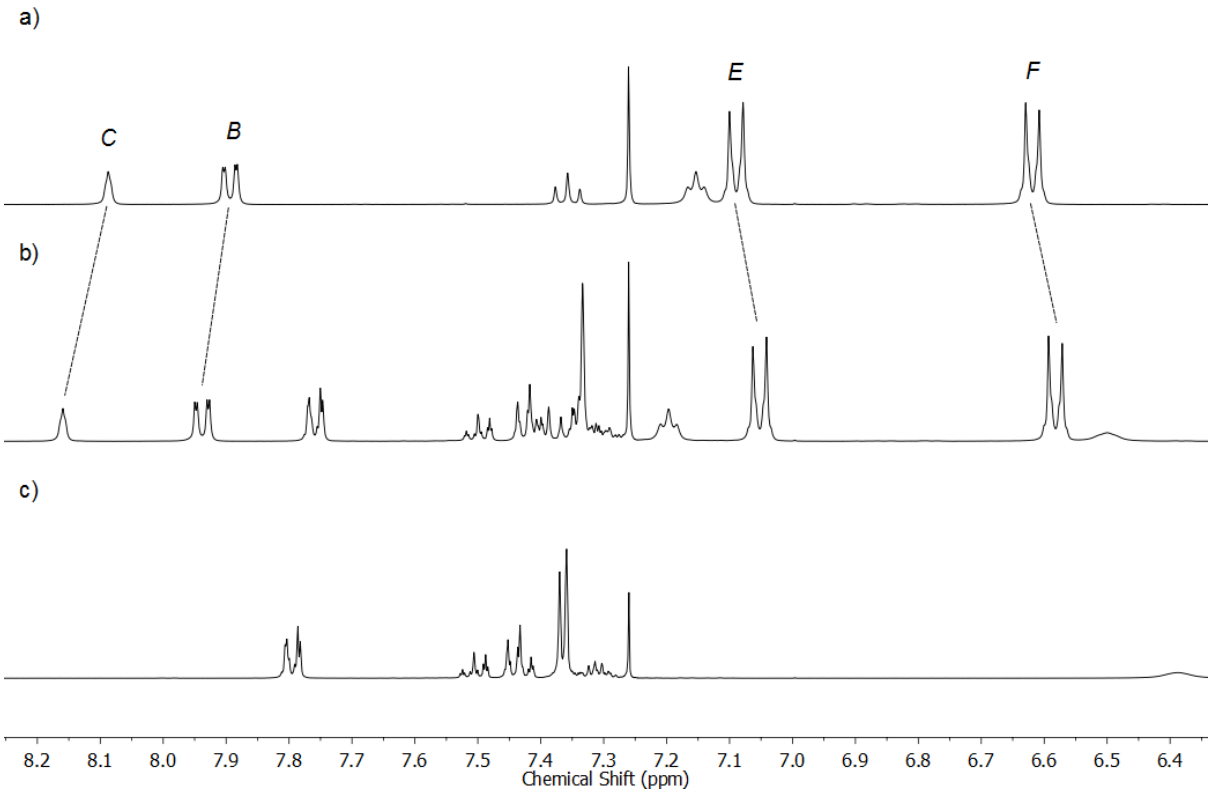


Figure S86 Partial ^{1}H NMR spectra (25 mM $CDCl_3$, 400 MHz) of a) macrocycle **3b**, b) **3b** and N-benzylbenzamide, and c) N-benzylbenzamide.

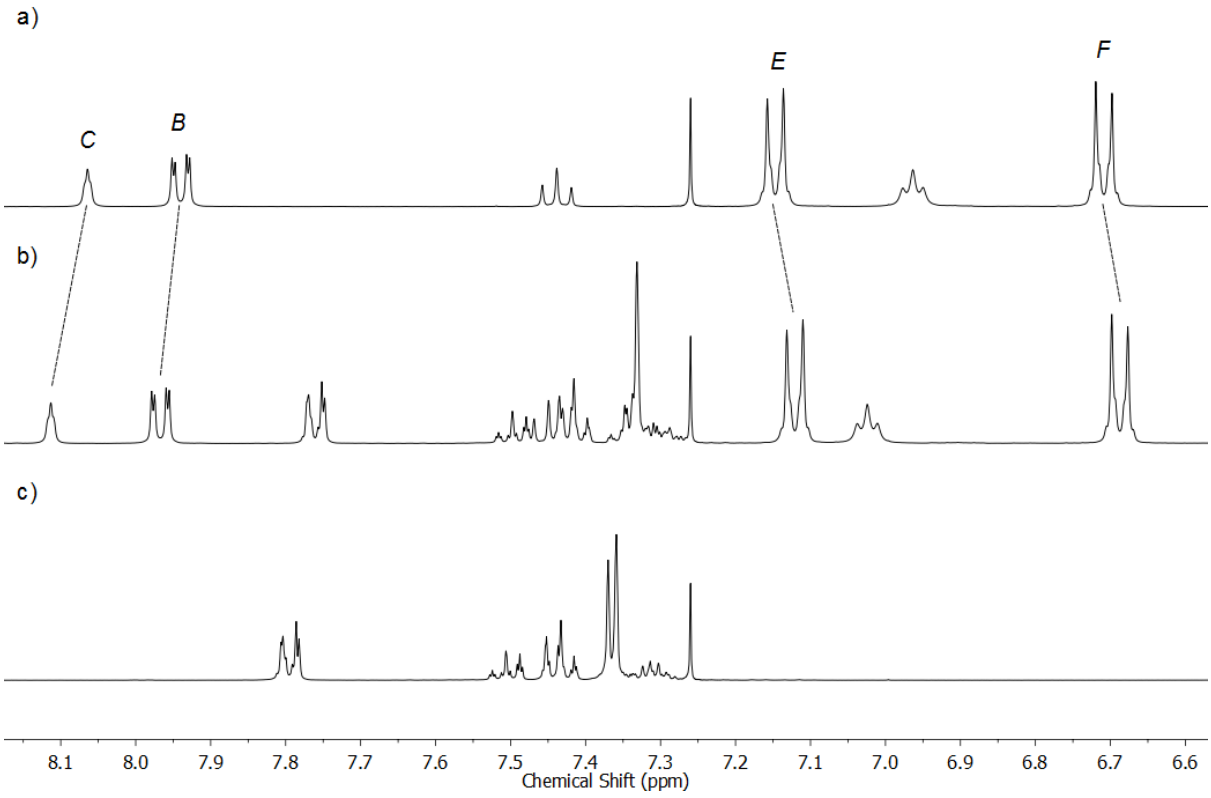


Figure S87 Partial ^{1}H NMR spectra (25 mM $CDCl_3$, 400 MHz) of a) macrocycle **3c**, b) **3c** and N-benzylbenzamide, and c) N-benzylbenzamide.

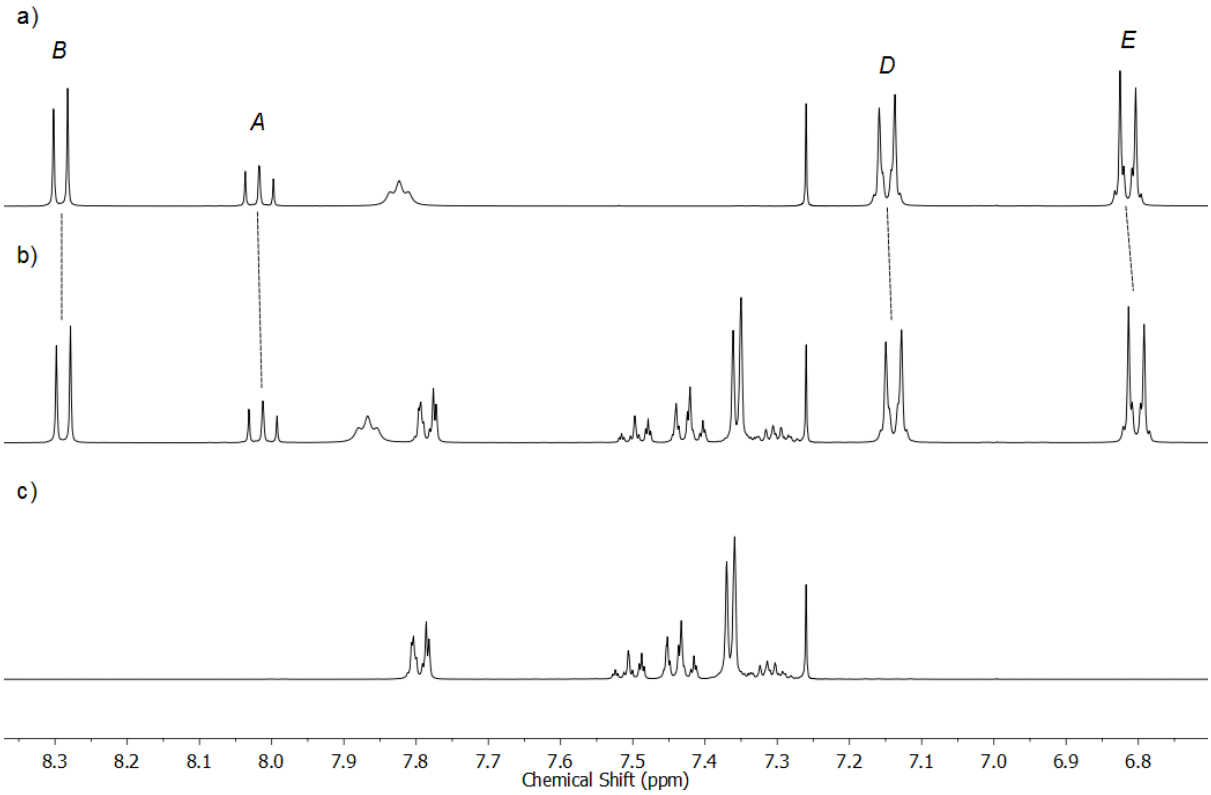


Figure S88 Partial ^{1}H NMR spectra (25 mM $CDCl_3$, 400 MHz) of a) macrocycle **3f**, b) **3f** and N-benzylbenzamide, and c) N-benzylbenzamide.

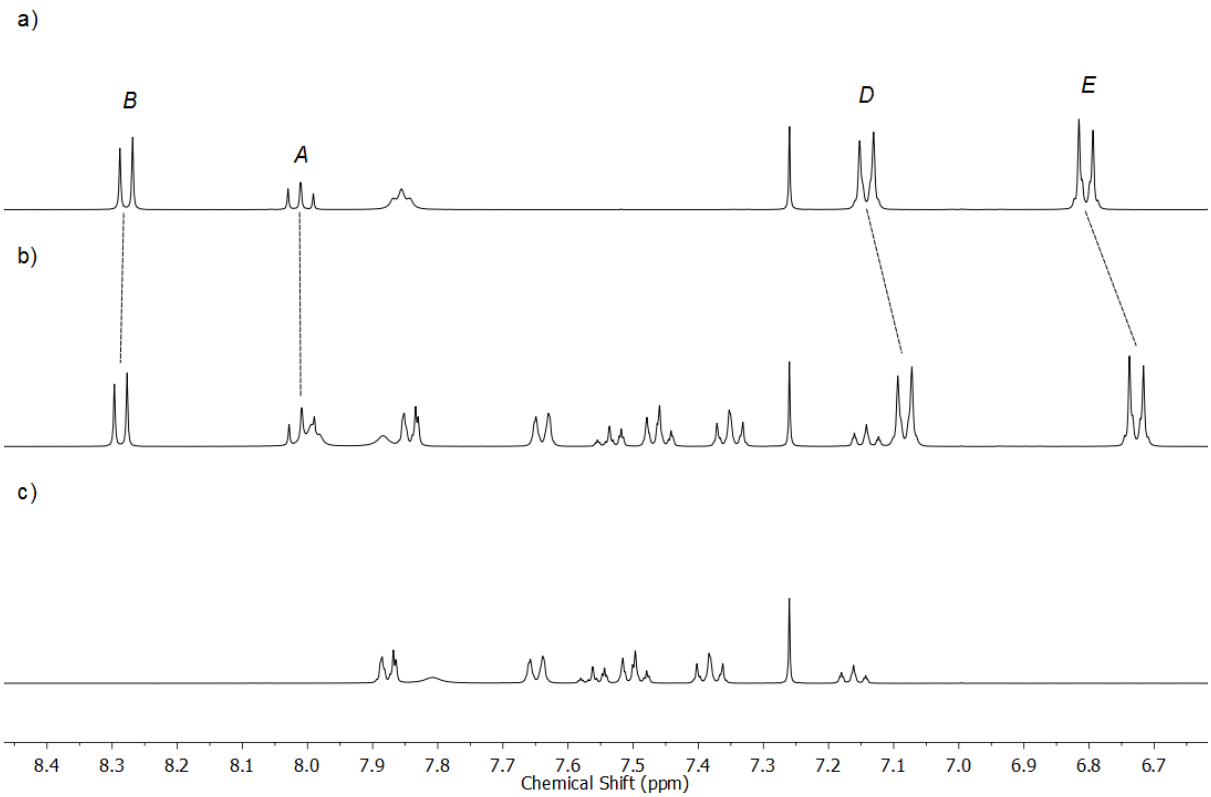


Figure S89 Partial ^{1}H NMR spectra (25 mM $CDCl_3$, 400 MHz) of a) macrocycle **3f**, b) **3f** and N-phenylbenzamide, and c) N-phenylbenzamide.

X-ray Data

X-ray Data for [2]catenane 4a

Crystals of **4a** were grown by vapour diffusion of pentane into a solution of the catenane in 1,2-dichloroethane.

Crystal data for **4a**: $2(C_{28}H_{30}N_2O_6)\cdot C_2H_4Cl_2$, M = 1080.03, triclinic, P-1 (no. 2), a = 8.9724(3), b = 17.8840(7), c = 18.7581(7) Å, α = 71.649(4), β = 78.938(3), γ = 75.953(3)°, V = 2749.61(19) Å^3, Z = 2, D_c = 1.304 g cm^{-3}, μ(Cu-Kα) = 1.606 mm^{-1}, T = 173 K, colourless blocky needles, Agilent Xcalibur PX Ultra A diffractometer; 10510 independent measured reflections (R_{int} = 0.0276), F^2 refinement,[5,6] R_1(obs) = 0.0543, wR_2(all) = 0.1644, 7638 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, completeness to θ_{full}(67.7°) = 98.4%], 714 parameters. CCDC 1868404.

The C10- to C18-based $-C_6H_4OCH_2CH_2-$ unit in the structure of **4a** was found to be disordered. Two orientations were identified of *ca*. 85 and 15% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically). The N–H hydrogen atoms on N8, N33, N48 and N73 were all located from ΔF maps and refined freely subject to an N–H distance constraint of 0.90 Å. One outlier reflection for which [I(obs) – I(calc)]/σ(W) was ca. 19 was omitted from the refinements.

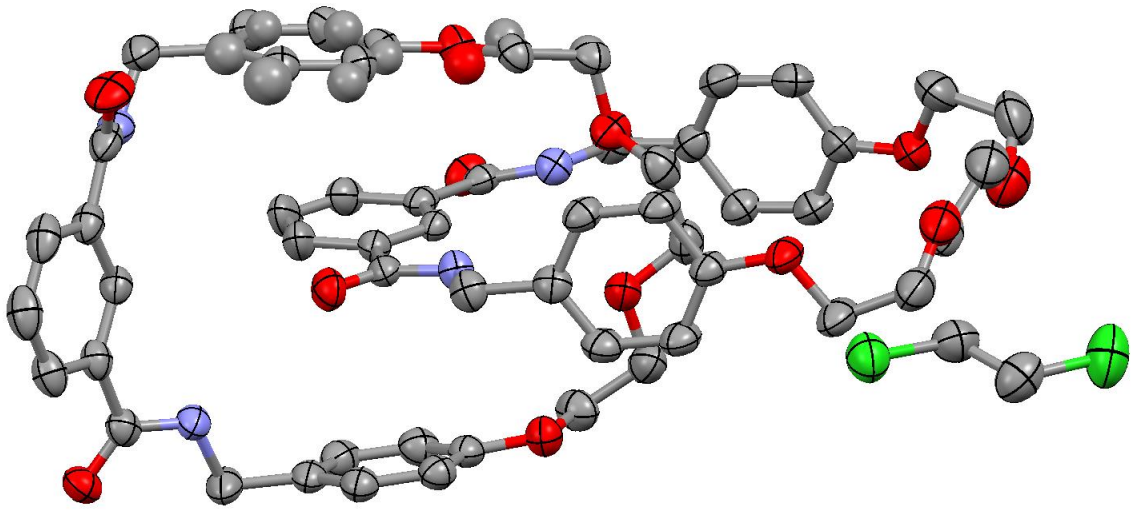


Figure S90 Ellipsoid plot of the asymmetric unit of **4a**·$C_2H_4Cl_2$. Ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

X-ray Data for [2]catenane 4g

Crystals of **4g** were grown by vapour diffusion of H_2O into a solution of the catenane in DMF.

Crystal data for **4g**: $2(C_{29}H_{33}N_3O_7)\cdot 6.25H_2O$, M = 1183.76, triclinic, P-1 (no. 2), a = 13.3255(6), b = 13.5278(6), c = 17.7443(8) Å, α = 90.033(3), β = 100.915(4), γ = 105.148(4)°, V = 3027.4(2) Å^3, Z = 2, D_c = 1.299 g cm^{-3}, μ(Mo-Kα) = 0.099 mm^{-1}, T = 173 K, colourless block, Agilent Xcalibur 3 E diffractometer; 11912 independent measured reflections (R_{int} = 0.0207), F^2 refinement,[5,6] R_1(obs) = 0.0468, wR_2(all) = 0.1109, 8665 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, completeness to θ_{full}(25.2°) = 98.6%], 835 parameters. CCDC 1889522.

The O62–C63 portion of one of the polyether chains in the structure of **4g** was found to be disordered. Two orientations were identified of *ca*. 84 and 16% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically). The O86-based water molecule was assigned a fixed occupancy of 25% based on its thermal parameter (and for simplicity). The four N–H hydrogen atoms on N8, N36, N48 and N76, and the twelve O–H hydrogen atoms on the O80-, O81-, O82-, O83-, O84-, and O85-based water molecules, were all located from Δ*F* maps and refined freely subject to X–H distance constraints of 0.90 Å. Unsurprisingly, the hydrogen atoms for the 25% occupancy O86-based water molecule could not be located. As a result, the atom list for the asymmetric unit is low by 0.5H (and that for the unit cell low by 1H) compared to what is actually presumed to be present. Three low angle reflections (resolution ca. 8 Å) for which the observed intensity was much less than the calculated intensity (likely indicating partial obscuration by the beam stop) were omitted from the refinements.

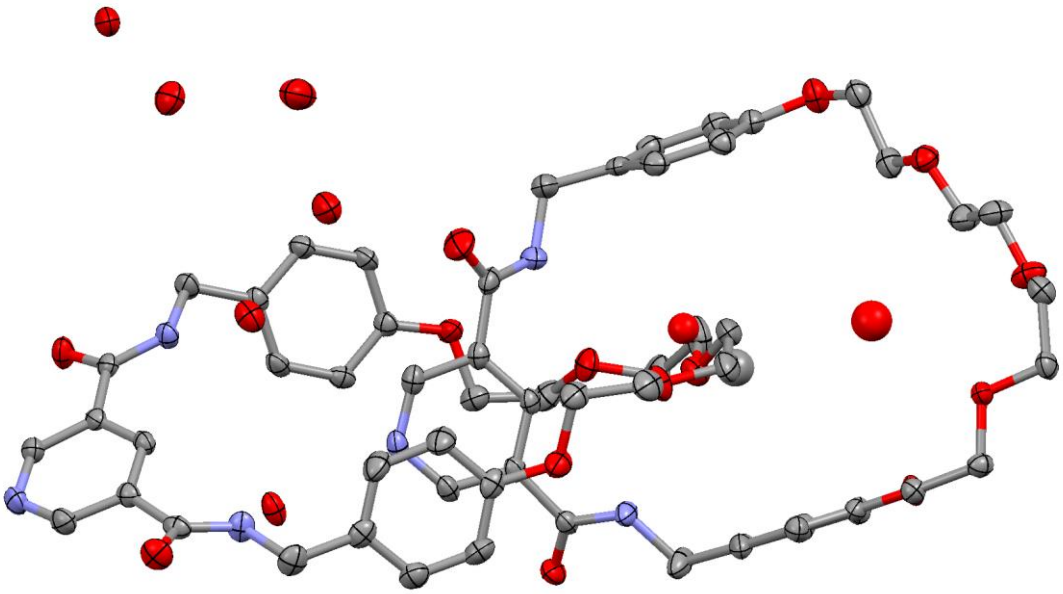


Figure S91 Ellipsoid plot of the asymmetric unit of **4g**·6.25H_2O. Ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

X-ray Data for {[Ag(4g)](OTf)}

Crystals of {[Ag(**4g**)](OTf)} were grown by vapour diffusion of Et_2O into a solution of 1:1 **4g**/AgOTf in DMF.

Crystal data for {[Ag(**4g**)](OTf)}: $[C_{58}H_{66}AgN_6O_{14}](CF_3O_3S)\cdot 4(C_4H_{10}O)$, M = 1624.58, monoclinic, *I*2/*a* (no. 15), a = 28.3764(9), b = 22.9821(8), c = 26.0316(10) Å, β = 110.512(4)°, V = 15900.2(11) $Å^3$, Z = 8, D_c = 1.357 g cm^{-3}, μ(Mo-Kα) = 0.361 mm^{-1}, T = 173 K, colourless tabular needles, Agilent Xcalibur 3 E diffractometer; 15974 independent measured reflections (R_{int} = 0.0244), F^2 refinement,[5,6] R_1(obs) = 0.0751, wR_2(all) = 0.2435, 11086 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, completeness to θ_{full}(25.2°) = 98.7%], 888 parameters. CCDC 1889521.

The $(CH_2CH_2O)_3$–C_6H_4 unit (labelled C60 to C74) of the N41-based macrocycle in the structure of {[Ag(**4g**)](OTf)} was found to be disordered. Two orientations were identified of *ca*. 69 and 31% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were

restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically). The S80-based triflate anion was also found to be disordered, and three orientations were identified of *ca*. 61, 20 and 19% occupancy. The geometries of all three orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and the atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientations were refined isotropically). The four presumed N–H hydrogen atoms on N8, N36, N48 and N76 could not be reliably located from Δ*F* maps and so they were added in idealised positions with an N–H distance constraint of 0.90 Å.

The included solvent was found to be highly disordered, and the best approach to handling this diffuse electron density was found to be the SQUEEZE routine of PLATON.[7] This suggested a total of 1374 electrons per unit cell, equivalent to 171.8 electrons per asymmetric unit. Before the use of SQUEEZE the solvent most resembled diethyl ether ($C_4H_{10}O$, 42 electrons), and 4 diethyl ether molecules corresponds to 168 electrons, so this was used as the solvent present. As a result, the atom list for the asymmetric unit is low by $4(C_4H_{10}O) = C_{16}H_{40}O_4$ (and that for the unit cell low by $C_{128}H_{320}O_{32}$) compared to what is actually presumed to be present. Five outlier reflections for which [I(obs) – I(calc)]/σ(W) was > 10 were omitted from the refinements, as was one low angle reflection (resolution ca. 8 Å) for which the observed intensity was much less than the calculated intensity (likely indicating partial obscuration by the beam stop).

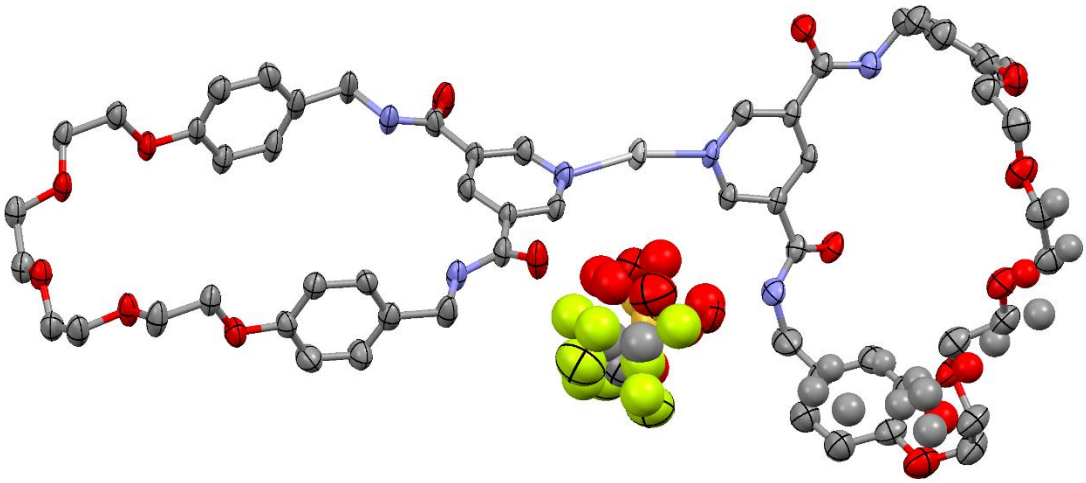


Figure S92 Ellipsoid plot of the asymmetric unit of {[Ag(**4g**)](OTf)}·4Et_2O. Ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

References

[1] M. Muraoka, H. Irie, Y. Nakatsuji, *Org. Biomol. Chem.* 2010, **8**, 2408-2413.
[2] M. J. Barrell, D. A. Leigh, P. J. Lusby, A. M. Z. Slawin, *Angew. Chem. Int. Ed.* 2008, **47**, 8036-8039.
[3] J. Bourlier, M. W. Hosseini, J.-M. Planeix, N. Kyritsakas, *New J. Chem.* 2007, **31**, 25-32.
[4] M. Ogawa, M. Nagashima, H. Sogawa, S. Kuwata, T. Takata, *Org. Lett.* 2015, **17**, 1664-1667.
[5] SHELXTL v5.1, Bruker AXS, Madison, WI, 1998.
[6] SHELX-2013, G.M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.
[7] A.L. Spek (2003, 2009) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands. See also A.L. Spek, *Acta. Cryst.*, 2015, **C71**, 9-18.