

Catechol-based macrocyclic aromatic ether-sulfones: Synthesis, characterization and ring-opening polymerization

Article

Supplemental Material

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Supplementary Material

Catechol-based macrocyclic aromatic ether-sulfones: Synthesis, characterization and ring-opening polymerization

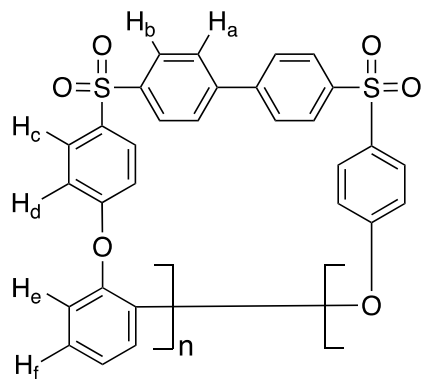
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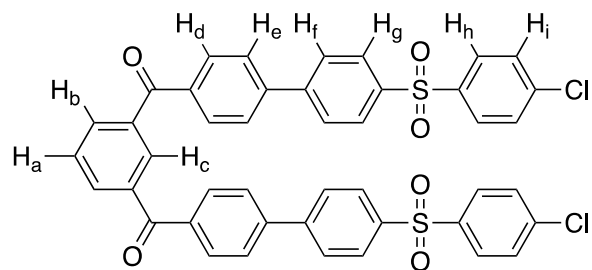
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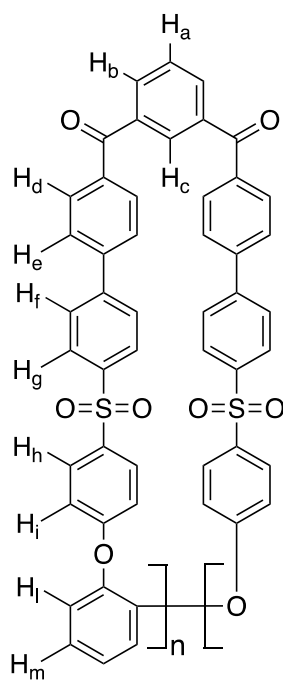
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2 ($n = 2$), **3** ($n = 3$), **4** ($n = 4$), **5** ($n = 5$)



7



8 ($n = 1$), **9** ($n = 2$)

Chart S1: Labelled structures for ^1H NMR assignments (refer to Experimental Section).

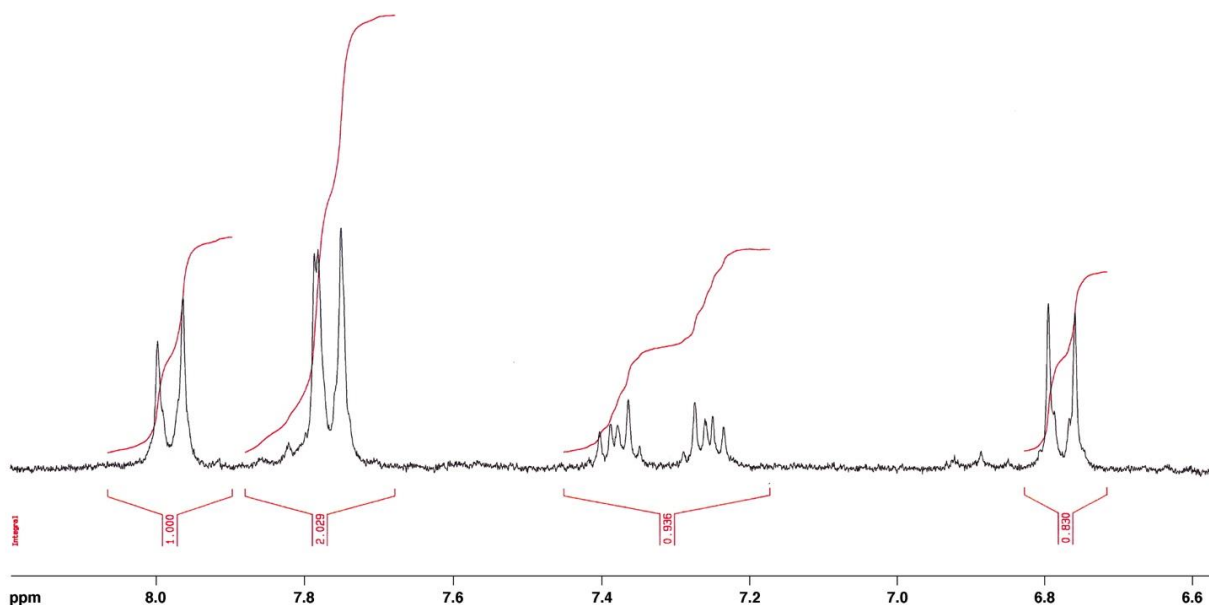


Figure S1: ¹H NMR spectrum of macrocycle **2** (250 MHz, CD₂Cl₂/CH₃SO₃H 4/1 v/v).

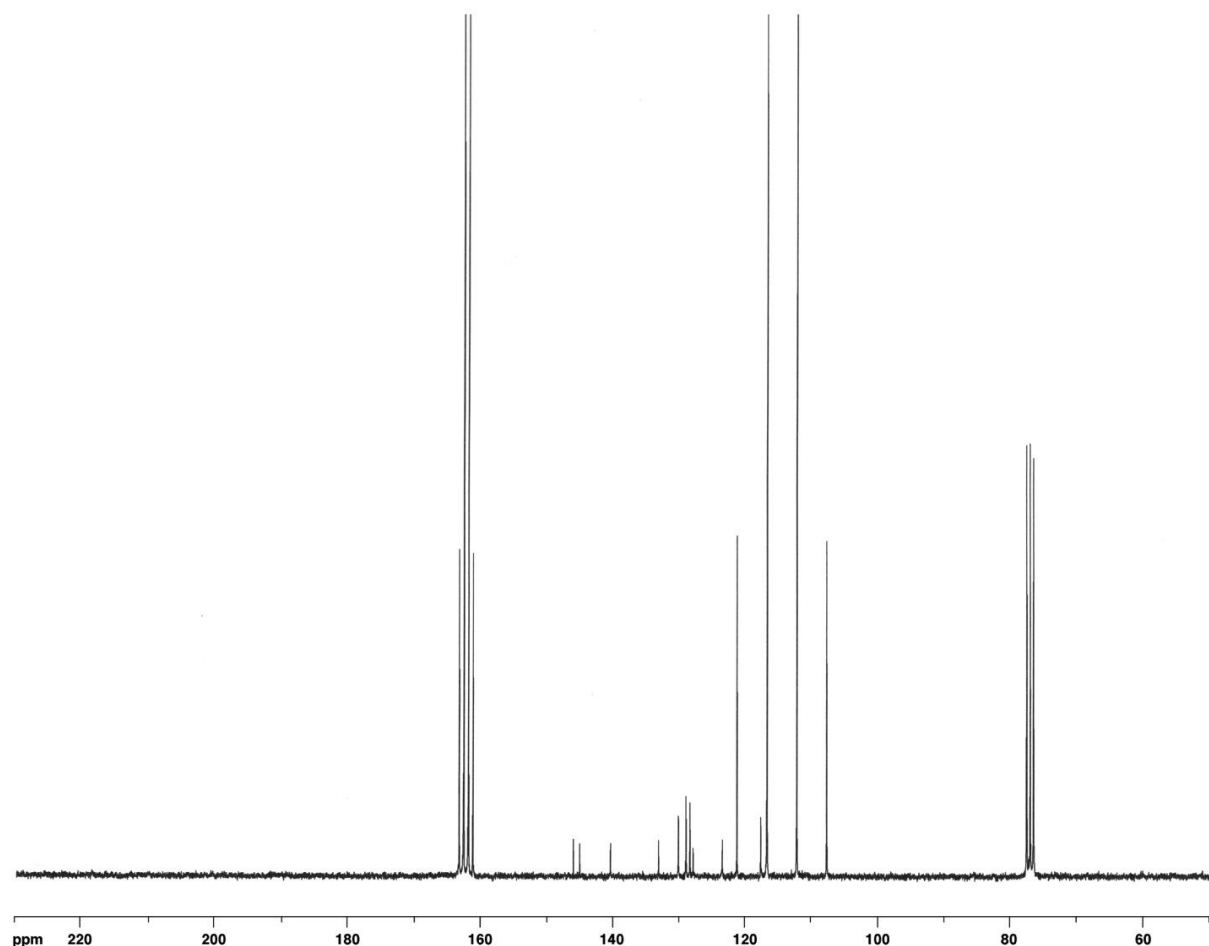


Figure S2: ¹³C NMR spectrum of macrocycle **2** (62.5 MHz, CDCl₃/CF₃CO₂H 5/1 v/v). *Note:* the strong quartet resonances centred at 114 and 162 ppm are due to trifluoroacetic acid co-solvent.

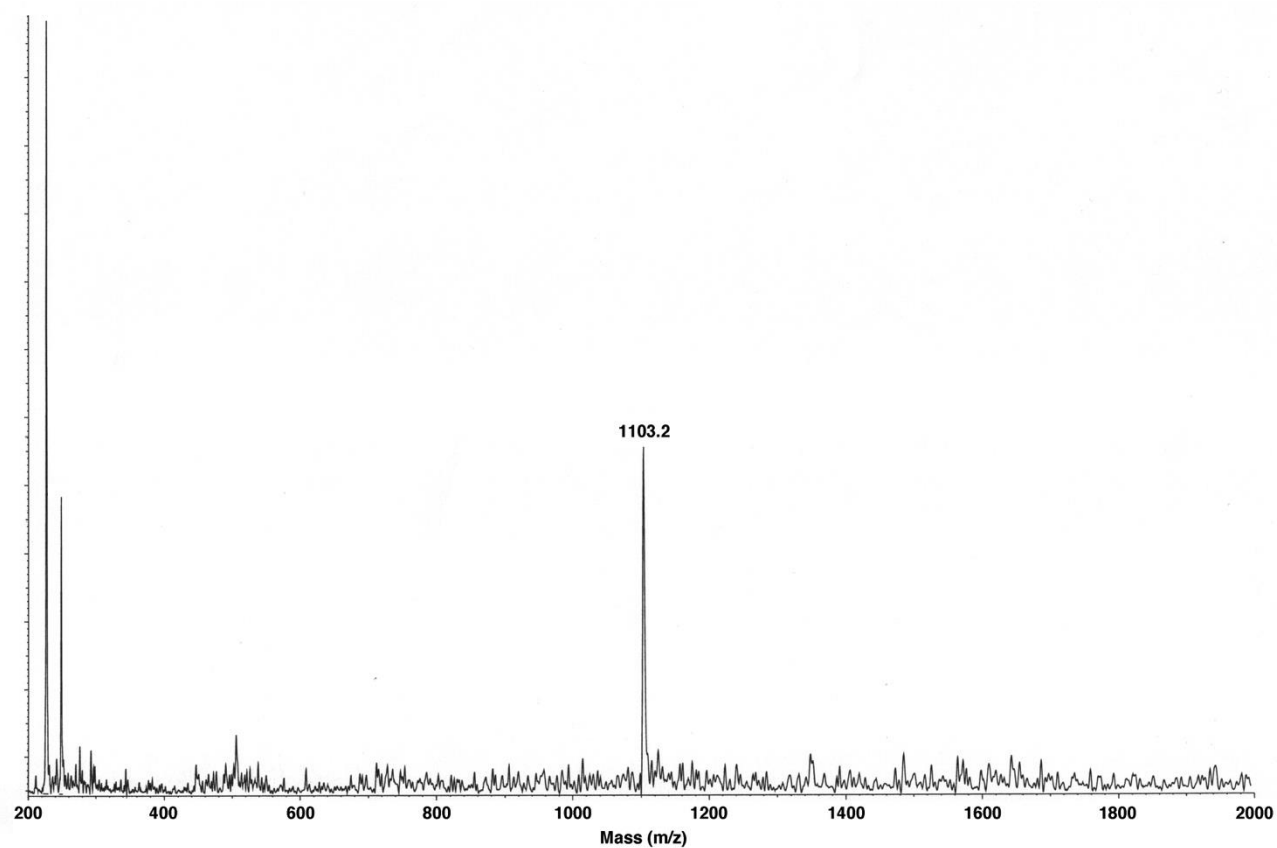


Figure S3: MALDI-TOF mass spectrum of macrocycle **2**. (Calc. m/z for $[\text{C}_{60}\text{H}_{40}\text{S}_4\text{O}_{12}\text{Na}]^+ = 1104.2$).

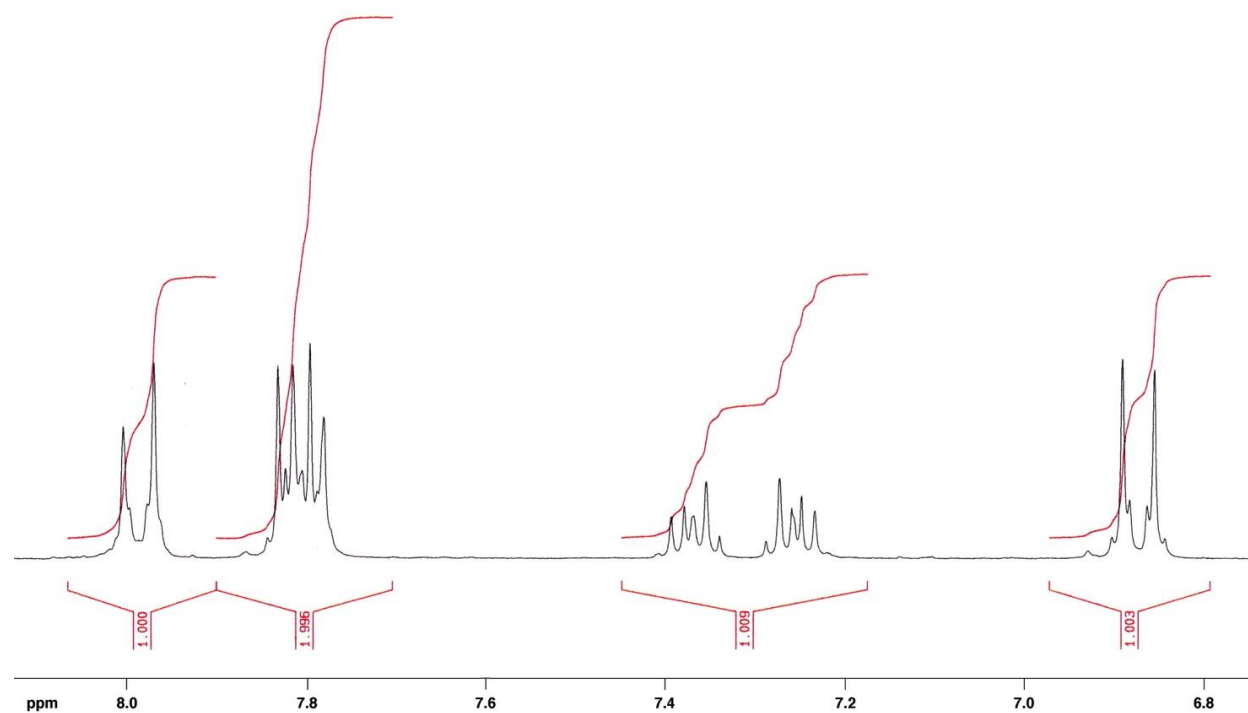


Figure S4: ^1H NMR spectrum of macrocycle **3** (250 MHz, $\text{CD}_2\text{Cl}_2/\text{CH}_3\text{SO}_3\text{H}$ 4/1 v/v).

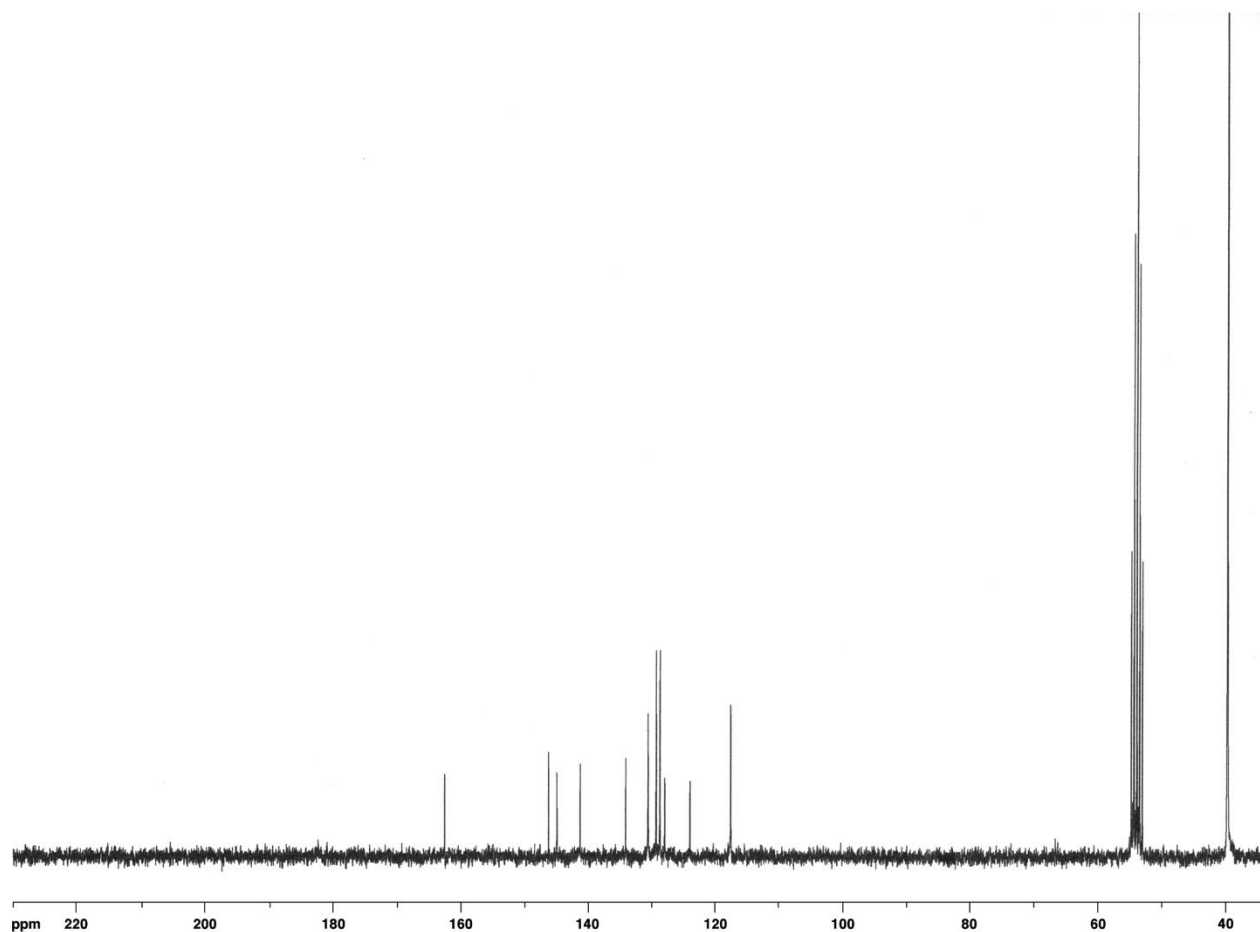


Figure S5: ^{13}C NMR spectrum of macrocycle **3** (62.5 MHz, $\text{CD}_2\text{Cl}_2/\text{CH}_3\text{SO}_3\text{H}$ 4/1 v/v).

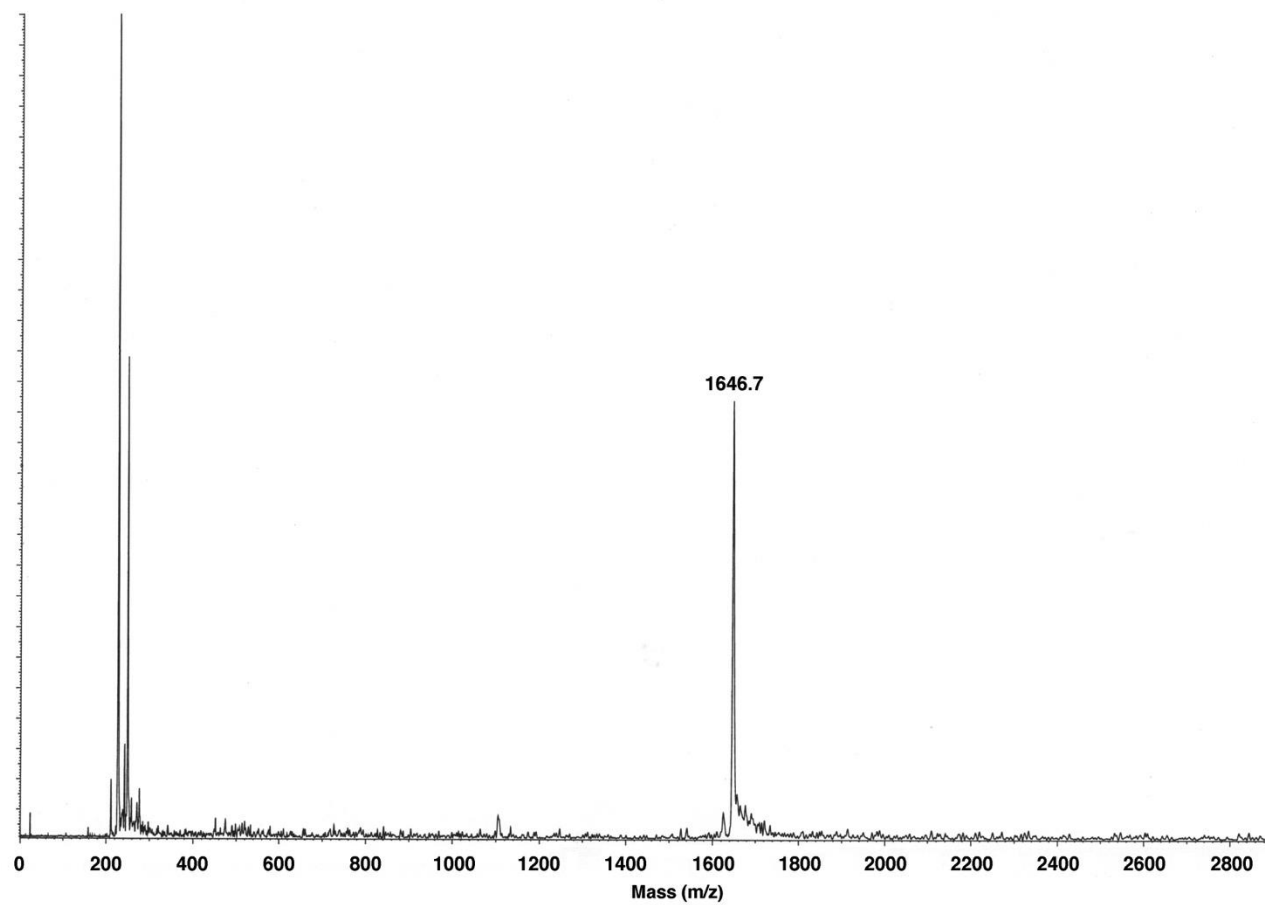


Figure S6: MALDI-TOF mass spectrum of macrocycle **3**. (Calc. m/z for $[\text{C}_{90}\text{H}_{60}\text{S}_6\text{O}_{18}\text{Na}]^+ = 1644.8$).

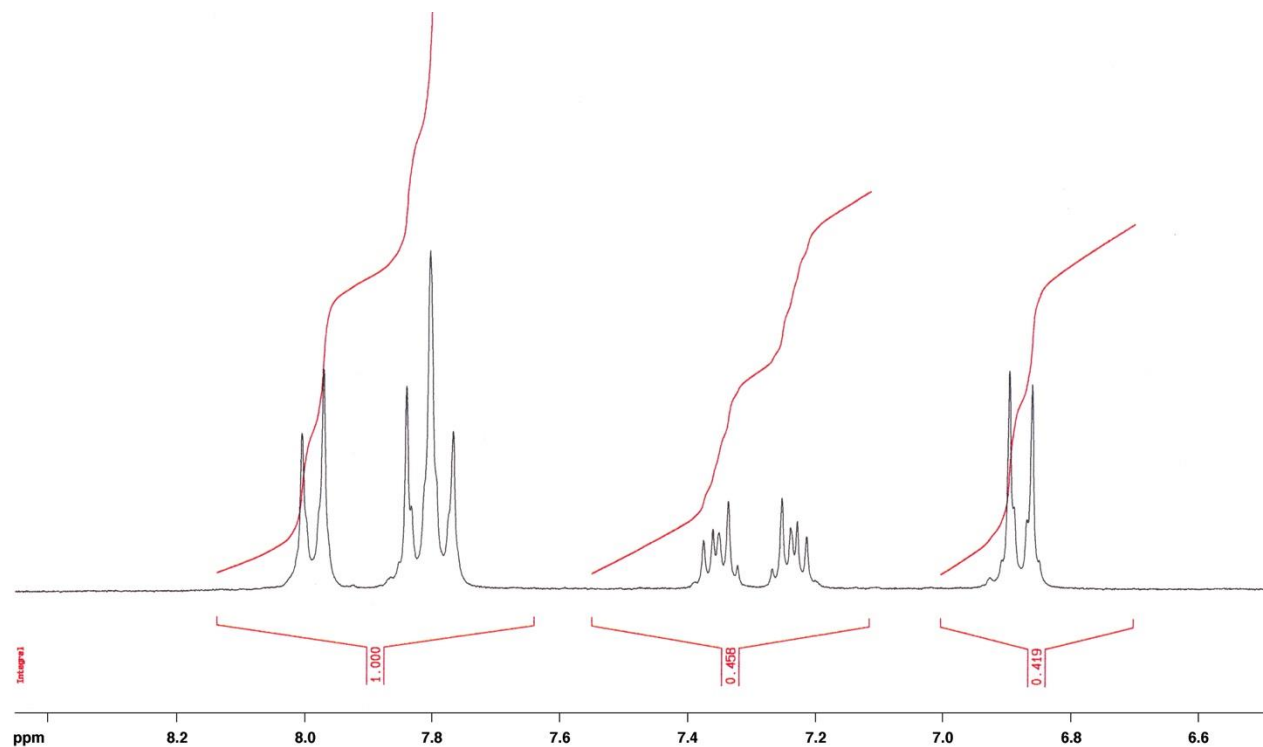


Figure S7: ^1H NMR spectrum of macrocycle **4** (250 MHz, $\text{CD}_2\text{Cl}_2/\text{CH}_3\text{SO}_3\text{H}$ 4/1 v/v).

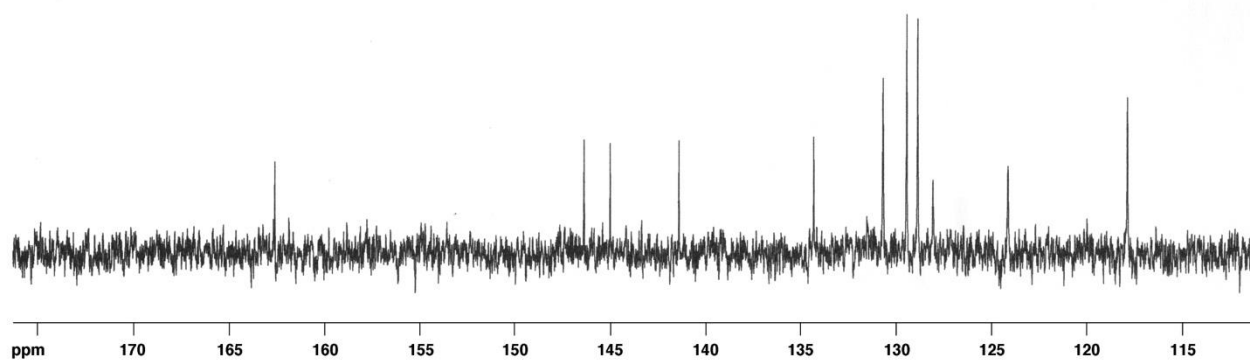


Figure S8: ^{13}C NMR spectrum of macrocycle **4** (62.5 MHz, $\text{CD}_2\text{Cl}_2/\text{CH}_3\text{SO}_3\text{H}$ 4/1 v/v).

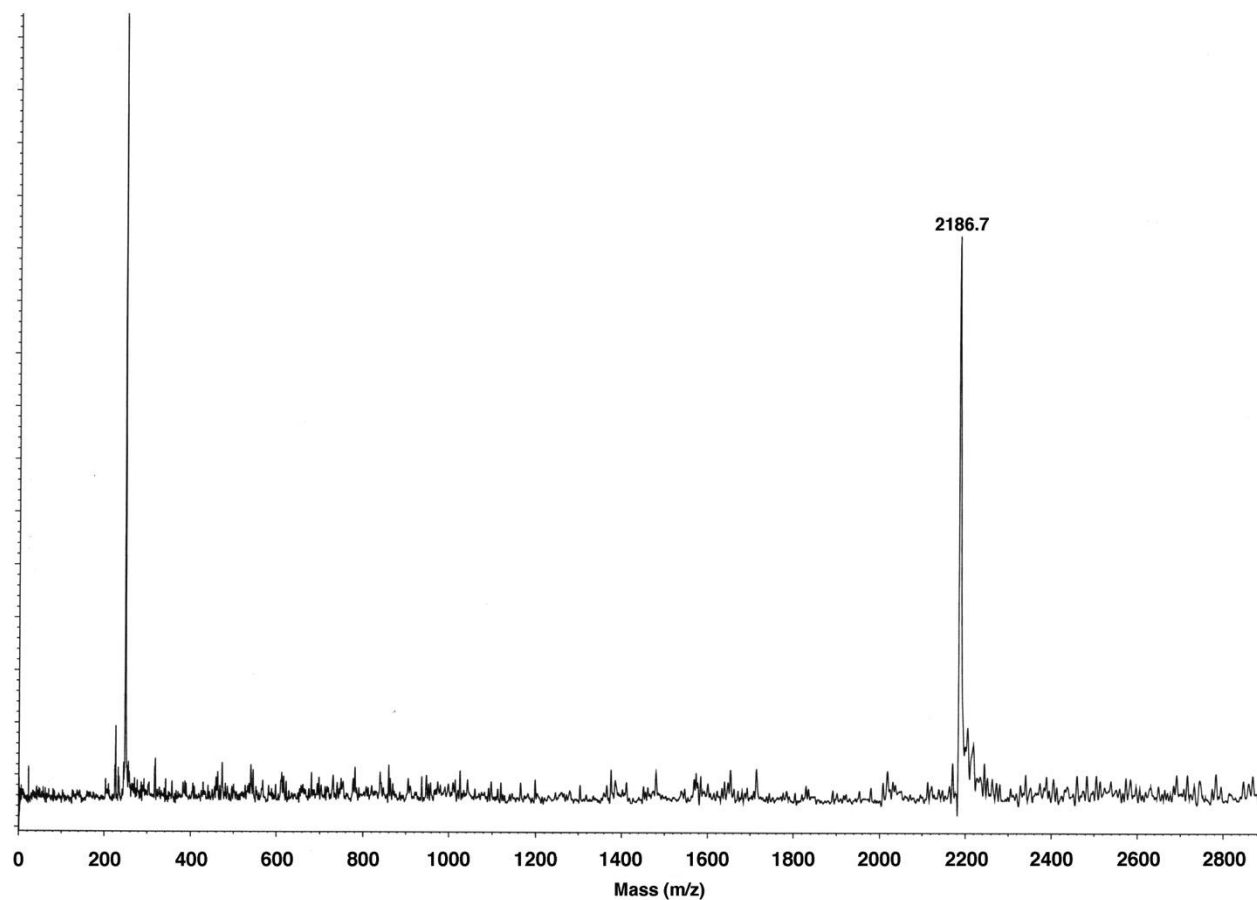


Figure S9: MALDI-TOF mass spectrum of macrocycle **4**. (Calc. m/z for $[\text{C}_{120}\text{H}_{80}\text{S}_8\text{O}_{24}\text{Na}]^+ = 2185.4$).

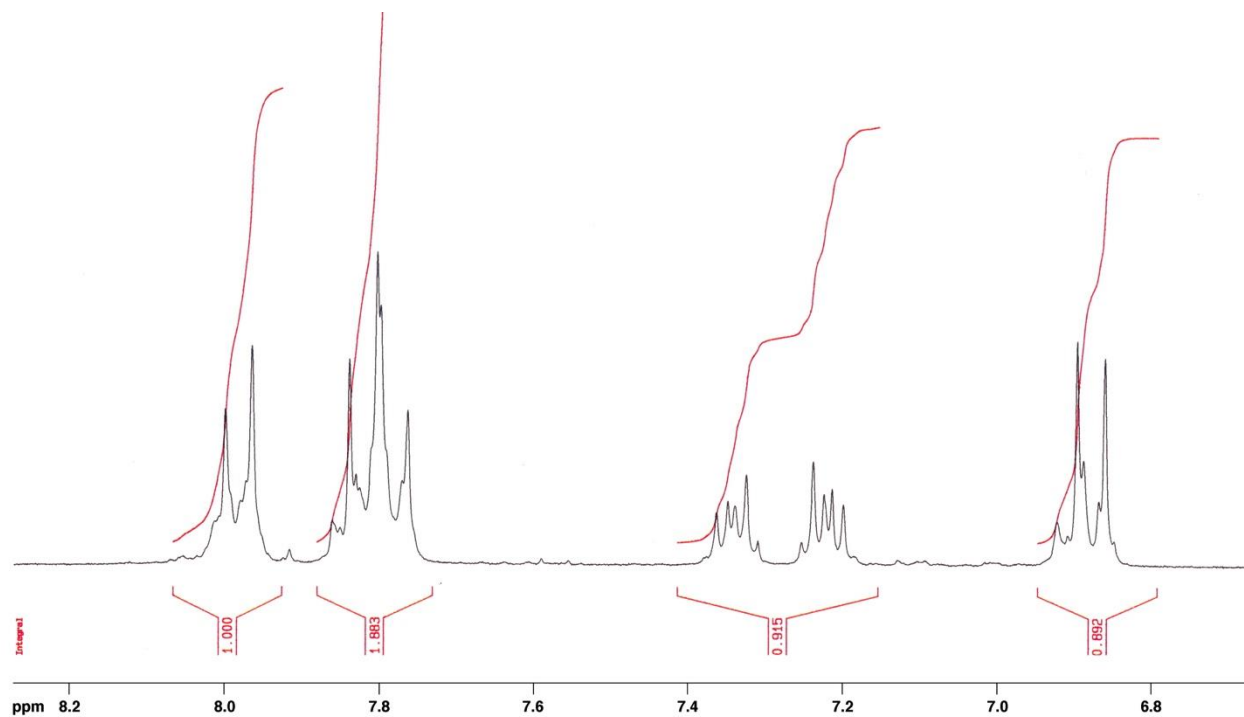


Figure S10: ^1H NMR spectrum of macrocycle **5** (250 MHz, $\text{CD}_2\text{Cl}_2/\text{CH}_3\text{SO}_3\text{H}$ 4/1 v/v).

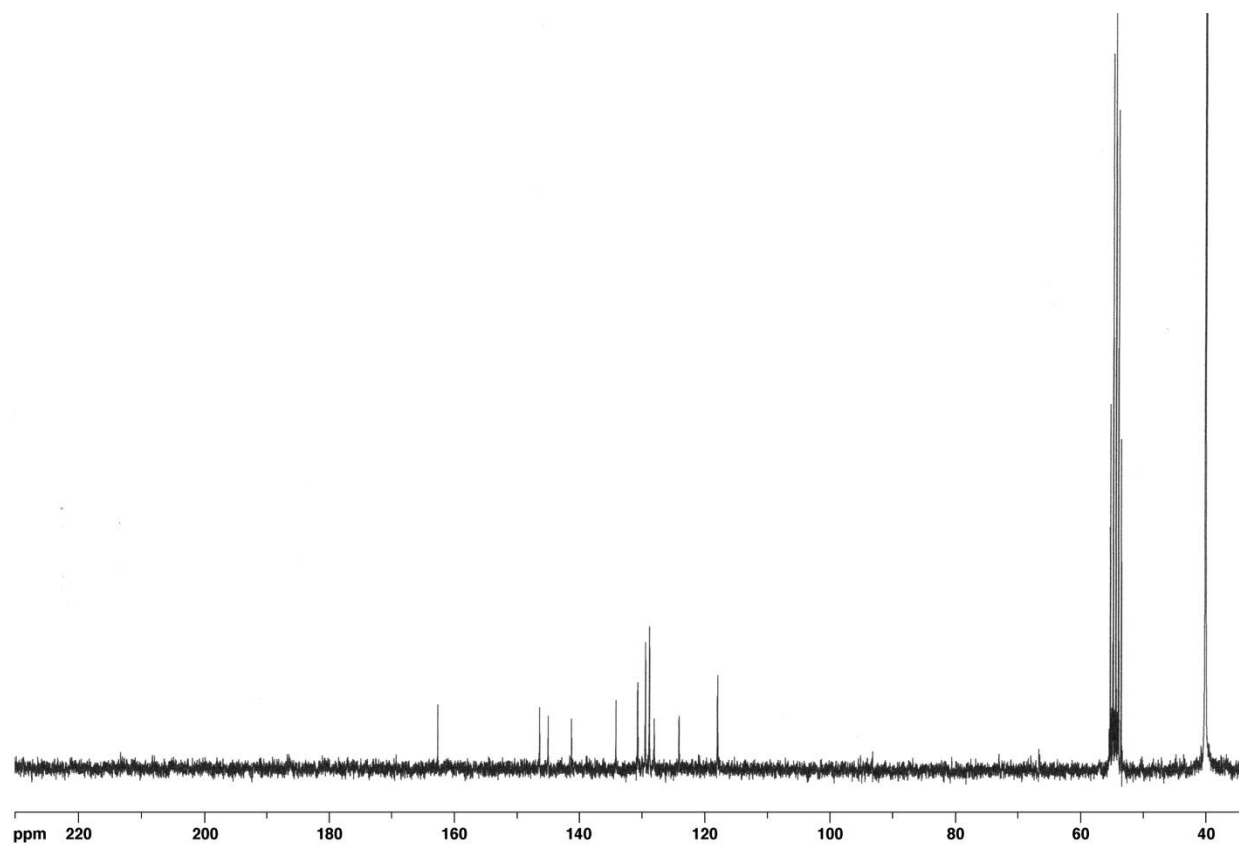


Figure S11: ^{13}C NMR spectrum of macrocycle **5** (62.5 MHz, $\text{CD}_2\text{Cl}_2/\text{CH}_3\text{SO}_3\text{H}$ 4/1 v/v).

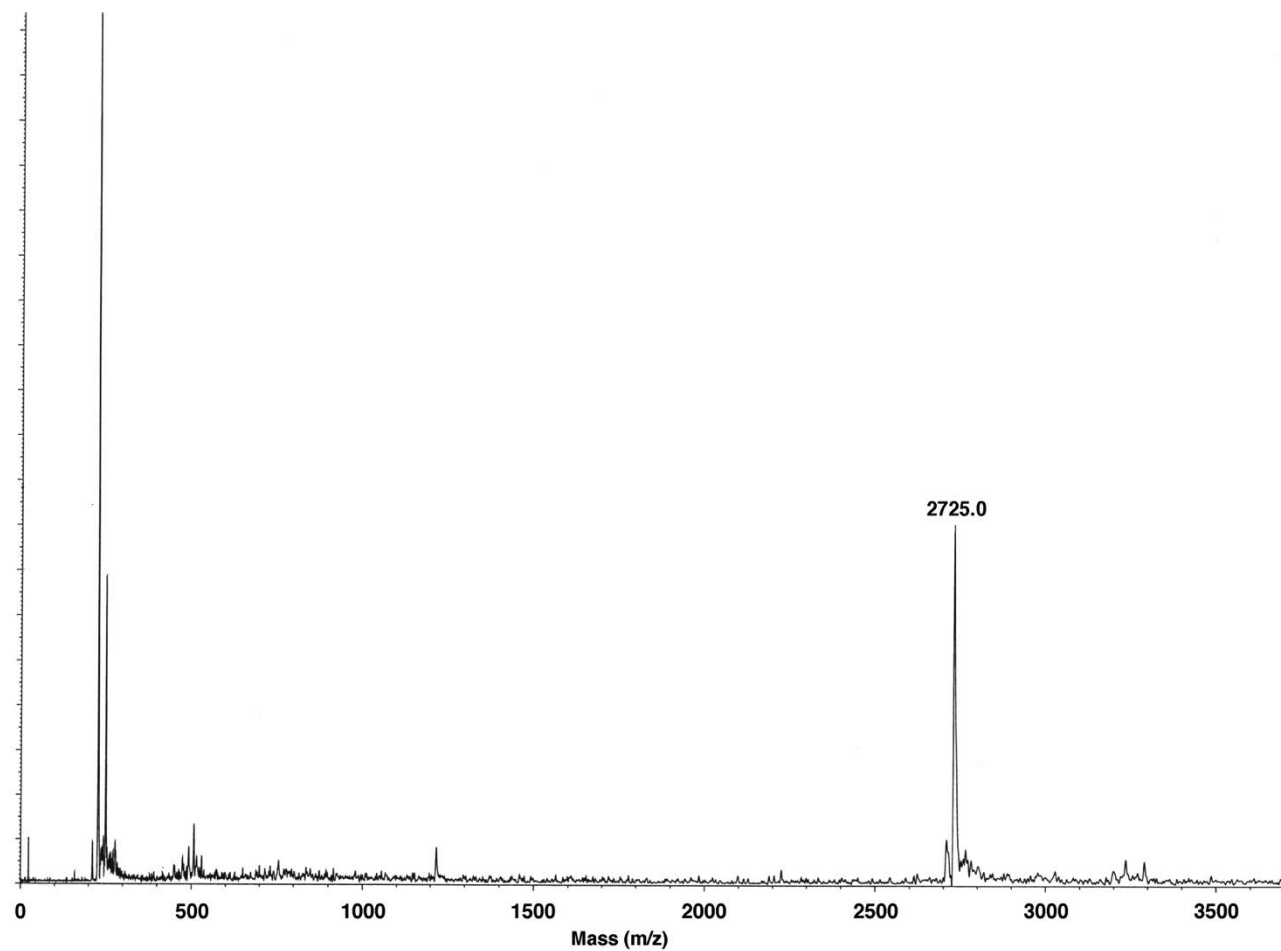


Figure S12: MALDI-TOF mass spectrum of macrocycle **5**. (Calc. m/z for $[\text{C}_{150}\text{H}_{100}\text{S}_{10}\text{O}_{30}\text{Na}]^+ = 2726.0$).

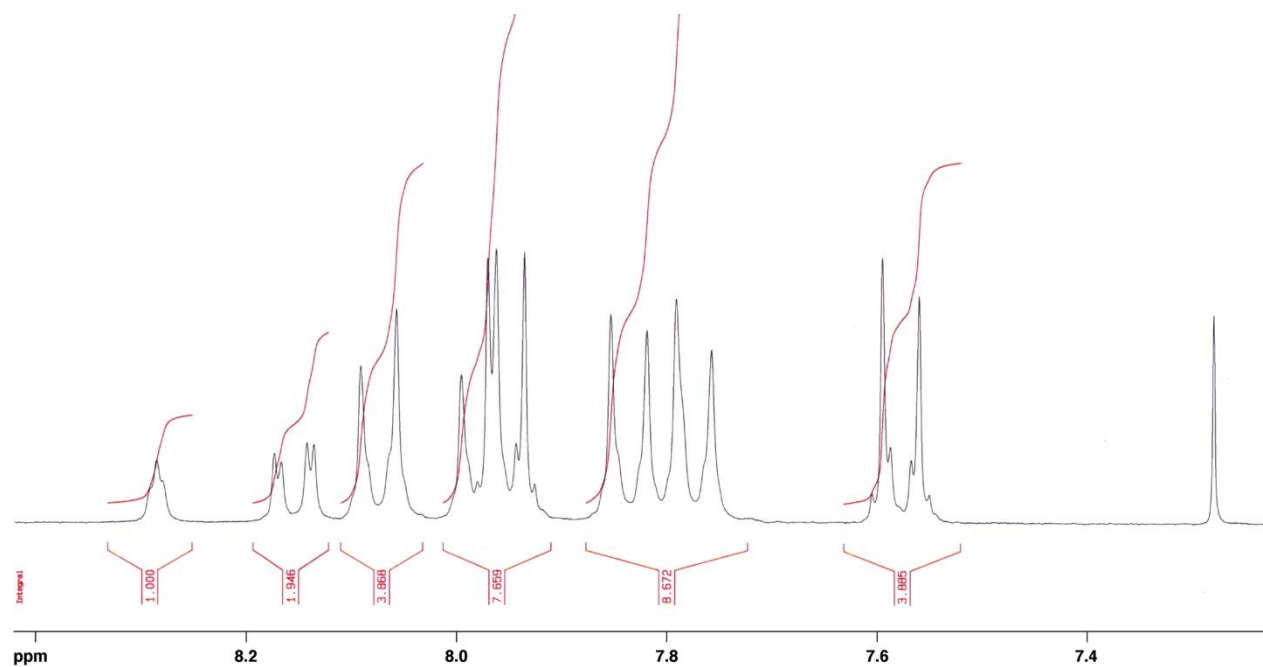


Figure S13: ¹H NMR spectrum of linear oligomer **7** (250 MHz, CDCl₃/CF₃COOH 5/1 v/v).

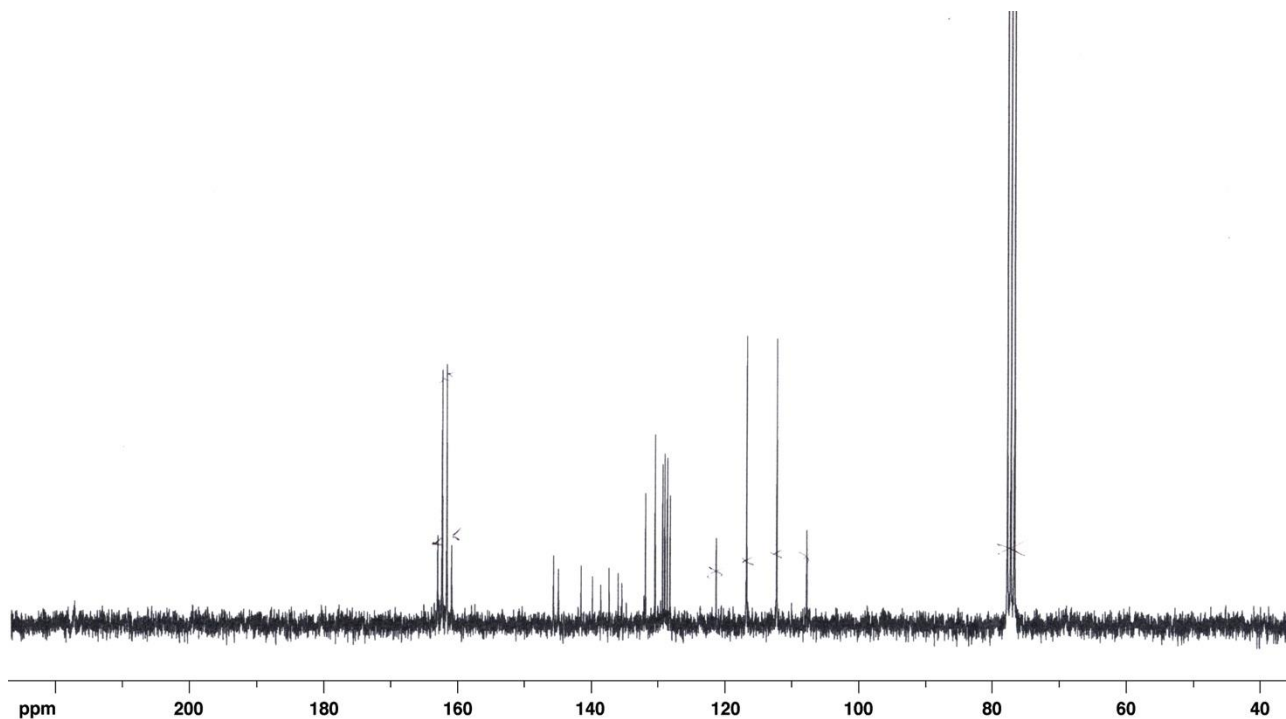


Figure S14: ¹³C NMR spectrum of linear oligomer **7** (62.5 MHz, CDCl₃/CF₃COOH 5/1 v/v). *Note:* the strong quartet resonances centred at 114 and 162 ppm are due to trifluoroacetic acid co-solvent.

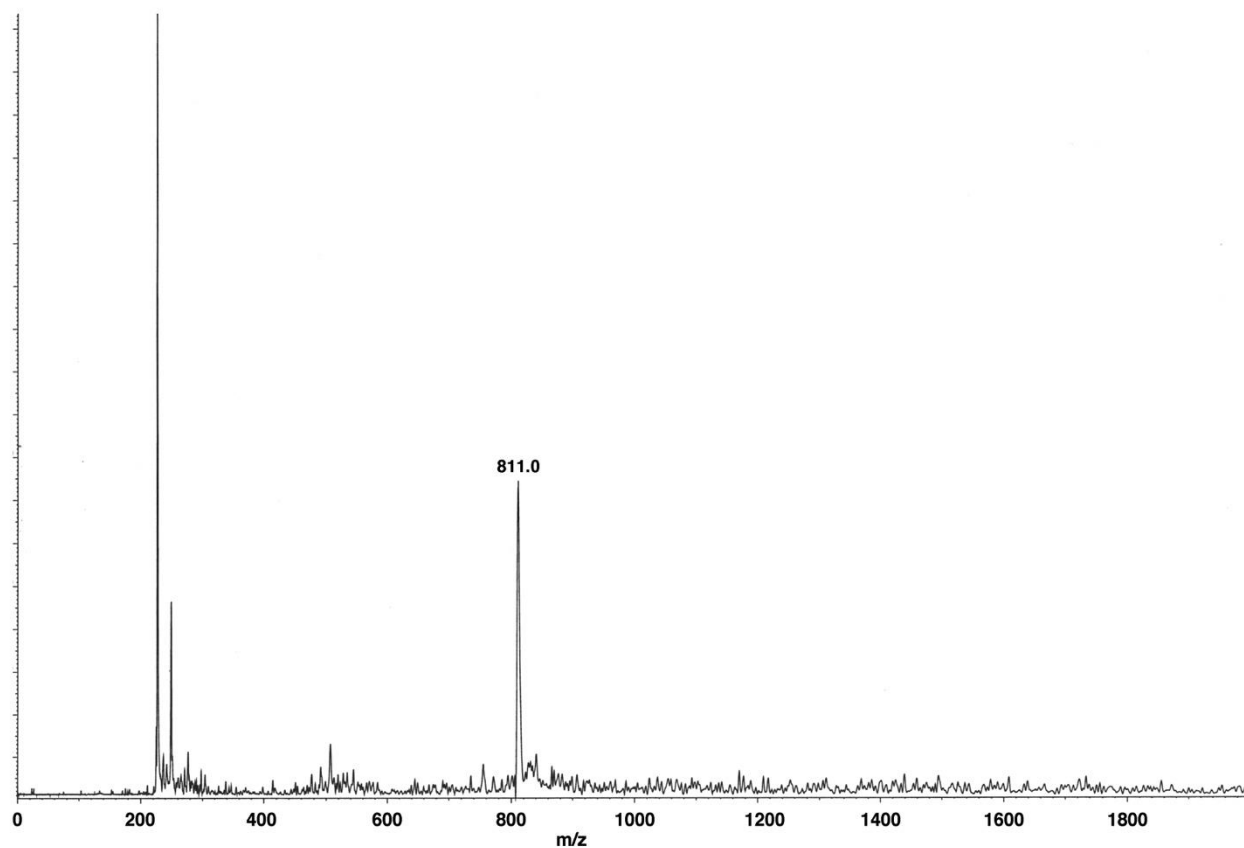


Figure S15: MALDI-TOF mass spectrum of linear oligomer **7**. (Calc. m/z for $[\text{C}_{44}\text{H}_{28}\text{S}_2\text{O}_6\text{Cl}_2\text{Na}]^+ = 810.7$).

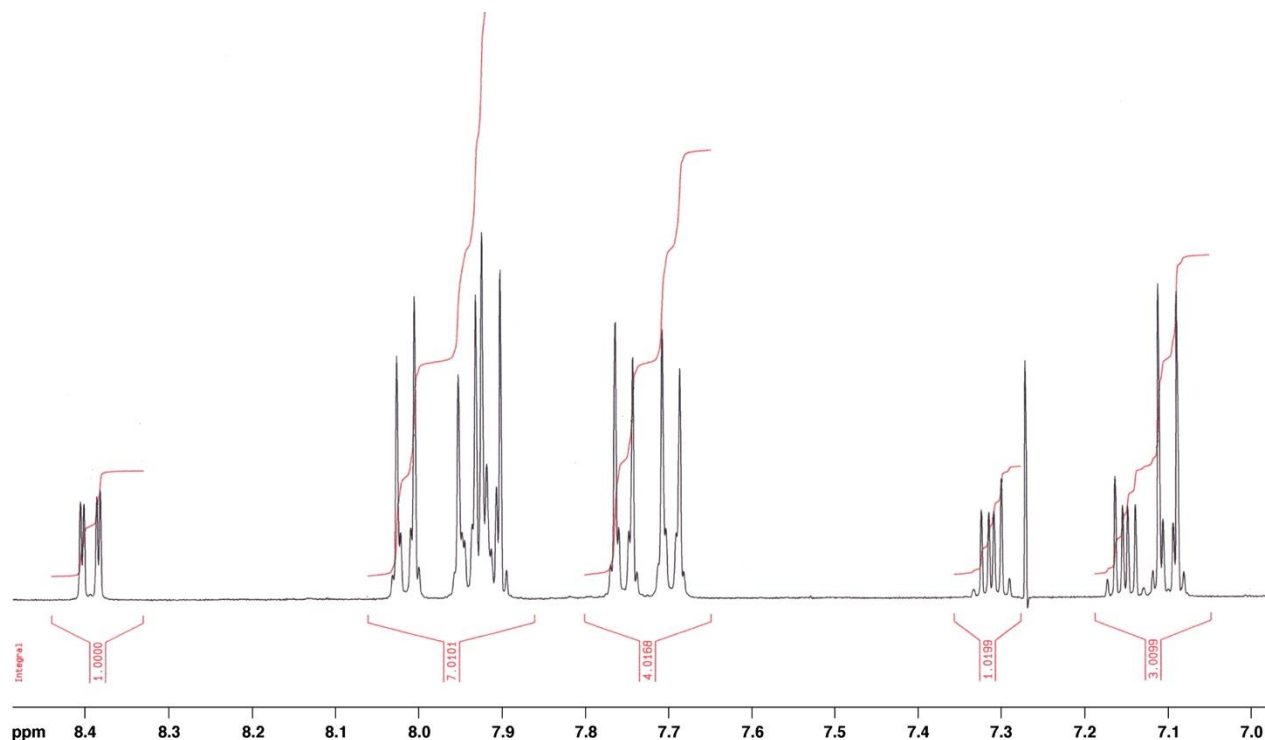


Figure S16: ^1H NMR spectrum of macrocycle **8** (400 MHz, $\text{CDCl}_3/\text{CF}_3\text{COOH}$ 5/1 v/v).

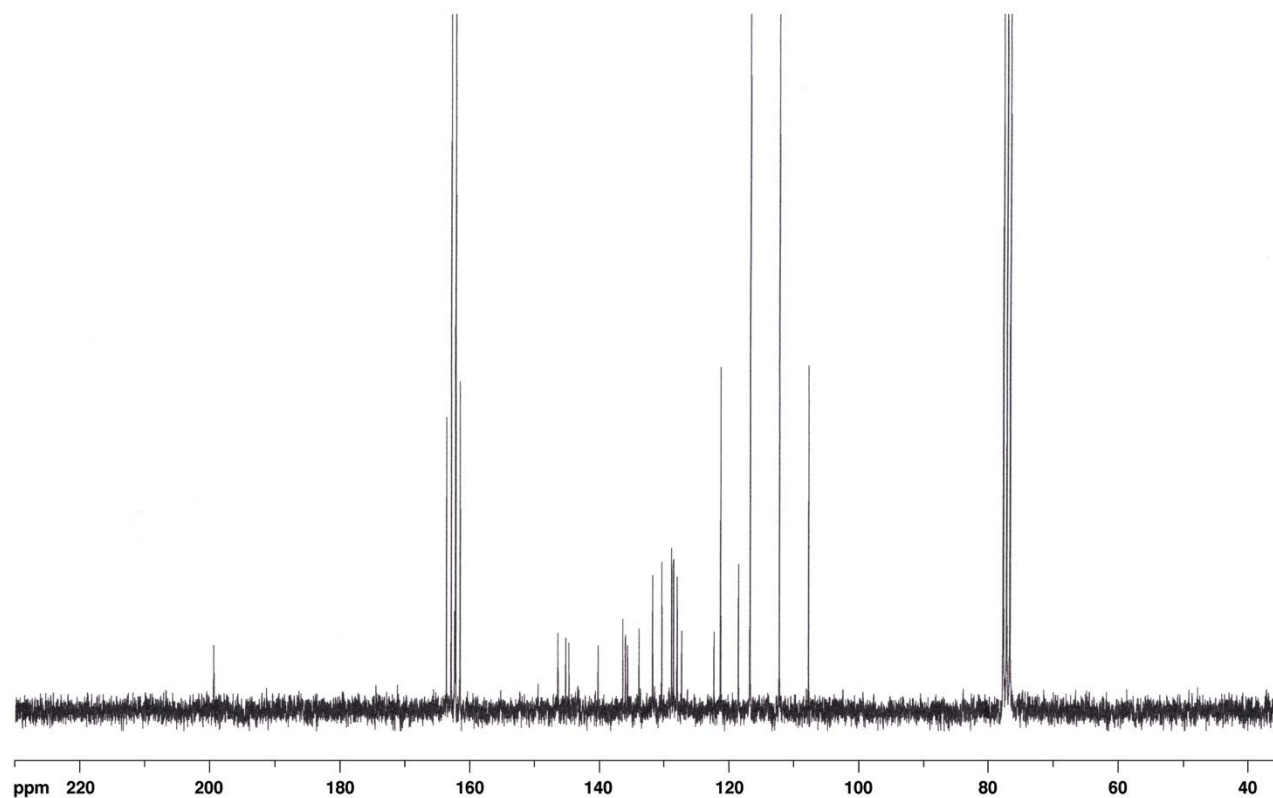


Figure S17: ^{13}C NMR spectrum of macrocycle **8** (100 MHz, $\text{CDCl}_3/\text{CF}_3\text{COOH}$ 5/1 v/v). Note: the strong quartet resonances centred at 114 and 162 ppm are due to trifluoroacetic acid co-solvent.

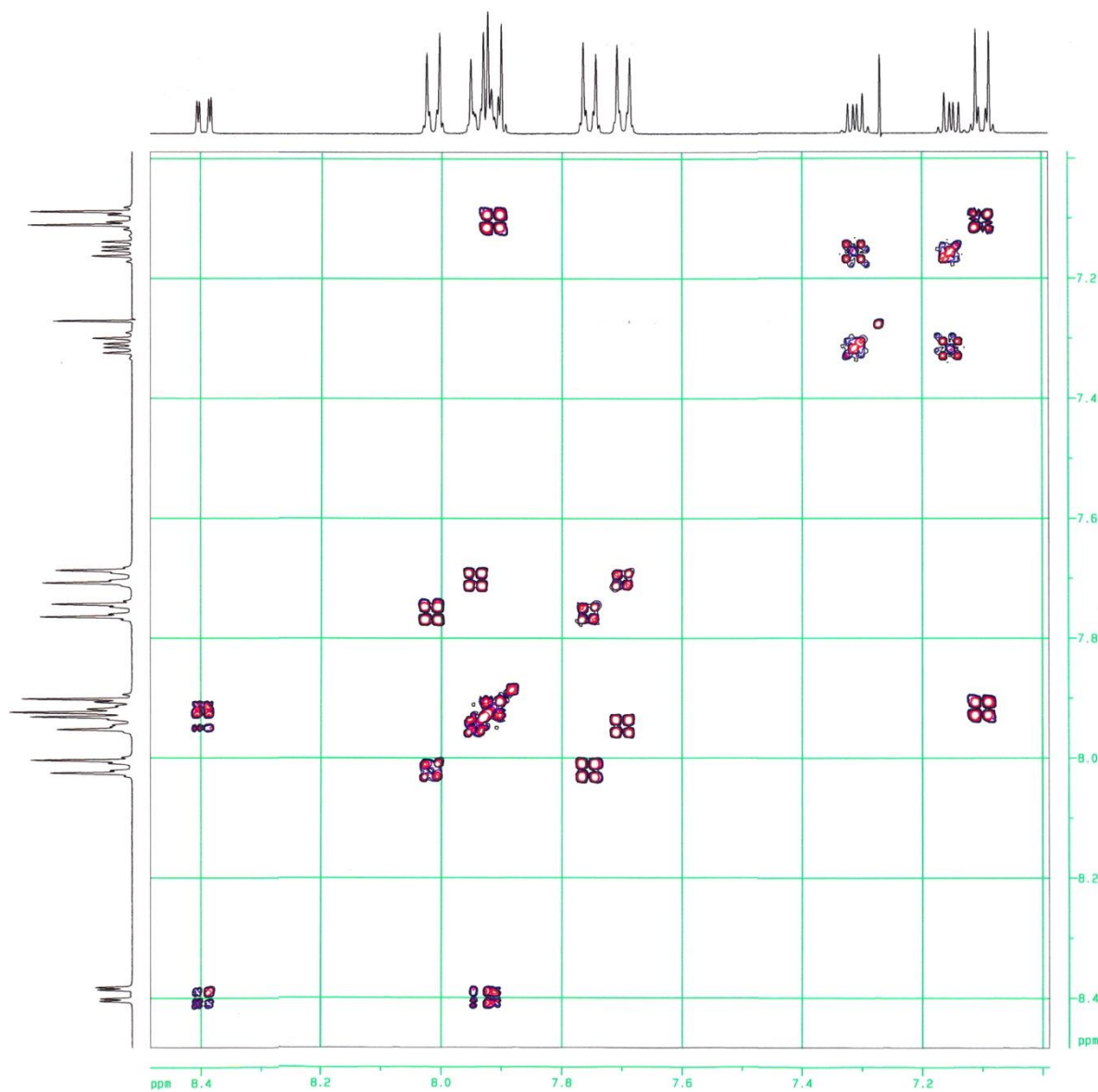


Figure S18: ^1H - ^1H COSY NMR spectrum of macrocycle **8** (400 MHz, $\text{CDCl}_3/\text{CF}_3\text{COOH}$ 5/1 v/v).

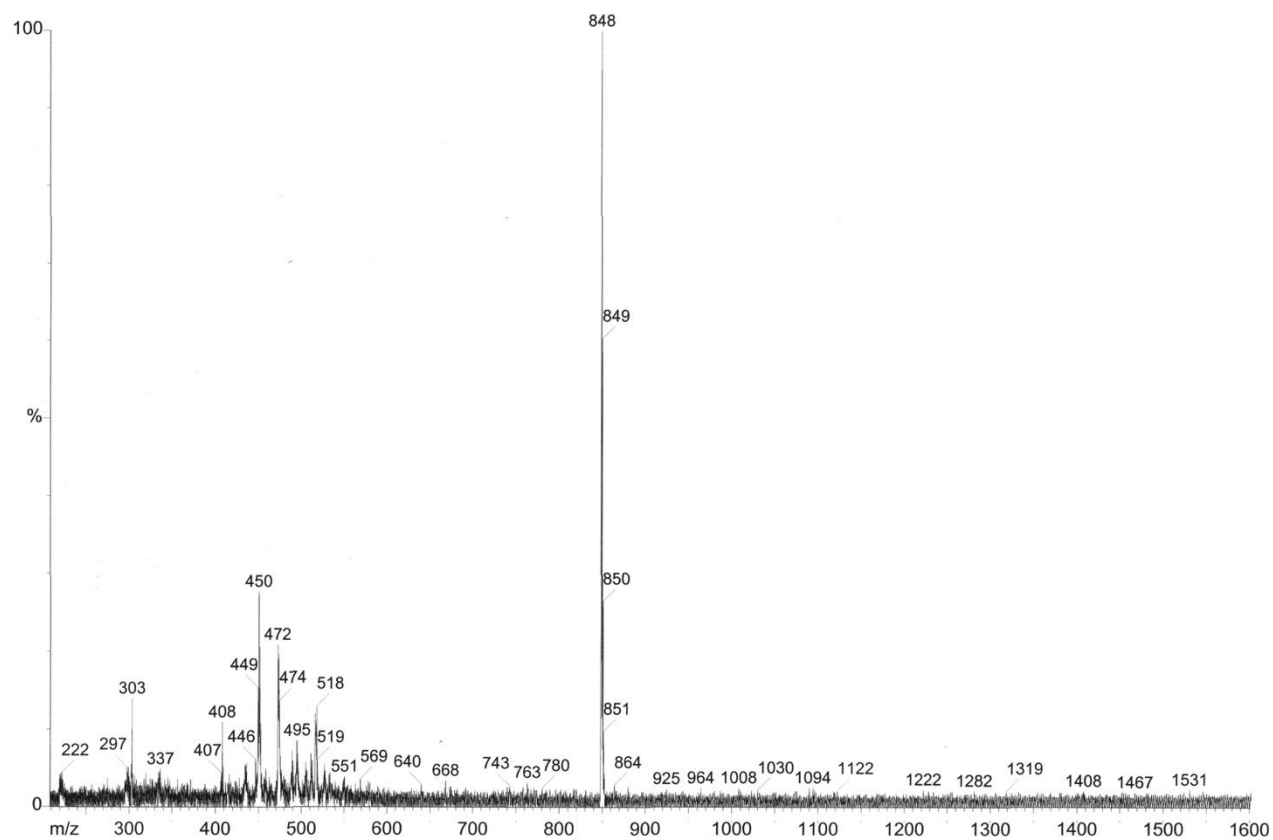


Figure S19: MALDI-TOF mass spectrum of macrocycle **8** (Calc. m/z for $[C_{50}H_{32}S_2O_8Na]^+ = 847.9$).

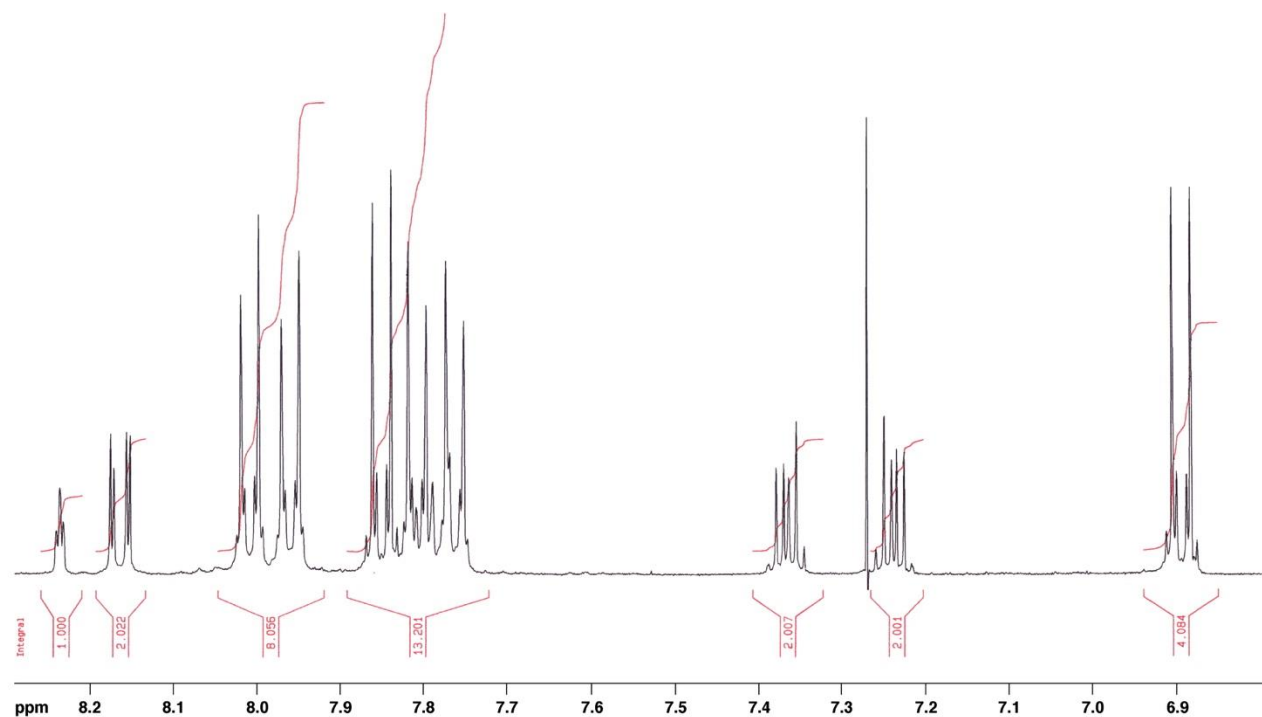


Figure S20: ¹H NMR spectrum of macrocycle **9** (400 MHz, CDCl₃/CF₃COOH 5/1 v/v).

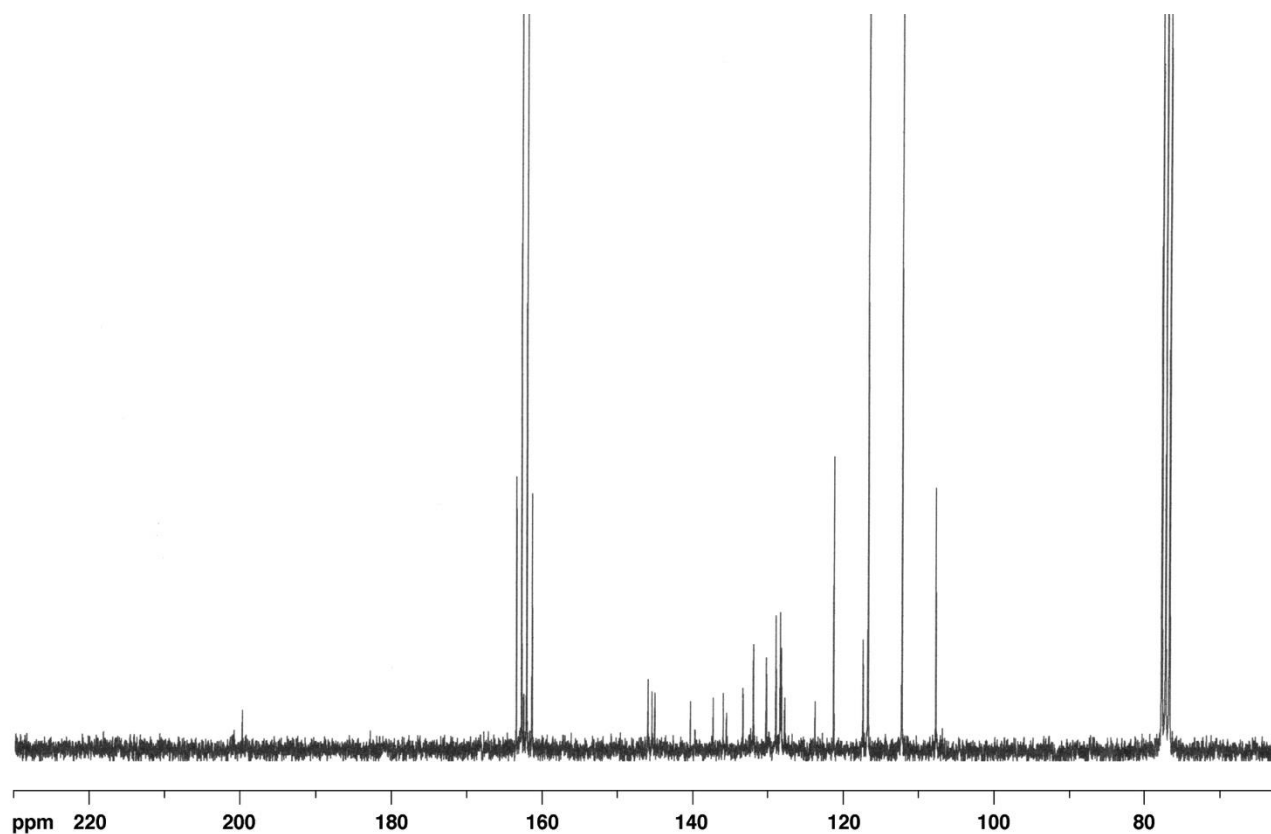


Figure S21: ¹³C NMR spectrum of macrocycle **9** (100 MHz, CDCl₃/CF₃COOH 5/1 v/v). *Note:* the strong quartet resonances centred at 114 and 162 ppm are due to trifluoroacetic acid co-solvent.

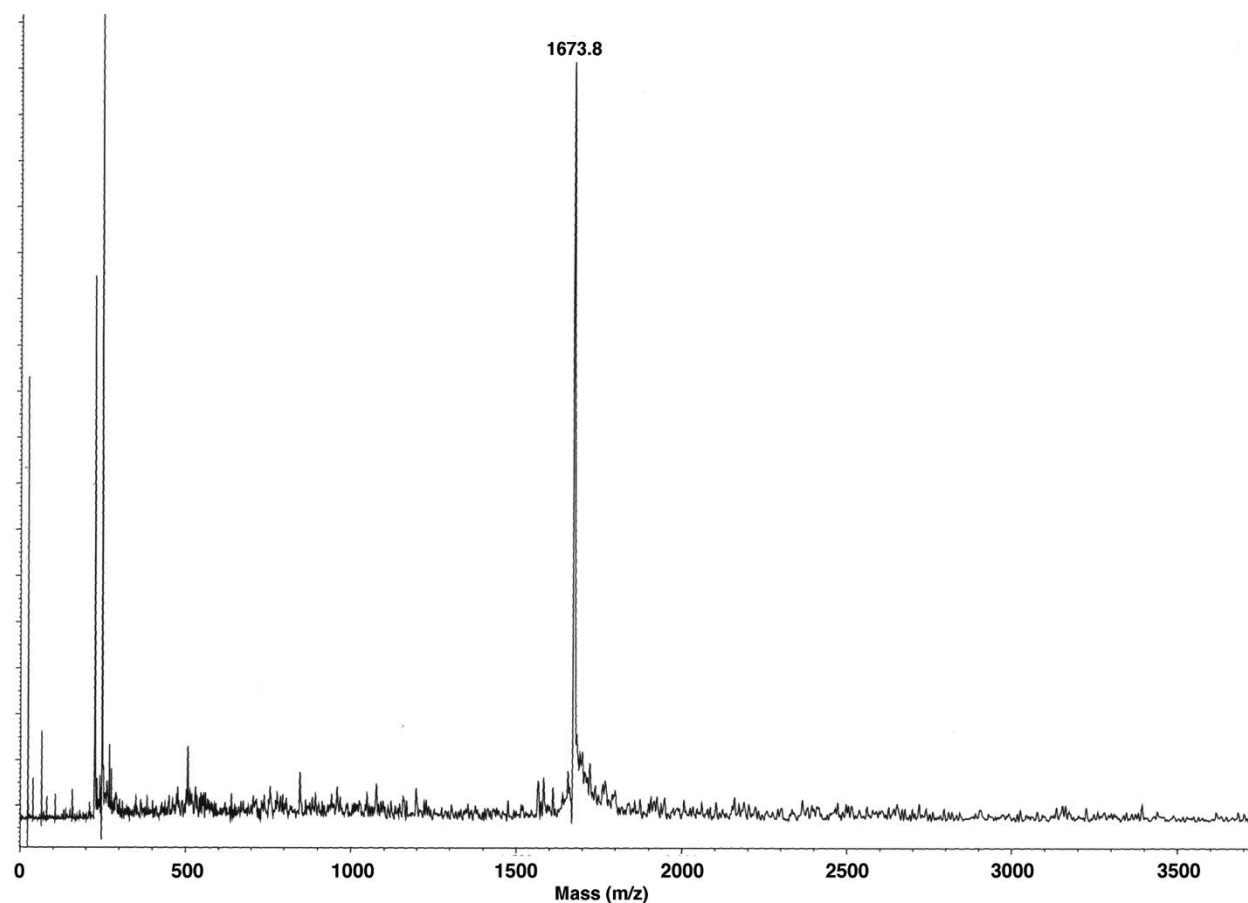


Figure S19: MALDI-TOF mass spectrum of macrocycle **9** (Calc. m/z for $[\text{C}_{100}\text{H}_{64}\text{S}_4\text{O}_{16}\text{Na}]^+ = 1672.8$).

Computational modelling of macrocycles **8** and **9**

Models of macrocycles **8** and **9** were constructed on a SGI-O2 workstation using the *Cerius2* suite of programs, v. 3.5, Accelrys, San Diego. Models were minimised initially using the Dreiding-II force field (molecular mechanics with charge-equilibration),^{S1} and the resulting models were then re-minimised with a modified version of this force field in which aromatic ether, ketone, and sulfone linkages were constrained to experimentally-established bond lengths and bond angles.

Atomic coordinates of the final models for **8** and **9** are available from the authors as electronic data files in pdb format. Email: fabio.arico@unive.it; or h.m.colquhoun@rdg.ac.uk

S1. Mayo, S. L.; Olafson, B. D.; Goddard III, W. A. *J. Phys. Chem.* **1990**, *94*, 8897-8909.