Supplementary Material

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

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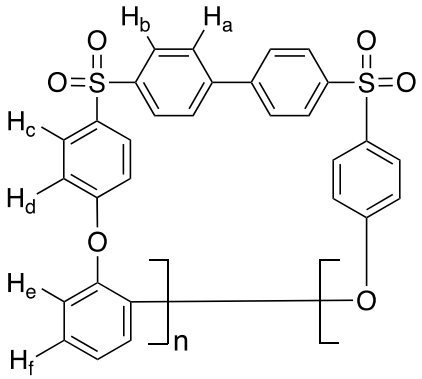
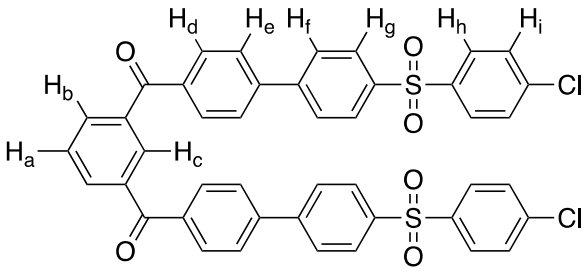


2 (n = 2), **3** (n = 3), **4** (n = 4), **5** (n = 5)



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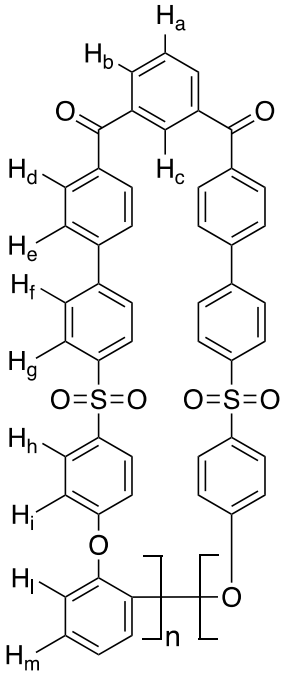

8 (n = 1), **9** (n = 2)

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

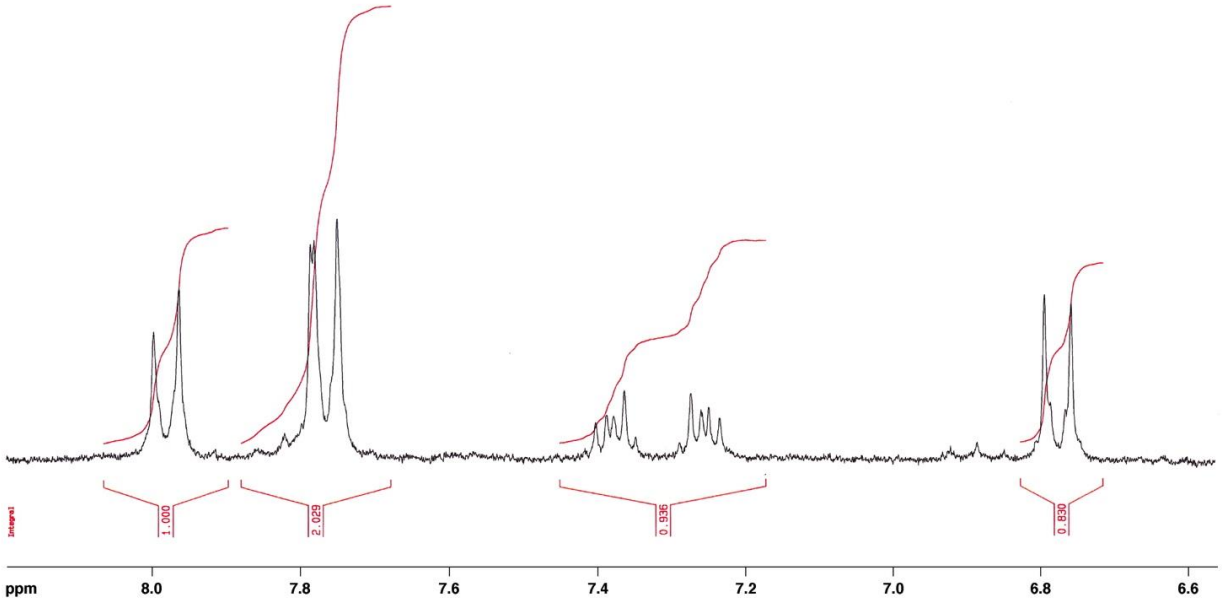

Figure S1: ^{1}H NMR spectrum of macrocycle **2** (250 MHz, CD_2Cl_2/CH_3SO_3H 4/1 v/v).

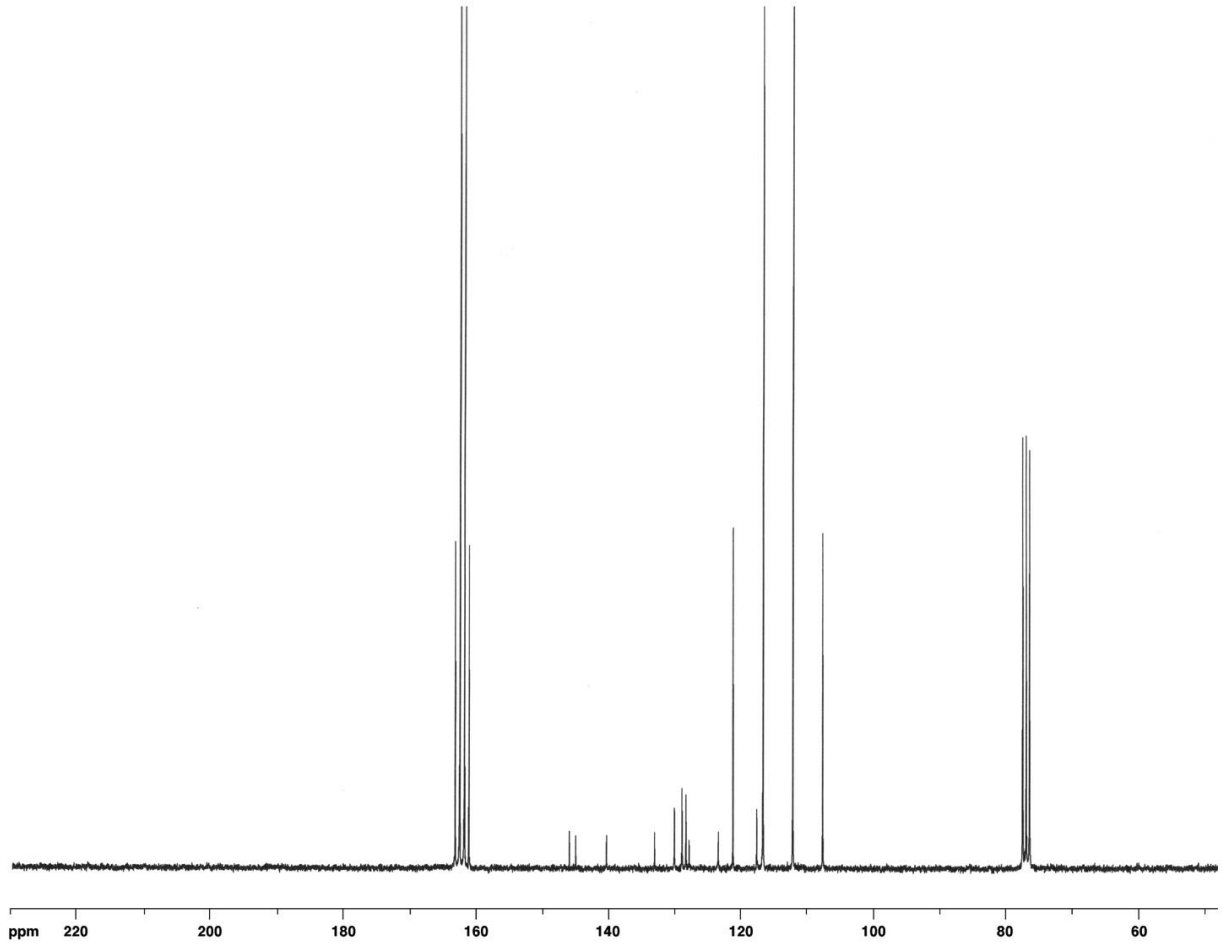

Figure S2: ^{13}C NMR spectrum of macrocycle **2** (62.5 MHz, $CDCl_3/CF_3CO_2H$ 5/1 v/v). *Note:* the strong quartet resonances centred at 114 and 162 ppm are due to trifluoroacetic acid co-solvent.

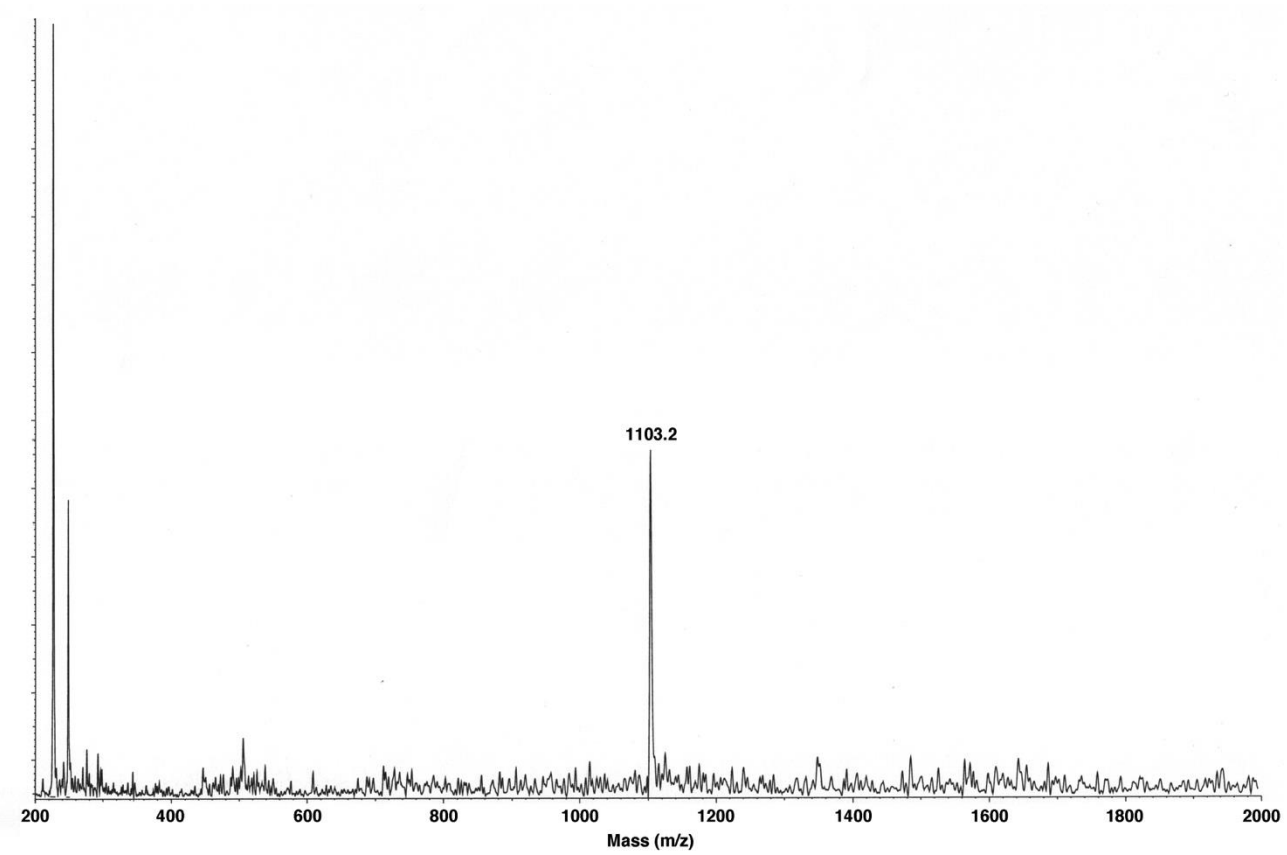

Figure S3: MALDI-TOF mass spectrum of macrocycle **2**. (Calc. *m*/*z* for $[C_{60}H_{40}S_4O_{12}Na]^+$ = 1104.2).

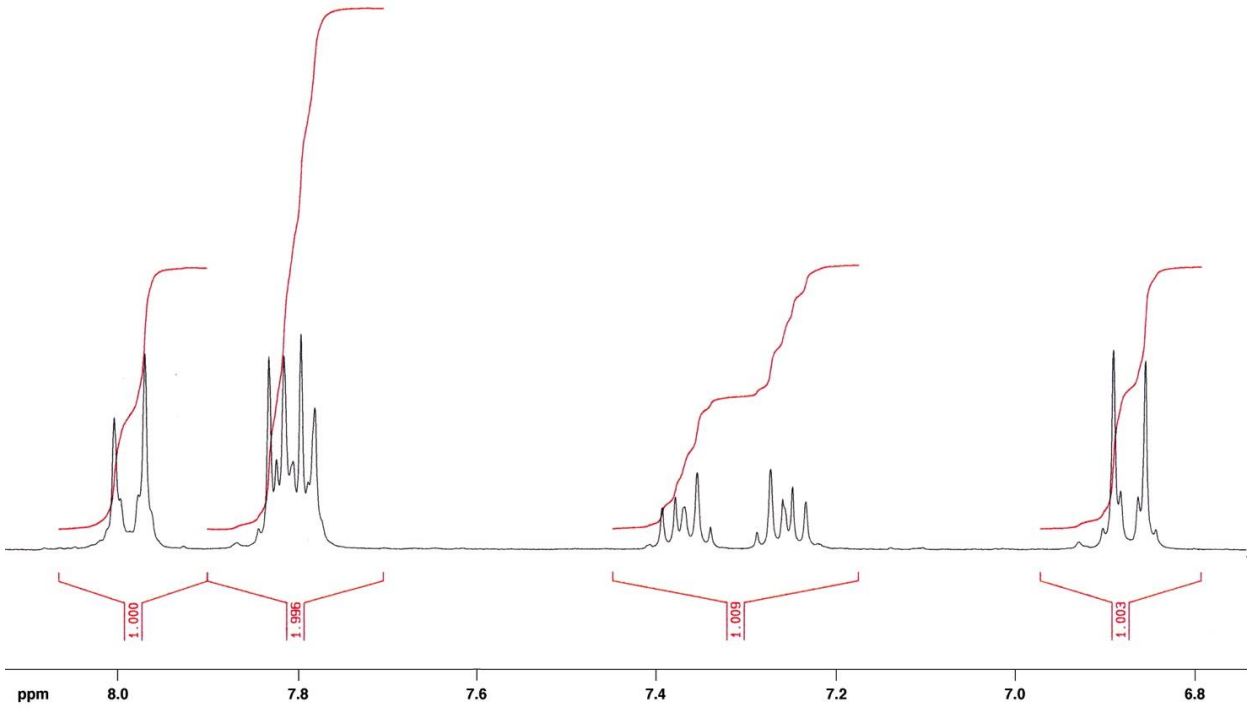

Figure S4: ^{1}H NMR spectrum of macrocycle **3** (250 MHz, CD_2Cl_2/CH_3SO_3H 4/1 v/v).

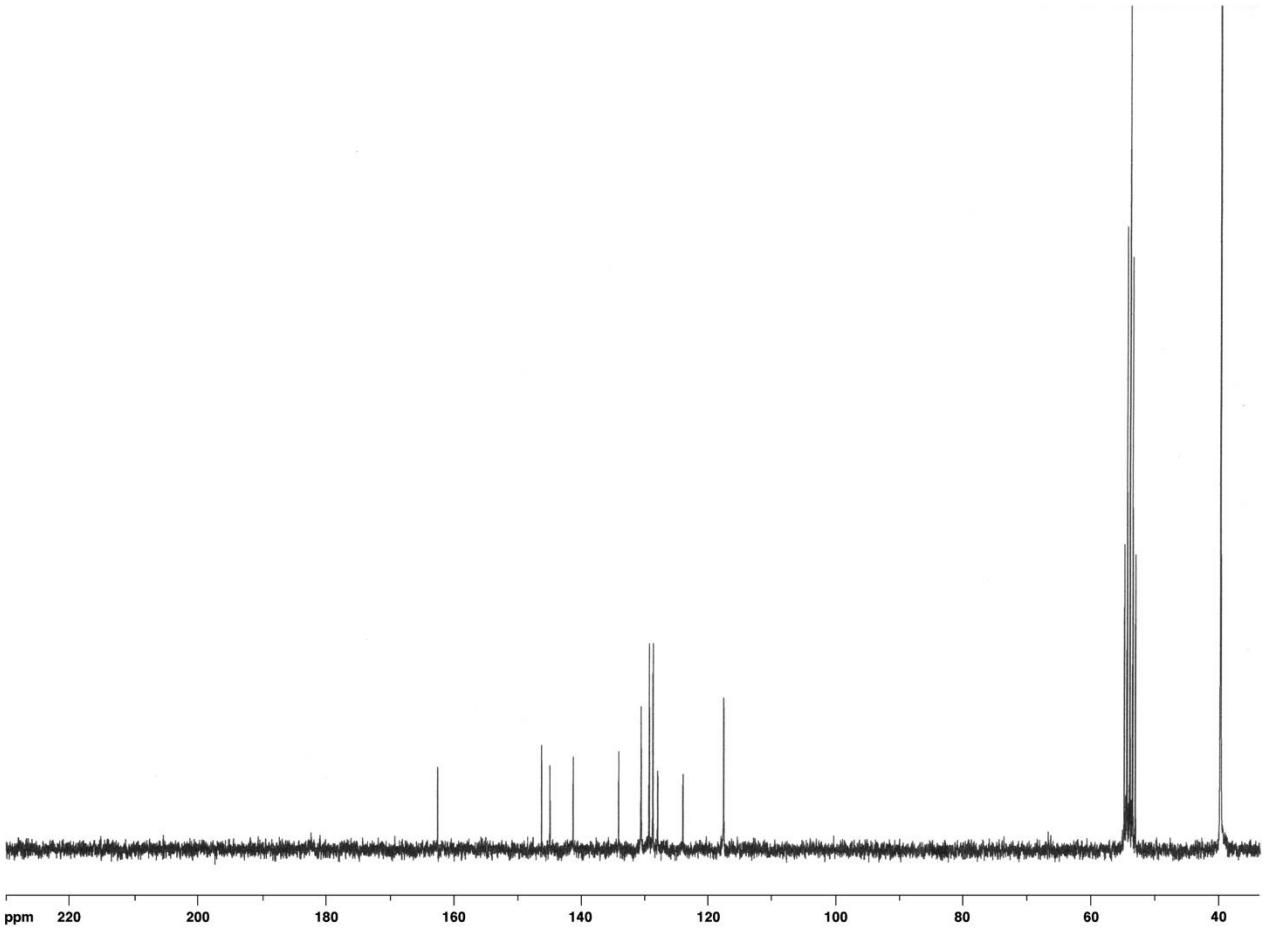

Figure S5: ^{13}C NMR spectrum of macrocycle **3** (62.5 MHz, CD_2Cl_2/CH_3SO_3H 4/1 v/v).

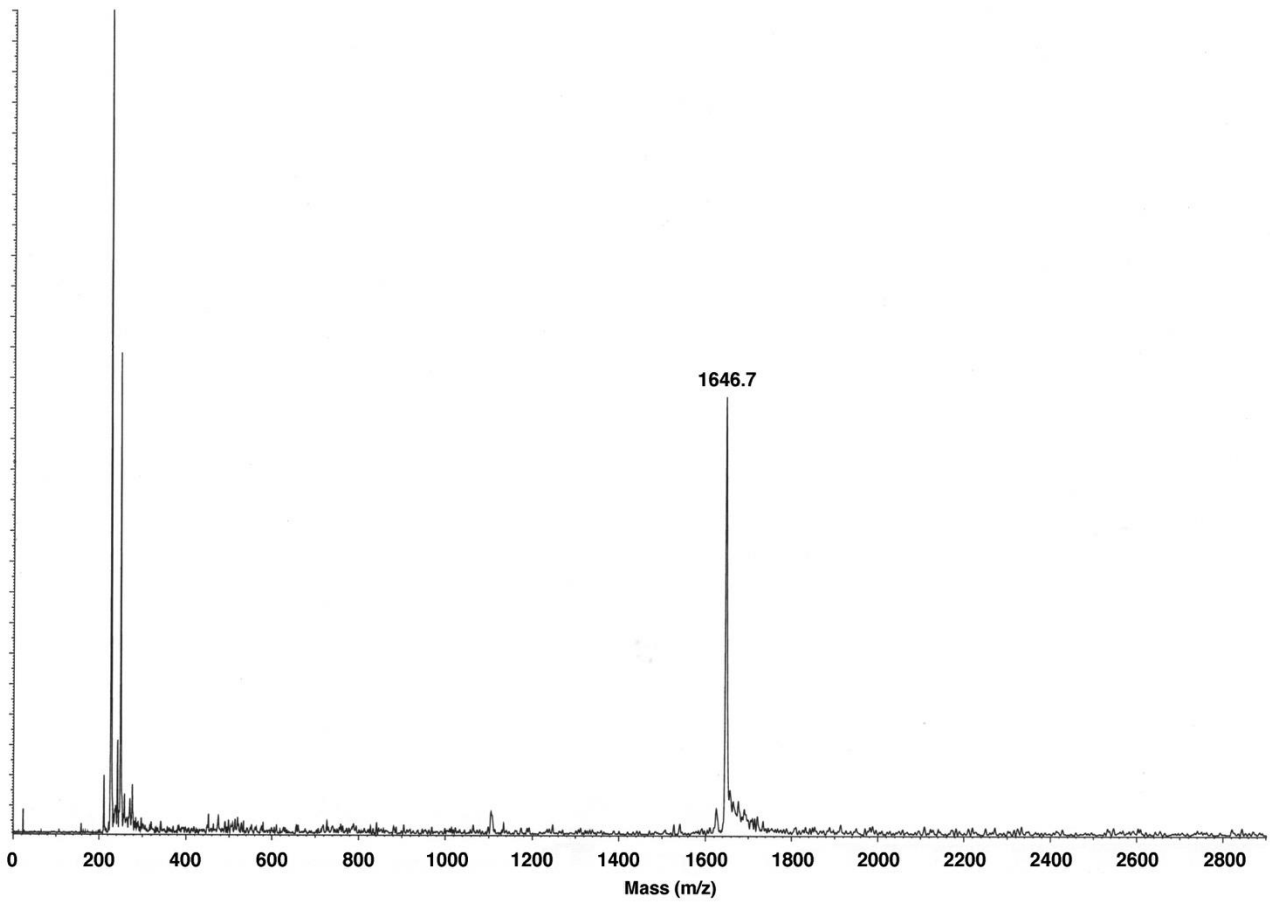

Figure S6: MALDI-TOF mass spectrum of macrocycle **3**. (Calc. *m*/*z* for $[C_{90}H_{60}S_6O_{18}Na]^+$ = 1644.8).

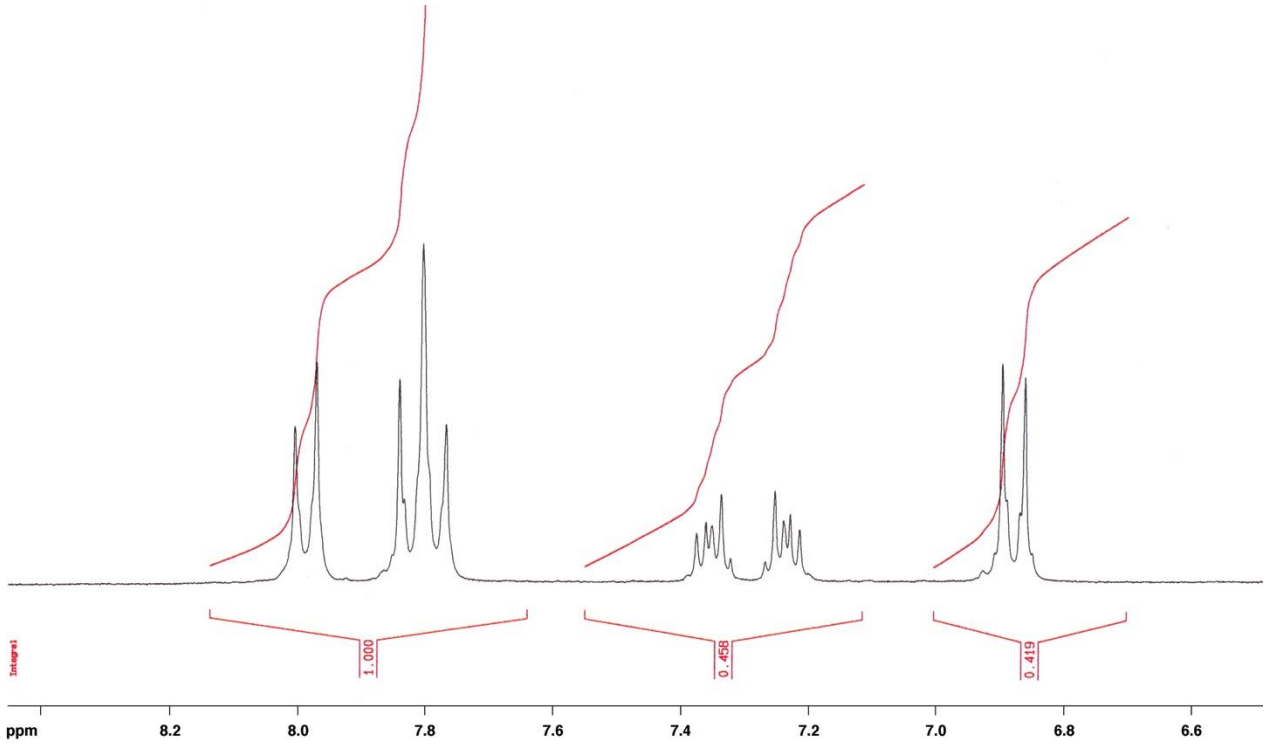

Figure S7: ^{1}H NMR spectrum of macrocycle **4** (250 MHz, CD_2Cl_2/CH_3SO_3H 4/1 v/v).

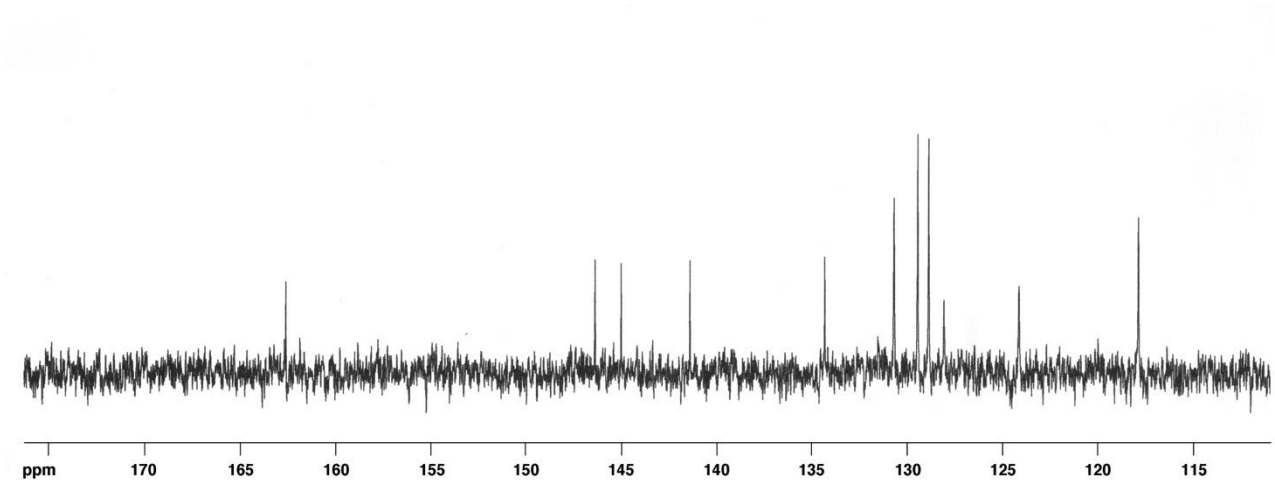

Figure S8: ^{13}C NMR spectrum of macrocycle **4** (62.5 MHz, CD_2Cl_2/CH_3SO_3H 4/1 v/v).

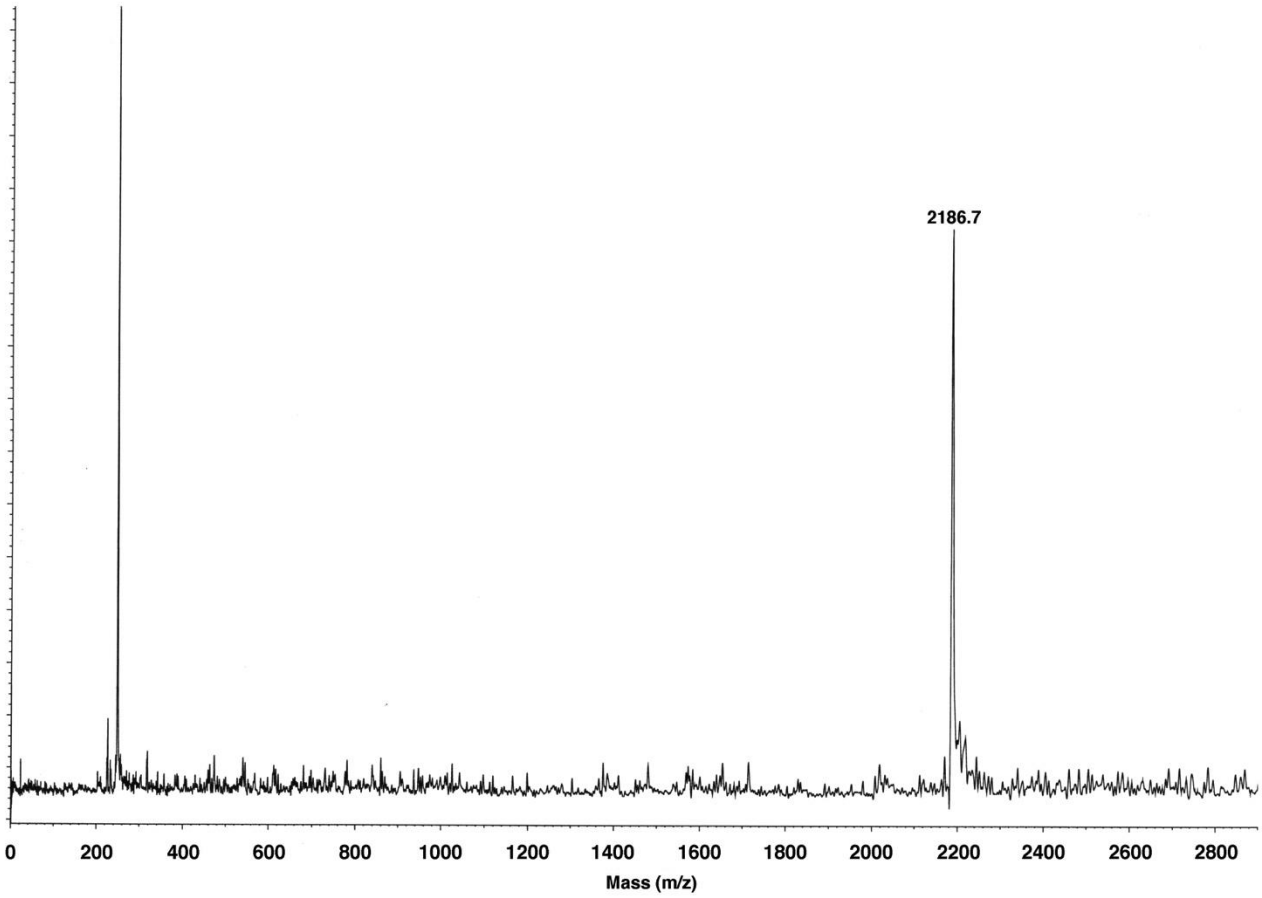

Figure S9: MALDI-TOF mass spectrum of macrocycle **4**. (Calc. *m/z* for $[C_{120}H_{80}S_8O_{24}Na]^+$ = 2185.4).

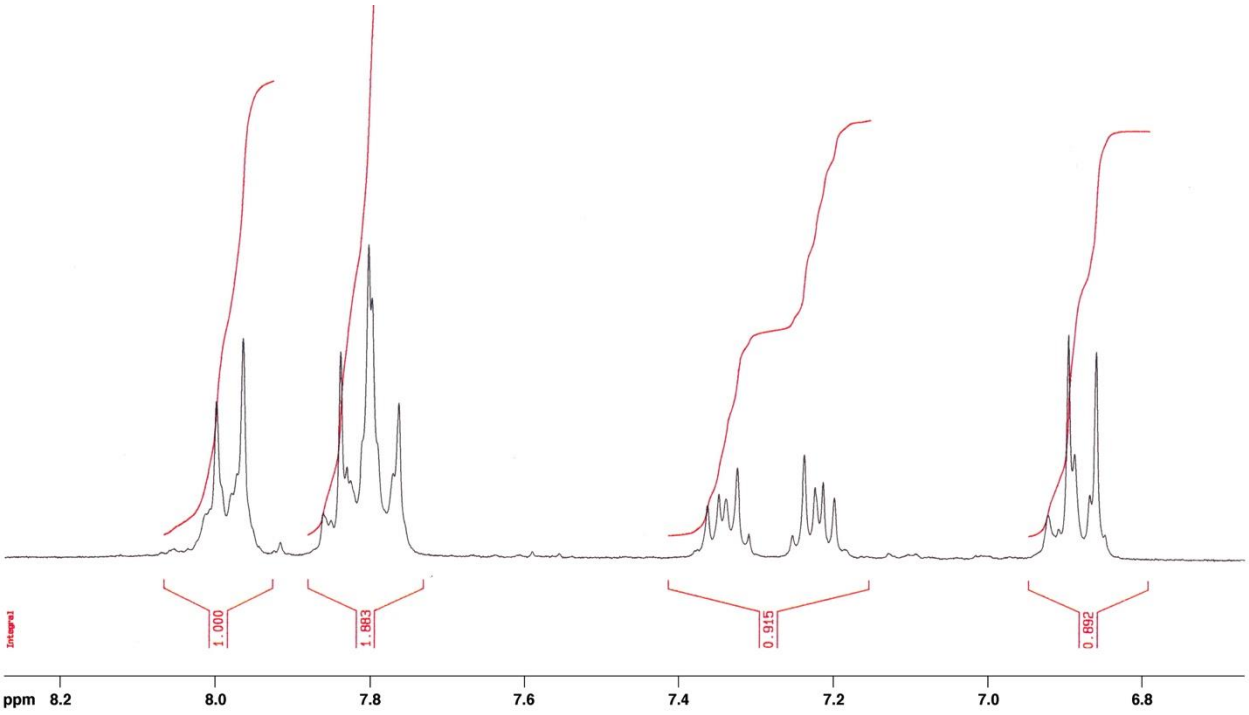

Figure S10: ^{1}H NMR spectrum of macrocycle **5** (250 MHz, CD_2Cl_2/CH_3SO_3H 4/1 v/v).

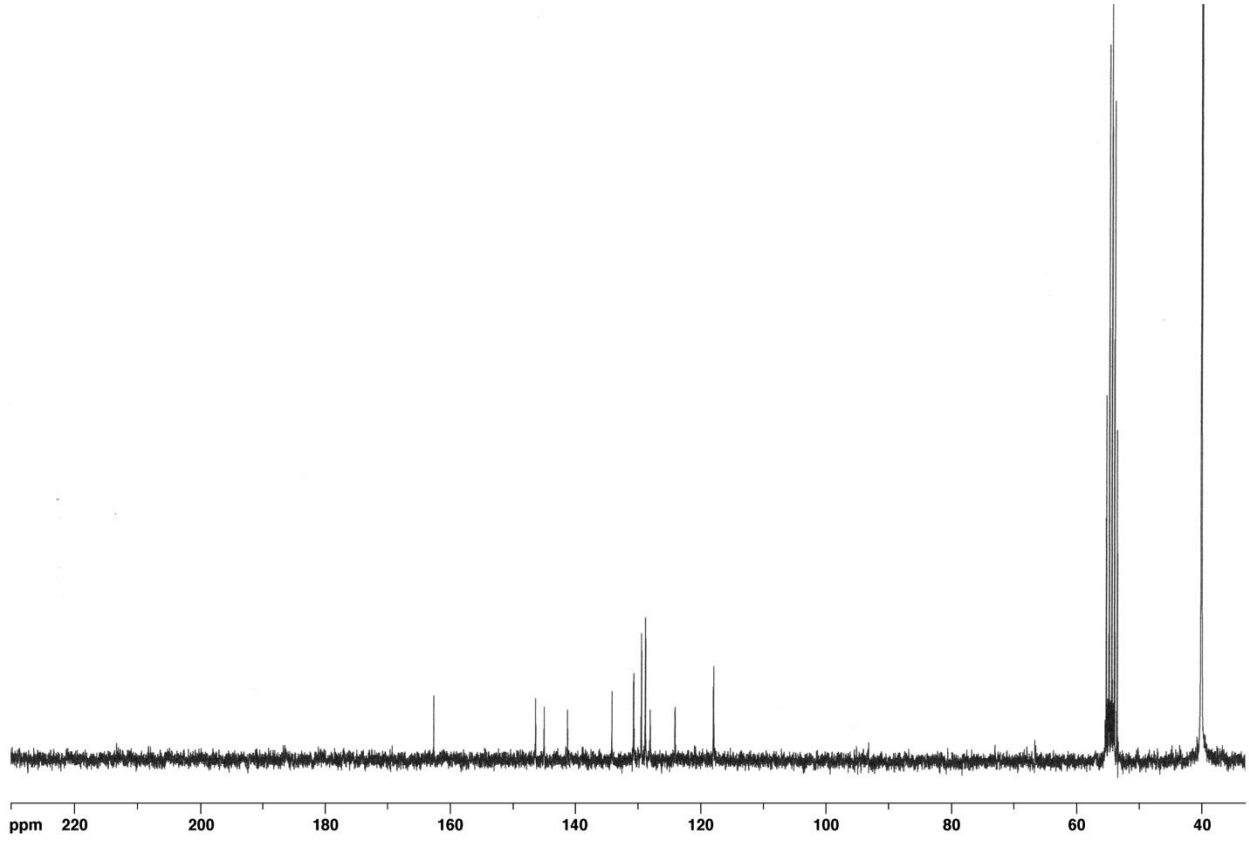

Figure S11: ^{13}C NMR spectrum of macrocycle **5** (62.5 MHz, CD_2Cl_2/CH_3SO_3H 4/1 v/v).

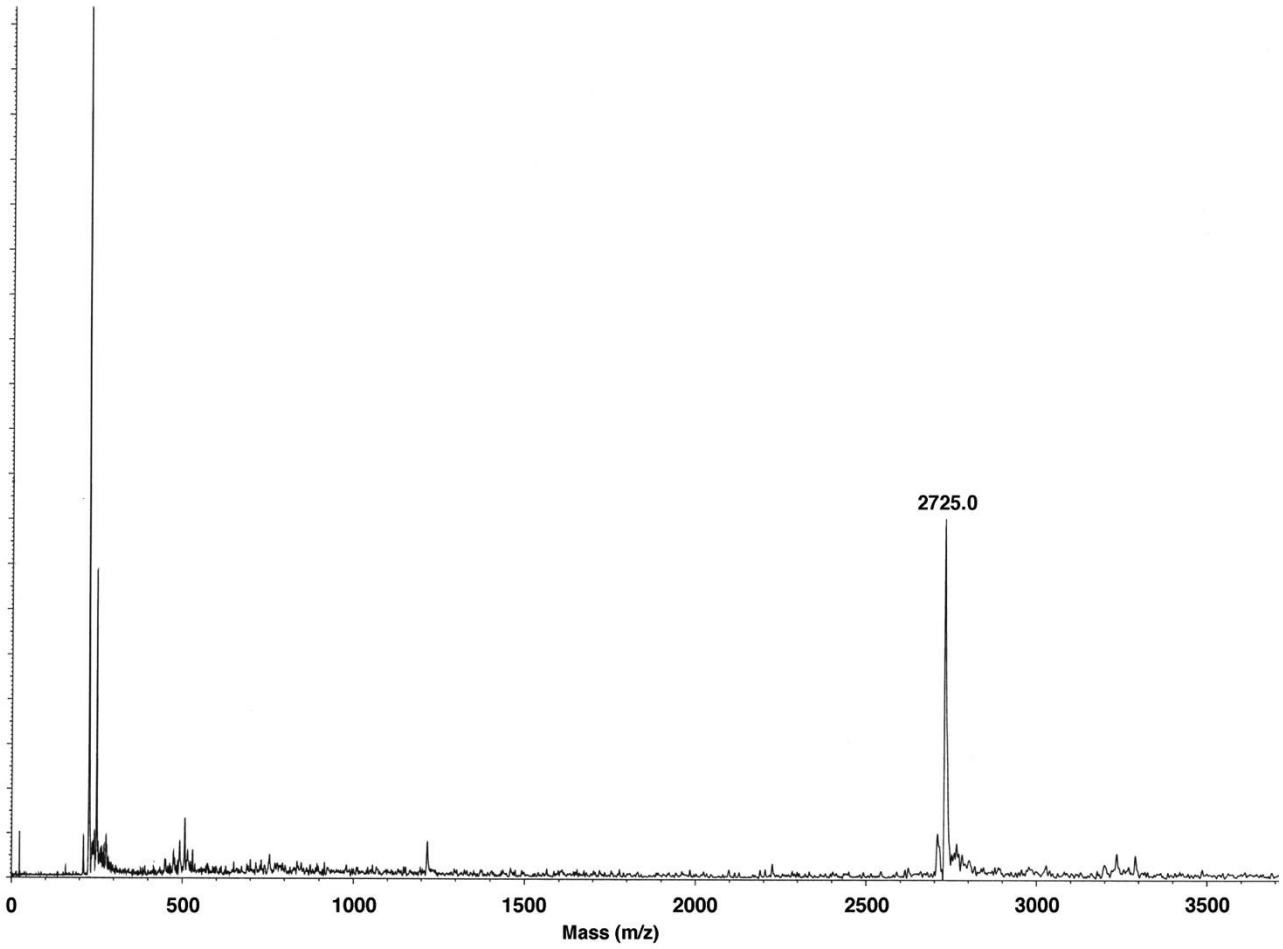

Figure S12: MALDI-TOF mass spectrum of macrocycle **5**. (Calc. *m*/*z* for $[C_{150}H_{100}S_{10}O_{30}Na]^+$ = 2726.0).

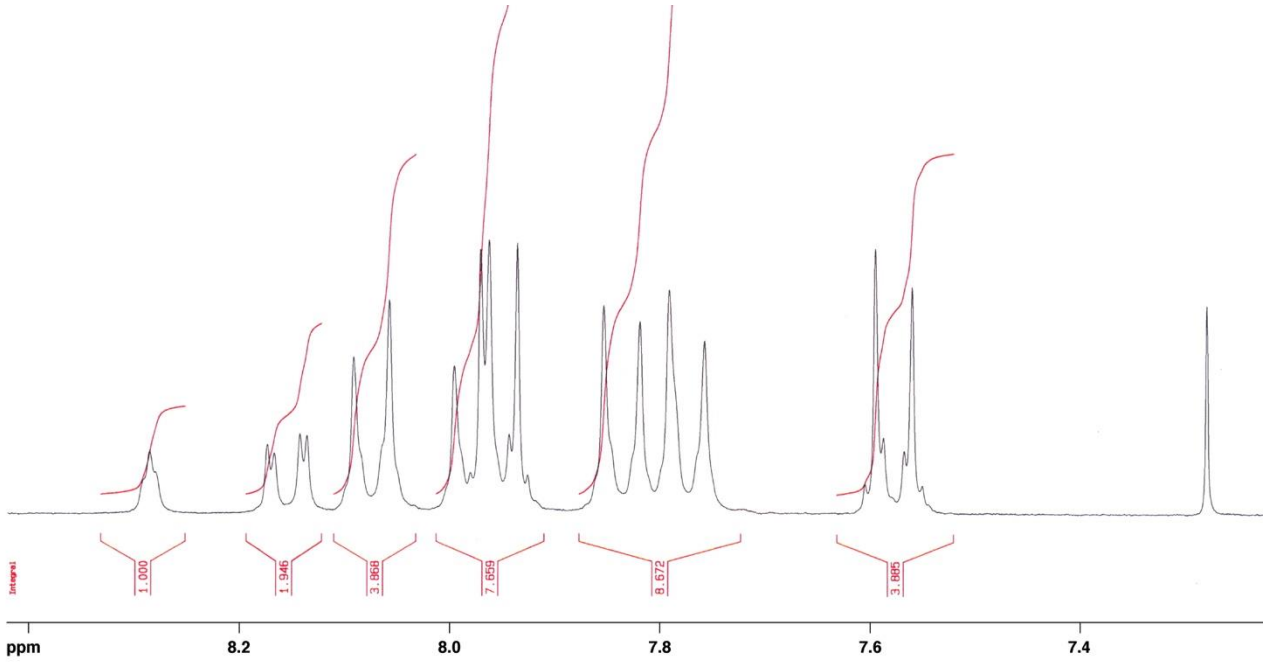

Figure S13: ^{1}H NMR spectrum of linear oligomer **7** (250 MHz, $CDCl_3/CF_3COOH$ 5/1 v/v).

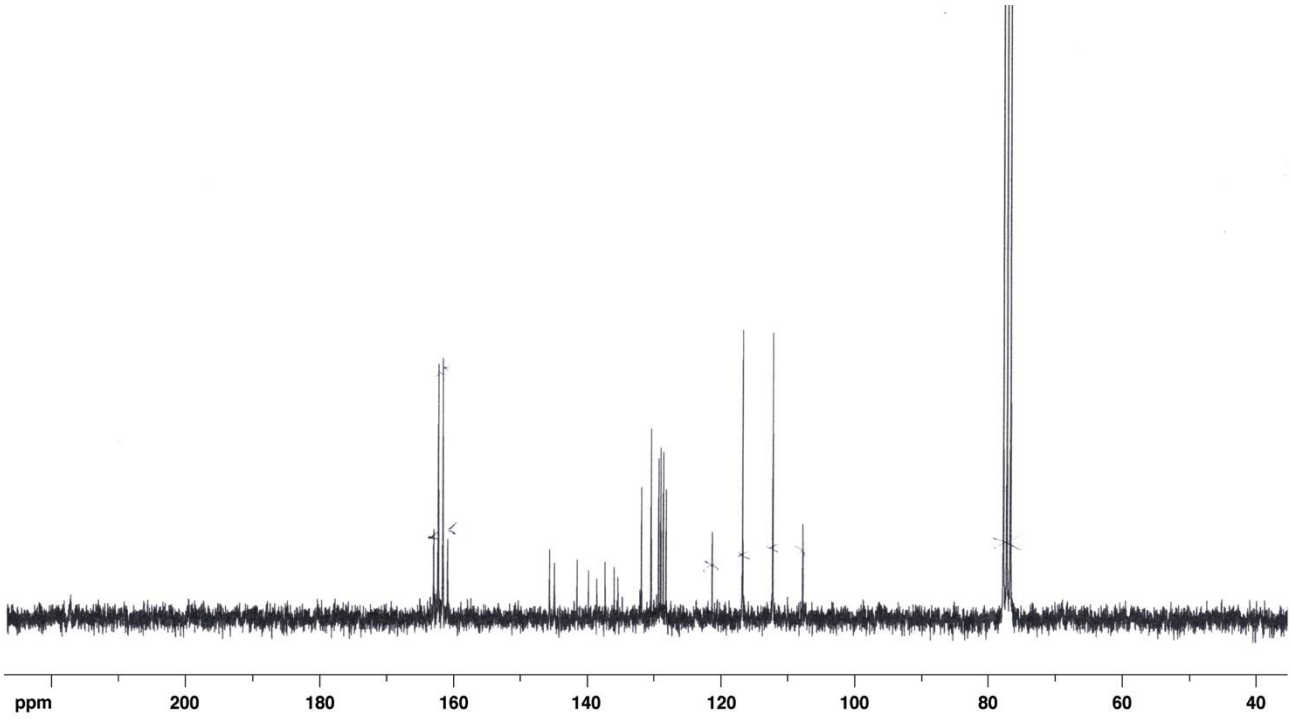

Figure S14: ^{13}C NMR spectrum of linear oligomer **7** (62.5 MHz, $CDCl_3/CF_3COOH$ 5/1 v/v). *Note:* the strong quartet resonances centred at 114 and 162 ppm are due to trifluoroacetic acid co-solvent.

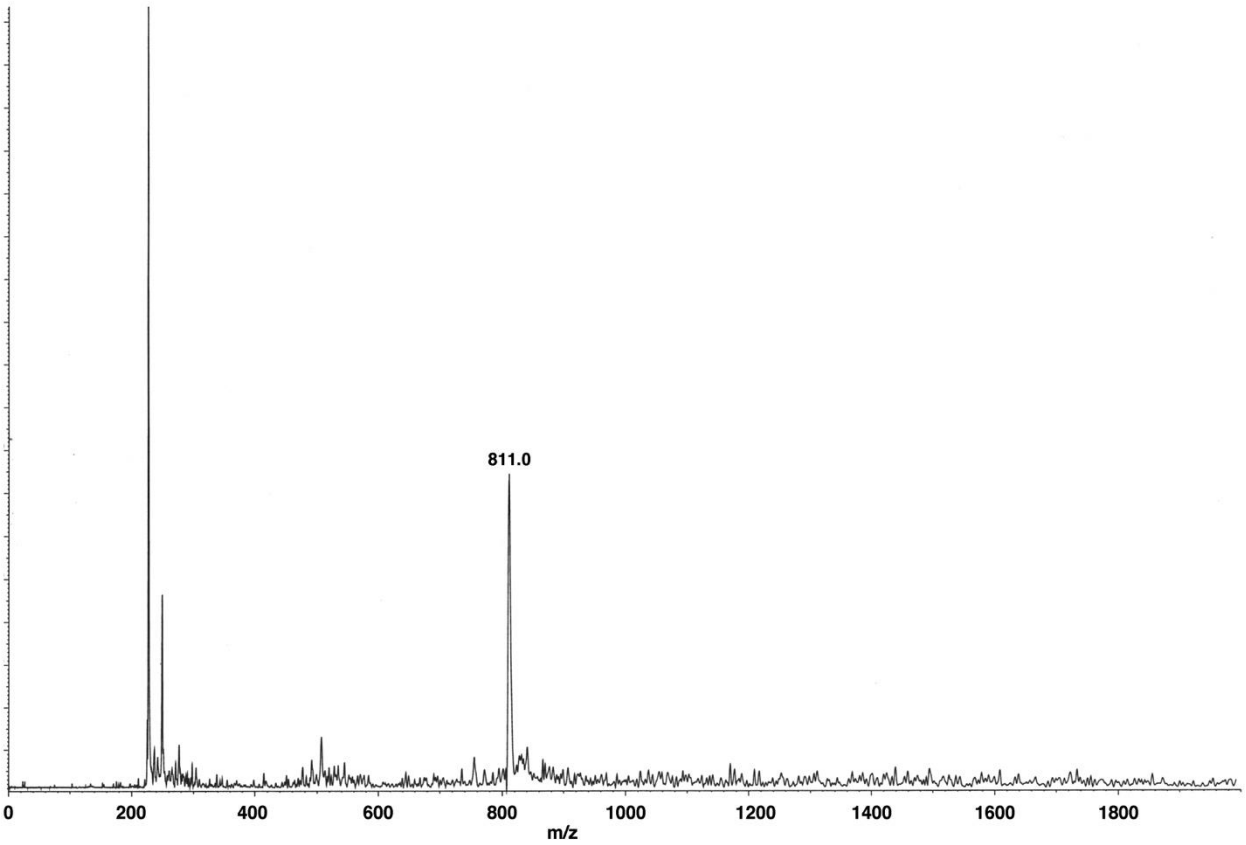

Figure S15: MALDI-TOF mass spectrum of linear oligomer **7**. (Calc. *m/z* for $[C_{44}H_{28}S_2O_6Cl_2Na]^+$ = 810.7).

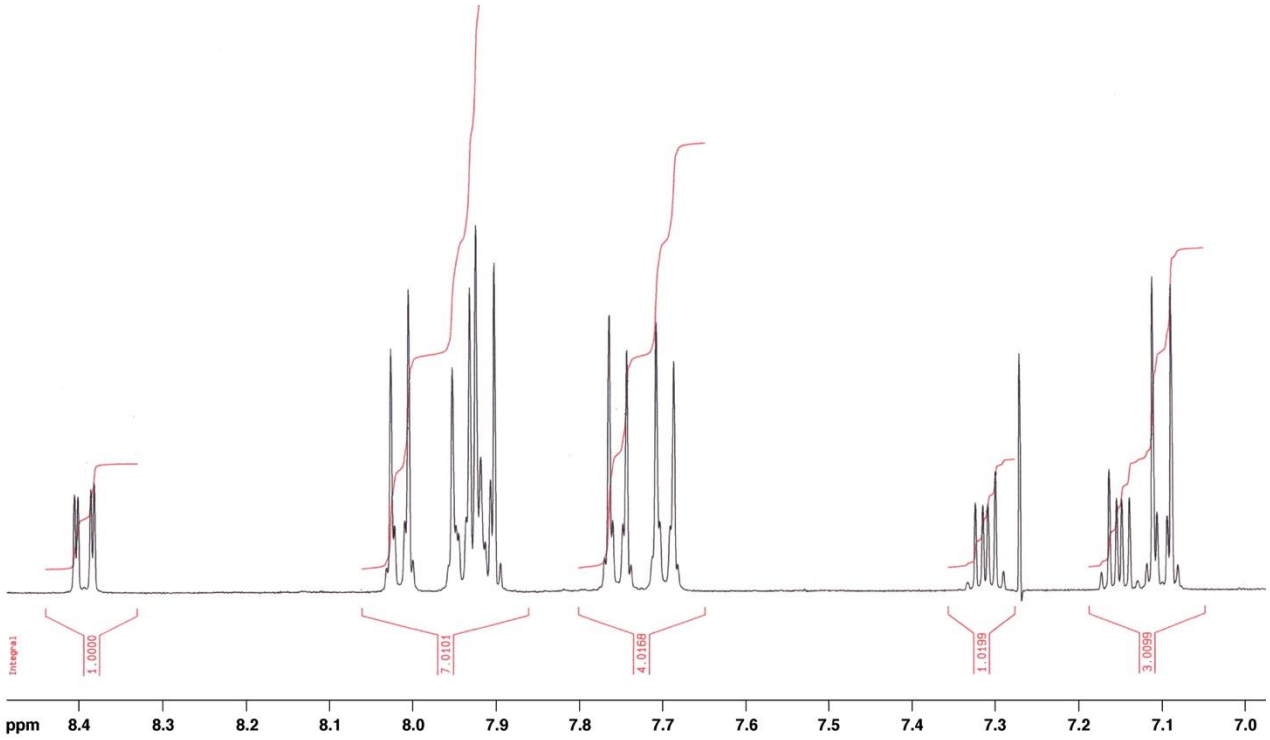

Figure S16: ^{1}H NMR spectrum of macrocycle **8** (400 MHz, $CDCl_3/CF_3COOH$ 5/1 v/v).

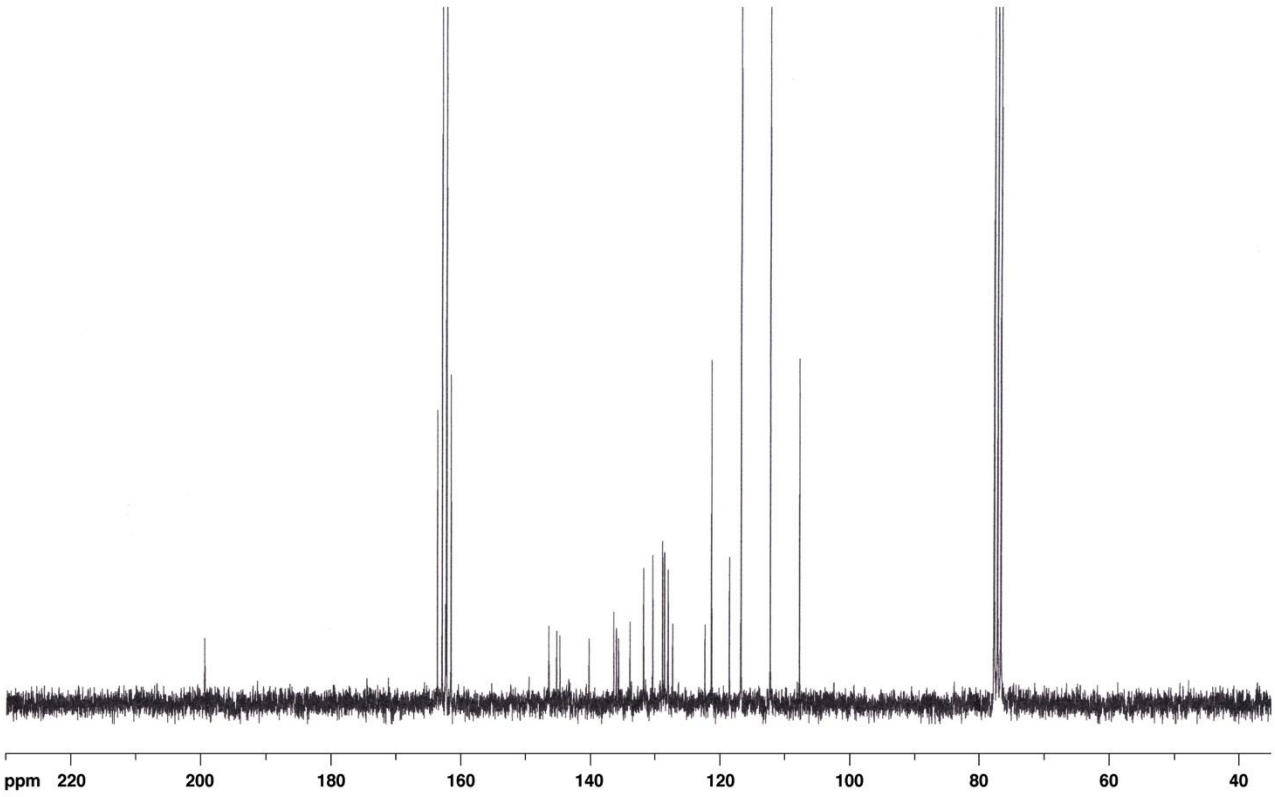

Figure S17: ^{13}C NMR spectrum of macrocycle **8** (100 MHz, $CDCl_3/CF_3COOH$ 5/1 v/v). *Note:* the strong quartet resonances centred at 114 and 162 ppm are due to trifluoroacetic acid co-solvent.

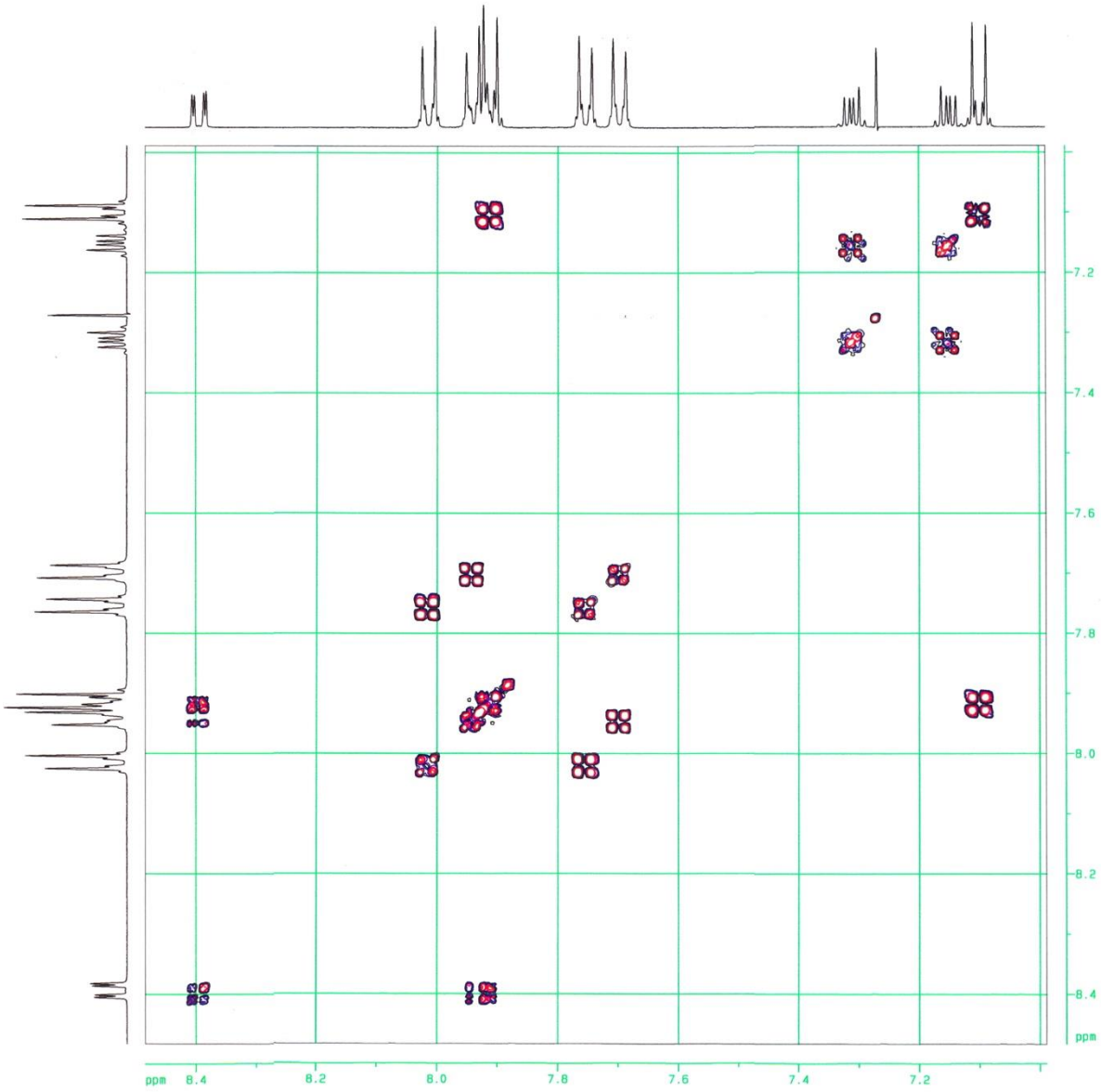

Figure S18: ^{1}H-^{1}H COSY NMR spectrum of macrocycle **8** (400 MHz, $CDCl_3$/CF_3COOH 5/1 v/v).

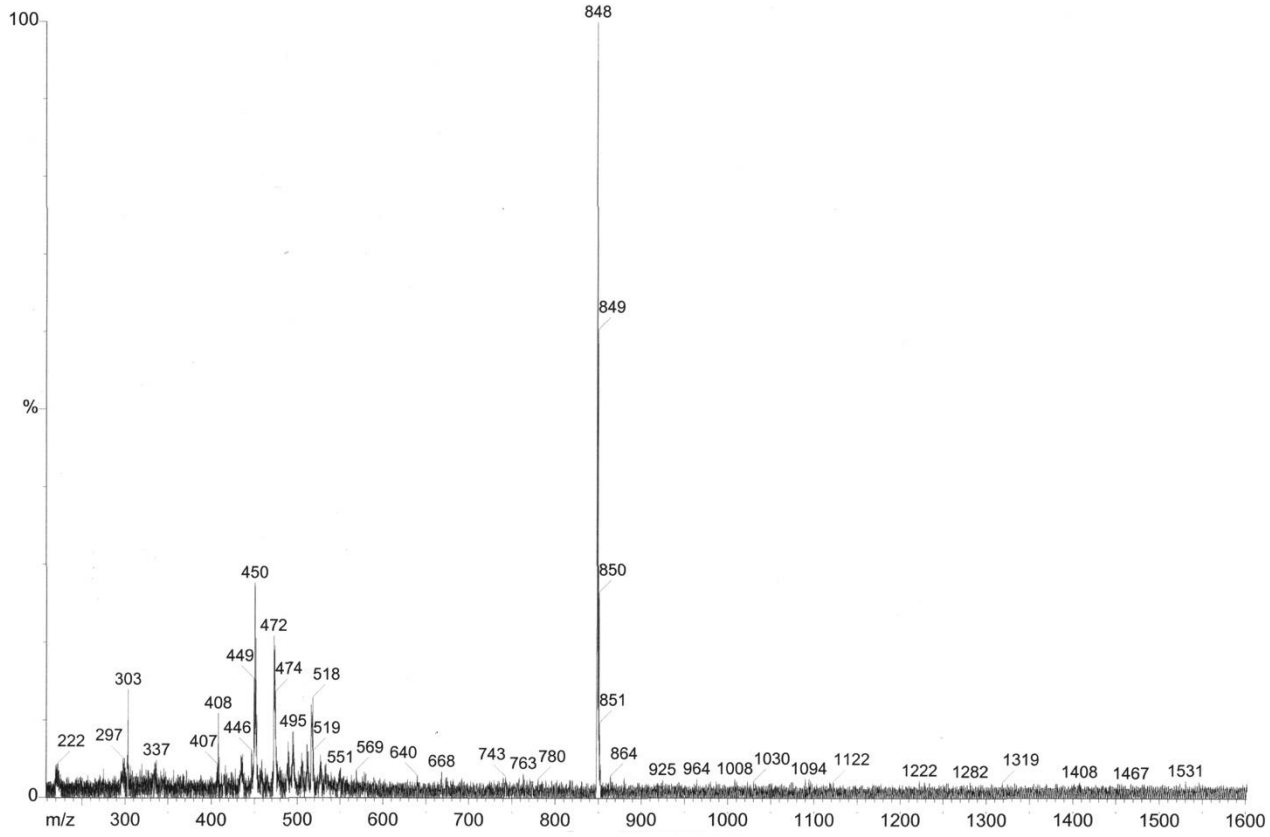

Figure S19: MALDI-TOF mass spectrum of macrocycle **8** (Calc. *m/z* for $[C_{50}H_{32}S_2O_8Na]^+$ = 847.9).

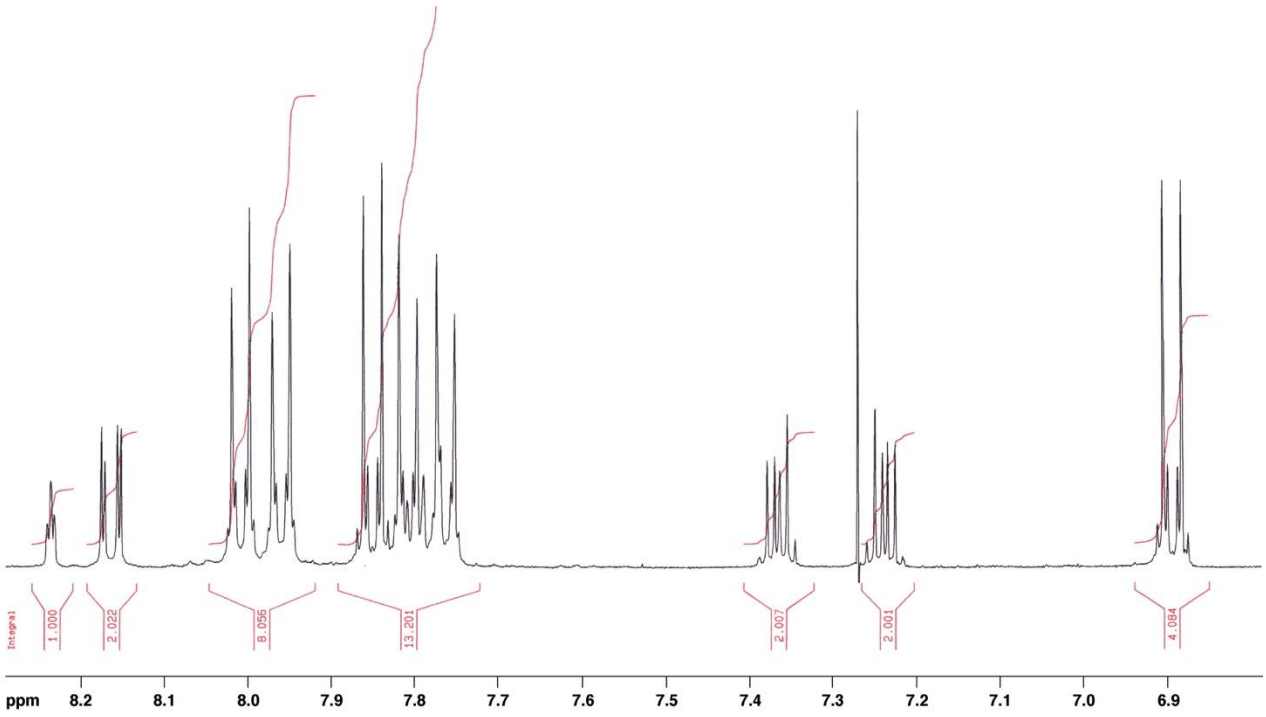

Figure S20: ^{1}H NMR spectrum of macrocycle **9** (400 MHz, $CDCl_3/CF_3COOH$ 5/1 v/v).

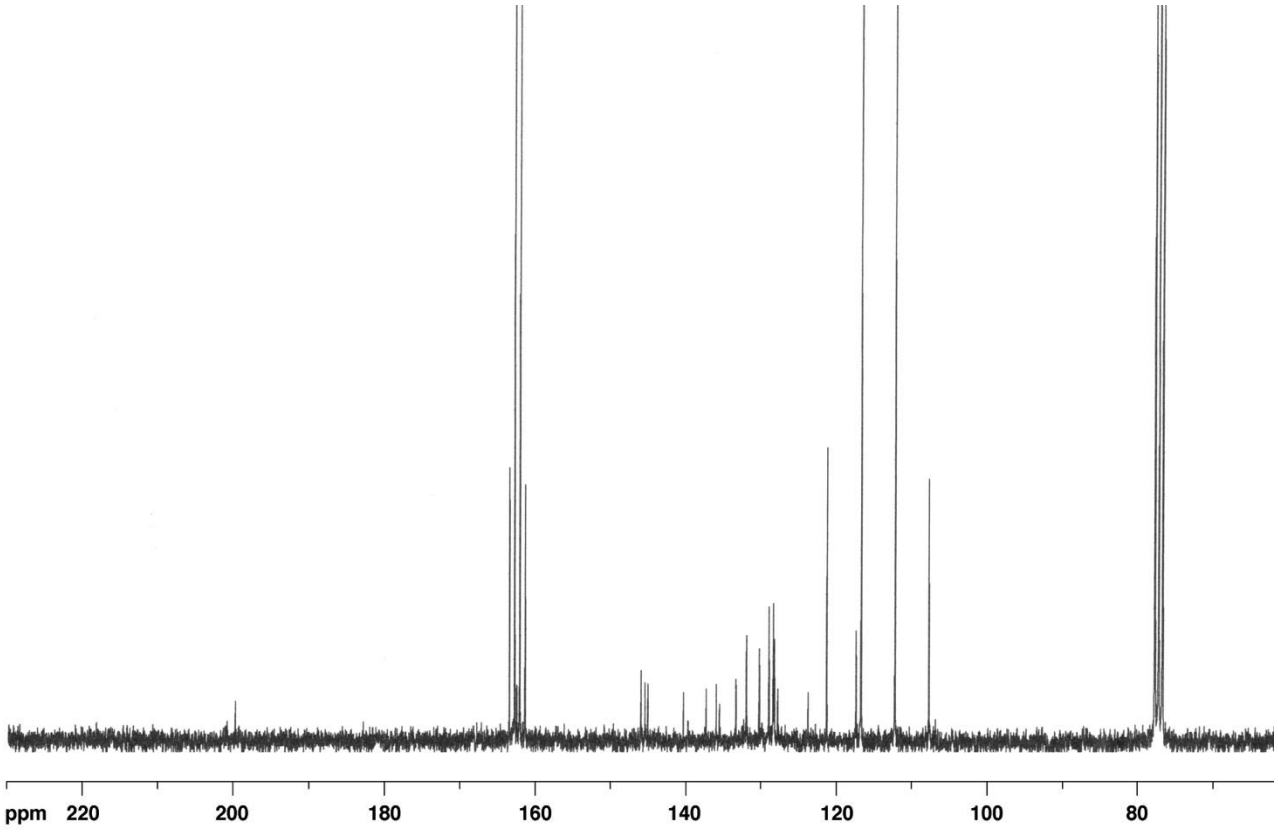

Figure S21: ^{13}C NMR spectrum of macrocycle **9** (100 MHz, $CDCl_3/CF_3COOH$ 5/1 v/v). *Note:* the strong quartet resonances centred at 114 and 162 ppm are due to trifluoroacetic acid co-solvent.

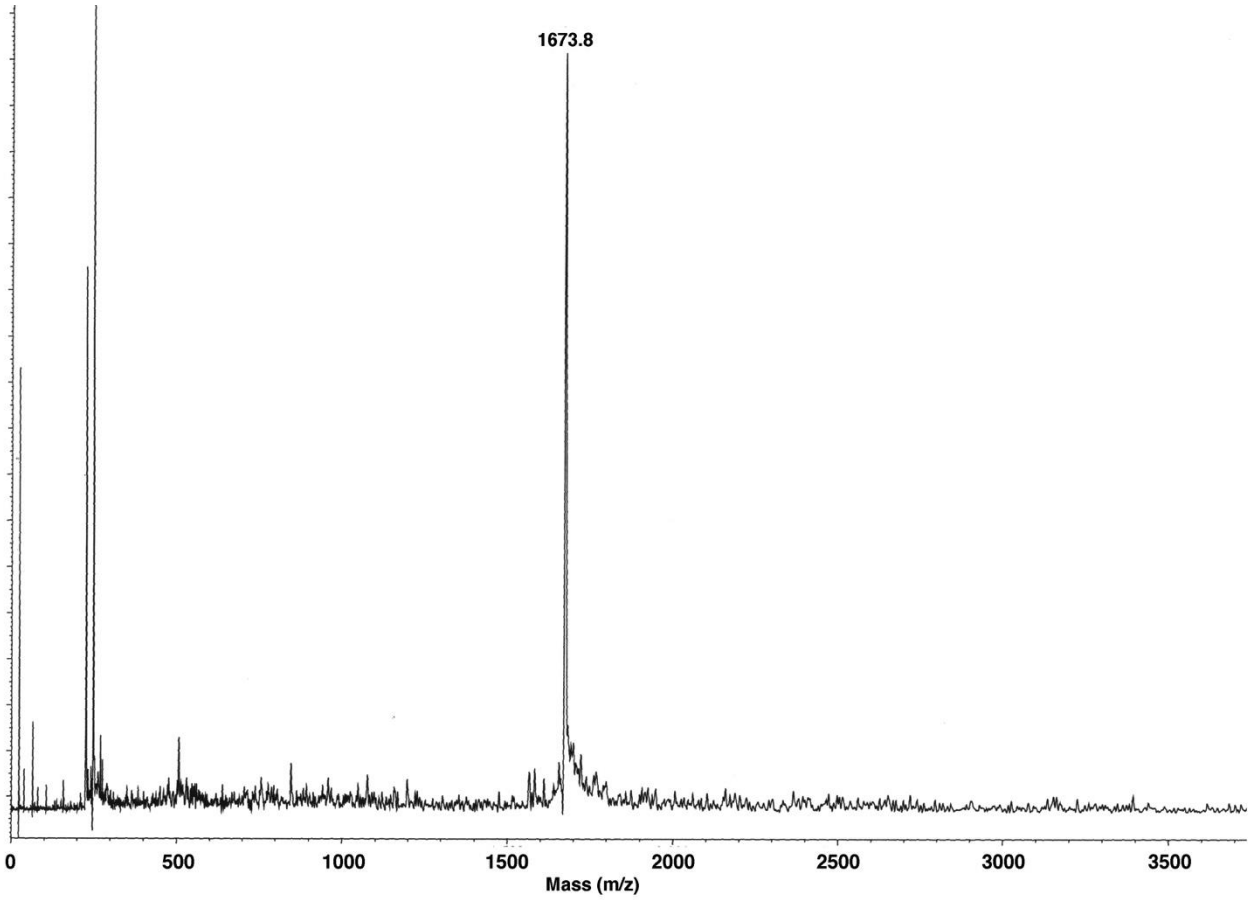

Figure S19: MALDI-TOF mass spectrum of macrocycle **9** (Calc. *m/z* for $[C_{100}H_{64}S_4O_{16}Na]^+$ = 1672.8).

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

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

