Electronic Supplementary Information

Synthesis and solid state structure of a hydrazone-disulfide macrocycle and its dynamic covalent ring-opening under acidic and basic conditions

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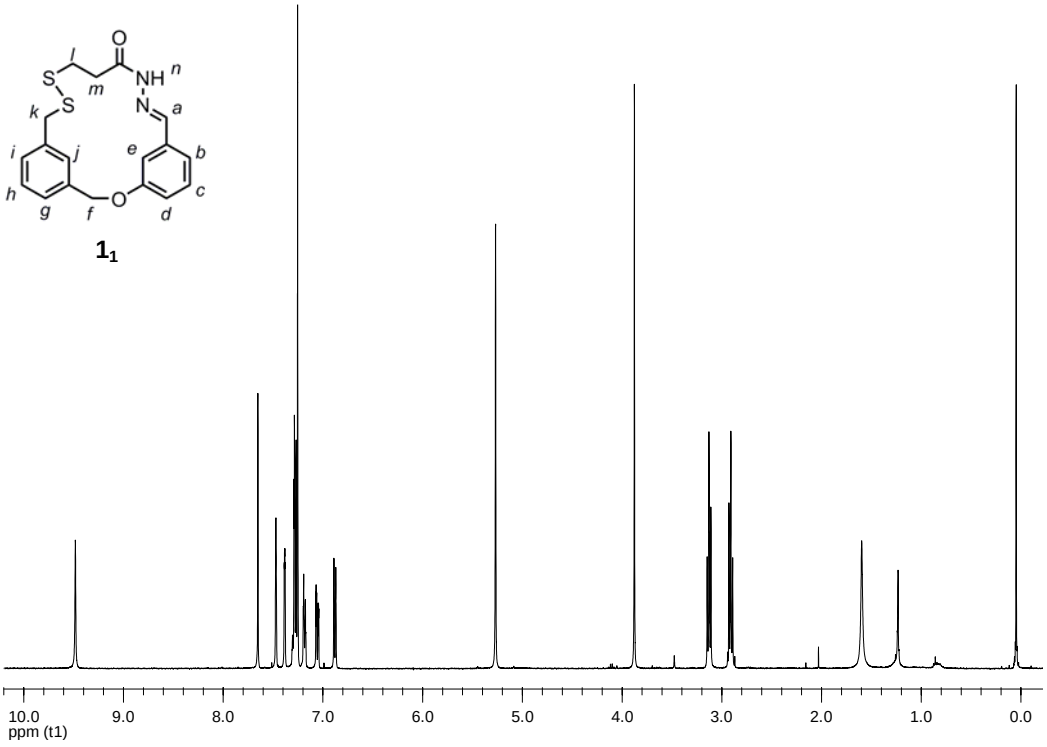
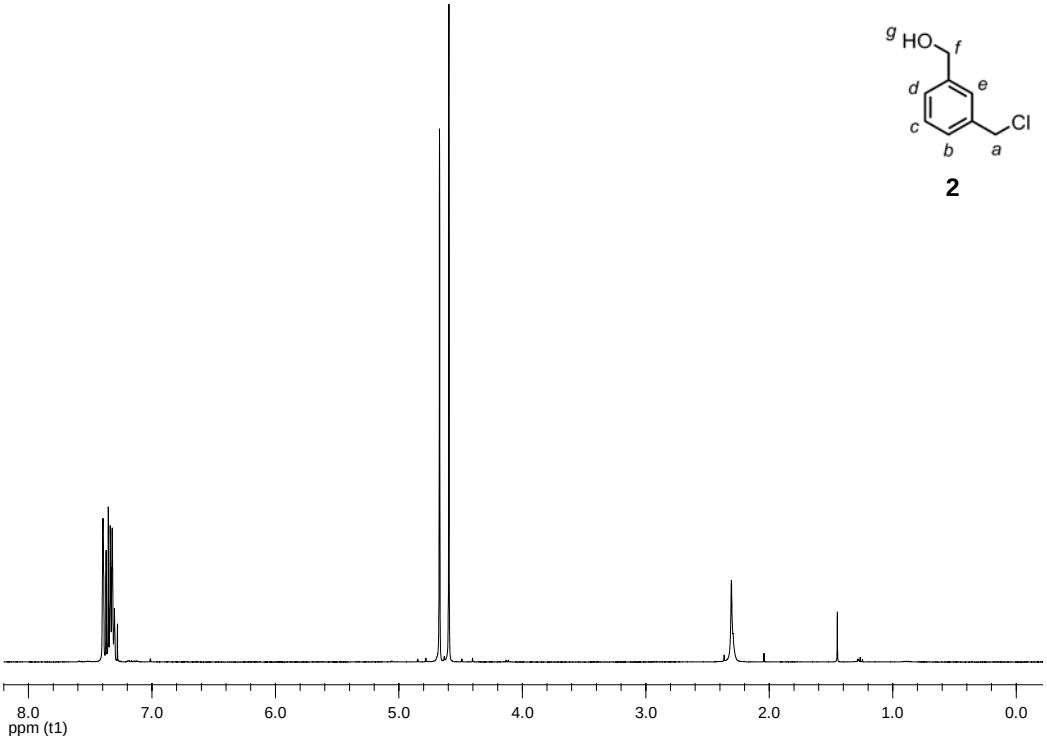
^{1}H NMR spectra of all compounds

400 MHz, 298 K, $CDCl_3$



1_1

400 MHz, 298 K, $CDCl_3$



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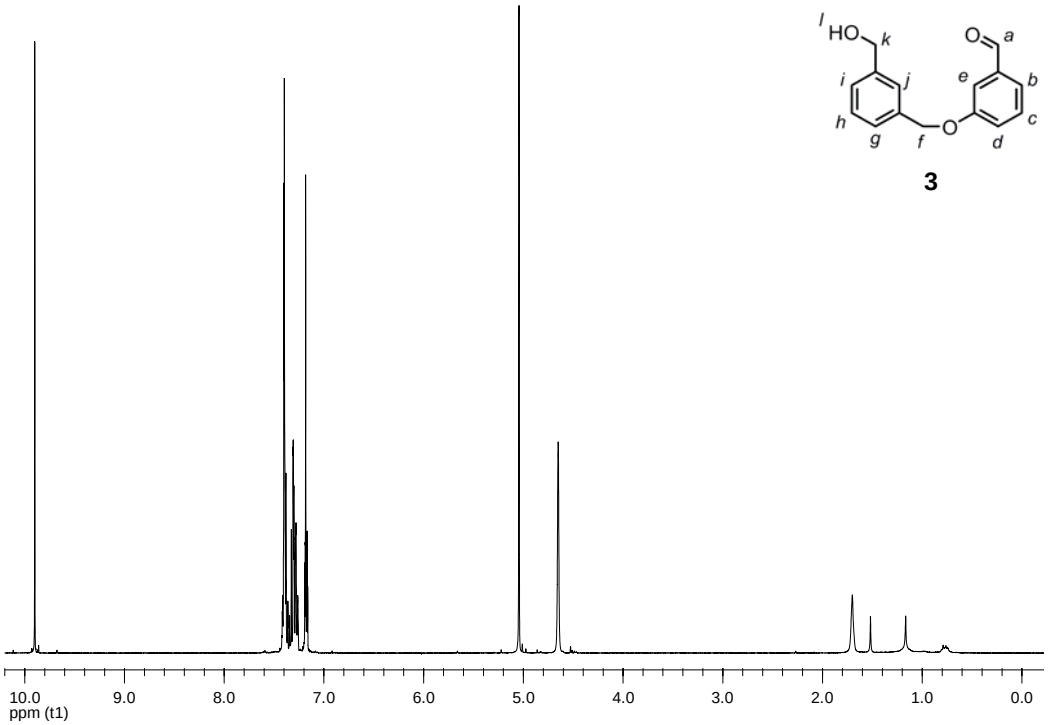

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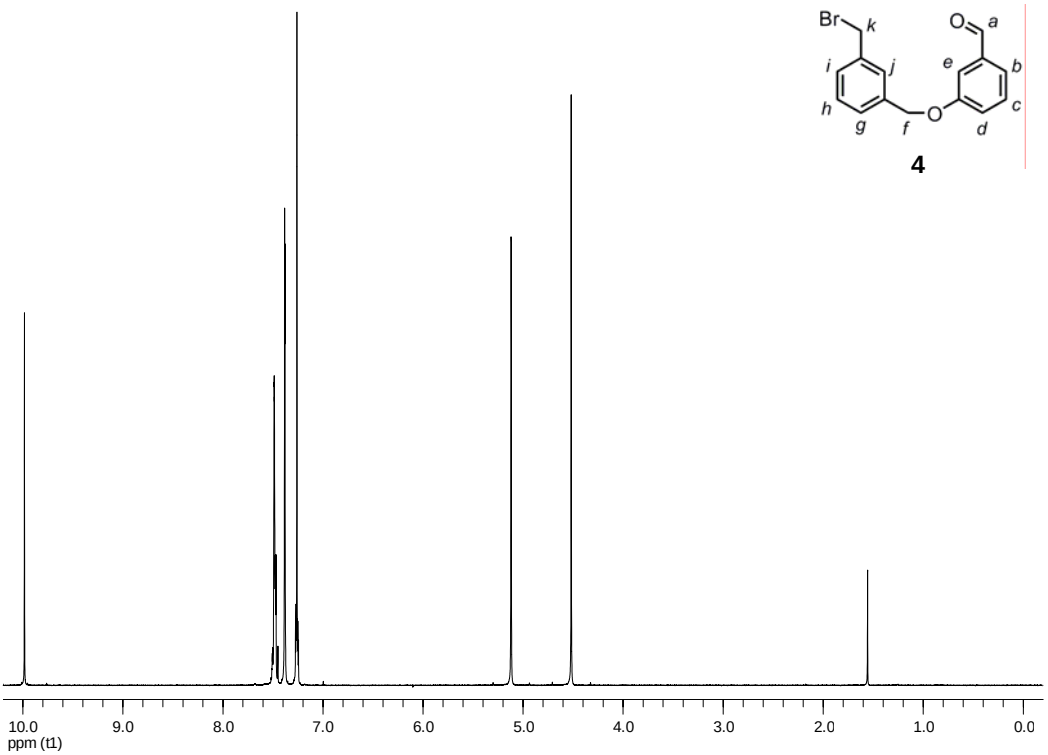
400 MHz, 298 K, $CDCl_3$



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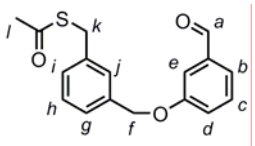
400 MHz, 298 K, $CDCl_3$



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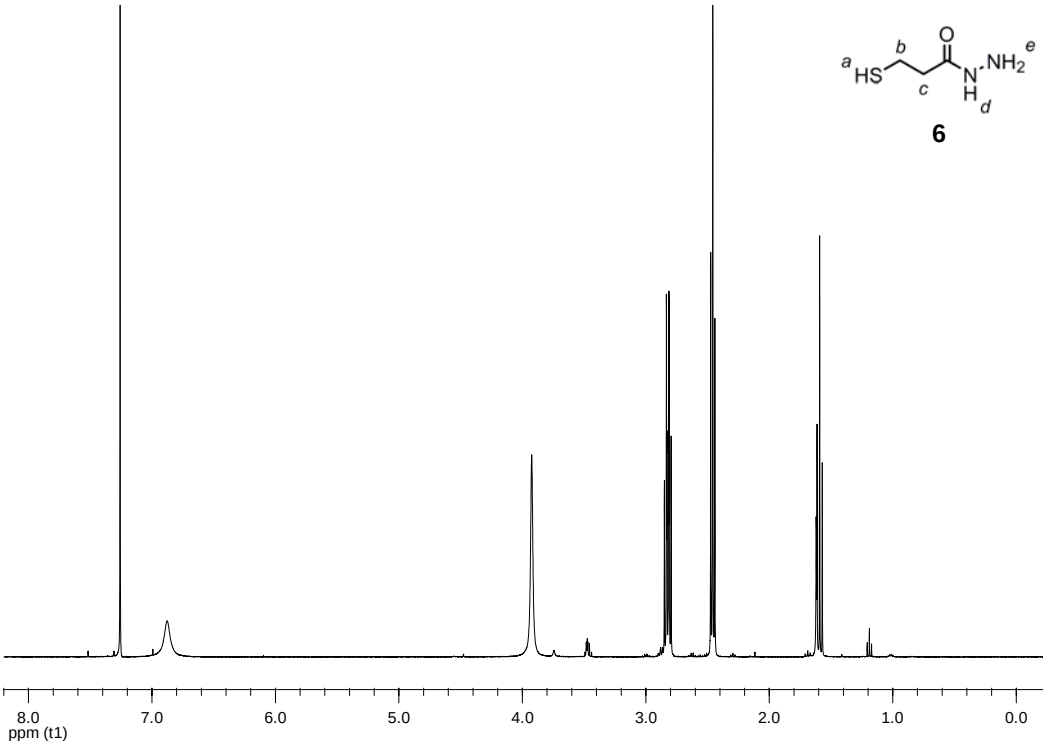
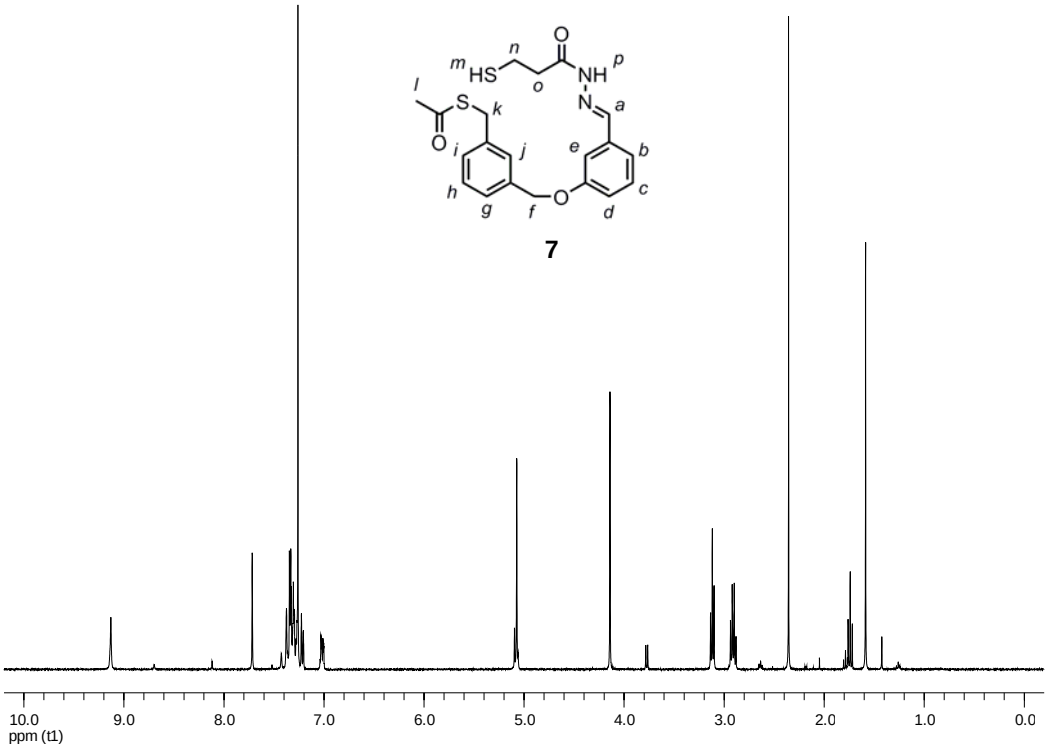
400 MHz, 298 K, $CDCl_3$



6

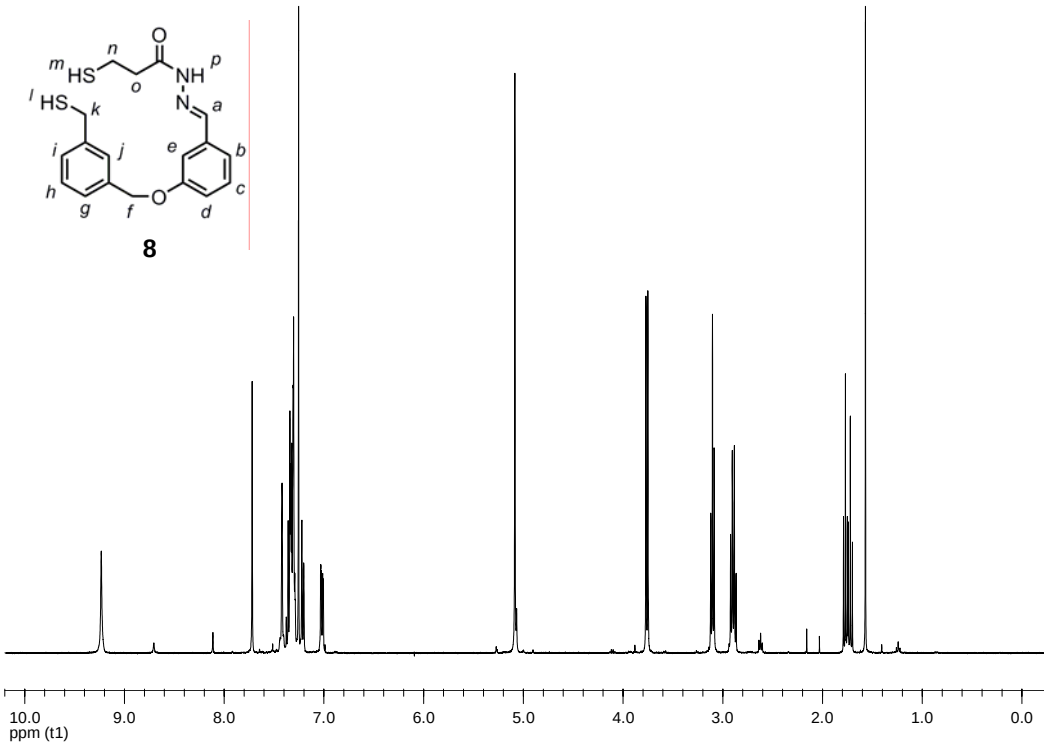
400 MHz, 298 K, $CDCl_3$



7

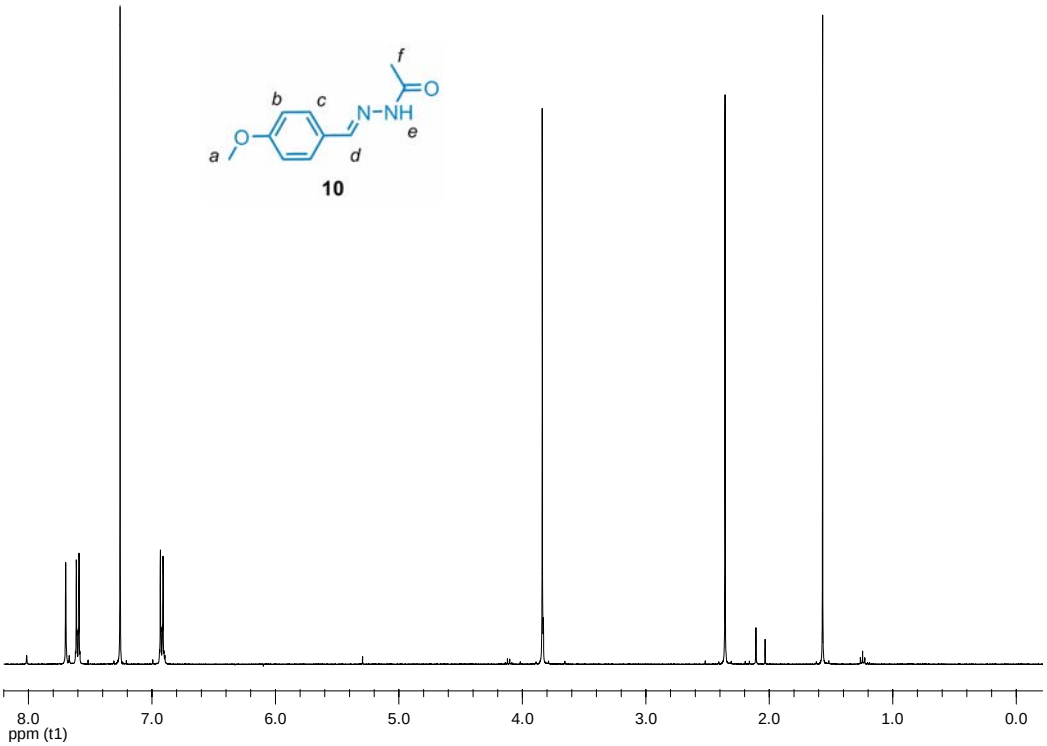
Spectrum shows a mixture of **7** and **8** (~85:15; see experimental section)

400 MHz, 298 K, $CDCl_3$



8

400 MHz, 298 K, $CDCl_3$



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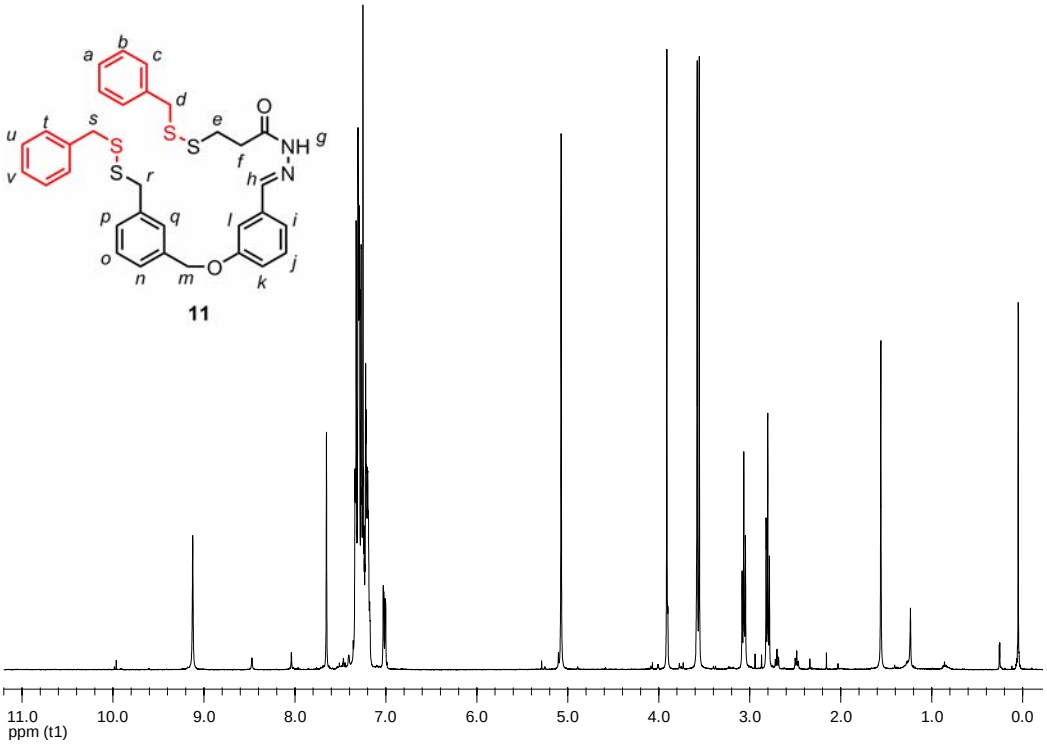
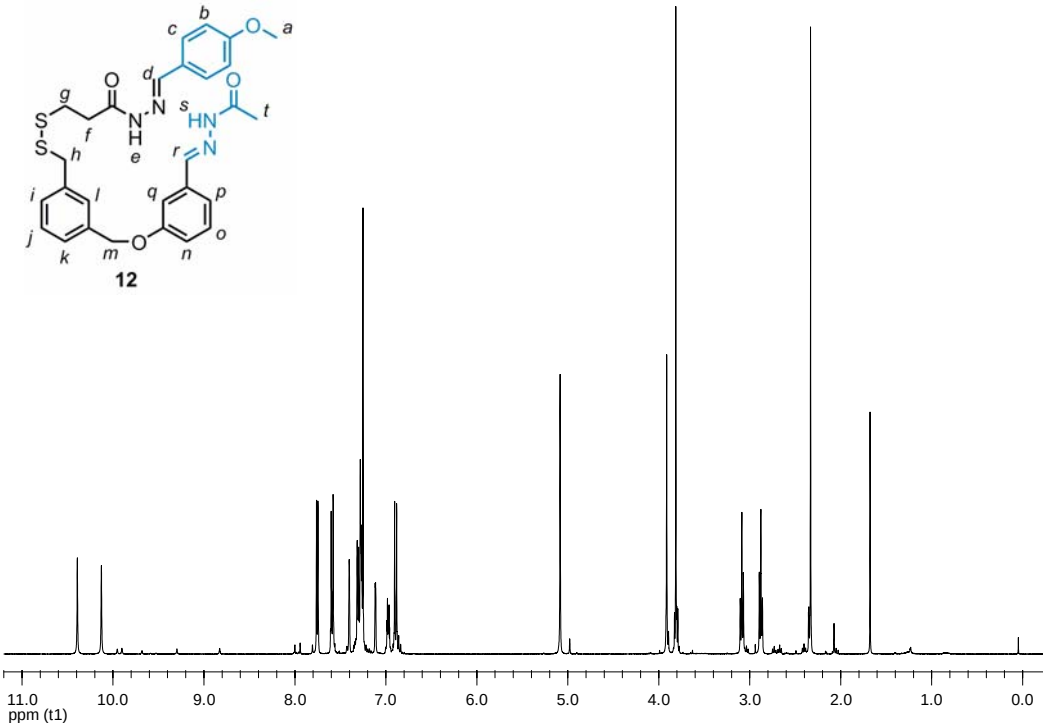
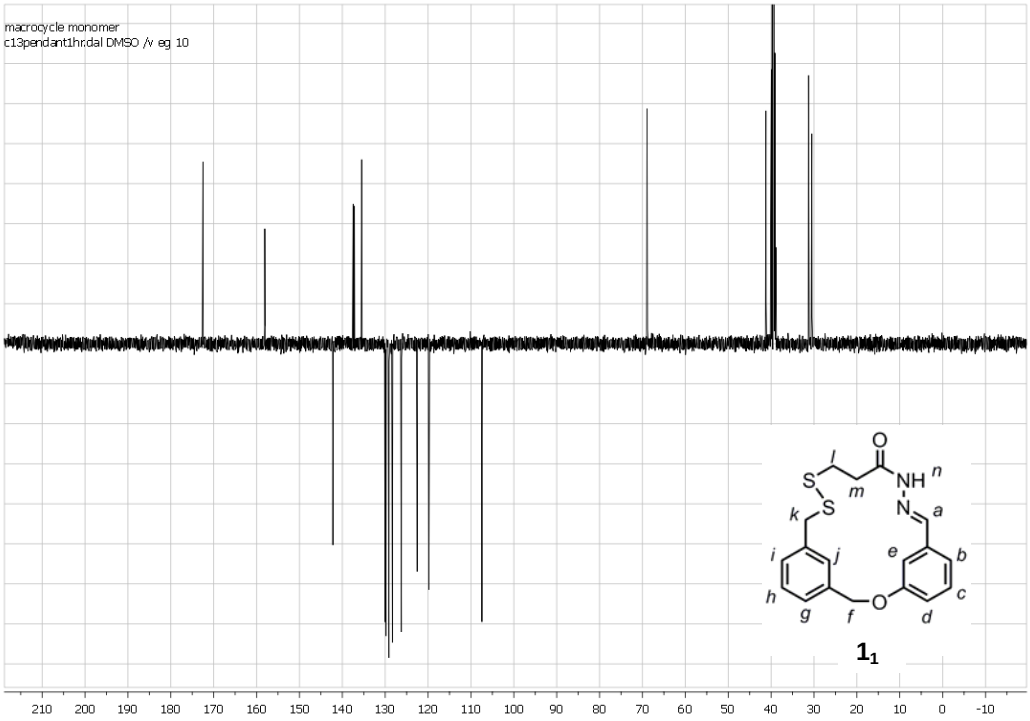


400 MHz, 298 K, $CDCl_3$



^{13}C NMR spectrum of macrocycle $\mathbf{1_1}$

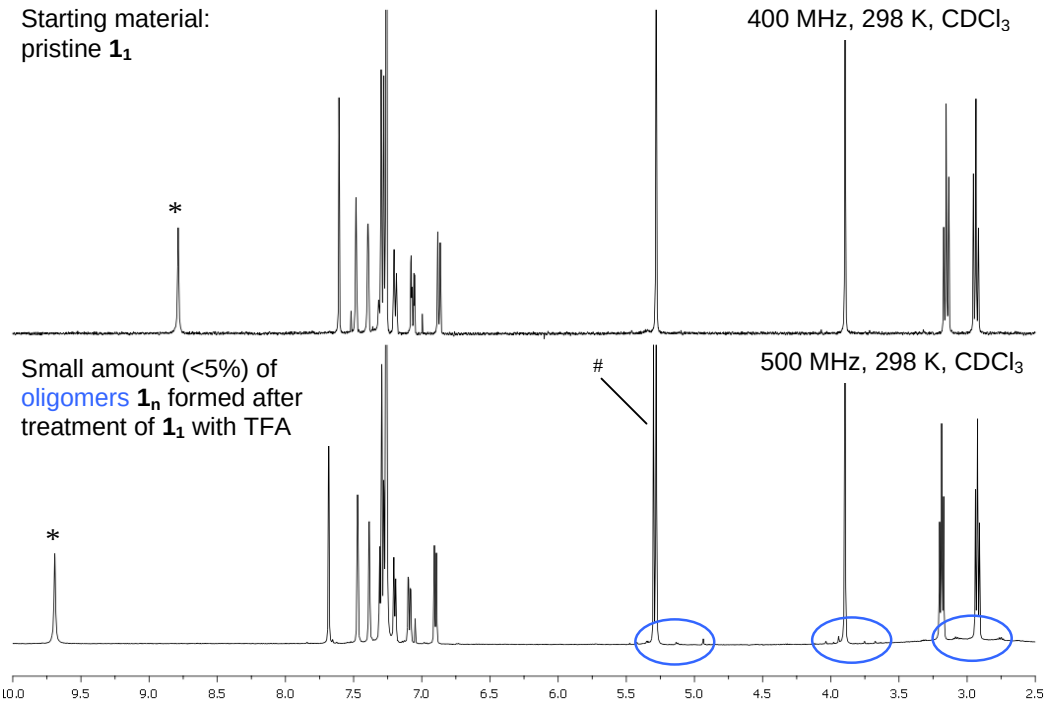
100 MHz, 298 K, DMSO-d_6



$\mathbf{1_1}$

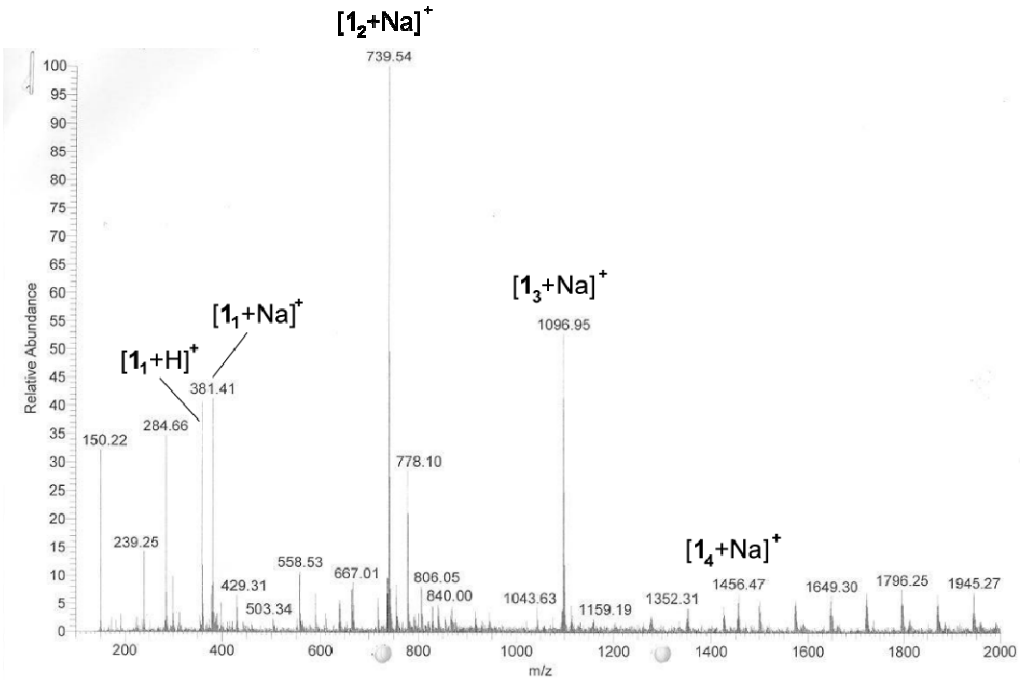
^{1}H NMR spectrum corresponding to ESI mass spectrum in Fig. 1b

^{1}H NMR:



*: hydrazone N-H proton, exchanges with solvent. #: residual CH_2Cl_2 peak (from workup).

ESI-MS (as shown in Fig. 1b):



Comments:

The ^{1}H NMR spectrum indicates that there is only a small amount of oligomers $\mathbf{1_n}$ (<5%) present and monomer $\mathbf{1_1}$ is by far the major compound in the mixture.

The relative peak heights in the ESI mass spectrum would, however, indicate that $\mathbf{1_2}$ is the major compound in the mixture.

Since low-resolution ESI mass spectrometry, unlike ^{1}H NMR spectroscopy, is not a quantitative analytical technique, we are certain that the mass spectrometric data is misleading. The most likely reason for this is the relatively low tendency of the monomer $\mathbf{1_1}$ to form a sodium-aggregate $[M+Na]^+$, whereas the oligomers under the ESI conditions seem to form rather stable sodium aggregates. Because only ionised particles will be able to reach the detector of the mass spectrometer, the different tendency to form $[M+Na]^+$ species will have an impact on the observed relative peak heights. This hypothesis is supported by the fact that only for the monomer $\mathbf{1_1}$, but not for $\mathbf{1_2}$ or $\mathbf{1_3}$, a significant $[M+H]^+$ peak is observed (the $[M+H]^+$ peaks are therefore probably a better indicator for the composition of the mixture).