Quantitative method for analysis of mixtures of homologues and stereoisomers of hemicucurbiturils allows to follow their formation and stability.

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Supplementary Material

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1 HPLC chromatogram of oligomeric mixture and structures of isolated oligomers

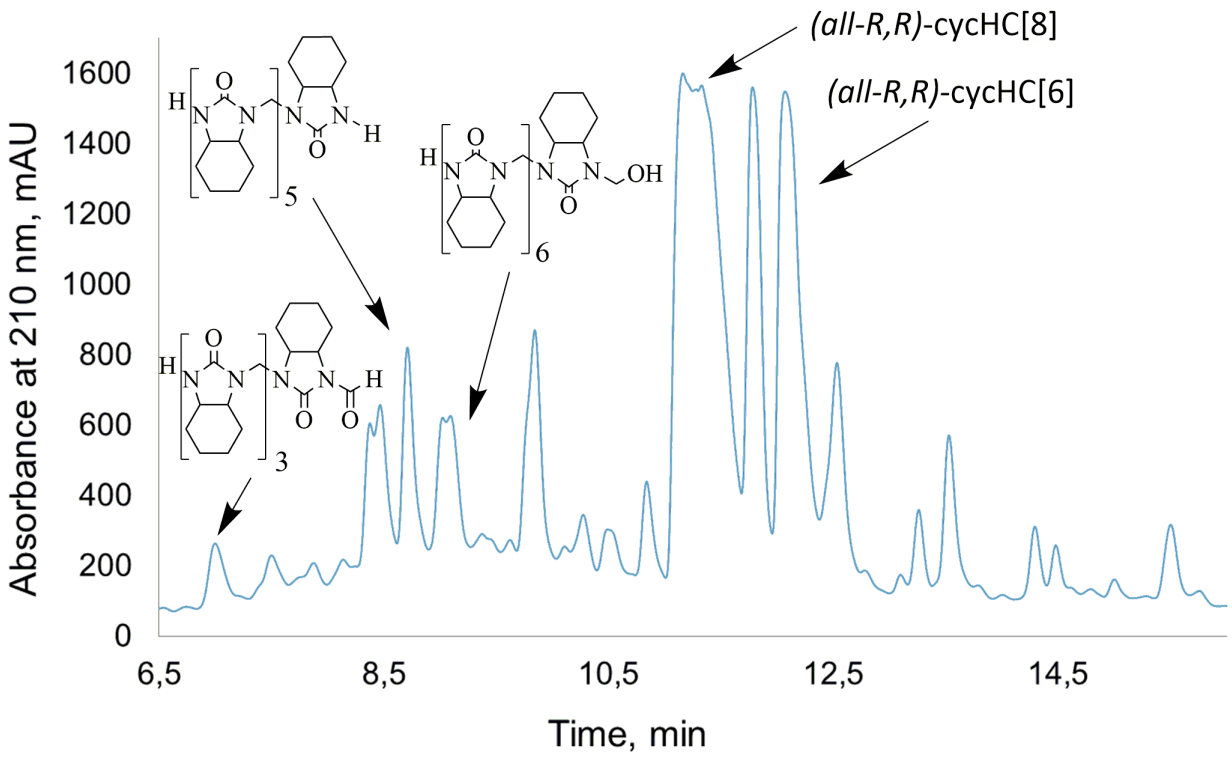

Figure S1. HPLC chromatogram of oligomeric mixture. Peaks and structures of isolated 4-, 6- and 7-membered oligomers are pointed out.

2 HRMS results for isolated oligomers and for cycHC[10,11,12]

Table S1. HRMS data of oligomers and *(all-R,R)*-cyclohexanohemicucurbituril homologues

Compound	Formula	Calculated m/z $[M+Na]^+$	Experimental m/z $[M+Na]^+$
4-membered oligomer	C32H48N8O5	647.3645	647.3654
6-membered oligomer	C47H72N12O6	923.5590	923.5562
7-membered oligomer	C58H84N14O8	1105.6678	1105.6666
(all-R,R)-cycHC[10]	C80H120N20O10	1534.9389	1543.9409
(all-R,R)-cycHC[11]	C88H132N22O11	1696.0338	1696.0319
(all-R,R)-cycHC[12]	C96H144N24O12	1848.1288	1848.1288

3 UV-measurements

3.1 *(all-R,R)*-cyclohexanohemicucurbit[8]uril

(*all-R,R*)-cycHC[8] with purity of 95 % was used for preparation of stock solution $9.51 \cdot 10^{-5}$ M. Into 2 ml of CH_3CN 20 μl of stock solution was added repeatedly 5 times resulting in solutions with concentrations shown on the Figure S2.

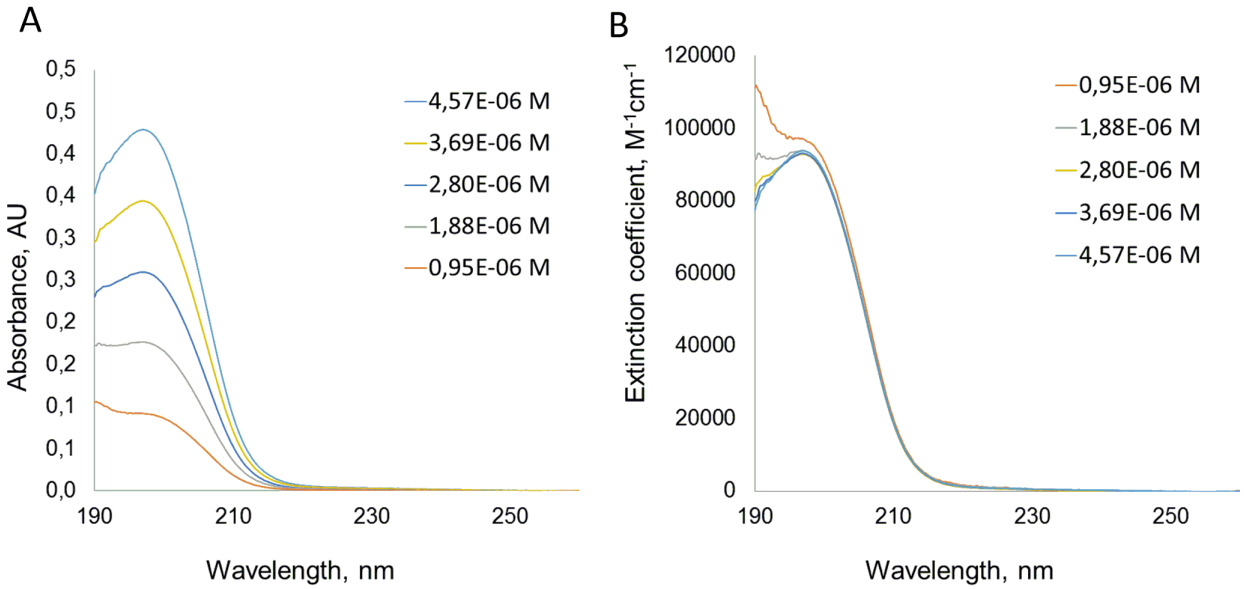

Figure S2. A) UV-spectra and B) molar extinction coefficient of *(all-R,R)*-cycHC[8] in acetonitrile.

3.2 *(all-R,R)*-cyclohexanohemicucurbit[6]uril

(*all-R,R*)-cycHC[6] with purity of 86 % was used for preparation of stock solution $6.95 \cdot 10^{-4}$ M. Into 2 ml of CH_3CN 20 μl of stock solution was added repeatedly 5 times resulting in solutions with concentrations shown on the Figure S3.

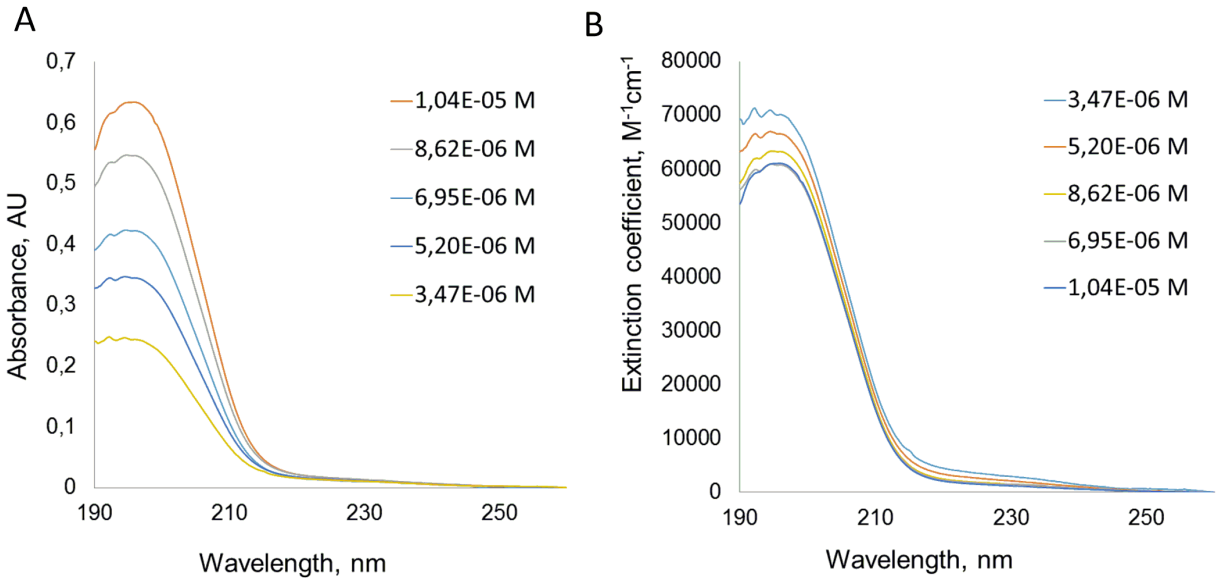

Figure S3. A) UV-spectra and B) molar extinction coefficient of *(all-R,R)*-cycHC[6] in acetonitrile.

3.3 *(all-R,S)*-cyclohexanohemicucurbit[6]uril

(*all-R,S*)-cycHC[6] with purity of 96 % was used for preparation of stock solution $8.90 \cdot 10^{-6}$ M. Into 2 ml of CH_3CN 20 μl of stock solution was added repeatedly 5 times resulting in solutions with concentrations shown on the Figure S4.

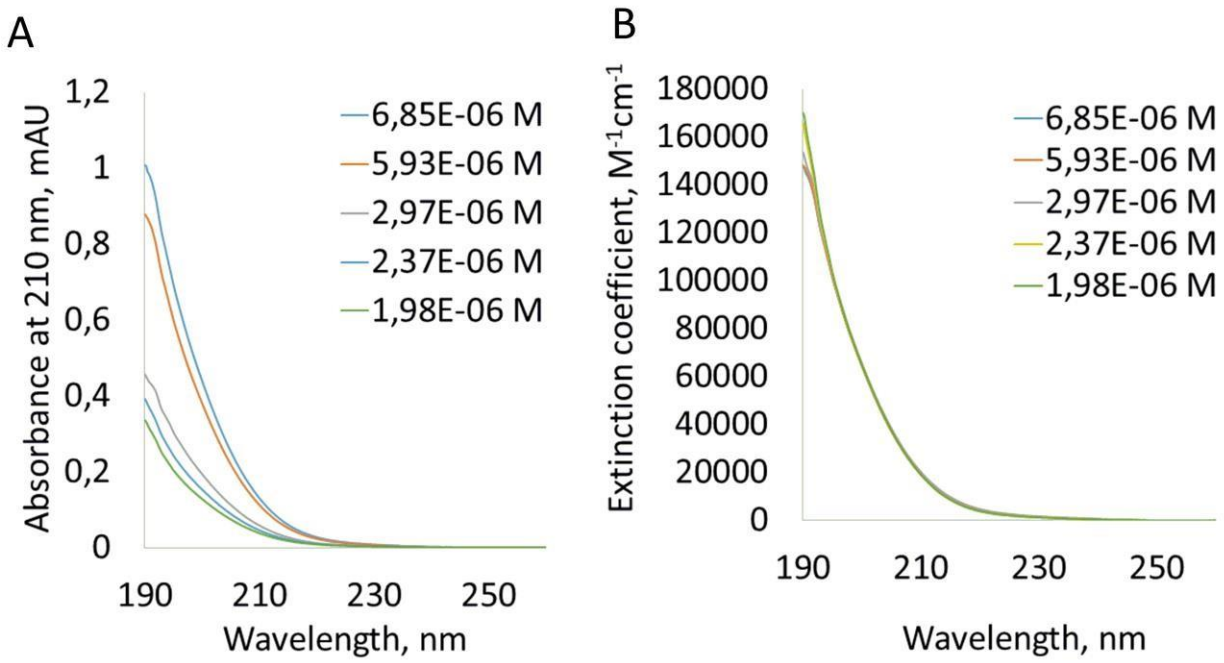

Figure S4. A) UV-spectra and B) molar extinction coefficient of *(all-R,S)*-cycHC[6] in acetonitrile.

3.4 *(R,R)*-cyclohex-1,2-diylurea

Into 2 ml of CH_3CN 20 μl of *(R,R)*-cyclohex-1,2-diylurea stock solution ($6.98*10^{-3}$ M) was added repeatedly 5 times resulting in solutions with concentrations shown on the Figure S5.

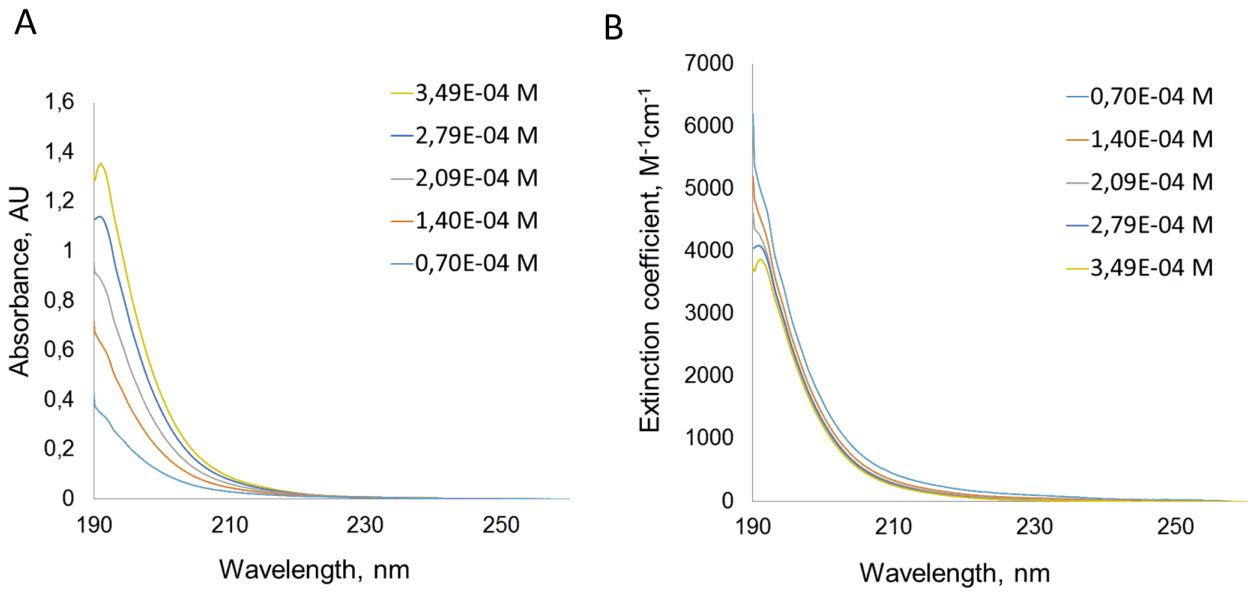

Figure S5. A) UV-spectra and B) molar extinction coefficient of *R,R*-cyclohex-1,2-diylurea in acetonitrile.

3.5 (*R,S*)-cyclohex-1,2-diylurea

Into 2 ml of CH_3CN 20 µl of *(R,S)*-cyclohex-1,2-diylurea stock solution ($7.40*10^{-3}$ M was added repeatedly 5 times resulting in solutions with concentrations shown on the Figure S6.

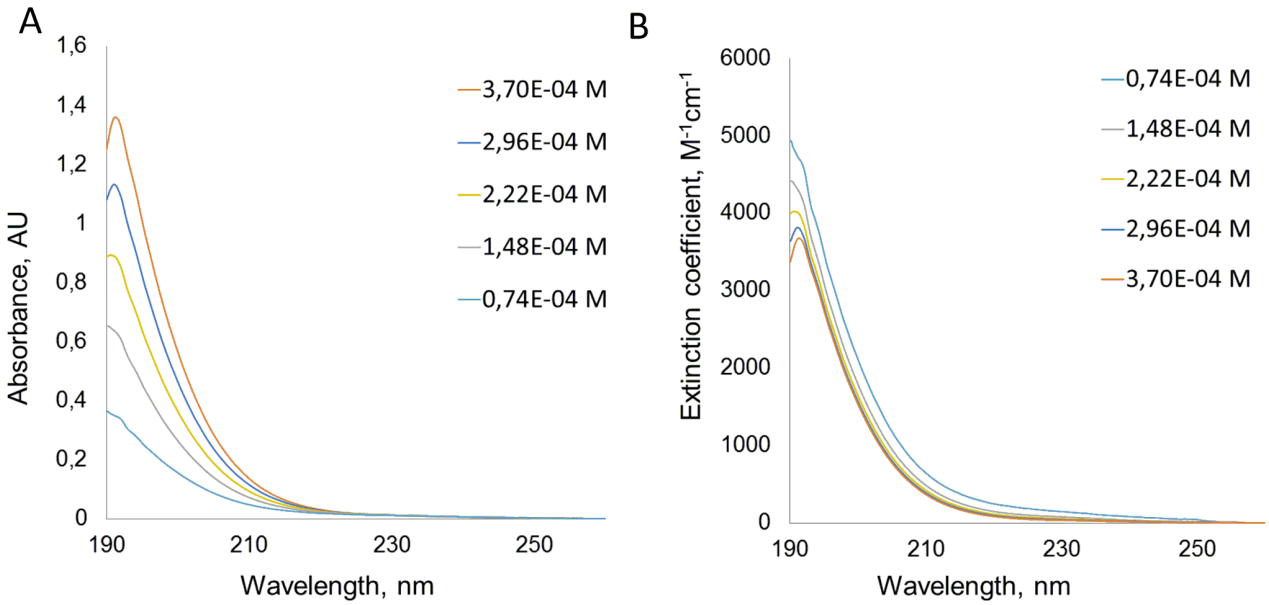

Figure S6. A) UV-spectra and B) molar extinction coefficient of (*R,S*)-cyclohex-1,2-diylurea in acetonitrile.

3.6 4-membered oligomer

Into 2 ml of CH_3CN 10 µl of 4-memebered oligomer stock solution ($1.5*10^{-3}$ M) was added repeatedly 5 times resulting in solutions with concentrations shown on the Figure S7.

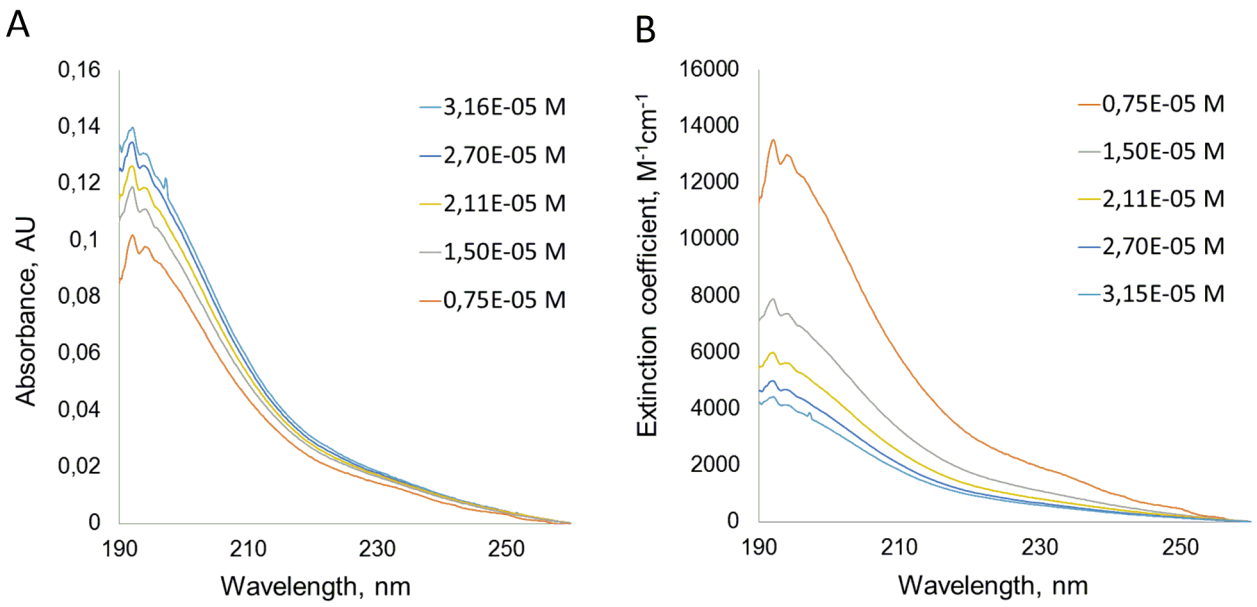

Figure S7. A) UV-spectra and B) molar extinction coefficient of 4-membered oligomer in acetonitrile.

3.7 6-membered oligomer

Into 2 ml of CH_3CN 10 µl of 6-memebered oligomer stock solution ($1.5*10^{-3}$ M) was added repeatedly 5 times resulting in solutions with concentrations shown on the Figure S8.

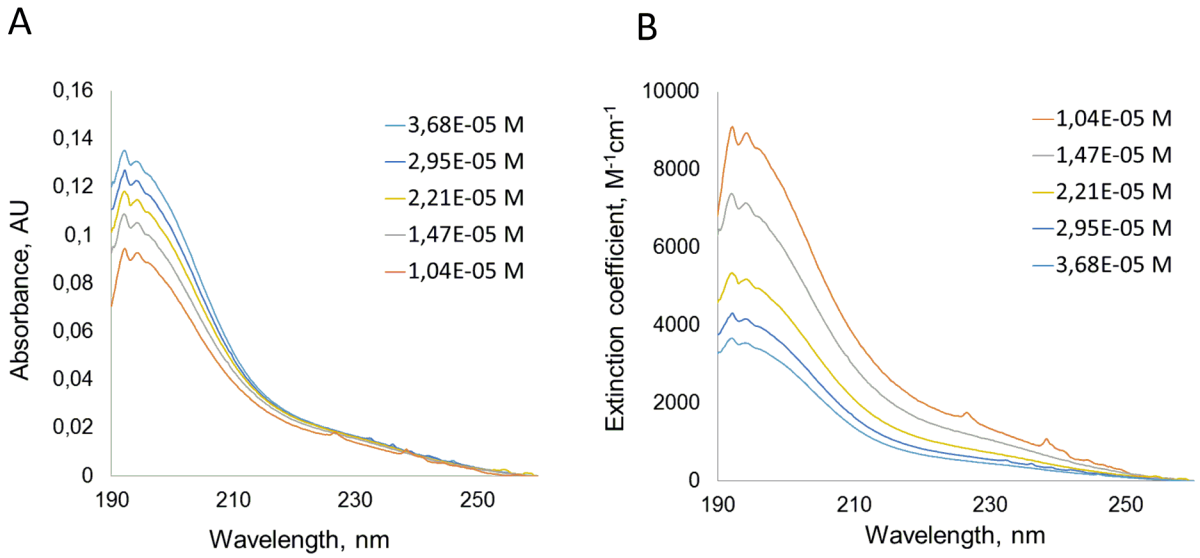

Figure S8. A) UV-spectra and B) molar extinction coefficient of 6-membered oligomer in acetonitrile.

3.8 7-membered oligomer

Into 2 ml of CH_3CN 10 µl of 7-memebered oligomer stock solution ($2.1*10^{-3}$ M) was added repeatedly 5 times resulting in solutions with concentrations shown on the Figure S9.

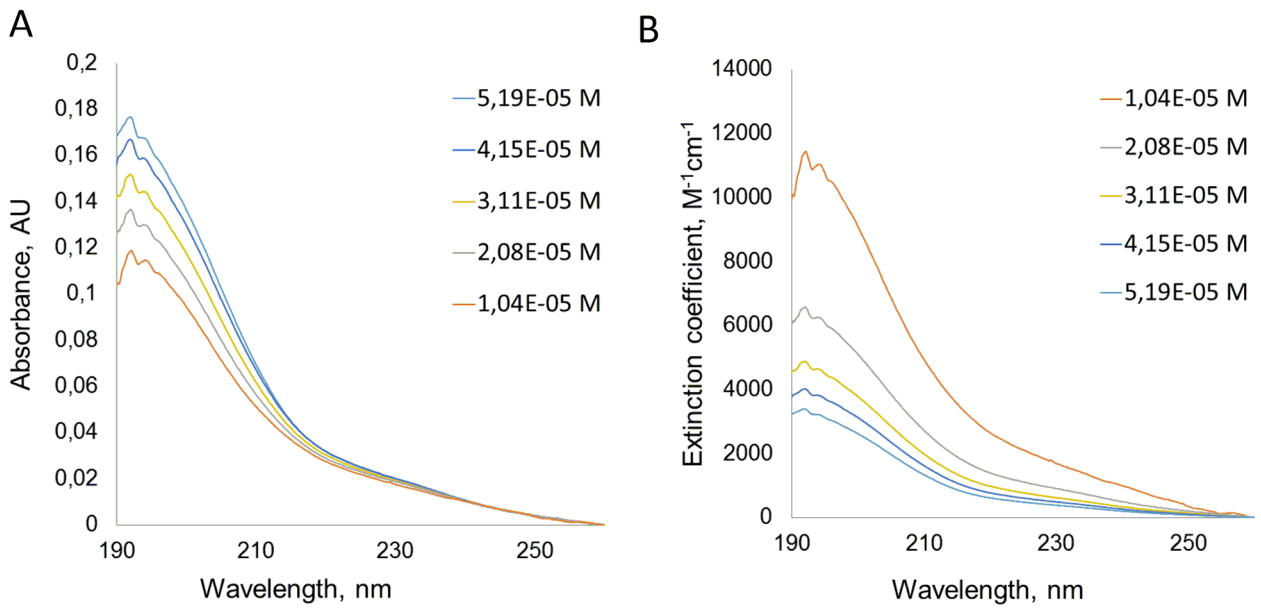

Figure S9. A) UV-spectra and B) molar extinction coefficient of 7-membered oligomer in acetonitrile.

4 HPLC and structures of cyclohex-1,2-diylurea diasteromers modelled by molecular mechanics

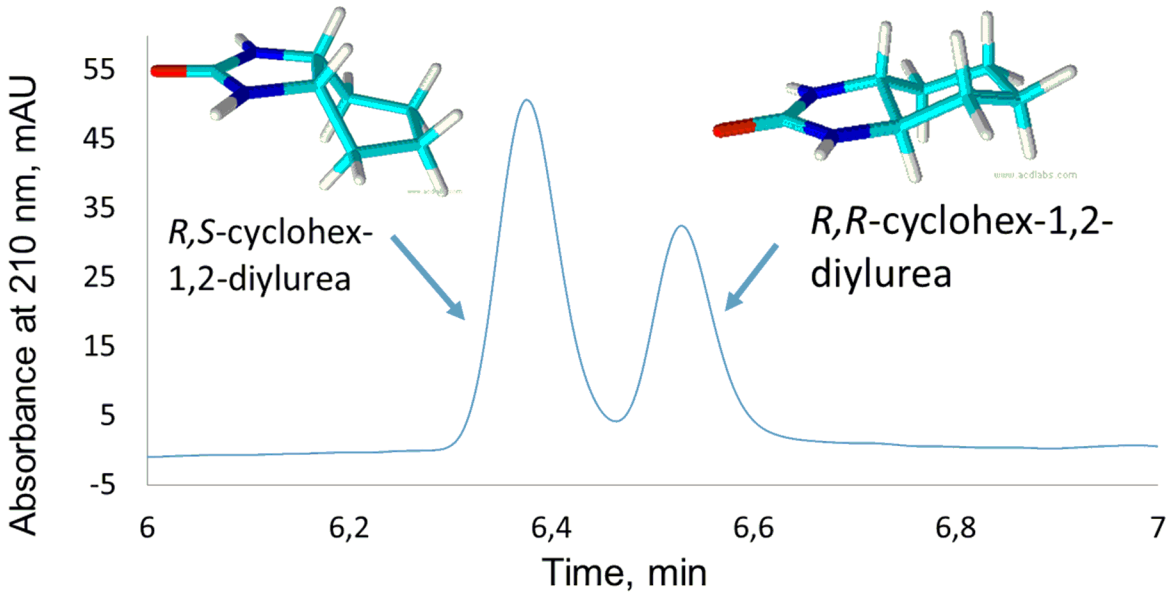

Figure S10. RP-HPLC chromatogram of (*R,S*)- and (*R,R*)-cyclohex-1,2-diylurea (46 and 62 µg/ml, respectively) in chloroform:methanol (1:9).

5 Stability analysis of hemicucurbit[6]uril by HPLC-UV

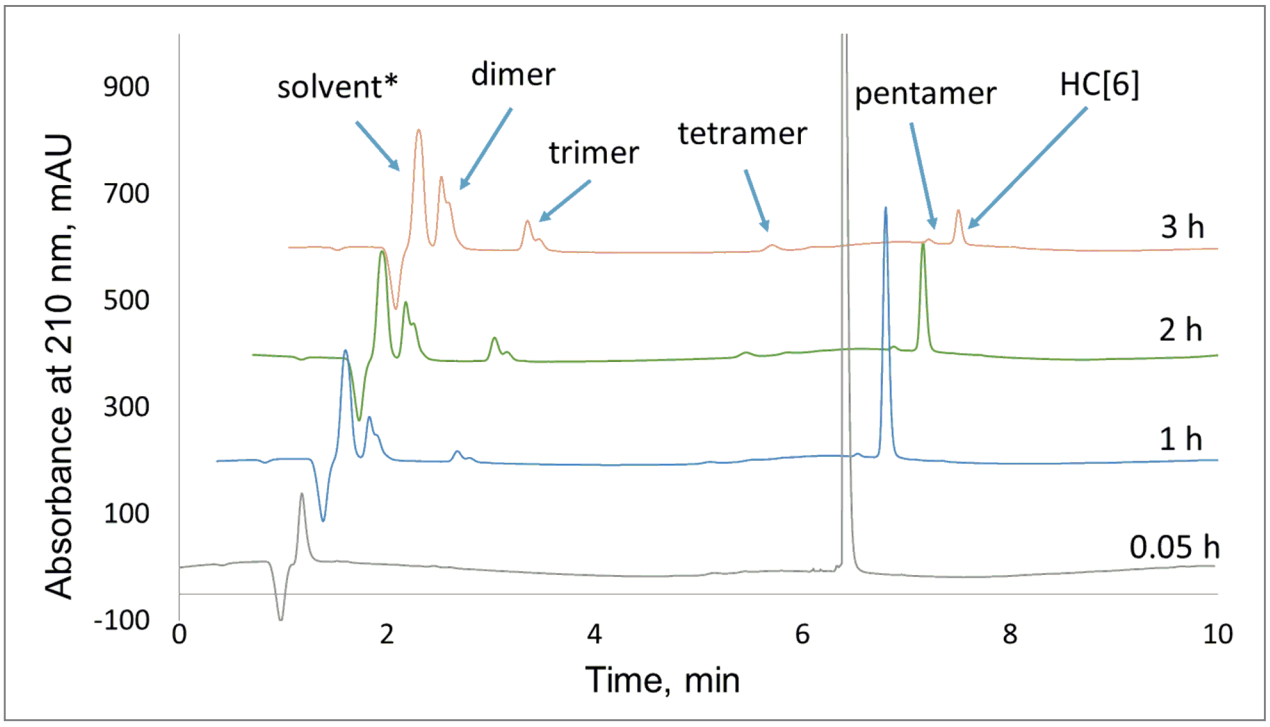

Figure S11. RP-HPLC analysis of degradation of a homogenous solution of HC[6] in 0,1 M HCl at 65 °C. *solvent peak contains hydrochloric acid aqueous and methanol solution.

6 Stability analysis of hemicucurbit[6]uril and hemicucurbit[12]uril by ^{1}H-NMR

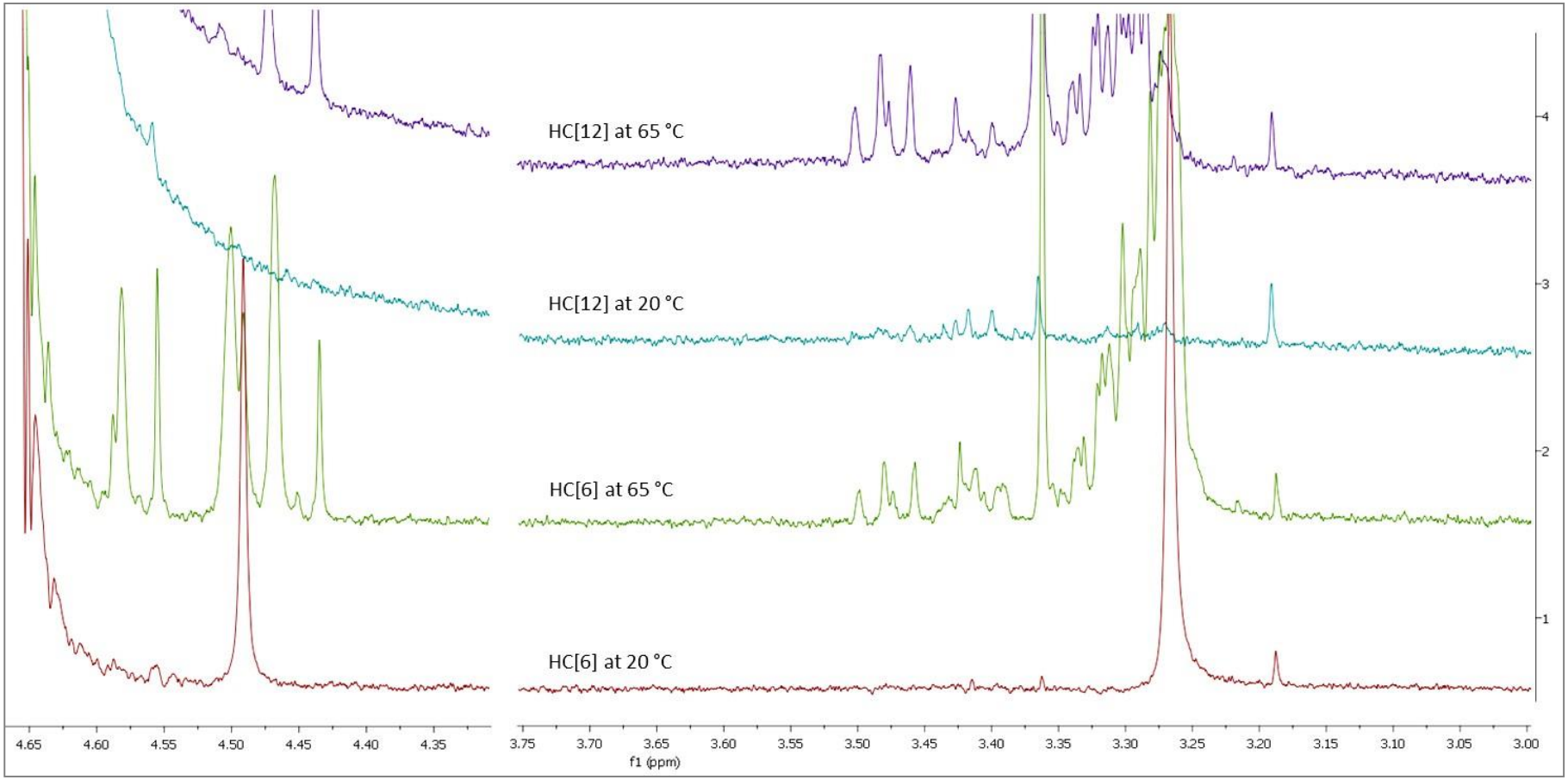

Figure S12. ^{1}H-NMR analysis of saturated solution of unsubstituted hemicucurbiturils in 0.1 M HCl in D_2O at room temperature and at elevated temperature on a Bruker Avance III 400 MHz spectrometer. Experimental conditions: 16 scans for HC[6] and 256 scans for HC[12], 30 degree flip angle, 1 second relaxation delay.