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for

Synthesis of a monofunctional glycoluril clip *via* cyclic imide formation on the convex site

Malgorzata Urbaniak, Mateusz Gosecki, Bartlomiej Gostynski, Monika Gosecka*

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Polymer Division,
ul. Sienkiewicza 112, 90-36 Lodz, Poland
E-mail: mdybko@cbmm.lodz.pl

Materials

Ethanolamine, 98% and organic acids: acetic acid, propionic acid and 2-ethylhexanoic acid were purchased from Sigma-Aldrich Co., Ltd. Deuterated solvents (DMSO-d_6 and $CDCl_3$-d_1) were also purchased from Sigma-Aldrich Co., Ltd and used without any purification.

Table 1. Thermodynamic potentials and equilibrium constant (K_{eq}) calculated for amidation reaction based on theoretical calculations.

Reaction	ΔH^{298}, kcal/mol	ΔG^{298}, kcal/mol	T, K	K_{eq}, M^{-1}
amidation	-8,8	-9,9	298	$2{,}0\cdot10^7$

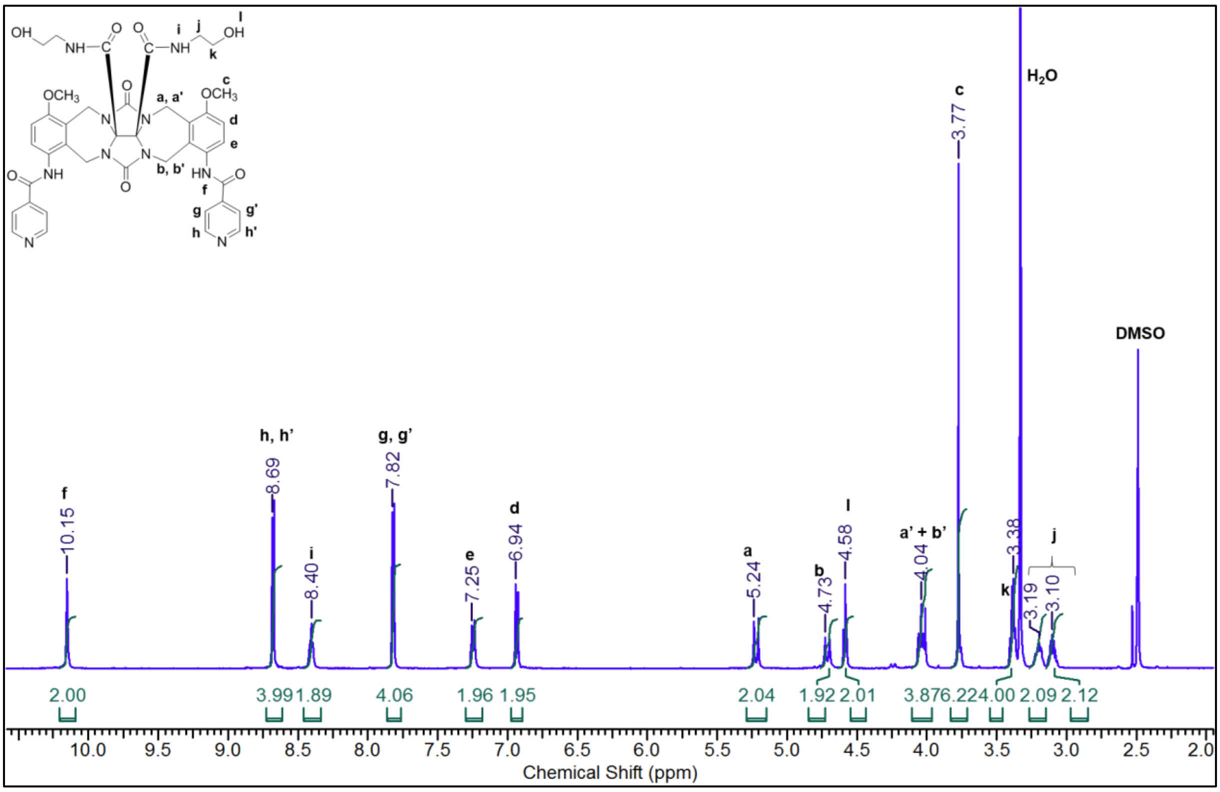


Figure 1. ^1H NMR spectrum of glycoluril clip **2** recorded in DMSO-d_6.

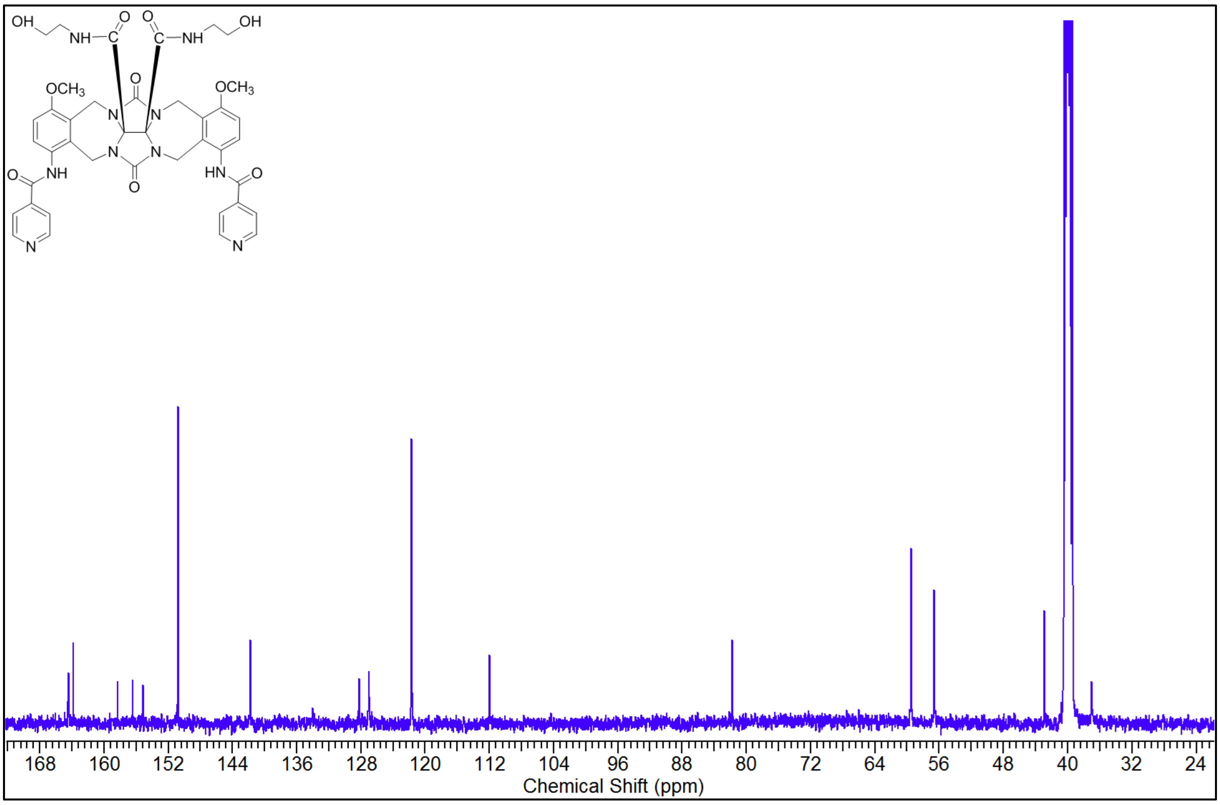


Figure 2. ^{13}C NMR spectrum of glycoluril clip **2** recorded in DMSO-d$_6$.

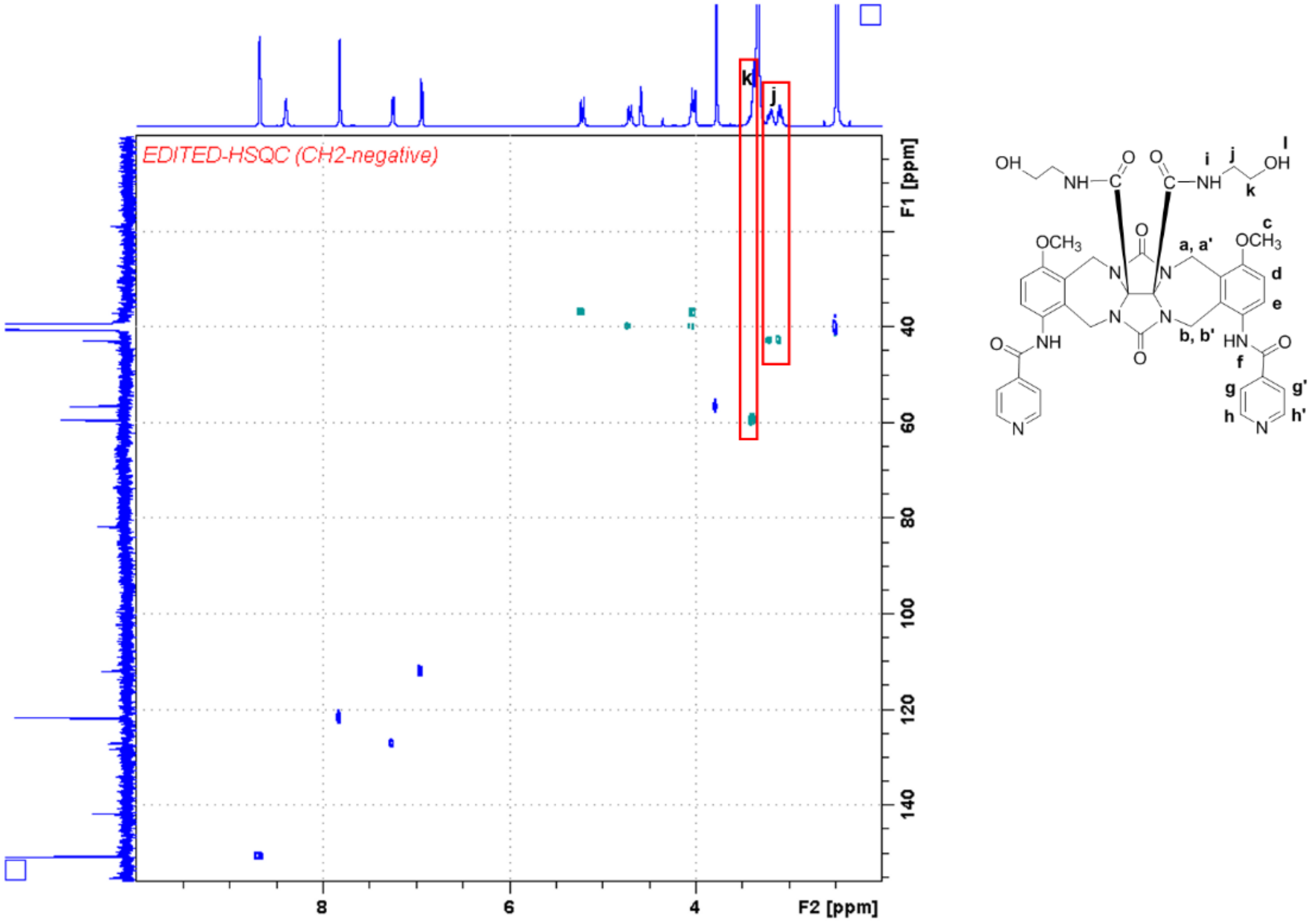


Figure 3. ^{1}H-^{13}C HSQC NMR spectrum of glycoluril clip ***2*** recorded in DMSO at 295 K.

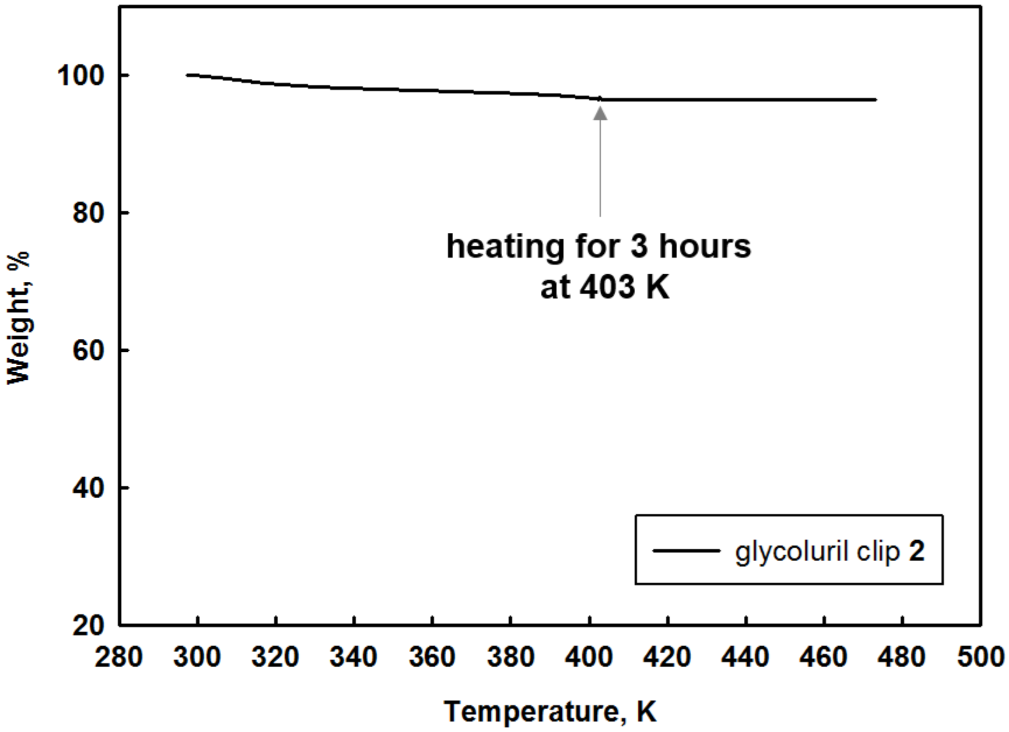


Figure 4. Thermogravimetric analysis of a monohydroxylated clip, ***2***.

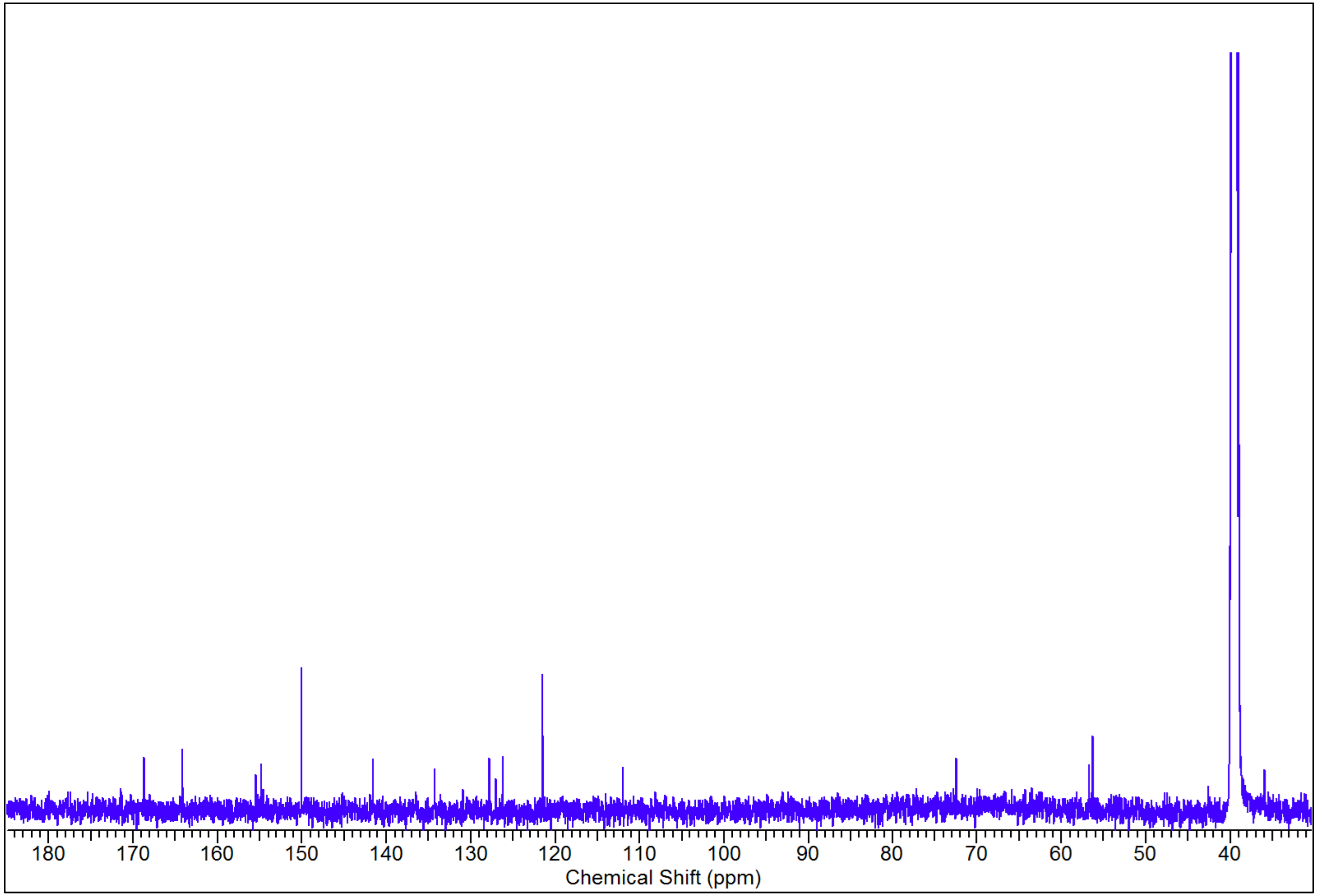


Figure 5. ^{13}C NMR spectrum of ***3*** clip derivative recorded in DMSO-d_6 at 295 K.

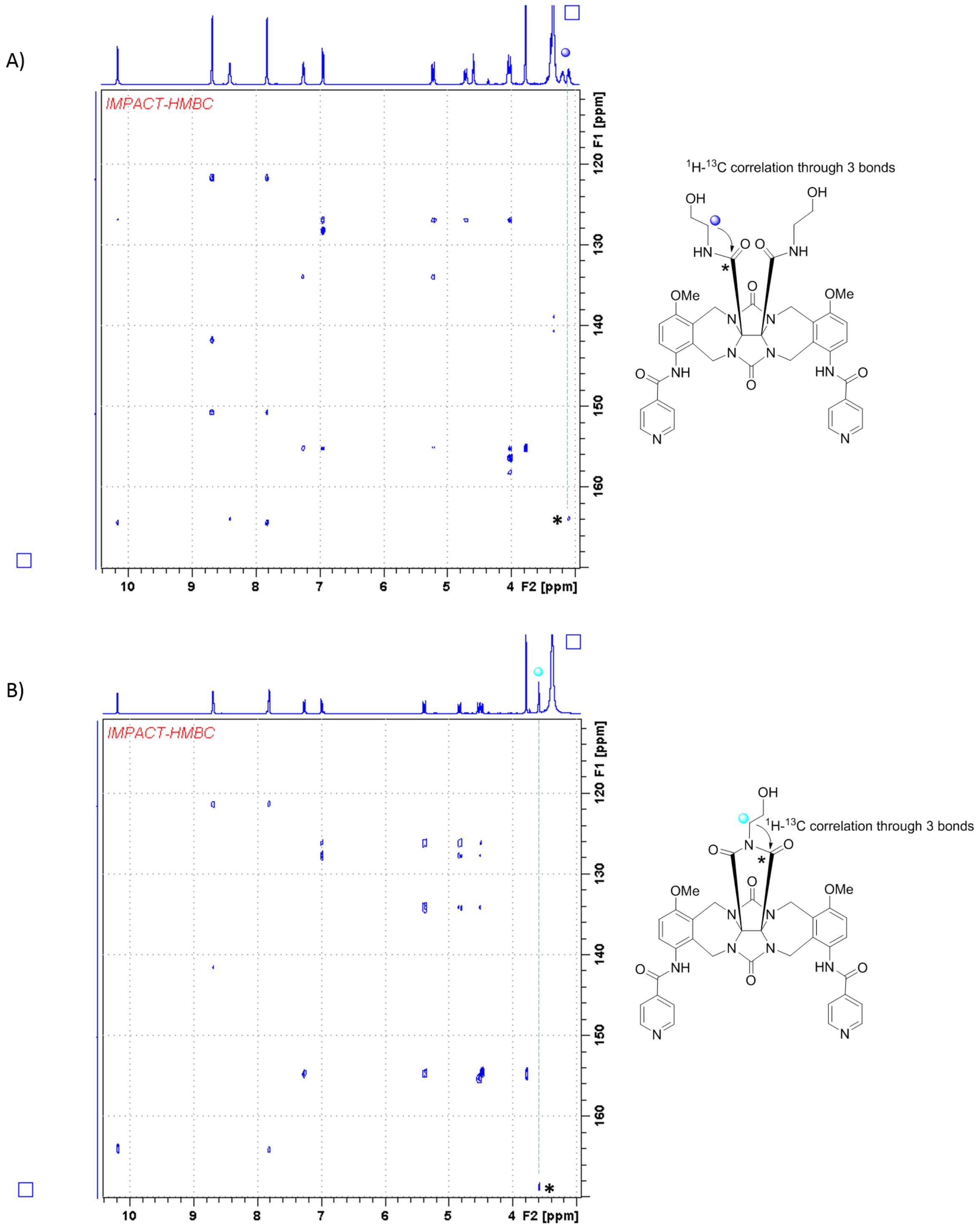
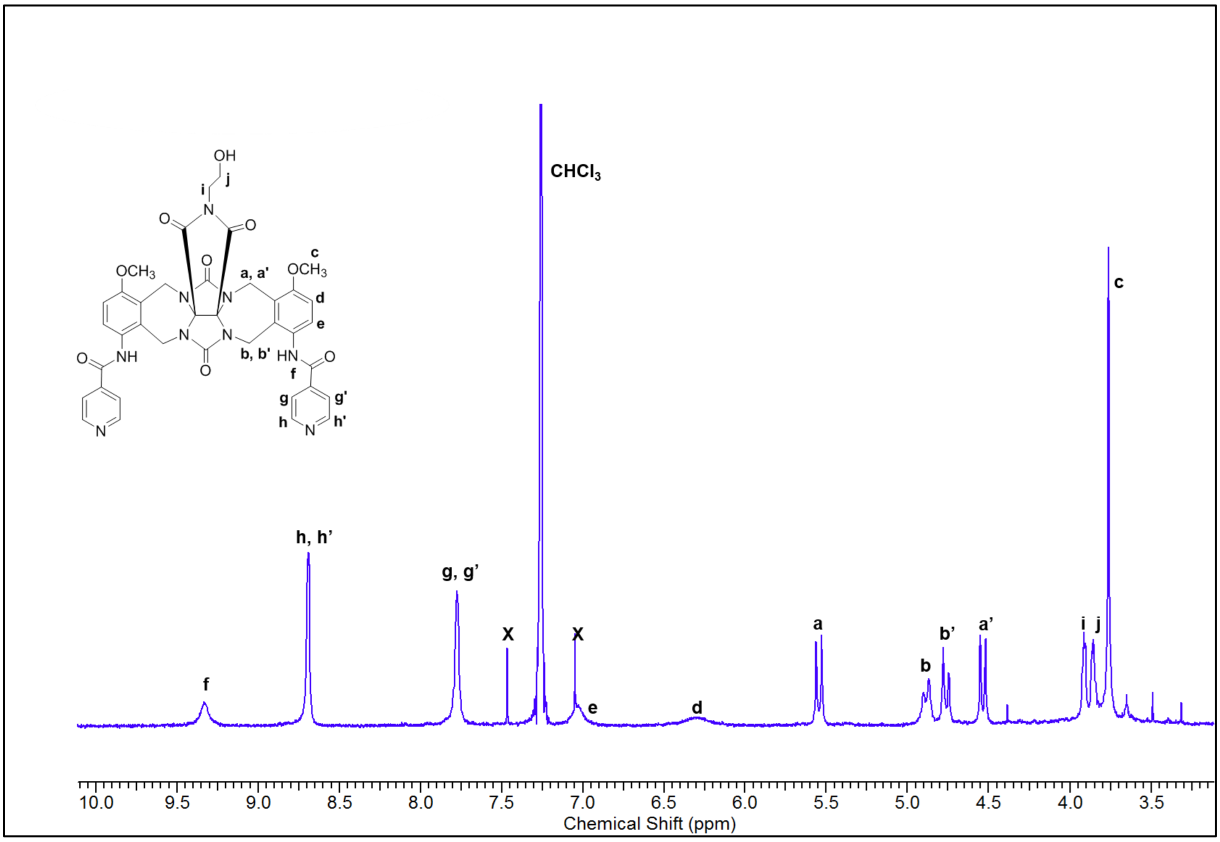
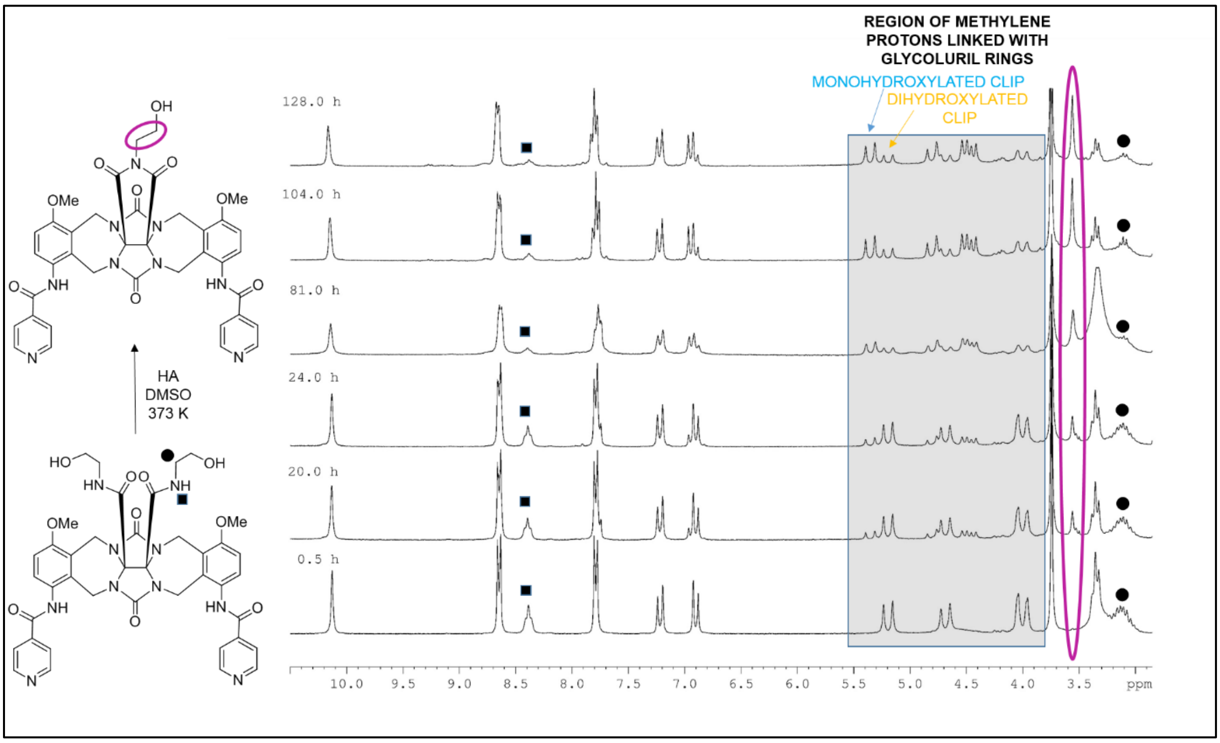


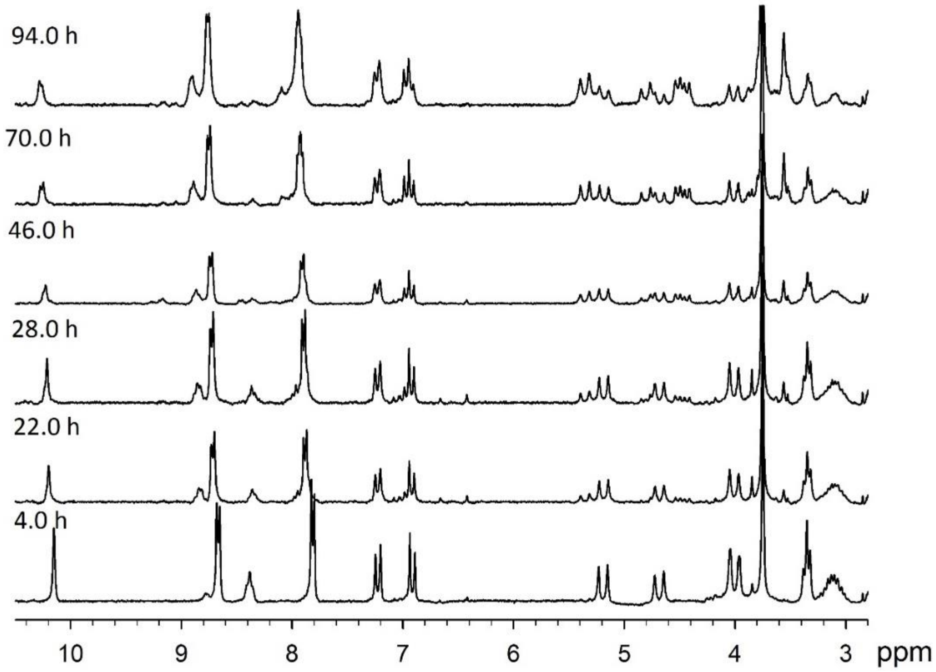
Figure 6. ^{1}H-^{13}C HMBC NMR spectrum of molecular clip derivative ***3*** with monohydroxyl group recorded in DMSO-d$_6$. The ^{1}H-^{13}C coupling *via* three bonds confirms the cyclization on the clip convex. Blue circle corresponds to methylene protons, whereas the asterisk is ascribed to carbonyl carbon atom.



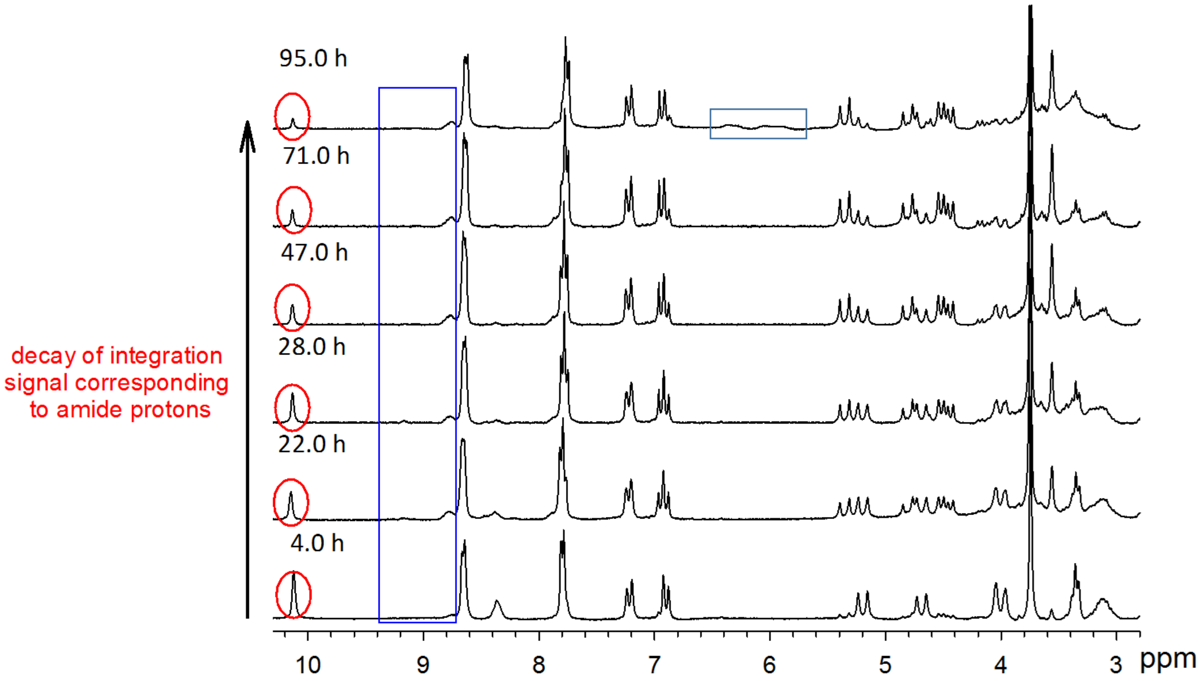
S-Figure 7. ^{1}H NMR spectrum of clip 3 recorded in CDCl3-d$_1$ at 295 K. X = ^{13}CHCl$_3$



S-Figure 8. The kinetics conversion of dihydroxylated glycoluril clip derivative into monohydroxylated glycoluril clip derivative at 373 K conducted in DMSO-d$_6$ in the presence propionic acid. The concentration of substrate was 10 mg/mL. The equimolar ratio of hydroxyl groups *versus* acid was applied.



S-Figure 9. The kinetics of dihydroxylated glycoluril clip derivative conversion into monohydroxylated glycoluril clip derivative at 403 K. The concentration of substrate was 10 mg/mL. The equimolar ratio of hydroxyl groups *vs* acid was applied.



S-Figure 10. The kinetics of dihydroxylated glycoluril clip derivative conversion into monohydroxylated glycoluril clip derivative at 423 K. The concentration of substrate was 10 mg/mL. The equimolar ratio of hydroxyl groups *vs* acid was applied.

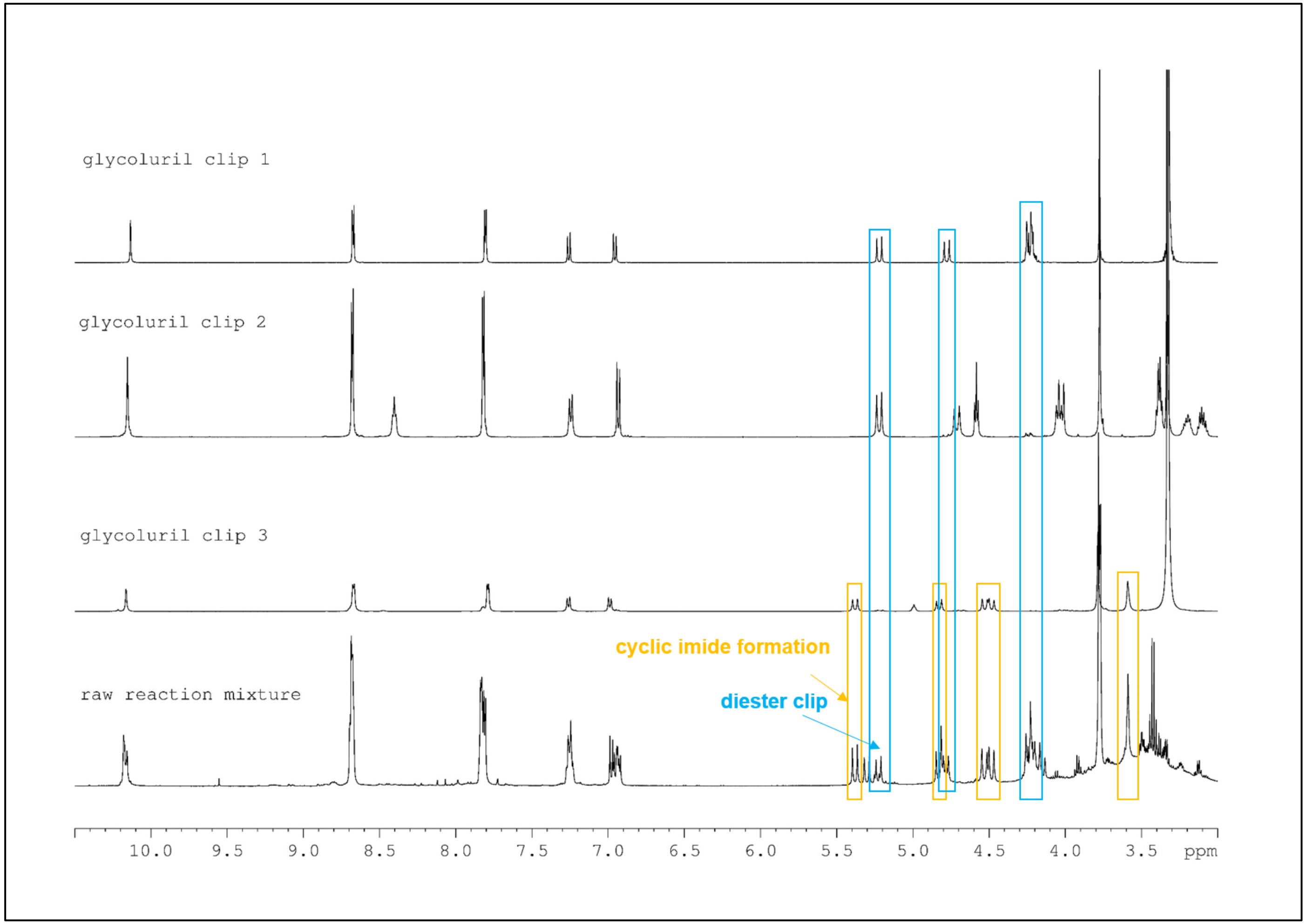
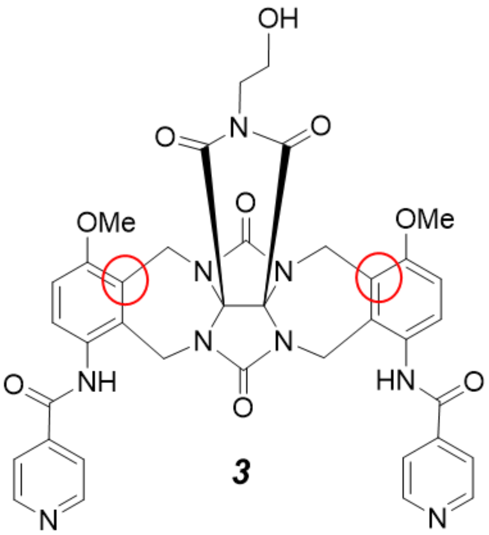
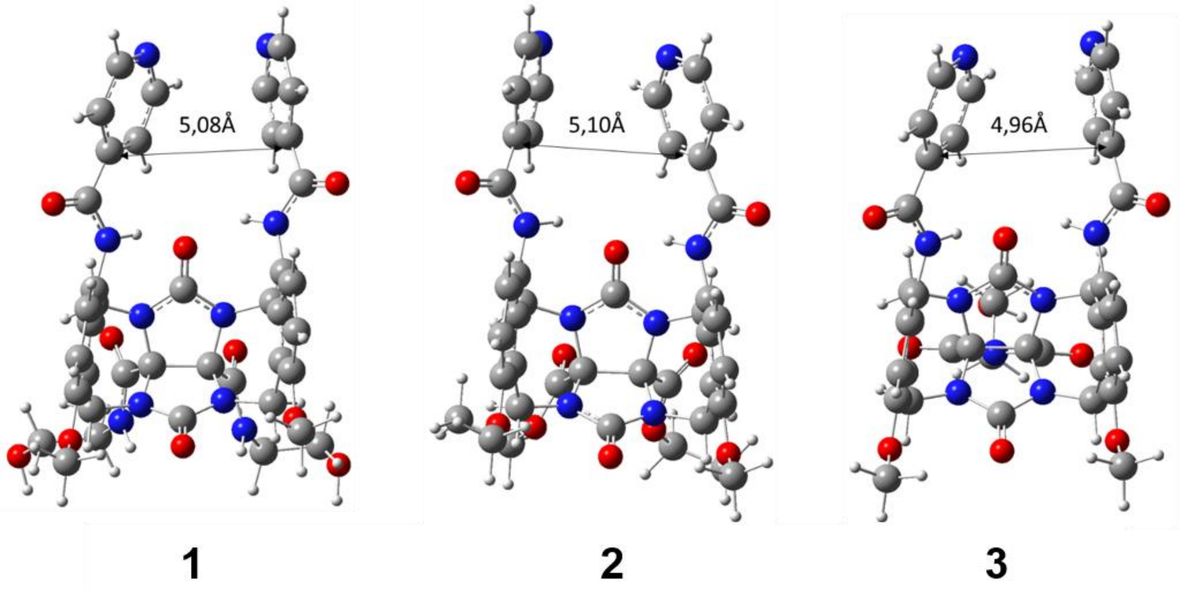


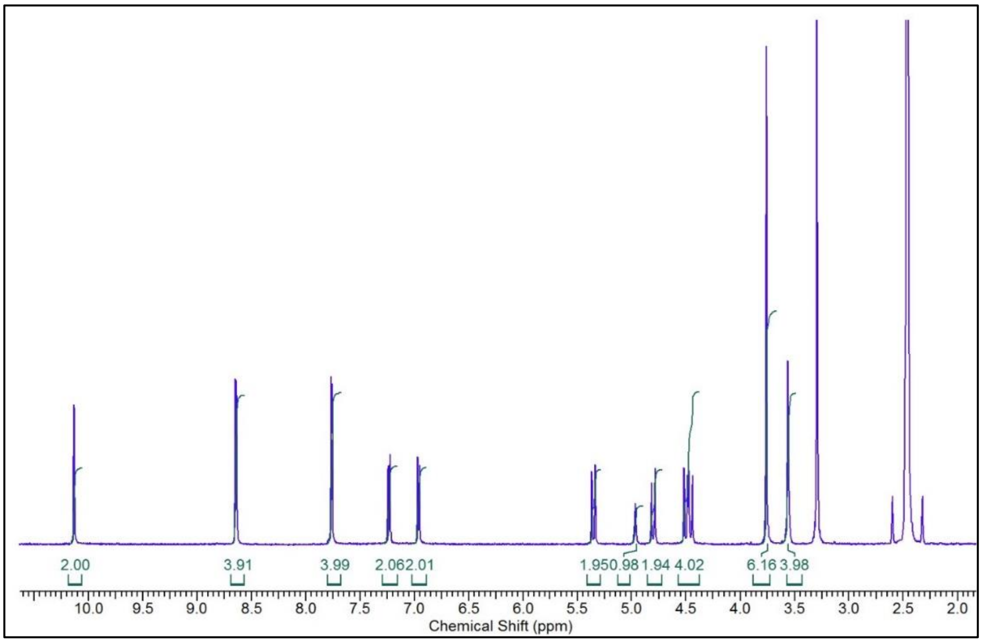
Figure S11. The comparison of ^{1}H NMR spectrum recorded for a direct reaction mixture of diester clip ***1*** into a clip ***3*** bearing a monohydroxyl cyclic imide on the convex site to ^{1}H NMR spectra recorded for pure glycoluril clips ***1***, ***2*** and ***3***.



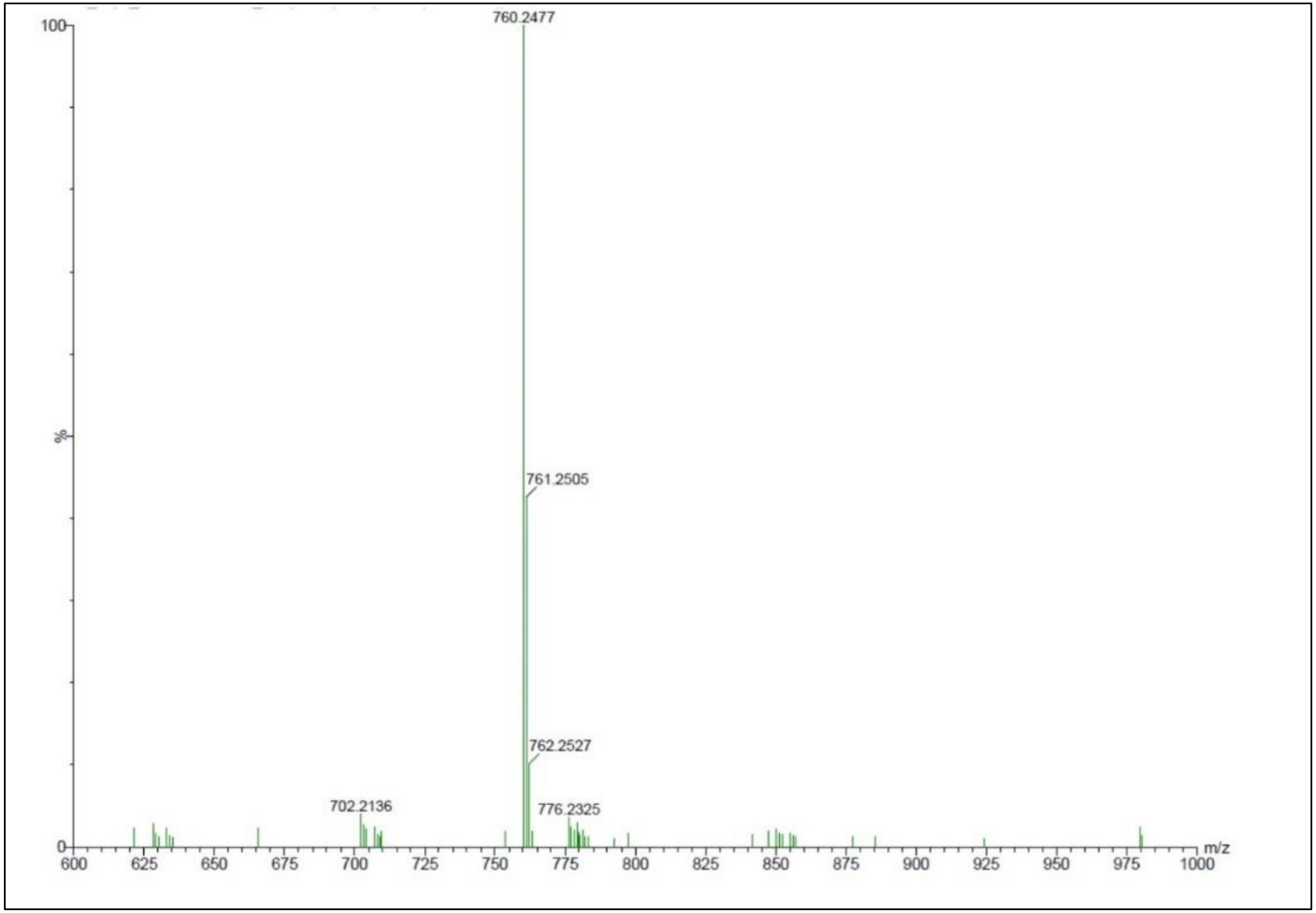
S-Figure 12. Exemplary structure of glycoluril clip monohydroxyl derivative. The cleft diameter of each glycoluril clip derivative was estimated based on the distance between the same type of phenyl carbon atom (assigned in red circles) belonging to the individual clip sidewalls.



S-Figure 13. Structures of glycoluril clips demonstrating the distance between pyridinyl carbon atoms within the clip cavity of molecular clips **1**, **2** and **3**.



S-Figure 14. ^{1}H NMR spectrum of glycoluril clip ***3*** after TGA analysis. The spectrum recorded in DMSO-d_6 (spectrometer 500 MHz).



S-Figure 15. ESI MS spectrum of monohydroxylated derivative of a glycoluril clip ***3*** upon TGA analysis.