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Supporting Information

Synthesis, characterisation, and remarkable biological properties of cyclodextrins bearing guanidinoalkylamino and aminoalkylamino groups on their primary side.

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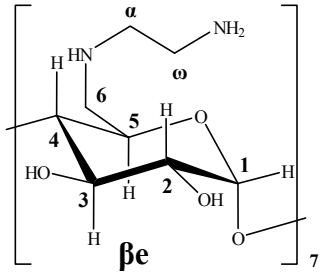
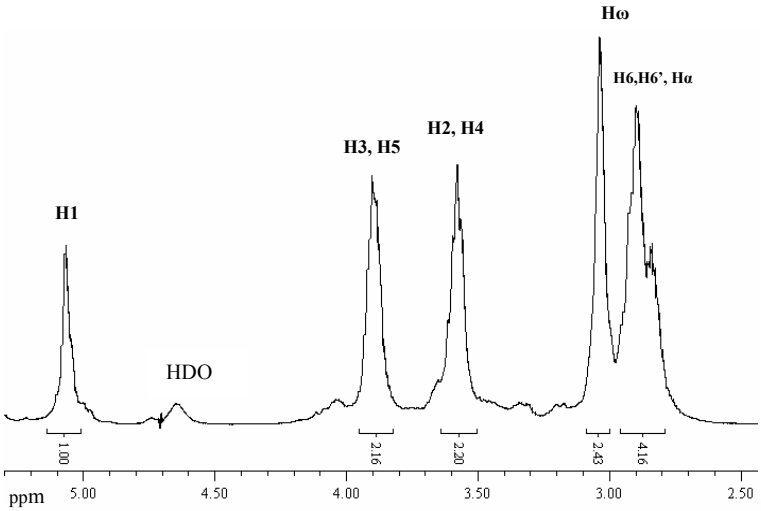
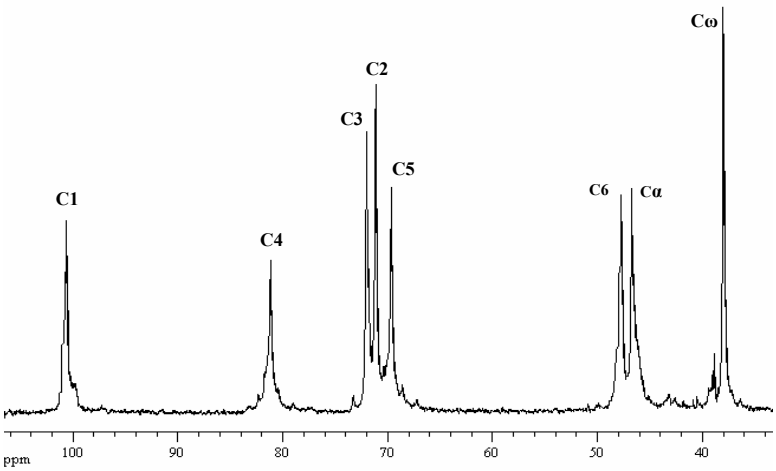
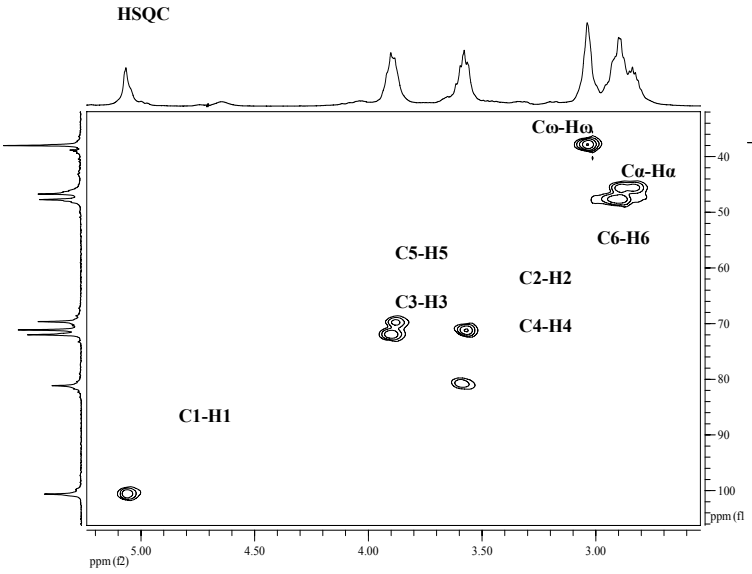


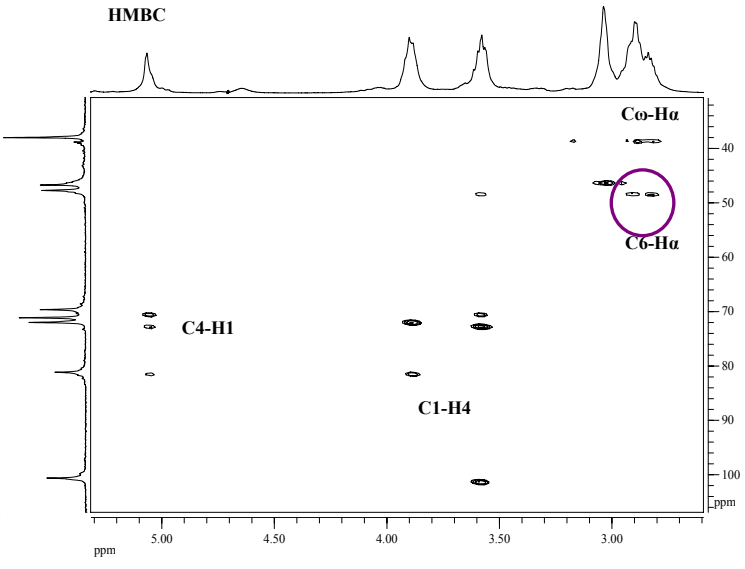
^{1}H NMR



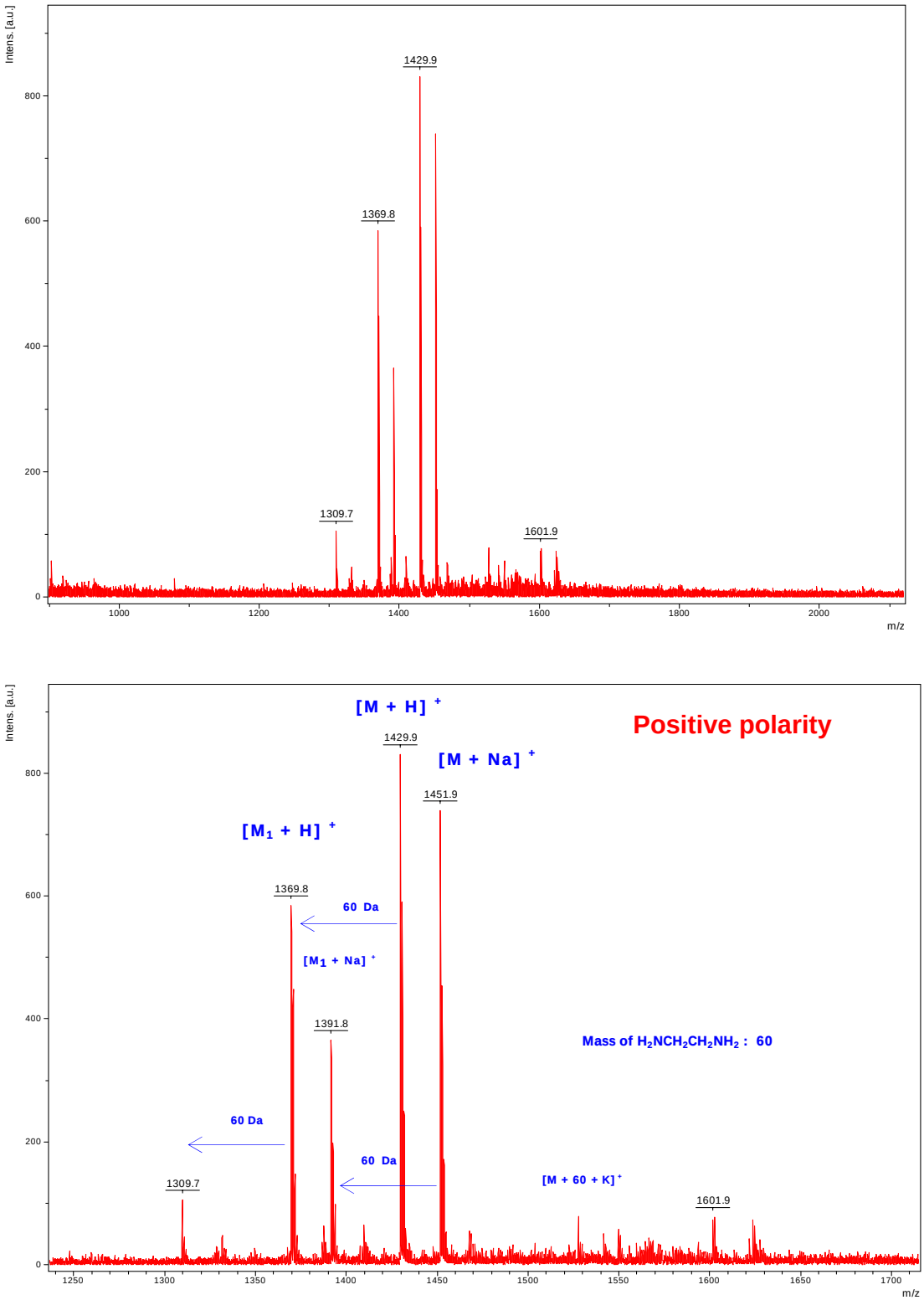
^{13}C NMR



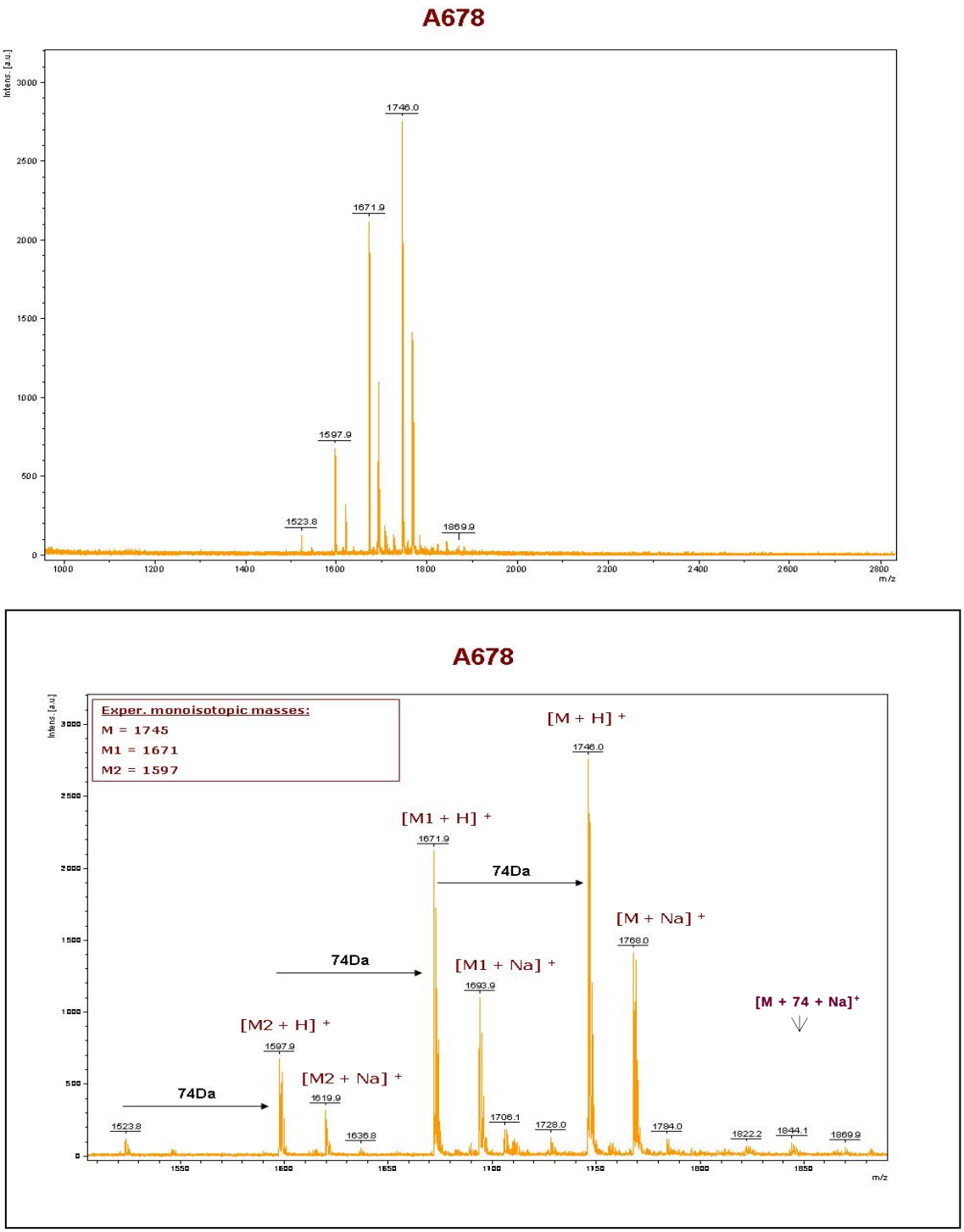




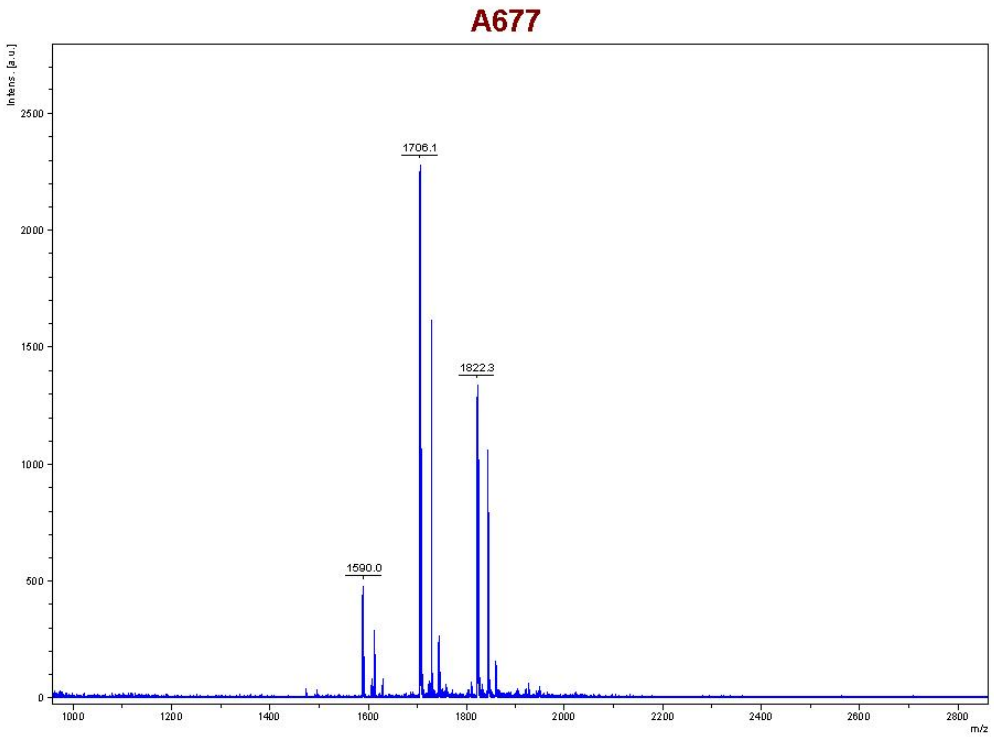
S1. ^{1}H, ^{13}C, HSQC and HMBC NMR spectra of **βe** with characteristic assignments.

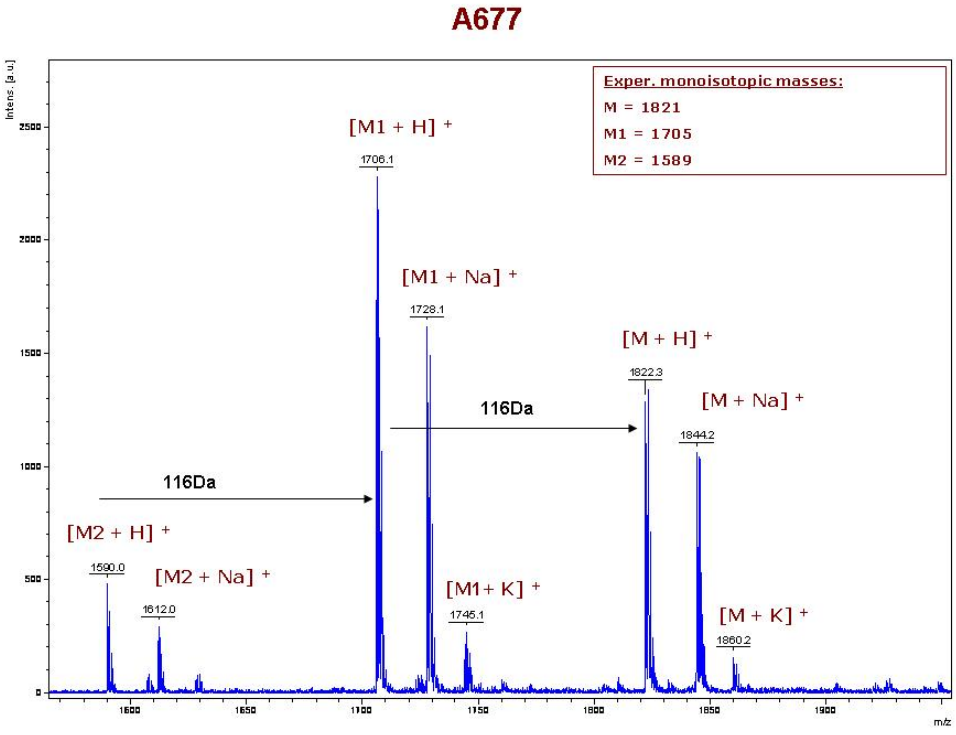


S2. Full (*top*) and expanded (*bottom*) MALDI-TOF Autoflex (Bruker Daltonics) spectrum of **βe** ($C_{56}H_{112}N_{14}O_{28}$). Theoretical monoisotopic mass = 1428.78**.** Matrix solution: 10 mg/ml of 2,5-dihydroxy benzoic acid in EtOH 80%. The spectrum shows a signal at *m/z* 1429.9 attributable to the protonated molecular ion of **βe** and a signal at *m/z* 1369.8 due to the loss of the $NH_2CH_2CH_2NH_2$ (*m/e* 60) group.

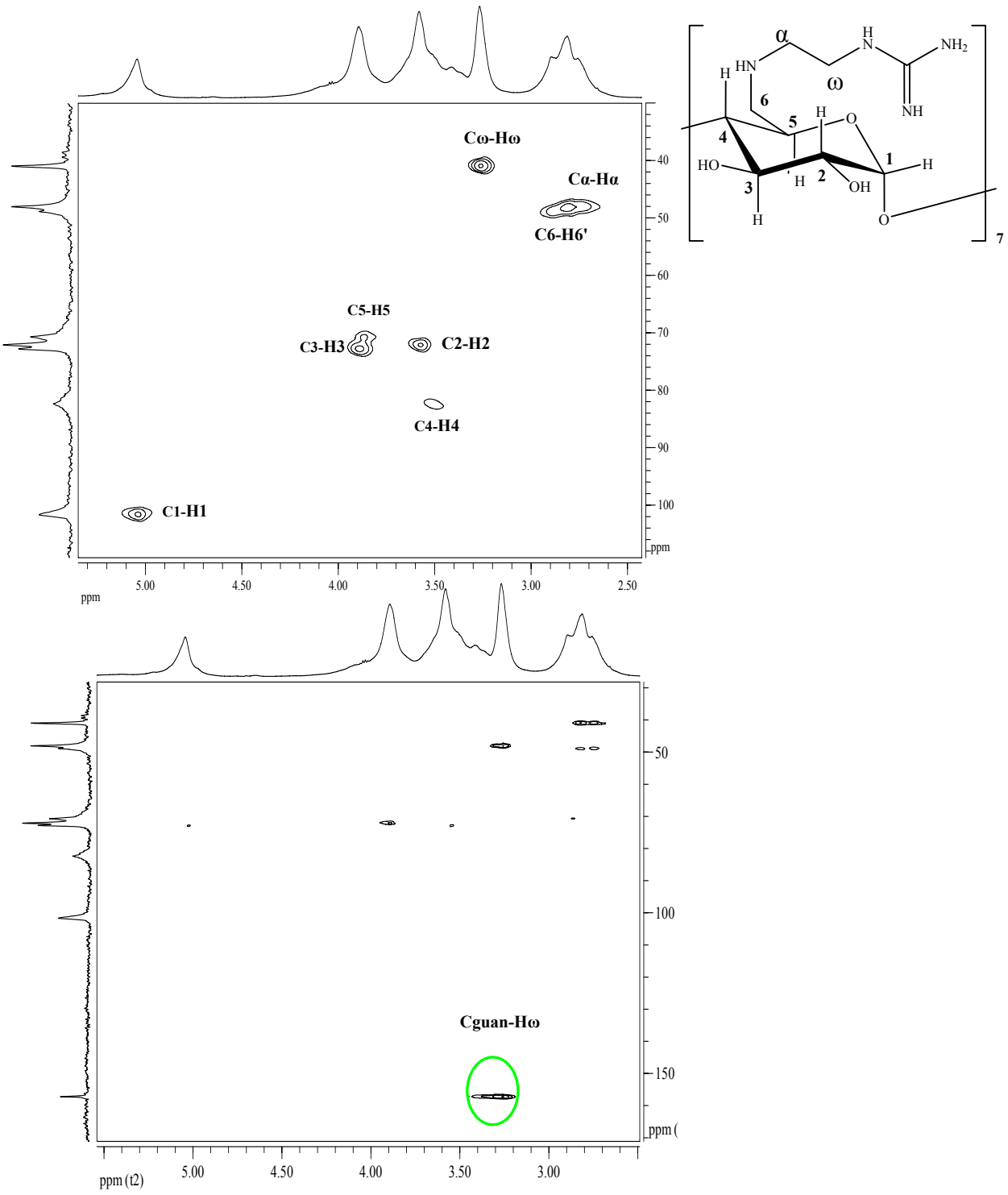


S3. Full (*top*) and expanded (*bottom*) MALDI-TOF Autoflex (Bruker Daltonics) spectrum of **γp** ($C_{72}H_{144}N_{16}O_{32}$). Theoretical monoisotopic mass = 1745.0. Matrix solution: 10 mg/ml of 2,5-dihydroxy benzoic acid in EtOH 80%. The spectrum shows a signal at *m/z* 1746 attributable to the protonated molecular ion of **γp** and signals at *m/z* 1671.9, 1597.9 and 1523.8 due to sequential loss of the $NH_2CH_2CH_2$ CH_2NH_2 (*m/e* 74) group.

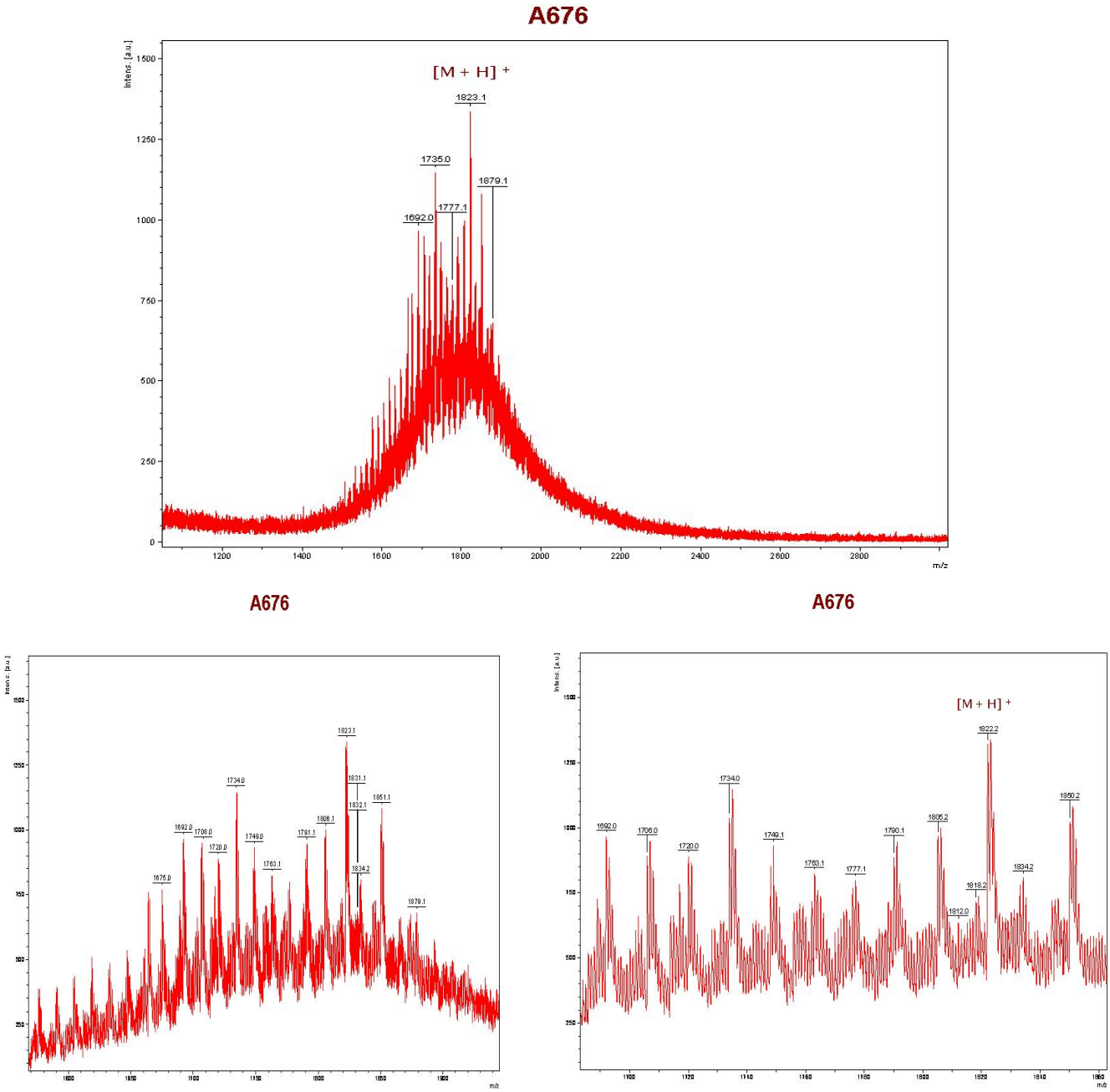




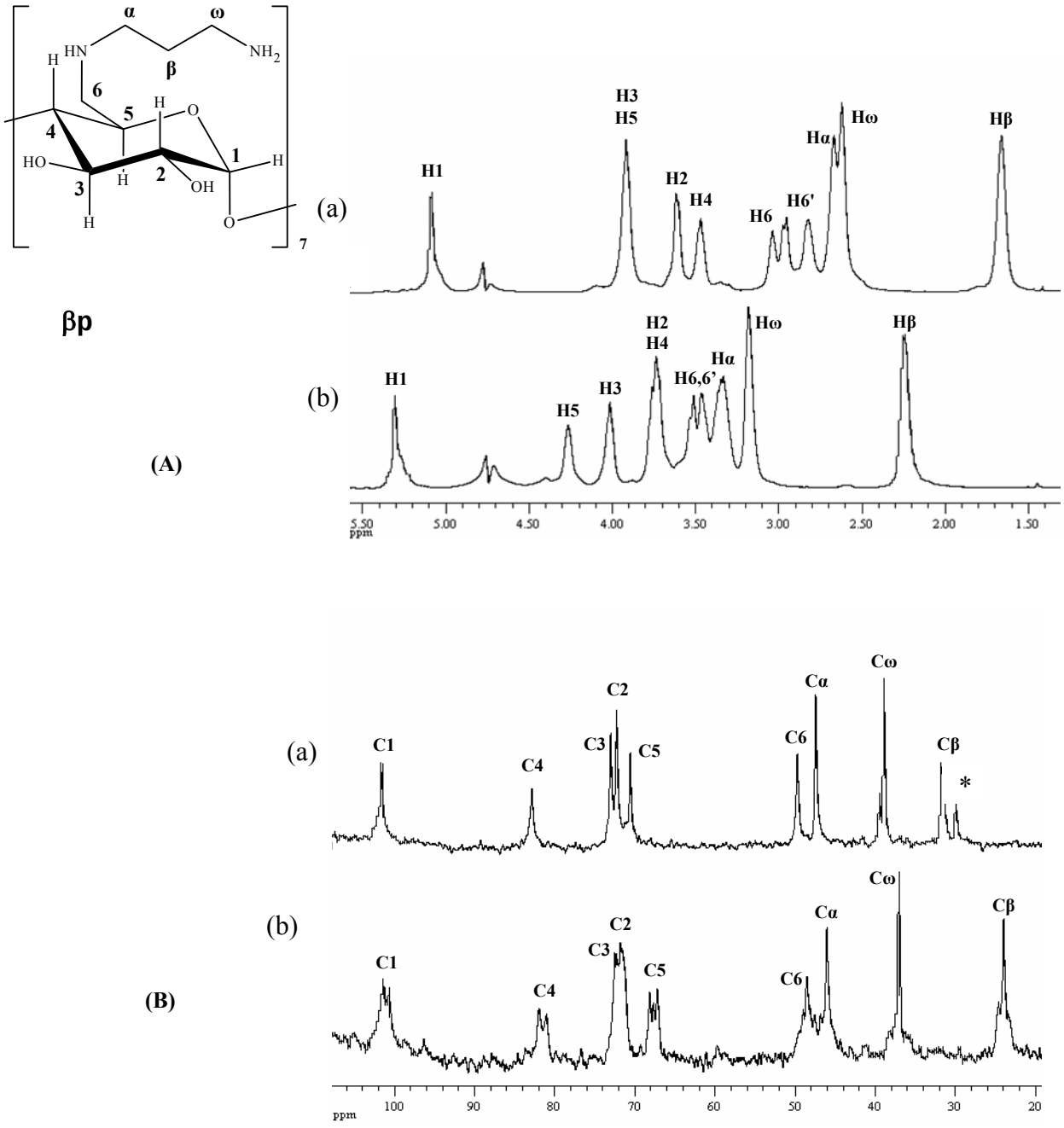
S4. Full (*top*) and expanded (*bottom*) MALDI-TOF Autoflex (Bruker Daltonics) spectrum of **βh** ($C_{84}H_{168}N_{14}O_{28}$). Theoretical monoisotopic mass = 1821.21. Matrix solution: 10 mg/ml of 2,5-dihydroxy benzoic acid in EtOH 80%. The spectrum shows a signal at *m/z* 1822.3 attributable to the protonated molecular ion and signals at *m/z* 1706.1, and 1590.0 due to sequential loss of the $NH_2CH_2(CH_2)_4CH_2NH_2$ (*m/e* 116) group.



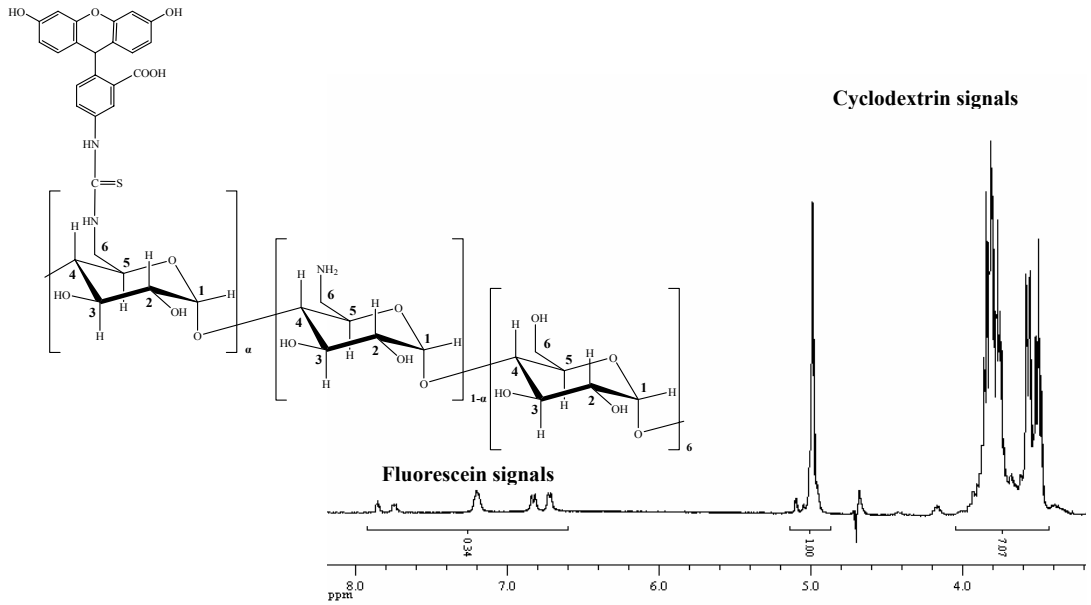
S5. 2D HSQC (top) and HMBC (bottom) NMR spectra of compound **βeg** (500 MHz, D_2O, 25°C).



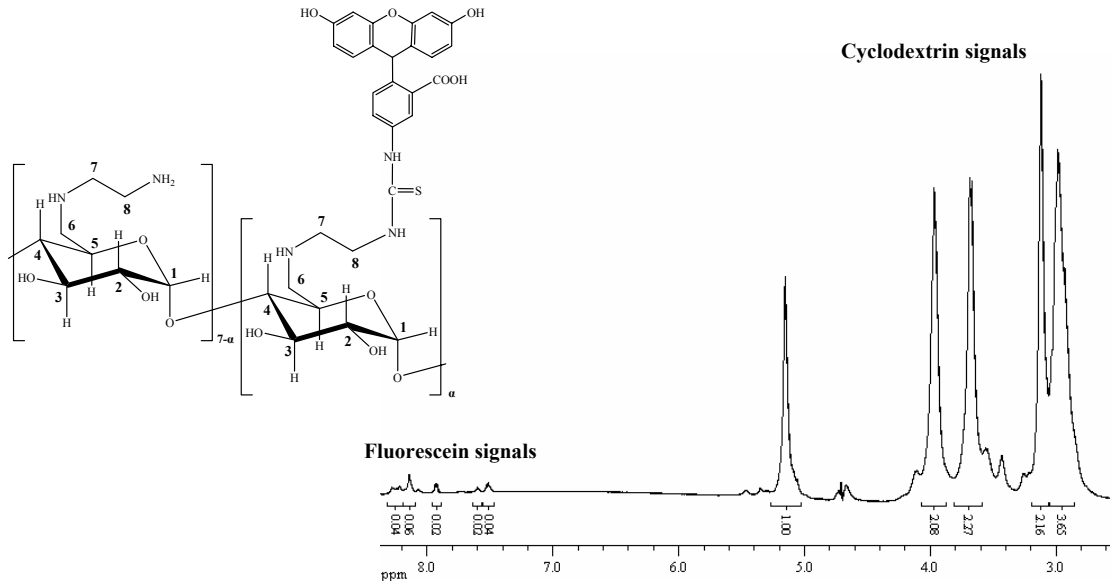
S6. MALDI-TOF Autoflex (Bruker Daltonics) spectrum of **βpg** ($C_{70}H_{140}N_{28}O_{28}$). Theoretical monoisotopic mass = 1821.04. Matrix solution: 10 mg of 2,5-dihydroxy benzoic acid/ml EtOH 80%. The spectrum shows a signal at *m/z* 1822 attributable to the protonated molecular ion of **βpg** and a signal at *m/z* 1763.1 due to loss of a $NH_2CH(NH)NH_2$ group (*m/e* 59).



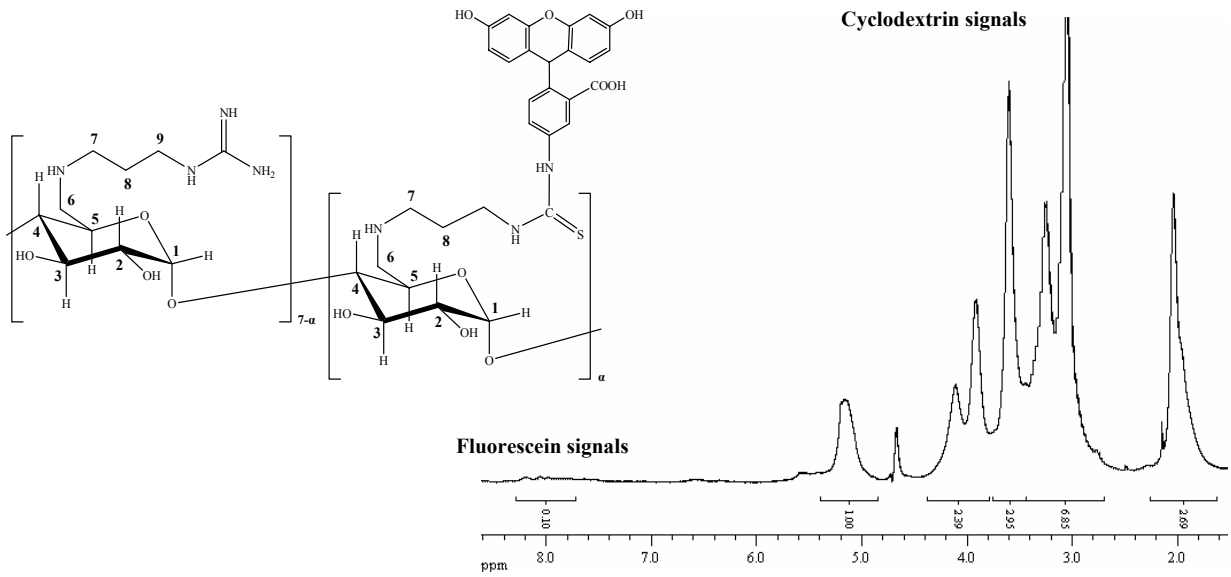
S7. (A) ^{1}H NMR, 500 MHz and (B) ^{13}C NMR 125 MHz spectrum of **βp** at pH (a) 1.2 and (b) 11.5 (D_2O, 25°C).
* free propylene diamine



S8. ^{1}H NMR spectrum (500 MHz) of fluorescein labelled *mono*(6-amino-6-deoxy)-β-cyclodextrin in D_2O, 25°C.



S9. ^{1}H NMR spectrum (500 MHz) of fluorescein labelled **βe** in D_2O, 25°C.



S10. ^{1}H NMR spectrum (500 MHz) of fluorescein labelled **βpg** in D_2O, 25°C.

(a) (b) (c)

S11. Fluorescent microscope images of HeLa cells incubated for 1h with (a) a mixture of βCD/fluorescein (200 μM/10 μM), (b) Fluorescein isothiocyanate (FITC, 20 μM) with the incubation medium and (c) fluorescein-labelled *mono*(6-amino-6-deoxy)-β-cyclodextrin (100 μM). No green fluorescence detected, thus no cell penetration has taken place.