A Prototype Calix[4]arene-based Receptor for Carbohydrate Recognition Containing Peptide and Phosphate Binding Groups

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Experimental section

General Methods: All moisture sensitive reactions were carried out under nitrogen atmosphere. Dry solvents were prepared according to standard procedures and stored over molecular sieves. Melting points are uncorrected and were determined in under nitrogen sealed capillaries with an Electrothermal apparatus. ^1H and ^{13}C NMR spectra were recorded at 300 and 400 MHz and 75 MHz, respectively, at 300 K unless otherwise specified (partially deuterated solvents were used as internal standard). The reported J values are referred to H,H coupling constants, unless other specifications. Mass spectra were registered in ESI and CI (CH_4) mode. Elemental analyses are reported as percentage. TLC, sheets and flash chromatography were performed on silica gel Carbohydrates **14a-c** were synthesised as described in literature.^[19] CDCl_3 used for ^1H NMR titration experiments was freshly dried over neutral aluminium oxide.

For reasons of clarity and in order to reduce space, the name calix[4]arene was used instead of the original IUPAC name: pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecane.

NMR titration experiments: ^1H NMR titration experiments with monosaccharides **13a-e** were performed by addition of a 8.8×10^{-3} M solution of the guest to a 1.0×10^{-3} M solution of the host, going from a 2:1 to a 1:9 host/guest ratio. On the contrary, with carbohydrates **14a-c**, a 1.0×10^{-4} M solution of the guest was titrated with a solution mixture of host (1.0×10^{-3} M) and guest (1.0×10^{-4} M) in order to keep constant the concentration of these carbohydrates which experience self-association at concentrations above 10^{-4} M.

Figure S1. ^1H NMR of compound **4a** in CDCl_3 (300 MHz, 300K)

Figure S2. ^1H NMR of compound **4b** in CDCl_3 (300 MHz, 300K)

Figure S3. ^1H NMR of compound **8** in CDCl_3 (300 MHz, 300K)

Figure S4. ¹H NMR in CDCl₃ (300 MHz, 300K) of compound **10a**

Figure S5. ^1H NMR in CDCl_3 (300 MHz, 300K) of compound **10b**

Figure S6. ^1H NMR (300 MHz, 300K) in a) CDCl_3 and b) $\text{DMSO}-d_6$ of compound **11a**

Figure S7. ^1H NMR in $\text{DMSO}-d_6$ (300 MHz, 300K) of compound **11b**

Figure S8.
COSY NMR in CDCl_3 of compound **10a**
(300 MHz, 300K).

Figure S9.

COSY NMR in DMSO- d_6
of compound **11a** (300 MHz, 300K).

Figure S10.

COSY NMR in CDCl_3
of receptor **12** (300 MHz, 300K)

Figure S11. a) ¹H NMR in CDCl₃ (400 MHz, 300K) of free receptor **12**.

b) ¹H NMR in CDCl₃ (400 MHz, 300K) of the mixture **12a**:octyl-β-glucopyranoside 1:5.

Figure S12. NOESY NMR in CDCl_3 of receptor **12** (300 MHz, 300K)

Figure S13. NOESY of the
1:1 complex between
receptor **12** and
 β -octylglucoside **13a**