Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting informations

Diastereoselective recognition of α-mannoside by hemicryptophane receptors

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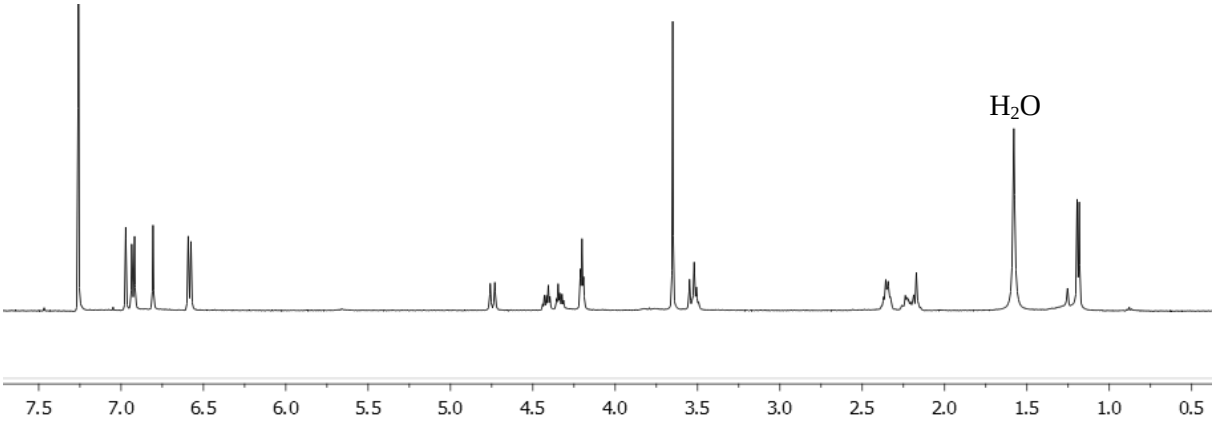
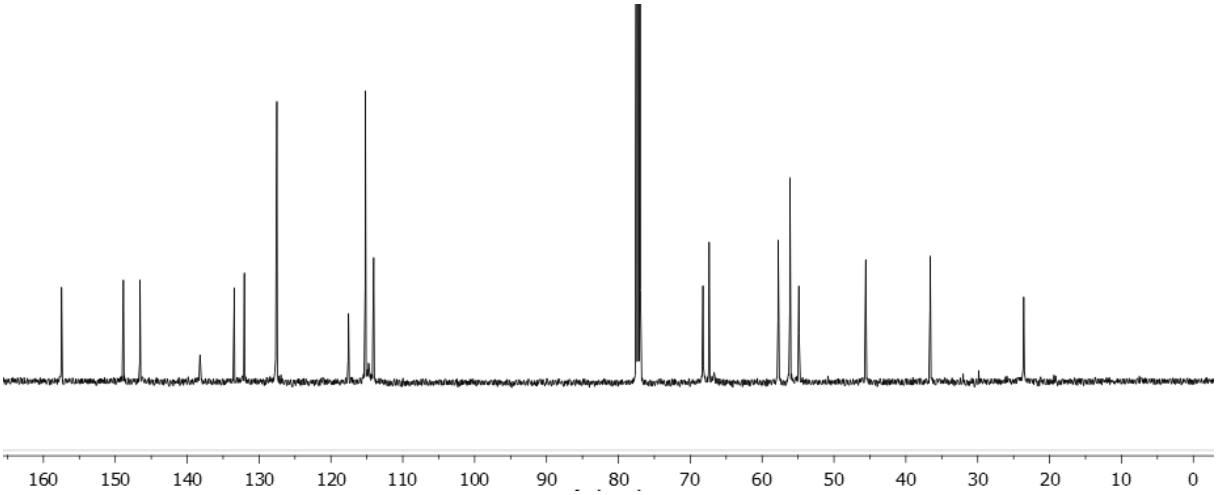
A) NMR spectra

1) *M-SSS*-**3**

^{1}H NMR ($CDCl_3$, 298 K, 500.10 MHz):

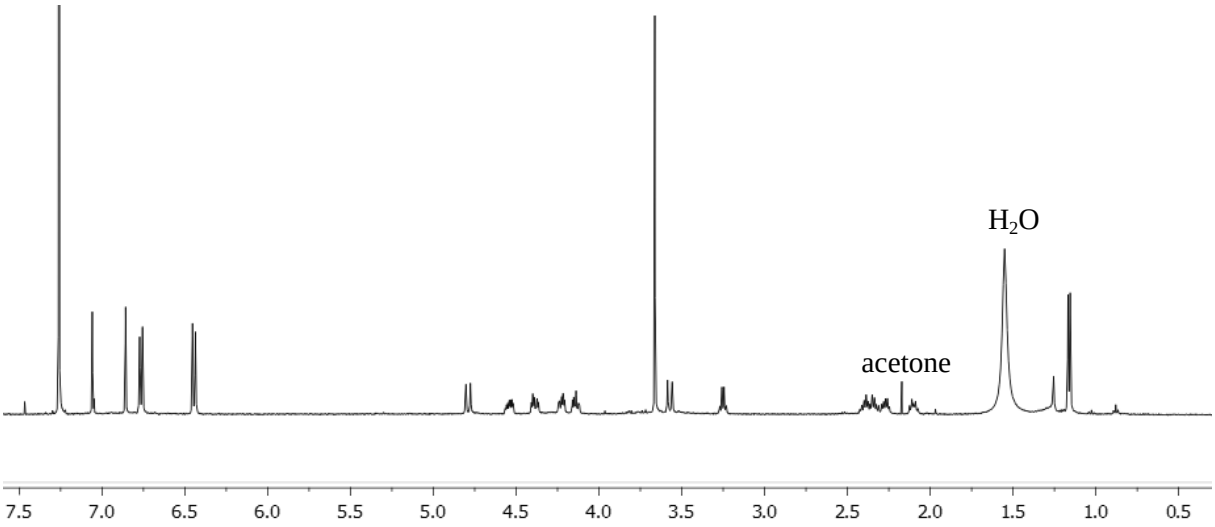


^{13}C NMR ($CDCl_3$, 298 K, 125.76 MHz):

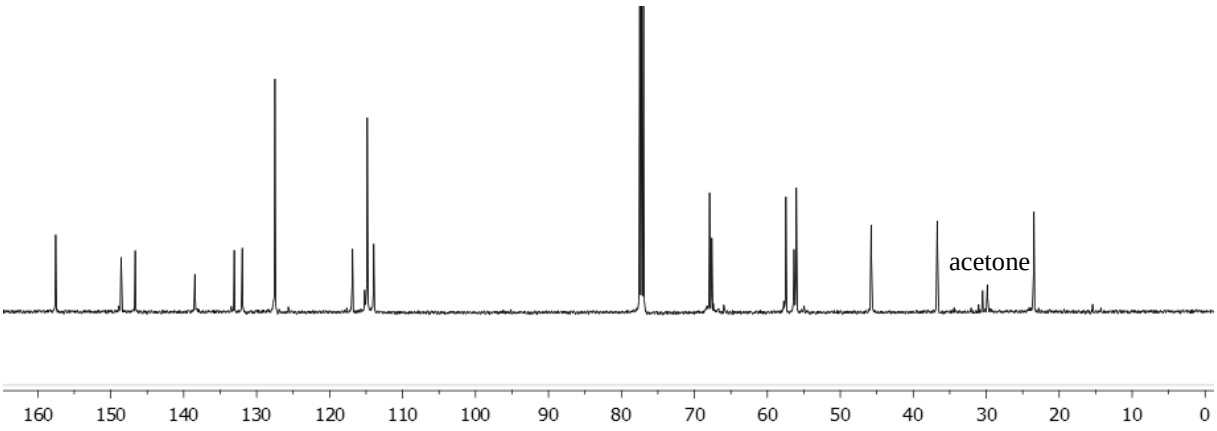


2) *P-SSS-***3**

^{1}H NMR ($CDCl_3$, 298 K, 500.10 MHz):

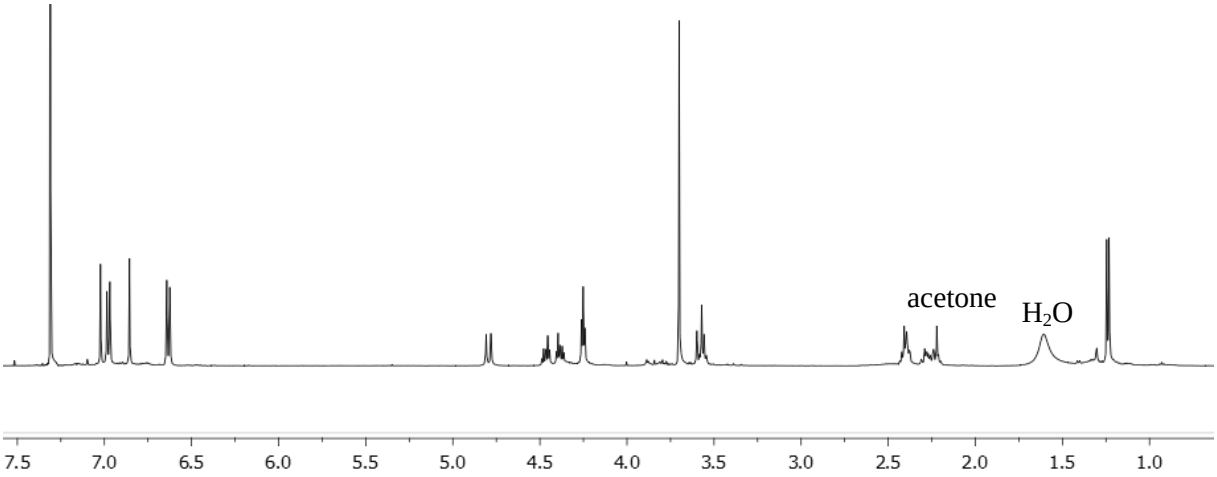


^{13}C NMR ($CDCl_3$, 298 K, 125.76 MHz):

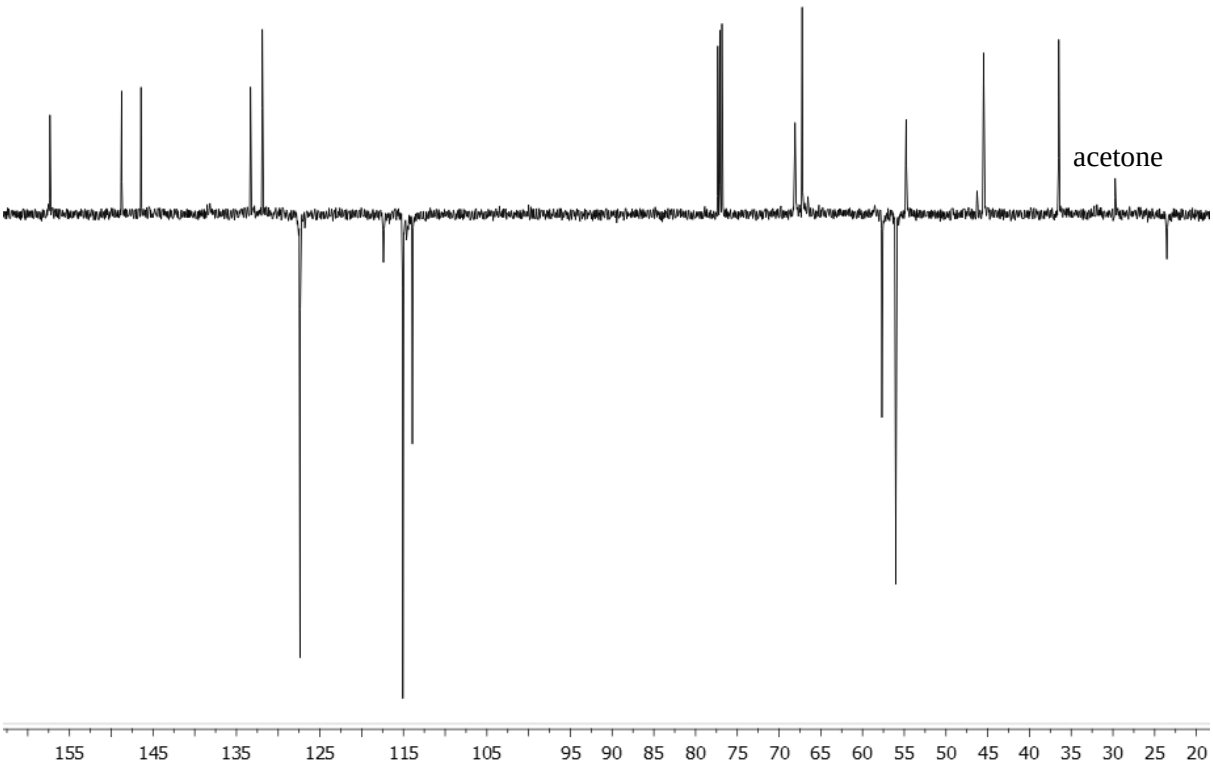


3) *P-RRR*-**3**

^{1}H NMR ($CDCl_3$, 298 K, 500.10 MHz):

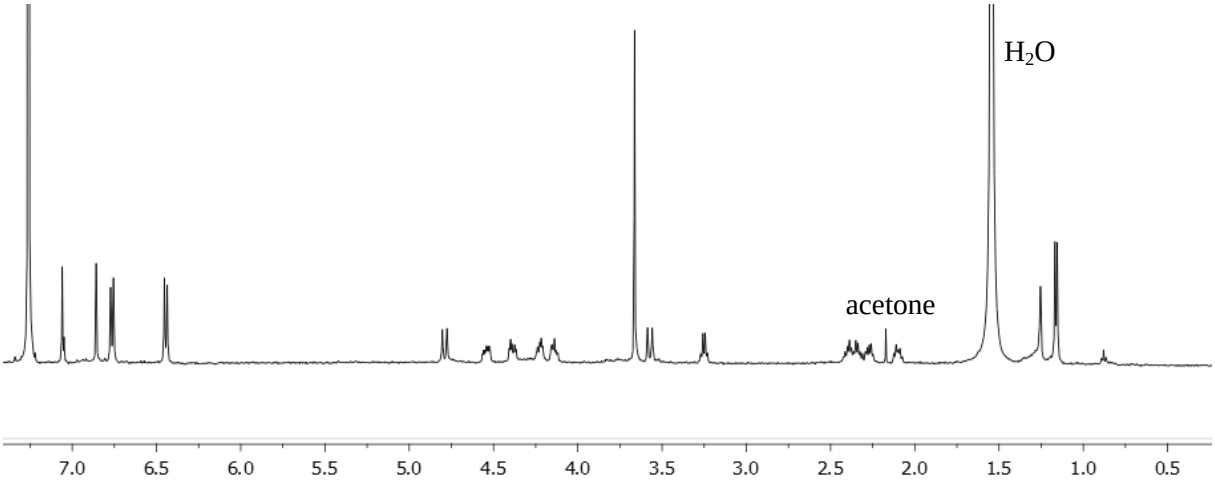


^{13}C NMR ($CDCl_3$, 298 K, 125.76 MHz):

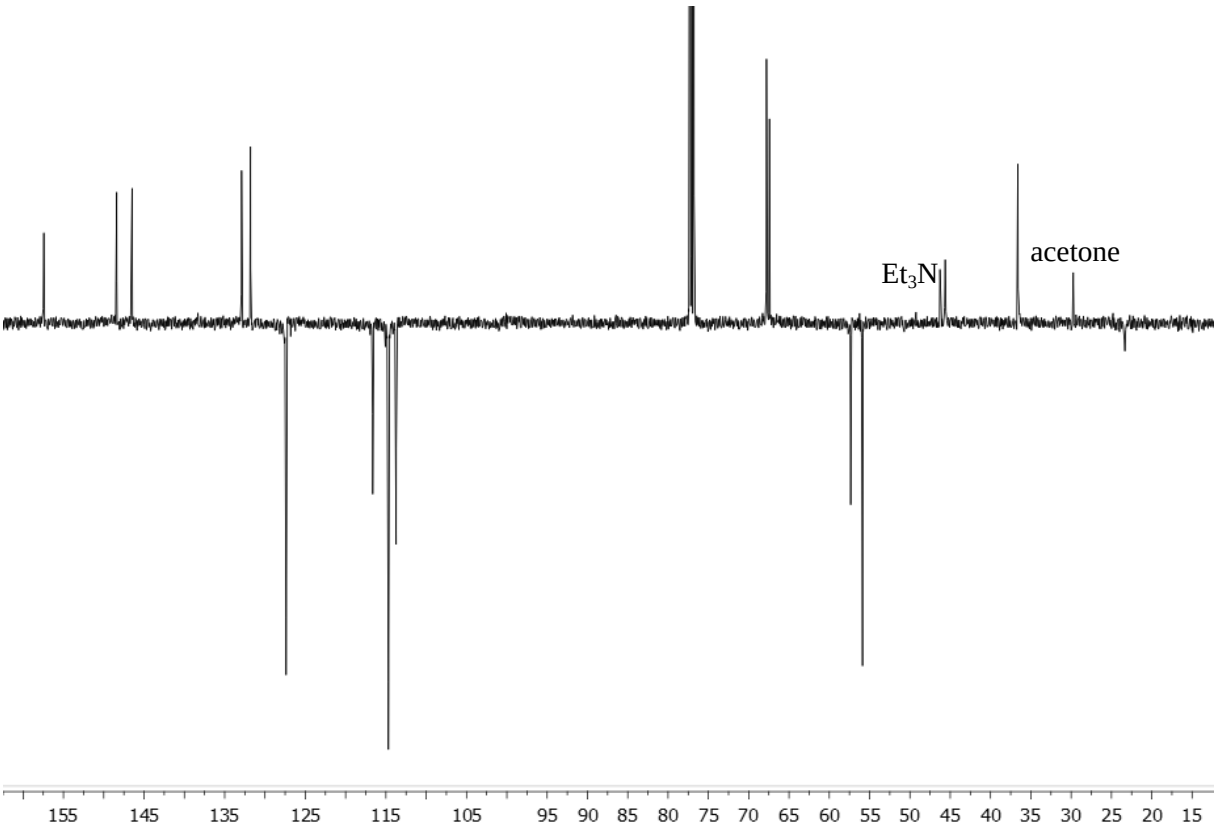


4) *M-RRR*-**3**

^{1}H NMR ($CDCl_3$, 298 K, 500.10 MHz):

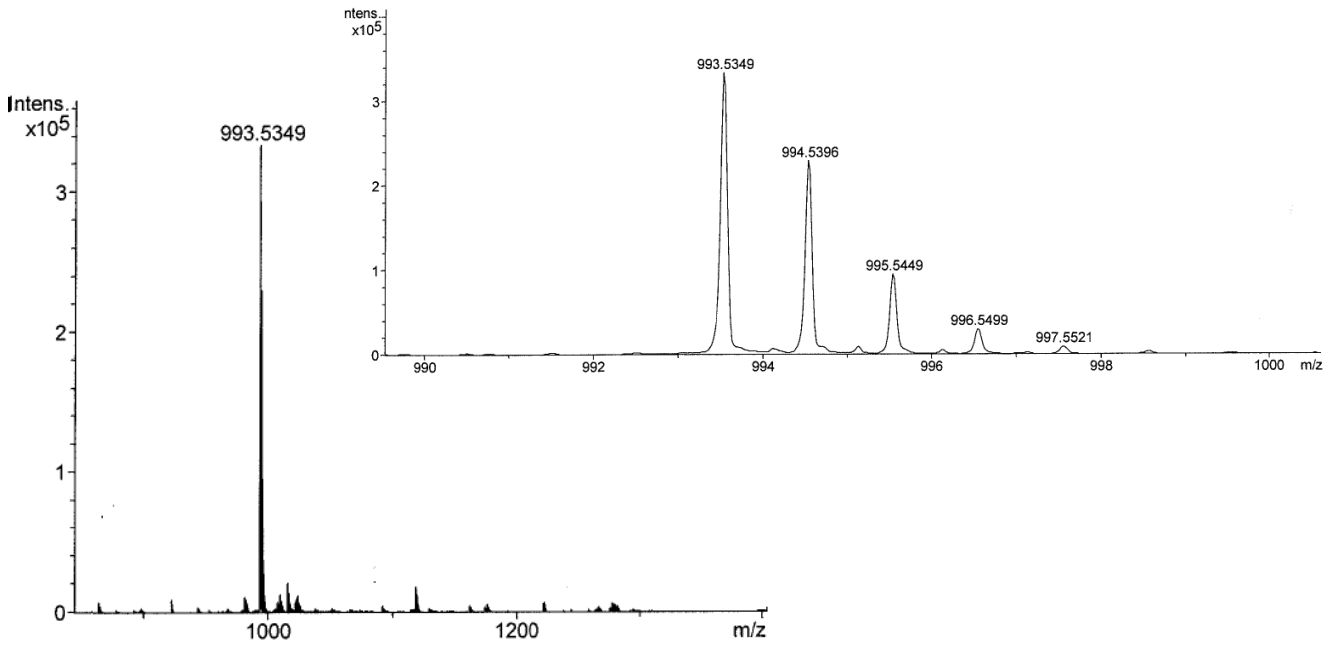


^{13}C NMR ($CDCl_3$, 298 K, 125.76 MHz):

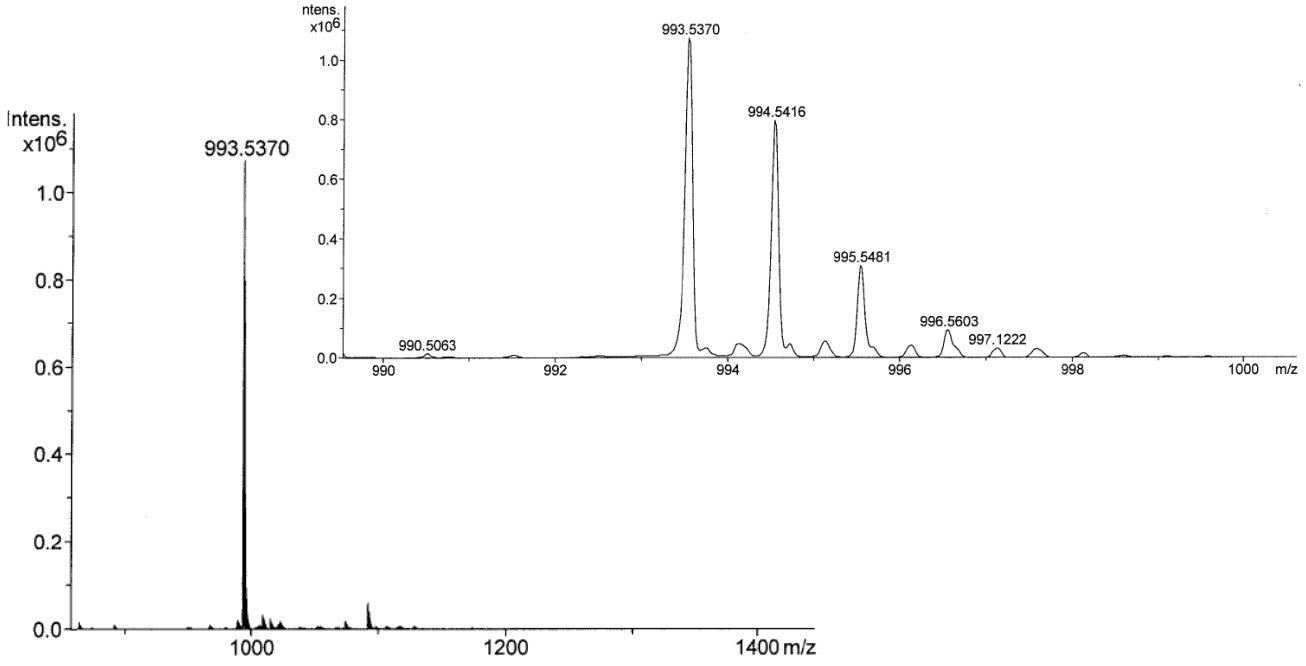


B) Masse spectra

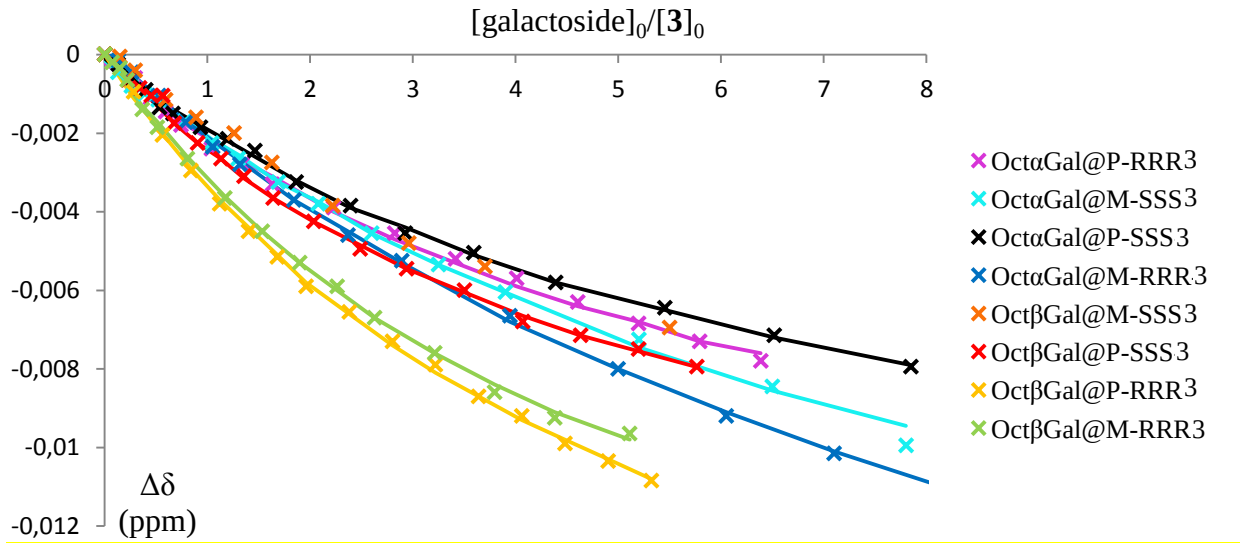
1) *M-SSS-***3**

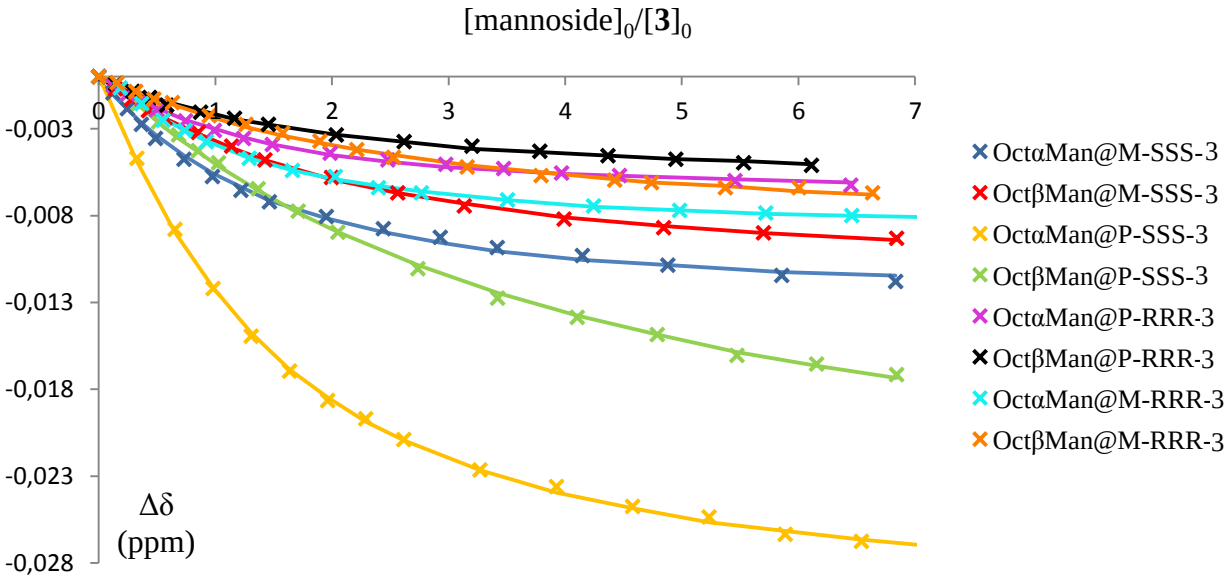


2) *P-SSS-***3**



C) ^{1}H NMR titration





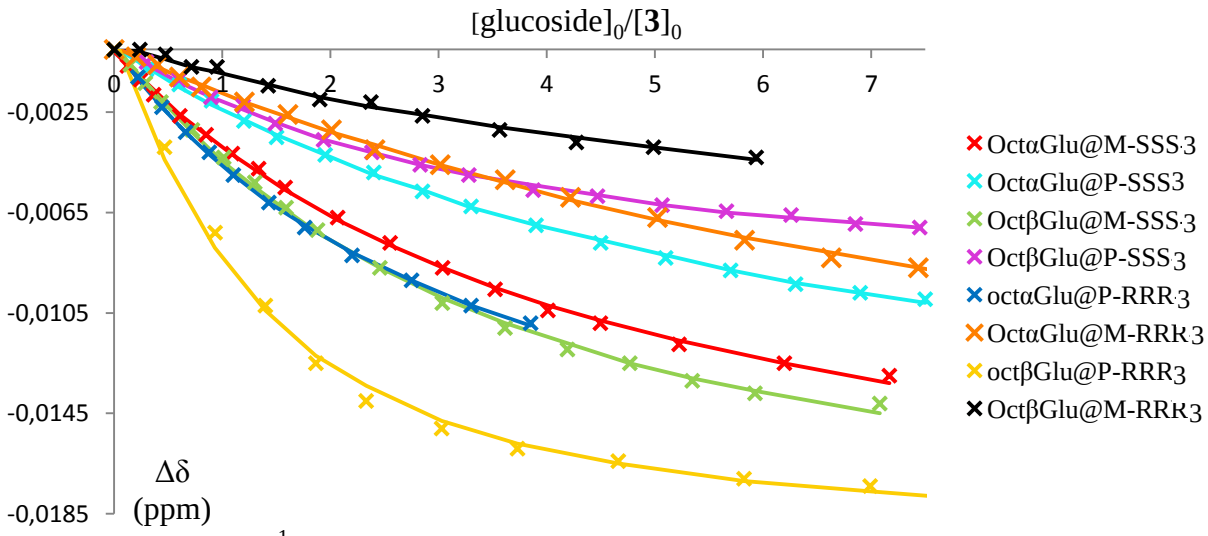


Figure S-1 ^{1}H NMR titration curves for the complexation of the carbohydrates by **3**

(Complexation induced shifts of either the OMe or the aromatic protons of the linkers were plotted as a function of the guest/host ratio; dots correspond to experimental data and the curves are those obtained after modeling by HypNMR 2008 with a model based on the formation of a 1:1 complex)

HypNMR2008 reports for the determination of the K_a values

Receptor: *M-SSS*-**3** guest: OctαMan

```
HypNMR2008

Converged in 5 iterations with sigma = 0,211595

                        standard
                 value  deviation  Comments
 1 log beta(HCsucre)  3.1491  0.044      3.15(4)
```

Receptor: *M-SSS*-**3** guest: OctβMan

```
HypNMR2008

Converged in 4 iterations with sigma = 0,087772

                        standard
                 value  deviation  Comments
 1 log beta(HCsucre)  2.9054  0.025      2.91(2)
```

Receptor: *P-SSS*-**3** guest: OctαMan

```
HypNMR2008

Converged in 5 iterations with sigma = 0,190596

                        standard
                 value  deviation  Comments
 1 log beta(HCsucre)  3.217  0.0155      3.22(2)
```

Receptor: *P-SSS*-**3** guest: OctβMan

HypNMR2008

Converged in 1 iterations with sigma = 0,191906

	value	standard deviation	Comments
1 log beta(HCsucre)	2.5875	0.037	2.59(4)

Receptor: *P-RRR*-**3** guest: OctαMan

HypNMR2008

Converged in 6 iterations with sigma = 0,083884

	value	standard deviation	Comments
1 log beta(HCsucre)	3.1886	0.0335	3.19(3)

Receptor: *P-RRR*-**3** guest: OctβMan

HypNMR2008

Converged in 6 iterations with sigma = 0,088926

	value	standard deviation	Comments
1 log beta(HCsucre)	2.9854	0.048	2.99(5)

Receptor: *M-RRR*-**3** guest: OctαMan

HypNMR2008

Converged in 4 iterations with sigma = 0,088440

	value	standard deviation	Comments
1 log beta(HCsucre)	3.3999	0.023	3.4(2)

Receptor: *M-RRR*-**3** guest: OctβMan

HypNMR2008

Converged in 5 iterations with sigma = 0,105480

	value	standard deviation	Comments
1 log beta(HCsucre)	2.8069	0.0401	2.81(4)

Receptor: *M-SSS*-**3** guest: OctαGlc

HypNMR2008

Converged in 5 iterations with sigma = 0,130351

	value	standard deviation	Comments
1 log beta(HCsucre)	2.3276	0.0367	2.33(4)

Receptor: *M-SSS*-**3** guest: OctβGlc

HypNMR2008

Converged in 1 iterations with sigma = 0,197642

	value	standard deviation	Comments
1 log beta(HCsucre)	2.5772	0.0417	2.58(4)

Receptor: *P-SSS*-**3** guest: OctαGlc

HypNMR2008

Converged in 4 iterations with sigma = 0,078563

	value	standard deviation	Comments
1 log beta(HCsucre)	2.149	0.0377	2.15(4)

Receptor: *P-SSS*-**3** guest: OctβGlc

HypNMR2008

Converged in 4 iterations with sigma = 0,099589

	value	standard deviation	Comments
1 log beta(HCsucre)	2.6024	0.0401	2.6(4)

Receptor: *P-RRR*-**3** guest: OctαGlc

HypNMR2008

Converged in 4 iterations with sigma = 0,068253

	value	standard deviation	Comments
1 log beta(HCsucre)	1.9762	0.0499	1.98(5)

Receptor: *P-RRR*-**3** guest: OctβGlc

HypNMR2008

Converged in 1 iterations with sigma = 0,427088

	value	standard deviation	Comments
1 log beta(HCsucre)	2.8584	0.0572	2.86(6)

Receptor: *M-RRR*-**3** guest: OctαGlc

HypNMR2008

Converged in 4 iterations with sigma = 0,099253

	value	standard deviation	Comments
1 log beta(HCsucre)	1.9207	0.078	1.92(8)

Receptor: *M-RRR*-**3** guest: OctβGlc

```
HypNMR2008

Converged in 4 iterations with sigma = 0,098564

                          standard
                  value   deviation   Comments
 1 log beta(HCsucre)  2.4307   0.11        2.4(1)
```

Receptor: *M-SSS*-**3** guest: OctαGal

```
HypNMR2008

Converged in 5 iterations with sigma = 0,085131

                          standard
                  value   deviation   Comments
 1 log beta(HCsucre)  1.4561   0.1388      1.5(1)
```

Receptor: *M-SSS*-**3** guest: OctβGal

```
HypNMR2008

Converged in 6 iterations with sigma = 0,195467

                          standard
                  value   deviation   Comments
 1 beta(HCsucre)      -6.2E+01  0.1129 Log beta cannot be updated
```

Receptor: *P-SSS*-**3** guest: OctαGal

```
HypNMR2008

Converged in 5 iterations with sigma = 0,109730

                          standard
                  value   deviation   Comments
 1 log beta(HCsucre)  2.0501   0.0757      2.05(8)
```

Receptor: *P-SSS*-**3** guest: OctβGal

```
HypNMR2008

Converged in 4 iterations with sigma = 0,057278

                          standard
                  value   deviation   Comments
 1 log beta(HCsucre)  1.1314   excessive   relative error on beta = 41%
```

Receptor: *P-RRR*-**3** guest: OctαGal

```
HypNMR2008

Converged in 6 iterations with sigma = 0,136277

                          standard
                   value  deviation  Comments
 1 log beta(HCsucre) 2.1515  0.1039    2.2(1)
```

Receptor: *P-RRR*-**3** guest: OctβGal

```
HypNMR2008

Converged in 4 iterations with sigma = 0,096084

                          standard
                   value  deviation  Comments
 1 log beta(HCsucre) 1.8334  0.1151    1.8(1)
```

Receptor: *M-RRR*-**3** guest: OctαGal

```
HypNMR2008

Converged in 4 iterations with sigma = 0,087180

                          standard
                   value  deviation  Comments
 1 log beta(HCsucre) 1.3692  0.1426    1.4(1)
```

Receptor: *M-RRR*-**3** guest: OctβGal

```
HypNMR2008

Converged in 3 iterations with sigma = 0,120747

                          standard
                   value  deviation  Comments
 1   log beta(HCsucre)  1.7737   0.1057     1.8(1)
```

D) Computational Details

Electronic TDDFT calculations were run using the Gaussian09 package[1] employing a set of different functionals (B3LYP, CAM-B3LYP, BH&HLYP) in combination with the SVP basis set on the first 36 excited states. Spectra were generated using the program SpecDis[2] by applying a Gaussian bandshape with exponential bandwith σ = 0.15 eV. The CD curves have been constructed using dipole-length computed rotatory strengths; dipole-velocity data differ by less than 10% for most transitions.

E) Bibliography

1. Gaussian 03: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian*, Wallingford, CT, 2009.
2. T. Bruhn, A. Schaumlöffel, Y. Hemberger, G. Bringmann, *Chirality* 2013, **25**, 243–249.