## Electronic supplementary material

**New macrocyclic compounds for molecular recognition studies**

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NMR SPECTRA

Figure S1. $^1$H NMR spectrum of compound 9 in CDCl$_3$

Figure S2. $^{13}$C NMR spectrum of compound 9 in CDCl$_3$
Figure S3. $^1$H NMR spectrum of compound 10 in CDCl$_3$

Figure S4. $^{13}$C NMR spectrum of compound 10 in CDCl$_3$

* can be exchanged
Figure S5. $^1$H NMR spectrum of host Ia in CDCl$_3$.

Figure S6. $^{13}$C NMR spectrum of host Ia in CDCl$_3$.  

* can be exchanged
Figure S7. 2D ($^1$H-$^{15}$N) gs-HMBC spectrum of host Ia in CDCl₃.

Figure S8. $^1$H NMR spectrum of host Ib in CDCl₃.
Figure S9. $^{13}$C NMR spectrum of host Ib in CDCl$_3$.

Figure S10. 2D ($^1$H-$^{15}$N) gs-HMBC spectrum of host Ib in CDCl$_3$.
Figure S11. Methyl biotin ester (1) chemical shifts in CDCl₃

MOLECULAR MODELING

The minimum energy conformations of complexes of hosts Ia-Ib with guests 1-4 are shown in Figures S12-S13.

Figure S12. The minimum energy conformations of complexes of host Ia.
Figure S13. The minimum energy conformations of complexes of host Ib.
NMR TITRATIONS

Ia:1 Biotin methyl ester

Figure S14. Starting and end point $^1$H NMR spectra of a typical titration experiment of Ia (5e-4 M) with increasing amounts of guest 1 (0-1.2 equiv).

Figure S15. Typical $^1$H NMR titration curve of Ia (5e-4 M) with increasing amounts of guest 1 (0-1.2 equiv).
Ia:2 Imidazolidone

Figure S16. Typical $^1$H NMR titration experiment of Ia (7e-4 M) with increasing amounts of guest 2 (0-5 equiv).

Figure S17. Typical $^1$H NMR titration curve of Ia (7e-4 M) with increasing amounts of guest 2 (0-5 equiv).
Ia:3 Trimethyleneurea

**Figure S18.** Typical $^1$H NMR titration experiment of Ia (8e-4 M) with increasing amounts of guest 3 (0-7 equiv).

**Figure S19.** Typical $^1$H NMR titration curve of Ia (8e-4 M) with increasing amounts of guest 3 (0-7 equiv).
Figure S20. Typical $^1$H NMR titration experiment of Ia (8e-4 M) with increasing amounts of guest 4 (0-50 equiv).

Figure S21. Typical $^1$H NMR curve of Ia (8e-4 M) with increasing amounts of guest 4 (0-50 equiv).
**Ib:1 Methylbiotin ester**

**Figure S22.** Typical $^1$H NMR titration experiment of Ib (1e-3 M) with increasing amounts of guest 1 (0-10 equiv).

**Figure S23.** Typical $^1$H NMR titration curve of Ib (1e-3 M) with increasing amounts of guest 1 (0-10 equiv).
**Ib:2 Imidazolidone**

Figure S24. Typical $^1$H NMR titration experiment of Ib (8e-4 M) with increasing amounts of guest 2 (0-6 equiv).

Figure S25. Typical $^1$H NMR titration curve of Ib (8e-4 M) with increasing amounts of guest 2 (0-6 equiv).
**Figure S26.** Typical $^1$H NMR titration experiment of Ib (1e-3 M) with increasing amounts of guest 3 (0-6 equiv).

**Figure S27.** Typical $^1$H NMR titration curve of Ib (1e-3 M) with increasing amounts of guest 3 (0-6 equiv).
**Ib:4 Barbital**

**Figure S28.** Typical $^1$H NMR titration experiment of Ib (5e-4 M) with increasing amounts of guest 4 (0-27 equiv).

**Figure S29.** Typical $^1$H NMR titration curve of Ib (5e-4 M) with increasing amounts of guest 4 (0-27 equiv).