Supporting Information

Trimethoxybenzene- and trimethylbenzene-based compounds bearing imidazole, indole and pyrrole groups as recognition units: Synthesis and evaluation of the binding properties towards carbohydrates

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1. Representative EQNMR plots (Figures S1-S11)
2. Representative mole ratio plots (Figures S12-S18)
3. $^1$H NMR titrations of compound 14a, 14b, 16a and 16b with the tested carbohydrates (Figures S19-S27)
4. $^1$H and $^{13}$C NMR spectra of compounds 12a/b-16a/b (Figures S28-47)
5. Partial $^1$H and $^{13}$C NMR spectra of compound 14a and 14b (chemical shifts of the amine-NH signals of the two compounds; Figure 48)
Plots of the chemical shifts of the receptor resonances as a function of added carbohydrate (EQNMR program).

Figure S1. Plot of the observed chemical shifts of the CH$_2$ resonances of 14a as a function of added β-glucoside 27a in CDCl$_3$ (1:1 binding model).

Figure S2. Plot of the observed chemical shifts of the NH-indole resonances of 14b as a function of added β-glucoside 27a in CDCl$_3$ (1:1 binding model).

Figure S3. Plot of the observed chemical shifts of the NH-pyrrole resonances of 16a as a function of added β-glucoside 27a in CDCl$_3$ (1:1 binding model).

Figure S4. Plot of the observed chemical shifts of the NH-pyrrole resonances of 16b as a function of added β-glucoside 27a in CDCl$_3$ (1:1 binding model).
Figure S5. Plot of the observed chemical shifts of the NH-indole resonances of 14a as a function of added β-galactoside 29a in CDCl₃ (“mixed” 1:1 and 2:1 receptor-sugar binding model).

Figure S6. Plot of the observed chemical shifts of the NH-indole resonances of 14a as a function of added α-galactoside 30a in CDCl₃ (1:1 binding model).

Figure S7. Plot of the observed chemical shifts of the CH₂ resonances of 15a as a function of added β-glucoside 27a in CDCl₃ (1:1 binding model).

Figure S8. Plot of the observed chemical shifts of the NH-pyrrole resonances of 16a as a function of added β-galactoside 29a in CDCl₃ (1:1 binding model).
Figure S9. Plot of the observed chemical shifts of the NH-pyrrole resonances of 16a as a function of added α-galactoside 30a in CDCl₃ (1:1 binding model).

Figure S10. Plot of the observed chemical shifts of the NH-pyrrole resonances of 16b as a function of added β-galactoside 29a in CDCl₃ (1:1 binding model).

Figure S11. Plot of the observed chemical shifts of the NH-pyrrole resonances of 16b as a function of added β-maltoside 31 in CDCl₃ (“mixed” 1:1 and 2:1 receptor-sugar binding model).

Representative mole ratio plots
**Figure S12.** Mole ratio plot: Titration of compound 14a with β-galactopyranoside 29a in CDCl₃ (analysis of the complexation-induced shift of the NH-indole signal of 14a).

**Figure S13.** Mole ratio plot: Titration of compound 14b with β-glucopyranoside 27a in CDCl₃ (analysis of the complexation-induced shift of the NH-indole signal of 14b).

**Figure S14.** Mole ratio plot: Titration of compound 16a with β-galactopyranoside 29a in CDCl₃ (analysis of the complexation-induced shift of the NH-pyrrole signal of 16a).
**Figure S15.** Mole ratio plot: Titration of compound 16b with β-glucopyranoside 27a in CDCl₃ (analysis of the complexation-induced shift of the NH-pyrrole signal of 16b).

**Figure S16.** Mole ratio plot: Titration of compound 16a with β-glucopyranoside 27a in CDCl₃ (analysis of the complexation-induced shift of the NH-pyrrole signal of 16a).

**Figure S17.** Mole ratio plot: Titration of compound 16b with β-galactopyranoside 29a in CDCl₃ (analysis of the complexation-induced shift of the NH-pyrrole signal of 16b).
3. **1H NMR titrations of compounds 14a, 14b, 16a and 16b with the tested carbohydrates.**

3.1 **1H NMR titrations of compound 14a with β-glucoside 27a.**

a) b) c) **Figure S19.** Partial 1H NMR spectra (400 MHz) of compound 14a ([14a] = 1.00 mM) after addition of 0.00 – 4.10 equiv of β-glucoside 27a in CDCl₃. Shown are chemical shifts of the CH-indole (a) and CH₂ signals of 14a (b,c).

3.2 **1H NMR titrations of compound 14b with β-glucoside 27a.**

a) b) c)
Figure S20. Partial $^1$H NMR spectra (400 MHz) of compound 14b ([14b] = 1.00 mM) after addition of 0.00 – 4.97 equiv of β-glucoside 27a in CDCl$_3$. Shown are chemical shifts of the NH-indole (a), CH-indole (b,c) and CH$_2$ (d) signals of 14b.

3.3 $^1$H NMR titrations of compound 16a with β-glucoside 27a.

a) b) c)

Figure S21. (a) Partial $^1$H NMR spectra (400 MHz) of compound 16a ([16a] = 1.00 mM) after addition of 0.00 – 5.01 equiv of β-glucoside 27a in CDCl$_3$. Shown are chemical shifts of the NH-pyrrole (a), CH-pyrrole (b) and CH$_2$/OCH$_3$ (c) signals of 16a.

3.4 $^1$H NMR titrations of compound 16a with β-galactoside 29a.
Figure S22. Partial $^1$H NMR spectra (400 MHz) of compound 16a ([16a] = 1.00 mM) after addition of 0.00 – 4.49 equiv of β-galactoside 29a in CDCl$_3$. Shown are chemical shifts of the NH-pyrrole (a), CH-pyrrole (b) and CH$_2$/OCH$_3$ (c) signals of 16a.

3.5 $^1$H NMR titrations of compound 16b with β-glucoside 27a.

Figure S23. Partial $^1$H NMR spectra (400 MHz) of compound 16b ([16b] = 1.01 mM) after addition of 0.00 – 4.98 equiv of β-glucoside 27a in CDCl$_3$. Shown are chemical shifts of the NH-pyrrole (a), CH-pyrrole (b) and CH$_2$/OCH$_3$ (c) signals of 16b.

3.6 $^1$H NMR titrations of compound 16b with β-galactoside 29a.
**Figure S24.** Partial $^1$H NMR spectra (400 MHz) of compound $16b$ ([16b] = 1.01 mM) after addition of 0.00 – 4.49 equiv of $\beta$-galactoside $29a$ in CDCl$_3$. Shown are chemical shifts of the NH-pyrrole (a), CH-pyrrole (b) and OCH$_3$ (c) signals of $16b$.

**3.7** $^1$H NMR titrations of compound $14a$ with $\alpha$-galactoside $30a$.

3.7.1 $^1$H NMR titrations of compound $14a$ with $\alpha$-galactoside $30a$.

**Figure S25.** Partial $^1$H NMR spectra (400 MHz) of compound $14a$ ([14a] = 1.00 mM) after addition of 0.00 – 4.51 equiv of $\alpha$-galactoside $30a$ in CDCl$_3$. Shown are chemical shifts of the CH-indole (a,b), CH$_2$ and OCH$_3$ (c) signals of $14a$. 
3.8 \(^1\)H NMR titrations of compound 15a with \(\beta\)-glucoside 27a.

![Partial 1H NMR spectra](image)

**Figure S26.** Partial \(^1\)H NMR spectra (400 MHz) of compound 15a ([15a] = 1.01 mM) after addition of 0.00 − 4.08 equiv of \(\beta\)-glucoside 27a in CDCl\(_3\). Shown are chemical shifts of the NH- (a), CH\(_2\) (b) and OCH\(_3\) (c) signals of 15a.

3.9 \(^1\)H NMR titrations of compound 16a with \(\alpha\)-galactoside 30a.

![Partial 1H NMR spectra](image)

**Figure S27.** Partial \(^1\)H NMR spectra (400 MHz) of compound 16a ([16a] = 1.00 mM) after addition of 0.00 − 5.01 equiv of \(\alpha\)-galactoside 30a in CDCl\(_3\). Shown are chemical shifts of the NH- (a), CH-pyrrole (b), CH\(_2\) and OCH\(_3\) (c) signals of 16a.

4 \(^1\)H and \(^{13}\)C NMR spectra of imidazole-, indole- and pyrrole-based compounds 12a/b-16a/b.

4.1 \(^1\)H and \(^{13}\)C NMR spectra of compound 12a.
Figure S28. $^1$H NMR spectrum of 12a in MeOD-d₄ (0.03 M).

Figure S29. $^{13}$C NMR spectrum of 12a in MeOD-d₄.

4.2 $^1$H and $^{13}$C NMR spectra of compound 13a.
Figure S30. $^1$H NMR spectrum of 13a in CDCl$_3$ + MeOD-d$_4$ (0.03 M).

Figure S31. $^{13}$C NMR spectrum of 13a in CDCl$_3$ + MeOD-d$_4$.

4.3 $^1$H and $^{13}$C NMR spectra of compound 14a.
**Figure S32.** $^1$H NMR spectrum of 14a in CDCl$_3$ (0.02 M).

**Figure S33.** $^{13}$C NMR spectrum of 14a in CDCl$_3$.

4.4 $^1$H and $^{13}$C NMR spectra of compound 15a.
Figure S34. $^1$H NMR spectrum of $^{15a}$ in CDCl$_3$ (0.03 M).

Figure S35. $^{13}$C NMR spectrum of $^{15a}$ in CDCl$_3$.

4.5 $^1$H and $^{13}$C NMR spectra of compound $^{16a}$. 
Figure S36. $^1$H NMR spectrum of 16a in CDCl$_3$ (0.03 M).

Figure S37. $^{13}$C NMR spectrum of 16a in CDCl$_3$.

4.6 $^1$H and $^{13}$C NMR spectra of compound 12b.
Figure S38. $^1$H NMR spectrum of 12b in MeOD-d$_4$ (0.06 M).

Figure S39. $^{13}$C NMR spectrum of 12b in MeOD-d$_4$.

4.7 $^1$H and $^{13}$C NMR spectra of compound 13b.
Figure S40. $^1$H NMR spectrum of 13b in MeOD-d$_4$ (0.04 M).

Figure S41. $^{13}$C NMR spectrum of 13b in MeOD-d$_4$.

4.8 $^1$H and $^{13}$C NMR spectra of compound 14b.
Figure S42. $^1$H NMR spectrum of 14b in CDCl$_3$ (0.03 M).

Figure S43. $^{13}$C NMR spectrum of 14b in CDCl$_3$.

4.9 $^1$H and $^{13}$C NMR spectra of compound 15b.
**Figure S44.** $^1$H NMR spectrum of 15b in CDCl$_3$ (0.02 M).

**Figure S45.** $^{13}$C NMR spectrum of 15b in CDCl$_3$.

4.10 $^1$H and $^{13}$C NMR spectra of compound 16b.
Figure S46. $^1$H NMR spectrum of 16b in CDCl$_3$ (0.04 M).

Figure S47. $^{13}$C NMR spectrum of 16b in CDCl$_3$. 
Partial $^1$H and $^{13}$C NMR spectra of compound 14a and 14b (chemical shifts of the amine-NH signals of the two compounds)

**Figure 48.** Partial $^1$H NMR spectra (400 MHz) of compound 14a (a) and 14b (b) in CDCl$_3$. Shown are chemical shifts of the NH (2.96 ppm and 1.70 ppm in the case of 14a and 14b, respectively), CH$_2$ and OCH$_3$ / CH$_3$ signals of 14a / 14b ([14a] = [14b]).