Chloride-Templated Macrocyclization and Anion-Binding Properties of C_2-Symmetric Macrocyclic Ureas from Sucrose

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Contents

1. Synthetic Procedures and Structural Analysis

1.1 Materials and Methods

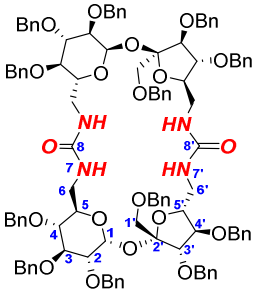
All reported NMR spectra were recorded with a Varian AM-600 (600 MHz ^{1}H, 150 MHz ^{13}C). Chemical shifts (δ) are reported in ppm relative to acetone-d_6 (δ 2.07) for ^{1}H and (δ 29.84) for ^{13}C. All significant resonances (carbon skeleton) were assigned by COSY (^{1}H-^{1}H), HSQC (^{1}H-^{13}C) and HMBC (^{1}H-^{13}C) correlations. IR spectra (CH_2Cl_2 film) were recorded with a JASCO FT/IR 6200. Mass spectra were recorded with an ESI/MS Mariner (PetSeptive Biosystem) mass spectrometer. Optical rotations were measured on Jasco P 2000 apparatus in $CHCl_3$ with a sodium lamp at r.t. Elemental analyses were obtained with a Perkin–Elmer 2400 CHN analyzer. Commercially available reagents and dry solvents were used as received. Compounds were purified using automatic flash chromatography system Grace Reveleris X2 with UV and ELSD detection and Grace Resolv or Reveleris cartridges. Analytical and preparative TLC were performed on Silica Gel 60 F_{254} (Merck).

1.2 Compounds synthesis

Macrocyclic urea-sucrose derivatives **3a** and **3b**

Triphosgene (23 mg, 0.08 mmol) was carefully added to a solution of 6,6'-diamino-6,6'-dideoxy-1',2,3,3',4,4'-hexa-*O*-benzylsucrose **1** (100 mg, 0.113 mmol) and Et_3N (90 µL, 0.678 mmol) in THF (30 mL) at -10 °C under an argon atmosphere. The reaction was allowed to warm to r.t. and stirred afterwards for one hour. To the resulting solution of diisocyanate-sucrose **2**, second portion of diamine **1** (100 mg, 0.113 mmol) in THF (30 mL) was added at r.t. *via* syringe within 30 min. The reaction mixture was stirred overnight, concentrated under reduced pressure, and the residue was purified by chromatography with EA:hexanes (3:7 v/v) to give two regioisomers **3a** (95 mg, 46%) and **3b** (90 mg, 44%) in the form of white amorphous foam.

Data for 3a

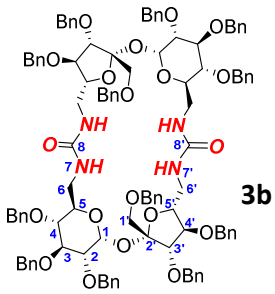


3a

^{1}H NMR (600 MHz, acetone-d_6)	δ 7.54 – 7.15 (m, 30H, H-Ar), 6.81 (d, J = 6.5 Hz, 1H, NH-7), 6.06 (dd, J = 7.3, 4.5 Hz, 1H, NH-7'), 5.49 (d, J = 3.4 Hz, 1H, H1), 4.91 (d, J = 12.8 Hz, 1H, CH_2Bn), 4.90 (d, J = 12.6 Hz, 1H, CH_2Bn), 4.81 (d, J = 11.3 Hz, 1H, CH_2Bn), 4.79 – 4.72 (m, 4H, CH_2Bn), 4.69 (d, J = 11.6 Hz, 1H, CH_2Bn), 4.64 (d, J = 11.7 Hz, 1H, CH_2Bn), 4.62 (d, J = 11.0 Hz, 1H, CH_2Bn), 4.52 (t, J = 7.6 Hz, 1H, H4'), 4.50 – 4.47 (m, 1H, H6), 4.47 (d, J = 12.1 Hz, 1H, CH_2Bn), 4.45 (d, J = 7.7 Hz, 1H, H3'), 4.40 (d, J = 12.1 Hz, 1H, CH_2Bn), 4.22 – 4.14 (m, 1H, H5), 4.12 – 4.02 (m, 1H, H6'), 3.99 (t, J = 9.3 Hz, 1H, H3), 3.86 – 3.79 (m, 1H, H5'), 3.55 (d, J = 11.2 Hz, 1H, H1'), 3.50 – 3.46 (m, 1H, H2), 3.47 (d, J = 11.1 Hz, 1H, H1'), 3.21 – 3.17 (m, 1H, H4), 3.18 – 3.13 (m, 1H, H6'), 2.77 – 2.68 (m, 1H, H6).
^{13}C NMR (151 MHz, acetone-d_6)	δ 159.88 (C8'), 159.84 (C8'), 158.76 (C8), 158.71 (C8), 140.21 140.12, 139.80, 139.77, 139.54, 139.43 (C_{quat}, 6x OCH_2Ph), 104.50 (C2'), 89.32 (C1), 86.60 (C4'), 85.31 (C3'), 82.36 (C3), 81.10 (C4), 80.76 (C2), 80.63 (C5'), 75.67 (OCH_2-Ph), 75.24 (OCH_2-Ph), 74.50 (C5), 73.70 (double intensity, OCH_2-Ph), 73.58 (OCH_2-Ph), 73.21 (C1'), 72.80 (OCH_2-Ph), 44.11 (C6'), 43.99 (C6'), 42.64 (C6), 42.53 (C6).
HRMS ESI	Calc. for $C_{110}H_{116}N_4O_{20}$ $[M+Na]^+$: 1835.8081, found: 1835.8092.
Anal (%)	Calc. for $C_{110}H_{118}N_4O_{21}$ (**3a**+H_2O): C 72.11, H 6.49, N 3.06, found: C 71.59, H 6.47, N 3.15.
IR (film)	ν_{max} 3363, 3062, 3030, 2916, 2867,1638, 1567, 1091, 1028, 994, 735,

		697 cm^{-1}
	$[\alpha]_D$	+48 (c = 0.25).

Data for 3b



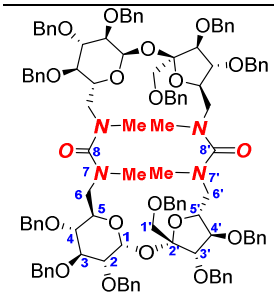
3b

^{1}H NMR (600 MHz, acetone-d_6)	δ 7.45 – 7.14 (m, 30H, H-Ar), 5.97 – 5.87 (m, 2H, NH-7, NH-7'), 5.63 (d, *J* = 3.2 Hz, 1H, H1), 4.91 (d, *J* = 11.3 Hz, 1H, $\underline{CH_2}$Bn), 4.89 (d, *J* = 10.9 Hz, 1H, $\underline{CH_2}$Bn), 4.83 (d, *J* = 11.6 Hz, 1H, $\underline{CH_2}$Bn), 4.76 (d, *J* = 11.9 Hz, 1H, $\underline{CH_2}$Bn), 4.75 – 4.69 (m, 4H, $\underline{CH_2}$Bn), 4.65 (d, *J* = 11.6 Hz, 1H, $\underline{CH_2}$Bn), 4.56 (d, *J* = 11.6 Hz, 1H, $\underline{CH_2}$Bn), 4.51 (d, *J* = 11.9 Hz, 1H, $\underline{CH_2}$Bn), 4.46 (d, *J* = 12.0 Hz, 1H, $\underline{CH_2}$Bn), 4.44 (d, *J* = 6.3 Hz, 1H, H3'), 4.23 – 4.17 (m, 2H, H4', H5), 4.03 (t, *J* = 9.3 Hz, 1H, H3), 3.97 (dd, *J* = 11.8, 6.0 Hz, 1H, H5'), 3.82 – 3.76 (m, 1H, H6'), 3.73 (d, *J* = 10.8 Hz, 1H, H1'), 3.64 (dd, *J* = 9.5, 3.8 Hz, 1H, H6), 3.59 (d, *J* = 10.9 Hz, 1H, H1'), 3.53 (dd, *J* = 9.7, 3.3 Hz, 1H, H2), 3.35 (t, *J* = 9.4 Hz, 1H, H6'), 3.33 – 3.26 (m, 2H, H6, H4).
^{13}C NMR (151 MHz, acetone-d_6)	158.41, 158.37 (double intensity), 158.33, 139.23, 138.95, 138.79, 138.77, 138.58, 138.47 (C_{quat}, 6x OCH_2Ph), 104.51 (C2'), 89.69 (1), 83.93 (C3'), 83.63 (C4'), 81.52 (C3), 80.22 (C5'), 80.06 (C2), 79.39 (C4), 74.88 (O$\underline{C}H_2$-Ph), 74.26 (O$\underline{C}H_2$-Ph), 72.95 (O$\underline{C}H_2$-Ph), 72.45 (O$\underline{C}H_2$-Ph), 72.09 (O$\underline{C}H_2$-Ph), 72.01 (O$\underline{C}H_2$-Ph), 71.21 (C5) 42.03, 41.95, 40.74, 40.63.
HRMS ESI	Calc. for $C_{110}H_{116}N_4O_{20}$ $[M+Na]^+$: 1835.8081, found: 1835.8097.
Anal (%)	Calc. for $C_{110}H_{118}N_4O_{21}$ (**3b**+H_2O): C 72.11, H 6.49, N 3.06, found: C 71.70, H 6.50, N 3.11.
IR (film)	ν_{max} 3355, 3317, 3030, 2918, 2869,1627, 1575, 1092, 1028, 1001, 735, 697 cm^{-1}
$[\alpha]_D$	+42 (c = 0.30).

Tetra-methylated sugar-urea derivatives **4a** and **4b**

A suspension of 60% NaH (22 mg, 0.57 mmol) was added in one portion to a solution of **3a** or **3b** (50 mg, 0.028 mmol each) and imidazole (1 mg) in DMF (0.5 mL). After stirring for 10 min at r.t., iodomethane (20 µL, 0.32 mmol) was added, the temperature was raised to 45°C, and the mixture was stirred for an additional hour at 45°C. The reaction was quenched with MeOH (1 mL) solvent was removed under vacuum, and oily residue was purified by a preparative TLC (EA:hexanes, **4a**: 65:50 v/v; **4b**: 50:50 v/v) to afford **4a** (42 mg, 82%) or **4b** (40 mg, 78%) as a white amorphous foam.

Data for 4a

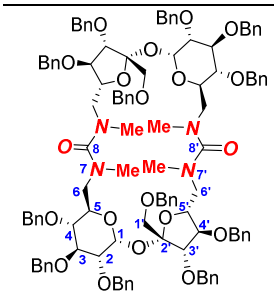


4a

^{1}H NMR (600 MHz, acetone-d_6)	δ 7.42 – 7.19 (m, 30H, H-Ar), 5.58 (d, *J* = 3.1 Hz, 1H, H1), 4.93 (d, *J* = 11.2 Hz, 1H, $\underline{CH_2}$Bn), 4.91 (d, *J* = 11.1 Hz, 1H, $\underline{CH_2}$Bn), 4.82 (d, *J* = 11.6 Hz, 1H, $\underline{CH_2}$Bn), 4.77 (d, *J* = 11.6 Hz, 1H, $\underline{CH_2}$Bn), 4.76 – 4.67 (m, 4H, $\underline{CH_2}$Bn), 4.64 (d, *J* = 11.3 Hz, 1H, $\underline{CH_2}$Bn), 4.60 (d, *J* = 11.6 Hz, 1H, $\underline{CH_2}$Bn), 4.49 (d, *J* = 12.1 Hz, 1H, $\underline{CH_2}$Bn), 4.46 – 4.42 (m, 2H, H5, H3'), 4.43 (d, *J* = 12.1 Hz, 1H, $\underline{CH_2}$Bn), 4.18 (t, *J* = 6.9 Hz, 1H, H4'), 4.13 (td, *J* = 7.5, 3.8 Hz, 1H, H5'), 4.08 (t, *J* = 9.3 Hz, 1H, H3), 3.71 (d, *J* = 11.1 Hz, 1H, H1'), 3.60 (d, *J* = 11.1 Hz, 1H, H1'), 3.60 – 3.57 (m, 1H, H6'), 3.53 (dd, *J* = 9.7, 3.2 Hz, 1H, H2), 3.49 (d, *J* = 13.7 Hz, 1H, H6), 3.45 (dd, *J* = 14.7, 3.7 Hz, 1H, H6'), 3.25 – 3.20 (m, 1H, H4), 3.08 (dd, *J* = 14.3, 8.9 Hz, 1H, H6), 2.78 (s, 3H, OMe), 2.72 (s, 3H, OMe).
^{13}C NMR (151 MHz,	δ 165.63 (C8), 165.06 (C8'), 139.18, 138.97, 138.89, 138.82, 138.51, 138.42 (C_{quat}, 6x OCH_2Ph), 104.69 (C2'), 89.95 (C1), 84.45 (C4'),

acetone-d_6)	83.51(C3'), 81.41 (C3), 80.86 (C4), 80.21 (C2), 78.77 (C5'), 74.79(O<u>C</u>H$_2$-Ph), 74.23 (O<u>C</u>H$_2$-Ph), 72.83 (O<u>C</u>H$_2$-Ph), 72.78 (O<u>C</u>H$_2$-Ph), 71.99 (O<u>C</u>H$_2$-Ph), 71.92 (O<u>C</u>H$_2$-Ph), 71.30 (C1'), 70.53 (C5), 54.81 (C6'), 53.62 (C6), 37.77 (Me), 35.68 (Me).
HRMS ESI	Calc. for $C_{114}H_{124}N_4O_{20}$ $[M+Na]^+$: 1891.8707, found: 1891.8730.

Data for 4b



4b

^{1}H NMR (600 MHz, acetone-d_6)	δ 7.45 – 7.10 (m, 30H, H-Ar), 5.62 (d, *J* = 3.0 Hz, 1H, H1), 4.96 (d, *J* = 11.2 Hz, 1H, <u>C</u>H$_2$Bn), 4.87 (d, *J* = 11.3 Hz, 1H, <u>C</u>H$_2$Bn), 4.84 (d, *J* = 11.9 Hz, 1H, <u>C</u>H$_2$Bn), 4.76 (d, *J* = 11.5 Hz, 1H, <u>C</u>H$_2$Bn), 4.69 (d, *J* = 11.9 Hz, 1H, <u>C</u>H$_2$Bn), 4.67 (d, *J* = 12.1 Hz, 3H, <u>C</u>H$_2$Bn), 4.61 (d, *J* = 11.8 Hz, 1H, <u>C</u>H$_2$Bn), 4.54 (d, *J* = 11.8 Hz, 1H, <u>C</u>H$_2$Bn), 4.44 (d, *J* = 12.0 Hz, 1H, <u>C</u>H$_2$Bn), 4.42 – 4.37 (m, 2H, H5, H3'), 4.38 (d, *J* = 12.2 Hz, 1H, <u>C</u>H$_2$Bn), 4.26 – 4.23 (m, 1H, H5'), 4.23 – 4.20 (m, 1H, H4'), 4.10 (t, *J* = 9.3 Hz, 1H, H3), 3.81 (d, *J* = 11.1 Hz, 1H, H1'), 3.75 (dd, *J* = 14.3, 2.6 Hz, 1H, H6'), 3.67 (d, *J* = 11.1 Hz, 2H, H6, H1'), 3.56 (dd, *J* = 9.7, 3.1 Hz, 1H, H2), 3.49 – 3.42 (m, 1H, H6), 3.40 (dd, *J* = 14.4, 7.4 Hz, 1H, H6'), 3.30 (t, *J* = 9.4 Hz, 1H, H4), 2.92 (s, 3H, OMe), 2.91 (s, 3H, OMe).
^{13}C NMR (151 MHz, acetone-d_6)	δ 164.07 (C=O), 139.27, 139.05, 138.95, 138.82, 138.60, 138.43 (C_{quat}, 6x OCH$_2$<u>Ph</u>), 105.60 (C2'), 90.58 (C1), 84.93 (C4'), 82.93 (C3'), 81.45 (C5'), 81.03 (C3), 80.64 (C4), 80.39 (C2), 74.80 (O<u>C</u>H$_2$-Ph), 73.71 (O<u>C</u>H$_2$-Ph), 72.80 (O<u>C</u>H$_2$-Ph), 72.70 (O<u>C</u>H$_2$-Ph), 71.92 (O<u>C</u>H$_2$-Ph), 71.61 (O<u>C</u>H$_2$-Ph), 70.64 (C1'), 70.61 (C5), 53.85 (C6'), 52.77 (C6), 38.80 (Me), 37.17 (Me).
HRMS ESI	Calc. for $C_{114}H_{124}N_4O_{20}$ $[M+Na]^+$: 1891.8707, found: 1891.8722.

Evaluation of anion influence on coupling between preisolated diisocyanate-sucrose **2** and diamino-sucrose **1**

Trial 1 – The chloride-free solution of diisocyanate-sucrose **2** (*this reaction was carried out under an argon atmosphere*) Triphosgene (23 mg, 0.08 mmol) was carefully added to a cooled -10 °C solution of diamino-sucrose **1** (100 mg, 0.113 mmol) in CH_2Cl_2 (30 mL) containing Et_3N (90 µL, 0.678 mmol). The reaction was allowed to reach r.t. and stirred for another hour. Water (10 mL) was added, the organic layer was separated, washed with water (4x10 mL), dried over magnesium sulfate, and concentrated to give crude di-isocyanate which was re-dissolved in THF (30 mL). To this chloride-free solution, second portion of **1** (100 mg, 0.113 mmol) in THF (30 mL) was added at r.t. *via* syringe within 30 min. The mixture was stirred overnight, concentrated, and the resulting oily residue was purified by chromatography with EA:hexanes (3:7; v/v) to give two regioisomers **3a** (43 mg, 21%) and **3b** (40 mg, 19%) in the form of white amorphous foam.

Trials 2 and 3 – Addition of TBACl or Et_3N·HCl salts to the chloride-free solution of **2**

The solution of diisocyanate-sucrose **2** in THF (15 mL) was prepared as above in Trial 1 using triphosgene (12.6 mg, 0.04 mmol), diamino-sucrose **1** (53 mg, 0.06 mmol), and Et_3N (50 µL, 0.36 mmol). To this solution was added successively either TBACl (100 mg, 0.36 mmol, 6.0 equiv) or Et_3N·HCl (50 mg, 0.36 mmol, 6.0 equiv) and the second portion of **1** (53 mg, 0.06 mmol) in THF (10 mL) at r.t. The mixture was stirred overnight, concentrated, and the resulting oily residue was purified by a preparative TLC (EA:hexanes 1:1 v/v) to give two regioisomers **3a** (TBACl: 47 mg, 43%; Et_3N·HCl: 45 mg, 41%) and **3b** (TBACl: 45 mg, 41%; Et_3N·HCl: 43 mg, 39%) in the form of white amorphous foam.

2. Copies of NMR spectra

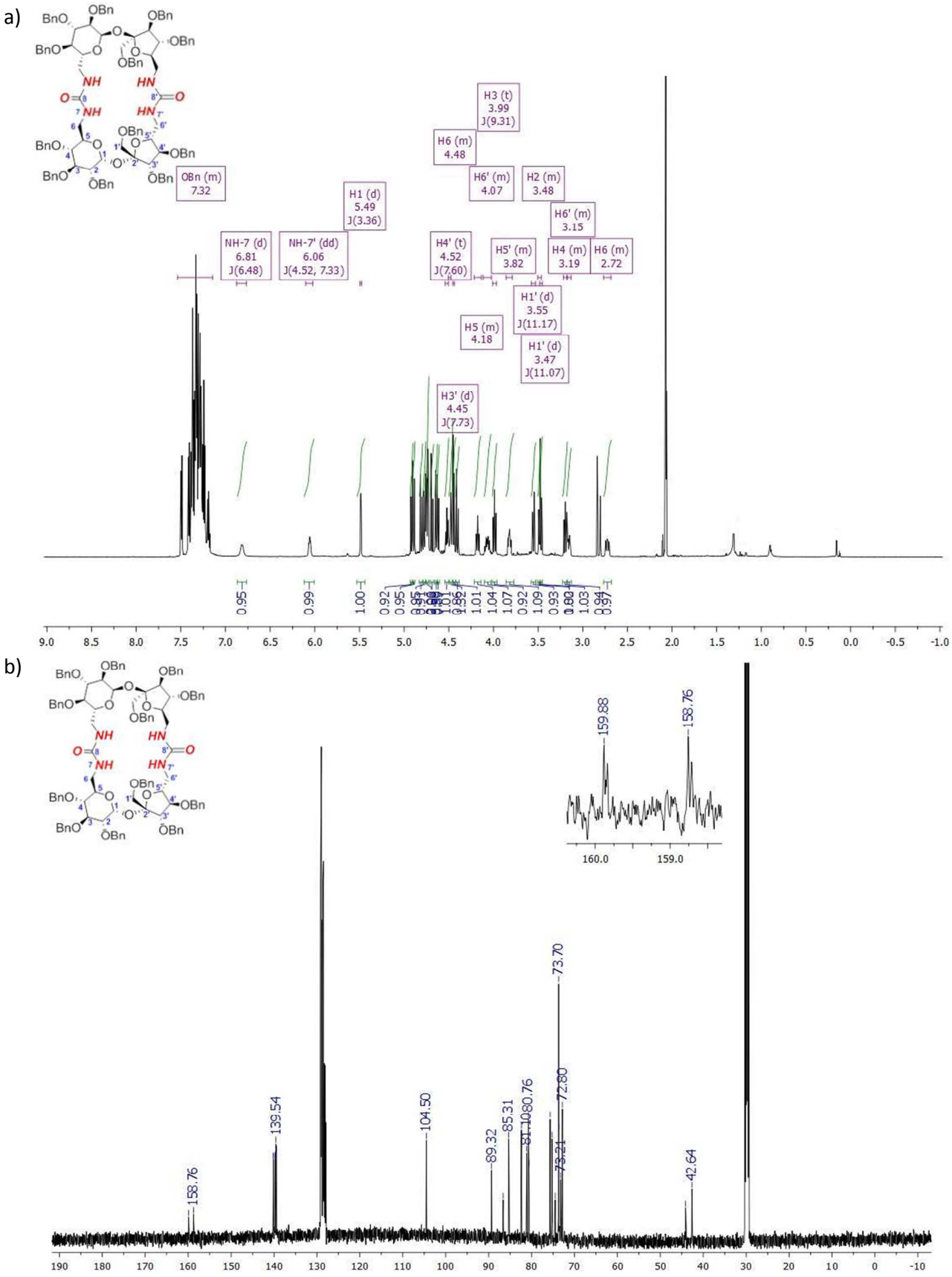


Fig. S1. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound **3a** in acetone-d_6.

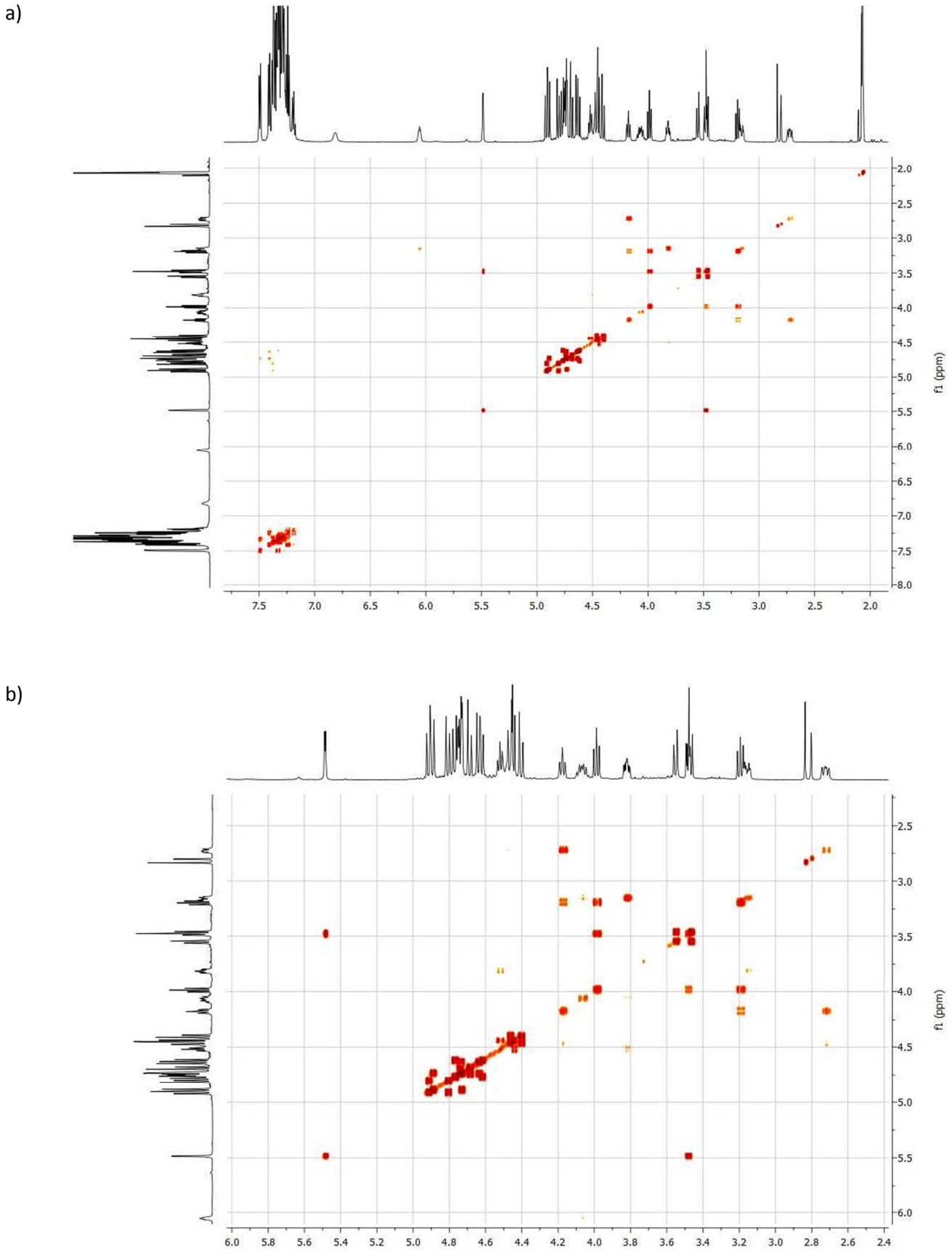


Fig. S2. COSY (^{1}H-^{1}H) spectra of compound **3a** in acetone-d_6.

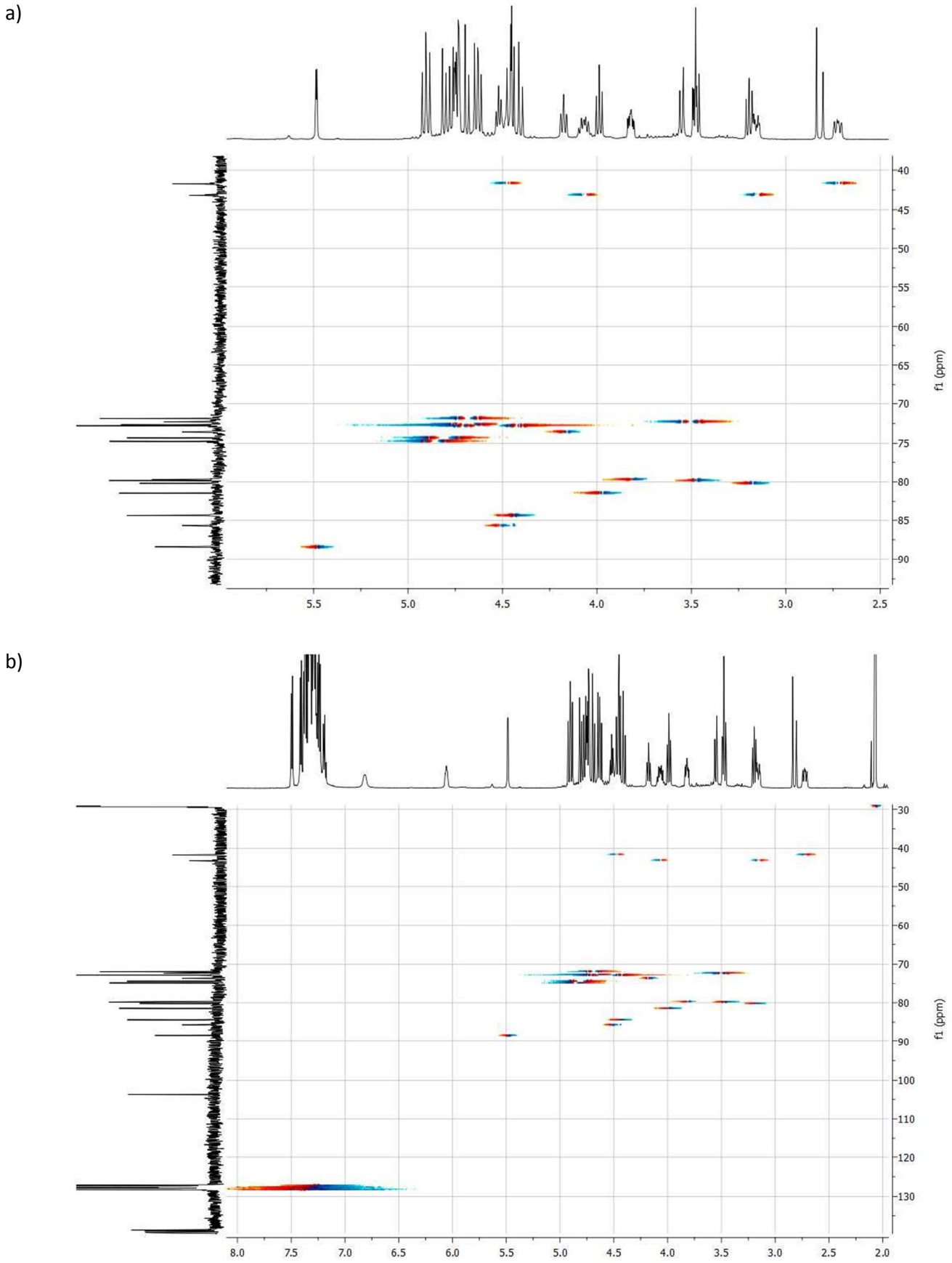


Fig. S3. HSQC (^{1}H-^{13}C) spectra of compound **3a** in acetone-d_6.

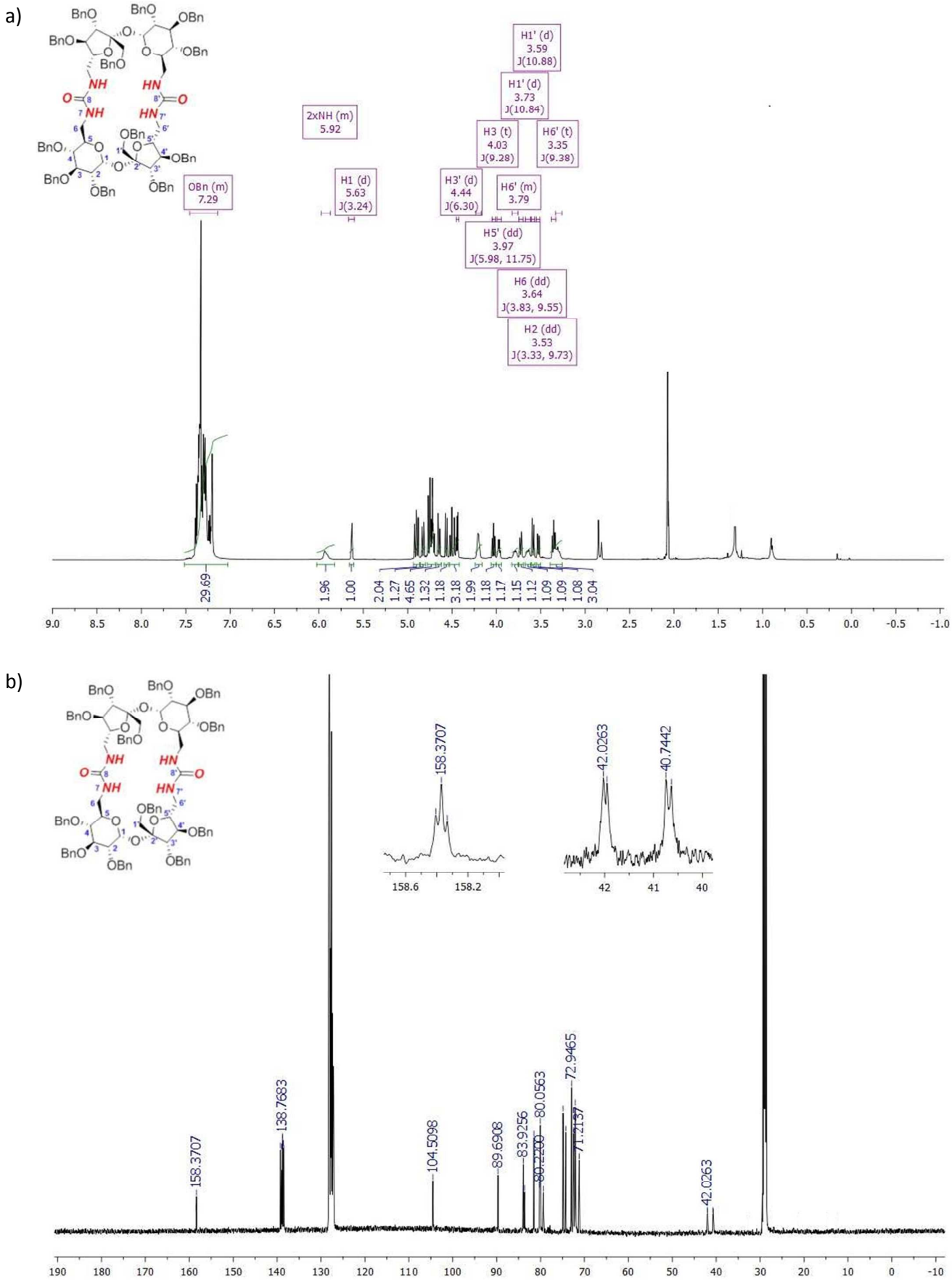
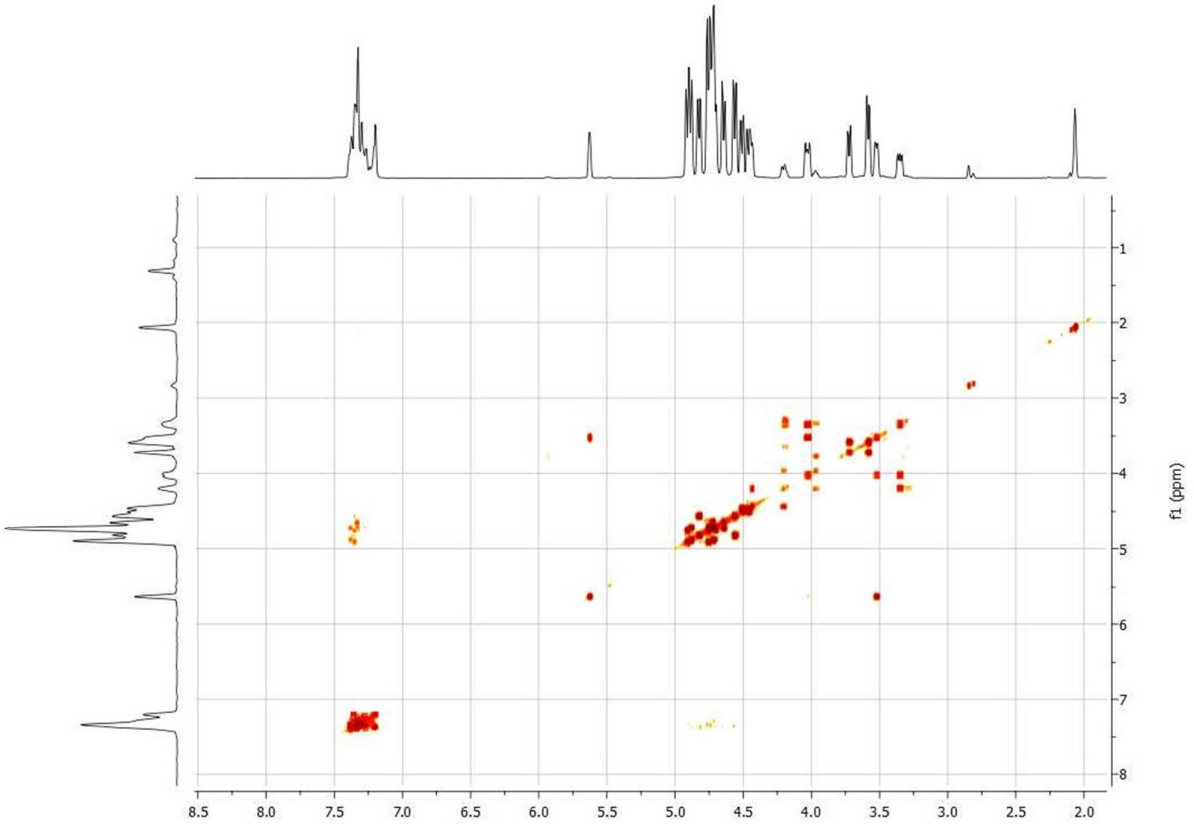


Fig. S4. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound **3b** in acetone-d_6.

a)



b)

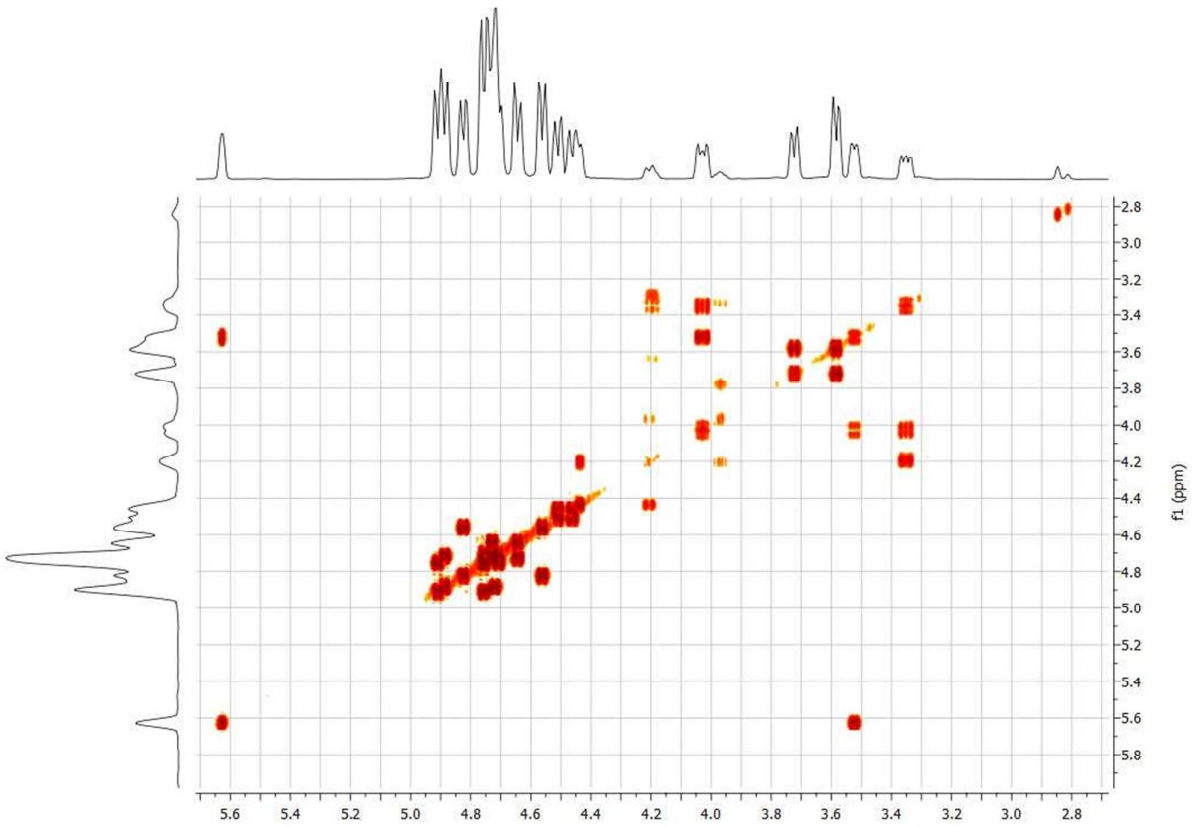


Fig. S5. COSY (^{1}H-^{1}H) spectra of compound **3b** in acetone-d_6.

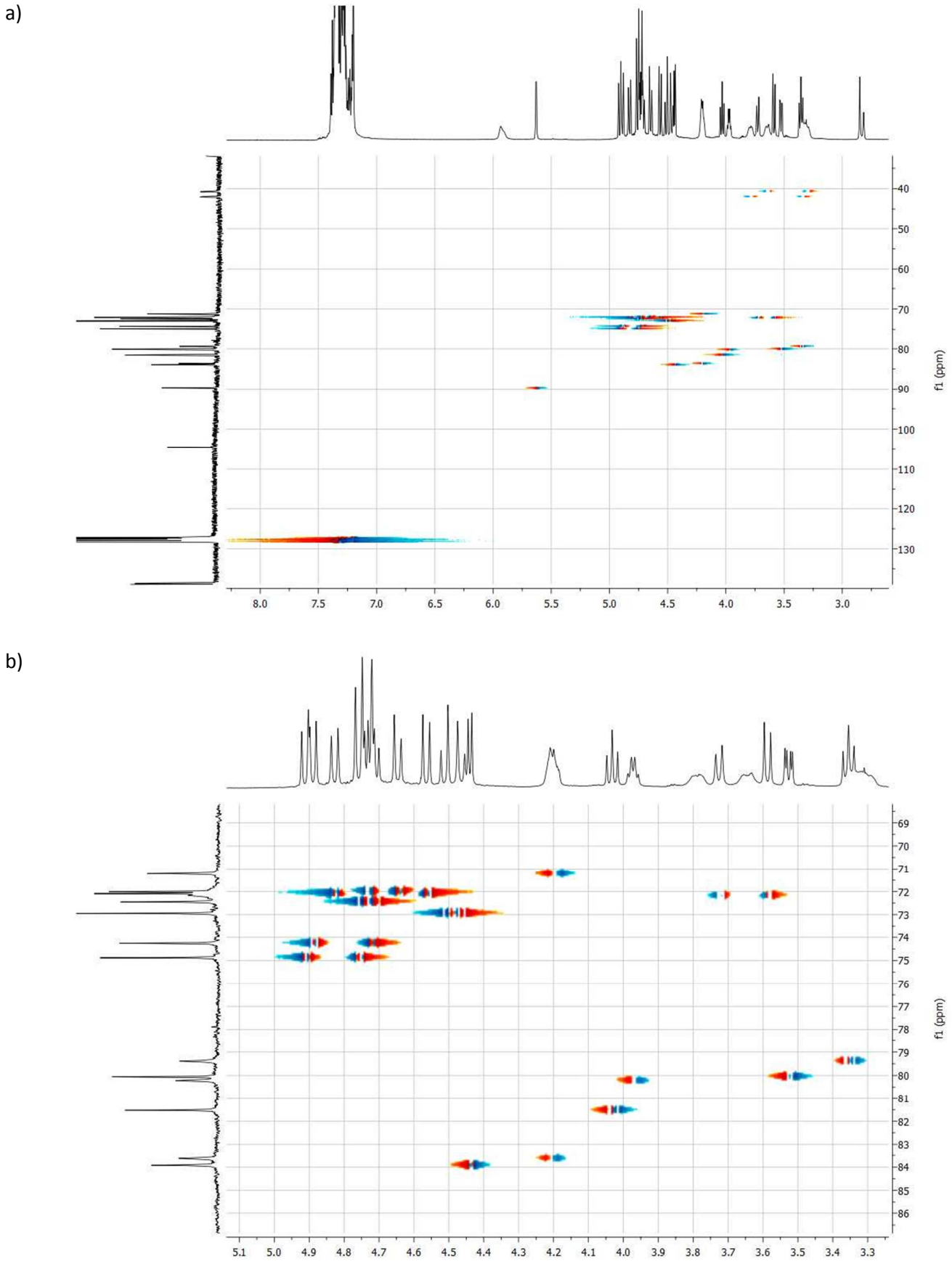


Fig. S6. HSQC (^{1}H-^{13}C) spectra of compound **3b** in acetone-d_6.

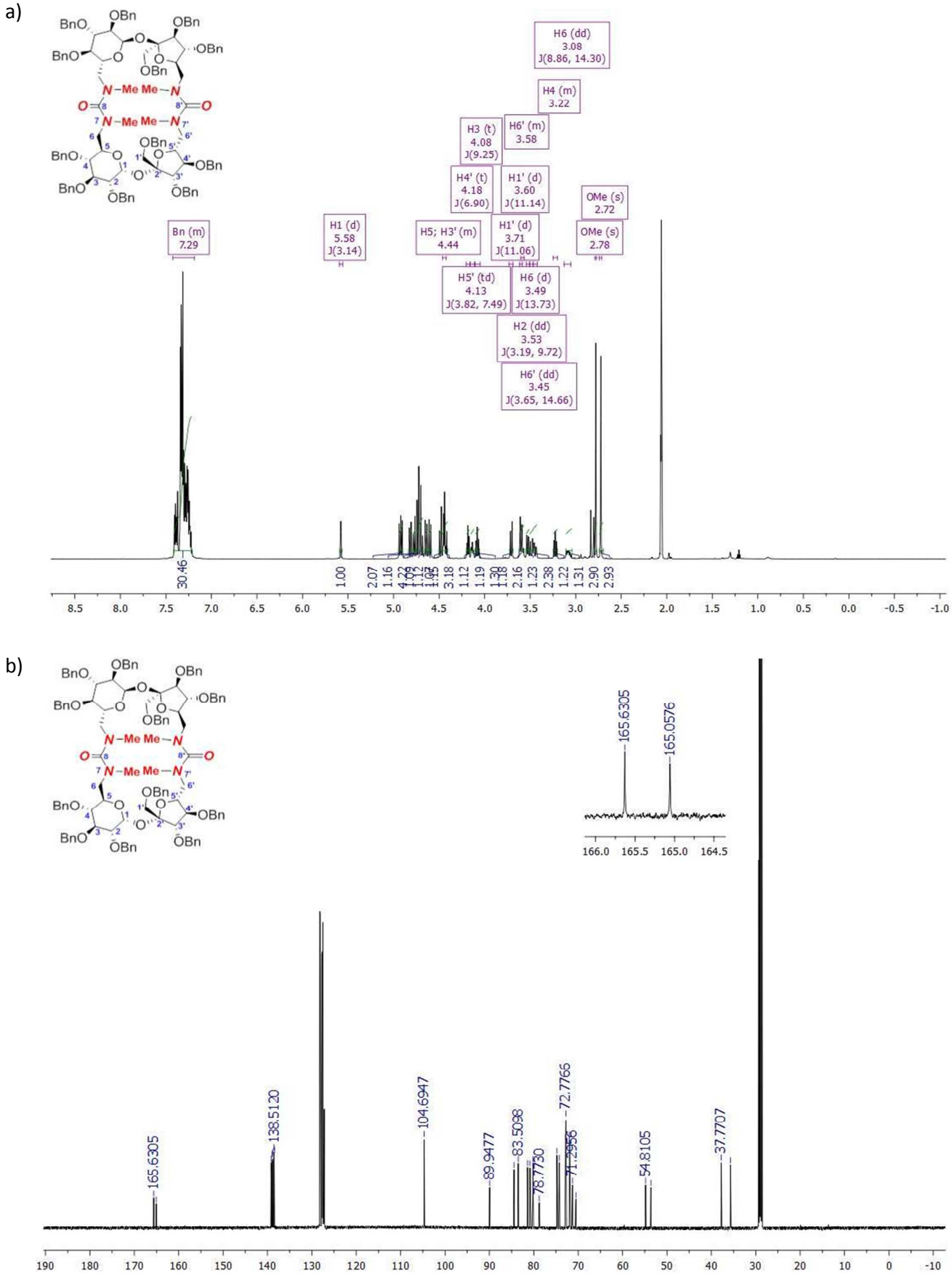
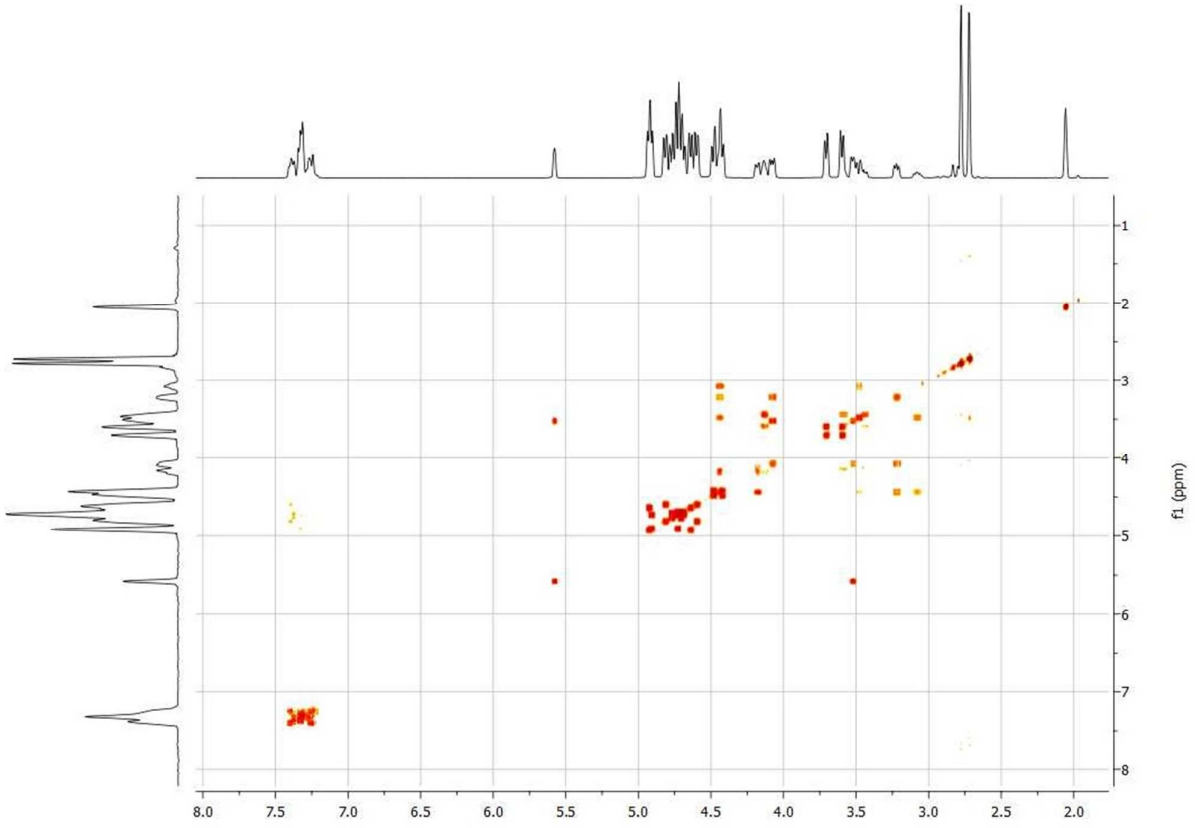


Fig. S7. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound **4a** in acetone-d_6.

a)



b)

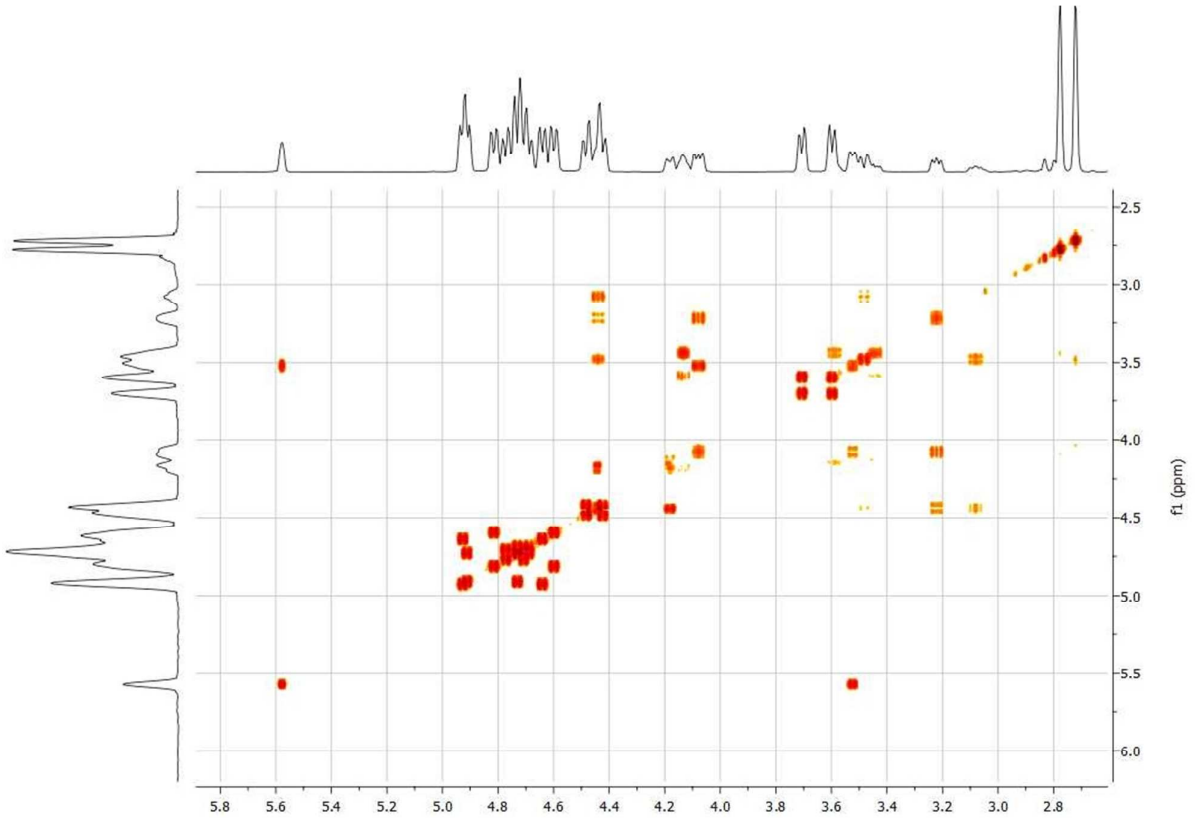


Fig. S8. COSY (^{1}H-^{1}H) spectra of compound **4a** in acetone-d_6.

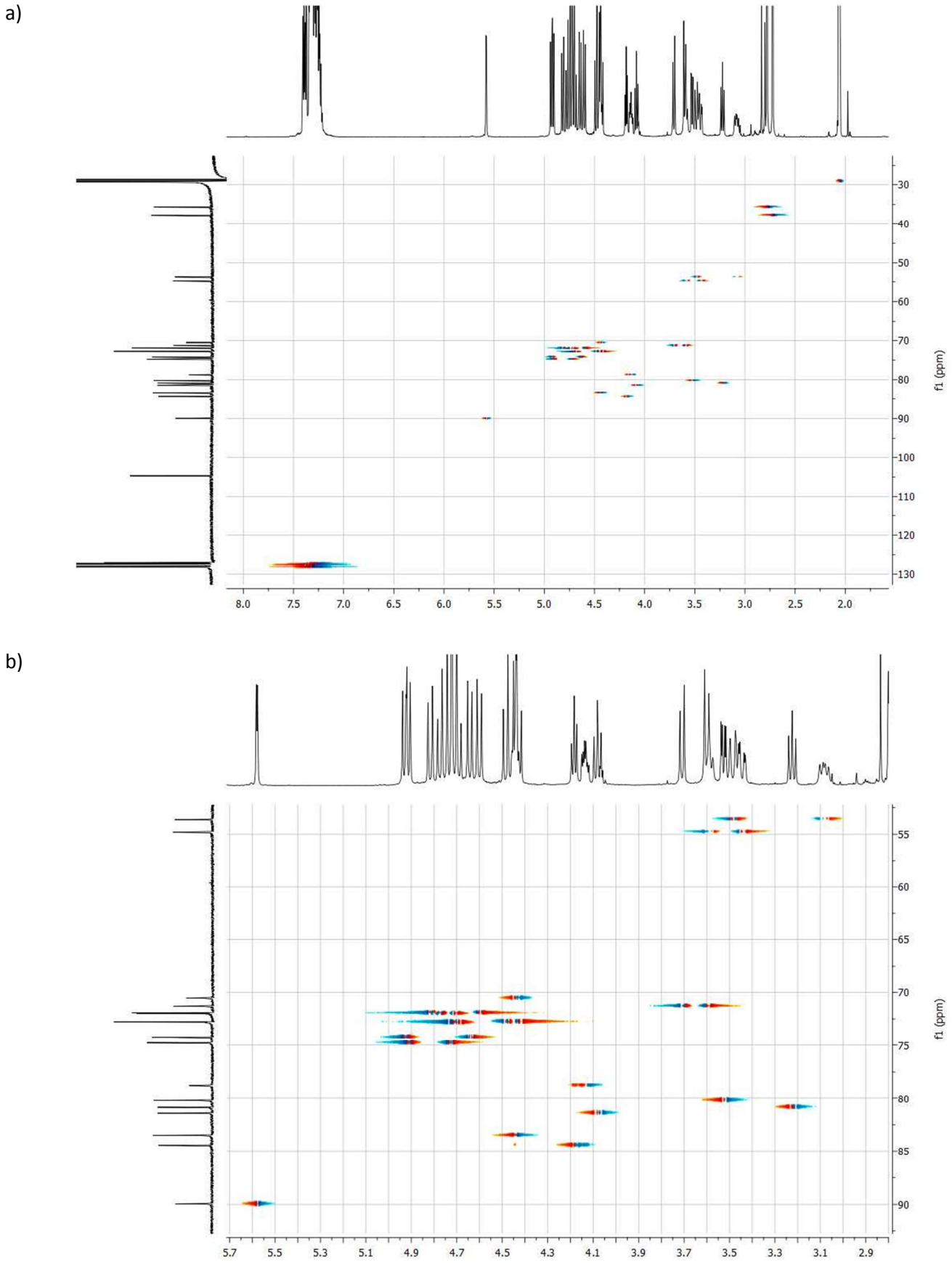


Fig. S9. HSQC (^{1}H-^{13}C) spectra of compound **3a** in acetone-d_6.

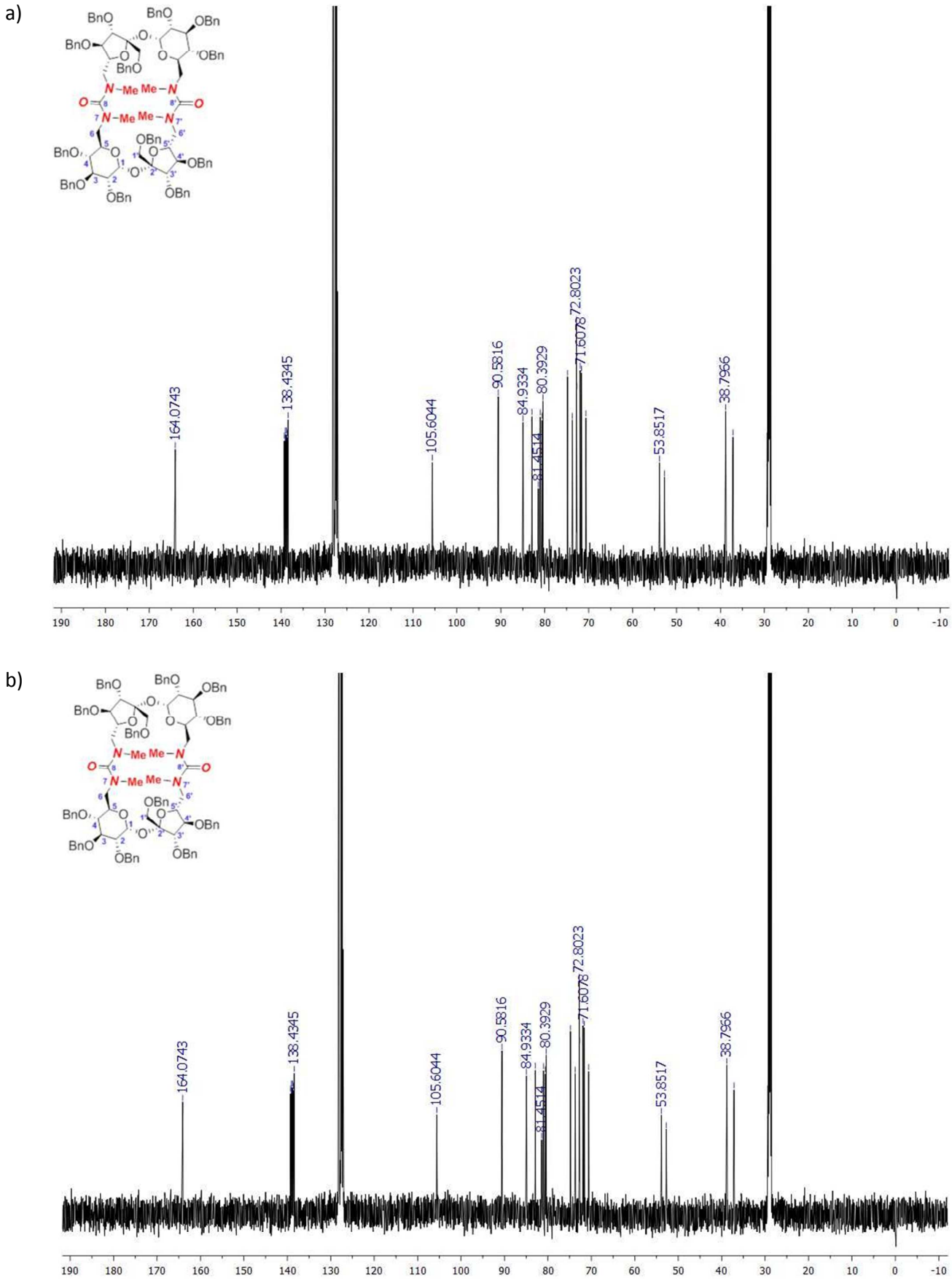
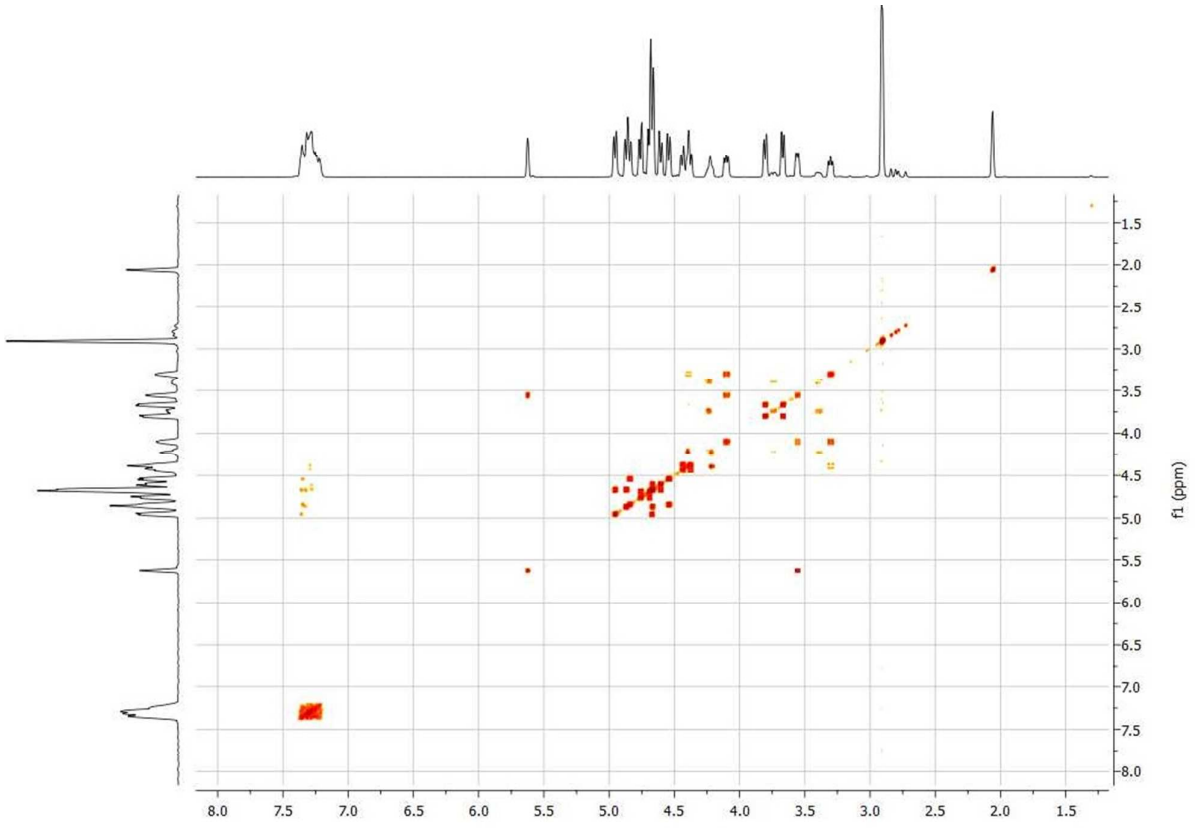


Fig. S10. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound **4b** in acetone-d_6.

a)



b)

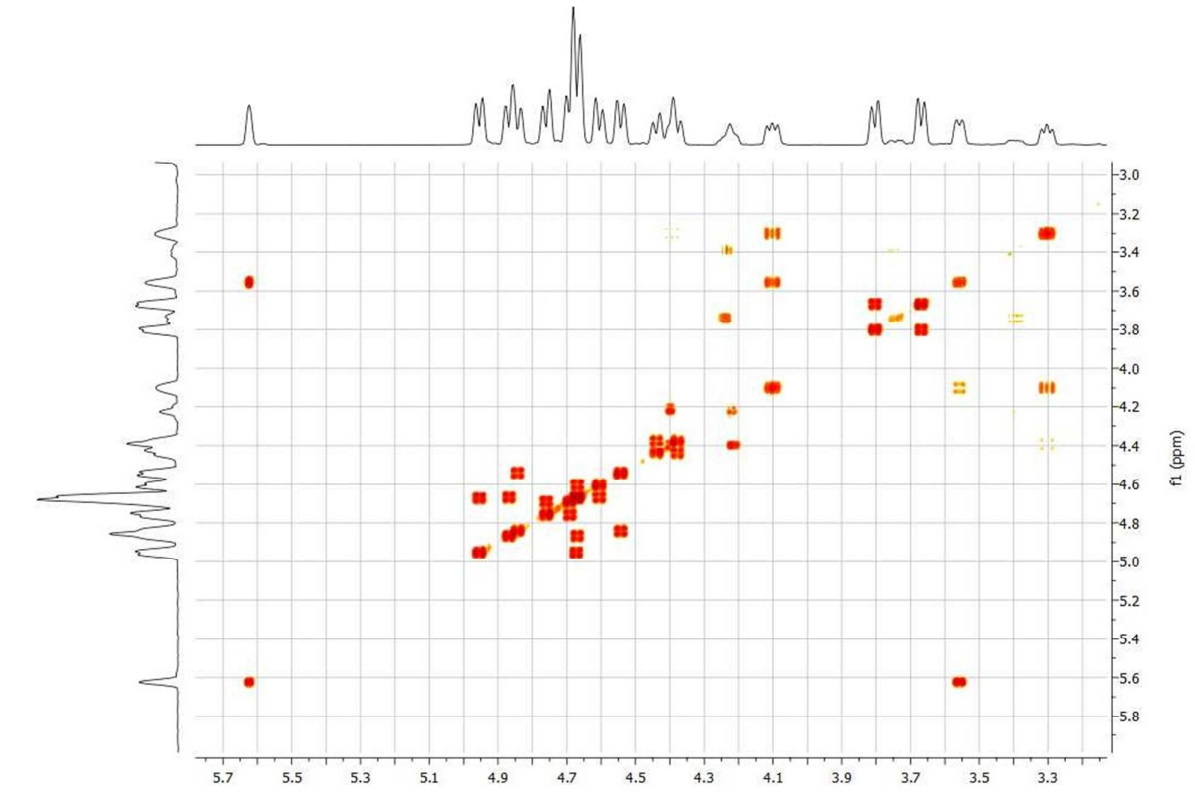


Fig. S11. COSY (^{1}H-^{1}H) spectra of compound **4b** in acetone-d_6.

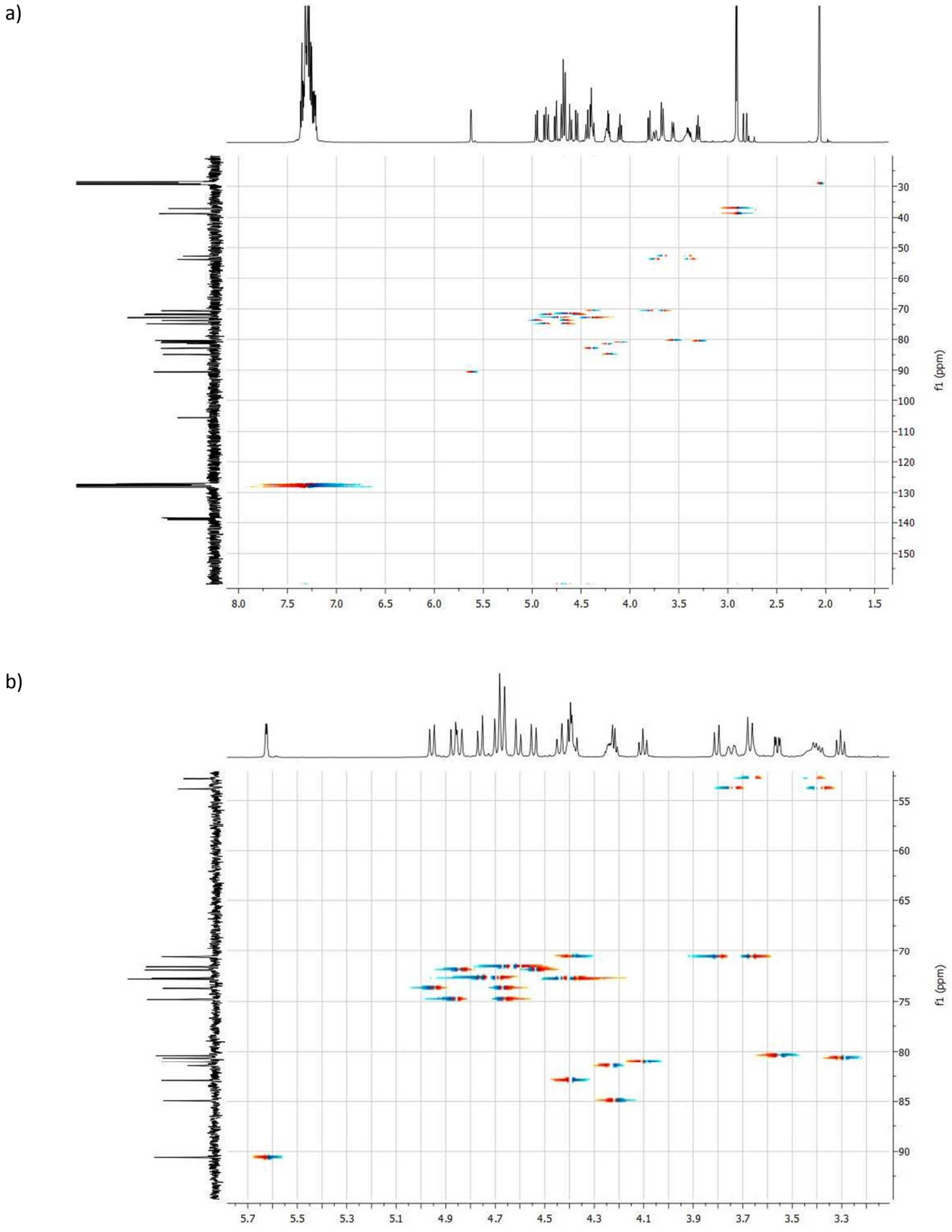


Fig. S12. HSQC (^{1}H-^{13}C) spectra of compound **4b** in acetone-d_6.

3. Titration experiments

3.1. General remarks

The tetrabuthylammonium salts of: chloride (TBACl), dihydrogenphosphate ($TBAH_2PO_4$), acetate ($TBAMeCO_2$), and benzoate ($TBAPhCO_2$) were commercially available and were used as received. The MeCN-d_3 of 99.80% isotopic purity was used as a deuterated solvent.

In order to determine the binding mode of receptors **3**, we initially examine two possible scenarios, *i.e.* simple 1:1 HG and fully-relaxed 1:1 + 1:2 H:G binding models (H – host, G – guest). A simultaneous nonlinear curve fitting for all protons belonging to the corresponding receptor and a TBA salt, and assuming a suitable binding model was carried out with the HypNMR 2008 Software.[1-3] This procedure provides more reliable K_a's (so-called 'global association constant") than fitting of the experimental data to a single chemical signal changes.[4, 5] Possible self-association phenomena involving the receptors **3** were excluded by additional dilution experiments (data not included).

For all titrations, except **3b** + $TBA^+H_2PO_4^-$, this procedure allows for the determination of the corresponding association constants (K_a's) and maximal chemical shift changes ($\Delta\delta_{max}$) of the protons belonging to either receptor or salt.

Although, a 1:1 + 1:2 binding model for the titrations of **3** with chloride gave better fit, the distribution of residuals is similar as in the 1:1 binding model.

In two cases, *i.e.* **3a** + $TBA^+H_2PO_4^-$ and **3b** + $TBA^+H_2PO_4^-$, the fitting of the experimental data to simultaneous 1:1 HG + G_2 binding model was significantly better than fitting to either 1:1 or 1:1 + 1:2 H:G binding models, respectively. The model assuming dimerization of $H_2PO_4^-$ is supported by the literature data[6] and observation, that chemical shift for the exchangeable protons of water and phosphate,[$] shows a concentration dependent behavior, *i.e.* it experiences a downfield resonance shift as the concentration of the phosphate salt increases (Fig. S13).

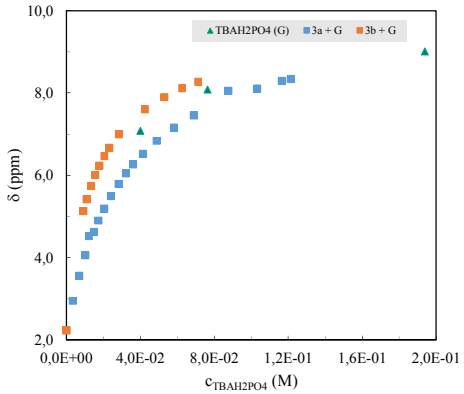


Figure S13. Experimental chemical shift changes for the exchangeable protons of water and phosphate in MeCN-d_3 at 298K: pure $TBAH_2PO_4$ (G) (green triangles), **3a** + G (blue squares), **3b** + G (orange squares).

The experimental binding isotherm for **3b**/$H_2PO_4^-$ complex is steeper than the corresponding binding isotherms recorded for either pure $TBA^+H_2PO_4^-$ or **3a**/$H_2PO_4^-$ complex, respectively, suggesting that self-dimerization of a $H_2PO_4^-$ anion is more pronounced in the former case. In other words, the K_{dim} should be higher for **3b** than for **3a** and pure $TBA^+H_2PO_4^-$, and such assumption is actually in accordance with the fitted binding constants (K_{dim} = 78 vs 3 M^{-1} for **3b** and **3a**, respectively, Tab. S1 entries 15 and 18). In conclusion, this clearly implies that addition of both studied macrocyclic sucrose-derived receptors **3a** and **3b** considerably influences the dimerization equilibrium of dihydrogenphosphate anion.

From steric considerations one can assume, that twelve benzyl substituents installed in each of receptors **3a** and **3b** generate steric hindrance effect on anion binding, which in principle disfavors binding of the second anionic guest.

[$] Many interconvertible forms of phosphate are possible, *e.g.* $H_2PO_4^-$ and HPO_4^{2-}, $(H_2PO_4)_2^{2-}$, etc.

In addition, rigidity of the macrocyclic scaffold and close proximity of two internally H-bonded urea groups in receptors **3**, allows for the assumption that simultaneous binding of the second anion (*i.e.* 1:1 + 1:2 H:G model) is rather strongly limited in these systems, *i.e.* receptors **3** are able to bind only one anion, either in a cooperative or non-cooperative fashion. This assumption, in particular for titrations of **3** with carboxylates, is supported by the comparable values of the chemical shift changes ($\Delta\delta_{max}$) for urea and anomeric sugar protons for both plausible 1:1 and 1:1+1:2 HG binding models (compare Tab. S3, entries 5 vs 6, 7 vs 8, 9 vs 10, and 11 vs 12).

Table S1. Titration details, global stability constants K_a (M^{-1}), and selected maximum signal shifts ($\Delta\delta_{max}$) of urea and CH anomeric protons for receptors **3a** and **3b** with various anions in MeCN-d_3 at 298 K[a]

Entry	Host	Guest[b]	c_{Host} (M)	c_{Guest} (M)	Binding model (H:G)	K_a (M^{-1})	$\Delta\delta_{max}$ (ppm)		
							NH■	NH▲	CH■ (dublet)
1	**3a**	Cl^-	0.0107	0.2900	1:1	259±3	1.81	0.40	0.09
2					1:1 + 1:2	483±38 (12±4)	2.02 [c]	0.43 [c]	0.08 [c]
3	**3b**	Cl^-	0.0100	0.2479	1:1	386±5	1.52	1.44	0.30
4					1:1 + 1:2	617± 2 (12±1)	1.64 [c]	1.56 [c]	0.31 [c]
5	**3a**	$MeCO_2^-$	0.0097	0.3188	1:1	2628±51	3.27	0.46	0.16
6					1:1 + 1:2	>10000	3.05 [c]	0.46 [c]	0.16 [c]
7	**3b**	$MeCO_2^-$	0.0105	0.2647	1:1	1390±26	2.26	1.96	0.16
8					1:1 + 1:2	>10000	2.26 [c]	1.95 [c]	0.16 [c]
9	**3a**	$PhCO_2^-$	0.0100	0.2813	1:1	3772±59	3.15	0.55	0.18
10					1:1 + 1:2	>10000	3.14 [c]	0.46 [c]	0.18 [c]
11	**3b**	$PhCO_2^-$	0.0106	0.2544	1:1	2958±96	2.27	2.13	0.10
12					1:1 + 1:2	>10000	2.30 [c]	2.12 [c]	0.21 [c]
13	**3a**	$H_2PO_4^-$	0.0107	0.2843	1:1	126±1	2.83	0.59	0.14
14					1:1 + 1:2	150±9 (5.4±2.5)	2.93 [c]	0.63 [c]	0.11 [c]
15					1:1 HG + G_2	122±1 (2.9±0.3)	2.93	0.61	0.15
16	**3b**	$H_2PO_4^-$	0.0108	0.2551	1:1	184±5	1.74	1.65	0.16
17					1:1 + 1:2	– [d]	N/A	N/A	N/A
18					1:1 HG + G_2	189±4 (78±8)	2.16	2.03	0.19

[a] Determined by the ^{1}H NMR titration experiments and nonlinear curve-fitting using HypNMR 2008 software[3]; [b] anions added as tetrabuthylammonium (TBA) salts; [c] maximal chemical shift ($\Delta\delta_{max}$) for the HG_2 complex; [d] fitting failed.

3.2 Changes of chemical shifts and calculated binding isotherms upon ^{1}H NMR titrations

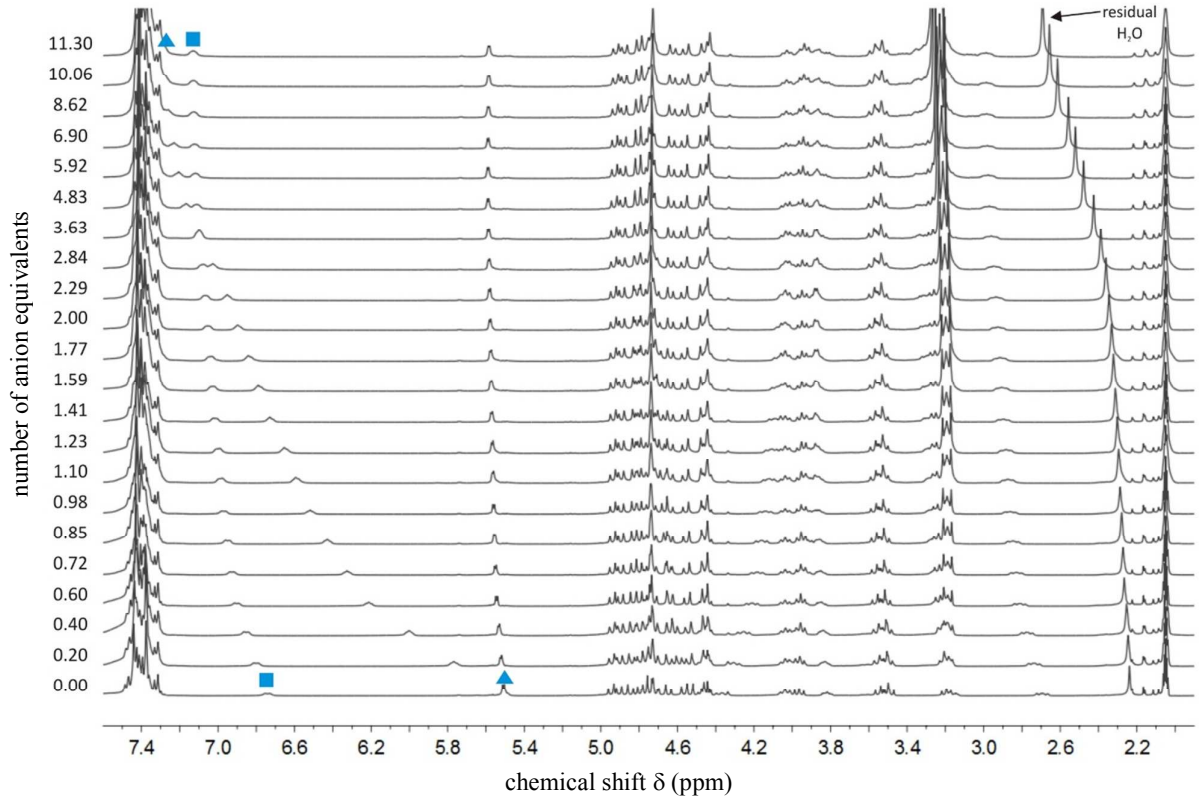


Figure S14. Stacked plots from the ^{1}H NMR titrations of receptor **3a** (in the range of 7.6−1.8 ppm) with TBACl.

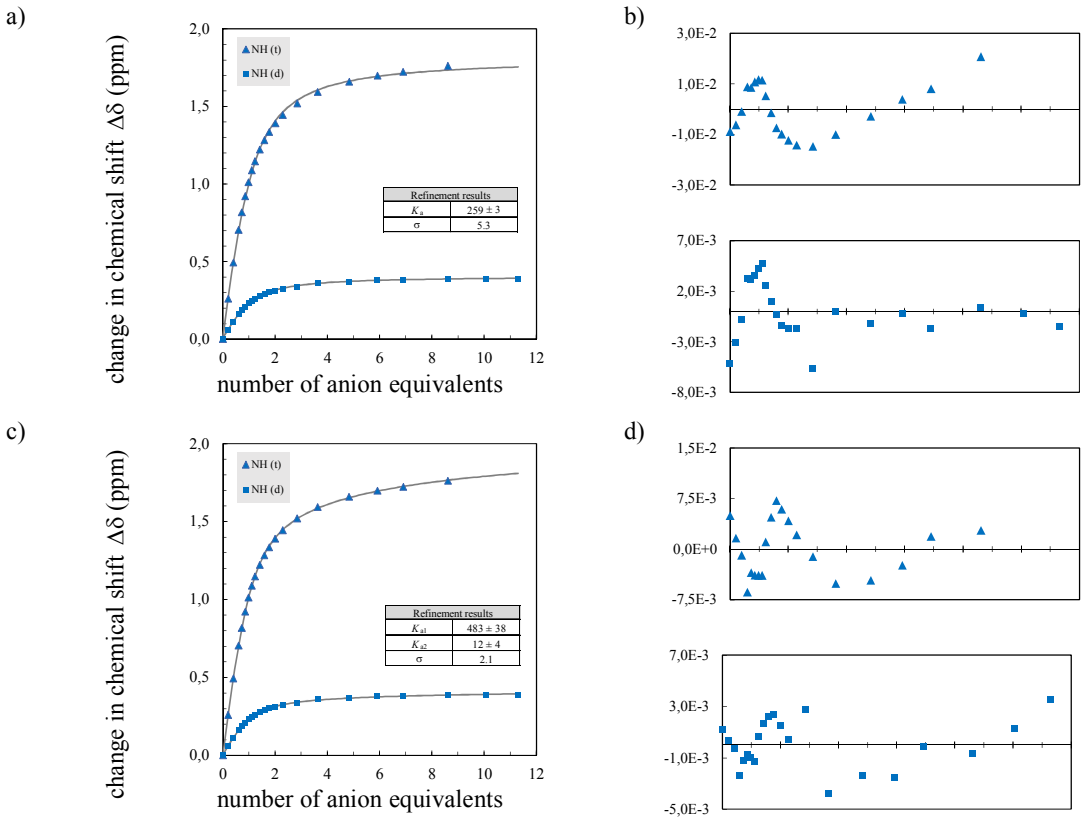


Figure S15. Experimental chemical shift changes (symbols) and calculated binding isotherms (lines) for titration of **3a** with TBACl (a, c) assuming simple 1:1 HG (a) or fully-relaxed 1:1 + 1:2 HG (c) binding model and distribution of residual for corresponding chemical shift for assumed binding model (b, d); H – host; G – guest.

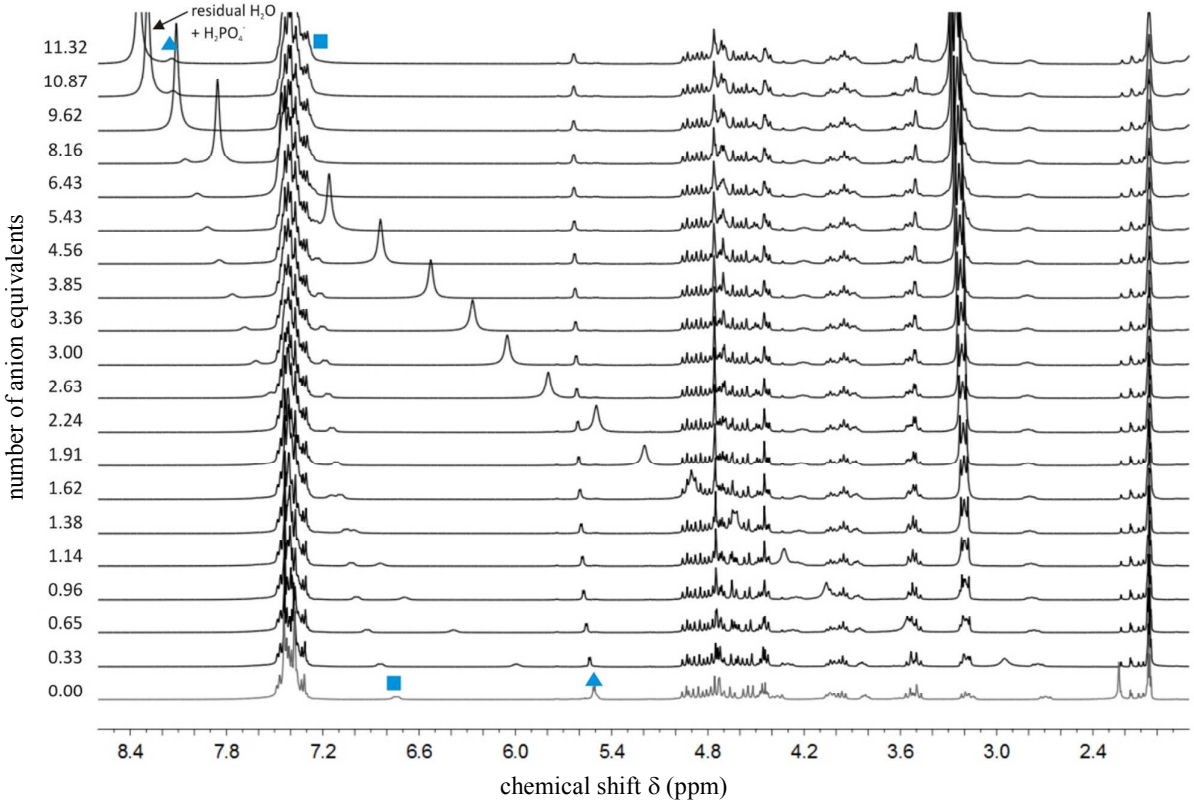


Figure S16. Stacked plots from ^{1}H NMR titrations of receptor **3a** (in the range of 8.6−1.8 ppm) with $TBAH_2PO_4$.

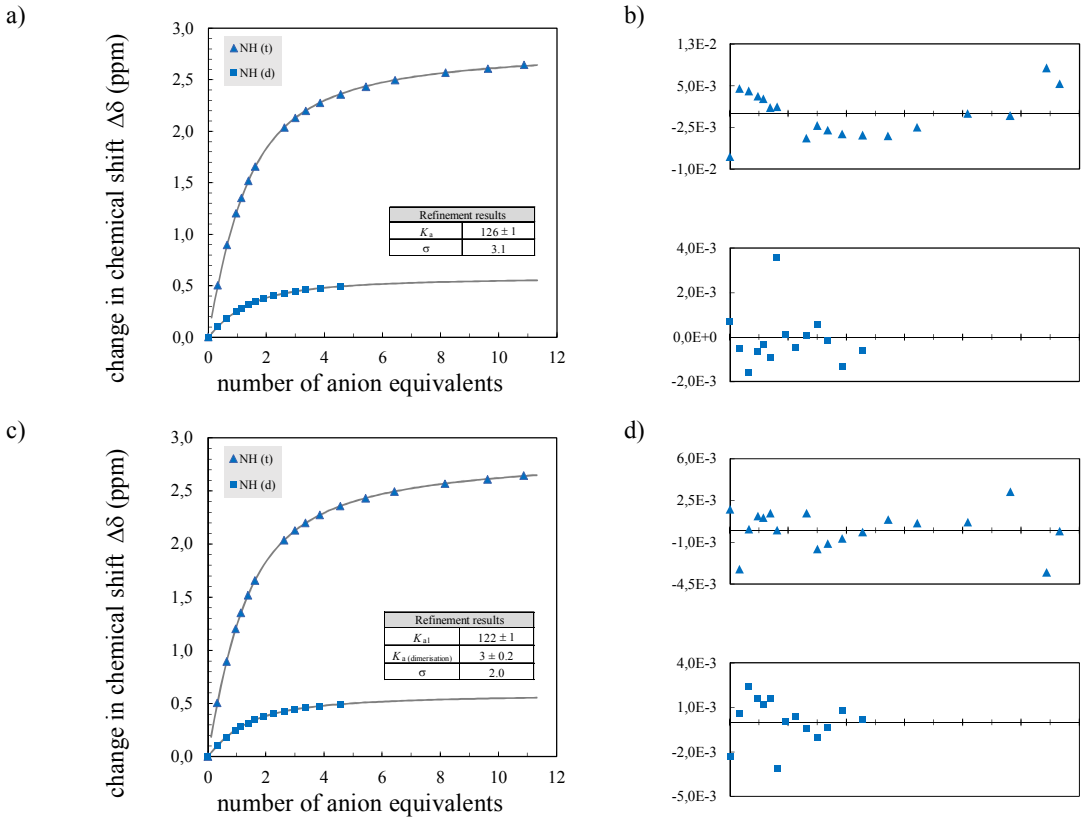


Figure S17. Experimental chemical shift changes (symbols) and calculated binding isotherms (lines) for titration of **3a** with $TBAH_2PO_4$ (a, c) assuming simple 1:1 HG (a) or fully-relaxed 1:1 HG + G_2 (c) binding model (see above for discussion on plausible binding mode of **3a** with this anion) and distribution of residual for corresponding chemical shift for assumed binding model (b, d); H – host; G – guest.

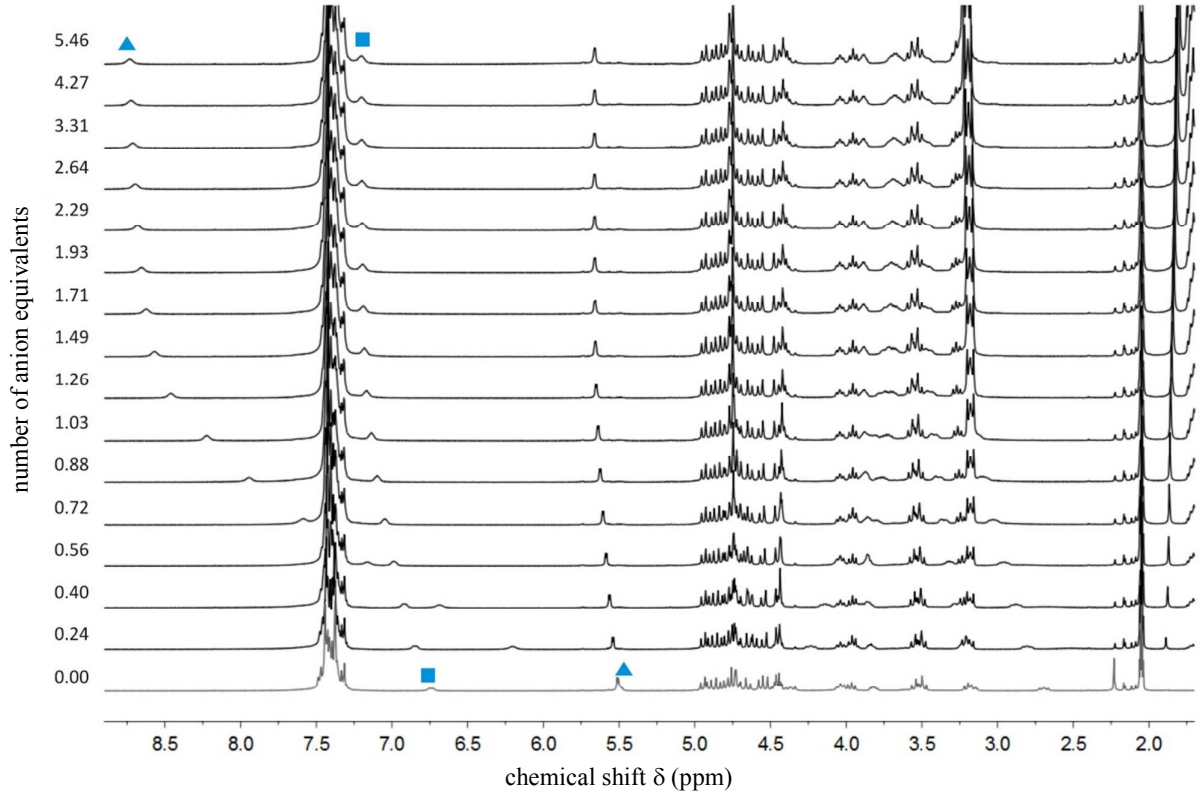


Figure S18. Stacked plots from the ^{1}H NMR titrations of receptor **3a** (in the range of 8.9−1.7 ppm) with $TBAMeCO_2$.

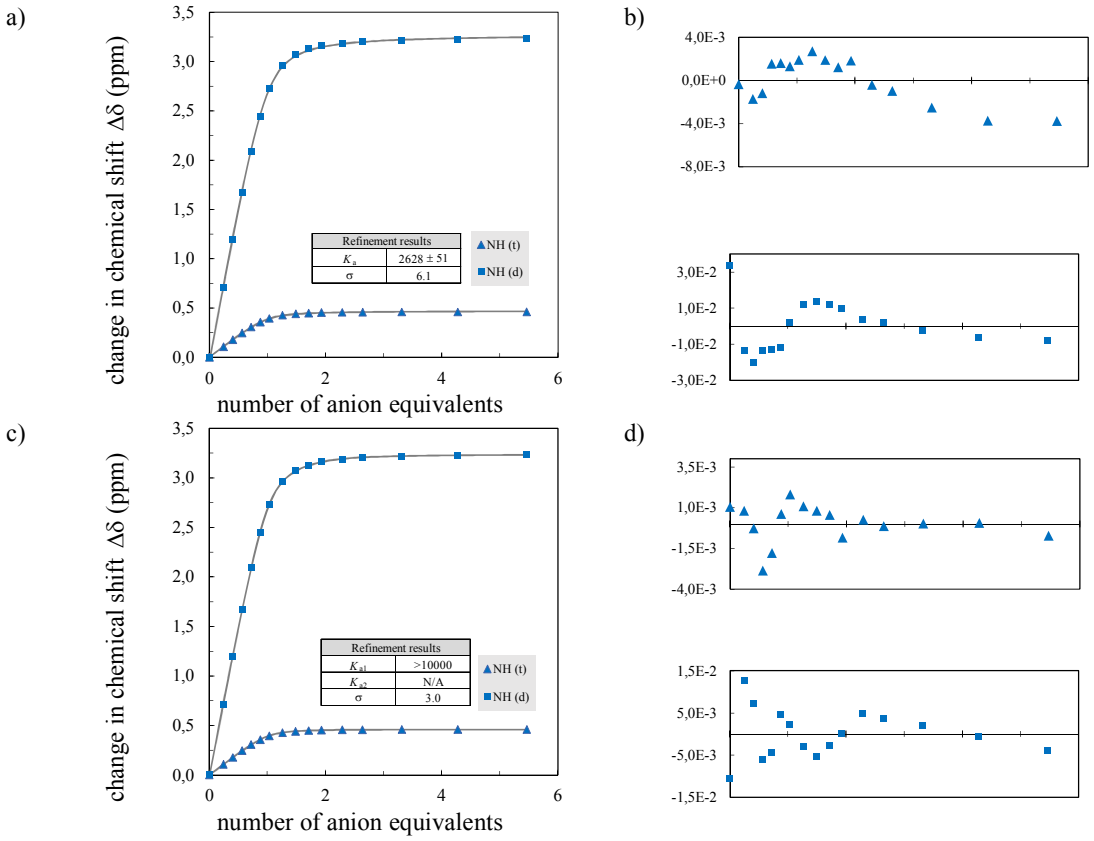


Figure S19. Experimental chemical shift changes (symbols) and calculated binding isotherms (lines) for titration of **3a** with $TBAMeCO_2$ (a, c) assuming simple 1:1 HG (a) or fully-relaxed 1:1 + 1:2 HG (c) binding model and distribution of residual for corresponding chemical shift for assumed binding model (b, d); H – host; G – guest.

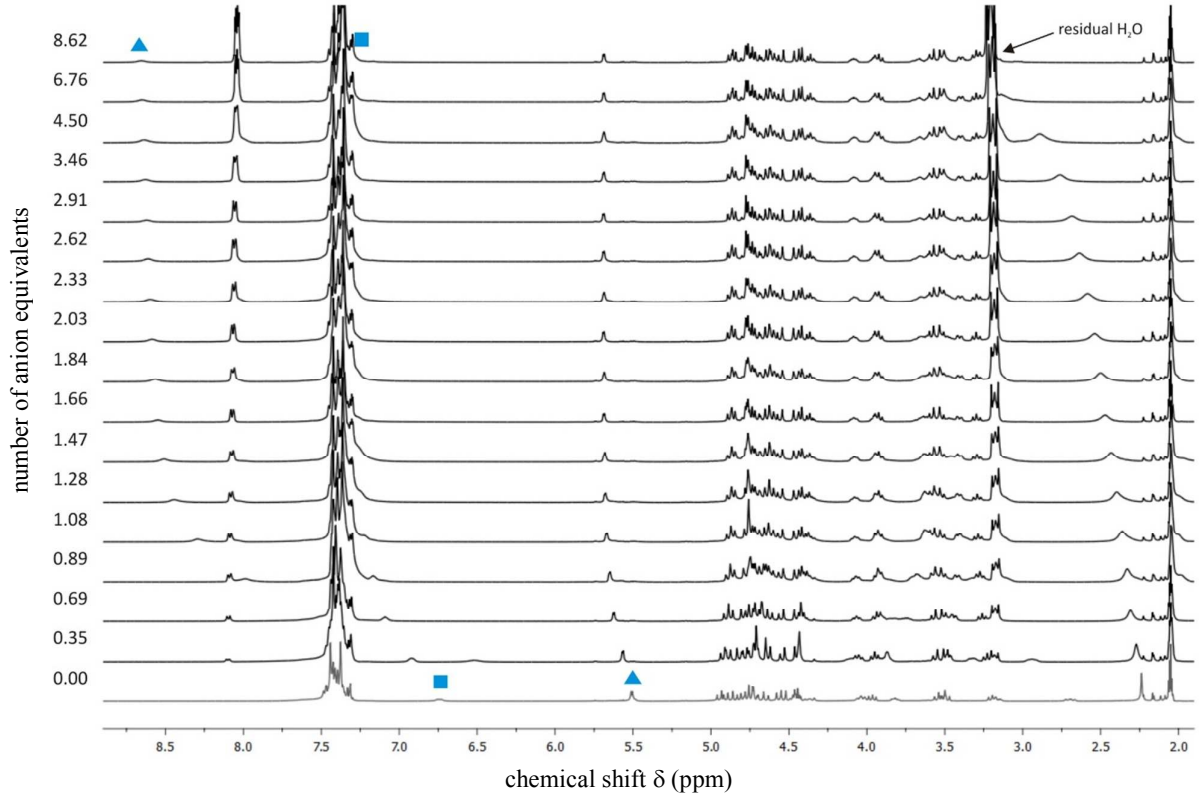


Figure S20. Stacked plots from ^{1}H NMR titrations of receptor **3a** (in the range of 8.9−1.7 ppm) with $TBAPhCO_2$.

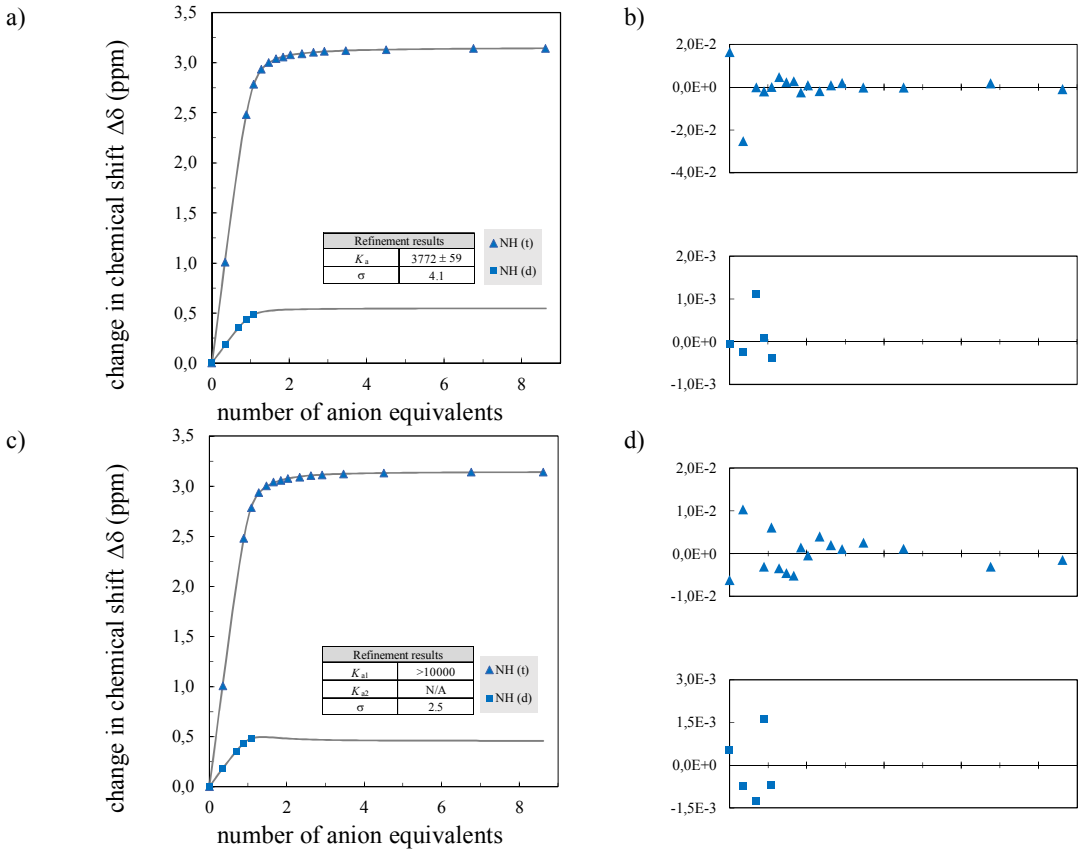


Figure S21. Experimental chemical shift changes (symbols) and calculated binding isotherms (lines) for titration of **3a** with $TBAPhCO_2$ (a, c) assuming simple 1:1 HG (a) or fully-relaxed 1:1 + 1:2 HG (c) binding model and distribution of residual for corresponding chemical shift for assumed binding model (b, d); H – host; G – guest.

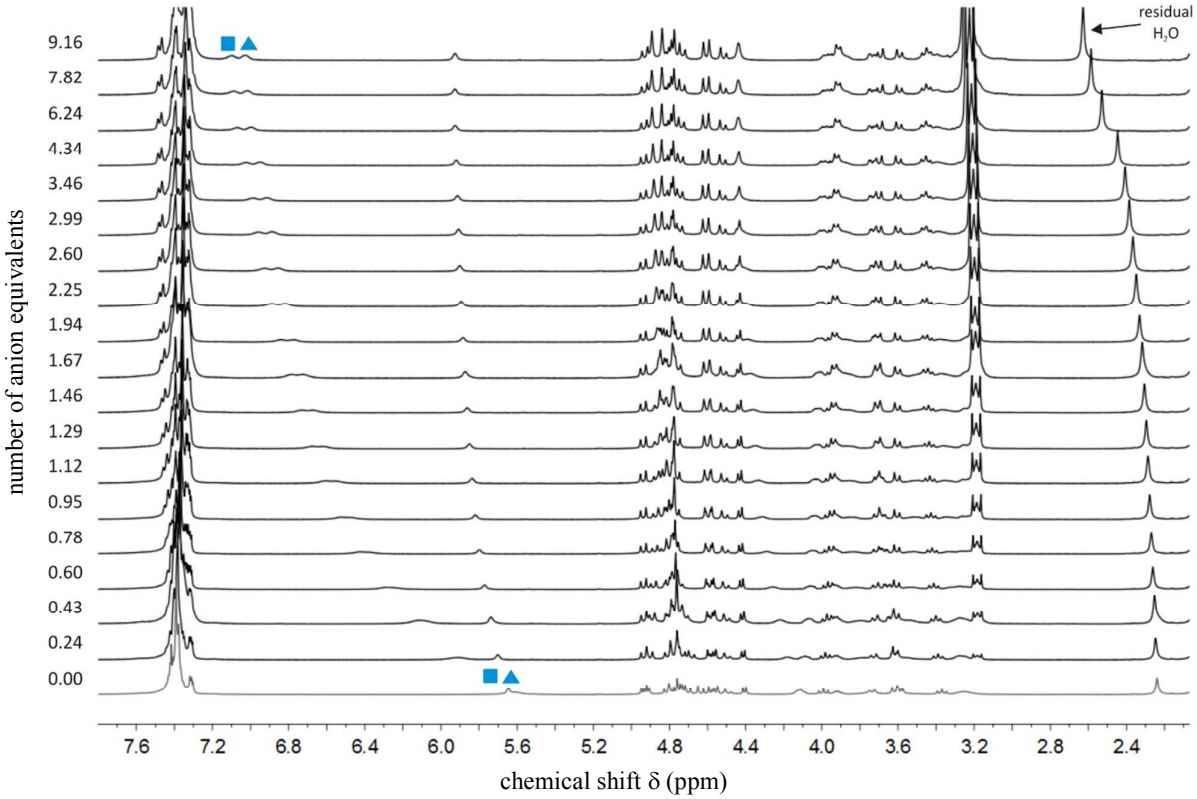


Figure S22. Stacked plots from ^{1}H NMR titrations of receptor **3b** (in the range of 7.8−2.1 ppm) with TBACl.

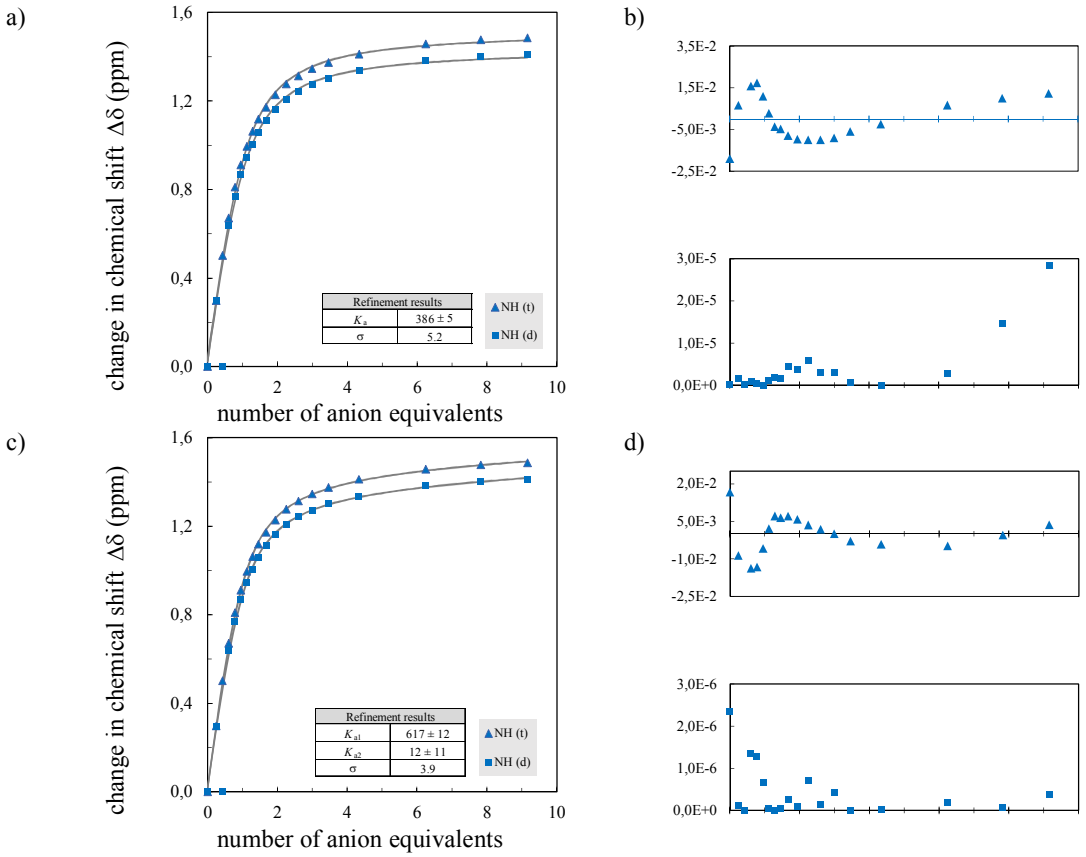


Figure S23. Experimental chemical shift changes (symbols) and calculated binding isotherms (lines) for titration of **3b** with TBACl (a, c) assuming simple 1:1 HG (a) or fully-relaxed 1:1 + 1:2 HG (c) binding model and distribution of residual for corresponding chemical shift for assumed binding model (b, d); H – host; G – guest.

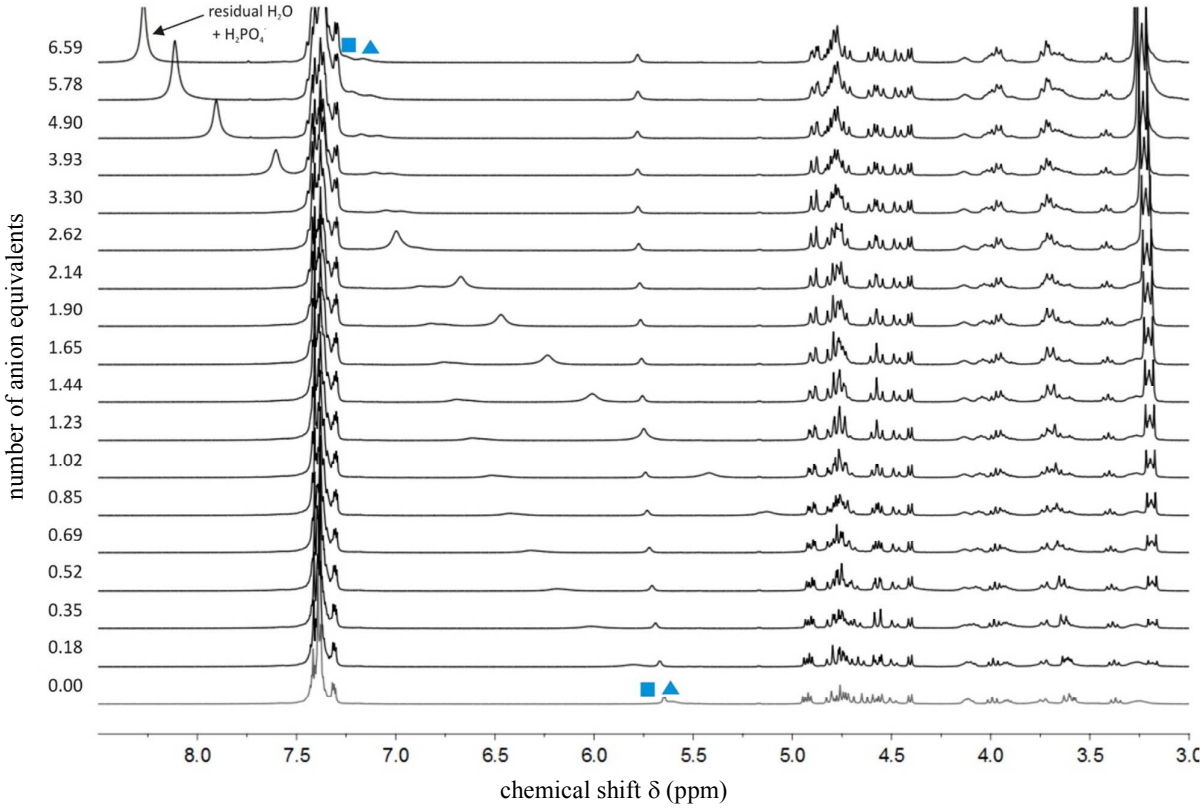


Figure S24. Stacked plots from ^{1}H NMR titrations of receptor **3b** (in the range of 8.5−3.0 ppm) with $TBAH_2PO_4$.

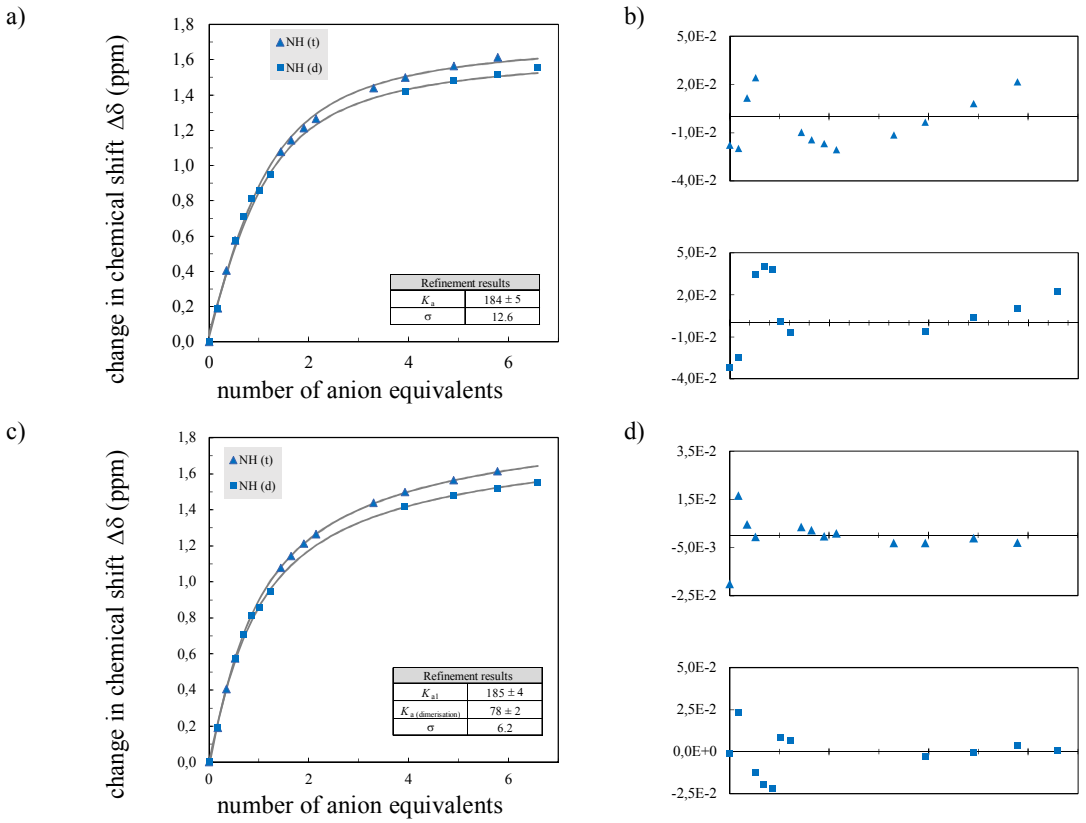


Figure S25. Experimental chemical shift changes (symbols) and calculated binding isotherms (lines) for titration of **3a** with $TBAH_2PO_4$ (a, c) assuming simple 1:1 HG (a) or fully-relaxed 1:1 HG + G_2 (c) binding model (see above for discussion on plausible binding mode of **3b** with this anion) and distribution of residual for corresponding chemical shift for assumed binding model (b, d); H – host; G – guest.

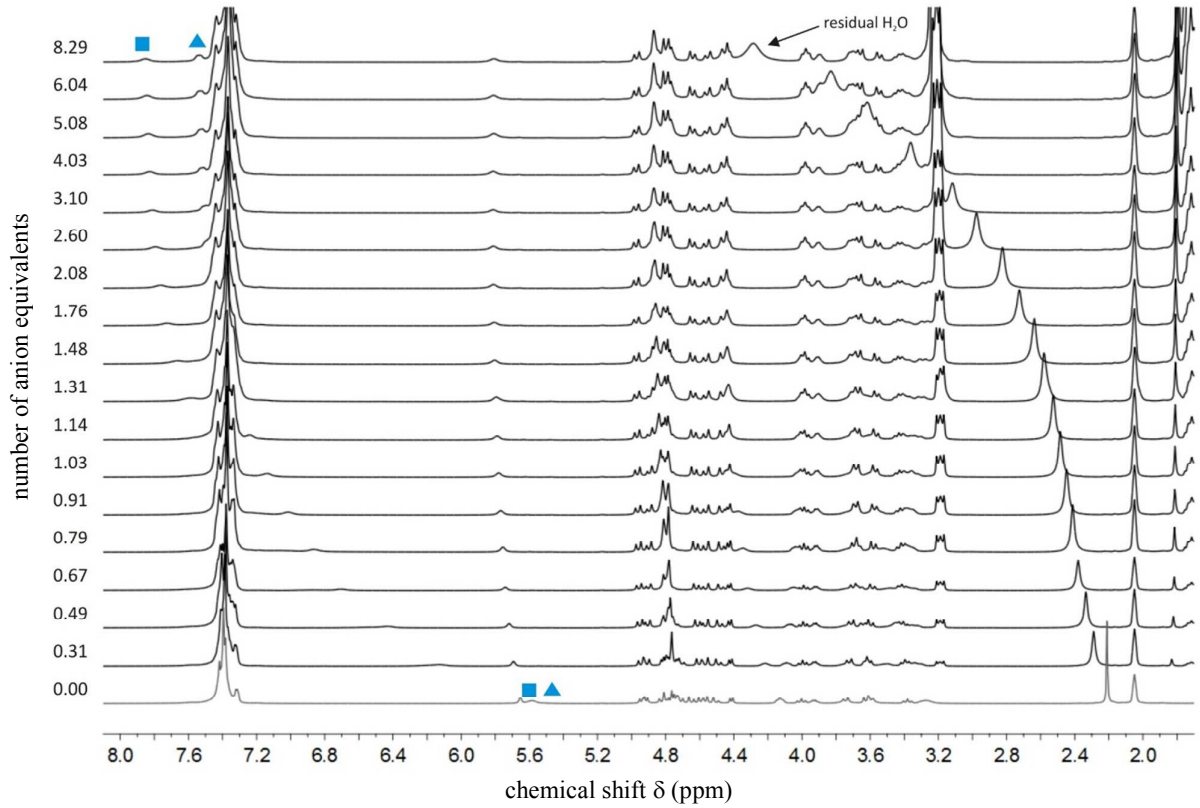


Figure S26. Stacked plots from ^{1}H NMR titrations of receptor **3b** (in the range of 8.1−1.7 ppm) with $TBAMeCO_2$.

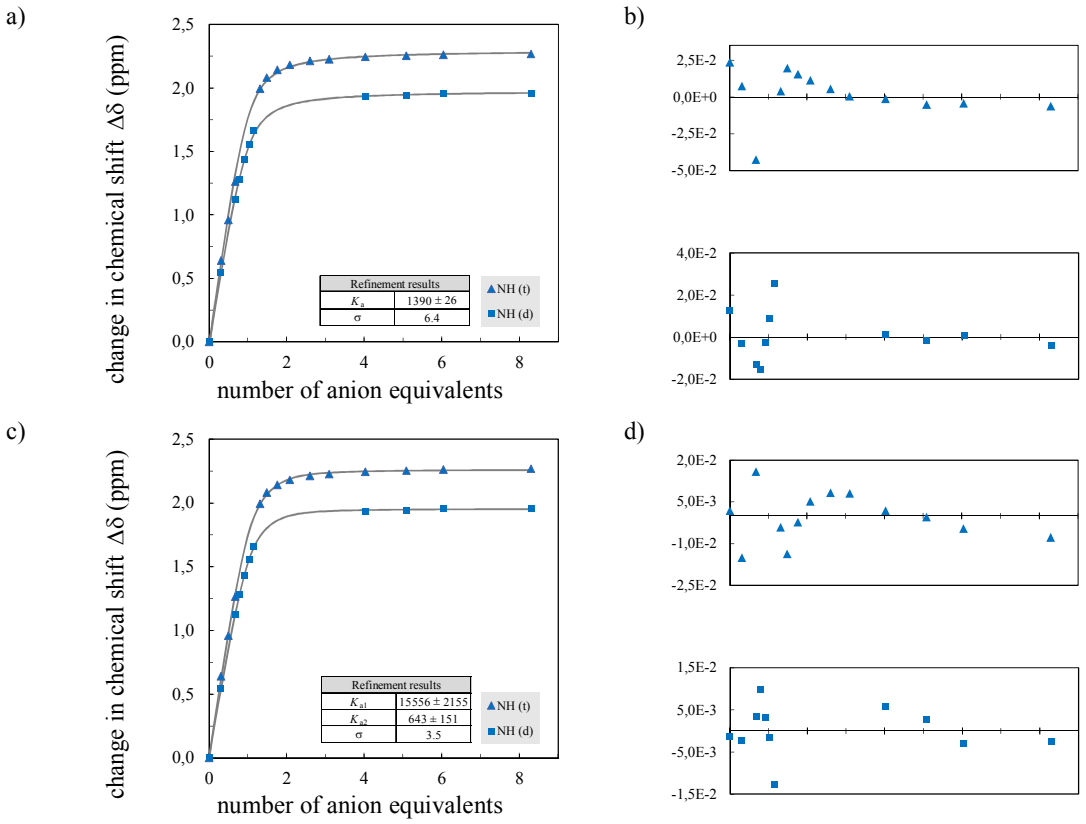


Figure S27. Experimental chemical shift changes (symbols) and calculated binding isotherms (lines) for titration of **3b** with $TBAMeCO_2$ (a, c) assuming simple 1:1 HG (a) or fully-relaxed 1:1 + 1:2 HG (c) binding model and distribution of residual for corresponding chemical shift for assumed binding model (b, d); H – host; G – guest.

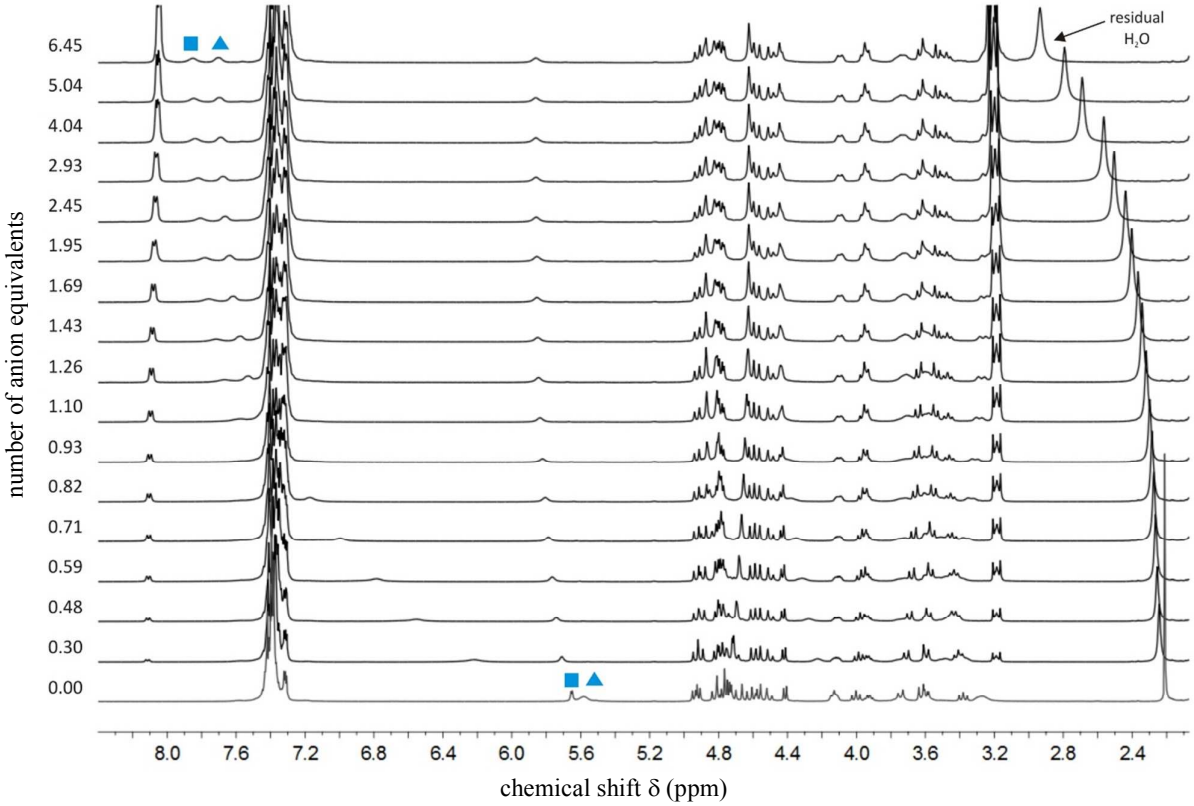


Figure S28. Stacked plots from ^{1}H NMR titrations of receptor **3b** (in the range of 8.4−2.1 ppm) with $TBAPhCO_2$.

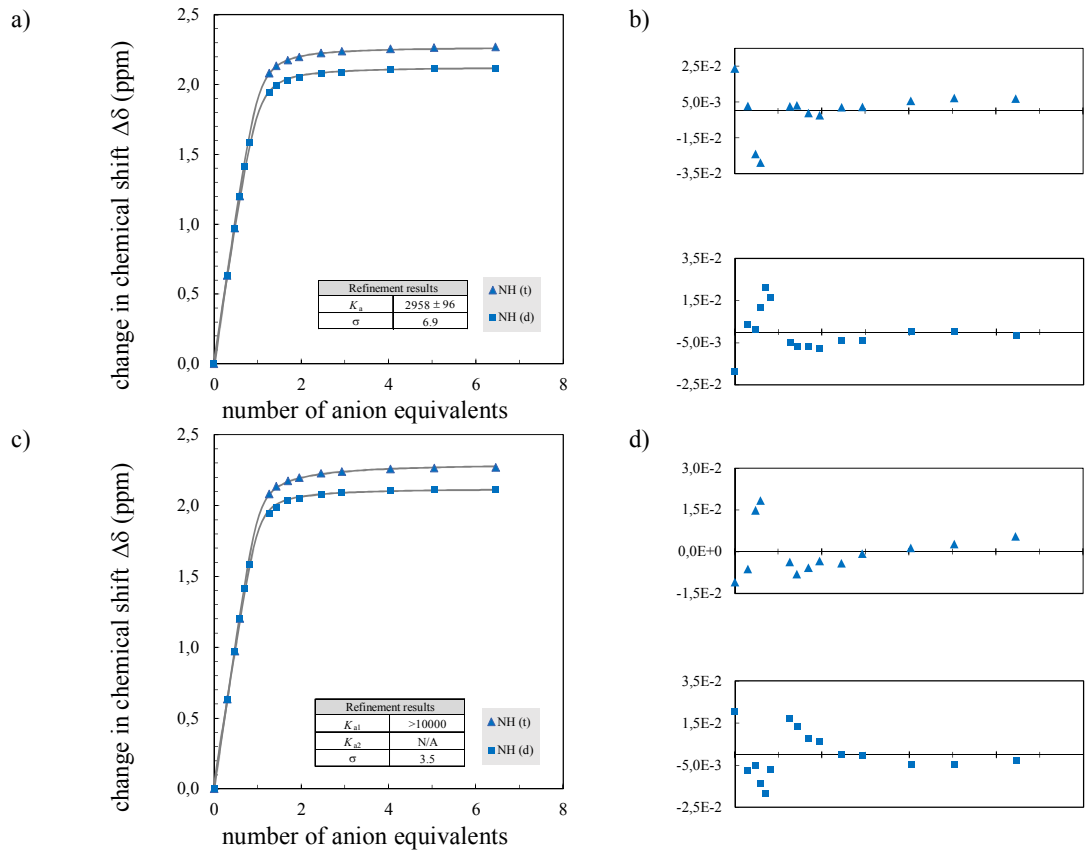


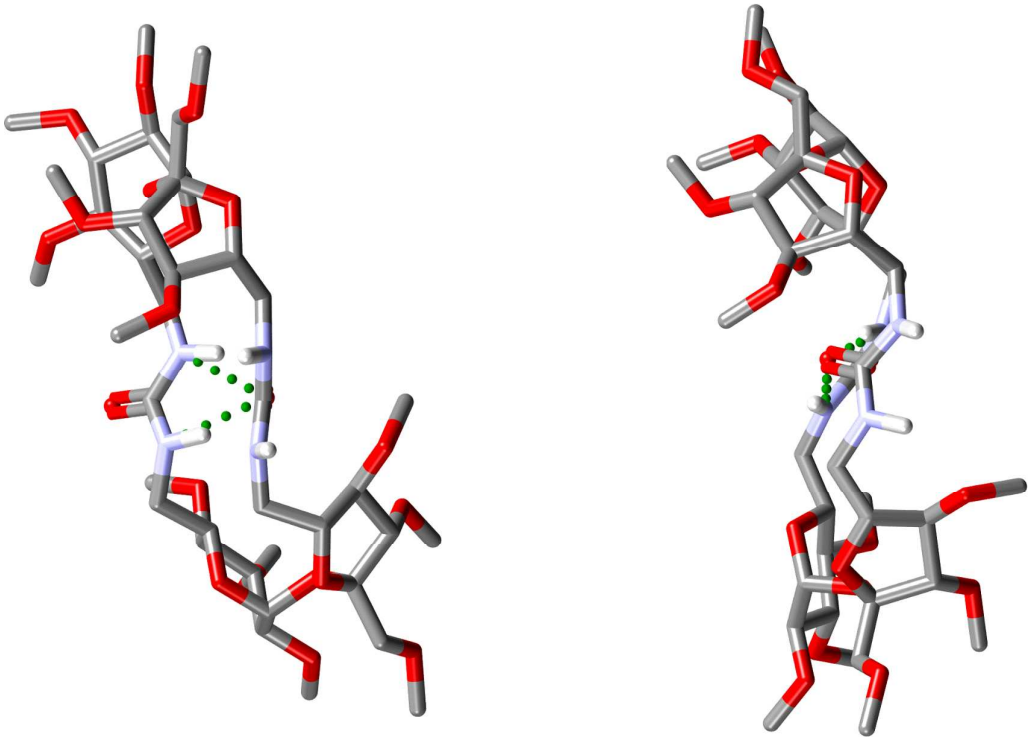
Figure S29. Experimental chemical shift changes (symbols) and calculated binding isotherms (lines) for titration of **3b** with $TBAPhCO_2$ (a, c) assuming simple 1:1 HG (a) or fully-relaxed 1:1 + 1:2 HG (c) binding model and distribution of residual for corresponding chemical shift for assumed binding model (b, d); H – host; G – guest.

3. DFT calculation studies

All calculations were performed in the gas-phase using Spartan'14 Parallel for Windows software package.[7]

In order to properly describe the hydrogen bonds and London dispersion forces associated with the anion binding we used the density theory (DFT) method with global hybrid functional M06-2X,[8] combined with the 6-31G* basis set. This functional proved to be robust and accurate in describing noncovalent supramolecular complexes.[9-12] To find lowest-energy structures for the methyl analogs of free macrocycles **3a** and **3b** as well as their acetate complexes we performed a conformational analysis search as described previously.[13] Notice that according to the theoretical predictions one can assume that breaking the internal H-bond is much easier for **3b** than for **3a** due to less-planar geometry of this internal H-bond as well as longer distances between the (urea) C=O and NH moieties in the former case (see Figs. S31a vs S31a). Although, the electronic energies for the complex of **3a** with acetate are comparable for both structures in which anion is bound either by two (cleft-binding) or four (cooperative binding) NH bond donors, one can assume that activation energies require to preorganize the binding moieties is considerably higher in the latter case.

a) **3a** (conf#1 – internal H-bonding) ΔE = 0 kJ/mol



b) **3a** (conf#2 – no internal H-bonding) ΔE = + 49.8 kJ/mol

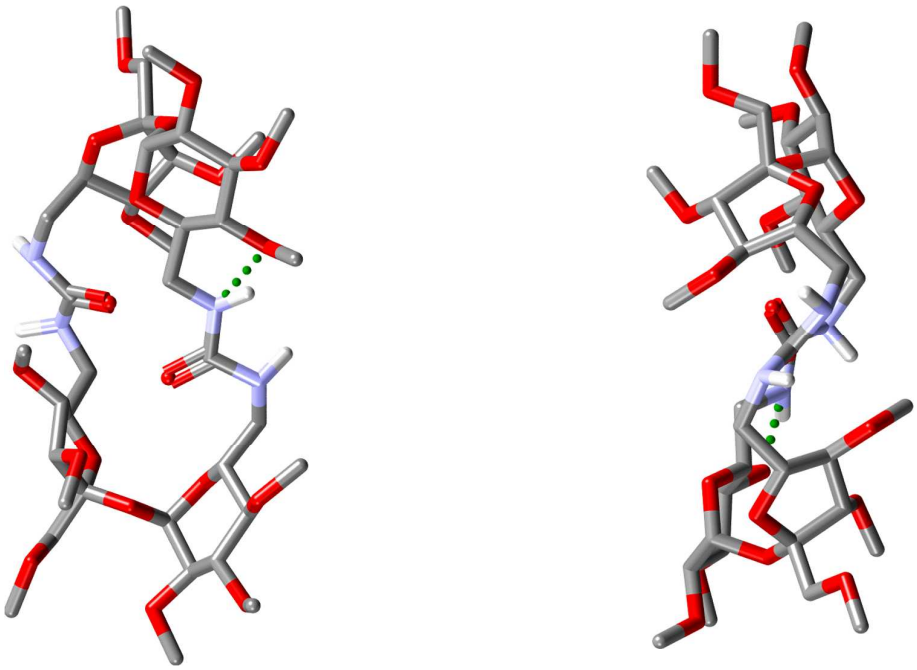
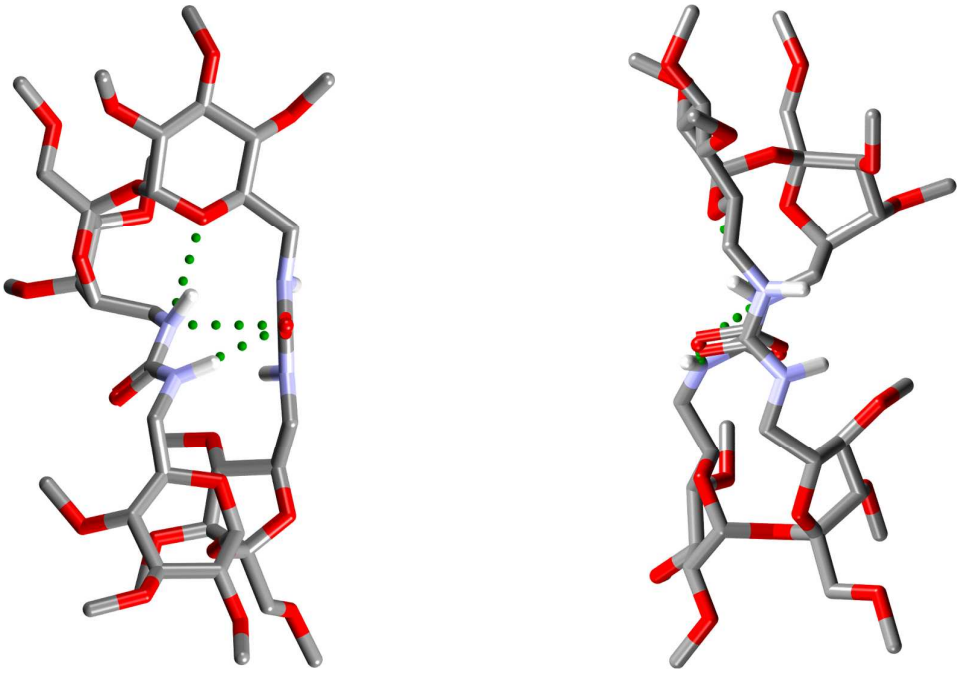


Fig. S30. Different views of the structures and relative energies of two lowest energy conformations of receptor **3a** exemplifying stabilization of the structure by intermolecular H-bonding (DFT/M06-2X/6-31G(d)); hydrogen bonds are shown in green dashed lines.

a) **3b** (conf#1 – internal H-bonding) ΔE = 0 kJ/mol



b) **3b** (conf#2 – no internal H-bonding) ΔE = +70.1 kJ/mol

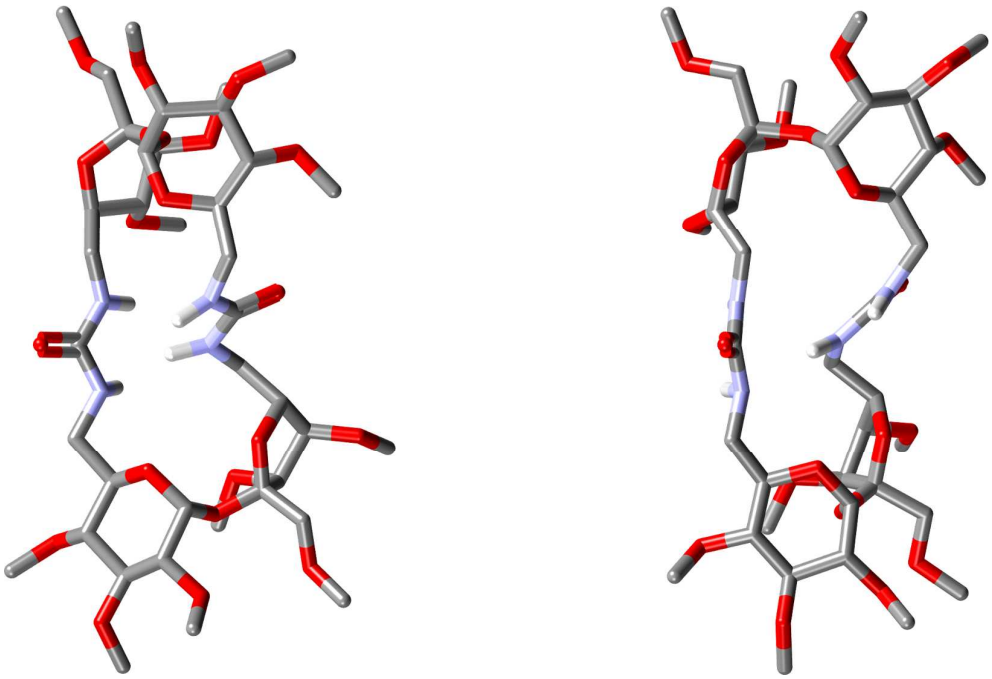
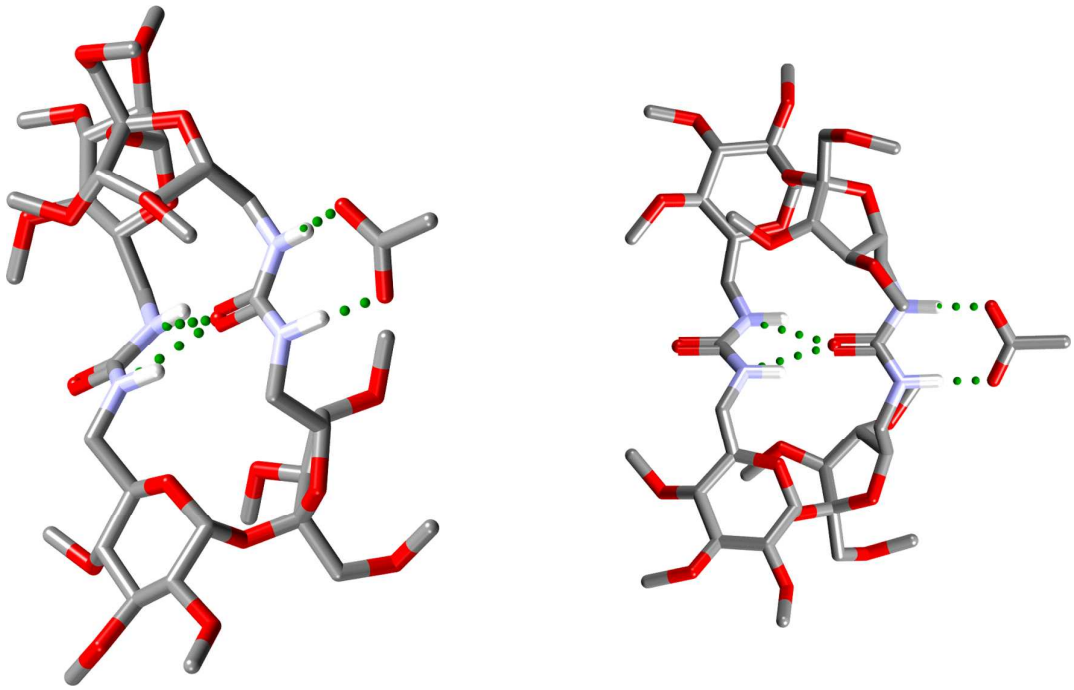


Fig. S31. Different views of the structures and relative energies of two lowest energy conformations of receptor **3b** exemplifying stabilization of the structure by intermolecular H-bonding (DFT/M06-2X/6-31G(d)); hydrogen bonds are shown in green dashed lines.

a) **3a**+$MeCO_2^-$ (conf#1 – cleft binding) ΔE = 0 kJ/mol



b) **3a**+$MeCO_2^-$ (conf#2 – cooperative binding) ΔE = +0.45 kJ/mol

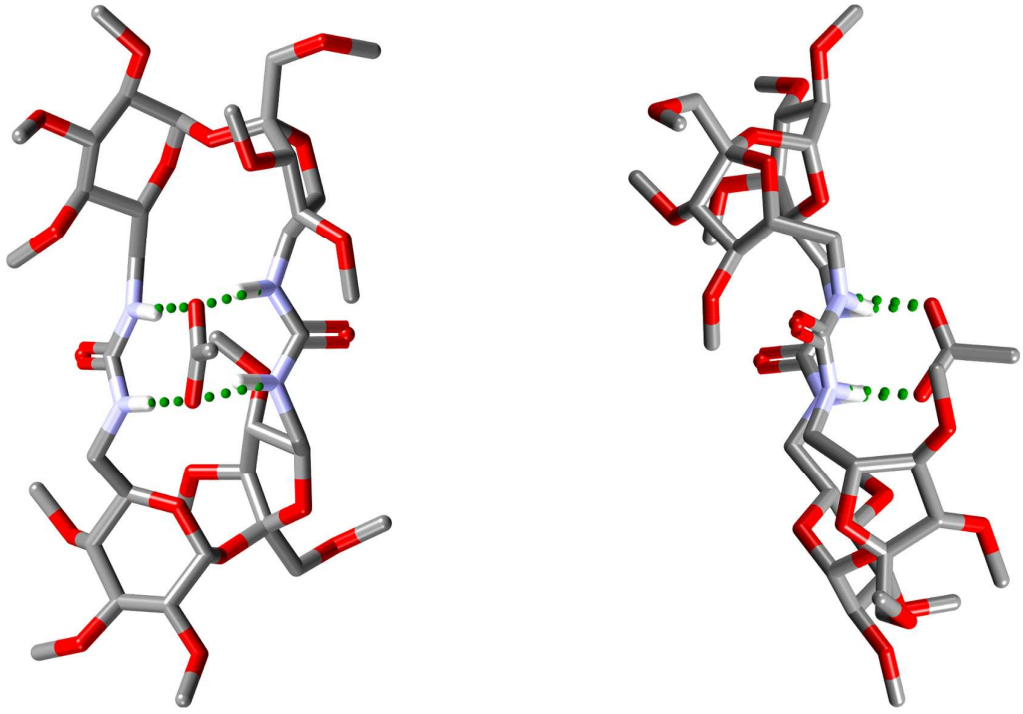
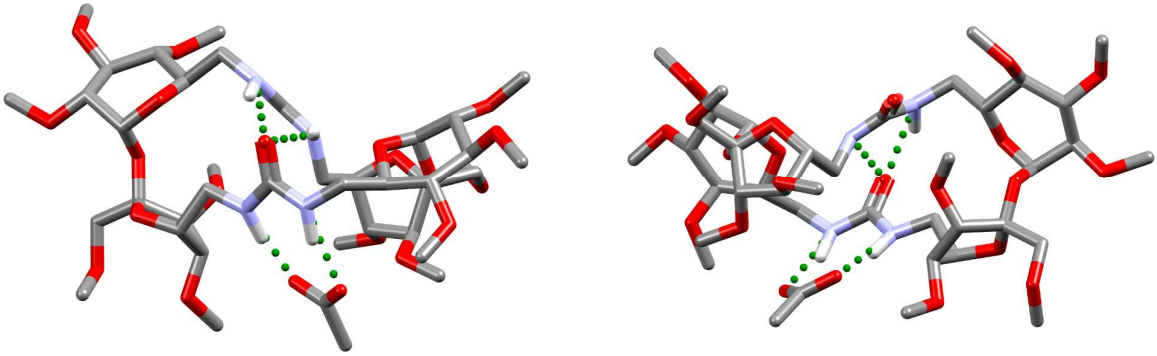


Fig. S32. Different views of the structures and relative energies of two lowest energy conformations exemplifying different binding modes for complexes of receptor **3a** with acetate (DFT/M06-2X/6-31G(d)); hydrogen bonds are shown in green dashed lines.

a) **3b**+$MeCO_2^-$ (conf#1 – cleft binding) ΔE = 0 kJ/mol



b) **3b**+$MeCO_2^-$ (conf#2 – cooperative binding) ΔE = -0.13 kJ/mol

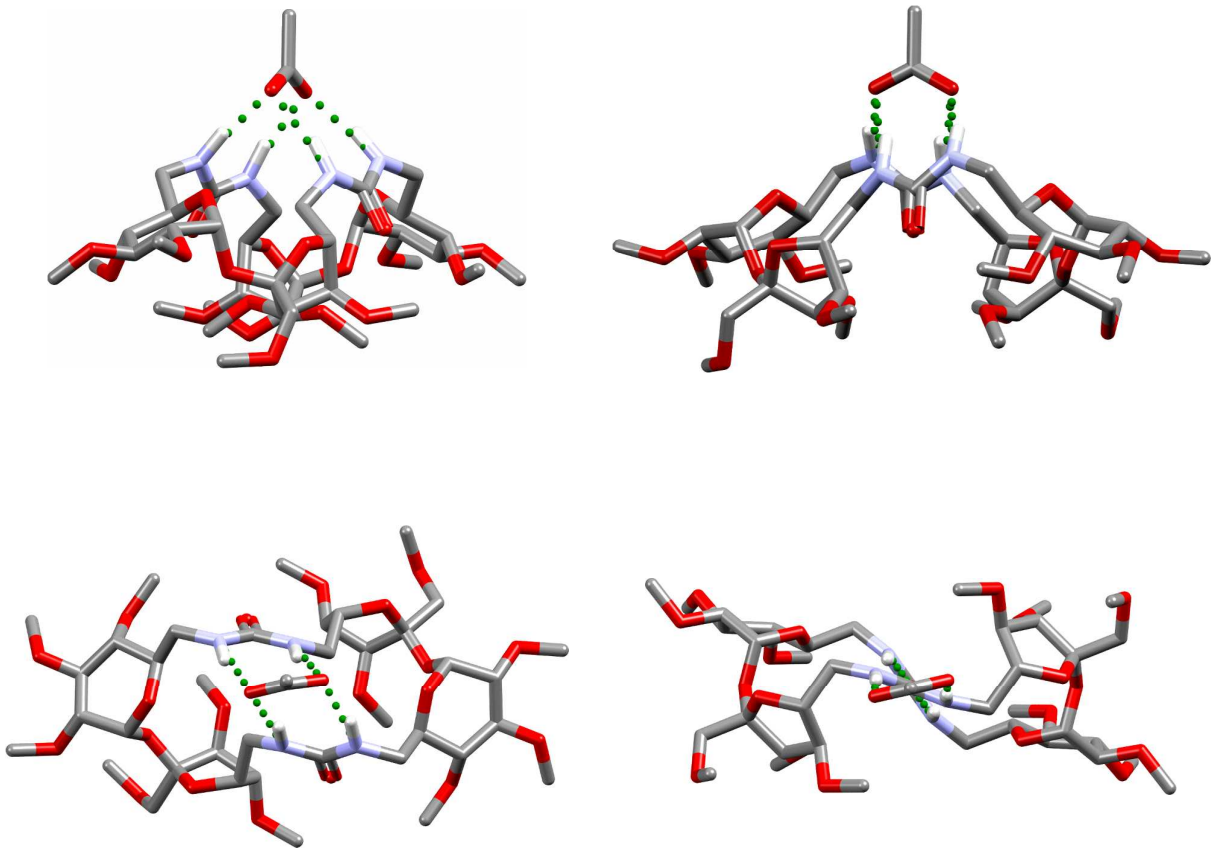


Fig. S33. Different views of the structures and relative energies of two lowest energy conformations exemplifying different binding modes for complexes of receptor **3b** with acetate (DFT/M06-2X/6-31G(d)); hydrogen bonds are shown in green dashed lines.

4. Cartesian coordinates of calculated structures

Table S2. Cartesian coordinates of the structures of methyl analogs of receptors **3a** and **3b** and their acetate complexes (DFT/M06-2X/6-31G(d)).

3a (conf#1)				**3a** (conf#2)				**3b** (conf#1)			
E = -3211.04809 au				E = -3211.04165 au				E = -3211.06060 au			
H	6.151377	-0.753927	-1.848405	H	5.422793	-1.323985	-1.701413	H	5.086934	-1.614215	-1.613302
C	5.532180	-0.109508	-1.219330	C	5.114121	-0.364048	-1.279987	C	4.973676	-0.541460	-1.448117
C	5.345296	2.090399	-0.074480	C	5.737900	1.984365	-0.784893	C	5.790740	1.737522	-2.016317
C	3.433832	0.980838	-1.286155	C	3.447859	1.275086	-1.576120	C	3.292965	1.126174	-1.528331
C	4.061018	2.307326	-0.871540	C	4.481510	2.405425	-1.546979	C	4.315752	2.195540	-1.982579
O	4.387476	0.174062	-1.976376	O	4.061082	0.091429	-2.083373	O	3.684940	-0.201985	-1.875202
C	6.283546	1.176857	-0.860131	C	6.260376	0.648195	-1.304902	C	5.989215	0.246317	-2.259585
H	5.101118	1.594612	0.875855	H	5.479298	1.854249	0.274912	H	6.212148	1.967943	-1.026939
H	3.112133	0.462938	-0.370517	H	3.090672	1.093662	-0.557908	H	3.193894	1.217185	-0.441700
H	4.318258	2.875967	-1.779581	H	4.786324	2.650386	-2.578240	H	4.057808	2.529381	-3.005598
H	6.572680	1.683163	-1.795677	H	6.593119	0.769558	-2.347840	H	5.819855	0.028419	-3.325456
O	5.206629	-0.728789	-0.002528	O	4.714309	-0.489621	0.057727	O	5.158413	-0.205870	-0.100369
C	2.219029	1.162664	-2.211928	C	2.242645	1.536824	-2.482962	C	1.934694	1.303028	-2.211046
H	2.342530	0.481479	-3.061176	H	2.518399	2.174308	-3.328717	H	2.051138	1.036975	-3.266270
H	2.159874	2.182183	-2.601664	O	3.961818	3.553707	-0.902838	H	1.627224	2.349656	-2.163517
O	3.108578	3.006575	-0.100464	O	6.737374	2.976453	-0.933683	O	4.326982	3.305217	-1.102550
O	5.978443	3.335517	0.162130	O	7.304477	0.127647	-0.512795	O	6.515646	2.413400	-3.025552
O	7.430095	0.781118	-0.147462	C	4.511757	-1.773068	0.578071	O	7.258925	-0.210157	-1.857210
C	5.294096	-2.125216	0.097175	C	3.650338	-1.613781	1.867808	C	5.093500	-1.219849	0.885763
C	4.524642	-2.488529	1.399186	C	2.262976	-2.071936	1.412809	C	4.259418	-0.659117	2.063410
C	3.097490	-2.641092	0.864323	C	2.562354	-3.040781	0.278255	C	2.841907	-1.034114	1.631510
C	3.282177	-3.143491	-0.562197	O	3.769095	-2.573021	-0.319673	C	3.052455	-2.369520	0.923134
O	4.603418	-2.775536	-0.949539	H	4.031737	-2.300187	2.642190	O	4.398547	-2.356556	0.452160
H	4.905076	-3.449206	1.786443	C	5.839255	-2.490339	0.795958	H	4.534947	-1.209066	2.977435
C	6.726891	-2.640563	-0.027873	H	6.394035	-2.512144	-0.154169	C	6.522764	-1.648687	1.184336
H	7.095366	-2.393339	-1.033794	H	5.630367	-3.531507	1.092032	H	7.152604	-0.760888	1.331906
H	6.698483	-3.737837	0.048046	C	7.925682	-2.183741	1.785651	H	6.900593	-2.180886	0.296600
C	8.882754	-1.943927	0.561714	O	6.570864	-1.821401	1.783809	C	7.796714	-2.983955	2.604541
O	7.542108	-2.081005	0.958782	C	6.886292	3.802278	0.201152	O	6.520317	-2.472499	2.319682
C	5.749156	3.840017	1.461130	H	7.657347	4.537906	-0.039507	C	6.680246	3.796833	-2.801456
H	6.220552	4.824116	1.509144	C	8.593533	0.559196	-0.895528	H	7.405716	4.149040	-3.537968
C	8.461646	1.742828	-0.075892	H	8.708400	1.640793	-0.785289	C	8.318170	0.089949	-2.741267
H	8.248789	2.519384	0.663674	H	8.806740	0.286612	-1.939607	H	8.601343	1.145213	-2.696587
H	8.620708	2.226841	-1.049016	C	3.560643	4.585316	-1.766946	H	8.046604	-0.151049	-3.778027
C	2.876247	4.334631	-0.526594	H	4.387888	4.905539	-2.415072	C	3.125456	4.037857	-0.999345
H	3.800119	4.926511	-0.482530	H	2.708955	4.291539	-2.395563	H	2.764045	4.348045	-1.992339
H	2.462089	4.355991	-1.540743	H	2.722253	-4.044771	0.705350	H	2.341210	3.471280	-0.482678
H	3.204621	-4.240003	-0.559642	C	1.494179	-3.095159	-0.807305	H	2.948743	-3.177691	1.660368
C	2.289390	-2.554601	-1.559656	H	1.905337	-3.602395	-1.685847	C	2.121430	-2.599556	-0.250562
H	2.566356	-2.853852	-2.574397	H	1.716768	-1.199233	1.027590	H	2.443864	-3.488334	-0.803553
H	2.659568	-1.634687	0.865681	O	1.523213	-2.745697	2.399370	H	2.485526	-0.262647	0.931542
O	2.262890	-3.536882	1.548238	O	3.551973	-0.309918	2.362910	O	1.902312	-1.207048	2.667916
O	4.480016	-1.513492	2.397587	C	0.870501	-1.858621	3.285151	O	4.331549	0.724322	2.253865
C	1.746896	-3.002886	2.754223	H	1.592247	-1.262661	3.857134	C	1.678172	-0.010605	3.402048
H	2.542710	-2.820755	3.484175	C	4.725646	0.188525	2.970925	H	2.546891	0.237813	4.020391
C	5.712155	-1.164023	2.998076	H	5.074554	-0.486700	3.764373	C	5.616035	1.209758	2.572745
H	6.274037	-2.056879	3.301131	H	5.532915	0.311594	2.242661	H	6.100852	0.582610	3.335390
H	6.330671	-0.578052	2.312458	N	0.286876	-3.791784	-0.398876	H	6.251595	1.254793	1.681071
N	0.917007	-2.967231	-1.316052	N	1.159779	2.180713	-1.753490	N	0.773673	-2.807728	0.257490
N	0.971285	0.890114	-1.539614	H	8.388076	-1.962463	0.814076	N	0.869869	0.491886	-1.663041
H	8.958464	-1.302990	-0.326605	H	1.229847	-2.071385	-1.086291	H	8.519836	-2.176430	2.791853
H	2.353145	-1.465979	-1.518233	H	0.336536	-4.796805	-0.305170	H	2.178467	-1.741891	-0.928715
H	0.689142	-3.926453	-1.539501	H	0.632476	2.892623	-2.240203	H	0.599880	-2.505766	1.212290
H	0.942813	0.025365	-1.006583	H	0.280521	-2.474060	3.968147	H	0.664802	-0.423808	-2.054652
H	1.048102	-3.743686	3.148370	H	5.950511	4.316454	0.443687	H	0.814518	-0.196610	4.045352
H	4.677881	3.934779	1.670103	H	8.418706	-1.596232	2.562523	H	5.740356	4.346737	-2.925015
H	9.414669	-1.471126	1.389847	N	-0.683830	1.889764	-0.356812	H	7.709037	-3.600891	3.500327
N	-0.581306	1.499245	0.030579	H	-0.888320	2.875141	-0.453567	N	-0.722241	0.070481	-0.058213
H	-0.459095	0.565633	0.407370	C	-0.694595	-3.138465	0.298945	H	-1.277460	-0.400957	-0.763657
C	0.123780	-2.357276	-0.379120	C	0.454739	1.359185	-0.888829	C	-0.267362	-2.745022	-0.632876
C	0.232174	1.913239	-0.994239	O	-0.639783	-1.946473	0.559063	C	0.383356	0.780916	-0.414358
O	0.469445	-1.339238	0.232266	O	0.852365	0.228456	-0.631640	O	-0.114250	-2.490083	-1.824737
O	0.257508	3.068799	-1.410955	N	-1.768989	-3.931566	0.681317	O	0.907247	1.619786	0.326473
N	-1.094810	-2.934541	-0.188044	H	-1.917305	-4.739663	0.086731	N	-1.500142	-3.012208	-0.081316
H	-1.466603	-3.506498	-0.940304	H	-5.144300	-0.595179	1.936000	H	-1.503819	-3.456383	0.826334
H	-4.698393	-0.082428	2.202479	C	-4.882314	0.260238	1.310625	H	-3.496594	1.079277	-1.246243
C	-4.633769	0.639570	1.385138	C	-4.888566	2.776088	1.126446	C	-4.053950	0.193526	-0.932981

C	-5.386026	2.870708	0.548467
C	-2.985733	2.028584	0.343465
C	-3.915946	3.254328	0.373344
O	-3.305464	1.064127	1.353470
C	-5.562421	1.825326	1.639368
H	-5.737003	2.439967	-0.402227
H	-3.078637	1.570588	-0.649681
H	-3.634454	3.919957	1.208364
H	-5.288148	2.266653	2.609683
O	-4.992177	0.034026	0.162211
C	-1.529383	2.402921	0.622005
H	-1.408449	2.435539	1.711666
H	-1.293822	3.390871	0.230621
O	-3.855276	3.947654	-0.855946
O	-6.186339	3.975664	0.908561
O	-6.880345	1.328856	1.676647
C	-5.361133	-1.327029	0.194459
C	-5.194037	-1.854300	-1.251206
C	-3.711357	-2.211354	-1.267556
C	-3.458410	-2.682891	0.162784
O	-4.467023	-2.092114	0.969106
H	-5.797202	-2.768008	-1.356014
C	-6.743695	-1.509496	0.813861
H	-7.446527	-0.782198	0.389259
H	-6.673646	-1.306076	1.893410
C	-8.388191	-3.116121	1.183189
O	-7.155330	-2.830541	0.573736
C	-6.484948	4.884717	-0.130733
H	-7.366155	5.446625	0.188607
C	-7.734925	1.991340	2.586907
H	-7.848984	3.046848	2.328874
H	-7.352378	1.909215	3.614048
C	-2.808354	4.880949	-1.043287
H	-2.589034	5.419352	-0.110185
H	-1.891320	4.409083	-1.413480
H	-3.583999	-3.774120	0.192408
C	-2.081232	-2.294005	0.671773
H	-1.987510	-1.203031	0.632226
H	-3.142748	-1.292474	-1.486399
O	-3.333171	-3.243983	-2.147979
O	-5.469127	-0.937432	-2.271472
C	-3.322229	-2.836828	-3.505251
H	-4.321155	-2.538451	-3.836786
C	-6.799053	-0.463683	-2.284219
H	-7.515557	-1.287435	-2.152191
H	-6.957152	0.283394	-1.497355
H	-9.182553	-2.453322	0.809816
H	-2.977921	-3.692713	-4.087802
H	-5.659096	5.577565	-0.318854
H	-8.640092	-4.149732	0.941080
H	-1.953539	-2.608561	1.712954
H	-3.162618	5.600479	-1.785883
H	-6.961126	0.001275	-3.258197
H	-6.709164	4.355532	-1.065282
H	-2.636343	-1.991981	-3.651597
H	9.369533	1.204650	0.208895
H	9.344956	-2.918538	0.348679
H	1.215792	-2.063199	2.558346
H	-8.702013	1.487134	2.529564
H	-8.327764	-3.005280	2.275061
H	6.202363	3.187366	2.221159
H	2.130593	4.753220	0.150844
H	5.459049	-0.575048	3.882416
C	-2.894583	1.352895	0.574832
C	-3.366361	2.695702	1.133018
O	-3.480685	0.294062	1.334819
C	-5.463105	1.570194	1.866395
H	-5.235519	2.756894	0.082201
H	-3.191919	1.264191	-0.477729
H	-3.015350	2.782488	2.174575
H	-5.155509	1.640386	2.923407
O	-5.419760	0.113918	0.024374
C	-1.385643	1.174699	0.690920
H	-1.052364	1.498158	1.688919
O	-2.788381	3.718302	0.341739
O	-5.274469	3.979445	1.755206
O	-6.863990	1.631346	1.768031
C	-5.392118	-1.159305	-0.604048
C	-4.352503	-1.183959	-1.758897
C	-3.148455	-1.849058	-1.104128
C	-3.820151	-2.835490	-0.155581
O	-5.011688	-2.179881	0.283276
H	-4.733320	-1.838988	-2.556984
C	-6.829621	-1.428210	-1.031810
H	-7.218384	-0.579767	-1.614287
H	-7.436372	-1.522429	-0.117057
C	-8.155897	-2.992990	-2.140127
O	-6.852529	-2.614341	-1.778447
C	-6.428408	4.580360	1.204034
H	-6.607094	5.495337	1.772758
C	-7.530511	0.644433	2.517898
H	-7.169236	0.619827	3.556044
H	-7.409180	-0.354500	2.077917
C	-2.449651	4.888595	1.063652
H	-3.328206	5.326270	1.543007
H	-1.691653	4.668054	1.828613
H	-4.099345	-3.729490	-0.735356
C	-2.991752	-3.236494	1.059911
H	-2.710904	-2.337125	1.612597
H	-2.587636	-1.100049	-0.531483
O	-2.302974	-2.545209	-1.977449
O	-3.999530	0.070265	-2.276111
C	-1.342665	-1.706439	-2.598664
H	-1.820804	-1.007946	-3.295556
C	-5.044229	0.731520	-2.953357
H	-5.537318	0.059112	-3.670039
H	-5.790501	1.121963	-2.251105
H	-8.641747	-2.220241	-2.753320
H	-0.663039	-2.364380	-3.145177
H	-6.264759	4.842557	0.149354
H	-8.078614	-3.913799	-2.720072
H	-3.586369	-3.882474	1.713029
H	-2.031190	5.593086	0.341446
H	-4.594683	1.565006	-3.496293
H	-7.297677	3.921593	1.281616
H	-0.777472	-1.142460	-1.844509
H	9.303405	0.043631	-0.244681
H	8.057991	-3.253466	2.006566
H	0.203384	-1.188817	2.729153
H	-8.590747	0.902649	2.515613
H	-8.778111	-3.176052	-1.252495
H	7.210814	3.216381	1.072988
H	3.253532	5.425066	-1.139629
H	4.456672	1.153722	3.406124
H	1.923912	0.563253	-2.871740
H	-1.134297	0.116113	0.591740
C	-6.005409	-1.299924	-1.315232
C	-3.730001	-2.142815	-0.675403
C	-5.038412	-2.477365	-1.400735
O	-3.201159	-0.909222	-1.153630
C	-5.319914	-0.014270	-1.762956
H	-6.302785	-1.182697	-0.264208
H	-3.937491	-2.059680	0.400728
H	-4.817931	-2.681582	-2.462127
H	-5.012791	-0.117416	-2.814129
O	-4.390209	0.258402	0.422134
C	-2.667851	-3.200160	-0.919586
H	-2.332864	-3.142204	-1.958729
H	-3.111423	-4.184941	-0.740567
O	-5.583103	-3.620970	-0.778048
O	-7.143487	-1.556150	-2.118878
O	-6.177133	1.097669	-1.611771
C	-4.046266	1.419649	1.152760
C	-3.917875	1.006354	2.658901
C	-2.498298	1.481393	3.018366
C	-1.791503	1.505055	1.670672
O	-2.810542	1.942951	0.765058
H	-4.671912	1.547069	3.247617
C	-5.090030	2.499793	0.928516
H	-5.101249	2.773248	-0.136098
H	-4.815328	3.383381	1.525487
C	-7.406110	2.770176	0.906951
O	-6.329608	1.973241	1.326694
C	-8.362432	-1.275368	-1.462532
H	-9.161873	-1.442876	-2.187503
C	-6.787914	1.503970	-2.819880
H	-7.367008	0.688759	-3.267097
H	-6.038653	1.849141	-3.545138
C	-6.242202	-4.502434	-1.664518
H	-7.055351	-3.999568	-2.196315
H	-5.537609	-4.918650	-2.398674
H	-0.992880	2.246178	1.634392
C	-1.253262	0.126264	1.280870
H	-0.473423	-0.162525	1.996404
H	-2.035801	0.787772	3.736207
O	-2.516568	2.798782	3.520778
O	-4.018937	-0.372075	2.882669
C	-2.873578	2.866192	4.879703
H	-3.878045	2.461136	5.066369
C	-5.360392	-0.817822	2.951842
H	-5.845247	-0.426716	3.857547
H	-5.934351	-0.496355	2.077446
H	-7.432580	2.841902	-0.188572
H	-2.859899	3.919629	5.163089
H	-8.507540	-1.945191	-0.604303
H	-8.322331	2.291907	1.259053
H	-2.056689	-0.615133	1.343354
H	8.172579	-3.601216	1.776352
H	9.162896	-0.532807	-2.438236
H	7.057382	3.991229	-1.788809
H	-7.346429	3.784018	1.329238
H	1.473809	0.827646	2.724084
H	3.360736	4.932149	-0.418636
H	5.485087	2.219036	2.966952
H	-2.156854	2.314164	5.503947
H	-8.395323	-0.236033	-1.112877
H	-6.643261	-5.316656	-1.057958
H	-7.453207	2.335585	-2.576822
H	-5.330623	-1.907992	3.000824

Table S2 continuation.

3b (conf#2)				**3a**+$MeCO_2^-$ (conf#1)				**3a**+$MeCO_2^-$ (conf#2)			
E = -3211.03392 au				E = -3439.54750 au				E = -3439.54733 au			
H	4.835150	-1.513776	-1.779433	H	4.776041	-0.824211	-1.282980	H	4.835313	-1.043853	-1.876225
C	4.848191	-0.462814	-1.482038	C	4.729059	0.225397	-0.988293	C	5.061478	-0.245876	-1.165412
C	5.948752	1.743963	-1.754176	C	5.682034	2.500880	-1.318020	C	6.471155	1.712316	-0.640638
C	3.378643	1.400675	-1.399706	C	3.159343	2.023764	-0.952306	C	3.905250	1.542111	-0.047171
C	4.538022	2.378106	-1.696755	C	4.243684	3.041661	-1.362451	C	5.229462	2.346851	0.008881
O	3.616033	0.079205	-1.875925	O	3.461421	0.688210	-1.361398	O	3.872888	0.466186	-0.991183
C	5.951893	0.290633	-2.205109	C	5.786190	1.038686	-1.726773	C	6.126991	0.694356	-1.717540
H	6.352020	1.778632	-0.726355	H	6.033984	2.580916	-0.279024	H	7.022127	1.182241	0.148314
H	3.237414	1.391376	-0.308407	H	3.065412	2.053149	0.139010	H	3.737067	1.132950	0.954150
H	4.359947	2.860184	-2.682193	H	4.054053	3.389453	-2.394849	H	5.070876	3.309959	-0.512820
H	5.720872	0.245724	-3.288107	H	5.586726	0.945881	-2.805061	H	5.695432	1.204042	-2.592219
O	5.000344	-0.326008	-0.097188	O	4.973564	0.373505	0.375683	O	5.588884	-0.767017	0.019210
C	2.087699	1.808304	-2.097869	C	1.798071	2.297088	-1.596085	C	2.751989	2.459564	-0.452830
H	2.195032	1.604461	-3.169878	H	1.842092	1.920370	-2.625183	H	2.935563	2.786180	-1.484182
H	1.898739	2.876258	-1.971012	H	1.571023	3.361627	-1.633576	H	2.748552	3.342337	0.193173
O	4.633163	3.368411	-0.690579	O	4.250194	4.147303	-0.473217	O	5.595395	2.607581	1.355612
O	6.781168	2.454917	-2.642882	O	6.544179	3.226757	-2.175443	O	7.307319	2.693551	-1.229300
O	7.164993	-0.375486	-1.923584	O	7.047672	0.498684	-1.404857	O	7.250724	-0.069879	-2.089900
C	5.160939	-1.481733	0.709651	C	4.821376	-0.717480	1.282167	C	5.054706	-1.949198	0.606505
C	4.565450	-1.121450	2.091210	C	3.647030	-0.463310	2.272480	C	4.145719	-1.604303	1.803415
C	3.089023	-1.535222	1.949426	C	2.604315	-1.542226	1.966809	C	2.749810	-1.589967	1.194945
C	3.101928	-2.595917	0.848682	C	3.202649	-2.377356	0.821783	C	2.851183	-2.634867	0.088513
O	4.408545	-2.562130	0.263969	O	4.553040	-1.925845	0.637822	O	4.249794	-2.689983	-0.272574
H	5.061056	-1.755077	2.850920	H	4.015952	-0.618556	3.297017	H	4.201615	-2.436472	2.523363
C	6.623345	-1.914031	0.686317	C	6.196124	-0.825867	1.951987	C	6.304202	-2.775724	0.929984
H	7.279403	-1.028410	0.737260	H	6.536407	0.183062	2.200149	H	7.052578	-2.120683	1.380716
H	6.818086	-2.411801	-0.279448	H	6.880044	-1.252389	1.201476	H	6.694872	-3.143168	-0.032084
C	8.141311	-3.314151	1.769257	C	5.853279	-2.917218	3.031464	C	5.325124	-4.896967	1.334597
O	6.840332	-2.781374	1.768066	O	6.217970	-1.555054	3.150647	O	6.100554	-3.828946	1.835506
C	7.254619	3.688024	-2.152333	C	6.806983	4.551883	-1.773473	C	7.911739	3.553904	-0.292355
H	7.909391	4.098792	-2.910615	H	7.671125	4.889227	-2.351805	H	8.656420	4.141111	-0.835322
C	8.168928	-0.238939	-2.899858	C	7.993523	0.564694	-2.447184	C	7.966291	0.452794	-3.185041
H	8.429648	0.779008	-3.039798	H	8.223323	1.599146	-2.718723	H	8.389459	1.436219	-2.959769
H	7.833166	-0.644955	-3.836529	H	7.635043	0.033174	-3.341062	H	7.323104	0.537976	-4.073507
C	3.584132	4.318653	-0.654248	C	3.150369	5.029937	-0.557751	C	4.678872	3.420038	2.058220
H	3.392436	4.727596	-1.662279	H	2.948588	5.308186	-1.603570	H	4.548432	4.389551	1.551178
H	2.658731	3.898324	-0.249153	H	2.235457	4.614150	-0.119254	H	3.694112	2.949784	2.175320
H	2.958027	-3.575981	1.315707	H	3.258835	-3.431094	1.122221	H	2.549316	-3.605191	0.498131
C	2.068971	-2.372195	-0.245006	C	2.413677	-2.280879	-0.484812	C	2.024127	-2.321109	-1.163889
H	2.085371	-3.206109	-0.956930	H	2.977191	-2.785956	-1.277280	H	1.916153	-3.233050	-1.763719
H	2.514113	-0.623606	1.648493	H	1.673686	-1.049744	1.655002	H	2.540703	-0.607431	0.751943
O	2.522686	-2.104997	3.114655	O	2.389709	-2.306262	3.135588	O	1.767611	-1.936072	2.133754
O	4.630718	0.235667	2.423026	O	3.050686	0.800565	2.149702	O	4.399464	-0.384687	2.445988
C	2.300085	-1.157148	4.131789	C	1.250240	-3.140612	3.030903	C	0.981521	-0.829494	2.526423
H	3.247102	-0.693134	4.462052	H	0.349814	-2.544185	2.827600	H	1.588019	-0.036804	2.982556
C	5.935846	0.689052	2.729898	C	3.823420	1.851038	2.682124	C	5.670790	-0.283089	3.041152
H	6.425348	0.023305	3.466487	H	4.108081	1.637265	3.722892	H	5.912031	-1.190856	3.614131
H	6.560846	0.742266	1.823322	H	4.727041	2.033367	2.087629	H	6.448836	-0.105934	2.289484
N	0.730365	-2.297283	0.326437	N	1.123340	-2.911071	-0.338219	N	0.742861	-1.741272	-0.848786
N	0.917070	1.093602	-1.613491	N	0.724101	1.661863	-0.880297	N	1.458737	1.841050	-0.387562
H	8.905060	-2.517341	1.832615	H	6.286933	-3.367924	2.129617	H	5.599465	-5.133355	0.298353
H	2.341424	-1.451565	-0.786016	H	2.283185	-1.233495	-0.769449	H	2.561678	-1.573206	-1.752418
H	1.825156	-1.681735	4.973921	H	1.103880	-3.938996	-0.157684	H	0.539555	-0.829638	-1.255484
H	6.449070	4.381988	-1.952018	H	0.751590	0.651704	-0.749944	H	1.090965	1.373380	-1.223736
H	8.227462	-3.967095	2.646579	H	1.142443	-3.642321	3.994825	H	0.250560	-1.201193	3.249196
N	-0.443294	0.528861	0.184631	H	5.958045	5.217337	-1.967192	H	7.184639	4.230976	0.172899
C	-0.301567	-2.824499	-0.419830	H	6.245330	-3.422337	3.917829	H	5.528206	-5.760209	1.973078
C	0.476637	1.427538	-0.355763	N	-0.745618	1.641559	0.890381	N	-0.610228	1.554129	0.539594
O	-0.162097	-3.584482	-1.356901	H	-0.755651	0.632209	0.751308	H	-0.891077	1.188788	-0.378241
O	0.860719	2.422991	0.241928	C	0.020960	-2.192446	-0.009245	C	-0.208625	-2.436615	-0.152617
N	-1.545404	-2.384777	0.009707	C	-0.015938	2.391710	0.009256	C	0.667028	2.000582	0.717490
H	-1.586671	-2.262859	1.020743	O	0.010940	-0.941337	-0.006553	O	-0.046946	-3.595546	0.226452
H	-4.181574	0.892135	-1.848461	O	-0.025172	3.630457	0.015752	O	1.067256	2.520033	1.765976
C	-4.569997	0.061728	-1.252168	N	-1.070495	-2.929360	0.317181	N	-1.340213	-1.700111	0.088123
C	-6.313551	-1.700870	-1.084709	H	-1.035120	-3.955253	0.133278	H	-1.460402	-0.847758	-0.459548
C	-3.899737	-2.056443	-0.478020	H	-4.759751	-0.911532	1.282538	H	-5.564206	-0.174421	2.316844
C	-5.180348	-2.720426	-1.004598	C	-4.728778	0.140783	0.995398	C	-5.088891	0.471608	1.573154
O	-3.566030	-0.915832	-1.252157	C	-5.715684	2.399339	1.342879	C	-5.020644	2.748298	0.548101
C	-5.839698	-0.491406	-1.878401	C	-3.186415	1.962523	0.970004	C	-2.966104	1.408987	1.092741
H	-6.551307	-1.383310	-0.056918	C	-4.285428	2.960852	1.388872	C	-3.553074	2.818176	0.972115

Table S2 continuation.

H	-4.085014	-1.754689	0.569050
H	-4.984449	-3.112020	-2.021690
H	-5.573053	-0.828404	-2.897251
O	-4.891407	0.467916	0.054474
C	-2.727125	-3.014278	-0.544368
H	-2.508441	-3.257955	-1.589669
H	-3.001150	-3.942049	-0.025157
O	-5.482133	-3.762481	-0.113062
O	-7.445489	-2.275747	-1.700979
O	-6.814793	0.528641	-1.924776
C	-4.320559	1.662016	0.490284
C	-4.283569	1.670557	2.038247
C	-2.975950	2.429170	2.332791
C	-2.100973	2.130499	1.113658
O	-2.980773	1.753348	0.050190
H	-5.169471	2.207929	2.418863
C	-5.097120	2.848695	-0.069214
H	-5.136904	2.759079	-1.174883
H	-4.556837	3.774112	0.193984
C	-7.216086	3.820934	-0.075599
O	-6.392885	2.827564	0.479638
C	-8.674941	-1.926427	-1.073488
H	-9.473312	-2.376369	-1.668793
C	-7.526481	0.576737	-3.145132
H	-8.019366	-0.379508	-3.353788
H	-6.856991	0.817838	-3.986252
C	-6.141033	-4.869666	-0.691725
H	-7.088165	-4.576340	-1.159556
H	-5.500383	-5.348899	-1.449586
H	-1.554084	3.030677	0.818315
C	-1.130256	0.987351	1.382522
H	-0.379632	1.323405	2.113706
H	-2.536989	2.020505	3.261901
O	-3.164157	3.815454	2.418191
O	-4.181032	0.380095	2.580380
C	-3.640358	4.234614	3.675069
H	-4.626542	3.798382	3.913346
C	-5.446083	-0.201112	2.854158
H	-5.973765	0.377105	3.629703
H	-6.067275	-0.236445	1.949678
H	-7.327692	3.678143	-1.166994
H	-3.731916	5.321072	3.629577
H	-8.723779	-2.328515	-0.039086
H	-8.202624	3.740955	0.402466
H	-1.685470	0.133304	1.806098
H	8.329476	-3.901409	0.855849
H	9.041759	-0.793886	-2.566991
H	7.817827	3.546650	-1.232879
H	-6.801393	4.825332	0.105004
H	1.622263	-0.354928	3.771725
H	3.922868	5.128975	-0.010237
H	5.837989	1.691990	3.154074
H	-2.931646	3.959234	4.476595
H	-8.813358	-0.832105	-1.036985
H	-6.325444	-5.580754	0.118333
H	-8.282840	1.367273	-3.049775
H	-5.262081	-1.215908	3.225858
H	0.565670	-1.876414	1.231914
H	0.452627	0.389147	-2.172221
H	-0.620431	-0.378267	-0.227539
O	-3.467615	0.619757	1.370186
C	-5.797555	0.932616	1.740886
H	-6.070821	2.481778	0.305119
H	-3.094934	2.001007	-0.121208
H	-4.099390	3.304153	2.423426
H	-5.595867	0.834785	2.818343
O	-4.977459	0.295177	-0.367104
C	-1.828463	2.252435	1.613706
H	-1.864513	1.866000	2.639514
H	-1.618609	3.320190	1.660314
O	-4.309754	4.072486	0.507402
O	-6.586327	3.106557	2.207222
O	-7.050893	0.375892	1.415902
C	-4.808563	-0.785974	-1.282298
C	-3.641823	-0.503394	-2.273835
C	-2.578099	-1.564302	-1.977289
C	-3.159023	-2.419521	-0.838029
O	-4.517047	-1.994236	-0.648257
H	-4.010557	-0.659661	-3.298253
C	-6.182822	-0.913395	-1.949715
H	-6.540986	0.091199	-2.190218
H	-6.857850	-1.356794	-1.200970
C	-5.808170	-2.991739	-3.043352
O	-6.194278	-1.634731	-3.153320
C	-6.867398	4.431202	1.815951
H	-7.733781	4.753234	2.399586
C	-7.998513	0.424820	2.457589
H	-8.244507	1.454862	2.731578
H	-7.632440	-0.103246	3.350449
C	-3.221784	4.969361	0.594764
H	-3.021036	5.243675	1.641808
H	-2.302371	4.569025	0.151376
H	-3.196696	-3.471657	-1.146918
C	-2.370112	-2.319623	0.468288
H	-2.254781	-1.272295	0.759427
H	-1.656376	-1.056725	-1.663095
O	-2.350891	-2.315230	-3.152302
O	-3.070171	0.771282	-2.145139
C	-1.196615	-3.129803	-3.055108
H	-0.306767	-2.519237	-2.847231
C	-3.867848	1.809625	-2.664796
H	-4.153534	1.598447	-3.705815
H	-4.771846	1.967241	-2.063813
H	-6.233726	-3.454826	-2.143920
H	-1.080498	-3.621742	-4.023061
H	-6.026121	5.105767	2.011532
H	-6.193054	-3.497271	-3.932595
H	-2.925318	-2.837857	1.258125
H	-3.519937	5.867941	0.048712
H	-3.260889	2.717370	-2.633737
H	-7.104476	4.486763	0.745583
H	-1.281749	-3.893992	-2.270326
H	8.895955	0.067965	-2.083282
H	4.764185	-3.044100	3.004965
H	1.348970	-3.896755	2.239789
H	-8.892766	-0.085077	2.091748
H	-4.717187	-3.101627	-3.018430
H	7.039884	4.602600	-0.701950
H	3.434890	5.928975	-0.005227
H	3.197488	2.745969	2.655424
C	0.052799	-6.150687	-0.031173
O	-1.029643	-5.596283	-0.351279
O	1.122498	-5.577633	0.306346
C	0.090304	-7.682334	-0.051252
H	0.856969	-8.015644	-0.757225
H	-0.878928	-8.096418	-0.332855
H	0.381452	-8.050081	0.937145
O	-3.772648	0.661408	2.012102
C	-5.800147	1.827431	1.483081
H	-5.080118	2.337817	-0.470944
H	-2.995156	0.932037	0.103502
H	-3.514499	3.302183	1.962634
H	-5.817263	2.280359	2.487797
O	-5.125845	-0.101696	0.293703
C	-1.535916	1.362877	1.628462
H	-1.404869	0.382458	2.109521
H	-1.364640	2.125402	2.396334
O	-2.868240	3.597372	0.018634
O	-5.601185	4.040287	0.605514
O	-7.117804	1.569409	1.053286
C	-5.614091	-1.418402	0.103560
C	-5.345060	-1.712960	-1.384102
C	-3.864713	-2.071352	-1.364866
C	-3.659496	-2.689814	0.036106
O	-4.857922	-2.380759	0.784769
H	-5.933783	-2.597785	-1.671041
C	-7.062734	-1.561126	0.590840
H	-7.611347	-0.646793	0.366011
H	-7.042682	-1.698516	1.684069
C	-7.345900	-3.909576	0.388480
O	-7.762736	-2.622668	-0.013305
C	-5.648695	4.692251	-0.644708
H	-6.066028	5.687085	-0.468375
C	-8.042583	2.620051	1.227031
H	-7.967993	3.368020	0.432489
H	-7.890908	3.126275	2.189286
C	-1.912986	4.484654	0.559825
H	-1.122730	3.965826	1.112911
H	-1.458850	5.004975	-0.286220
H	-3.631962	-3.779517	-0.084685
C	-2.446543	-2.199663	0.856196
H	-2.816132	-1.406008	1.513997
H	-3.285566	-1.149411	-1.507551
O	-3.600511	-2.978987	-2.410259
O	-5.560589	-0.661063	-2.278776
C	-2.219546	-3.215168	-2.595326
H	-1.667189	-2.273712	-2.717179
C	-6.876338	-0.159475	-2.274612
H	-7.616902	-0.972300	-2.249565
H	-7.042865	0.506033	-1.416713
H	-7.227356	-3.962369	1.479208
H	-2.123147	-3.814468	-3.503740
H	-4.651203	4.780188	-1.084145
H	-8.128274	-4.603938	0.072589
H	-2.065858	-3.012433	1.479419
H	-2.398644	5.220604	1.217365
H	-7.001664	0.411131	-3.198193
H	-6.302501	4.151216	-1.345520
H	-1.778468	-3.765147	-1.752134
H	8.769999	-0.255007	-3.401244
H	4.251956	-4.677177	1.362908
H	0.455519	-0.420057	1.657045
H	-9.037165	2.166356	1.210324
H	-6.394442	-4.201574	-0.070282
H	8.403424	2.984749	0.508389
H	5.111274	3.593172	3.046206
H	5.638123	0.575017	3.715927
C	-0.845751	0.438461	-2.804256
O	-1.641809	0.403660	-1.819423
O	0.402434	0.520652	-2.721106
C	-1.483392	0.391295	-4.189064
H	-1.806708	1.402567	-4.457691
H	-2.371404	-0.245894	-4.172250
H	-0.764981	0.044028	-4.933361

Table S2 continuation.

3b+$MeCO_2^-$ (conf#1)				**3b**+$MeCO_2^-$ (conf#2)			
E = -3439.55401 au				E = -3439.55406 au			
H	4.847082	-0.445608	-2.234119	H	4.895056	-2.075824	-0.920599
C	4.844903	0.338820	-1.476655	C	4.910079	-1.046796	-0.558766
C	6.112274	2.199483	-0.415051	C	6.294116	0.911272	0.045713
C	3.521839	2.146181	-0.752810	C	3.916563	1.047177	-1.060580
C	4.765963	2.947047	-0.304594	C	5.180597	1.793405	-0.555024
O	3.822757	1.235858	-1.810603	O	4.194980	-0.284629	-1.491329
C	6.160600	1.106765	-1.475727	C	6.330739	-0.500443	-0.517190
H	6.283332	1.714488	0.557860	H	6.091644	0.828421	1.123792
H	3.148406	1.590384	0.110005	H	3.183812	1.018043	-0.250193
H	4.850466	3.860240	-0.923967	H	5.632658	2.342303	-1.403436
H	6.289198	1.570405	-2.466235	H	6.704833	-0.477697	-1.551285
O	4.645622	-0.192406	-0.197616	O	4.374641	-0.949265	0.732867
C	2.398108	3.026426	-1.304101	C	3.308800	1.742655	-2.285107
H	2.672458	3.347019	-2.314294	H	3.942891	1.515074	-3.148189
H	2.282802	3.920877	-0.688549	H	3.329474	2.826077	-2.134402
O	4.699115	3.304796	1.066970	O	4.873163	2.705770	0.487372
O	7.174022	3.096473	-0.699832	O	7.577173	1.478635	-0.157011
O	7.181814	0.164059	-1.241279	O	7.121779	-1.365769	0.268768
C	4.353141	-1.572067	-0.020652	C	3.507437	-1.981500	1.193199
C	3.195010	-1.725107	1.024360	C	2.290428	-1.353678	1.930967
C	2.187279	-2.642846	0.306706	C	1.135852	-2.238789	1.452010
C	2.487813	-2.381377	-1.164323	C	1.561149	-2.586968	0.021809
O	3.905204	-2.174853	-1.201391	O	2.992922	-2.729345	0.127379
H	3.578038	-2.207314	1.934957	H	2.418416	-1.418878	3.018819
C	5.663225	-2.228317	0.410445	C	4.303320	-2.947094	2.076733
H	6.087758	-1.616979	1.213305	H	5.185477	-3.273537	1.501518
H	6.356339	-2.201470	-0.444138	H	3.658395	-3.803812	2.284226
C	5.417657	-4.537763	-0.065147	C	5.662497	-1.414935	3.294508
O	5.504534	-3.527661	0.917973	O	4.679086	-2.427035	3.328646
C	7.469050	3.995817	0.343213	C	7.797198	2.682397	0.541612
H	8.409583	4.486359	0.079393	H	8.867640	2.893484	0.475213
C	8.494947	0.617424	-1.473956	C	8.478733	-1.424250	-0.108932
H	8.855213	1.266453	-0.669124	H	8.975939	-0.459083	0.021900
H	8.560723	1.176563	-2.417384	H	8.581053	-1.736923	-1.158331
C	3.664635	4.192976	1.434005	C	4.016962	3.776241	0.147568
H	3.667325	5.087366	0.790493	H	4.420223	4.345639	-0.705351
H	2.681078	3.711917	1.395007	H	3.001438	3.434843	-0.088136
H	2.276520	-3.269181	-1.766455	H	1.176571	-3.556883	-0.300000
C	1.713090	-1.185329	-1.709673	C	1.206898	-1.513121	-1.014641
H	2.131272	-0.875747	-2.672516	H	2.088347	-1.353002	-1.638585
H	1.160987	-2.375047	0.581760	H	0.181712	-1.702142	1.484568
O	2.427406	-4.004674	0.579155	O	1.116710	-3.383515	2.282959
O	2.540918	-0.520256	1.325289	O	2.010372	-0.038800	1.523993
C	1.762937	-4.429290	1.748982	C	-0.067028	-4.135584	2.144244
H	2.153334	-3.918594	2.642719	H	-0.945599	-3.537256	2.423560
C	3.169098	0.265188	2.315866	C	2.681503	0.966635	2.247457
H	3.259349	-0.303363	3.254516	H	2.449303	0.892581	3.320147
H	4.162158	0.604097	1.997736	H	3.765345	0.924631	2.097032
N	0.343324	-1.606022	-1.888329	N	0.125407	-1.882363	-1.908403
N	1.122912	2.348497	-1.369170	N	1.961910	1.338028	-2.599862
H	6.244591	-4.446872	-0.784971	H	5.224926	-0.430285	3.086568
H	1.818509	-0.331936	-1.021732	H	0.994069	-0.565633	-0.500380
H	-0.075109	-2.238660	-1.186208	H	0.204071	-1.477306	-2.843248
H	0.934494	1.740166	-2.167364	H	1.780462	0.620615	-3.306706
H	1.951617	-5.500409	1.852139	H	0.023733	-4.991646	2.817439
H	6.687325	4.754552	0.467756	H	7.235049	3.518176	0.108930
H	5.507654	-5.490872	0.462311	H	6.126061	-1.394407	4.285346
N	-0.607825	1.246122	-0.325455	N	-0.289573	1.256969	-2.097534
H	-0.943566	1.126639	-1.275283	H	-0.423621	0.704737	-2.947843
C	-0.535885	-0.845243	-2.600707	C	-1.103096	-2.191056	-1.414025
C	0.555304	1.945329	-0.180527	C	0.958655	1.650109	-1.728665
O	-0.225231	0.228764	-3.146184	O	-1.264813	-2.618893	-0.258001
O	1.041022	2.223126	0.920272	O	1.171185	2.284864	-0.680122
N	-1.778272	-1.401505	-2.670302	N	-2.146282	-2.048516	-2.284579
H	-1.986556	-2.227738	-2.084339	H	-2.011211	-1.439315	-3.096121
H	-3.137203	2.377733	-0.023094	H	-4.930337	1.675627	-1.216179
C	-3.824524	1.629973	-0.422887	C	-4.952067	0.736204	-0.659912
C	-5.995121	1.151955	-1.533637	C	-6.343540	-1.021238	0.403133
C	-3.791212	-0.214616	-1.913522	C	-4.019512	-1.429652	-0.756063

Table S2 continuation.

C	-5.275872	0.007656	-2.280319	C	-5.252264	-2.025134	-0.031112
O	-3.152870	0.977442	-1.464447	O	-4.337834	-0.230969	-1.463322
C	-5.081469	2.257115	-1.013415	C	-6.380395	0.277556	-0.393601
H	-6.485088	0.700319	-0.658244	H	-6.129932	-0.752622	1.448584
H	-3.745186	-0.971044	-1.118055	H	-3.246779	-1.222222	-0.007853
H	-5.344532	0.238961	-3.360076	H	-5.742966	-2.748710	-0.709999
H	-4.784134	2.908884	-1.849264	H	-6.872561	0.097338	-1.361839
O	-4.218333	0.717778	0.561389	O	-4.294918	0.852624	0.570074
C	-2.938094	-0.671320	-3.103425	C	-3.471028	-2.380032	-1.825086
H	-2.610564	0.210693	-3.661528	H	-4.150754	-2.351108	-2.683058
H	-3.533427	-1.298855	-3.775738	H	-3.464252	-3.402848	-1.438094
O	-6.060048	-1.140172	-1.989773	O	-4.893014	-2.678735	1.175847
O	-6.966526	1.771055	-2.362398	O	-7.634194	-1.603758	0.312066
O	-5.681294	3.017754	0.010593	O	-7.025046	1.324592	0.295149
C	-3.683340	0.776409	1.876801	C	-3.601298	2.050427	0.887524
C	-3.389888	-0.686398	2.352801	C	-2.390492	1.679080	1.809747
C	-1.892285	-0.681274	2.692784	C	-1.202929	2.368315	1.126805
C	-1.367176	0.553457	1.956793	C	-1.641593	2.407738	-0.340290
O	-2.472579	1.464732	1.940451	O	-3.058590	2.658403	-0.248484
H	-3.972416	-0.913825	3.256465	H	-2.534490	2.082487	2.821205
C	-4.711004	1.519598	2.728382	C	-4.615678	2.995224	1.530154
H	-5.695335	1.091516	2.515477	H	-5.150898	2.431524	2.300769
H	-4.715753	2.572463	2.407535	H	-5.346289	3.294196	0.762367
C	-3.439716	2.169007	4.628215	C	-3.713653	5.170305	1.283287
O	-4.505744	1.397828	4.112679	O	-4.034561	4.109423	2.155813
C	-8.063894	0.944297	-2.671633	C	-7.855972	-2.649077	1.229546
H	-8.804905	1.575755	-3.168451	H	-8.919151	-2.896351	1.175454
C	-6.686803	3.911543	-0.405517	C	-8.422152	1.199381	0.423051
H	-7.629653	3.398998	-0.621905	H	-8.701569	0.465218	1.185653
H	-6.382139	4.458574	-1.308411	H	-8.882440	0.895099	-0.526851
C	-5.657715	-2.340650	-2.616078	C	-4.064172	-3.813486	1.034580
H	-5.607739	-2.219771	-3.709361	H	-4.517096	-4.545675	0.346394
H	-4.695378	-2.709062	-2.237431	H	-3.060957	-3.549270	0.679479
H	-0.560795	1.071076	2.481561	H	-1.220522	3.258110	-0.879475
C	-0.897660	0.143301	0.569441	C	-1.340476	1.110902	-1.108218
H	-0.005136	-0.481364	0.715218	H	-1.109801	0.303228	-0.395746
H	-1.437155	-1.607069	2.308316	H	-0.282879	1.789760	1.265407
O	-1.736721	-0.591070	4.096413	O	-1.088126	3.662334	1.682385
O	-3.584682	-1.648651	1.354524	O	-2.116166	0.302149	1.835648
C	-0.418850	-0.876629	4.495351	C	0.111248	4.313408	1.335270
H	-0.130234	-1.896073	4.199917	H	0.983970	3.750010	1.693013
C	-4.920310	-2.046756	1.142980	C	-2.889881	-0.439730	2.749275
H	-5.348403	-2.463314	2.067958	H	-2.711383	-0.090816	3.777617
H	-5.542562	-1.218344	0.787423	H	-3.958768	-0.386271	2.520879
H	-3.426524	3.170072	4.175729	H	-4.595198	5.464838	0.693507
H	-0.384666	-0.791605	5.583693	H	0.083725	5.293117	1.819618
H	-7.784217	0.118782	-3.336827	H	-7.263061	-3.540103	0.990553
H	-3.616266	2.262893	5.703582	H	-3.409701	6.009017	1.914761
H	-1.656692	-0.485877	0.090196	H	-2.240667	0.815643	-1.652963
H	-6.834091	4.620820	0.413158	H	-8.798984	2.184658	0.709080
H	-2.472572	1.689160	4.460468	H	-2.895426	4.912737	0.608013
H	-8.501604	0.510144	-1.761817	H	-7.601360	-2.339343	2.252654
H	-6.429510	-3.078179	-2.382062	H	-3.993057	-4.266274	2.027346
H	-4.873844	-2.818262	0.371000	H	-2.565740	-1.478693	2.653628
H	4.465469	-4.513091	-0.597924	H	6.419874	-1.613435	2.527373
H	9.126357	-0.272500	-1.536127	H	8.949758	-2.175356	0.529518
H	7.583991	3.469511	1.300675	H	7.504703	2.588713	1.595886
H	3.877282	4.502618	2.460446	H	3.987811	4.432302	1.021818
H	2.523834	1.133970	2.460385	H	2.311995	1.916831	1.852992
H	0.307324	-0.177186	4.058676	H	0.224474	4.436190	0.252271
H	0.685998	-4.239099	1.659208	H	-0.221382	-4.481336	1.116171
C	-2.059570	-3.599037	0.000664	C	-0.152014	-0.514631	-4.990035
O	-0.911162	-3.105823	0.182288	O	-1.239091	-0.308862	-4.386731
O	-2.805216	-3.401034	-0.989930	O	0.972085	-0.644386	-4.439483
C	-2.563445	-4.538346	1.099355	C	-0.220568	-0.650762	-6.511506
H	-3.520116	-4.989529	0.827637	H	-0.619336	-1.640764	-6.756943
H	-2.679787	-3.965401	2.024067	H	0.769701	-0.548461	-6.957529
H	-1.822802	-5.324056	1.278605	H	-0.908651	0.092016	-6.921313

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