Enhanced binding of methyl alkylammonium cations through preorganization of a water-soluble calix[4]pyrrole

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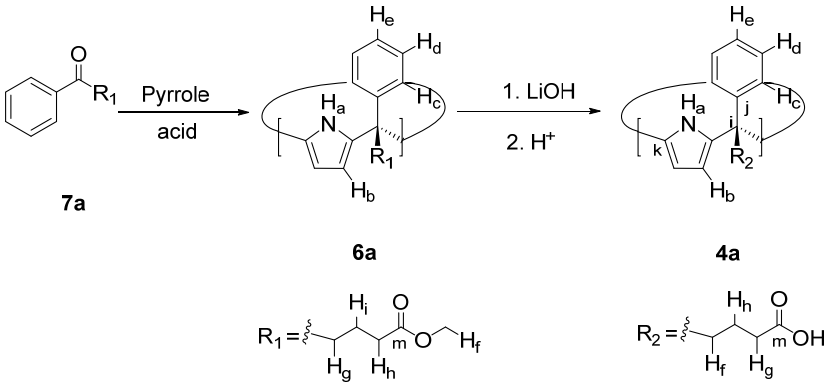
Supporting Information

1. General information and instruments

Reagents were obtained from commercial suppliers and used without further purification unless otherwise stated. All solvents were commercially obtained and used without further purification except pyrrole which was distilled and freshly used. Dry solvents were taken from a solvent system MB SPS 800. THF was dried, distilled and degassed by three freeze-pump-thaw cycles before used in the cross-coupling reactions. Routine ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker Avance 300 (300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR), Bruker Avance 400 (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR), Bruker Avance 500 (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR) or Bruker Avance 500 with cryoprobe (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR). Deuterated solvents used are indicated in the characterization and chemical shifts are given in ppm. Residual solvent peaks were used as reference.[1] All NMR *J* values are given in Hz. COSY, NOESY, ROESY, HMQC and HMBC experiments were recorded to help with the assignation of ^{1}H and ^{13}C signals. High-resolution mass spectra (HRMS) were obtained on a Bruker HPLC-TOF (MicroTOF Focus) and Bruker HPLC-QqTOF (MaXis Impact). Both with ESI as ionization mode. IR spectra were recorded on a Bruker Optics FTIR Alpha spectrometer equipped with a DTGS detector, KBr beam splitter at 4 cm^{-1} resolution using a one bounce ATR accessory with diamond windows. Melting points were measured on a MP70 Melting Point System Mettler Toledo instrument. ITC titrations were carried out on a Microcal VP-ITC MicroCalorimeter. Column chromatography purifications were performed with silica gel technical grade, pore size 60 Å, 230-400 mesh particle size, 40-63 μm particle size and Thin layer chromatography (TLC) analyses on silica gel 60 F254.

2. Synthesis and characterization data

2.1 Tetra-acid aryl-extended calix[4]pyrrole 4a



Scheme S 1. Synthesis of water-soluble calix[4]pyrrole **4a**

Tetra-ester calix[4]pyrrole 6a: A solution of methyl 5-oxo-5-phenylpentanoate **7a**[2] (1g, 5 mmol, 1 equiv.) in dry CH_2Cl_2 (16 mL) was stirred under argon atmosphere and protected from the light by covering the flask with aluminum foil. Then, HCl 37% (0.3 mL, 0.01 mmol, 2 equiv.) was added dropwise to the solution. Finally, freshly distilled pyrrole (0.3 mL, 5 mmol, 1 equiv.) was added slowly for 5min. The reaction was stirred under argon atmosphere at room temperature for 3 days. After, that the solution mixture was diluted with 20 mL of CH_2Cl_2 and washed with Na_2CO_3 (2x20 mL), brine (1x20 mL) and water (1x20 mL). The organic layer was dried (Na_2SO_4), filtered and concentrated to dryness. The crude was purified by column chromatography on silica gel (50g, 80:18:2 CH_2Cl_2:Hexane:MTBE) affording the tetra-α **6a** as white solid. Compound **6a** was recrystallized from 3:2 CH_3OH:CH_2Cl_2 (137 mg, 11%). Rf = 0.25 (80:18:2 CH_2Cl_2:Hexane: MTBE). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 7.93 (s, 4H); 7.24-7.12 (m, 20H); 5.83 (d, J = 2.34 Hz, 8H); 3.63 (s, 12H); 2.38-2.32 (m, 8H); 2.30 (t, J = 7.01 Hz, 8H); 1.63 (m, 8H). ^{13}C{^{1}H} NMR (125 MHz, 298K, $CDCl_3$): δ (ppm) = 174.4; 145.5; 135.6; 128.9; 127.4; 126.6; 106.4; 51.6; 49.2; 38.8; 33.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{64}H_{68}N_4NaO_8$ 1043.4929; Found 1043.4928. FTIR ν (cm^{-1}): 3370; 2949; 1734; 1708; 1437; 1202; 1175; 764; 703. M.p.106.4ºC.

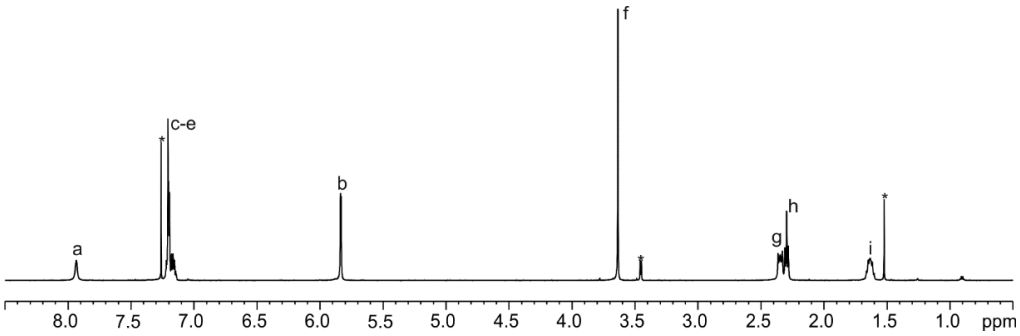


Figure S 1. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of compound **6a**. See Scheme S 1 for proton assignment. *Residual solvent peak

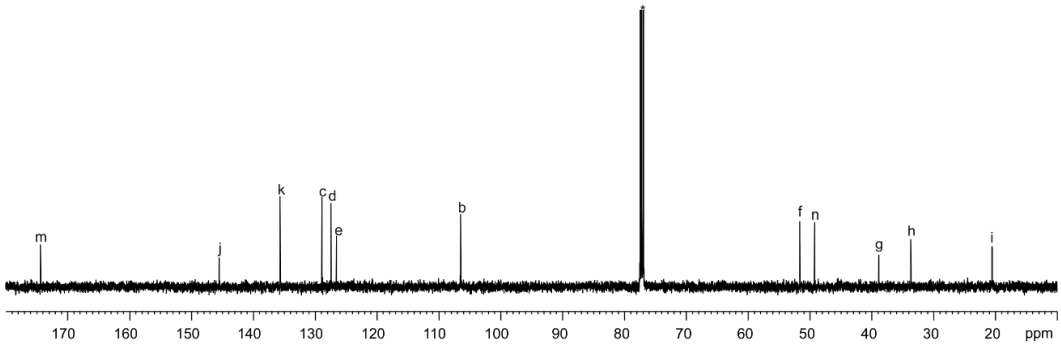


Figure S 2. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 298 K) spectrum of **6a**. See Scheme S 1 for carbon assignment. *Residual solvent peak.

Tetra-acid calix[4]pyrrole 4a: Tetra-ester aryl-extended calix[4]pyrrole **6a** (100 mg, 0.1 mmol, 1 equiv.) was dissolved in THF (30 mL). LiOH (23.4 mg, 0.98 mmol) was dissolved in water (10 mL) and added to the above solution. The mixture was stirred at 40ºC for 24 h. After that, THF was removed and the aqueous layer was transferred to a separatory funnel and washed with CH_2Cl_2 (30 mL). Then, the aqueous phase was acidified with 1 N HCl until pH = 3 and the white precipitate was extracted with EtOAc (3x30 mL). The organic phase was dried with Na_2SO_4, filtered and concentrated affording the product as a white solid (84 mg, 94% yield). ^{1}H NMR (500 MHz, $(CD_3)_2CO$, 298 K): δ (ppm) = 9.14 (s, 4H); 7.30 (t, J = 7.21Hz, 8H); 7.12 (t, J = 7.21 Hz, 4H); 6.91 (d, J = 7.21 Hz, 4H); 5.97 (d, J = 2.37 Hz, 8H); 2.24 (m, 8H); 2.11 (t, J = 7.40 Hz, 8H); 1.14 (m, 8H). $^{13}C\{^{1}H\}$ NMR (125 MHz, 298K, $(CD_3)_2CO$): δ (ppm) = 174.4; 146.1; 136.6; 128.4; 128.1; 126.7; 104.5; 59.8; 47.6; 33.7; 30.7. HRMS (ESI-TOF) m/z: $[M-H]^-$ Calcd for $C_{60}H_{59}N_4O_8$ 963.4338; Found 963.4323. FTIR ν (cm^{-1}): 3418; 2921; 1701; 1422; 1290; 1205; 756; 707. M.p. > 150ºC (decompose).

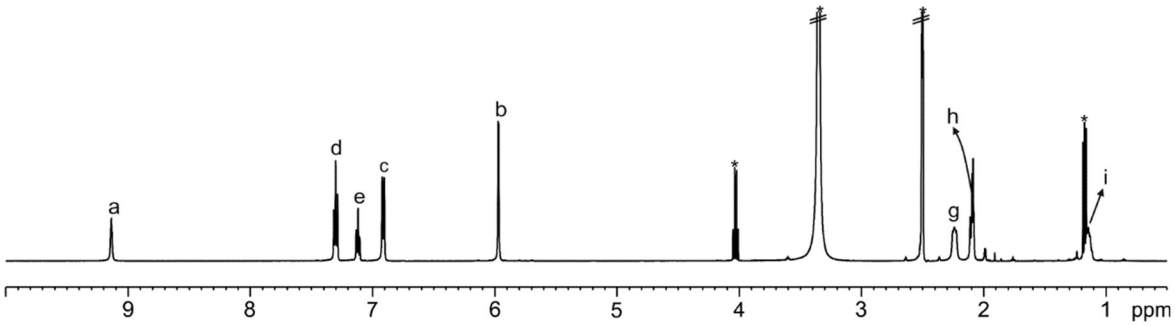


Figure S 3. ^{1}H NMR (500 MHz, $(CD_3)_2CO$, 298 K) spectrum of compound **4a**. See Scheme S 1 for proton assignment. *Residual solvent peak

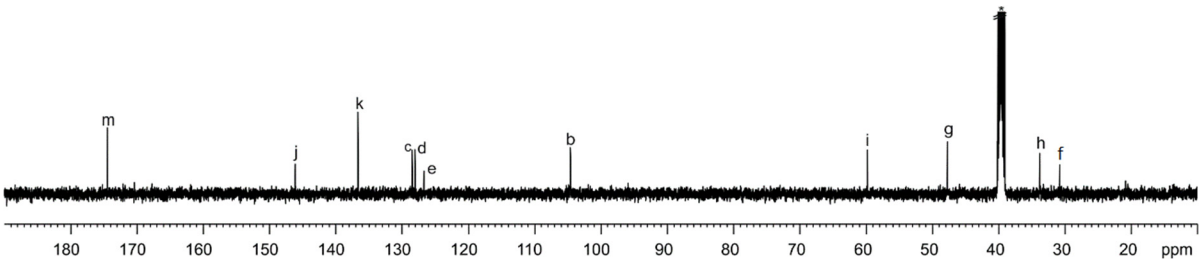
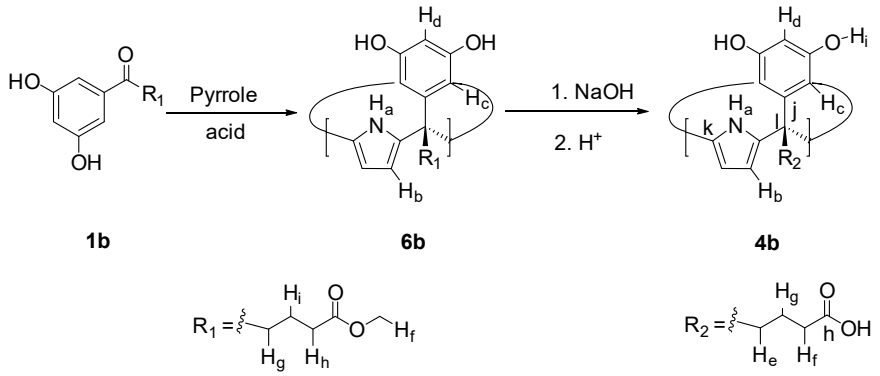


Figure S 4. $^{13}C\{^{1}H\}$ NMR (125 MHz, $(CD_3)_2CO$, 298 K) spectrum of **6a**. See Scheme S 1 for carbon assignment. *Residual solvent peak.

2.2 Tetra-acid aryl-extended calix[4]pyrrole 4b



Scheme S 2. Synthesis of water-soluble calix[4]pyrrole **4b**

Tetra-*α* tetra-ester **6b** aryl-extended calix[4]pyrrole was synthesized following a procedure described by our research group.[3]

Tetra-acid calix[4]pyrrole 4b: Tetra-ester aryl-extended calix[4]pyrrole **6b** (30 mg, 0.025 mmol, 1 equiv.) was dissolved in a mixture of THF: 3M NaOH (1:1) (10 mL). The reaction was refluxed for 3h. After that, the THF was removed, and the aqueous phase was washed with DCM (10 mL). Then, the aqueous phase was acidified with 1N HCl and a brown solid precipitated. The solid was collected by centrifugation and washed with DCM (2x5mL). Finally, the compound was dried under vacuum obtaining a pale brown solid (24 mg, 88% yield). ^{1}H NMR (400 MHz, $(CD_3)_2CO$, 298 K): δ (ppm) = 8.66 (s, 4H); 8.01 (s, 8H); 6.16 (t, J = 4.05 Hz, 1H); 6.08 (d, J = 2.41 Hz, 8H); 6.08 (d, J = 2.41 Hz, 8H); 2.37 (m, 8H); 2.27 (t, J = 7.40 Hz, 8H); 1.47 (m, 8H). $^{13}C\{^{1}H\}$ NMR (100 MHz, 298K, $(CD_3)_2CO$): δ (ppm) = 173.8; 157.2; 149.1; 136.9; 108.5; 104.8; 101.6; 48.3; 39.7; 33.6; 20.8. HRMS (ESI-TOF) m/z: [M-H$^-$] Calcd for $C_{60}H_{59}N_4O_{16}$ 1091.3917; Found 1091.3932.

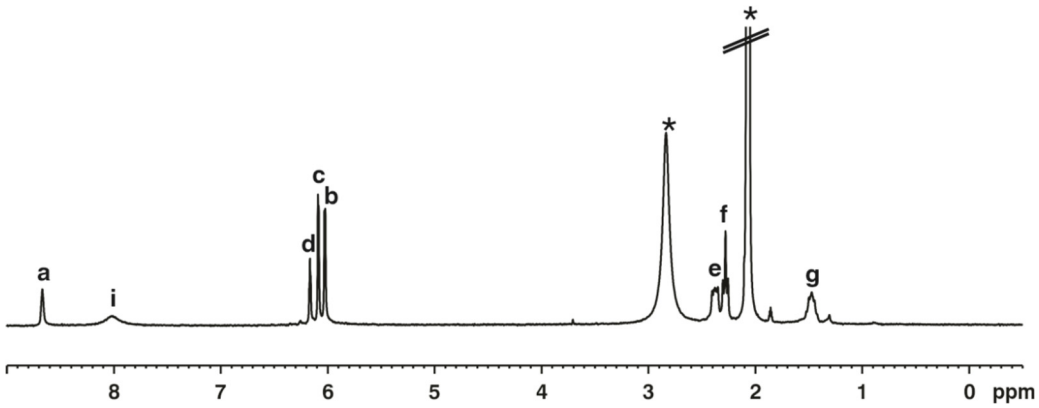


Figure S 5. ^{1}H NMR (400 MHz, $(CD_3)_2CO$, 298 K) spectrum of compound **4b**. See Scheme S 2 proton assignment. *Residual solvent peak

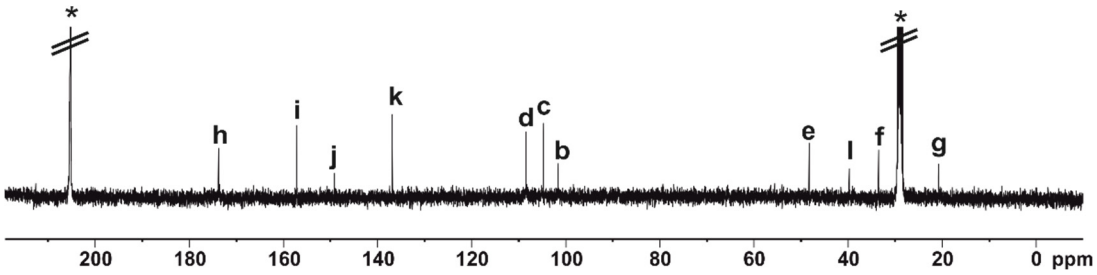


Figure S 6. $^{13}C\{^{1}H\}$ NMR (100 MHz, $(CD_3)_2CO$, 298 K) spectrum of **4b**. See Scheme S 2 for carbon assignment. *Residual solvent peak.

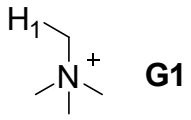
3. NMR binding studies

For reverse titrations a solution of the host (1-2.5 mM) was prepared in 0.01 M borate/sodium hydroxide buffer in D_2O (pD ~ 10) and 0.01 M NaCl. Subsequently, 0.5 mL of the solution were placed in an NMR tube. A solution of the guest was prepared at 8-10-fold higher concentration using the host's solution ([G] = 8-20 mM and [H] = 1-2.5 mM). Immediately, the 0.5 mL of the host solution was titrated by manually injecting incremental amounts of the titrant's solution using a Hamilton Glass micro syringe. For the direct titrations the maximum concentration of the calix[4]pyrrole was 2.5-3 mM due to solubility reasons. We performed the direct titrations to determine the chemical shift values of the protons signals of the methyl and methylene protons of the tetraalkylammonium cations in the 1:1 complex and compare them with those obtained in the reverse titrations. Not surprisingly, in the direct titrations the proton signals of the alkylammonium cations (increase % of free) moved in opposite direction to that observed in the reverse titration (increase % of bound). A ^{1}H NMR spectrum of the mixture was acquired after each injection and vigorous hand shaking of the NMR tube and sonication for few seconds was performed.

The titrations data were mathematically analyzed using the HypNMR 2008 software and a 1:1 theoretical binding model. For the determination of the binding constants (*K*a) we exclusively selected proton signals belonging to the binding partner placed initially in the NMR tube (β-Pyrroles/ortho or $-CH_3$/$-CH_2-$ protons). We fixed the value of the chemical shift for the protons of the free species initially placed in the NMR tube and calculated the log β by manually adjusting the fit of the experimental data to a 1:1 model in order to obtain the minimum sigma value. Next, we fixed the determined *K*a value and the chemical shift of the free added species and fit the chemical shift changes of this species to a 1:1 binding model. The fit returned the chemical shift value for the protons in the bound species. We determined the complexation induced shift (CIS) value by subtracting the chemical shift value of the bound species returned from the fit from that of the free species.

3.1 ^{1}H NMR spectroscopic titration experiments free tetra-acid C[4]P 4a

3.1.1 ^{1}H NMR spectroscopic titration experiments leading to G1⊂4a



G1

Figure S 7. Line-drawing structure of tetramethylammonium chloride guest (**G1**)

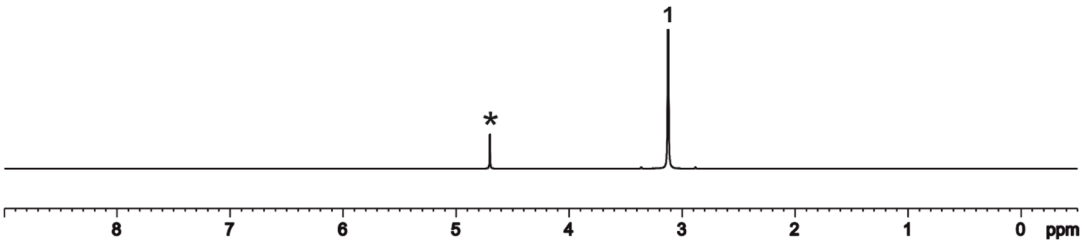


Figure S 8. ^{1}H NMR spectrum (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) of tetramethylammonium chloride **G1**. *Residual solvent peaks

Reverse titration: addition of incremental amounts of G1 to a 4a solution - G1⊂4a

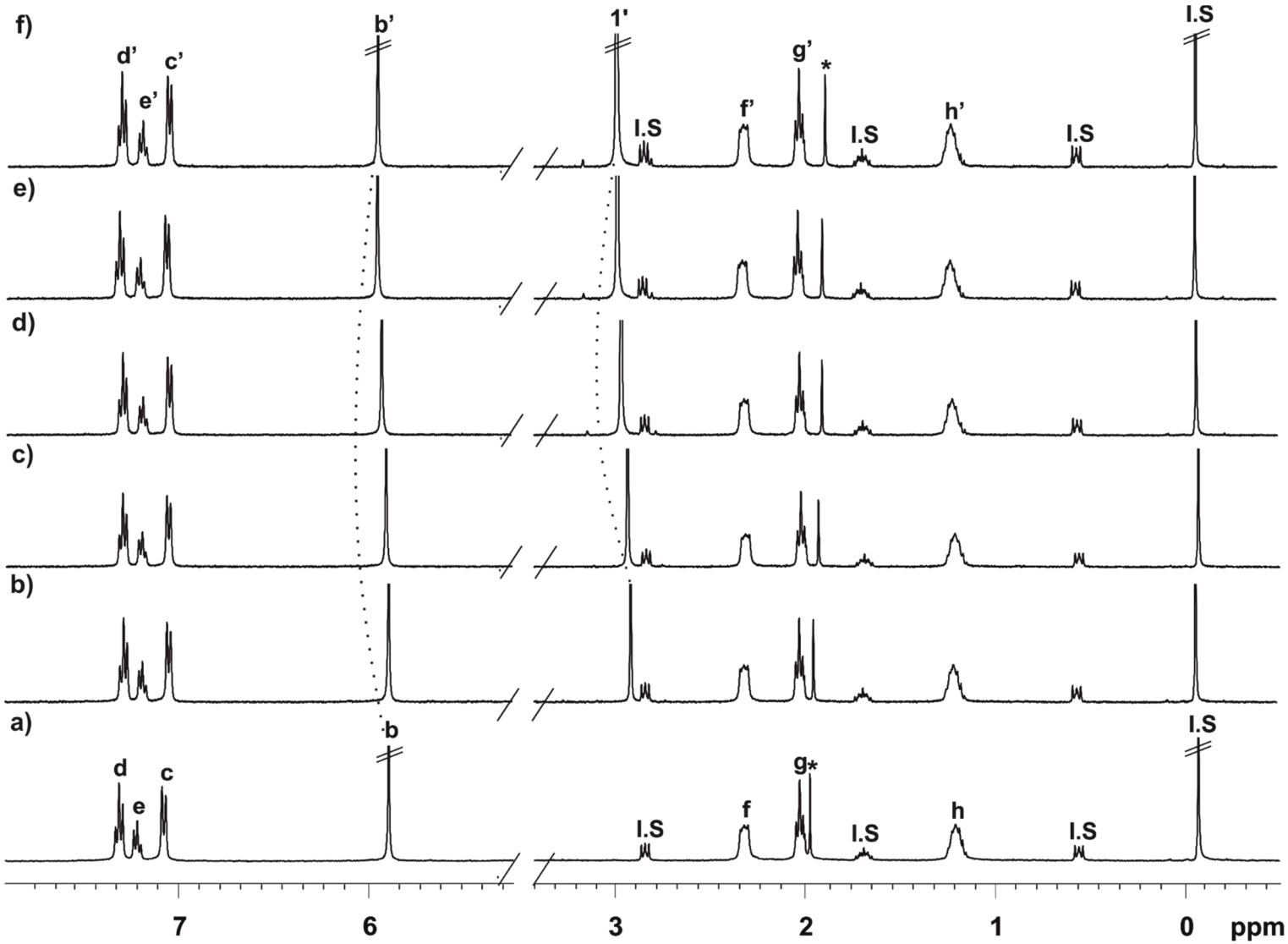


Figure S 9. Selected regions of ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of tetra-acid **4a** with **TMACl G1**: a) 0; b) 0.5; c) 1.0; d)1.5; e) 2.0 and f) 2.5 equiv. of **G1**. Primed letters and numbers correspond to proton signal of bound components. See **Scheme S 1** and **Figure S 7** for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

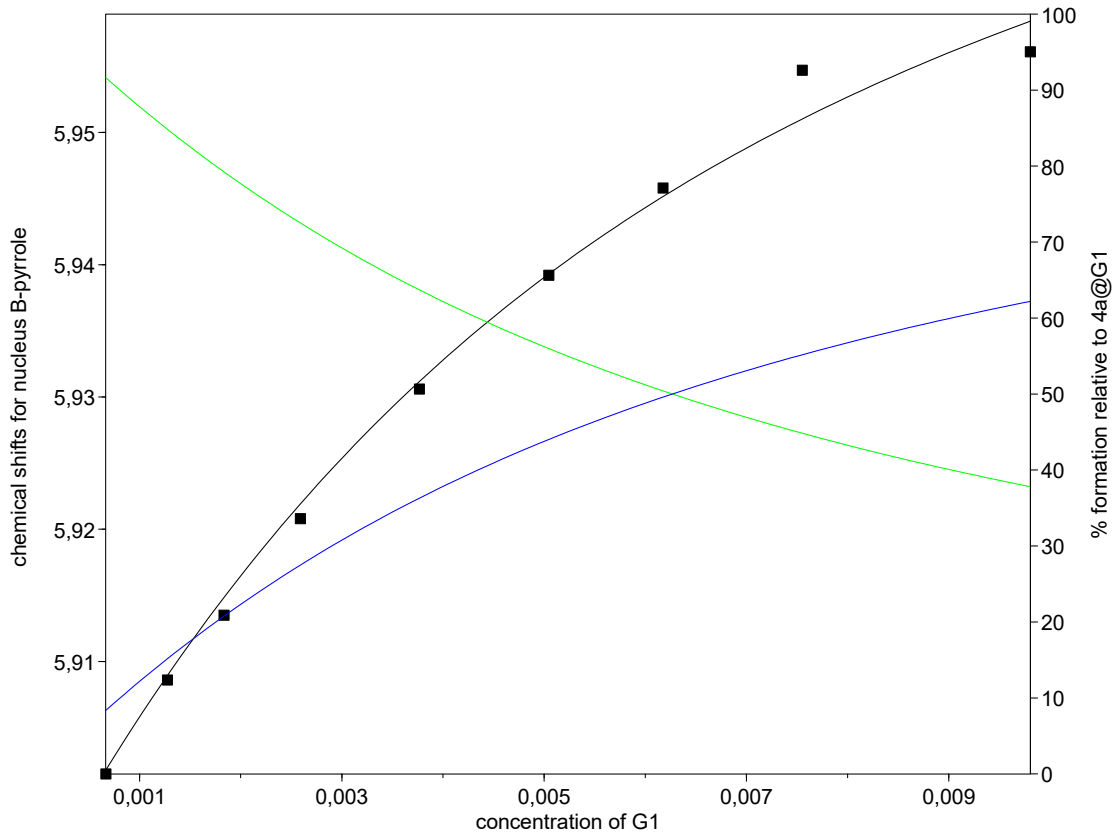


Figure S 10. Fit of the NMR titration data (signal **b**, β-pyrrole proton) to a 1:1 binding model (black line). The fit returned K_a (**G1⊂4a**) = 2.3 x 10^2 M^{-1}. The speciation shows the concentration (%) of free tetra-acid **4a** (green line) and 1:1 complex (blue line) throughout the titration.

Table S 1. Chemical shifts of the proton signals of free and bound **4a**/ **G1** of the **G1⊂4a** (δ, ppm) and calculated complexation-induced shifts ($\Delta\delta$, ppm).

Signal	δ_{free}	δ_{bound} (1:1 complex)	$\Delta\delta$ (1:1 complex)
1	3.11	2.45	-0.66
H-ortho (Hc)	7.07	7.04	-0.03
β-pyrrole (Hb)	5.90	5.99	0.09

Direct titration: addition of incremental amounts of 4a to a G1 solution - G1⊂4a

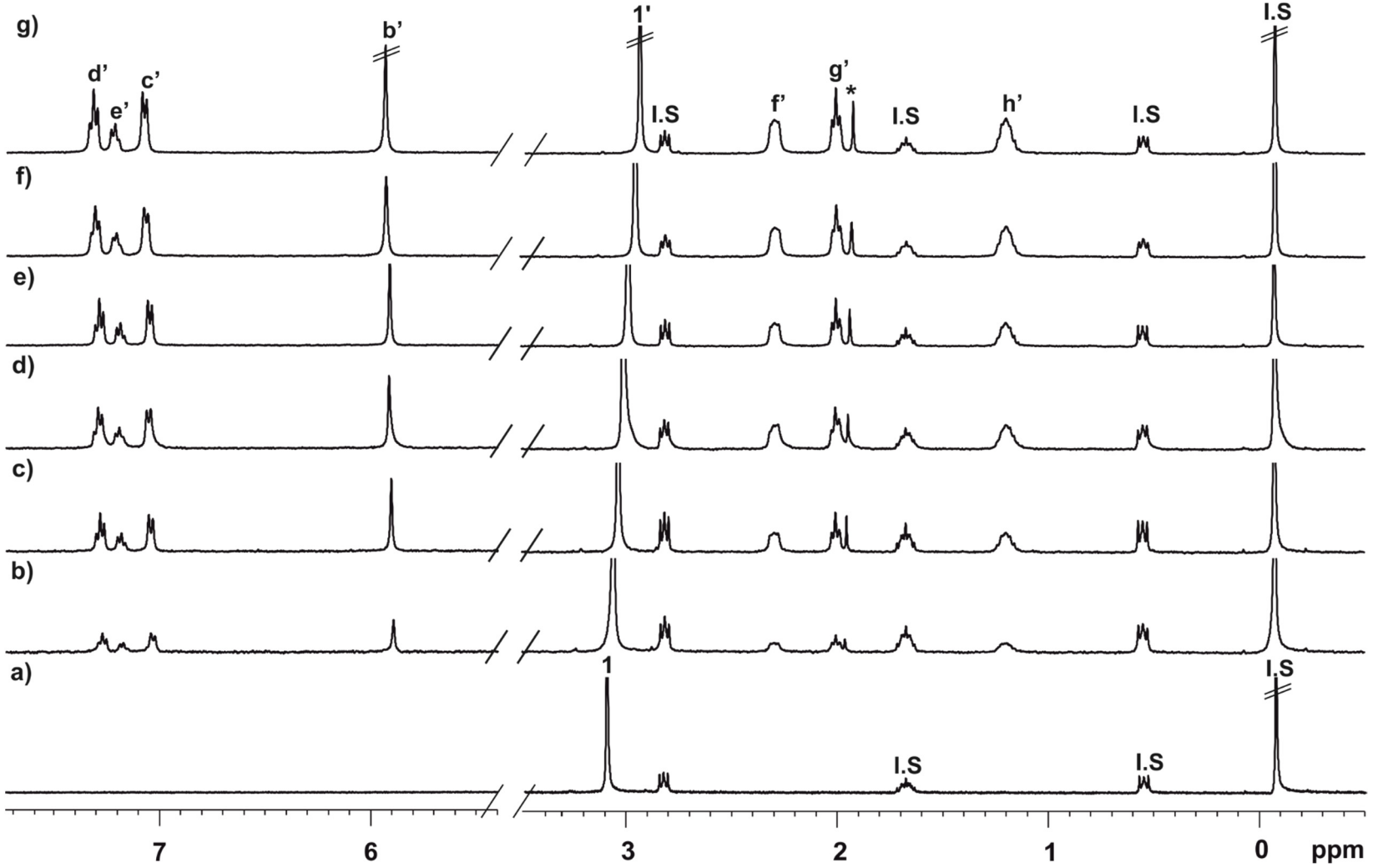


Figure S 11. Selected regions of ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **TMACl G1** with tetra-acid **4a** : a) 0; b) 0.11; c) 0.24; d) 0.36; e) 0.48; f) 0.57 and g) 0.72 equiv. of **4a**. Primed letters and numbers correspond to proton signal of bound components. See **Scheme S 1** and **Figure S 7** for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

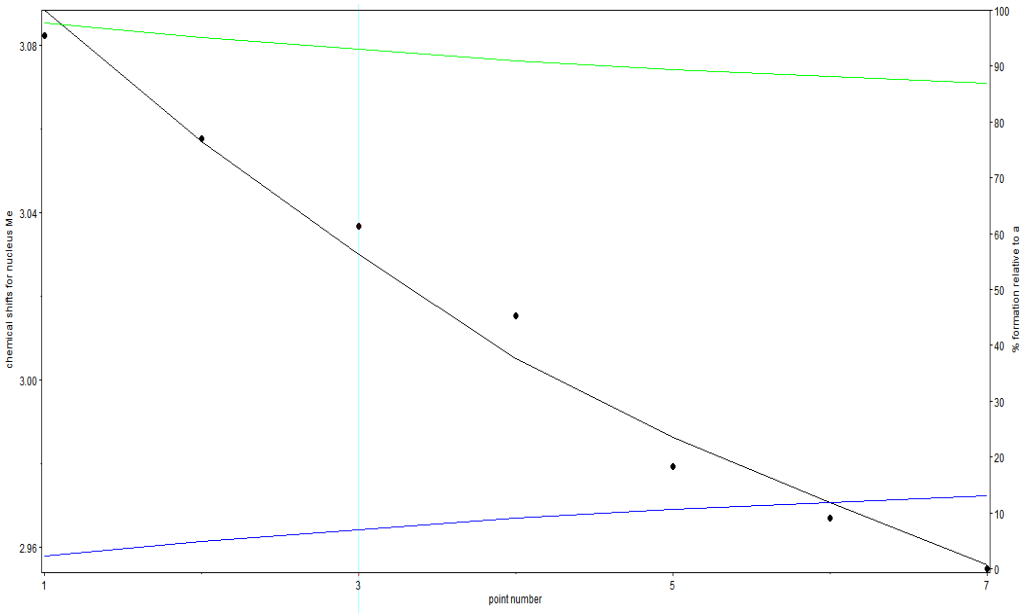
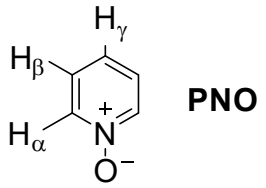


Figure S 12. Fit of the NMR titration data (signal **1'**, -CH_3 proton) to a 1:1 binding model (black line). Owing to the reduced formation of the complex we did not considered the K_a and CIS values from the fit as reliable and accurate. The speciation shows the concentration (%) of free **G1** (green line) and 1:1 complex (blue line) throughout the titration.

3.2 ^{1}H NMR spectroscopic titration experiments Gx⊂(5@4a)



PNO

Figure S 13. Line-drawing structure of pyridine *N*-oxide (**PNO**)

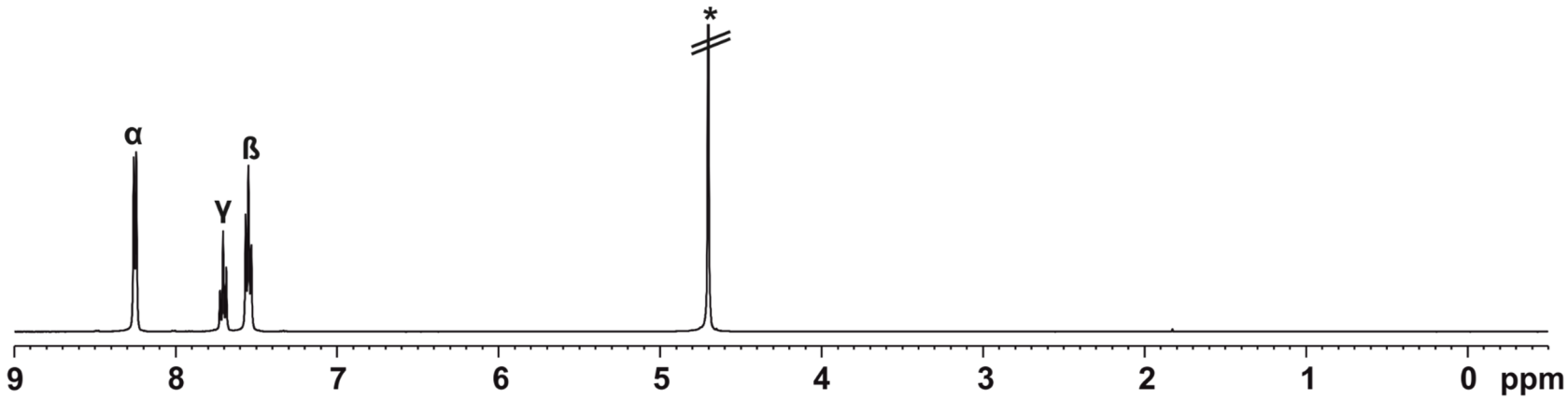


Figure S 14. ^{1}H NMR spectrum (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) of pyridine *N*-oxide (PNO) **5**. *Residual solvent peaks

3.2.1 ^{1}H NMR spectroscopic titration experiments 5@4a

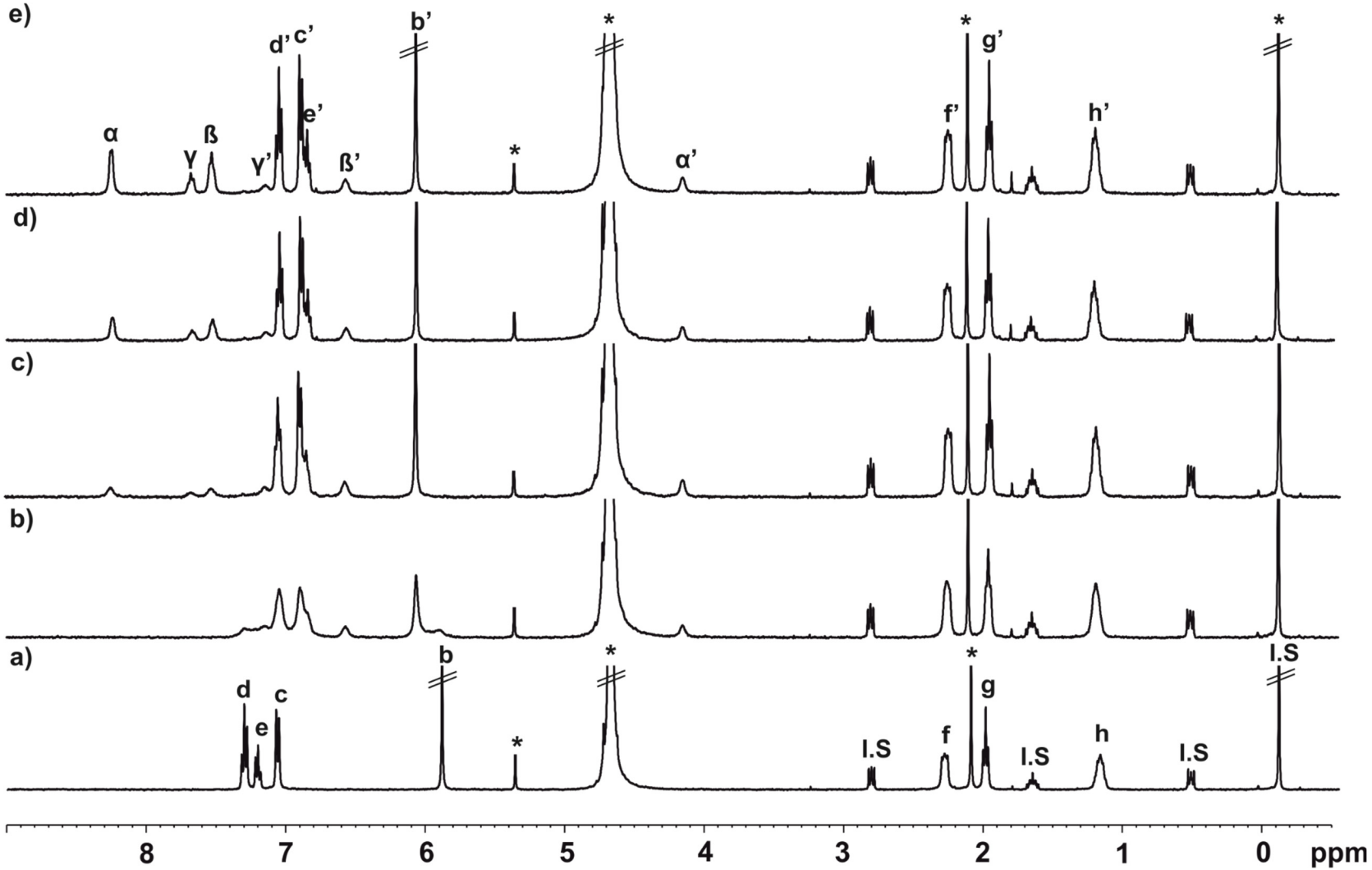


Figure S 15. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of tetra-acid **4a** with pyridine *N*-oxide (**5**): a) 0; b) 0.6; c) 1.2; d) 2.0 and e) 3.0 equiv. Primed letters and numbers correspond to proton signal of bound components. See **Scheme S 1** and Figure S 14 for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks

3.2.2 ^{1}H NMR spectroscopic titration experiments leading to G1⊂(PNO@4a)
Reverse titration adding incremental amounts of G1 to a solution of PNO@4a

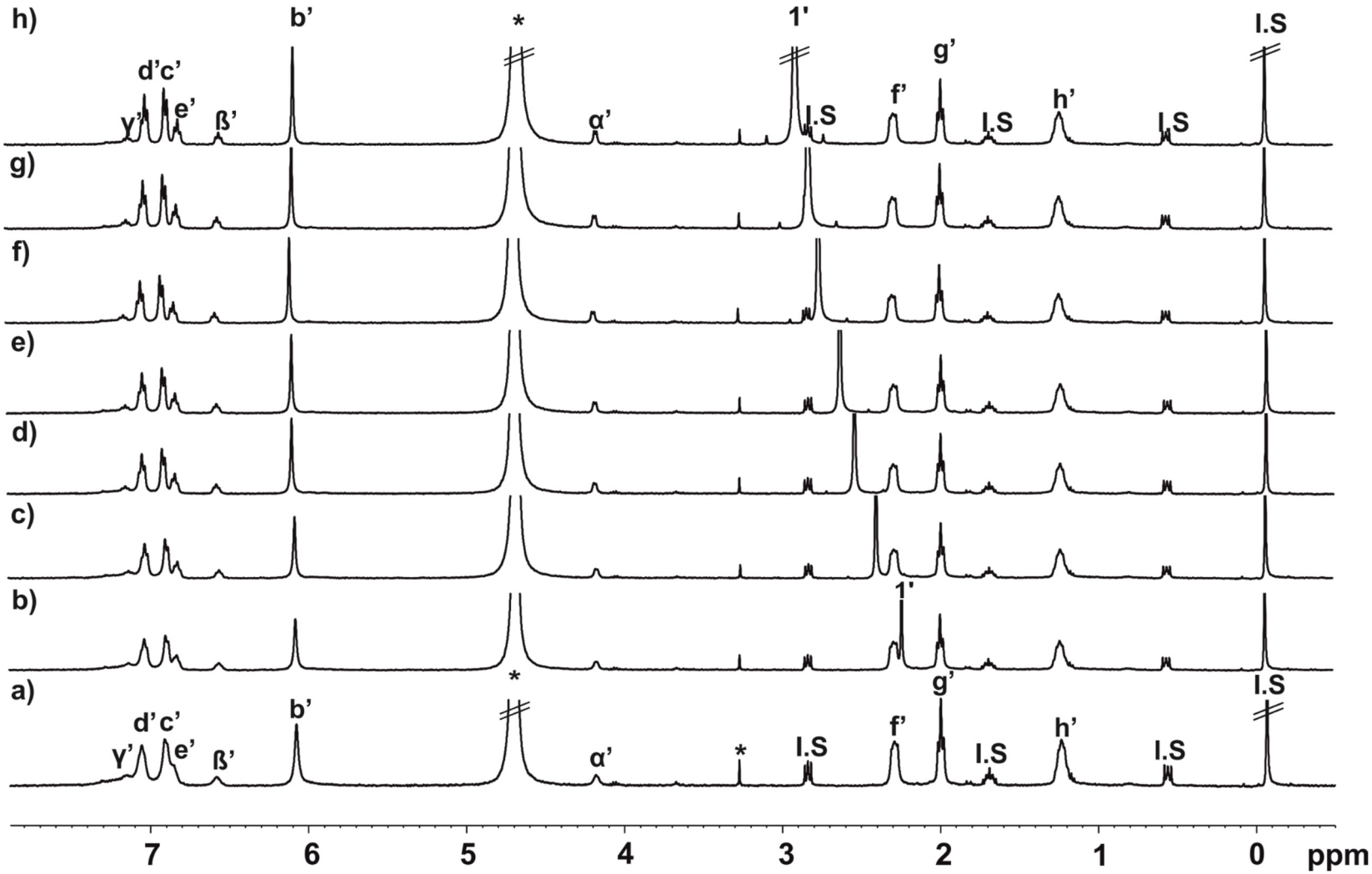


Figure S 16. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **PNO@4a** (1.3 equiv. of **PNO**) with **G1**: a) 0; b) 0.5; c) 1.0; d)1.5; e) 2.0; f) 3.0; g) 4.0 and h) 5.8equiv. of **G1**. Primed letters and numbers correspond to proton signal of bound components. See **Scheme S 1**, **Figure S 7** and **Figure S 13**for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

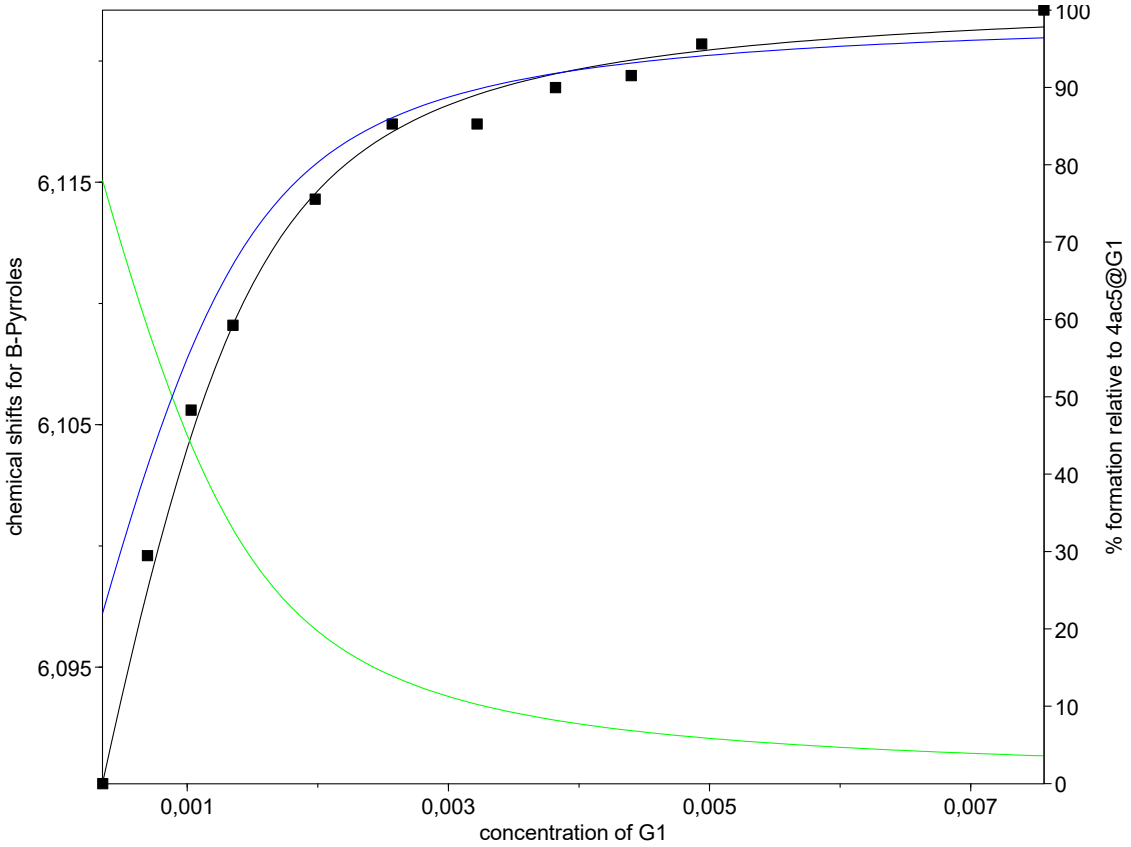


Figure S 17. Fit of the NMR titration data (signal **b**, β-pyrrole proton) to a 1:1 binding model (black line). The fit returned K_a (**G1⊂(PNO@4a**) = 4.4 x 10^3 M^{-1}. The speciation shows the concentration (%) of free **PNO@4a** (green line) and the 1:1 complex (blue line) throughout the titration.

Table S 2. Chemical shifts of the proton signals of free **PNO@4a/G1** and bound in the **G1⊂(PNO@4a)** (δ, ppm) complex and the calculated complexation-induced shifts ($\Delta\delta$, ppm).

Signal	δ_{free}	δ_{bound} (1:1 complex)	$\Delta\delta$ (1:1 complex)
1	3.096	2.00	-1.10
H-ortho (Hc)	6.90	6.93	0.03
β-pyrrole (Hb)	6.08	6.12	0.04

Direct titration: addition of incrementa amounts of 5@4a to a solution of G1 - G1⊂(5@4a)

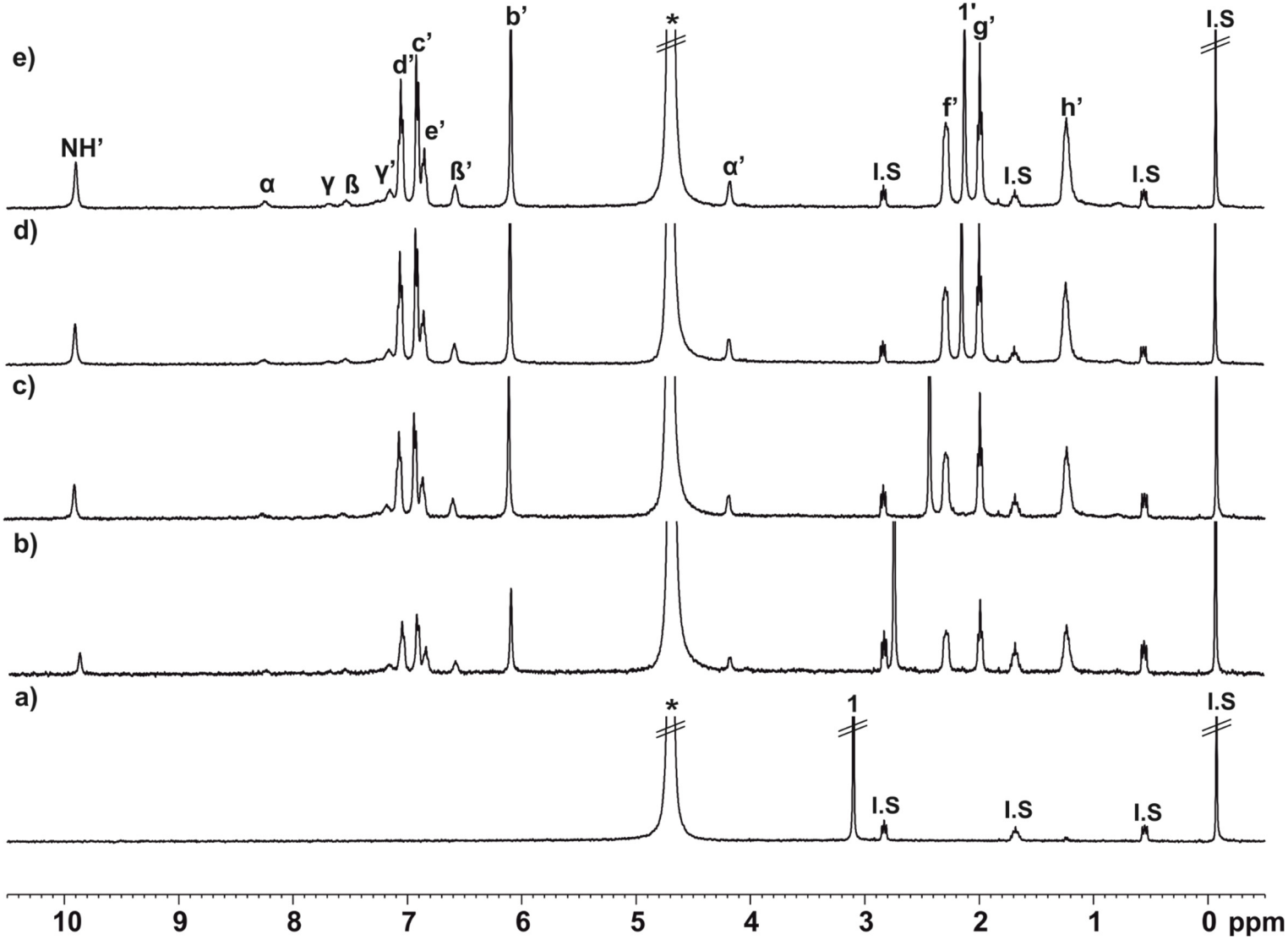


Figure S 18. [1]H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **5@4a** (1.2 equiv. of **5**) with **G1**: a) 0; b) 0.5; c) 1.0; d) 2.0 and e) 2.5 equiv. **5@4a**. Primed letters and numbers correspond to proton signal of bound components. See **Figure S 7**, **Figure S 13** and **Scheme S 1** for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

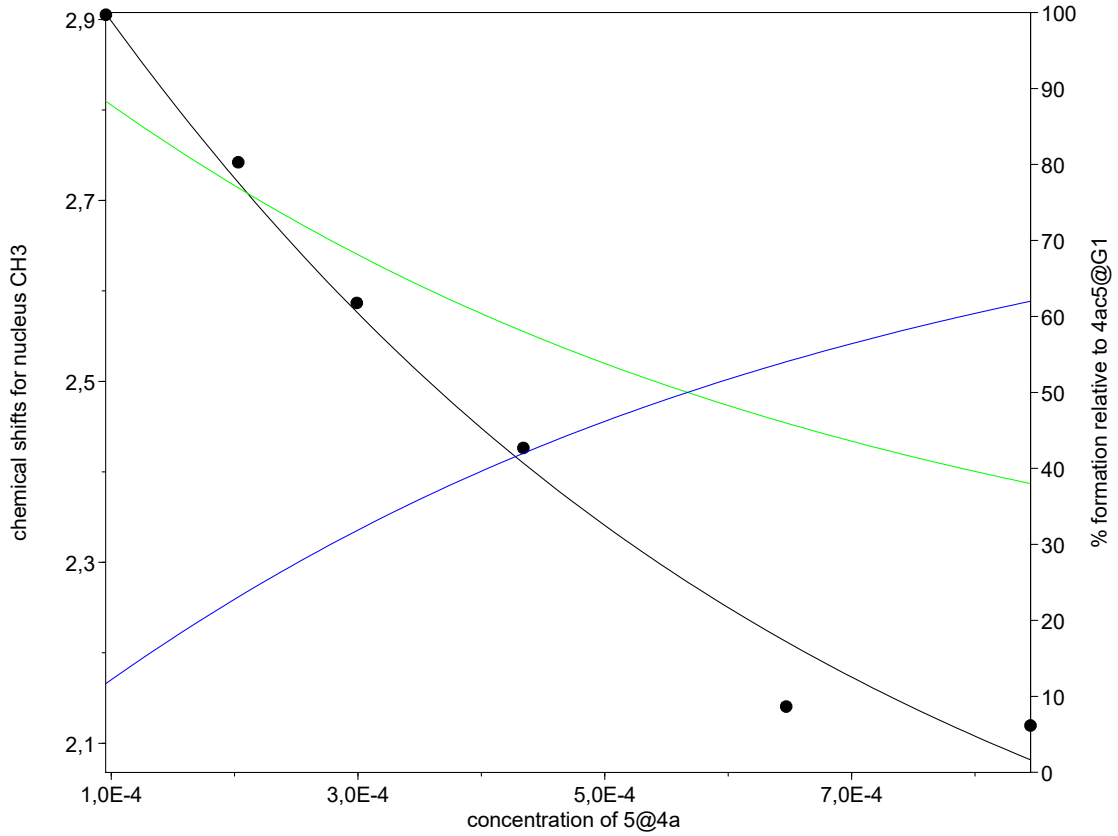
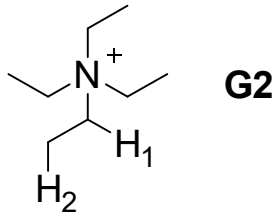


Figure S 19. Fit of the NMR titration data (signal **1'**, -CH_3 proton) to a 1:1 binding model (black line). The fit returned K_a (**G1⊂(5@4a)**) = 2.8 x 10^3 M^{-1}. The speciation shows the concentration (%) of free **G1** (green line) and 1:1 complex (blue line) throughout the titration.

Table S 3. Chemical shifts of the proton signals of free and bound **G1** in the **G1⊂(5@4a)** (δ, ppm) and calculated complexation-induced shifts ($\Delta\delta$, ppm).

Signal	δ_{free}	δ_{bound} (1:1 complex)	$\Delta\delta$ (1:1 complex)
1	3.10	1.47	-1.63

3.2.3 ^{1}H NMR spectroscopic titration experiments leading to G2⊂(5@4a*)*



G2

Figure S 20. Line-drawing structure of tetraethylammonium chloride guest (**G2**)

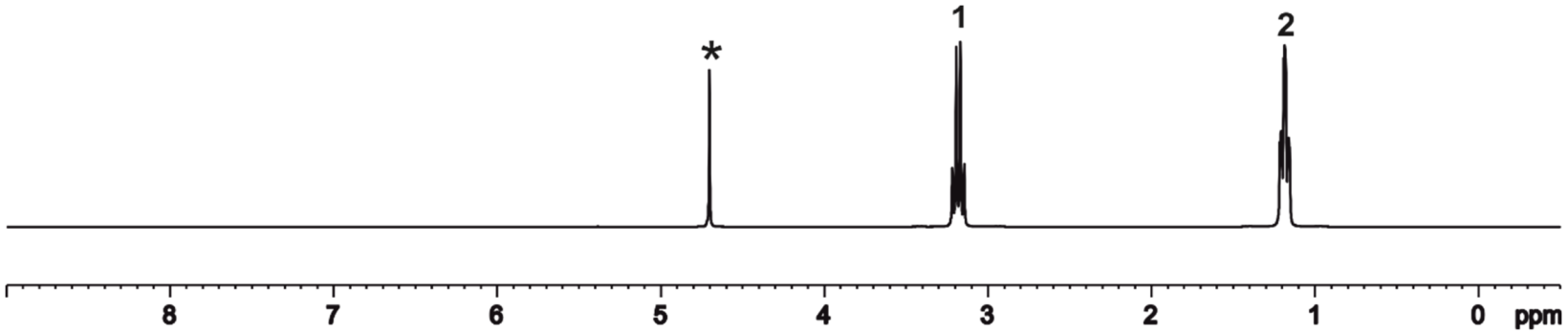


Figure S 21. ^{1}H NMR spectrum (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) of tetraethylammonium chloride **(G2)**. *Residual solvent peaks

Reverse titration: incremental addition of G2 to a solution of 5@4a - G2⊂(5@4a)

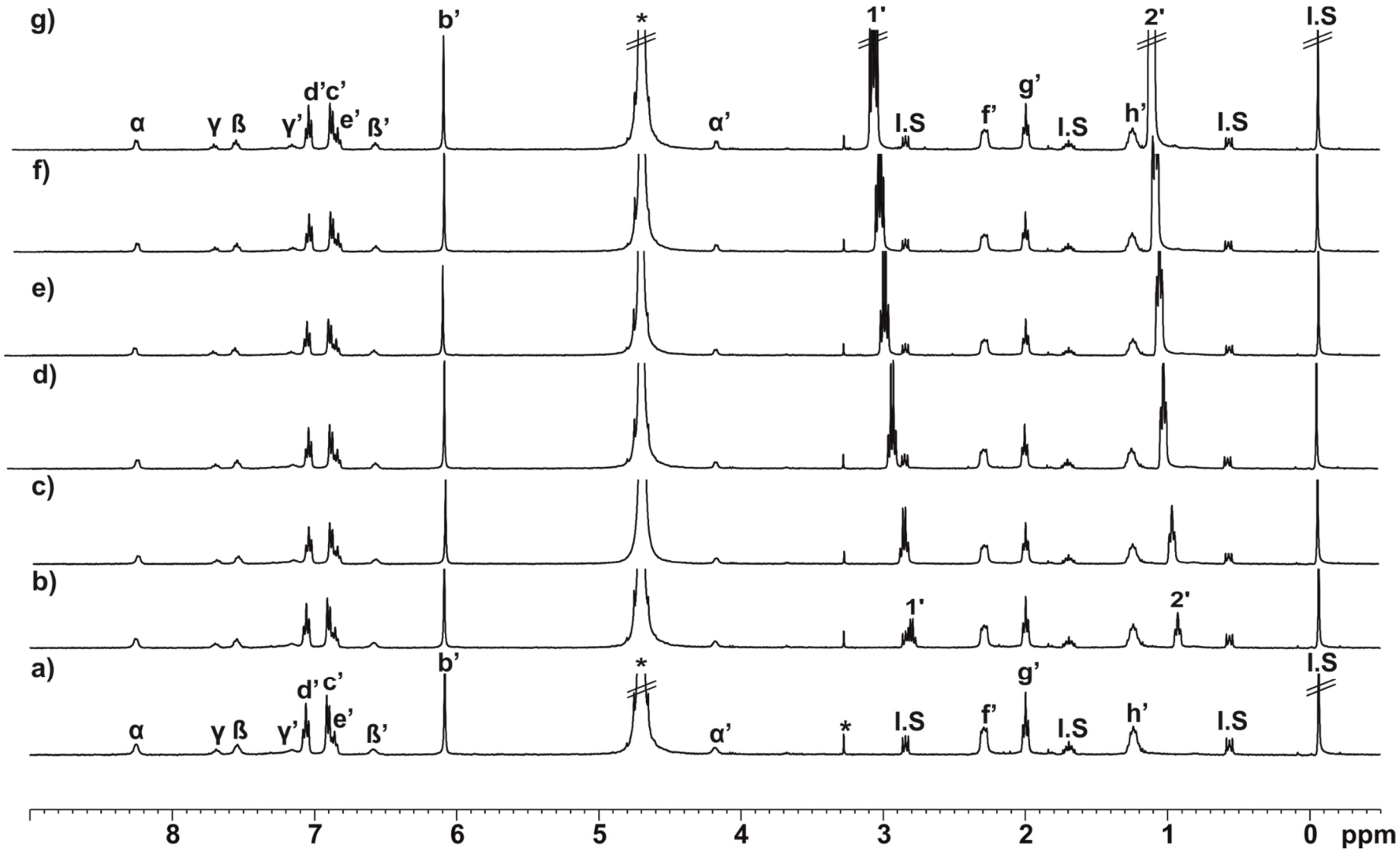


Figure S 22. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **5@4a** (1.4 equiv. of **5**) with **G2**: a) 0; b) 0.5; c) 1.0; d) 1.5; e) 2.0; f) 3.0; g) 4.0 and h) 5.5equiv. of **G2**. Primed letters and numbers correspond to proton signal of bound components. See **Scheme S 1**, **Figure S 13** and Figure S 21 for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

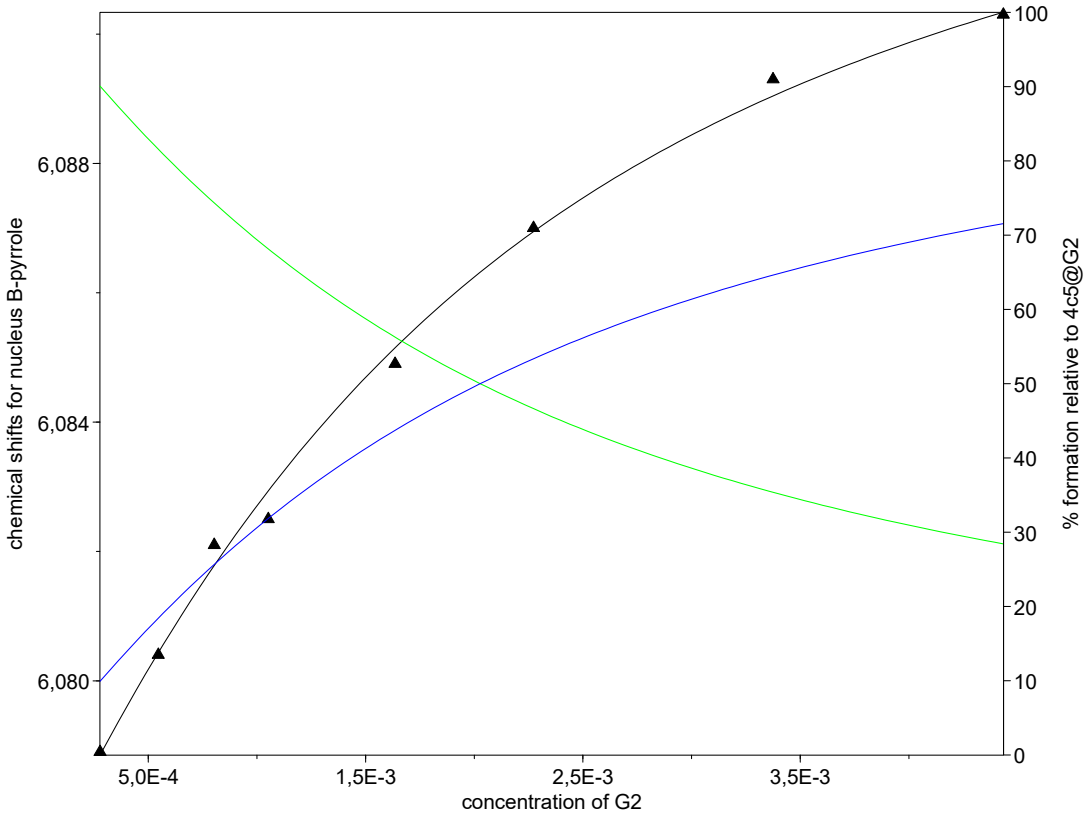


Figure S 23. Fit of the NMR titration data (signal **b**, β-pyrrole proton) to a 1:1 binding model (black line). The fit returned K_a (**G2⊂(5@4a)**) = 7.4 x 10^2 M^{-1}. The speciation shows the concentration (%) of free **5@4a** (green line) and 1:1 complex (blue line) throughout the titration.

Table S 4. Chemical shifts of the proton signals of free and bound **5@4a/G2**/ **G2⊂(5@4a)** (δ, ppm) and calculated complexation-induced shifts ($\Delta\delta$, ppm).

Signal	δ_{free}	δ_{bound} (1:1 complex)	$\Delta\delta$ (1:1 complex)
1	3.10	2.00	-1.10
2	1.18	0.44	-0.74
H-ortho (Hc)	6.90	6.88	-0.02
β-pyrrole (Hb)	6.08	6.10	0.00

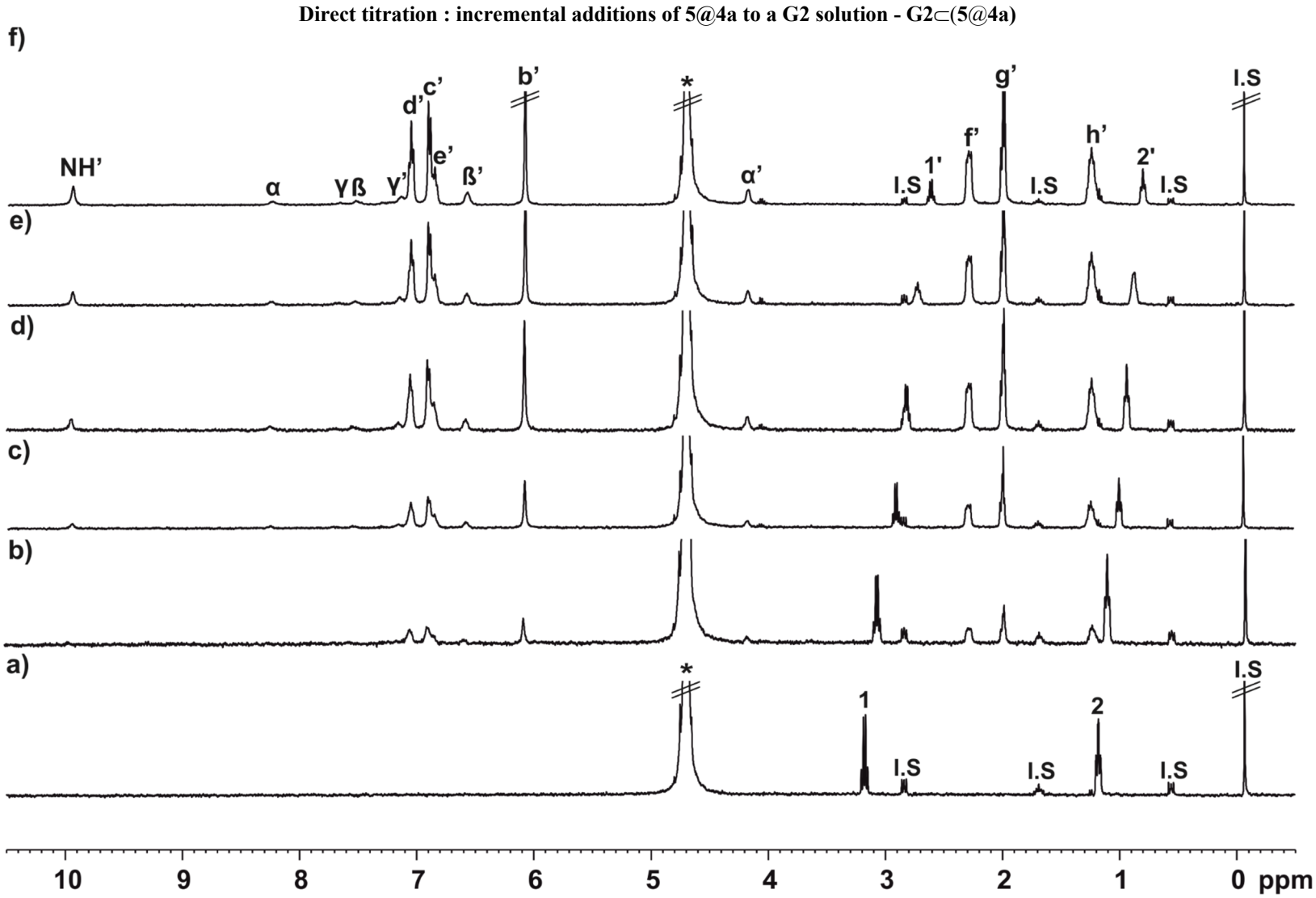


Figure S 24. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **5@4a** (1.2 equiv. of **5**) with **G2**: a) 0; b) 0.5; c) 1.0; d) 2.0 and e) 2.5 equiv. **5@4a**. Primed letters and numbers correspond to proton signal of bound components. See **Scheme S 1**, **Figure S 13**and Figure S 21 for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

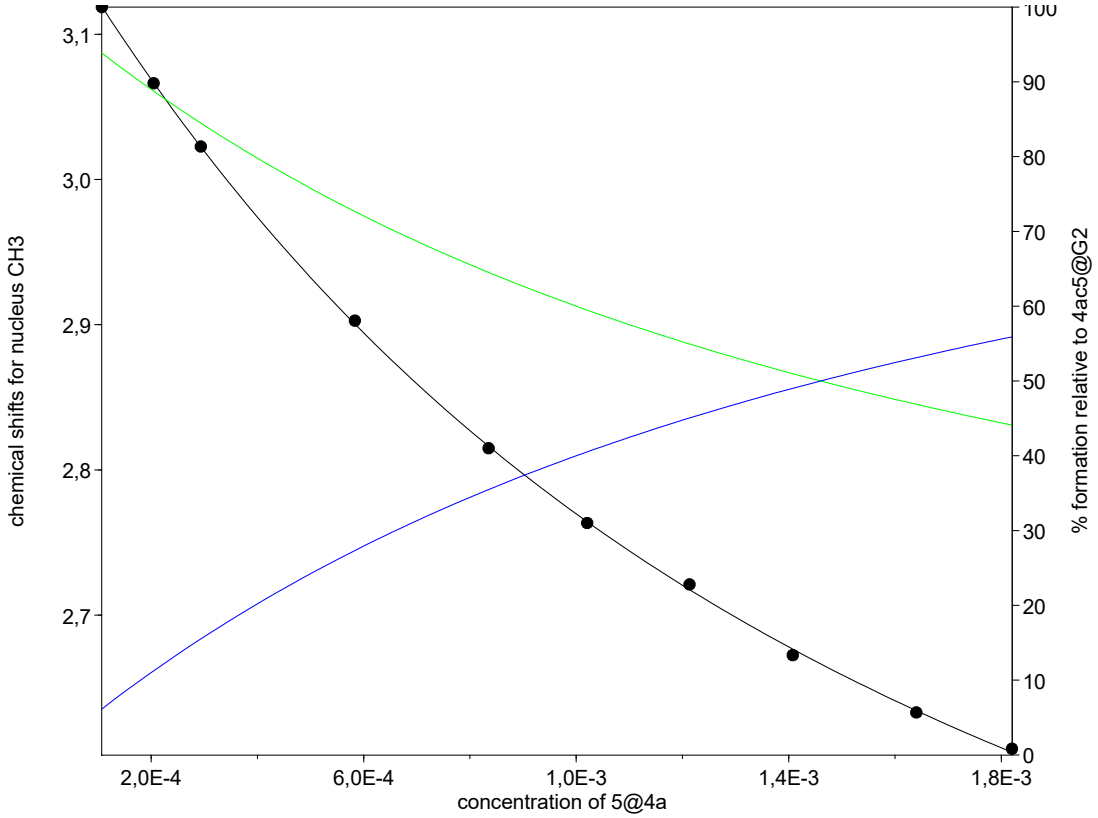


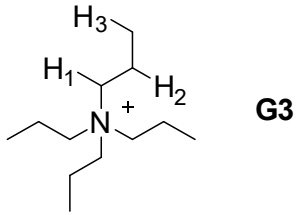
Figure S 25. Fit of the NMR titration data (signal **1'**, -CH_2 proton) to a 1:1 binding model (black line). The fit returned K_a (**G2⊂(5@4a)**) = 7.2 x 10^2 M^{-1}. The speciation shows the concentration (%) of free **G2** (green line) and 1:1 complex (blue line) throughout the titration.

Table S 5. Chemical shifts of the proton signals of free and bound **G2** of the **G2⊂(5@4a)** (δ, ppm) and complexation-induced shifts ($\Delta\delta$, ppm).

Signal	δ_{free}	δ_{bound} (1:1 complex)	$\Delta\delta$ (1:1 complex)
1	3.17	2.11	-1.06
2	1.18	0.46	-0.72

Figure S 25 shows the theoretical speciation profile of the titration of guest **G2** with complex **5@4a** to form (**G2⊂(5@4a)** complex (60%) considering Ka (**G2⊂(5@4a)** = 7.2 x 10^2 M^{-1}. To have an accurate measurement the complex formation should reach at least a formation of 80%. Nevertheless, the K_a and CIS values are in agreement with the reverse titrations.

3.2.4 ^{1}H NMR spectroscopic titration experiments leading to G3⊂(5@4a)



G3

Figure S 26. Line-drawing structure of tetrapropylammonium chloride guest (**G3**)

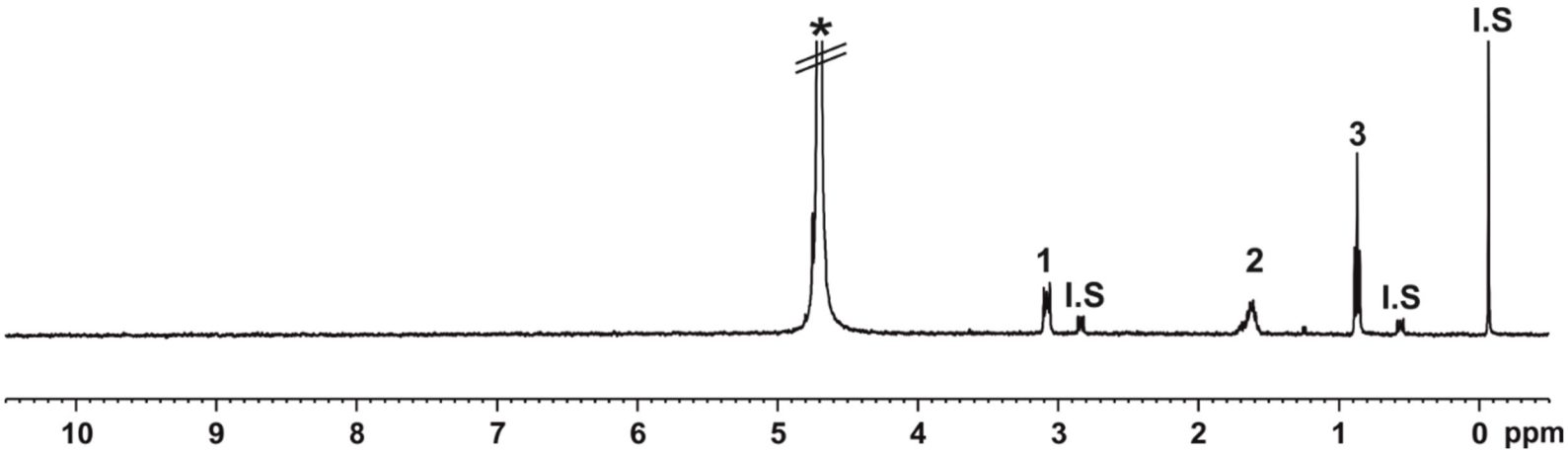


Figure S 27. ^{1}H NMR spectrum (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) of tetrapropyl ammonium chloride **(G3)**. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.) *Residual solvent peaks

Reverse titration: incremental addition of G3 to a solution of 5@4a - *G3⊂(5@4a)*

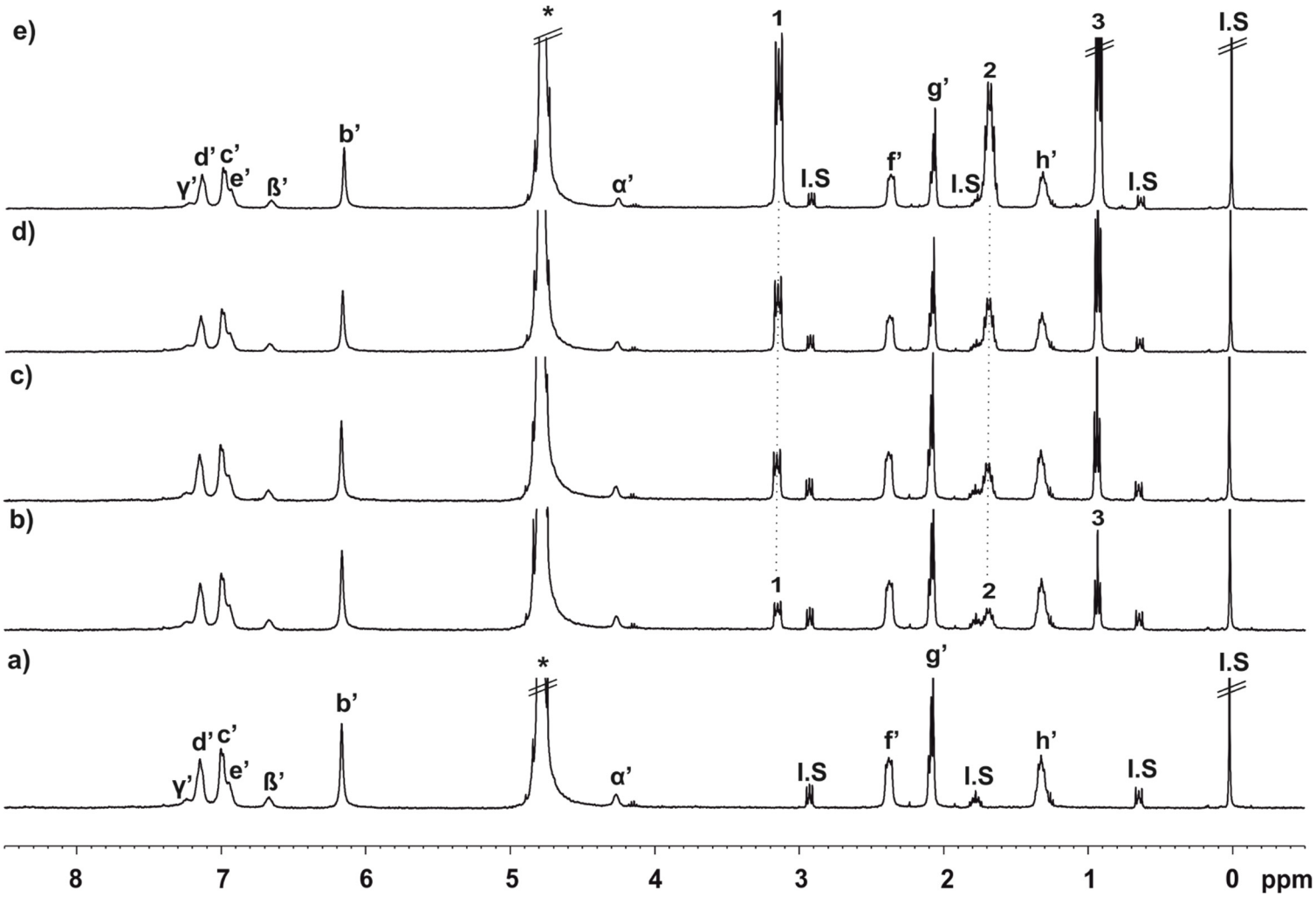


Figure S 28. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **5@4a** (1.1 equiv. of **5**) with **G3**: a) 0; b) 0.5; c) 1.0; d) 2.0 and e) 5.0 equiv. of **G3**. Primed letters and numbers correspond to proton signal of bound components. See Figure S 15 and Figure S 27 for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

The binding with TPACl (**G3**) did not show significant chemical shift changes data to determine an accurate binding constant from the fit to a theoretical binding model.

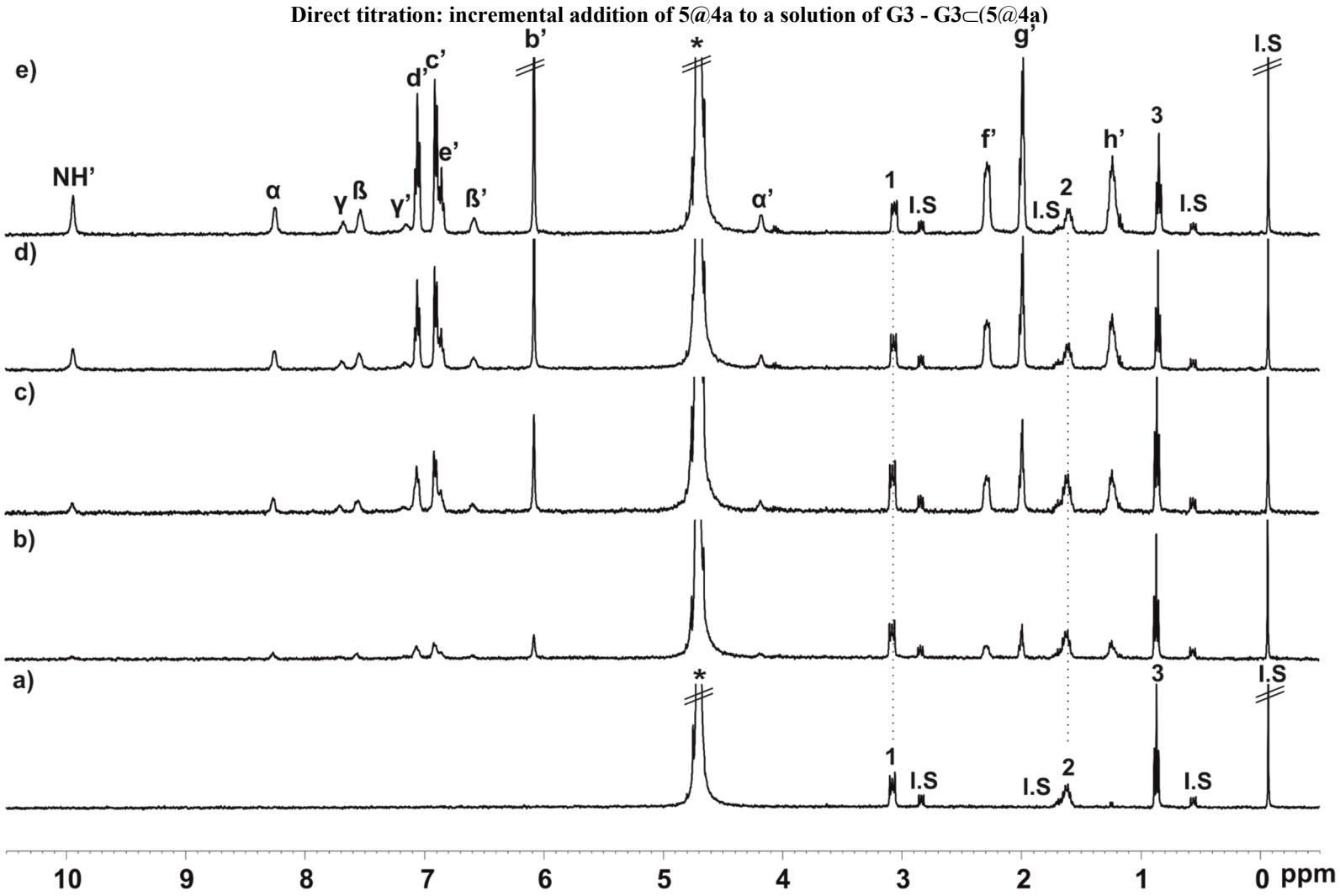
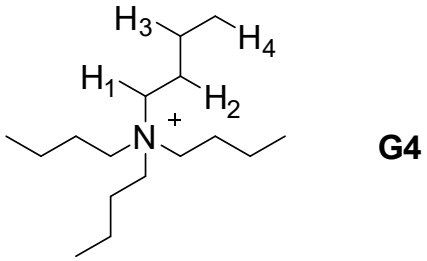


Figure S 29. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of 5@**4a** (1.5 equiv. of **5**) with **G3**: a) 0; b) 0.5; c) 1.0; d) 2.0 and e) 2.5 equiv. **5**@**4a**. Primed letters and numbers correspond to proton signal of bound components. See Figure S 27 for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

The binding with TPACl (**G3**) does not show significant chemical shift changes, and we cannot use the obtained data to determine an accurate binding constant from the fit to a theoretical binding model.

3.2.5 ^{1}H NMR spectroscopic titration experiments leading to G4⊂(5@4a)



G4

Figure S 30. Line-drawing structure of tetrabutylammonium chloride guest (**G4**)

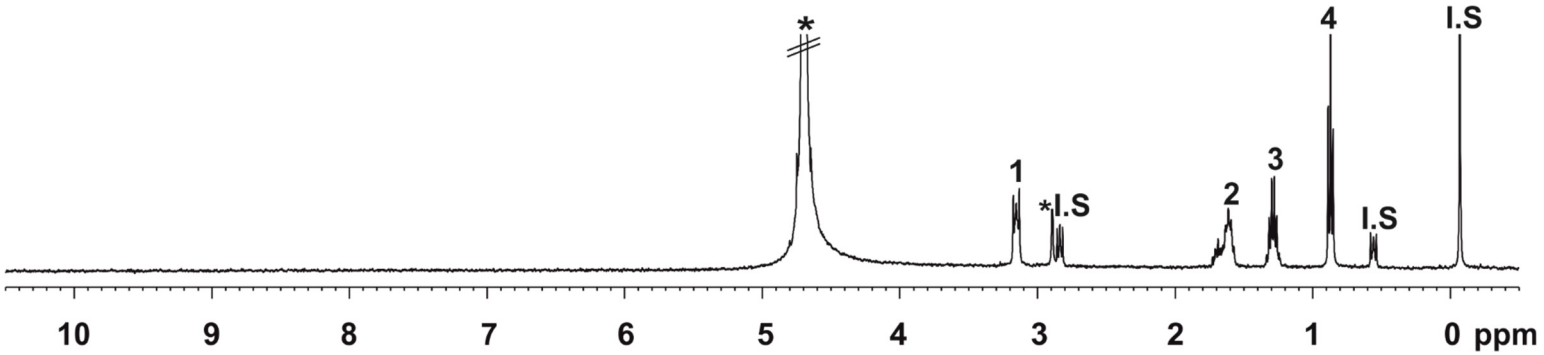


Figure S 31. ^{1}H NMR spectrum (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) of tetrabutylammonium chloride **(G4)**. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.) *Residual solvent peaks

Reverse titration: incremental addition of G4 to a solution of 5@4a - G4⊂(5@4a)

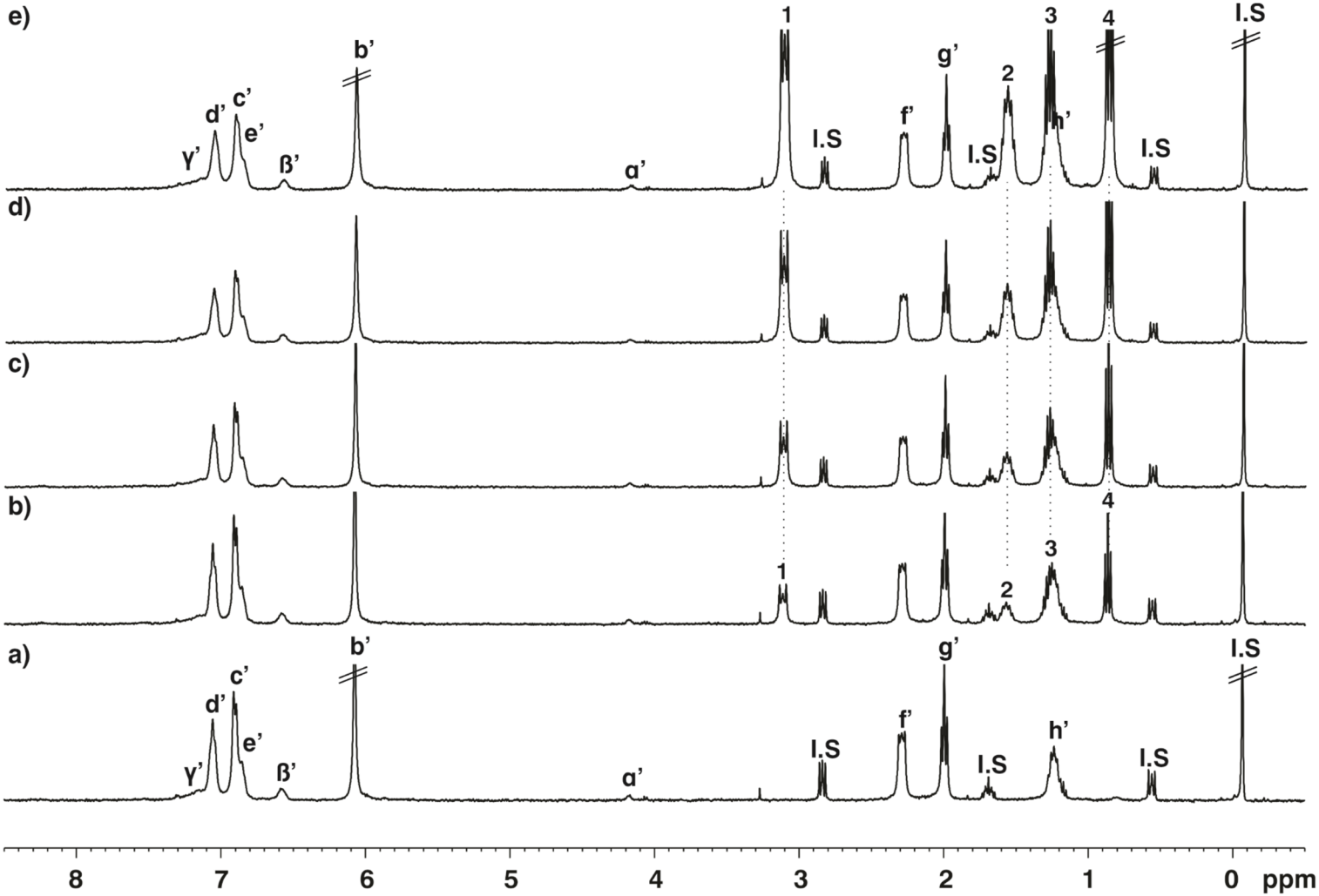


Figure S 32. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of 5@**4a** (1.1 equiv of **5**) with **G4**: a) 0; b) 0.5; c) 1.0; d) 2 and e) 3 equiv. of **G4**. Primed letters and numbers correspond to proton signal of bound components. See **Scheme S 1**, **Figure S 13** and **Figure S 30**for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

The binding with TBACl (**G4**) did not show significant chemical shift changes, which made it difficult to determine an accurate binding constant from the fit to a theoretical binding model.

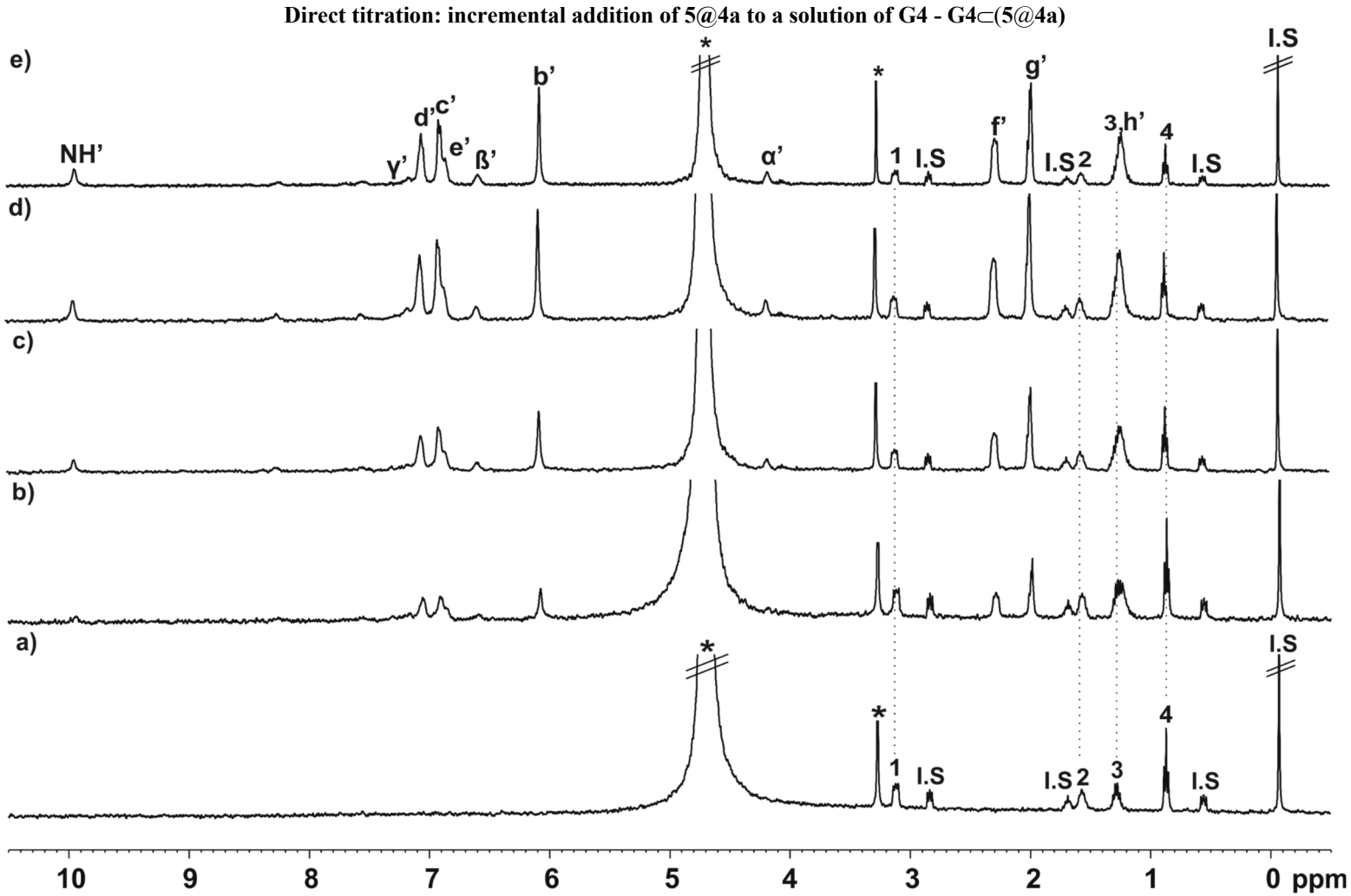
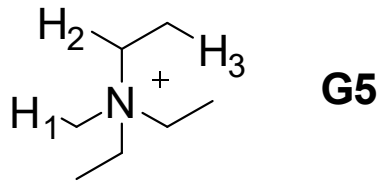


Figure S 33. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **5**@**4a** (1.5 equiv. of **5**) with **G4**: a) 0; b) 0.5; c) 1.0; d)2 and e) 2.5 equiv. 5@**4a**. Primed letters and numbers correspond to the proton signal of bound components. See **Scheme S 1**, **Figure S 13** and **Figure S 30** for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

The binding with TBACl (**G4**) did not show significant chemical shift changes, so an accurate binding constant from the fit to a theoretical binding model could not be determined.

3.2.6 ^{1}H NMR spectroscopic titration experiments leading to G5⊂(5@4a)



G5

Figure S 34. Line-drawing structure of methyltriethyl ammonium chloride guest (**G5**)

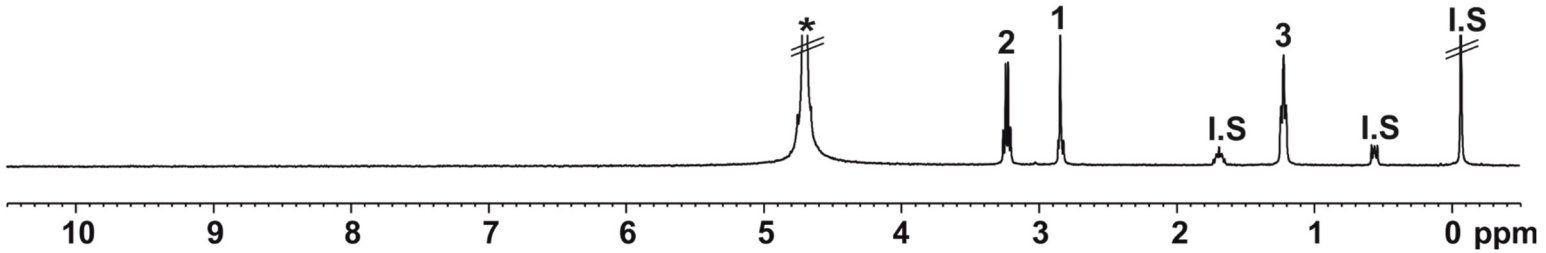


Figure S 35. ^{1}H NMR spectrum (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) of methyltriethyl ammonium chloride **(G5)**. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.) *Residual solvent peaks

Reverse titration: incremental addition of G5 to a solution of 5@4a - G5⊂(5@4a)

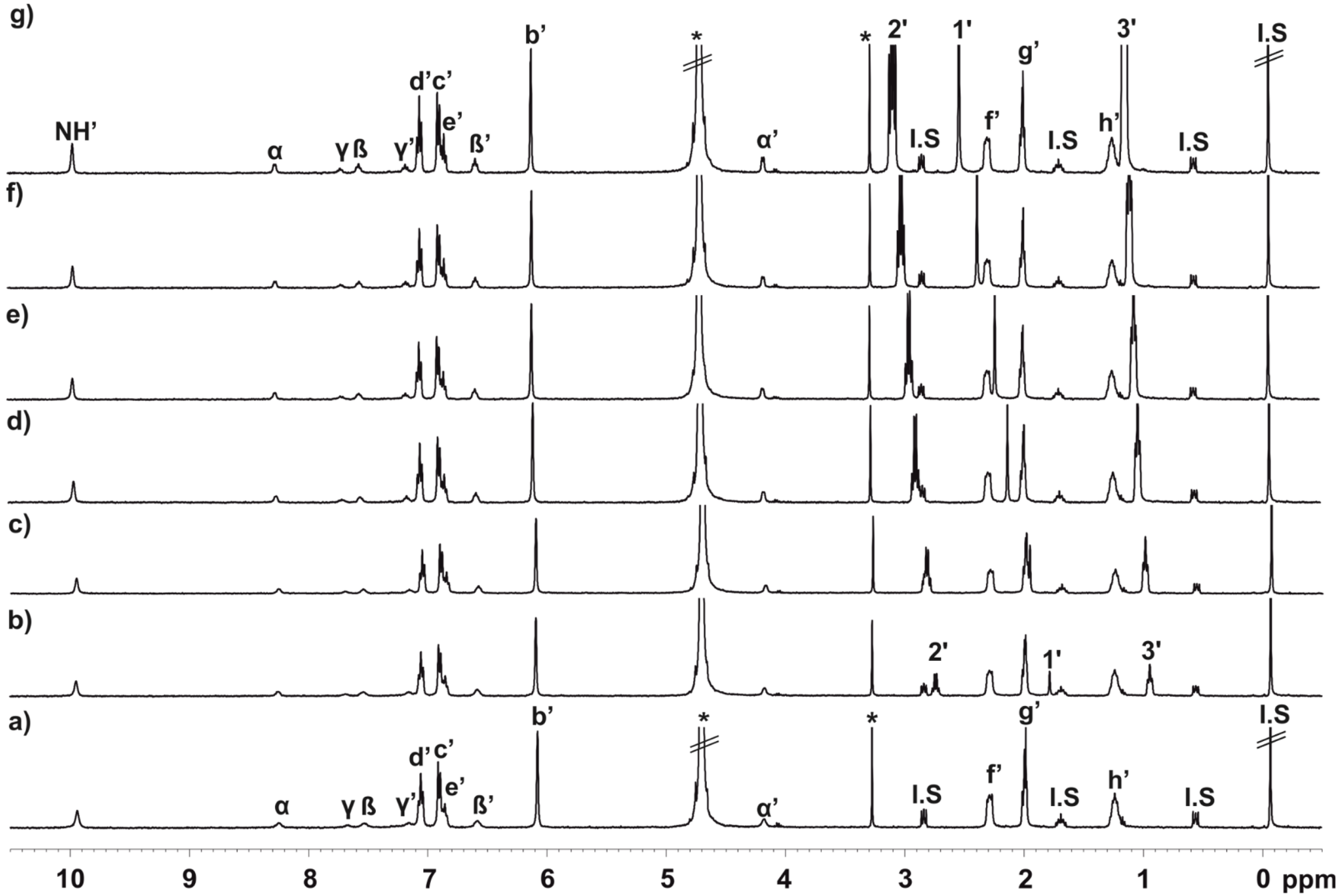


Figure S 36. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **5@4a** (1.1 equiv. of **5**) with **G5**: a) 0; b) 0.5; c) 1.0; d) 2 and e) 5.6 equiv. of **G5**. Primed letters and numbers correspond to proton signal of bound components. See **Scheme S 1**, **Figure S 13** and **Figure S 34** for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

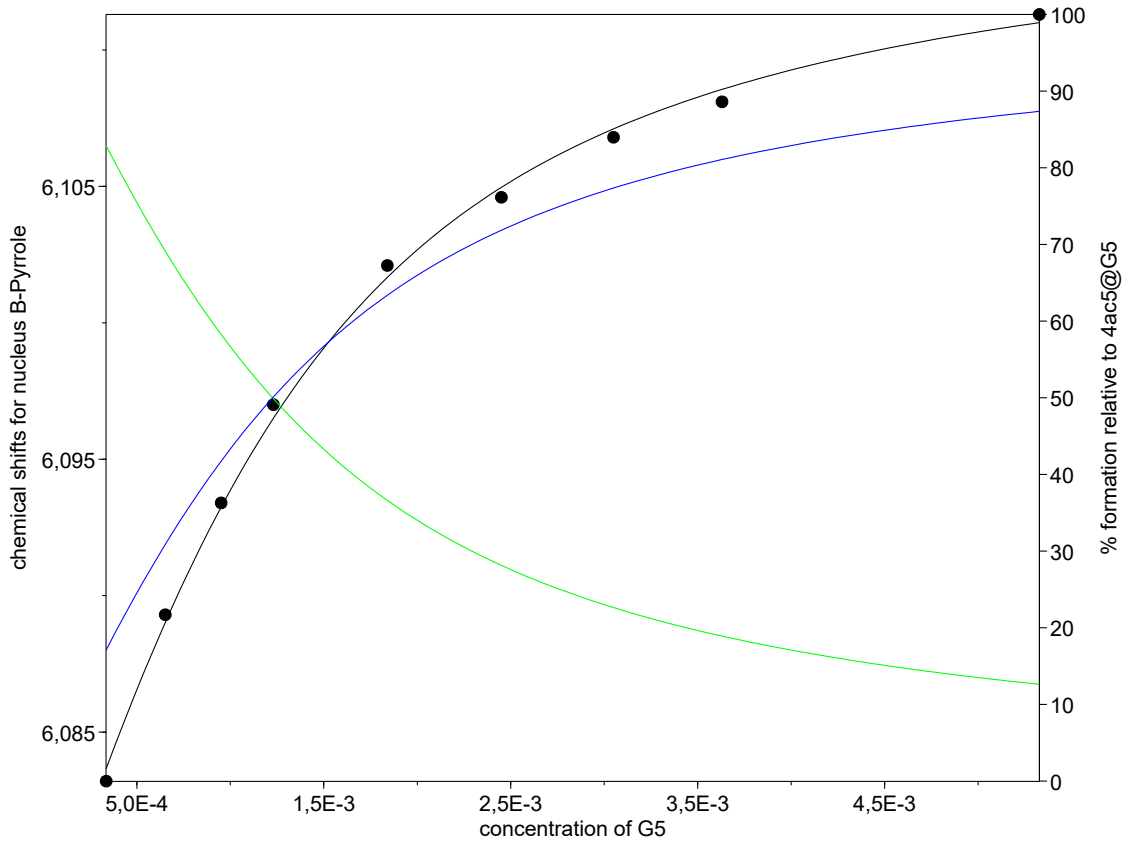


Figure S 37. Fit of the NMR titration data (signal **b**, β-pyrrole proton proton) to a 1:1 binding model (black line). The fit returned K_a (**G5⊂(5@4a)**) = 1.3x 10^3 M^{-1}. The speciation shows the concentration (%) of free **5@4a** (green line) and 1:1 complex (blue line) throughout the titration.

Table S 6. Chemical shifts of the proton signals of free and bound 5@**4a/G5** / **G5⊂(5@4a)** (δ, ppm) and calculated complexation-induced shifts ($\Delta\delta$, ppm).

Signal	δ_{free}	δ_{bound} (1:1 complex)	$\Delta\delta$ (1:1 complex)
1	2.85	0.91	-1.94
2	3.23	2.37	-0.86
3	1.22	0.73	-0.49
H-ortho (Hc)	6.90	6.88	-0.02
β-pyrrole (Hb)	6.08	6.12	0.04

Direct titration: incremental addition of 5@4a to a solution of G5 - G5⊂(5@4a)

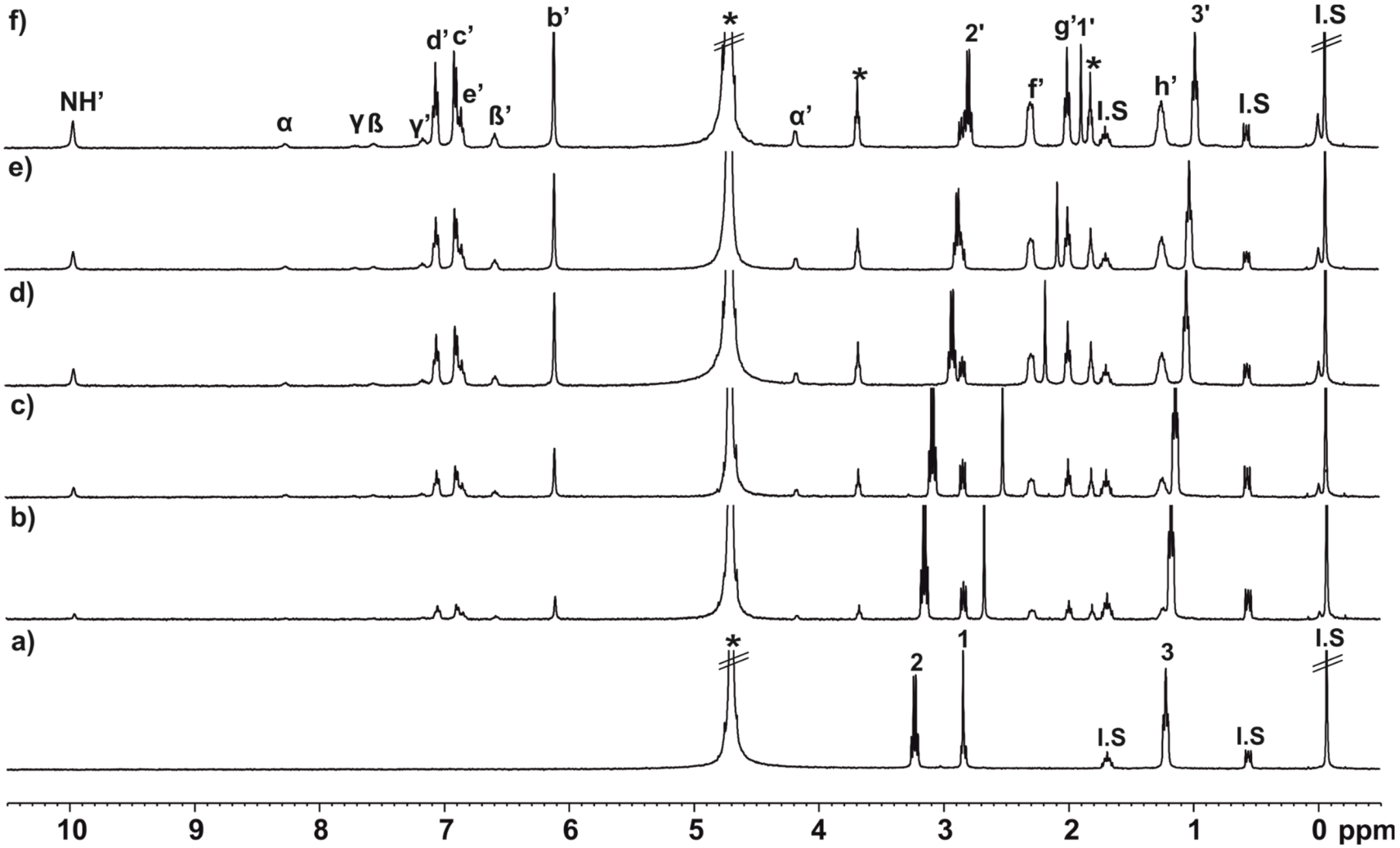


Figure S 38. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **5@4a** (1.1 equiv. of **5**) with **G5**: a) 0; b) 0.5; c) 1.0; d) 2.0 and e) 2.5 equiv. **5@4a**. Primed letters and numbers correspond to proton signal of bound components. See **Scheme S 1**, **Figure S 13** and **Figure S 34** for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

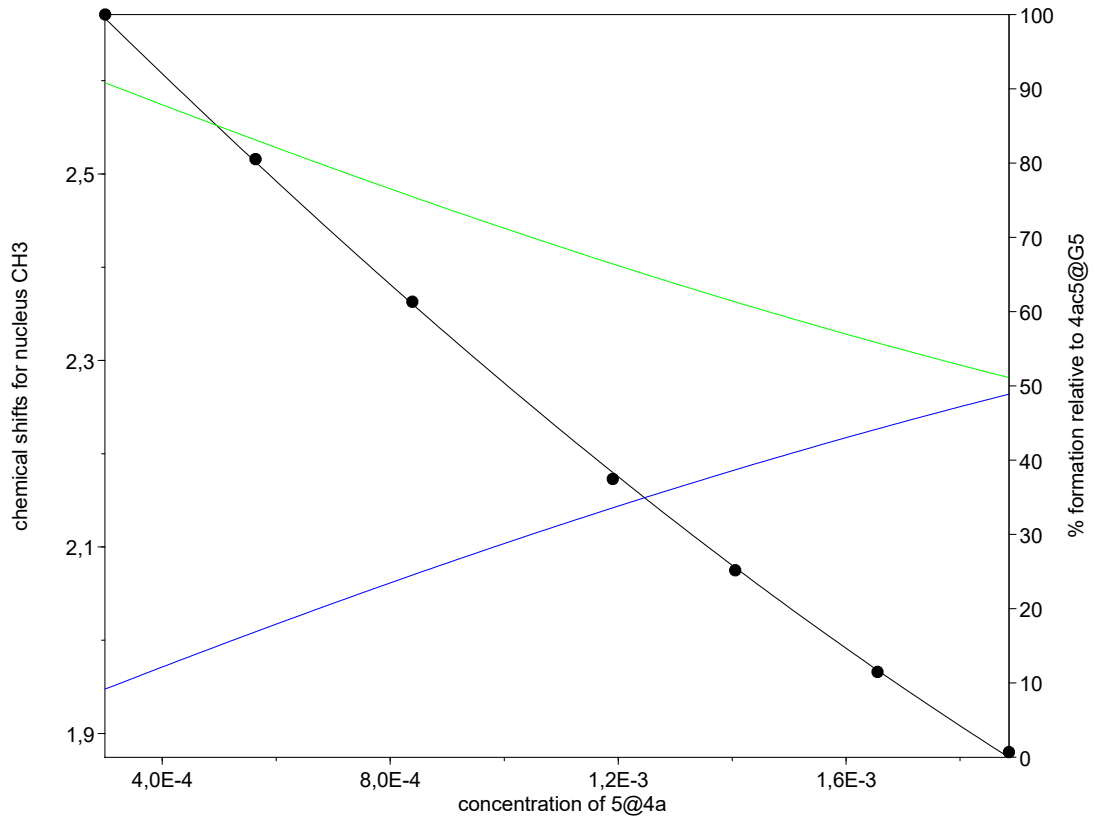


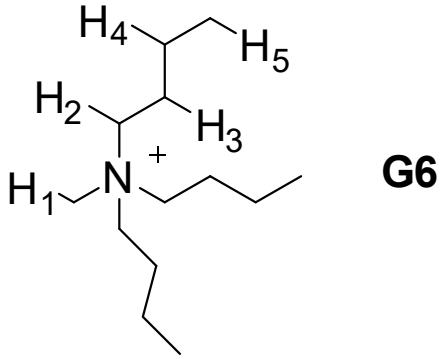
Figure S 39. Fit of the NMR titration data (signal **1'**, -CH_3 proton) to a 1:1 binding model (black line). The fit returned K_a (**G5⊂(5@4a)**) = 1.5x 10^3 M^{-1}. The speciation shows the concentration (%) of free **G5** (green line) and 1:1 complex (blue line) throughout the titration.

Table S 7. Chemical shifts of the proton signals of free and bound **G5** of the **G5⊂(5@4a)** (δ, ppm) and calculated complexation-induced shifts ($\Delta\delta$, ppm).

Signal	δ_{free}	δ_{bound} (1:1 complex)	$\Delta\delta$ (1:1 complex)
1	2.85	0.85	-2.00
2	3.23	2.31	-0.92
3	1.22	0.73	-0.49

As we observed before for the direct titration of **G2** with **5@4a**, the extent of complexation is lower than 60%. Although this value is not enough to accurately determine the association constant, the estimated value agrees with that derived from the reverse titration.

3.2.7 ^{1}H NMR spectroscopic titration experiments leading to G6⊂(5@4a)



G6

Figure S 40. Line-drawing structure of methyltributylammonium chloride guest (**G6**)

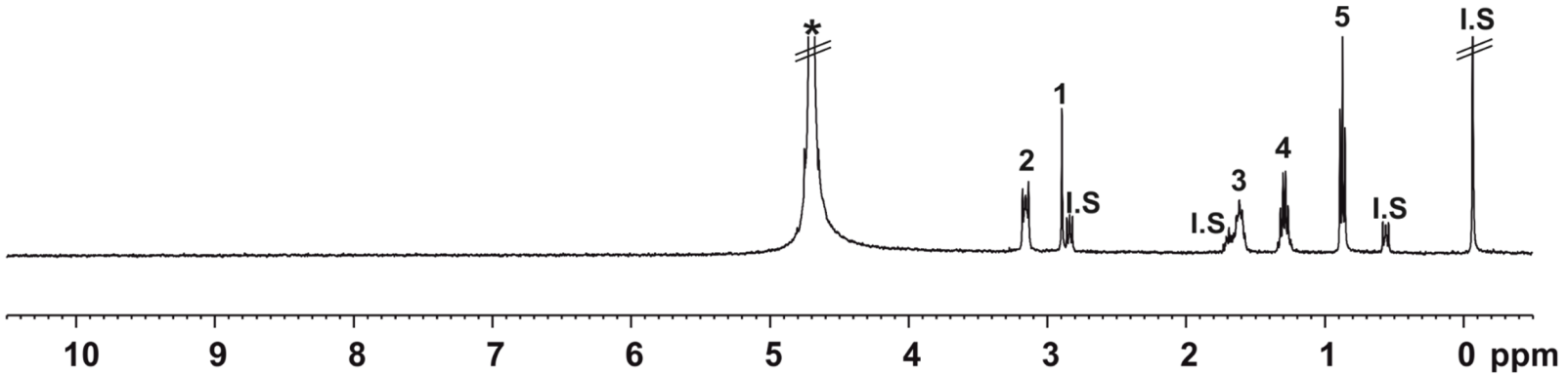


Figure S 41. ^{1}H NMR spectrum (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) of methyltributylammonium chloride **(G6)**. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.) *Residual solvent peaks

Reverse titration: incremental addition of G6 to a solution of 5@4a - G6⊂(5@4a)

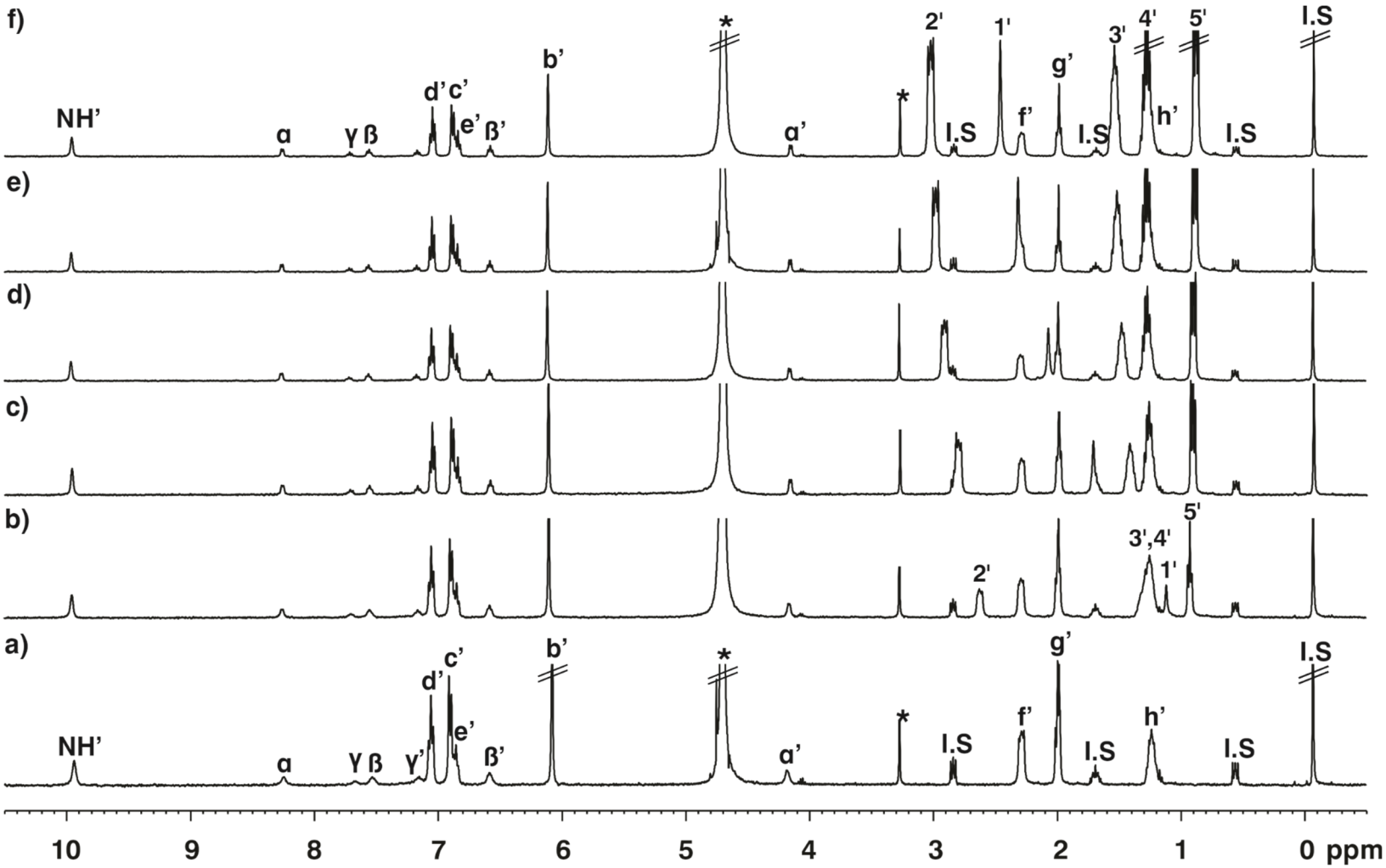


Figure S 42. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **5@4a** (1.3 equiv. of **5**) with **G6**: a) 0; b) 0.5; c) 1.0; d) 1.5; e) 2.0 and f) 4.0 equiv. of **G6**. Primed letters and numbers correspond to proton signal of bound components. See **Scheme S 1**, **Figure S 13** and **Figure S 40**for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

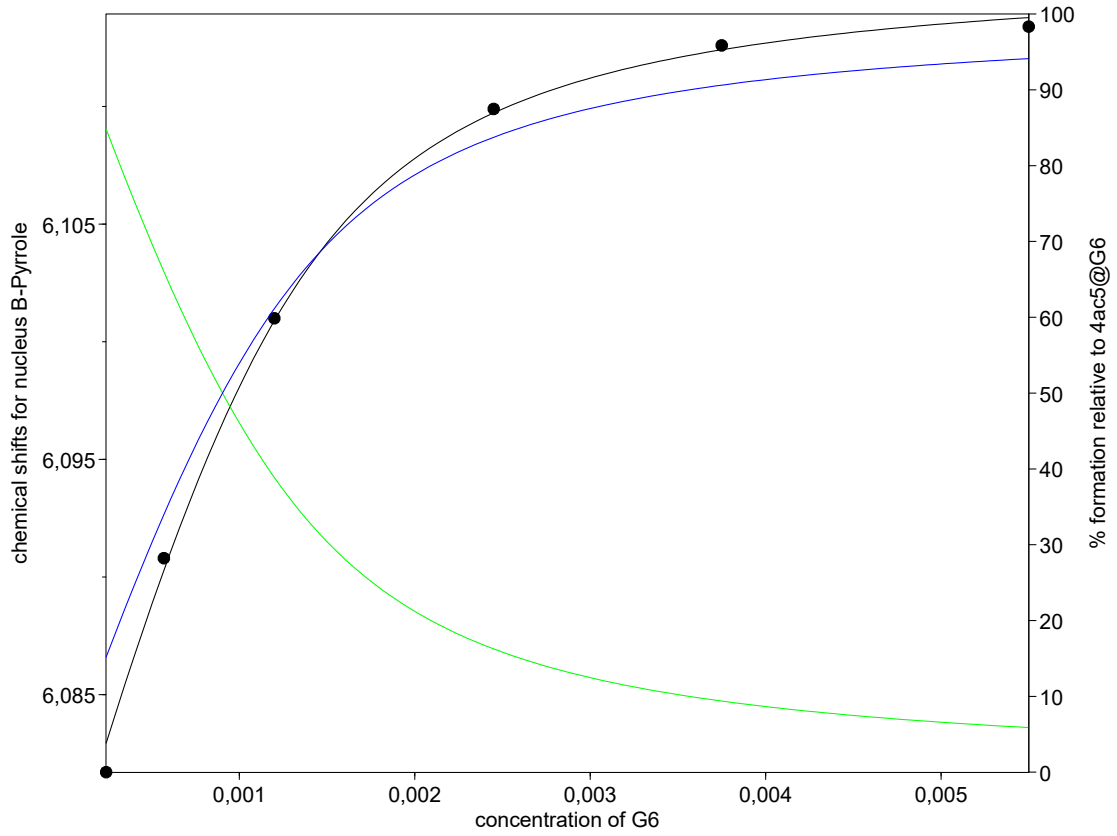


Figure S 43. Fit of the NMR titration data (signal **b**, β-pyrrole proton) to a 1:1 binding model (black line). The fit returned K_a (**G6**⊂(**5**@**4a**)) = 3.2x 10^3 M^{-1}. The speciation shows the concentration (%) of free **G6** (green line) and 1:1 complex (blue line) throughout the titration.

Table S 8. Chemical shifts of the proton signals of free and bound **5**@**4a**/**G6** of the **G6**⊂(**5**@**4a**) (δ, ppm) and calculated complexation-induced shifts ($\Delta\delta$, ppm).

Signal	δ_{free}	δ_{bound} (1:1 complex)	$\Delta\delta$ (1:1 complex)
1	2.91	0.57	-2.34
2	3.17	2.45	-0.72
3	1.63	1.21	-0.42
4	1.31	1.23	-0.08
H-ortho (Hc)	6.90	6.88	-0.02
β-pyrrole (Hb)	6.08	6.12	0.04

Direct titration: incremental addition of 5@4a to a solution of G6 - G6⊂(5@4a)

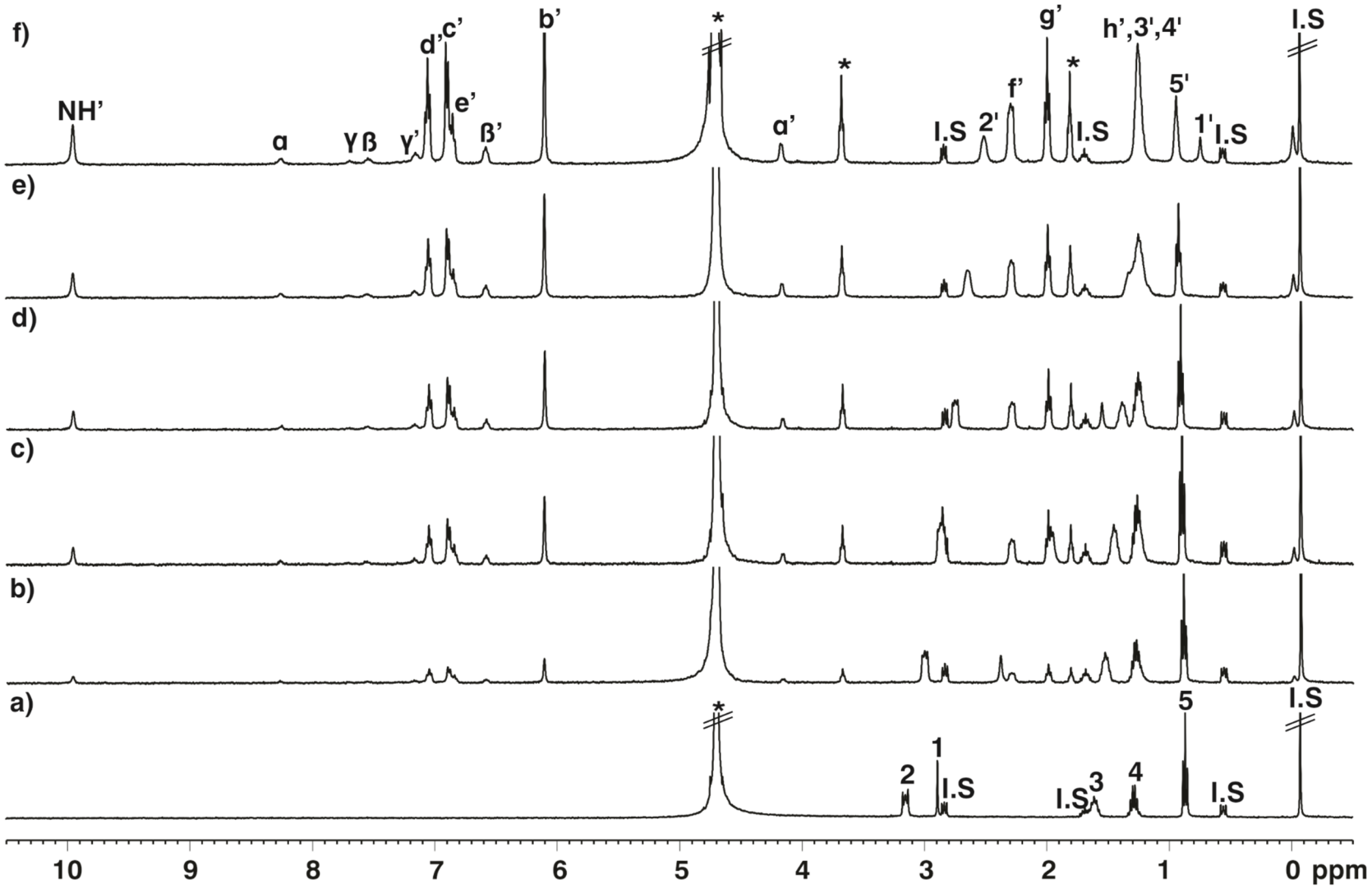


Figure S 44. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **5**@**4a**(1.1 equiv. of **5**) with **G6**: a) 0; b) 0.25; c) 0.5; d) 0.7; e) 0.96 and f) 1.28 equiv. **5**@**4a**. Primed letters and numbers correspond to proton signal of bound components. See **Scheme S 1**, **Figure S 13** and **Figure S 40** for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

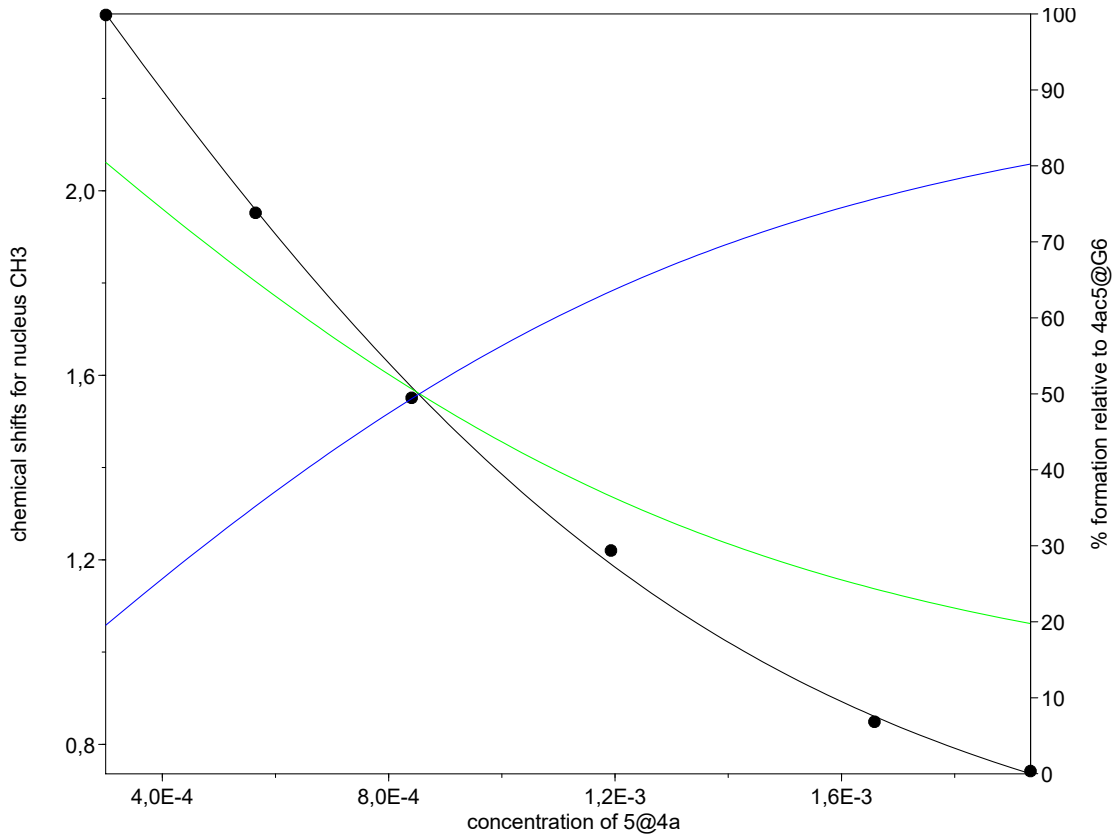
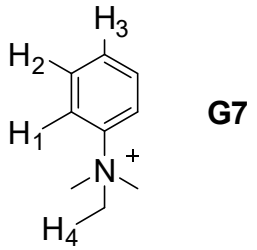


Figure S 45. Fit of the NMR titration data (signal **4'**, -CH_3 proton) to a 1:1 binding model (black line). The fit returned K_a (**G6⊂(5@4a)**) = 4.3x 10^3 M^{-1}. The speciation shows the concentration (%) of free **G6** (green line) and 1:1 complex (blue line) throughout the titration.

Table S 9. Chemical shifts of the proton signals of free and bound **G6** of the **G6⊂(5@4a)** (δ, ppm) and calculated complexation-induced shifts ($\Delta\delta$, ppm).

Signal	δ_{free}	δ_{bound} (1:1 complex)	$\Delta\delta$ (1:1 complex)
1	2.91	0.21	-2.70
2	3.17	2.33	-0.84

3.2.8 ^{1}H NMR spectroscopic titration experiments leading to G7⊂(5@4a)



G7

Figure S 46. Line-drawing structure of trimethylphenylammonium chloride guest (**G7**)

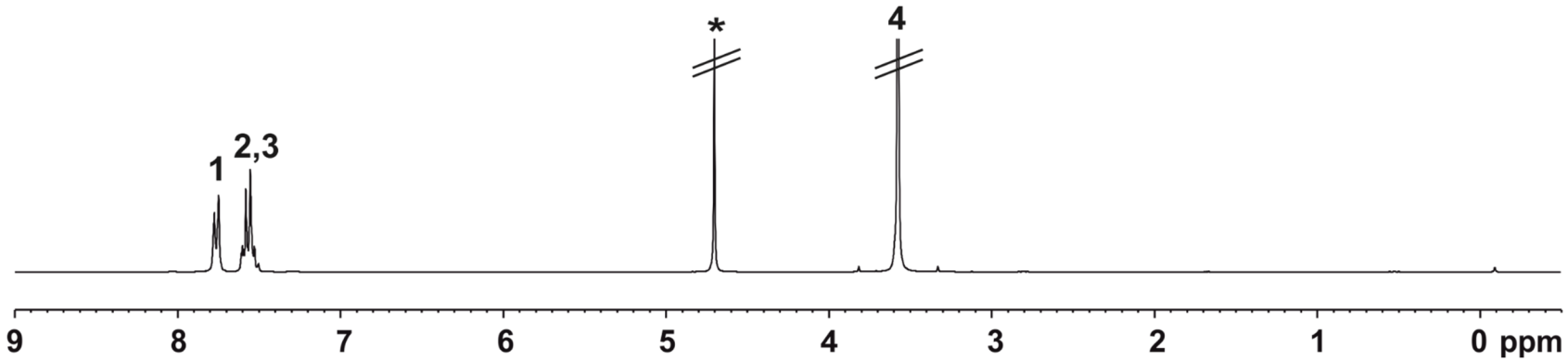


Figure S 47. ^{1}H NMR spectrum (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) of trimethylphenylammonium chloride **(G7)**. *Residual solvent peaks

Reverse titration: incremental addition of G7 to a solution of 5@4a - G7⊂(5@4a)

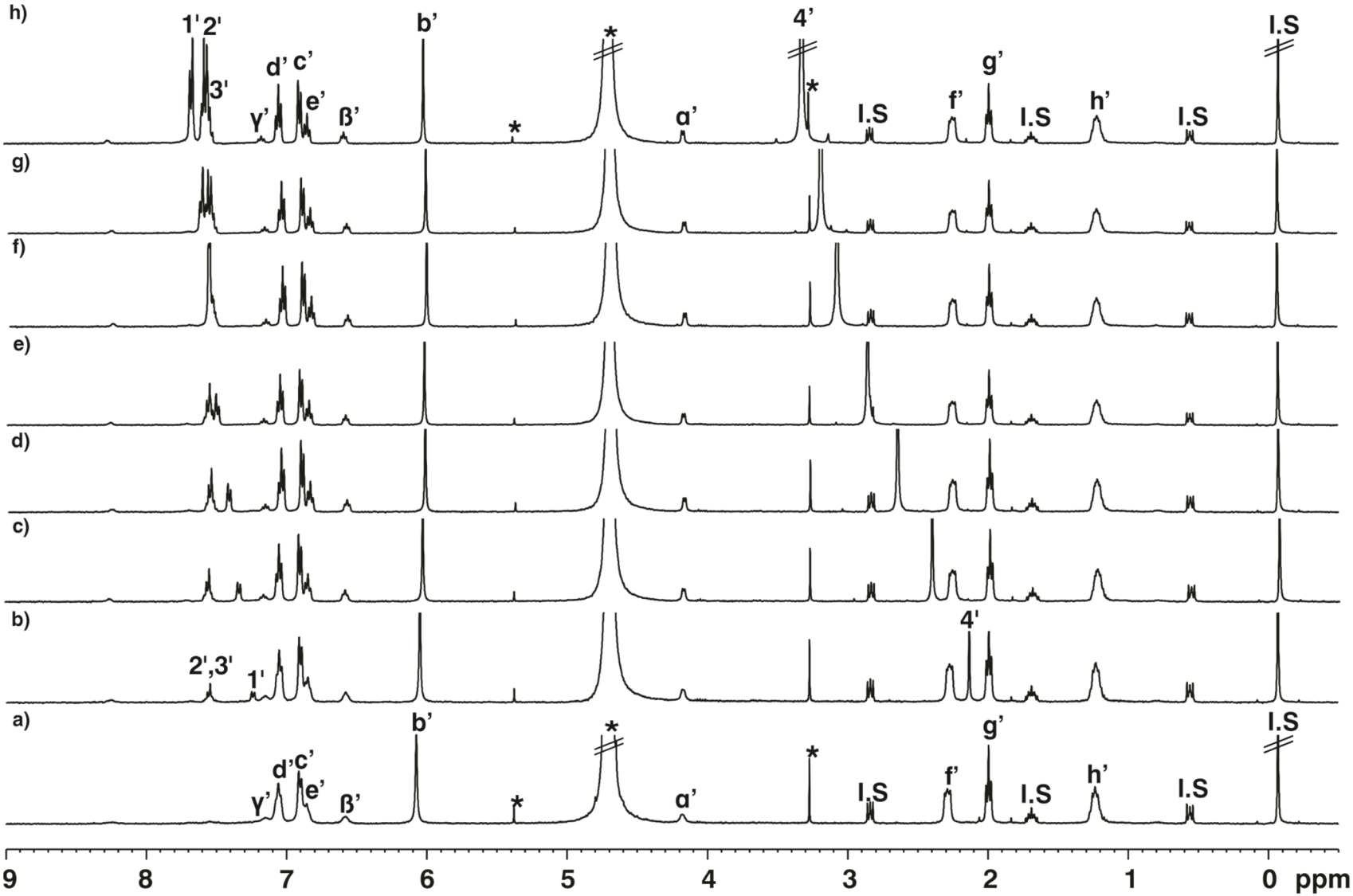


Figure S 48. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **5@4a** (1.3 equiv. of **5**) with **G7**: a) 0; b) 0.5; c) 1.0; d) 1.5; e) 2.0; f) 3.0; g) 4.0 and h) 5.0 equiv. of **G7**. Primed letters and numbers correspond to proton signal of bound components. See **Scheme S 1**, **Figure S 13** and **Figure S 46** for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

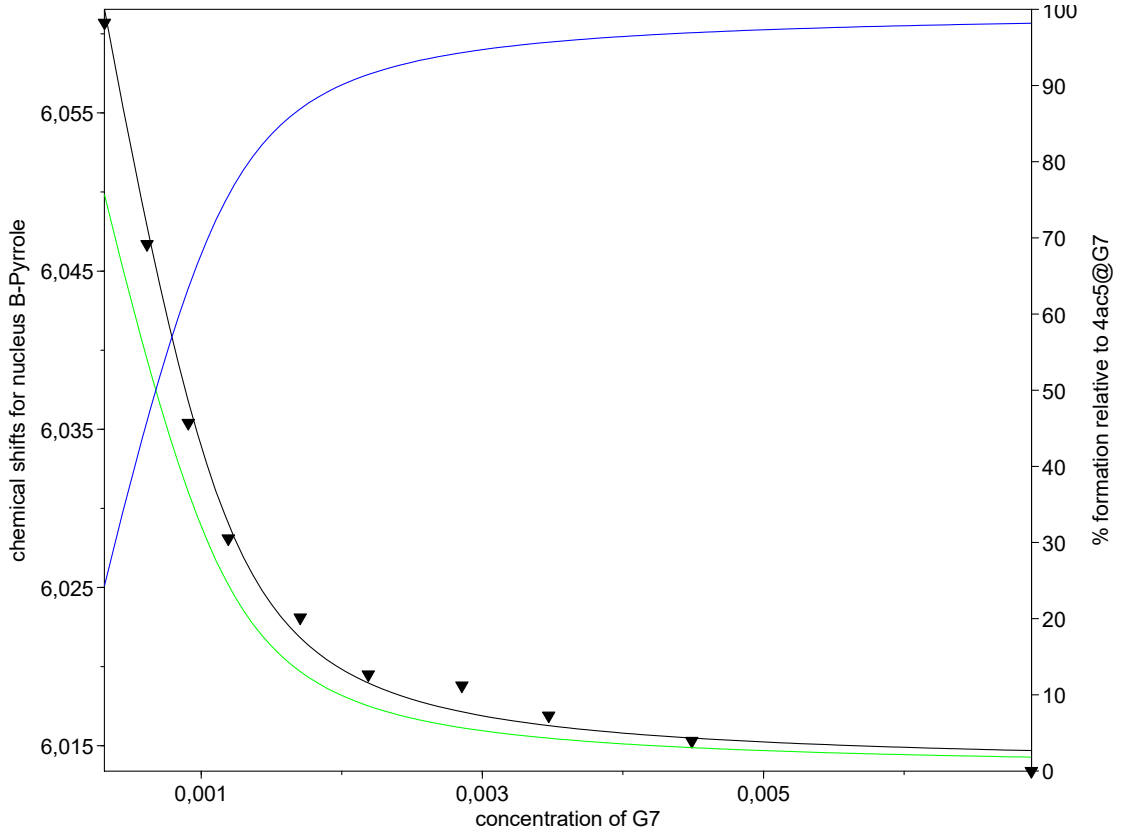
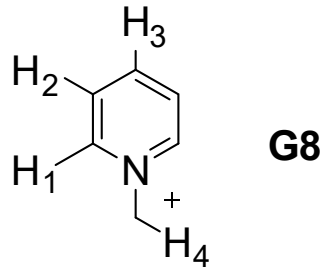


Figure S 49. Fit of the NMR titration data (signal **b**, β-pyrrole proton) to a 1:1 binding model (black line). The fit returned K_a (**G7**⊂(**5**@**4a**)) = 1.1x 10^4 M^{-1}. The speciation shows the concentration (%) of free **G7** (green line) and 1:1 complex (blue line) throughout the titration.

Table S 10. Chemical shifts of the proton signals of free and bound **5@4a/G7** of the **G7**⊂(**5**@**4a**) (δ, ppm) and calculated complexation-induced shifts ($\Delta\delta$, ppm).

Signal	δ_{free}	δ_{bound} (1:1 complex)	$\Delta\delta$ (1:1 complex)
1	7.76	7.16	-0.6
4	3.57	1.97	-1.60
H-ortho (Hc)	6.90	6.89	-0.01
β-pyrrole (Hb)	6.08	6.02	-0.06

3.2.9 ^{1}H NMR spectroscopic titration experiments leading to G8⊂(5@4a)



G8

Figure S 50. Line-drawing structure of methylpyridinium chloride guest (**G8)**

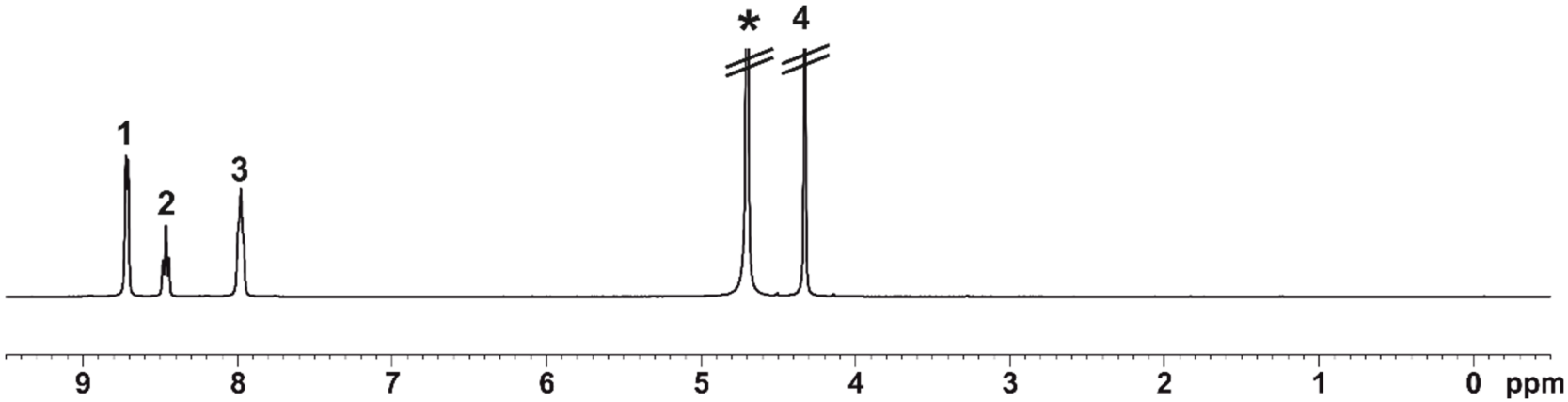


Figure S 51. ^{1}H NMR spectrum (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) of methyltributylammonium chloride **(G8)**. *Residual solvent peaks

Reverse titration: incremental addition of G8 to a solution of 5@4a - G8⊂(5@4a)

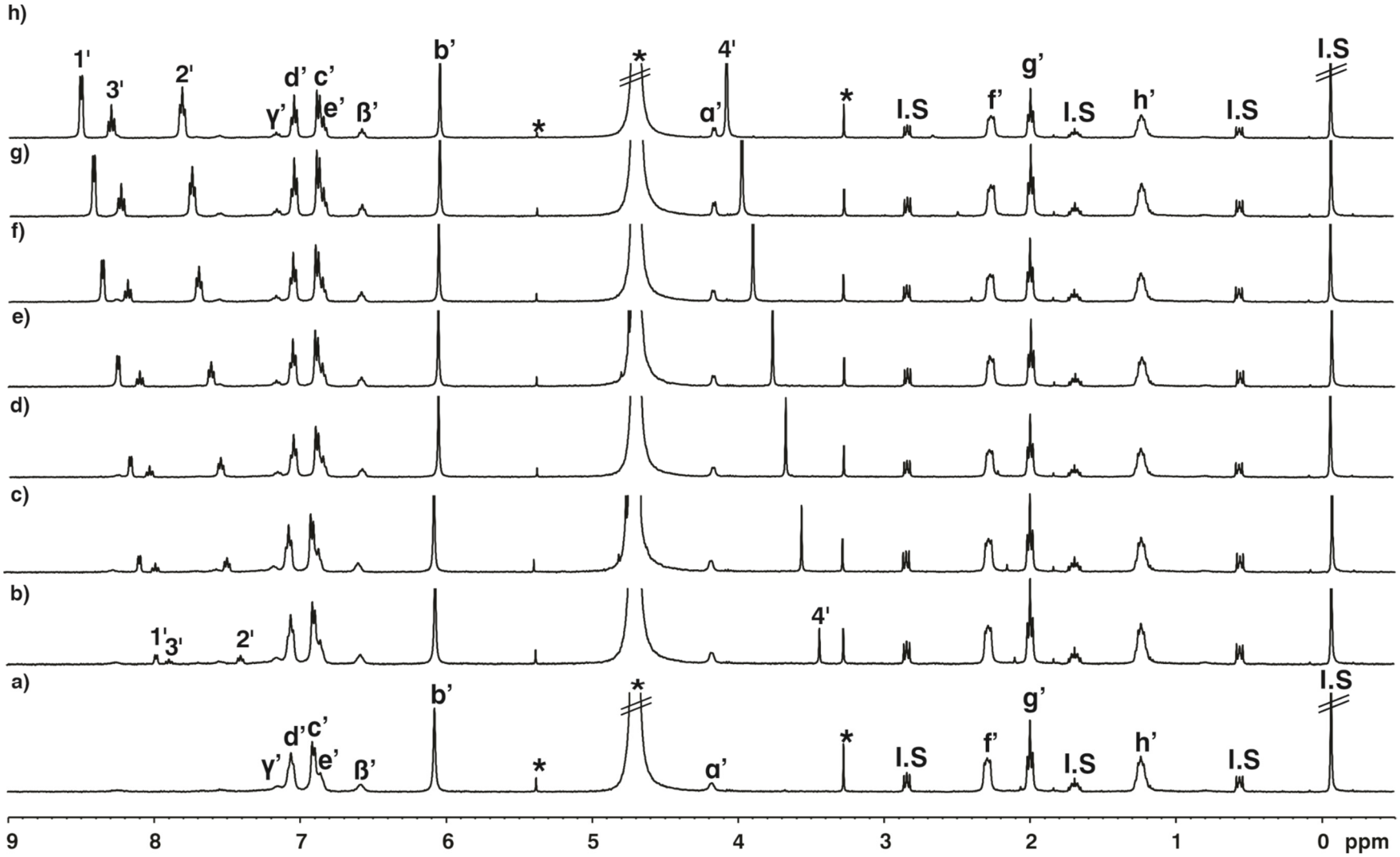


Figure S 52. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **5**@**4a** (1.1 equiv. of **5**) with **G8**: a) 0; b) 0.5; c) 1.0; d) 1.5; e) 2.0; f) 3.0; g) 4.0 and h) 5.0 equiv. of **G8**. Primed letters and numbers correspond to proton signal of bound components. See **Scheme S 1**, **Figure S 13** and **Figure S 50**for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

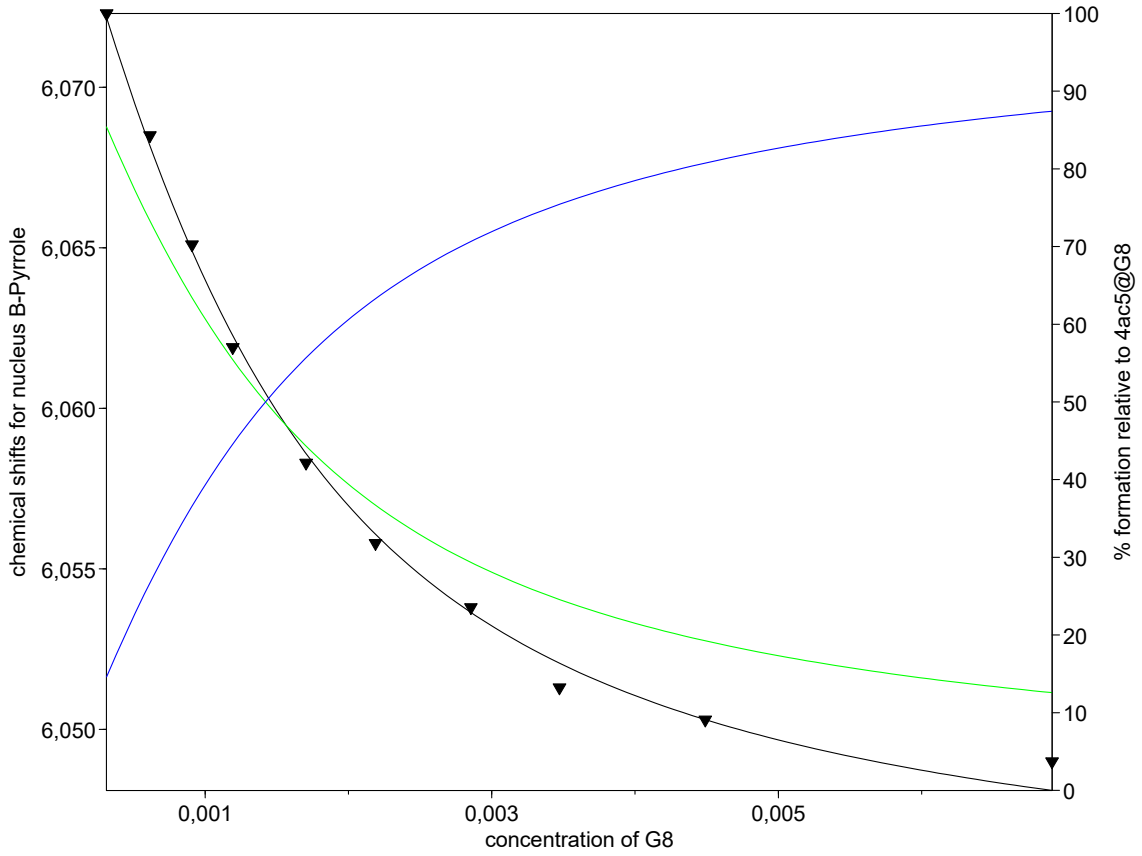


Figure S 53. Fit of the NMR titration data (signal **b**, β-pyrrole proton proton) to a 1:1 binding model (black line). The fit returned K_a (**G8⊂(5@4a)**) = 1.2x 10^3 M^{-1}. The speciation shows the concentration (%) of free **5@4a** (green line) and 1:1 complex (blue line) throughout the titration.

Table S 11. Chemical shifts of the proton signals of free and bound **5@4a/G8** of the **G8⊂(5@4a)** (δ, ppm) and calculated complexation-induced shifts ($\Delta\delta$, ppm).

Signal	δ_{free}	δ_{bound} (1:1 complex)	$\Delta\delta$ (1:1 complex)
1	8.72	7.37	-1.35
2	8.46	7.41	-1.05
3	7.98	6.92	-1.06
4	4.33	2.71	-1.62
H-ortho (Hc)	6.90	6.88	-0.02
β-pyrrole (Hb)	6.08	6.04	-0.04

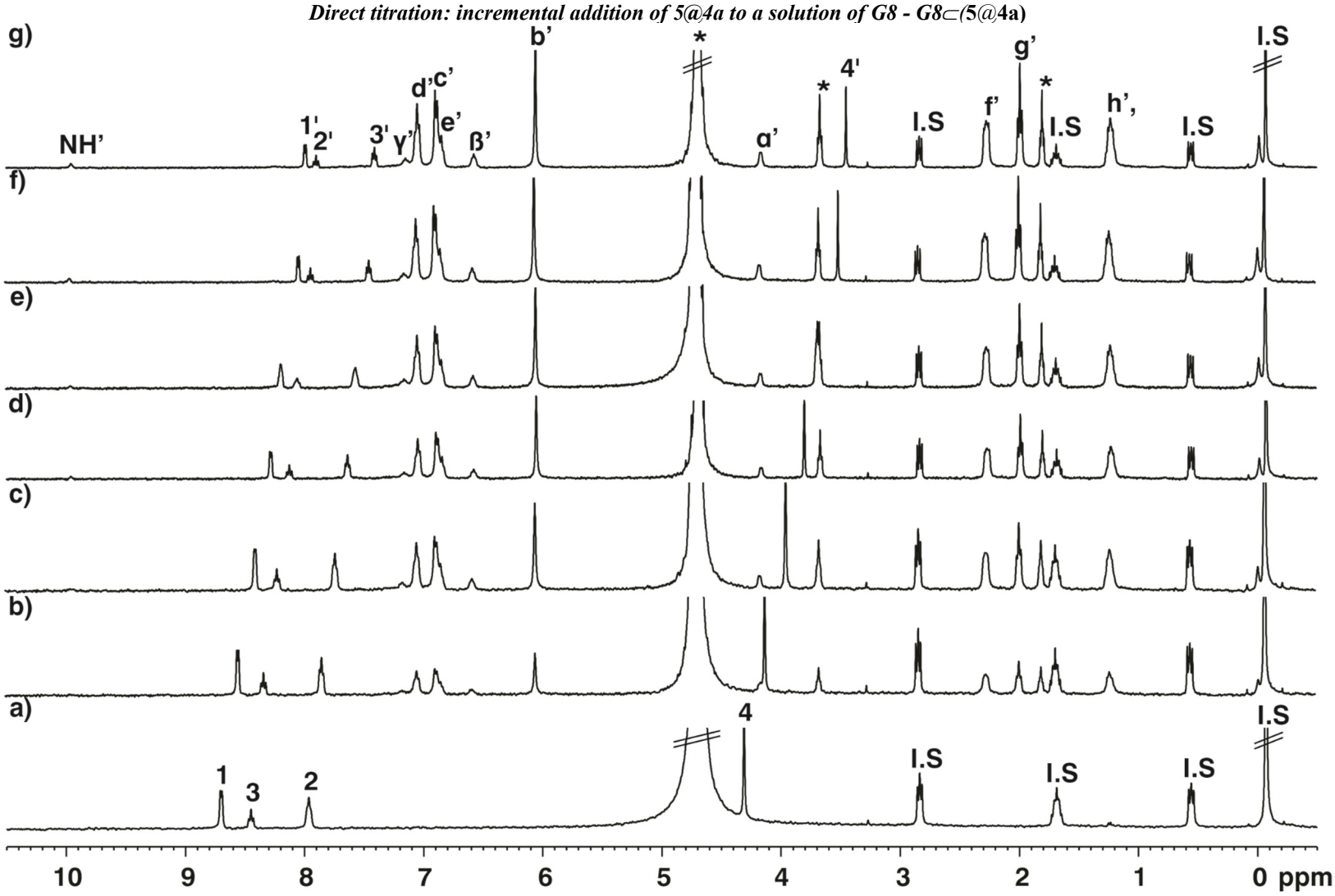


Figure S 54. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **5@4a** (1.1 equiv. of **5**) with **G8**: a) 0; b) 0.18; c) 0,37; d) 0.53; e) 0.84; f) 1.0 and g) 1.15 equiv. **5@4a**. Primed letters and numbers correspond to the proton signal of bound components. See **Scheme S 1**, **Figure S 13** and **Figure S 50** for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

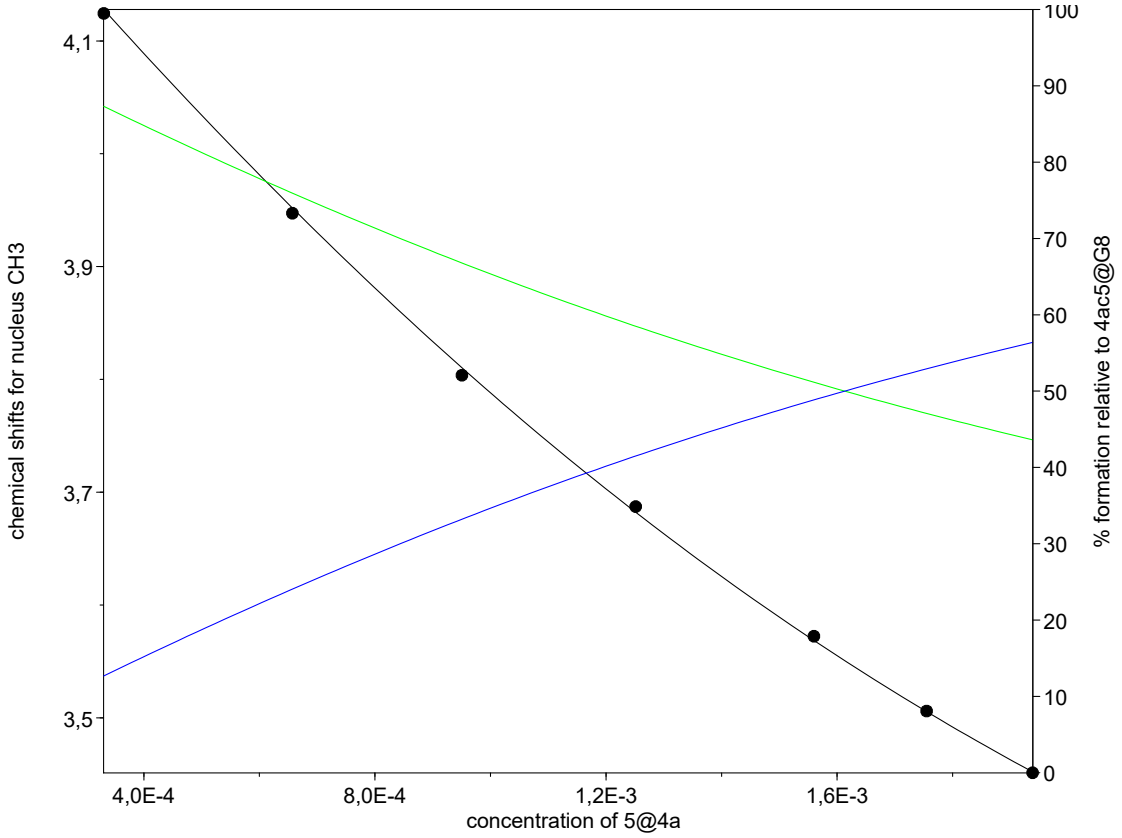


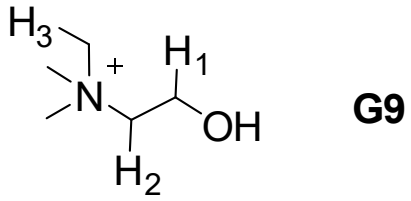
Figure S 55. Fit of the NMR titration data (signal **4'**, -CH_3 proton) to a 1:1 binding model (black line). The fit returned K_a (**G8⊂(5@4a)**) = 1.3 x 10^3 M^{-1}. The speciation shows the concentration (%) of free **G8** (green line) and 1:1 complex (blue line) throughout the titration.

Table S 12. Chemical shifts of the proton signals of free and bound **G8** of the **G8⊂(5@4a)** (δ, ppm) and calculated complexation-induced shifts ($\Delta\delta$, ppm).

Signal	δ_{free}	δ_{bound} (1:1 complex)	$\Delta\delta$ (1:1 complex)
1	8.72	7.41	-1.31
2	8.46	7.44	-1.02
3	7.98	6.95	-0.97
4	4.33	2.78	-1.55

As we expected, for direct titrations with binding constants lower than 3000 M^{-1} the binding constant cannot be accurately determined due to the low solubility of receptor **4a**. However, the estimated value is in agreement with the values derived from reverse titrations.

3.2.10 ^{1}H NMR spectroscopic titration experiments leading to G9⊂(5@4a)



G9

Figure S 56. Line-drawing structure of Choline chloride guest (**G9)**

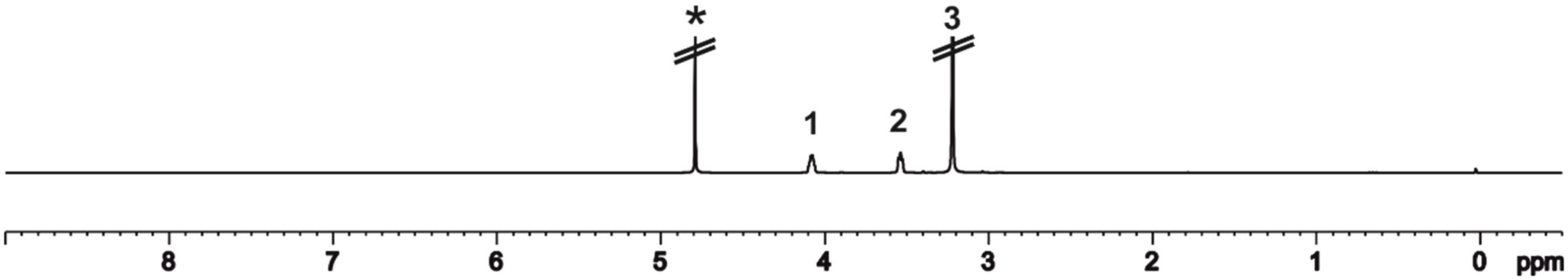


Figure S 57. ^{1}H NMR spectrum (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) of Choline chloride **(G8)**. *Residual solvent peaks

Reverse titration: incremental addition of G9 to a solution of 5@4a - G9⊂(5@4a)

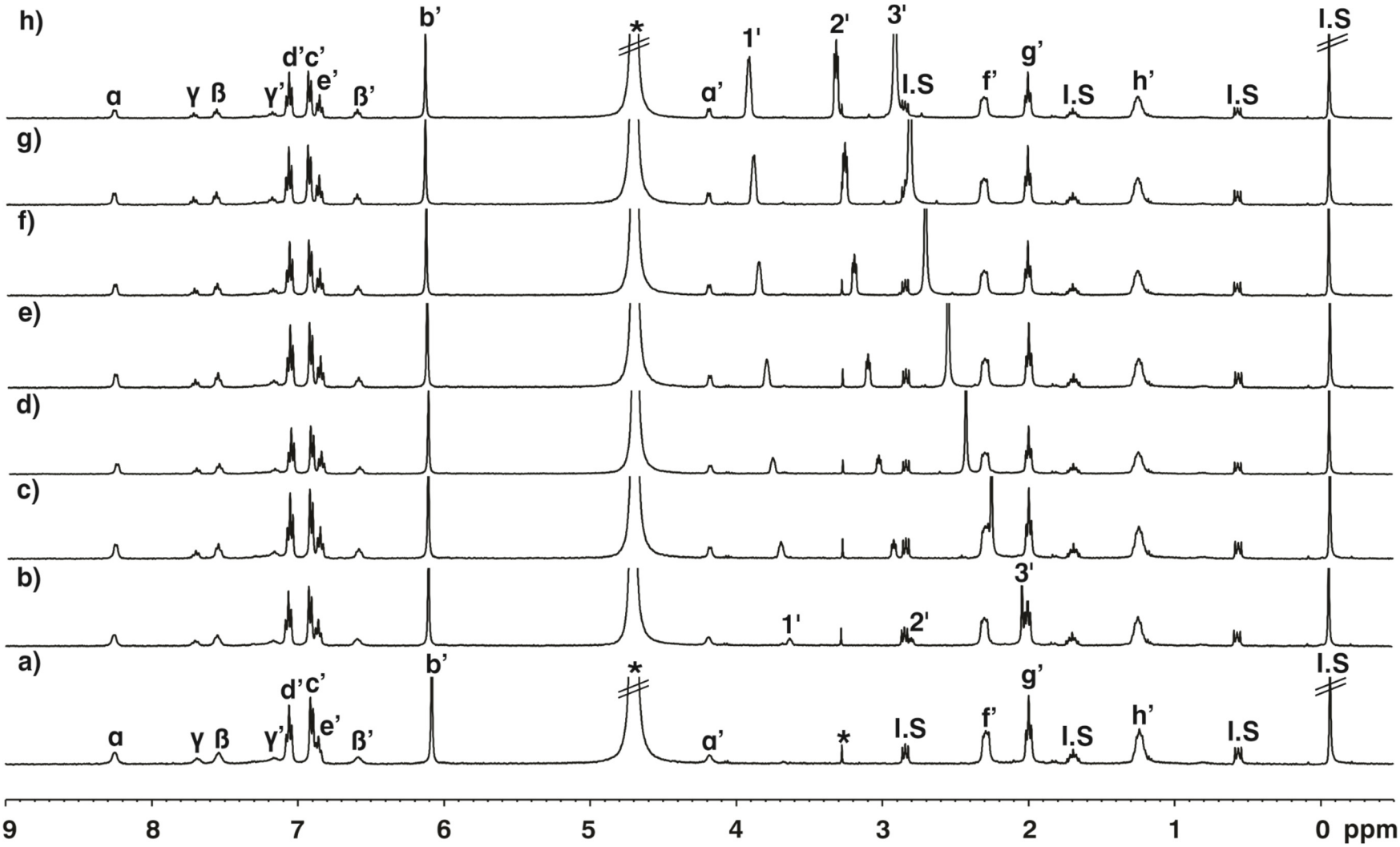


Figure S 58. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **5@4a** (1.1 equiv. of **5**) with **G9**: a) 0; b) 0.5; c) 1.0; d) 1.5; e) 2.0; f) 3.0; g) 4.0 and h) 5.0 equiv. of **G9**. Primed letters and numbers correspond to the proton signal of bound components. See **Scheme S 1**, **Figure S 13** and **Figure S 56** for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

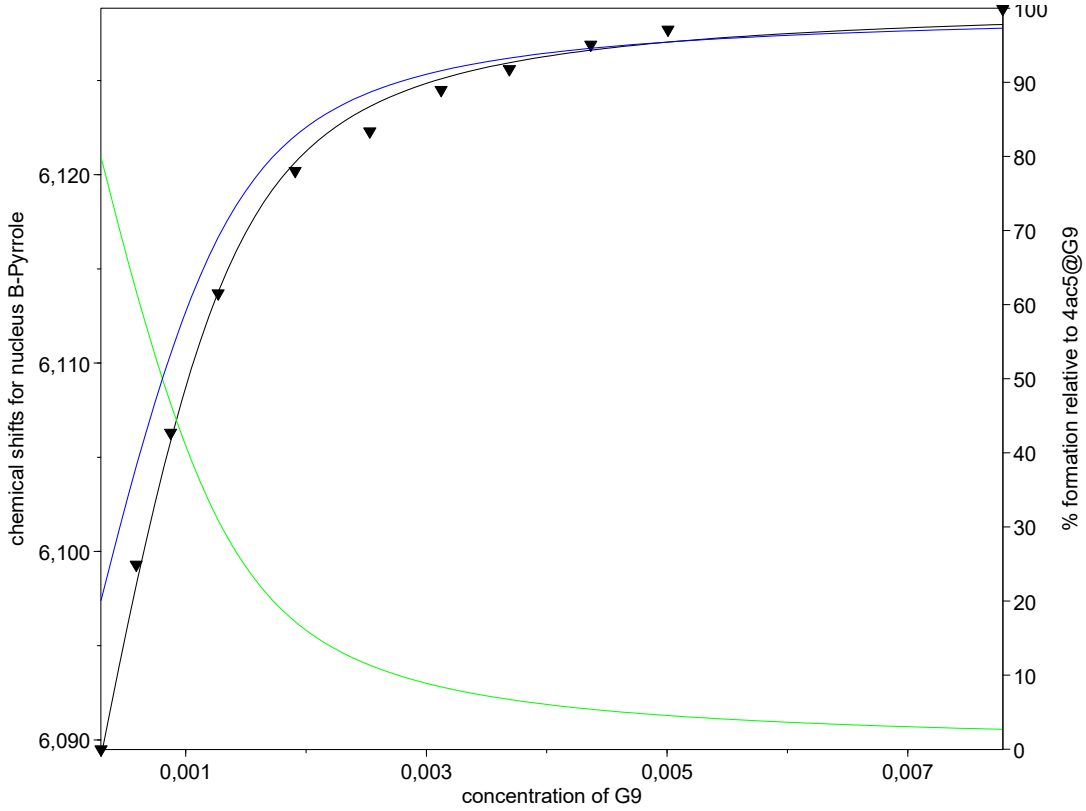


Figure S 59. Fit of the NMR titration data (signal **b**, β-pyrrole proton proton) to a 1:1 binding model (black line). The fit returned K_a (**G9⊂(5@4a)**) = 9.8 x 10^3 M^{-1}. The speciation shows the concentration (%) of free **5@4a** (green line) and 1:1 complex (blue line) throughout the titration.

Table S 13. Chemical shifts of the proton signals of free and bound **5@4a/G9** of the **G9⊂(5@4a)** (δ, ppm) and calculated complexation-induced shifts ($\Delta\delta$, ppm).

Signal	δ_{free}	δ_{bound} (1:1 complex)	$\Delta\delta$ (1:1 complex)
1	3.98	3.56	-0.42
2	3.44	2.68	-0.76
3	3.12	1.80	-1.32
H-ortho (Hc)	6.90	6.93	0.03
β-pyrrole (Hb)	6.08	6.13	0.05

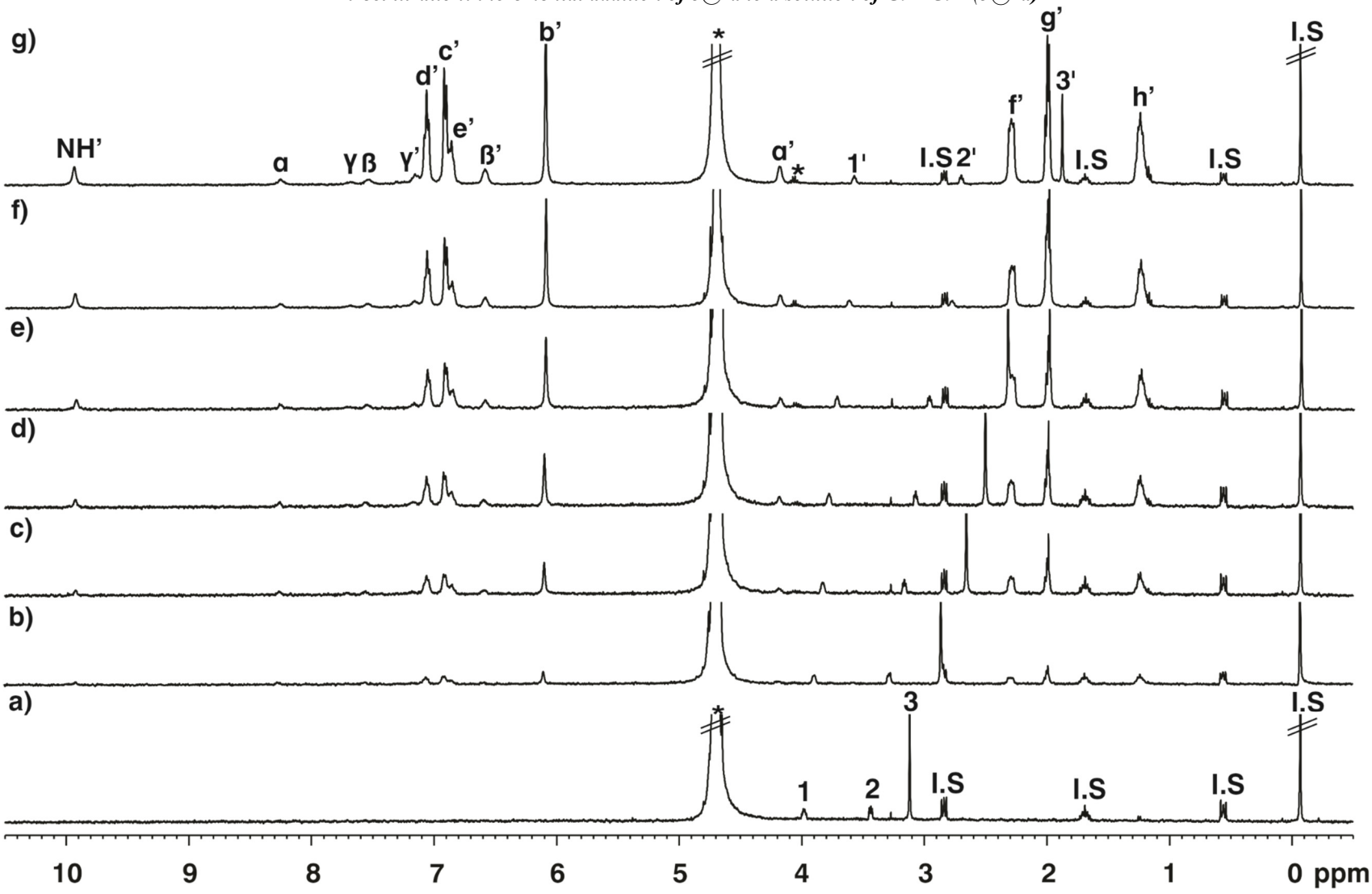


Figure S 60. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **5**@**4a** (1.1 equiv. of **5**) with **G9**: a) 0; b) 0.25; c) 0.5; d) 0.75; f) 1.1; g) 1.6 and h) 2.1 equiv. **5**@**4a**. Primed letters and numbers correspond to the proton signal of bound components. See **Scheme S 1**, **Figure S 13** and **Figure S 56** for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

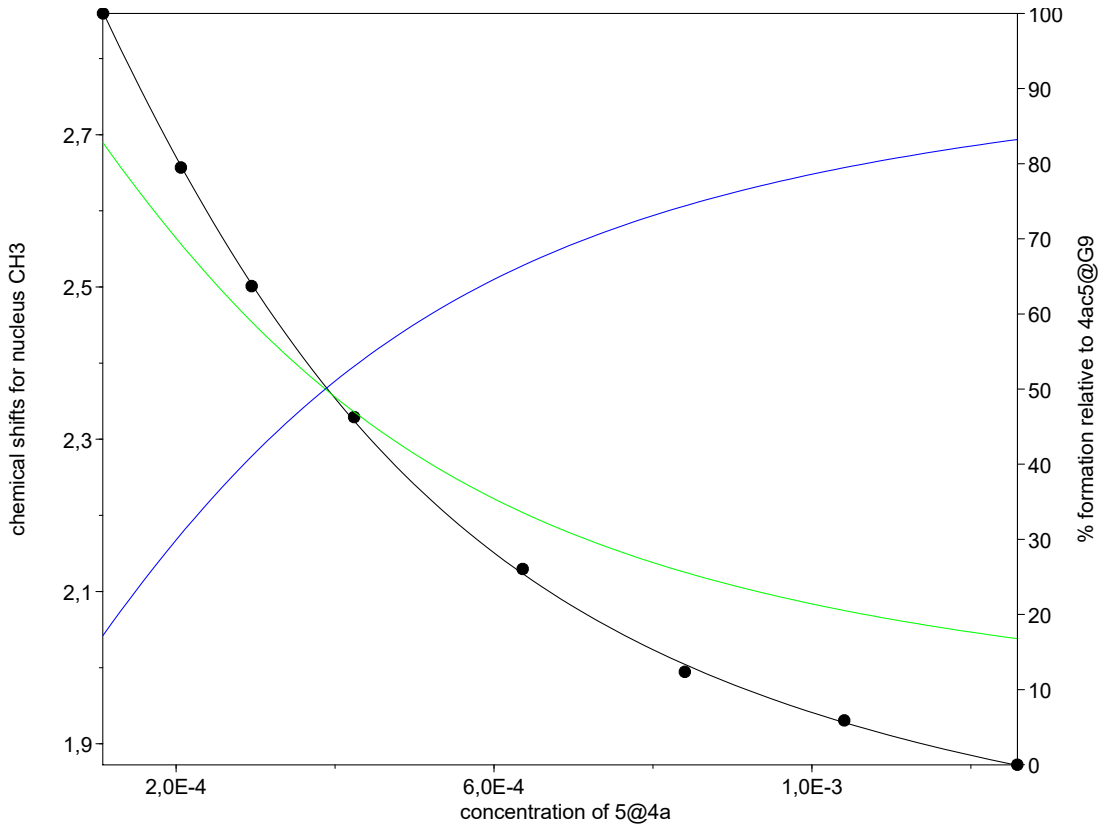
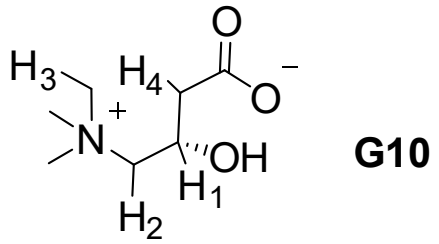


Figure S 61. Fit of the NMR titration data (signal **3'**, -CH_3 proton) to a 1:1 binding model (black line). The fit returned K_a (**G9⊂(5@4a)**) = 5.9x 10^3 M^{-1}. The speciation shows the concentration (%) of free **G9** (green line) and 1:1 complex (blue line) throughout the titration.

Table S 14. Chemical shifts of the proton signals of free and bound **G9** of the **G9⊂(5@4a)** (δ, ppm) and calculated complexation-induced shifts ($\Delta\delta$, ppm).

Signal	δ_{free}	δ_{bound} (1:1 complex)	$\Delta\delta$ (1:1 complex)
1	3.98	3.50	-0.48
2	3.44	2.57	-0.87
3	3.12	1.66	-1.46

3.2.11 ^{1}H NMR spectroscopic titration experiments leading to G10⊂(5@4a)



G10

Figure S 62. Line-drawing structure of L-Carnitine chloride guest (**G10)**

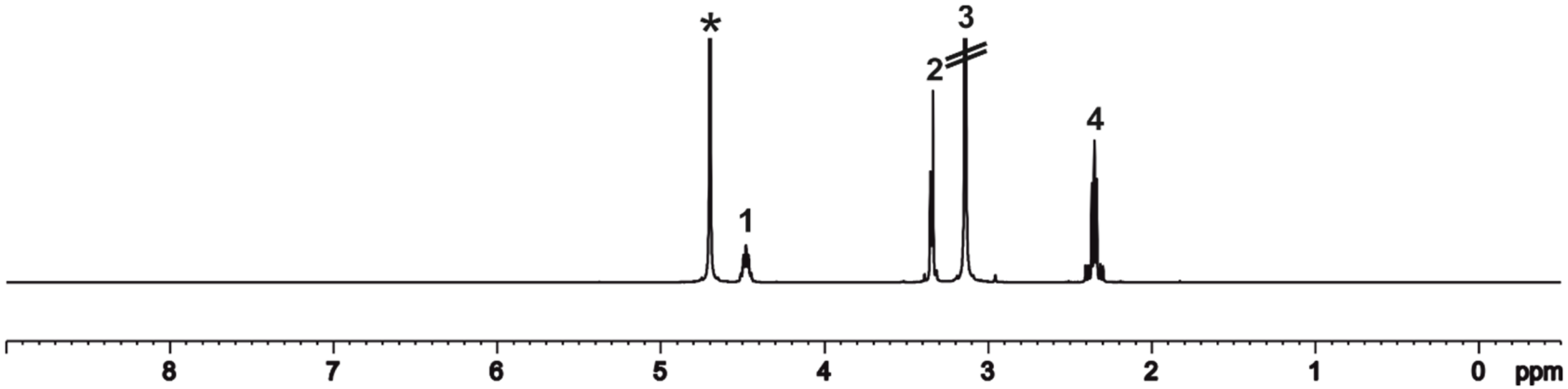


Figure S 63. ^{1}H NMR spectrum (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) of L-Carnitine chloride **(G10)**. *Residual solvent peaks

Reverse titration: incremental addition of G10to a solution of 5@4a - G10⊂(5@4a)

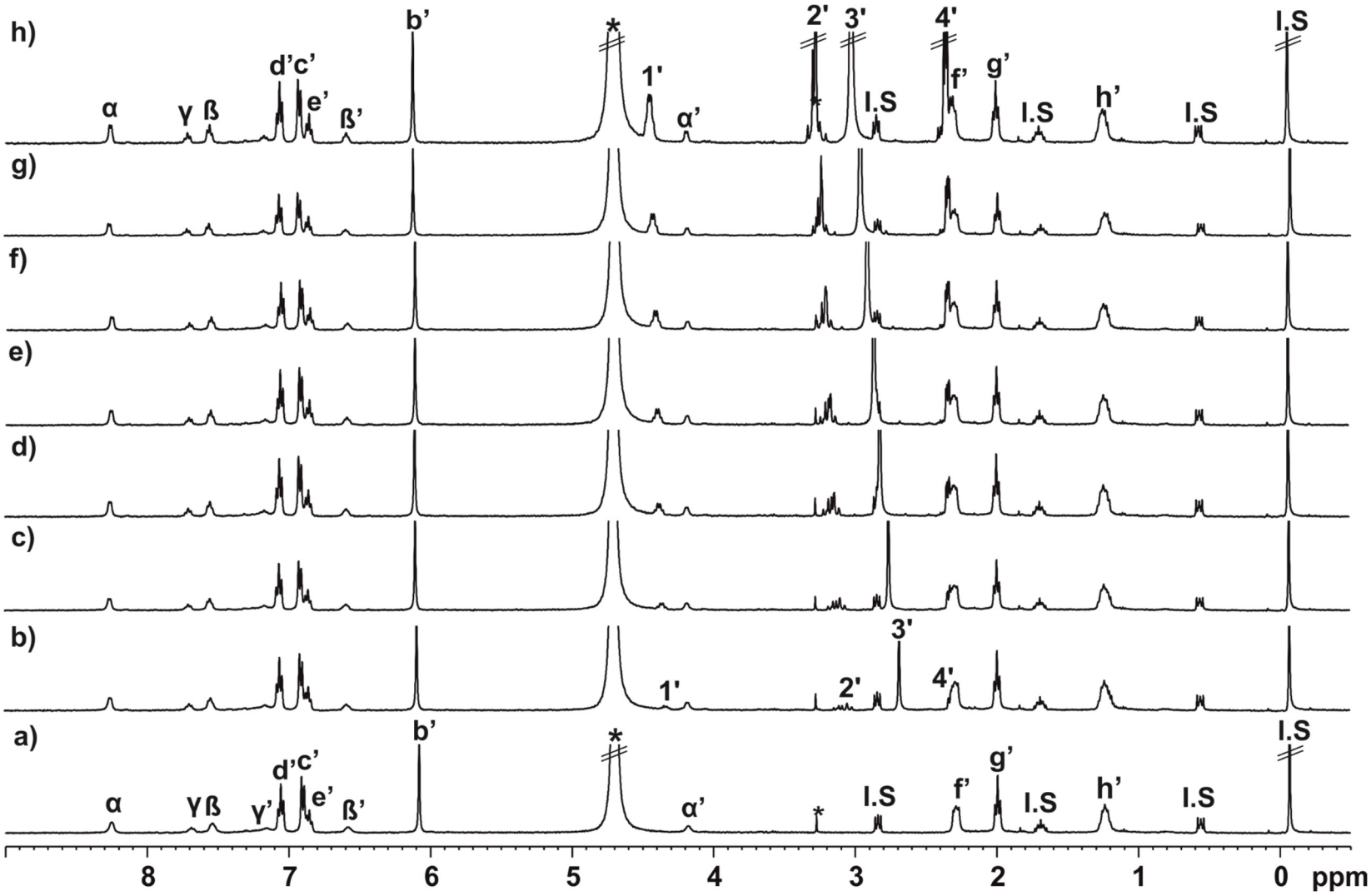


Figure S 64. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **5@4a** (1.1equiv of **5**) with **G10**: a) 0; b) 0.5; c) 1.0; d) 1.5; e) 2.0; f) 3.0; g) 4.0 and h) 5.0 equiv. of **G10**. Primed letters and numbers correspond to proton signal of bound components. See **Scheme S 1**, **Figure S 13** and **Figure S 62** for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

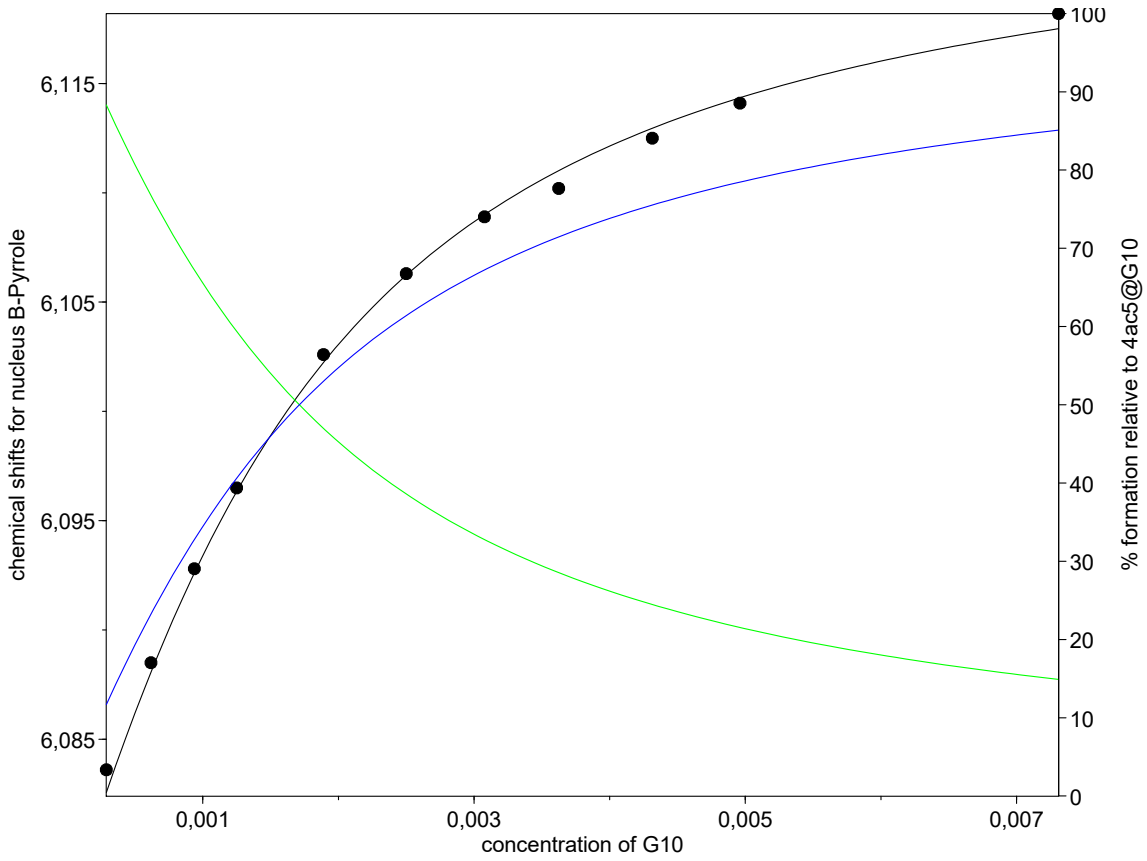


Figure S 65. Fit of the NMR titration data (signal **b**, β-pyrrole proton) to a 1:1 binding model (black line). The fit returned K_a (**G10⊂(5@4a)**) = 7.9 x 10^2 M^{-1}. The speciation shows the concentration (%) of free **5@4a** (green line) and 1:1 complex (blue line) throughout the titration.

Table S 15. Chemical shifts of the proton signals of free and bound **5@4a/G10** of the **G10⊂(5@4a)** (δ, ppm) and calculated complexation-induced shifts ($\Delta\delta$, ppm).

Signal	δ_{free}	δ_{bound} (1:1 complex)	$\Delta\delta$ (1:1 complex)
1	4.48	4.17	-0.31
2	3.35	2.79	-0.56
3	3.14	2.12	-1.02
4	2.35	2.28	-0.07
H-ortho (Hc)	6.90	6.92	-0.02
β-pyrrole (Hb)	6.08	6.12	-0.04

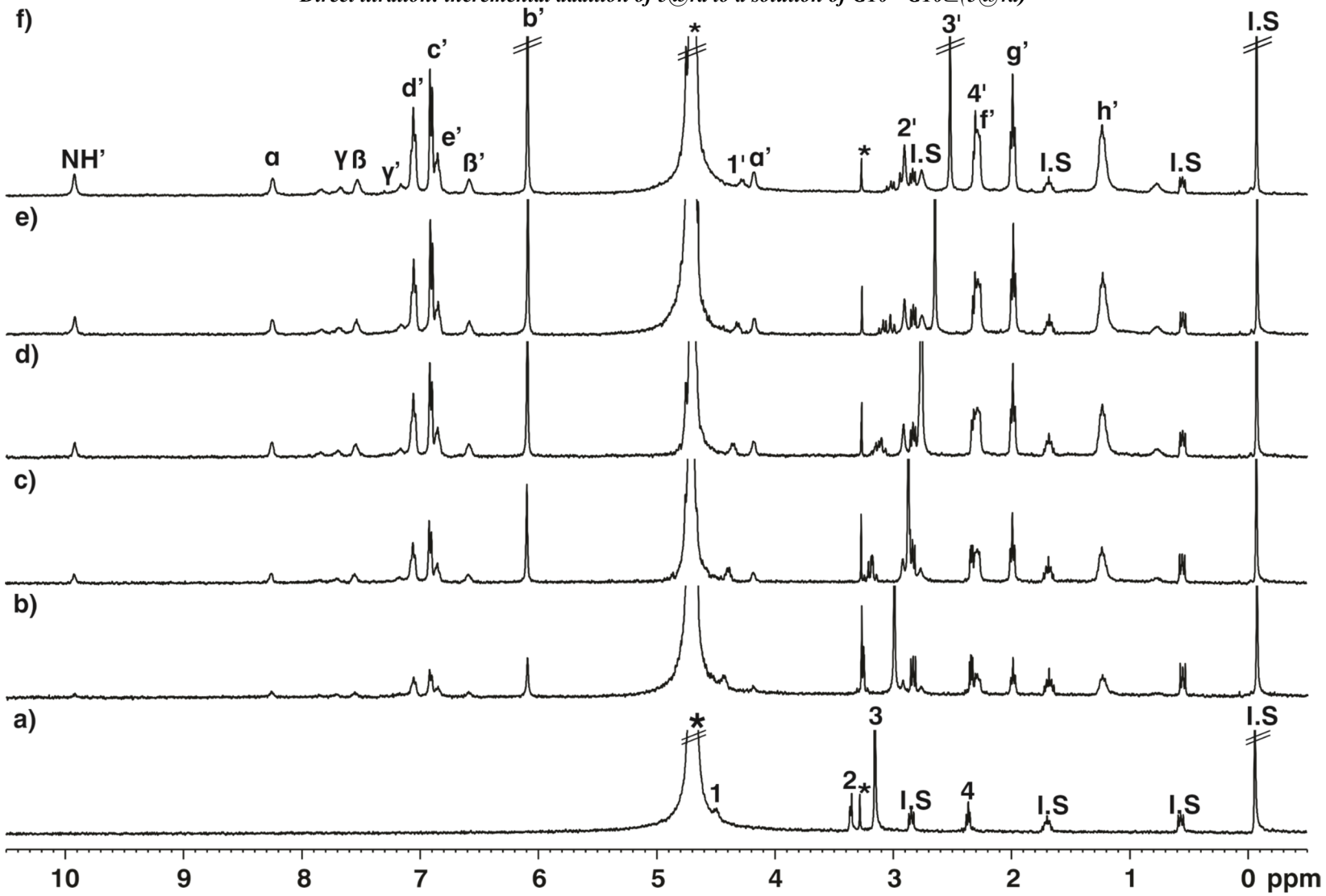


Figure S 66. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **5@4a** (1.1equiv of **5**) with **G10**: a) 0; b) 0.25; c) 0.5; d) 0.7; e) 1.06 and f) 1.5equiv. of **5@4a**. Primed letters and numbers correspond to proton signal of bound components. See **Scheme S 1**, **Figure S 13** and **Figure S 62** for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

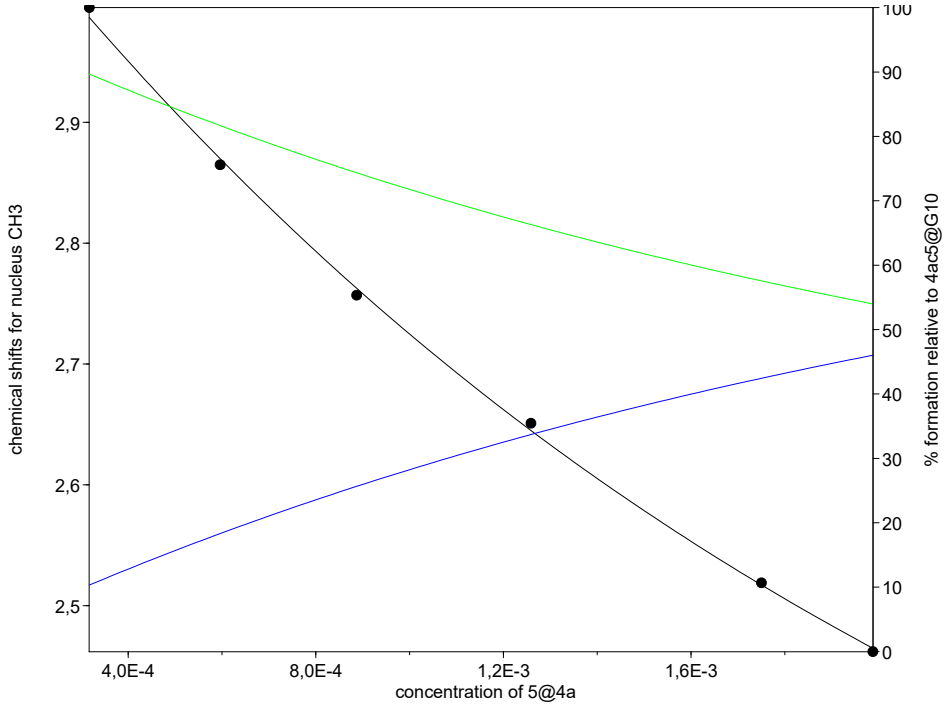


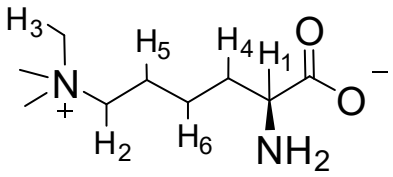
Figure S 67. Fit of the NMR titration data (signal **3'**, -CH_3 proton) to a 1:1 binding model (black line). The fit returned K_a (**G10⊂(5@4a)**) = 5.5x 10^2 M^{-1}. The speciation shows the concentration (%) of free **G10** (green line) and 1:1 complex (blue line) throughout the titration.

Table S 16. Chemical shifts of the proton signals of free and bound **G10** of the **G10⊂(5@4a)** (δ, ppm) and calculated complexation-induced shifts ($\Delta\delta$, ppm).

Signal	δ_{free}	δ_{bound} (1:1 complex)	$\Delta\delta$ (1:1 complex)
1	4.48	3.98	-0.5
2	3.35	2.35	-1.00
3	3.14	1.67	-1.47
4	2.35	2.27	-0.08

As observed in previous direct titrations, under these conditions less than 60% of complex is formed with L-Carnitine. However, the results of CIS and estimated binding constant are in agreement with reverse titrations.

3.2.12 ^{1}H NMR spectroscopic titration experiments leading to G11⊂(5@4a)



G11

Figure S 68. Line-drawing structure of L-Trimethylysine chloride guest (**G11)**

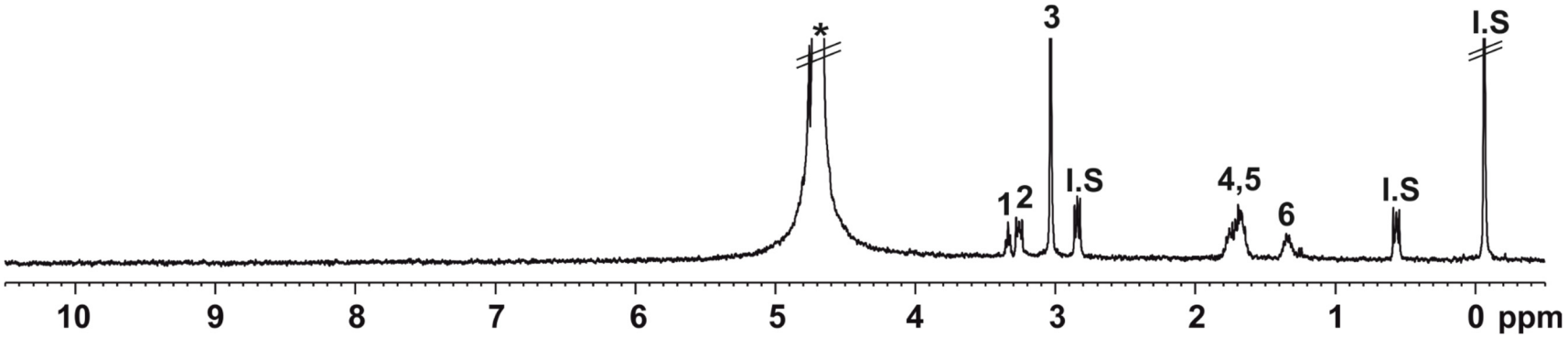


Figure S 69. ^{1}H NMR spectrum (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) of L-TMLys **(G11)**. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.) *Residual solvent peaks

Reverse titration: incremental addition of G11 to a solution of 5@4a - G11⊂(5@4a)

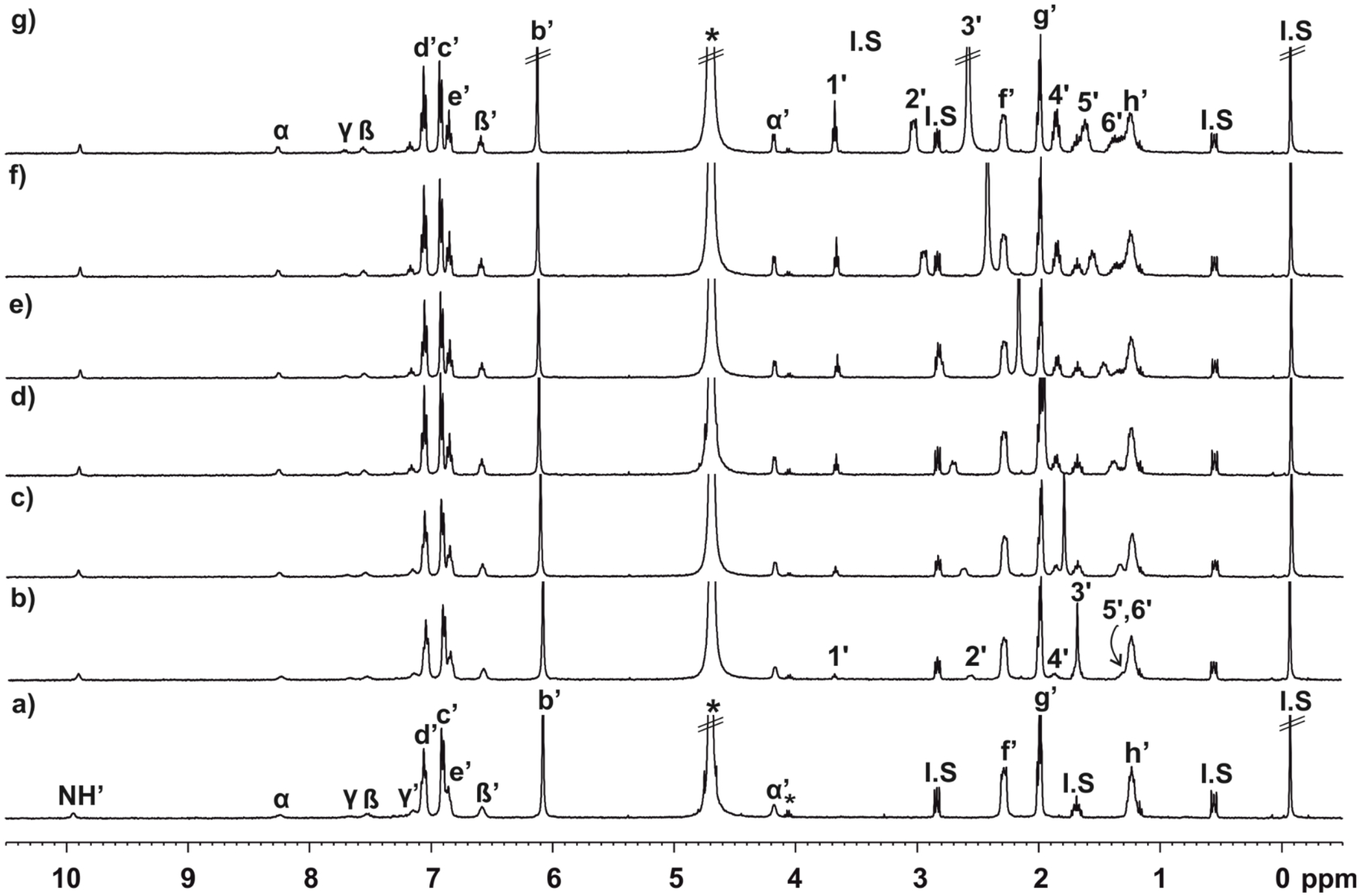


Figure S 70. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **5@4a** (1.1equiv of **5**) with **G11**: a) 0; b) 0.5; c) 1.0; d) 2.0; e) 3.0; f) 4.0 and g) 5 equiv. of **G11**. Primed letters and numbers correspond to the proton signal of bound components. See **Scheme S 1**, **Figure S 13** and **Figure S 68**for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

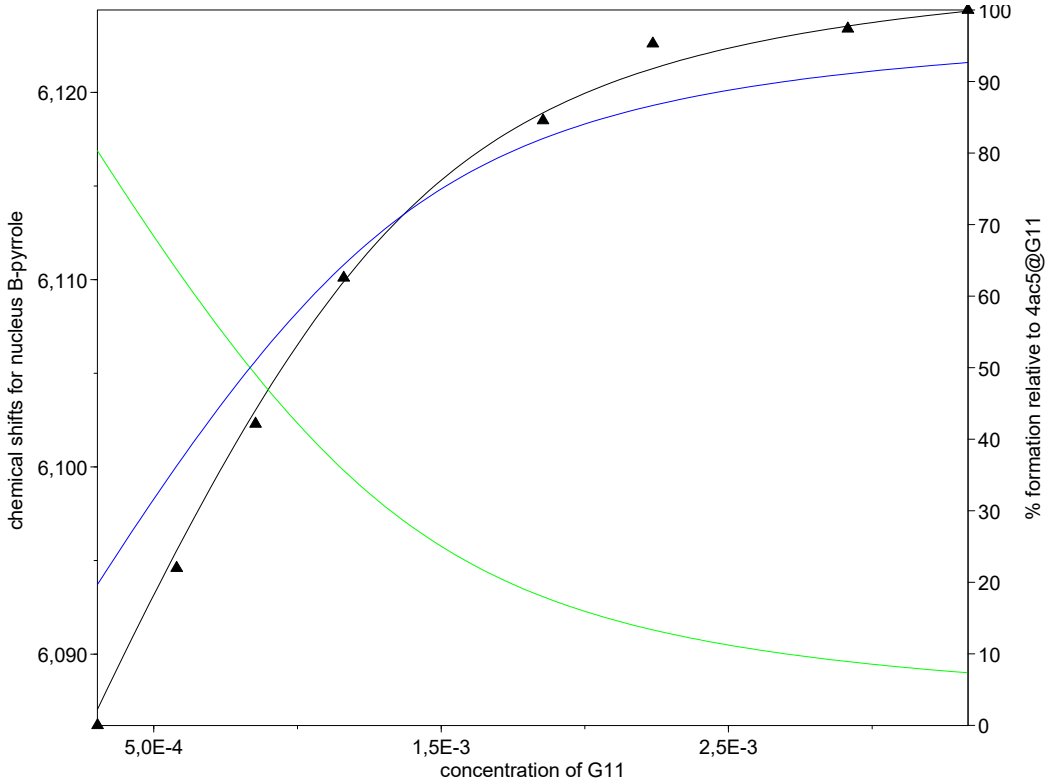


Figure S 71. Fit of the NMR titration data (signal **b**, β-pyrrole proton) to a 1:1 binding model (black line). The fit returned K_a (**G11⊂(5@4a)**) = 6.1 x 10^3 M^{-1}. The speciation shows the concentration (%) of free **5@4a** (green line) and 1:1 complex (blue line) throughout the titration.

Table S 17. Chemical shifts of the proton signals of free and bound **5@4a/G11** of the **G11⊂(5@4a)** (δ, ppm) and calculated complexation-induced shifts ($\Delta\delta$, ppm).

Signal	δ_{free}	δ_{bound} (1:1 complex)	$\Delta\delta$ (1:1 complex)
1	3.33	3.83	-0.50
2	3.27	2.41	-0.86
3	3.04	1.39	-1.65
5	1.79	1.18	-0.61
H-ortho (Hc)	6.90	6.92	-0.02
β-pyrrole (Hb)	6.08	6.13	-0.05

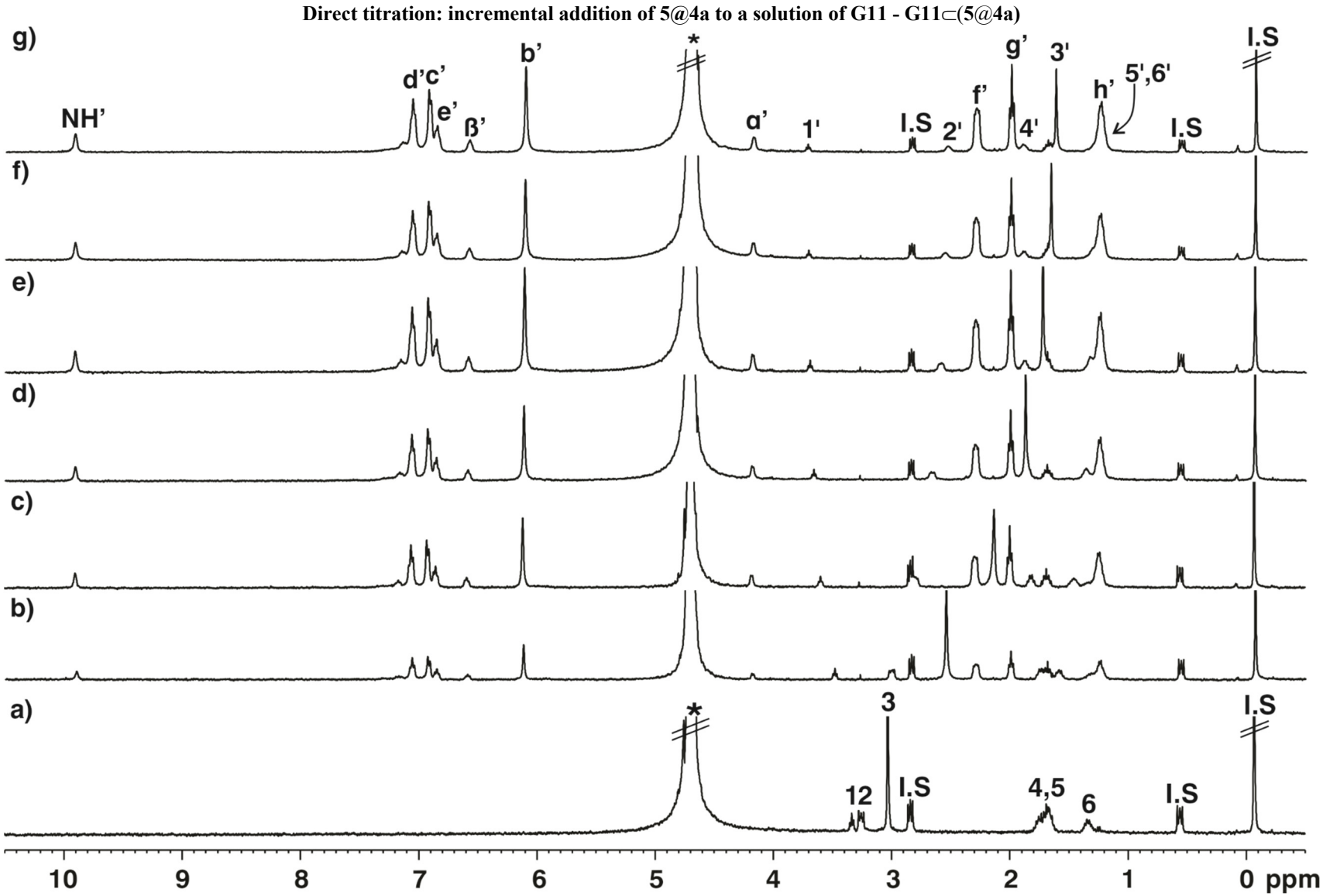


Figure S 72. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **5@4a** (1.1equiv of **5**) with **G11**: a) 0; b) 0.35; c) 0.71; d) 1.03; e) 1.33; f) 1.47 and g) 1.69 equiv. **5@4a**. Primed letters and numbers correspond to proton signal of bound components. See **Scheme S 1**, **Figure S 13** and **Figure S 68** for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

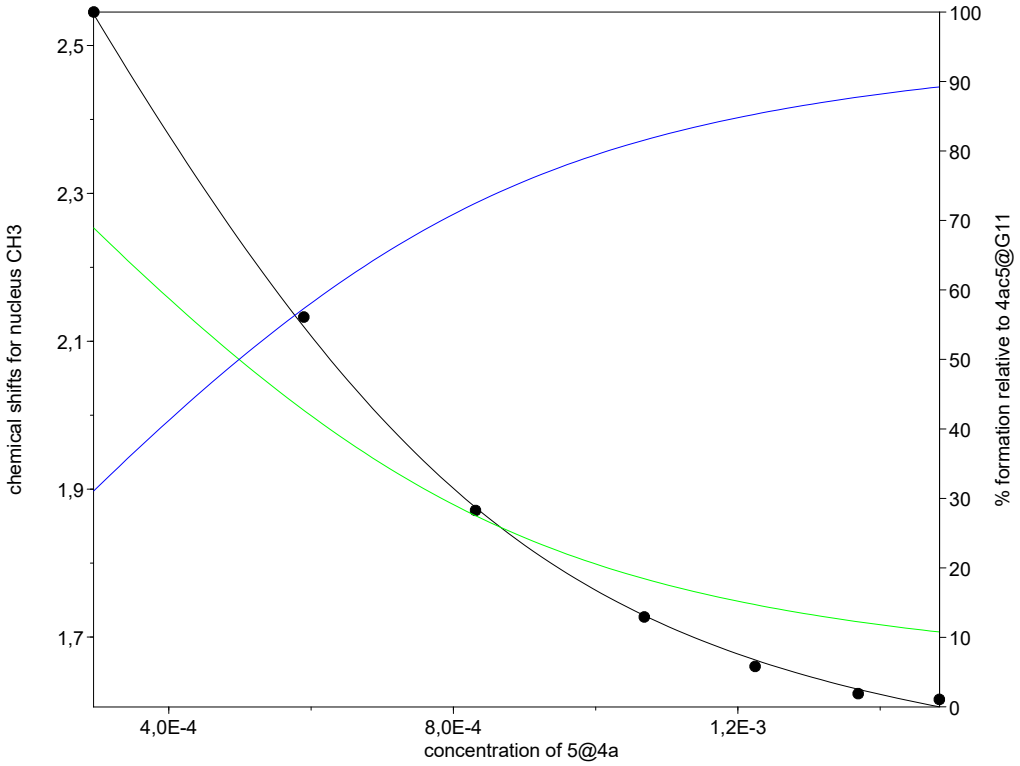
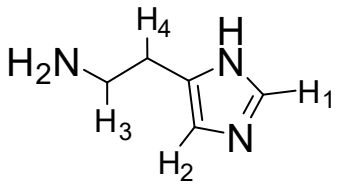


Figure S 73. Fit of the NMR titration data (signal **3'**, -CH_3 proton) to a 1:1 binding model (black line). The fit returned K_a (**G11⊂(5@4a)**) = 1.1 x 10^4 M^{-1}. The speciation shows the concentration (%) of free **G11** (green line) and 1:1 complex (blue line) throughout the titration.

Table S 18. Chemical shifts of the proton signals of free and bound **G11** of the **G11⊂(5@4a)** (δ, ppm) and calculated complexation-induced shifts ($\Delta\delta$, ppm).

Signal	δ_{free}	δ_{bound} (1:1 complex)	$\Delta\delta$ (1:1 complex)
1	3.33	3.77	0.44
2	3.27	2.44	-0.83
3	3.04	1.43	-1.61
4	1.72	1.91	-0.19
5	1.68	1.25	-0.43

3.2.13 ^{1}H NMR spectroscopic titration experiments leading to G12⊂(5@4a)



G12

Figure S 74. Line-drawing structure of Histamine guest (**G12)**

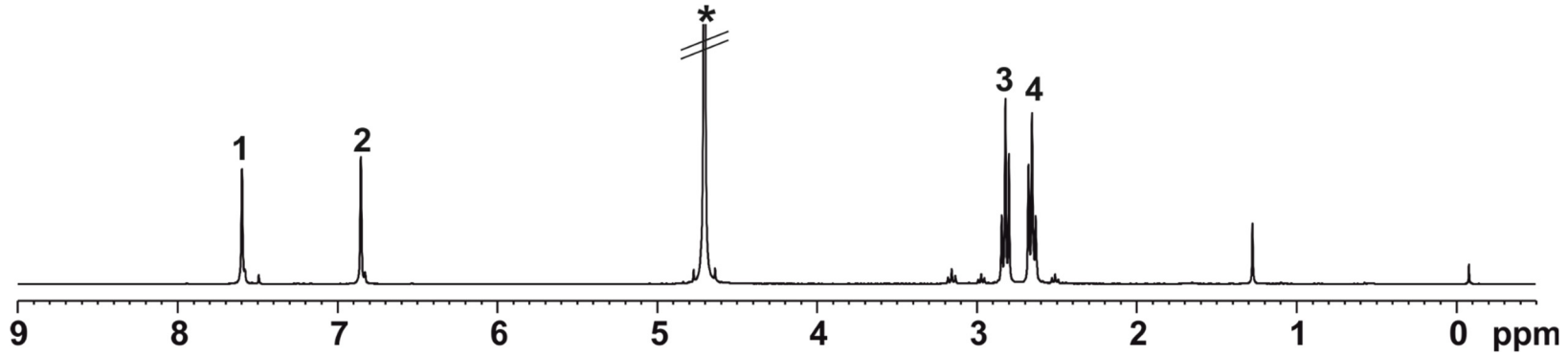


Figure S 75. ^{1}H NMR spectrum (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) of Histamine **(G12)**. *Residual solvent peaks

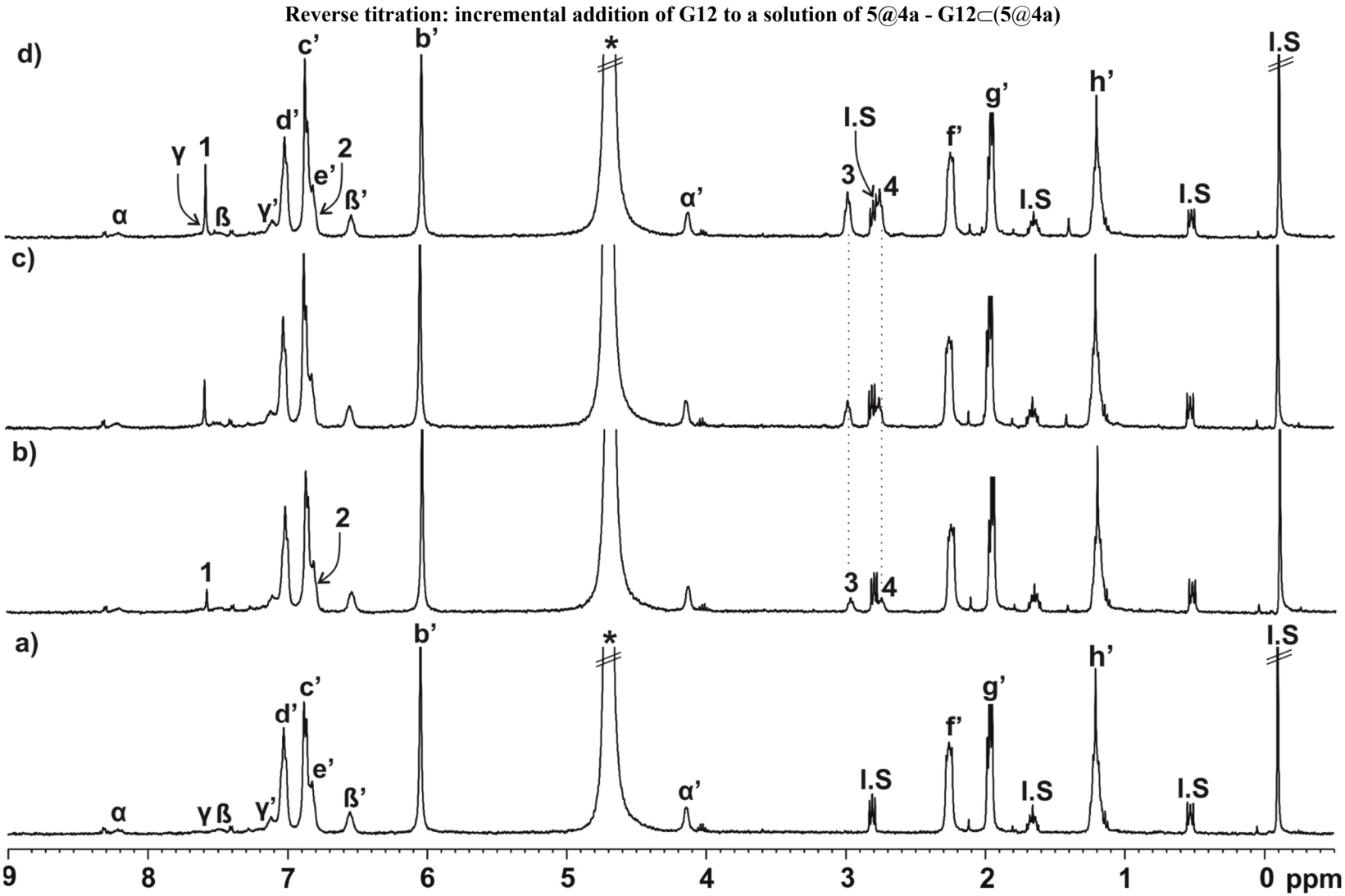
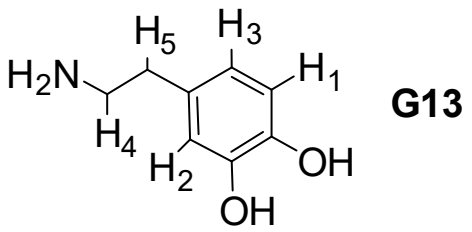


Figure S 76. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **5@4a** (1.1 equiv. of **5**) with **G12**: a) 0; b) 0.5; c) 1.0 and d) 2.0 equiv. of **G12**. Primed letters and numbers correspond to the proton signal of bound components. See **Scheme S 1**, **Figure S 13** and **Figure S 74** for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

3.2.14 ^{1}H NMR spectroscopic titration experiments leading to G13⊂(5@4a)



G13

Figure S 77. Line-drawing structure of Dopamine guest (**G13)**

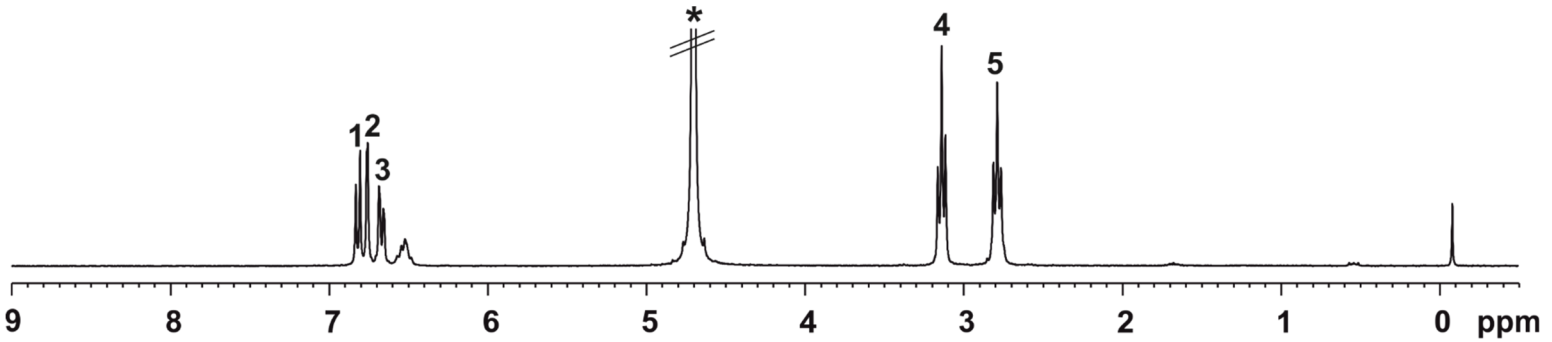


Figure S 78. ^{1}H NMR spectrum (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) of Dopamine **(G13)**. *Residual solvent peaks

Reverse titration: incremental addition of G13 to a solution of 5@4a - G13⊂(5@4a)

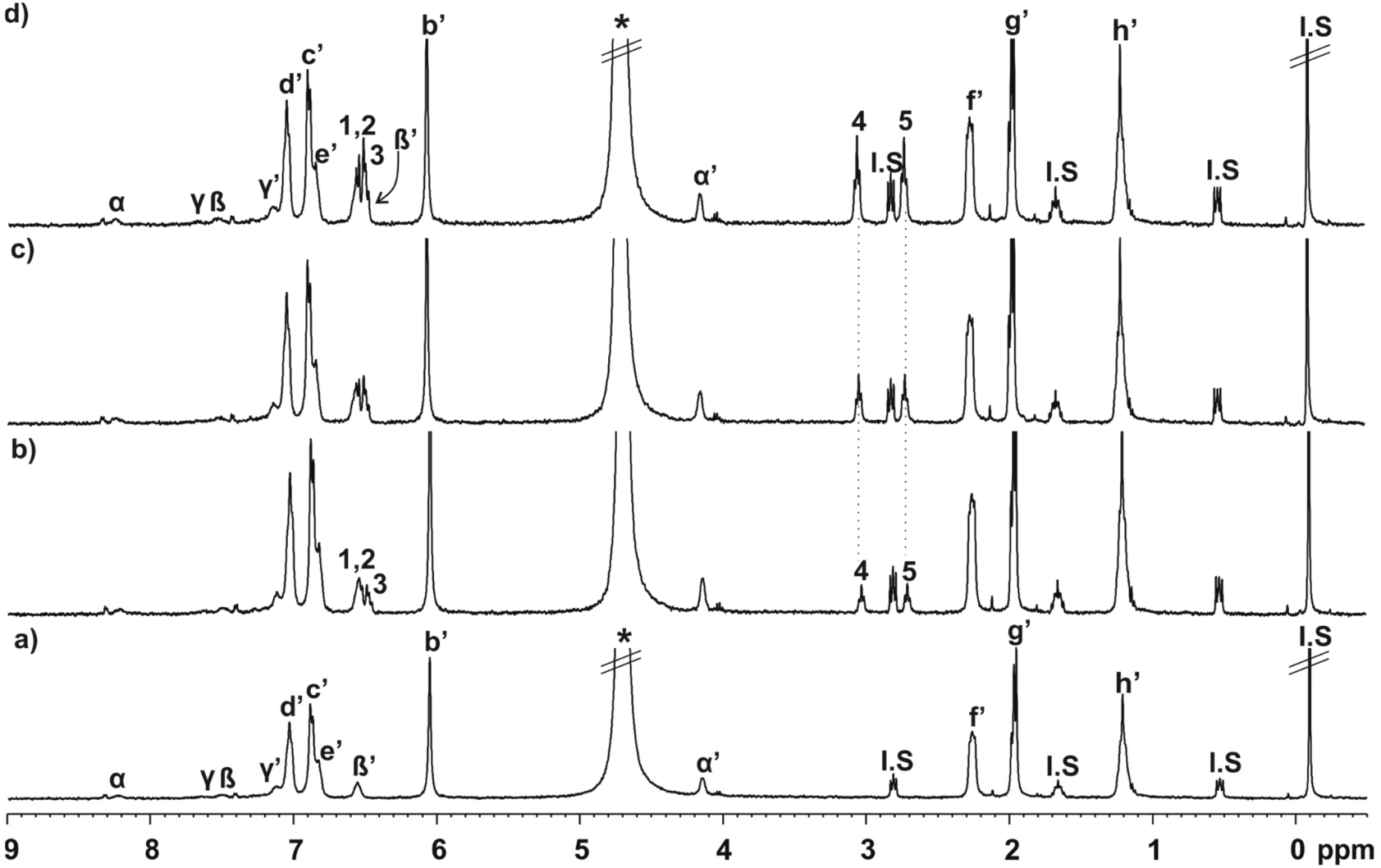
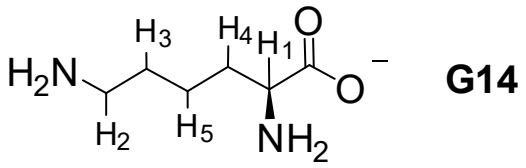


Figure S 79. [1]H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **5@4a** (1.1 equiv. of **5**) with **G13**: a) 0; b) 0.5; c) 1.0 and d) 2.0 equiv. of **G13**. Primed letters and numbers correspond to the proton signal of bound components. See **Scheme S 1**, **Figure S 13** and **Figure S 77**for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

3.2.15 ^{1}H NMR spectroscopic titration experiments leading to G14⊂(5@4a)



G14

Figure S 80. Line-drawing structure of L-Lysine guest (**G14)**

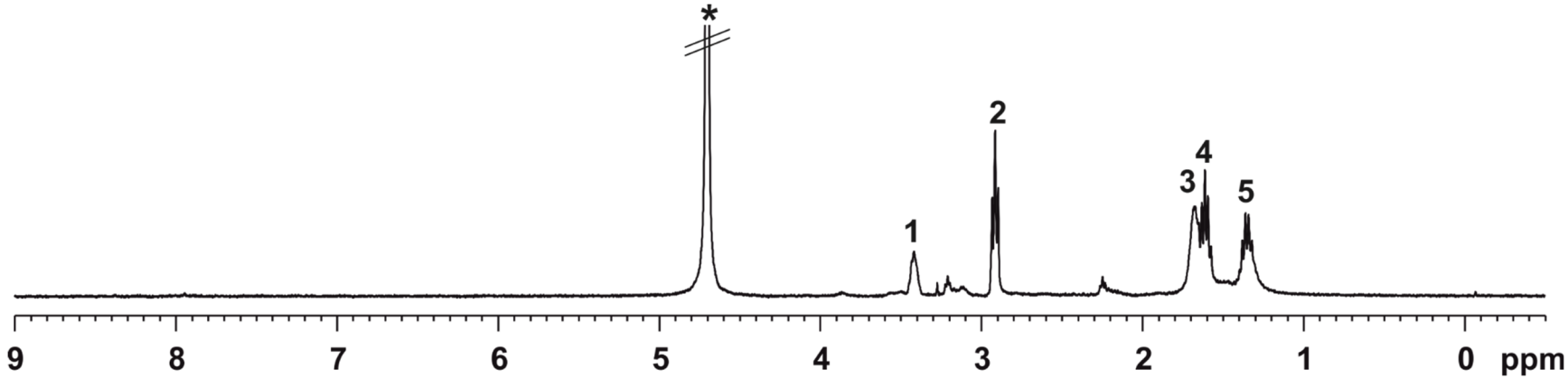


Figure S 81. ^{1}H NMR spectrum (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) of L-Lysine **(G14)**. *Residual solvent peaks

Reverse titration: incremental addition of G14 to a solution of 5@4a - G14⊂(5@4a)

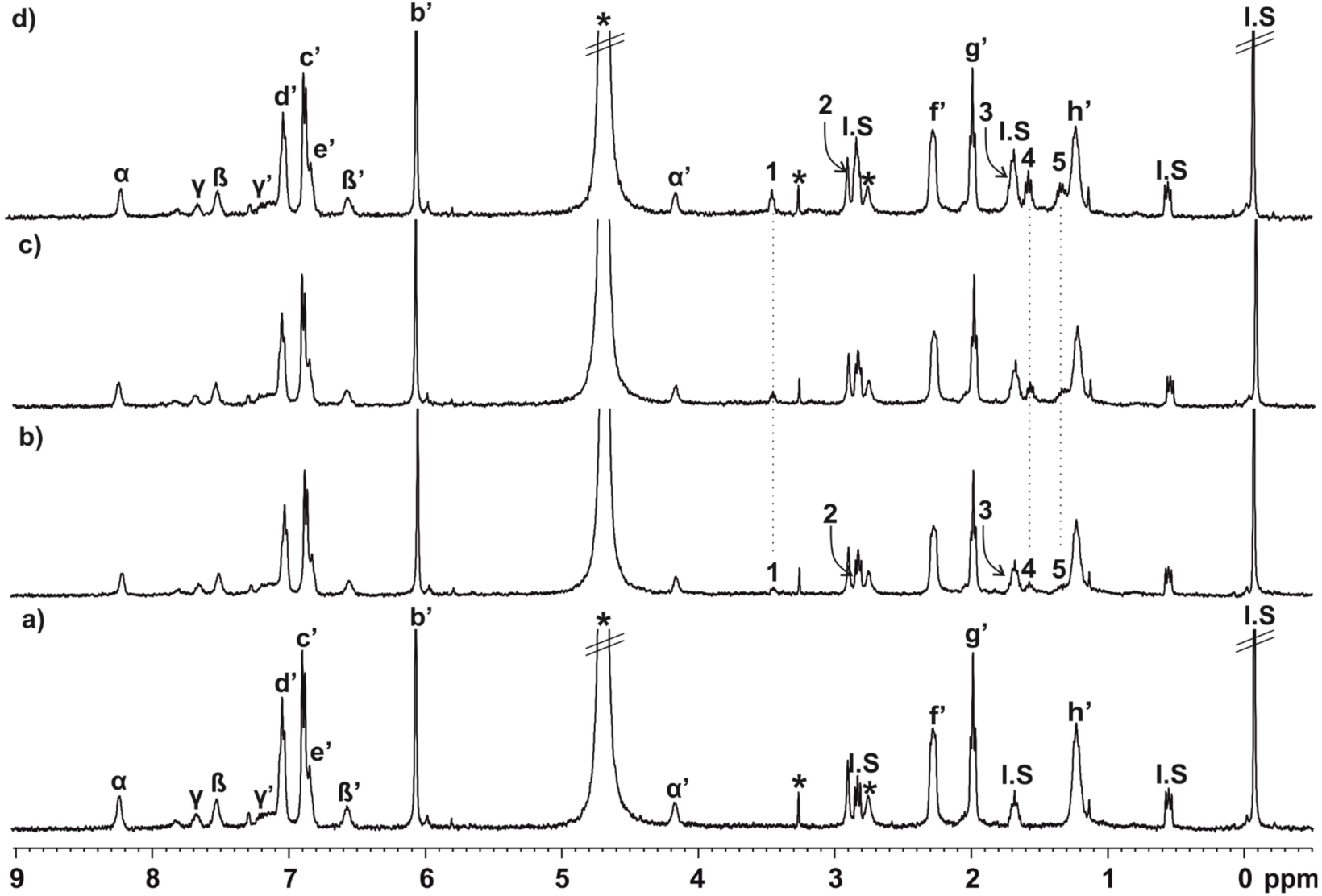


Figure S 82. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **5@4a** (1.1 equiv. of **5**) with **G14**: a) 0; b) 0.5; c) 1.0 and d) 2.0 equiv. of **G14**. Primed letters and numbers correspond to the proton signal of bound components. See **Scheme S 1**, **Figure S 13** and **Figure S 80** for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

3.3 ^{1}H NMR spectroscopic titration experiments tetra-acid C[4]P 4b

3.3.1 ^{1}H NMR spectroscopic titration experiments 5@4b

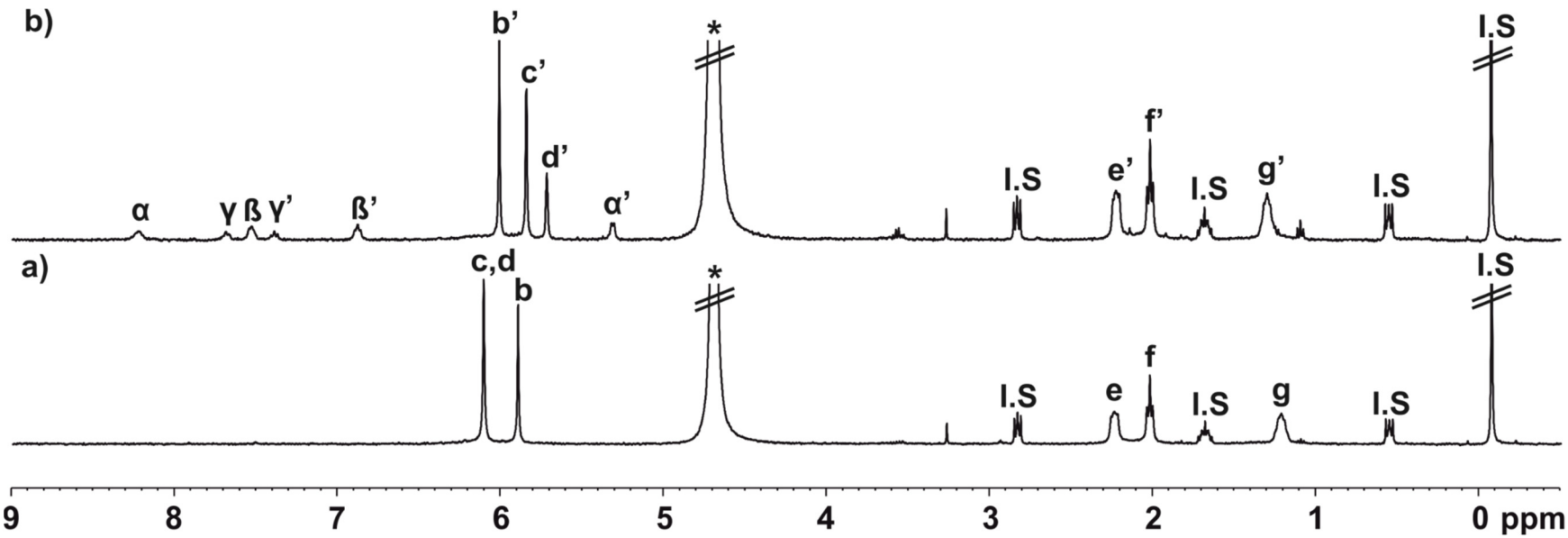


Figure S 83. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **4b** with **5**: a) 0 and b)1.5 equiv. of **5**. Primed letters and numbers correspond to the proton signal of bound components. See **Scheme S 2** and **Figure S 13** for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peaks.

3.3.2 ^{1}H NMR spectroscopic titration experiments leading to G9⊂(5@4b)

Reverse titration: incremental addition of G9 to a solution of 5@4b - G9⊂(5@4b)

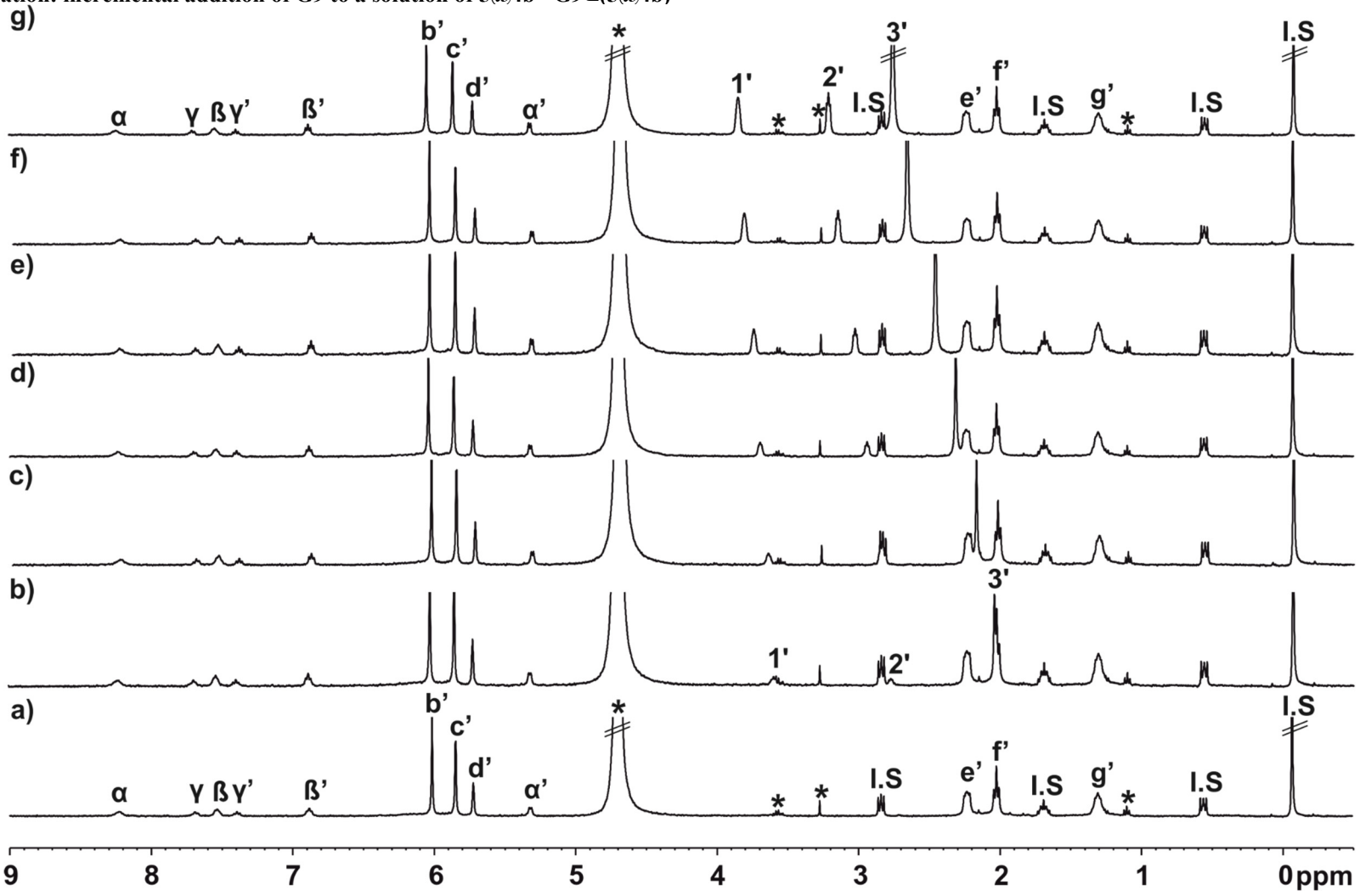


Figure S 84. ^{1}H NMR (400 MHz, D_2O, 0.01 M borate/sodium hydroxide buffer, pD = 10, 0.01 M NaCl, 298 K) spectra of the titration of **5**@**4b** (1.4 equiv. of **5**) with **G9**: a) 0; b) 0.5; c) 1.0; d) 1.5; e) 2; f) 3; and g) 4 equiv. of **G9**. Primed letters and numbers correspond to the proton signal of bound components. See **Scheme S 2**, **Figure S 56** and **Figure S 13** for proton assignments. Sodium 3-(trimethylsilyl)-1-propanesulfonate (I.S.). *Residual solvent peak

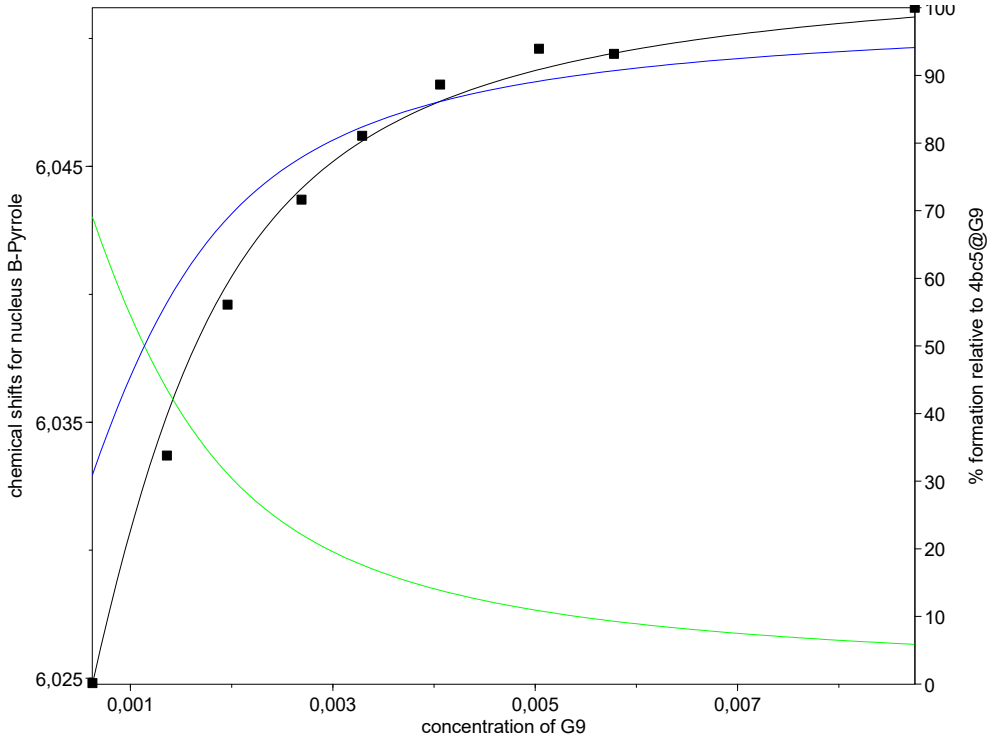


Figure S 85. Fit of the NMR titration data (signal **3'**, -CH_3 proton) to a 1:1 binding model (black line). The fit returned K_a (**G9⊂(5@4b)**) = 2.5x 10^3 M^{-1}. The speciation shows the concentration (%) of free **G9** (green line) and 1:1 complex (blue line) throughout the titration.

Table S 19. Chemical shifts of the proton signals of free and bound **5@4b/G9** of the **G9⊂(5@4b)** (δ, ppm) and calculated complexation-induced shifts ($\Delta\delta$, ppm).

Signal	δ_{free}	δ_{bound} (1:1 complex)	$\Delta\delta$ (1:1 complex)
1	4.07	3.28	-0.79
2	3.44	2.40	-1.04
3	3.12	1.45	-1.67
H-ortho (Hc)	5.85	5.87	0.02
β-pyrrole (Hb)	6.01	6.05	0.04

4. ITC Experiment

ITC experiments were performed using a MicroCal VP-ITC MicroCalorimeter with the VP Viewer 2000 software. Titrations were carried out in 0.01 M borate/sodium hydroxide buffer in H_2O (pH ~ 10) and 0.01 M NaCl at 298 K by adding small aliquots (8-16 µL, 16-32 s) of a solution of the guest into a solution of the host. The concentration of the guest solution was 7-10 times more concentrated than the host solutions (see corresponding figures for details). The association constants and the thermodynamic parameters were obtained from the fit of the titration data to the "one set of sites" binding model using the Microcal ITC Data Analysis module.

4.1 **Titration G7⊂(5@4a)**

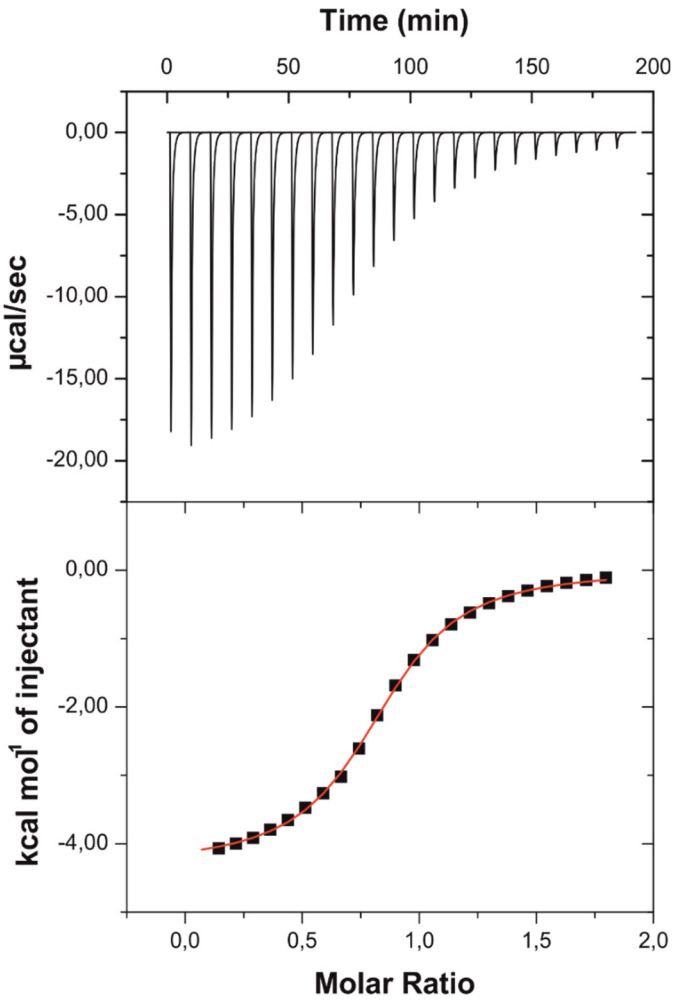


Figure S 86. top) Trace shows raw data for the titration of guest into host: [**G7**] = 9.6 mM and [**5@4a**] = 1.2 mM. Titration was performed at 298 K. bottom) Binding isotherm of the calorimetric titration shown on top. The enthalpy of binding for each injection is plotted versus the molar ratio of guest/host in the cell. The continuous line represents the least-squares-fit of the data to the "one set of sites" binding model.

Table S 20. Binding constant value (K_a) and thermodynamic parameters of the interaction between **5@4a** and **G7** in buffer at pH =10 determined by ITC.

5@4a	K_a(M^{-1})	ΔG (kcal·mol^{-1})	ΔH (kcal·mol^{-1})	ΔS (kcal·mol^{-1})
G7	1.2±0.4 x 10^4	-5.5±0.1	-4.8±0.2	1.3±0.1

5. Calculations

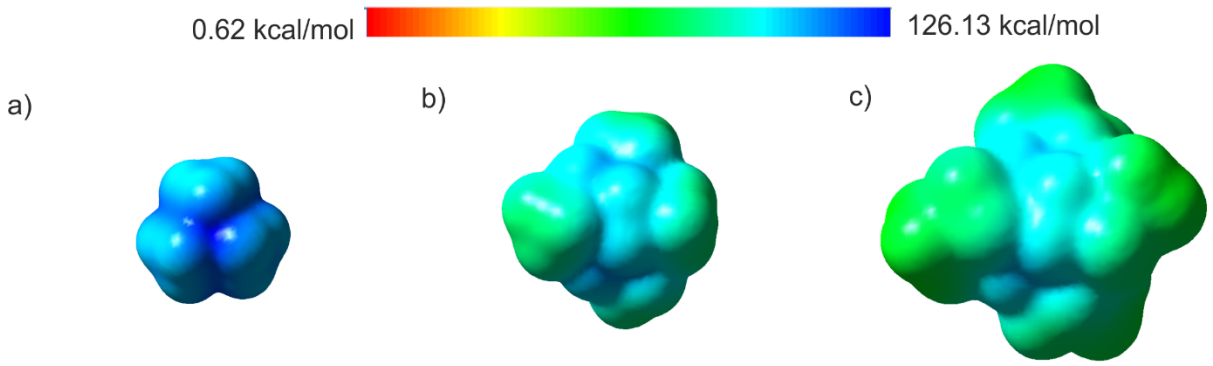


Figure S 87. Electrostatic surface potentials (ESP) calculated using DFT at the RI-BP86-D3BJ-def2-SVP level of theory and mapped to an electron density of 0.001 electron/bohr^3 (van der Waals surface): a) TMA; b) TEA and c) TPA. Boundaries of ESP values are given in kcal/mol·e

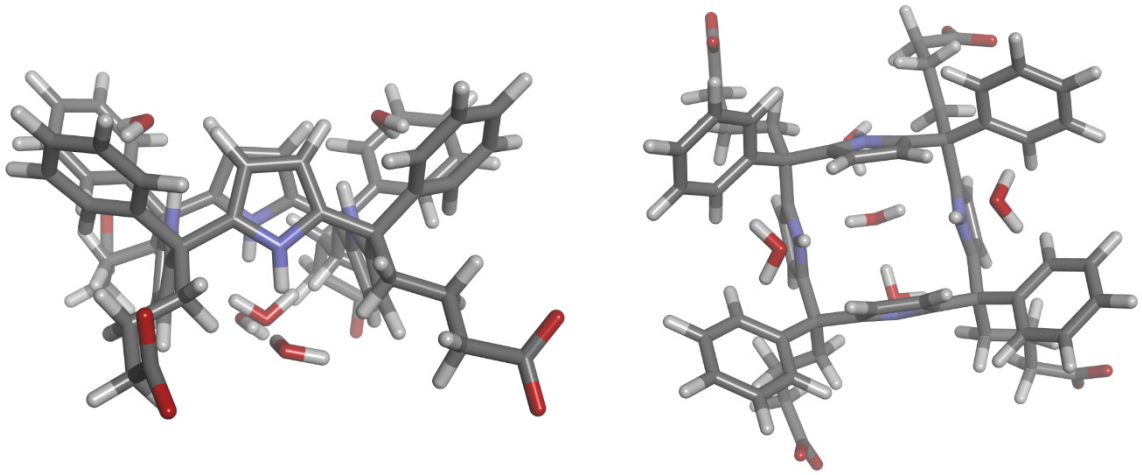


Figure S 88. Side and top views of the energy minimized structure of **4a** in 1,3-alternate conformation at the RI-BP86-D3BJ-def2-SVP COSMO.

Cartesian coordinates of **4a** in 1,3-alternate conformation. The number of atoms and calculated electronic energy are reported in the two first lines.

143

Energy = -3521.739638286

C -5.4790987 -7.2969694 -0.0537190

C -5.1393639 -8.5547472 0.4723718

H -5.8732932 -9.1268879 1.0606521

C -3.8567550 -9.0895530 0.2483930

H -3.6026729 -10.0823225 0.6465454

C -2.8901377 -8.3784638 -0.4923396

C -4.5325444 -6.5937581 -0.8201963

H -4.7925524 -5.6142902 -1.2508778

C	-3.2558038	-7.1324724	-1.0406539
H	-2.5233586	-6.5774705	-1.6435618
C	5.0681649	-3.2539885	-0.3031263
C	5.7199922	-4.3985465	0.1863819
H	6.7003443	-4.3109461	0.6791255
C	5.1196651	-5.6630755	0.0542610
H	5.6397437	-6.5559183	0.4329132
C	3.8565804	-5.8114124	-0.5590243
C	3.2225322	-4.6563866	-1.0636832
H	2.2380022	-4.7506918	-1.5412750
C	3.8201810	-3.3916718	-0.9354675
H	3.3005709	-2.5036473	-1.3276100
O	8.7225725	-9.7091600	6.1520371
O	9.0759333	-11.9076370	5.7369975
O	-0.5966926	-13.6992331	7.0934411
O	0.7275484	-15.5224211	6.8650019
O	-3.4395763	-8.4426696	-4.5552537
O	-2.8252154	-9.6912610	-6.3421206
O	5.6785768	-7.0362919	-4.4238744
O	5.2160541	-8.7198094	-5.8675076
N	3.4890305	-7.9155280	1.6830999
H	2.8705957	-7.1629884	2.0222893
N	1.7811992	-9.9645529	3.9302895
H	2.2222200	-10.8093976	3.5033506
N	-1.1083881	-9.8481921	1.5338365
H	-1.3752475	-8.9500491	1.9754851
N	0.8656550	-8.1101969	-1.0463647
H	1.1494018	-8.8834788	-1.6788285
C	3.7815308	-8.1366499	0.3531862
C	4.7026278	-9.1922984	0.3141647
H	5.1527125	-9.6176815	-0.5887703
C	4.9596297	-9.5923676	1.6699558
H	5.6412739	-10.3873592	1.9917274
C	4.1941808	-8.7706507	2.5022564

C	3.9658982	-8.7077510	4.0047281
C	4.5164534	-7.3959804	4.5924433
C	5.4124240	-6.5825029	3.8691582
H	5.6975120	-6.8744464	2.8484902
C	5.9524034	-5.4136645	4.4376495
H	6.6438013	-4.7918903	3.8484885
C	5.6105357	-5.0445153	5.7487282
C	4.7354953	-5.8611329	6.4877209
H	4.4669775	-5.5879605	7.5198597
C	4.1979514	-7.0250133	5.9159902
H	3.5127414	-7.6548365	6.5015120
C	-1.9191589	-10.6134068	4.4205051
C	4.6762005	-9.8932313	4.7343763
H	4.3854226	-10.8365882	4.2273051
H	4.2431722	-9.9607036	5.7550033
C	6.2004002	-9.7937198	4.8382582
H	6.6430651	-9.5826002	3.8412559
H	6.4915920	-8.9329463	5.4730445
C	6.8475350	-11.0437661	5.4342422
H	6.7407949	-11.9237787	4.7636703
H	6.3157708	-11.3179591	6.3766586
C	8.3541052	-10.8680610	5.7975396
C	2.4574870	-8.7899995	4.2027321
C	1.5004610	-7.8180950	4.5065861
H	1.7079445	-6.7726679	4.7575858
C	0.2146558	-8.4427665	4.4232753
H	-0.7571090	-7.9684714	4.5910620
C	0.4186801	-9.7779841	4.0659823
C	-0.5628054	-10.9018448	3.7492178
C	-1.9682500	-10.2650020	5.7867122
H	-1.0286977	-10.1707299	6.3484880
C	-3.1939818	-10.0339629	6.4293069
H	-3.2064494	-9.7561431	7.4945920
C	-4.4032521	-10.1526701	5.7199013

C	-4.3712105	-10.5262612	4.3663613
H	-5.3081666	-10.6391785	3.7996334
C	-3.1385068	-10.7603687	3.7275376
H	-3.1232377	-11.0747883	2.6743561
C	-0.0183945	-12.2517897	4.3132353
H	0.2923012	-12.0745361	5.3617902
H	0.8963459	-12.5268260	3.7472786
C	-1.0068179	-13.4205409	4.3235400
H	-1.8661201	-13.1498710	4.9700602
H	-1.4060310	-13.6045561	3.3032159
C	-0.3736679	-14.6899380	4.8964029
H	0.5617032	-14.9584534	4.3569987
H	-1.0576562	-15.5573936	4.7528660
C	-0.0465812	-14.6219988	6.4220872
C	-0.7023302	-10.9642737	2.2361966
C	-0.4610182	-11.9688326	1.2954357
H	-0.1047712	-12.9808411	1.5119509
C	-0.7464788	-11.4210330	-0.0056697
H	-0.6535337	-11.9340677	-0.9683512
C	-1.1615328	-10.0970632	0.1775710
C	-1.5041113	-8.9737257	-0.7909349
C	-1.5034711	-9.4652937	-2.2692449
H	-0.5402599	-9.9724399	-2.4798271
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H	-2.6581312	-11.3059894	-2.0670052
H	-3.6215349	-9.8519893	-2.4589810
C	-2.6377657	-10.6960065	-4.1682414
H	-3.3583884	-11.5111928	-4.4060209
H	-1.6420225	-11.0832853	-4.4797110
C	-2.9935256	-9.4947778	-5.1014175
C	-0.4206809	-7.9255353	-0.5688511
C	-0.3915228	-6.8235966	0.2878620
H	-1.2426243	-6.4436881	0.8620914

C	0.9501488	-6.3326074	0.3135246
H	1.3322461	-5.5004758	0.9133769
C	1.7152759	-7.1480883	-0.5253780
C	3.2243882	-7.2096419	-0.7206559
C	3.6176403	-7.7800167	-2.1124057
H	3.2713226	-8.8329752	-2.1499734
H	4.7229922	-7.7999504	-2.1832678
C	3.0783826	-7.0285606	-3.3293421
H	1.9840491	-6.8689898	-3.2221565
H	3.5622611	-6.0322680	-3.3797086
C	3.3852414	-7.7705664	-4.6313601
H	2.8717910	-7.2711963	-5.4842707
H	2.9746877	-8.8046361	-4.6110117
C	4.9000781	-7.8539790	-4.9984570
H	-6.4778353	-6.8708131	0.1262549
H	5.5287885	-2.2607479	-0.1906794
H	6.0269590	-4.1285576	6.1945164
H	-5.3642638	-9.9619336	6.2214586
O	2.9694872	-12.1358241	2.5040577
O	2.2421506	-10.9423300	0.1603861
O	1.6436370	-10.5389872	-2.4661258
H	2.7016127	-11.7781362	1.6085817
H	3.9280266	-11.9457091	2.5147248
H	2.6817630	-10.0622523	0.2894399
H	1.2730183	-10.8214026	0.3358006
H	2.3933287	-10.5668475	-3.0901668
H	2.0194684	-10.8689179	-1.6044832
O	-2.7284549	-7.7516182	2.8349003
O	3.0453321	-5.0601055	2.5588361
H	-2.9957402	-8.5170407	3.3900839
H	-3.3092208	-7.8556081	2.0491454
H	3.6110187	-4.9852968	1.7602641
H	3.6937281	-5.3279621	3.2451155

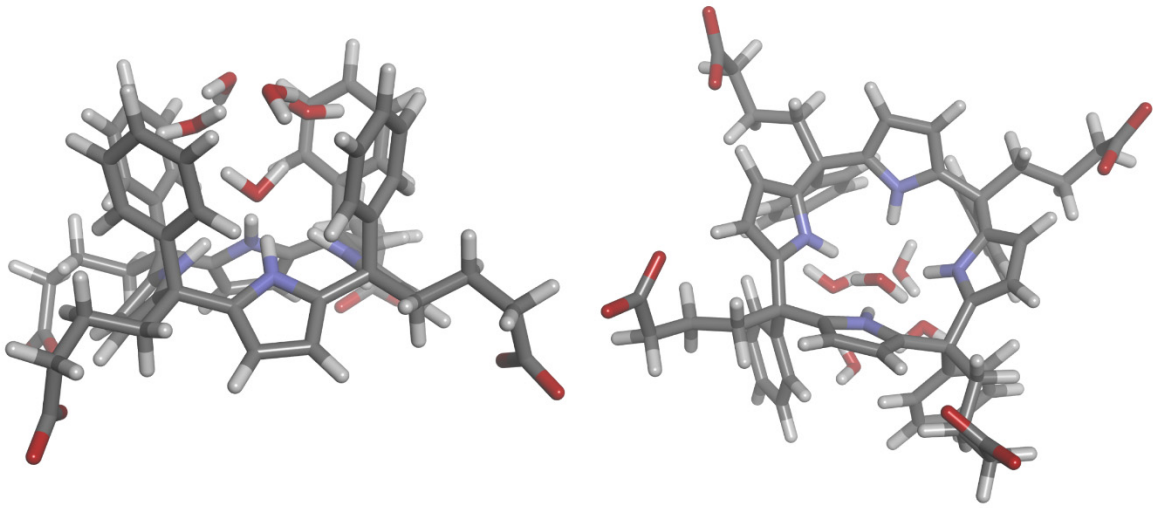

Figure S 89. Side and top views of the energy minimized structure of **4a** in cone conformation at the RI-BP86-D3BJ-def2-SVP COSMO.

Cartesian coordinates of **4a** in cone conformation. The number of atoms and calculated electronic energy are reported in the two first lines.

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Energy = -3521.782451197

C	2.6082756	2.2590953	-4.5460780
C	3.4510365	1.1400435	-4.4575332
H	4.0396916	0.9660703	-3.5438098
C	3.5404563	0.2321650	-5.5263478
H	4.1825538	-0.6552694	-5.4409750
C	2.7990255	0.4280276	-6.7067579
C	1.8679931	2.4720080	-5.7258496
H	1.1979325	3.3422999	-5.8081633
C	1.9688025	1.5660823	-6.7944688
H	1.3731927	1.7235936	-7.7068669
C	4.0506754	6.3955768	-8.9854850
C	3.1423192	5.3822288	-8.6381645
H	2.4718647	5.5181052	-7.7760591
C	3.0790436	4.1961921	-9.3907687
H	2.3515263	3.4178229	-9.1235961
C	3.9219520	3.9965153	-10.5020565
C	4.8426336	5.0138832	-10.8338170
H	5.5022798	4.8715418	-11.7034194

C	4.9062688	6.2051813	-10.0895440
H	5.6209681	6.9917566	-10.3764981
O	9.2904899	1.8016974	-15.5214653
O	11.3891855	1.5813470	-16.3309219
O	6.9961138	-6.1247102	-7.1495472
O	8.8094683	-7.4447609	-6.8655747
O	1.2771758	-4.6569759	-7.3113732
O	-0.9484342	-4.9618478	-7.0605438
O	0.3682360	1.8075726	-13.8800699
O	-0.3110215	3.2232098	-15.5053151
N	6.1724205	2.0357960	-11.1857199
H	6.1098953	1.9096028	-10.1703392
N	7.9857070	-0.0512895	-9.3750161
H	7.4641068	0.6791856	-8.8588574
N	5.2487859	-1.0915158	-7.8222267
H	5.5006814	-0.1114643	-7.9802088
N	3.4611974	1.1009770	-9.5476597
H	4.2404569	1.4637921	-8.9711209
C	5.1130426	2.3813574	-12.0062575
C	5.6005367	2.3754802	-13.3156742
H	5.0206782	2.6159934	-14.2126179
C	6.9902300	2.0281409	-13.2701470
H	7.6945322	1.9598043	-14.1140521
C	7.3240731	1.8319061	-11.9287037
C	8.6576854	1.5116026	-11.2764762
C	9.0777797	2.5961628	-10.2627410
C	8.5834250	3.9121756	-10.3377844
H	7.7886245	4.1455931	-11.0603475
C	9.1076054	4.9280337	-9.5201564
H	8.7076298	5.9506868	-9.5969120
C	10.1430702	4.6465023	-8.6146401
C	10.6356371	3.3298259	-8.5188682
H	11.4497340	3.0944164	-7.8155451
C	10.1017700	2.3167585	-9.3324860

H	10.5037476	1.2939791	-9.2715402
C	7.9778636	-0.9286300	-6.4487446
C	9.7708409	1.4615262	-12.3741826
H	9.4305565	0.7808075	-13.1797744
H	10.6672048	0.9983545	-11.9123506
C	10.1781801	2.7972643	-13.0039493
H	9.2782732	3.3311876	-13.3691123
H	10.6430033	3.4460832	-12.2313440
C	11.1459951	2.6029991	-14.1736561
H	12.0327086	2.0069392	-13.8614818
H	11.5568317	3.5862469	-14.4964216
C	10.5520171	1.9292114	-15.4487193
C	8.6065450	0.1513822	-10.5967269
C	9.1811552	-1.0636191	-10.9720227
H	9.7545849	-1.2457764	-11.8866139
C	8.9075089	-2.0097615	-9.9351338
H	9.2282874	-3.0559885	-9.9093941
C	8.1709521	-1.3556260	-8.9443195
C	7.6512406	-1.8849941	-7.6145322
C	9.1182347	-0.1013790	-6.4697199
H	9.7323580	-0.0572539	-7.3803997
C	9.4865242	0.6545498	-5.3426715
H	10.3783295	1.2984564	-5.3850812
C	8.7276901	0.5836985	-4.1628299
C	7.5843771	-0.2392582	-4.1279473
H	6.9853639	-0.3132378	-3.2070768
C	7.2098897	-0.9758235	-5.2653655
H	6.3218702	-1.6231451	-5.2348607
C	8.3952423	-3.2332774	-7.3307923
H	9.4751796	-3.0502923	-7.5104561
H	8.0578950	-3.9683951	-8.0885305
C	8.2338354	-3.8668668	-5.9459325
H	8.6850488	-3.2081364	-5.1744310
H	7.1588222	-3.9681968	-5.6978717

C	8.8772176	-5.2543806	-5.8868223
H	8.9104996	-5.6144290	-4.8337238
H	9.9397792	-5.2165374	-6.2149778
C	8.1645279	-6.3667186	-6.7156944
C	6.1538724	-2.1332418	-7.6959338
C	5.4126042	-3.3116223	-7.5871555
H	5.8418281	-4.3158702	-7.4485355
C	4.0237469	-2.9550392	-7.6377769
H	3.1572930	-3.6274807	-7.5430575
C	3.9479660	-1.5666287	-7.7764942
C	2.7475538	-0.6364710	-7.8229552
C	1.4425279	-1.4678948	-7.5990679
H	1.4399821	-2.3068122	-8.3237152
H	0.5863858	-0.8106390	-7.8566742
C	1.2189475	-2.0364121	-6.1951703
H	2.1115196	-2.6107558	-5.8773930
H	1.0982241	-1.2034029	-5.4702943
C	-0.0035080	-2.9558152	-6.1429868
H	-0.9110353	-2.4359673	-6.5241389
H	-0.2400381	-3.2147325	-5.0860485
C	0.1233877	-4.3056039	-6.9144414
C	2.6420149	0.0466677	-9.1791173
C	1.7258994	-0.1403514	-10.2162095
H	0.9264465	-0.8889143	-10.2335509
C	1.9951365	0.8387762	-11.2246703
H	1.4312648	1.0187805	-12.1524378
C	3.0740903	1.6072419	-10.7806642
C	3.7563542	2.7890981	-11.4499341
C	2.8808457	3.2801560	-12.6475913
H	2.7191451	2.4246261	-13.3330638
H	3.4784898	4.0334337	-13.2014940
C	1.5193380	3.8883220	-12.3044959
H	0.9475710	3.1848497	-11.6672679
H	1.6612866	4.8162815	-11.7099337

C	0.7026404	4.1952201	-13.5618442
H	1.2717382	4.8555097	-14.2542231
H	-0.2086916	4.7756372	-13.2930454
C	0.2189237	2.9627582	-14.3868391
O	6.0043552	1.7879233	-8.2311164
H	2.5370488	2.9713294	-3.7104177
H	4.1027288	7.3234714	-8.3965762
H	10.5539118	5.4405830	-7.9736935
H	9.0154536	1.1720865	-3.2788590
H	6.0746477	1.7238176	-7.2201270
H	6.1308978	2.7911433	-8.3209765
O	8.3063417	3.6624767	-6.3183748
O	4.6205456	4.1405846	-5.9918356
H	8.9809250	3.2264328	-6.8811490
H	7.7215208	4.1172886	-6.9937892
H	3.7678361	3.7287659	-6.2477187
H	5.1418882	3.3577342	-5.6438385
O	6.3072248	4.3747768	-7.9402664
H	6.0898476	5.0135798	-8.6534864
H	5.5464451	4.4288787	-7.2549460
O	6.3328028	2.1309251	-5.6600436
H	6.5276582	1.3798192	-5.0576756
H	7.2156774	2.6358415	-5.7963561

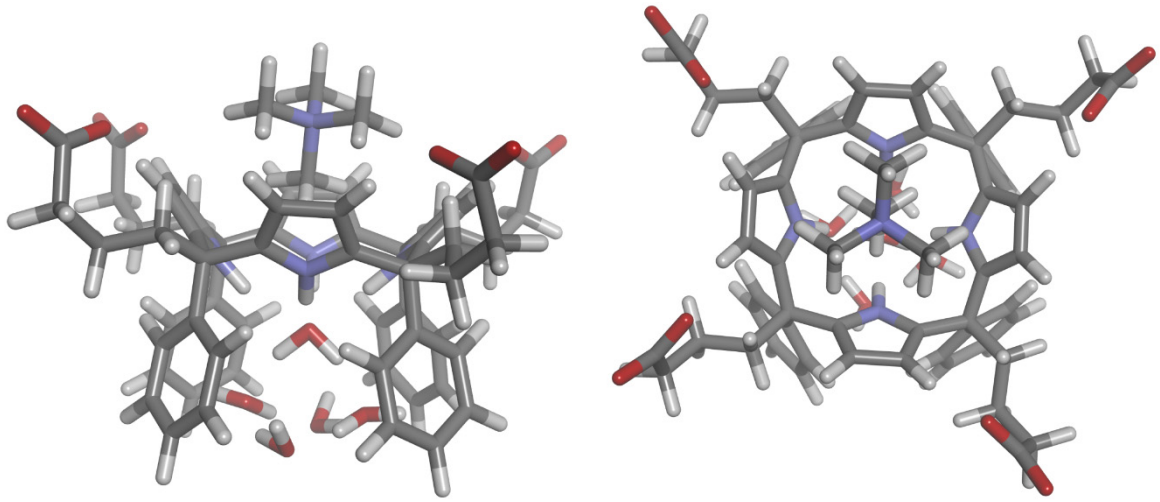

Figure S 90. Side and top views of the energy minimized structure of **G1⊂4a** in 1,3-alternate conformation at the RI-BP86-D3BJ-def2-SVP COSMO.

Cartesian coordinates of **4a@G1**. The number of atoms and calculated electronic energy are reported in the two first lines.

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Energy = -3735.925951519

C	2.6463121	2.2567056	-4.4489293
C	3.4640488	1.1188816	-4.3698258
H	4.0458251	0.9214470	-3.4565977
C	3.5365576	0.2202760	-5.4478627
H	4.1592508	-0.6807942	-5.3677202
C	2.8067813	0.4470905	-6.6306918
C	1.9101702	2.4954474	-5.6260663
H	1.2551419	3.3778334	-5.6986949
C	1.9972512	1.6012247	-6.7057484
H	1.4063787	1.7824265	-7.6166951
C	4.0988488	6.4467320	-9.0187236
C	3.1797900	5.4491604	-8.6534149
H	2.5130638	5.6056272	-7.7920679
C	3.1010633	4.2531908	-9.3880953
H	2.3646418	3.4880457	-9.1071481
C	3.9394248	4.0275747	-10.4980261
C	4.8694102	5.0296458	-10.8487485
H	5.5238884	4.8693689	-11.7189246
C	4.9486977	6.2307089	-10.1223784

H	5.6699527	7.0057290	-10.4239173
O	9.2178435	1.5706268	-15.4914568
O	11.3110573	1.3711045	-16.3211350
O	7.0132807	-6.0600590	-7.4104416
O	8.7462203	-7.4409189	-6.9599554
O	1.2889690	-4.5884576	-7.6221900
O	-0.8804929	-5.0184215	-7.1558825
O	0.4167834	1.7564441	-13.8263525
O	-0.2872196	3.1134681	-15.4904204
N	6.1893885	2.0943923	-11.1456088
H	6.1532337	2.0650647	-10.1216837
N	8.0331467	-0.0091616	-9.3079230
H	7.5125342	0.7256599	-8.7976087
N	5.2555619	-1.0355683	-7.6900036
H	5.5059240	-0.0445109	-7.7186024
N	3.4447091	1.1592957	-9.4852829
H	4.2336043	1.5187091	-8.9171866
C	5.1097298	2.3612225	-11.9688814
C	5.5597748	2.2125102	-13.2828583
H	4.9561309	2.3624902	-14.1835026
C	6.9468413	1.8543397	-13.2398367
H	7.6315856	1.7066780	-14.0898525
C	7.3178661	1.8014300	-11.8945321
C	8.6643081	1.5232832	-11.2491807
C	9.0778710	2.6327245	-10.2621913
C	8.5793095	3.9451709	-10.3703501
H	7.7950277	4.1630663	-11.1084560
C	9.0833286	4.9785331	-9.5620481
H	8.6788575	5.9971187	-9.6645814
C	10.1052100	4.7194982	-8.6348017
C	10.6077196	3.4089953	-8.5114595
H	11.4146565	3.1918578	-7.7942744
C	10.0925959	2.3778429	-9.3147126
H	10.5015594	1.3598461	-9.2285305

C	7.9770558	-0.9037298	-6.3842380
C	9.7614408	1.4541468	-12.3599151
H	9.4300860	0.7237491	-13.1243736
H	10.6794364	1.0435391	-11.8902802
C	10.1059819	2.7677403	-13.0662908
H	9.1783871	3.2417282	-13.4444945
H	10.5563614	3.4776688	-12.3399189
C	11.0596810	2.5442450	-14.2425046
H	11.9834861	2.0188538	-13.9122888
H	11.4091268	3.5232422	-14.6414795
C	10.4737860	1.7522910	-15.4525593
C	8.6288965	0.1758785	-10.5460025
C	9.1617413	-1.0540693	-10.9341734
H	9.7069907	-1.2512290	-11.8623226
C	8.8901603	-1.9916385	-9.8899982
H	9.1828762	-3.0456072	-9.8716821
C	8.1961221	-1.3185683	-8.8818681
C	7.6601192	-1.8477155	-7.5591867
C	9.1141668	-0.0712312	-6.3920626
H	9.7364243	-0.0198766	-7.2968108
C	9.4698184	0.6810402	-5.2587962
H	10.3600326	1.3275677	-5.2905540
C	8.7003192	0.6028630	-4.0862242
C	7.5616246	-0.2266237	-4.0635897
H	6.9556278	-0.3077822	-3.1480208
C	7.2015552	-0.9625176	-5.2060676
H	6.3171739	-1.6146380	-5.1820986
C	8.3819314	-3.2078211	-7.2838212
H	9.4715910	-3.0241736	-7.3914669
H	8.0857552	-3.9125131	-8.0856931
C	8.1221847	-3.8942280	-5.9411420
H	8.5214064	-3.2736343	-5.1110460
H	7.0305153	-3.9923536	-5.7772065
C	8.7496393	-5.2900288	-5.8971175

H	8.6868548	-5.7054648	-4.8660851
H	9.8379206	-5.2451124	-6.1257640
C	8.1121266	-6.3512302	-6.8470369
C	6.1634664	-2.0827706	-7.6793054
C	5.4276732	-3.2663660	-7.7737846
H	5.8604532	-4.2782602	-7.7421410
C	4.0393720	-2.9088294	-7.8250342
H	3.1717887	-3.5861956	-7.8414639
C	3.9576073	-1.5158625	-7.7664195
C	2.7494250	-0.5947375	-7.7651719
C	1.4573171	-1.4467592	-7.5541428
H	1.4326389	-2.2354666	-8.3326122
H	0.5896736	-0.7787109	-7.7348500
C	1.2943101	-2.1223076	-6.1908581
H	2.2060090	-2.7072808	-5.9557469
H	1.1939975	-1.3506001	-5.3975339
C	0.0833450	-3.0585657	-6.1655381
H	-0.8446238	-2.5149250	-6.4540224
H	-0.1031770	-3.4161820	-5.1279941
C	0.1772910	-4.3296983	-7.0665643
C	2.6248540	0.1052041	-9.1101617
C	1.7188877	-0.0984951	-10.1530286
H	0.9177509	-0.8447944	-10.1647971
C	1.9945934	0.8668968	-11.1741995
H	1.4375239	1.0333781	-12.1097526
C	3.0667457	1.6449802	-10.7316182
C	3.7617468	2.8061609	-11.4223538
C	2.8951190	3.2741098	-12.6349446
H	2.7265316	2.4019501	-13.2974561
H	3.5028885	4.0058446	-13.2064134
C	1.5362991	3.8987837	-12.3126480
H	0.9629094	3.2218425	-11.6483785
H	1.6804054	4.8484115	-11.7536429
C	0.7207419	4.1577916	-13.5818122

H	1.2886814	4.7971287	-14.2944994
H	-0.1949355	4.7414854	-13.3364723
C	0.2491443	2.8939138	-14.3662862
O	6.0114310	1.8559652	-8.1959472
H	2.5886904	2.9615817	-3.6061282
H	4.1624813	7.3829199	-8.4443856
H	10.5001422	5.5272446	-8.0010587
H	8.9772051	1.1896308	-3.1978226
N	4.9185022	-2.0131400	-11.9767038
C	4.3967212	-1.1232849	-13.0692255
C	3.7933545	-2.8282900	-11.4045229
C	5.9885448	-2.9165895	-12.5155270
C	5.5099136	-1.1640486	-10.8909787
H	5.2286495	-0.4991341	-13.4406934
H	3.0367613	-2.1282472	-11.0060918
H	4.1899485	-3.4426237	-10.5772903
H	6.3658312	-3.5440520	-11.6895116
H	6.8087387	-2.2914952	-12.9097530
H	6.3462835	-0.5844047	-11.3178707
H	5.8738527	-1.8277853	-10.0875752
H	3.6180770	-0.4687758	-12.6349418
H	3.9808958	-1.7513421	-13.8761120
H	3.3668910	-3.4609526	-12.2019699
H	5.5621100	-3.5462982	-13.3155832
H	4.7291031	-0.4896962	-10.5074139
H	6.0977105	1.7901730	-7.1856067
H	6.1314699	2.8616067	-8.2768618
O	8.3109786	3.7098665	-6.2840786
O	4.6245129	4.1708493	-5.9558703
H	8.9847385	3.2822190	-6.8541920
H	7.7232104	4.1716590	-6.9521310
H	3.7729392	3.7548497	-6.2083941
H	5.1508201	3.3912873	-5.6087463
O	6.3109611	4.4403109	-7.8989263

H 6.0988944 5.0923808 -8.6016751

H 5.5503699 4.4870296 -7.2129167

O 6.3490567 2.1654383 -5.6238570

H 6.5415651 1.4230620 -5.0097123

H 7.2287692 2.6780468 -5.7550358

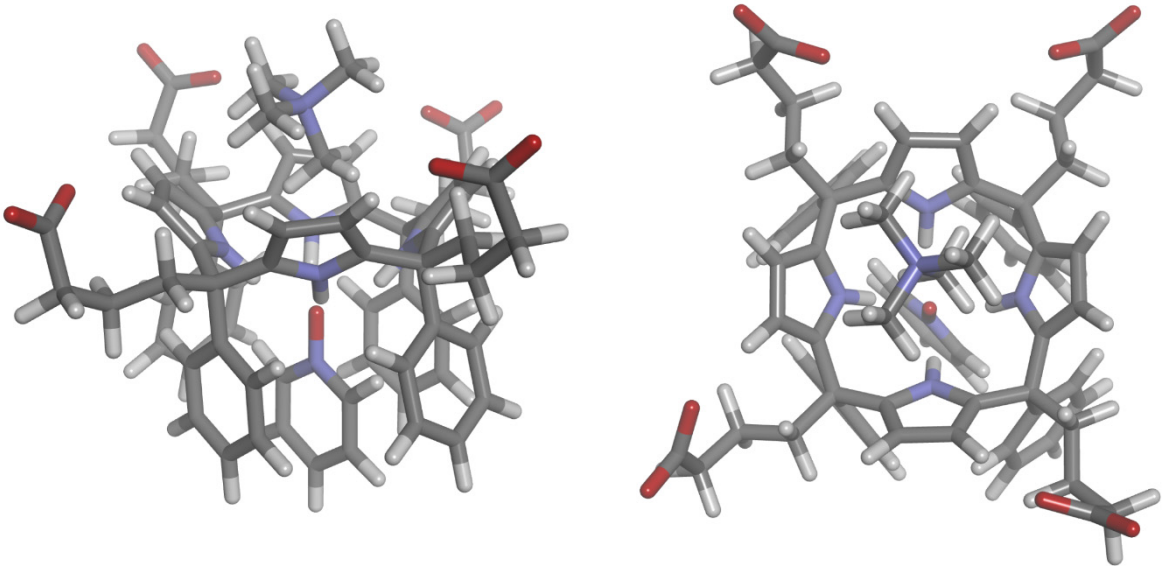

Figure S 91. Side and top views of the energy minimized structure of **G1⊂5@4a** in 1,3-alternate conformation at the RI-BP86-D3BJ-def2-SVP COSMO.

Cartesian coordinates of **G1⊂5@4a**. The number of atoms and calculated electronic energy are reported in the two first lines.

157

Energy = -3677.261761692

C 2.2825606 1.5407057 -4.5606429

C 3.0375969 0.3616457 -4.4302660

H 3.5059558 0.1097590 -3.4666375

C 3.2014869 -0.4980545 -5.5291133

H 3.7846167 -1.4236054 -5.4228203

C 2.6219770 -0.1964941 -6.7792225

C 1.6838772 1.8428187 -5.7969511

H 1.0852831 2.7596804 -5.9109153

C 1.8505816 0.9787630 -6.8924124

H 1.3739471 1.2149174 -7.8558761

C 4.6333592 5.5614364 -8.1764785

C 3.5752671 4.6494958 -8.0337422

H 2.9221555 4.6941339 -7.1492872

C	3.3511726	3.6648976	-9.0103151
H	2.5202036	2.9586613	-8.8844901
C	4.1850473	3.5617316	-10.1418754
C	5.2307101	4.4980328	-10.2844222
H	5.8786232	4.4444229	-11.1707139
C	5.4570316	5.4848239	-9.3130421
H	6.2900767	6.1927366	-9.4393657
O	9.1716468	0.9480726	-15.5092040
O	11.2276291	0.5334336	-16.3528677
O	7.4906193	-6.0740311	-6.5790743
O	9.2155202	-7.1642189	-5.6051527
O	1.7359104	-5.2949773	-8.1230723
O	-0.4306256	-5.9328365	-8.0283724
O	-0.0762676	3.5600919	-15.2164239
O	0.5088003	1.9693104	-13.7215007
N	6.3331498	1.7429313	-11.0603158
H	6.3192384	1.8021672	-10.0285264
N	8.1081172	-0.2763667	-9.2139791
H	7.5218530	0.4566313	-8.7800130
N	5.2721117	-1.3404274	-7.6670253
H	5.4474692	-0.3221988	-7.6695556
N	3.5323354	0.6802979	-9.5414012
H	4.3081853	1.0039706	-8.9373510
C	5.2442756	2.0537958	-11.8514844
C	5.6343695	1.8557915	-13.1780946
H	5.0007357	2.0094493	-14.0579288
C	7.0024576	1.4245129	-13.1751458
H	7.6465175	1.2198250	-14.0447854
C	7.4184659	1.3797629	-11.8410340
C	8.7869659	1.1123716	-11.2338589
C	9.2212366	2.2889093	-10.3313031
C	8.7729655	3.6020575	-10.5832206
H	8.0654516	3.7769809	-11.4055318
C	9.2199519	4.6808514	-9.8024022

H	8.8517189	5.6960563	-10.0141698
C	10.1293617	4.4656502	-8.7521270
C	10.5961311	3.1629165	-8.5011711
H	11.3128767	2.9809381	-7.6860110
C	10.1477850	2.0880082	-9.2869464
H	10.5193773	1.0717194	-9.0900110
C	7.8586458	-0.7027257	-6.3014110
C	9.8437001	0.9510539	-12.3706016
H	9.4725412	0.1764285	-13.0717755
H	10.7689173	0.5538400	-11.9040539
C	10.1979903	2.2048577	-13.1747585
H	9.2725509	2.6788614	-13.5573028
H	10.6931494	2.9478416	-12.5136231
C	11.1012950	1.8744296	-14.3650786
H	12.0162472	1.3331962	-14.0362298
H	11.4707705	2.8140852	-14.8350656
C	10.4372670	1.0373479	-15.5024857
C	8.7654407	-0.1778170	-10.4283391
C	9.3916246	-1.4073908	-10.6494088
H	10.0034209	-1.6671451	-11.5190727
C	9.1118938	-2.2476508	-9.5231556
H	9.4586911	-3.2749119	-9.3716939
C	8.3205269	-1.5138390	-8.6373943
C	7.7236236	-1.8826971	-7.2862063
C	8.9871463	0.1428393	-6.3497765
H	9.7499091	-0.0239180	-7.1230611
C	9.1427750	1.1984319	-5.4378711
H	10.0213035	1.8569910	-5.5131138
C	8.1747748	1.4241315	-4.4444350
C	7.0602130	0.5732336	-4.3680465
H	6.2930224	0.7355611	-3.5959815
C	6.9085989	-0.4811760	-5.2834792
H	6.0318378	-1.1372233	-5.2137598
C	8.5220878	-3.0982792	-6.7270333

H	9.5973282	-2.8194111	-6.7305478
H	8.4013708	-3.9428321	-7.4336936
C	8.1230351	-3.5920776	-5.3360322
H	8.3254993	-2.8020168	-4.5809835
H	7.0310305	-3.7836523	-5.3178067
C	8.8570512	-4.8819043	-4.9603069
H	8.6644915	-5.1368408	-3.8937596
H	9.9599924	-4.7481370	-5.0314772
C	8.4868279	-6.1467106	-5.7969280
C	6.2714580	-2.2815210	-7.4963989
C	5.6808231	-3.5424032	-7.6204282
H	6.2067989	-4.4963893	-7.4703418
C	4.2804527	-3.3391871	-7.8577580
H	3.4976854	-4.1068683	-7.9618428
C	4.0498411	-1.9604353	-7.8721629
C	2.7546326	-1.1699304	-7.9724282
C	1.5399940	-2.1478767	-7.9441601
H	1.6850303	-2.8917848	-8.7530930
H	0.6347008	-1.5568683	-8.1953043
C	1.2806762	-2.9053112	-6.6391057
H	2.2109501	-3.4047086	-6.3038260
H	0.9969854	-2.1890118	-5.8388962
C	0.1853268	-3.9618112	-6.8089571
H	-0.7536239	-3.5042108	-7.1936158
H	-0.0870621	-4.3934446	-5.8194839
C	0.5329920	-5.1640181	-7.7409353
C	2.6881159	-0.3869434	-9.2767103
C	1.7844836	-0.4560212	-10.3416554
H	0.9687025	-1.1795990	-10.4401925
C	2.0851978	0.6112799	-11.2521056
H	1.5365453	0.8983039	-12.1625011
C	3.1707975	1.3104524	-10.7208053
C	3.9249574	2.5196052	-11.2510174
C	3.0951805	3.1950050	-12.3839642

H	2.8826138	2.4307993	-13.1565952
H	3.7436759	3.9633423	-12.8554408
C	1.7678419	3.8316745	-11.9695803
H	1.1665277	3.0926013	-11.4032660
H	1.9578189	4.6848513	-11.2833997
C	0.9588258	4.2978069	-13.1825952
H	1.5514509	5.0004765	-13.8099946
H	0.0719880	4.8831979	-12.8501429
C	0.4248046	3.1713498	-14.1214512
O	5.9869014	1.3899924	-8.2245647
N	6.1110481	2.3333684	-7.3049048
C	7.1659206	3.1961569	-7.3668307
H	7.8513116	3.0368208	-8.2062965
C	7.3119793	4.1937942	-6.4085065
H	8.1718321	4.8710574	-6.4927104
C	6.3758907	4.3133318	-5.3707397
C	5.3032558	3.4118410	-5.3307791
H	4.5396450	3.4552139	-4.5433321
C	5.1842637	2.4284566	-6.3079226
H	4.3752650	1.6899438	-6.3469470
H	6.4809223	5.0959351	-4.6069907
H	2.1586131	2.2192944	-3.7029007
H	4.8202465	6.3225924	-7.4046957
H	10.4726126	5.3081057	-8.1328287
H	8.2850840	2.2619213	-3.7400755
N	5.1167553	-2.4111254	-11.9251653
C	4.5861419	-1.4508275	-12.9519489
C	3.9899692	-3.2442398	-11.3832750
C	6.1610512	-3.2941999	-12.5412475
C	5.7433216	-1.6313919	-10.8059534
H	5.4155602	-0.8044990	-13.2904958
H	3.8130075	-0.8218781	-12.4715293
H	3.5423722	-3.8205741	-12.2113848
H	3.2487872	-2.5598194	-10.9328192

H 4.3880438 -3.9134889 -10.6015968

H 6.9760193 -2.6565808 -12.9263938

H 5.7055853 -3.8756020 -13.3616555

H 6.5540773 -3.9713867 -11.7630605

H 6.5933360 -1.0589238 -11.2145273

H 4.9854408 -0.9482716 -10.3931923

H 6.0886040 -2.3355780 -10.0283360

H 4.1588868 -2.0242704 -13.7931354

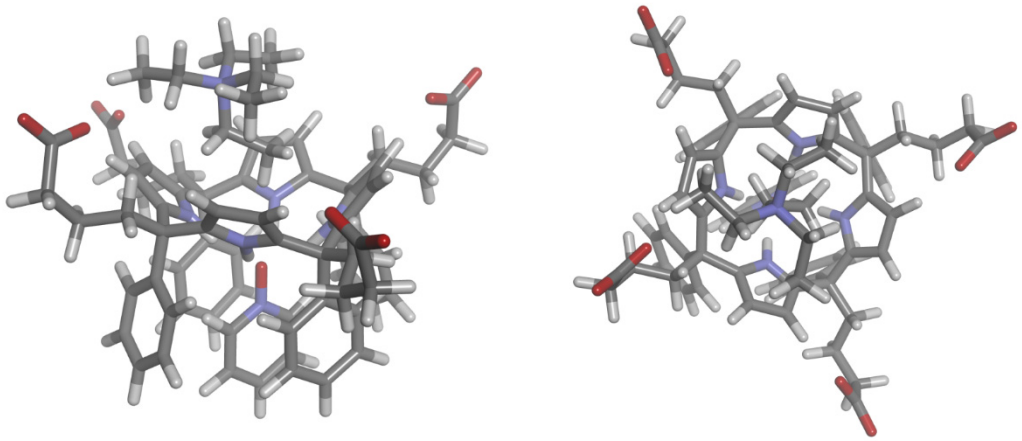

Figure S 92. Side and top views of the energy minimized structure of **G2⊂5@4a** at the RI-BP86-D3BJ-def2-SVP COSMO.

The number of atoms and calculated electronic energy are reported in the two first lines.

169

Energy = -3833.974712527

C 2.3152131 1.6698422 -4.5149073

C 3.0581220 0.4818349 -4.3979890

H 3.5154843 0.2069767 -3.4343088

C 3.2280117 -0.3594448 -5.5098605

H 3.8042125 -1.2924444 -5.4251398

C 2.6646816 -0.0303175 -6.7606571

C 1.7332380 1.9986196 -5.7528727

H 1.1446055 2.9237602 -5.8599657

C 1.9042133 1.1541095 -6.8612671

H 1.4464831 1.4048535 -7.8306157

C 4.7761536 5.7766548 -7.9889783

C 3.7260521 4.8553968 -7.8528250

H	3.0948914	4.8627742	-6.9508416
C	3.4829488	3.9023090	-8.8547907
H	2.6605233	3.1850644	-8.7377262
C	4.2882451	3.8372490	-10.0097841
C	5.3264260	4.7841170	-10.1440449
H	5.9492536	4.7567028	-11.0491919
C	5.5720920	5.7389192	-9.1467767
H	6.4035510	6.4508559	-9.2694115
O	9.3016035	0.9807049	-15.3608675
O	11.2449398	1.1684513	-16.5220190
O	7.8183716	-5.8469162	-6.9332305
O	9.3274204	-7.0570066	-5.7471701
O	1.7887449	-4.8438389	-8.6841719
O	-0.2389917	-5.8300118	-8.3830149
O	-0.4554094	4.0275173	-14.7021740
O	0.6675782	2.3927328	-13.6024297
N	6.4311545	2.1004224	-11.0173615
H	6.4302746	2.1249297	-9.9874259
N	8.1718508	-0.0518031	-9.2706332
H	7.5905763	0.6705622	-8.8145468
N	5.3472464	-1.1683642	-7.7401868
H	5.5361173	-0.1551638	-7.7725714
N	3.6307977	0.9250019	-9.4938322
H	4.4331526	1.2043373	-8.9083143
C	5.3145762	2.3846172	-11.7820639
C	5.6698751	2.1606632	-13.1147309
H	5.0099430	2.3007344	-13.9769541
C	7.0404107	1.7380301	-13.1455757
H	7.6610169	1.5001356	-14.0267471
C	7.4926002	1.7168040	-11.8244594
C	8.8614466	1.4042576	-11.2418468
C	9.3254567	2.5347027	-10.2998017
C	8.9024290	3.8663674	-10.4957489

H	8.1936614	4.0779951	-11.3079273
C	9.3705698	4.9029743	-9.6722593
H	9.0159992	5.9318442	-9.8408351
C	10.2804177	4.6305439	-8.6357010
C	10.7252906	3.3105267	-8.4426353
H	11.4417052	3.0798992	-7.6384613
C	10.2535931	2.2776242	-9.2685591
H	10.6023191	1.2449282	-9.1210634
C	7.9572571	-0.5746702	-6.3686418
C	9.9122409	1.2794032	-12.3908035
H	9.5460015	0.5288340	-13.1210200
H	10.8477659	0.8859985	-11.9385825
C	10.2374355	2.5497373	-13.1822430
H	9.2963941	3.0051733	-13.5507252
H	10.7211485	3.2998585	-12.5153625
C	11.1389514	2.2483817	-14.3855476
H	12.0673219	1.7249323	-14.0581717
H	11.4892777	3.1956159	-14.8533814
C	10.4930937	1.3803473	-15.5360810
C	8.8321308	0.0862956	-10.4791034
C	9.4524179	-1.1382594	-10.7393284
H	10.0704372	-1.3597940	-11.6148579
C	9.1574726	-2.0194118	-9.6467406
H	9.4991117	-3.0515050	-9.5195311
C	8.3645804	-1.3144528	-8.7389273
C	7.7970385	-1.7235483	-7.3846484
C	9.0931903	0.2613433	-6.4012483
H	9.8372570	0.1126716	-7.1958477
C	9.2762571	1.2757856	-5.4498531
H	10.1594978	1.9300261	-5.5178552
C	8.3298547	1.4704777	-4.4298754
C	7.2055468	0.6316068	-4.3729925
H	6.4496701	0.7717585	-3.5847771

C	7.0249335	-0.3806732	-5.3285199
H	6.1426031	-1.0314569	-5.2786361
C	8.6244403	-2.9430121	-6.8702921
H	9.6975604	-2.6584573	-6.9273184
H	8.4649224	-3.7969892	-7.5598527
C	8.3084161	-3.4566148	-5.4638576
H	8.5466373	-2.6739727	-4.7080843
H	7.2210630	-3.6592204	-5.3833701
C	9.0764588	-4.7483062	-5.1571259
H	8.9347868	-5.0414114	-4.0929384
H	10.1740213	-4.5877649	-5.2710761
C	8.6985440	-6.0053437	-6.0326784
C	6.3379464	-2.1191185	-7.5435677
C	5.7200919	-3.3728006	-7.5369516
H	6.2466227	-4.3302242	-7.3834174
C	4.3134271	-3.1555733	-7.7215245
H	3.5220036	-3.9138249	-7.8222946
C	4.1032112	-1.7797453	-7.8420002
C	2.8203647	-0.9717783	-7.9738554
C	1.5870697	-1.9281753	-8.0107115
H	1.7411492	-2.6356869	-8.8502359
H	0.6992996	-1.3057680	-8.2474925
C	1.2655593	-2.7755225	-6.7755102
H	2.1816422	-3.2692422	-6.3982139
H	0.8990163	-2.1225710	-5.9503057
C	0.2178361	-3.8495397	-7.1104674
H	-0.7134602	-3.3734307	-7.4957225
H	-0.0930311	-4.3883686	-6.1882701
C	0.6250019	-4.9556046	-8.1610953
C	2.7811566	-0.1466490	-9.2582087
C	1.8441977	-0.1418159	-10.2985990
H	1.0136306	-0.8455058	-10.4076646
C	2.1344788	0.9596279	-11.1678317

H	1.5698895	1.2899147	-12.0583814
C	3.2478056	1.6119801	-10.6367850
C	4.0047833	2.8311951	-11.1440752
C	3.1489343	3.5576948	-12.2305637
H	2.8756023	2.8244053	-13.0148888
H	3.7993296	4.3249203	-12.7031981
C	1.8497836	4.2103063	-11.7486026
H	1.2639308	3.4711966	-11.1646303
H	2.0861798	5.0497816	-11.0562152
C	0.9871560	4.7088090	-12.9148081
H	1.5827692	5.3735853	-13.5829889
H	0.1544838	5.3447033	-12.5398009
C	0.3365995	3.5977278	-13.8239179
O	6.1093982	1.5947752	-8.1926759
N	6.2305008	2.4892885	-7.2330839
C	7.2853755	3.3659396	-7.2564402
H	7.9695444	3.2478151	-8.1033571
C	7.4251260	4.3179287	-6.2580448
H	8.2851113	4.9980764	-6.3244657
C	6.4900193	4.3907777	-5.2075745
C	5.4199755	3.4777280	-5.2101647
H	4.6511208	3.4733050	-4.4258235
C	5.3010588	2.5384216	-6.2249663
H	4.4947456	1.7990224	-6.2935917
H	6.5923468	5.1405752	-4.4103963
H	2.1856647	2.3343385	-3.6453840
H	4.9828257	6.5083911	-7.1927820
H	10.6414812	5.4415035	-7.9832462
H	8.4594361	2.2805751	-3.6956858
N	4.8512073	-3.3564606	-11.9004668
C	4.3336281	-2.7207024	-13.1786058
C	3.7878604	-4.3403941	-11.3643303
C	6.1131676	-4.1470506	-12.2043005

C	5.1047504	-2.2914596	-10.8235314
H	5.1076529	-2.0045160	-13.5055833
C	2.9906687	-2.0202421	-13.0500741
H	3.3770591	-4.8454275	-12.2624869
H	2.9885599	-3.7162868	-10.9256224
C	4.2501424	-5.3499263	-10.3294686
C	7.3088983	-3.3815248	-12.7526327
H	5.7896254	-4.9419720	-12.9083372
H	6.3895379	-4.6374228	-11.2537791
C	5.7071156	-0.9828149	-11.2829841
H	4.1200508	-2.1017529	-10.3619666
H	5.7295355	-2.7811264	-10.0521002
H	4.2958079	-3.5423945	-13.9243916
H	2.7810435	-1.4908037	-13.9997742
H	2.9846934	-1.2497891	-12.2539403
H	2.1563895	-2.7203246	-12.8583850
H	3.3239363	-5.6639903	-9.7924109
H	4.8925345	-4.8904236	-9.5545345
H	4.7721721	-6.2213982	-10.7708372
H	8.0779840	-4.1297381	-13.0300496
H	7.7657477	-2.7169541	-11.9954200
H	7.0864086	-2.7867724	-13.6592228
H	5.8317154	-0.3827619	-10.3677009
H	5.0486800	-0.3931026	-11.9470200
H	6.7083569	-1.0564499	-11.7378922

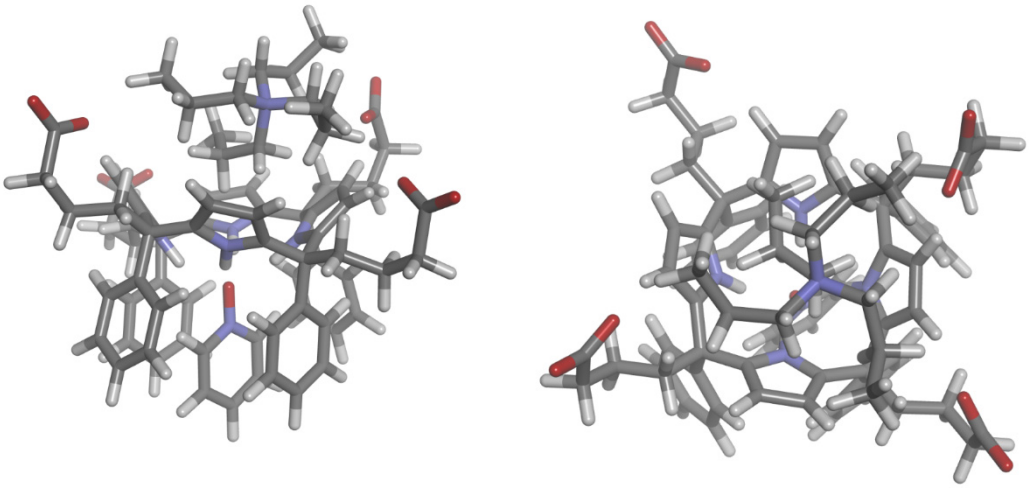

Figure S 93. Side and top views of the energy minimized structure of **G3⊂5@4a** at the RI-BP86-D3BJ-def2-SVP.

The number of atoms and calculated electronic energy are reported in the two first lines.

181

Energy = -3991.142943314

C	2.2980156	1.5288310	-4.3436683
C	2.8610266	0.2409302	-4.4060665
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C	2.9054489	-0.4566355	-5.6237619
H	3.3553236	-1.4595492	-5.6770994
C	2.3939392	0.1175440	-6.8089618
C	1.7640678	2.1010044	-5.5115023
H	1.3178494	3.1079326	-5.4821709
C	1.8113726	1.4010329	-6.7294175
H	1.4049295	1.8501280	-7.6492064
C	5.3329636	6.0764841	-7.8952207
C	4.1997518	5.2710287	-7.7038358
H	3.6076395	5.3591756	-6.7801731
C	3.8176760	4.3392109	-8.6820588
H	2.9266364	3.7133560	-8.5340082
C	4.5559784	4.1930633	-9.8728965
C	5.6939301	5.0083674	-10.0534987
H	6.2720426	4.9089283	-10.9830809
C	6.0809551	5.9375343	-9.0775211
H	6.9796589	6.5533229	-9.2380028

O	8.6984744	0.2507308	-15.2780852
O	10.5432922	0.0757316	-16.5997583
O	7.1277293	-5.8497826	-7.0740903
O	8.4868685	-7.2052509	-5.8548611
O	1.7146929	-4.4937576	-9.2850808
O	-0.3976415	-4.9486368	-9.9761849
O	-0.1695163	5.6670733	-14.2702463
O	0.4346572	3.7996467	-13.1413804
N	6.3462515	2.1538870	-10.9720230
H	6.4051480	2.2160671	-9.9464628
N	7.8353264	-0.2118298	-9.2807507
H	7.2792970	0.5576614	-8.8731103
N	5.0104037	-0.9823121	-7.8283523
H	5.2708383	0.0135757	-7.8090098
N	3.4777286	1.3063735	-9.5210835
H	4.3612792	1.3775861	-8.9985007
C	5.2501700	2.5948203	-11.6916678
C	5.4918294	2.2716713	-13.0292821
H	4.8126386	2.4792930	-13.8624909
C	6.7728594	1.6312675	-13.1085744
H	7.2930457	1.2520954	-14.0043578
C	7.2906709	1.5815205	-11.8111189
C	8.6444488	1.1259766	-11.2878049
C	9.2617546	2.2258844	-10.3932571
C	9.0099446	3.5919610	-10.6430569
H	8.3498054	3.8602521	-11.4796662
C	9.5759609	4.5914015	-9.8352633
H	9.3528296	5.6492287	-10.0450720
C	10.4128610	4.2467532	-8.7592878
C	10.6932871	2.8907384	-8.5159725
H	11.3500377	2.6018611	-7.6800509
C	10.1264798	1.8946233	-9.3277952
H	10.3459511	0.8331388	-9.1379746
C	7.6000449	-0.6136505	-6.2802156

C	9.6130897	0.8417258	-12.4765481
H	9.1467972	0.0588048	-13.1091805
H	10.5470584	0.4231969	-12.0460195
C	9.9766816	1.9947065	-13.4163767
H	9.0555812	2.5186423	-13.7391510
H	10.6011818	2.7471542	-12.8813953
C	10.7127715	1.4726631	-14.6590554
H	11.6404759	0.9292923	-14.3639247
H	11.0619094	2.3216445	-15.2881364
C	9.9044980	0.5031869	-15.6119535
C	8.5347048	-0.1576531	-10.4740965
C	9.1999734	-1.3807152	-10.6035671
H	9.8497722	-1.6652771	-11.4360865
C	8.8981830	-2.1688634	-9.4459747
H	9.2631621	-3.1757735	-9.2245186
C	8.0495349	-1.4133581	-8.6310679
C	7.3850169	-1.7431450	-7.3016866
C	8.7794498	0.1588295	-6.2915989
H	9.5111707	-0.0049298	-7.0952932
C	9.0215490	1.1245252	-5.3032058
H	9.9409450	1.7296228	-5.3483997
C	8.0899920	1.3323087	-4.2720732
C	6.9127853	0.5668996	-4.2488494
H	6.1616976	0.7289959	-3.4601219
C	6.6716454	-0.3950398	-5.2414673
H	5.7464622	-0.9862921	-5.2264591
C	8.0734841	-3.0291916	-6.7479698
H	9.1637809	-2.8189443	-6.6953945
H	7.9227619	-3.8465765	-7.4806608
C	7.5936219	-3.5802579	-5.4041031
H	7.8168263	-2.8579503	-4.5859720
H	6.4919184	-3.7006824	-5.4312625
C	8.2374609	-4.9419290	-5.1051945
H	7.9411016	-5.2940297	-4.0920979

H	9.3477054	-4.8494463	-5.0668008
C	7.9166400	-6.1189171	-6.1090213
C	5.9087520	-2.0031006	-7.5509261
C	5.2173032	-3.2084268	-7.6650386
H	5.6580001	-4.2000248	-7.4868793
C	3.8699876	-2.8997474	-8.0304593
H	3.0658554	-3.6172347	-8.2718155
C	3.7522151	-1.5056107	-8.1144334
C	2.4950476	-0.6366487	-8.1609498
C	1.2389641	-1.5459875	-8.3792348
H	1.4166562	-2.0671204	-9.3406156
H	0.3744627	-0.8704471	-8.5293068
C	0.8281130	-2.6000651	-7.3428999
H	1.7115217	-3.1397241	-6.9556356
H	0.3503377	-2.1070784	-6.4655240
C	-0.1360755	-3.6174844	-7.9808305
H	-1.0682372	-3.1207026	-8.3312814
H	-0.4584906	-4.3606165	-7.2163950
C	0.4441878	-4.4303556	-9.2032569
C	2.4616084	0.3911268	-9.2919441
C	1.4136609	0.7482726	-10.1501650
H	0.4582703	0.2253551	-10.2479549
C	1.8132248	1.8918772	-10.9100431
H	1.2365378	2.4236694	-11.6854517
C	3.1046462	2.2194505	-10.4997940
C	4.0681212	3.2768205	-11.0110908
C	3.3438620	4.1885046	-12.0570744
H	2.8417981	3.5423199	-12.8048916
H	4.1299546	4.7635871	-12.5923125
C	2.2999771	5.1605600	-11.4959212
H	1.5723675	4.5996982	-10.8734651
H	2.7995991	5.8942587	-10.8243028
C	1.5344383	5.8986542	-12.5994612
H	2.2411510	6.3541751	-13.3317666

H	0.9691515	6.7568566	-12.1720068
C	0.5035515	5.0353797	-13.4119738
O	6.0229576	1.6658797	-8.1860095
N	6.1963848	2.5063678	-7.1922916
C	7.3010988	3.3184772	-7.1824132
H	7.9809767	3.1918287	-8.0327881
C	7.4903017	4.2232738	-6.1483110
H	8.3868555	4.8569707	-6.1849137
C	6.5551496	4.3122701	-5.1009069
C	5.4321415	3.4678612	-5.1400283
H	4.6599598	3.4820380	-4.3590085
C	5.2648549	2.5723423	-6.1875198
H	4.4124934	1.8885923	-6.2881914
H	6.6972704	5.0256034	-4.2769405
H	2.2736841	2.0802994	-3.3897087
H	5.6413327	6.7961373	-7.1208814
H	10.8439429	5.0299794	-8.1153893
H	8.2704795	2.1011187	-3.5048396
N	5.5405721	-3.5764610	-11.8524225
C	4.3863611	-3.7761568	-12.8264628
C	5.5431275	-4.8038800	-10.9179347
C	6.8715511	-3.5505789	-12.5972271
C	5.3682415	-2.3224538	-10.9884880
H	4.4158837	-2.9019955	-13.4936520
C	2.9945035	-3.9754136	-12.1953631
H	5.4421766	-5.6776707	-11.5938446
H	4.6051421	-4.7139664	-10.3413619
C	6.7268235	-4.9842473	-9.9714304
C	7.2810605	-2.3571181	-13.4636673
H	6.8861212	-4.4931000	-13.1843123
H	7.6257085	-3.6372896	-11.7970505
C	5.0155579	-0.9859382	-11.6355930
H	4.6001883	-2.5837751	-10.2387057
H	6.3254969	-2.2282843	-10.4433982

H	4.6765259	-4.6600238	-13.4314395
H	2.2952681	-3.2908789	-12.7154660
H	2.9606356	-3.6489657	-11.1345539
C	2.4299369	-5.3986832	-12.2476501
H	6.3523931	-5.4923196	-9.0596099
H	7.0645930	-4.0012065	-9.5898339
C	7.9193014	-5.8176734	-10.4527403
H	8.3186386	-2.6154766	-13.7704864
H	7.4158474	-1.4649574	-12.8232658
C	6.5005550	-1.9890221	-14.7249679
H	5.1105422	-0.2879102	-10.7801094
C	3.6220289	-0.7783651	-12.2283854
H	5.7891477	-0.6431029	-12.3427587
H	1.4567215	-5.4223473	-11.7122213
H	3.0908772	-6.1183935	-11.7233231
H	2.3013872	-5.7501622	-13.2964848
H	8.5128344	-6.1110251	-9.5637988
H	8.5896898	-5.2930784	-11.1652099
H	7.5796023	-6.7565962	-10.9420034
H	7.1239557	-1.2690168	-15.3006168
H	5.5382683	-1.4883691	-14.4935843
H	6.2854956	-2.8793704	-15.3552006
H	3.4388331	0.3054592	-12.3437586
H	2.8282202	-1.1683731	-11.5643546
H	3.4952168	-1.2302950	-13.2327152

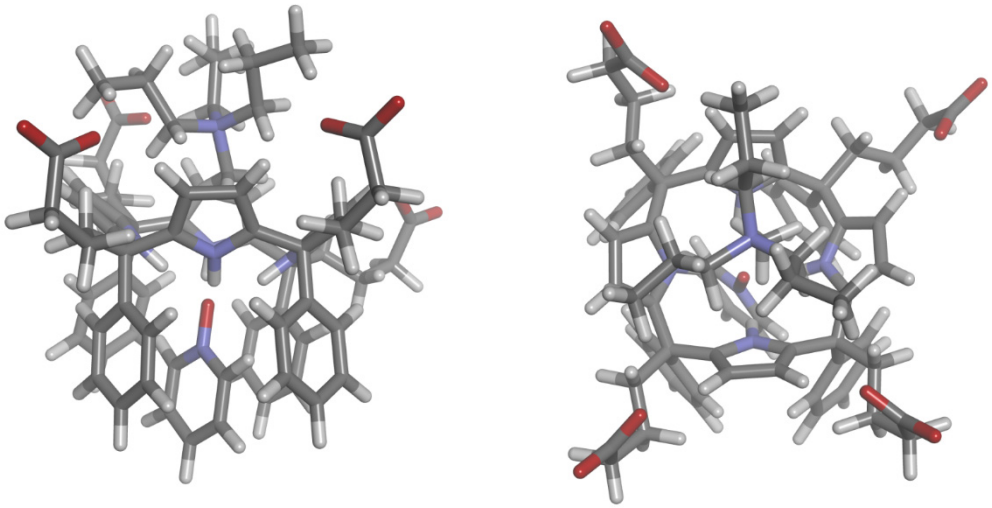

Figure S 94. Side and top views of the energy minimized structure of **G5⊂5@4a** at the RI-BP86-D3BJ-def2-SVP.

The number of atoms and calculated electronic energy are reported in the two first lines.

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Energy = -3912.569847426

C	2.6969911	2.2154453	-4.2492865
C	3.2737871	0.9333915	-4.2795817
H	3.7472284	0.5181127	-3.3758763
C	3.2578848	0.1752805	-5.4623319
H	3.7122795	-0.8246471	-5.4869111
C	2.6701236	0.6807779	-6.6422492
C	2.0862941	2.7204658	-5.4113195
H	1.6224761	3.7196377	-5.4049549
C	2.0700036	1.9578410	-6.5903652
H	1.5873943	2.3479646	-7.4993687
C	5.3550781	6.3341642	-7.6875115
C	4.2129861	5.5361299	-7.5178929
H	3.6502663	5.5656760	-6.5721599
C	3.7862866	4.6797432	-8.5458036
H	2.8918962	4.0597420	-8.4049027
C	4.4962047	4.5864163	-9.7597152
C	5.6318998	5.4092928	-9.9235962
H	6.1891925	5.3597272	-10.8694526
C	6.0593819	6.2698716	-8.9020709
H	6.9631570	6.8813204	-9.0500221

O	8.3333512	0.6408432	-15.3042995
O	9.9461557	0.6115153	-16.9091968
O	7.2099271	-5.4161569	-8.1082334
O	8.4369287	-7.0586133	-7.1282842
O	1.1208474	-3.7743953	-8.9867977
O	-0.9421449	-4.6111936	-8.5259273
O	0.5395447	3.9134797	-13.2419665
O	-0.3721196	5.7717641	-14.1652720
N	6.3361308	2.6692582	-10.9820902
H	6.4201113	2.6927250	-9.9555501
N	7.9001080	0.2399524	-9.4358467
H	7.2858836	0.9531139	-9.0083113
N	5.1203411	-0.6155298	-7.7529707
H	5.3925968	0.3706231	-7.6403460
N	3.4899020	1.7697975	-9.3473718
H	4.3471051	1.9197404	-8.7944047
C	5.1982841	3.0808850	-11.6498868
C	5.3760953	2.7547857	-12.9963586
H	4.6520963	2.9496084	-13.7943736
C	6.6608039	2.1373476	-13.1363856
H	7.1334291	1.7431635	-14.0531539
C	7.2456187	2.1004471	-11.8669828
C	8.6370324	1.6752411	-11.4237766
C	9.2826609	2.7893852	-10.5706130
C	9.0008999	4.1495472	-10.8230491
H	8.2968756	4.4004085	-11.6290635
C	9.5925780	5.1646005	-10.0545962
H	9.3472278	6.2174447	-10.2654368
C	10.4860396	4.8421558	-9.0175292
C	10.7927554	3.4924127	-8.7707859
H	11.4915101	3.2214764	-7.9632454
C	10.1980152	2.4795097	-9.5413692
H	10.4345206	1.4219331	-9.3482943
C	7.7336720	-0.4214427	-6.4112638

C	9.5331201	1.4057868	-12.6729906
H	9.0593618	0.5794380	-13.2421454
H	10.5153756	1.0461982	-12.3007834
C	9.7736888	2.5374286	-13.6767149
H	8.8215587	3.0593528	-13.8963623
H	10.4579698	3.3028307	-13.2419673
C	10.3532618	1.9817580	-14.9881697
H	11.3128231	1.4489495	-14.7904541
H	10.6212256	2.8123678	-15.6774139
C	9.4531419	0.9806507	-15.8218119
C	8.6118975	0.3828329	-10.6177446
C	9.3737165	-0.7798639	-10.7705824
H	10.0424481	-0.9980713	-11.6075339
C	9.1173704	-1.6218110	-9.6449789
H	9.5393593	-2.6123043	-9.4580886
C	8.1892150	-0.9717999	-8.8305722
C	7.5168668	-1.4379341	-7.5469495
C	8.8055746	0.4935384	-6.4360352
H	9.4643717	0.5142331	-7.3152244
C	9.0286142	1.3805954	-5.3709284
H	9.8591343	2.1013449	-5.4312855
C	8.1873166	1.3639714	-4.2478013
C	7.1200676	0.4504324	-4.2056016
H	6.4435791	0.4318920	-3.3367797
C	6.8963920	-0.4297339	-5.2739236
H	6.0548479	-1.1344653	-5.2426235
C	8.1961567	-2.7883889	-7.1609151
H	9.2813690	-2.5866157	-7.0288805
H	8.0778437	-3.4729610	-8.0254838
C	7.6673531	-3.5681807	-5.9570593
H	7.9013266	-3.0374203	-5.0049161
H	6.5633534	-3.6378519	-6.0215403
C	8.2557259	-4.9877538	-5.9403589
H	7.9191651	-5.5376233	-5.0335721

H	9.3669881	-4.9473080	-5.8604013
C	7.9299447	-5.9128883	-7.1821017
C	6.0314819	-1.6600260	-7.7997455
C	5.3173795	-2.8207619	-8.1104791
H	5.7659426	-3.8268840	-8.1766568
C	3.9357337	-2.4541839	-8.2489176
H	3.0774456	-3.1122275	-8.4686653
C	3.8355852	-1.0789007	-8.0109435
C	2.6241887	-0.1599783	-7.9352204
C	1.3136835	-1.0042494	-7.9259703
H	1.2969706	-1.6074410	-8.8562936
H	0.4638987	-0.2903180	-7.9698817
C	1.0904430	-1.9837107	-6.7699677
H	1.9995447	-2.5993198	-6.6183427
H	0.9214921	-1.4275838	-5.8188753
C	-0.0962179	-2.9143690	-7.0608061
H	-1.0283976	-2.3226734	-7.2135145
H	-0.3042351	-3.5649625	-6.1827562
C	0.0406441	-3.8656231	-8.3119437
C	2.5569304	0.7674277	-9.1407332
C	1.5877111	0.9106318	-10.1383742
H	0.7011167	0.2806793	-10.2569684
C	1.9428282	2.0364015	-10.9526738
H	1.3798141	2.4688616	-11.7962807
C	3.1280526	2.5570792	-10.4302537
C	4.0114263	3.6934898	-10.9176917
C	3.2155417	4.5894624	-11.9183541
H	2.7994717	3.9477262	-12.7211178
H	3.9424882	5.2846212	-12.3921825
C	2.0472928	5.3834483	-11.3264370
H	1.3819561	4.6889823	-10.7732019
H	2.4288698	6.1214672	-10.5846558
C	1.2250993	6.0956895	-12.4075057
H	1.8857488	6.7187499	-13.0544676

H	0.5113480	6.8132095	-11.9444758
C	0.3829286	5.1659056	-13.3593599
O	6.0956450	2.0770568	-8.1819279
N	6.4283868	2.8933721	-7.2047836
C	7.5411330	3.6863651	-7.3293670
H	8.0884706	3.5812982	-8.2728488
C	7.9038991	4.5481001	-6.3037461
H	8.8007130	5.1638676	-6.4543809
C	7.1365620	4.6152119	-5.1256968
C	6.0003928	3.7902847	-5.0282531
H	5.3553812	3.7843401	-4.1395998
C	5.6575179	2.9409539	-6.0704354
H	4.7905324	2.2702914	-6.0636056
H	7.4169504	5.2911022	-4.3057453
H	2.7183798	2.8149175	-3.3248469
H	5.7032062	6.9888351	-6.8735866
H	10.9410809	5.6385157	-8.4069820
H	8.3491230	2.0724723	-3.4205265
N	5.0466921	-1.5572740	-12.0092386
C	6.1359283	-2.4391498	-11.4001569
C	5.4091181	-1.0439605	-13.3995214
C	3.6463615	-2.1662690	-11.9054547
C	4.9939744	-0.3193351	-11.1469558
H	6.9570682	-1.7433782	-11.1446779
H	4.8490421	-0.0949904	-13.5084771
C	5.1540420	-1.9154305	-14.6235529
H	3.3368564	-1.9976003	-10.8548192
C	3.4570255	-3.6437173	-12.2309252
H	4.8960404	-0.6332043	-10.0975623
H	4.1225797	0.2882875	-11.4470050
C	6.7041990	-3.5859703	-12.2316193
H	5.7181303	-2.7996733	-10.4400831
H	6.4776903	-0.7565492	-13.3440563
H	3.0037199	-1.5245558	-12.5413346

H	5.9226719	0.2496982	-11.3050048
H	4.0800270	-2.1935495	-14.6821595
H	5.7270372	-2.8603771	-14.5657052
C	5.5691200	-1.1224655	-15.8745989
C	1.9765195	-4.0239120	-12.0809715
H	3.8198109	-3.8752035	-13.2533943
H	4.0558431	-4.2542207	-11.5252684
H	5.8974542	-4.2327664	-12.6251102
C	7.6678013	-4.4263696	-11.3793245
H	7.2488498	-3.1785299	-13.1094464
H	6.6085734	-0.7246858	-15.8004213
H	4.9032537	-0.2457819	-16.0188972
H	5.4906113	-1.7547915	-16.7826206
H	1.6238683	-3.9438625	-11.0244927
H	1.3319078	-3.3831637	-12.7206962
H	1.8202904	-5.0747548	-12.4000850
H	7.2101016	-4.8376482	-10.4534579
H	8.5332893	-3.8157667	-11.0585599
H	8.0603948	-5.2783038	-11.9715009

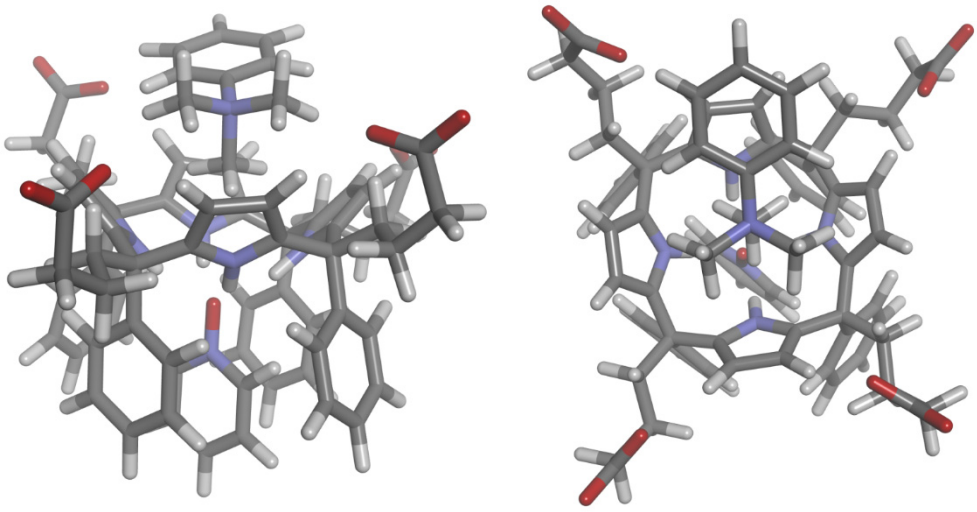

Figure S 95. Side and top views of the energy minimized structure of **G7⊂5@4a** at the RI-BP86-D3BJ-def2-SVP.

The number of atoms and calculated electronic energy are reported in the two first lines.

164

Energy = -3868.451087750

C	2.2321390	1.0087198	-3.6864428
C	2.8749519	-0.2418701	-3.6880670
H	3.3292777	-0.6320462	-2.7635068
C	2.9439260	-1.0022667	-4.8668283
H	3.4393520	-1.9831969	-4.8678929
C	2.3792537	-0.5296321	-6.0709814
C	1.6453870	1.4807504	-4.8742973
H	1.1312844	2.4548958	-4.8899198
C	1.7162354	0.7163807	-6.0502377
H	1.2522664	1.0811220	-6.9790304
C	4.7957103	5.1955492	-7.0736397
C	3.6667106	4.3667427	-6.9816593
H	3.0371238	4.3860186	-6.0788264
C	3.3410261	3.4911138	-8.0297905
H	2.4572013	2.8459311	-7.9475348
C	4.1426865	3.4087055	-9.1867781
C	5.2593371	4.2676643	-9.2771603
H	5.8803943	4.2293919	-10.1829074
C	5.5864965	5.1464450	-8.2344040
H	6.4786717	5.7858372	-8.3231849
O	8.8528567	0.2550830	-14.6865900
O	10.7748002	0.2939178	-15.9047487
O	7.2366388	-6.6441217	-6.8559302
O	8.5509588	-8.0295266	-5.6328267
O	1.0274475	-5.1204996	-8.2322898
O	-0.9991124	-6.0226235	-7.7530094
O	0.5276458	2.2982838	-12.9114066
O	-0.5221158	4.0235037	-13.9434154
N	6.1619978	1.5743682	-10.2877467
H	6.1706438	1.5473426	-9.2569586
N	7.7723835	-0.7789821	-8.6883258
H	7.2155420	-0.0548346	-8.2025789
N	4.9072314	-1.7735590	-7.1198526
H	5.1534211	-0.7759166	-7.0335867

N	3.2630105	0.5685357	-8.7515698
H	4.0849646	0.7686783	-8.1596885
C	5.0561235	1.9614622	-11.0254609
C	5.3747841	1.7678518	-12.3710287
H	4.7098126	1.9698613	-13.2159089
C	6.7147330	1.2663608	-12.4397831
H	7.3041083	1.0231843	-13.3371546
C	7.1858819	1.1581047	-11.1302582
C	8.5408127	0.7246960	-10.5980171
C	9.1056756	1.7764730	-9.6224701
C	8.7867029	3.1434810	-9.7641608
H	8.0906380	3.4400881	-10.5610397
C	9.3388282	4.1070376	-8.9049437
H	9.0653805	5.1664064	-9.0299582
C	10.2278796	3.7230337	-7.8860098
C	10.5685842	2.3658471	-7.7468592
H	11.2664189	2.0488634	-6.9558078
C	10.0153692	1.4061929	-8.6094681
H	10.2839576	0.3444477	-8.5050949
C	7.5346653	-1.4380801	-5.7900612
C	9.5534049	0.5641475	-11.7755794
H	9.1258386	-0.1552960	-12.5036802
H	10.4758823	0.1130035	-11.3524242
C	9.9340336	1.8159349	-12.5712115
H	9.0158846	2.3420502	-12.9009273
H	10.4938911	2.5267618	-11.9212045
C	10.7714386	1.4568557	-13.8065860
H	11.6948056	0.9094203	-13.5061263
H	11.1341032	2.3813697	-14.3088021
C	10.0674629	0.5827901	-14.9158902
C	8.4336913	-0.6225975	-9.8955587
C	9.0152060	-1.8583756	-10.1975596
H	9.6275946	-2.0721281	-11.0790054
C	8.7058664	-2.7608876	-9.1278437

H	9.0098613	-3.8084283	-9.0391295
C	7.9358262	-2.0623077	-8.1967802
C	7.3230410	-2.5104436	-6.8762303
C	8.6820637	-0.6178064	-5.7960200
H	9.4034699	-0.7213632	-6.6177596
C	8.9045204	0.3294816	-4.7852289
H	9.7947255	0.9758995	-4.8351644
C	7.9877893	0.4695753	-3.7305749
C	6.8530830	-0.3569786	-3.6989614
H	6.1183185	-0.2578407	-2.8849939
C	6.6341100	-1.3026595	-4.7121120
H	5.7444099	-1.9435216	-4.6801789
C	8.0585022	-3.8101268	-6.4272332
H	9.1455189	-3.5776739	-6.3958575
H	7.9032198	-4.5954812	-7.1958617
C	7.6265585	-4.4325381	-5.0987067
H	7.8303109	-3.7312253	-4.2575677
H	6.5304883	-4.6030478	-5.1174106
C	8.3326276	-5.7730155	-4.8585527
H	8.0940800	-6.1632237	-3.8443626
H	9.4395380	-5.6379980	-4.8665207
C	8.0010101	-6.9255557	-5.8831412
C	5.8448561	-2.7944017	-7.0984416
C	5.1661809	-3.9892224	-7.3546866
H	5.6341779	-4.9869256	-7.3468104
C	3.7743415	-3.6672719	-7.5245277
H	2.9340713	-4.3603757	-7.7122069
C	3.6372515	-2.2836692	-7.3633764
C	2.4069421	-1.3862380	-7.3527675
C	1.1124856	-2.2569928	-7.3749848
H	1.1580482	-2.9224740	-8.2618569
H	0.2553145	-1.5646261	-7.5123470
C	0.8376730	-3.1598041	-6.1683066
H	1.7444131	-3.7510226	-5.9281174

H	0.6124226	-2.5410308	-5.2696699
C	-0.3188656	-4.1271868	-6.4558554
H	-1.2378245	-3.5625063	-6.7391065
H	-0.5938979	-4.6897376	-5.5365306
C	-0.0672915	-5.1966189	-7.5896791
C	2.3740854	-0.4798206	-8.5769477
C	1.4808308	-0.4285502	-9.6527052
H	0.6293840	-1.1002563	-9.8006774
C	1.8431991	0.6786658	-10.4891270
H	1.3224017	1.0531493	-11.3884424
C	2.9534946	1.2863394	-9.8985916
C	3.7850294	2.4741642	-10.3588919
C	2.9797997	3.2925149	-11.4161927
H	2.6824482	2.6105548	-12.2380004
H	3.6712647	4.0506242	-11.8437620
C	1.7018297	3.9758358	-10.9230381
H	1.0745593	3.2333160	-10.3882592
H	1.9572531	4.7700571	-10.1851807
C	0.8864090	4.5633379	-12.0824329
H	1.5194084	5.2454313	-12.6966370
H	0.0611637	5.2018940	-11.6960672
C	0.2329123	3.5226745	-13.0708065
O	5.8281101	0.9483532	-7.4875218
N	6.0492467	1.7974148	-6.5016690
C	7.1579179	2.6052924	-6.5374687
H	7.7989286	2.4778878	-7.4158695
C	7.3993585	3.5068276	-5.5120465
H	8.2983524	4.1328931	-5.5899376
C	6.5118957	3.6004267	-4.4220311
C	5.3834160	2.7591135	-4.4137929
H	4.6472867	2.7750938	-3.5988478
C	5.1652518	1.8672326	-5.4538230
H	4.3111068	1.1835244	-5.5147006
H	6.6942494	4.3111035	-3.6036823

H	2.1833688	1.6089500	-2.7637041
H	5.0668844	5.8621537	-6.2405515
H	10.6540502	4.4767906	-7.2048237
H	8.1471937	1.2292712	-2.9499500
N	4.7621811	-2.5718362	-11.3077430
C	5.7877899	-3.6210438	-10.9666161
C	4.8878289	-2.0737763	-12.7225311
C	3.4005866	-3.1410836	-11.0008238
C	4.9936402	-1.3686308	-10.4272354
H	6.7973086	-3.1805972	-11.0146766
C	3.7409110	-1.6470119	-13.4090154
H	3.4258378	-3.5428616	-9.9713541
H	4.9043389	-1.6839391	-9.3765759
H	4.2370651	-0.6109590	-10.6889200
H	5.6015549	-3.9385996	-9.9229484
C	6.1665519	-1.8682773	-13.2634643
H	2.6536225	-2.3302948	-11.0295831
H	6.0006298	-0.9788305	-10.6446139
H	5.6817692	-4.4665464	-11.6689996
H	3.1706189	-3.9358270	-11.7309930
H	2.7409997	-1.7323867	-12.9686573
C	3.8856573	-1.0426143	-14.6677103
C	6.3071244	-1.2588514	-14.5209913
H	2.9851244	-0.6848341	-15.1890217
C	5.1604107	-0.8550774	-15.2230245
H	5.2704353	-0.3459558	-16.1927792
H	7.0722620	-2.1147055	-12.6935311
H	7.3212528	-0.9973018	-14.8872464

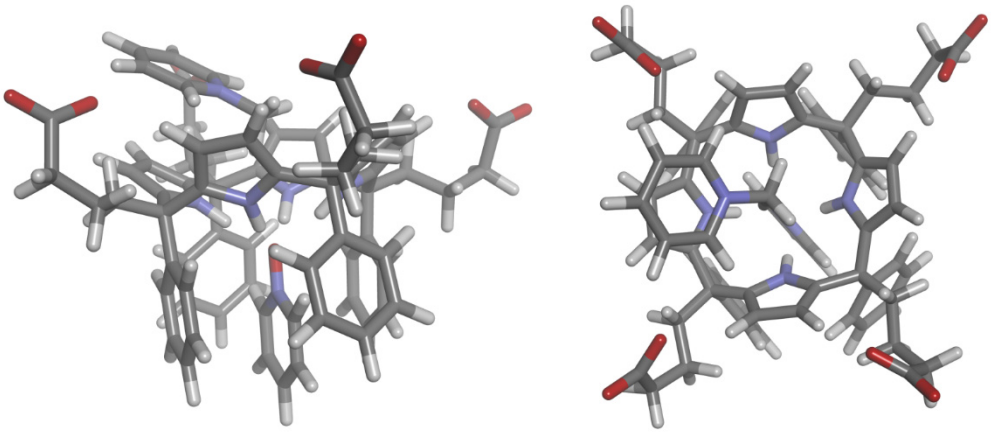

Figure S 96. Side and top views of the energy minimized structure of **G8⊂5@4a** at the RI-BP86-D3BJ-def2-SVP.

The number of atoms and calculated electronic energy are reported in the two first lines.

155

Energy = -3750.598326463

C	2.3447035	1.9511451	-4.2913660
C	3.0297494	0.7277451	-4.1928314
H	3.5124698	0.4379355	-3.2466580
C	3.1137812	-0.1298313	-5.3023228
H	3.6506868	-1.0845449	-5.2251489
C	2.5152571	0.2134428	-6.5335535
C	1.7335017	2.2993113	-5.5092796
H	1.1888690	3.2523770	-5.6033881
C	1.8144802	1.4360215	-6.6136105
H	1.3226775	1.6970926	-7.5635216
C	4.8150474	5.9051559	-8.0078390
C	3.7729274	4.9976763	-7.7632589
H	3.2142298	5.0342742	-6.8155901
C	3.4430902	4.0217747	-8.7179133
H	2.6237979	3.3196333	-8.5201133
C	4.1546657	3.9152443	-9.9288341
C	5.1937096	4.8415307	-10.1660290
H	5.7521943	4.7801578	-11.1109642
C	5.5213869	5.8241476	-9.2207210
H	6.3482297	6.5218619	-9.4265977

O	8.8518024	-0.3497075	-14.7338565
O	10.5355700	-0.2669594	-16.2585517
O	7.7316906	-5.5089857	-8.1379173
O	8.9546972	-7.1831811	-7.2054844
O	1.1711288	-4.7132581	-7.9609725
O	-0.8528924	-5.4799298	-7.2920686
O	0.2995772	2.7545071	-13.3795260
O	-0.6193665	4.4812285	-14.5244719
N	6.1712595	2.0710498	-10.8927684
H	6.2006266	2.1937844	-9.8694286
N	7.8512042	-0.0637655	-9.0904911
H	7.1874435	0.6359710	-8.7127436
N	5.0489270	-1.0630056	-7.5014602
H	5.2637238	-0.0577431	-7.4436395
N	3.3505643	1.0424125	-9.3306296
H	4.1780761	1.2934390	-8.7693444
C	5.0340249	2.3050170	-11.6420177
C	5.3164833	1.8925900	-12.9466935
H	4.6201935	1.9415318	-13.7901670
C	6.6688050	1.4159191	-12.9732451
H	7.2316359	1.0151333	-13.8301583
C	7.1862357	1.5479410	-11.6791719
C	8.5830150	1.3193326	-11.1221730
C	9.0590605	2.5529954	-10.3294006
C	8.6763476	3.8564896	-10.7110209
H	7.9959967	3.9775654	-11.5658339
C	9.1413809	4.9795272	-10.0078947
H	8.8197816	5.9858276	-10.3188603
C	10.0056923	4.8235939	-8.9098761
C	10.4104540	3.5309250	-8.5327369
H	11.0857439	3.3902214	-7.6738569
C	9.9430484	2.4103740	-9.2377451
H	10.2561900	1.3962593	-8.9456512
C	7.5625073	-0.6785609	-6.0446308

C	9.5982548	1.0527524	-12.2746899
H	9.2805743	0.1165833	-12.7770761
H	10.5862115	0.8696899	-11.8017849
C	9.7712397	2.0739341	-13.4006953
H	8.7825801	2.4247746	-13.7557000
H	10.3089018	2.9800416	-13.0363605
C	10.5332939	1.4318482	-14.5742641
H	11.5524019	1.1249907	-14.2422845
H	10.7051118	2.1747414	-15.3831354
C	9.9061619	0.1509247	-15.2635063
C	8.6249327	0.0871530	-10.2323078
C	9.4514209	-1.0347887	-10.3132034
H	10.1692551	-1.2424532	-11.1101123
C	9.1688646	-1.8672369	-9.1913039
H	9.6179233	-2.8393149	-8.9762753
C	8.1687628	-1.2469631	-8.4390988
C	7.4768890	-1.7277157	-7.1683140
C	8.4832202	0.3883254	-6.0768862
H	9.1433000	0.4971538	-6.9483243
C	8.5502063	1.3212321	-5.0289649
H	9.2565304	2.1631958	-5.0976010
C	7.7052752	1.1976549	-3.9156103
C	6.7974007	0.1256659	-3.8601245
H	6.1273459	0.0137715	-2.9931745
C	6.7257663	-0.7972065	-4.9128010
H	6.0059671	-1.6278850	-4.8768139
C	8.2598675	-3.0127591	-6.7599323
H	9.3074649	-2.7052311	-6.5533035
H	8.2632532	-3.6602542	-7.6602013
C	7.7666828	-3.9436571	-5.6524365
H	7.9536713	-3.5148870	-4.6401002
H	6.6713095	-4.0834050	-5.7336051
C	8.4671274	-5.3108928	-5.7965735
H	8.1038189	-6.0180594	-5.0193310

H	9.5584210	-5.2003693	-5.5984305
C	8.3670920	-6.0812935	-7.1828463
C	6.0147689	-2.0570464	-7.4486481
C	5.3560392	-3.2753615	-7.6534625
H	5.8608304	-4.2525492	-7.6902487
C	3.9579779	-2.9970322	-7.8200334
H	3.1377195	-3.7229761	-7.9499372
C	3.7917796	-1.6129197	-7.7119926
C	2.5351561	-0.7567111	-7.7346338
C	1.2693286	-1.6657295	-7.6199768
H	1.3033877	-2.4194520	-8.4331585
H	0.3867661	-1.0164821	-7.7999063
C	1.0674766	-2.4183697	-6.3009535
H	1.9834376	-2.9948692	-6.0575265
H	0.9101053	-1.6920196	-5.4721601
C	-0.1150168	-3.3914263	-6.3754958
H	-1.0332698	-2.8671154	-6.7291431
H	-0.3695019	-3.7734019	-5.3616554
C	0.0929754	-4.6480016	-7.2985377
C	2.4384485	0.0437065	-9.0261148
C	1.4439451	0.0975344	-10.0068322
H	0.5715646	-0.5608163	-10.0625582
C	1.7567245	1.1681173	-10.9075297
H	1.1738814	1.5164794	-11.7765292
C	2.9415080	1.7476336	-10.4534053
C	3.7722281	2.8881898	-11.0163292
C	2.9619245	3.6409895	-12.1193908
H	2.5862250	2.9033940	-12.8566647
H	3.6690823	4.3132845	-12.6525665
C	1.7580895	4.4498665	-11.6248607
H	1.1070064	3.7925254	-11.0128718
H	2.1080833	5.2682650	-10.9559686
C	0.9307036	5.0268819	-12.7792931
H	1.5816729	5.6024350	-13.4782286

H	0.1915903	5.7663713	-12.3972866
C	0.1265987	3.9827353	-13.6403393
O	5.8728451	1.6764878	-8.0689352
N	6.1000445	2.5840775	-7.1408947
C	7.1142832	3.4927607	-7.3111721
H	7.6765046	3.3984116	-8.2461072
C	7.3647248	4.4507253	-6.3391039
H	8.1850113	5.1567136	-6.5256368
C	6.5804050	4.5037969	-5.1708335
C	5.5451722	3.5596099	-5.0280622
H	4.8919104	3.5352143	-4.1457668
C	5.3154573	2.6137105	-6.0163280
H	4.5347825	1.8458524	-5.9678616
H	6.7712091	5.2577235	-4.3942649
H	2.2851682	2.6284768	-3.4240194
H	5.0871459	6.6580710	-7.2520597
H	10.3609488	5.7045293	-8.3515060
H	7.7426802	1.9407134	-3.1033950
N	6.2972699	-2.1646114	-11.3773954
C	7.0012342	-1.8762968	-12.5049422
C	8.0394492	-2.7021706	-12.9287882
C	6.6051697	-3.2527010	-10.6215475
C	5.2339732	-1.2495423	-10.9122614
C	8.3582137	-3.8371330	-12.1608934
C	7.6397268	-4.1138053	-10.9845380
H	4.9083606	-0.5982628	-11.7413305
H	4.3870785	-1.8319368	-10.5064733
H	5.6464104	-0.6242631	-10.1033252
H	6.7398743	-0.9482998	-13.0316490
H	8.5777277	-2.3606313	-13.8327644
H	6.0200117	-3.3829715	-9.6980815
H	9.1881061	-4.4935261	-12.4658320
H	7.8573221	-4.9421569	-10.2802400

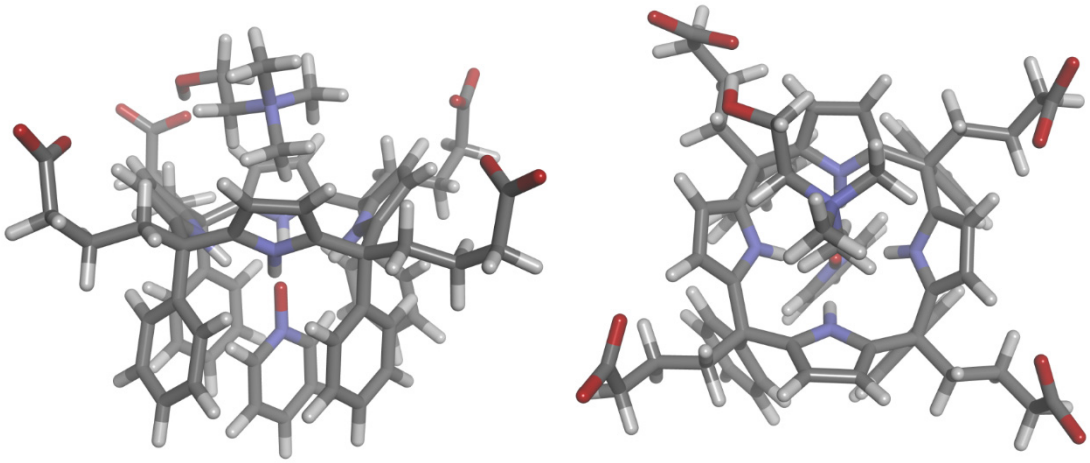

Figure S 97. Side and top views of the energy minimized structure of **G9⊂5@4a** at the RI-BP86-D3BJ-def2-SVP COSMO.

The number of atoms and calculated electronic energy are reported in the two first lines.

161

Energy = -3791.738623142

C	2.4097827	1.5119420	-4.4047420
C	3.1620465	0.3273685	-4.3154737
H	3.6500669	0.0533228	-3.3678137
C	3.2931729	-0.5124024	-5.4337001
H	3.8684411	-1.4457493	-5.3580846
C	2.6862519	-0.1825883	-6.6629908
C	1.7845573	1.8425746	-5.6204619
H	1.1902203	2.7654407	-5.7026258
C	1.9221370	1.0004964	-6.7369313
H	1.4289503	1.2605235	-7.6856116
C	4.5357952	5.5520868	-8.1635946
C	3.4470386	4.6688319	-8.0765109
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H 6.5763163 -1.1237491 -11.4942937

H 5.1804487 -1.0536618 -10.3475170

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