

Supplementary material**Modulation and Binding Properties of Extended Glycoluril Molecular Clips**Prasad Polavarapu,^a Helena Melander,^a Vratislav Langer,^b Adolf Gogoll,^{a*} Helena Grennberg^{a,*}

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1. NMR Titrations of clip 1.

(a) Clip 1 with H₂O.

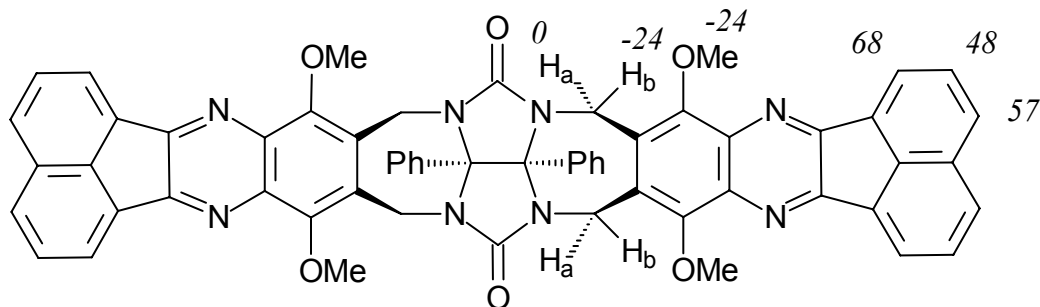


Figure S1: Temperature dependent ¹H NMR chemical shift changes $\Delta\delta$ (ppb) for clip 1 in the presence of water. Numbers correspond to the chemical shift difference $\Delta\delta$ in ppb when the temperature was varied from 25 °C to -55 °C. ($\Delta\delta = \delta_{-55\text{ °C}} - \delta_{25\text{ °C}}$).

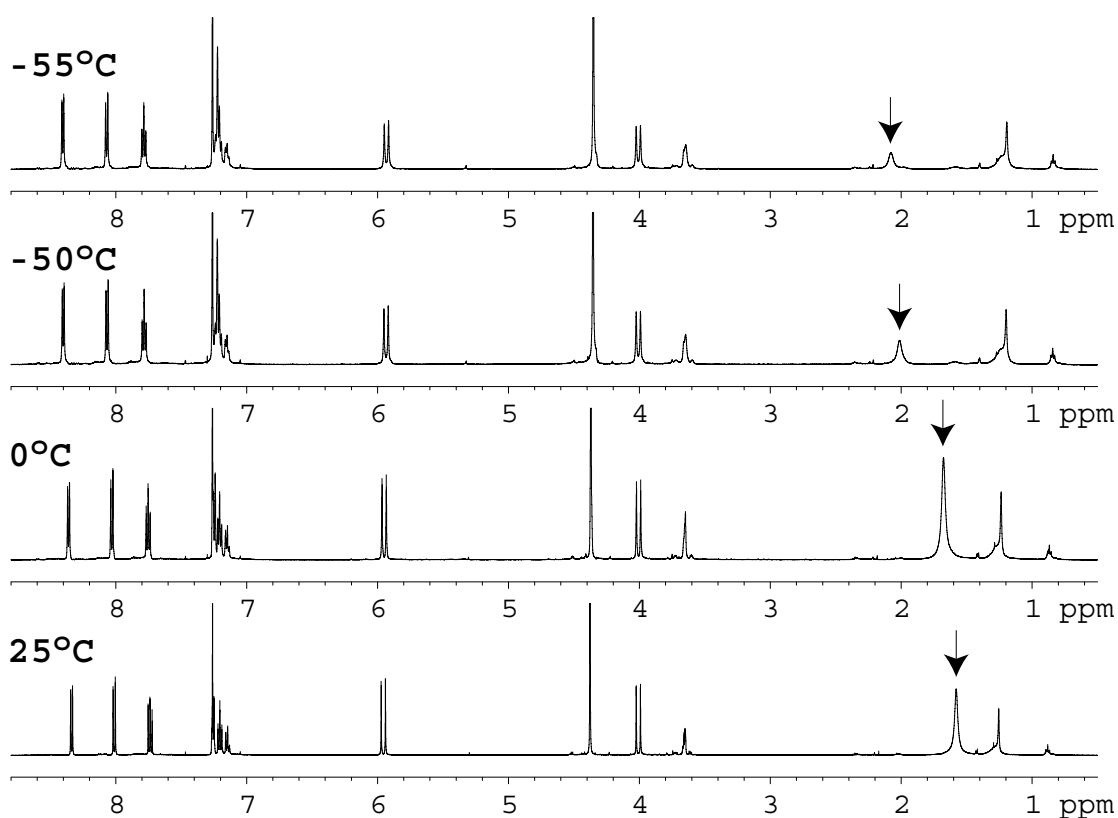


Figure S2: ¹H NMR spectra of clip 1 in the presence of water (500 MHz, CDCl₃ solution) recorded at the indicated temperatures. The arrow indicates the position of the water signal.

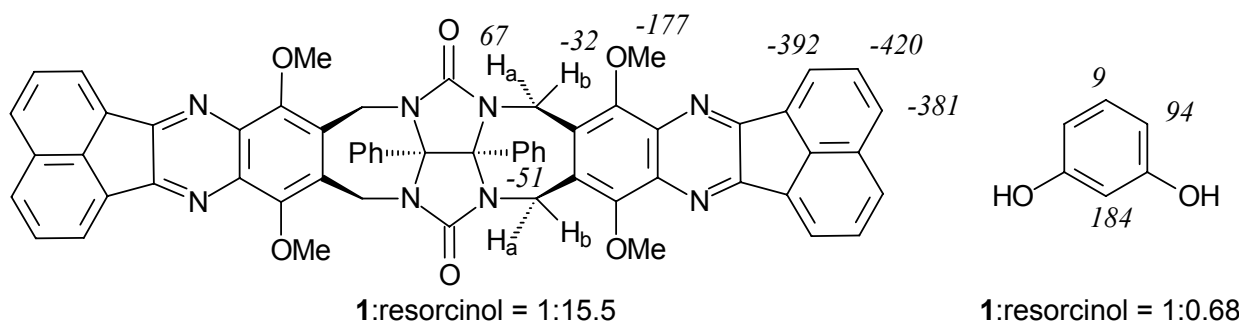
(b) Clip 1 with resorcinol.

Figure S3: ^1H NMR chemical shift changes $\Delta\delta$ (ppb) for clip 1 and resorcinol. Values for clip 1 correspond to a clip:resorcinol ratio of 1:15.5. Values for resorcinol correspond to a clip>resorcinol ratio of 1:0.68. $\Delta\delta = \delta_{(1+\text{resorcinol})} - \delta_1$ (or $\delta_{(\text{resorcinol})}$).

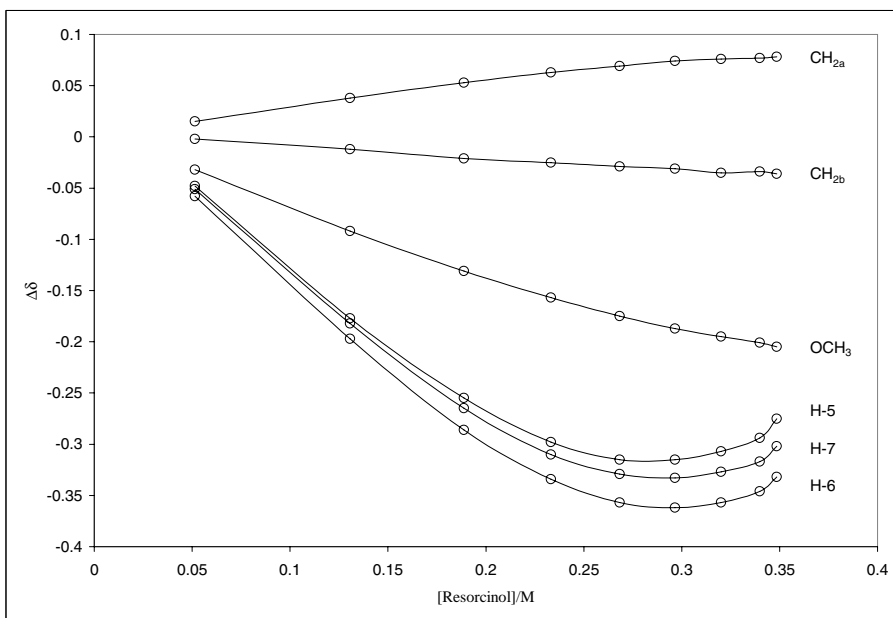


Figure S4: Chemical shift changes vs. resorcinol concentration for selected protons of clip 1 (CDCl_3 solution, 500 MHz, 25°C). $[\text{clip } 1] = 0.082 \text{ M}$.

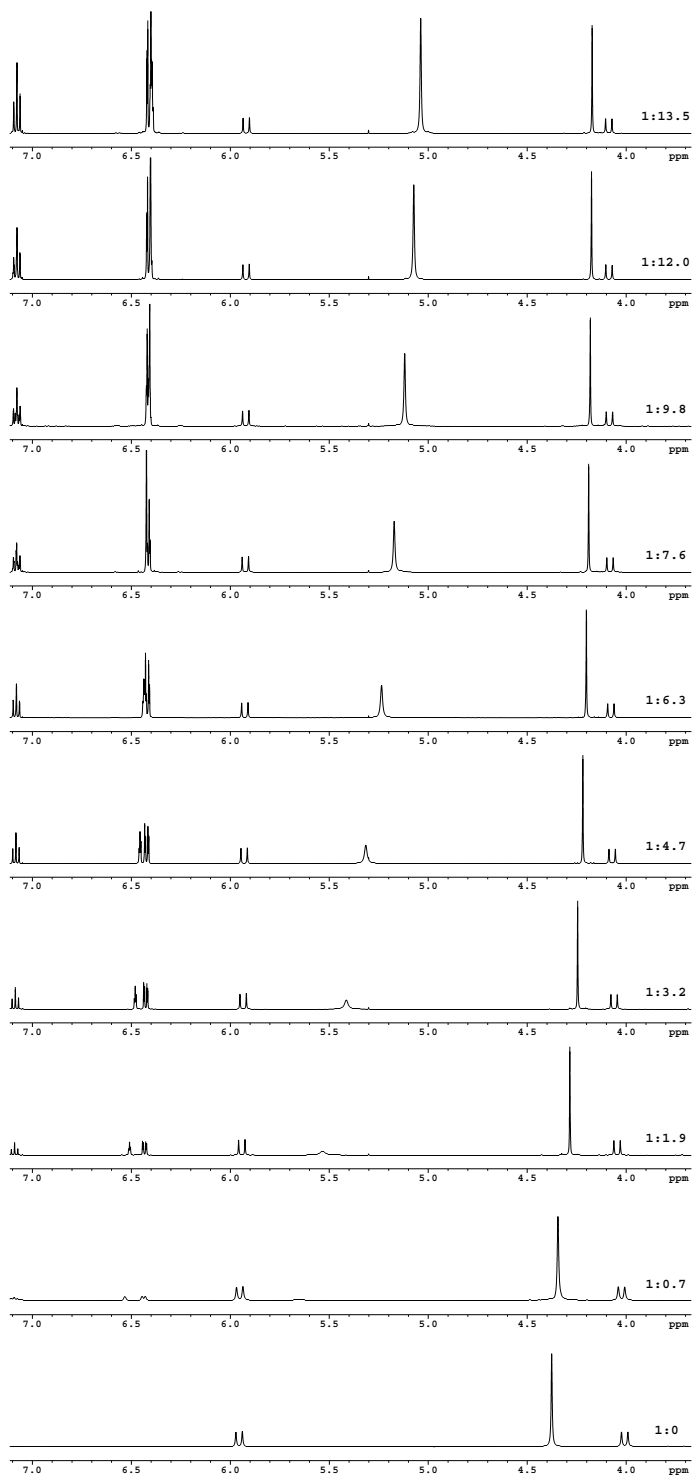


Figure S5: Expansions of ^1H NMR spectra showing resorcinol and aliphatic clip proton signals observed upon titration of a solution of clip **1** with resorcinol (CDCl_3 solution, 500 MHz, 25°C). Molecular ratios of clip **1**:resorcinol are indicated.

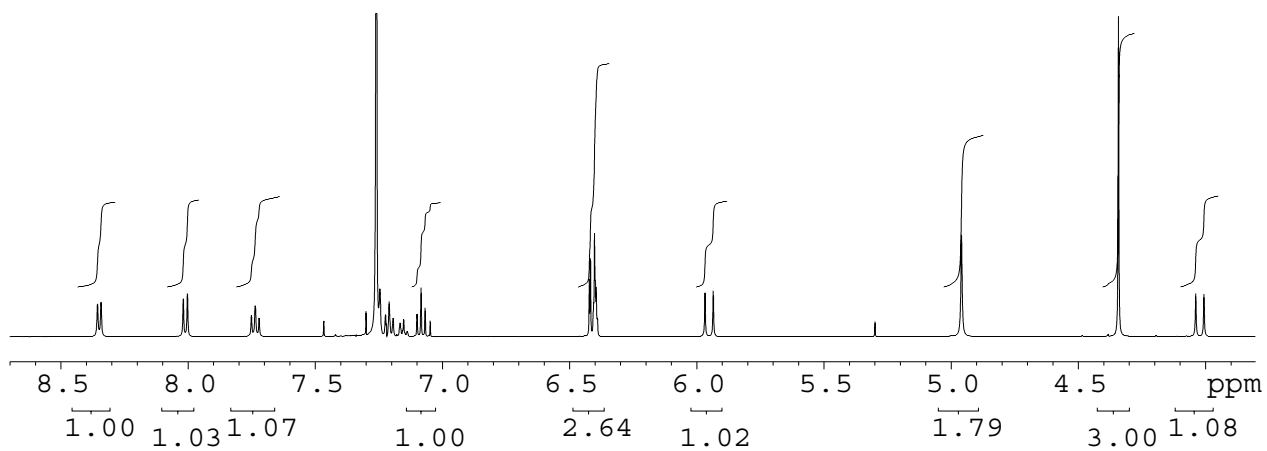
Clip 1 – resorcinol precipitate

Figure S6: ¹H NMR spectrum of collected precipitate obtained from a solution of clip **1** + excess of resorcinol (500 MHz, CDCl₃ solution).

(c) Clip 1 with AgClO₄.

Table S1: ¹H NMR chemical shift changes for clip **1** upon addition of AgClO₄. $\Delta\delta = \delta_{(1+Ag^+)} - \delta_1$. Solvent CDCl₃:CD₃OD 9:1.

1:Ag ⁺		H _{2a}	H _{2b}	H ₅	H ₆	H ₇	CH ₃	Ph
1:0	δ	3.952	5.840	8.251	7.644	7.927	4.244	7.114
1:0.2	δ	3.954	5.839	8.231	7.630	7.913	4.241	7.120
	Δδ	0.002	0.001	-0.020	-0.014	-0.014	0.003	0.006
1:0.6	δ	3.958	5.835	8.192	7.601	7.885	4.234	7.121
	Δδ	0.006	-0.010	-0.060	-0.043	-0.042	-0.01	0.007
1:0.8	δ	3.959	5.835	8.175	7.589	7.873	4.231	7.122
	Δδ	0.007	-0.010	-0.080	-0.055	-0.054	-0.013	0.008
1:1	δ	3.973	5.830	8.1(br)	7.52(br)	7.82(br)	4.213	7.13
	Δδ	0.021	-0.010	-0.150	-0.124	-0.107	-0.031	0.016
1:1.2	δ	3.995	5.816	small and broad peaks			4.177(br)	7.15(br)
	Δδ	0.043	-0.020				-0.067	0.036
1:2	δ	4.018(br)	5.755	No peaks			4.076	7.2
	Δδ	0.066	-0.090				-0.168	0.086
1:3	δ	-	5.730				4.037	7.21
	Δδ		-0.110				-0.207	0.096
1:4.4	δ	4.120	5.735				4.010	7.22
	Δδ	0.168	-0.110				-0.234	0.106
1:7	δ	Very small and broad signals						
1:11	δ	All signals corresponding to 1 disappear						

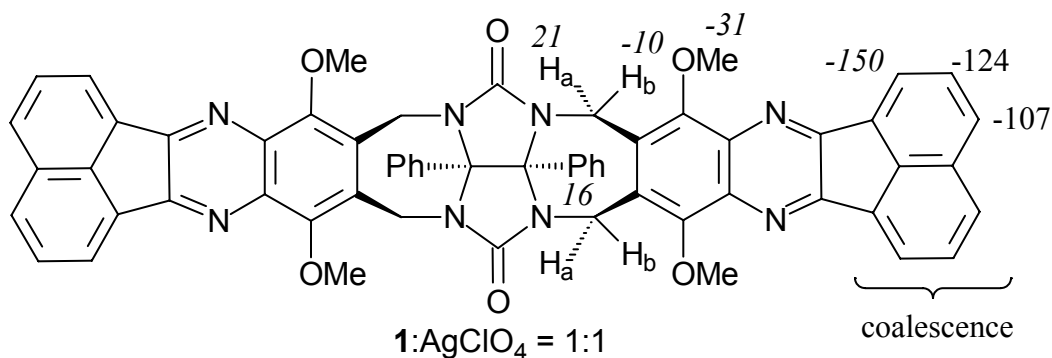


Figure S7: ¹H NMR chemical shift changes $\Delta\delta$ (in ppb) for clip **1** for clip:Ag⁺ ratio of 1:1.

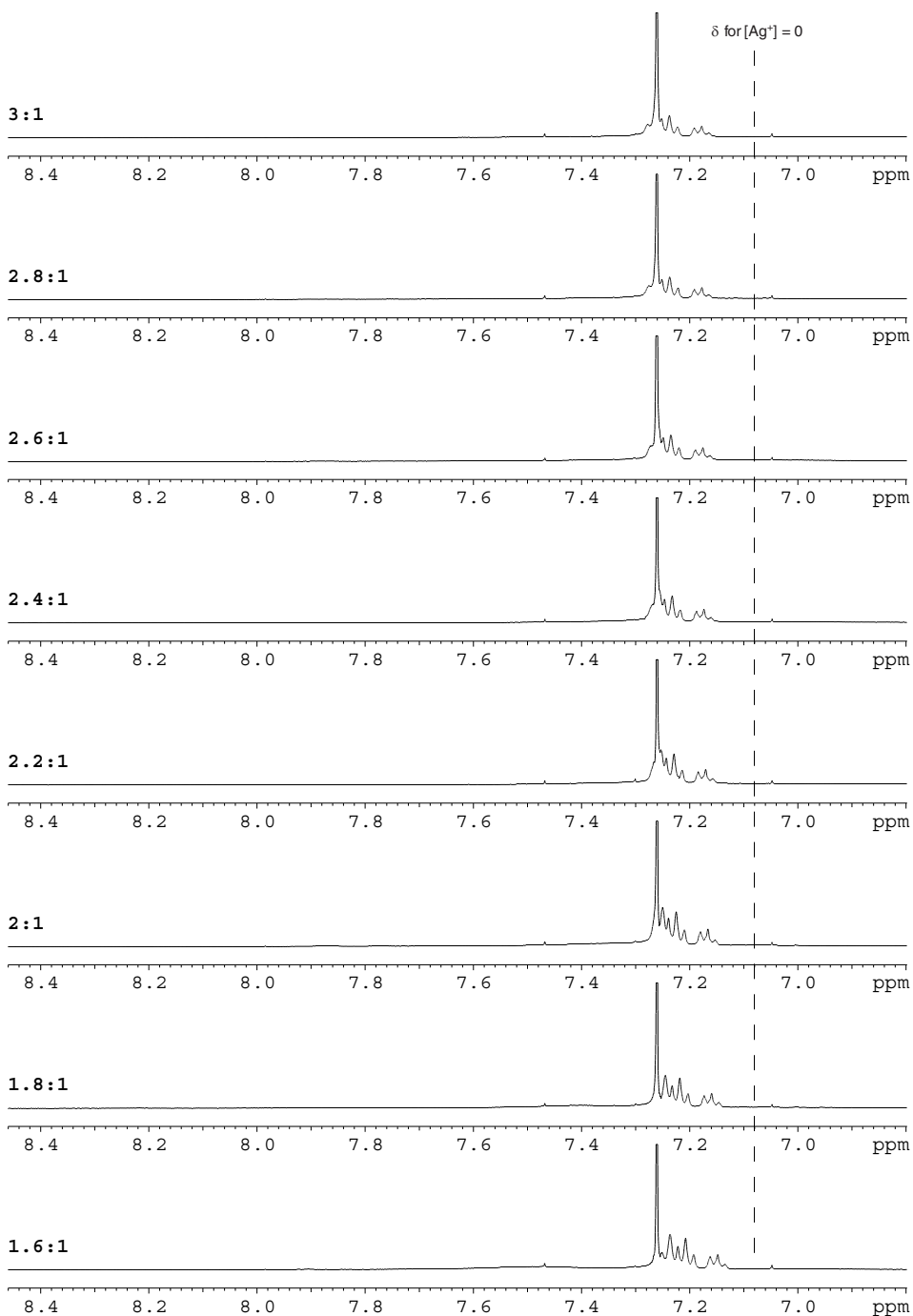


Figure S8: Expansion of aromatic region of ^1H NMR spectra with various $\text{Ag}^+:\text{clip 1}$ ratios (500 MHz, solvent $\text{CDCl}_3:\text{MeOH-d}_4$ 9:1) (continued from **Error! Reference source not found.**). Aliquots of AgClO_4 solution added to clip 1, ratios indicated on left hand side of spectra. The dashed line indicates the δ of *para*-Ph protons in the absence of Ag^+ (continued overleaf).

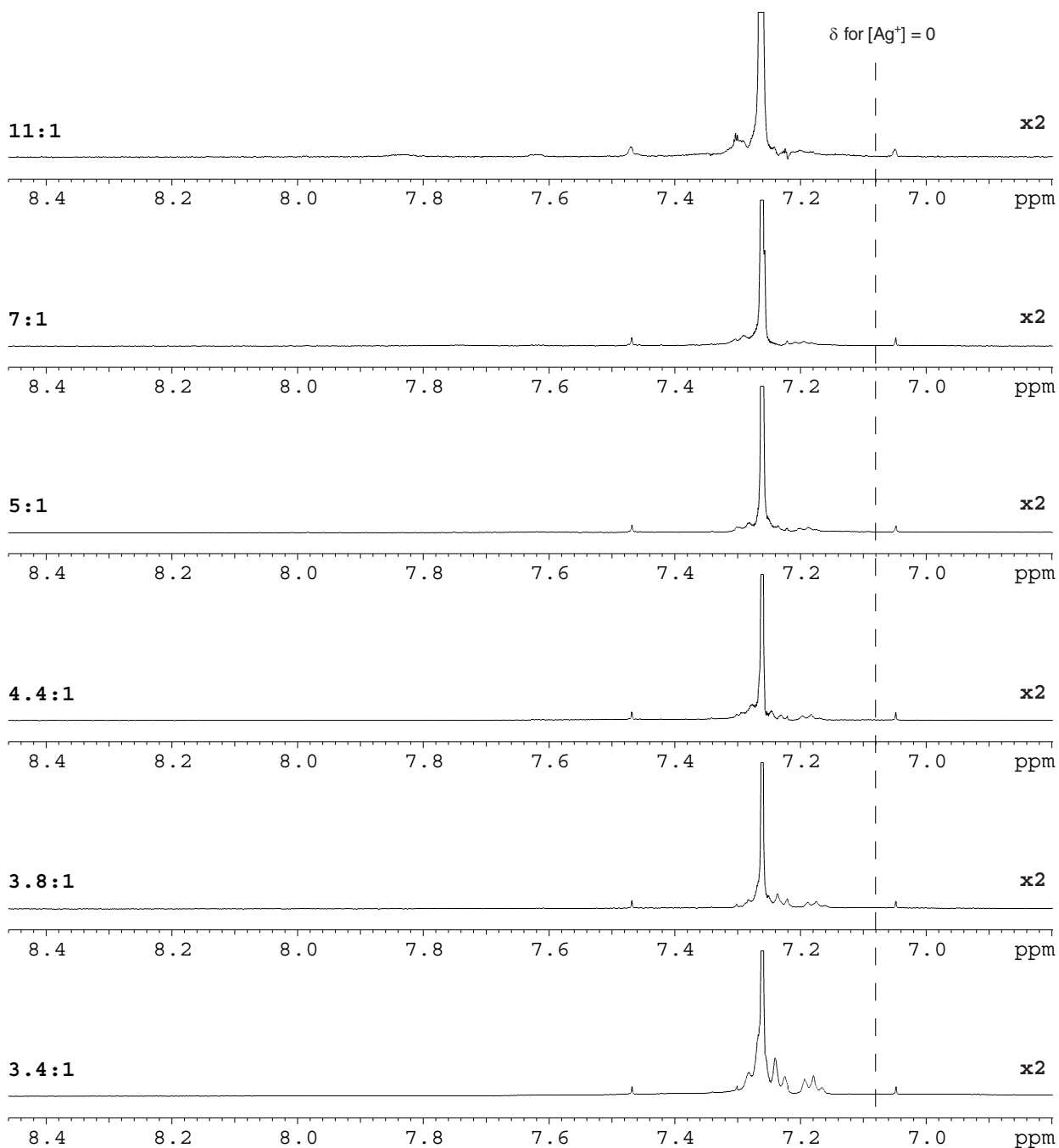


Figure S9: Expansion of aromatic region of ^1H NMR spectra with various Ag^+ : clip **1** ratios (500 MHz, solvent $\text{CDCl}_3:\text{MeOH}-d_4$ 9:1) (continued from previous Figure). Aliquots of AgClO_4 solution added to clip **1**, ratios indicated on left hand side of spectra. The vertical scale was increased two times compared to Figures for lower Ag^+ : clip **1** ratios.

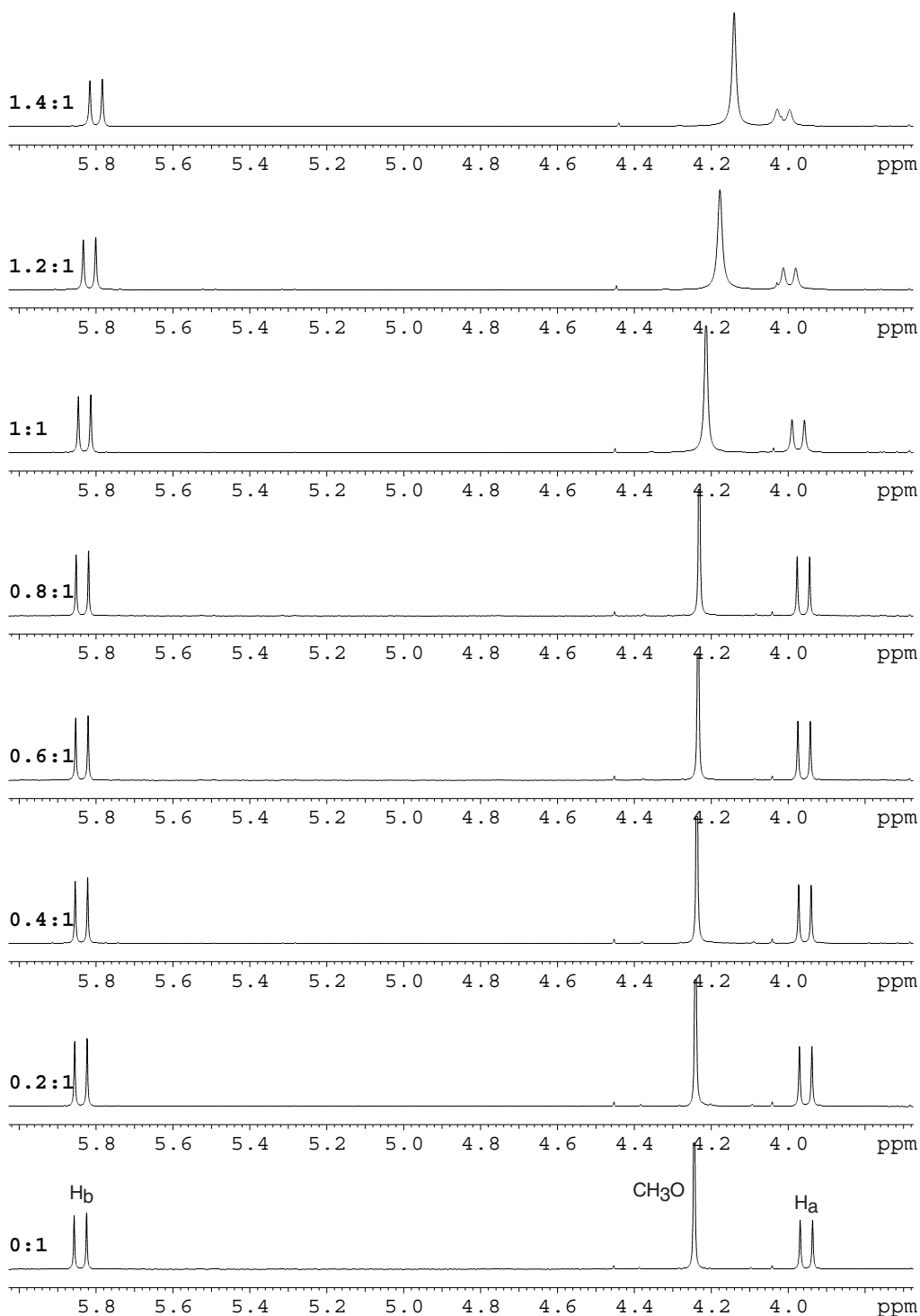


Figure S10: Expansion of aliphatic region of ^1H NMR spectra with various Ag^+ : clip **1** ratios (500 MHz, solvent CDCl_3 : MeOH-d_4 9:1). Aliquots of AgClO_4 solution added to clip **1**, ratios indicated on left hand side of spectra. Observe the change of chemical shift as well as broadening of the CH_2 proton oriented towards the outside of the cleft and the methoxy protons starting to change beyond the 1:1 ratio (continued overleaf).

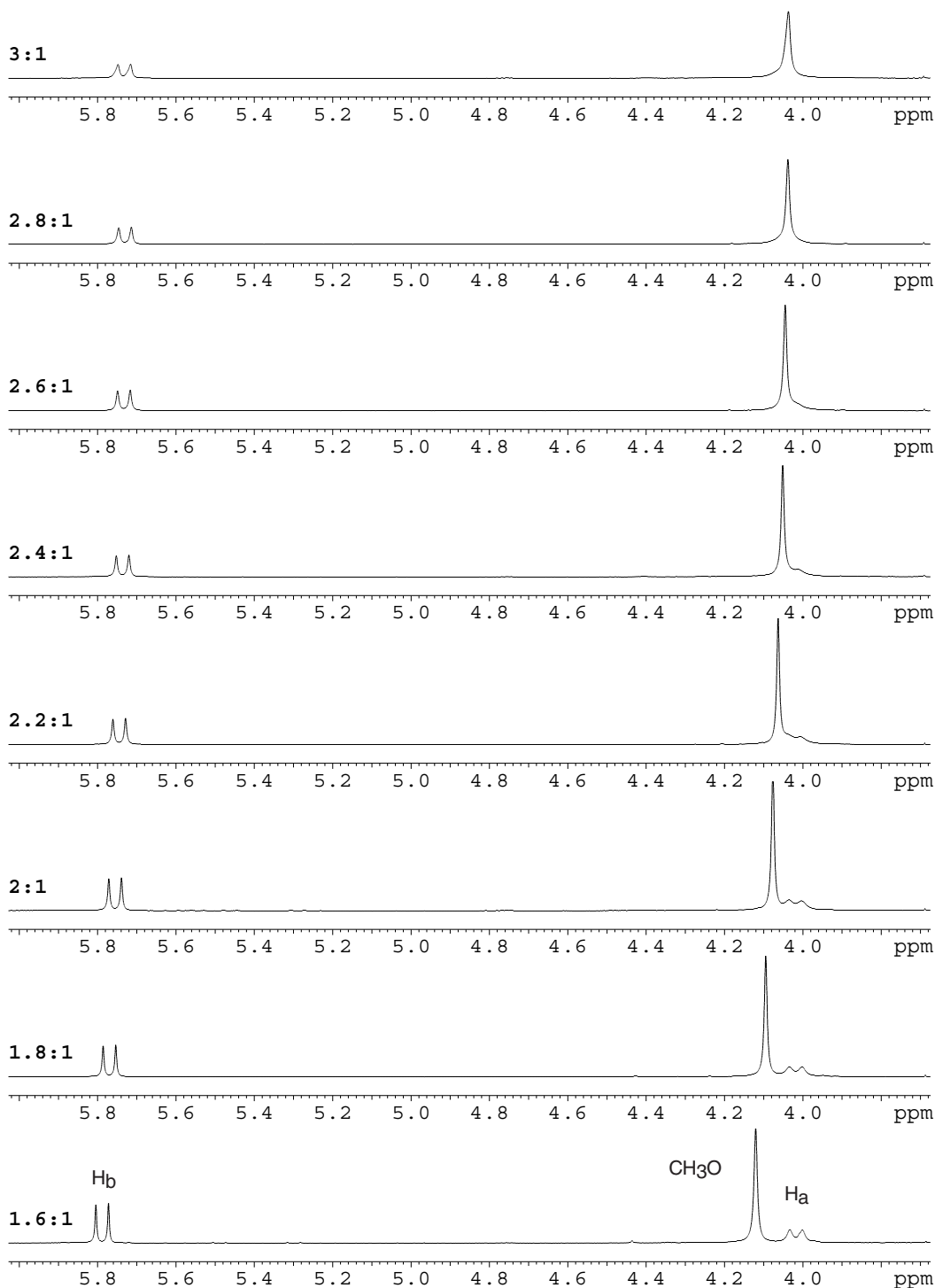


Figure S11: Expansion of the aliphatic region of ^1H NMR spectra with variable Ag^+ : clip **1** ratios (500 MHz, solvent CDCl_3 : MeOH-d_4 9:1) (continued from previous Figure). Aliquots of AgClO_4 solution added to clip **1**, ratios indicated on left hand side of spectra. Observe the change of chemical shift as well as broadening of the CH_2 proton oriented outside of the cleft (H_a) and the methoxy protons starting to change beyond the 1:1 ratio (continued overleaf).

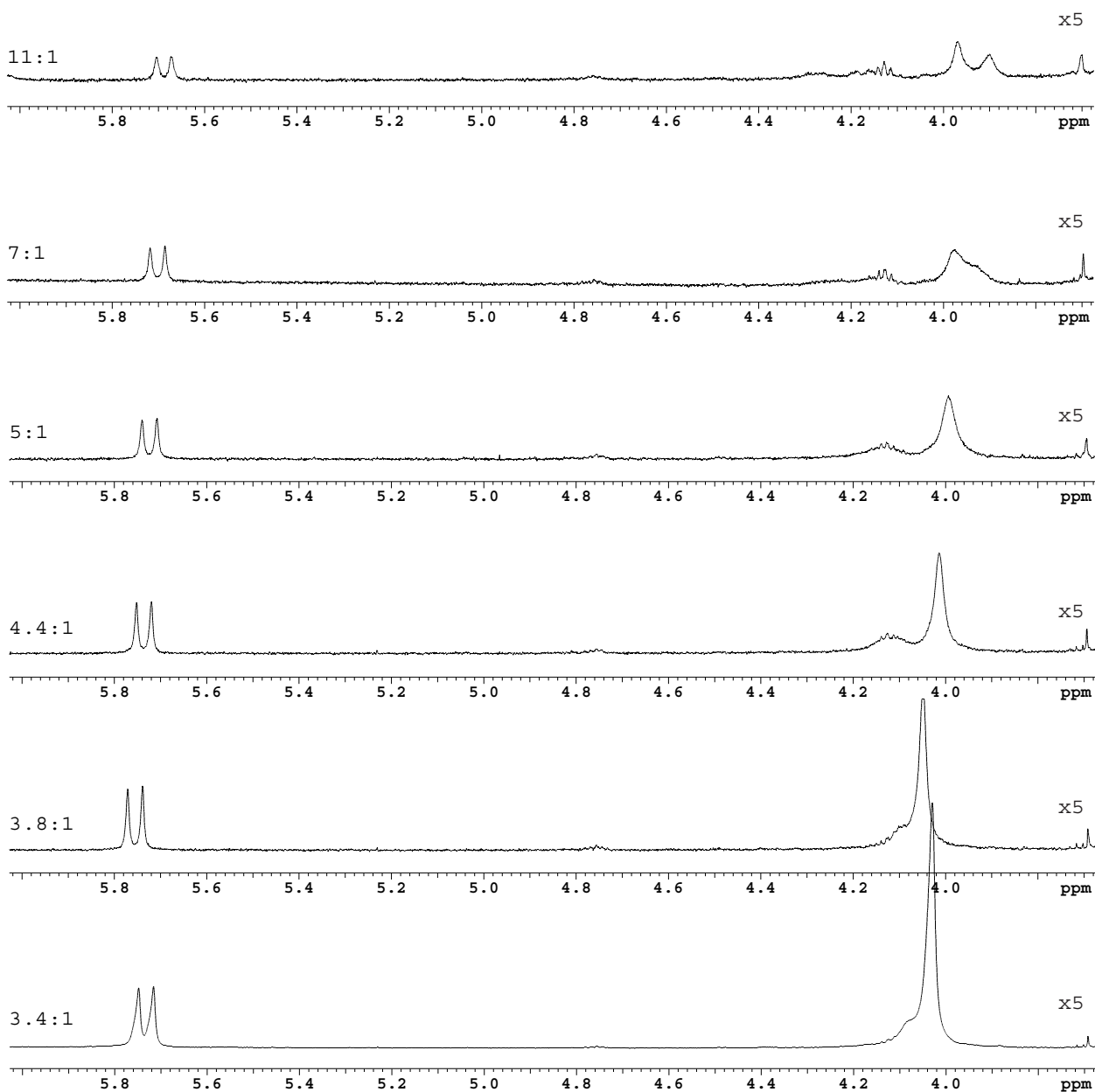
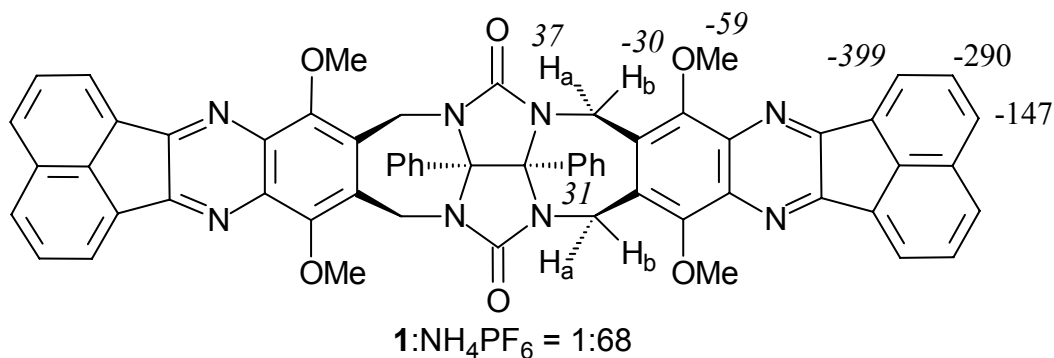


Figure S12: Expansion of the aliphatic region of ^1H NMR spectra with variable Ag^+ : clip 1 ratios (500 MHz, solvent $\text{CDCl}_3:\text{MeOH-d}_4$ 9:1) (continued from previous Figure). Aliquots of AgClO_4 solution added to clip 1, ratios indicated on left hand side of spectra.

(d) Clip 1 with NH₄PF₆Figure S13: ¹H NMR chemical shift changes $\Delta\delta$ (in ppb) for clip **1** for clip:NH₄⁺ ratio of 1:68.Table S2: ¹H NMR chemical shift changes for clip **1** upon addition of NH₄PF₆. $\Delta\delta = \delta_{(1+\Delta g^+)} - \delta_1$. Solvent CDCl₃:CD₃OD 7:3.

1:NH ₄ ⁺		H ₅	H ₆	H ₇	Ph
1:0	δ	8.141	7.540	7.831	7.059
1:1.1	δ	8.106	7.513	7.818	7.062
	$\Delta\delta$	-0.035	-0.027	-0.013	0.003
1:2.3	δ	8.062	7.481	7.801	7.065
	$\Delta\delta$	-0.079	-0.059	-0.030	0.006
1:3.4	δ	8.016	7.446	7.783	7.069
	$\Delta\delta$	-0.125	-0.094	-0.048	0.010
1:5.1	δ	7.991	7.427	7.774	7.070
	$\Delta\delta$	-0.150	-0.113	-0.057	0.011
1:6.8	δ	7.960	7.404	7.762	7.073
	$\Delta\delta$	-0.181	-0.136	-0.069	0.014
1:8.5	δ	7.922	7.377	7.748	7.075
	$\Delta\delta$	-0.219	-0.163	-0.083	0.016
1:10.8	δ	7.901	7.361	7.741	7.077
	$\Delta\delta$	-0.240	-0.179	-0.090	0.018
1:13.7	δ	7.879	7.346	7.732	7.078
	$\Delta\delta$	-0.262	-0.194	-0.099	0.019
1:17.1	δ	7.853	7.326	7.722	7.081
	$\Delta\delta$	-0.288	-0.214	-0.109	0.022
1:22.8	δ	7.810	7.295	7.707	7.084
	$\Delta\delta$	-0.331	-0.245	-0.124	0.025
1:28.5	δ	7.798	7.286	7.702	7.085
	$\Delta\delta$	-0.343	-0.254	-0.129	0.026
1:34.2	δ	7.778	7.272	7.695	7.086
	$\Delta\delta$	-0.363	-0.268	-0.136	0.027
1:39.9	δ	7.766	7.260	7.691	7.088
	$\Delta\delta$	-0.375	-0.280	-0.140	0.029
1:51.3	δ	7.753	7.260	7.686	7.089
	$\Delta\delta$	-0.388	-0.280	-0.145	0.030
1:68.3	δ	7.742	7.250	7.684	7.090
	$\Delta\delta$	-0.399	-0.290	-0.147	0.031

