

## Supporting information

### A Repertoire of Cross-talk from the First to the Sixth Nucleotide Residue in Single Stranded Hexameric-RNA by Tandem Electrostatic Nearest-neighbour Interactions

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**Table S1.** The dimerization and oligomerization shift estimated from  $^1\text{H}$  chemical shift at the neutral (N) state at 298 K for aromatic protons of compounds **2a**, **3a** and **4 – 8** using appropriate monomeric reference compounds (**1a**, **1f** or **1g**)<sup>†,‡,‡</sup>.

Compounds	$\Delta\delta_{\text{N}(\underline{\text{M}}-\underline{\text{O}})}^{\text{a}}$					
GpA ( <b>2a</b> )	0.104 <b>Gp</b> <sup>†</sup>	- (H8) - (H2) <b>pA</b>	-	-	-	-
GpC ( <b>3a</b> )	-0.029 <b>Gp</b> <sup>†</sup>	-	-	-	-	0.396 (H5) 0.113 (H6) <b>pC</b> <sup>‡</sup>
GpApA ( <b>4</b> )	0.107 <b>Gp</b> <sup>†</sup>	0.259 (H8) 0.151 (H2) <b>pAp</b> <sup>‡</sup>	(H8) (H2) <b>pA</b>	-	-	-
GpApC ( <b>5</b> )	0.052 <b>Gp</b> <sup>†</sup>	0.215 (H8) 0.121 (H2) <b>pAp</b> <sup>‡</sup>	-	-	-	0.442 (H5) 0.266 (H6) <b>pC</b> <sup>‡</sup>
GpA <sup>1</sup> pA <sup>2</sup> pC ( <b>6</b> )	0.088 <b>Gp</b> <sup>†</sup>	0.258 (H8) 0.196 (H2) <b>pA</b> <sup>1</sup> <b>p</b> <sup>‡</sup>	0.405 (H8) 0.323 (H2) <b>pA</b> <sup>2</sup> <b>p</b> <sup>‡</sup>	-	-	0.507 (H5) 0.331 (H6) <b>pC</b> <sup>‡</sup>
GpA <sup>1</sup> pA <sup>2</sup> pA <sup>3</sup> pC ( <b>7</b> )	0.123 <b>Gp</b> <sup>†</sup>	0.277 (H8) 0.377 (H2) <b>pA</b> <sup>1</sup> <b>p</b> <sup>‡</sup>	0.409 (H8) 0.406 (H2) <b>pA</b> <sup>2</sup> <b>p</b> <sup>‡</sup>	0.464 (H8) 0.230 (H2) <b>pA</b> <sup>3</sup> <b>p</b> <sup>‡</sup>	-	0.570 (H5) 0.361 (H6) <b>pC</b> <sup>‡</sup>
GpA <sup>1</sup> pA <sup>2</sup> pA <sup>3</sup> pA <sup>4</sup> pC ( <b>8</b> )	0.135 <b>Gp</b> <sup>†</sup>	0.287 (H8) 0.379 (H2) <b>pA</b> <sup>1</sup> <b>p</b> <sup>‡</sup>	0.402 (H8) 0.467 (H2) <b>pA</b> <sup>2</sup> <b>p</b> <sup>‡</sup>	0.493 (H8) 0.226 (H2) <b>pA</b> <sup>3</sup> <b>p</b> <sup>‡</sup>	0.524 (H8) 0.457 (H2) <b>pA</b> <sup>4</sup> <b>p</b> <sup>‡</sup>	0.592 (H5) 0.376 (H6) <b>pC</b> <sup>‡</sup>

<sup>a</sup>The chemical shift difference [ $\Delta\delta_{\text{N}(\underline{\text{M}}-\underline{\text{O}})}$ , in ppm] between the monomer ( $\underline{\text{M}} = \text{NpEt} / \text{EtpNpEt} / \text{EtpN}$ , where N = G, A or C) and Oligomers ( $\underline{\text{O}}$ ) at the neutral (N) state.  $\Delta\delta_{\text{N}(\underline{\text{M}}-\underline{\text{O}})} > 0$  signifies shielding and  $\Delta\delta_{\text{N}(\underline{\text{M}}-\underline{\text{O}})} < 0$  signifies deshielding

<sup>†</sup> $\delta([\text{GpEt}(\mathbf{1a})] - \text{Dimer}(\mathbf{2a}$  or  $\mathbf{3a})$  or oligomer  $\mathbf{4}$ ,  $\mathbf{5}$ ,  $\mathbf{6}$ ,  $\mathbf{7}$  or  $\mathbf{8}) = [\Delta\delta_{\text{N}(\underline{\text{M}}-\underline{\text{O}})}]$

<sup>‡</sup> $\delta([\text{EtpApEt}(\mathbf{1f})] - \text{oligomer} \mathbf{4}$ ,  $\mathbf{5}$ ,  $\mathbf{6}$ ,  $\mathbf{7}$  or  $\mathbf{8}) = [\Delta\delta_{\text{N}(\underline{\text{M}}-\underline{\text{O}})}]$ .

<sup>‡</sup> $\delta([\text{EtpC}(\mathbf{1g})] - \text{Dimer}(\mathbf{3a})$  or oligomer  $\mathbf{5}$ ,  $\mathbf{6}$ ,  $\mathbf{7}$  or  $\mathbf{8}) = [\Delta\delta_{\text{N}(\underline{\text{M}}-\underline{\text{O}})}]$ .

**Table S2.** The dimerization and oligomerization shift estimated from  $^1\text{H}$  chemical shift at the deprotonated (D) state at 298 K for aromatic protons of compounds **2a**, **3a** and **4 – 8** using appropriate monomeric reference compounds (**1a**, **1f** or **1g**)<sup>†,‡,§</sup>.

Compounds	$\Delta\delta_{\text{D}(\underline{\text{M}}-\underline{\text{O}})}^{\text{a}}$					
GpA ( <b>2a</b> )	0.096 <b>Gp</b> <sup>†</sup>	- (H8) - (H2) <b>pA</b>	-	-	-	-
GpC ( <b>3a</b> )	-0.001 <b>Gp</b> <sup>†</sup>	-	-	-	-	0.176 (H5) 0.079 (H6) <b>pC</b> <sup>‡</sup>
GpApA ( <b>4</b> )	0.110 <b>Gp</b> <sup>†</sup>	0.204 (H8) 0.164 (H2) <b>pAp</b> <sup>‡</sup>	(H8) (H2) <b>pA</b>	-	-	-
GpApC ( <b>5</b> )	0.063 <b>Gp</b> <sup>†</sup>	0.098 (H8) 0.123 (H2) <b>pAp</b> <sup>‡</sup>	-	-	-	0.343 (H5) 0.196 (H6) <b>pC</b> <sup>‡</sup>
GpA <sup>1</sup> pA <sup>2</sup> pC ( <b>6</b> )	0.082 <b>Gp</b> <sup>†</sup>	0.181 (H8) 0.198 (H2) <b>pA</b> <sup>1</sup> <b>p</b> <sup>‡</sup>	0.310 (H8) 0.327 (H2) <b>pA</b> <sup>2</sup> <b>p</b> <sup>‡</sup>	-	-	0.485 (H5) 0.310 (H6) <b>pC</b> <sup>‡</sup>
GpA <sup>1</sup> pA <sup>2</sup> pA <sup>3</sup> pC ( <b>7</b> )	0.125 <b>Gp</b> <sup>†</sup>	0.208 (H8) 0.385 (H2) <b>pA</b> <sup>1</sup> <b>p</b> <sup>‡</sup>	0.348 (H8) 0.420 (H2) <b>pA</b> <sup>2</sup> <b>p</b> <sup>‡</sup>	0.439 (H8) 0.238 (H2) <b>pA</b> <sup>3</sup> <b>p</b> <sup>‡</sup>	-	0.564 (H5) 0.371 (H6) <b>pC</b> <sup>‡</sup>
GpA <sup>1</sup> pA <sup>2</sup> pA <sup>3</sup> pA <sup>4</sup> pC ( <b>8</b> )	0.141 <b>Gp</b> <sup>†</sup>	0.251 (H8) 0.403 (H2) <b>pA</b> <sup>1</sup> <b>p</b> <sup>‡</sup>	0.351 (H8) 0.478 (H2) <b>pA</b> <sup>2</sup> <b>p</b> <sup>‡</sup>	0.494 (H8) 0.231 (H2) <b>pA</b> <sup>3</sup> <b>p</b> <sup>‡</sup>	0.530 (H8) 0.475 (H2) <b>pA</b> <sup>4</sup> <b>p</b> <sup>‡</sup>	0.596 (H5) 0.390 (H6) <b>pC</b> <sup>‡</sup>

<sup>a</sup> The chemical shift difference [ $\Delta\delta_{\text{D}(\underline{\text{M}}-\underline{\text{O}})}$  in ppm] between the monomer ( $\underline{\text{M}}$  = NpEt / EtpNpEt / EtpN, where N = G, A or C) and Oligomers ( $\underline{\text{O}}$ ) at the deprotonated (D) states respectively.  $\Delta\delta_{\text{D}(\underline{\text{M}}-\underline{\text{O}})} > 0$  signifies shielding and  $\Delta\delta_{\text{D}(\underline{\text{M}}-\underline{\text{O}})} < 0$  signifies deshielding.

<sup>†</sup> $\delta([\text{GpEt}(\mathbf{1a})] - \text{Dimer}(\mathbf{2a}$  or  $\mathbf{3a})$  or oligomer **4**, **5**, **6**, **7** or **8**) = [ $\Delta\delta_{\text{D}(\underline{\text{M}}-\underline{\text{O}})}$ ]

<sup>‡</sup> $\delta([\text{EtpApEt}(\mathbf{1f})] - \text{oligomer } \mathbf{4}, \mathbf{5}, \mathbf{6}, \mathbf{7}$  or  $\mathbf{8}) = [\Delta\delta_{\text{D}(\underline{\text{M}}-\underline{\text{O}})}]$ .

<sup>§</sup> $\delta([\text{EtpC}(\mathbf{1g})] - \text{Dimer}(\mathbf{3a})$  or oligomer **5**, **6**, **7** or **8**) = [ $\Delta\delta_{\text{D}(\underline{\text{M}}-\underline{\text{O}})}$ ].

**Table S3.** The endocyclic  ${}^3J_{1'2'}$  (in Hz) from  ${}^1\text{H}$  NMR at 298 K for the respective pentofuranose moiety in each nucleotydic unit in **1a**, **2a**, **3a** and **4 – 8**.<sup>a</sup>

Compounds		${}^3J_{1'2'}$ in the neutral (N) and deprotonated (D) states						
		Gp	pA <sup>1</sup> p	pA <sup>2</sup> p	pA <sup>3</sup> p	pA <sup>4</sup> p	pA	pC
GpEt ( <b>1a</b> )	N	6.5	-	-	-	-	-	-
	D	7.3	-	-	-	-	-	-
GpA ( <b>2a</b> )	N	4.4	-	-	-	-	4.5	-
	D	6.2	-	-	-	-	5.1	-
GpC ( <b>3a</b> )	N	3.4	-	-	-	-	-	2.8
	D	6.2	-	-	-	-	-	3.9
GpA <sup>1</sup> pA ( <b>4</b> )	N	4.2	3.4	-	-	-	3.6	-
	D	6.3	4.2	-	-	-	4.1	-
GpApC ( <b>5</b> )	N	3.4	2.7	-	-	-	-	2.8
	D	6.4	3.8	-	-	-	-	3.1
GpA <sup>1</sup> pA <sup>2</sup> pC ( <b>6</b> )	N	4.3	2.4	2.3	-	-	-	2.7
	D	6.5	3.7	2.7	-	-	-	2.8
GpA <sup>1</sup> pA <sup>2</sup> pA <sup>3</sup> pC ( <b>7</b> )	N	4.6	3.0	2.3	2.1	-	-	2.7
	D	6.2	4.5	2.6	2.0	-	-	2.6
GpA <sup>1</sup> pA <sup>2</sup> pA <sup>3</sup> pA <sup>4</sup> pC ( <b>8</b> )	N	4.8	3.5	2.1	2.0	2.1	-	2.7
	D	6.2	4.6	3.3	1.1	1.9	-	2.6

<sup>a</sup> All spectra are taken in 500 MHz or 600 MHz spectrometer. The error in measurement of  ${}^3J_{1'2'}$  is  $\pm 0.1$  Hz.

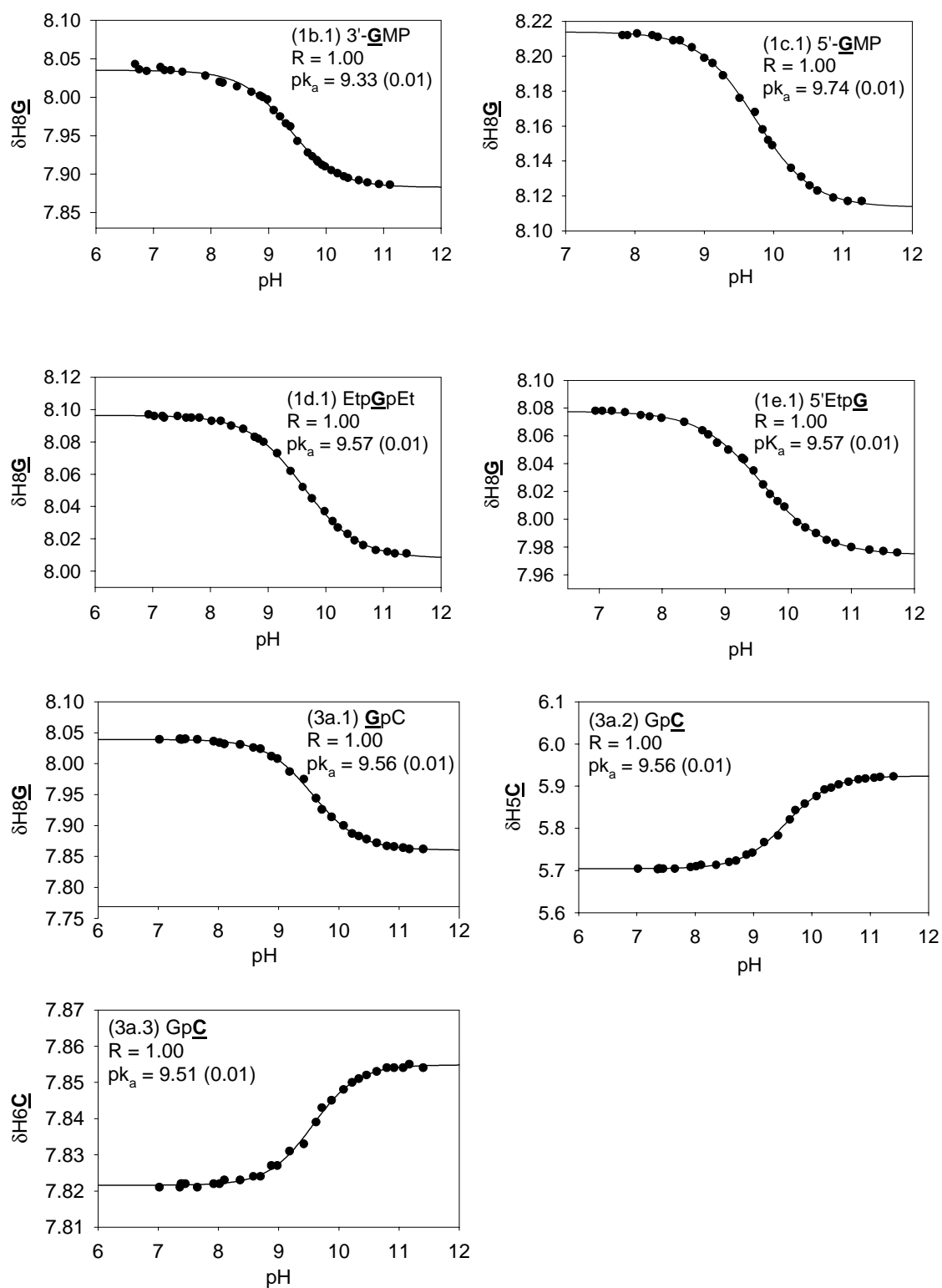
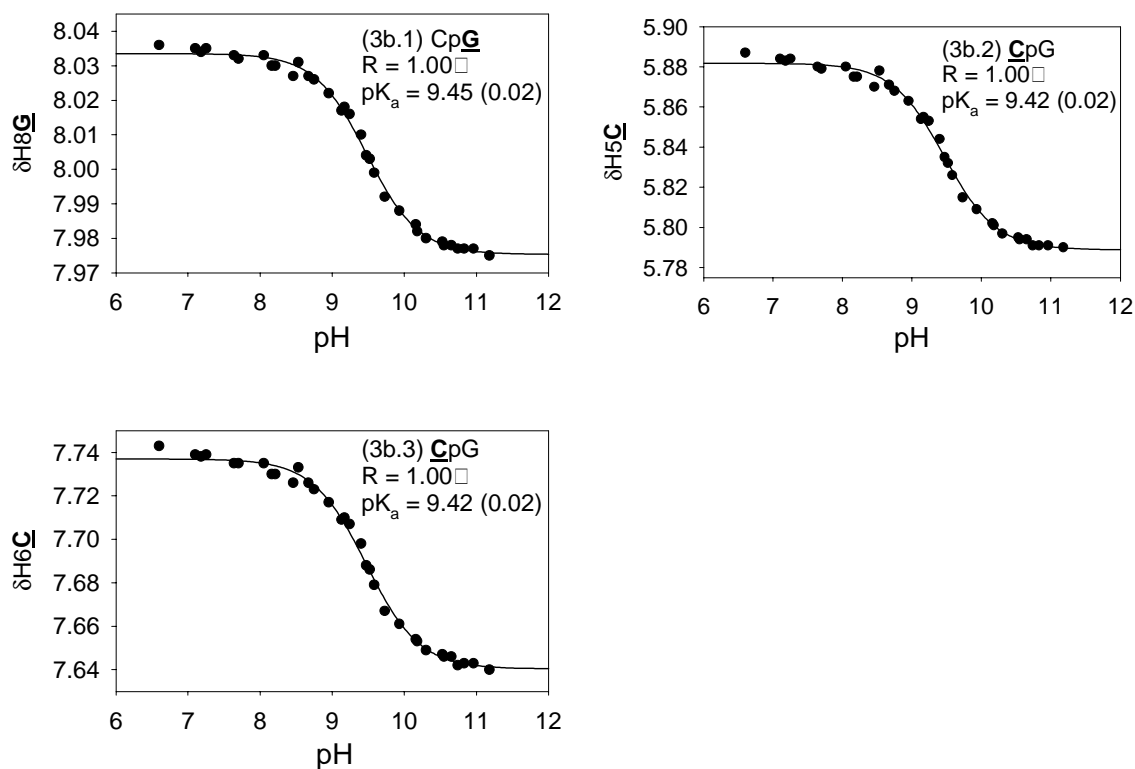


Figure S1 (Contd.)



**Figure S1.** Plot of pH-dependent ( $6.55 \leq \text{pH} \leq 11.8$ )  $^1\text{H}$  chemical shifts ( $\delta\text{H}$ ) for different aromatic protons for compounds **1b** – **1e** (Panels **1b.1** – **1e.1**), **3a** (Panels **3a.1** – **3a.3**), and **3b** (Panels **3b.1** – **3b.3**) to give the  $\text{pK}_a$  at the inflection point. Chemical shift variations at 26 – 32 different pH values have been measured in an interval of 0.15 – 0.3 pH units to obtain the sigmoidal curves. Each graph shows chemical shift change with pH for one particular aromatic proton in a compound. The name of the compound along with the particular aromatic proton chosen, the correlation coefficient ( $R$ ) obtained from curve fitting, and the  $\text{pK}_a$  values obtained from Hill plot analyses [see experimental section in text and Figure S2 for details] are shown in the respective graphs.

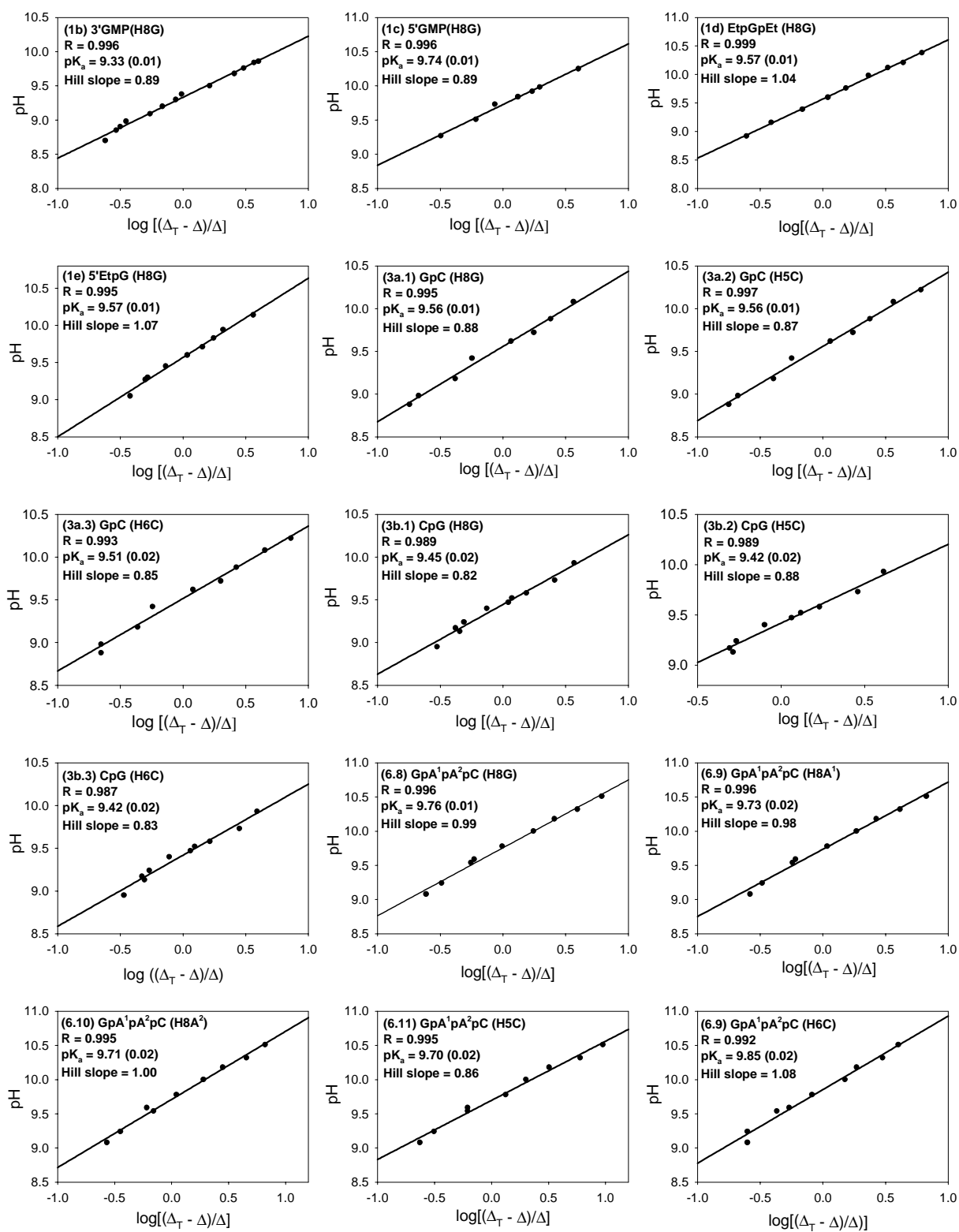
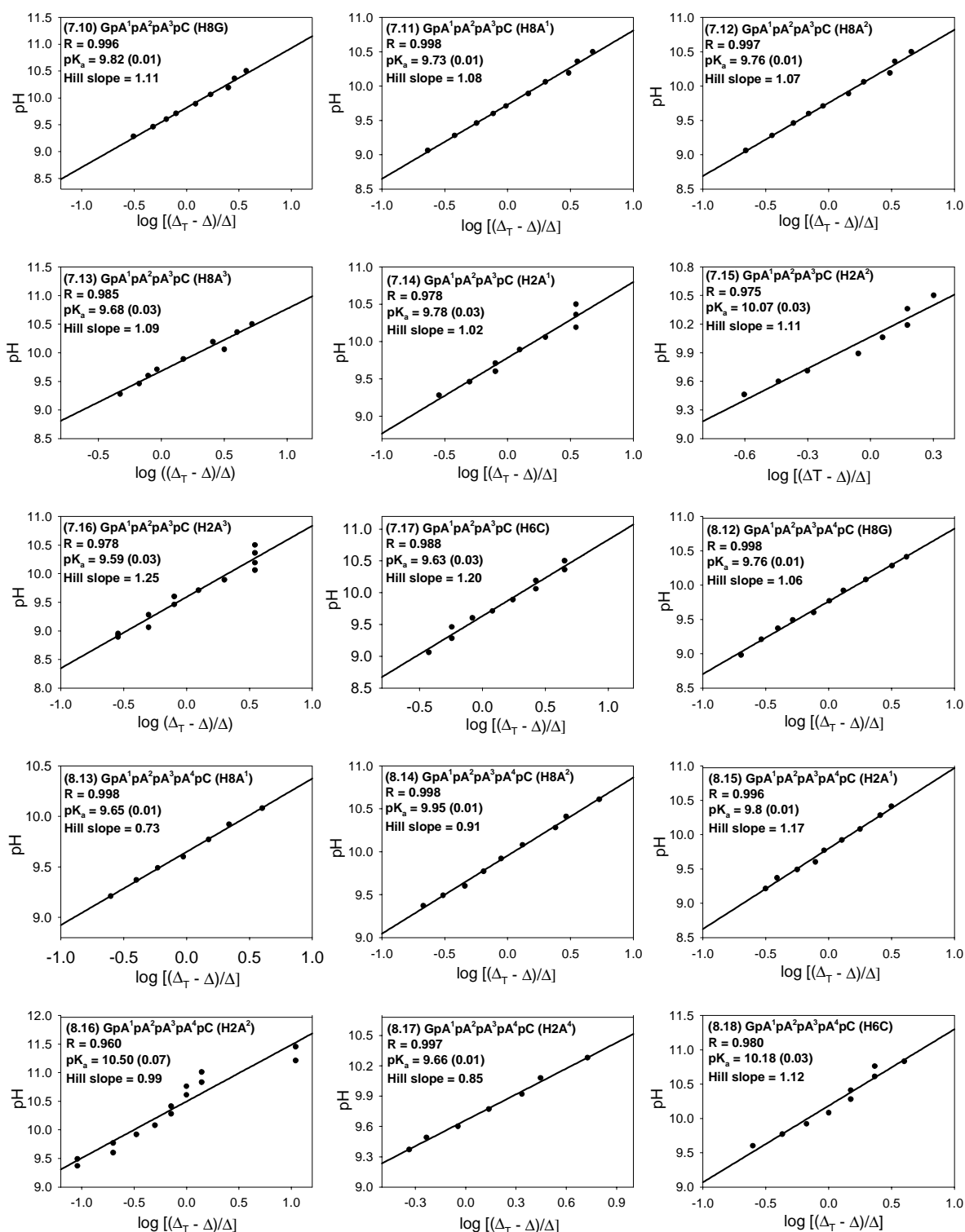


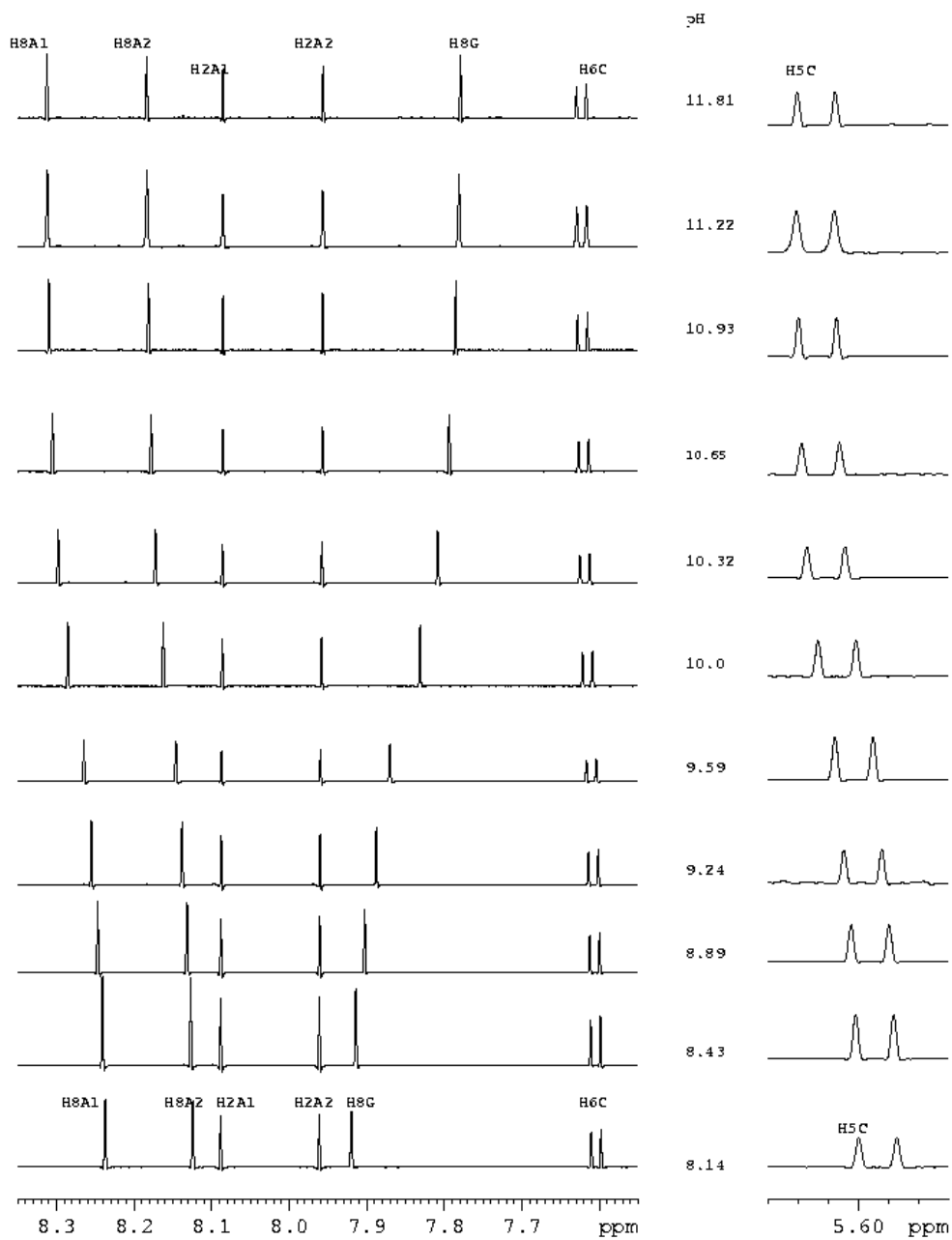
Figure S2 (Contd.)

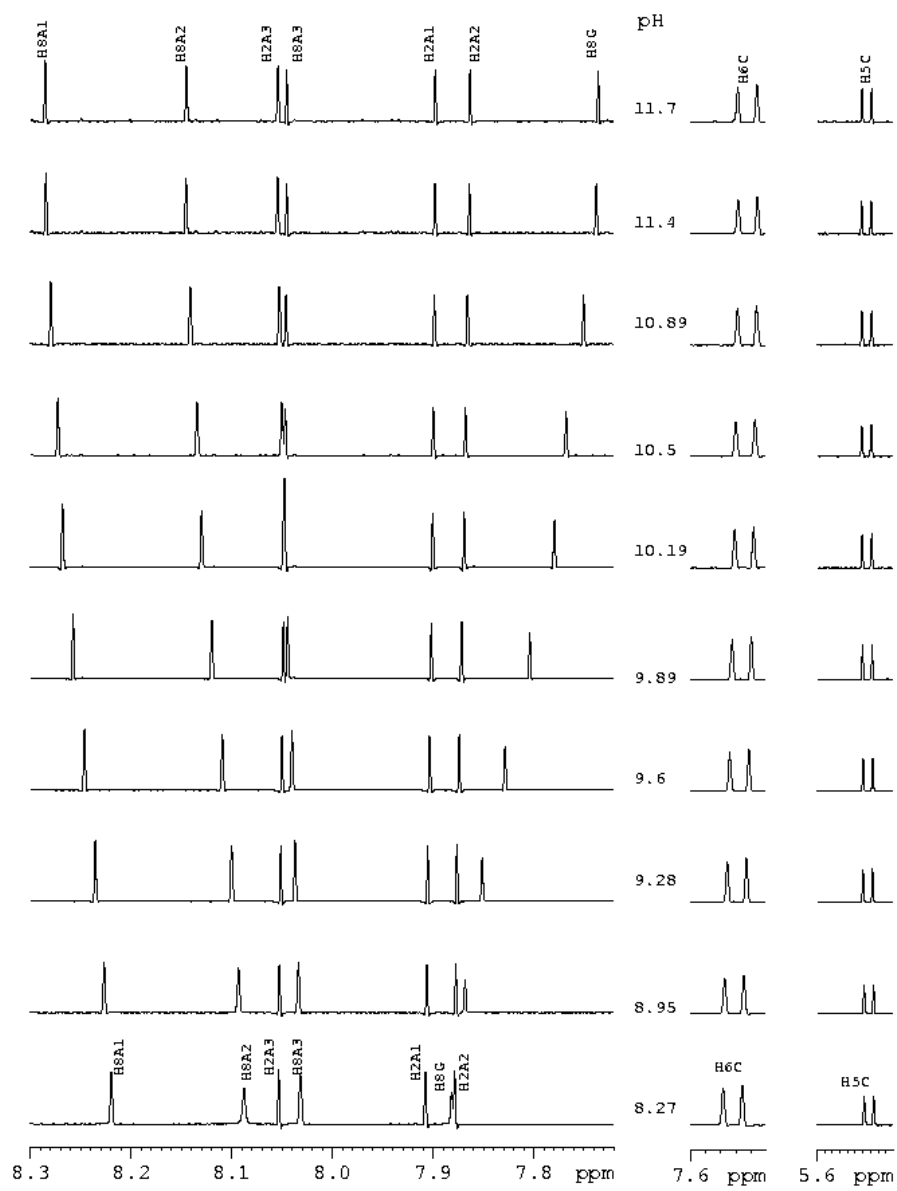




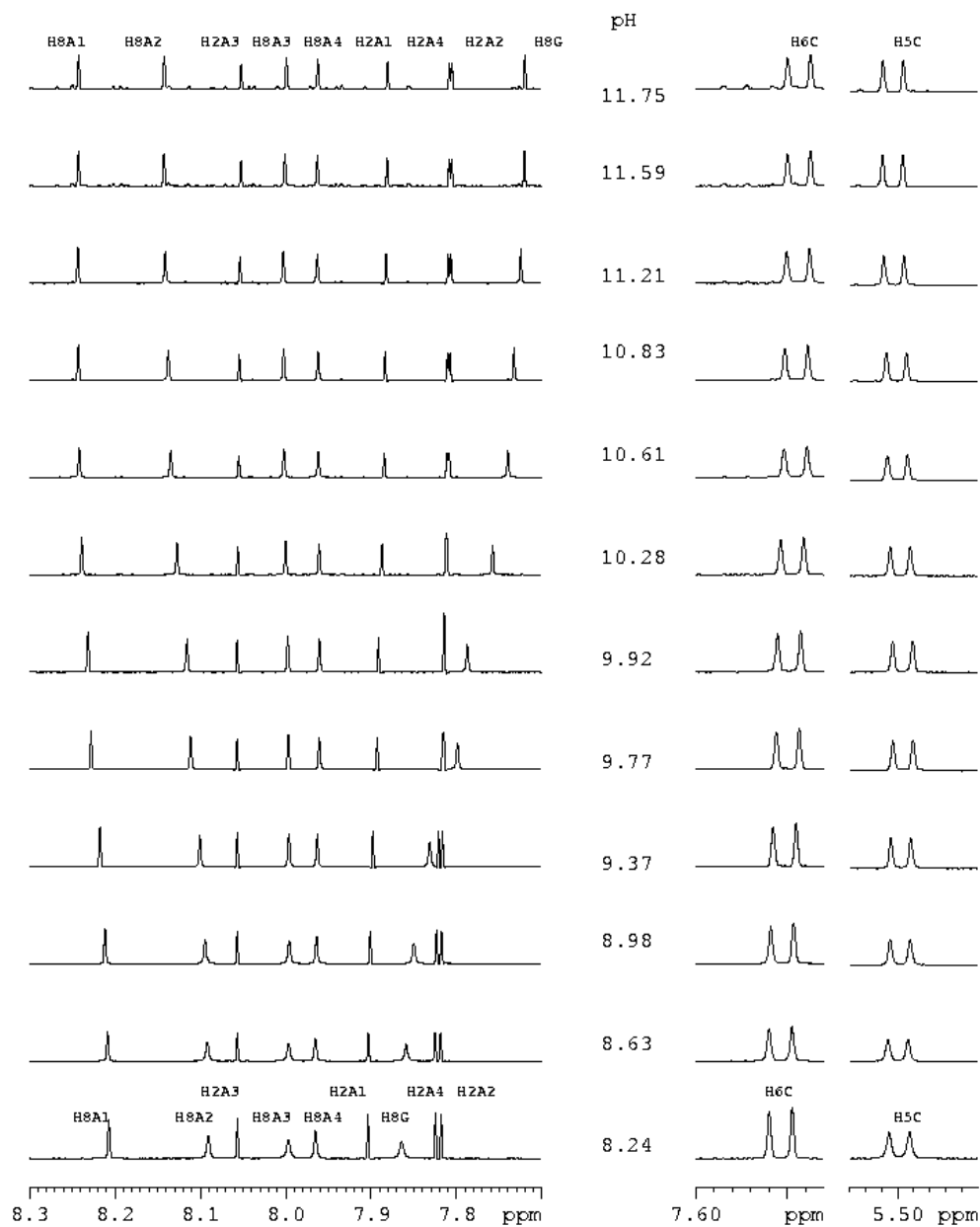
**Figure S2.** The Hill plots for compounds **1b** – **1e** (Panels **1b.1** – **1e.1**), **3a** (Panels **3a.1** – **3a.3**), **3b** (Panels **3b.1** – **3b.3**) and **6** – **8** (Panels **6.1** – **8.18**). The plot of  $\log[(\Delta_T - \Delta)/\Delta]$  as a function of pH gave a straight line with Hill slope as slope and  $pK_a$  as intercept of the straight line. Name of the compounds, values for the correlation coefficient (R),  $pK_a$  obtained from the Hill plot analyses and the value of Hill slope are shown in the respective graphs.

(A)



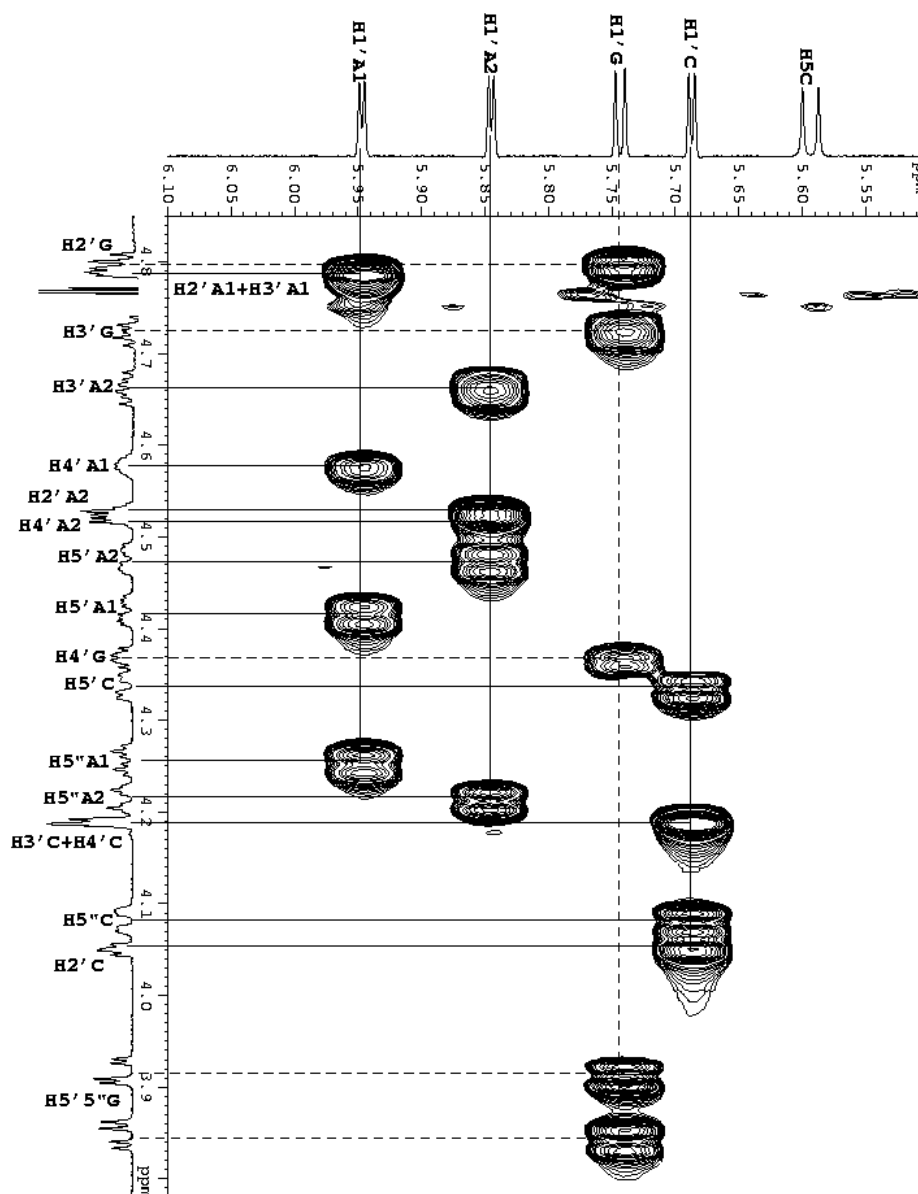
**(B)**

(C)

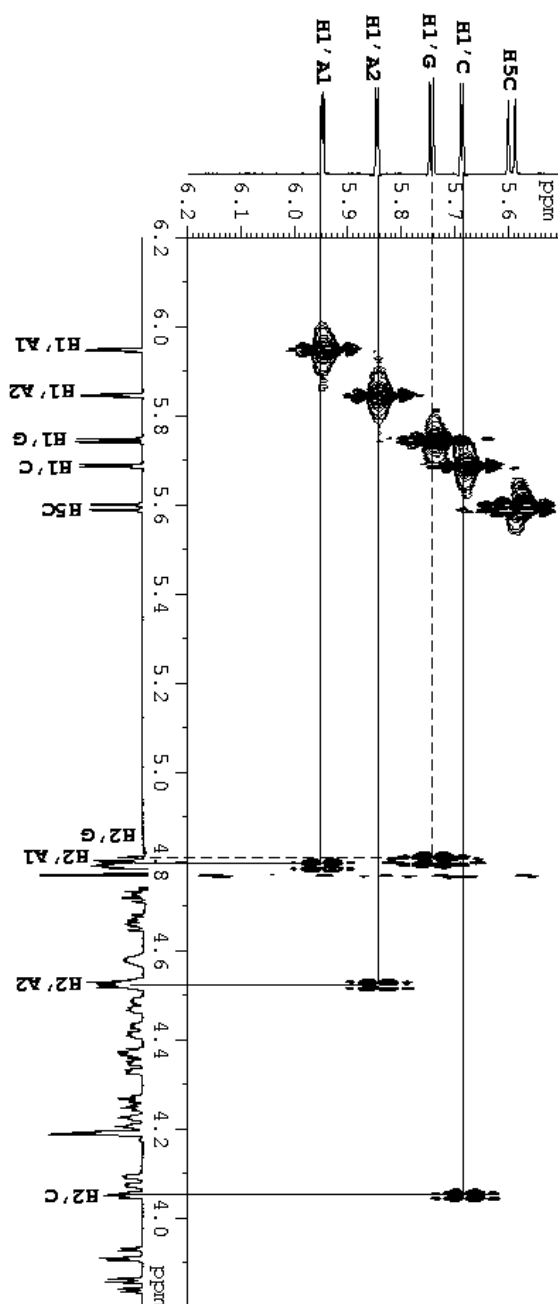


**Figure S3.** Panels (A), (B) and (C) show stack plots of the pH-dependent  $^1\text{H}$  NMR chemical shifts pH-dependent chemical shifts (in  $\text{D}_2\text{O}$ ) of the aromatic protons for compounds **6** – **8** at 298 K. It is only 10 – 12 pHs (including two plateaus at two extreme pHs) those are shown out of total ~25 – 30 pHs (used for the titration plots) in panel (A) for  $\text{GpA}^1\text{pA}^2\text{pC}$  (**6**), panel (B) for  $\text{GpA}^1\text{pA}^2\text{pA}^3\text{pC}$  (**7**) and panel (C) for  $\text{GpA}^1\text{pA}^2\text{pA}^3\text{pA}^4\text{pC}$  (**8**). All NMR measurements have been performed in 500 MHz

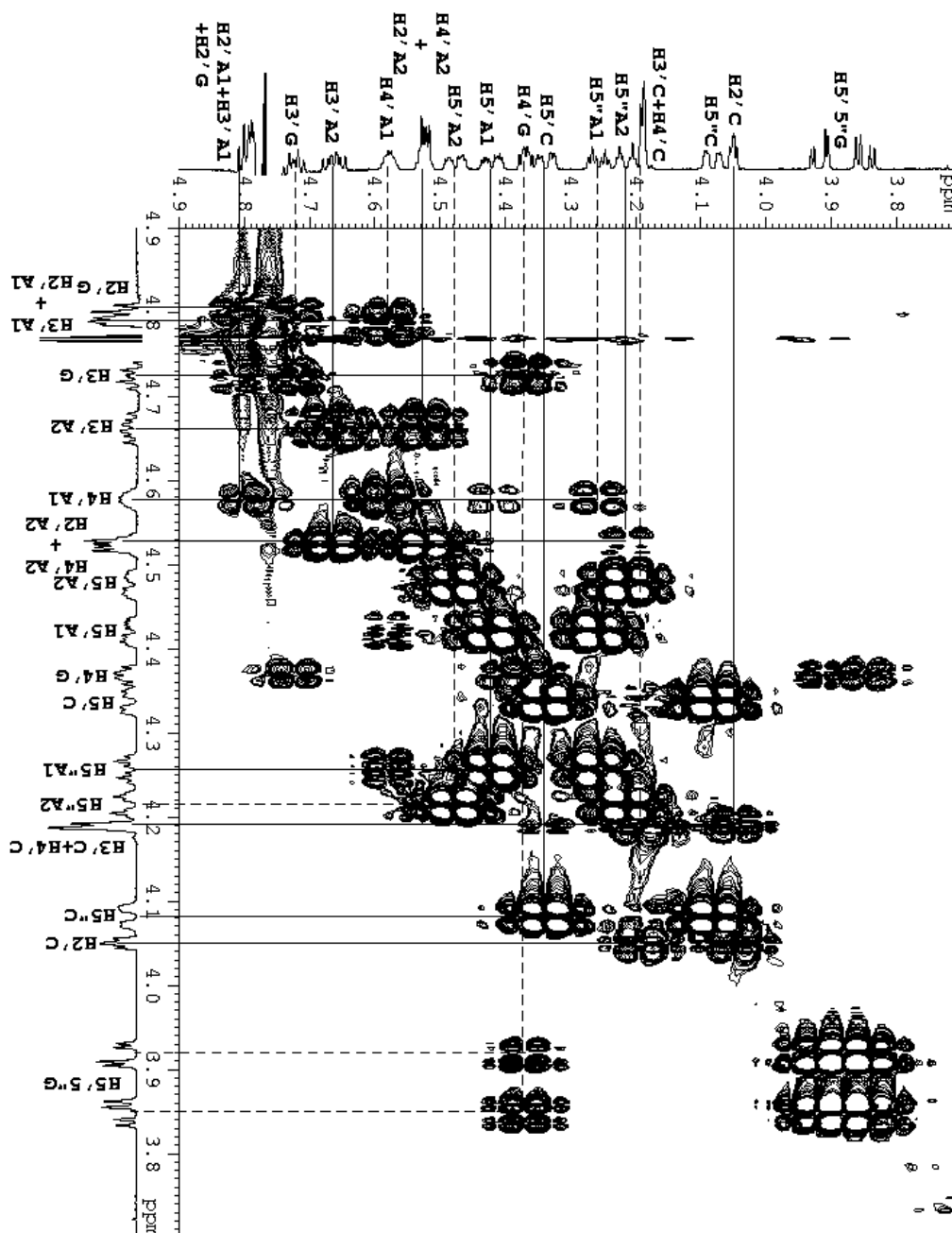
and/or 600 MHz spectrometers with  $\delta_{\text{DSS}} = 0.015$  ppm as internal standard. The pH values are corrected with the deuterium effect. The assignments for all compounds have been performed on the basis of selective homo- ( $^1\text{H}$ ) and heteronuclear ( $^{31}\text{P}$ ) decoupling experiments as well as using  $^1\text{H}$  NOESY,  $^1\text{H}$  COSY,  $^{31}\text{P}$  decoupled  $^1\text{H}$  COSY, TOCSY and  $^{31}\text{P}$  -  $^1\text{H}$  correlation spectroscopy for **6** – **8** at 298 and also at 283 K (for **7** and **8**) in the neutral pH (see Figure S4).



**Figure S4A1.** Expanded TOCSY spectra of H2'/H3'/H4'/H5'/H5'' region (4.85 – 3.8 ppm in F1 direction) to the anomeric (H1') region (6.1 – 5.5 ppm in F2 direction) for GpA<sup>1</sup>pA<sup>2</sup>pC (**6**) at 298 K.

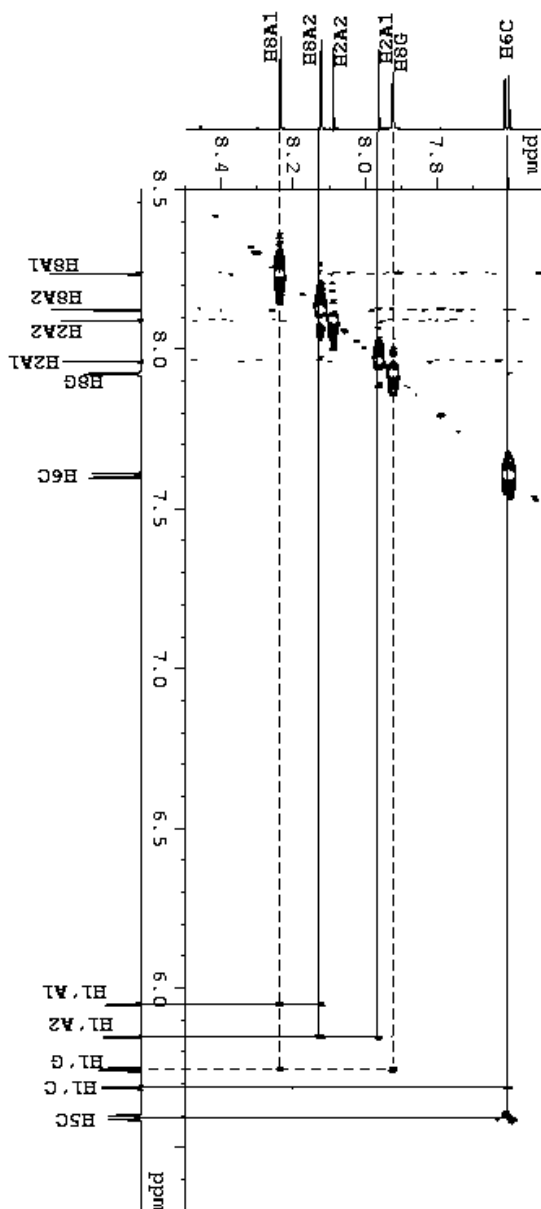


**Figure S4A2.** Expanded DQF-COSY spectra of the anomeric (H1') region (6.2 – 5.5 ppm in F1 direction) to the anomeric and H2'/H3'/H4'/H5'/H5'' region (6.2 – 3.8 ppm in F2 direction) for GpA<sup>1</sup>pA<sup>2</sup>pC (**6**) at 298 K.

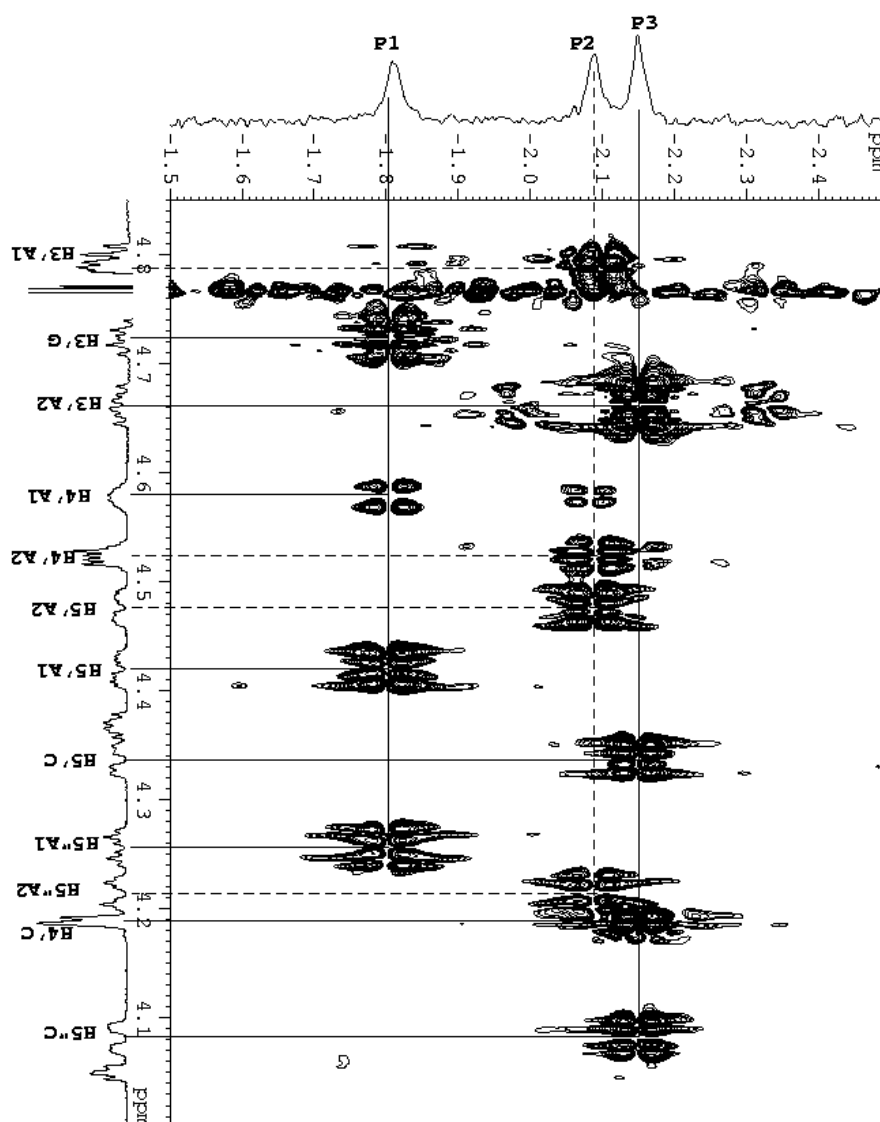


**Figure S4A3.** Expanded DQF-COSY spectra of H2'/H3'/H4'/H5'/H5'' region (4.9 – 3.7 ppm in F1 direction) to H2'/H3'/H4'/H5'/H5'' region (4.9 – 3.7 ppm in F2 direction) for GpA<sup>1</sup>pA<sup>2</sup>pC (6) at 298 K.

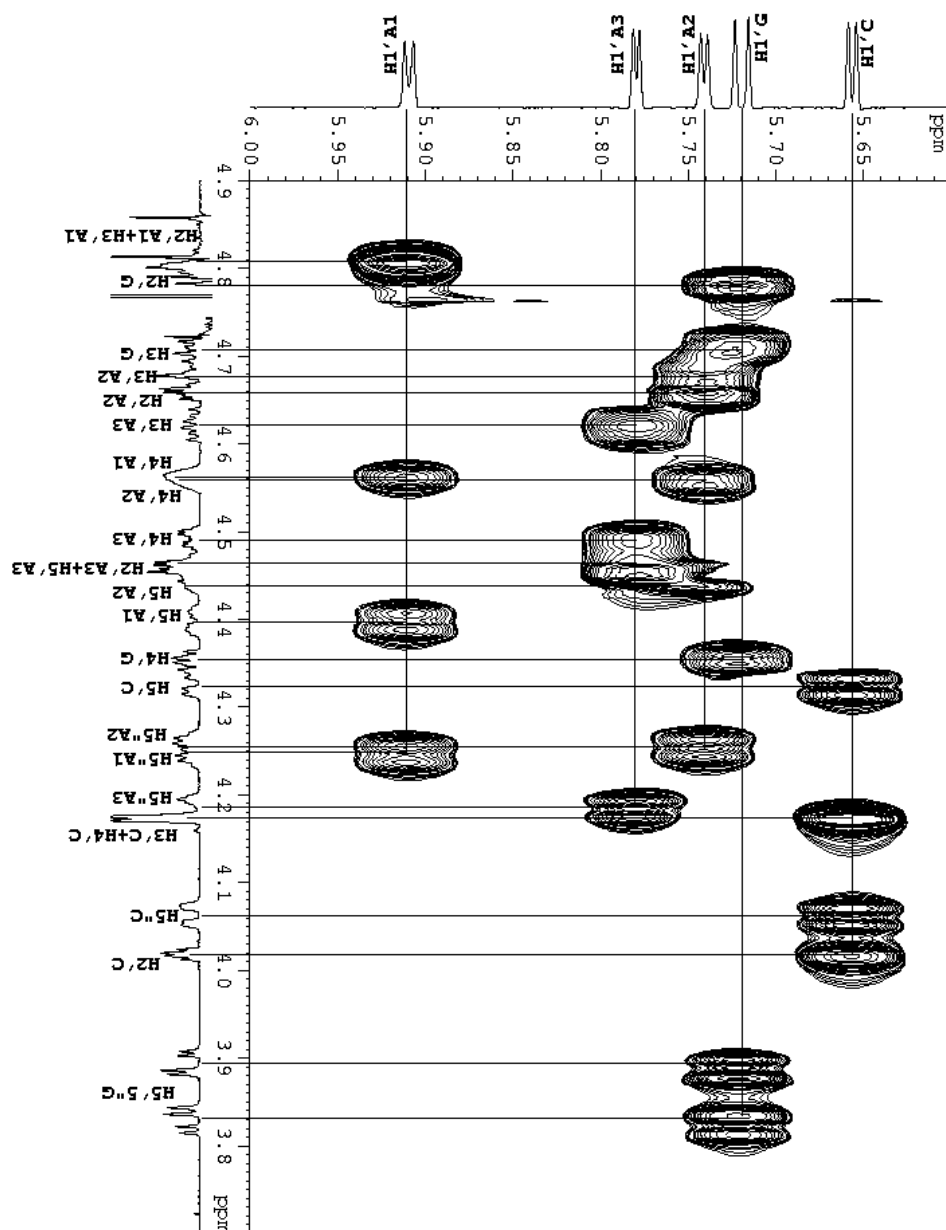




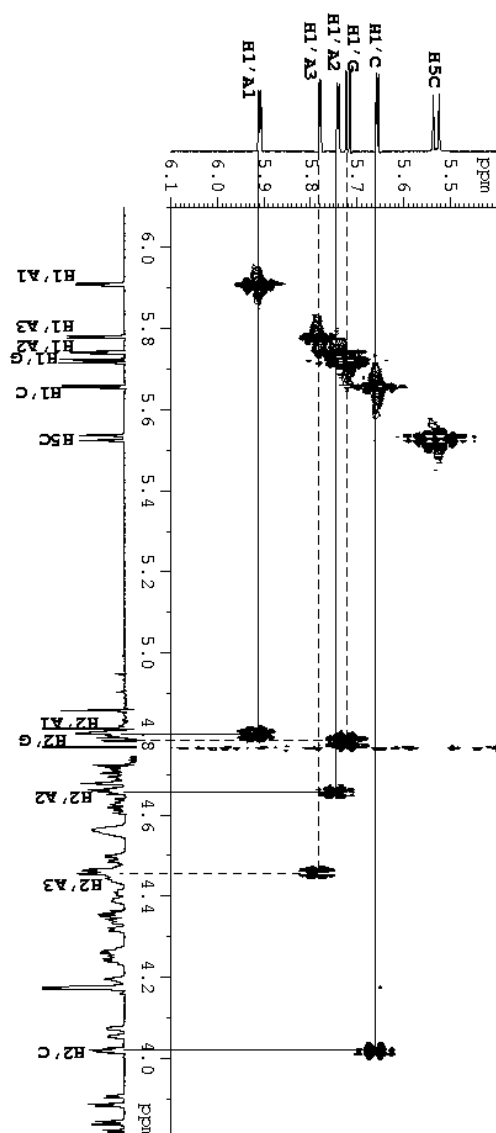
**Figure S4A4.** Expanded NOESY spectra (mixing time  $\tau = 800$  ms) of the aromatic (H8/H2/H5/H6) region (8.5 – 7.4 ppm in F1 direction) to the aromatic (H8/H2/H5/H6) and anomeric (H1') region (8.5 – 5.3 ppm in F2 direction) for GpA<sup>1</sup>pA<sup>2</sup>pC (**6**) at 298 K. The spectra showed some inter-residual cross-peaks [H1'A<sup>1</sup>  $\leftrightarrow$  H8A<sup>2</sup>; H1'A<sup>2</sup>  $\leftrightarrow$  H2A<sup>1</sup>; H1'G  $\leftrightarrow$  H8A<sup>1</sup>], thereby helping for assigning A<sup>1</sup> and A<sup>2</sup>.



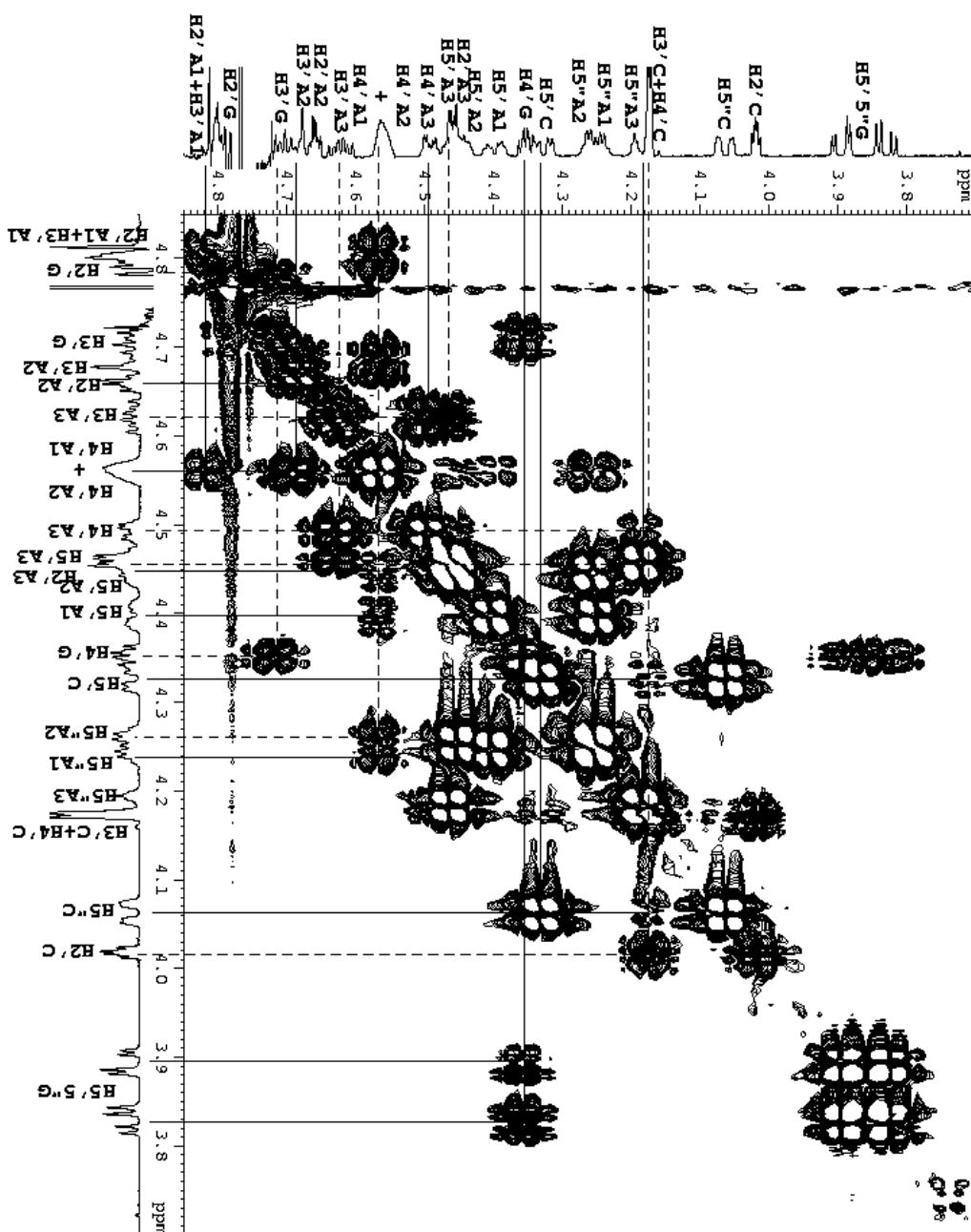
**Figure S4A5.** Expanded  $^{31}\text{P}$ - $^1\text{H}$  correlation spectroscopy of  $^{31}\text{P}$  region (-1.5 – 2.5 ppm in F1 direction) to H2'/H3'/H4'/H5'/H5'' region (4.9 – 4.0 ppm in F2 direction) for GpA<sup>1</sup>pA<sup>2</sup>pC (6) at 298 K.



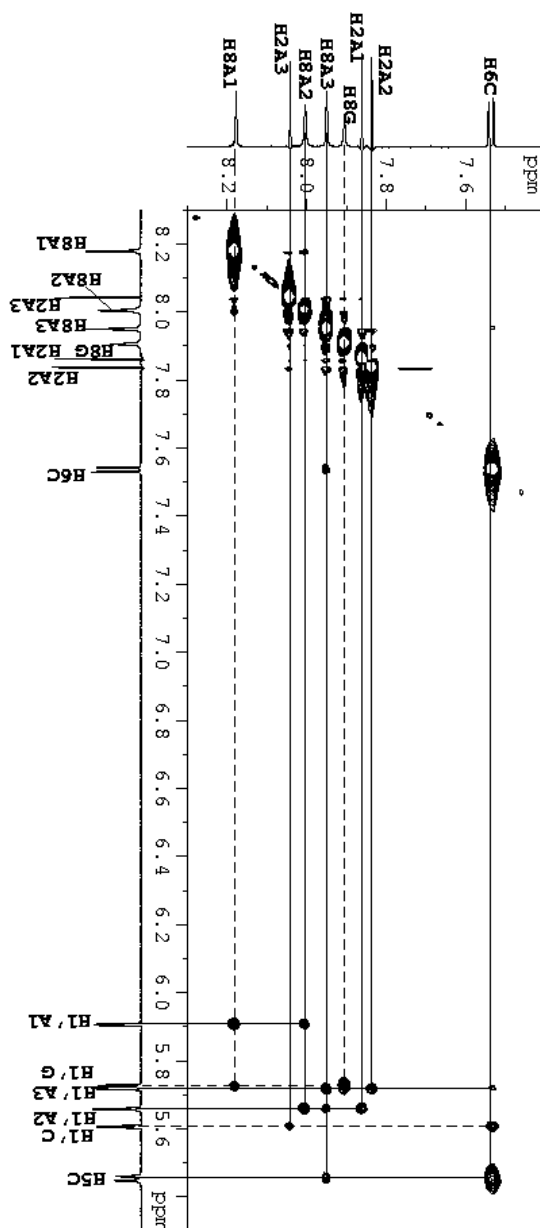
**Figure S4B1.** Expanded TOCSY spectra of the anomeric (H1') region (6.0 – 5.6 ppm in F1 direction) to H2'/H3'/H4'/H5'/H5'' region (4.9 – 3.7 ppm in F2 direction) for GpA<sup>1</sup>pA<sup>2</sup>pA<sup>3</sup>pC (7) at 298 K.



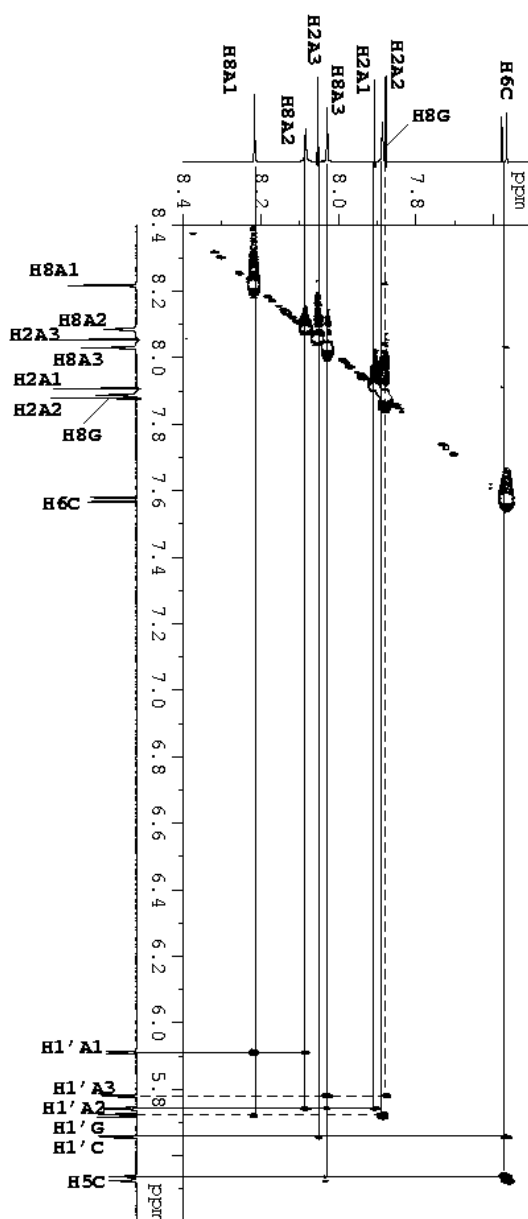
**Figure S4B2.** Expanded DQF-COSY spectra of the anomeric (H1') region (6.1 – 5.4 ppm in F1 direction) to the anomeric and H2'/H3'/H4'/H5'/H5'' region (6.1 – 3.8 ppm in F2 direction) for GpA<sup>1</sup>pA<sup>2</sup>pA<sup>3</sup>pC (**7**) at 298 K.



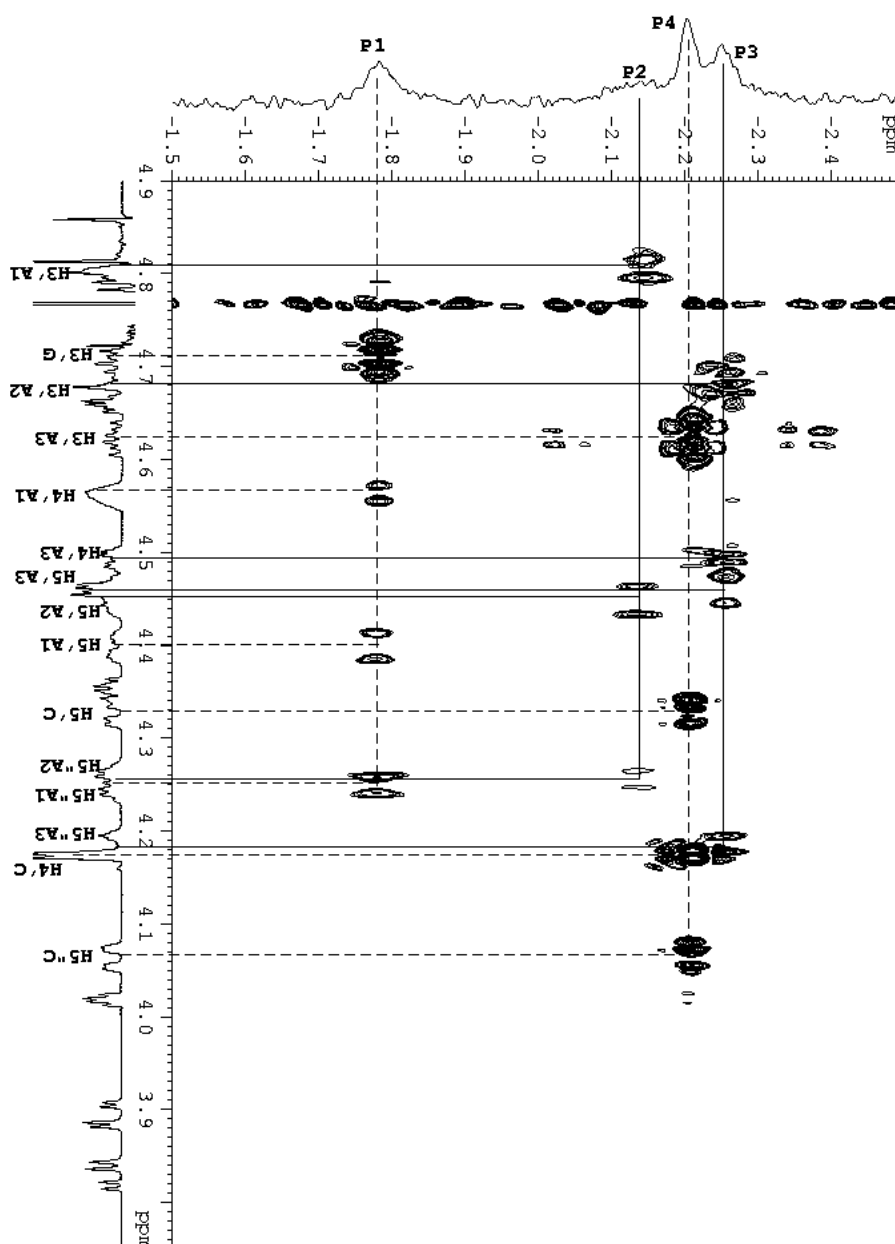
**Figure S4B3.** Expanded DQF-COSY spectra of H2'/H3'/H4'/H5'/H5'' region (4.85 – 3.7 ppm in F1 direction) to H2'/H3'/H4'/H5'/H5'' region (4.85 – 3.7 ppm in F2 direction) for GpA<sup>1</sup>pA<sup>2</sup>pA<sup>3</sup>pC (7) at 298 K.



**Figure S4B4.** Expanded NOESY spectra (mixing time  $\tau = 800$  ms) of the aromatic (H8/H2/H5/H6) region (8.3 – 7.4 ppm in F1 direction) to the anomeric (H1') region (8.3 – 5.3 ppm in F2 direction) for GpA<sup>1</sup>pA<sup>2</sup>pA<sup>3</sup>pC (7) at 283 K. NOESY spectra at 283 K. The spectra showed some inter-residual cross-peaks [H1'A<sup>1</sup> ↔ H8A<sup>2</sup>, H1'A<sup>2</sup> ↔ H8A<sup>3</sup>, H1'A<sup>2</sup> ↔ H2A<sup>1</sup>, H1'A<sup>3</sup> ↔ H2A<sup>2</sup>, H1'A<sup>3</sup> ↔ H6C, H1'G ↔ H8A<sup>1</sup>, H1'C ↔ H2A<sup>3</sup>]; the underlined cross-peak is the extra one found at 283 K compared to 298 K, see Panel **B5**], thereby helping for assigning A<sup>1</sup> to A<sup>3</sup>. Temperature-dependent <sup>1</sup>H NMR experiments (data not shown) have been performed from 298 to 283 K (in 5 K steps) to assign the corresponding anomeric protons at 283 K in order to make full assignments of the aromatic protons at 298 K.

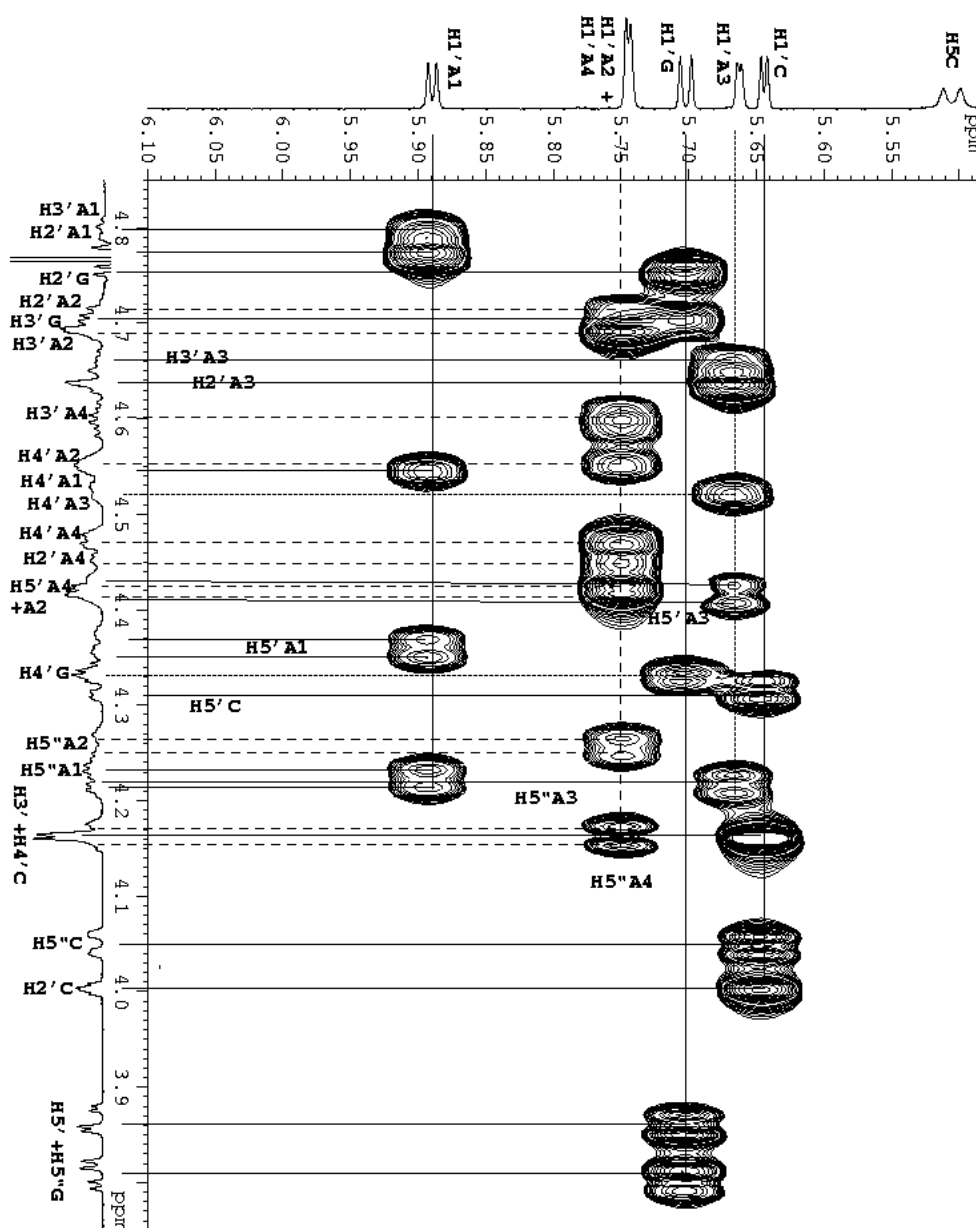


**Figure S4B5.** Expanded NOESY spectra (mixing time  $\tau = 800$  ms) of the aromatic (H8/H2/H5/H6) region (8.4 – 7.5 ppm in F1 direction) to the anomeric (H1') region (8.4 – 5.4 ppm in F2 direction) for GpA<sup>1</sup>pA<sup>2</sup>pA<sup>3</sup>pC (**7**) at 298 K. The spectra showed some inter-residual cross-peaks [H1'A<sup>1</sup>  $\leftrightarrow$  H8A<sup>2</sup>, H1'A<sup>2</sup>  $\leftrightarrow$  H8A<sup>3</sup>, H1'A<sup>2</sup>  $\leftrightarrow$  H2A<sup>1</sup>, H1'A<sup>3</sup>  $\leftrightarrow$  H2A<sup>2</sup>, H1'G  $\leftrightarrow$  H8A<sup>1</sup>, H1'C  $\leftrightarrow$  H2A<sup>3</sup>], thereby helping for assigning A<sup>1</sup> and A<sup>3</sup>.

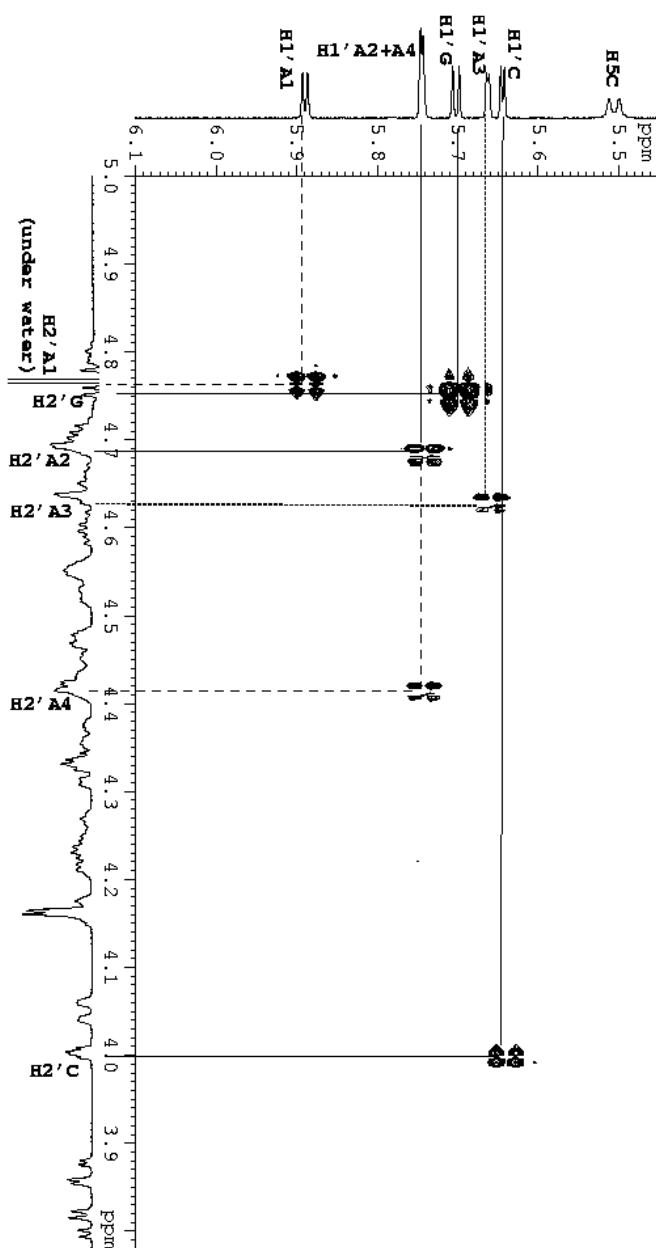


**Figure S4B6.** Expanded  $^{31}\text{P}$ - $^1\text{H}$  correlation spectroscopy of  $^{31}\text{P}$  region (-1.5 – 2.5 ppm in F1 direction) to H2'/H3'/H4'/H5'/H5'' region (4.9 – 3.75 ppm in F2 direction) for GpA<sup>1</sup>pA<sup>2</sup>pA<sup>3</sup>pC (7) at 298 K. The spectra showed some inter-residual cross-peaks [H1'A<sup>1</sup> ↔ H8A<sup>2</sup>; H1'A<sup>2</sup> ↔ H2A<sup>1</sup>; H1'G ↔ H8A<sup>1</sup>], thereby helping for assigning A<sup>1</sup> and A<sup>2</sup>.

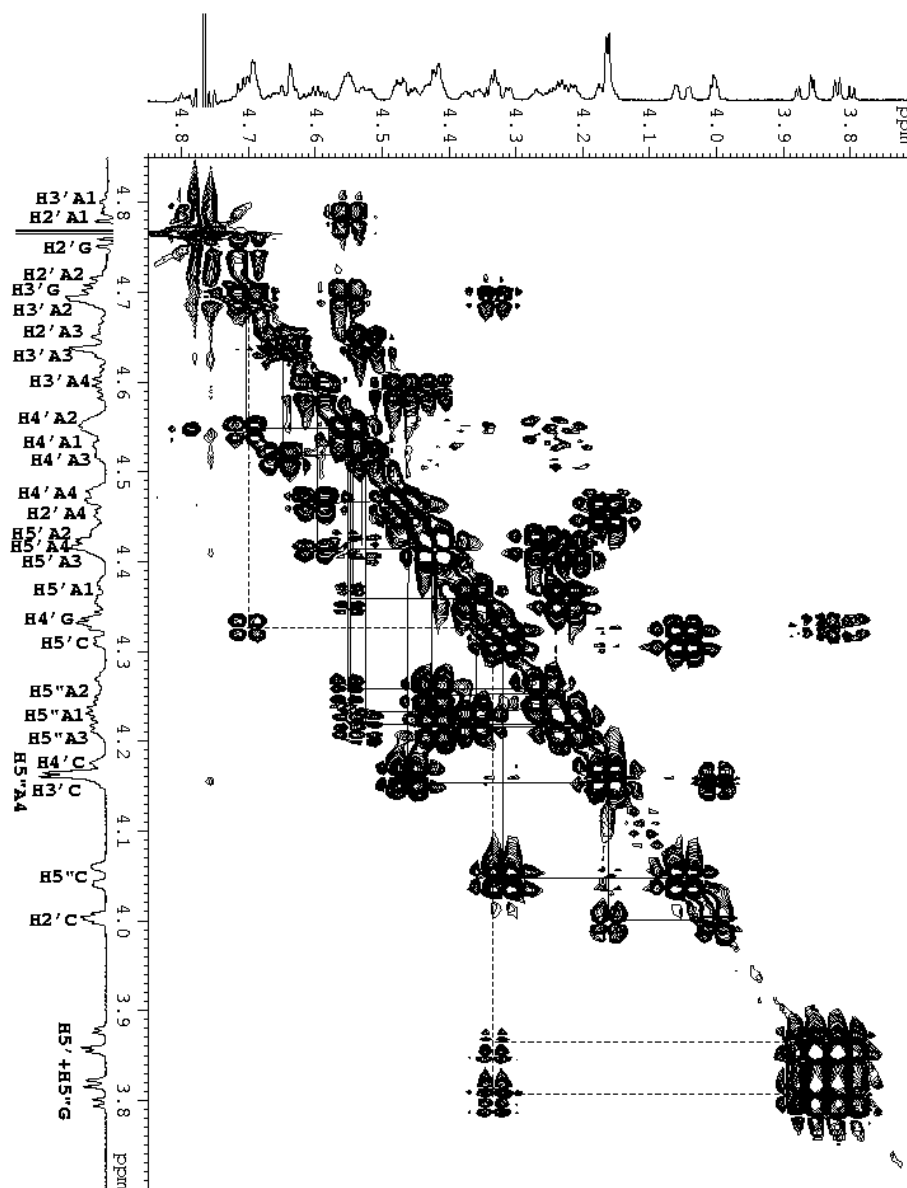




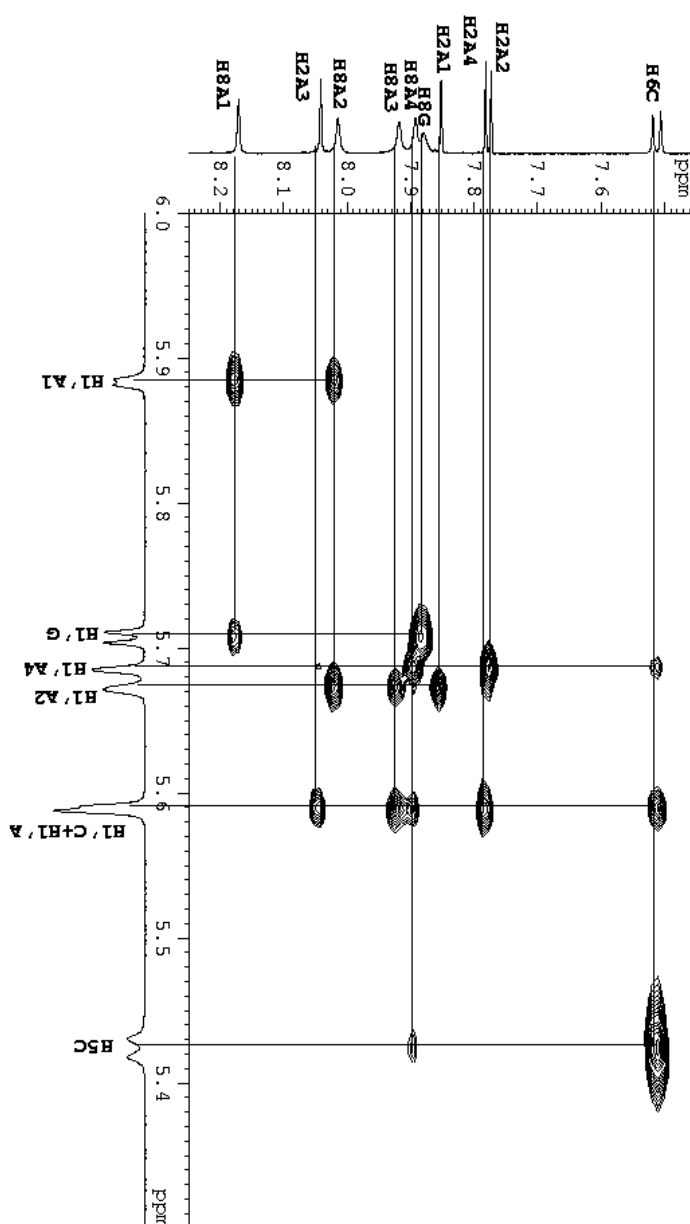
**Figure S4C1.** Expanded TOCSY spectra of the anomeric (H1') region (6.1 – 5.5 ppm in F1 direction) to H2'/H3'/H4'/H5'/H5'' region (4.9 – 3.8 ppm in F2 direction) for GpA<sup>1</sup>pA<sup>2</sup>pA<sup>3</sup>pA<sup>4</sup>pC (**8**) at 298 K.



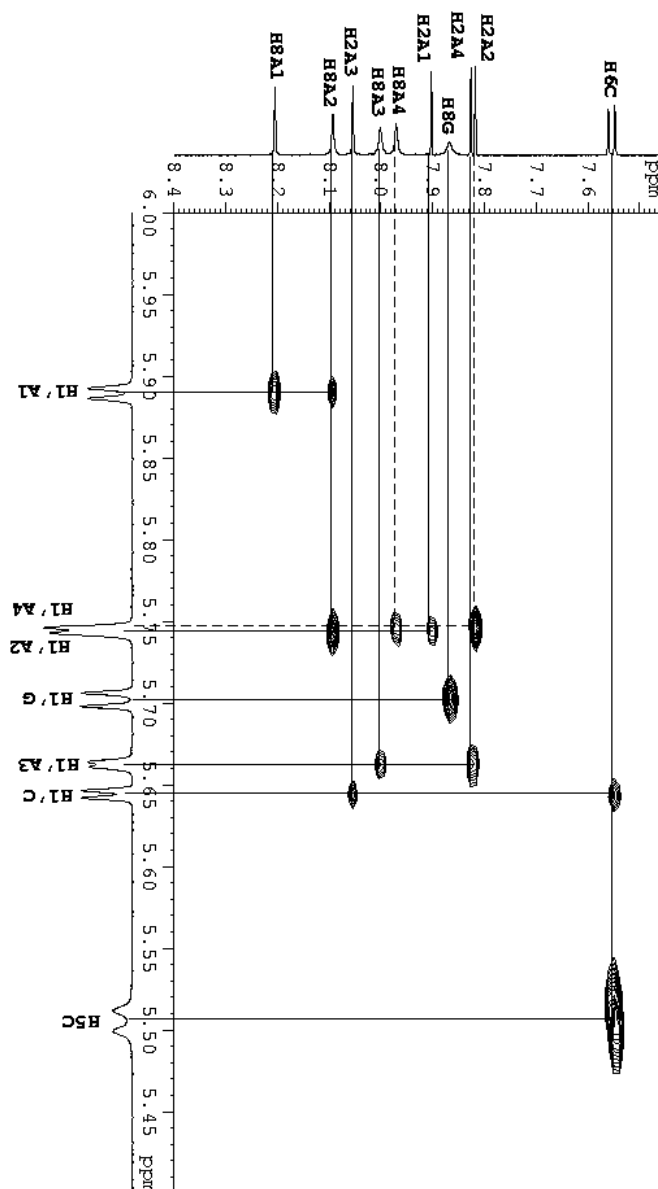
**Figure S4C2.** Expanded DQF-COSY spectra of the anomeric (H1') region (6.1 – 5.45 ppm in F1 direction) to H2'/H3'/H4'/H5'/H5'' region (5.0 – 3.78 ppm in F2 direction) for GpA<sup>1</sup>pA<sup>2</sup>pA<sup>3</sup>pA<sup>4</sup>pC (**8**) at 298 K.



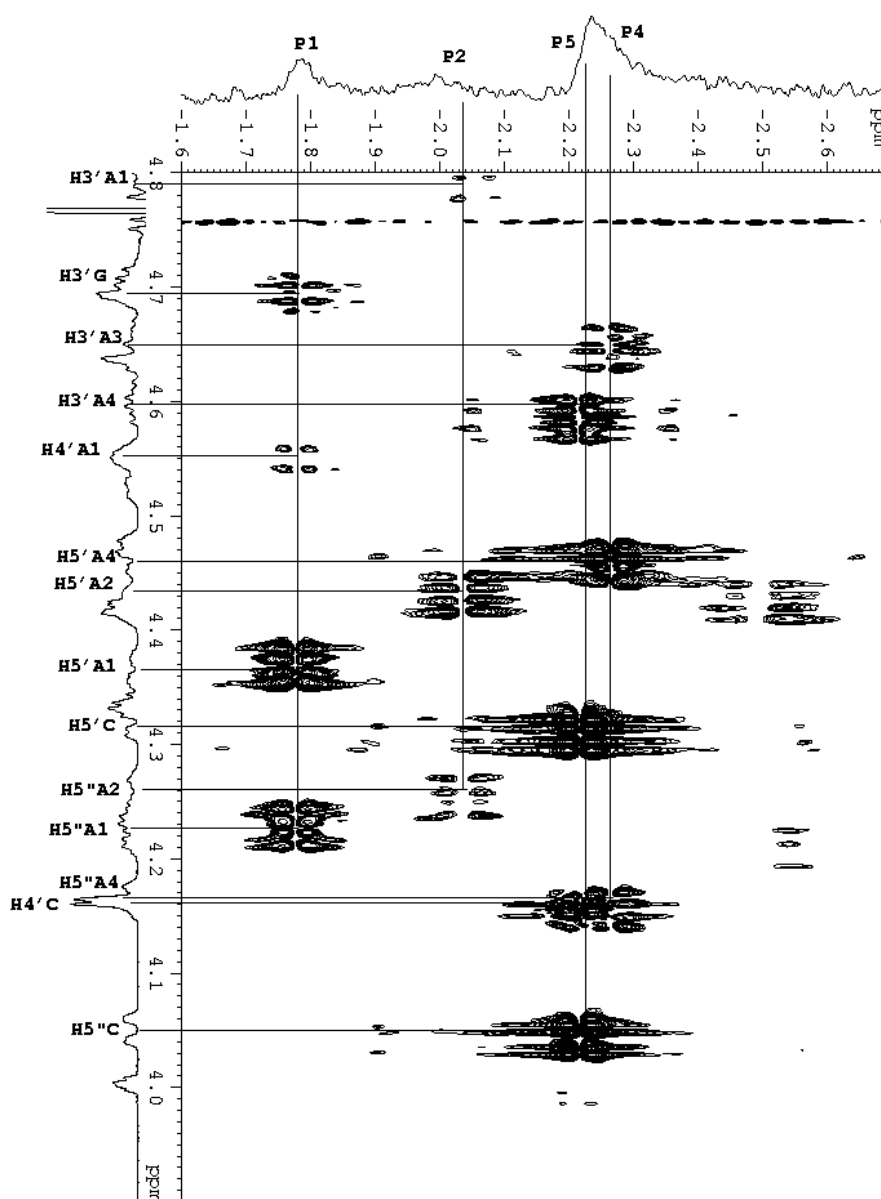
**Figure S4C3.** Expanded DQF-COSY spectra of H2'/H3'/H4'/H5'/H5'' region (4.85 – 3.7 ppm in F1 direction) to H2'/H3'/H4'/H5'/H5'' region (4.85 – 3.7 ppm in F2 direction) for GpA<sup>1</sup>pA<sup>2</sup>pA<sup>3</sup>pA<sup>4</sup>pC (**8**) at 298 K.



**Figure S4C4.** Expanded NOESY spectra ( $\tau = 800$  ms) of the H8/H2/H5/H6 region (8.15 – 7.45 ppm in F1 direction) to the anomeric (H1') region (6.0 – 5.3 ppm in F2 direction) for GpA<sup>1</sup>pA<sup>2</sup>pA<sup>3</sup>pA<sup>4</sup>pC (**8**) at 283 K. NOESY spectra at 283 K. The spectra showed some inter-residual cross-peaks [H1'A<sup>1</sup> ↔ H8A<sup>2</sup>, H1'A<sup>2</sup> ↔ H8A<sup>3</sup>, H1'A<sup>2</sup> ↔ H2A<sup>1</sup>, H1'A<sup>3</sup> ↔ H8A<sup>4</sup>, H1'A<sup>4</sup> ↔ H6C, H1'G ↔ H8A<sup>1</sup>, H1'C ↔ H2A<sup>3</sup>, H1'C ↔ H2A<sup>4</sup>; the underlined cross-peaks are the extra ones found at 283 K compared to 298 K, see Panel C5], thereby helping for assigning A<sup>1</sup> to A<sup>4</sup>. Temperature-dependent <sup>1</sup>H NMR experiments (data not shown) have been performed from 298 to 283 K (in 5 K steps) to assign the corresponding anomeric protons at 283 K in order to make full assignments of the aromatic protons at 298 K.



**Figure S4C5.** Expanded NOESY spectra (mixing time  $\tau = 800$  ms) of the aromatic (H8/H2/H5/H6) region (8.4 – 7.45 ppm in F1 direction) to the aromatic (H8/H2/H5/H6) and anomeric (H1') region (6.0 – 5.4 ppm in F2 direction) for GpA<sup>1</sup>pA<sup>2</sup>pA<sup>3</sup>pA<sup>4</sup>pC (**8**) at 298 K. The spectra showed some inter-residual cross-peaks [H1'A<sup>1</sup> ↔ H8A<sup>2</sup>, H1'A<sup>2</sup> ↔ H2A<sup>1</sup>, H1'A<sup>3</sup> ↔ H2A<sup>4</sup>, H1'A<sup>4</sup> ↔ H2A<sup>2</sup>, H1'C ↔ H2A<sup>3</sup>], thereby helping for assigning A<sup>1</sup> and A<sup>3</sup>.



**Figure S4C6.** Expanded  $^{31}\text{P}$ - $^1\text{H}$  correlation spectroscopy of  $^{31}\text{P}$  region (-1.6 – 2.5 ppm in F1 direction) to H2'/H3'/H4'/H5'/H5'' region (4.8 – 3.9 ppm in F2 direction) for GpA<sup>1</sup>pA<sup>2</sup>pA<sup>3</sup>pA<sup>4</sup>pC (**8**) at 298 K.