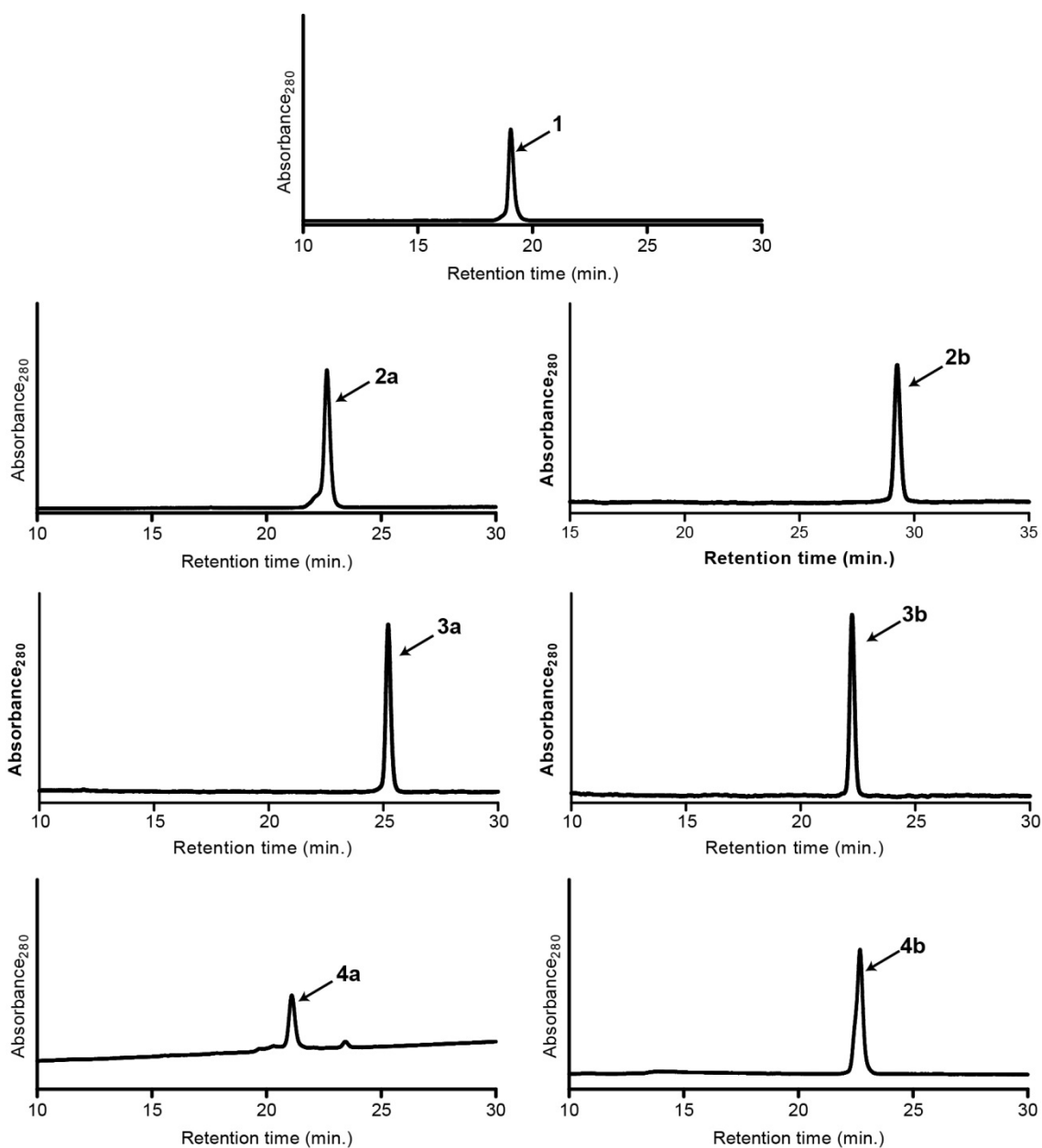


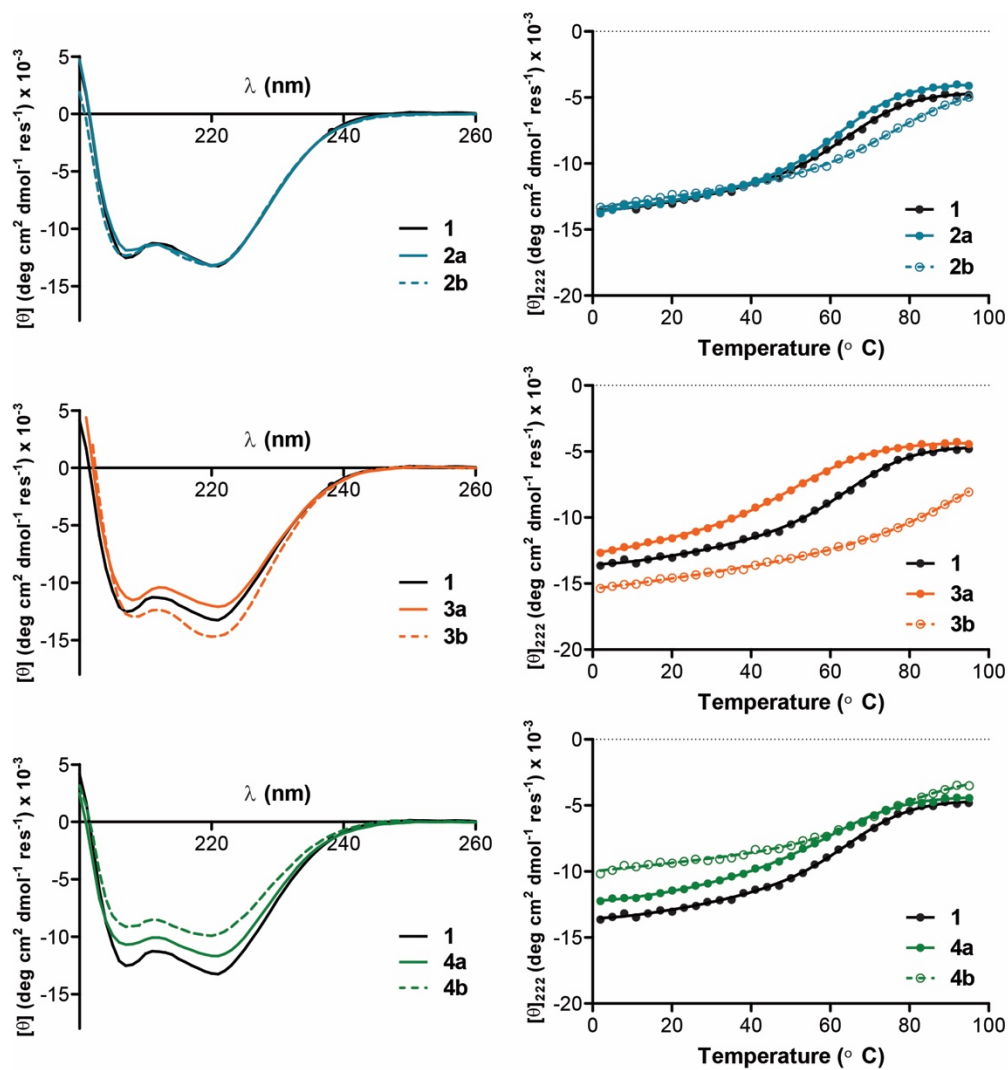
## Thermodynamic Origin of $\alpha$ -Helix Stabilization by Side-Chain Cross-Links in a Small Protein

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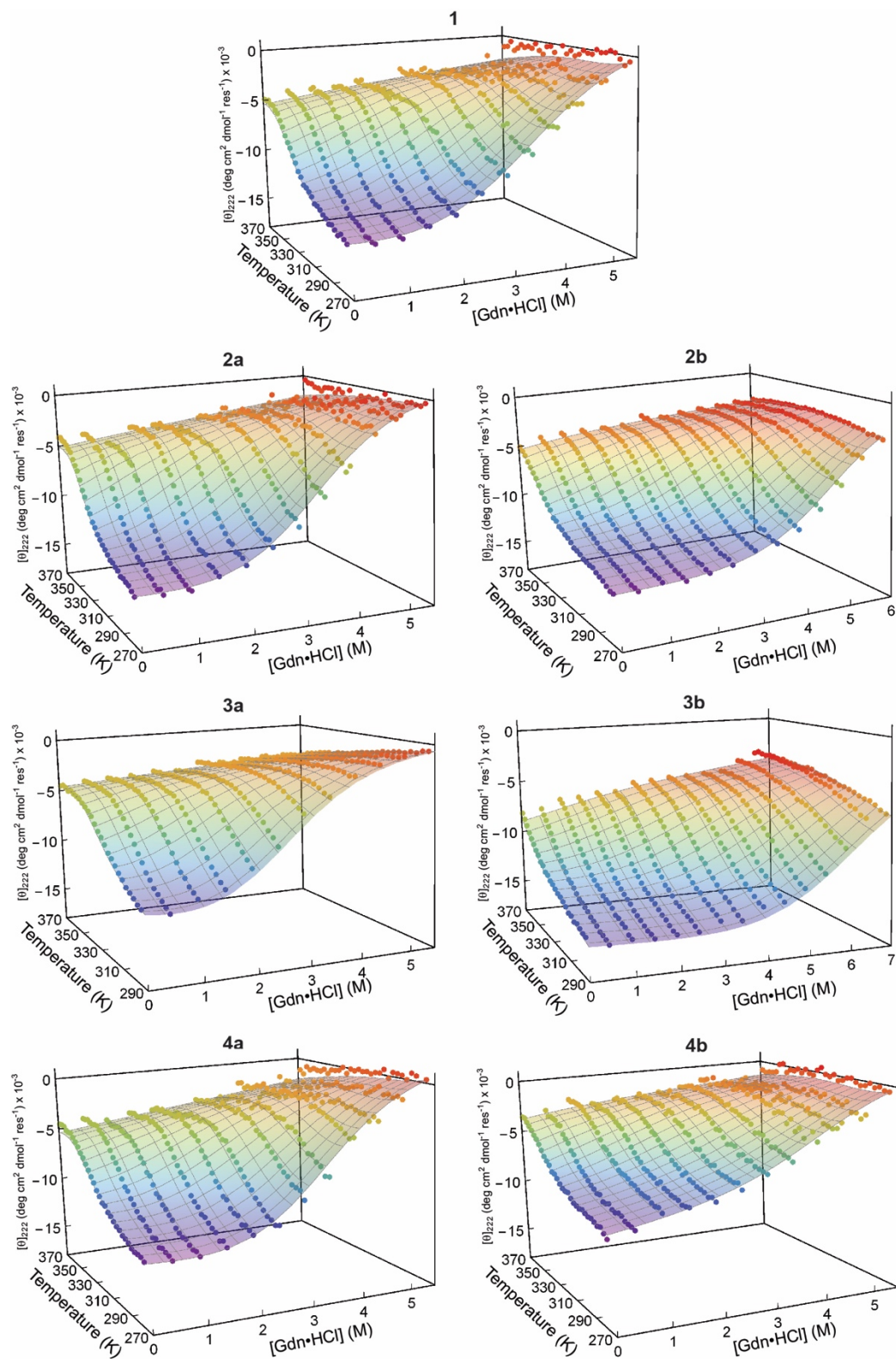
### Supporting Information



**Fig. S1.** Analytical HPLC chromatograms of purified peptides **1**, **2a-4a** and **2b-4b**.



**Fig. S2.** Circular dichroism (CD) data for peptides **1**, **2a-4a** and **2b-4b** at 50  $\mu\text{M}$  concentration. Left: CD scans acquired at 20  $^{\circ}\text{C}$ . Right: CD thermal melts obtained by monitoring molar ellipticity at 222 nm as a function of temperature; circles represent measured ellipticity values, while dashed or solid lines represent the nonlinear fit to a two-state thermal denaturation model.



**Fig. S3.** Thermal-chemical denaturation plots for peptides **1**, **2a-4a** and **2b-4b**. Raw data (points) are fit (surface) to extract thermodynamic parameters for the folding equilibrium.

**Table S1.** MALDI-TOF data for peptides **1**, **2a-4a** and **2b-4b**.

<b>Peptide</b>	<b>[M+H]<sup>+</sup> (<i>m/z</i>)</b>	
	<b>Calculated</b>	<b>Observed</b>
<b>1</b>	4151.3	4151.1
<b>2a</b>	4138.2	4138.0
<b>2b</b>	4120.2	4120.3
<b>3a</b>	4146.8	4146.0
<b>3b</b>	4146.8	4146.5
<b>4a</b>	4212.3	4212.3
<b>4b</b>	4163.2	4163.0