

Influence of Linker Structure on the Affinity of Anion Binding Biscyclopeptides

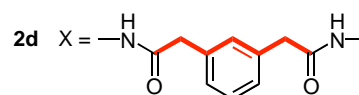
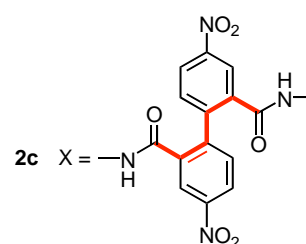
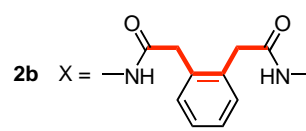
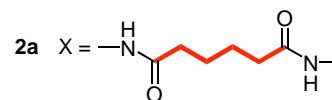
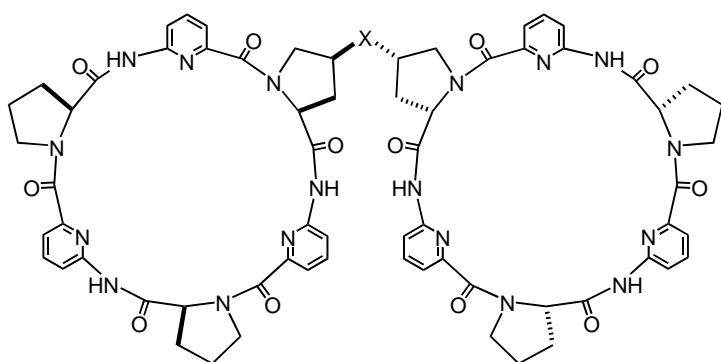
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Structures:

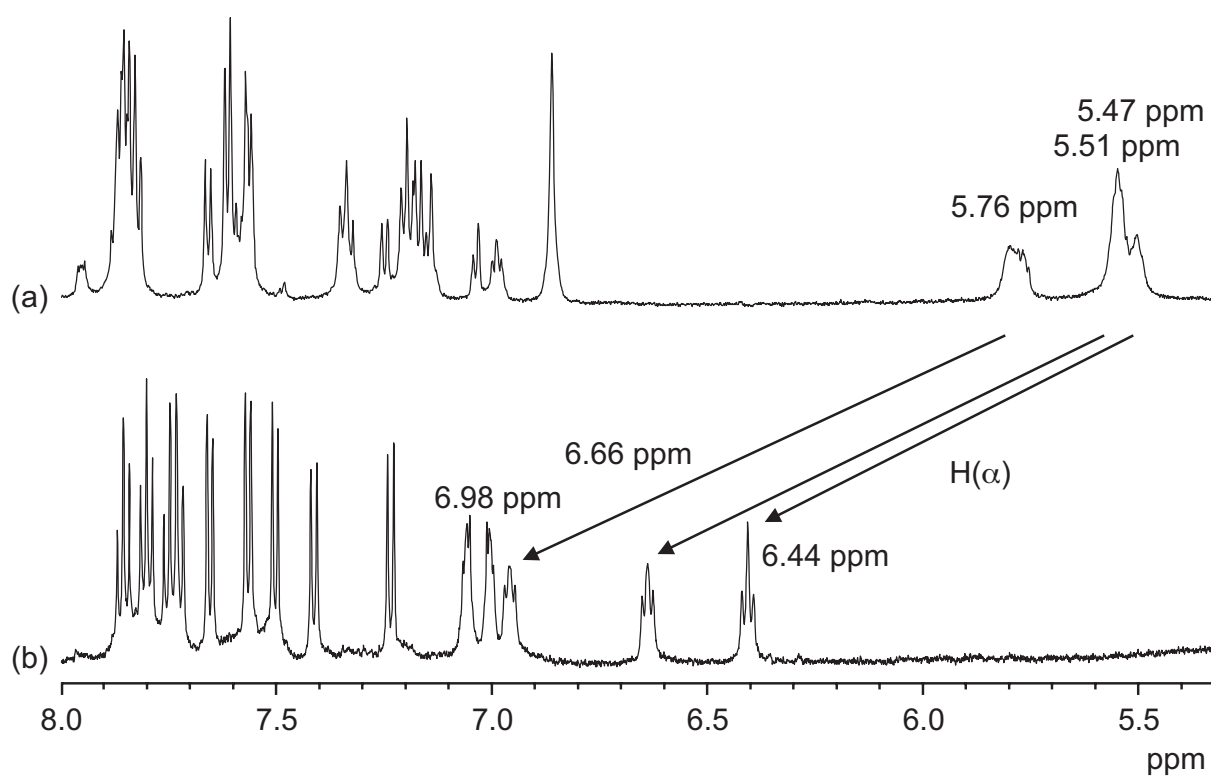


ITC Experiments: Concentrations of biscyclopeptides **2b-d** and of salts in the ITC titrations. All salts were used with sodium as counterion.

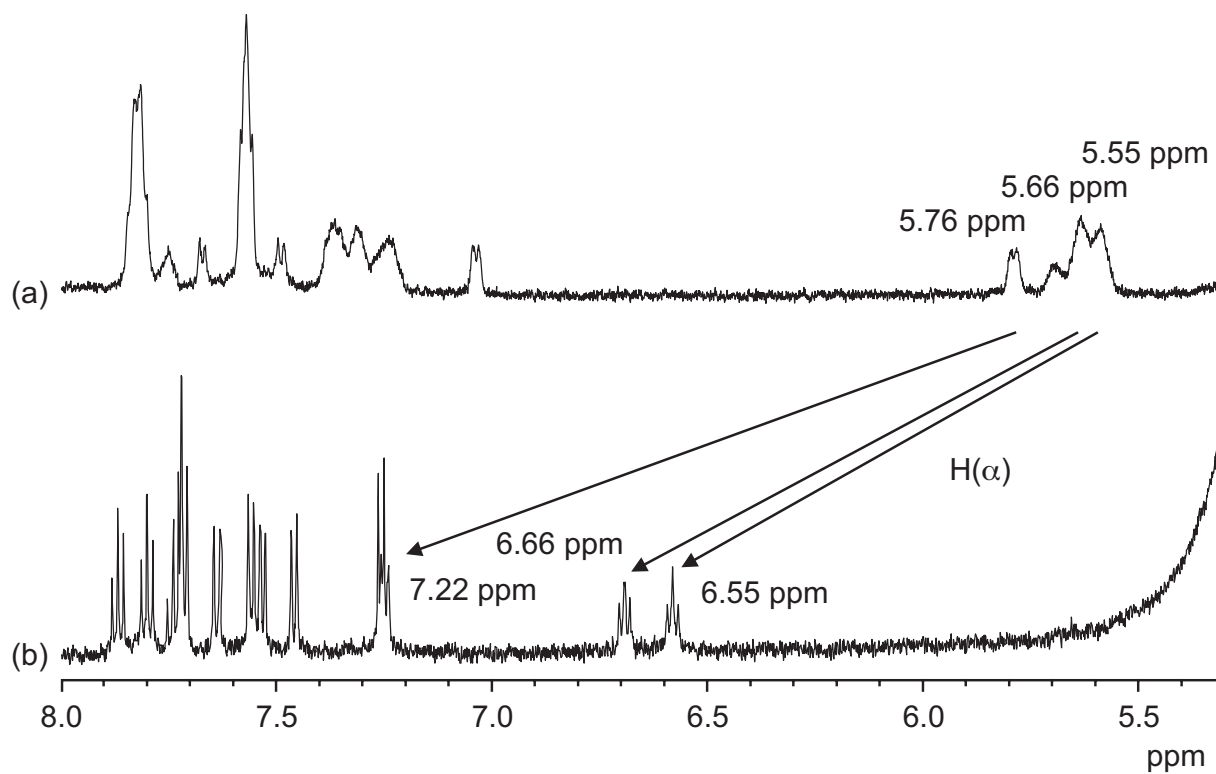
receptor	receptor concentration / mM	sulphate / mM	iodide / mM	bromide / mM	chloride / mM
2b	0.45 mM	14	14	14	40 ^a
2c	0.25 mM	2.5	2.5	5	15
2d	0.25 mM	2.5	5	15	40

^a A receptor concentration of 0.5 mM was used in this titration.

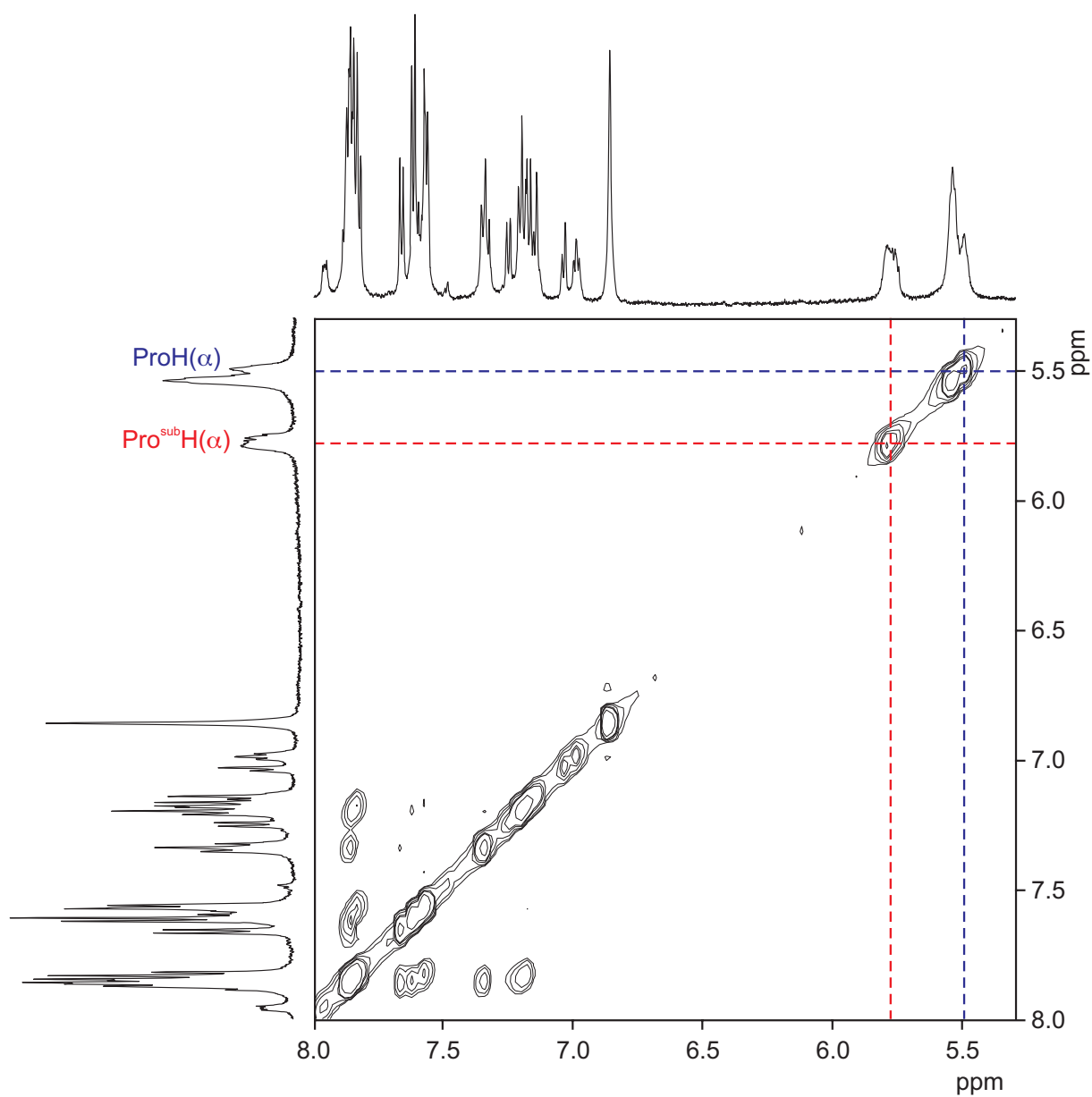
^1H NMR spectrum: **2b** (1 mM) in $\text{D}_2\text{O}/\text{CD}_3\text{OD}$ 1:1 (a), **2b** (1 mM) + 5 equiv of Na_2SO_4 in $\text{D}_2\text{O}/\text{CD}_3\text{OD}$ 1:1 (b).



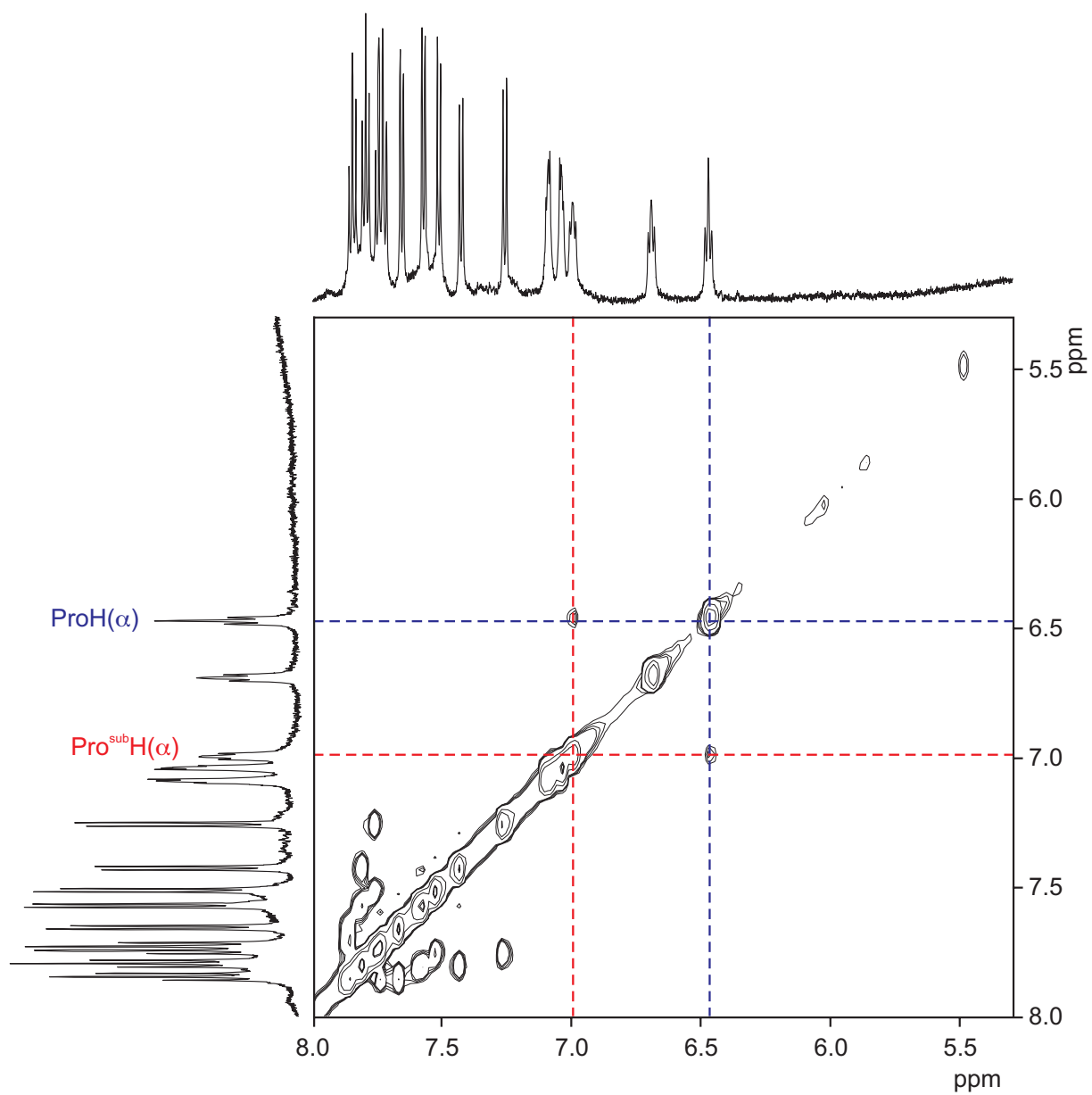
^1H NMR spectrum: **2c** (1 mM) in $\text{D}_2\text{O}/\text{CD}_3\text{OD}$ 1:1 (a), **2c** (1 mM) + 5 equiv of Na_2SO_4 in $\text{D}_2\text{O}/\text{CD}_3\text{OD}$ 1:1 (b).



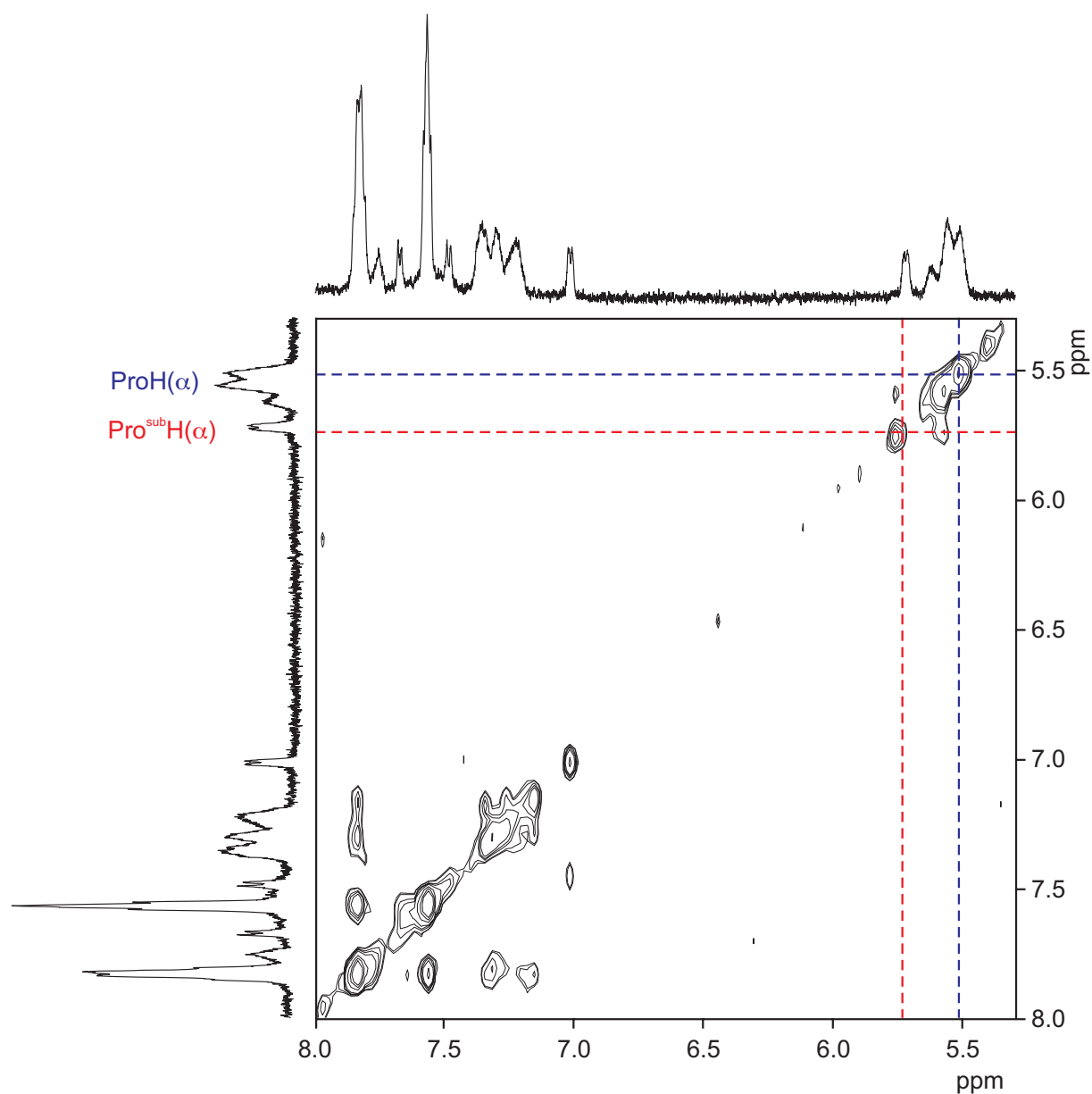
NOESY NMR spectrum: 2b (1 mM) in D₂O/CD₃OD 1:1 (mixing time 300 ms) (Bruker Avance 600).



NOESY NMR spectrum: 2b (1 mM) + 5 equiv of Na₂SO₄ in D₂O/CD₃OD 1:1 (mixing time 300 ms) (Bruker Avance 600).

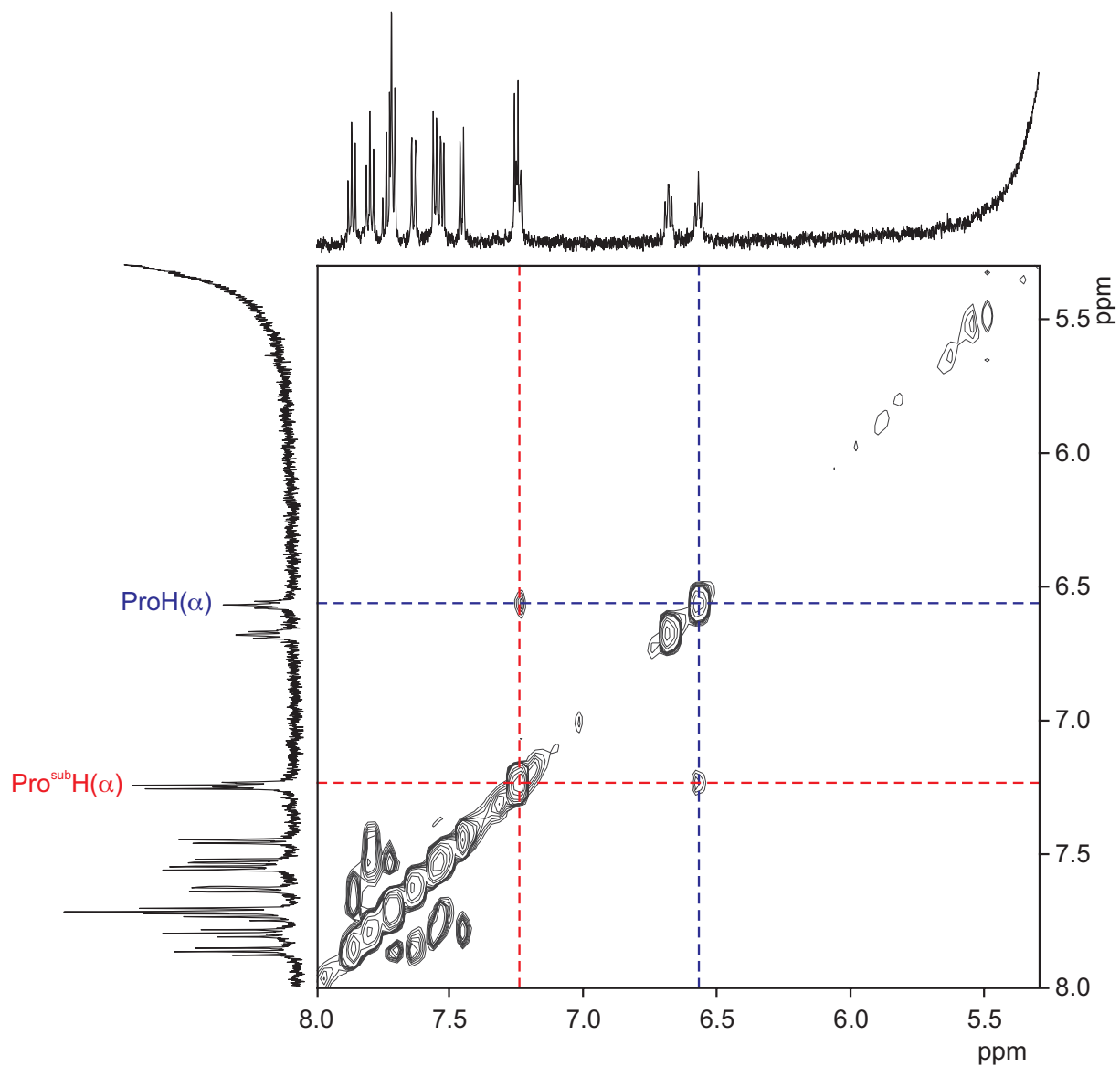


NOESY NMR spectrum: 2c (1 mM) in D₂O/CD₃OD 1:1 (mixing time 300 ms) (Bruker Avance 600).

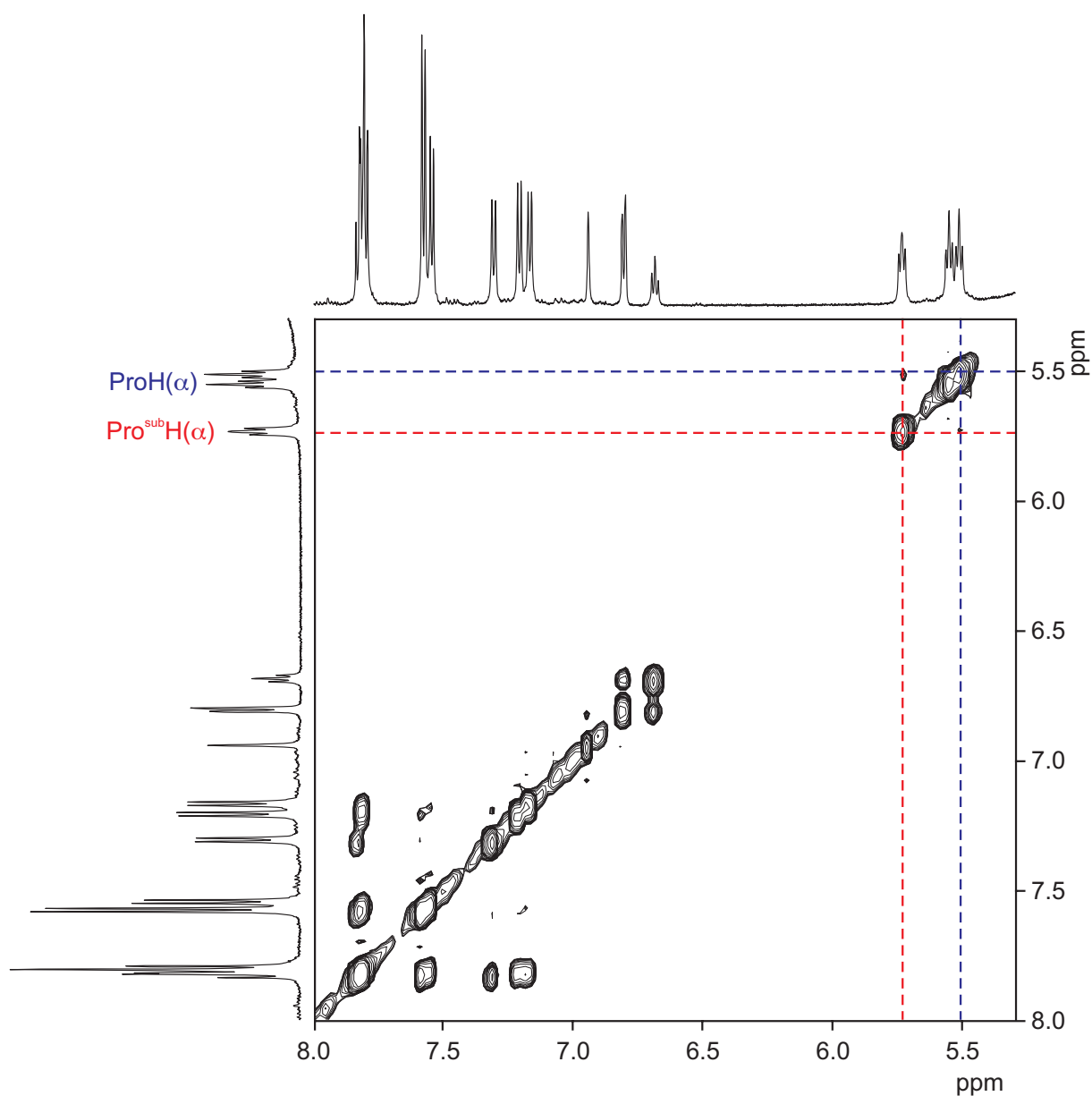


NOESY NMR spectrum: 2c (1 mM) + 5 equiv of Na₂SO₄ in D₂O/CD₃OD 1:1 (mixing time 300 ms)

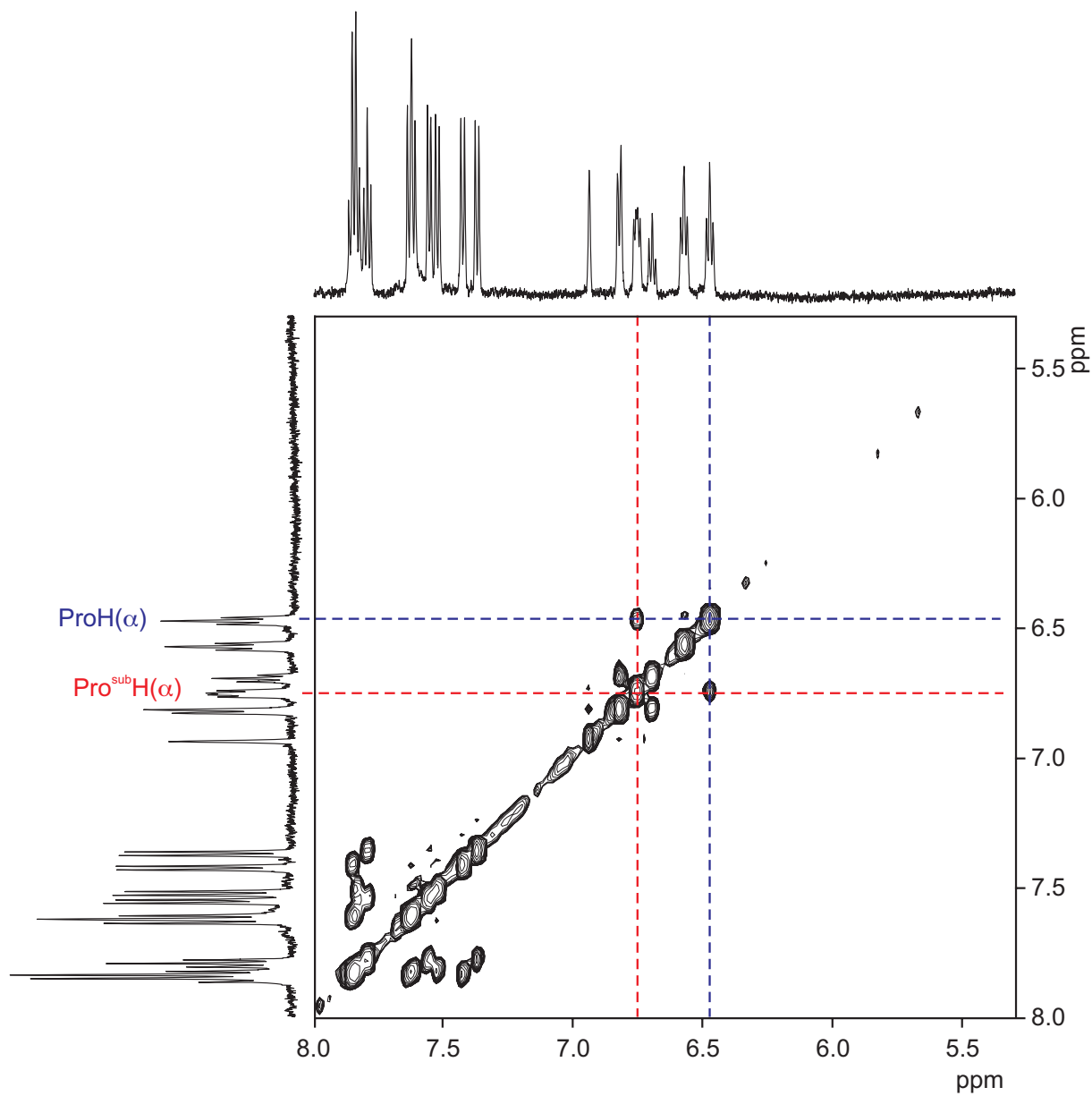
(Bruker Avance 600).



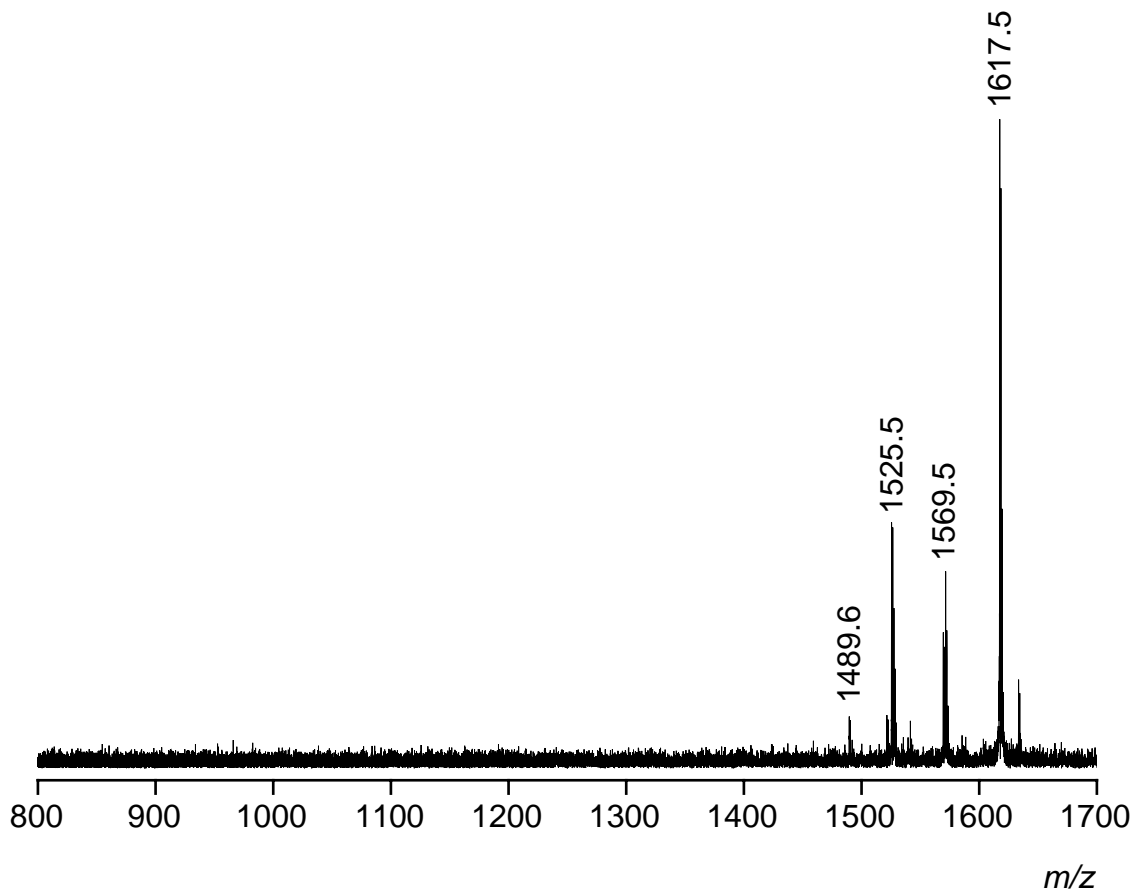
NOESY NMR spectrum: 2d (1 mM) in D₂O/CD₃OD 1:1 (mixing time 300 ms) (Bruker Avance 600).



NOESY NMR spectrum: 2d (1 mM) + 1 equiv of Na₂SO₄ in D₂O/CD₃OD 1:1 (mixing time 300 ms) (Bruker Avance 600).

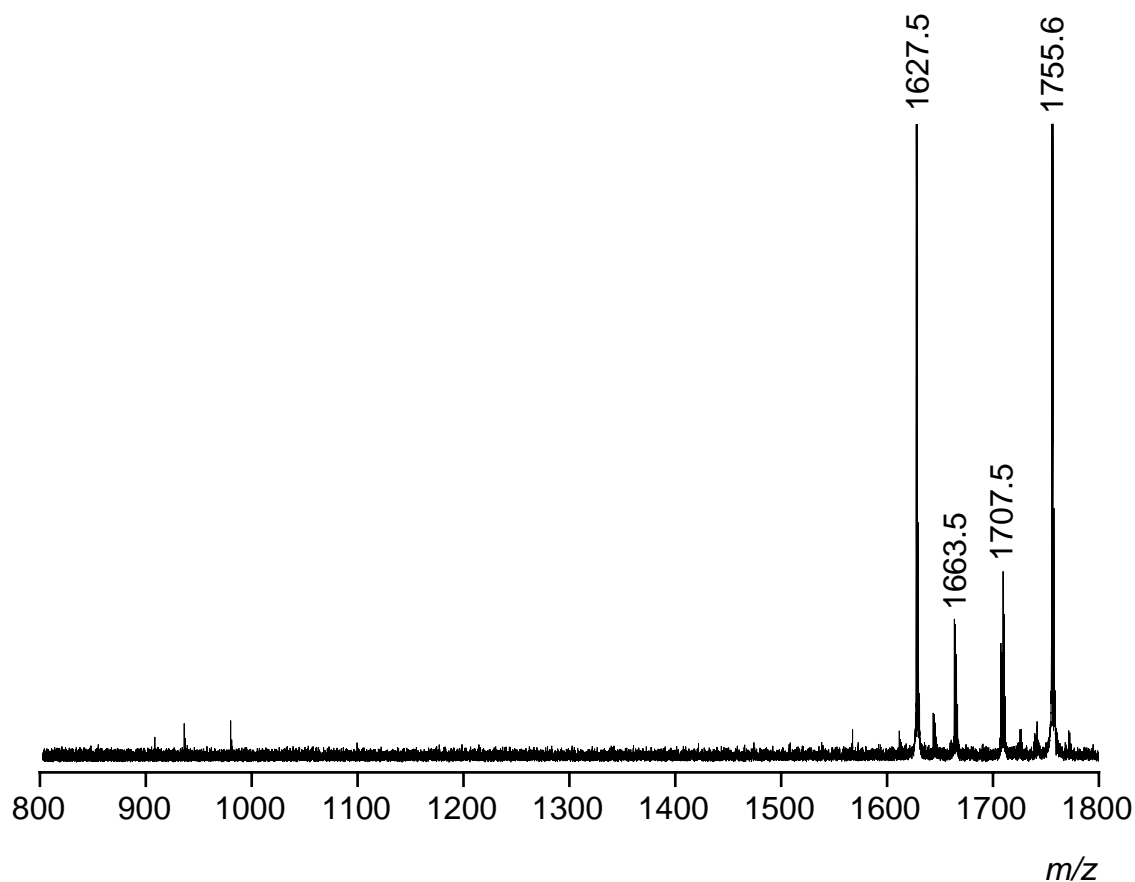


ESI mass spectrum: 2b in 1:1 (v/v) water/methanol (0.1 mM) after the addition of 0.33 equivalents of each NaCl, NaBr, and NaI.



		<i>m/z calcd.</i>	<i>m/z exp.</i>
2b - H ⁺	C ₇₆ H ₇₃ N ₂₀ O ₁₄	1489.6	1489.6
2b + Cl ⁻	C ₇₆ H ₇₄ N ₂₀ O ₁₄ · Cl	1525.5	1525.5
2b + Br ⁻	C ₇₆ H ₇₄ N ₂₀ O ₁₄ · Br	1569.5	1569.5
2b + I ⁻	C ₇₆ H ₇₄ N ₂₀ O ₁₄ · I	1617.5	1617.5

ESI mass spectrum: 2c in 1:1 (v/v) water/methanol (0.1 mM) after the addition of 0.33 equivalents of each NaCl, NaBr, and NaI.



		<i>m/z calcd.</i>	<i>m/z exp.</i>
2c - H ⁺	C ₈₀ H ₇₁ N ₂₂ O ₁₈	1627.5	1627.5
2c + Cl ⁻	C ₈₀ H ₇₂ N ₂₂ O ₁₈ · Cl	1663.5	1663.5
2c + Br ⁻	C ₈₀ H ₇₂ N ₂₂ O ₁₈ · Br	1707.5	1707.5
2c + I ⁻	C ₈₀ H ₇₂ N ₂₂ O ₁₈ · I	1755.4	1755.6