Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Supplementary information

Effect of ester chemical structure and peptide bond conformation in fragmentation pathways of differently metal cationized cyclodepsipeptides

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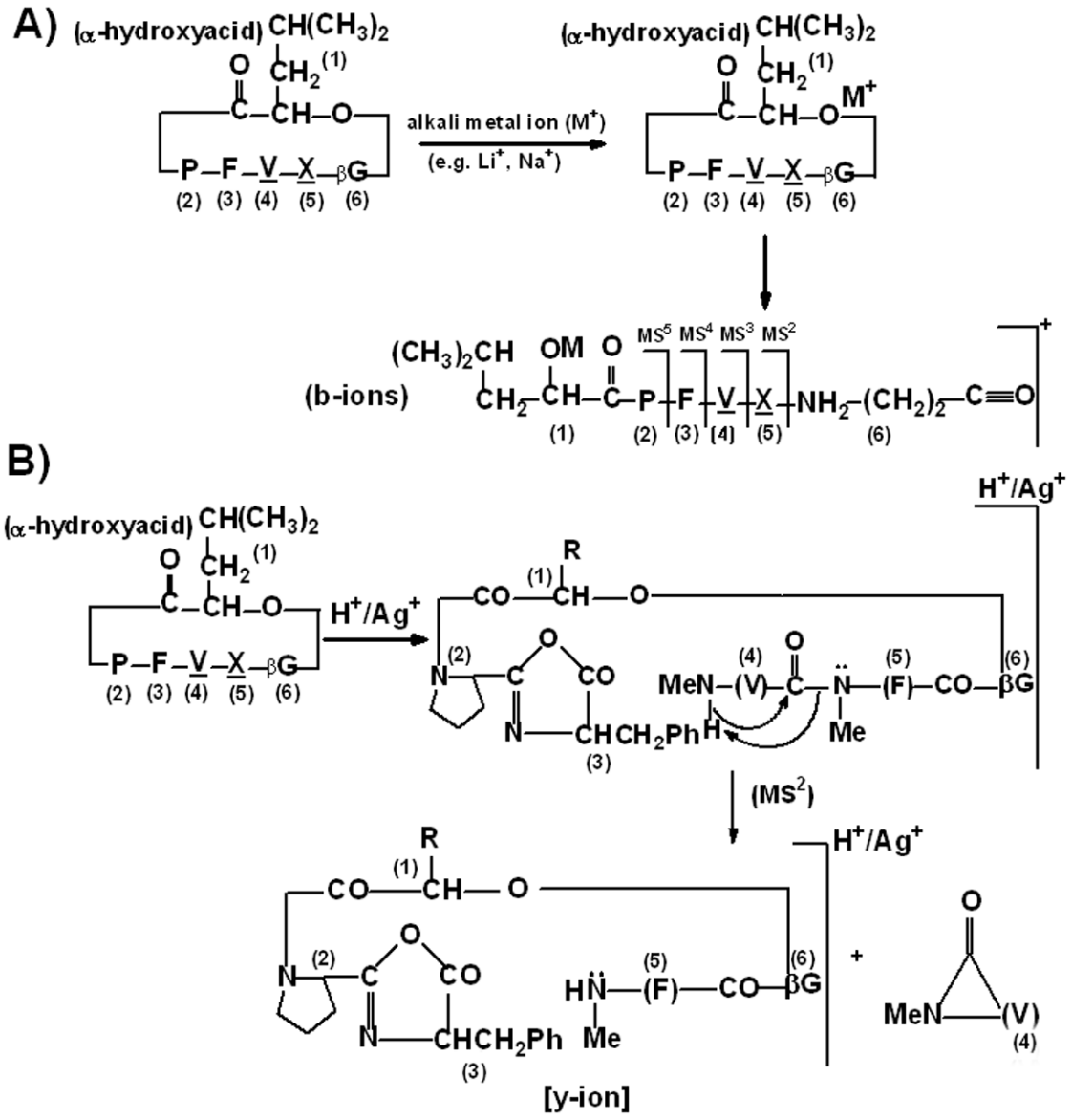
Short title: MS^n analysis of metal ion added cyclodepsipeptide



Scheme S1: Schematic representation of plausible mechanism for **(A)** generation of b-ions in presence of alkali metal ions (e.g. Li^+, Na^+) and **(B)** generation of y-ions in presence of H^+ and Ag^+ from isaridin molecules

Table S1

a) Formation of product ions (m/z) from protonated and several metal-ion adducts of isariin-II (MW 567.4 Da) and isariin-III (MW 567.3 Da) during MS^n experiments along with the assigned partial sequence information obtained from fragmentation study

Metal ions	MS (m/z)	MS^2 (m/z)	MS^3 (m/z)	MS^4 (m/z)	MS^5 (m/z)	MS^6 (m/z)	Partial sequence
Isariin-II							
H^+	568.5	469.2	398.1	284.9			LAV (b-ions)
Na^+	590.4	491.1	307.0				LAV (b-ions)
K^+	606.4	507.3	436.2	322.9			LAV (b-ions)
Li^+	574.4	475.2	404.2	291.0	191.9		VLAV (b-ions)
Ag^+	676.3	577.0	506.1	392.8	293.9	236.8	GVLAV (b-ions)
Isariin-III							
H^+	568.5	497.1	426.0	313.1	213.9		VLAA (b-ions)
Na^+	590.2	519.2	448.1	335.0	235.9		VLAA (b-ions)
K^+	606.4	535.1	464.2	351.0			LAV (b-ions)
Li^+	574.3	503.2	432.1	319.0	219.8		VLAA (b-ions)
Ag^+	676.4	605.1	534.0	420.9			VLAA (b-ions)

Continued…

b) Formation of product ions (m/z) from protonated and several metal-ion adducts of isaridin-I (MW 655.4 Da) and isaridin-III (717.5 Da) during MS^n experiments along with the assigned partial sequence information obtained from fragmentation study

Metal ions	MS (m/z)	MS^2 (m/z)	MS^3 (m/z)	MS^4 (m/z)	MS^5 (m/z)	MS^6 (m/z)	Partial sequence
Isaridin-I							
H^+	656.4	543.2	430.1	359.1	244.9		V-V-βG-αHyL (y-ions)*
	656.4		472.2	359.1	211.9		F-V-V-βG (b-ions)
Na^+	678.5	606.7		381.1	233.9		F-V-V-βG (b-ions)*
	678.5	547.2 ($-H_2O$)	434.2	363.1			V-V-βG (y-ions)
K^+	694.5	563.1 (581-H_2O)					V-V-βG (y-ions) [from MS^2]
Li^+	662.4	590.2	478.2	365.0	217.9		F-V-V-βG (b-ions)
Ag^+	762.3 (764.3)	649.1	536.0	465.1	350.9		V-V-βG-αHyL (y-ions)
Isaridin-III							
H^+	718.4	605.3	444.2	373.1			V-F-βG (y-ions)*
	718.4		486.2	373.1			VFβG (b-ions)
Na^+	740.5	627.3	466.2	395.1			VFβG (y-ions)
	740.5	651.3	508.2	395.1	248.0		FVFβG (b-ions)*
K^+	756.4	643.2	482.1	410.9			V-F-βG (y-ions)
	756.4	524.2	411.1				V-F-βG (b-ions)
Li^+	724.4	635.2 (653.2-H_2O)	492.2 (474.2)	379.0	231.9		F-V-F-βG (b-ions))
Ag^+	826.2 (824.2)	713.2	534.1 (552.1-H_2O)	463.0	349.0		V-F-βG-αHyL (y-ions)

(* indicated more intense peaks in case of mixed b and y -ions)

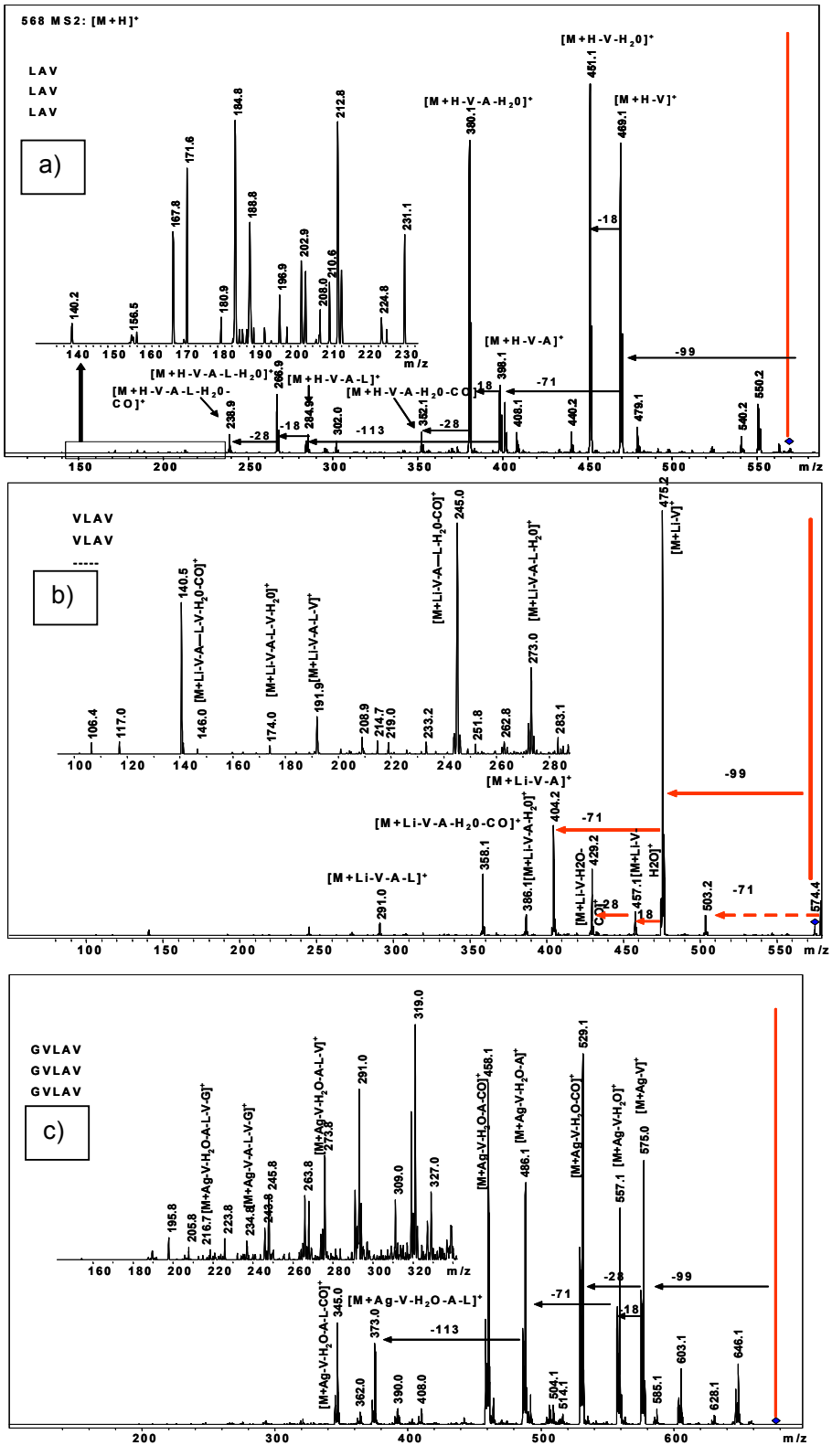


Figure S1. Presentation of MS^2 data of β-hydroxyacid containing peptide isariin-II (molecular mass 567.4) as a) protonated species, b) Li^+ adduct and c) Ag^+ adduct

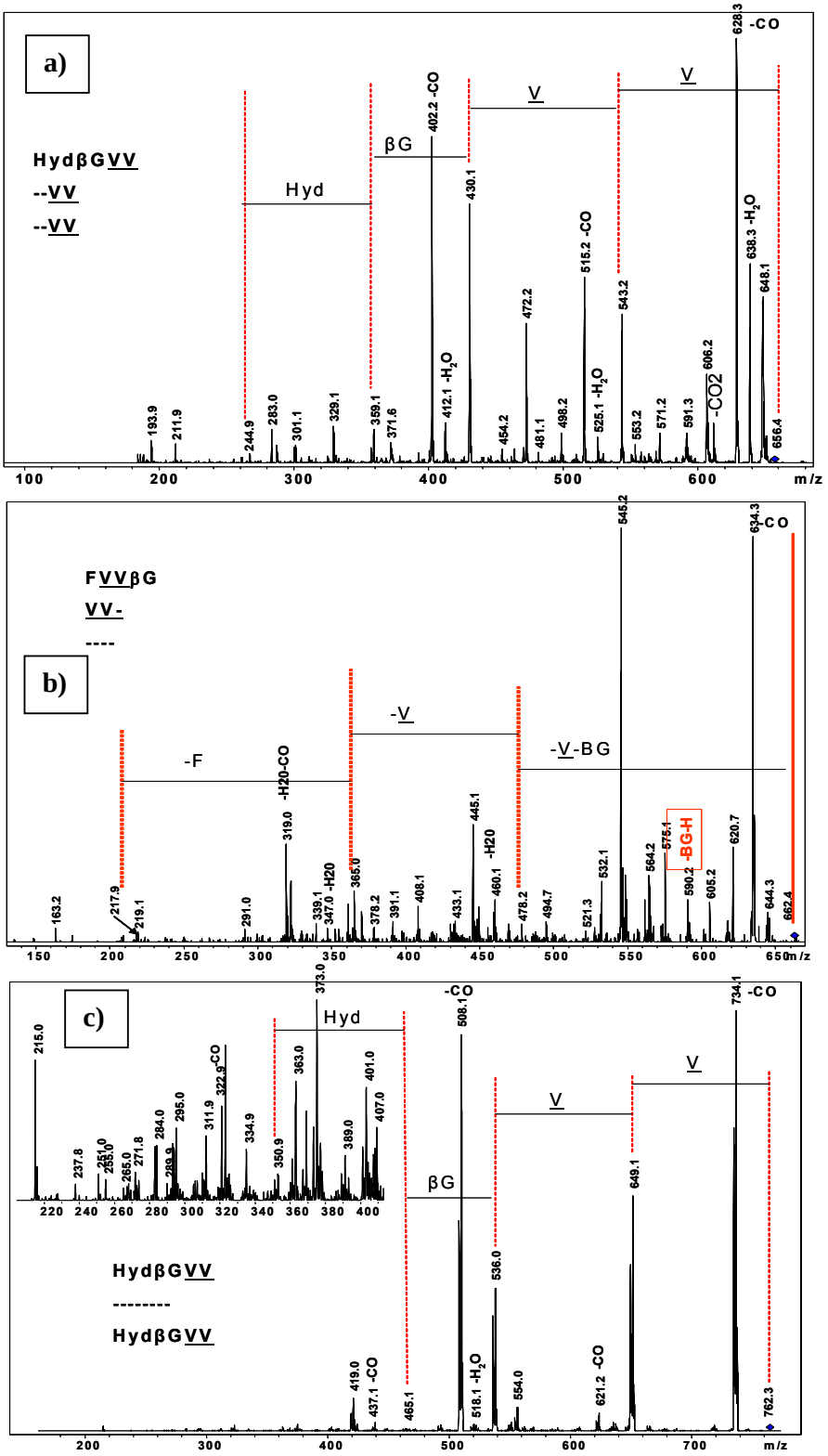


Figure S2. Presentation of MS^2 data of α-hydroxyacid containing peptide isaridin-I (molecular mass 655.4) as a) protonated species, b) Li^+ adduct and c) Ag^+ adduct

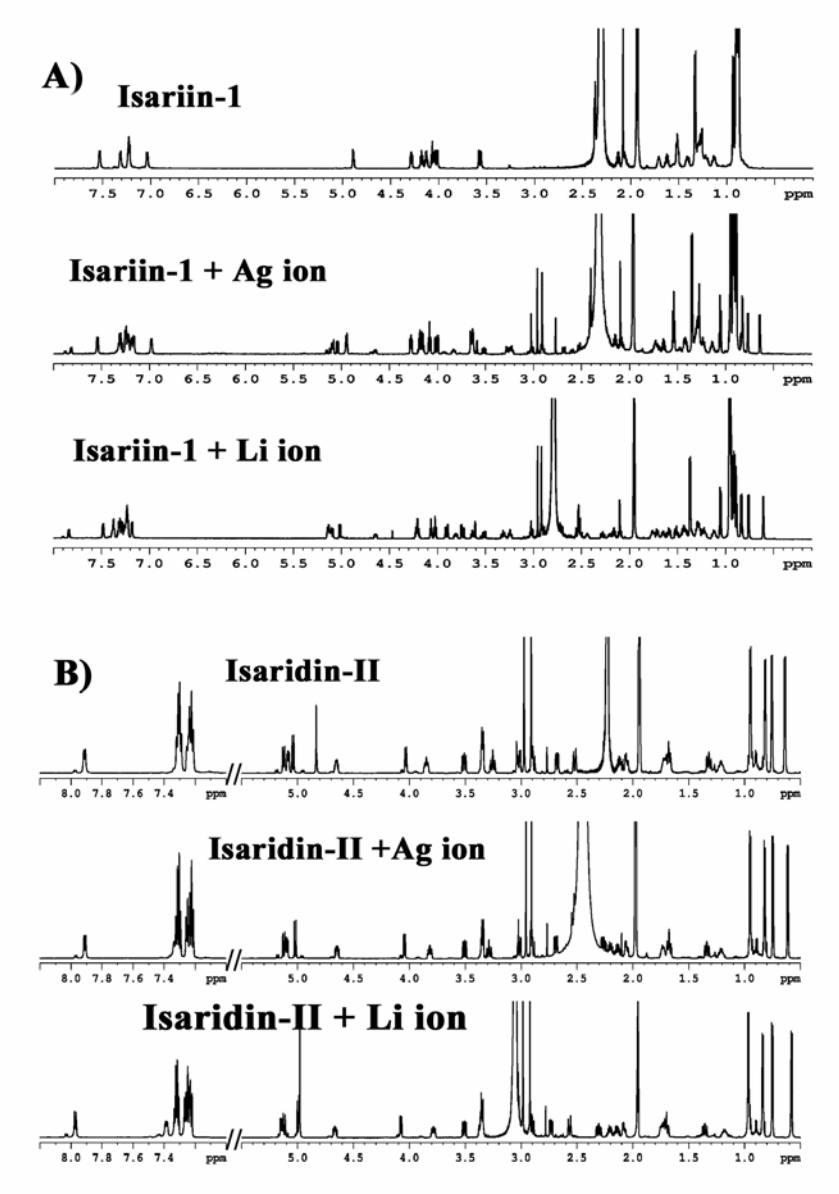


Figure S3: 1D ^{1}H-NMR spectra of free and metal ion (Ag^{+} and Li^{+}) complexes of A) isariin-I and B) isaridin-II, recorded on a Bruker AV 700 system attached with a cryo probe

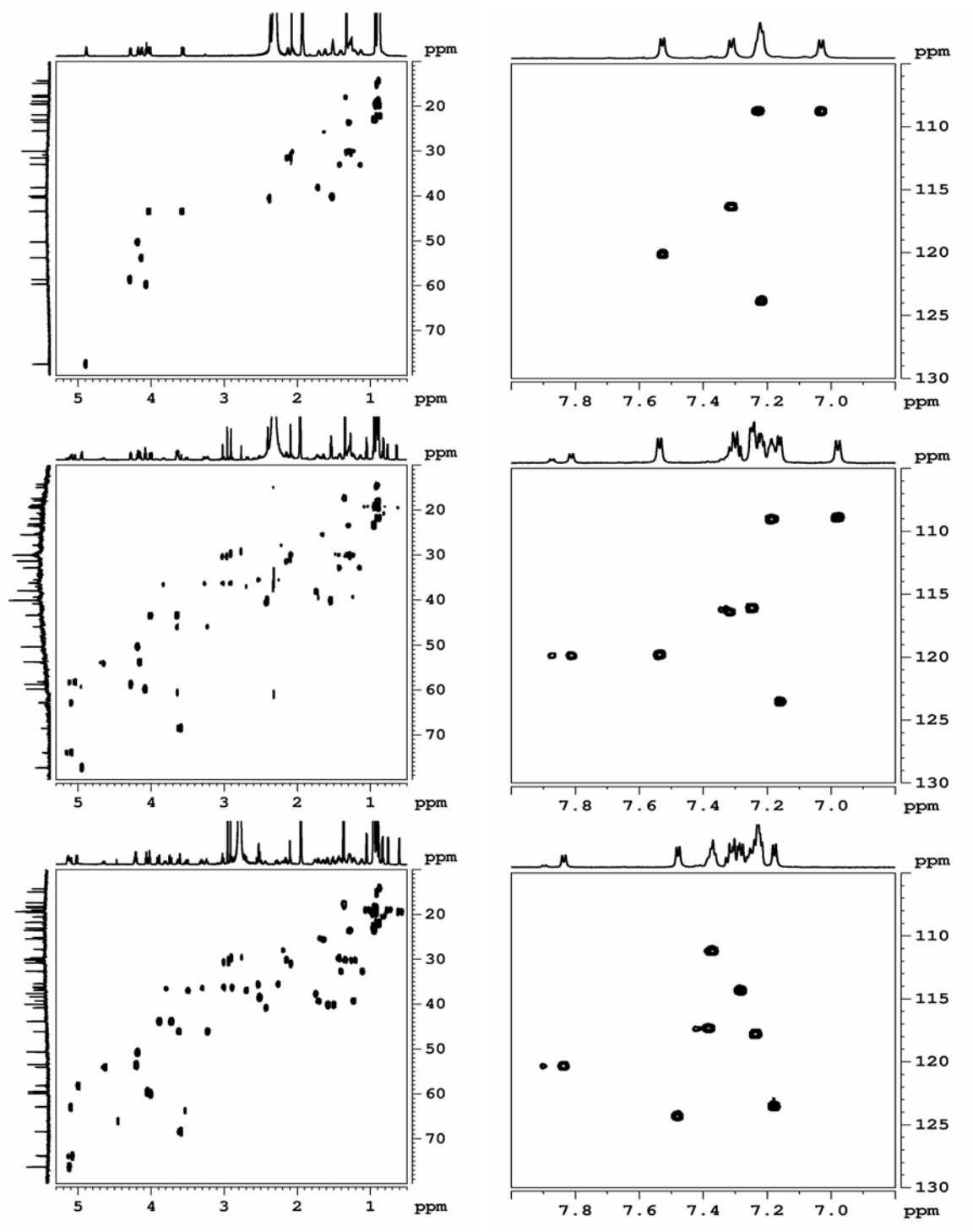
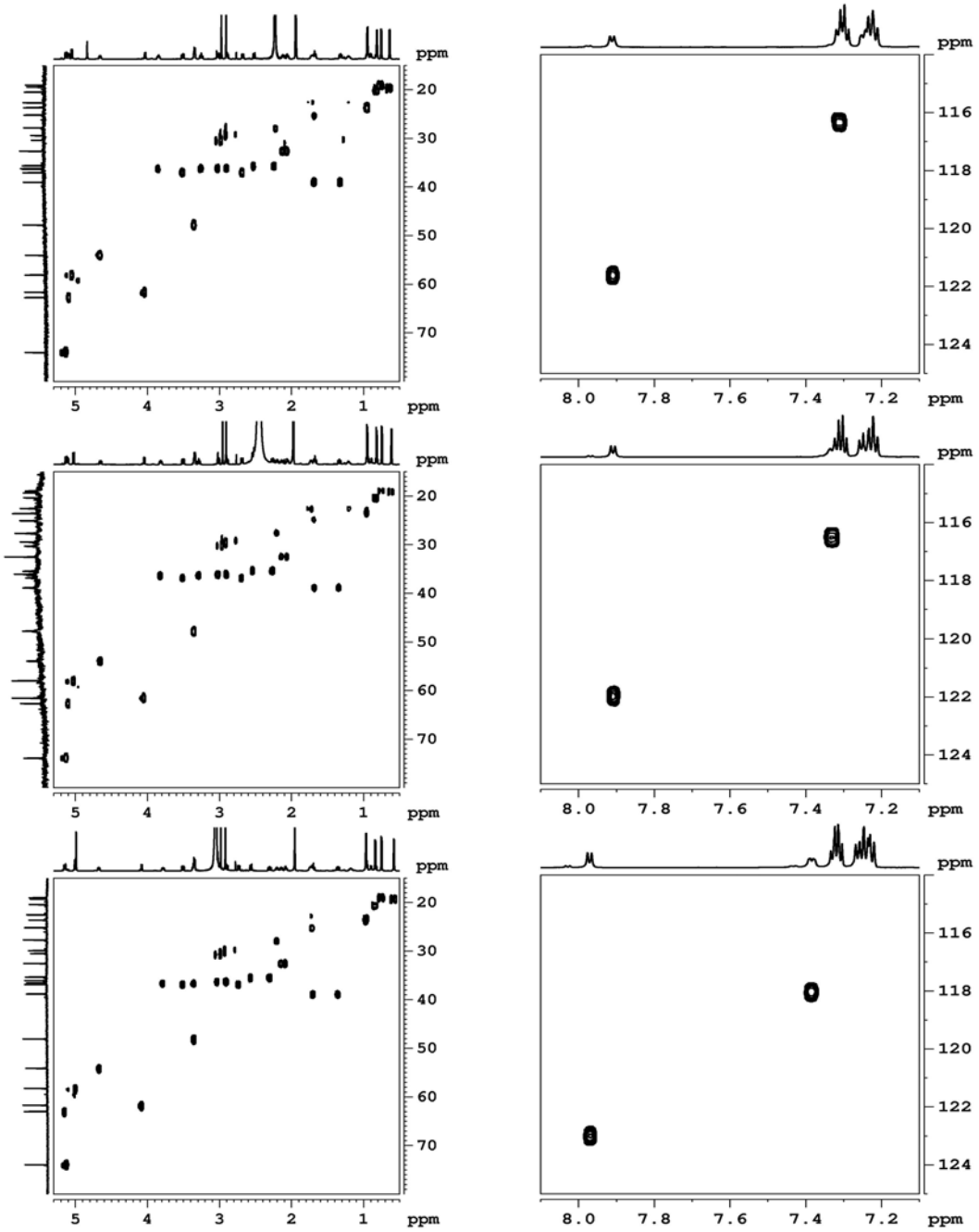


Figure S4. 2D NMR data of free and metal ion adduct of β-hydroxy acid containing peptide isariin-I (Molecular Mass 595.4): Panel A: ^{1}H-^{13}C HSQC and Panel B: ^{1}H-^{15}N HSQC. Top row: Free isariin-I, Middle row: isariin-I+ $AgClO_4$, Bottom row: isariin-I + $LiClO_4$.



Panel – A Panel – B

Figure S5. 2D NMR data of free and metal ion adduct of α-hydroxy acid containing peptide isaridin-II (Molecular Mass 703.4): Panel A: ^{1}H-^{13}C HSQC and Panel B: ^{1}H-^{15}N HSQC. Top row: Free isaridin-II, Middle row: isaridin-II+ $AgClO_4$, Bottom row: isaridin-II + $LiClO_4$.

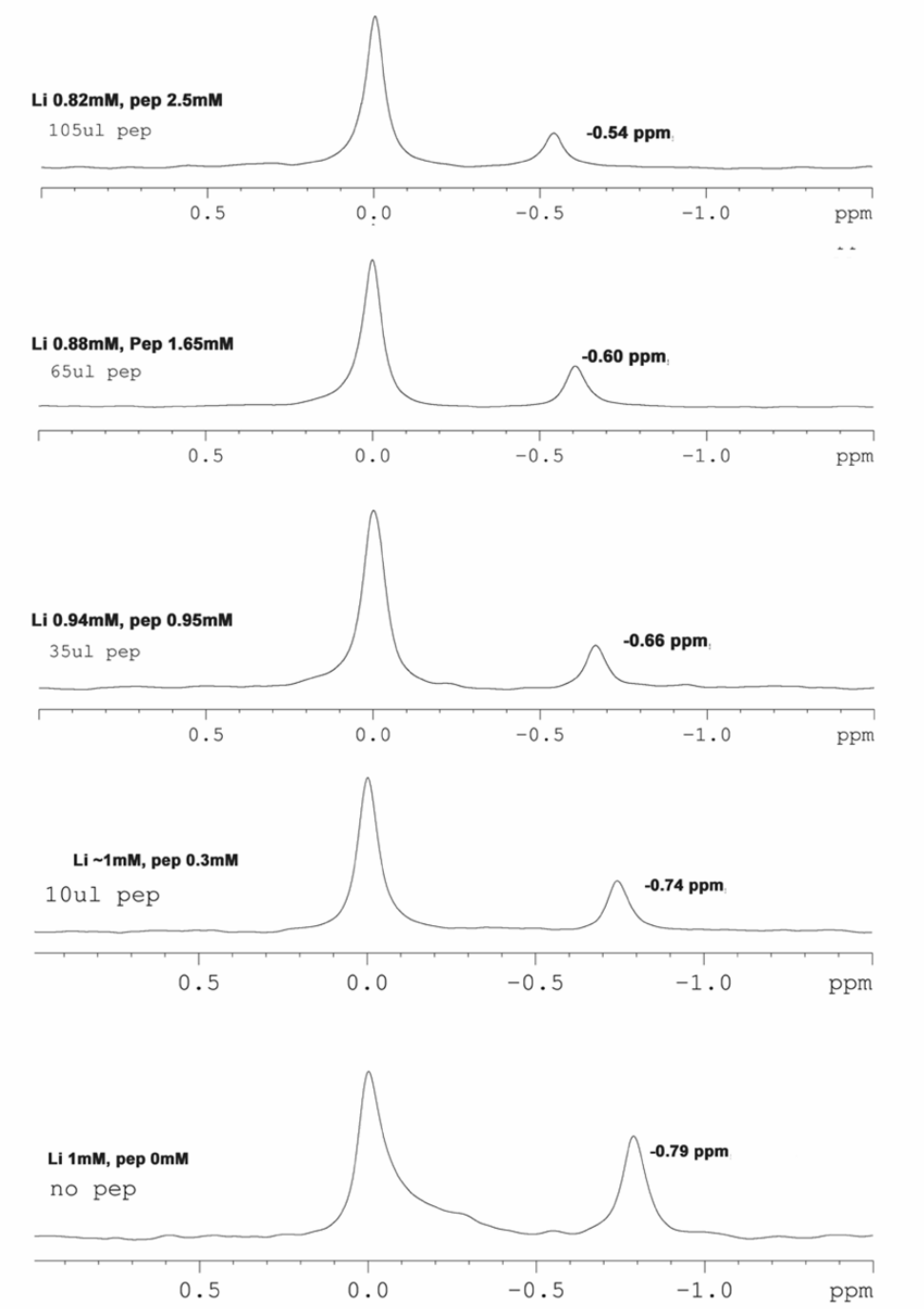


Figure S6. Change in Chemical shift of ^{7}Li upon successive addition of isaridin-II molecule (molecular mass 703.4) in CD_3CN solution using LiCl in H_2O as external reference