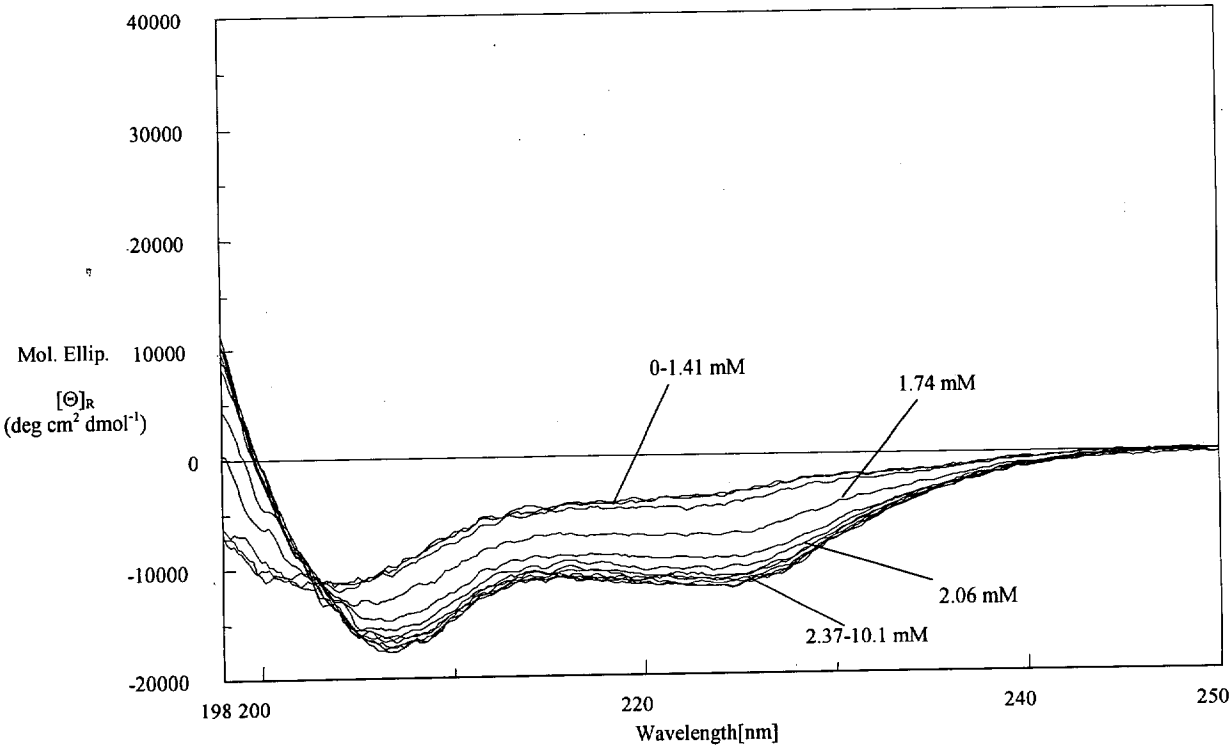
SUPPORTING INFORMATION

a



b

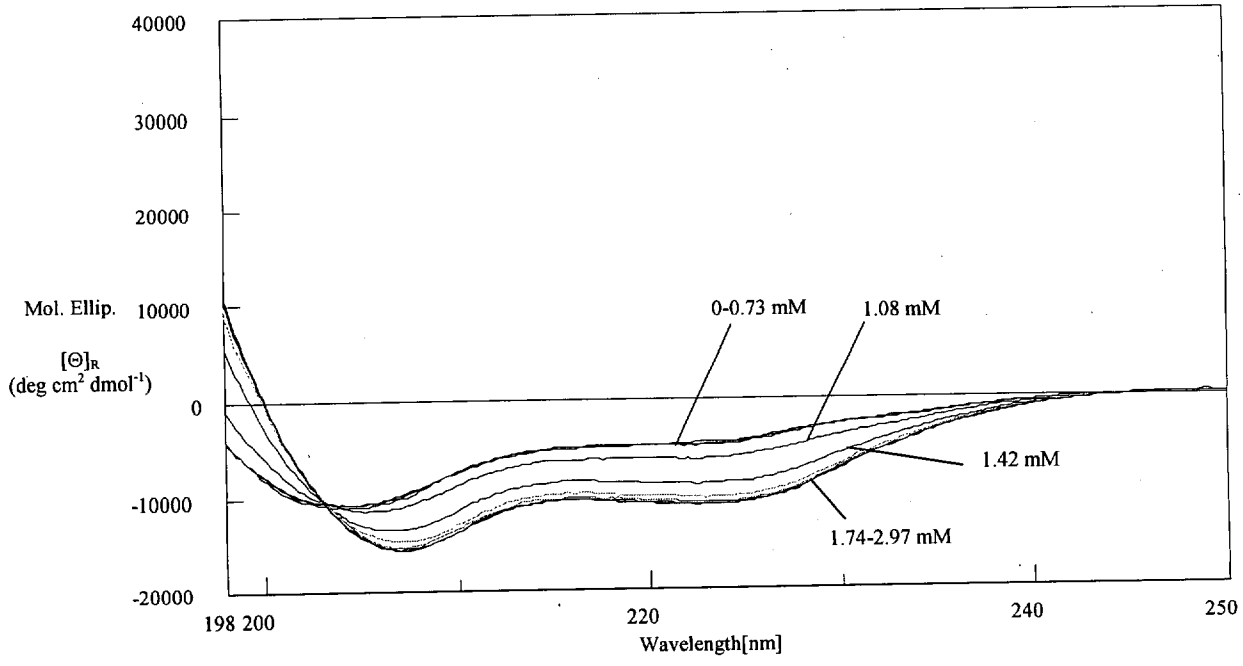


Figure 1. CD spectra of analog **I** (a) $5.2 \cdot 10^{-5}$ M and **II** (b) $4.24 \cdot 10^{-5}$ M, in water at increasing concentrations of DPC (indicated in the spectra).

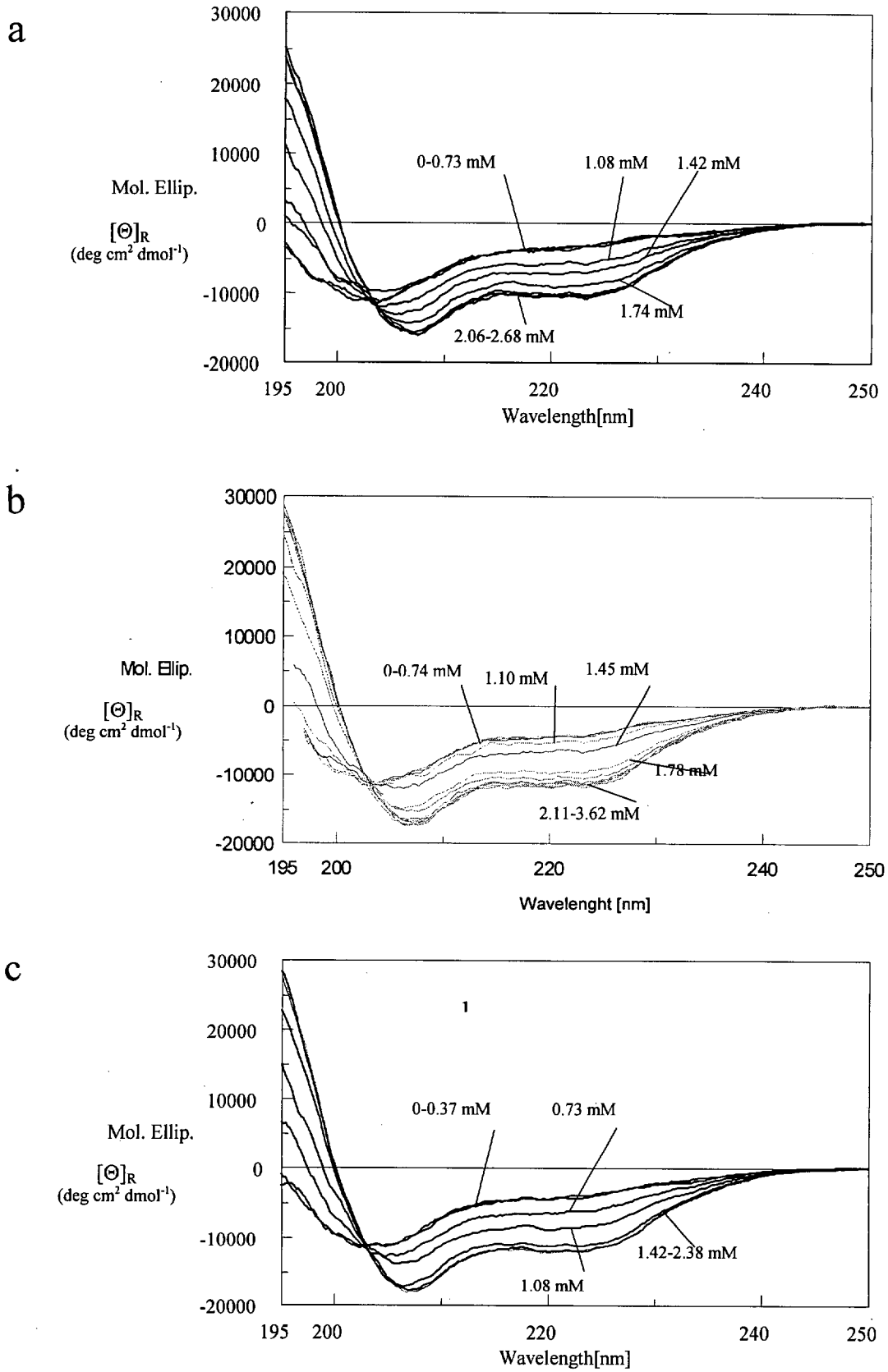


Figure 2. CD spectra of analog **III** (a) $4.91 \cdot 10^{-5}$M, analog **IV** $5.0 \cdot 10^{-5}$M (b), analog **V** (c) $5.22 \cdot 10^{-5}$M in water at increasing concentrations of DPC (indicated in the spectra).

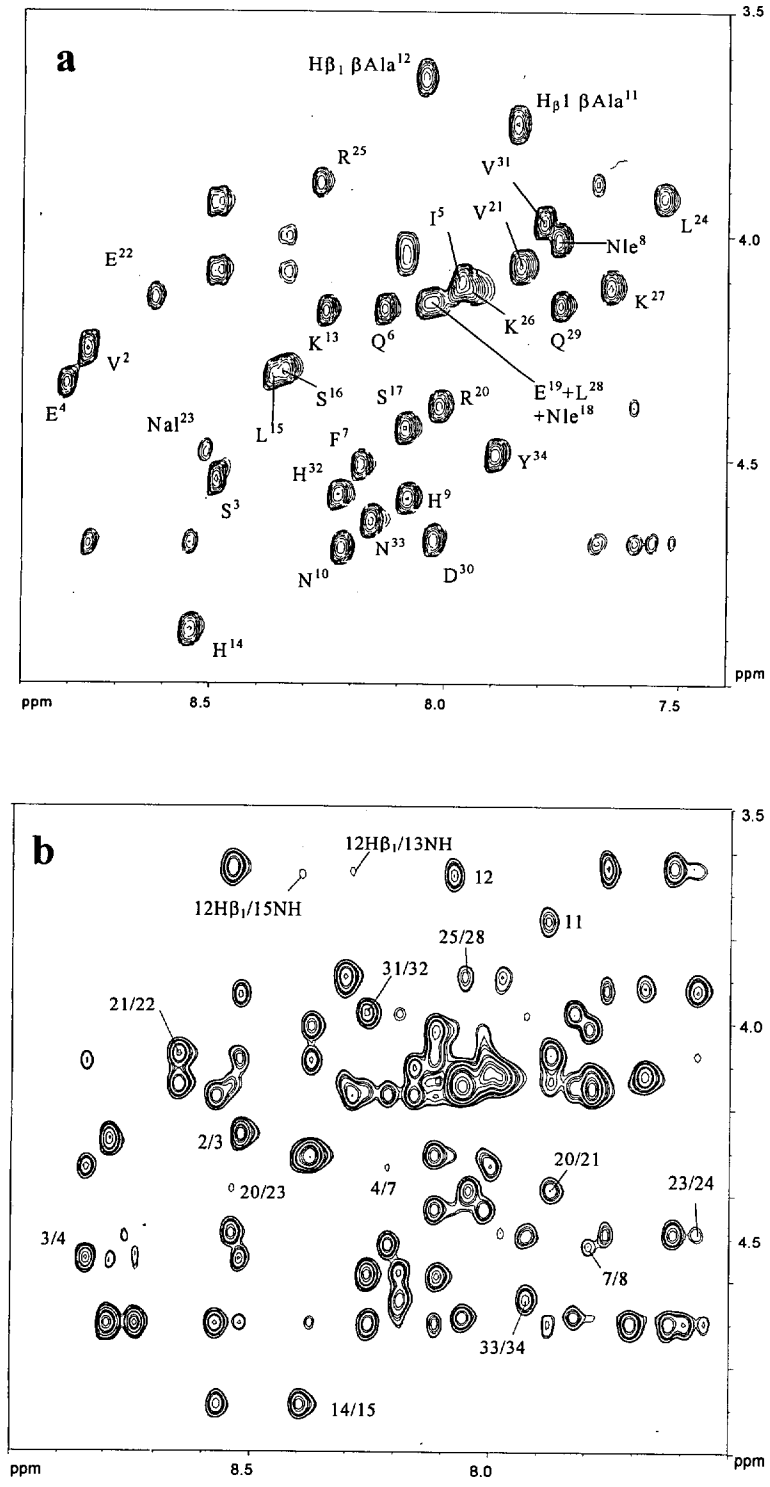


Figure 3. Fingerprint region of the TOCSY (a) and NOESY (b) spectra at 600 MHz of a 1.5 mM solution of **analog I,** in DPC micelles, T=313K.

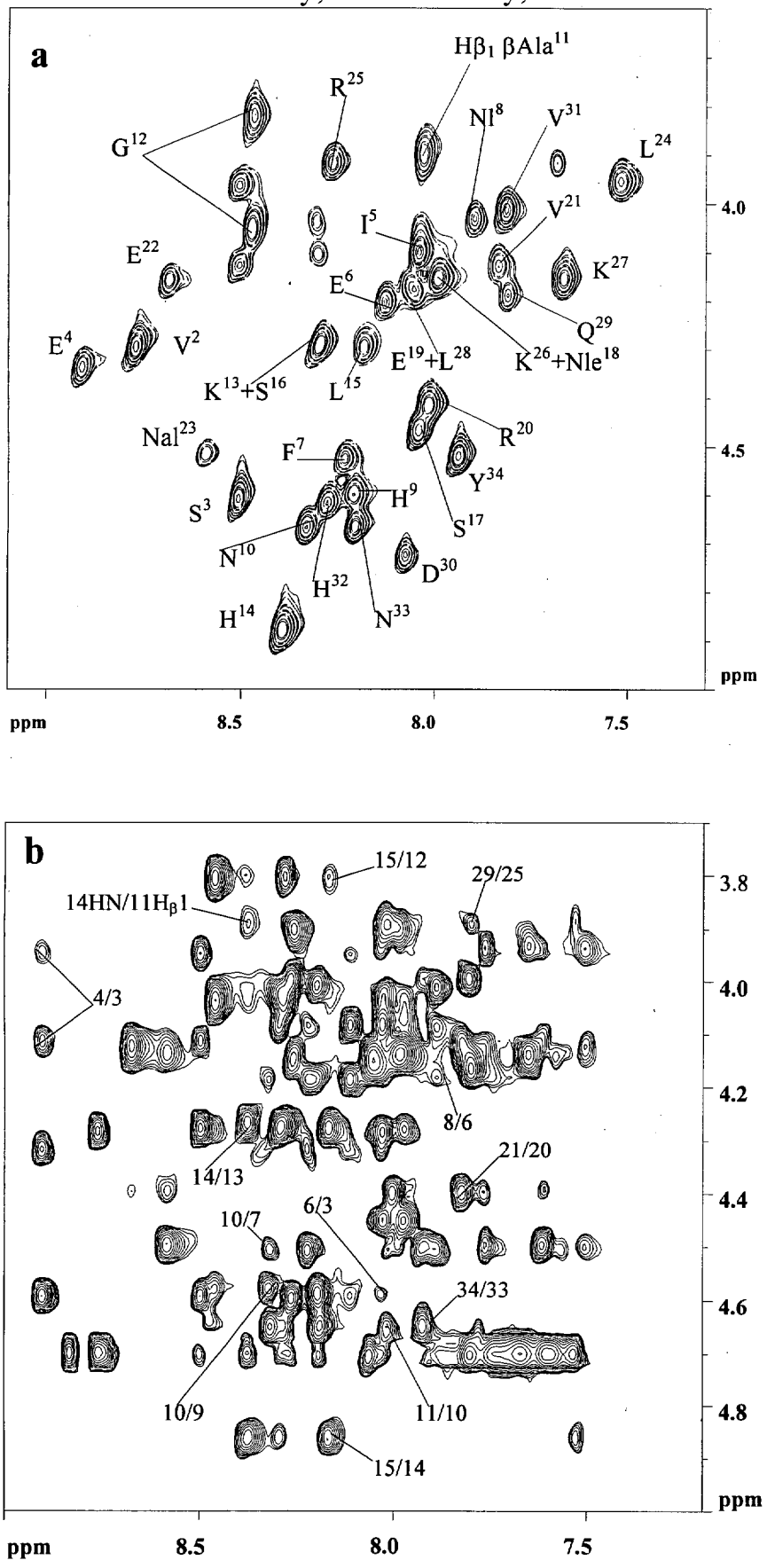


Figure 4. Fingerprint region of the TOCSY (a) and NOESY (b) spectra at **660** MHz of a 1.5 mM solution of **analog III,** in DPC micelles, T=313K.

Residue	δNH	δαH	δβH	δ others
Ala[1]		4.31	1.62	
Val[2]	8.76	4.25	2.22	γ 1.07
Ser[3]	8.49	4.54	3.93, 4.08	
Glu[4]	8.81	4.33	2.18	γ 2.54
Ile[5]	7.96	4.10	1.99	γ 1.32, δ 0.95
Gln[6]	8.13	4.16	2.18	γ 2.41; δ_{NH2} 6.88, 7.52
Phe[7]	8.18	4.51	3.27	Aromatic 7.26, 7.34
Nle[8]	7.76	4.00	1.81	γ 1.25,1.38; δ 0.95
His[9]	8.08	4.58	3.31, 3.40	H^2 7.36; H^4 8.73
Asn[10]	8.22	4.70	2.82, 2.90	γ_{NH2} 7.01, 7.66
βAla[11]	7.85	2.31, 2.49	3.22, 3.75	
βAla[12]	8.04	2.57	2.97, 3.65	
Lys[13]	8.26	4.16	1.76	γ 1.40
His[14]	8.54	4.88	3.35, 3.45	H^2 7.45, H^4 8.78
Leu[15]	8.36	4.30	1.75, 1.83	δ 0.94, 0.99
Ser[16]	8.34	4.29	4.00, 4.08	
Ser[17]	8.09	4.42	4.04	
Nle[18]	7.98	4.13	1.91	γ 1.36, 1.53
Glu[19]	8.04	4.15	2.22	γ 2.46
Arg[20]	8.01	4.38	2.07	γ 1.79, 1.93; δ 3.30, ε_{NH} 7.59
Val[21]	7.84	4.06	2.38	γ 1.06, 1.13
Glu[22]	8.62	4.13	2.29	γ 2.58 7.51, 7.57, 7.84, 8.02, 7.59, 7.73, 7.98
Nal[23]	8.51	4.48	3.39, 3.63	Aromatic H^1 7.73, H^3 7.57, H^4 7.98, $H^{5,8}$ 7.84, 8.02, $H^{6,7}$
Leu[24]	7.53	3.91	1.56, 1.88	γ 1.68; δ 0.93
Arg[25]	8.27	3.87	1.95, 2.03	γ 1.67, 1.79; δ 3.26; ε_{NH} 7.67
Lys[26]	7.94	4.12	1.92	γ 1.50, 1.59
Lys[27]	7.65	4.11	1.59, 1.65	γ 0.64, 0.99; ε 2.37, 2.53
Leu[28]	8.02	4.14	1.86	γ 1.67; δ 0.91
Gln[29]	7.75	4.15	2.25	γ 2.51, 2.57; δ_{NH2} 6.85, 7.55
Asp[30]	8.02	4.68	2.97	
Val[31]	7.79	3.96	2.29	γ 1.00, 1.07
His[32]	8.23	4.58	3.26, 3.39	H^2 7.34, H^4 8.71
Asn[33]	8.16	4.63	2.74, 2.83	γ_{NH2} 6.89, 7.59
Tyr[34]	7.89	4.49	3.04, 3.16	Aromatic 6.86, 7.20

Table 1. Proton chemical shifts (ppm) of analog **I** ([$Nle^{8,18}$,β-$Ala^{11,12}$,Nal^{23},Tyr^{34}]bPTH(1-34)NH_2).

Residue	δNH	δαH	δβH	δ others
Ala[1]		4.29	1.63	
Val[2]	8.73	4.24	2.21	γ 1.06
Ser[3]	8.48	4.54	3.92, 4.09	
Glu[4]	8.84	4.31	2.18	γ 2.54
Ile[5]	7.94	4.08	1.99	γ_{CH2} 1.31, δ 0.95
Gln[6]	8.07	4.09	2.19	γ 2.42, δ_{NH2} 6.87, 7.50
Phe[7]	8.19	4.45	3.30	Aromatic 7.26, 7.33
Nle[8]	7.73	3.93	1.83	γ 1.28, 1.41, δ 0.94
His[9]	8.08	4.46	3.36, 3.40	H^2 7.36, H^4 8.71
Asn[10]	8.13	4.62	2.82, 2.92	γ_{NH2} 6.98, 7.61
Leu	7.66	4.20	1.39, 1.73	γ 1.54; δ 0.88, 0.91
βAla[12]	7.73	2.39, 2.48	3.28, 3.66	
βAla[13]	8.04	2.47	3.30, 3.50	
His[14]	8.42	4.78	3.22, 3.39	H^2 7.39, H^4 8.72
Leu[15]	8.87	4.29	1.75, 1.87	γ 1.81 , δ 0.95, 1.00
Ser[16]	8.42	4.26	3.98, 4.05	-
Ser[17]	8.06	4.42	4.01, 4.07	-
Nle[18]	8.00	4.11	1.90	γ 1.34, 1.52
Glu[19]	8.02	4.17	2.21	γ 2.58
Arg[20]	7.98	4.37	2.06	γ 1.78, 1.91; δ 3.30, ε_{NH}7.58
Val[21]	7.82	4.06	2.36	γ 1.05, 1.12
Glu[22]	8.63	4.13	2.27	γ 2.55
Nal[23]	8.51	4.46	3.39, 3.65	Aromatic H^1 7.71, H^3 7.54, H^4 7.98, $H^{5,8}$ 7.83, 8.00, $H^{6,7}$
Leu[24]	7.51	3.90	1.54, 1.87	γ 1.68, δ 0.94
Arg[25]	8.25	3.86	1.95, 2.02	γ 1.65, 1.79, δ 3.25, ε_{NH} 7.65
Lys[26]	7.94	4.10	1.91	γ 1.49, 1.58, , ε 3.06
Lys[27]	7.63	4.10	1.56, 1.64	γ 0.62, 0.97, δ 1.35; ε 2.35, 2.51
Leu[28]	8.01	4.13	1.84	γ 1.65, δ 0.90
Gln[29]	7.73	4.14	2.24	γ 2.55, δ 6.84, 7.53
Asp[30]	8.01	4.65	2.94	
Val[31]	7.78	3.95	2.27	γ 0.98, 1.06
His[32]	8.20	4.56	3.25, 3.37	H^2 7.33, H^4 8.69
Asn[33]	8.13	4.62	2.73, 2.82	γ_{NH2} 6.88, 7.58
Tyr[34]	7.87	4.47	3.04, 3.16	Aromatic 6.84, 7.18

Table 2. Proton chemical shifts (ppm) of analog **II** ([$Nle^{8,18}$,β-$Ala^{12,13}$,Nal^{23},Tyr^{34}]bPTH(1-34)NH_2).

Residue	δNH	δαH	δβH	δothers
Ala[1]		4.32	1.63	
Val[2]	8.77	4.31	2.22	γ 1.09
Ser[3]	8.50	4.59	3.95, 4.10	
Glu[4]	8.91	4.31	2.22	γ 2.58
Ile[5]	8.04	4.08	2.02	γ 1.35-1.61, δ,γ 0.98
Gln[6]	8.12	4.20	2.21	γ 2.46, δ_{NH2}=7.57
Phe[7]	8.23	4.50	3.30	Aromatic 7.30, 7.39
Nle[8]	7.90	4.02	1.87	γ 1.39-1.47, δ 0.91-0.97, ε 1.31
His[9]	8.20	4.58	3.38, 3.42	H^2, H^4 8.78, 7.40
Asn[10]	8.33	4.65	2.87, 2.91	γ 7.06, 7.71
βAla[11]	8.02	3.18, 3.90	2.32, 2.68	
Gly[12]	8.46	4.07, 3.80		
Lys[13]	8.27	4.28	1.87	γ 1.44-1.49, δ 1.73, ε 3.04
His[14]	8.38	4.85	3.25, 3.4	H^2, H^4 8.83, 7.54
Leu[15]	8.17	4.28	1.86	γ 1.75, δ 0.97-1.03
Ser[16]	8.27	4.28	4.03, 4.09	
Ser[17]	8.03	4.45	4.05, 4.09	
Nle[18]	7.98	4.14	1.95	γ 1.37, δ 0.95
Glu[19]	8.06	4.16	2.25	γ 2.49, 2.65
Arg[20]	8.01	4.39	2.06, 2.12	γ 1.82, 1.96, δ 3.33, ε_{NH}=7.60
Val[21]	7.83	4.12	2.41	γ 1.09, 1.16
Glu[22]	8.68	4.12	2.30, 2.34	γ 2.63
Nal[23]	8.59	4.49	3.38, 3.66	Aromatic H^1 7.76; H^3 7.60; H^4 8.02; $H^{5,8}$ 7.90, 8.00;
Leu[24]	7.51	3.95	1.56, 1.89	γ 1.65, δ 0.93-0.96
Arg[25]	8.26	3.89	1.99, 2.05	γ 1.70, 1.81, δ 3.29, ε 7.65
Lys[26]	7.98	4.14	1.95	γ 1.52, 1.58, δ 1.81, ε 3.10
Lys[27]	7.66	4.14	1.63, 1.69	γ 1.63, 1.70, δ 1.40, ε 0.73, 1.05
Leu[28]	8.04	4.16	1.87	γ 1.70, δ 0.93
Gln[29]	7.08	4.18	2.26	γ 2.53, 2.60, δ_{NH2} 7.59
Asp[30]	8.07	4.70	3.02	
Val[31]	7.81	4.01	2.30	γ 1.02, 1.10
His[32]	8.27	4.59	3.27, 3.41	H^2, H^4 8.76, 7.40
Asn[33]	8.20	4.65	2.77, 2.85	γ 6.70-7.57
Tyr[34]	7.93	4.49	3.07, 3.19	Aromatic 7.30, 7.24, 7.40

Table 3. Proton chemical shifts (ppm) of analog **III(** [$Nle^{8,18}$,β-Ala^{11},Nal^{23},Tyr^{34}]bPTH(1-34)NH_2)

Residue	δNH	δαH	δβH	δ others
Ala[1]		4.25	1.58	
Val[2]	8.71	4.25	2.17	g 1.04
Ser[3]	8.39	4.59	4.11 , 3.92	
Glu[4]	8.91	4.22	2.18	g 2.53
Ile[5]	8.01	3.99	1.95	g 1.51, 1.33; g, δ 0.93
Gln[6]	8.04	4.14	2.28, 2.23	g 2.44; δ 7.49, 6.87
Phe[7]	8.23	4.40	3.26	Aromatics 7.28, 7.19
Nle[8]	8.00	3.90	1.89, 1.85	g 1.53, 1.38; d 1.31 ; ε 0.94
His[9]	8.17	4.54	3.38	H^2 8.82 ; H^4 7.58
Asn[10]	8.21	4.60	2.85	d 7.63, 7.14
hLeu[11]	7.67	2.60, 2.13	4.36	g 1.65, 1.57; δ1.11 ; ε 0.84
Gly[12]	8.48	4.04, 3.69		
Lys[13]	8.19	4.19	1.87	g 1.45, 1.37 ; d 1.68 ; ε 2.98
His[14]	8.24	4.84	3.49, 3.12	H^2 8.82 ; H^4 7.59
Leu[15]	7.90	4.20	1.82, 1.72	γ 1.82 ; δ 0.98, 0.91
Ser[16]	8.21	4.20	3.99	
Ser[17]	7.85	4.41	4.02	
Nle[18]	7.85	4.07	1.90	g 1.55, 1.36 ; d 0.91
Glu[19]	7.98	4.09	2.18	g 2.59, 2.41
Arg[20]	7.84	4.38	2.10 , 2.00	g 1.00, 1.78 ; d 3.28 ; ε_{NH} 7.54
Val[21]	7.72	4.13	2.36	g 1.10, 1.04
Glu[22]	8.72	4.10	2.26	g 2.53
Nal[23]	8.63	4.45	3.62, 3.29	Aromatic H^1 7.71, H^3 7.52, H^4 7.95, $H^{5,8}$ 7.83, 7.98, $H^{6,7}$
Leu[24]	7.35	3.90	1.82, 1.53	γ 1.53; δ 0.91, 0.86
Arg[25]	8.16	3.85	1.96	g 1.76, 1.65 ; d 3.25 ; ε_{NH} 7.62
Lys[26]	7.96	4.09	1.89	g 1.57, 1.48; d 1.81; ε 3.06
Lys[27]	7.57	4.13	1.65, 1.58	g 1.02, 0.70; d 1.37; ε 2.54, 2.37
Leu[28]	7.97	4.11	1.81, 1.65	γ 1.81, 1.65; δ 0.87
Gln[29]	7.72	4.11	2.21	g 2.53, 2.47 ; δ_{NH_2} 7.51, 6.82
Asp[30]	7.99	4.66	2.93	
Val[31]	7.75	3.95	2.25	g 1.04, 0.96
His[32]	8.21	4.56	3.41, 3.23	H^2 8.68 ; H^4 7.32
Asn[33]	8.13	4.60	279, 2.71	d 7.55, 6.85
Tyr[34]	7.86	4.47	3.14, 3.02	Aromatic 7.30, 7.02 ; NH_2 7.15, 6.82

Table 4. Proton chemical shifts (ppm) of analog **IV** ([Nle[8,18],β-hLeu[11],Nal[23],Tyr[34]]bPTH(1-34)NH_2)

Residue	δNH	δαH	δβH	δ others
Ala[1]		4.22	1.59	
Val[2]	8.70	4.25	2.20	γ 1.05
Ser[3]	8.48	4.56	3.94, 4.11	
Glu[4]	8.89	4.26	2.19	γ 2.51
Ile[5]	8.01	3.99	1.99	γ 1.33; γ0.95; δ 1.58
Gln[6]	8.04	4.10	2.20	γ 2.45, δ_{NH2} 7.51
Phe[7]	8.27	4.42	3.28, 3.32	Aromatic 7.28,, 7.36
Nle[8]	7.98	3.87	1.95	γ 1.35, 1.82; δ 1.35; ε 0.95
His[9]	8.24	4.42	3.40	$H^2$8.74; H^4 7.33
Asn[10]	8.25	4.59	2.91	γ_{NH2} 7.07, 7.71
Leu[11]	7.99	4.11	1.52	γ 1.52; δ 0.89, 1.04
βAla[12]	7.95	2.45, 2.61	3.18, 3.89	
Lys[13]	8.10	4.01	1.77, 1.84	γ 1.34, δ 1.66, ε_{NH2} 2.97
His[14]	8.16	4.77	3.40, 3.49	H^2 8.83; H^4 7.44
Leu[15]	8.28	4.26	1.86	γ 1.76, δ 0.95
Ser[16]	8.22	4.20	4.00	
Ser[17]	7.86	4.42	4.00	
Nle[18]	7.86	4.08	1.91	γ 1.55; δ 1.34, ε 0.91
Glu[19]	8.30	4.10	2.20	γ 2.42, 2.60
Arg[20]	7.90	4.37	1.99, 2.09	γ 1.99, 2.09, δ 3.29, ; ε_{NH} 7.54
Val[21]	7.74	4.08	2.37	γ 1.05, 1.10
Glu[22]	8.73	4.08	2.27	γ 2.54
Nal[23]	8.60	4.45	3.28, 3.62	Aromatic H^1 7.71, H^3 7.57, H^4 7.98, $H^{5,8}$ 7.86, 8.01, $H^{6,7}$
Leu[24]	7.37	3.91	1.52, 1.84	γ1.60, δ 0.89, 0.93
Arg[25]	8.19	3.88	1.97	γ1.65,1.77, δ 3.25; , ε_{NH}7.61
Lys[26]	7.96	4.09	1.89	γ1.51, δ 1.75, ε_{NH2} 3.06
Lys[27]	7.59	4.09	1.58, 1.65	γ 0.67, 1.00; δ 1.34; ε_{NH2} 2.36,2.56
Leu[28]	7.99	4.11	1.84	γ_{CH} 1.65; δ 0.95
Gln[29]	7.73	4.11	2.22	γ 2.48,2.54; δ_{NH2} 7.53
Asp[30]	8.00	4.65	2.93	
Val[31]	7.76	3.94	2.26	γ 0.97, 1.04
His[32]	8.21	4.54	3.23, 3.35	H^2 8.71; H^4 7.32
Asn[33]	8.13	4.61	2.72-2.80	γ_{NH2} 2.72, 2.80
Tyr[34]	7.87	4.45	3.02-3.13	aromatics 7.03, 7.16

Table 5. Proton chemical shifts (ppm) of analog **V** ([Nle[8,18], β-Ala[12],Nal[23],Tyr[34]]bPTH(1-34)NH_2)

Residue	**δNH**	**δαH**	**δβH**	**δ others**
Ala[1]		4.36	1.46	
Val[2]	8.72	4.28	2.22	γ 1.08
Ser[3]	8.50	4.59	3.96, 4.14	
Glu[4]	8.91	4.31	2.22	γ 2.56
Ile[5]	8.02	4.06	2.01	γ 1.37; γ, δ 0.98
Gln[6]	8.07	4.13	2.22	γ 2.46;δ_{NH2} 6.91, 7.52
Phe[7]	8.27	4.47	3.32	aromatic 7.27, 7.35
Nle[8]	7.92	3.94	1.87, 1.93	γ 1.37, 1.52; δ 0.98
His[9]	8.22	4.46	3.39	H^2 8.72; H^4 7.37
Asn[10]	8.34	4.65	2.91, 2.96	γ_{NH2} 7.03, 7.70
Leu[11]	8.02	4.22	1.74	γ 1.66; δ 0.92
Gly[12]	8.33	3.82		
βAla[13]	7.71	2.46, 2.56	3.30, 3.82	
His[14]	8.17	4.64	3.34	H^2 8.78; H^4 7.34
Leu[15]	8.77	4.27	1.88, 1.97	γ 1.77; δ 0.97
Ser[16]	8.21	4.26	4.04, 4.10	
Ser[17]	7.98	4.45	4.02, 4.05	
Nle[18]	7.92	3.94	1.87, 1.93	γ 1.37, 1.52; δ 0.97
Glu[19]	8.11	4.15	2.23	γ 2.48
Arg[20]	8.02	4.39	2.03, 2.10	γ 1.80, 1.92; δ 3.31; ε_{NH} 7.56
Val[21]	7.79	4.09	2.40	γ 1.08, 1.14
Glu[22]	8.69	4.13	2.28	γ 2.60
Nal[23]	8.56	4.48	3.34, 3.64	Aromatic H^1 7.72, H^3 7.56, H^4 7.98, $H^{5,8}$ 7.85, 8.02, $H^{6,7}$
Leu[24]	7.47	3.94	1.88	γ 1.68; δ 0.97, 1.56
Arg[25]	8.26	3.89	1.98, 2.02	γ 1.68, 1.81; δ 3.28
Lys[26]	7.98	4.13	1.93	γ 1.51, 1.58; δ 1.81
Lys[27]	7.63	4.12	1.60	γ 1.02; δ 1.40; ε 3.89
Leu[28]	8.03	4.16	1.86	γ 1.66; δ 0.92
Gln[29]	7.76	4.16	2.25	γ 2.51-2.57; δ_{NH2} 7.55, 6.86
Asp[30]	8.03	4.69	2.99	
Val[31]	7.78	3.98	2.30	γ 1.00
His[32]	8.24	4.58	3.26-3.39	H^2 8.71; H^4 7.34
Asn[33]	8.17	4.64	2.75, 2.83	γ_{NH2} 6.90, 7.58
Tyr[34]	7.90	4.49	3.05, 3.17	Aromatic 6.87, 7.20

Table 6. Proton chemical shifts (ppm) of analog **VI** ([Nle[8,18],β-Ala[13],Nal[23],Tyr[34]]bPTH(1-34)NH_2)