Supplementary Material (ESI) for Chemical Communications

Two prolines with a difference: Contrasting stereoelectronic effects of 4*R*/*S*-aminoproline on triplex stability in collagen peptides [Pro(X)-Pro(Y)-Gly]$_n$

*M.Umashankara, I. Ramesh Babu and Krishna N. Ganesh **

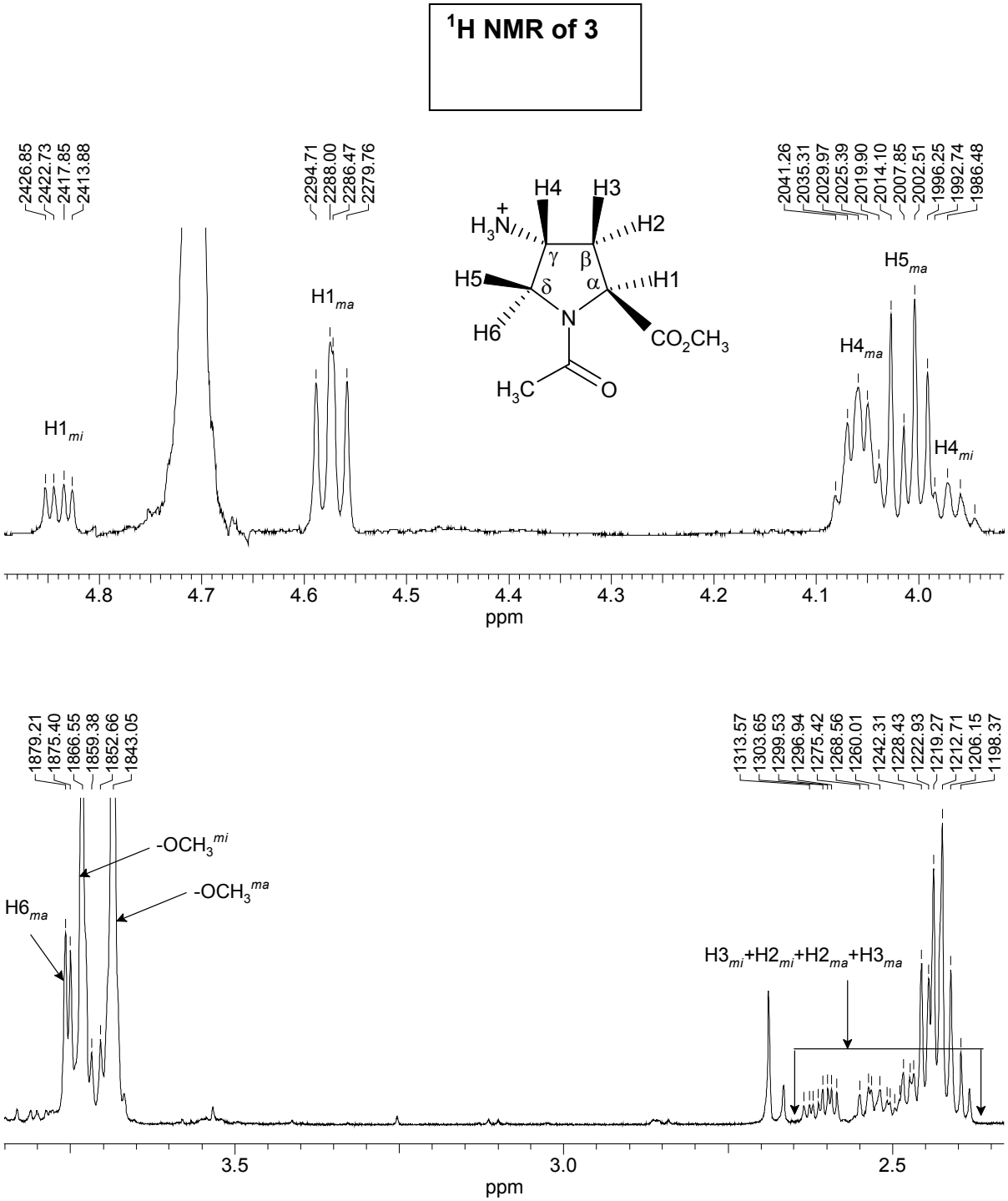
Division of Organic Chemistry (Synthesis),

National Chemical Laboratory,

Pune 411008, India

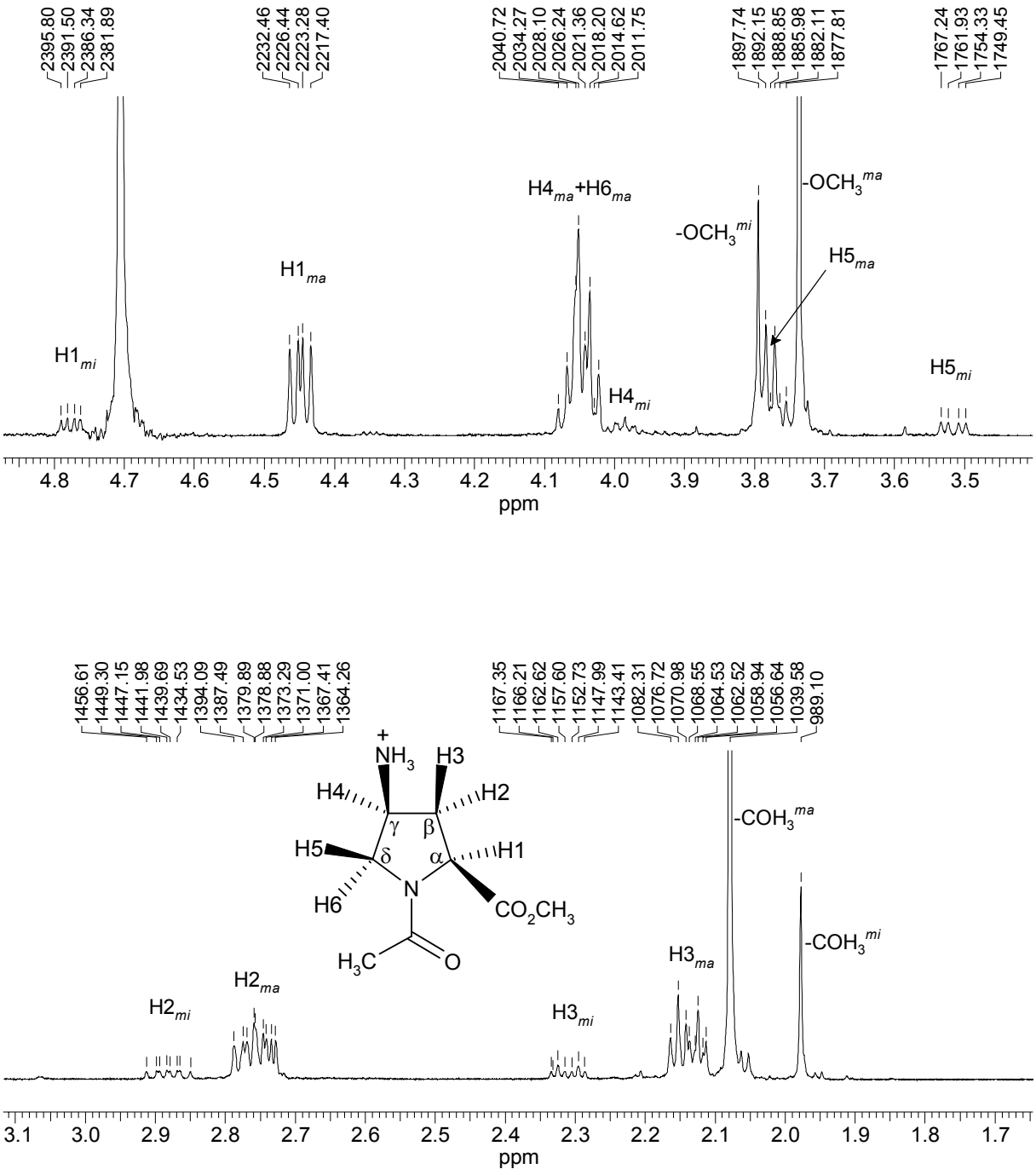
Fax: (91) 20 589 3153

E-mail: kng@ems.ncl.res.in



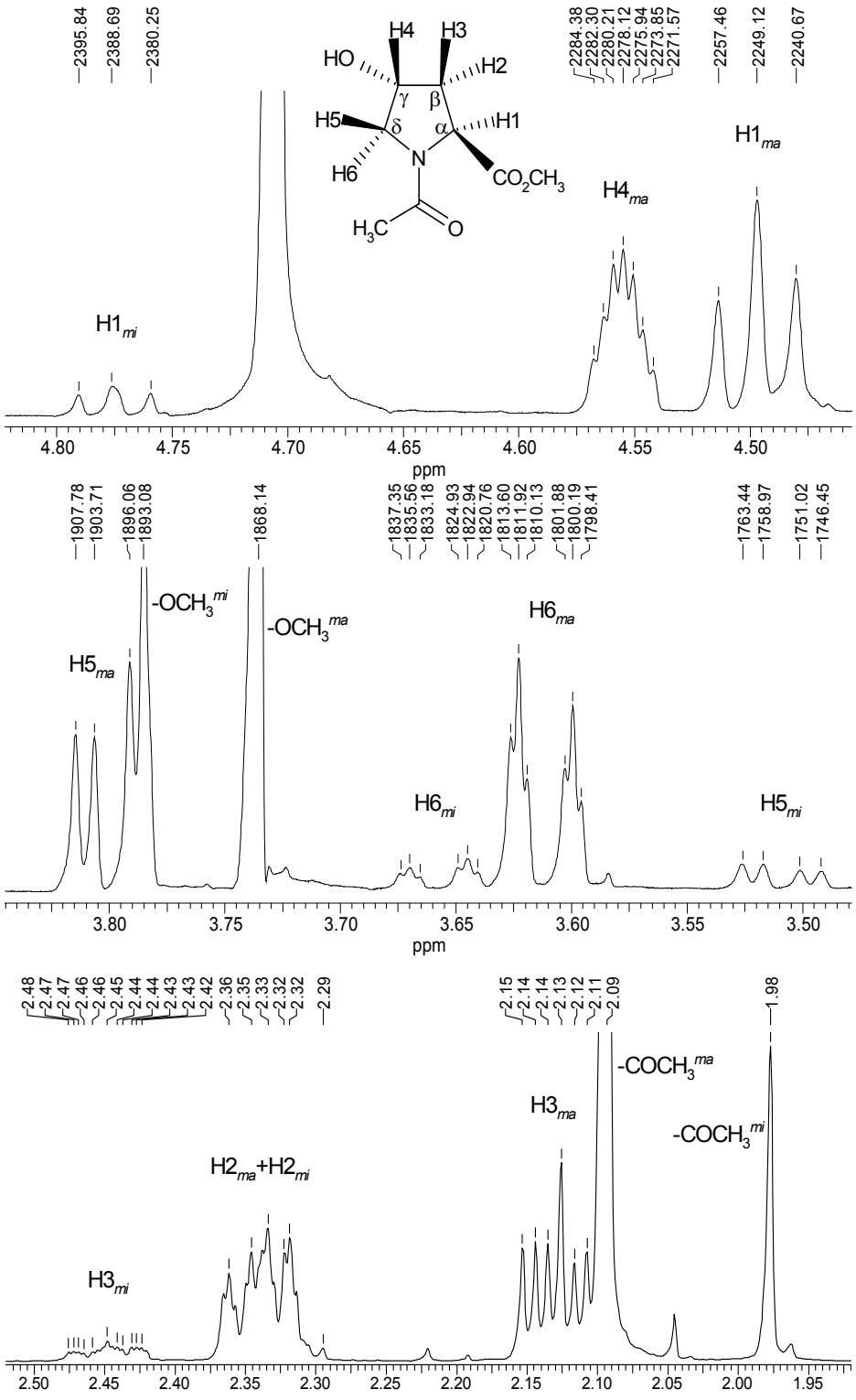
Expanded 500 MHz ^{1}H-NMR spectrum of Ac-Amp-OMe$^+$ **3** in D_2O; *ma* is the major isomer (*Z*) and *mi* is the minor isomer (*E*). Spectrum was recorded on a Bruker-DRX 500 instrument using a 5 mm QNP probe.

^{1}H NMR of 4



Expanded 500 MHz ^{1}H-NMR spectrum of Ac-amp-OMe$^+$ **4** in D_2O; *ma* is the major isomer (*Z*) and *mi* is the minor isomer (*E*). Spectrum was recorded on a Bruker-DRX 500 instrument using a 5 mm QNP probe.

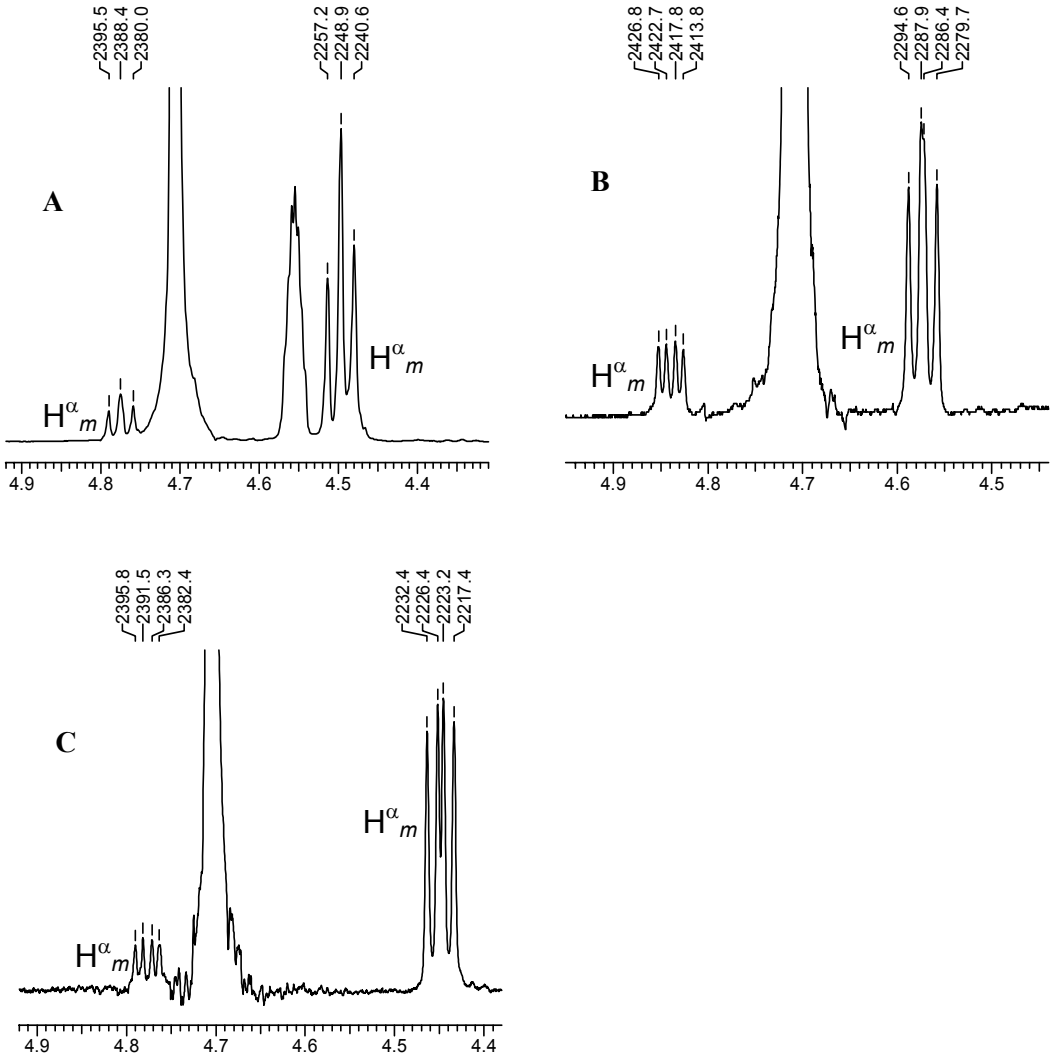
^{1}H NMR of 4*R*-OAc-Hyp



Expanded 500 MHz ^{1}H-NMR spectrum of Ac-Hyp-OMe in D_2O. *ma* is the major isomer (*Z*) and *mi* is the minor isomer (*E*). Spectrum was recorded on a Bruker-DRX 500 instrument using a 5 mm QNP probe.

H^{α} regions of the ^{1}H-NMR spectra

H^{α} regions of the ^{1}H-NMR spectra of **A** Ac-Hyp-OMe; **B** Ac-Amp-OMe^{+} **3**; and **C** Ac-amp-OMe^{+} **4**; *ma* is the major isomer (*Z*) and *mi* is the minor isomer (*E*). NMR spectra were recorded in D_2O at 500 MHz with a 5mm probe.



Analysis of vicinal coupling constants for ring pucker assignments

Vicinal coupling constants of compounds **3**,**4** extracted from 500 MHz spectra and the derived pucker type for the pyrrolidine ring

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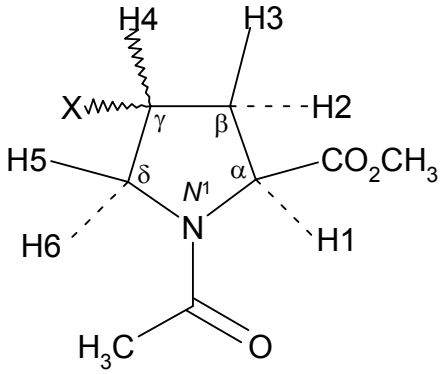
	J_{H-H}								Derived pucker type
	Vicinal J_{H-H} values(Hz)						W type J_{H-H}		
	J_{1-2}	J_{1-3}	J_{2-4}	J_{3-4}	J_{4-5}	J_{4-6}	J_{2-6}	J_{3-5}	
J_{calc} for γ-exo pucker[a]	*8.10*	*10.36*	*0.93*	*3.82*	*3.26*	*0.62*			
J_{cal} for γ-endo pucker[a]	*10.50*	*2.80*	*3.85*	*1.10*	*0.81*	*3.42*			
Ac-Hyp-OMe	7.95	8.74	2.38	4.37	3.97	1.59	1.99		γ-*exo*
Ac-Amp-OMe$^+$ **3**	6.71	8.24	--	--	5.95	3.82			γ-*exo*
Ac-amp-OMe$^+$ **4**	8.95	5.85	6.51	5.58	3.26	6.51			γ-*endo*

a) Idealized coupling constants for γ-*exo* and γ-*endo* conformation (from reference 8b)

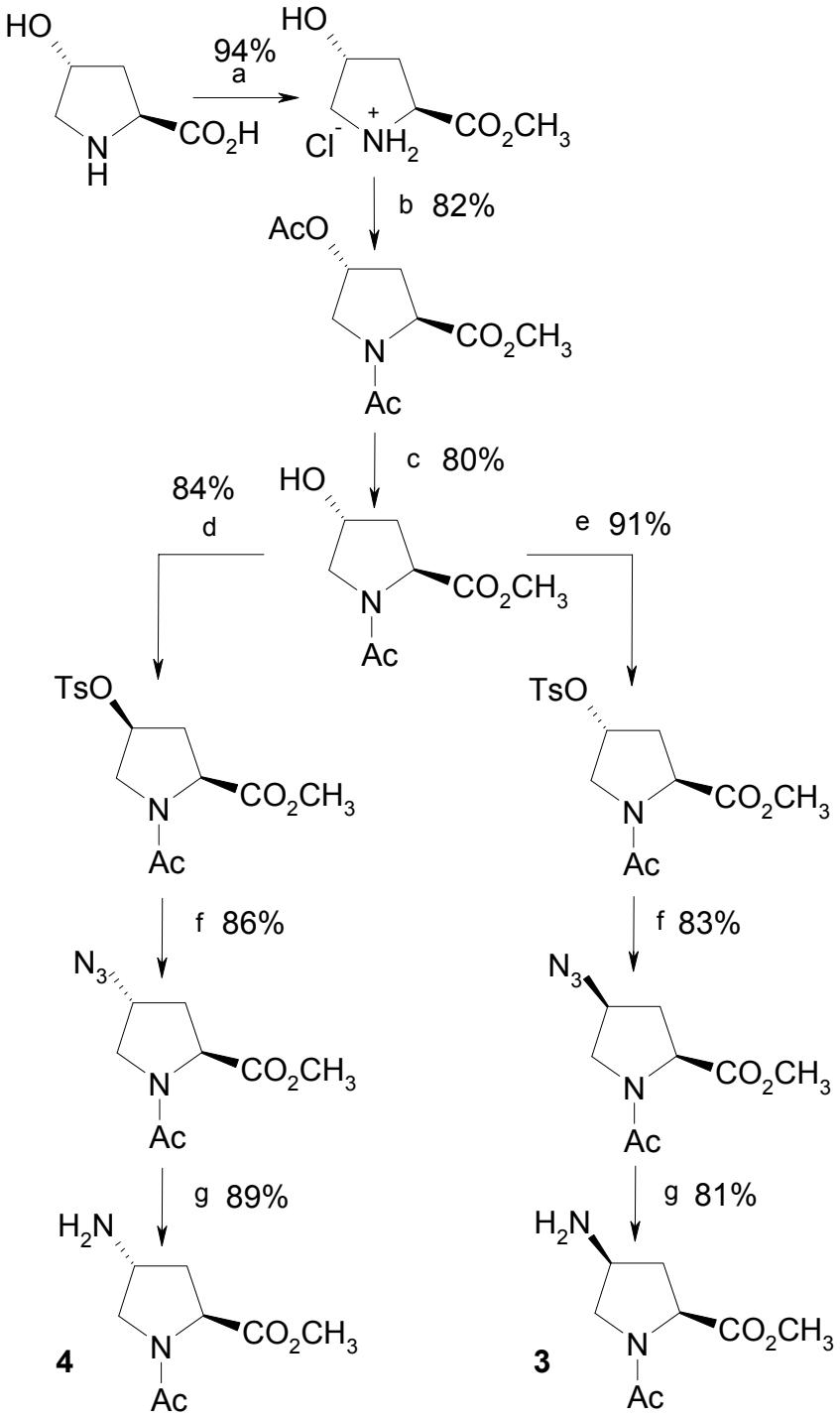
b) Obtained from decoupled spectra (see Appendix).



X = 4*R*-OH, 4*R*-N_3, 4*S*-N_3, 4*R*-NH_3^+, 4*S*-NH_3^+

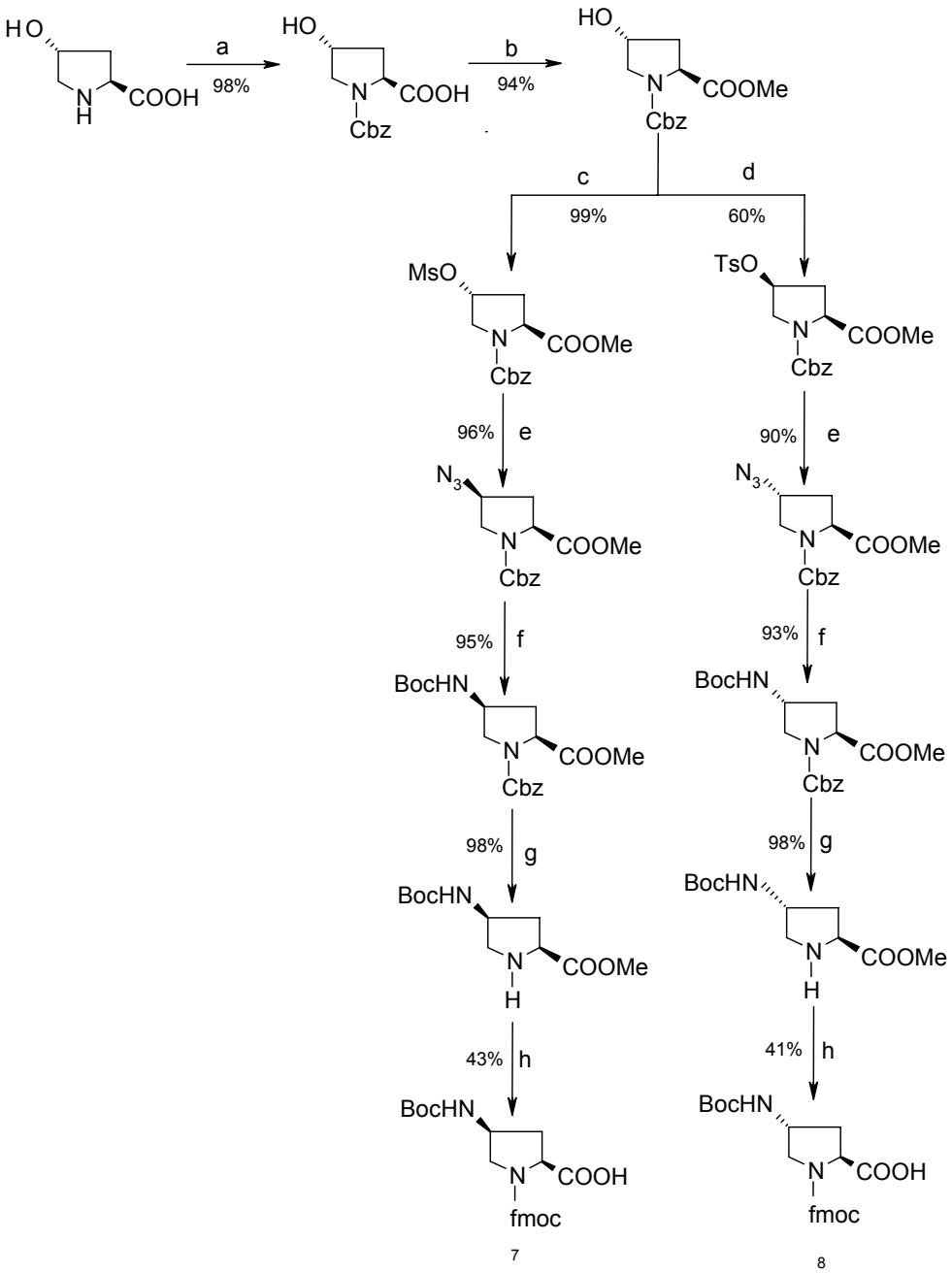
Numbering scheme used to identify the peaks of ^{1}H-NMR spectra of 4-substituted proline model compounds Ac-Xaa-OMe.

Synthesis of Amp (3) and amp (4) monomers for NMR studies



a) MeOH, $SOCl_2$; b. Ac_2O; c) MeOH, K_2CO_3; d) PPh_3, DEAD, TsOMe, THF; e) TsCl, pyridine; f) NaN_3, DMF at 55 °C; g) Pd-C, H_2, MeOH

Synthesis of Monomers 7 and 8

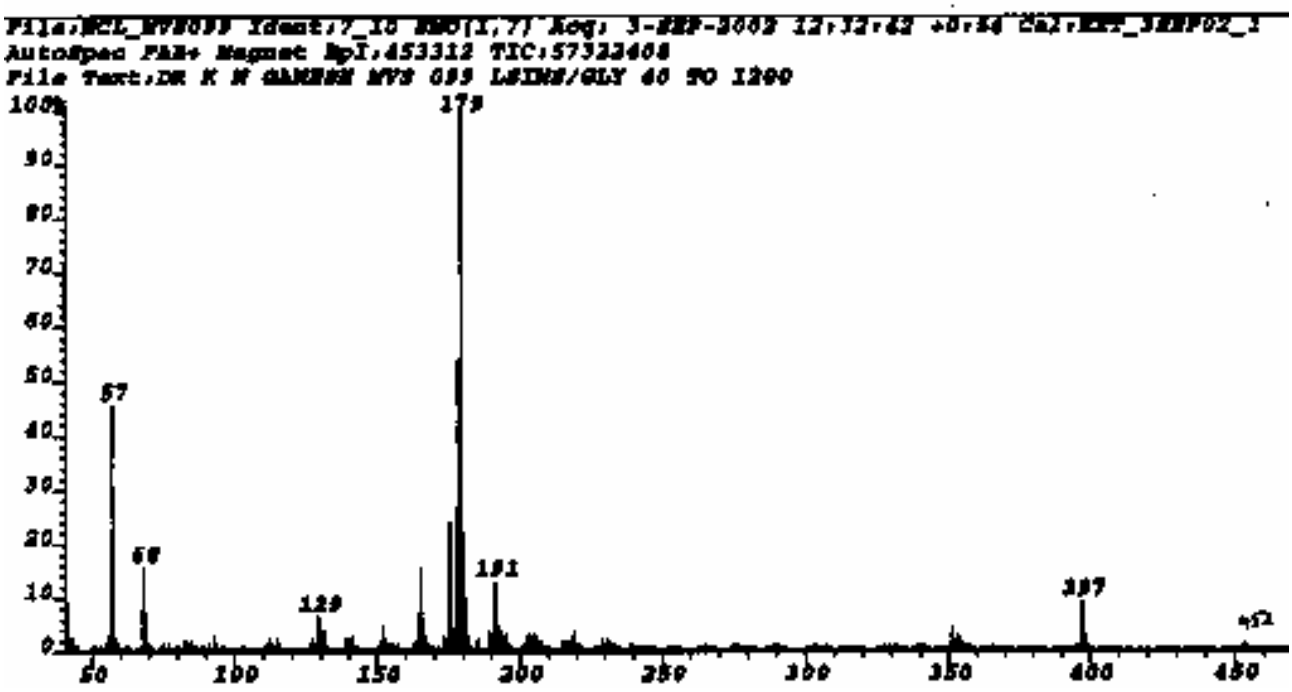


a)$NaHCO_3$, CbzCl , H_2O : b)Me0H/ $SOCl_2$; c)MsCl / Py ; d)PPh_3 , DIAD, P-Ts 0Me,THF ;

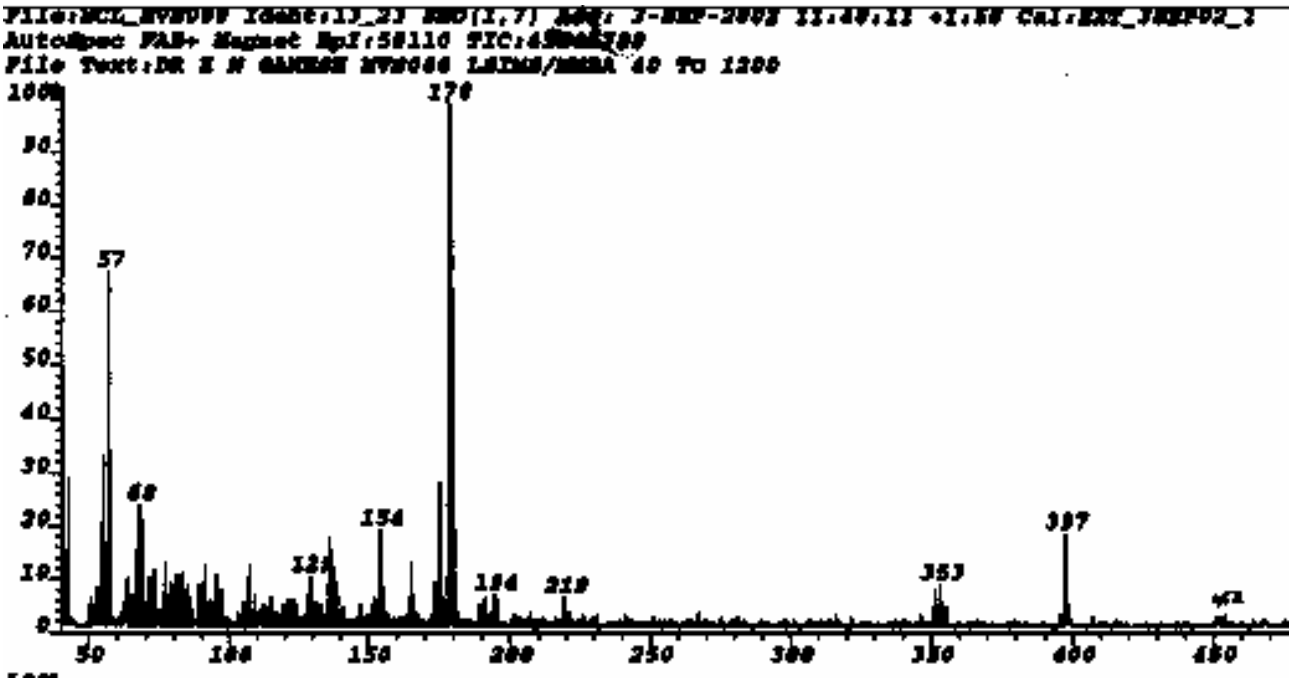
e) DMF/ NaN_3 ; f)Raney Ni/H_2, EtOAc, $(Boc)_2O$; g)10% Pd/C,MeOH ; h) i) MeOH/NaOH,

ii) Na_2CO_3, Fmoc Cl, H_2O : Dioxan

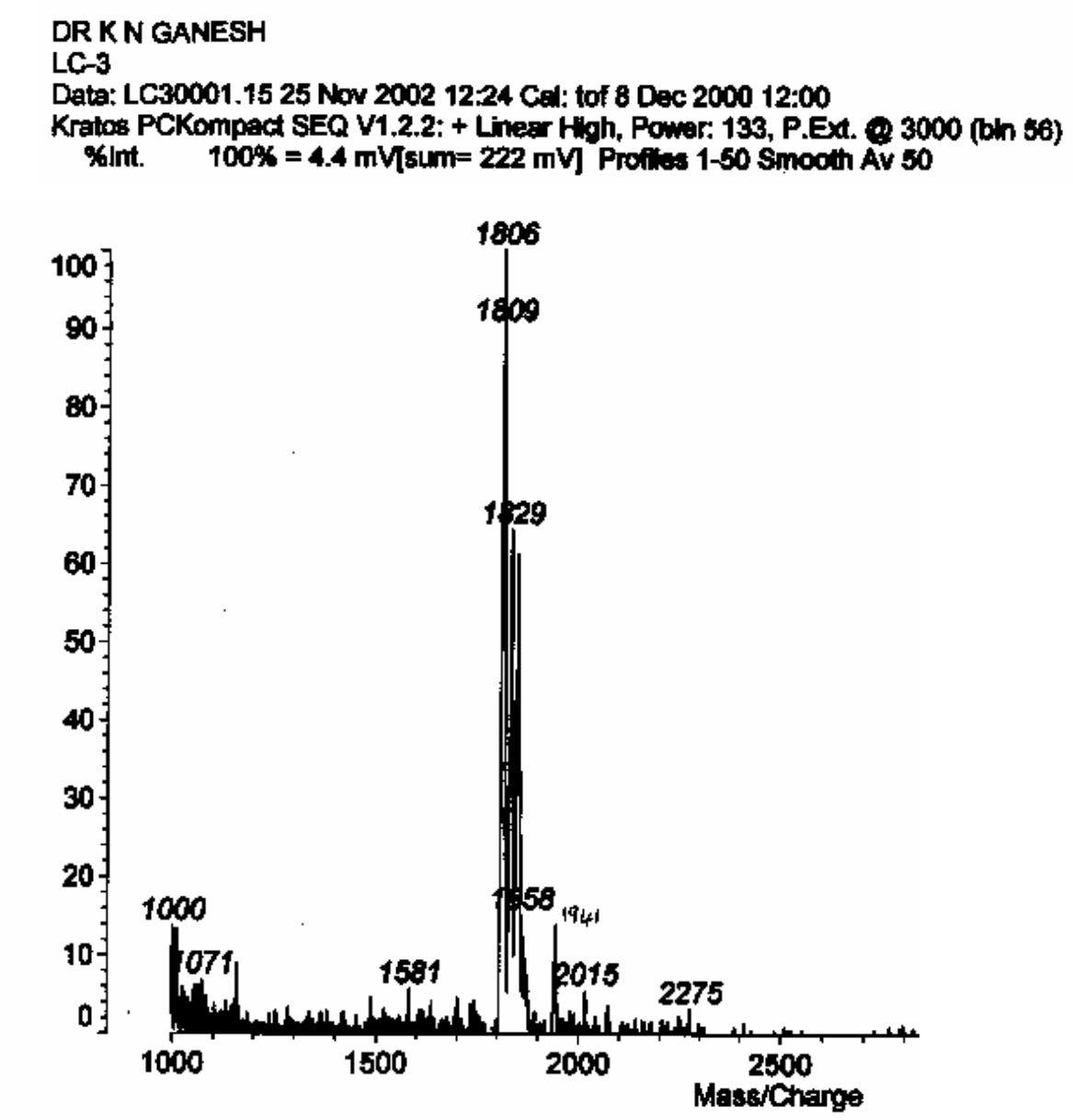
FAB Mass spectrum of compound **7**



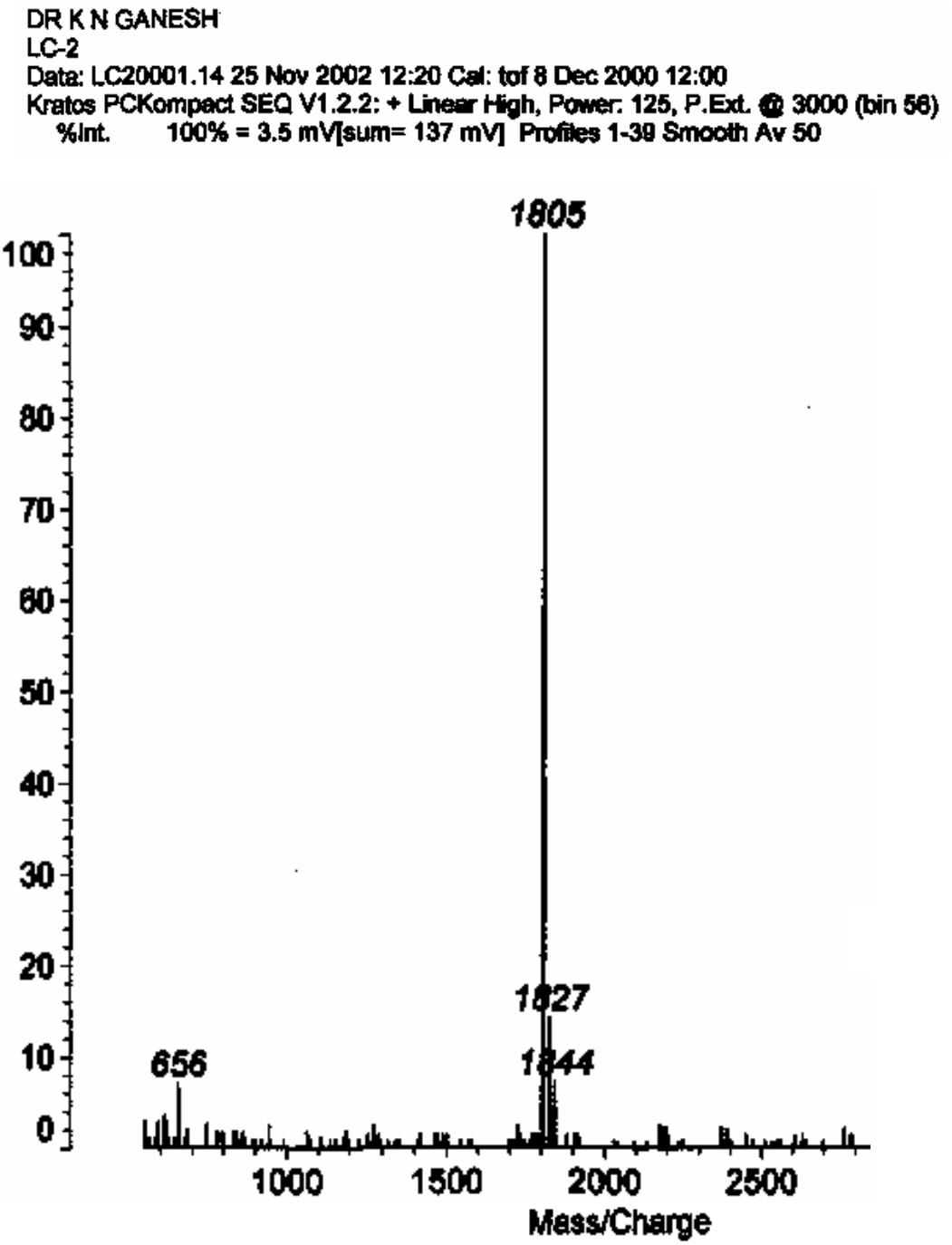
FAB Mass spectrum of compound **8**



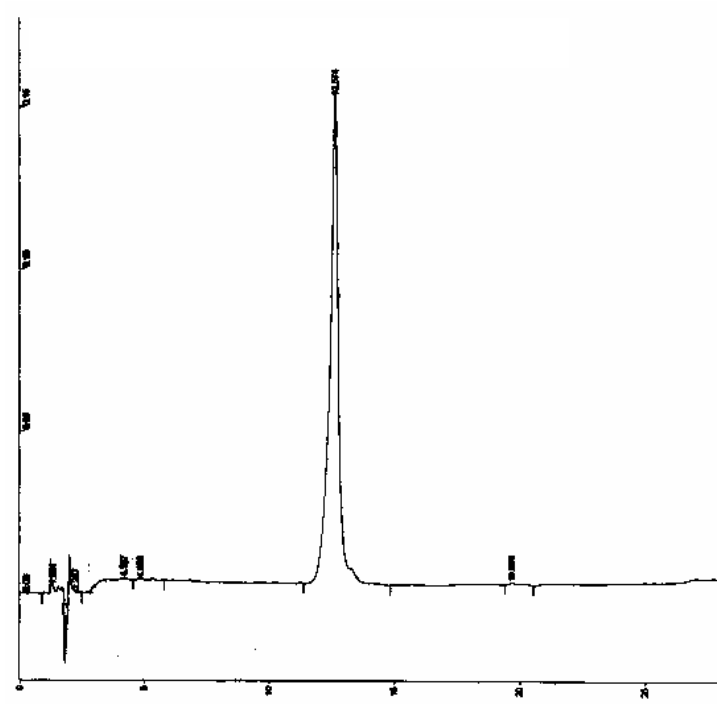
MALDI-TOF Mass spectrum of peptide **5**



MALDI-TOF Mass spectrum of peptide **6**

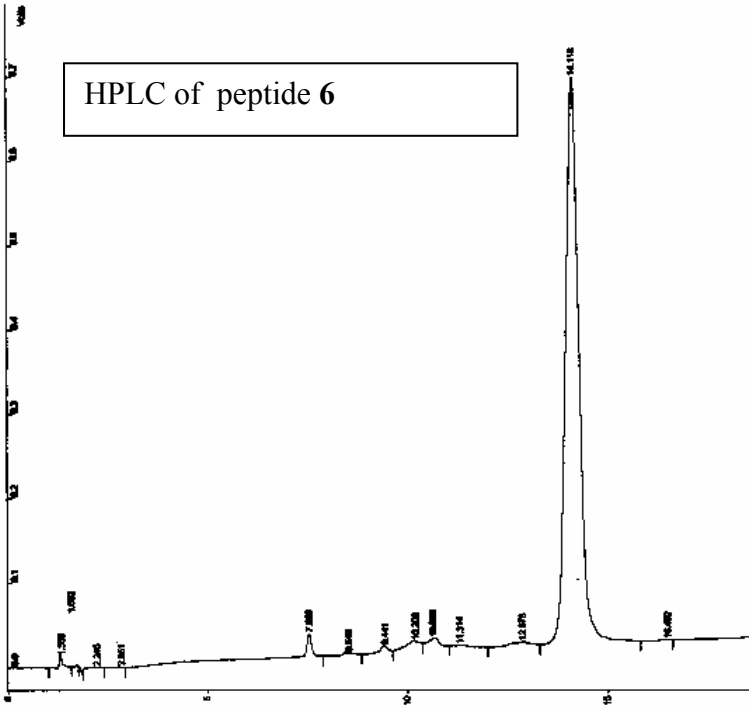


HPLC of peptide **5**



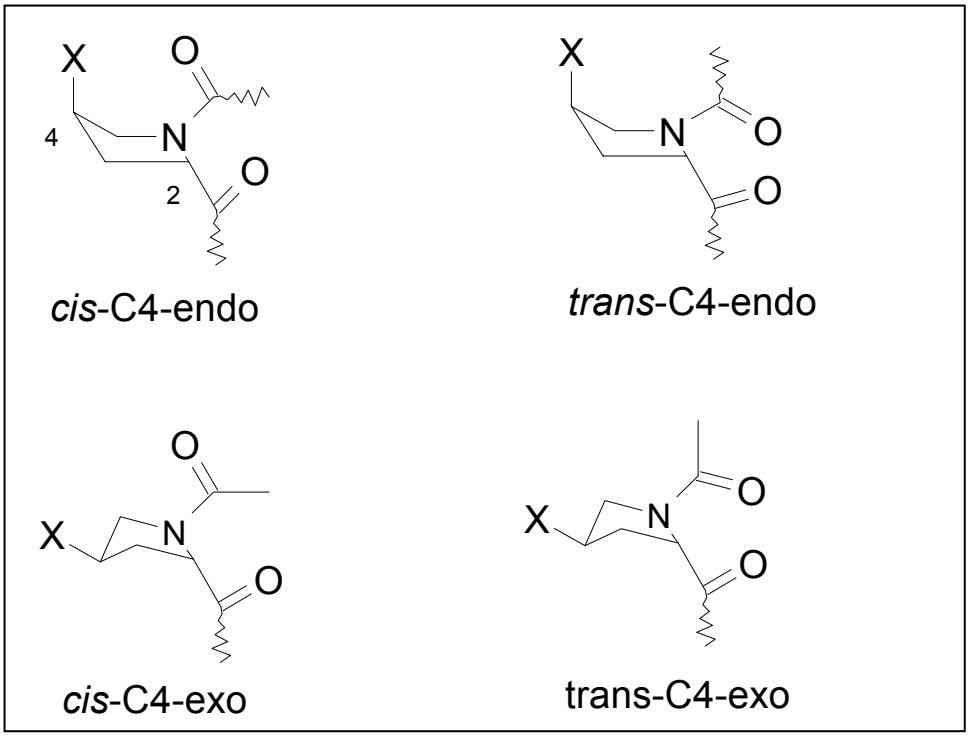
Time in mins

HPLC of peptide **6**



Time in mins

Exo and Endo Puckers **S12**



R_{pn} values for the collagen peptides calculated from the CD spectra measured at 10 °C

	R_{pn} values			
	pH 3.0	**pH 7.0**	**pH 9.0**	**pH 12.0**
Ac-Phe.(Pro.Amp.Gly)$_6$-NH$_2$ **9**	0.17	0.15	0.09	0.17
Ac-Phe(amp.Pro.Gly)$_6$-NH$_2$ **7**	0.12	0.08	0.08	-
Ac-Phe(Amp.Pro.Gly)$_6$-NH$_2$ **8**	0.08	0.08	-	-