Electronic Supplementary Material (ESI) for RSC Advances.

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S.I. Table 1 Physical properties of their peptides and copper(II)-peptides listing the yield and purity in terms of percentage, melting/decomposing point and their chiral optical rotation value at room temperature (25°C).

P/CuP	% Yield	% Purity	Melting point/°C	$\alpha[D]^{25°C}$
P1	74.0	80.0	191.0 (m)	-12
CuP1	65.0		205.2 (d)	214
P2	74.2	84.0	210.0 (m)	-14
CuP2	56.0		220.6 (d)	85
P3	83.1	73.0	200.0 (m)	1
CuP3	53.3		208.5 (d)	93
P4	70.0	99.5	162.4 (m)	-10
CuP4	48.1		245.0 (d)	227
P5	65.6	99.2	130.0 (m)	-4
CuP5	49.6		210.6 (d)	460

m-melted d-decomposed

S.I. Table 2 The secondary structures of peptides and their CuP analyzed at different temperatures

Peptides	Secondary structures		
	4°C	25°C	60°C
P1	β-sheet (53.2%)	**β-sheet (52.2%)**	β-sheet (38.3%)
CuP1	Random (67.2%)	**Random (67.6%)**	Random (71.5%)
P2	Random (62.8%)	**β-sheet (82.9%)**	β-sheet (82.9%)
CuP2	Random (58.6%)	**Random (68.7%)**	Random (70.7%)
P3	Random (50.7%)	**Random (47.5%)**	Random (53.2%)
CuP3	β-turn (57.2%)	**Random (42.4%)**	Random (81.4%)
P4	β-sheet (40.9%)	**β-sheet (38.1%)**	β-sheet (75.8%)
CuP4	β-sheet (49.6%)	**α-helix (39.5%)**	β-sheet (96.3%)
P5	β-sheet (80.1%)	**β-sheet (40.2%)**	β-sheet (80.3%)
CuP5	β-sheet (53.4%)	**Random (38.3%)**	β-turn (43.9%)

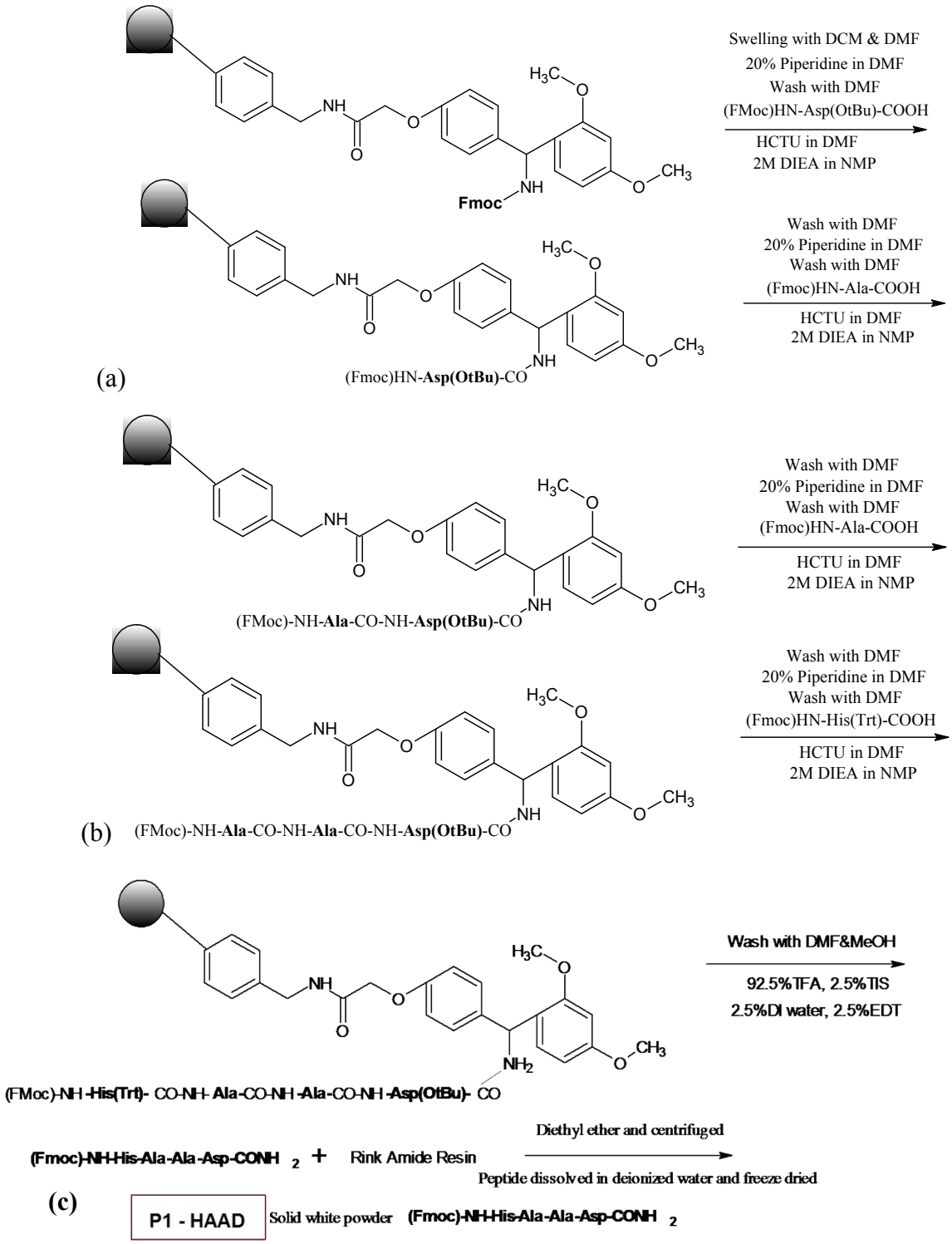
S.I Table 3 UV spectral analysis of P1-P5 and copper bound to P1-P5 in compliment with the FTIR spectral analysis with the peak assignments

P/MP	UV Spectral Analysis			FTIR Analysis	
	UV-Visible		Assignment	Wavenumber (υ) (type of peak)/ cm^{-1}	Assignment
	λ/nm	log ε/ $L \cdot cm^{-1} \cdot mol^{-1}$			
P1	π-π* transition at 200-270 nm & n-π* transition at 270-330 nm. (no peaks observed at 400-750 for all peptides and copper(II)-peptides) [31]			3277 (s,sh) 1251 (w,sh) 1188 (s,sh) 1626 (s,sh) 1437 (w,b) 1538 (s,sh)	2° amine (3280-3250 cm^{-1}) C-N (imidazole ring) C-O stretch of COOH Amide I & C=O bond Amide II
P2				3277 (s,sh) 1250 (w,sh) 1180 (s,sh) 1628 (s,sh) 1434 (w,b) 1540 (s,sh)	2° amine C-N (imidazole ring) C-O stretch of COOH Amide I & C=O bond Amide II
P3				3279 (s,sh) 1255 (w,sh) 1183 (s,sh) 1628 (s,sh) 1433 (w,b) 1537 (s,sh)	2° amine C-N (imidazole ring) C-O stretch of COOH Amide I & C=O bond Amide II
P4				3298 (s,sh) 1266 (w,sh) 1133 (s,sh) 1659 (s,sh) 1431 (w,sh) 1546 (s,sh)	1° amine (3400-3280 cm^{-1}) C-N (imidazole ring) C-O stretch of COOH Amide I & C=O bond Amide II
P5				3318 (s,sh) 1138 (s,sh) 1650 (s,sh) 1431 (w,sh) 1522 (s,sh)	1° amine C-O stretch of COOH Amide I & C=O bond Amide II
CuP1	714 458 239	2.04 1.98 3.84	d-d transition charge transfer Cu-N=C imidazole	All the bands observed for peptides were observed here. Another amide II band was observed around 1460 cm^{-1} (s,sh) for all the copper peptides. Another peak (s,b) was observed in the range 3400-3600 cm^{-1} due to a combination of the 2° amine and acetate (COO) from the copper(II) acetate [25]. s-strong, w- weak, sh-sharp, b-broad	
CuP2	708 530 268	1.60 1.72 3.74	d-d transition charge transfer Cu-N=C imidazole		
CuP3	737 648 270	2.17 2.23 3.85	d-d transition charge transfer Cu-N=C imidazole		
CuP4	747 518 307	2.31 1.25 2.60	d-d transition charge transfer Cu-N=C imidazole		
CuP5	749 264	1.16 1.93	d-d transition Cu-N=C imidazole		

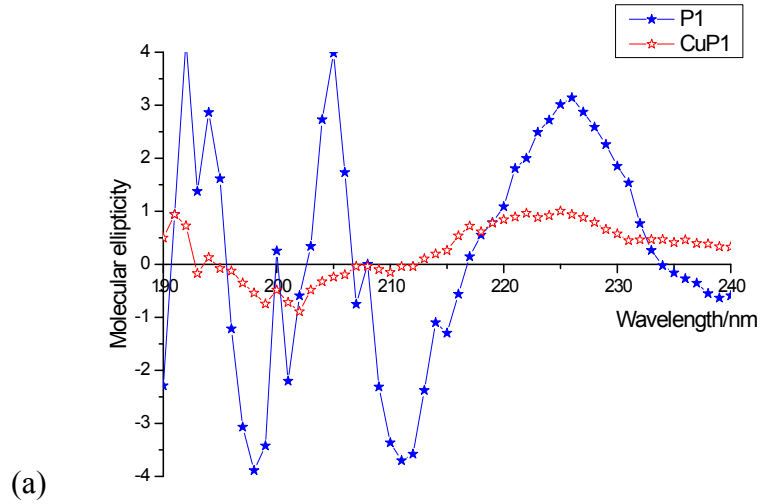
S.I. Table 4 HPLC CHIRALCAK column analysis of aldol enantiomers from Reaction 1 and Reaction 2 with different catalysts

Catalyst	(S)-2-[(R)-hydroxy(4-nitrophenyl)methyl] cyclohexan-1-one				(S)-2-[(R)-hydroxy(4-methoxyphenyl)methyl] cyclohexan-1-one			
	R_TA/min	R_TB/min	% Area A	% Area B	R_TA/min	R_TB/min	% Area A	% Area B
No catalyst[a]	10.2	-	97.1	-	7.50	-	1.24	-
Proline[b]	10.3	14.9	86.6	13.4	7.50	10.4	62.0	0.190
P1	10.9	15.3	3.30	2.10	7.50	-	13.7	-
CuP1	10.8	14.5	35.2	2.40	7.46	10.2	85.9	1.98
P2	10.6	14.7	10.6	16.9	7.50	-	3.41	-
CuP2	10.5	14.5	80.5	4.80	7.50	10.2	7.03	1.33
P3	10.7	14.6	68.2	1.98	7.50	10.2	11.1	0.140
CuP3	10.6	14.4	18.5	2.03	7.50	10.2	9.14	0.430
P4	10.7	14.4	75.2	0.750	7.49	10.2	32.9	0.260
CuP4	10.5	-	96.0	-	7.50	-	1.60	-
P5	No product peaks at 10-15 mins				7.49	10.3	87.2	0.420
CuP5	10.7	-	16.08	-	7.49	10.3	17.0	0.490

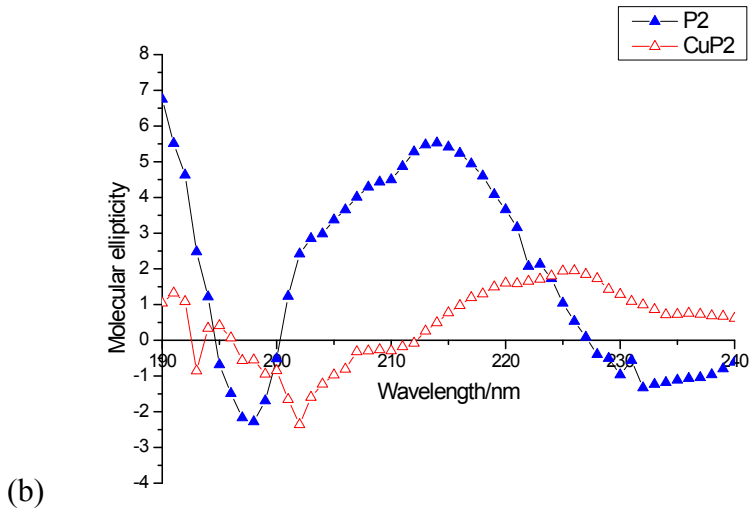
%ee= [(Peak Area A (R) – Peak Area B (S))/(Peak Area A (R) + Peak Area B (S))]*100



S.I. Scheme 1 SPPS scheme of P1; (a) Fmoc deprotection of rink amide resin and coupling of 1st amino acid from C-terminal; (b) Fmoc deprotection of 1st amino acid and coupling of 2nd and 3rd amino acid; (c) Fmoc deprotection of 2nd and 3rd amino acid and coupling of final (4th) amino acid; (d) Cleaving peptide from resin using cleavage cocktail mixture.



(a)



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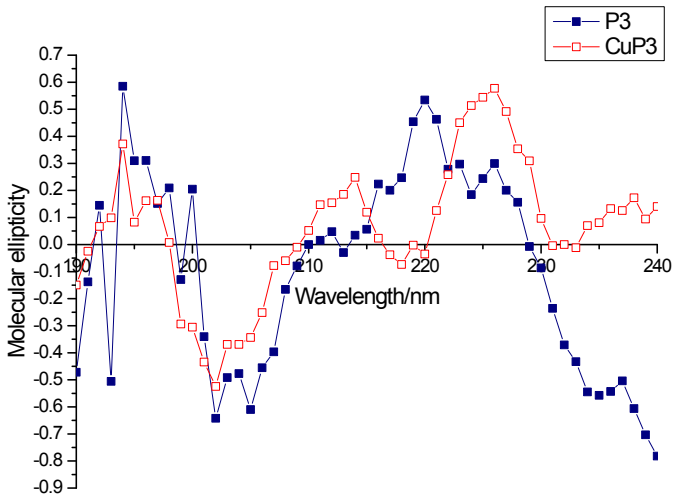
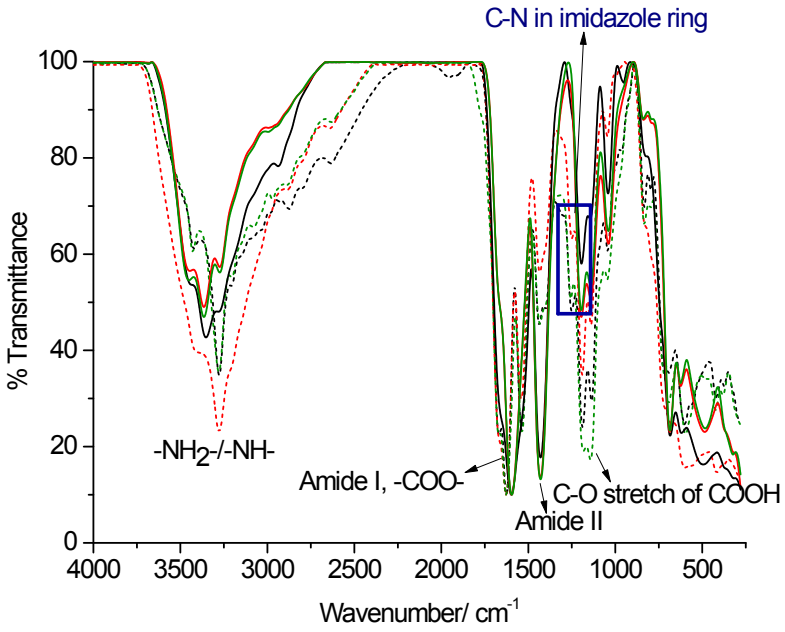
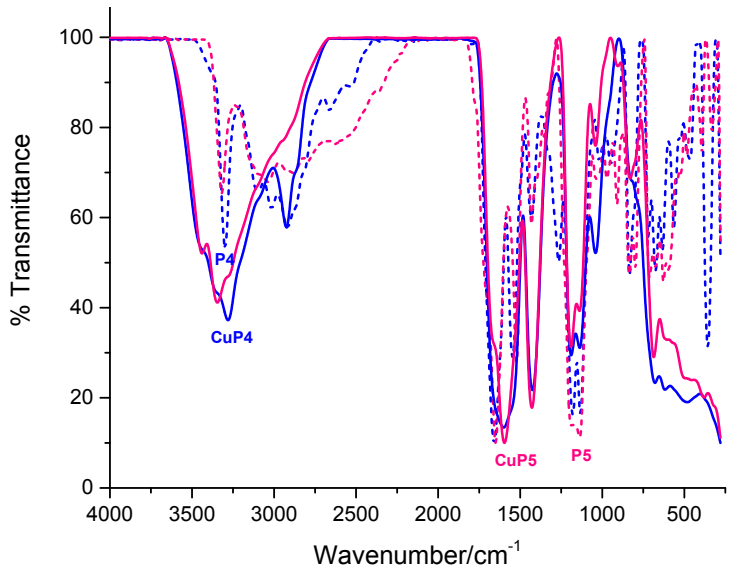


(c)

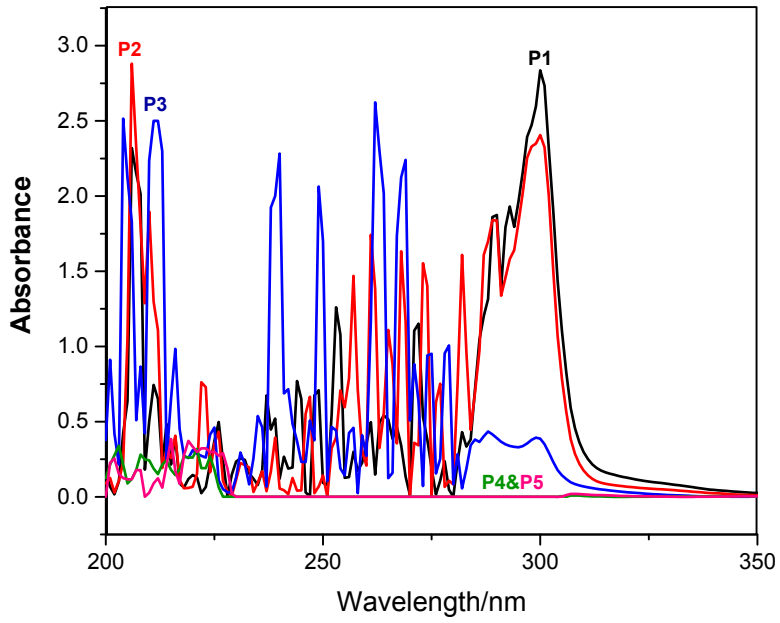
S.I. Figure 1 CD spectra of (a) P1 & CuP1 (5 mM, 400 µL), (b) P2 & CuP2 (5 mM, 400 µL) and (c) P3 & CuP3 (5 mM, 400 µL) analyzed at room temperature (25°C), their secondary structures opted by their highest percentage as shown in S.I. Table 2.



S.I. Figure 2 FTIR analysis of the P1-P3 and CuP1-CuP3. The dotted lines represent the peptides while the solid lines of the same colour represent the respective copper(II)-peptides; black: P1, red: P2 and green: P3. Most of the major peaks as assigned in the graph were shifted to the right for copper-peptides as compared to their parent peptides (in the range of 2000-500 cm^{-1}). The amide peaks (terminal end) of copper(II) peptides were shifted to the left when compared to their peptides (3400-3200 cm^{-1}).

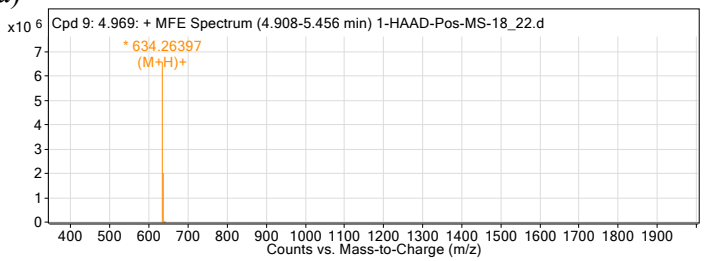


S.I. Figure 3 FTIR analysis of P4, CuP4, P5 and CuP5. The dotted lines represent the peptides while the solid lines of the same colour represent the respective copper(II)-peptides; blue: P4 and pink: P5.



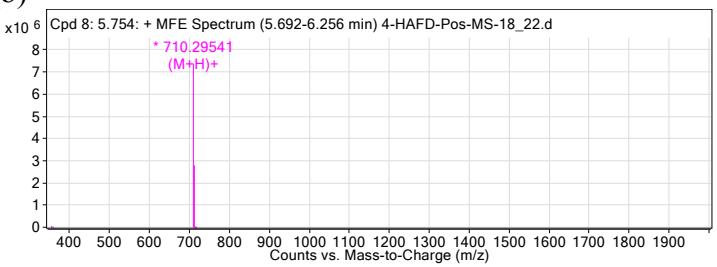
S.I. Figure 4 UV-Vis spectrum of P1-P5. 0.1M of P1-P3 are denoted by black, red and blue dotted lines, respectively, where as 0.01 M of P4 and P5 are denoted by green and pink dotted lines, respectively. The transitions that include n-π* and π- π* (peptides) appear around 270- 330 nm and 200-270 nm respectively. These transitions occur due to the presence of double bonds, cyclised rings and aromatic rings of the amino acids and amide bonds [21]. Hence they appear as several peaks clustered together as observed in the spectra of peptides.

(a)



Compound Label	*m/z*	RT	Algorithm	Mass
HAAD Fmoc	634.26397	4.969	Find by Molecular Feature	633.25686

(b)



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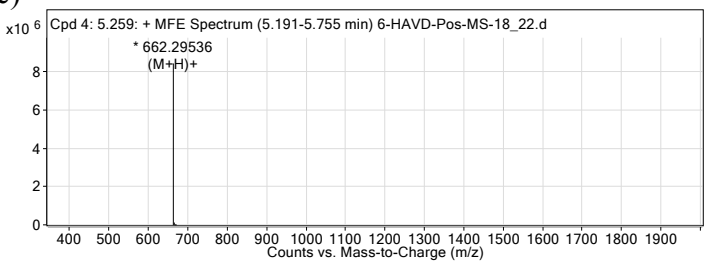
HAFD w Fmoc	710.29541	5.754	Find by Molecular Feature	709.28869

(c)



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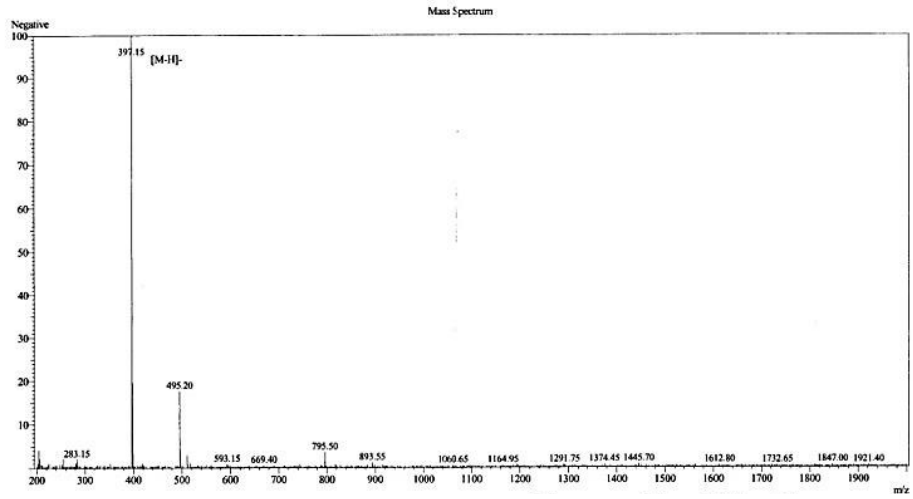
HAVD Fmoc	662.29536	5.259	Find by Molecular Feature	661.28848

(d)



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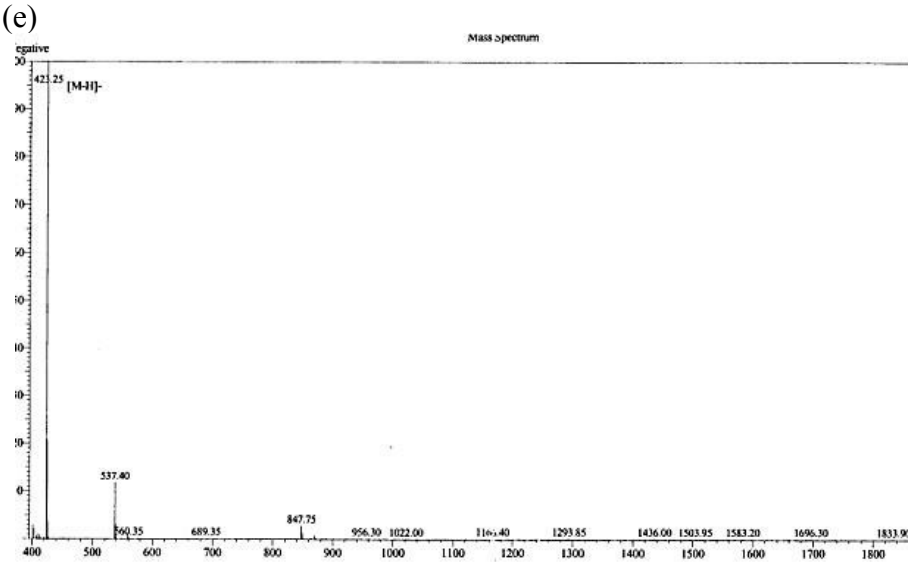
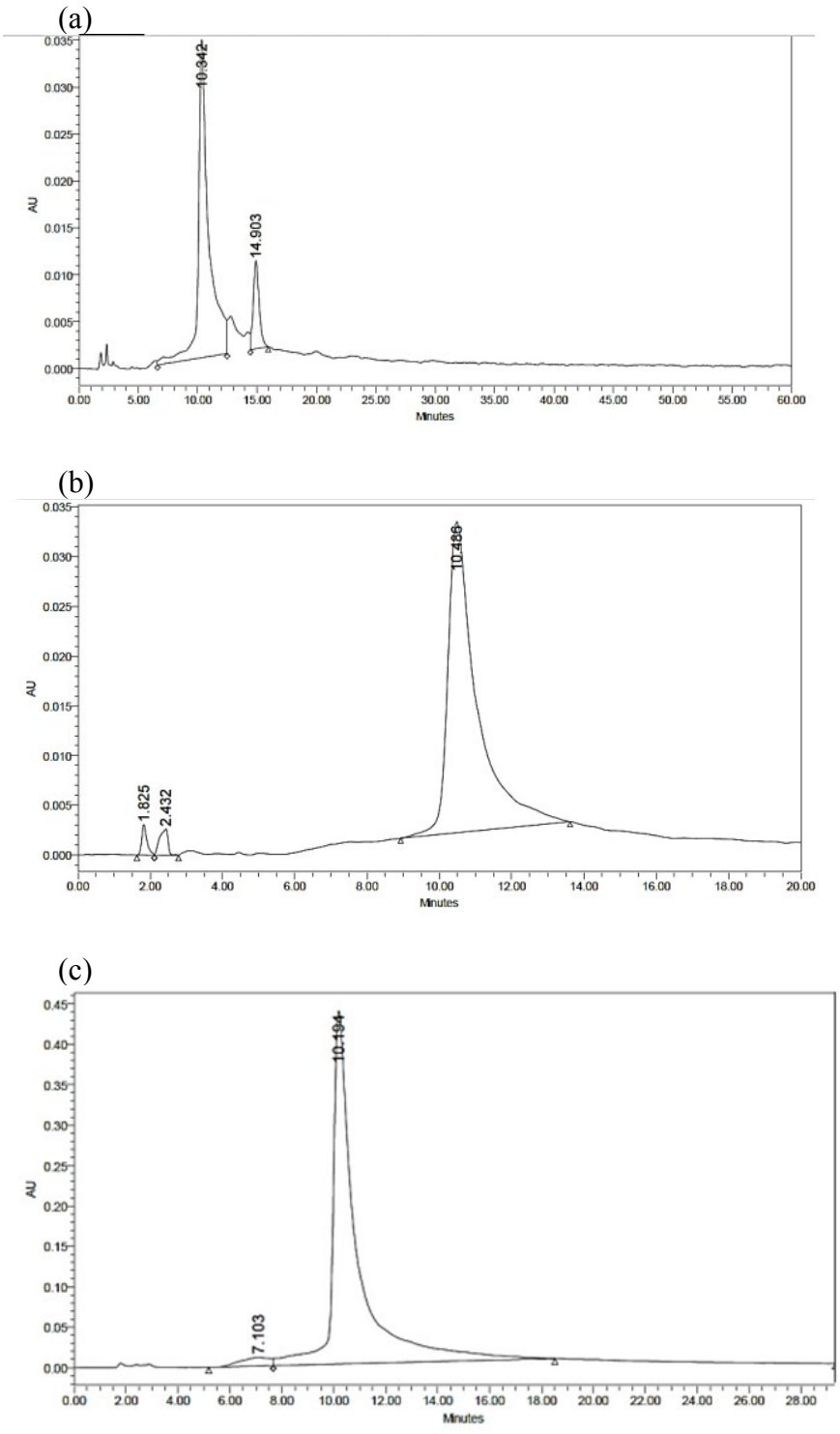
AGHD w/o Fmoc	398.4032	7.242	Find by Molecular Feature	397.1503

(e)



Compound Label	*m/z*	RT	Algorithm	Mass
PGHD wo Fmoc	424.42	7.690	Find by Molecular Feature	423.2513

S.I. Figure 5 LC-MS of peptides P1-P5.



S.I. Figure 6 HPLC chromatograms of aldol reaction between p-nitrobenzaldehyde & cyclohexanone with catalysts (a) Proline (b) CuP4 (c) No catalyst.