Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary Information

Amide bond hydrolysis of peptoids

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Materials

Rink Amide resin was purchased from Novabiochem. Reagents like piperdine, ethanolamine, naphthalen-1-ylmethanamine, 2-methoxyethan-1-amine, (S)-(+)-1-methoxy-2- propylamine, (S)-1-(2-naphthyl)ethylamine; (S)-(-)-1 phenylethylamine, phenylmethanamine; (R)-3,3-dimethylbutan-2-amine were purchased from Sigma Aldrich and Alfa Aesar Chemical company. Estradiol was purchased from Alfa Aesar company. N,N'-diisopropylcarbodiimide (DIC) was purchased from Chem-Impex Int'l Inc. Bromoacetic acid was purchased from Merck. Metal salts are purchased of analytical grade. All used solvents were HPLC grade of which dimethylforamide (DMF), toluene and dichloromethane (DCM) solvents were purchased from Bio-Lab Ltd. Acetonitrile (ACN) and water were obtained from Sigma-Aldrich.

Instrumentations

Reversed-phase HPLC on a Jasco UV-2075 instrument (analytical C18 column, Luna 5µm, 100 Å, 2.0 x 50 mm) was used to analyze synthesized peptoids. Linear gradient of 5–95% ACN in water with 0.1% TFA (flow rate is 700 µL/min) over 10 min was used. Preparative HPLC was performed using a phenomenex C18 column (Luna 15µm, 100 Å 21.20x100mm) on a Jasco UV-2075 instrument using 5–95% ACN in water with 0.1% TFA as solvent for elution. A linear gradient of the solvent is used over 50 min at a flow rate of 5 mL/min. Mass spectrometry was performed on Waters LCT Premier mass [ESI+, direct probe ACN:H_2O (95:5), flow rate 0.2 ml/min] and Advion expression mass under electrospray ionization (ESI) [ESI+, direct probe ACN:H_2O (70:30), flow rate 0.3 ml/min].

Preparation of peptoid oligomers

Peptoids were manually prepared in fritted syringes by the sub-monomer method on Rink amide resin at room temperature. [1] In a typical synthesis, rink-amide resin (100 mg) was measured and swallowed in DCM for a period of 40 minutes. De-protection of the resin was carried out by piperidine solution (20%, solvent: DMF) followed by 20 minutes shaking in ambient condition. Next, piperidine was washed by DMF for three times with one minute duration (1 mL/ 25 mg resin each time). Bromoacetylation was done by addition of 20 eq. Bromoacetic acid (1.2 M in DMF, 8.5 mL/g resin) together with 24 eq. of diisopropylcarbodiimide (2 mL g^{-1} resin), shaking for 20 min in room temperature. Afterwards, the bromoacetylation reagents were properly washed from the resin by DMF (1 mL/ 25 mg resin each time, three times with one minute duration each time). After washing, 20 eq. of the primary amine (1.0 M in DMF, 10 mL/g resin) was added under shaking for next 20 minutes at room temperature and later washed three times by DMF. Bromoacetylations and amine displacement steps were repeated till the desired sequence was loaded on the resin. When the synthesis of the desired sequence was finished, they were

cleaved from solid support for initial analysis. Approximately 4-6 mg of the resin were dispersed in a 95% TFA in water (40 mLg-1 resin) for 20 minutes. The cleavage cocktail was evaporated under nitrogen gas and the peptoid oligomers were resuspended in 0.5 mL HPLC solvent (1:1 HPLC grade acetonitrile: HPLC grade water). To cleave the peptoid oligomers from solid support for preparative HPLC the beads were treated with 5ml of 95% TFA in water for 30 minutes. The cleavage cocktail was evaporated under low pressure, resuspended in 2 mL HPLC solvent, and lyophilized overnight

Characterization of the peptoid oligomers

The peptoids were characterized by analytical HPLC using a C18 column using a specific solvent gradient of 5% to 95% solvent B (0.1% TFA in HPLC grade acetonitrile) over solvent A (0.1% TFA in HPLC grade water) for 10 minutes under a constant flow rate of 0.7 mL/min with 214 nm UV absorbance. In case of preparative HPLC at 230 nm, C18 column was used where the solvent gradient was 5% to 95% solvent B (0.1% TFA in HPLC grade acetonitrile) over solvent A (0.1% TFA in HPLC grade water), duration 50 minutes, flow rate 5 mL/min. The collected peptoids were lyophilized overnight. The pure peptoids were further analysed by RP-HPLC [C18 column with a linear gradient of 5–95% ACN in water (0.1% TFA) over 10 min at a flow rate of 700 µL/min and 214 nm UV absorbance].

Table S1. Peptoid oligomer sequences with their molecular weights [*Nnap:* naphthalen-1-ylmethanamine; *Nme*: 2-methoxyethan-1-amine; *Nsmp:* (S)-(+)-1-methoxy-2- propylamine, *Ns1npe:* (S)-1-(2- naphthyl)ethylamine; *Nspe:* (S)-(-)-1 phenylethylamine*, Npm*: phenylmethanamine*; Nr1tbe*: (R)-3,3-dimethylbutan-2-amine*, Nbp:* 2-(2, 2'-bipyridine-6-yloxy) ethylamine; *Npl:* chloropropyl group; *Nhse*: an ethanol group, *Nestradiol*: an estrogen steroid hormone]

Entry	Peptoid oligomers (C-terminus to N-terminus)	Molecular weight Calc: Found
1	**P1** (*N*pm- *Nhse- Nr1tbe*)	406.25:407.4
2	**P2** (*Nbp- Nhse- Nr1tbe*)	514.29:515.62
3	**P3** (*Nbp- Nhse- Npm*)	Ref 2.
4	**P4** (*Nbp- Nhse- Nspe*)	534.26:535.45
5	**P5** (*Nbp- Nhse- Nnap*)	570.26:571.4
6	**P6** (*Nbp- Nhse- Ns1npe*)	584.27:585.57
7	**P7** (*Nbp- Nhse- Nme*)	488.24:489.24
8	**P8** (*Nbp- Nhse- Nsmp*)	502.25:503.38
9	**P9** (*Npl- Nme- Npm- Nme-Npm-Nr1tbe*)	815.43:816.42
10	**P9a** (*Npl-Nme-Npm-Nme-Nspe*)	688.33:689.45
11	**P9b** (*Npl- Nme-Npm-Nme -Npm*)	674.32:675.39
12	**P9c** (*Npl- Nme -Npm- Nsmp*)	541.26:542.1
13	**P10** (*Nr1tbe- Nr1tbe- Nr1tbe- Nr1tbe)*	581.49:582.66
14	**P11** (*Nspe- Nspe- Nspe- Nspe)*	661.36:662.76
15	**PSteroid** (*Nestradiol - Nhse- Nr1tbe)*	711.47:712.39

Peptoid and metal ion interactions

Peptoids are mixed with metal ions (1:1, mole/mole) in ACN:Water (1:1, v/v), and kept 4 hrs on shaker followed by measuring in ESI-MS. In case of obtaining crystal structures, the same was kept for slow evaporation which produces small crystals for x-ray analysis after 3-4 days.

In 1:1 ratio, for ESI-MS measurements, the peptoid and metal ion concentration were kept at 50µM whereas for obtaining crystal structure, the same was at 1mM concentration to have enough complex in solution for crystallization.

DFT analysis

In case of geometry optimization for P3 (CCDC: 1559281)[2], P5 (table S2) and P7 (table S2), the peptoid structures were taken from crystal structure. For P4, P6 and P8 the alpha methyl substitution on N-terminal was introduced from crystal structure (S)-(-)-1 phenylethylamine.[3] The peptoids were optimized was optimized by DFT-D3 calculations (considering the dispersion correction) at the level of B3-LYP with def2-SVP for every atoms, def2-TZVP for Cu(II) and COSMO for water, using Turbomole software package (OS: MACOSX, V 7.3). The coordinates for P10 were taken from reported crystal structure. [4]

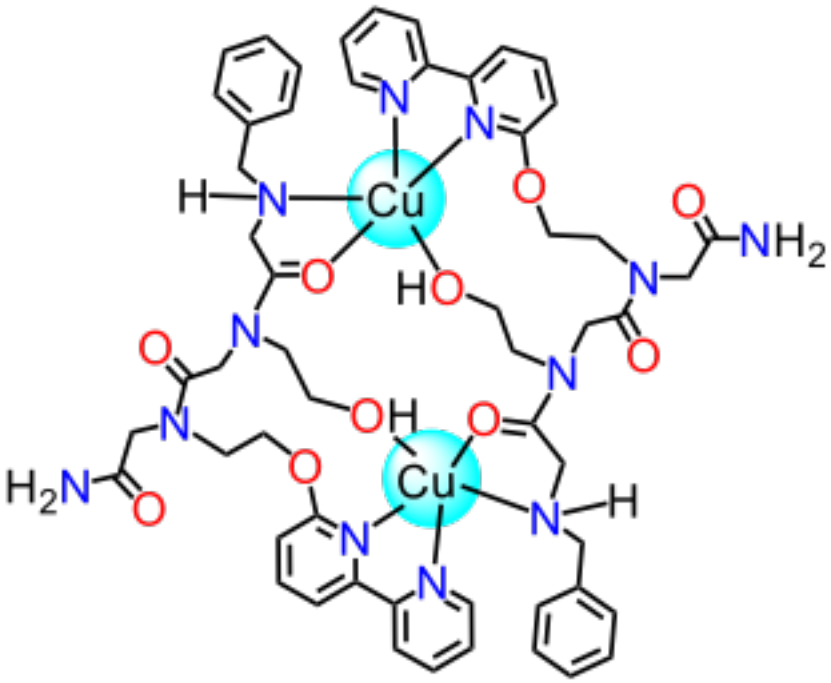

Figure S1. Schematic view of $(P3)_2Cu_2$, named 'Metallopeptoid 7' in the reported article (ref 2).

HPLC traces of peptoids

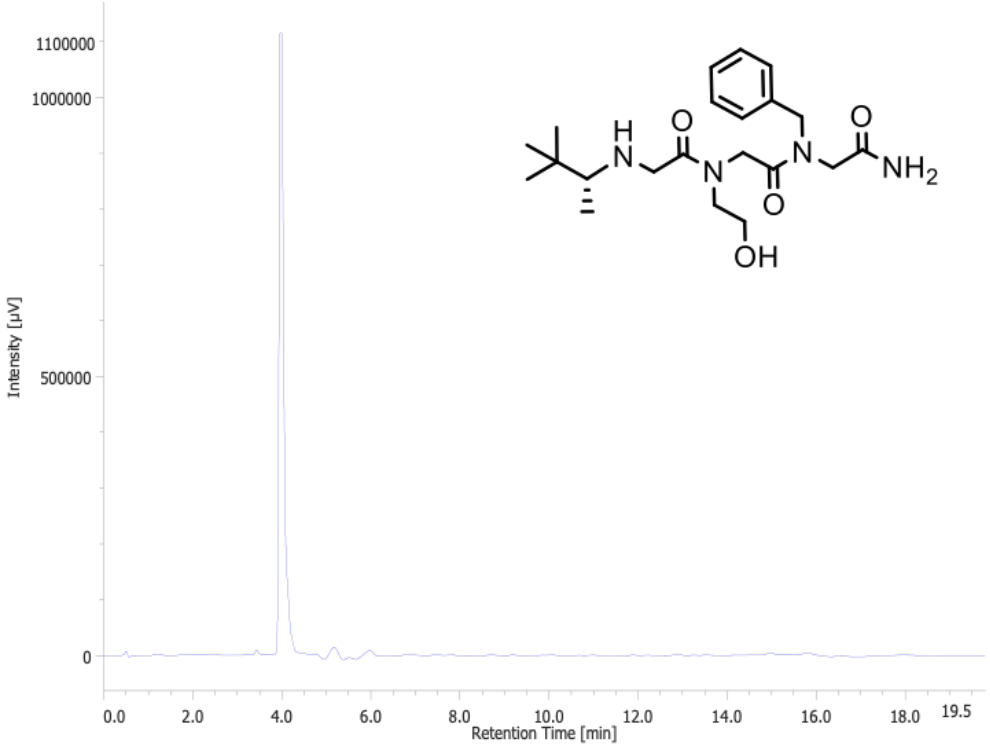

Figure S2. HPLC traces of pure peptoid **P1**.

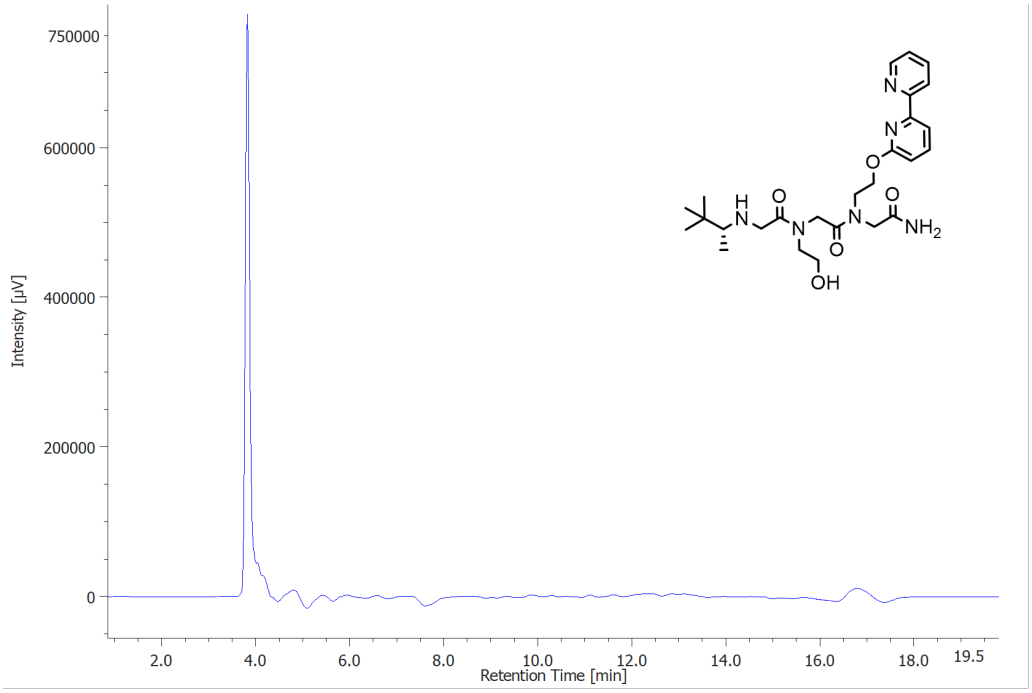

Figure S3. HPLC traces of pure peptoid **P2**.

We have reported the peptoid P3 before and the HPLC traces could thus be obtained in literature.[5]

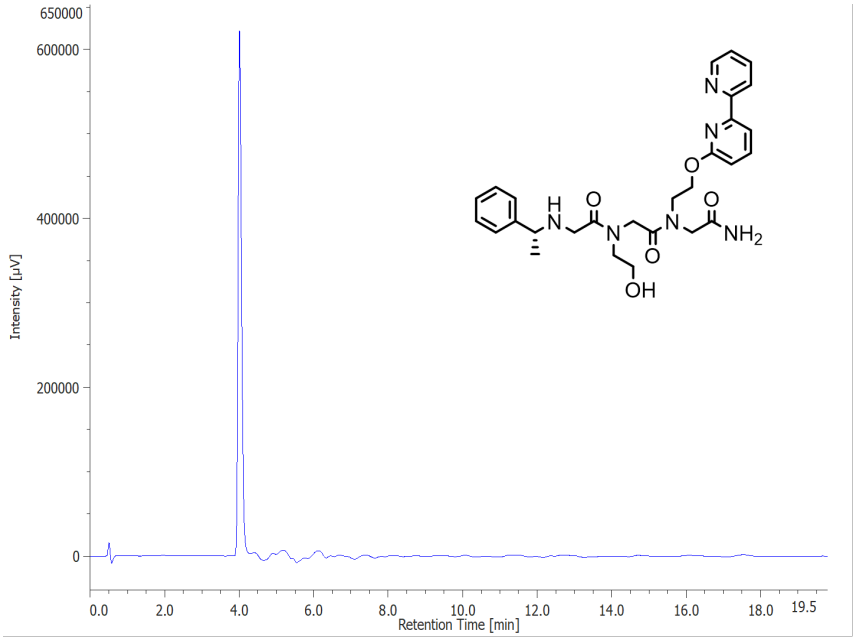

Figure S4. HPLC traces of pure peptoid **P4**.

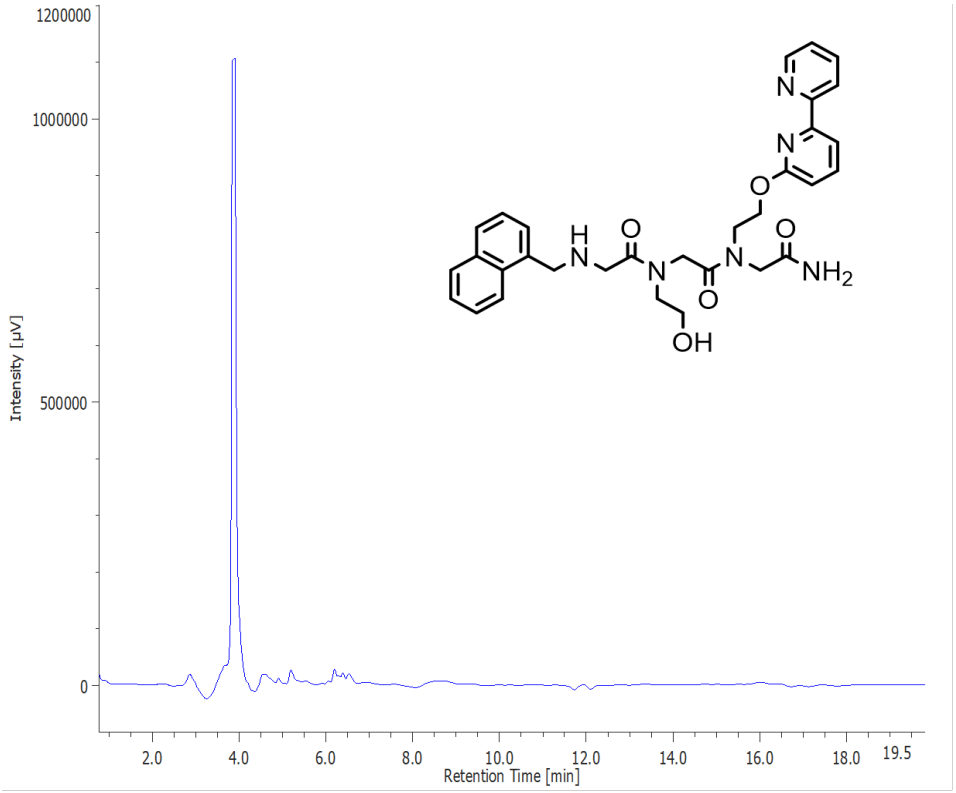

Figure S5. HPLC traces of pure peptoid **P5**.

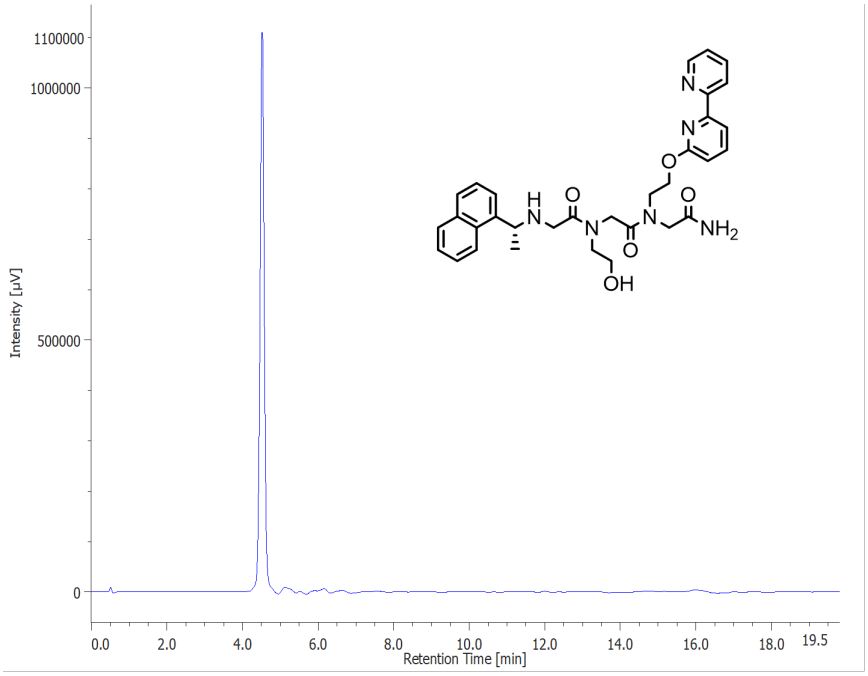

Figure S6. HPLC traces of pure peptoid **P6**.

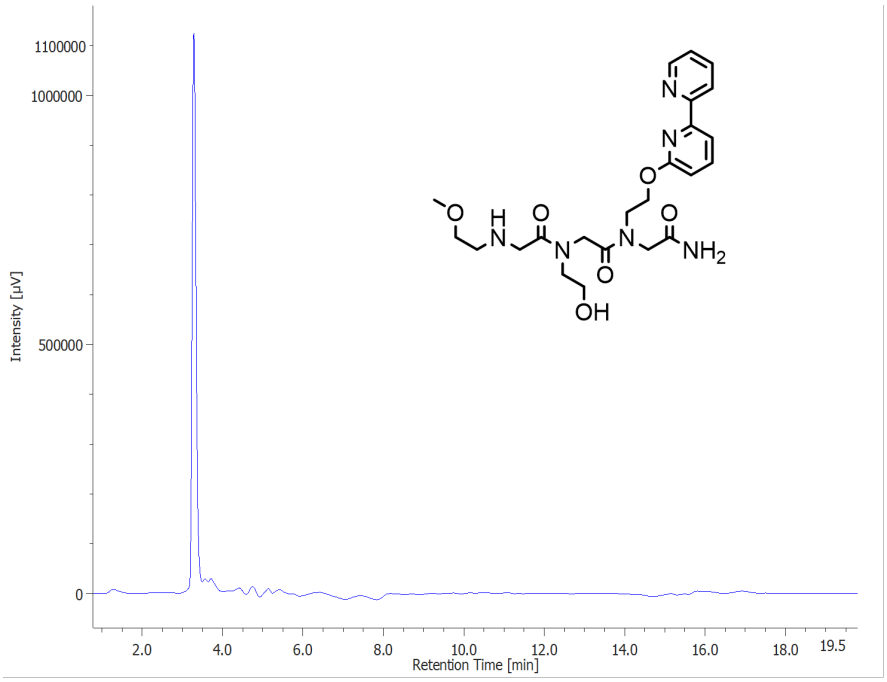

Figure S7. HPLC traces of pure peptoid **P7**.

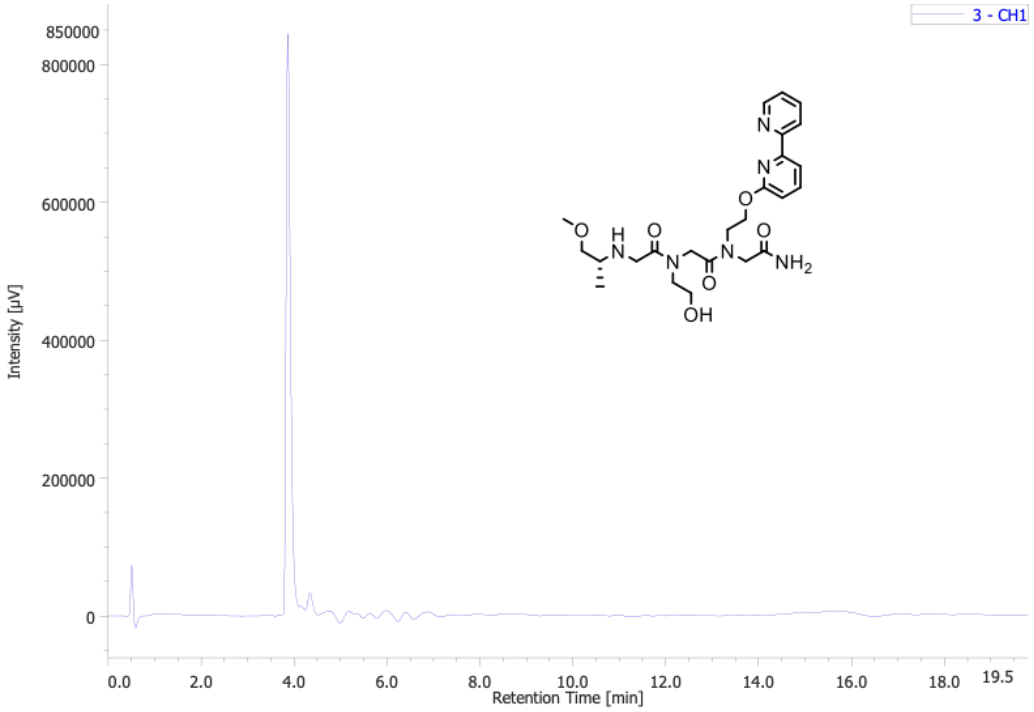

Figure S8. HPLC traces of pure peptoid **P8**.

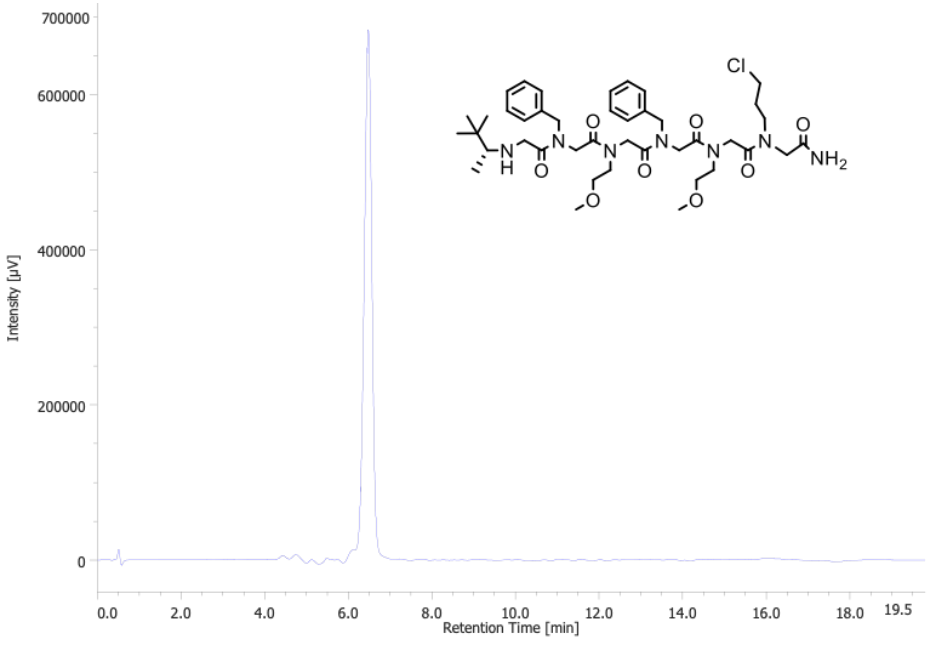

Figure S9. HPLC traces of pure peptoid **P9**.

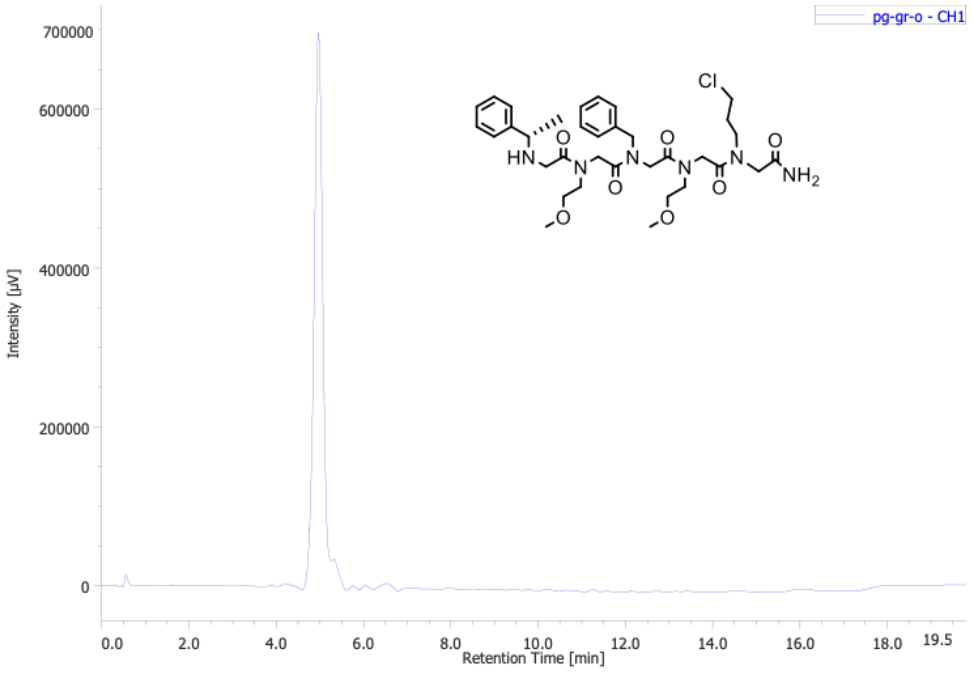

Figure S10. HPLC traces of pure peptoid **P9a**.

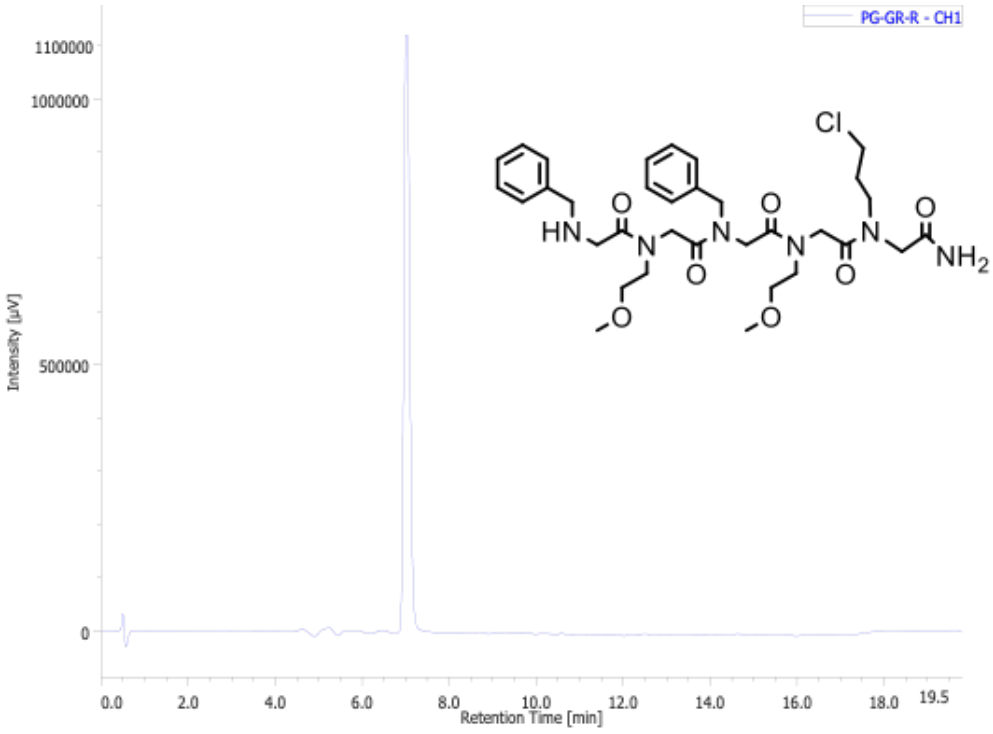

Figure S11. HPLC traces of pure peptoid **P9b**.

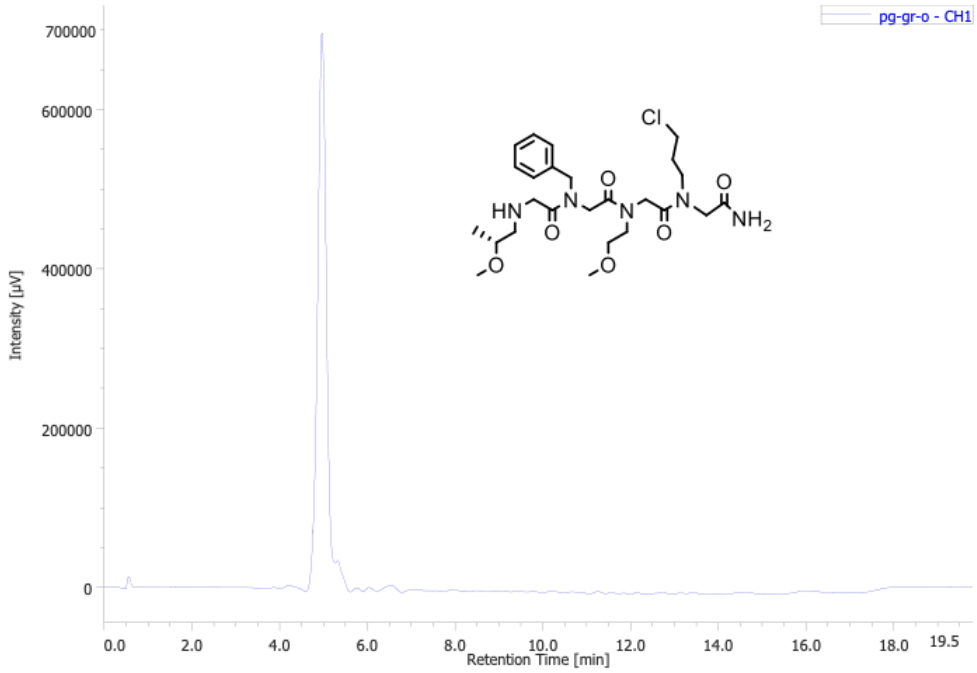

Figure S12. HPLC traces of pure peptoid **P9c**.

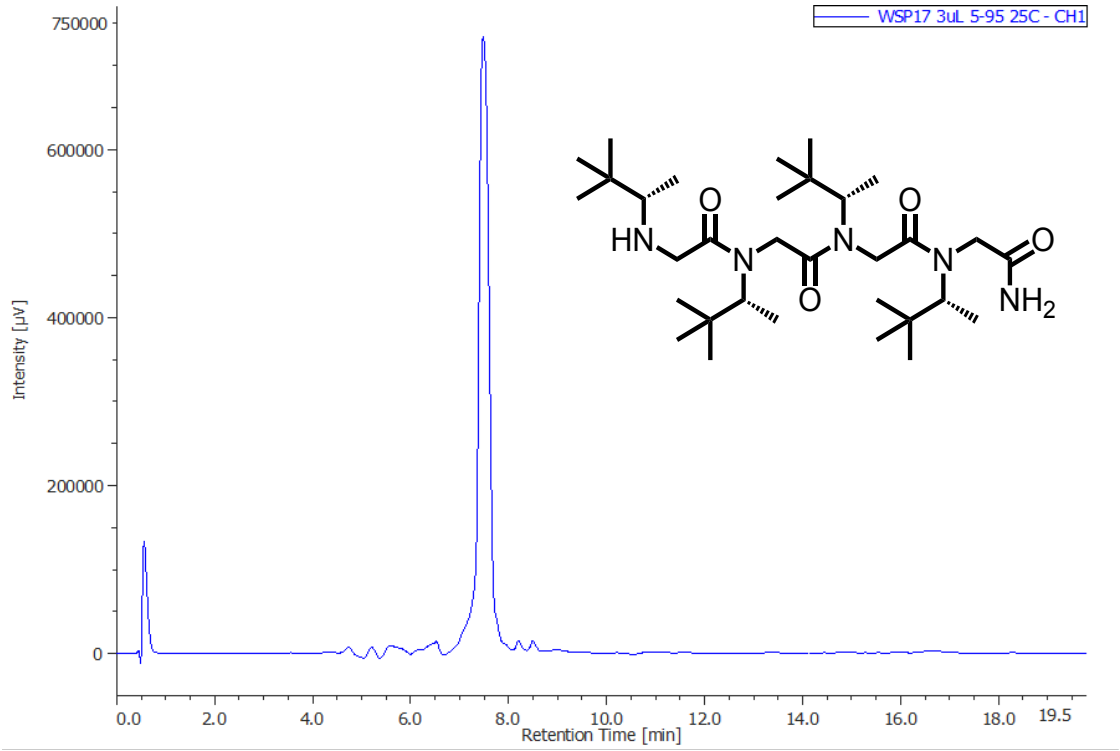

Figure S13. HPLC traces of pure peptoid **P10**.

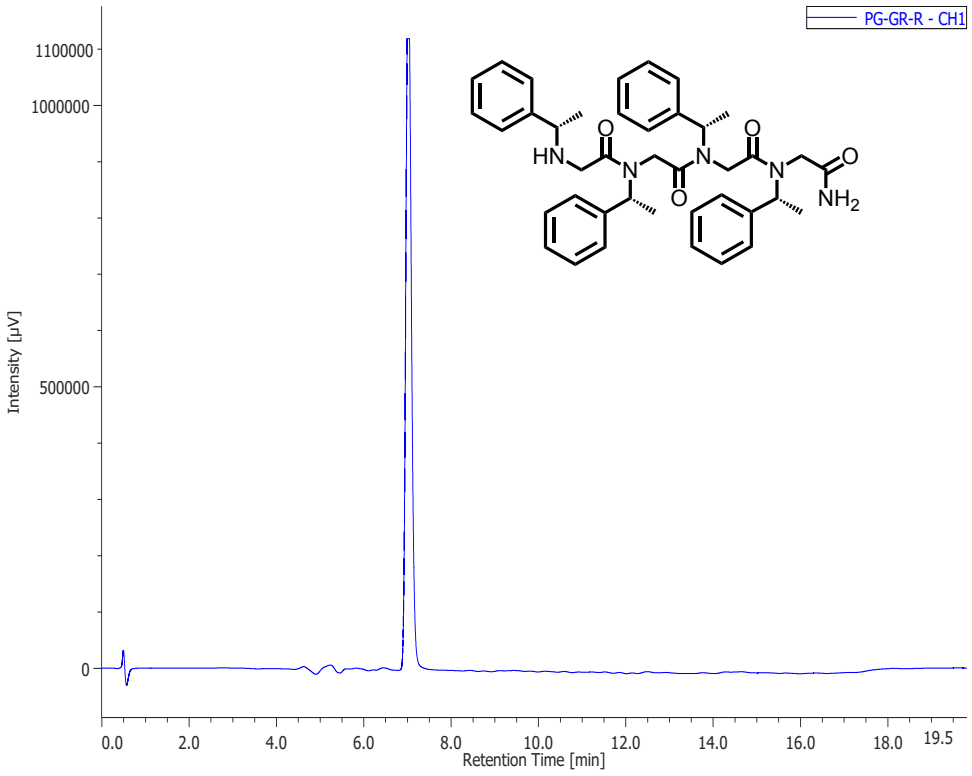

Figure S14. HPLC traces of pure peptoid **P11**.

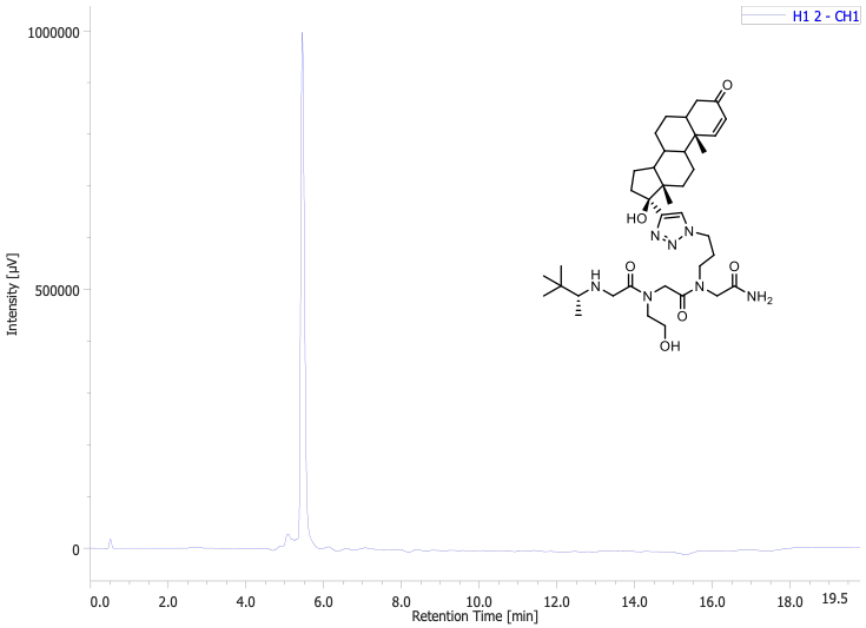

Figure S15. HPLC traces of pure peptoid **PSteroid**.

ESI-MS of peptoids

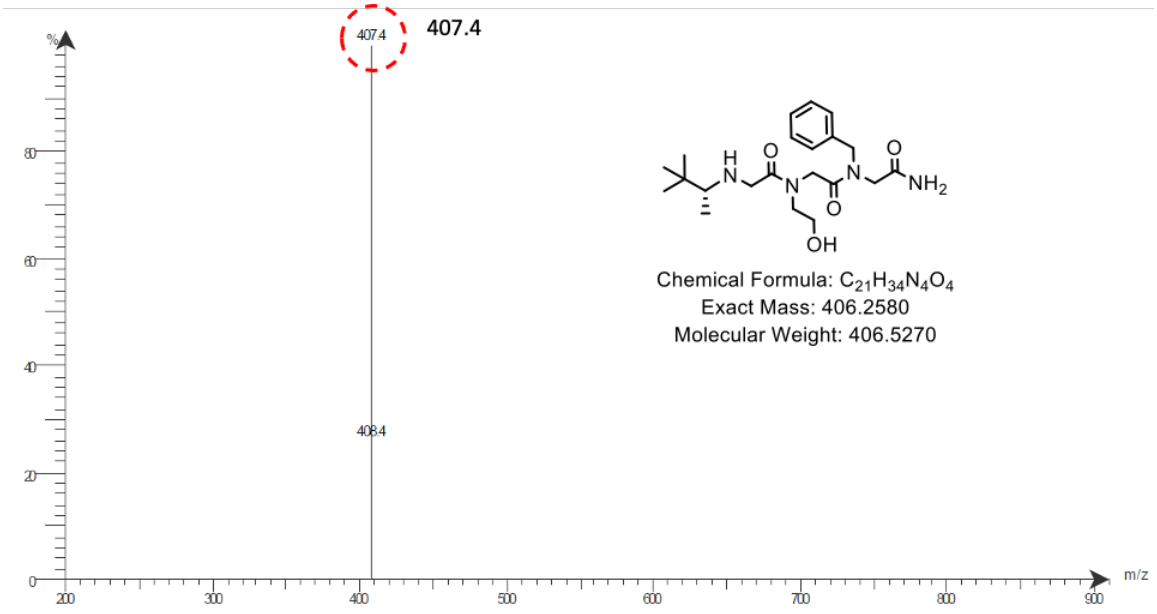

Figure S16. ESI-MS of **P1** in ACN:water.

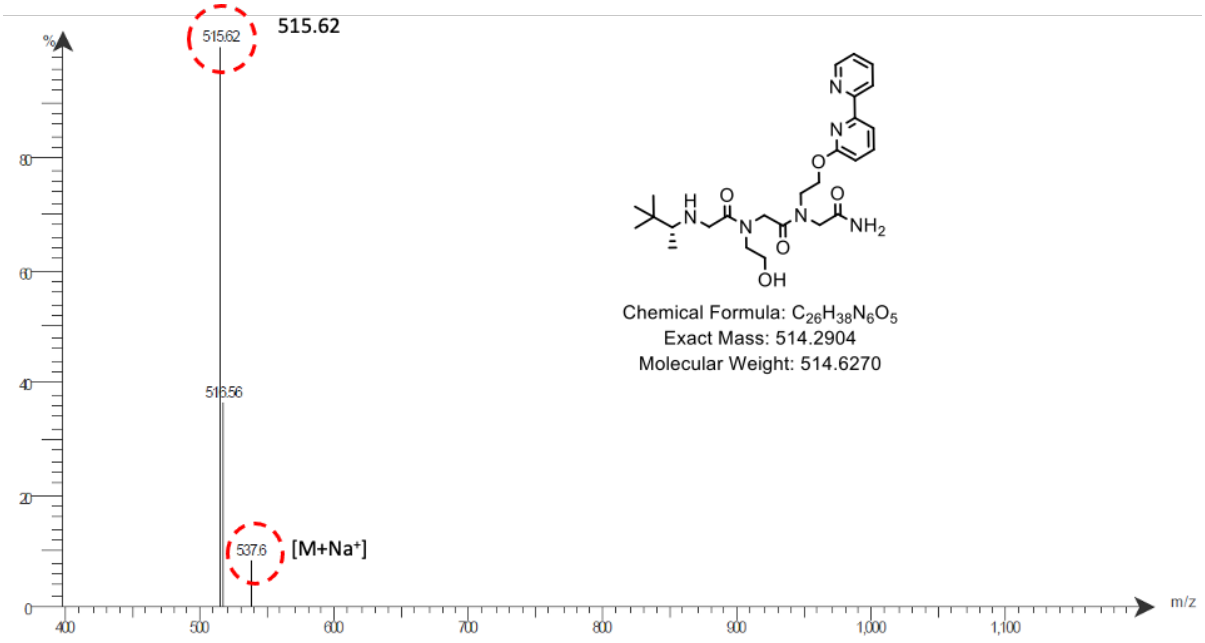

Figure S17. ESI-MS of **P2** in ACN:water.

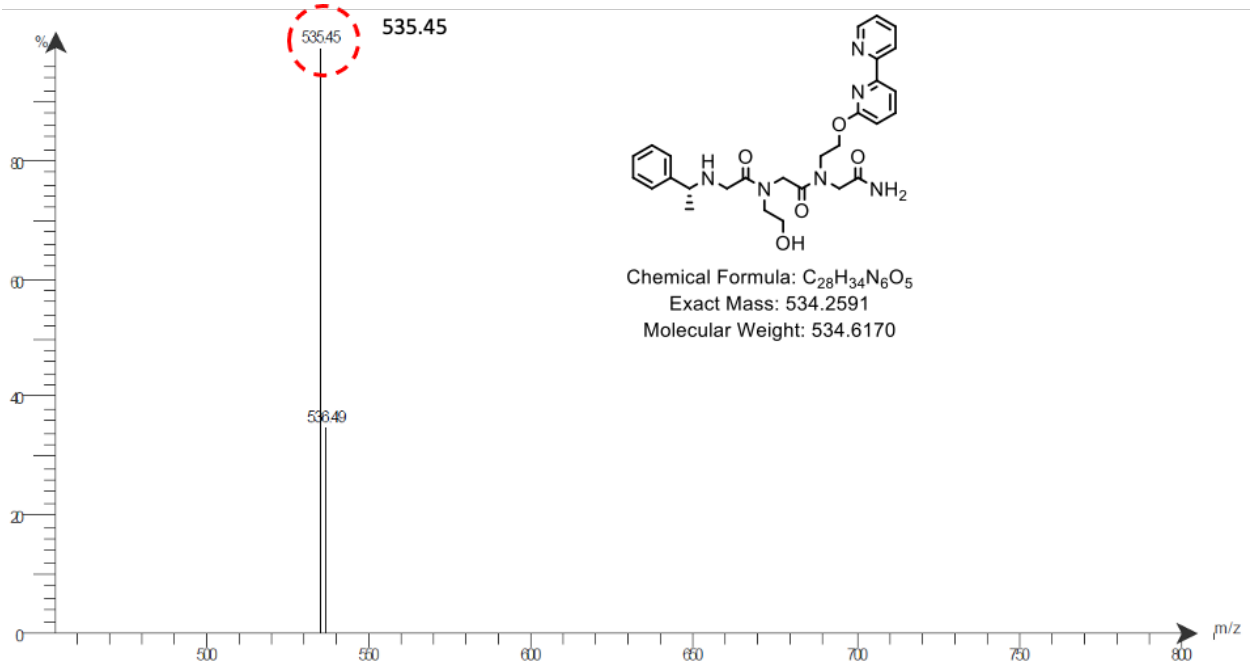

Figure S18. ESI-MS of **P4** in ACN:water.

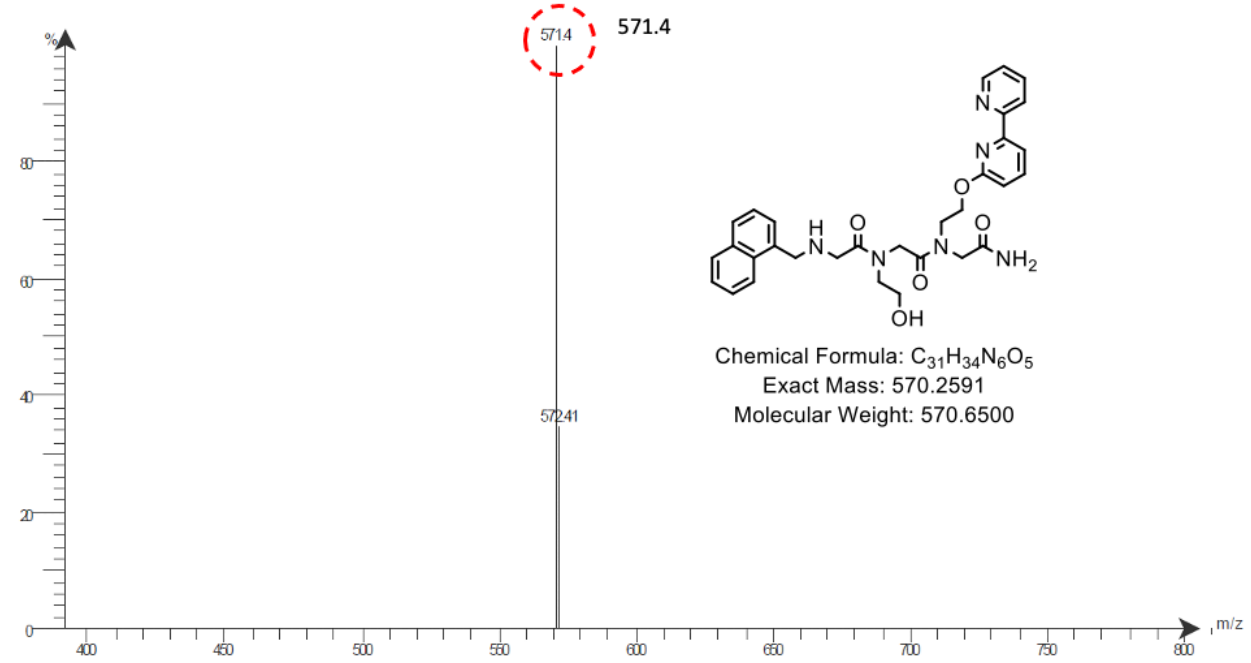

Figure S19. ESI-MS of **P5** in ACN:water.

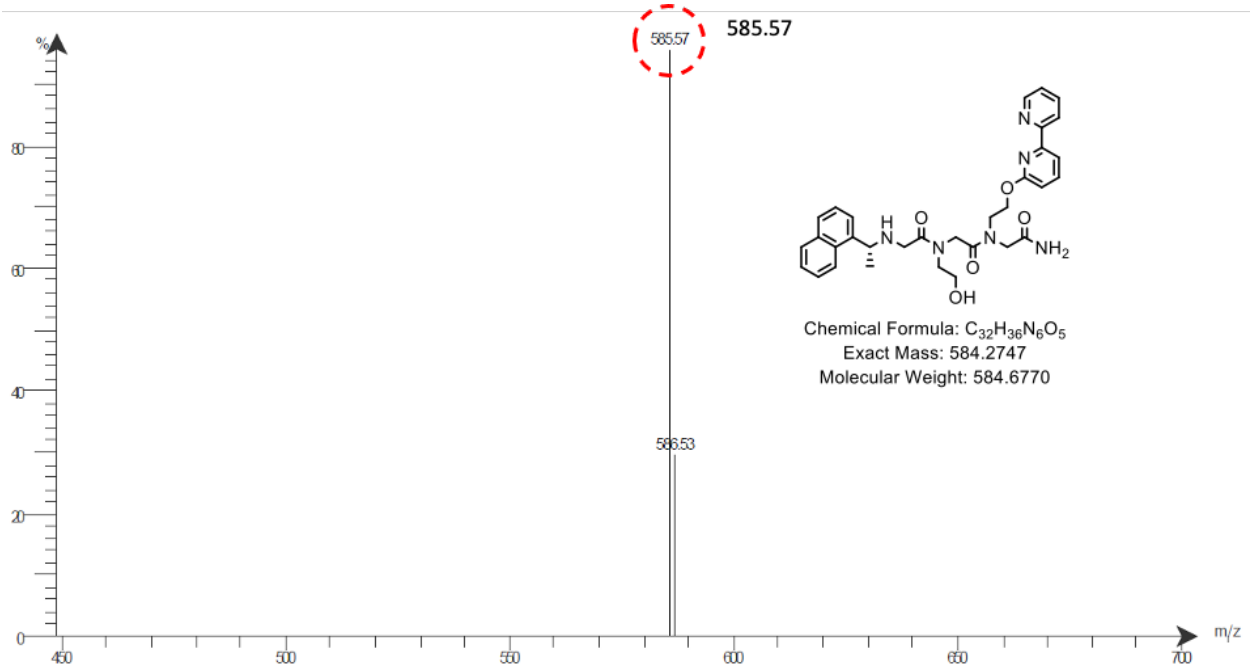

Figure S20. ESI-MS of **P6** in ACN:water.

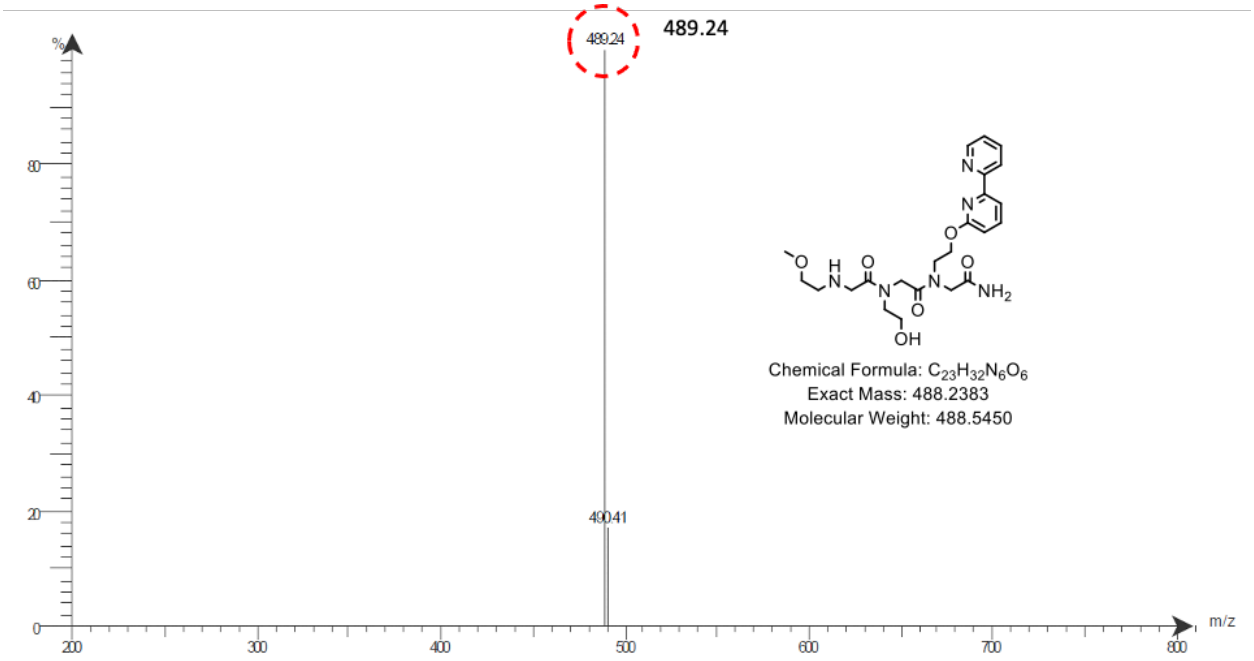

Figure S21. ESI-MS of **P7** in ACN:water.

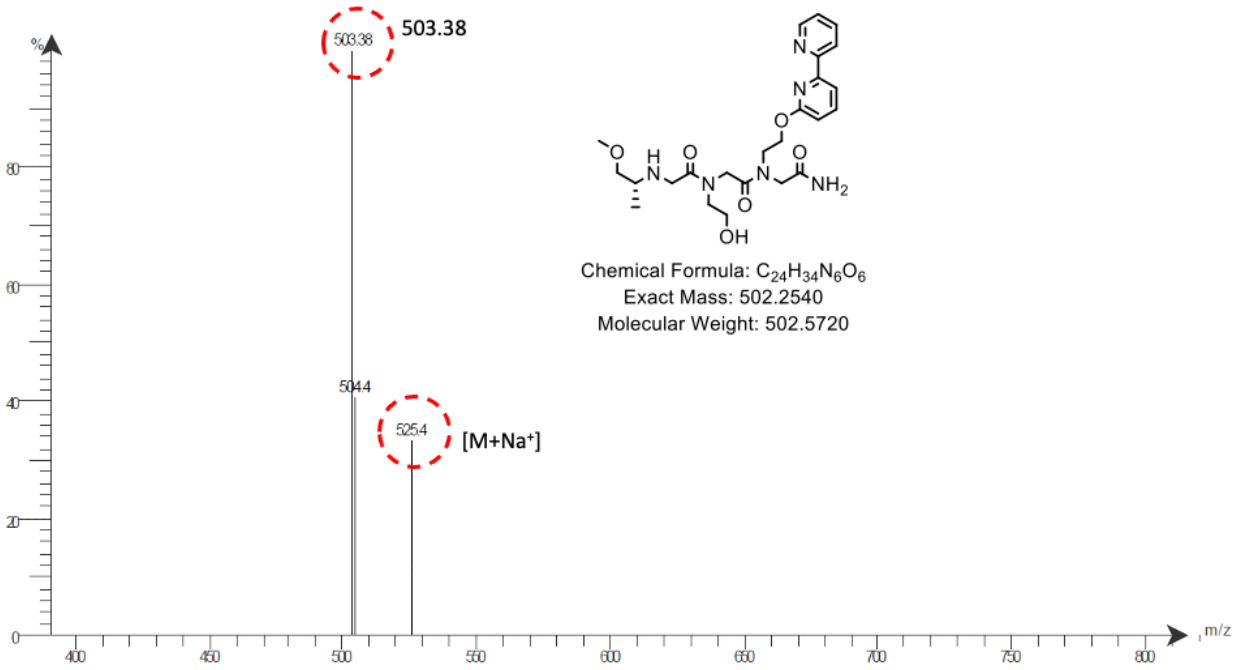

Figure S22. ESI-MS of **P8** in ACN:water.

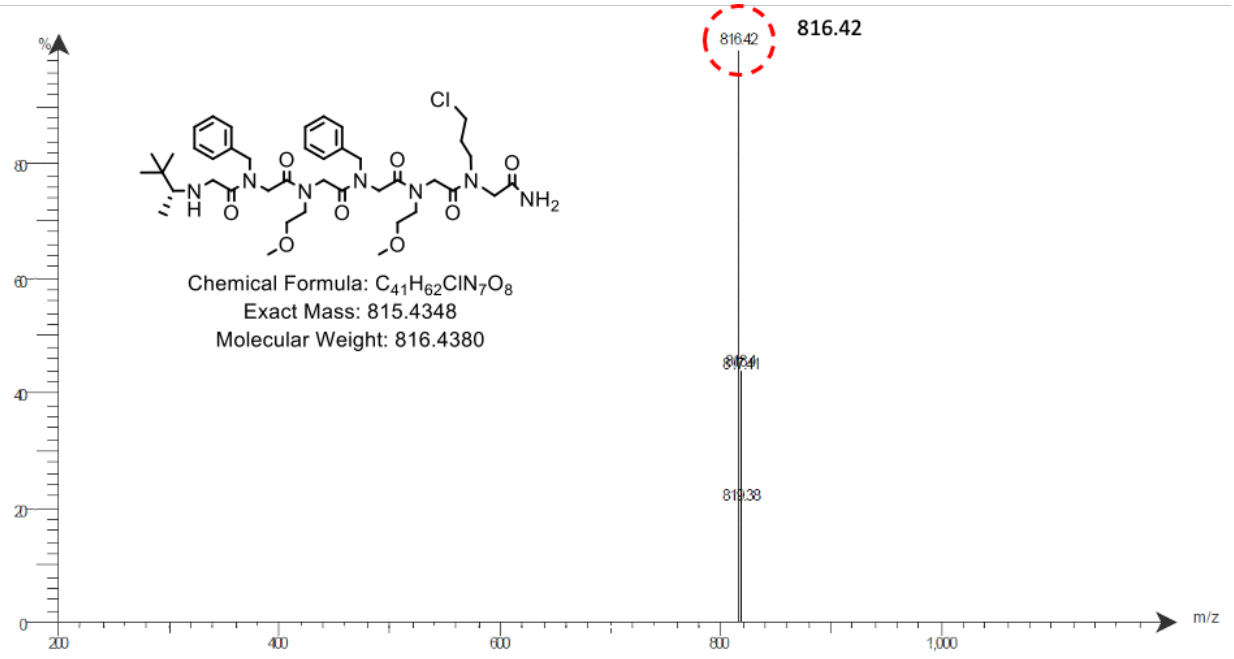

Figure S23. ESI-MS of **P9** in ACN:water.

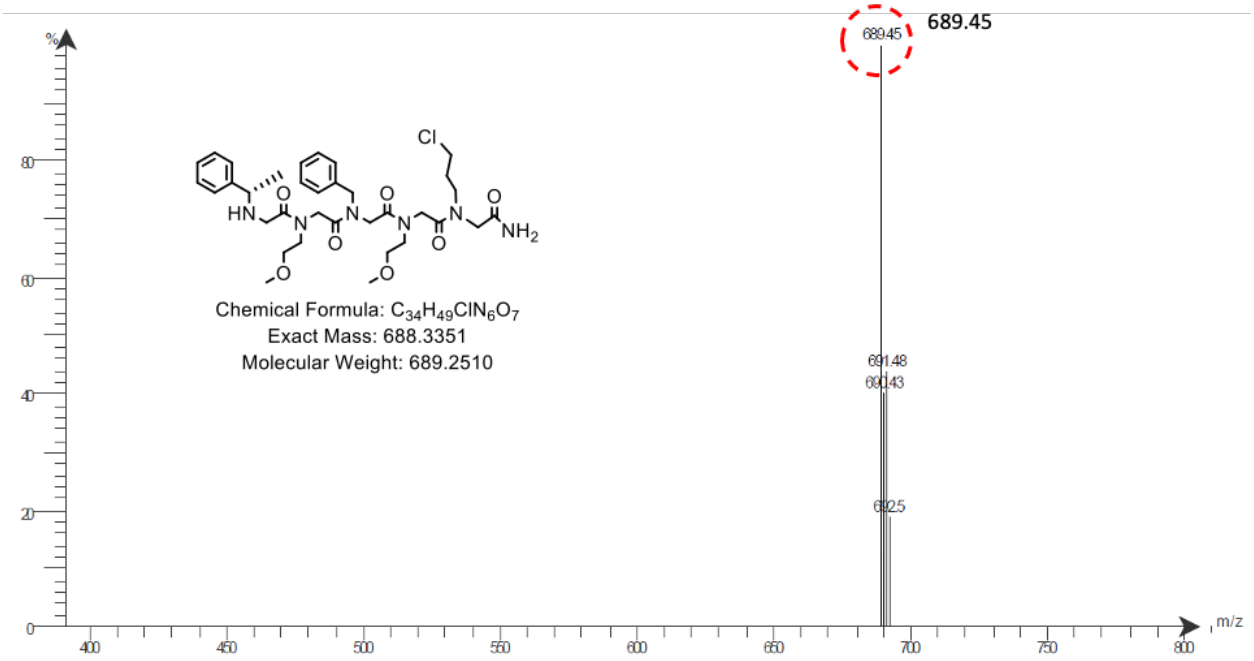

Figure S24. ESI-MS of **P9a** in ACN:water.

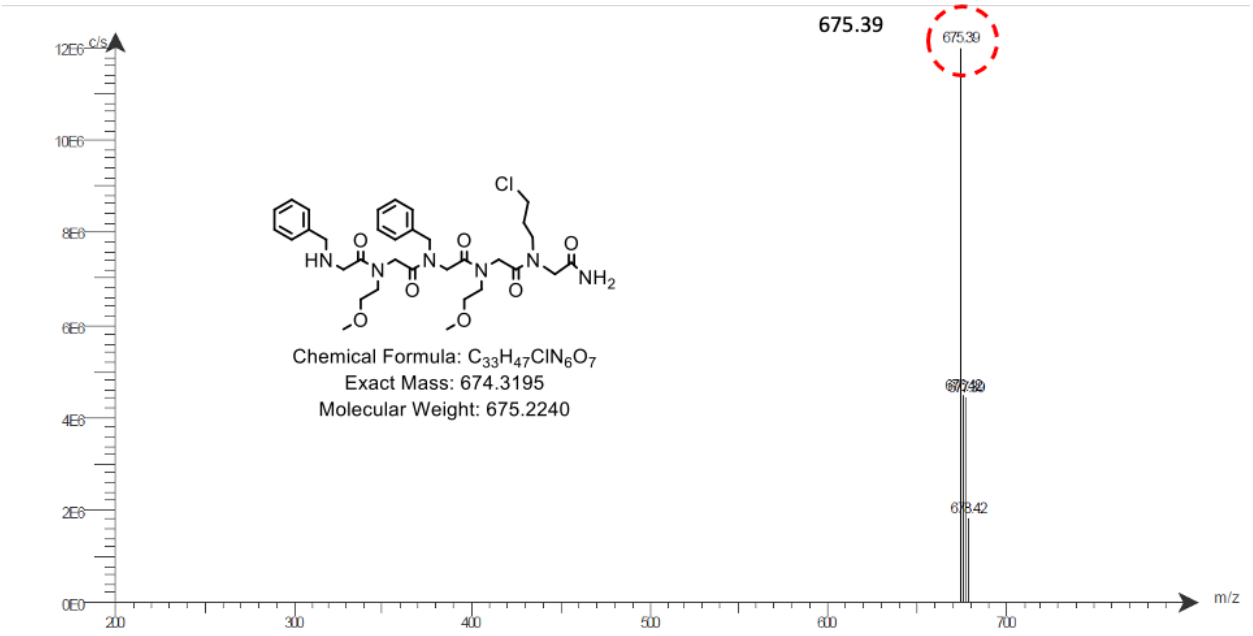

Figure S25. ESI-MS of **P9b** in ACN:water.

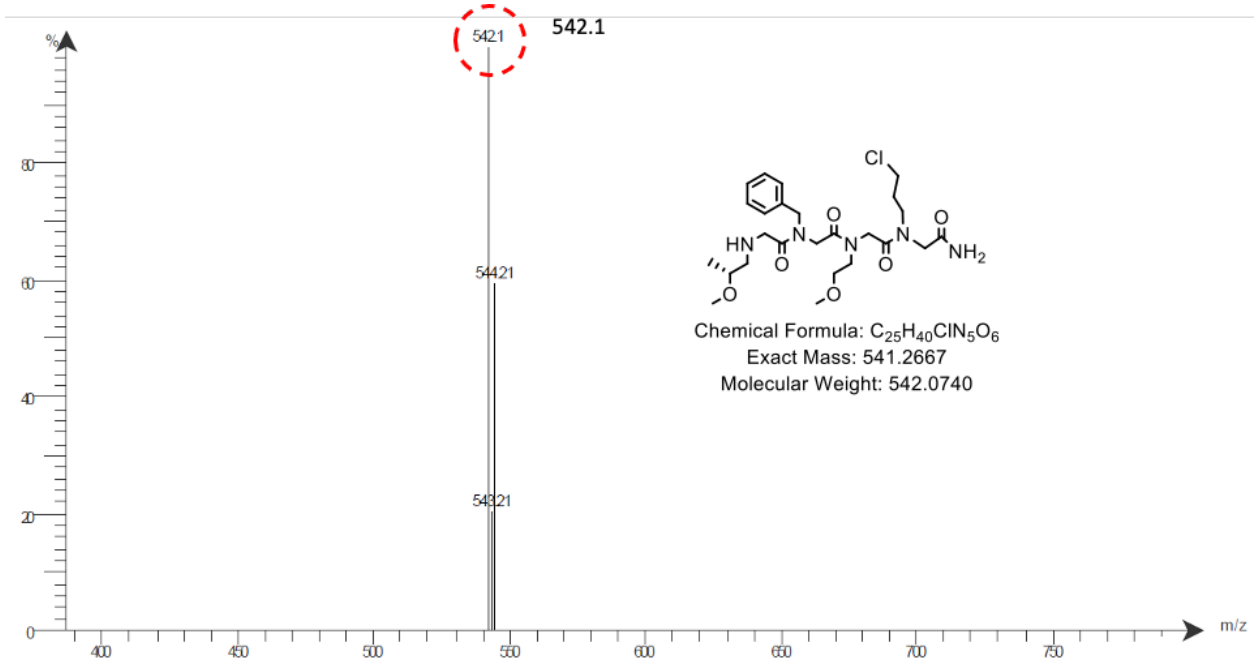

Figure S26. ESI-MS of **P9c** in ACN:water.

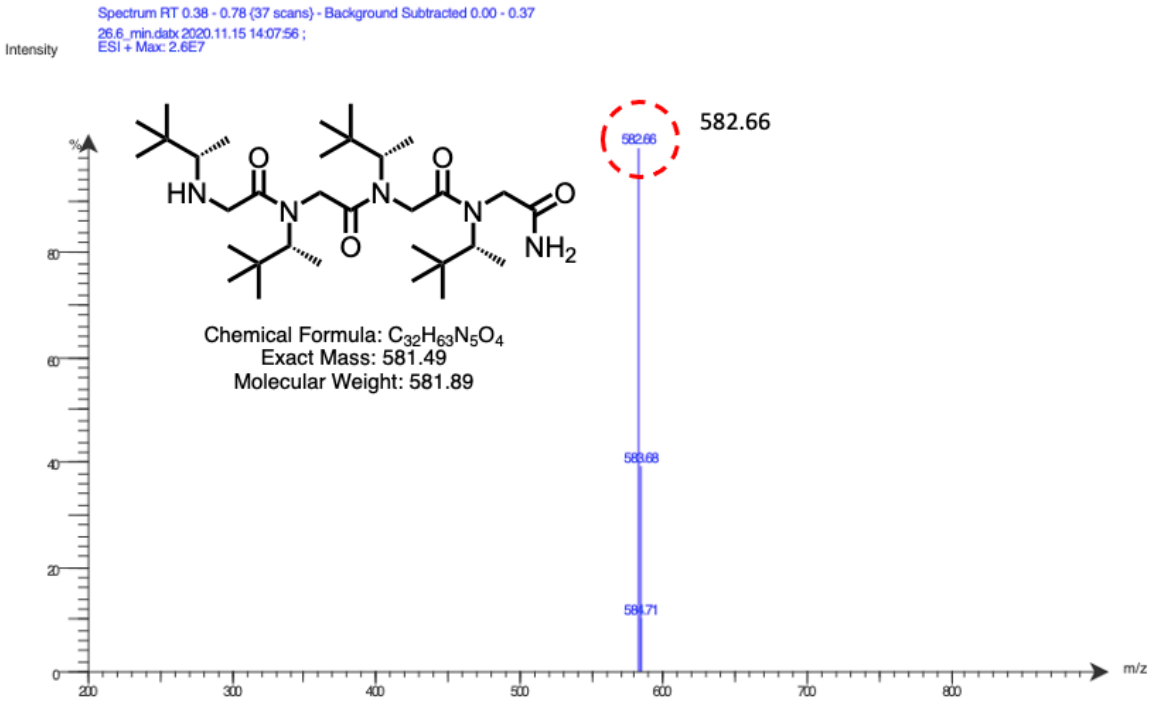

Figure S27. ESI-MS of **P10** in ACN:water.

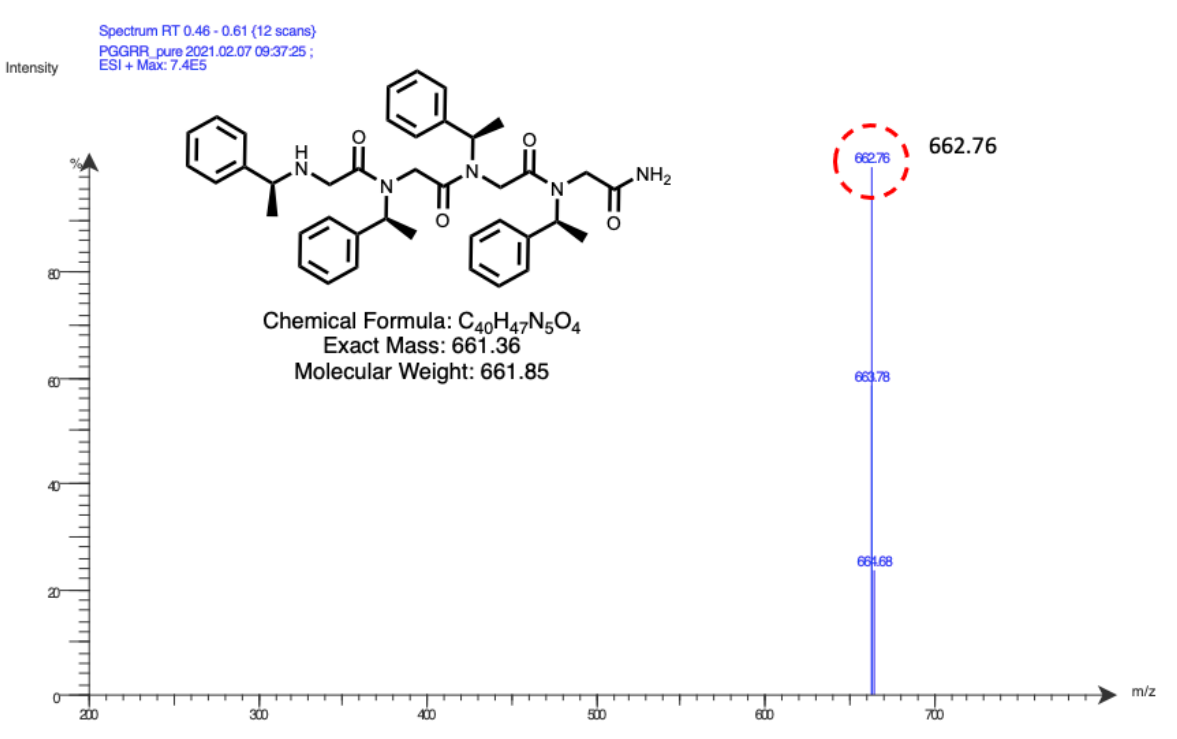

Figure S28. ESI-MS of **P11** in ACN:water.

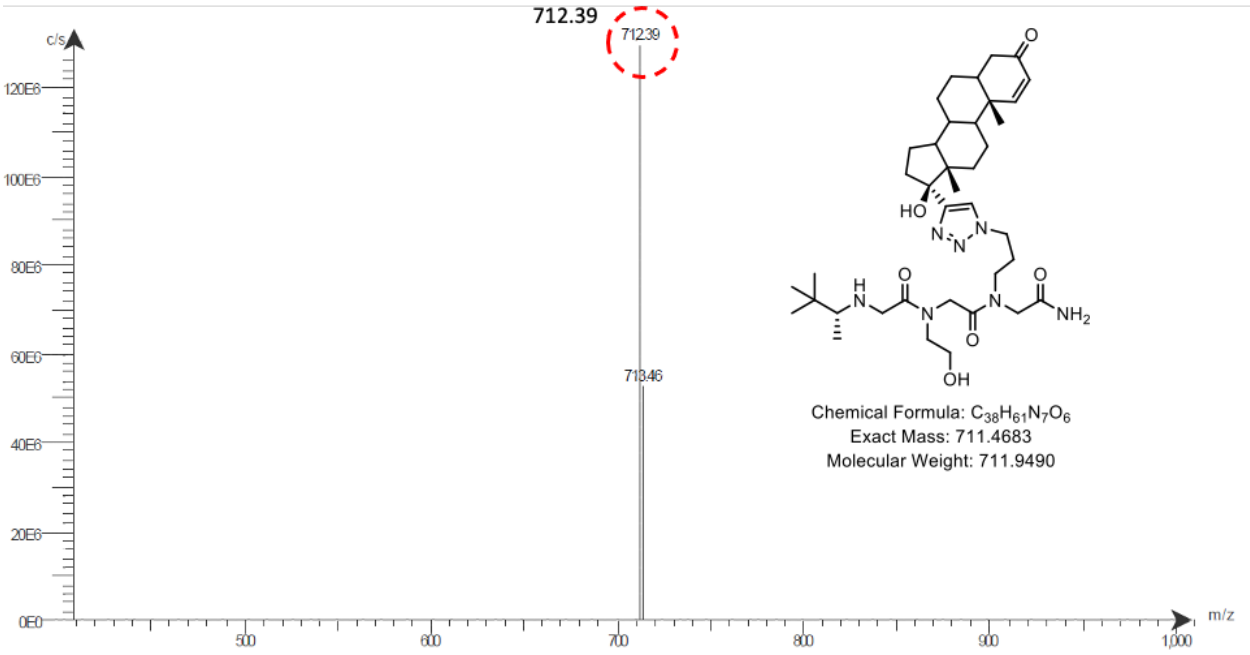

Figure S29. ESI-MS of **PSteroid** in ACN:water.

^{1}H-NMR of P1

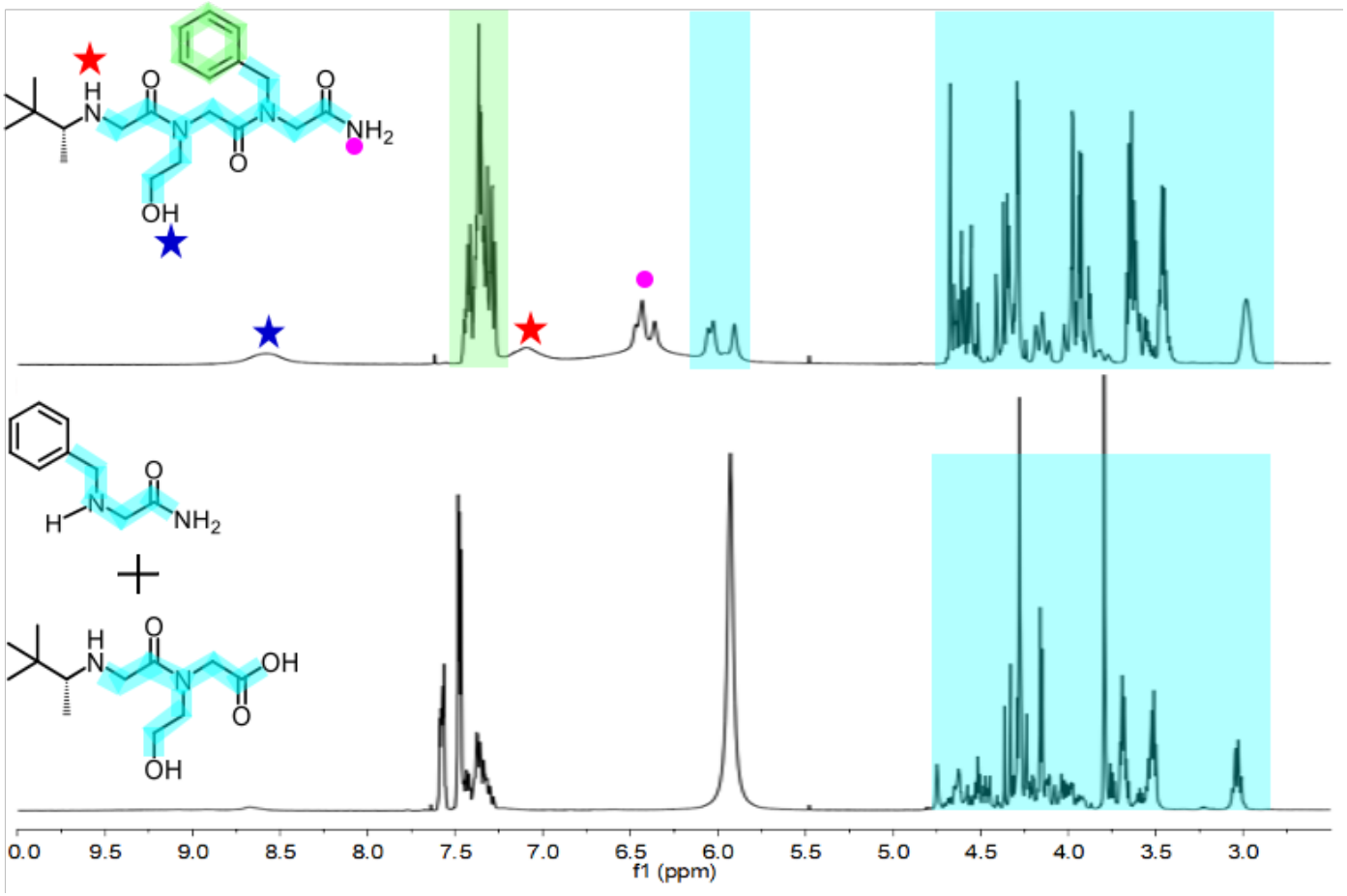

Figure S30. ^{1}H-NMR of **P1** before and after addition of deuterated hydrochloric acid (DCl), measured after 10 minutes of DCl mixing. The ^{1}H-NMR shows clear indication of shifting the signal (7.25-7.75ppm region) and/or appearing new signals (5.75-6 ppm region), indicating the formation of new products.

Table S2. Crystallographic information of the crystal structures used in the manuscript.

Parameters for crystallography	Cleaved structure of **P1**	Cu (II) mediated cleaved structure of **P2**	Cu (II) mediated cleaved structure of **P4**	Cu (II) mediated cleaved structure of **P6**	Cu (II) mediated cleaved structure of **P8**	Cu (II) mediated duplex of **P5**	Cu (II) mediated duplex of **P7**
Formula	$C_9H_{12.50}ClN_2O$	$C_{16}H_{19}Cl_2CuN_5O_{10}$	$C_{14}H_{16}Cl_2CuN_4O_{10}$	$C_{16}H_{19}Cl_2CuN_5O_{10}$	$C_{14}H_{16}Cl_2CuN_4O_{10}$	$C_{70}H_{84}Cl_4Cu_2N_{16}O_{28}$	$C_{98}H_{141}C_{l8}Cu_4\ N_{27}O_{59}$
Formula weight	200.16	575.80	534.75	575.80	534.75	1866.41	3179.19
T(K)	296(2)	200(2)	200(2)	200(2)	200(2)	150(2)	100(2)
Crystal color	colorless	Blue	Blue	Blue	Blue	Blue	Blue
Crystal system	monoclinic	orthorhombic	triclinic	orthorhombic	triclinic	monoclinic	orthorhombic
Space group	P n	P n a 2_1	P -1	P n a 2_1	P -1	P 21/n	P b c n
a(Å), b(Å), c(Å)	5.612(10), 4.705(9), 37.06(7)	7.8052(6) 25.0379(18) 11.0594(8)	8.3536(11) 10.1478(13) 11.5065(15)	7.8431(11) 25.178(3) 11.0713(16)	8.341(3) 10.126(4) 11.518(4)	17.360(3) 9.5805(16) 24.673(4)	23.575(3) 25.656(3) 21.546(4)
α(°), β(°), γ (°)	90, 91.35(4), 90	90 90 90	78.360(3) 87.561(3) 83.315(3)	90 90 90	78.746(7) 87.630(8) 83.013(9)	90 95.134(4) 90	90 90 90
V ($Å^3$)	978(3)	2161.3(3)	948.7(2)	2186.3(5)	946.8(6)	4087.1(12)	13032(3)
Z	4	4	2	4	2	2	4
Crystal dimensions (mm)	0.105 x 0.070 x 0.030	0.210 x 0.150 x 0.150	0.180 x 0.150 x 0.150	0.120 x 0.090 x 0.030	0.120 x 0.060 x 0.030	0.270 x 0.120 x 0.090	0.240 x 0.150 x 0.120
F (000)	422	1172	542	1172	542	1932	6568
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
θ Range (°)	4.332- 23.970	1.627- 25.063	1.807- 25.184	1.618- 25.056	1.803- 25.013	1.378-25.124	1.506- 25.079
Absorption correction	'multi-scan'	'multi-scan'	'multi-scan'	'multi-scan'	'multi-scan'	'multi-scan'	'multi-scan'
R factor (%)	17.49	3.98	5.97	5.77	5.43	9.62	6.88
Goodness-of-fit	1.634	0.979	0.986	0.887	0.969	1.086	1.025
CCDC number	2171365	2169565	2169562	2169564	2169563	2169566	2169567

Crystal Structure of cleaved metallopeptoid/metallopeptoid duplexes

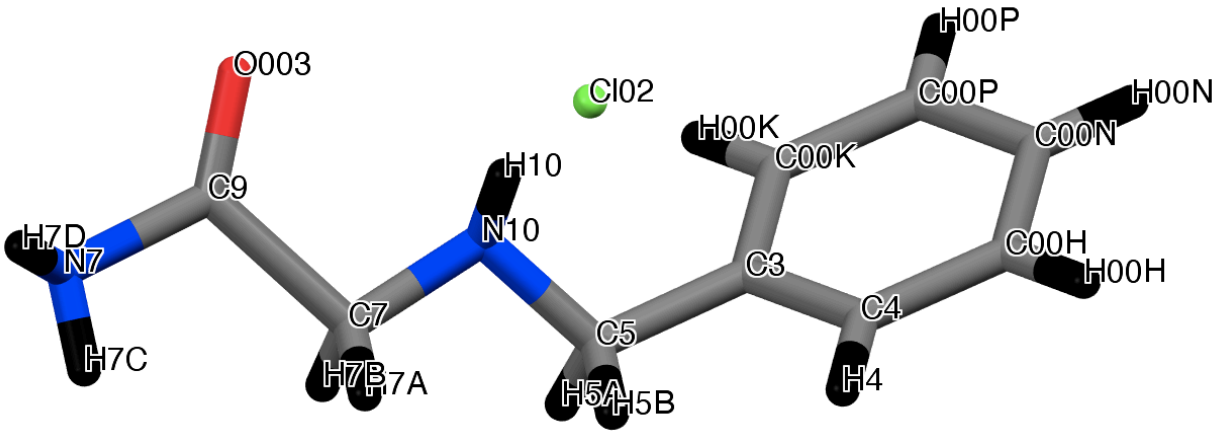

Figure S31. Crystal structure of cleaved **P1**, cleaved by proton.

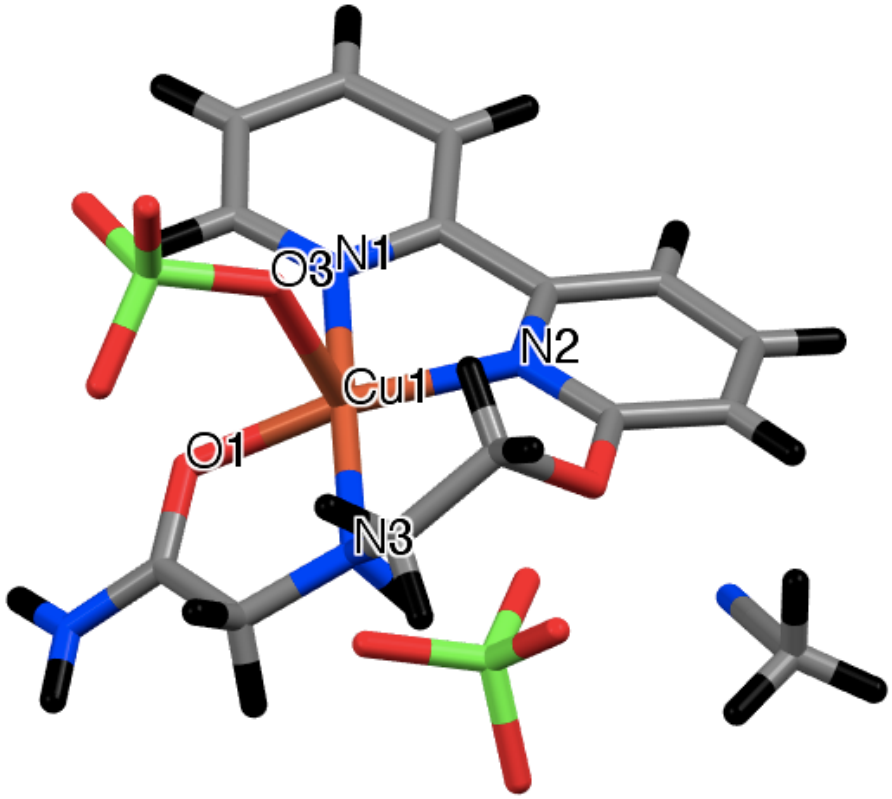

Figure S32. Crystal structure of cleaved **P2**, cleaved by Cu(II).

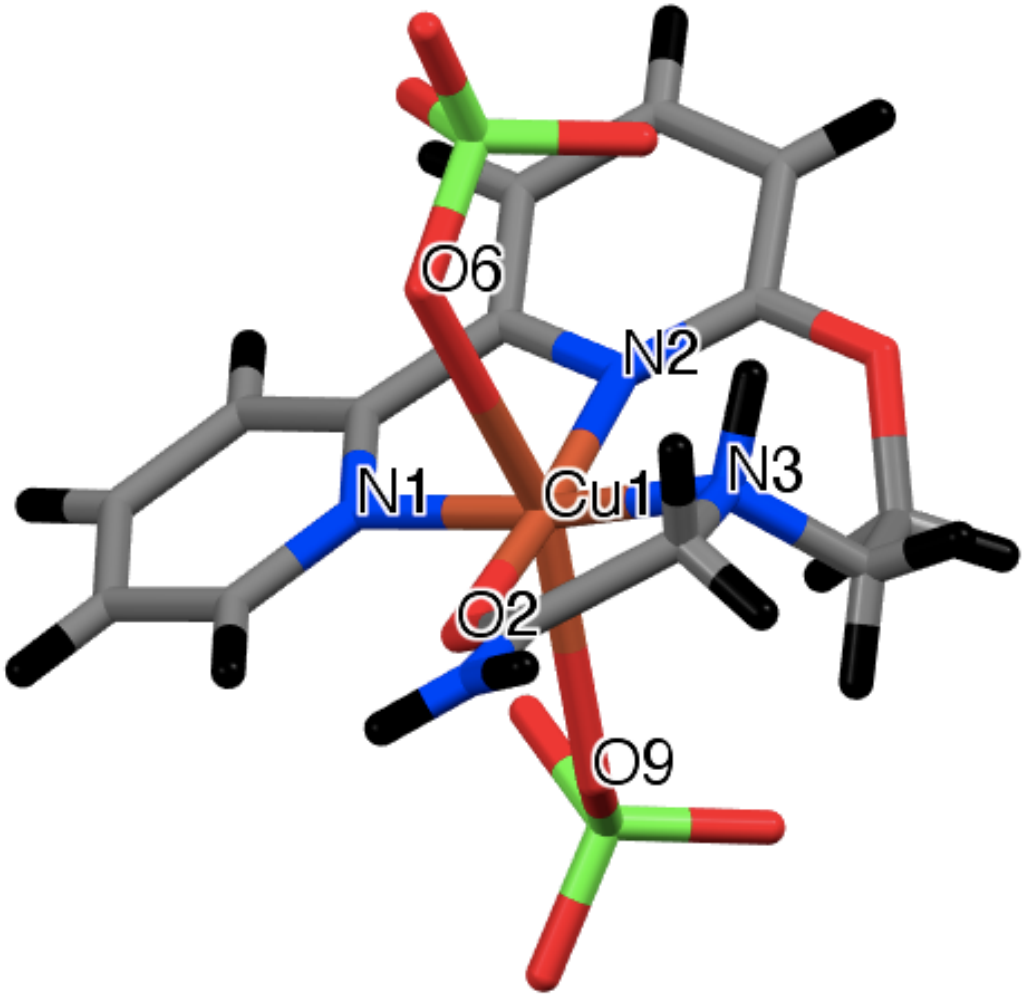

Figure S33. Crystal structure of cleaved **P4**, cleaved by Cu(II).

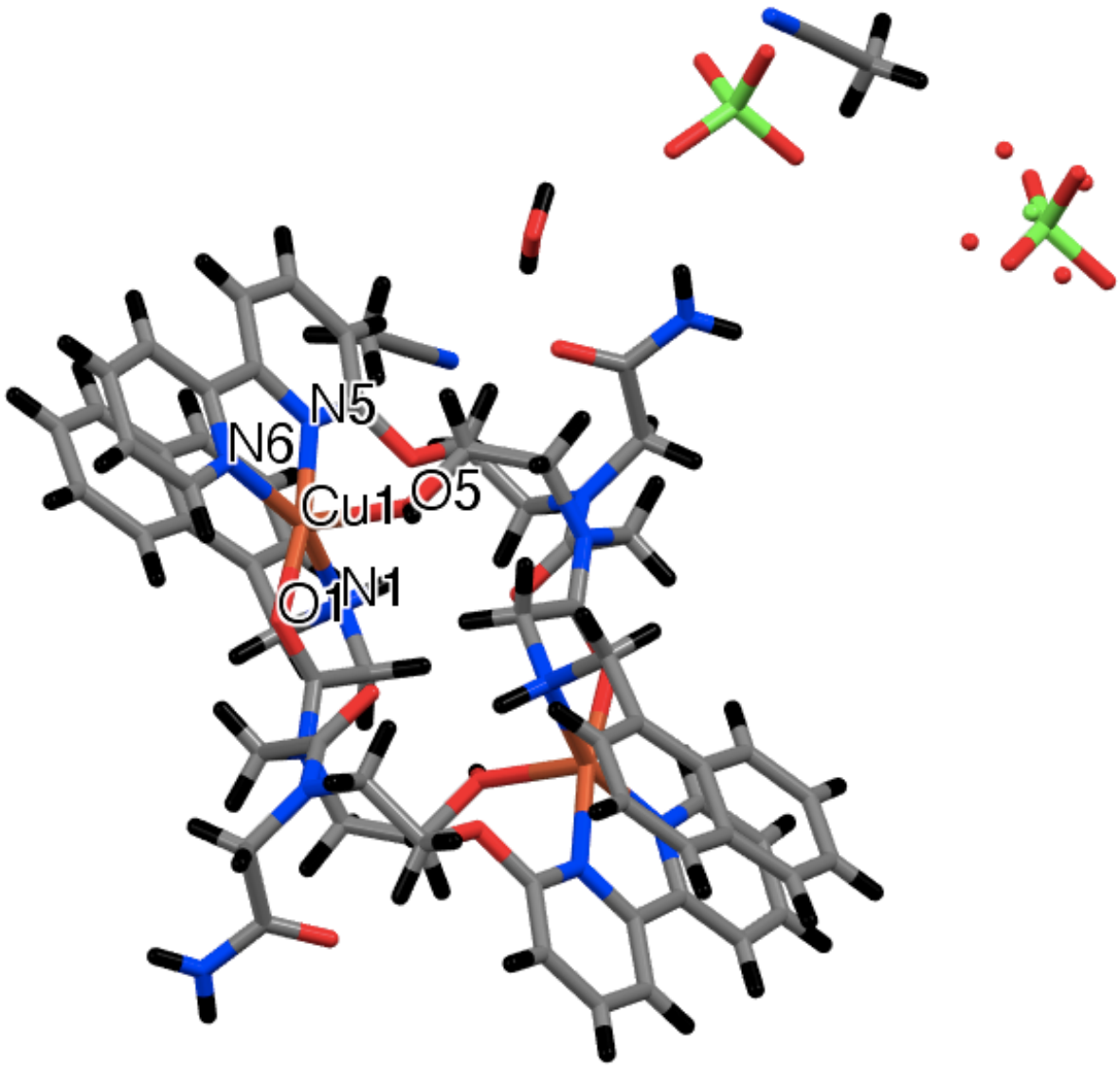

Figure S34. Crystal structure of duplex **P5** with Cu(II).

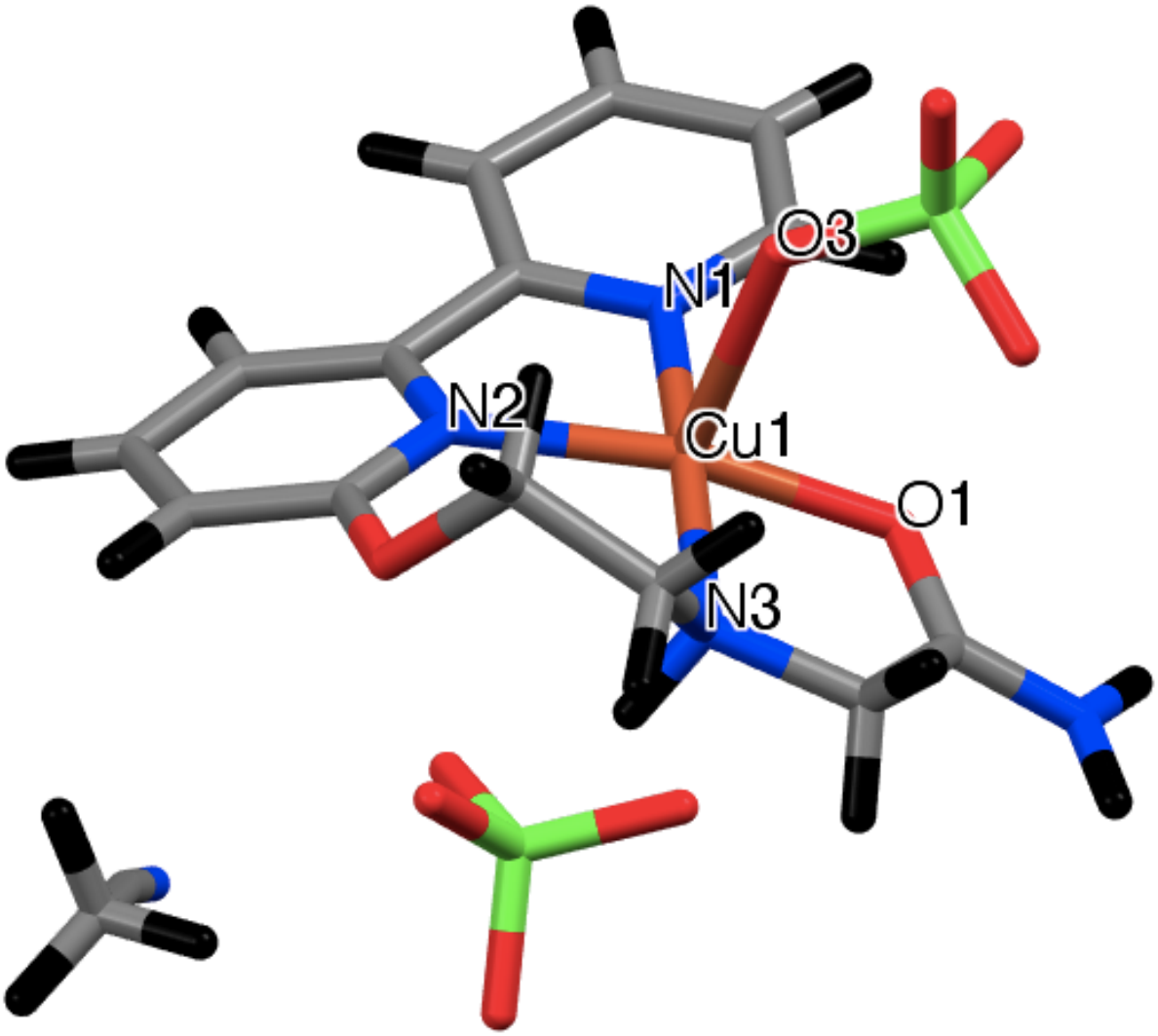

Figure S35. Crystal structure of cleaved **P6**, cleaved by Cu(II).

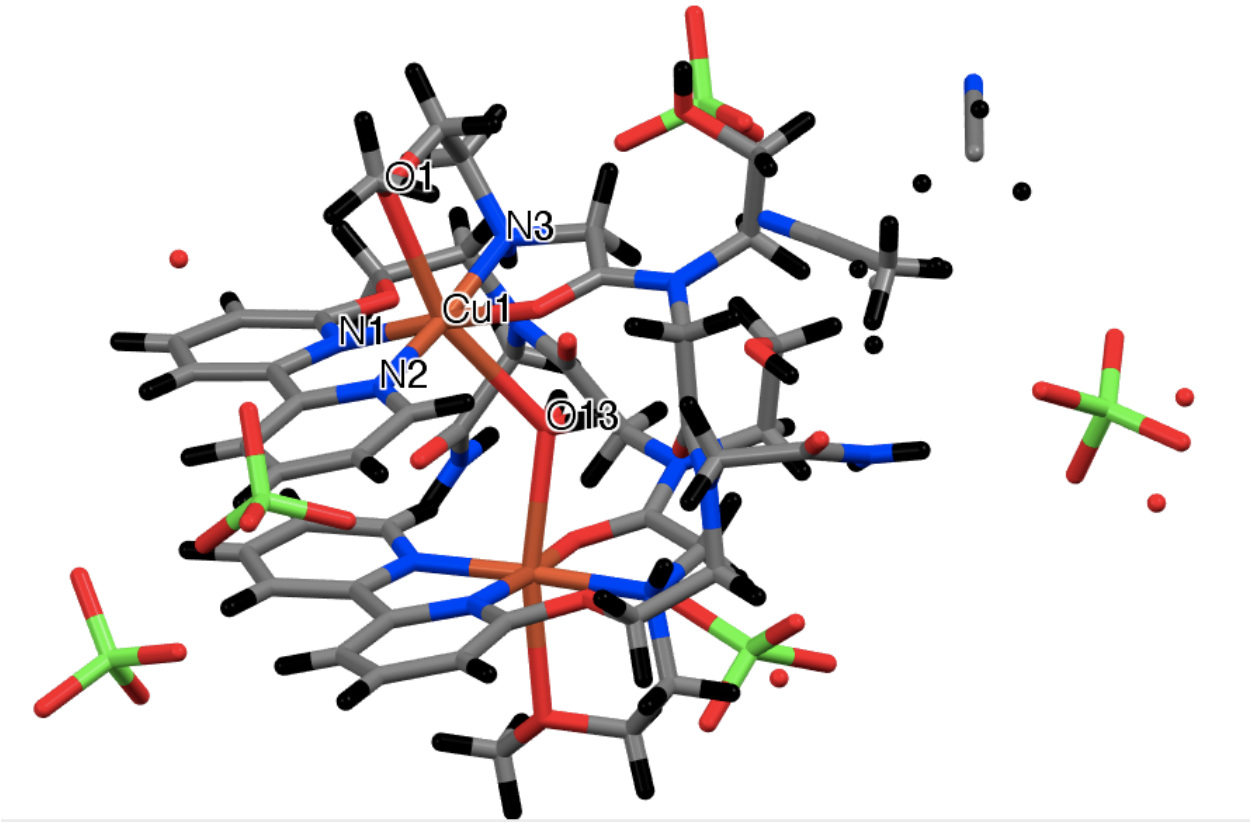

Figure S36. Crystal structure of duplex **P7** with Cu(II).

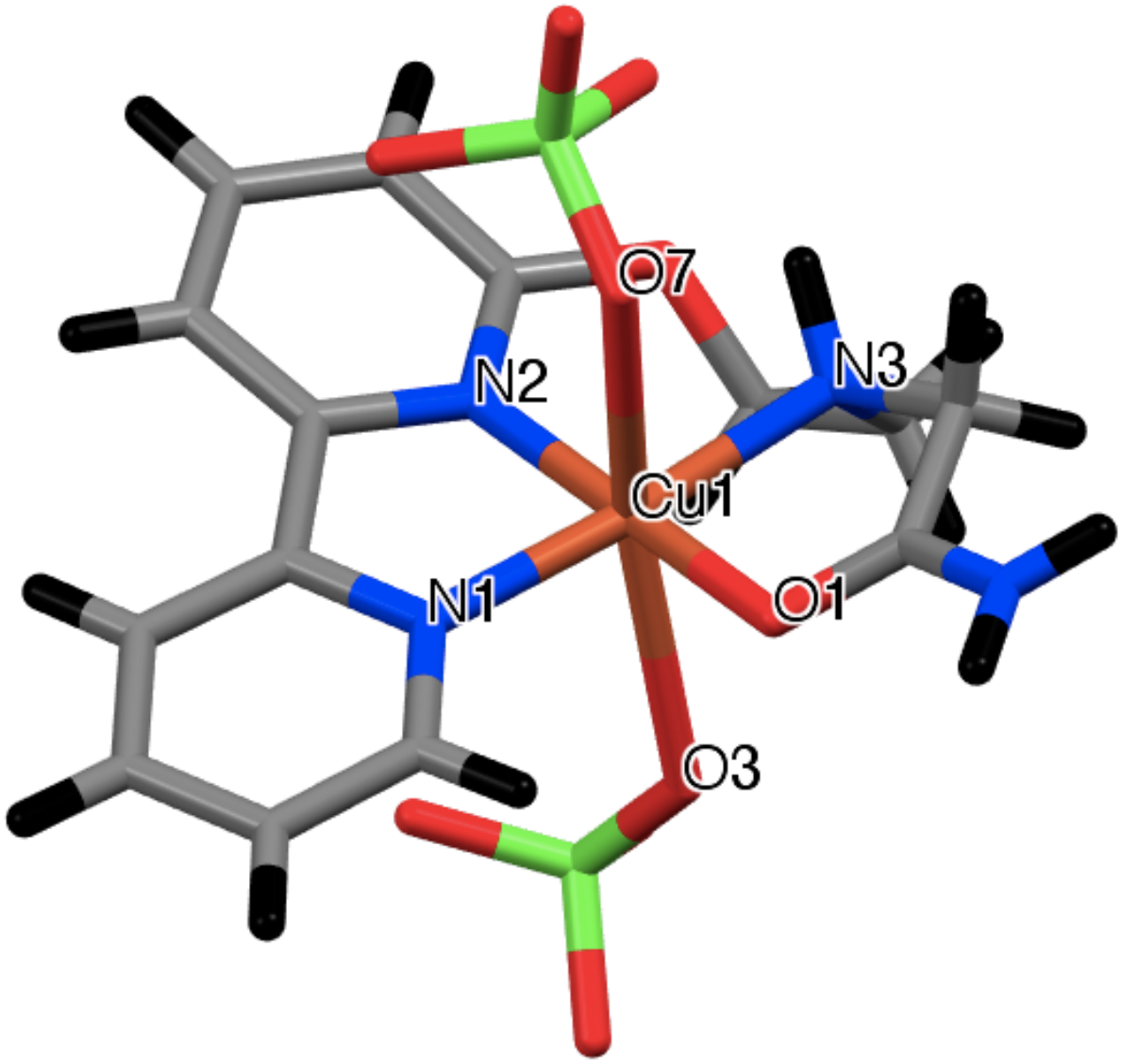

Figure S37. Crystal structure of cleaved **P8**, cleaved by Cu(II).

ESI-MS of peptoids with Cu^{2+}

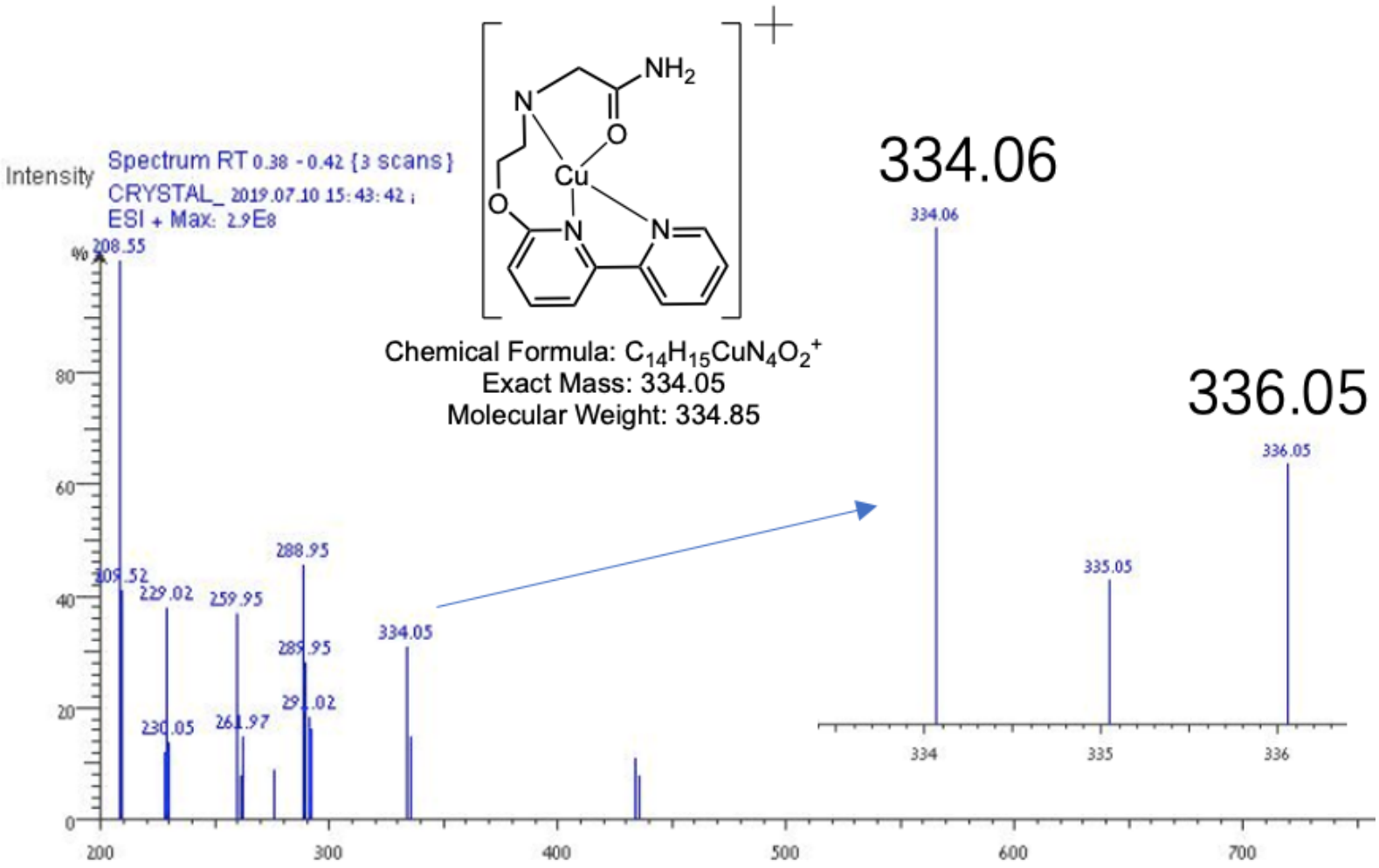

Figure S38. ESI-MS of the crystals (showed in fig. S32) obtained via Cu(II) mediated cleavage of peptoid **P2**, $[CPCu-H]^+$, 334.06/336.05 belongs to the isotopes of Cu(63.5/65/5), solvent: ACN:Water (1:1, v/v).

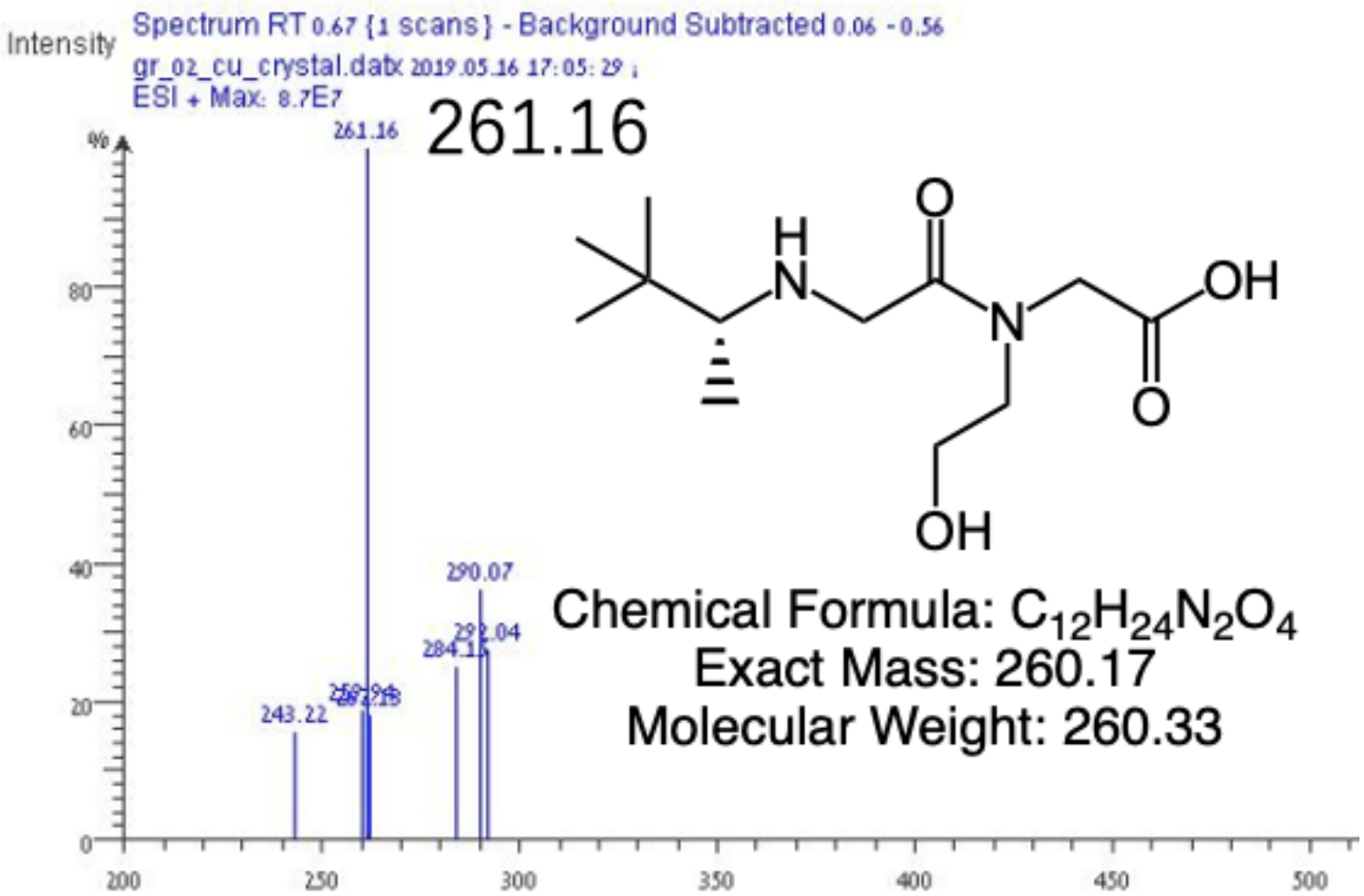

Figure S39. ESI-MS of the solution from which the crystal was obtained for Cu(II) mediated cleavage of peptoid **P2**, CPCu. The measurement was performed after collecting all the crystals out from the solution, cleaved tail [261.16 (cleaved peptoid tail+H^+), 284.12 (cleaved peptoid tail+H^++Na^+)].

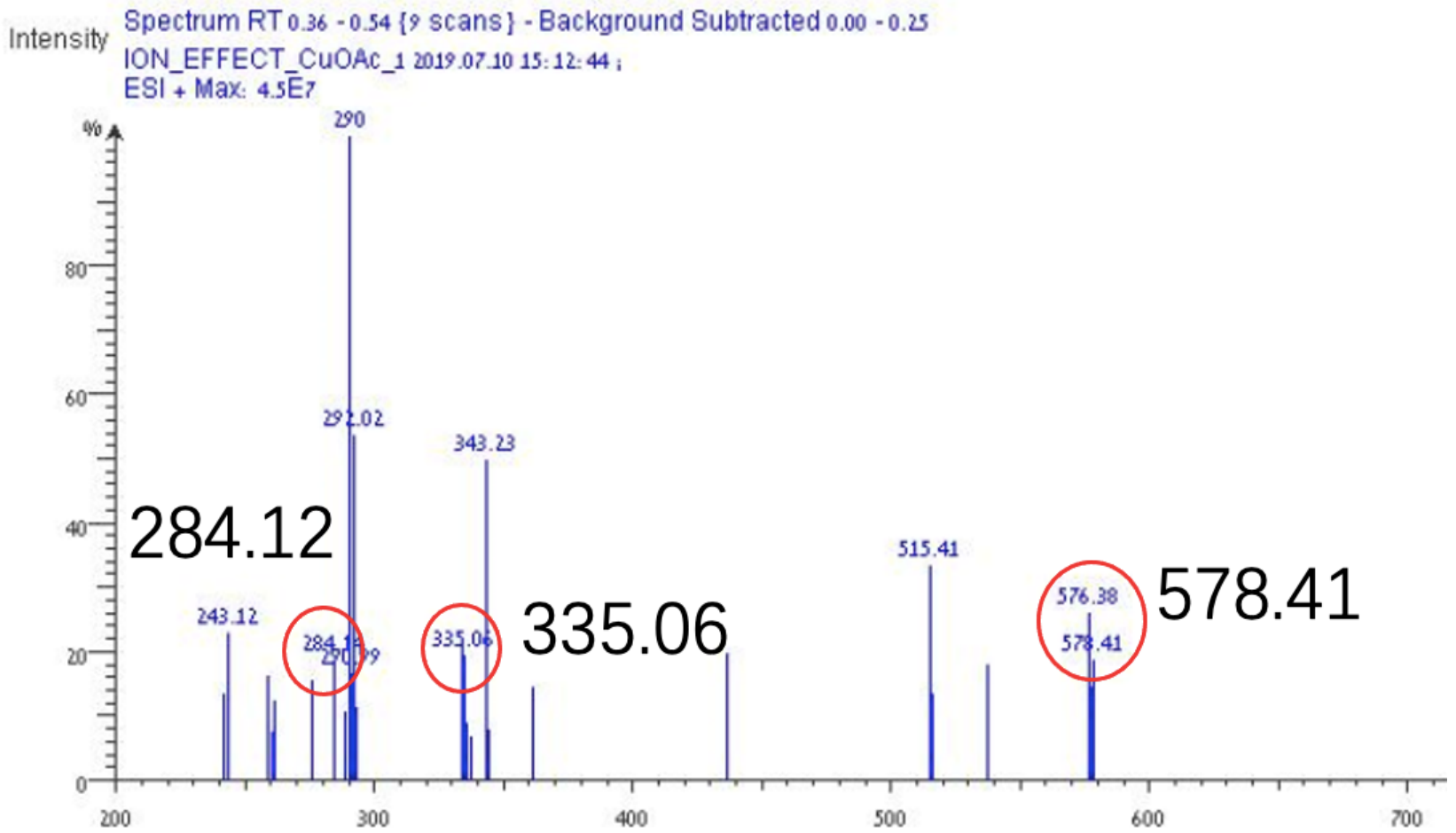

Figure S40. ESI-MS of **P2** with $Cu(OAc)_2$, cleaved product: 335.06 (see fig. S38 inset for chemical structure which is proposed based on crystal structure Fig. S32), cleaved tail [284.12 (cleaved peptoid tail+H^++Na^+), see fig. S39 inset for chemical structure], **P2**Cu intramolecular complex at 578.41.

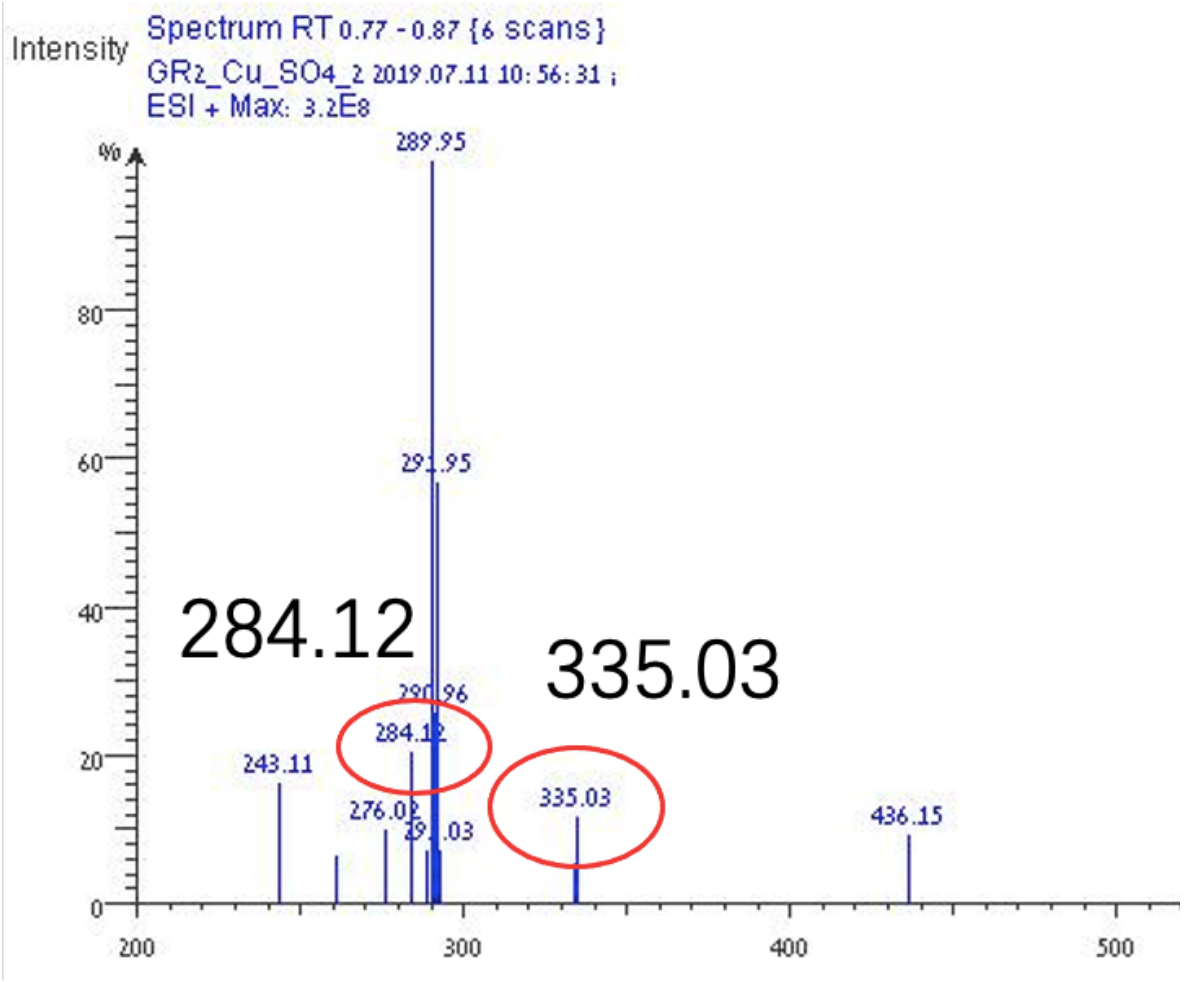

Figure S41. ESI-MS of **P2** with $CuSO_4$, cleaved product: 335.06 (see fig. S38 inset for chemical structure which is proposed based on crystal structure Fig. S32), cleaved tail [284.12 (cleaved peptoid tail+H^++Na^+), see fig. S39 inset for chemical structure].

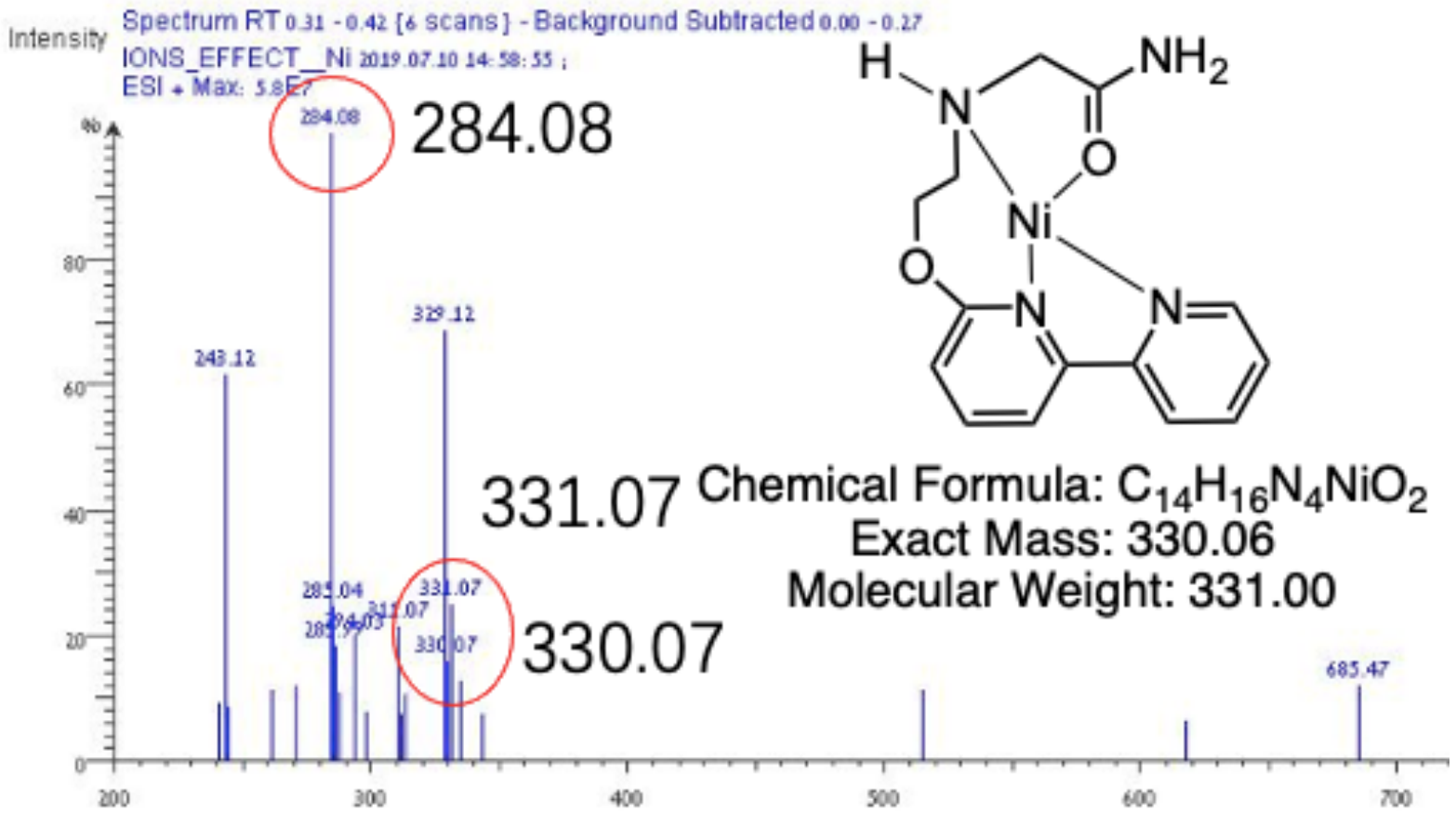

Figure S42. ESI-MS of peptoid **P2** with Ni(II), cleaved peptoid with Ni(II) {331.07 amu, this is proposed based on crystal structure Fig. S32 with Cu(II)} and cleaved peptoid tail mass was obtained [284.08 (cleaved peptoid tail+H^++Na^+), see fig. S39 inset for chemical structure].

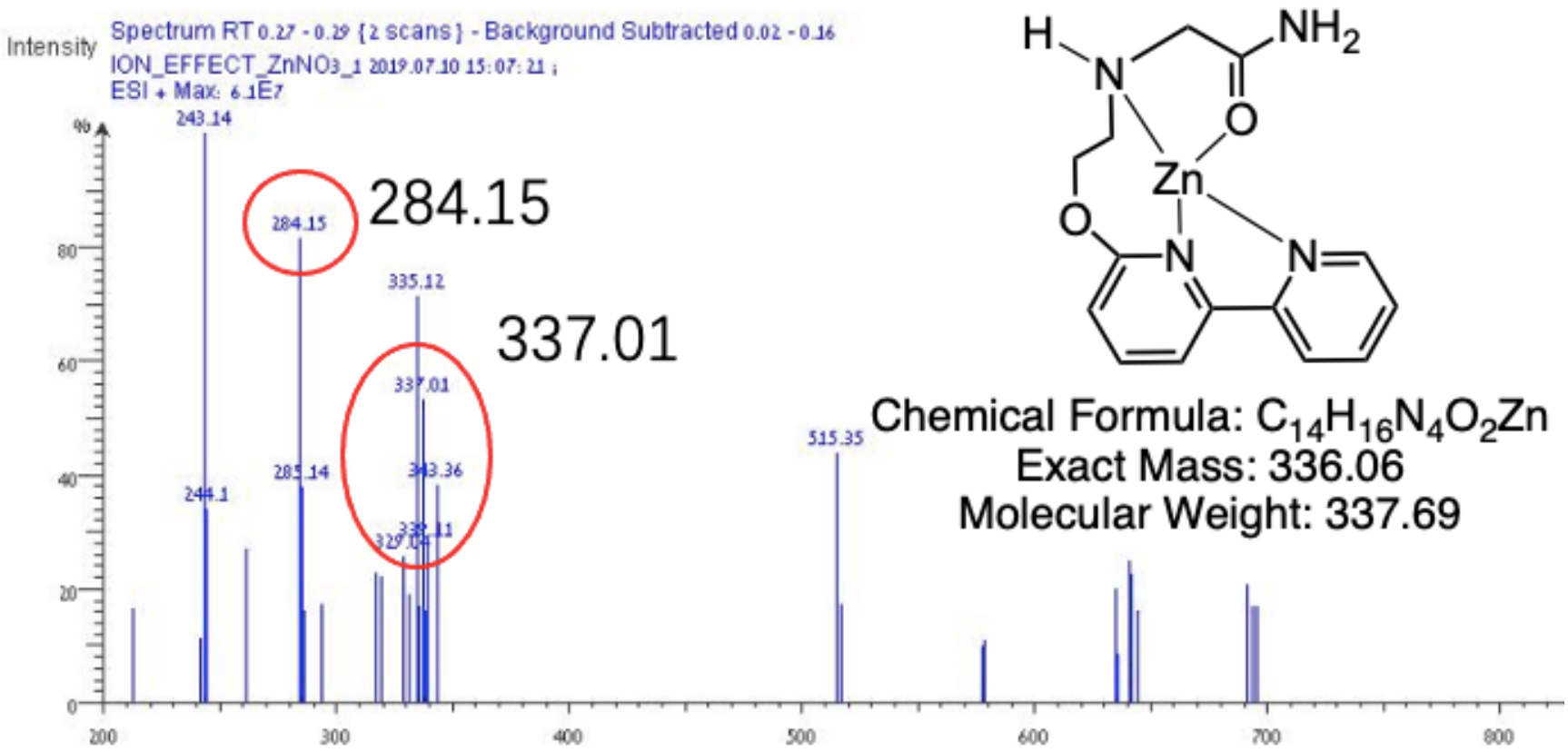

Figure S43. ESI-MS of peptoid **P2** with Zn(II), cleaved peptoid with Zn(II) {337.69 amu, this is proposed based on crystal structure Fig. S32 with Cu(II)} and cleaved peptoid tail mass was obtained [284.15 (cleaved peptoid tail+Na^+),see fig. S39 inset for chemical structure].

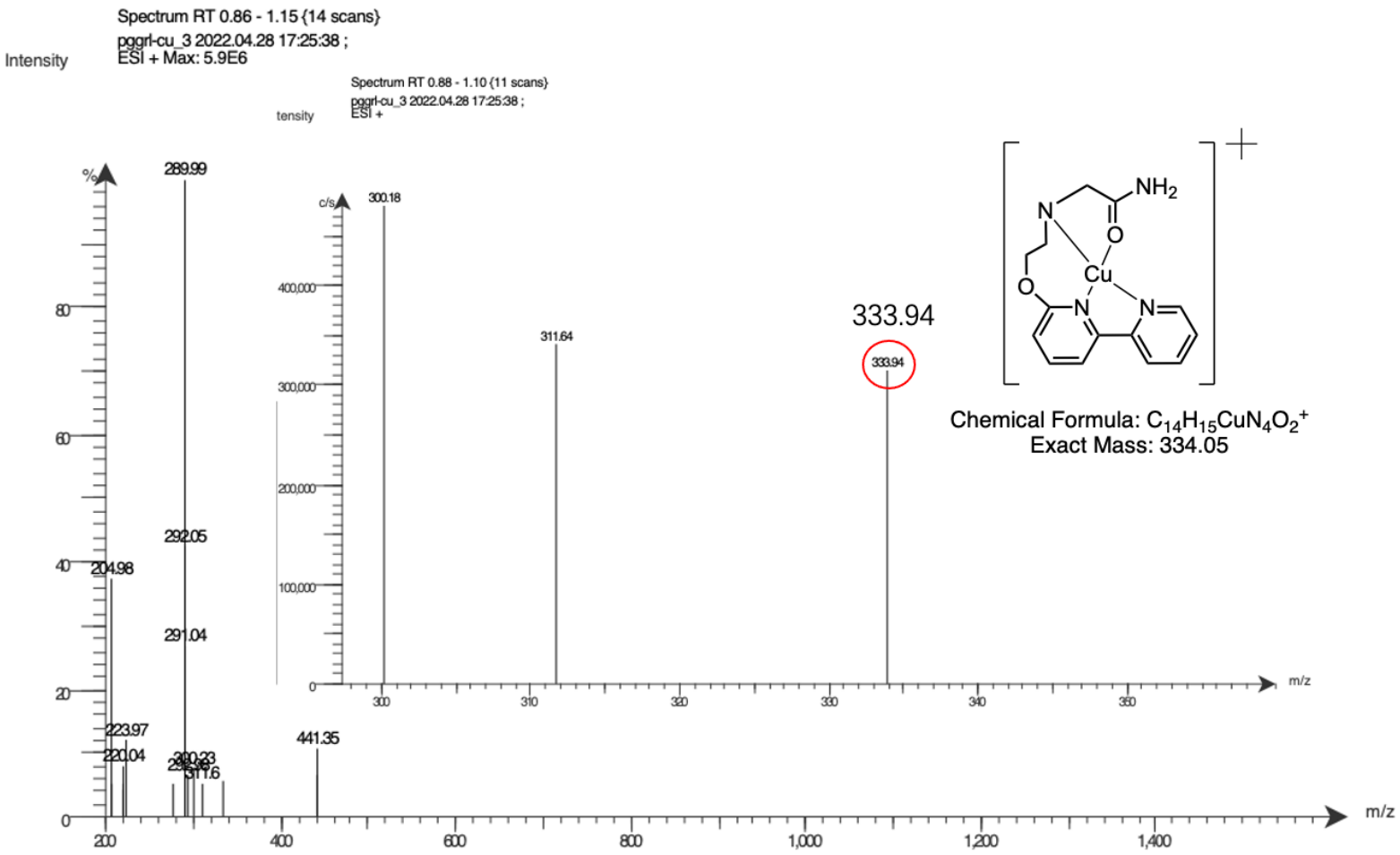

Figure S44. ESI-MS of peptoid **P4** with Cu(II) after 4 hrs, no trace of dimer was found and cleaved peptoid with Cu(II) {333.94 amu} was noticed, (see fig. S38 inset for chemical structure which is proposed based on crystal structure Fig. S32)

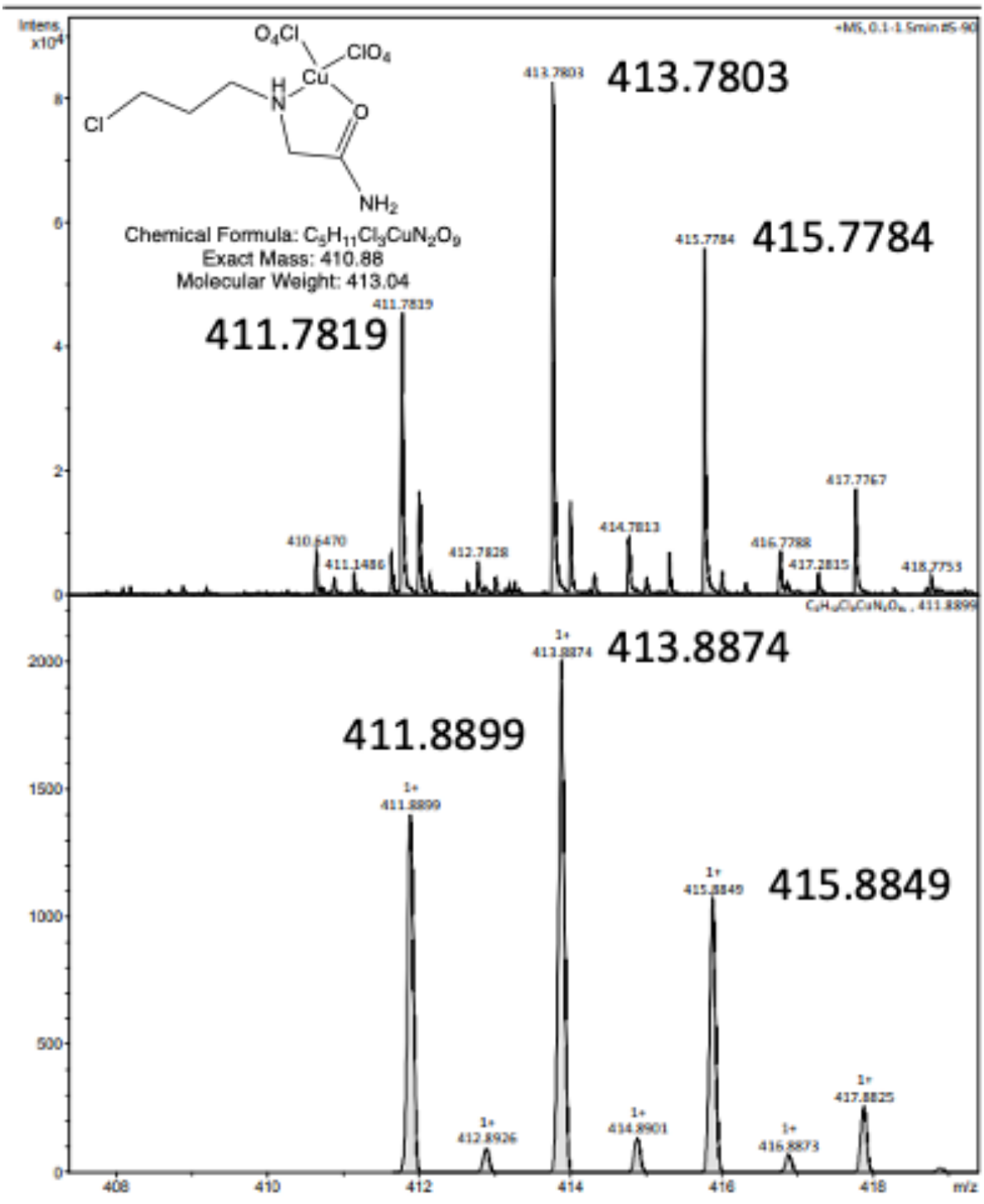

Figure S45. ESI-MS of peptoid **P9** with Cu (II), cleaved peptoid with Cu(II) (inset) was obtained, top: experimental data, down: simulated, [this geometry is proposed based on crystal structure of peptoid **P2** treated with Cu(II) Fig. S32, and and ESI-MS traces of crystal and the solution after taking out the crystals (fig. S38-S39) the cleavage is considered in the same position as happened with **P2**, **P4**, **P6** and **P8**].

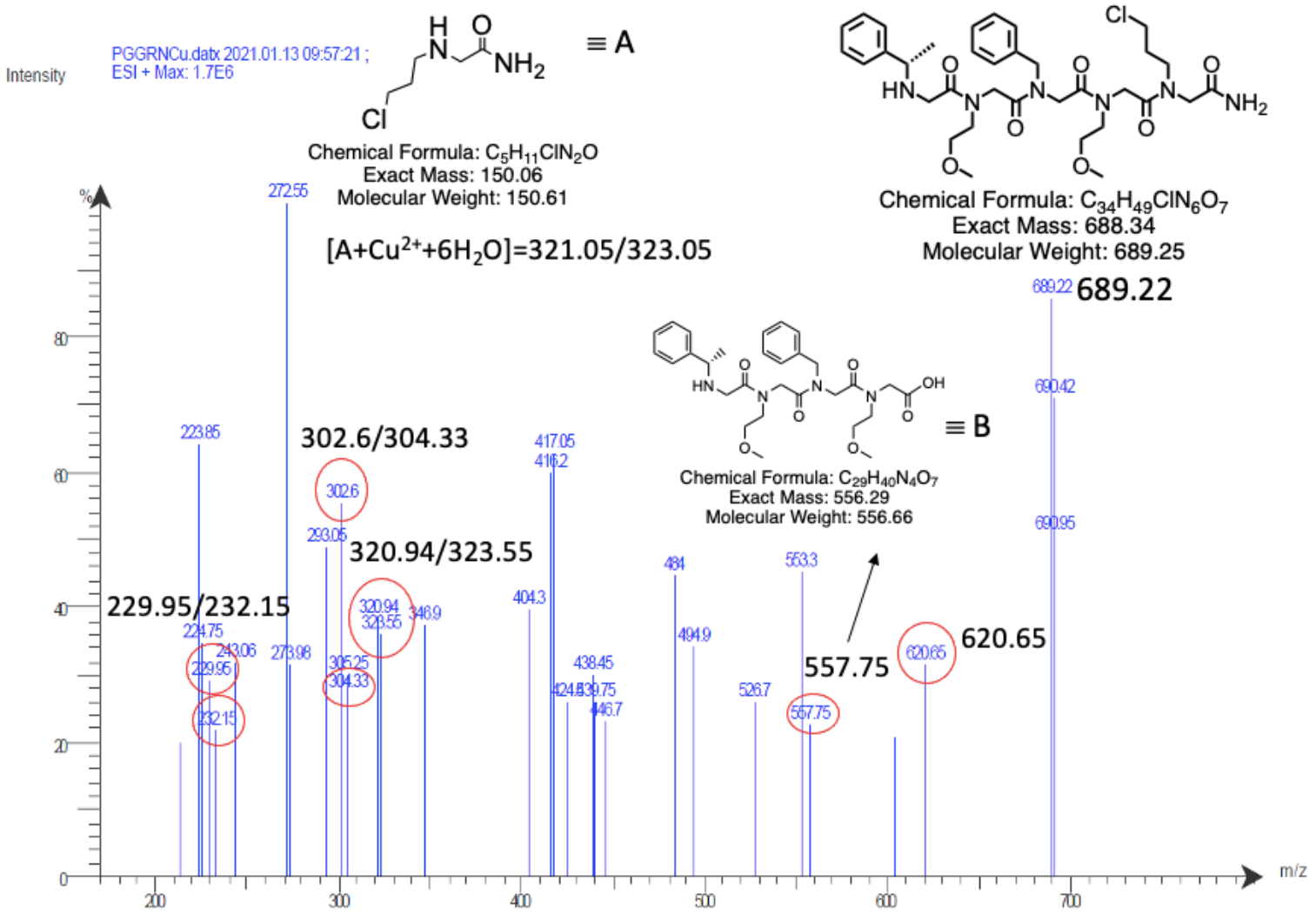

Figure S46. ESI-MS of peptoid P9a with Cu (II), cleaved peptoid with Cu(II) was obtained, [A+Cu^{2+}+6H_2O]=321.05/323.05, [A+Cu^{2+}+5H_2O]=302.03/304.03, [A+Cu^{2+}+H_2O]=229.99/231.99, B+ACN+Na^{+}: 620.31, [the geometries are proposed based on crystal structure of peptoid **P2** treated with Cu(II) Fig. S32 and ESI-MS traces of crystal and the solution after taking out the crystals (fig. S38-S39), the cleavage is considered in the same position as happened with **P2**, **P4**, **P6** and **P8**].

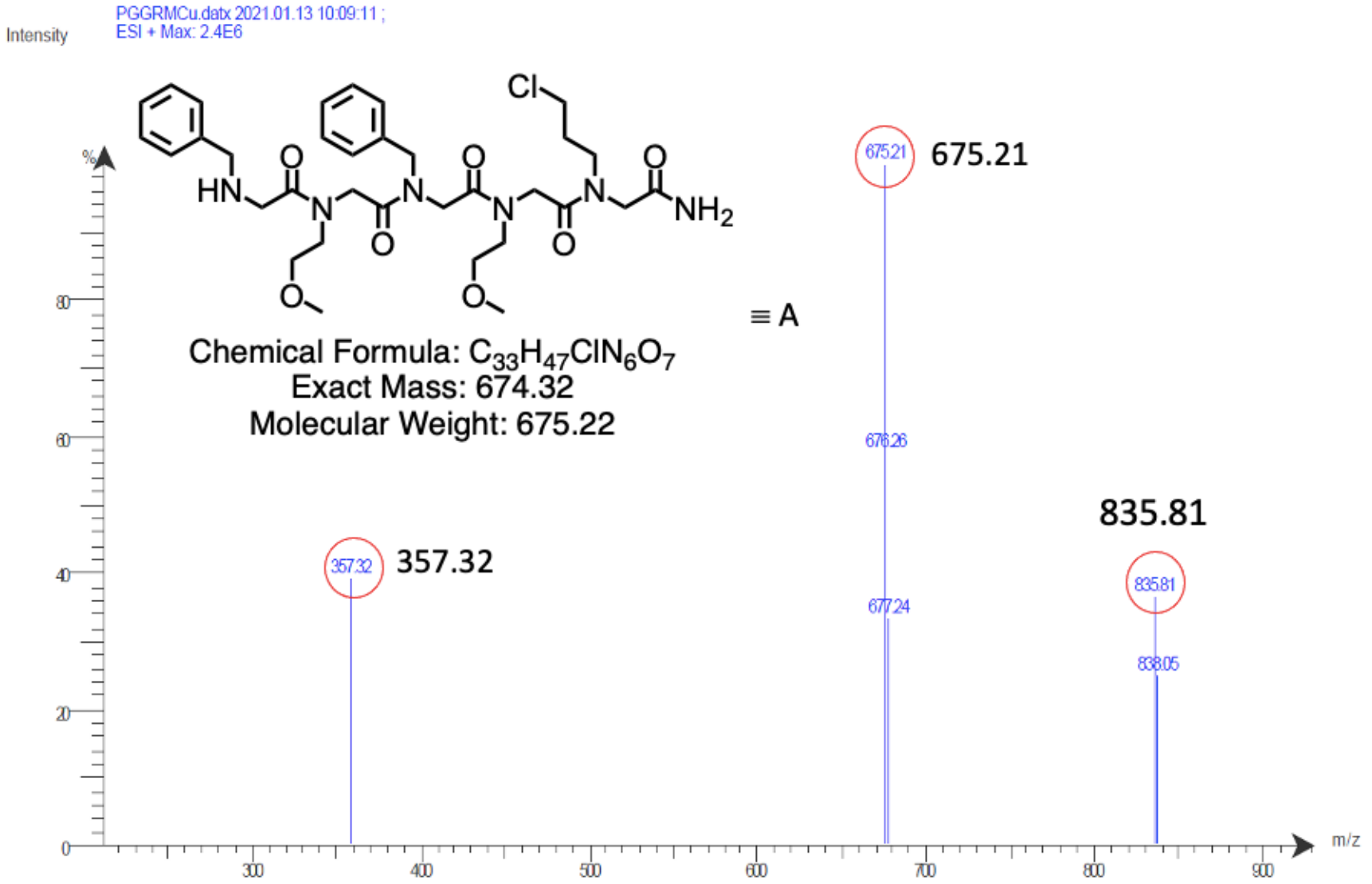

Figure S47. ESI-MS of peptoid **P9**b with Cu (II), no cleavage was observed, $[A+H^{+}+K^{+}]^{2+}$, *m/z*= 714.29/2= 357.145, $[A-H^{+}+Cu^{2+}+ClO_4]$=835.19.

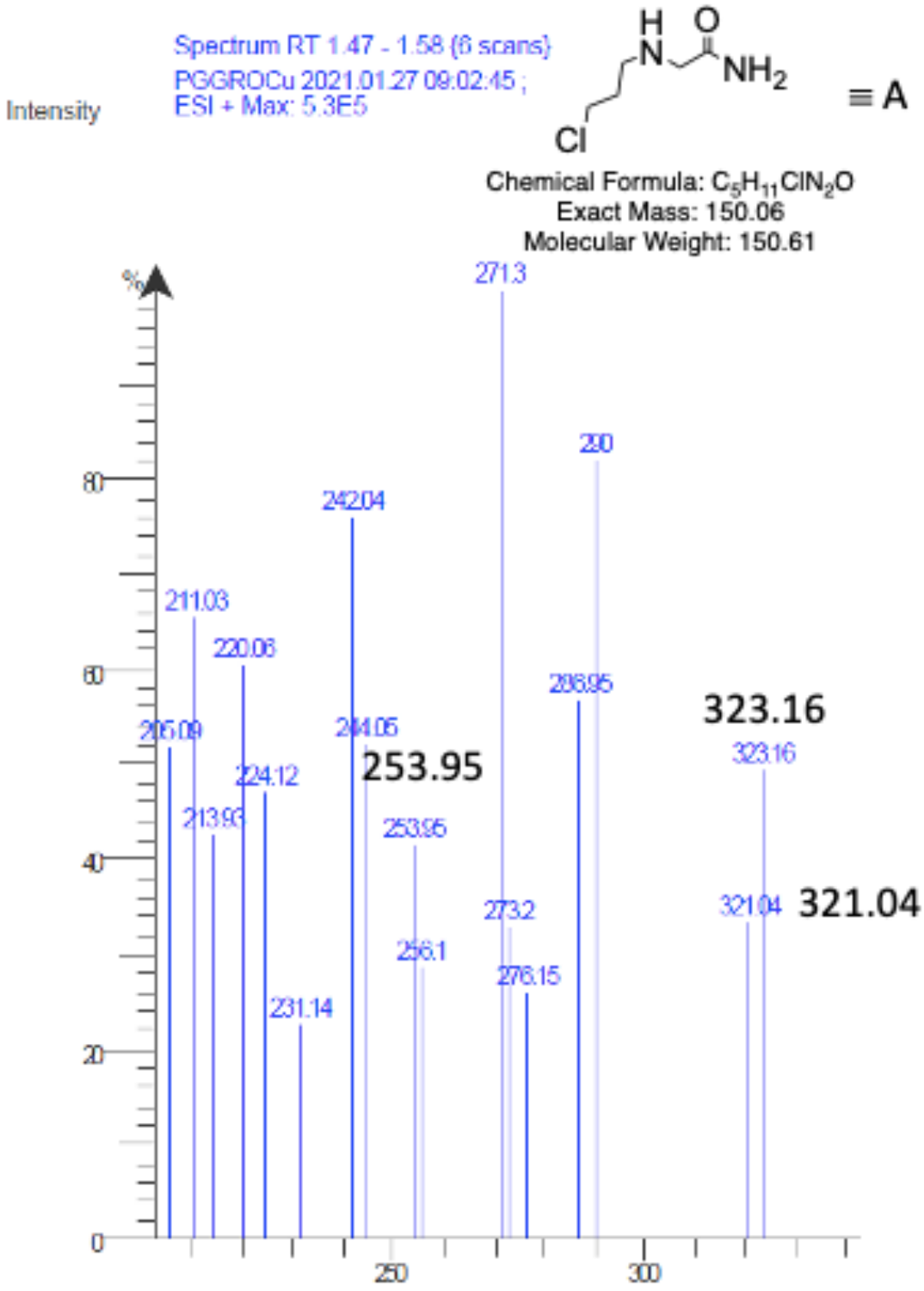

Figure S48. ESI-MS of peptoid **P9c** with Cu (II), cleaved peptoid (inset) with Cu(II) was obtained, [A+Cu^{2+}+$6H_2O$]= 321.05 /323.05, [A+Cu^{2+}+CH_3CN]= 254.01, [the geometry is proposed based on crystal structure Fig. S32 and ESI-MS traces of crystal and the solution after taking out the crystals (fig. S38-S39), the cleavage is considered in the same position as happened with **P2**, **P4**, **P6** and **P8**].

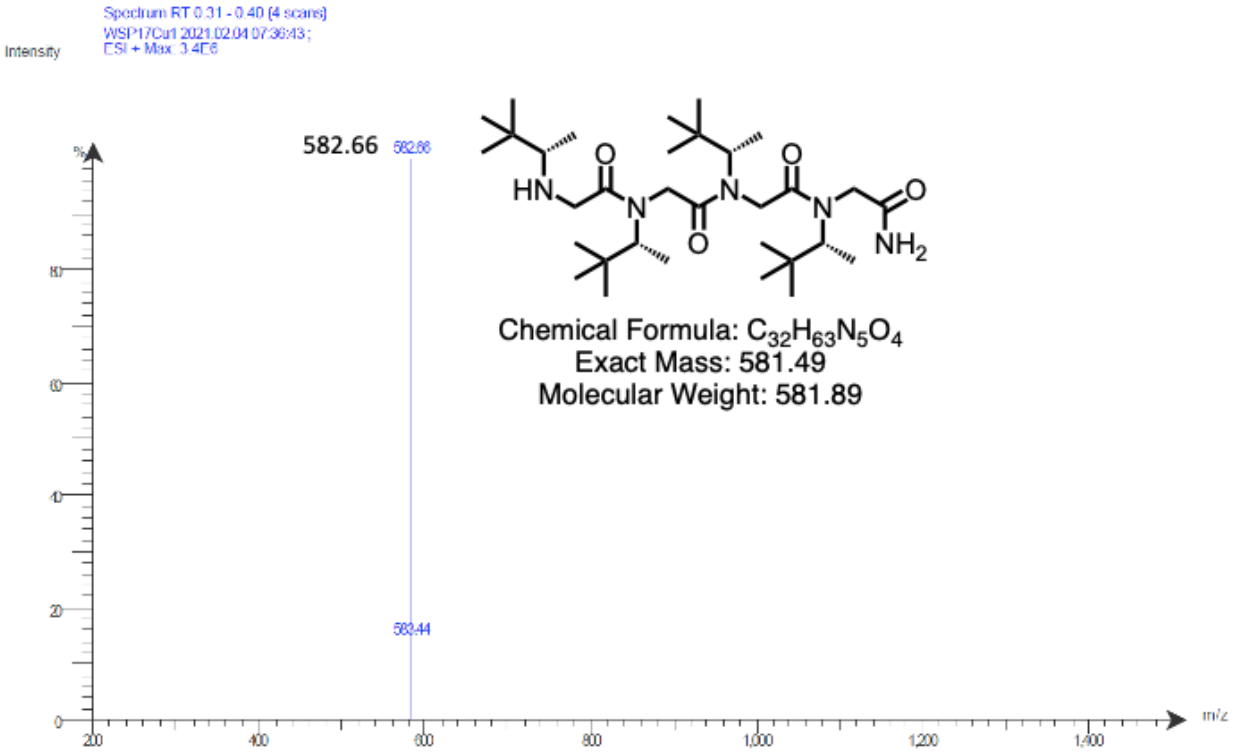

Figure S49. ESI-MS of peptoid **P10** with Cu (II), no cleavage was observed.

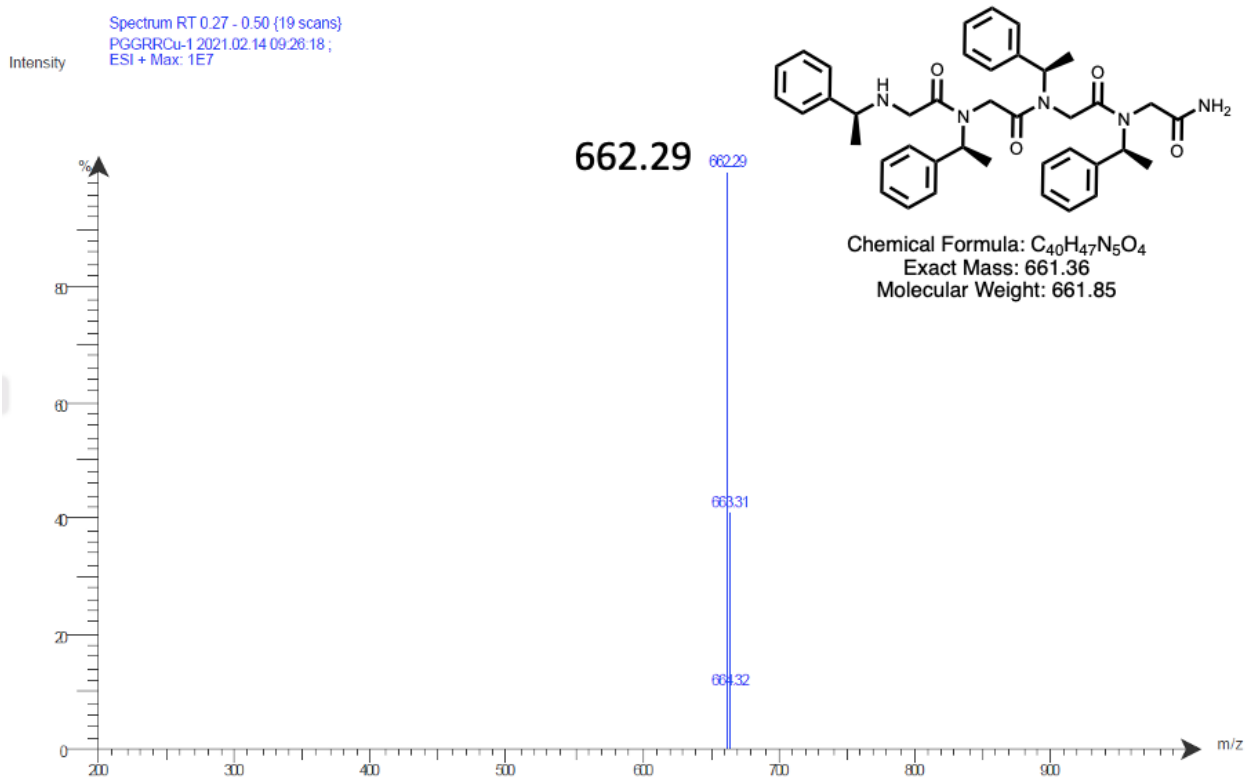

Figure S50. ESI-MS of peptoid **P11** with Cu (II), no cleavage was observed.

DFT-D3 optimized structure of peptoids

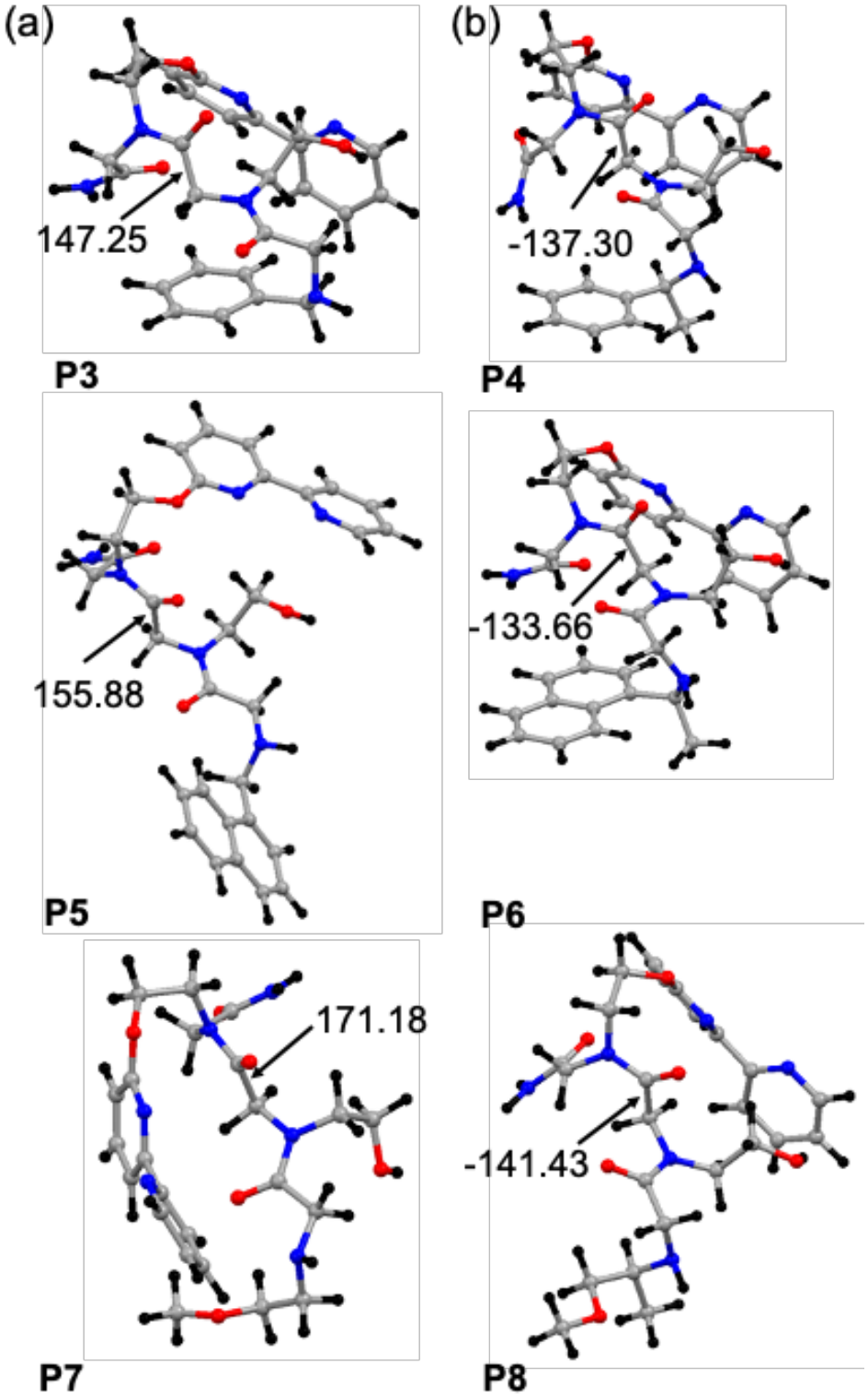

Figure S51. DFT-D3 optimized structure of **P3**-**P8**, arrow shows the specific bond for which the ψ angle is mentioned (color: Blue: N,Red: O, Grey: C, Black: H).

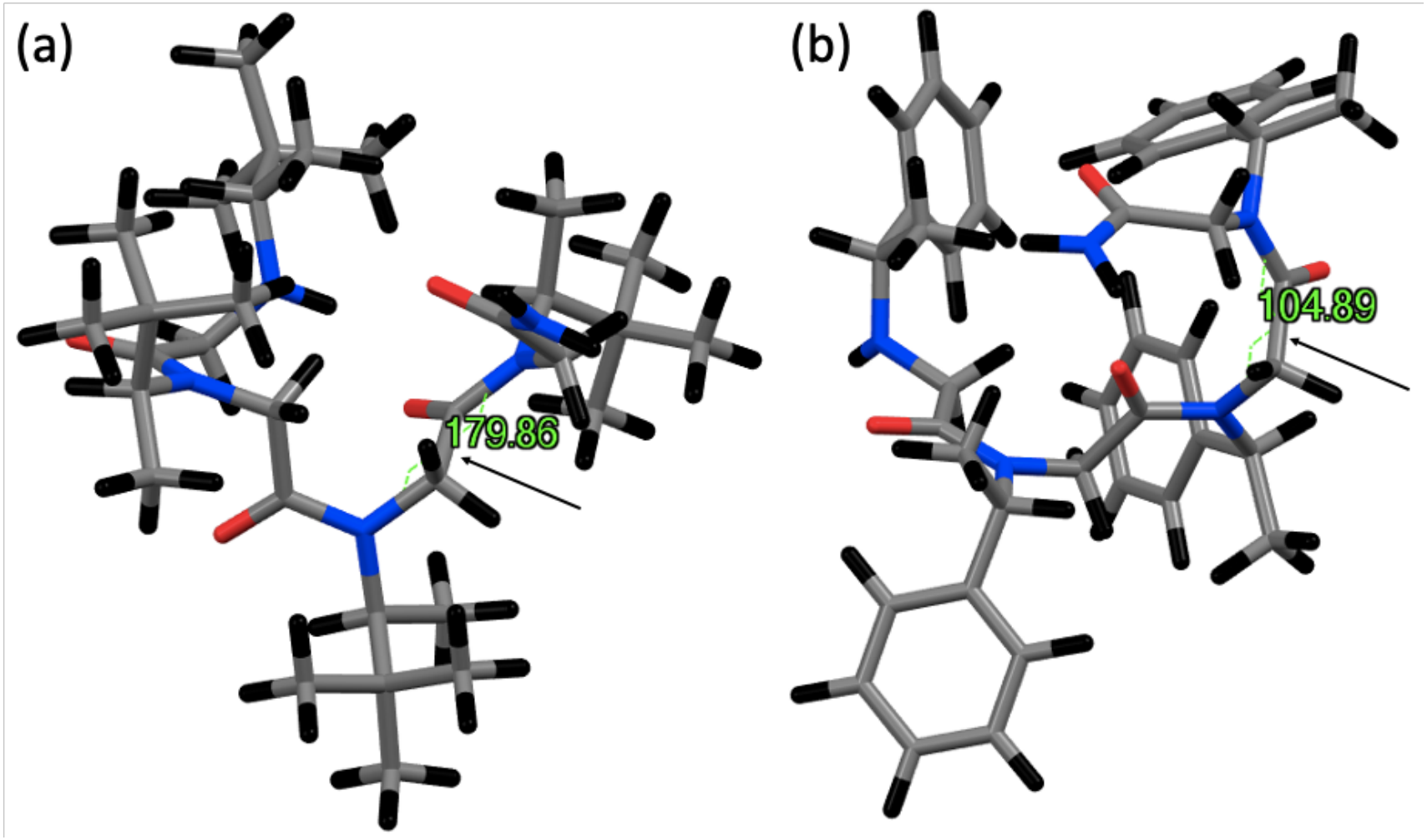

Figure S52. DFT-D3 optimized structure of (a)**P10** and (b) **P11**, arrow shows the specific bond for which the ψ angle is mentioned (color: Blue: N,Red: O, Grey: C, Black: H).

Proposed mechanism of Cu^{2+} assisted amide bond hydrolysis

Taking **P5** as a model, the concerted pathway should consist of one transition state whereas for the stepwise pathway two transition states could be expected. In the stepwise pathway, nucleophilic attack on the amide carbon followed by second nucleophilic attack towards cleavage of the C-N amide bond. In concerted pathway, the N-protonation influences the enhancement of N-C(O) bond length whereas C=O bond length is shortened. For both pathways, two water molecules (nucleophile and auxiliary) are participating in the reaction. After coordination with the Cu center, the backbone nitrogen of the first amine substitution is positively charged, and thus it should facilitate its nucleophilic attack to the proton, eventually making the concerted pathway more appropriate.

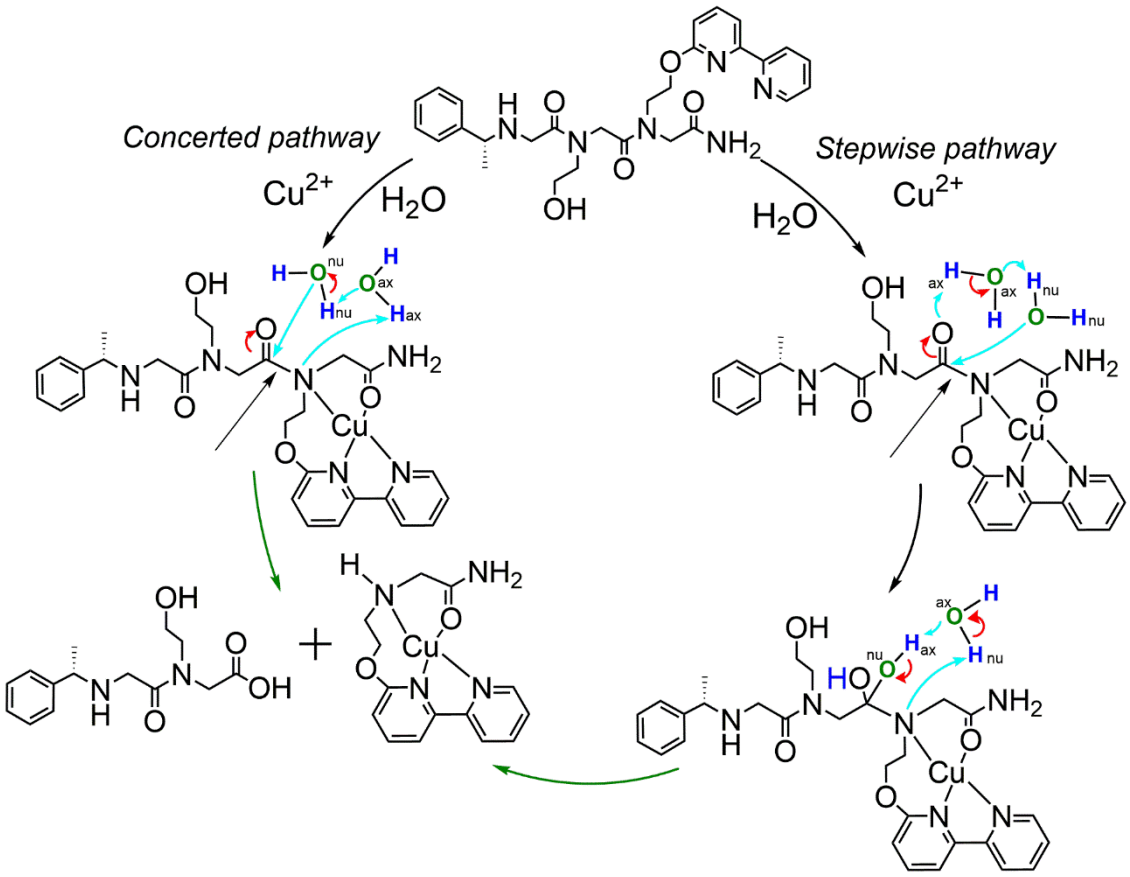

Figure S53. proposed mechanism for amide bond hydrolysis, black arrow shows the specific amide bond, cyan arrow: nucleophilic attack; red: electron pulling from a bond by more negative atom.

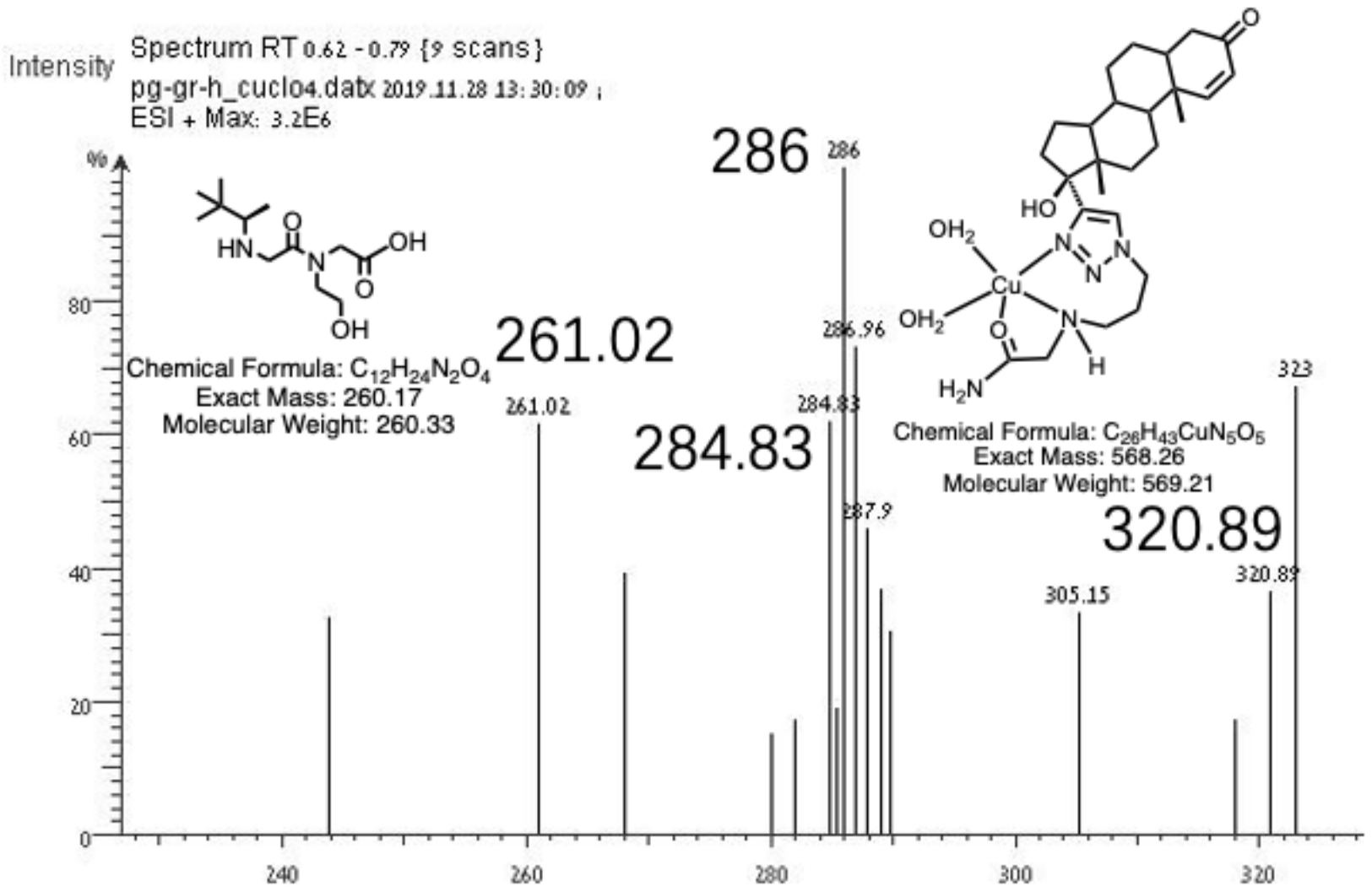

Figure S54. ESI-MS of peptoid **PSteroid** with Cu (II), half mass of the cleaved peptoid ligated with Cu observed at 284.83, full mass of the tail portion of the peptoid was observed at 261.02. the mass at 320.89 can be assigned to the half mass of [cleaved peptoid+Cu(II)+6H_2O]: 320.13, . [the geometries are proposed based on crystal structure Fig. S32 and ESI-MS traces of crystal and the solution after taking out the crystals (fig. S38-S39), the cleavage is considered in the same position as happened with **P2**, **P4**, **P6** and **P8**].

Table S3. Coordinates of **P3.**

70

O	5.5285976	10.4903180	-2.6543647
O	6.3026554	9.4274089	0.5180648
O	7.5472183	5.6867315	-0.9914498
O	2.7911856	9.1086039	-1.8468659
O	4.8248958	6.3318360	2.7528209
N	6.0702746	5.8771076	-4.2056038
N	5.1790445	8.5155067	-3.6669708
N	4.3745478	10.5267814	0.0255240
N	4.9669414	6.9613487	0.5749833
N	4.4066796	3.6921976	1.4227351
N	0.9939515	10.4275937	-1.4227391
C	6.3368002	4.5781489	-4.0422896
C	5.3559571	3.5796761	-4.0515728
C	4.0309294	3.9650034	-4.2713254
C	3.7465114	5.3194118	-4.4540545
C	4.7960416	6.2533862	-4.3991134
C	4.5083022	7.7153430	-4.5041919
C	3.5422328	8.2035471	-5.3951778
C	3.3083398	9.5818991	-5.4183517
C	3.9848822	10.4114287	-4.5281443
C	4.8845065	9.8068496	-3.6287181
C	4.9527713	11.6721019	-2.1062207

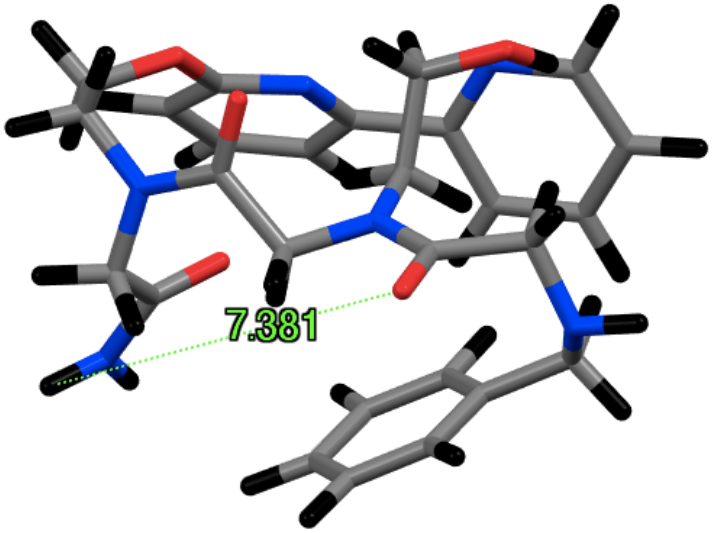

Figure S55. Distance between C-terminal -NH_2 and carbonyl group after second amine substitution for **P3**.

C	5.1016464	11.6343101	-0.5866450
C	2.9275135	10.6077570	0.0453337
C	2.2451134	9.9754828	-1.1813332
C	5.0772408	9.4328174	0.4529274
C	4.2692482	8.2033165	0.8699994
C	5.2943476	6.7438921	-0.8400583
C	6.7772698	6.8699674	-1.2056886
C	5.0941941	6.0537116	1.5823429
C	5.5229366	4.6205933	1.2426507
C	3.4822846	3.6183787	0.2976724
C	2.5307731	4.8000691	0.2139154
C	2.1886314	5.3498270	-1.0293300
C	1.3156471	6.4381811	-1.1201943
C	0.7622669	6.9877391	0.0405303
C	1.0926436	6.4422665	1.2877565
C	1.9712109	5.3578832	1.3731986
H	7.2503133	5.0153261	-1.6282444
H	4.7786111	2.7641767	1.6103276
H	0.4536915	10.0072543	-2.1729472
H	0.5580481	11.1505644	-0.8607511
H	7.3915887	4.3107308	-3.9038856
H	5.6291201	2.5337116	-3.8978798
H	3.2279207	3.2241281	-4.2883882
H	2.7190142	5.6552457	-4.6021070

H 3.0116987 7.5323648 -6.0717252

H 2.5971009 10.0095976 -6.1295914

H 3.8164566 11.4883415 -4.5312975

H 5.4732408 12.5609881 -2.5035446

H 3.8907419 11.7495421 -2.3858898

H 4.7365151 12.5905381 -0.1757797

H 6.1590310 11.5202361 -0.3197774

H 2.5250818 10.1177263 0.9453831

H 2.6416566 11.6675303 0.1320897

H 3.2978684 8.1659801 0.3645775

H 4.0986418 8.2399999 1.9552427

H 4.9032534 5.7750487 -1.1841651

H 4.7412934 7.5028398 -1.4100418

H 7.2289881 7.6556408 -0.5876407

H 6.8239855 7.1742310 -2.2623115

H 6.2950344 4.3636637 1.9835231

H 5.9900729 4.5485738 0.2489788

H 4.0081924 3.5161202 -0.6776494

H 2.8901059 2.6946724 0.4260308

H 2.6357708 4.9407147 -1.9386260

H 1.1007186 6.8813247 -2.0945353

H 0.1000831 7.8549781 -0.0251285

H 0.6750622 6.8754732 2.2011459

H 2.2655513 4.9563406 2.3441996

Table S4. Coordinates of **P4**

73

O	5.5271816	10.7507820	-3.0489240
O	6.7893966	8.6721984	-0.8463790
O	7.1611063	4.2712992	-1.8040755
O	2.4211243	10.6541552	-0.9772946
O	5.3212620	7.8461188	2.2361163
N	5.3583409	6.0967327	-4.4574972
N	4.7415069	8.6974270	-3.5708515
N	5.1825581	10.1551414	-0.1873259
N	5.2052245	6.5736105	0.3829402
N	4.9745002	4.3792217	2.4250373
N	1.7662239	9.7783977	1.0147942
C	5.6904581	4.8058453	-4.5443566
C	4.8231258	3.7594379	-4.2044694
C	3.5397541	4.0879279	-3.7568658
C	3.1789181	5.4338020	-3.6830718
C	4.1188989	6.4148780	-4.0488923
C	3.7725329	7.8654830	-3.9861896
C	2.4945070	8.3211829	-4.3331545
C	2.2437322	9.6973714	-4.2691035
C	3.2477261	10.5579966	-3.8425981
C	4.4845885	9.9948220	-3.4759679
C	5.3322372	11.7687487	-2.0605769

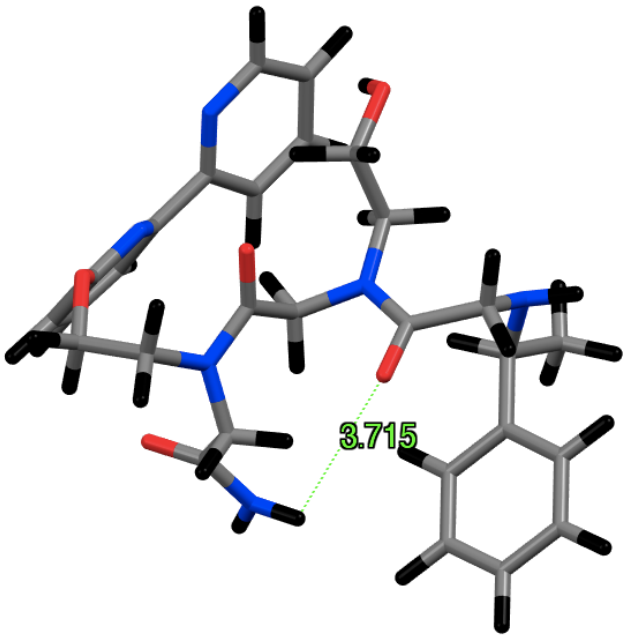

Figure S56. Distance between C-terminal -NH_2 and carbonyl group after second amine substitution for **P4**.

C	5.9143674	11.2966074	-0.7288981
C	4.0951233	10.3886823	0.7514922
C	2.6864732	10.2863086	0.1600643
C	5.6586846	8.8922818	-0.4330441
C	4.6637266	7.7360785	-0.2985535
C	5.5263119	5.3806040	-0.3902317
C	6.8197703	5.5109870	-1.2029371
C	5.4493885	6.7381745	1.7106023
C	5.8472524	5.5383895	2.5698504
H	6.4644775	4.0364594	-2.4407114
H	5.2300543	3.6721447	3.1128765
H	0.7865222	9.7621130	0.7456559
H	2.0108187	9.5087178	1.9616951
H	6.7049639	4.5865740	-4.8964164
H	5.1470237	2.7199945	-4.2922748
H	2.8315022	3.3081754	-3.4668907
H	2.1889070	5.7228999	-3.3270631
H	1.7245128	7.6280454	-4.6739368
H	1.2678501	10.0942560	-4.5593352
H	3.0818756	11.6334256	-3.7828026
H	5.8677046	12.6688157	-2.4028534
H	4.2637158	11.9977419	-1.9447204
H	5.8860014	12.1282042	-0.0071044
H	6.9608090	10.9967635	-0.8727304

H	4.2119823	9.7107597	1.6085535
H	4.1969482	11.4158729	1.1366869
H	4.4251024	7.4516027	-1.3327014
H	3.7266149	8.0302561	0.1887158
H	5.6040498	4.5282498	0.2963652
H	4.6838148	5.1718713	-1.0738360
H	7.6499727	5.7786921	-0.5308589
H	6.7282859	6.3176198	-1.9515356
H	5.8771273	5.9466536	3.5958044
H	6.8759054	5.2338571	2.3054198
C	3.3783619	5.4524470	4.8177363
C	2.9073189	6.3497506	5.7817306
C	2.0643283	7.4039075	5.4085131
C	1.6995588	7.5533675	4.0653805
C	2.1817001	6.6575532	3.1047688
C	3.0214673	5.5953785	3.4687546
C	3.5279619	4.6165633	2.4132758
C	2.8076067	3.2679585	2.5086458
H	4.0408640	4.6352586	5.1182011
H	3.1990259	6.2264177	6.8282874
H	1.6941223	8.1056804	6.1604924
H	1.0328302	8.3694783	3.7712275
H	1.9061248	6.7861871	2.0533878
H	3.2785740	5.0543234	1.4318714

H	1.7183224	3.4037459	2.4151010
H	3.0091384	2.7845737	3.4814830
H	3.1524235	2.5944127	1.7058746

Table S5. Coordinates of **P5**.

76

O	8.2878020	0.7290312	8.9398593
O	5.3898956	0.5838797	10.7913622
O	4.2061498	4.3854117	11.1125924
O	3.0331270	1.8842547	12.6320557
O	7.9462139	1.6236411	13.3588660
N	10.7051948	0.4840054	10.2029710
N	7.4899825	2.3412595	10.3182547
N	3.8601171	1.9531888	9.8046320
N	3.4994778	5.6006882	9.3285995
N	4.1234812	2.8083015	14.3446629
N	6.2069913	2.4529115	16.0567609
C	12.3496558	-0.1208410	8.4761921
C	13.7159682	0.0941262	8.5146952
C	14.6349956	-0.8712853	8.0298131
C	14.1763774	-2.0587558	7.5031512
C	12.7793215	-2.3297049	7.4420690
C	12.2834680	-3.5473860	6.8946558
C	10.9279026	-3.7965557	6.8368468

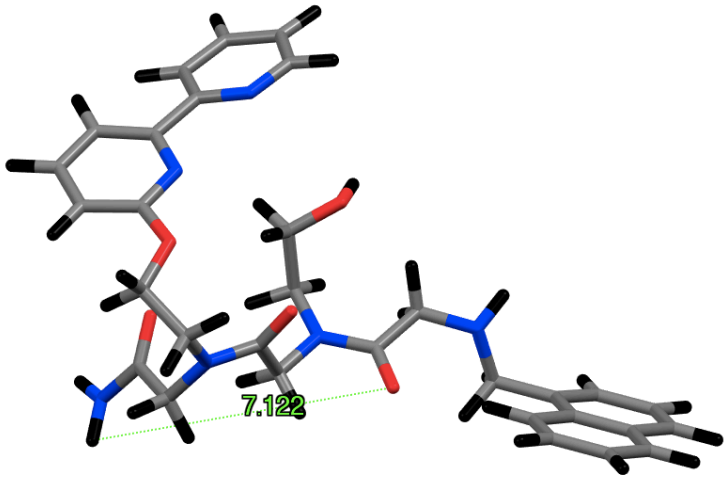

Figure S57. Distance between C-terminal -NH_2 and carbonyl group after second amine substitution for **P5**.

C	10.0086691	-2.8347423	7.3287247
C	10.4535197	-1.6437383	7.8689363
C	11.8483032	-1.3543890	7.9382895
C	11.4014973	0.9315056	8.9997025
C	9.7515120	1.4376565	10.7229223
C	8.4485769	1.4550501	9.9220706
C	6.2746001	2.4222156	9.5356644
C	5.1352098	1.5799786	10.1255845
C	3.5602359	3.1854943	9.1080141
C	3.7850340	4.4471791	9.9636077
C	2.7358276	1.2113089	10.3692161
C	2.1011930	1.9125083	11.5610537
C	3.0574602	2.8626906	13.5595502
C	2.0526605	3.8398129	13.7026408
C	2.2335090	4.7993999	14.6951296
C	3.3762686	4.7695028	15.4993947
C	4.3071416	3.7395482	15.2887692
C	5.5706572	3.6352840	16.0817904
C	6.0891625	4.7366203	16.7869817
C	7.2999153	4.5989657	17.4665685
C	7.9630953	3.3707407	17.4227617
C	7.3665824	2.3302073	16.7019895
C	7.0870275	2.6168380	12.8140693
C	7.5767595	3.2136646	11.4936495

H 8.6835942 2.0726380 13.7948761

H 11.3895301 0.2708615 10.9262809

H 3.6136134 6.4826068 9.8178295

H 3.1433773 5.6226551 8.3797005

H 14.0959075 1.0339422 8.9253977

H 15.7074911 -0.6652711 8.0762397

H 14.8761140 -2.8087120 7.1238935

H 13.0001339 -4.2830342 6.5186520

H 10.5588416 -4.7347031 6.4139319

H 8.9361422 -3.0428872 7.2816249

H 9.7401285 -0.9191257 8.2655697

H 11.9663075 1.8734557 9.1665505

H 10.6362169 1.1527973 8.2393545

H 10.1454988 2.4779975 10.7544382

H 9.4899805 1.1769137 11.7575650

H 6.4809151 2.0147166 8.5345672

H 6.0062343 3.4779242 9.4274089

H 2.5056568 3.1596582 8.7952419

H 4.1414041 3.2760428 8.1769281

H 3.1054027 0.2252863 10.6754098

H 1.9682434 1.0727813 9.5912274

H 1.8410127 2.9491610 11.2992691

H 1.1711288 1.3925944 11.8516457

H 1.1639210 3.8522746 13.0728957

H	1.4775940	5.5742782	14.8452308
H	3.5190178	5.5154446	16.2808357
H	5.5706119	5.6957986	16.7871805
H	7.7236437	5.4448047	18.0135939
H	8.9170645	3.2178768	17.9319909
H	7.8566740	1.3509655	16.6438183
H	6.9553899	3.4477803	13.5278246
H	6.1005128	2.1568535	12.6861242
H	6.9486124	4.0924841	11.2828072
H	8.6076263	3.5810593	11.6096515

Table S6. Coordinates of **P6**.

79

O	5.5774400	12.3973311	-1.4049604
O	7.3475299	9.9978836	0.2948712
O	7.8061875	5.7211194	-1.2284080
O	2.8929547	10.6274184	0.8203545
O	6.2665578	8.7661102	3.3919867
N	5.2473131	7.8582285	-3.1841137
N	4.7583659	10.3692284	-2.0027503
N	5.7124089	11.2262759	1.3031852
N	6.0760718	7.6413394	1.4523684
N	6.1435340	5.2513027	3.3319555
N	2.3754899	12.0407094	2.5174504

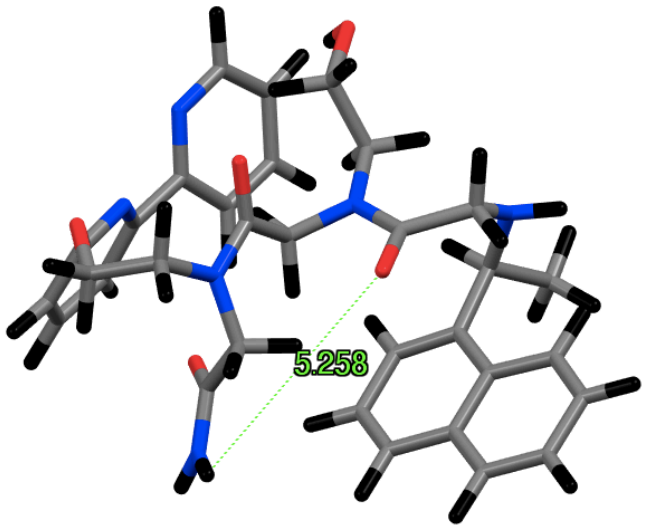

Figure S58. Distance between C-terminal -NH_2 and carbonyl group after second amine substitution for **P6**.

C	5.5799132	6.5833742	-3.4077765
C	4.8033366	5.4971984	-2.9880186
C	3.6140142	5.7643956	-2.3035589
C	3.2481483	7.0924906	-2.0865677
C	4.0932280	8.1182210	-2.5486489
C	3.7439199	9.5519627	-2.3242650
C	2.4217920	10.0015609	-2.4236555
C	2.1650730	11.3568788	-2.1974354
C	3.2127264	12.2016787	-1.8506252
C	4.4972701	11.6404708	-1.7404207
C	5.5407319	13.1842017	-0.2114547
C	6.3238913	12.4864802	0.8970905
C	4.6704827	11.2787786	2.3151615
C	3.2355662	11.2980643	1.7875136
C	6.2501336	10.0529687	0.8406640
C	5.3827324	8.8013812	0.9186093
C	6.3860504	6.5350976	0.5613487
C	7.5126562	6.8524776	-0.4258081
C	6.3989906	7.7095832	2.7697082
C	6.9203704	6.4742070	3.4971793
C	4.6802495	5.2803271	3.1915973
C	4.0976728	3.9538722	3.6934495
H	7.0126665	5.5075838	-1.7402416
H	6.4446415	4.5611373	4.0144388

H 1.3881631 12.0371637 2.2822553

H 2.6796454 12.6097316 3.2982622

H 6.5190918 6.4115195 -3.9466815

H 5.1220883 4.4733427 -3.1961578

H 2.9813684 4.9496836 -1.9434936

H 2.3319045 7.3361421 -1.5462914

H 1.6174150 9.3167251 -2.6954266

H 1.1504854 11.7508402 -2.2942473

H 3.0495998 13.2649188 -1.6682553

H 6.0092419 14.1544082 -0.4380279

H 4.5001752 13.3741100 0.0983923

H 6.3967432 13.1620390 1.7648736

H 7.3388037 12.2703330 0.5408414

H 4.7639053 10.3987396 2.9703629

H 4.8562745 12.1584914 2.9489539

H 5.1025424 8.5942426 -0.1205823

H 4.4529487 8.9637879 1.4676935

H 6.6543924 5.6544200 1.1584591

H 5.4754068 6.2739487 -0.0069557

H 8.4291371 7.1055876 0.1295944

H 7.2518306 7.7357849 -1.0349891

H 6.9947010 6.8070308 4.5463085

H 7.9524153 6.2848412 3.1484274

H 4.4568565 5.3171152 2.1106019

H	3.0261812	3.8959980	3.4525761
H	4.2096258	3.8407795	4.7827221
H	4.6090298	3.1103437	3.2022207
C	3.9529408	6.4963159	3.7658553
C	3.1199073	7.1968310	2.9097260
C	2.4298861	8.3640354	3.3106076
C	2.5856723	8.8442973	4.5915270
C	3.4065724	8.1506901	5.5239774
C	3.5561814	8.6236635	6.8582580
C	4.3399923	7.9484592	7.7701297
C	5.0140499	6.7648581	7.3788989
C	4.8955103	6.2850936	6.0900323
C	4.0936525	6.9527004	5.1189240
H	3.0167917	6.8524267	1.8770089
H	1.8065952	8.8922550	2.5870114
H	2.0850933	9.7634805	4.9065717
H	3.0314322	9.5381926	7.1485916
H	4.4439869	8.3218966	8.7920946
H	5.6353955	6.2300446	8.1017735
H	5.4324581	5.3806241	5.8093099

Table S7. Coordinates of **P7**.

67

O	6.0382101	17.4400492	6.9892324
O	5.7557203	16.1305871	10.0301168
O	2.2665707	17.5092826	12.0436365
O	6.9883451	15.5294862	13.7351432
O	3.5327979	11.1000895	13.5855850
O	9.4339232	13.3385665	13.2459456
N	5.7229403	18.8818499	9.5545409
N	4.9312352	16.2961637	12.1322377
N	6.4293684	13.3226513	13.7524697
N	3.9947666	12.8157270	15.0047577
N	9.3975301	14.7932613	11.5344098
N	10.6699430	16.9581141	10.2433125
C	7.4934403	12.9955930	14.7026013
C	6.1432735	16.1425275	6.4606081
C	4.7755660	17.7090898	7.5622587
C	4.8530379	18.9791023	8.3953473
C	5.3128621	16.8359359	10.9316015
C	5.1559455	18.3545323	10.7740754
C	4.2747520	11.9960784	13.9736249
C	5.6097497	12.2327280	13.2563478
C	8.7456602	12.3979944	14.0651865
C	9.0035838	13.6098591	11.9852919

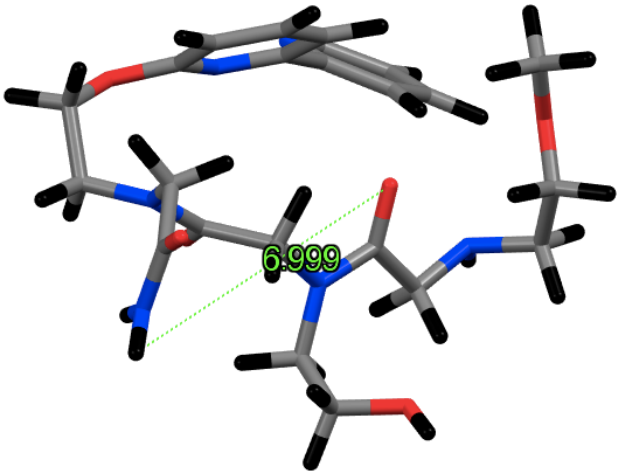

Figure S59. Distance between C-terminal -NH_2 and carbonyl group after second amine substitution for **P7**.

C 8.2378327 12.7136483 11.2164924

C 7.8451263 13.1259848 9.9459291

C 8.2171904 14.3880785 9.4830940

C 9.0091252 15.1924093 10.3132649

C 9.4458491 16.5462460 9.8651472

C 8.5888907 17.3424626 9.0882457

C 9.0344074 18.5981603 8.6752282

C 10.3113344 19.0211375 9.0480488

C 11.0840576 18.1616388 9.8391810

C 6.2740991 14.6217189 13.3357648

C 5.1344126 14.8829434 12.3433870

C 4.2936543 17.0304831 13.2202220

C 2.7761156 16.9110736 13.2193653

H 1.3222790 17.3085875 11.9834421

H 6.1597659 19.7772188 9.7412304

H 3.1360958 12.6854355 15.5306898

H 4.6568648 13.5096417 15.3298369

H 7.1020760 12.2777949 15.4412847

H 7.7642124 13.9197422 15.2278772

H 7.1659843 16.0147787 6.0743504

H 5.4291222 15.9718486 5.6291243

H 5.9560022 15.3757017 7.2365660

H 4.4585527 16.8605236 8.1922163

H 4.0122485 17.8447160 6.7663264

H	5.2384913	19.7835485	7.7473599
H	3.8115627	19.2598292	8.6715518
H	4.0762840	18.5802873	10.8890209
H	5.6623948	18.8302358	11.6284000
H	6.1732582	11.2918740	13.3359221
H	5.3842454	12.3481595	12.1875211
H	9.4494516	12.1344155	14.8672714
H	8.5210317	11.4703482	13.5149345
H	7.9590141	11.7288583	11.5863140
H	7.2470847	12.4595112	9.3195709
H	7.9053407	14.7413008	8.5020722
H	7.5721842	17.0286243	8.8556027
H	8.3720530	19.2309331	8.0805682
H	10.7042816	19.9952741	8.7474652
H	12.0882490	18.4674446	10.1580834
H	5.3944500	14.4280492	11.3767887
H	4.2050702	14.4098517	12.6962470
H	4.5769692	18.0891024	13.1787018
H	4.6846179	16.6467773	14.1745067
H	2.4849223	15.8445018	13.2845420
H	2.3935330	17.4065306	14.1335286

Table S8. Coordinates of **P8**.

70

O	5.7046624	11.5652912	-2.1665628
O	6.5544120	9.5276245	0.1621307
O	7.1023497	5.2006764	-0.9735693
O	2.4297965	11.0452256	-0.8262102
O	4.8502769	8.5989562	3.0074278
N	5.6013774	6.9403987	-3.7832961
N	4.9595984	9.5620566	-2.8964421
N	4.8699905	11.0005204	0.5967935
N	4.9233231	7.4068021	1.0970311
N	4.8746565	5.1784185	3.1730685
N	1.2135945	10.9603200	1.0891727
C	5.8734615	5.6324388	-3.8237433
C	4.9150462	4.6370833	-3.5989097
C	3.6020481	5.0350862	-3.3314112
C	3.3046833	6.3977104	-3.3126346
C	4.3368728	7.3239895	-3.5450152
C	4.0637084	8.7912574	-3.5327811
C	2.9279428	9.3192869	-4.1574878
C	2.7576987	10.7086943	-4.1511307
C	3.6875498	11.5084560	-3.5000705
C	4.7607749	10.8719417	-2.8496724
C	5.3225798	12.5942273	-1.2481709

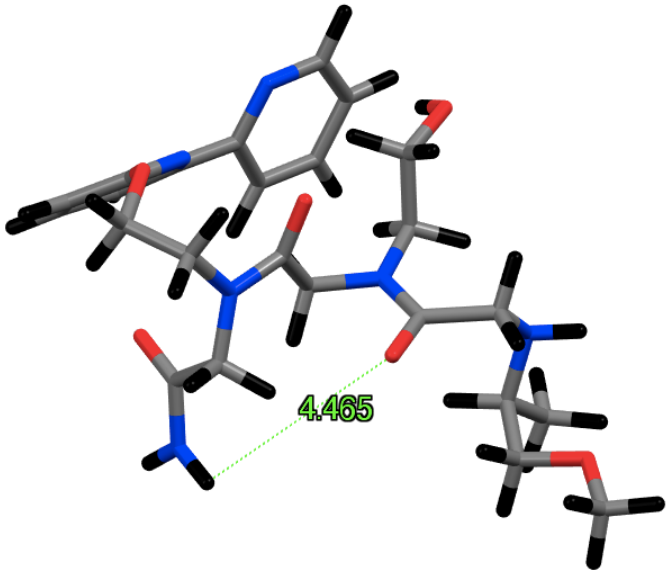

Figure S60. Distance between C-terminal -NH_2 and carbonyl group after second amine substitution for **P8**.

C	5.6660218	12.1470655	0.1706052
C	3.6106537	11.2302146	1.2765936
C	2.3665344	11.0684350	0.3969731
C	5.3751538	9.7424082	0.4124909
C	4.3820714	8.5759808	0.4283755
C	5.3292309	6.2513929	0.3069695
C	6.6748003	6.4272732	-0.4034009
C	5.1334865	7.5426449	2.4314238
C	5.7124070	6.3697488	3.2204172
C	3.4790837	5.3520453	3.5887523
C	2.7872864	3.9902360	3.5682861
H	6.4629152	4.9457878	-1.6544248
H	5.3055423	4.4616710	3.7568937
H	0.3321109	10.9023942	0.5892430
H	1.1873066	10.9868775	2.1021172
H	6.9117518	5.3557956	-4.0401731
H	5.1933055	3.5816904	-3.6380397
H	2.8216635	4.2949793	-3.1392984
H	2.2917840	6.7446665	-3.1008898
H	2.2160233	8.6677454	-4.6662931
H	1.9039365	11.1624953	-4.6603851
H	3.5845141	12.5938990	-3.4771539
H	5.8890185	13.5059431	-1.4971627
H	4.2471890	12.8049508	-1.3323887

H	5.4999708	12.9861237	0.8635871
H	6.7260530	11.8653072	0.2163119
H	3.5413438	10.5741826	2.1579052
H	3.6087258	12.2632951	1.6574482
H	4.2070089	8.3347010	-0.6289617
H	3.4167349	8.8361259	0.8758519
H	5.3666021	5.3759275	0.9668142
H	4.5416520	6.0551421	-0.4411260
H	7.4398797	6.7268254	0.3291558
H	6.6136785	7.2333918	-1.1554169
H	5.8774373	6.7638103	4.2390338
H	6.7027798	6.1140246	2.8075539
H	2.9869343	6.0045496	2.8447680
H	1.7095419	4.0956930	3.7661932
H	3.2123002	3.3353021	4.3461491
H	2.9213230	3.5048176	2.5898802
O	4.0514304	5.3276723	5.9143671
C	3.9911999	5.9010104	7.1982794
C	3.3205766	6.0484012	4.9446970
H	4.6051016	5.2878516	7.8746972
H	2.9537839	5.9294369	7.5869360
H	4.3840260	6.9372003	7.2019597
H	3.6869151	7.0914536	4.8855395
H	2.2461037	6.0977774	5.2158255

Table S9. Coordinates of geometry for **P3Cu** as per **fig. 3a(i)**.

76

O	5.6334530	10.2527784	-3.0280708
O	6.7075977	9.2420748	0.3568035
O	7.0749820	6.0009380	-1.9121341
O	3.3574070	8.7015125	-1.7643436
O	4.6918887	6.7906200	3.2796791
N	4.9624225	5.8571022	-3.9112488
N	4.8936711	8.4508817	-4.1287509
N	4.8782151	10.4599926	-0.2200505
N	5.1414752	7.0365526	1.0703821
N	4.2812795	3.9679438	2.4932017
N	1.6318170	10.1668360	-1.8648967
C	5.0934983	4.5448755	-3.6885600
C	4.3146882	3.6132400	-4.3718129
C	3.3879429	4.0753373	-5.3075711
C	3.2599086	5.4476615	-5.5312114
C	4.0677047	6.3272874	-4.8099658
C	4.0042347	7.7984871	-4.9122818
C	3.0748660	8.4925831	-5.6758513
C	3.0732498	9.8913414	-5.6010310
C	3.9410366	10.5492375	-4.7404804
C	4.8293242	9.7775008	-3.9681984

C	5.3813596	11.5280718	-2.4209365
C	5.6995883	11.4344377	-0.9368093
C	3.4393954	10.6136009	-0.2928702
C	2.8099500	9.7330485	-1.3862566
C	5.4880838	9.3881510	0.3673573
C	4.5990778	8.3867768	1.1032109
C	5.4364976	6.4791876	-0.2428226
C	6.9298629	6.3460445	-0.5130542
C	5.0627265	6.2953951	2.2185857
C	5.4349732	4.8065357	2.1864664
C	3.6246500	3.3601040	1.3452950
C	2.8680770	4.3528745	0.4825660
C	2.7812640	4.1602838	-0.9048249
C	2.1029910	5.0758195	-1.7147681
C	1.5059765	6.2043118	-1.1474610
C	1.5787585	6.4009647	0.2350075
C	2.2507384	5.4804656	1.0441329
Cu	6.1382109	7.2727687	-3.1695394
H	8.0334013	5.9603826	-2.1303604
H	4.5457170	3.2439973	3.1548743
H	1.1339453	9.6080941	-2.5507351
H	1.1928804	11.0195144	-1.5360788
H	5.8415506	4.2482271	-2.9518226
H	4.4410341	2.5489109	-4.1701582

H 2.7639535 3.3727394 -5.8633143

H 2.5411089 5.8237056 -6.2585656

H 2.3601093 7.9675563 -6.3071756

H 2.3721949 10.4682501 -6.2073058

H 3.9342864 11.6350004 -4.6621955

H 6.0221677 12.2900558 -2.8905937

H 4.3329539 11.8172663 -2.5848705

H 5.5545736 12.4388685 -0.5037219

H 6.7466200 11.1455736 -0.7927350

H 2.9616696 10.3636102 0.6660526

H 3.2029864 11.6729883 -0.4680774

H 3.5793231 8.3579569 0.7026699

H 4.5362623 8.6950657 2.1565614

H 4.9309352 5.5161286 -0.3832683

H 4.9775586 7.1584710 -0.9809023

H 7.3819834 5.5369840 0.0795868

H 7.4415273 7.2929655 -0.3005985

H 6.1769659 4.6934200 2.9909227

H 5.9330365 4.5008484 1.2509544

H 4.3335316 2.8060491 0.6924660

H 2.9152263 2.6078663 1.7335533

H 3.2658392 3.2900576 -1.3569525

H 2.0508748 4.9147883 -2.7937597

H 0.9970448 6.9331938 -1.7805809

H	1.1149808	7.2825845	0.6854962
H	2.3262031	5.6409718	2.1211846
Cl	8.8684100	7.7347341	-3.8639209
O	9.8158971	8.7186688	-4.3805961
O	8.1780980	6.9679114	-4.9365185
O	9.5186534	6.7943283	-2.9051429
O	7.7497046	8.4988926	-3.0901694

Table S10. Coordinates of geometry for **P3Cu** as per **fig. 3a(ii)**.

76

O	5.1047066	11.9146388	-3.3947726
O	6.5029630	8.4388535	-0.6025488
O	8.2948024	6.0509684	0.8442447
O	2.0588312	8.3343439	-2.0040786
O	4.6670632	7.7274072	1.9586358
N	2.8923313	7.7954366	-4.6230256
N	4.2334171	10.1052166	-4.5933149
N	4.4399387	9.3171877	-1.1749162
N	5.3649425	6.1346364	0.5368715
N	4.6919190	5.2555911	3.7155623
N	0.9074779	8.8933366	-0.1508046
C	2.1720735	6.6748052	-4.4991121
C	1.7464664	5.9621394	-5.6151791
C	2.0881161	6.4473777	-6.8804480

C	2.8339563	7.6191601	-6.9916729
C	3.2337297	8.2865061	-5.8284218
C	4.0233945	9.5349521	-5.8182674
C	4.5309025	10.0851642	-6.9847561
C	5.2891533	11.2617409	-6.9050742
C	5.4831000	11.8558803	-5.6753992
C	4.9161817	11.2499576	-4.5348584
C	4.4109304	11.6092107	-2.1867320
C	5.1818151	10.5957523	-1.3397904
C	3.2572120	9.4859695	-0.2783888
C	2.0152718	8.8602991	-0.8648300
C	5.3254833	8.2436897	-0.7206609
C	4.6800850	6.8843477	-0.4896876
C	6.2022488	5.0093113	0.1312860
C	7.6227033	5.4350305	-0.2393535
C	5.2593707	6.6567535	1.7872849
C	5.7919263	5.8794786	2.9891223
C	4.1587152	4.0379748	3.1162214
C	3.2327961	4.3070714	1.9423343
C	3.2692784	3.5033207	0.7950263
C	2.4245969	3.7620899	-0.2899180
C	1.5179354	4.8253024	-0.2335472
C	1.4641677	5.6232605	0.9157903
C	2.3179110	5.3688386	1.9912354

H	8.6030438	5.3562134	1.4432459
H	4.9888875	5.0673099	4.6699266
H	0.0399431	8.5310337	-0.5395106
H	0.8731243	9.3361647	0.7625947
H	1.9306542	6.3598638	-3.4823043
H	1.1598769	5.0510993	-5.4910779
H	1.7714335	5.9165200	-7.7804920
H	3.0956217	8.0084049	-7.9741012
H	4.3612689	9.6082971	-7.9478085
H	5.7102251	11.7072428	-7.8084827
H	6.0413906	12.7835905	-5.5490102
H	4.3421601	12.5702593	-1.6634962
H	3.3834662	11.2826135	-2.4165822
H	5.4092007	11.0022632	-0.3438359
H	6.1340788	10.3675842	-1.8283743
H	3.4757072	9.0607786	0.7156140
H	3.0651758	10.5577594	-0.1326523
H	4.7597789	6.3429448	-1.4399413
H	3.6159386	6.9636810	-0.2397629
H	6.2287289	4.2617333	0.9334021
H	5.7228093	4.5210498	-0.7296312
H	7.5872941	6.1684207	-1.0584877
H	8.1672245	4.5468529	-0.6105206
H	6.2547978	6.6319260	3.6430126

H	6.5819590	5.1666313	2.6998307
H	4.9548856	3.3351012	2.7910698
H	3.5888910	3.5112396	3.9008920
H	3.9822046	2.6756180	0.7396769
H	2.4776764	3.1327645	-1.1822738
H	0.8542467	5.0305625	-1.0779645
H	0.7570318	6.4530299	0.9728591
H	2.3075673	6.0117517	2.8732135
Cu	3.7038018	8.6939792	-3.0801308
Cl	6.6945516	7.7984227	-4.0289346
O	7.0329147	9.1929707	-3.6563128
O	7.7363266	6.8556622	-3.5784626
O	5.3919246	7.4023856	-3.3030763
O	6.4591387	7.6864920	-5.4835135

Table S11. Coordinates of geometry for **P5Cu** as per **fig. 3b(i)**.

79

O	4.9341880	9.8205832	-2.6462223
O	5.6806021	8.7002053	0.2793187
O	5.3187011	6.5622965	-1.3982099
O	2.8198071	8.2108704	-1.8552892
O	5.0017072	7.9051989	3.2815986
N	4.3702992	5.6685745	-4.4886966
N	4.6117294	8.2593817	-4.2200583

N	3.9150370	10.0764939	-0.1058671
N	4.2574661	6.7354538	1.4948986
N	4.7998961	4.5199175	3.4734225
N	1.5141834	9.8517153	-2.7116422
C	4.4420947	4.3321543	-4.4788349
C	4.6967696	3.6002077	-5.6377574
C	4.8669607	4.2845538	-6.8398752
C	4.8191905	5.6792739	-6.8406073
C	4.5869134	6.3500830	-5.6395786
C	4.6554935	7.8172960	-5.5006792
C	4.8252497	8.6961440	-6.5644574
C	4.9774364	10.0584043	-6.2826500
C	5.0058372	10.5006769	-4.9665579
C	4.8459292	9.5497866	-3.9440488
C	4.8129350	11.1662609	-2.1720284
C	4.8026700	11.1042842	-0.6502644
C	2.5145322	10.1346528	-0.4829867
C	2.2784539	9.3267030	-1.7663173
C	4.4706756	8.9203296	0.3612179
C	3.5447530	7.9128420	1.0545562
C	4.2703115	5.5563456	0.6277037
C	5.3814144	5.5179813	-0.4182711
C	4.9741632	6.8496384	2.6520152
C	5.7097545	5.6164688	3.1806003

C	5.1812643	4.4234548	6.5876561
C	5.7265053	4.8572445	7.7987444
C	5.4604471	6.1503844	8.2659066
C	4.6535201	7.0045601	7.5084984
C	4.1132281	6.5655107	6.2947935
C	4.3616249	5.2696229	5.8239904
C	3.7825860	4.8024532	4.4914321
C	2.8781868	3.5791791	4.6475083
H	5.6162665	7.3917459	-0.9663066
H	5.3323751	3.6855334	3.7194516
H	1.2740762	9.3086679	-3.5381195
H	1.0597265	10.7523908	-2.5940388
H	4.2915749	3.8304495	-3.5240371
H	4.7519012	2.5122603	-5.5851105
H	5.0529171	3.7428228	-7.7693795
H	4.9848201	6.2358016	-7.7622400
H	4.8440926	8.3374443	-7.5919048
H	5.1007956	10.7736724	-7.0981828
H	5.1720638	11.5505882	-4.7313732
H	5.6628528	11.7807510	-2.5077304
H	3.8867142	11.6037121	-2.5791329
H	4.4964898	12.0903583	-0.2678283
H	5.8099564	10.8830801	-0.2820812
H	1.8683928	9.7108687	0.2999041

H	2.2088473	11.1815812	-0.6079580
H	2.7398805	7.6019098	0.3816375
H	3.1034022	8.4230311	1.9247182
H	4.3558199	4.6659555	1.2651372
H	3.2965559	5.5041175	0.1264484
H	5.3005525	4.5662710	-0.9609114
H	6.3711466	5.5515941	0.0663153
H	6.2759256	5.9778686	4.0583359
H	6.4426499	5.2728637	2.4332703
H	5.4017289	3.4121668	6.2334269
H	6.3608542	4.1843289	8.3821874
H	5.8854773	6.4909406	9.2138194
H	4.4479567	8.0194030	7.8598437
H	3.5032640	7.2432611	5.6922373
H	3.1634092	5.6284918	4.1017248
H	2.0731642	3.7796386	5.3704734
H	3.4483110	2.7075020	5.0098360
H	2.4282650	3.3136668	3.6783822
Cu	3.8140548	6.8712983	-2.9711867
Cl	2.0053844	4.2048560	-2.1214952
O	2.3792399	5.7044611	-2.1140445
O	1.5707949	3.8345785	-3.4832151
O	3.1973660	3.4174427	-1.7109829
O	0.9198549	4.0619793	-1.1382353

Table S12. Coordinates of geometry for **P5Cu** as per **fig. 3b(ii)**.

79

O	5.4456303	9.8230716	-2.9978109
O	6.0568449	9.8352964	-0.0790030
O	9.6737487	6.9068893	-0.4022545
O	1.1495182	9.5359129	-1.0416025
O	4.7304046	7.9037866	2.2092865
N	1.3504269	7.6161203	-3.3085122
N	3.8658247	8.2331341	-3.5622159
N	3.8233369	9.7028875	-0.7669565
N	6.0941580	7.0652661	0.6277487
N	6.5209343	5.0725820	2.8029363
N	0.6909521	10.3917758	0.9936290
C	0.0374159	7.4617906	-3.1227202
C	-0.6991906	6.5580774	-3.8861193
C	-0.0309841	5.7895329	-4.8400050
C	1.3437766	5.9533098	-5.0183023
C	2.0148436	6.8902023	-4.2336937
C	3.4526737	7.2036643	-4.3473655
C	4.3417386	6.5510466	-5.1897030
C	5.6744145	6.9850291	-5.2236497
C	6.0678107	8.0892916	-4.4785826
C	5.1053534	8.7173774	-3.6761238

C	4.4721188	10.8804988	-2.8494504
C	4.0336128	11.0350269	-1.3990455
C	2.9905778	9.8158241	0.4653354
C	1.5286816	9.9216067	0.0929460
C	5.1370229	9.1219928	-0.3577390
C	5.1722568	7.6143242	-0.3363200
C	7.3510974	6.4765765	0.1792088
C	8.4450718	7.5207593	-0.0713639
C	5.7220495	7.2281946	1.9297774
C	6.5065259	6.5105527	3.0215766
C	4.5783389	4.5371205	5.1233054
C	3.6809312	4.8186277	6.1569620
C	2.4106218	5.3281806	5.8625457
C	2.0513813	5.5574713	4.5304487
C	2.9545904	5.2788666	3.4993656
C	4.2244265	4.7580675	3.7837968
C	5.2030650	4.4447702	2.6549567
C	5.3849402	2.9374456	2.4686424
H	9.5899312	6.5015849	-1.2778280
H	7.0680503	4.6168920	3.5325678
H	-0.3069569	10.4198828	0.7966823
H	1.0116515	10.7317703	1.8952331
H	-0.4198837	8.0725314	-2.3421409
H	-1.7727999	6.4578416	-3.7219819

H	-0.5760432	5.0637604	-5.4468810
H	1.8803114	5.3644244	-5.7613995
H	4.0157089	5.7180835	-5.8108373
H	6.3954755	6.4772843	-5.8672190
H	7.0752664	8.5027128	-4.5269451
H	4.9570038	11.8047571	-3.1909678
H	3.6146734	10.6764466	-3.5066050
H	3.0896284	11.5941522	-1.3749726
H	4.7756806	11.5893703	-0.8097582
H	3.1418497	8.9171966	1.0839799
H	3.3139653	10.6764444	1.0706806
H	5.4417379	7.2669295	-1.3444320
H	4.1622673	7.2483069	-0.1389917
H	7.6823821	5.7477710	0.9285270
H	7.1543520	5.9099213	-0.7472047
H	8.6098869	8.1002348	0.8515946
H	8.1211104	8.2436936	-0.8441176
H	6.0253191	6.8230614	3.9659539
H	7.5451698	6.8802886	3.0386623
H	5.5711673	4.1459150	5.3657653
H	3.9728699	4.6405779	7.1956291
H	1.7065419	5.5493601	6.6692771
H	1.0632338	5.9616062	4.2928252
H	2.6764136	5.4645139	2.4594480

H	4.7591851	4.8362620	1.7262295
H	4.4165387	2.4539889	2.2701586
H	5.8156605	2.4760377	3.3734183
H	6.0608387	2.7375931	1.6225875
Cu	2.5616672	8.6122174	-2.0874535
Cl	2.4315959	5.4428651	-1.0237885
O	2.1728227	6.8888823	-0.5863116
O	1.2045451	4.9130848	-1.6563303
O	3.5626092	5.4499665	-1.9931927
O	2.7893697	4.6557379	0.1791061

Table S13. Coordinates of geometry for **P10**.

104

N	3.8092574	8.6307056	18.0774823
O	6.0127510	7.3786156	10.3285112
O	8.5095200	6.8516200	13.2707173
O	7.7918456	10.3471145	14.7837728
O	4.2213916	9.2274110	15.9241189
N	5.8601464	7.0992366	12.5853889
N	8.2572704	7.7112201	15.3664798
N	6.4580063	10.7291424	16.5940710
N	6.0415983	10.1118025	12.3934950
C	5.2196400	5.7790051	12.4291432

C 7.7898471 7.3419977 14.1369722

C 3.6683748 5.8412241 12.6313813

C 4.4865252 9.2938164 17.1183652

C 7.2219960 13.0977993 17.0248693

C 7.2311849 9.9406801 15.7986743

C 5.2087245 12.2099278 11.2369504

C 9.9162315 6.2205620 16.5479489

C 6.2146983 7.8011146 11.4699501

C 5.9438152 4.7092762 13.2564387

C 6.2732456 12.1501222 16.2203390

C 3.2623086 6.2967474 14.0459532

C 9.6872592 7.5019461 15.6778526

C 4.7923328 12.5433712 16.2351216

C 3.9973042 12.7518759 10.4557801

C 5.6543177 10.1502059 17.6507858

C 3.7062613 10.7042564 12.7307073

C 6.4150787 12.1614588 10.2820447

C 10.3375013 8.7840723 16.2114118

C 6.2852368 7.5415839 13.8969051

C 3.0787027 4.4426344 12.3658392

C 4.9019011 10.7648538 11.7678516

C 7.4279826 8.4822688 16.2657634

C 3.0686323 6.8226720 11.6080693

C 6.8618930 9.1858752 11.6562225

C	8.6857596	12.6935051	16.7692557
C	9.3578368	4.9947492	15.8014073
C	5.5378939	13.1696103	12.3953170
C	7.0170567	14.5380540	16.5172401
C	11.4314027	6.0233632	16.7466268
C	6.9596229	13.0504268	18.5405922
C	9.2353030	6.3035954	17.9264992
H	5.3744950	5.5308419	11.3711518
H	5.6302088	3.7037925	12.9381631
H	5.7477108	4.7895656	14.3385613
H	7.0294484	4.7961377	13.1007775
H	6.6095473	12.1992089	15.1777747
H	2.1650921	6.2299782	14.1548239
H	3.5516814	7.3389774	14.2550893
H	3.7049066	5.6560493	14.8286187
H	10.1426980	7.2902130	14.7021955
H	4.6478716	13.4750140	15.6693324
H	4.3930811	12.7060850	17.2492726
H	4.1984402	11.7558864	15.7497384
H	3.1247723	12.9228934	11.1072233
H	3.6954727	12.0494739	9.6577588
H	4.2472157	13.7162398	9.9785947
H	5.2331282	10.9538448	18.2654276
H	6.2682536	9.5471351	18.3377106

H 2.7950692 11.1556074 12.3064214

H 3.9418859 11.2138706 13.6778237

H 3.4957205 9.6540139 12.9824331

H 7.3277582 11.8292004 10.8026913

H 6.6133971 13.1634350 9.8620232

H 6.2302809 11.4726635 9.4389765

H 11.4331771 8.6873659 16.1957976

H 10.0438573 9.0250936 17.2466161

H 10.0584872 9.6322902 15.5693202

H 5.7309460 6.9853307 14.6597481

H 6.0045220 8.5958863 14.0193755

H 1.9759325 4.4927997 12.3502207

H 3.3658018 3.7170471 13.1450197

H 3.4132081 4.0482537 11.3895330

H 4.6472676 10.1576652 10.8797663

H 7.8980540 8.5008226 17.2552320

H 6.4564435 7.9910512 16.4042115

H 1.9697235 6.8568324 11.7105397

H 3.3141153 6.5242392 10.5756840

H 3.4549414 7.8416670 11.7634044

H 7.8153601 9.0667428 12.1912015

H 7.1035533 9.5140661 10.6290401

H 9.3669064 13.3862801 17.2930797

H 8.9247334 12.7151790 15.6938714

H	8.8943072	11.6762502	17.1391017
H	9.5487147	4.0760966	16.3830496
H	9.8257814	4.8827819	14.8096806
H	8.2688995	5.0768817	15.6511761
H	6.3939191	12.8063383	12.9907398
H	4.6824615	13.3040311	13.0776325
H	5.8127803	14.1645876	12.0039430
H	7.7749646	15.2073021	16.9594483
H	6.0248435	14.9340145	16.7887070
H	7.1191447	14.5914929	15.4181761
H	11.6263026	5.0490210	17.2272019
H	11.8684889	6.8039910	17.3906993
H	11.9646872	6.0370272	15.7796645
H	6.5473883	10.6497773	13.0883173
H	4.0415970	8.7163150	19.0615648
H	7.6094004	13.7792553	19.0555682
H	7.1873625	12.0563380	18.9605392
H	5.9162436	13.3048544	18.7925005
H	9.4992079	5.4161226	18.5274841
H	8.1363630	6.3196598	17.8371610
H	9.5537302	7.1929541	18.4971406
H	3.0036047	8.0675033	17.8211945

Table S14. Coordinates of geometry for **P11**.

96

O	6.4358060	9.0124027	-1.0326839
O	2.0520745	7.0813979	-0.4629119
O	4.2511602	6.9658089	2.0387272
N	4.2067361	8.9718210	-0.6222512
N	6.3769698	7.5834970	1.6042900
N	4.7948661	4.6446837	3.2469621
N	1.4184255	7.9226719	1.5453245
C	3.0665739	9.1608815	0.2597372
C	2.1707491	7.9243817	0.4178339
C	5.5073471	8.9888588	-0.2228981
C	5.8720896	8.9144406	1.2646307
C	5.4482495	6.6977653	2.0639723
C	5.9161789	5.3800465	2.7052117
C	4.4623318	3.1776286	6.0327488
C	4.9922300	2.5608975	7.1698680
C	5.8501150	3.2661529	8.0249086
C	6.1763861	4.5938006	7.7318927
C	5.6458586	5.2083821	6.5904817
C	4.7844336	4.5126473	5.7284206
C	4.2293612	5.2147247	4.4969440
C	2.7034730	5.3635997	4.4974578
H	0.8538172	7.0976604	1.7284257

H	1.6987406	8.4697380	2.3521704
H	3.3901144	9.5192929	1.2403554
H	2.4300243	9.9616473	-0.1583589
H	5.0540588	9.1544983	1.9474466
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H	6.6282649	5.6028310	3.5161910
H	6.4767258	4.7788276	1.9869359
H	3.8030663	2.6254067	5.3620409
H	4.7335779	1.5218124	7.3923105
H	6.2614530	2.7816575	8.9145390
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H	4.6212404	6.2392330	4.5201317
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H	2.1902322	4.3970602	4.5637205
H	2.3927960	5.8755621	3.5731572
C	4.4228620	6.6003249	-2.4987937
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C	5.8269849	5.8428247	-4.3250646
C	6.0372232	7.1740527	-4.6986853
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C	3.9148860	9.0367058	-2.0788046
C	4.1225601	10.4610482	-2.5991917

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H	4.8375276	4.5298617	-2.9200734
H	6.2883238	5.0270002	-4.8876799
H	6.6710873	7.4100922	-5.5583003
H	5.6265272	9.2437901	-4.2790369
H	2.8443909	8.8018031	-2.1456400
H	3.7786829	10.5493978	-3.6424683
H	5.1824775	10.7519704	-2.5488588
H	3.5357390	11.1692269	-1.9905515
C	7.5383306	5.7929496	-0.5227216
C	7.7674052	4.5946186	-1.1997132
C	8.5882001	3.6097996	-0.6351617
C	9.1866297	3.8414482	0.6061922
C	8.9599004	5.0474280	1.2831159
C	8.1272986	6.0306432	0.7319895
C	7.8323883	7.3498099	1.4376264
C	8.5946256	7.6000674	2.7410704
H	6.8977817	6.5538537	-0.9746169
H	7.2937756	4.4300100	-2.1683049
H	8.7603115	2.6671037	-1.1616912
H	9.8307924	3.0819114	1.0566920
H	9.4277876	5.2030668	2.2563216
H	8.1343864	8.1294826	0.7254200
H	9.6816593	7.5756434	2.5638112

H	8.3572268	6.8572080	3.5188680
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C	4.9370480	3.0632930	1.3253158
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H	4.7604895	1.1717779	0.5436789
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H	2.5591563	1.4738547	-0.4468567
C	3.2386631	2.2625943	-2.9676853
C	3.8379004	2.1930092	-4.2275260
C	5.2308045	2.0859514	-4.3396278
C	6.0085511	2.0470941	-3.1796894
C	5.4018289	2.1191922	-1.9189619
C	4.0110897	2.2327637	-1.7921989
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H	7.0966631	1.9661347	-3.2531151
H	6.0268815	2.0948570	-1.0258850
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H 3.2021622 4.4783482 -0.2474100

H 2.0401815 3.5785533 0.7625800

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