

Supporting Information

for

Base Moiety Selectivity in Cleavage of Short Oligoribonucleotides by Di- and Tri-nuclear Zn(II) Complexes of Azacrown-derived Ligands

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1. General

The cleavage products were purified by RP-HPLC on a Hypersil ODS column (250 x 4.6 mm, particle size 5 μm ; flow rate 1 mL min⁻¹; buffer A = 0.05 mol L⁻¹ NH₄OAc and B = A containing 50 % MeCN). Mass spectra were verified on a Bruker micrOTOF-Q ESI-MS system.

2. Cleavage of 5'-CUACUA-3'

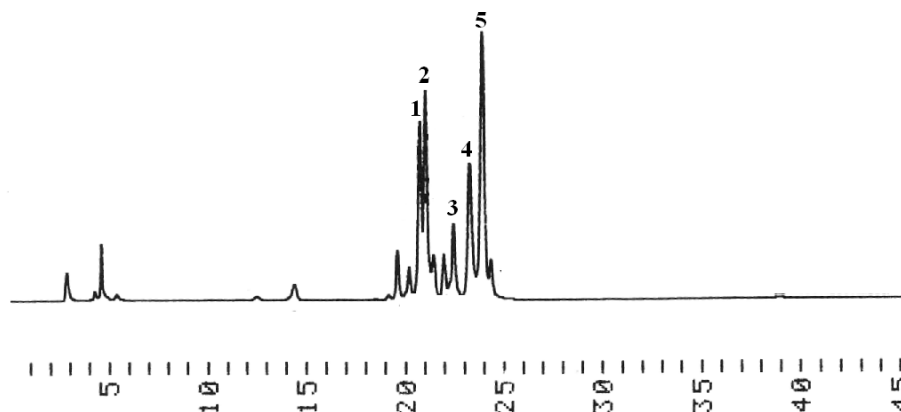


Figure 1. RP-HPLC chromatogram for the cleavage of the sequence 5'-CUACUA-3' in the presence of $(\text{Zn}^{2+})_3\text{L}^3$.

Table 1. Mass spectrometric and RP-HPLC analysis for the cleavage products of sequence 5'-CUACUA-3' promoted by $(\text{Zn}^{2+})_3\text{L}^3$.

Peak	Sequence	t_R / min	Observed masses m/z	Calculated masses m/z
1	5'-CUACp-3'	20.16	1262.2 $[\text{M} - \text{H}]^-$ 630.6 $[\text{M} - 2\text{H}]^{2-}$ 420.1 $[\text{M} - 3\text{H}]^{3-}$	1262.8 630.9 420.2
2	5'-CUACUp-3'	20.99	783.6 $[\text{M} - 2\text{H}]^{2-}$ 522.1 $[\text{M} - 3\text{H}]^{3-}$ 391.3 $[\text{M} - 4\text{H}]^{4-}$	784.0 522.3 391.5
3	A**	22.50		
4	5'-CUACUA-3'	23.24	908.1 $[\text{M} - 2\text{H}]^{2-}$ 605.1 $[\text{M} - 3\text{H}]^{3-}$ 453.6 $[\text{M} - 4\text{H}]^{4-}$ 362.7 $[\text{M} - 5\text{H}]^{5-}$	908.6 605.4 453.8 362.8
5	5'-UA-3'	23.88	572.1 $[\text{M} - \text{H}]^-$	572.4

**Based on the HPLC analysis with the adenosine reference sample.

3. Cleavage of 5'-CAGGCA-3'

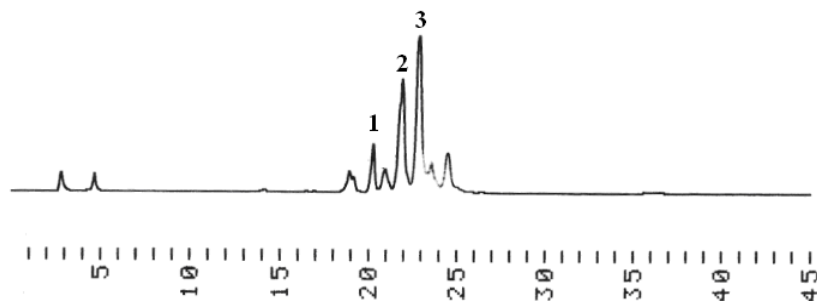


Figure 2. RP-HPLC chromatogram for the cleavage of the sequence 5'-CAGGCA-3' in the presence of $(\text{Zn}^{2+})_3\text{L}^3$.

Table 2. Mass spectrometric and RP-HPLC analysis for the cleavage products of sequence 5'-CAGGCA-3' promoted by $(\text{Zn}^{2+})_3\text{L}^3$.

Peak	Sequence	t_R / min	Observed masses m/z	Calculated masses m/z
1	5'-CAGp-3'	20.27	996.2 $[\text{M} - \text{H}]^-$ 497.6 $[\text{M} - 2\text{H}]^{2-}$	996.6 497.8
2	5'-GCA-3'	21.92	916.2 $[\text{M} - \text{H}]^-$ 457.6 $[\text{M} - 2\text{H}]^{2-}$	916.6 457.8
3	5'-CAGGCA-3'	22.91	947.2 $[\text{M} - 2\text{H}]^{2-}$ 631.1 $[\text{M} - 3\text{H}]^{3-}$ 473.1 $[\text{M} - 4\text{H}]^{4-}$	947.6 631.4 473.3

4. Cleavage of 5'-CAAGAC-3'

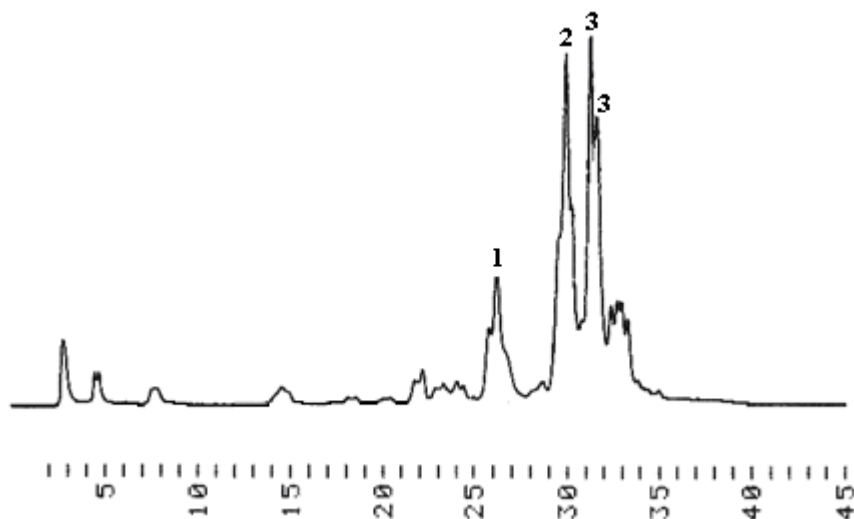


Figure 3. RP-HPLC chromatogram for the cleavage of the sequence 5'-CAAGAC-3' in the presence of $(\text{Zn}^{2+})_3\text{L}^3$.

Table 3. Mass spectrometric and RP-HPLC analysis for the cleavage products of sequence 5'-CAAGAC-3' promoted by $(\text{Zn}^{2+})_3\text{L}^3$.

Peak	Sequence	t_R / min	Observed masses m/z	Calculated masses m/z
1	5'-CAAGp-3'	25.79	662.1 $[\text{M} - 2\text{H}]^{2-}$ 441.1 $[\text{M} - 3\text{H}]^{3-}$	662.4 441.3
2	*5'-AC-3' ja 5'-GAC-3'	29.90	*571.1 $[\text{M} - \text{H}]^-$ 916.2 $[\text{M} - \text{H}]^-$ 457.6 $[\text{M} - 2\text{H}]^{2-}$	*571.4 916.6 457.8
3	5'-CAAGAC-3'	31.23	939.2 $[\text{M} - 2\text{H}]^{2-}$ 625.8 $[\text{M} - 3\text{H}]^{3-}$ 469.1 $[\text{M} - 4\text{H}]^{4-}$ 375.1 $[\text{M} - 5\text{H}]^{5-}$	939.6 626.1 469.3 375.2

5. Cleavage of 5'-CAGUCA-3'

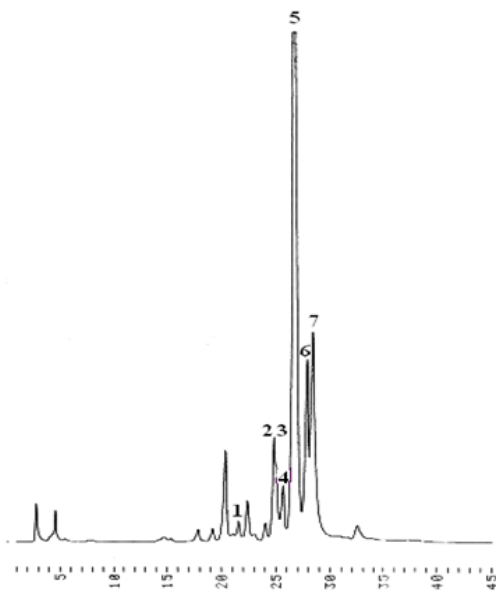


Figure 4. RP-HPLC chromatogram for the cleavage of the sequence 5'-CAGUCA-3' in the presence of $(\text{Zn}^{2+})_3\text{L}^3$.

Table 4. Mass spectrometric and RP-HPLC analysis for the cleavage products of sequence 5'-CAGUCA-3' promoted by $(\text{Zn}^{2+})_3\text{L}^3$.

Peak	Sequence	t_R / min	Observed masses m/z	Calculated masses m/z
1	5'-CAGp-3'	21.06	497.6 $[\text{M} - 2\text{H}]^{2-}$ 331.4 $[\text{M} - 3\text{H}]^{3-}$	497.8 331.5
2	5'-CA-3'	24.82	571.1 $[\text{M} - \text{H}]^-$	571.4
3	5'-CAp-3'	25.00	325.2 $[\text{M} - 2\text{H}]^{2-}$	325.2
4	5'-CAGUp-3'	25.67	650.6 $[\text{M} - 2\text{H}]^{2-}$ 433.4 $[\text{M} - 3\text{H}]^{3-}$	650.9 433.6
5	5'-UCA-3'	26.75	877.2 $[\text{M} - \text{H}]^-$ 438.1 $[\text{M} - 2\text{H}]^{2-}$	877.6 438.3
6	5'-GUCA	27.86	1222.2 $[\text{M} - \text{H}]^-$ 610.6 $[\text{M} - 2\text{H}]^{2-}$ 406.7 $[\text{M} - 3\text{H}]^{3-}$	1222.8 610.9 406.9
7	5'-CAGUCA-3'	28.38	927.6 $[\text{M} - 2\text{H}]^{2-}$ 618.1 $[\text{M} - 3\text{H}]^{3-}$ 463.3 $[\text{M} - 4\text{H}]^{4-}$ 370.5 $[\text{M} - 5\text{H}]^{5-}$	928.1 618.4 463.5 370.6

6. Cleavage of 5'-CGACGA-3'

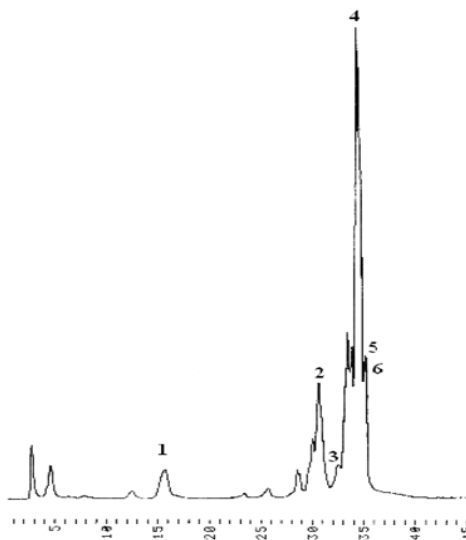


Figure 5. RP-HPLC chromatogram for the cleavage of the sequence 5'-CGACGA-3' in the presence of $(\text{Zn}^{2+})_3\text{L}^3$.

Table 5. Mass spectrometric and RP-HPLC analysis for the cleavage products of sequence 5'-CGACGA-3' promoted by $(\text{Zn}^{2+})_3\text{L}^3$.

Peak	Sequence	t_R / min	Observed masses m/z	Calculated masses m/z
1	5'-CGp-3'	15.71	667.1 [M - H] ⁻ 333.0 [M - 2H] ²⁻	667.4 333.2
2	*5'-CGACGp-3' and 5'-CGACp-3	30.56	*822.6 [M - 2H] ²⁻ *548.1 [M - 3H] ³⁻ *410.8 [M - 4H] ⁴⁻ 650.1 [M - 2H] ²⁻ 433.0 [M - 3H] ³⁻	* 823.0 * 548.3 * 411.0 650.4 433.3
3	A**	32.54		
4	5'-CGACGA-3'	34.11	947.1 [M - 2H] ²⁻ 631.1 [M - 3H] ³⁻ 473.1 [M - 4H] ⁴⁻	947.6 631.4 473.3
5	*5'-ACGA-3' and 5'-GACGA-3'	35.04	*622.1 [M - 2H] ²⁻ *414.4 [M - 3H] ³⁻ 794.6 [M - 2H] ²⁻ 529.4 [M - 3H] ³⁻ 396.8 [M - 4H] ⁴⁻	* 622.4 * 414.6 795.0 529.7 397.0
6	5'-GA-3'	35.23	611.1 [M - H] ⁻	611.4

**Based on the HPLC analysis with the adenosine reference sample.

7. Cleavage of 5'-CGAGCA-3'

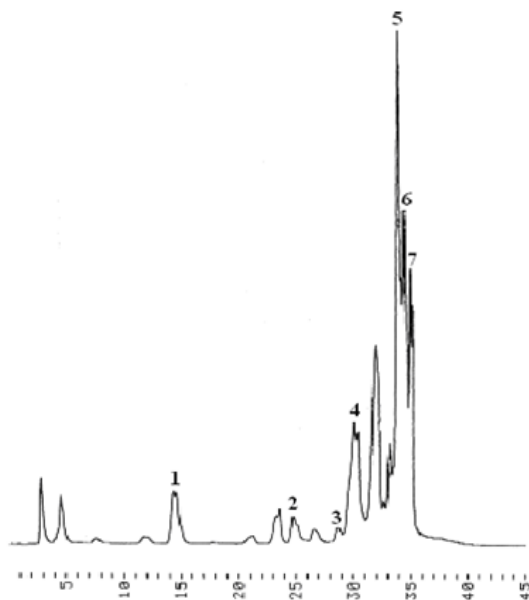


Figure 6. RP-HPLC chromatogram for the cleavage of the sequence 5'-CGAGCA-3' in the presence of $(\text{Zn}^{2+})_3\text{L}^3$.

Table 6. Mass spectrometric and RP-HPLC analysis for the cleavage products of sequence 5'-CGAGCA-3' promoted by $(\text{Zn}^{2+})_3\text{L}^3$.

Peak	Sequence	t_R / min	Observed masses m/z	Calculated masses m/z
1	5'-CGp-3'	14.30	667.1 $[\text{M} - \text{H}]^-$ 333.0 $[\text{M} - 2\text{H}]^{2-}$	667.4 333.2
2	5'-CGAp-3'	24.76	497.6 $[\text{M} - 2\text{H}]^{2-}$ 331.4 $[\text{M} - 3\text{H}]^{3-}$	497.8 331.5
3	5'-CGAGp-3'	28.71	670.1 $[\text{M} - 2\text{H}]^{2-}$ 446.2 $[\text{M} - 3\text{H}]^{3-}$	670.4 446.6
4	5'-CA-3'	30.06	571.1 $[\text{M} - \text{H}]^-$	571.4
5	5'-GCA-3'	33.71	916.2 $[\text{M} - \text{H}]^-$ 457.6 $[\text{M} - 2\text{H}]^{2-}$	916.6 457.8
6	*5'-GAGCA-3' and 5'-CGAGCA-3'	34.27	*794.6 $[\text{M} - 2\text{H}]^{2-}$ *529.4 $[\text{M} - 3\text{H}]^{3-}$ *396.8 $[\text{M} - 4\text{H}]^{4-}$ 947.2 $[\text{M} - 2\text{H}]^{2-}$ 631.1 $[\text{M} - 3\text{H}]^{3-}$ 473.1 $[\text{M} - 4\text{H}]^{4-}$ 378.3 $[\text{M} - 5\text{H}]^{5-}$	*795.0 *529.7 *397.0 947.6 631.4 473.3 378.4
7	5'-AGCA-3'	34.54	1245.2 $[\text{M} - \text{H}]^-$ 622.1 $[\text{M} - 2\text{H}]^{2-}$ 414.4 $[\text{M} - 3\text{H}]^{3-}$	1245.8 622.4 414.6

8. Cleavage of 5'-CAUUCA-3'

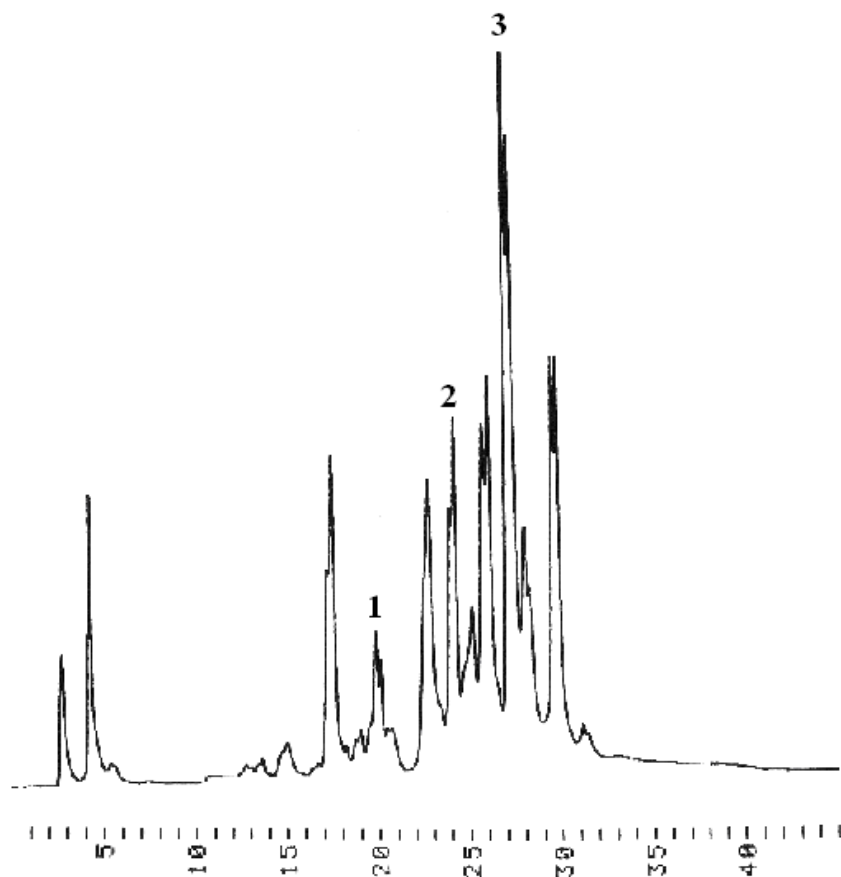


Figure 7. RP-HPLC chromatogram for the cleavage of the sequence 5'-CAUUCA-3' in the presence of $(\text{Zn}^{2+})_3\text{L}^3$.

Table 7. Mass spectrometric and RP-HPLC analysis for the cleavage products of sequence 5'-CAUUCA-3' promoted by $(\text{Zn}^{2+})_3\text{L}^3$.

Peak	Sequence	t_R / min	Observed masses m/z	Calculated masses m/z
1	5'-CAUp-3'	19.90	957.1 $[\text{M} - \text{H}]^-$ 478.1 $[\text{M} - 2\text{H}]^{2-}$ 318.4 $[\text{M} - 3\text{H}]^{3-}$	957.6 478.3 318.5
2	5'-UCA-3'	24.27	877.2 $[\text{M} - \text{H}]^-$ 438.1 $[\text{M} - 2\text{H}]^{2-}$	877.6 438.3
3	5'-CAUUCA-3'	27.15	908.2 $[\text{M} - 2\text{H}]^{2-}$ 605.1 $[\text{M} - 3\text{H}]^{3-}$ 453.6 $[\text{M} - 4\text{H}]^{4-}$	908.6 605.4 453.8

9. Cleavage of 5'-CAAUAC-3'

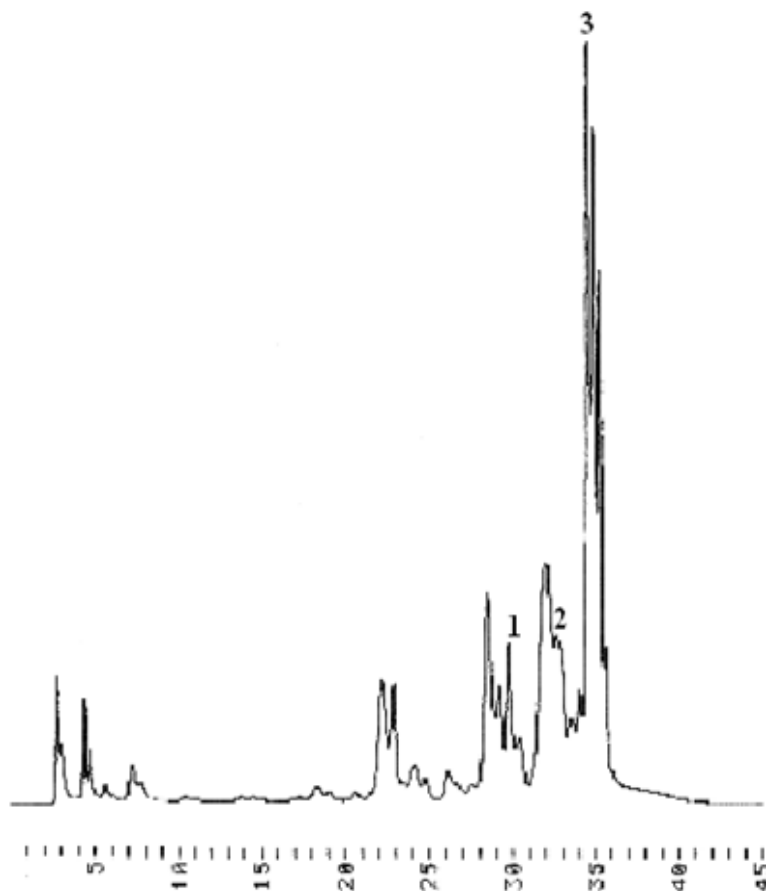


Figure 8. RP-HPLC chromatogram for the cleavage of the sequence 5'-CAAUAC-3' in the presence of $(\text{Zn}^{2+})_3\text{L}^3$.

Table 8. Mass spectrometric and RP-HPLC analysis for the cleavage products of sequence 5'-CAAUAC-3' promoted by $(\text{Zn}^{2+})_3\text{L}^3$.

Peak	Sequence	t_R / min	Observed masses m/z	Calculated masses m/z
1	5'-CAAUp-3'	29.72	642.6 $[\text{M} - 2\text{H}]^{2-}$ 428.0 $[\text{M} - 3\text{H}]^{3-}$	642.9 428.3
2	5'-AC-3'	32.59	571.1 $[\text{M} - \text{H}]$	571.4
3	5'-CAAUAC-3'	34.35	919.6 $[\text{M} - 2\text{H}]^{2-}$ 612.8 $[\text{M} - 3\text{H}]^{3-}$ 459.3 $[\text{M} - 4\text{H}]^{4-}$ 367.3 $[\text{M} - 5\text{H}]^{5-}$	920.1 613.1 459.5 367.4

10. Cleavage of 5'-CAAUAC-3'

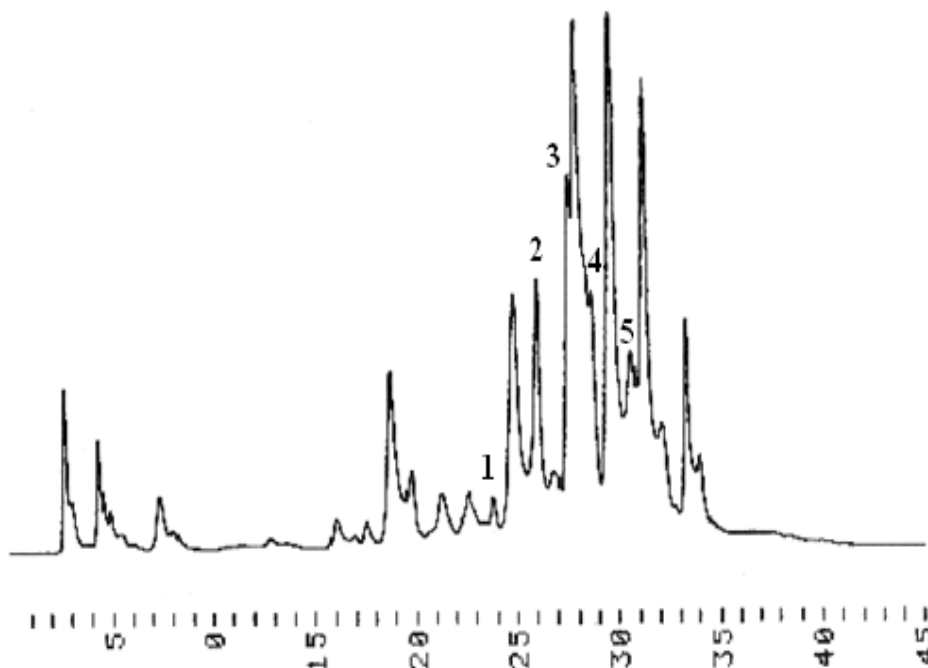


Figure 9. RP-HPLC chromatogram for the cleavage of the sequence 5'-CAAUAC-3' in the presence of $(\text{Zn}^{2+})_2\text{L}^1$.

Table 9. Mass spectrometric and RP-HPLC analysis for the cleavage products of sequence 5'-CAAUAC-3' promoted by $(\text{Zn}^{2+})_2\text{L}^1$.

Peak	Sequence	t_R / min	Observed masses m/z	Calculated masses m/z
1	5'-CAAp-3'	23.75	980.6 $[\text{M} - \text{H}]^-$ 489.6 $[\text{M} - 2\text{H}]^{2-}$ 326.0 $[\text{M} - 3\text{H}]^{3-}$	980.6 489.8 326.2
2	5'-CAAUp-3'	26.00	642.6 $[\text{M} - 2\text{H}]^{2-}$ 428.1 $[\text{M} - 3\text{H}]^{3-}$ 320.0 $[\text{M} - 4\text{H}]^{4-}$	642.9 428.3 320.9
3	5'-UAC-3'	27.52	877.2 $[\text{M} - \text{H}]^-$ 438.1 $[\text{M} - 2\text{H}]^{2-}$	877.6 438.3
4	5'-AC-3'	28.00	571.1 $[\text{M} - \text{H}]^-$	571.4
5	5'-CAAUAC-3'	30.64	919.6 $[\text{M} - 2\text{H}]^{2-}$ 612.8 $[\text{M} - 3\text{H}]^{3-}$ 459.3 $[\text{M} - 4\text{H}]^{4-}$	920.1 613.1 459.5