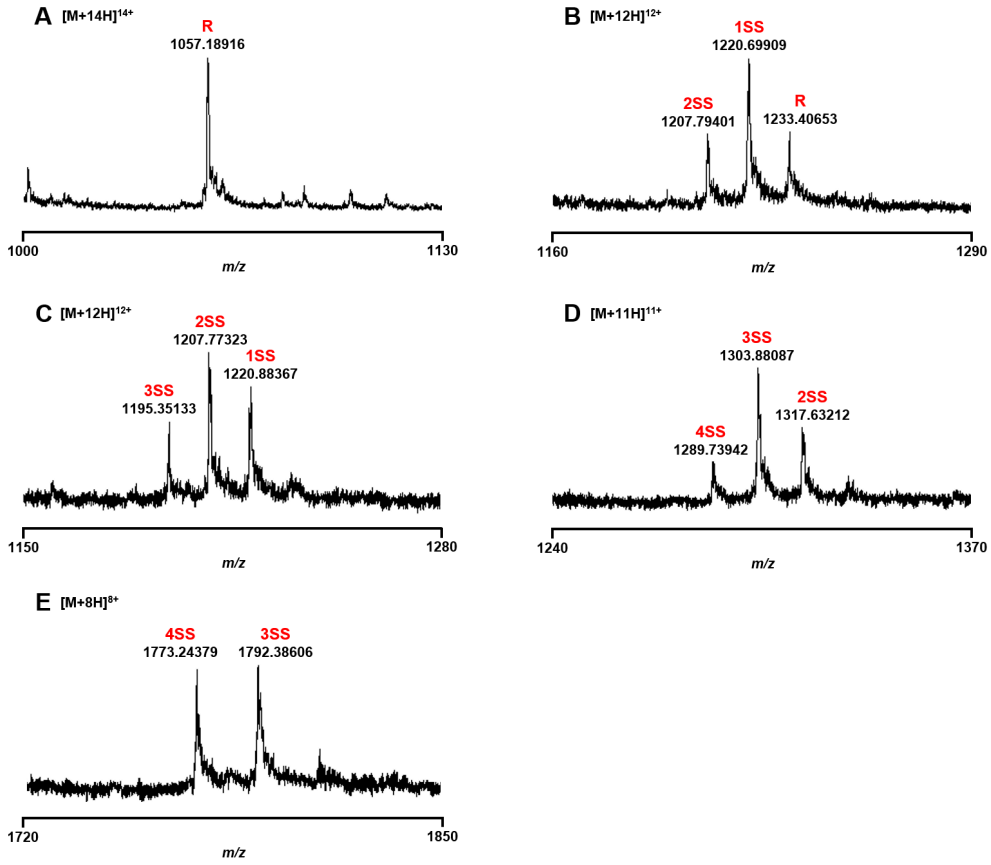

Figure S1. ESI mass spectra of the SS intermediates generated by the reaction of αLA with DHS^{ox}. The reaction was carried out in Tris-HCl buffer (pH 8.0) containing 2 mM EDTA. After 1 min, the reaction was quenched by AEMTS. The samples obtained were analyzed with the ESI(+) mode. (**A**) R; (**B**) 1 eq DHS^{ox} was added to R; (**C**) 2 eq DHS^{ox} was added to R; (**D**) 3 eq DHS^{ox} was added to R; (**E**) 4 eq DHS^{ox} was added to R.

Table S1. Assignment of the peaks observed in Figure S1. [a]

Species	Expected M^{+}	[M+8H]$^{8+}$	[M+11H]$^{11+}$	[M+12H]$^{12+}$	[M+14H]$^{14+}$
R + 8×AEMTS	14784.9862			1233.40653 (1233.0899)	1057.18916 (1057.0782)
1SS + 6×AEMTS	14632.9420			1220.69909 1220.88367 (1220.4196)	
2SS + 4×AEMTS	14480.8978		1317.63212 (1317.4530)	1207.79401 1207.77323 (1207.7492)	
3SS + 2×AEMTS	14328.8536	1792.38606 (1792.1144)	1303.88087 (1303.6308)	1195.35133 (1195.0789)	
4SS	14176.8094	1773.24379 (1773.1089)	1289.73942 (1289.8086)		

[a] The calculated mass numbers are shown in parentheses.

Figure S2. RP-HPLC chromatograms obtained by the oxidation of R (10 μM) with 1 eq DHS^{ox} at pH 6.8 and 5 °C in the absence of EDTA. The reaction was acid-quenched after 20 h. For HPLC analysis conditions, see the experimental section. (**A**) In the absence of $CaCl_2$; (**B**) In the presence of 5 mM $CaCl_2$.

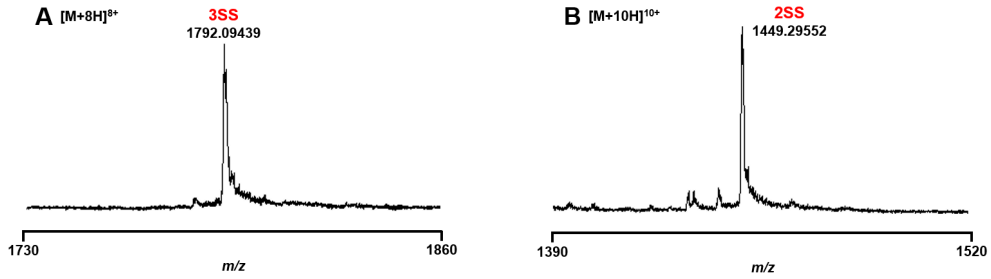

Figure S3. ESI mass spectra of I-1 and I-2 quenched by AEMTS. (**A**) I-1; (**B**) I-2.

Table S2. Assignment of the peaks observed in Figure S3. [a]

	Expected M^+	$[M+8H]^{8+}$	$[M+10H]^{10+}$
I-1 (3SS) + 2×AEMTS	14328.8536	1792.09439 (1792.1144)	
I-2 (2SS) + 4×AEMTS	14480.8978		1449.29552 (1449.0975)

[a] The calculated mass numbers are shown in parentheses.

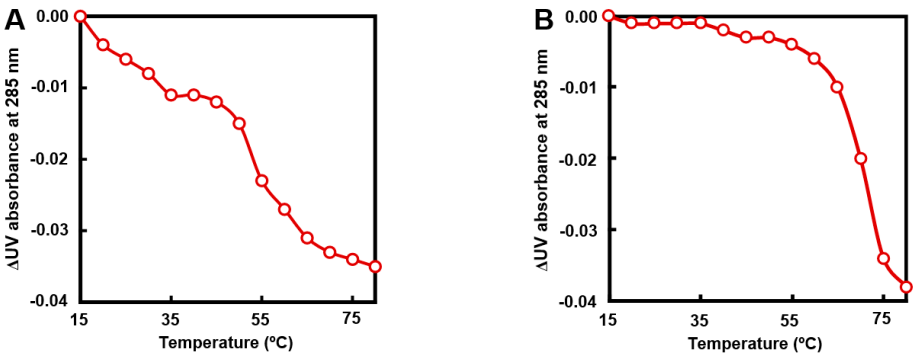

Figure S4. The thermal denaturation curves of αLA (10 μM) in the absence (**A**) and presence (**B**) of 5 mM $CaCl_2$.