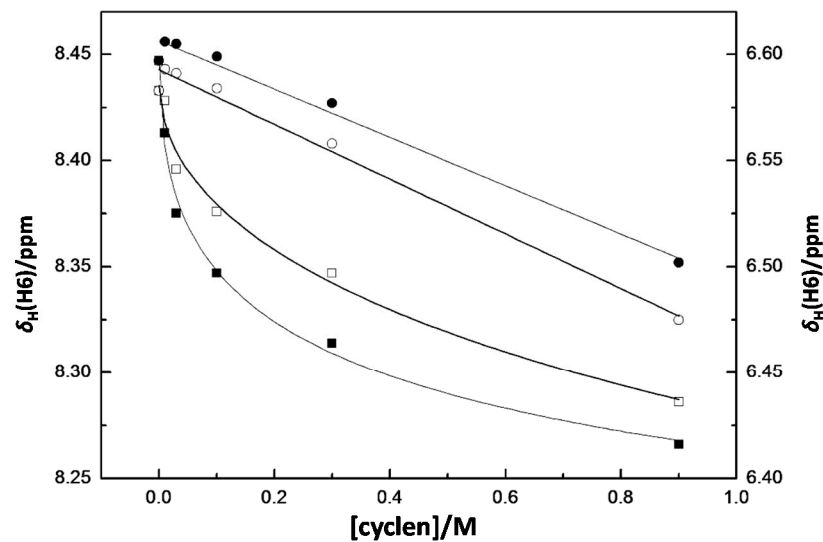


Supplementary Information

A



B

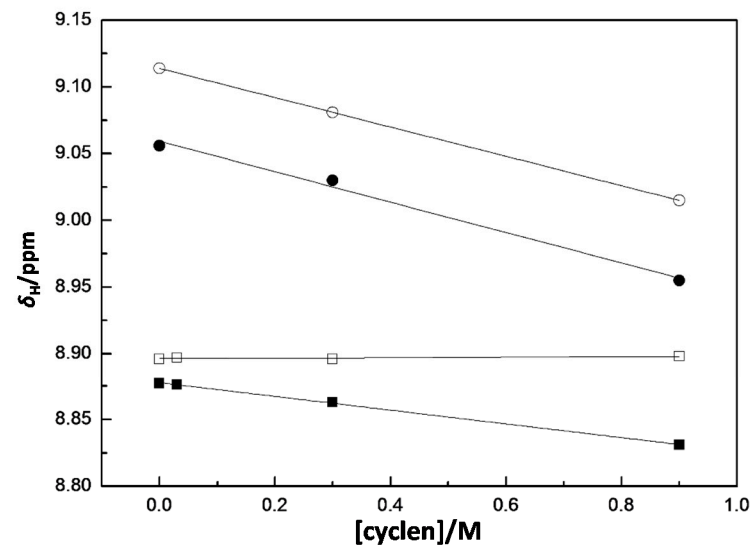


Figure S1. Dependence of the chemical shift of (A) H5 (hollow symbols) and H6 (solid symbols) of uridine and (B) H2 (hollow symbols) and H8 (solid symbols) of adenosine on the concentration of cyclen in D₂O at 90 °C. Cyclen was protonated with either 1.2 (squares) or 2.1 (circles) eq. of deuterium chloride prior to the NMR titration.

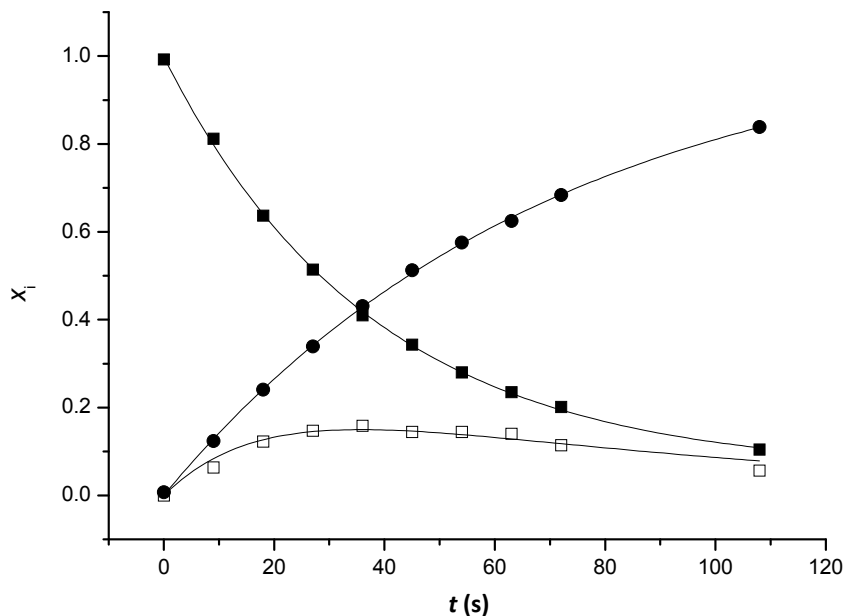


Figure S2. Time-dependent mole fractions of 3',5'-UpU (■), 2',5'-UpU (□) and uridine (●) in 20 mM **11a** titrated with 4.5 equivalents (eq.) of HClO₄; $T = 90\text{ }^{\circ}\text{C}$, pH = 2.6, $I(\text{NaClO}_4) = 1.0\text{ mol}\cdot\text{L}^{-1}$.

Table S1. Observed pseudo first-order rate constants for the cleavage of UpU in the presence of **11a**; $T = 90\text{ }^{\circ}\text{C}$, $I(\text{NaClO}_4) = 1.0\text{ mol}\cdot\text{L}^{-1}$.

[11a]/mmol·L ⁻¹	$k_{\text{obs}}(\text{cleavage})/10^{-5}\cdot\text{s}^{-1}$			
	+ 3.5 eq. HClO ₄	+ 3.8 eq. HClO ₄	+ 4.5 eq. HClO ₄	+ 5.0 eq. HClO ₄
10	2.44	1.51	4.12	0.48
20	3.44	6.01	15.7	15.9
30	9.41	11.9	28.4	35.7
40	8.28	18.3	-	-
50	13.9	23.1	47.7	78.6
70	-	-	103	130

Table S2. Observed pseudo first-order rate constants for the isomerization of UpU in the presence of **11a**; $T = 90\text{ }^{\circ}\text{C}$, $I(\text{NaClO}_4) = 1.0\text{ mol}\cdot\text{L}^{-1}$.

[11a]/mmol·L ⁻¹	$k_{\text{obs}}(\text{isomerization})/10^{-5}\cdot\text{s}^{-1}$			
	+ 3.5 eq. HClO ₄	+ 3.8 eq. HClO ₄	+ 4.5 eq. HClO ₄	+ 5.0 eq. HClO ₄
10	1.71	2.34	3.10	0.31
20	4.43	7.19	10.2	7.43
30	5.17	14.4	19.3	15.2
40	9.95	17.3	-	-
50	11.9	16.4	46.6	25.1
70	-	-	28.5	35.4

Table S3. Observed pseudo first-order rate constants for the cleavage of UpU in the presence of **11b**; $T = 90\text{ }^{\circ}\text{C}$, $I(\text{NaClO}_4) = 1.0\text{ mol}\cdot\text{L}^{-1}$.

[11b]/mmol·L ⁻¹	$k_{\text{obs}}(\text{cleavage})/10^{-5}\cdot\text{s}^{-1}$		
	+ 3.5 eq. HClO ₄	+ 3.8 eq. HClO ₄	+ 4.5 eq. HClO ₄
10	4.96	13.5	8.59
30	19.8	43.1	59
40	42.7	-	-
50	63.1	77	79

Table S4. Observed pseudo first-order rate constants for the isomerization of UpU in the presence of **11b**; $T = 90\text{ }^{\circ}\text{C}$, $I(\text{NaClO}_4) = 1.0\text{ mol}\cdot\text{L}^{-1}$.

[11b]/mmol·L ⁻¹	$k_{\text{obs}}(\text{isomerization})/10^{-5}\cdot\text{s}^{-1}$		
	+ 3.5 eq. HClO ₄	+ 3.8 eq. HClO ₄	+ 4.5 eq. HClO ₄
10	3.57	8.05	8.16
30	18.5	29.2	41.9
40	26.8	-	-
50	44.6	49.4	240