SUPPORTING INFORMATION

Oxidation of 5-methylaminomethyl uridine (mnm₅U) by oxone leads to aldonitrone derivatives

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Figure S1. HR-ESI-MS analysis of 1
Figure S2. NMR analysis of 1: (A) HMBC, (B) NOESY
Figure S3. HR-ESI-MS analysis of 3 and 4
Figure S4. HR-MS analysis of 5 and 6
Figure S5. HR-MS analysis of 2 and its hydrolysis product 7
Figure S6. NMR analysis of 2 + 7: (A) HSQC, (B) HMBC, (C) NOESY

Figure S1. High resolution negative electrospray ionization mass spectrum of the isolated mnm₅U oxidation product 1. [M-H]⁻ signal observed at m/z = 300.0833 amu.
Figure S2_A. HMBC of 1. Correlation between H signals δ 7.78 and 9.79 ppm with carbon atoms of the nucleobase and correlation between the methyl protons δ 3.75 ppm and the carbon atom of aldonitrone δ 132.5 ppm. 278 K

Figure S2_B. NOESY between the methyl group δ = 3.75 ppm and the aldonitrone H δ = 7.78 ppm of product 1 in D₂O (blue circle). A correlation between the nucleobase H6 δ = 9.79 ppm and the H5’ proton of ribose δ = 3.63 ppm is also observed.
Figure S3. LC/ESI-HR-MS (positive mode) analysis of the irradiation of aldonitrone 1 (Rt = 21.6 min) leading to oxaziridine 3 + 4 mixture. Left: chromatogram, right: in-line mass spectra of 3 and 4. Sodium adduct of molecular peak [M+Na]^+ and deglycosylated fragment [b+H]^+.
Figure S4. LC/ESI-HR-MS (positive mode) analysis of the reversion of the oxaziridine 3 + 4 mixture after 1 h at 60 °C to aldonitrone 1 (Rt = 21.6 min) with concomitant formation of aldehyde 5 (Rt = 22.6 min), and amide 6 (Rt = 26.7 min) derivatives. Left: chromatogram, right: in-line mass spectra. Sodium adduct of molecular peak [M+Na]^+ and deglycosylated fragment [b+H]^+.
Figure S5. LC/ESI-HR-MS (positive mode) analysis of isolated 2 showing 2 at Rt = 18.3 min and its hydrolysis product, hydroxylamine derivative (7) (Rt = 19.4 min). Left: chromatogram, right: in-line mass spectra.
**Figure S6_A.** Edited-HSQC of the mixture 2 + 7 (1H-NMR spectrum, Figure 13). Correlation between the protons of the CH₂ group at C5 (under the signal of water) and carbon δ 60.5 ppm of product 2 in D₂O is highlighted. Red color refers to CH, CH₃ and blue color to CH₂ protons.

**Figure S6_B.** HMBC of the mixture of 2 + 7 (corresponding ¹H-NMR spectrum: Figure 13).
Figure S6_C. NOESY between one of the protons of the terminal methylene of 2 δ 6.70 ppm and the signal under the peak of solvent (δ 4.5 ppm) attributed to the other CH$_2$ group. Another correlation between the CH$_2$ protons of 7 δ 3.44 ppm and the nucleobase H6 of 7 δ 7.66 ppm. (corresponding $^1$H-NMR spectrum: Figure 13).