## **Electronic Supplementary Material**

## Photochemical Conversion of a Cytidine Derivative to a Thymidine Analog via [2+2]-Cycloaddition

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Figure S1: FT-IR spectra in the carbonyl spectral region of 1, purified photoproduct 4a/4b, dC and dU on CaF<sub>2</sub> disks.



**Figure S2**: <sup>1</sup>H-NMR analysis of **1** (top) and isolated photoproduct **4** (bottom) in DMSO $d_3$ . In the photoproduct, protons a, b, and c (marked in red) are upfield shifted due to the loss of the double bond. In addition, the amide proton e (marked in red) is evident in the photoproduct. For simplicity, only the straight [2+2]-cycloadduct is shown.



Figure S3: <sup>1</sup>H-NMR of 3'-5'-bis-O-(*tert*-butyldimethylsilyl)-thymidine (6) in CDCl<sub>3</sub>.



Figure S4: <sup>13</sup>C-NMR of 3'-5'-bis-*O*-(*tert*-butyldimethylsilyl)-thymidine (6) in CD<sub>3</sub>OD.



**Figure S5**: <sup>1</sup>H-NMR of 3'-5'-bis-*O*-(*tert*-butyldimethylsilyl)-5-cinnamyloxymethyl-deoxyuridine (**8**) in CDCl<sub>3</sub>.



**Figure S6**: <sup>13</sup>C-NMR of 3'-5'-bis-*O*-(*tert*-butyldimethylsilyl)-5-cinnamyloxymethyl-deoxyuridine (**8**) in CDCl<sub>3</sub>.



**Figure S7**: <sup>1</sup>H-NMR of 3'-5'-bis-*O*-(*tert*-butyldimethylsilyl)-5-cinnamyloxymethyl-deoxycytidine (**10**) in CDCl<sub>3</sub>.



Figure S8: <sup>1</sup>H-NMR of 5-cinnamyloxymethyl-deoxycytidine (1) in CDCl<sub>3</sub>.



Figure S9: <sup>13</sup>C-NMR of 5-cinnamyloxymethyl-deoxycytidine (1) in CDCl<sub>3</sub>.



Figure S10: <sup>1</sup>H-NMR of photoproduct 4 in DMSO-*d*<sub>3</sub>.



**Figure S11**: <sup>13</sup>C-NMR of photoproduct **4** in DMSO-*d*<sub>3</sub>.