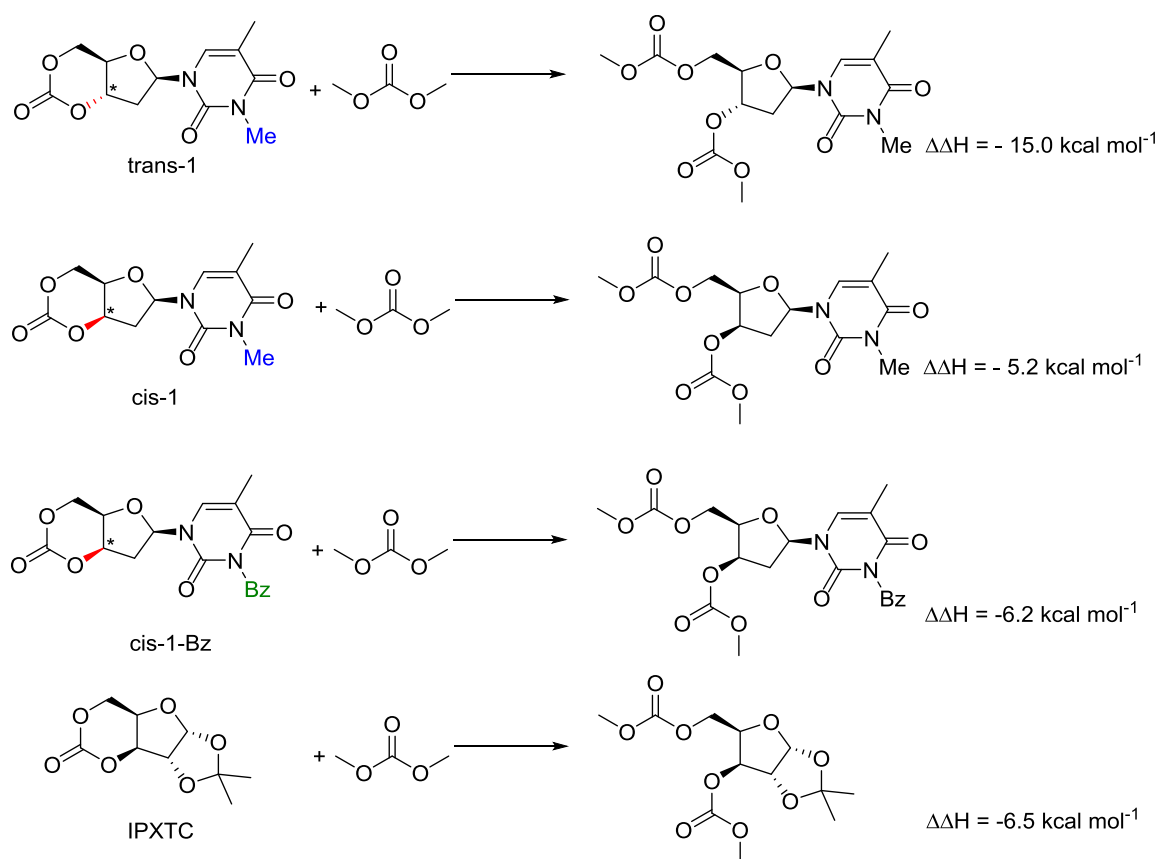## Ring Strain

Ring-strain was evaluated by calculating the enthalpy of ring-opening with dimethyl carbonate (DMC), such that the same number of bonds are formed as broken. Ring strain calculations at the rωb97xd/6-311++G(2d,p)/cpcm=dichloromethane/298 K level of theory highlight the highly strained nature of the *trans*-configured furanose-cored monomer compared to the corresponding isolated *cis*-configured cyclic carbonates. In addition, the calculations give an indication of the ROP potential of the *cis*-thymidine based monomers reported here (**1** and **1**-Bz), which form equilibrium polymerisations.

Isodesmic reaction with DMC

Scheme S1. Consideration of ring-stain by calculation of the enthalpy of isodesmic ring-opening with dimethyl carbonate (DMC) at rωb97xd/6-311++G(2d,p)/cpcm=dichloromethane/298 K level of theory. The synthesis and ROP of isopropylidene-D-xylofuranose-3,5-cyclic carbonate (IPXTC) was reported by Gross and coworkers.[15] Reported elsewhere,[16] $\Delta\Delta H_{ring\ strain}$ for the cyclic *trans*-4,6-carbonate monomers of protected D-glucose and D-mannose sugars, at the same level of theory, are -9.8 and -9.5 kcal mol^{-1}, respectively.

	Structure	H /Hartrees
Starting Materials	Trans_1	-1026.301977
	Cis_1	-1026.317516
	Cis_1_Bz	-1331.296124
	xyloseCC	-801.309791
	DMC	-343.512814
Products	DMC_Trans_1	-1369.838650
	DMC_Cis_1	-1369.838544
	Cis_1_Bz	-1674.818767
	DMC_xylose	-1144.832963

Table S1. Computed Gibbs Free Energies at the rωB97XD/6-311++g(2d,p)/cpcm=dichloromethane/298K level of theory for the isodesmic ring-opening with dimethyl carbonate (DMC) of *trans*-**1**, *cis*-**1,** cis-**1**-Bz and IPXTC. The values for the glucose and mannose monomers have been reported previously.[16]
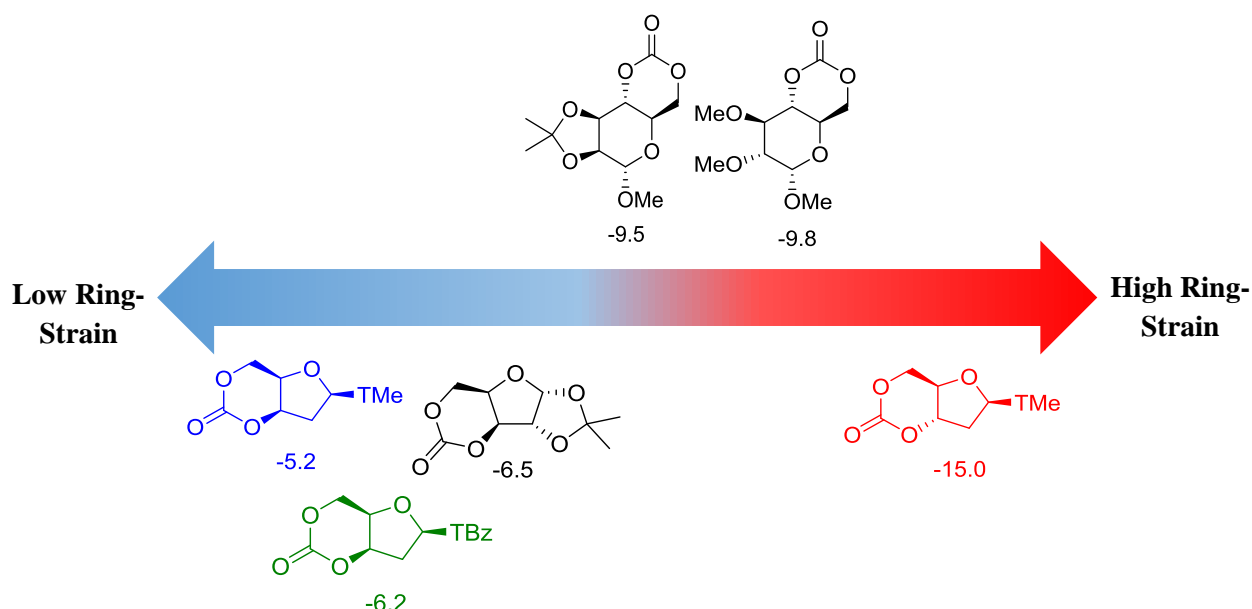

Figure S1. Illustrative summary of calculated enthalpies (ΔΔH) for ring-opening with DMC performed at the rωb97xd/6-311++G(2d,p)/cpcm=dichloromethane/298 K level of theory.

Full coordinates for all the stationary points, together with computed free Gibbs energy and vibrational frequency data, are available via the corresponding Gaussian 09 output files, stored in the digital repository: DOI: 10.6084/m9.figshare.4309469 (private link for review purposes: https://figshare.com/s/f64826384c01aca6289f).