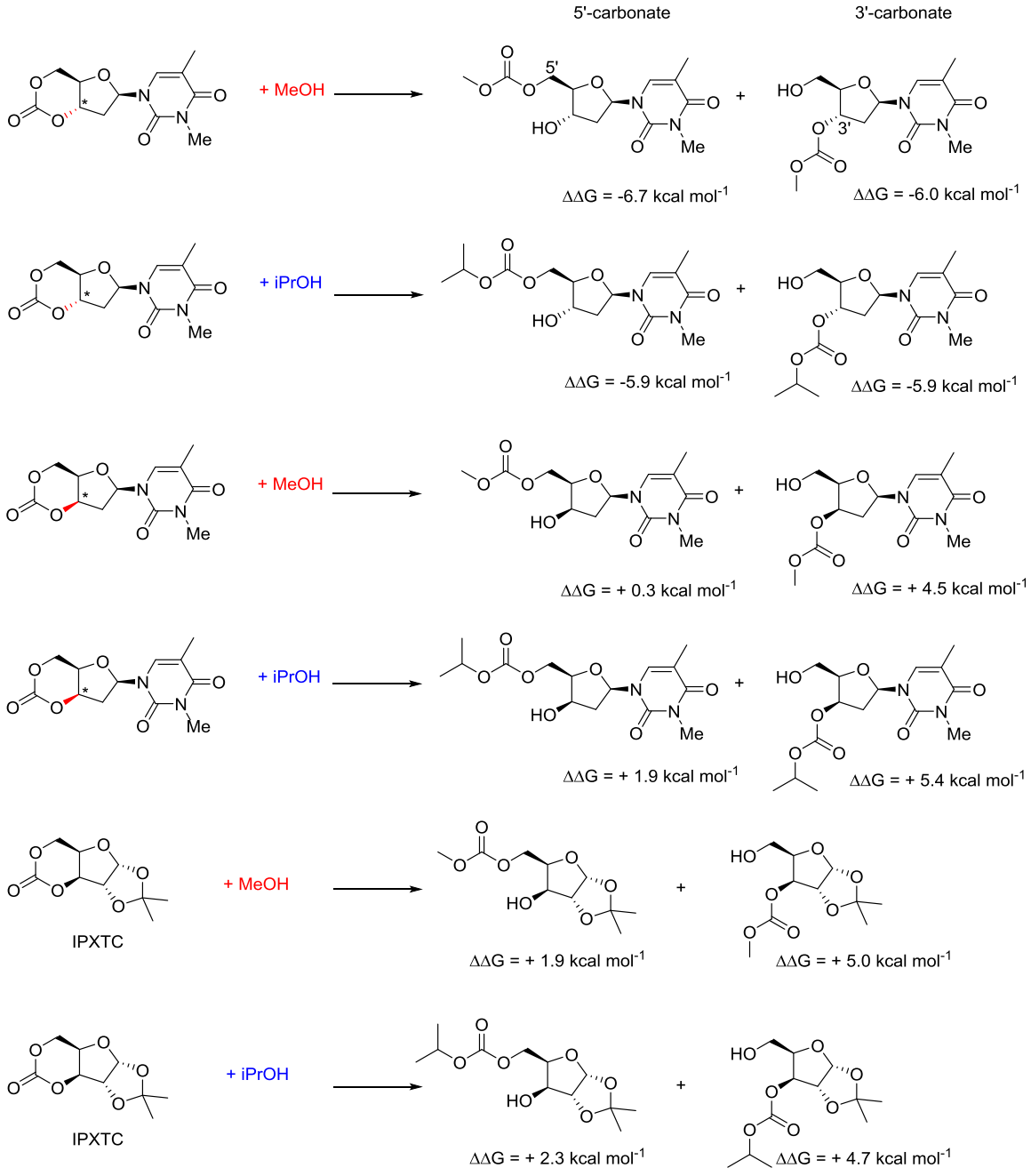
Thermodynamics of Ring-Opening with MeOH and ^{i}PrOH



Scheme S1. Gibbs Free energy (ΔΔG) for the ring-opening of *cis*-**1** (reported here) and *trans*-**1** (hypothetical) with primary and secondary alcohols computed at the 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) (calculated for comparison) was reported by Gross and coworkers.[15] Reported previously[16] and at the same level of theory, ring-opening with MeOH of the *trans*-4,6-cyclic carbonate monomer derived from D-mannose to place the carbonate at the primary or secondary positions was -0.9 and +3.9 kcal mol^{-1}, respectively and for the corresponding D-glucose cyclic carbonate -0.2 and +2.8 kcal mol^{-1}.

	Structure	***G /Hartrees***	***ΔG/ kcalmol^{-1}***
Starting Materials	Trans_1	-1026.367241	
	Cis_1	-1026.381294	
	xyloseCC	-801.362796	
	MeOH	-115.702205	
	iPrOH	-194.286844	
Trans-**1**	Trans_1+ MeOH	-1142.069446	0.0
	MeOH_trans1_3	-1142.080069	-6.7
	MeOH_trans1_5	-1142.079064	-6.0
	Trans_1 + iPrOH	-1220.654085	0.0
	PrOH_trans1_3	-1220.66344	-5.9
	PrOH_trans1_5	-1220.66355	-5.9
Cis-**1**	cis_1+ MeOH	-1142.083499	0.0
	MeOH_cis1_3	-1142.07635	4.5
	MeOH_cis1_5	-1142.083087	0.3
	cis_1 + iPrOH	-1220.668138	0.0
	PrOH_cis1_3	-1220.659461	5.4
	PrOH_ cis1_5	-1220.665093	1.9
IPXTC	xyloseCC+ MeOH	-917.065001	0.0
	MeOH_xylose_3	-917.057093	5.0
	MeOH_xylose_5	-917.061942	1.9
	xyloseCC+ iPrOH	-995.64964	0.0
	PrOH_xylose_3	-995.64208	4.7
	PrOH_xylose_5	-995.646029	2.3

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

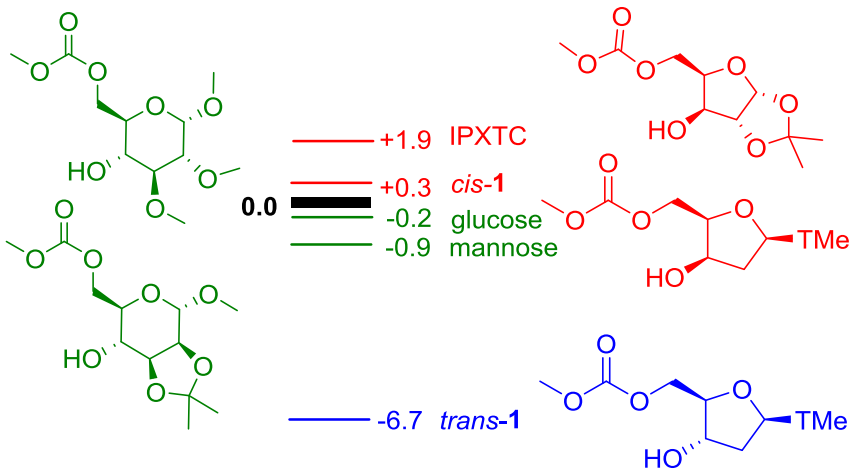


Figure S1. Illustrative overview of calculated ring-opening thermodynamics for sugar-based cyclic carbonates at the rωb97xd/6-311++G(2d,p)/cpcm=dichloromethane/298 K level of theory. Only ring-opening with MeOH to give a primary carbonate is shown.

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.4309487 (private link for review purposes: https://figshare.com/s/7420dc1db475151e7968).