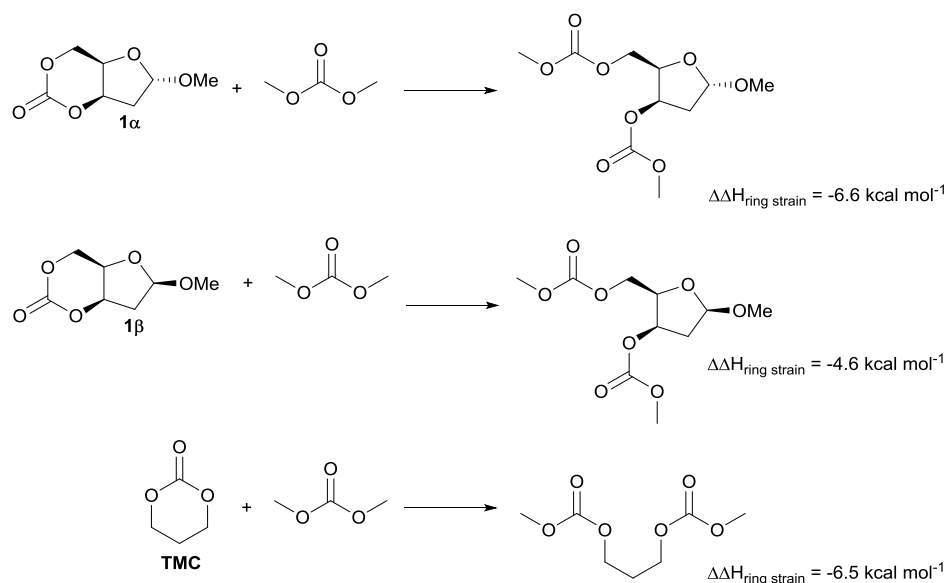


### Isodesmic reaction with dimethylcarbonate



**Scheme S1** Consideration of the ring strain of **1 $\alpha$** , **1 $\beta$**  and **TMC** by calculation of the enthalpy of isodesmic ring-opening with dimethylcarbonate ( $\Delta\Delta H_{\text{ring strain}}$ ).

Structure	H (Hartree)	$\Delta\Delta H \text{ (kcal mol}^{-1}\text{)}$
Dimethyl carbonate (DMC)	-343.512814	-
<b>1<math>\alpha</math></b>	-648.698158	-
<b>1<math>\beta</math></b>	-648.700746	-
<b>TMC</b>	-381.611588	-
<i>DMC + 1<math>\alpha</math></i>	-992.210972	0.0 (reference)
<b>1<math>\alpha</math> oligocarbonate</b>	-992.221438	<b>-6.6</b>
<i>DMC + 1<math>\beta</math></i>	-992.213560	0.0 (reference)
<b>1<math>\beta</math> oligocarbonate</b>	-992.220930	<b>-4.6</b>
<i>DMC + TMC</i>	-725.124402	0.0 (reference)
<b>TMC oligocarbonate</b>	-725.134702	<b>-6.5</b>

**Table S1** Computed Gibbs Free Energies at the rwB97XD/6-311++g(2d,p)/cpcm=dichloromethane/298K level of theory for the isodesmic ring-opening with dimethyl carbonate (DMC) of **1 $\alpha$** , **1 $\beta$**  and TMC.