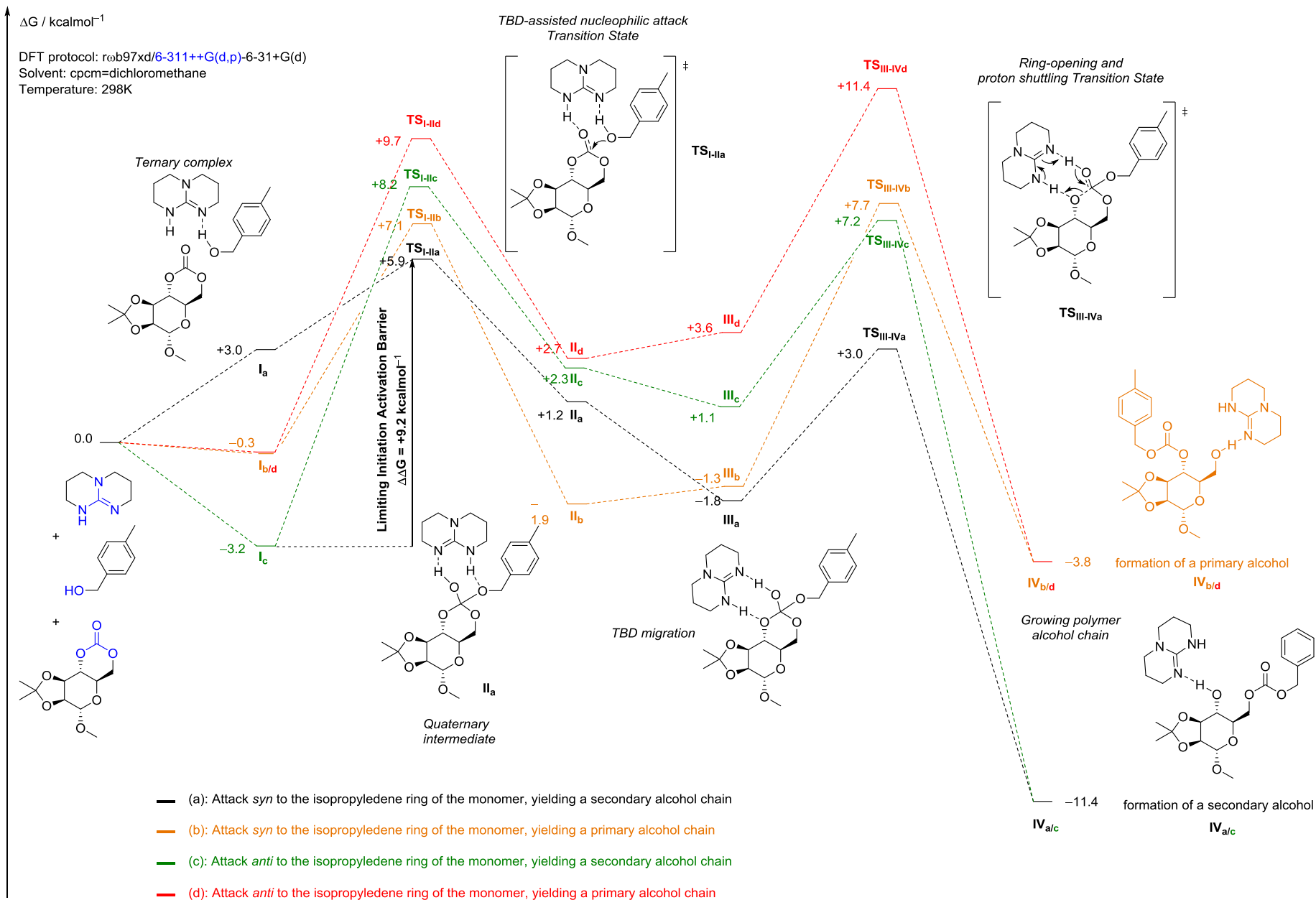
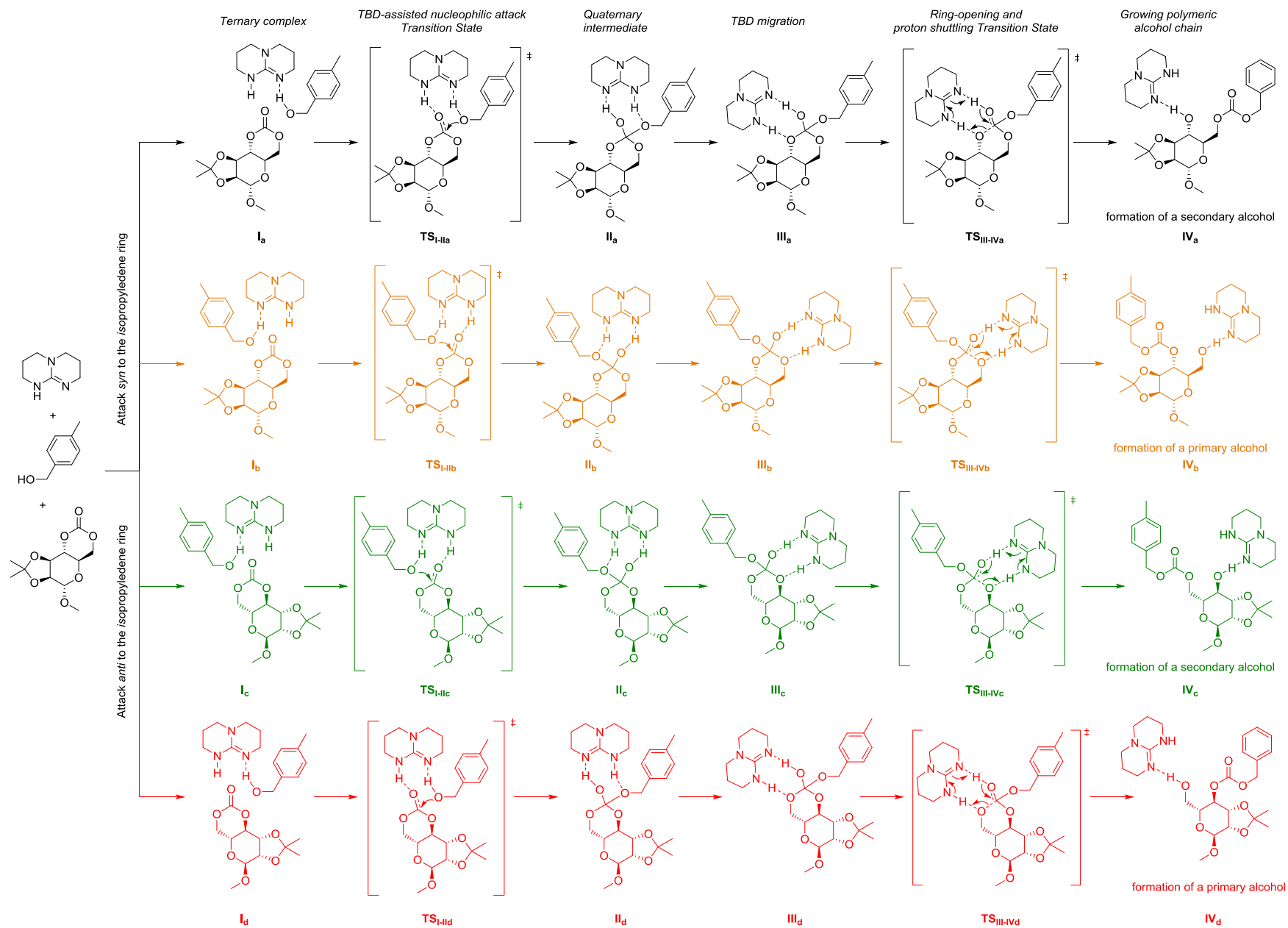


## DFT Modelling of the Initiation Step in the ROP of **1**

The reaction between TBD, 4-methyl benzylalcohol initiator, and one molecule of cyclic carbonate **1** (to account for the initiation step) was examined using DFT calculations. A mixture of the split-valence triple  $\zeta$  with polarization *and* diffuse functions 6-311++G(d,p) basis set (for the carbonate, guanidine and alcohol moieties of **1**, TBD and 4-MeBnOH respectively) and split-valence double  $\zeta$  6-31+g(d) basis set (for the rest) was selected to account for potential anions and nonbonding (hydrogen bonding) interactions, while allowing the models to scale up to the maximum size of 76 atoms.



**Figure 1:** ROP of 1, catalysed by TBD and initiated by 4-MeBnOH: calculated Gibbs Free energy profile for the initiation step.



**Figure 2:** Initiation step for the ROP of 1, catalysed by TBD and initiated by 4-MeBnOH: regiochemistries envisaged.

	Structure	G (Hartree)	$\Delta G$ (kcal mol <sup>-1</sup> )
Starting Materials	TBD	-438.513199	-
	D-Mannose based monomer <b>1</b>	-954.701846	-
	4MeBnOH	-385.796245	-
	<b>1</b> +TBD+4MeBnOH	-1779.011290	0 (reference)
Attack <i>syn</i> to the isopropylidene ring of the monomer, yielding a <i>secondary</i> alcohol chain	<b>I<sub>a</sub></b>	-1779.006520	2.99321793
	<b>TS<sub>I-IIa</sub></b>	-1779.001811	5.948157811
	<b>II<sub>a</sub></b>	-1779.009453	1.152734033
	<b>III<sub>a</sub></b>	-1779.014208	-1.831071262
	<b>TS<sub>III-IVa</sub></b>	-1779.006571	2.961214971
	<b>IV<sub>a/d</sub></b>	-1779.029512	-11.434469
Attack <i>syn</i> to the isopropylidene ring of the monomer, yielding a <i>primary</i> alcohol chain	<b>I<sub>b</sub></b>	-1779.011747	-0.286771613
	<b>TS<sub>I-IIb</sub></b>	-1778.999971	7.102774371
	<b>II<sub>b</sub></b>	-1779.014334	-1.910137396
	<b>III<sub>b</sub></b>	-1779.013411	-1.330946589
	<b>TS<sub>III-IVb</sub></b>	-1778.99895	7.74346106
	<b>IV<sub>b/d</sub></b>	-1779.017319	-3.783251761
Attack <i>anti</i> to the isopropylidene ring of the monomer, yielding a <i>secondary</i> alcohol chain	<b>I<sub>c</sub></b>	-1779.0164	-3.20657099
	<b>TS<sub>I-IIc</sub></b>	-1778.998181	8.226015481
	<b>II<sub>c</sub></b>	-1779.007654	2.281622724
	<b>III<sub>c</sub></b>	-1779.009583	1.071157863
	<b>TS<sub>III-IVc</sub></b>	-1778.999836	7.187488086
	<b>IV<sub>c/a</sub></b>	-1779.029512	-11.434469
Attack <i>anti</i> to the isopropylidene ring of the monomer, yielding a <i>primary</i> alcohol chain	<b>I<sub>d</sub></b>	-1779.011747	-0.286771613
	<b>TS<sub>I-IId</sub></b>	-1778.999971	7.102774371
	<b>II<sub>d</sub></b>	-1779.014334	-1.910137396
	<b>III<sub>d</sub></b>	-1779.013411	-1.330946589
	<b>TS<sub>III-IVd</sub></b>	-1778.99895	7.74346106
	<b>IV<sub>d/b</sub></b>	-1779.017319	-3.783251761

**Table 1:** Computed Gibbs Free Energies at the rwB97XD/6-311+g(d,p)/6-31+g(d)/cpcm=dichloromethane/298K level of theory for the ring-opening of **1** by 4-methyl benzyl alcohol promoted by TBD (initiation step).