







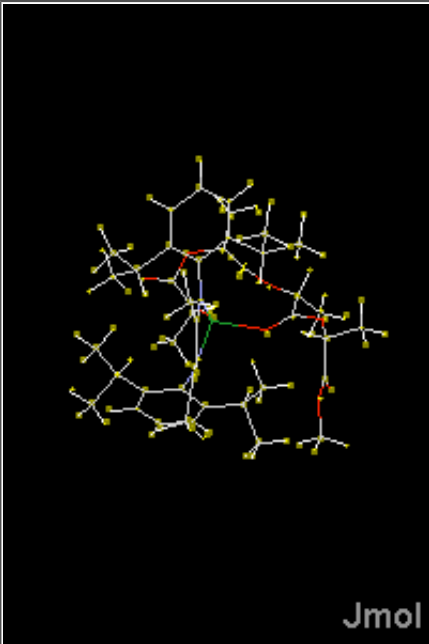
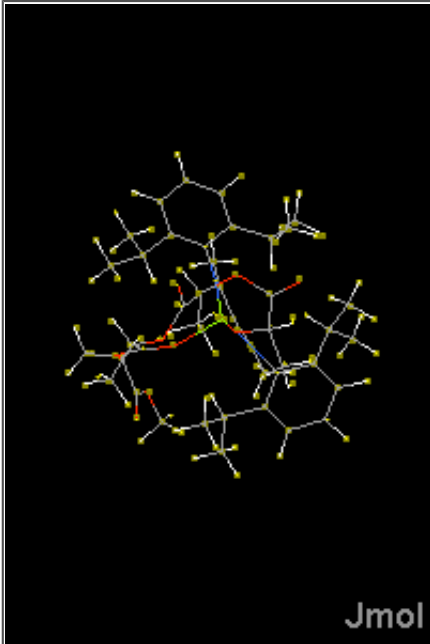
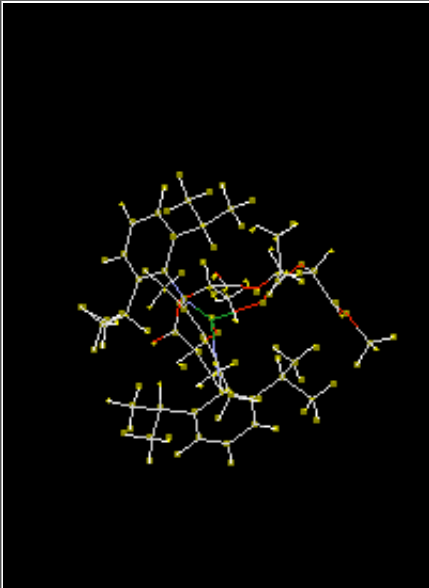
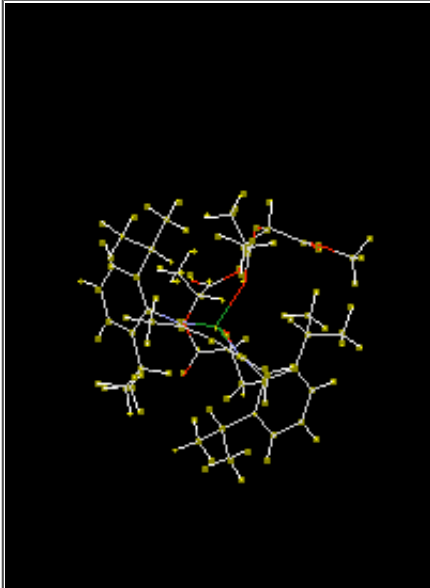


4. Table S2. Commentary on the Four diastereomeric Stationary points of TS2

Storyboard:

1. We seek to explain why RR,SS diastereomer is the lowest of the four transition states involving final ring opening (TS2) and corresponding to the rate limiting step in the overall mechanism.
2. The SS component (of RR,SS) comprises two equatorial methyl groups. One of these exhibits a close (attractive?) contact to the face of one aryl ring: . Crystallographically, many examples are known of approaches to within about 3.2 Å (measured between the ring centroid and the carbon atom of the methyl), which matches the predicted distance for this transition state. The other S-methyl group of this lactide unit also approaches the face of the other aryl ring, although here the predicted contact is not so close (4.1 Å): .
3. This di-equatorial arrangement also minimises steric interactions between the two SS methyl groups. In contrast, a RR configuration for these methyls places them di-axial: . The difference in (total) energy between the RRSS and RRRR diastereomers (4.0 kcal<sup>-1</sup>) quantifies the difference in the sum of these two effects. The free energy difference ( $\Delta G_{298}$ ) of 1.4 kcal<sup>-1</sup> agrees better with experiment. We also note at this stage that a similar energy difference occurs for the SSSS/SSRR pair (4.0 kcal<sup>-1</sup> in total energy, 2.7 in  $\Delta G_{298}$ ).
4. The stereochemistry of the RR lactide ring (of RR,SS) is mediated by different interactions. Firstly, steric repulsion between the two RR methyl groups:  is avoided, whereas in the SS,SS isomer, the repulsion is rather greater .
5. Secondly, the RR configuration (of RR,SS) also avoids a close contact between a methyl and an isopropyl group:  whereas such contact cannot be avoided with the SS configuration (of SS,SS): . These effects cumulatively amount to a difference in the total energy of 6.2 kcal<sup>-1</sup> (RRSS vs SSSS or RRRR vs SSRR) and of 6.6 (RRSS vs SSSS) or 7.9 kcal<sup>-1</sup> (RRRR vs SSRR) in  $\Delta G_{298}$ .
6. In total energy, the various effects are almost exactly additive, which means that the SS,RR isomer is doubly disfavoured (10.2 kcal<sup>-1</sup>) compared to the RR,SS configuration: .

The additivity is not so precise in  $\Delta G_{298}$  due to non-additivity in the Rigid-Rotor-Harmonic-Oscillator approximation in dealing with very low frequency contributions to the entropy.

Total energies (Hartree) [Corrected for $\Delta G_{298}$ (Hartree)] {C-O cleaving bond length,Å}					
RRSS	vib on	vib off	RRRR	vib on	vib off
-2612.17812 [-2611.26219] {2.289}			-2612.17174 [-2611.26002] {2.179}		
					
Jmol			Jmol		
SSRR	vib on	vib off	SSSS	vib on	vib off
-2612.16180 [-2611.24743] {2.154}			-2612.16815 [-2611.25173] {2.240}		
					
Jmol			Jmol		

7. Overall therefore, the tacticity is induced by a possible attractive interaction between one methyl and the face of any aryl ring, and avoidance of repulsion between the two methyls of one lactide, and between another methyl and one of the (four) isopropyl substituents on one of the (two) aryl rings.