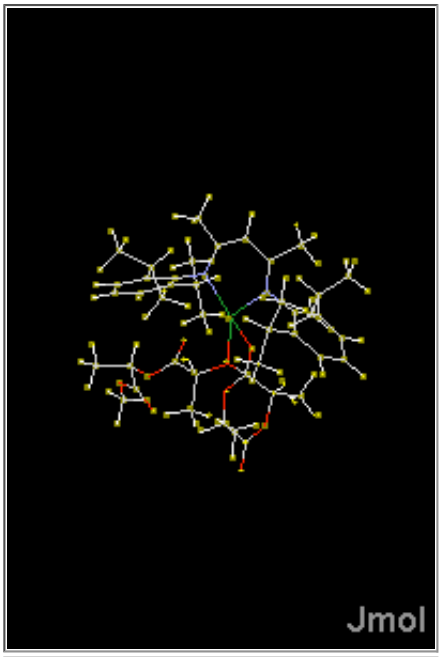
5. Table S3. Commentary on the Four diasteromeric Stationary points of TS1

Storyboard:

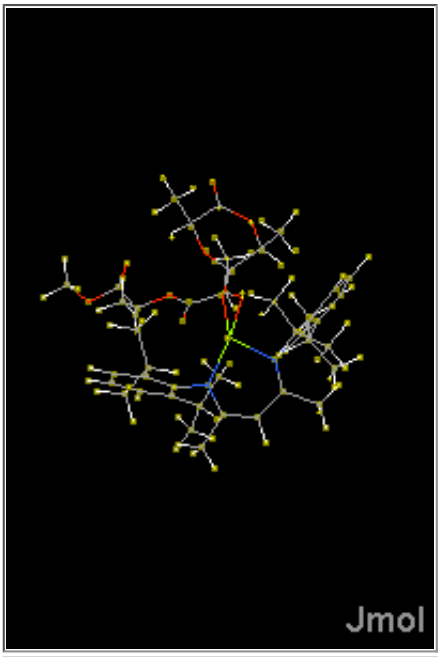
1. The SS,SS diasteromer is the lowest of the four for TS1, here the forming O-C bond is antiperiplanar to the C-Me bond. One of the methyl groups of the lactide interacts with the adjacent aryl ring in a presumed weak π interaction.
2. The difference between SS,SS and SS,RR amounts to 4.6 (total) or 5.8 (ΔG). In the SS,RR isomer, the antiperiplanar interaction is between the forming O-C bond and another C-O bond.
3. The analogous difference between RR,SS and RR,RR is 3.7 (total) or 2.9 (ΔG) with identical antiperiplanar arrangements.
4. The difference between SS,SS/RR,SS amounts to 2.1 (total) or 3.8 (ΔG); and SS,RR/RR,RR is 1.2 and 1.0 respectively. The additivity of these effects is relatively poor compared to TS2, which suggests that non-local stereoelectronic effects may be more significant here.
5. Steric factors are also important, in particular the separation between the two methyls of the coordinated lactide monomer, and the methyl group of the lactate chelate. In the energetically preferred (SS,SS) isomer, these three substituents are orientated on opposing faces, whereas a much closer approach is observed in the highest energy isomer, (RR,RR).

Total energies (Hartree)
[Corrected for ΔG_{298} (Hartree)] {C-O forming bond length,Å}

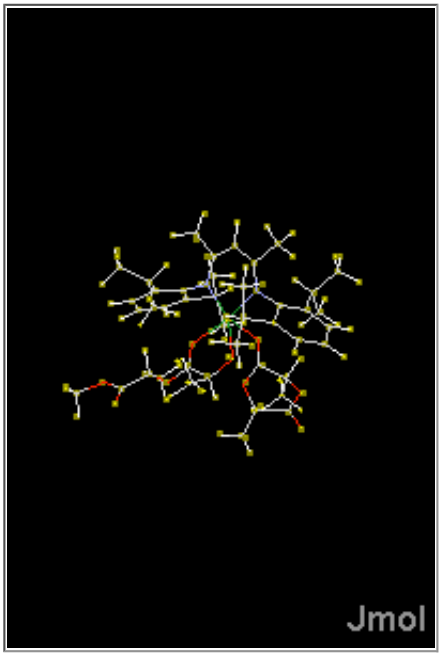
RRSS	vib on	vib off
-2612.18938[-2611.2755] {1.737}		



RRRR	vib on	vib off
-2612.18356[-2611.2708] {2.157}		



SSRR	vib on	vib off
-2612.18541[-2611.2724] {2.003}		



SSSS	vib on	vib off
-2612.1928[-2611.2816] {1.941}