



















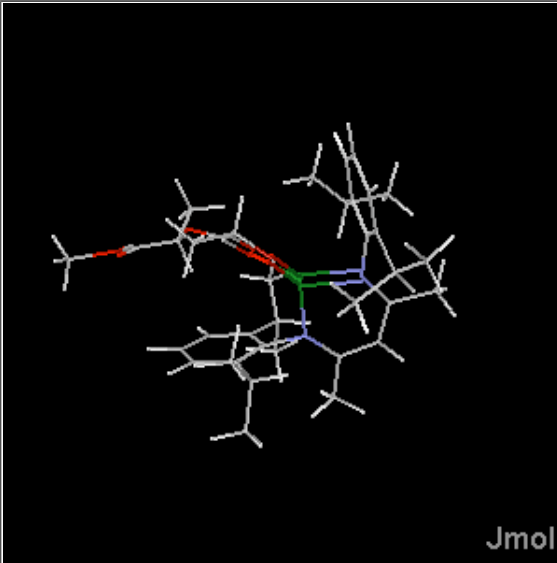
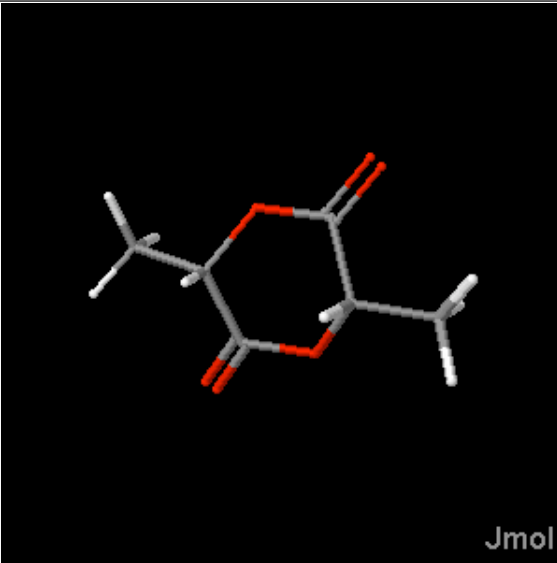
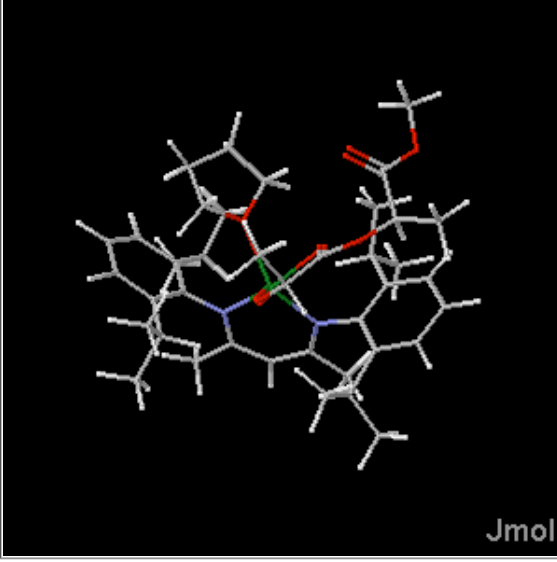
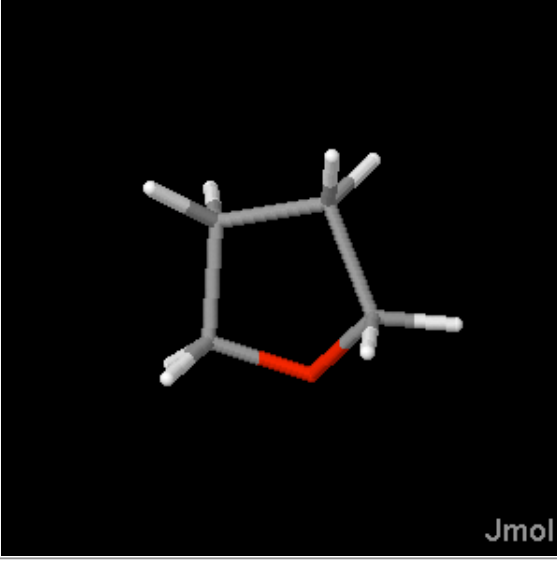
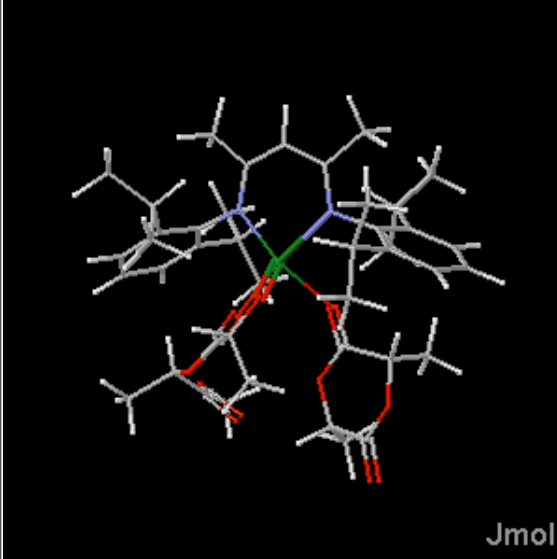
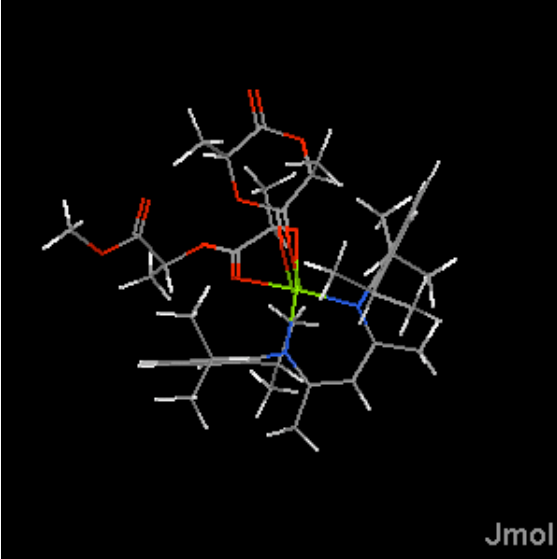


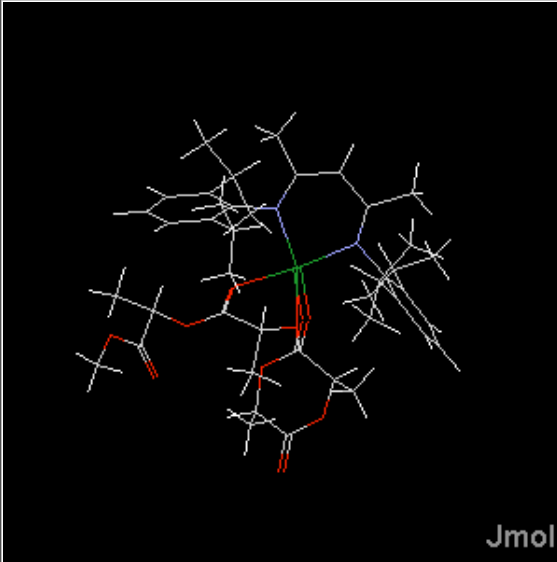
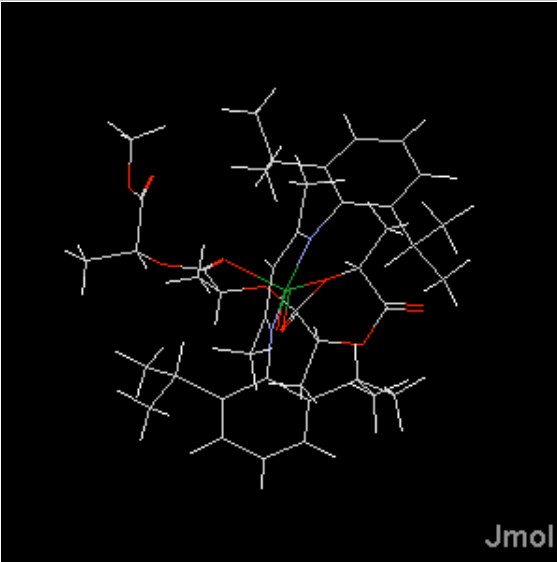
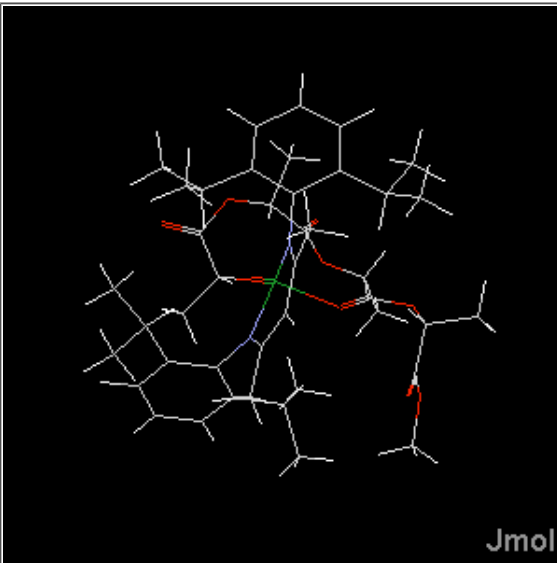
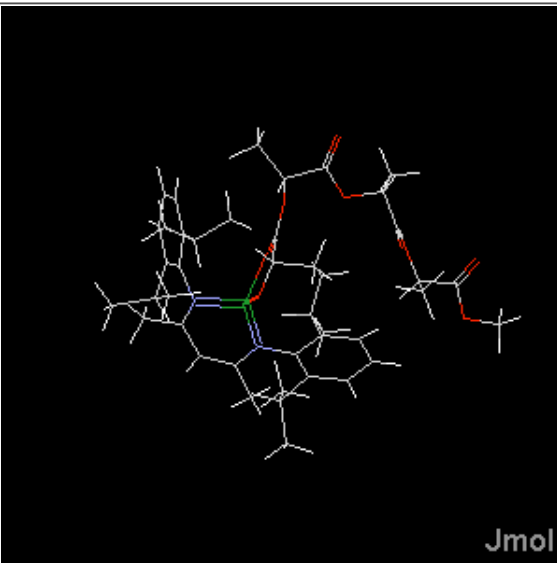
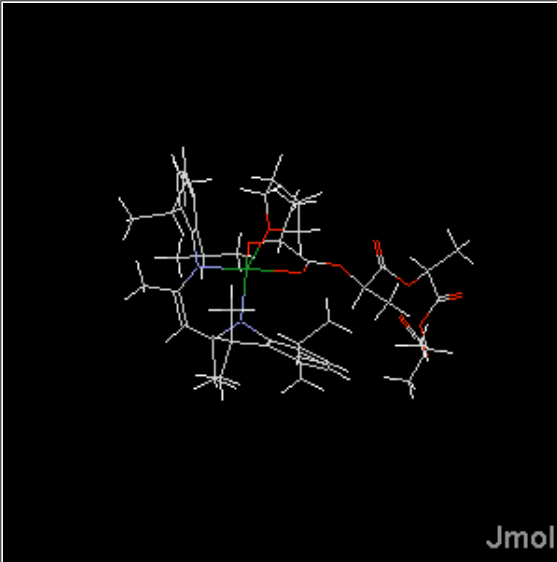
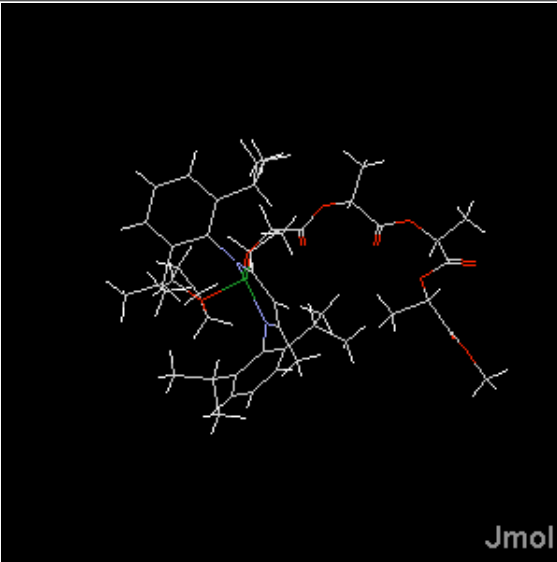
3. Table S1. Commentary on the Stationary points on the potential surface^a for the overall mechanism, illustrated using the RR,SS stereoisomer.

Storyboard:

1. In this terminology, RR (of RR,SS) refers to the configuration of the two chiral centres of the previously ring-opened lactide unit  whilst SS refers to the newly co-ordinated lactide unit  which is about to be ring-opened (see Int1 window).
2. The lowest energy of the first lactide (RR) is that of a 5-ring coordinated species: .
3. The reactant is solved by one molecule of THF , but the solvent is then displaced by a second (SS) lactide monomer.  The coordination of the THF solvent is closer to equatorial rather than axial.
4. The geometry of the resulting intermediate (Int1) is mediated by a weak O...C=O electrostatic interaction  (3.01Å).
5. The first transition state involves O...C=O bond formation  in which the weak O...C=O electrostatic interaction is strengthened  (2.88Å).
6. The geometry of this transition state is controlled by the stereoelectronic antiperiplanar orientation of the incoming O...C bond and the C-C bond .
7. The original alkyl-oxygen coordination to Mg is preserved in this transition state .
8. as it also is in the resulting tetrahedral intermediate. .
9. The tetrahedral intermediate undergoes a (rocker-switch like) reorganisation of the Mg-O coordination, accompanied by a conformational change. Thus the original alkyl-oxygen...Mg bond breaks  and a new alkyl-oxygen...Mg bond forms .
10. This change in conformation now sets up the final C-O bond cleavage .
11. which after further Mg...O de-coordination,  and re-coordination by the terminal C=O group .
12. results in the product with extruded polymer chain .
13. The rate-determining transition state has an imaginary normal mode  vib on  vib off  which reveals both O-C cleavage and concomitant C=O...Mg de-coordination with a computed wave

Total energies (Hartree)/Relative energies (kcal ⁻¹) [Corrected for ΔG ₂₉₈ (Hartree)/relative ΔG ₂₉₈ , kcal ⁻¹], {IEFPCM solvation model} ^b	
RR-Reactant	SS-Lactide
-2077.83601 [-2077.06000] {-2077.78925}	-534.35128 [-534.24493] {-534.35364}
Total: 2612.18729 [2611.30493] {2612.14289}	
	
RR-Reactant+THF	THF
-2310.29905 [-2309.40424] {-2310.25064}	-232.44540 [-232.35690] {-232.44402}
Total: 2612.18729 [2611.30493] {2612.14289}	
	
Int1 (=Reactant + ketide - thf)	TS1
-2612.20735/0.0 [-2611.29448/0.0] {-2612.155852}	-2612.18938/11.3 [-2611.27550/11.9]
	

- number of 49 cm⁻¹. This unusually low value for a transition mode arises in part because of the highly correlated nature of the vibration, in which most atoms of the reaction centre participate, and hence the relatively large mass-weighting of this vibration.
14. TS2 has Wiberg bond indices in the NAO basis^b: C–O_{acyl} 0.15 [0.15], O_{acyl}–Mg 0.09 [0.09], O_{carbonyl}–Mg 0.03 [0.03], O_{carbonyl}–C 1.65 [1.65] with considerable ionic nature (natural charge on Mg +1.68) [1.68].
15. The product re-coordinates a solvent THF molecule [1] in such a manner as to minimise repulsions to the methyl group [1]. This means in effect that the THF solvent and the polymer chain have to be coordinated di-equatorial to the Mg. This methyl group thus avoids clashing with the isopropyl group [1]. The extruding (and conformationally flexible) polymer chain folds back across the same face as the THF solvent. The energy reported here is considered an upper bound, since not all the conformational space of this chain has been explored. Alternative modes of coordination such as having the THF and the polymer chain effectively di-axial at the Mg centre are significantly higher in energy [1].
16. The thermochemistry of the overall mechanism is (respectively, as difference in total energy gas phase, with IEFPCM solvation correction for THF,^b and for ΔG gas phase):
1. (TS2,THF) – (RR–reactant+THF,lactide): 17.1, 16.5, 18.9 kcal mol⁻¹.
 2. TS2 – Int1(RR–reactant+lactide): 18.3, 13.7, 20.2 kcal mol⁻¹
 3. (RR–reactant,lactide) – (Product): –16.9, –7.7^c, –0.9,
 4. (RR–reactant+thf,lactide) – (Product+thf): –11.4, –2.6, +1.5

T11	T12
-2612.18950 [-2611.27569]	-2612.19235 [-2611.27650]
	
TS2	Product
-2612.17810/18.4 [-2611.26220/20.2] {-2612.134079}	-2612.21424 [-2611.30626/-7.4] {-2612.155228}
	
Product.thf	Product.thf isomer
-2844.66854 [-2843.64665]	2844.65185 [-2843.63036]
	

^aThese calculations are all based on the B3LYP density functional procedure, employing a 6–311G(3d) basis for Mg, 6–31G(d) for the lactide and core ligand units, and STO–3G for the 2,6–di–isopropyl aryl ligand substituents. The Gaussian 98 and 03 programs were used; a) Gaussian 98 (Revision A.11): (b) Gaussian 03 (Revision B.04): Gaussian, Inc., Pittsburgh (PA), 2003. ^b Reed, A. E.; Curtiss, L. A.; Weinhold, F., *Chem. Rev.*, 1988, **88**, 899 – 926. ^b M. T. Cancas, B. Mennucci, and J. Tomasi, *J. Chem. Phys.*, 1997, **107**, 3032. ^c Errors in convergence may render this value suspect.