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SUPPORTING INFORMATIONS

Living and Immortal Ring-Opening Polymerization of Cyclic Esters

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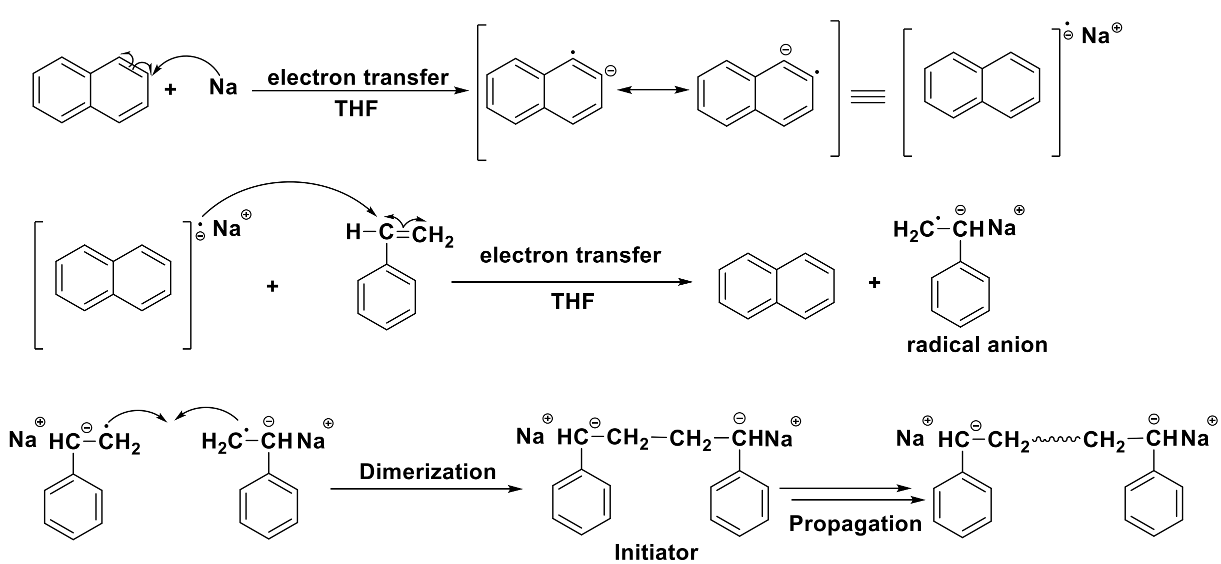
(ACZ-5940-2022)

ABSTRACT

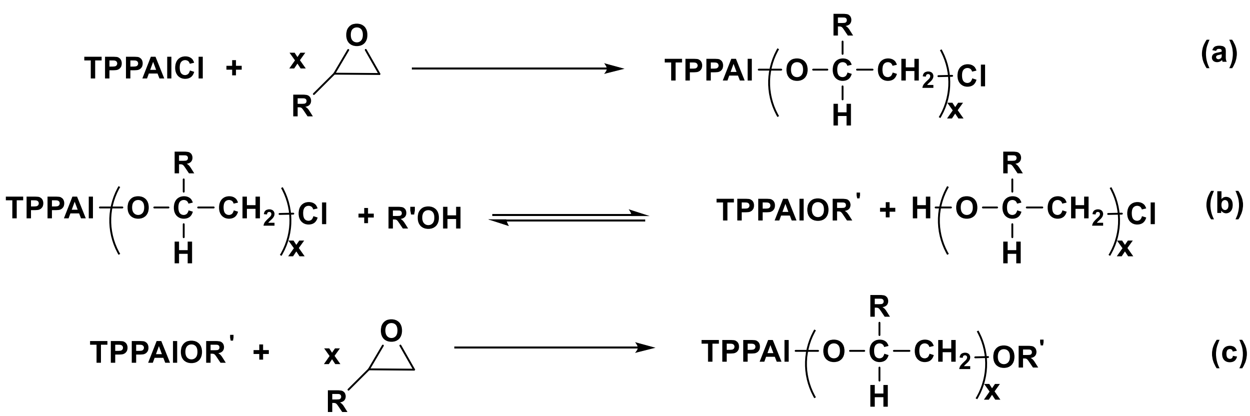
The limited availability of fossil fuels on the Earth has led researchers to develop new materials that are derived from renewable feedstocks. The polymers produced from the ROP of cyclic esters like (LA and ε-CL) are biodegradable, biocompatible, and bioassimilable and thus find major applications in various field. The ROP are catalyzed by the metal-based organometallic catalyst and metal-free organocatalyst. This review exemplifies the living and immortal ROP. The advantage of such polymerization is that they produce polymers with controlled molecular weight distribution. For the immortal ROP, more than one polymer chain grows from the single catalytic site in the presence of chain transfer agents (CTAs), and thus catalyst loading is low, which make the process economically more viable. The nature of CTAs and loading of CTAs with respect to the catalyst is crucial as the catalyst should be effective in the presence of CTAs. The review also discusses functionalized CTAs employed for the polymerization in some instances where functionalized polymers are generated.

KEYWORDS

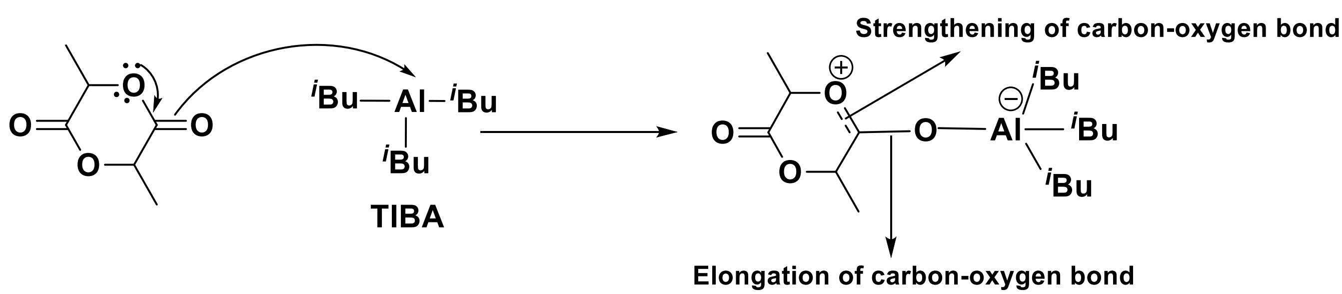
Ring-opening polymerization, immortal polymerization, living polymerization, chain transfer agents.



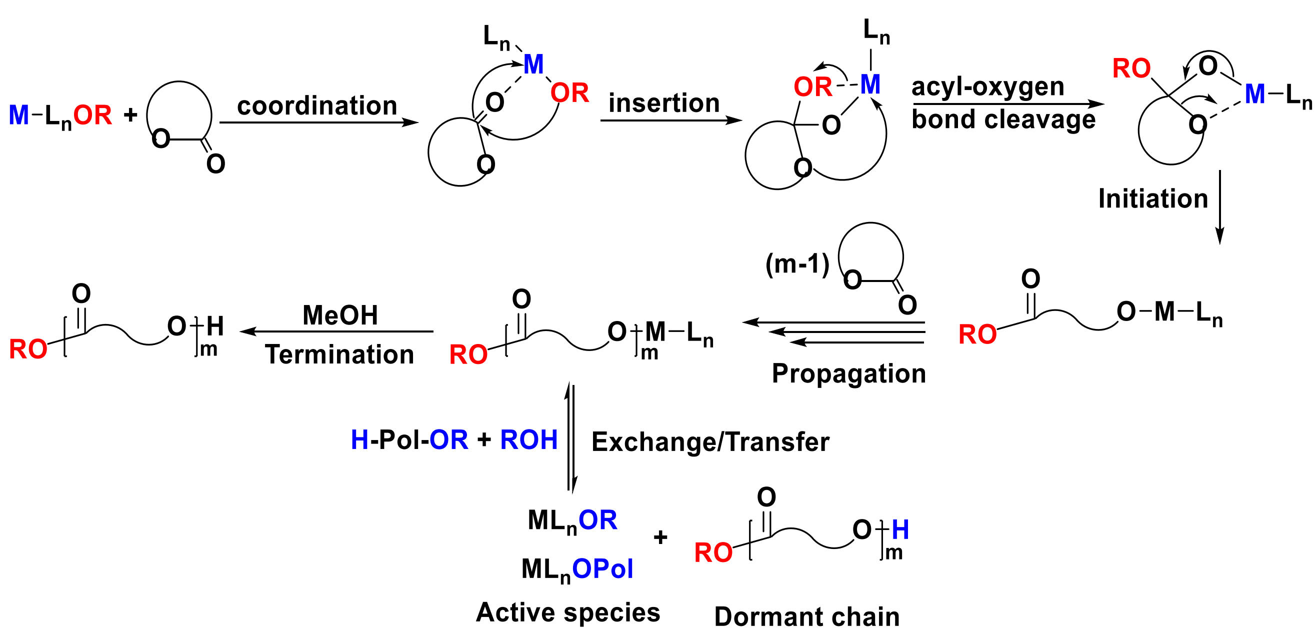
Scheme S1. Initiation and propagation steps for polystyrene formation.



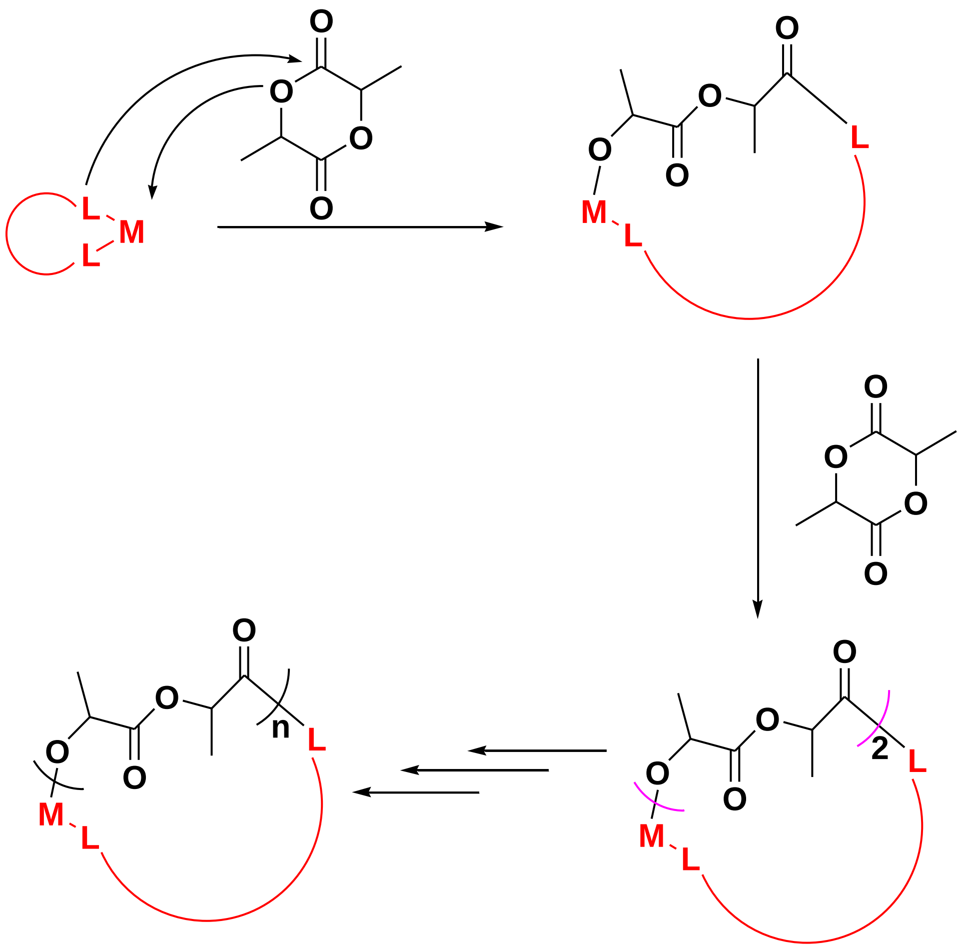
Scheme S2. Polymerization of epoxide catalysed by aluminium porphyrin-alcohol system.



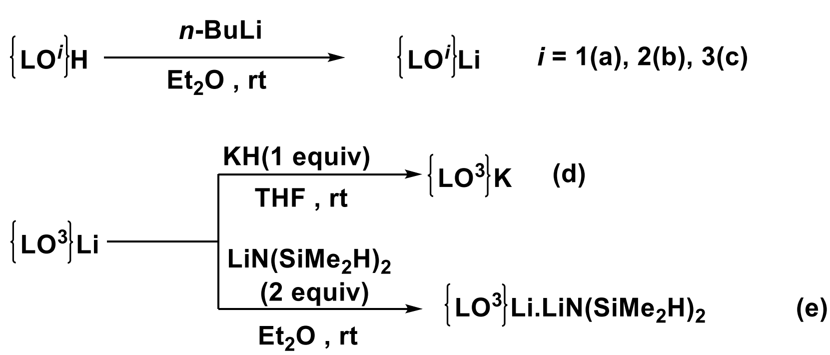
Scheme S3. Coordination of lactide to TIBA.



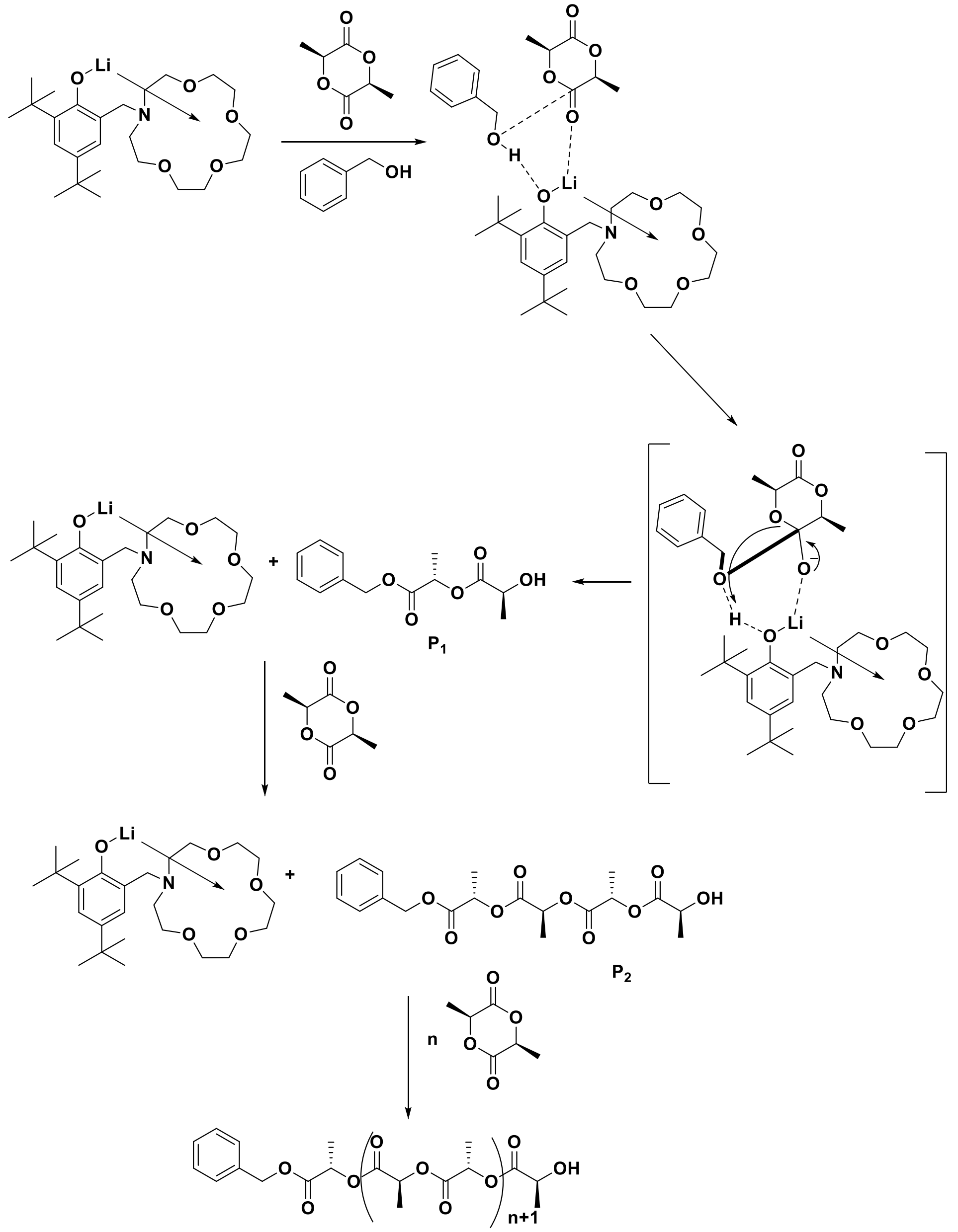
Scheme S4. Coordination-insertion mechanism of ROP.



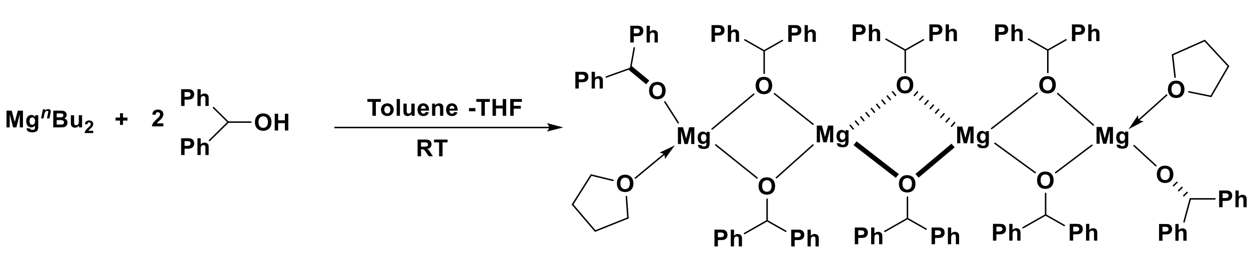
Scheme S5. Activated monomer mechanism of ROP.



Scheme S6. Synthesis of lithium and potassium complexes.

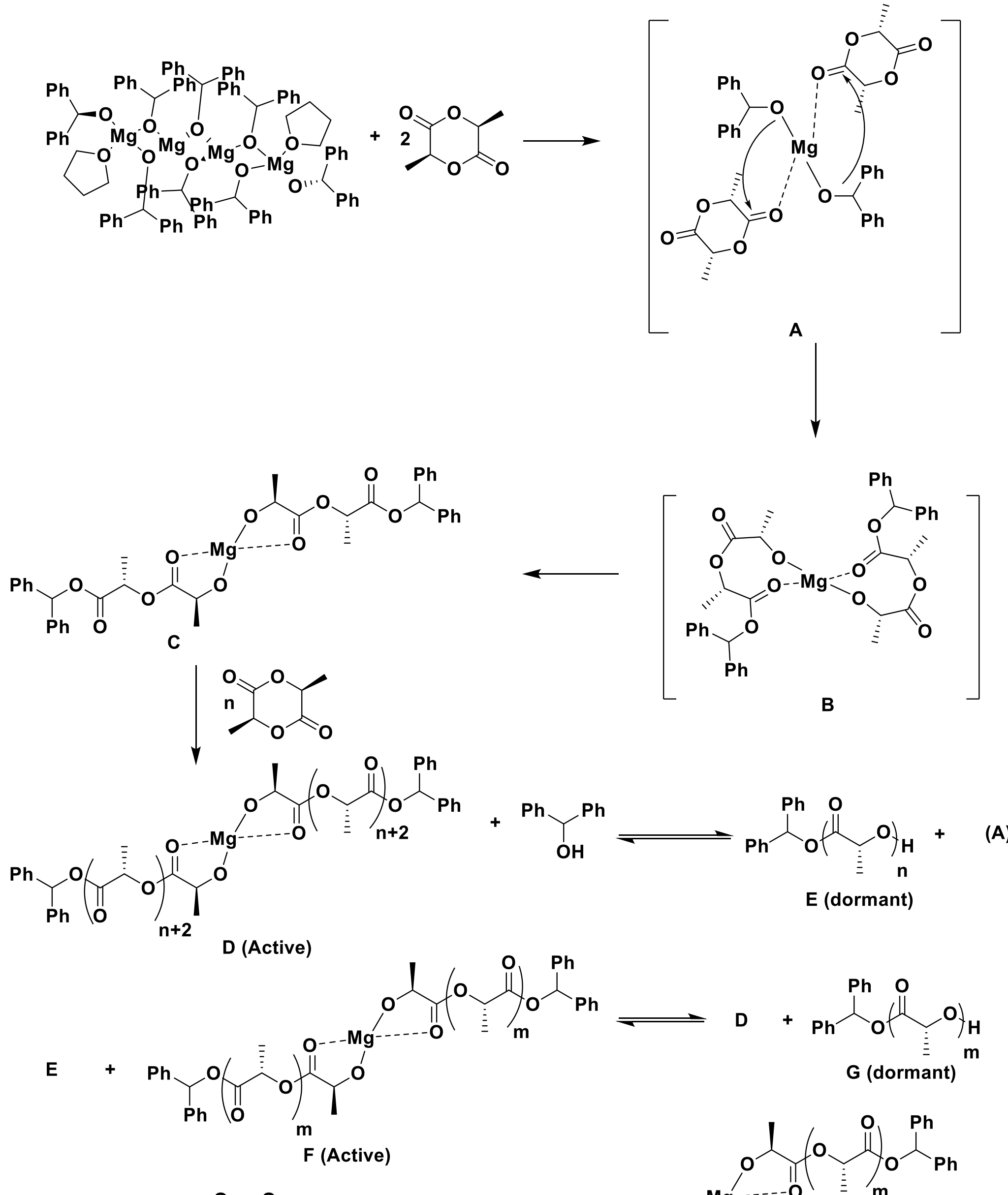


Scheme S7. Activated monomer mechanism for ROP of *L*-LA.

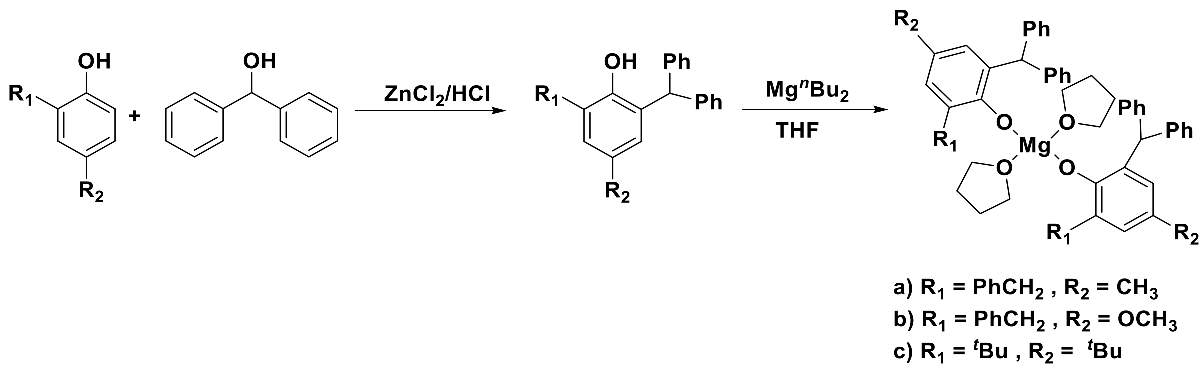


(a)

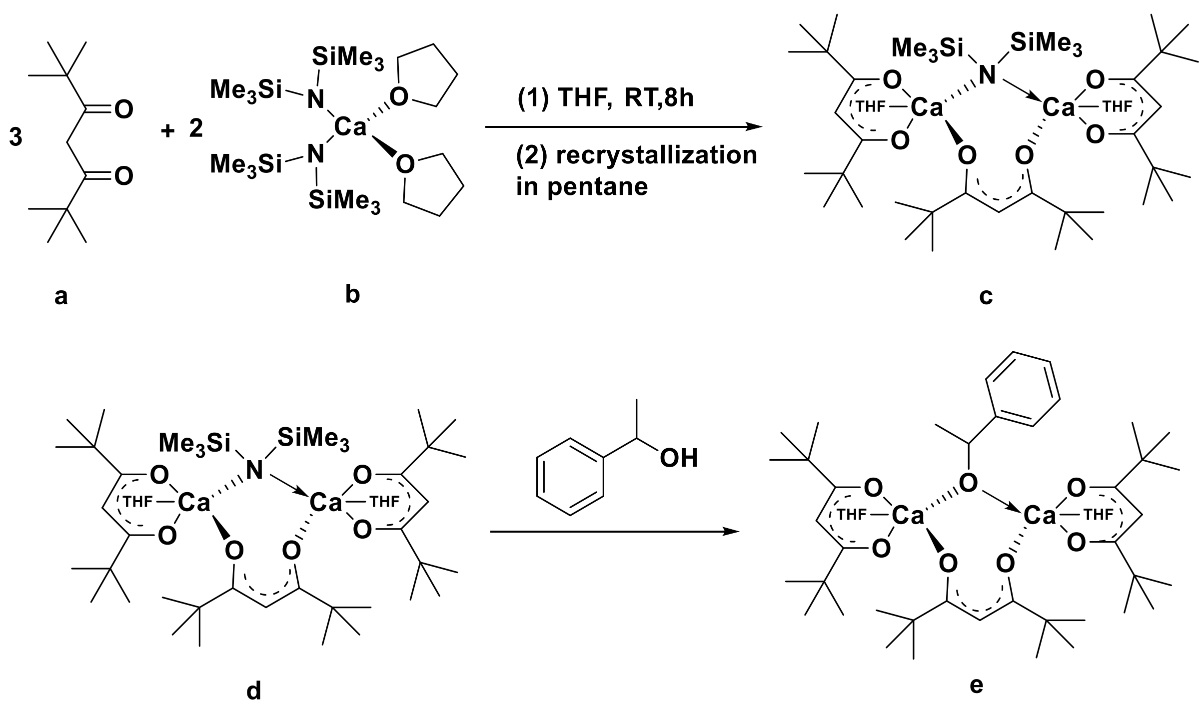
Scheme S8. Reaction between benzhydrol and $Mg^{n}Bu_2$.



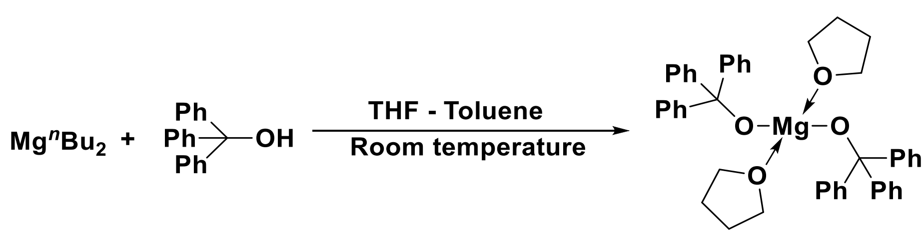
Scheme S9. Proposed coordination-insertion mechanism for ROP of *L*-LA.



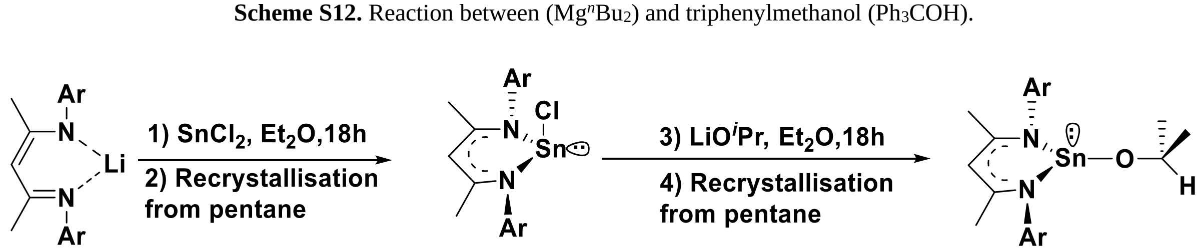
Scheme S10. Synthesis of magnesium-phenoxide complexes.



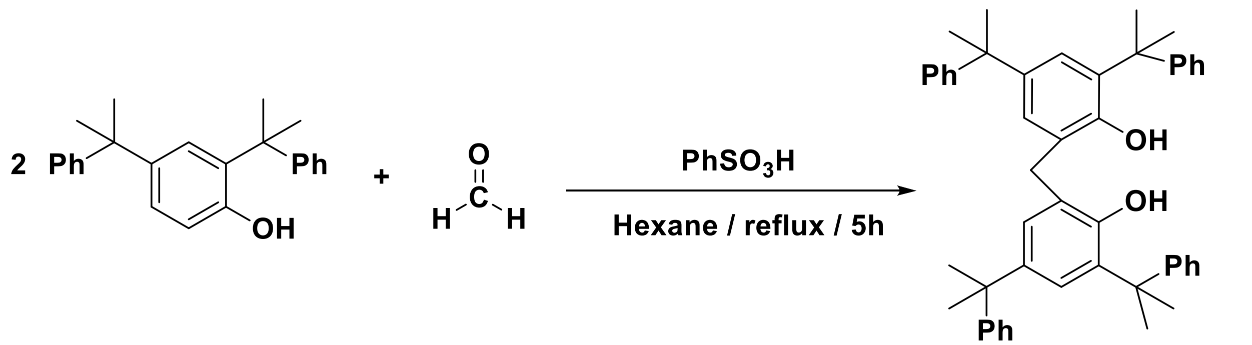
Scheme S11. Synthesis of *β*-diketonate calcium complexes.



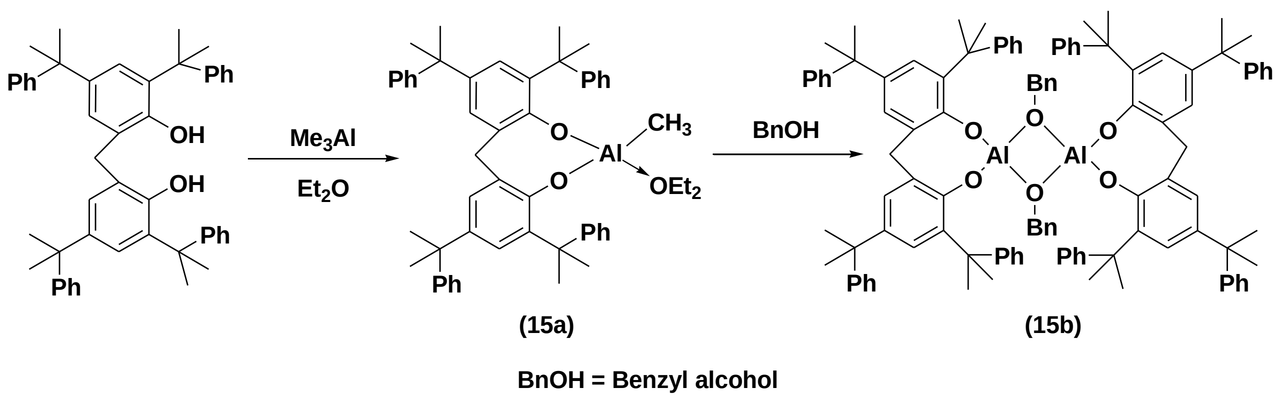
Scheme S12. Reaction between ($Mg^{n}Bu_2$) and triphenylmethanol (Ph_3COH).



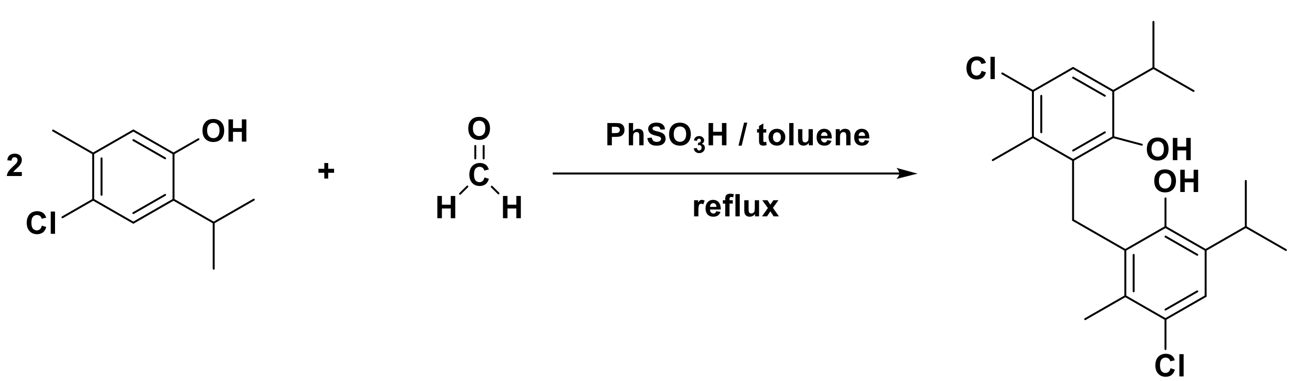
Scheme S13. Synthesis of tin complexes.



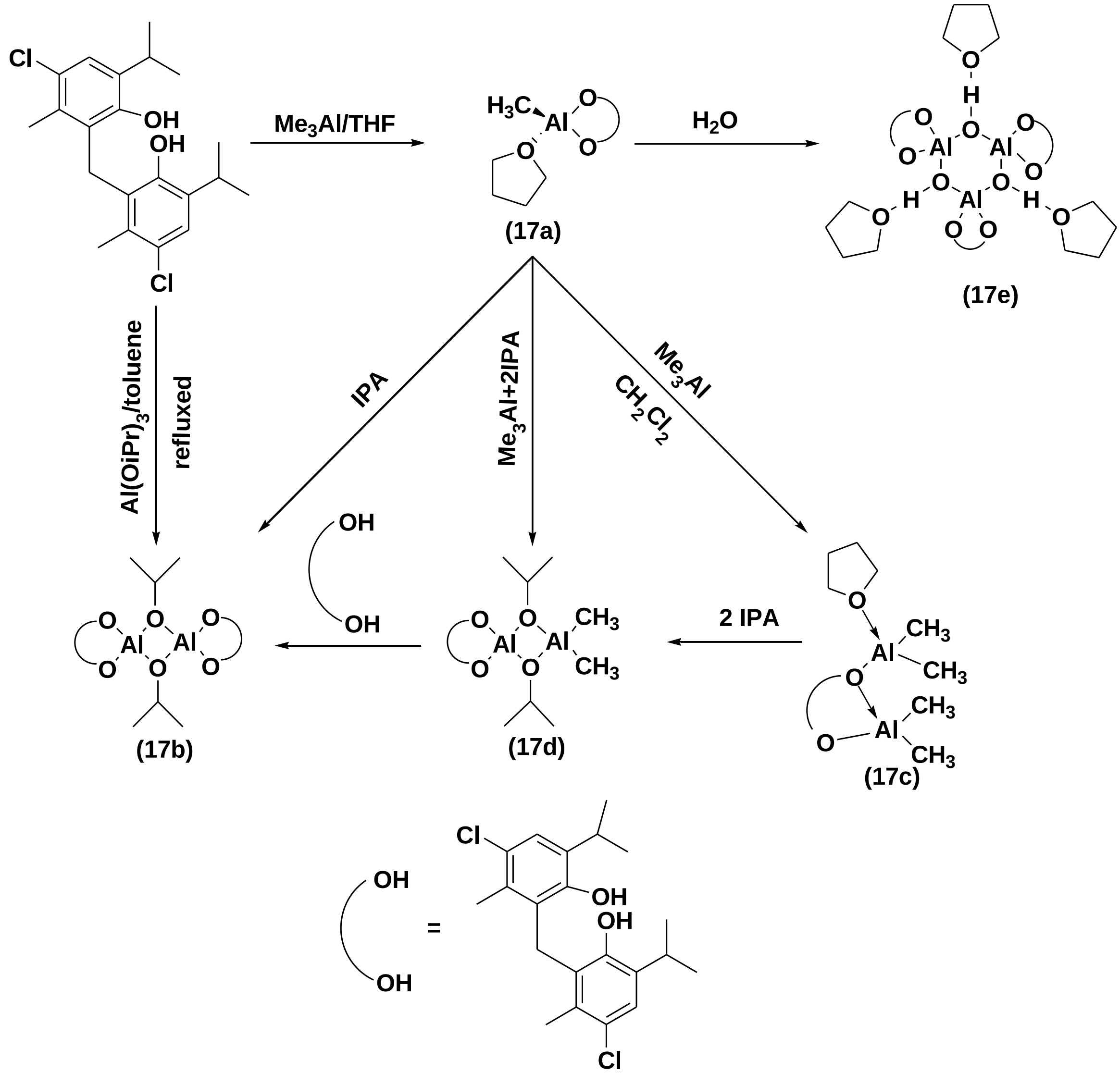
Scheme S14. Synthesis of 2,2'-methylenebis(4,6-di(1-methyl-1-phenylethyl) phenol).



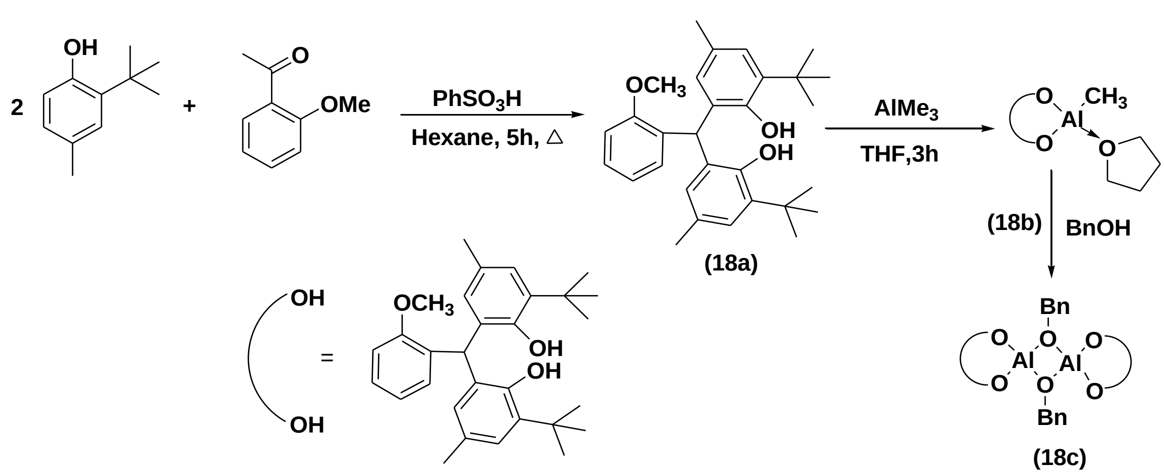
Scheme S15. Synthesis of aluminium complexes.



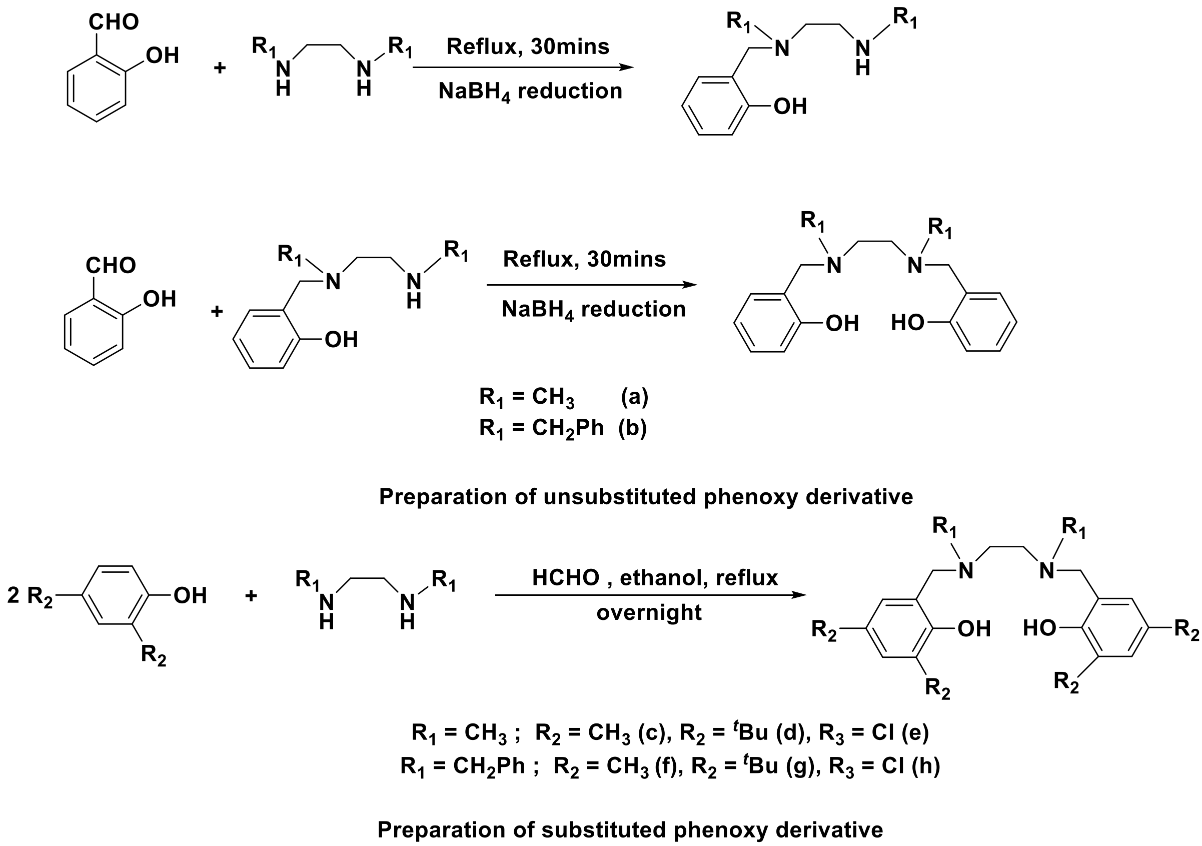
Scheme S16. Synthesis of 2,2'-methylenebis(4-chloro-6-isopropyl-3-methylphenol.



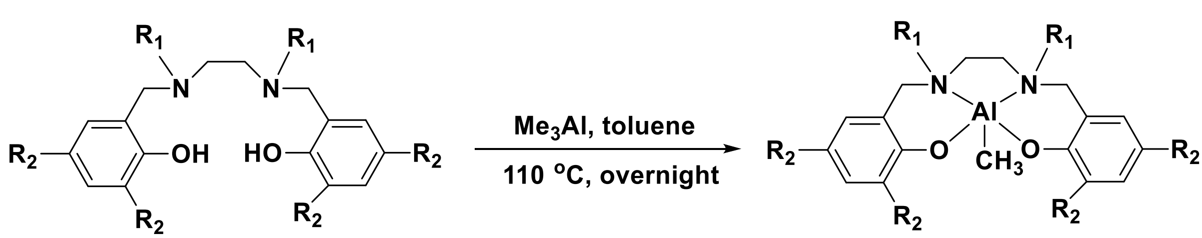
Scheme S17. Synthesis of five aluminium complexes.



Scheme S18. Synthesis of bisphenol derivative and aluminium complexes.

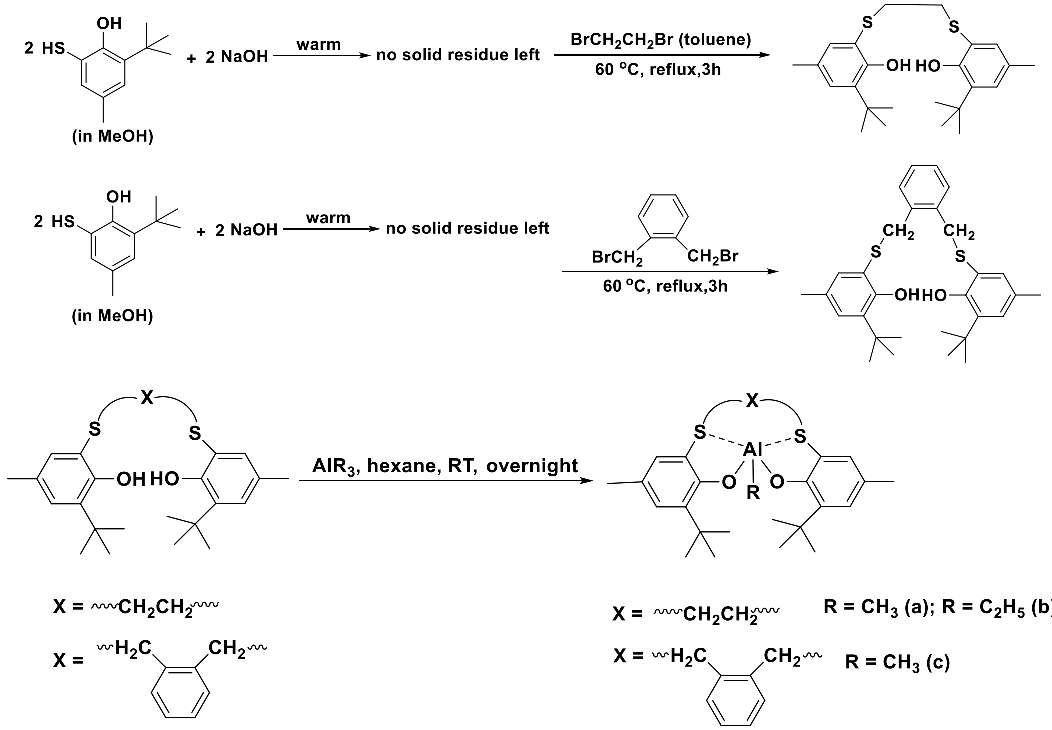


Scheme S19. Synthesis of phenoxy amine ligands.

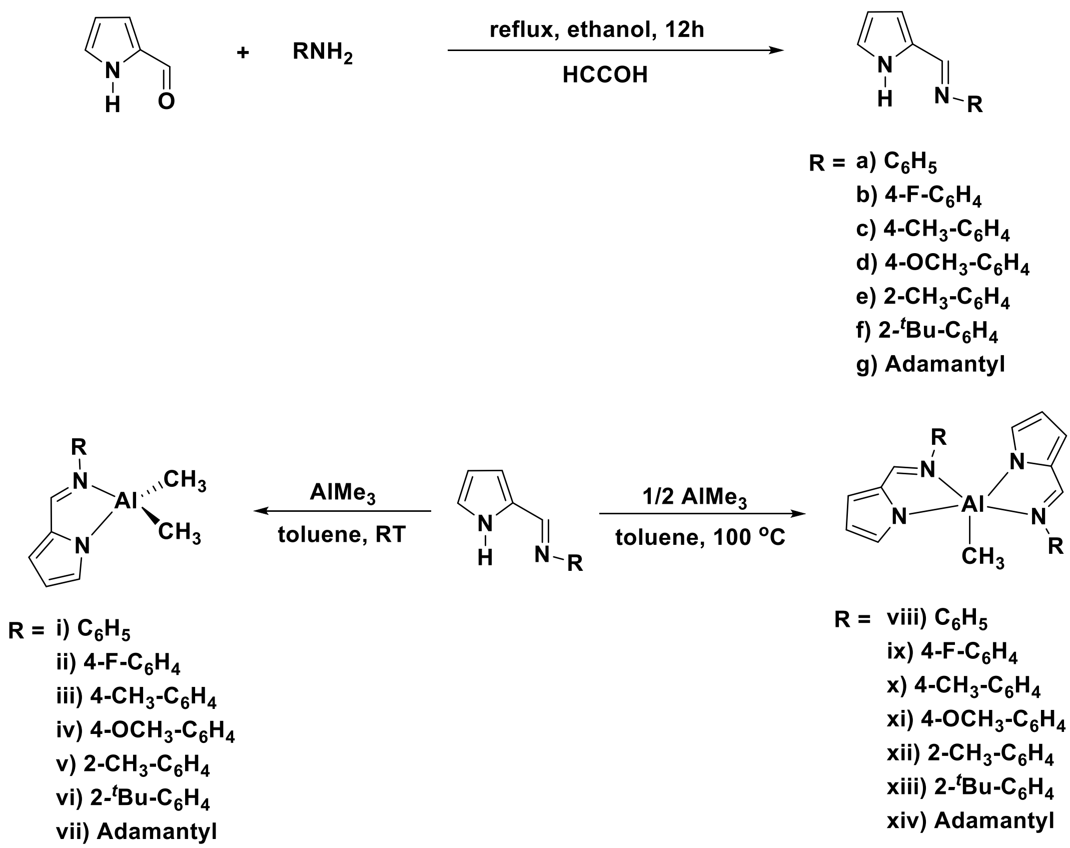


R_1 = CH_3 ; R_2= H (a), R_2 = CH_3 (c), R_2 = ^{t}Bu (d), R_3 = Cl (e)
R_1 = CH_2Ph ; R_2= H (b) R_2 = CH_3 (f), R_2 = ^{t}Bu (g), R_3 = Cl (h)

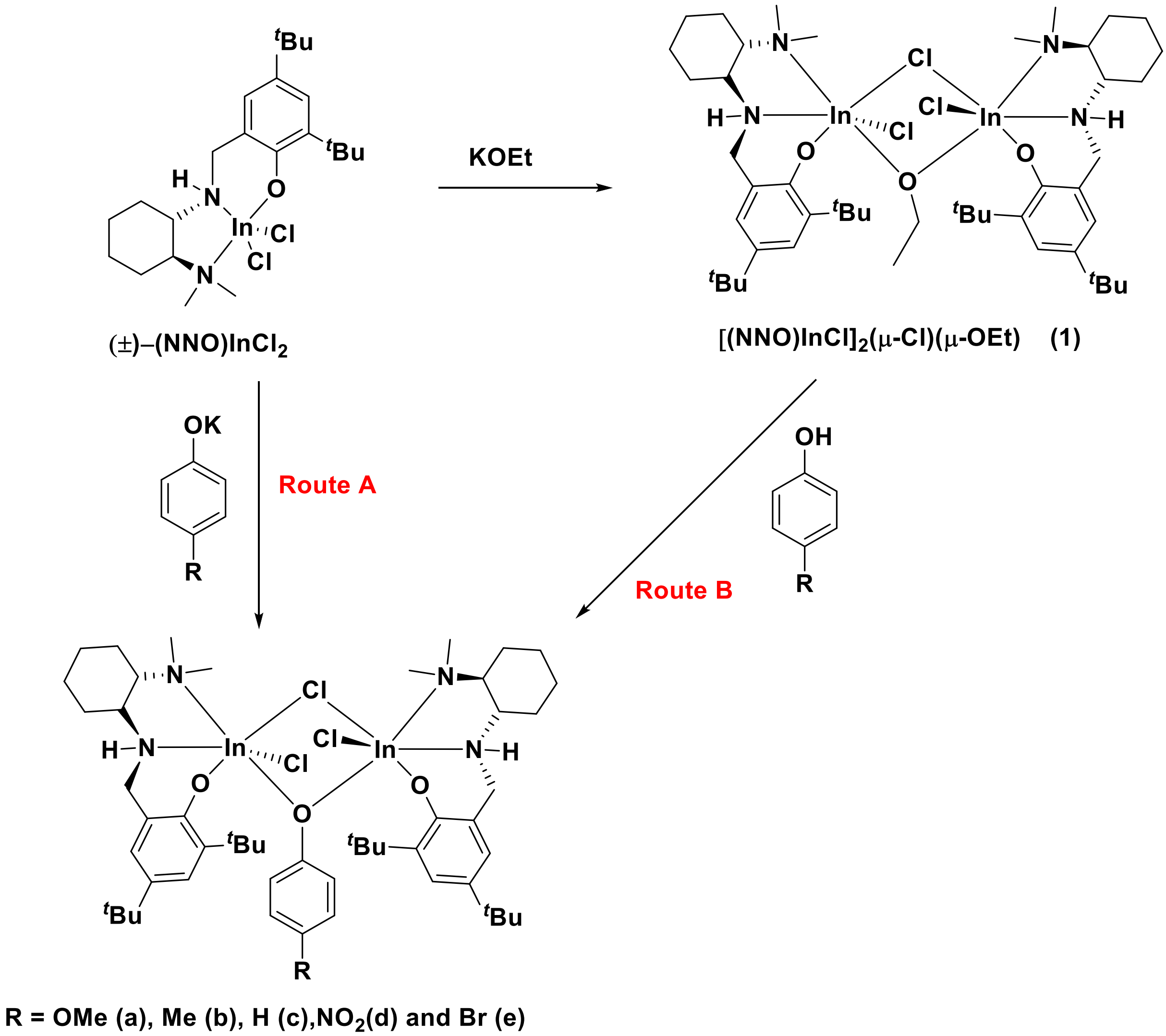
Scheme S20. Synthesis of aluminium complexes.



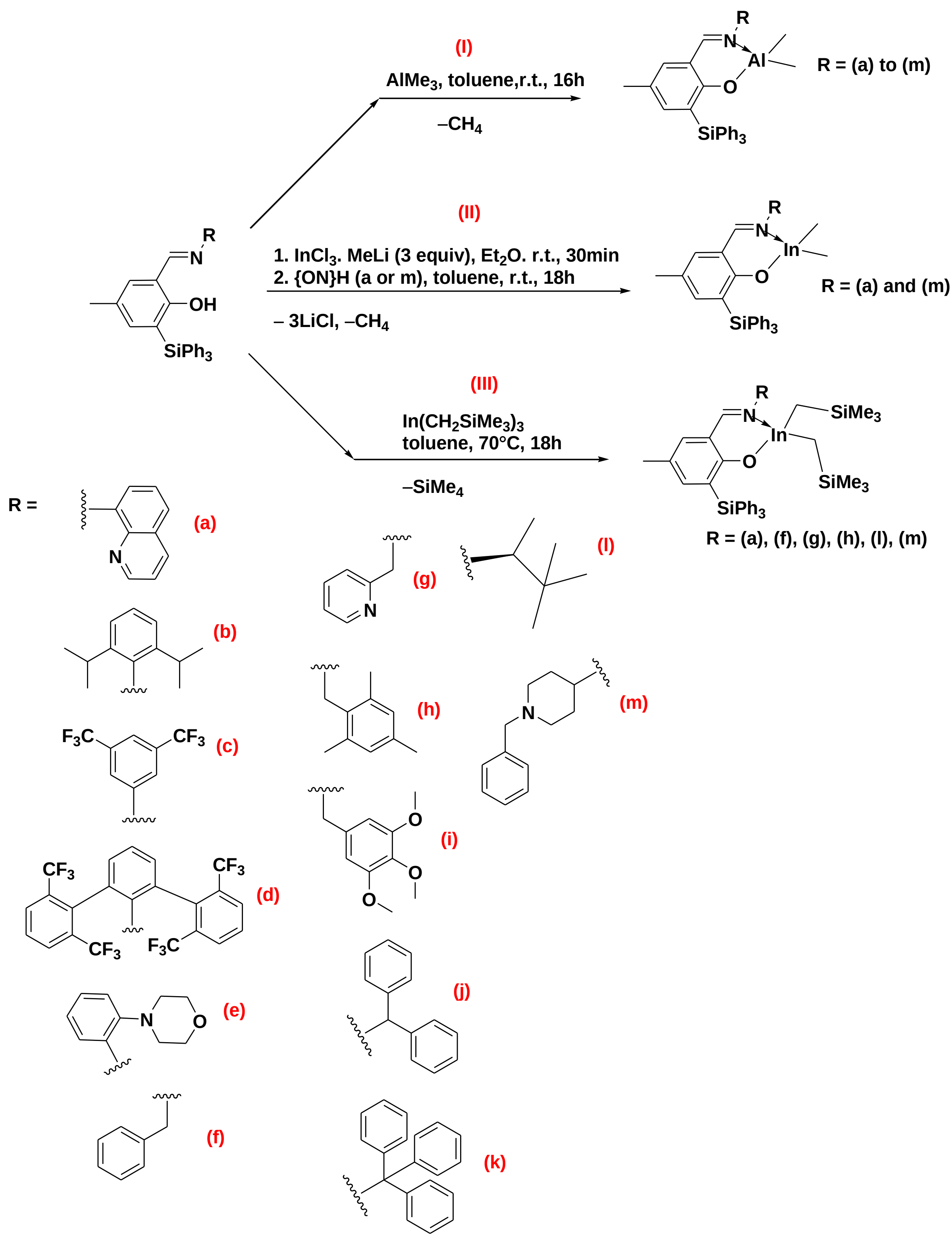
Scheme S21. Synthesis of 1,ω-dithiaalkanediyl bisphenol ligand and aluminium complexes.



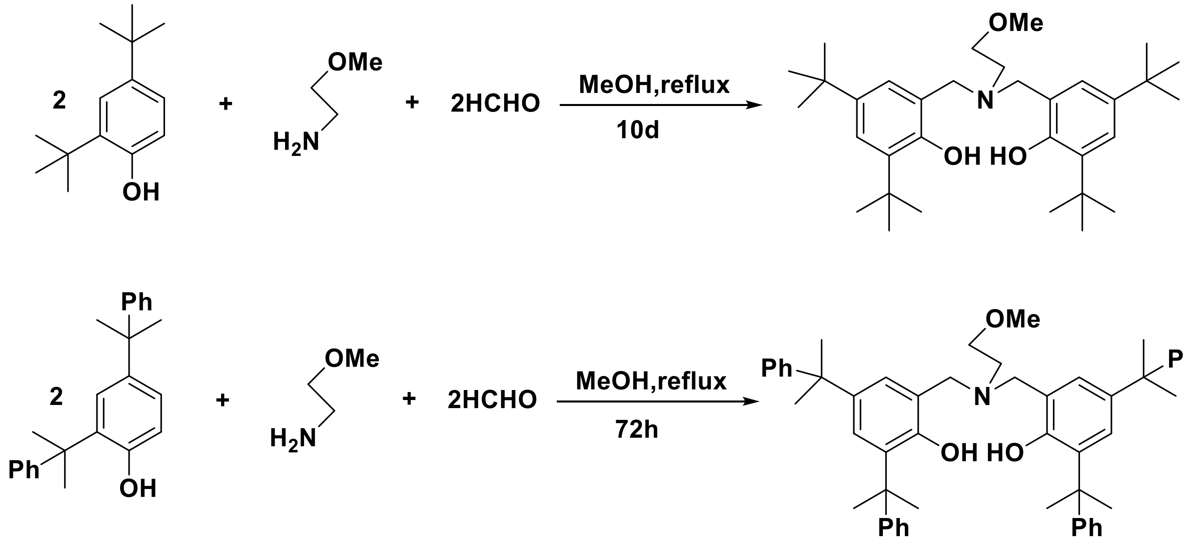
Scheme S22. Synthesis of pyrrolyaldiminate ligand and corresponding aluminium complexes.



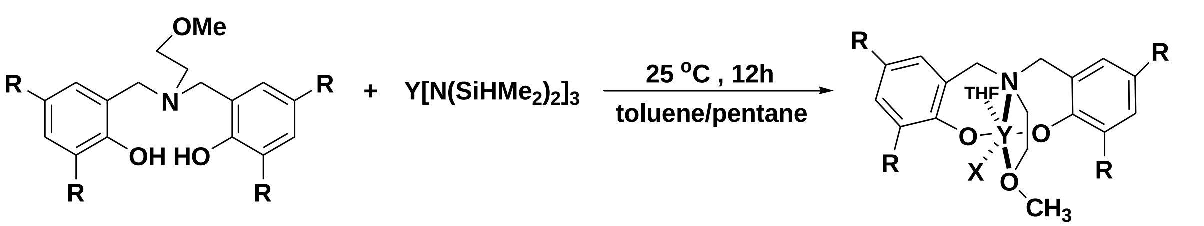
Scheme S23. Synthesis of dinuclear Indium complex.



Scheme S24. Synthetic routes of aluminium and indium complexes.



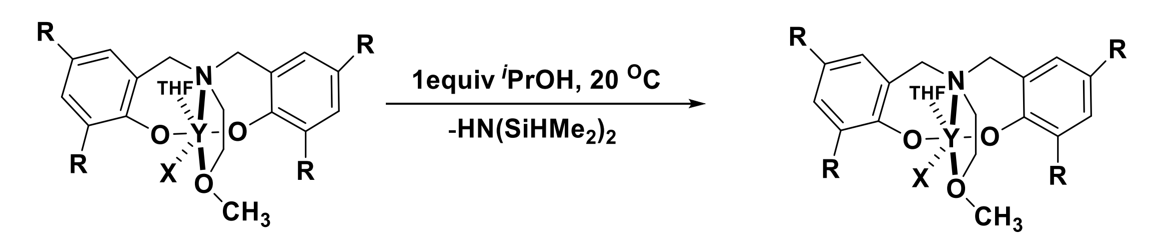
Scheme S25. Synthesis of amino-alkoxy-bis(phenolate) ligands.



a : R = ^{t}Bu
b : R = CMe_2Ph

26a : R = ^{t}Bu , X = $N(SiHMe_2)_2$
26b : R = CMe_2Ph , X = $N(SiMe_2)_2$

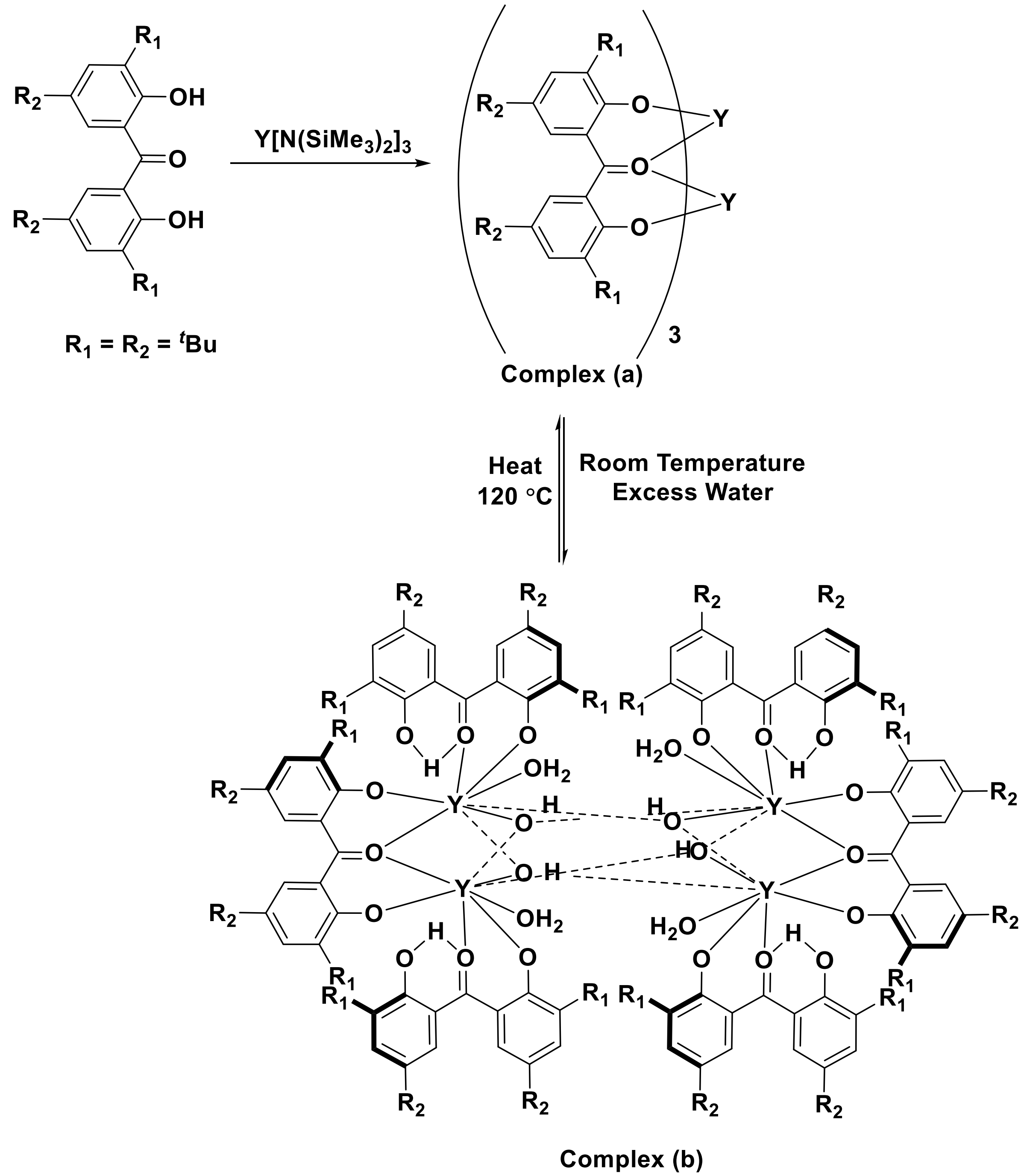
Scheme S26. Synthesis of yttrium amido complexes.



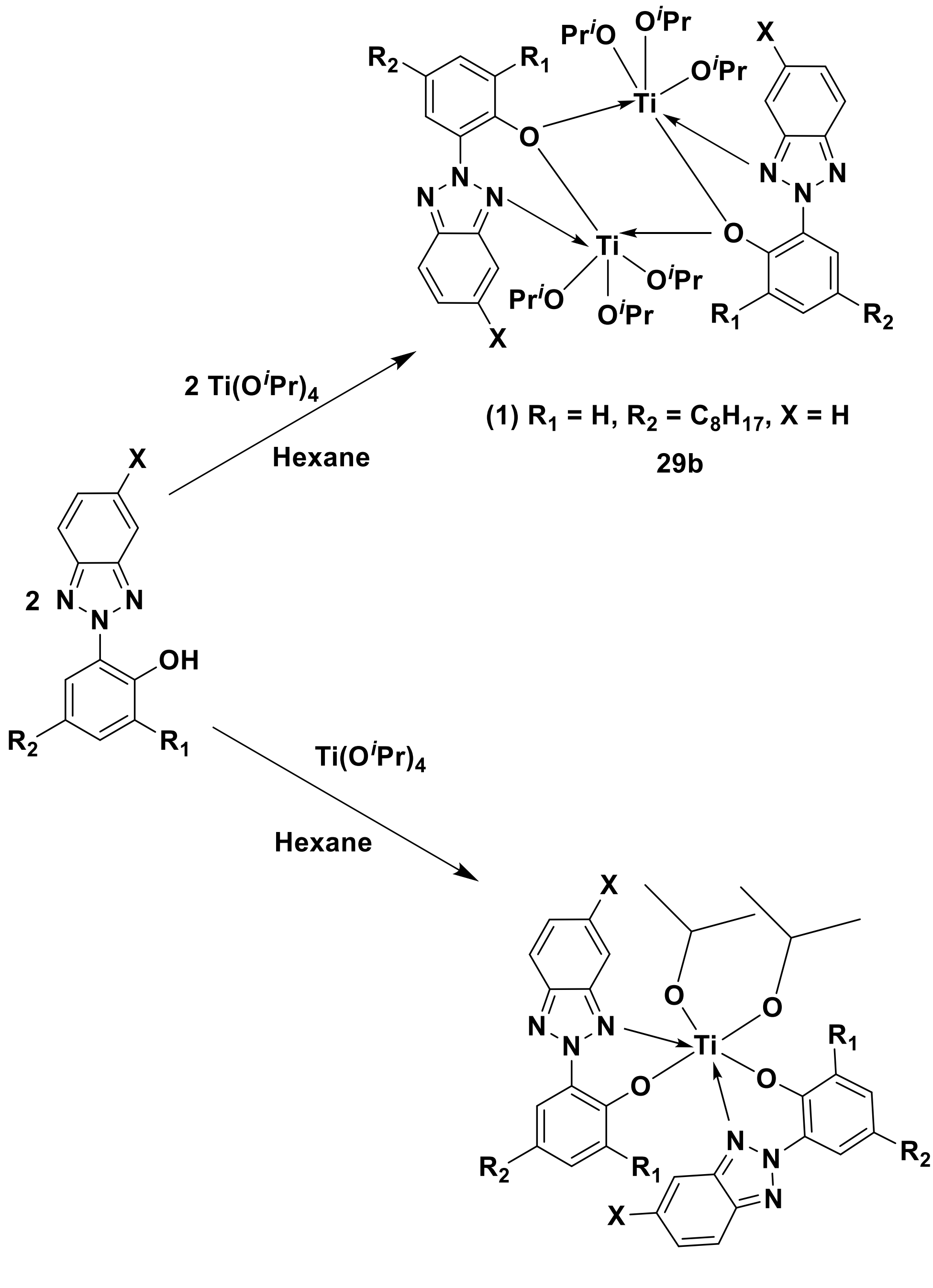
8a : R = ^{t}Bu , X = $N(SiHMe_2)_2$
8b : R = CMe_2Ph , X = $N(SiMe_2)_2$

9a : R = ^{t}Bu , X = O^iPr
9b : R = CMe_2Ph , X = O^iPr

Scheme S27. Synthesis of yttrium isopropoxide complexes.

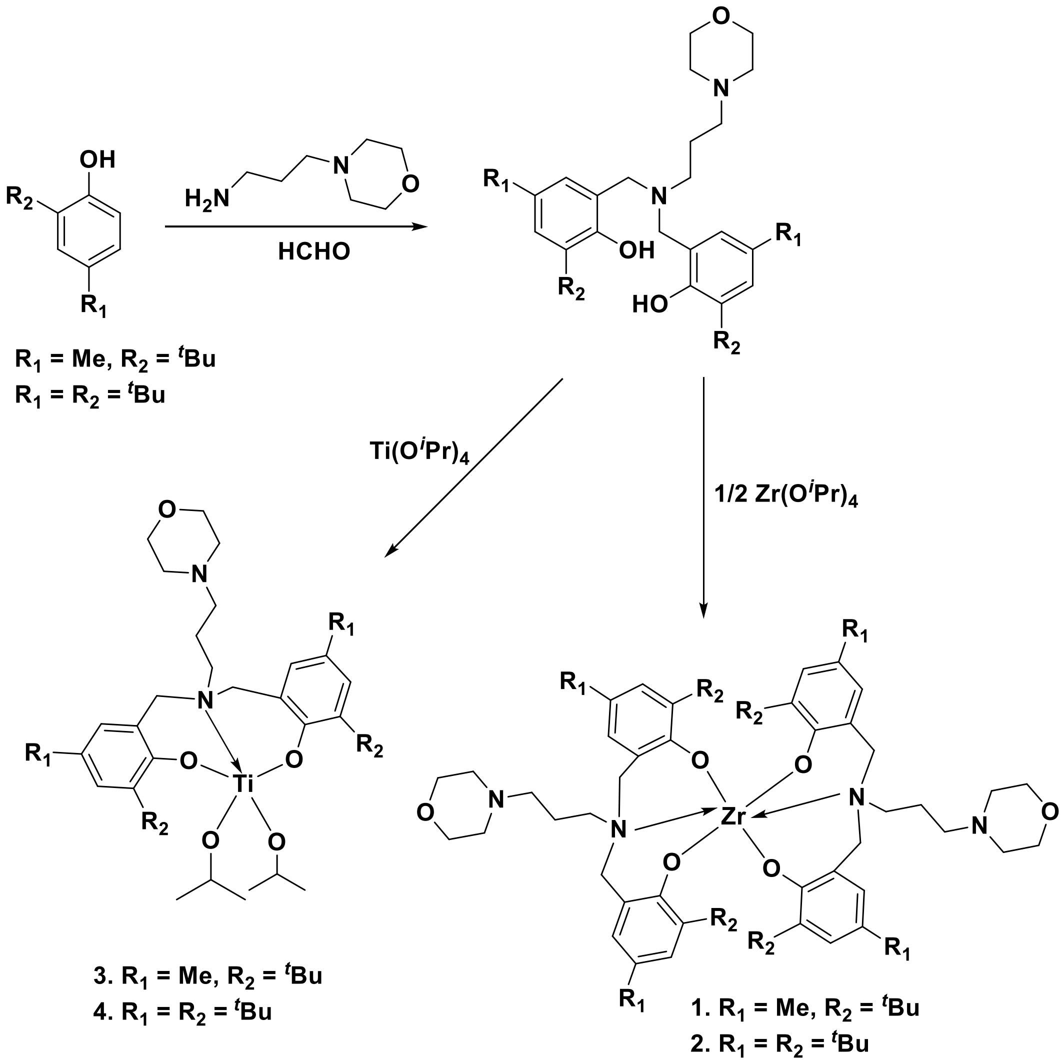


Scheme S28. Synthesis of binuclear yttrium complexes.

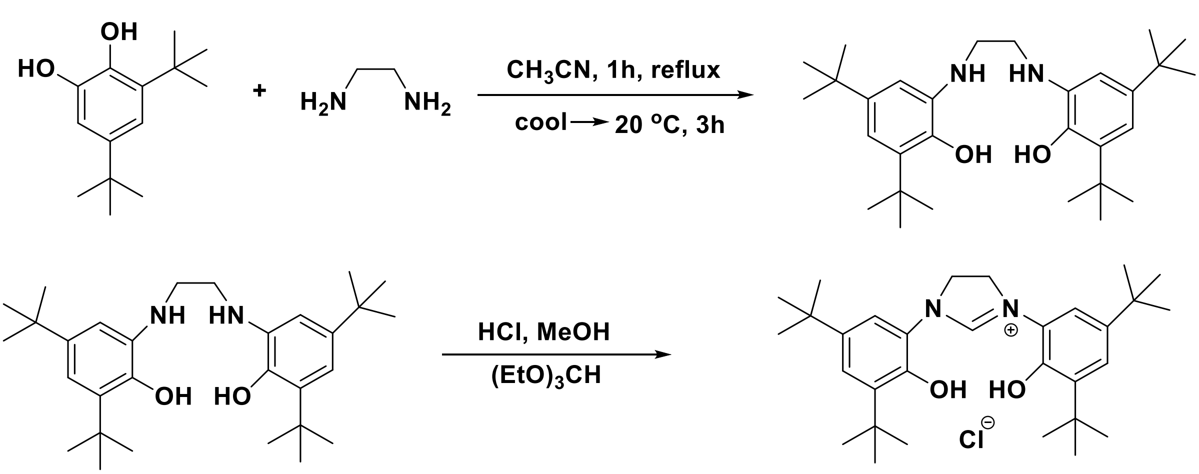


(2) R_1 = H, R_2 = C_8H_{17}, X = H
(3) R_1 = R_2 = ^{t}Bu, X = H
(4) R_1 = ^{t}Bu, R_2 = CH_3, X = Cl
29a

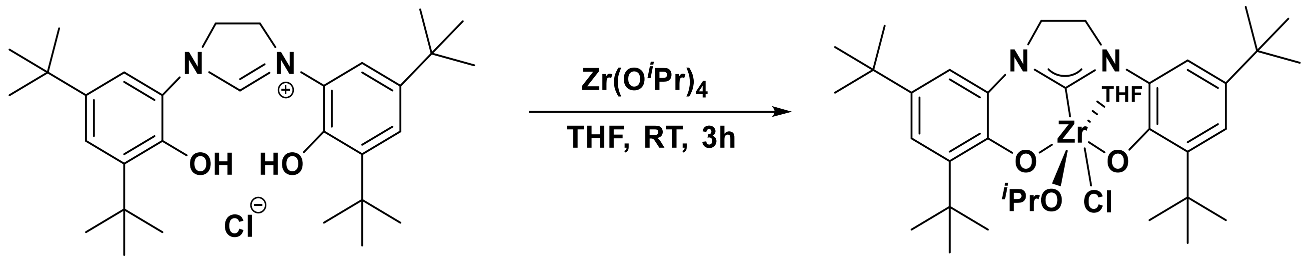
Scheme S29. Synthetic routes for titanium complexes.



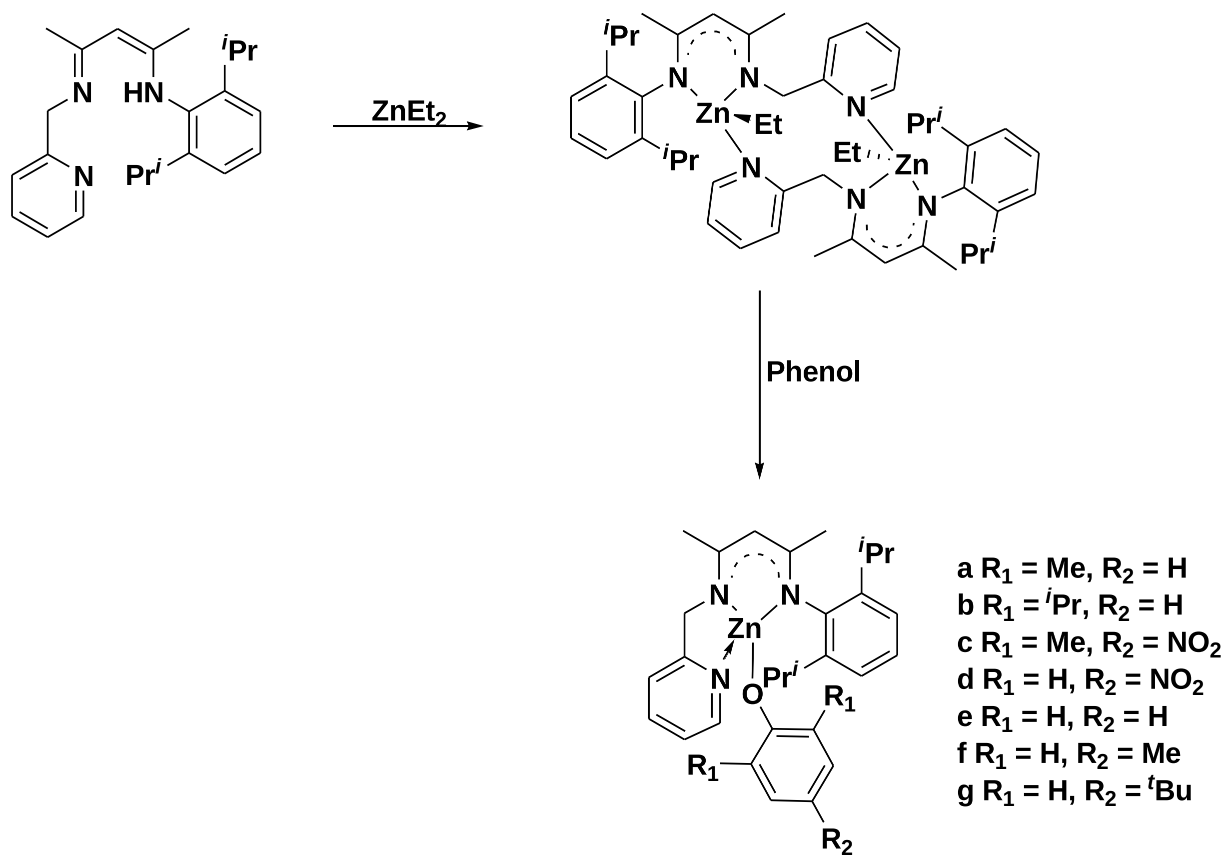
Scheme S30. Synthetic route for Ti and Zr complex.



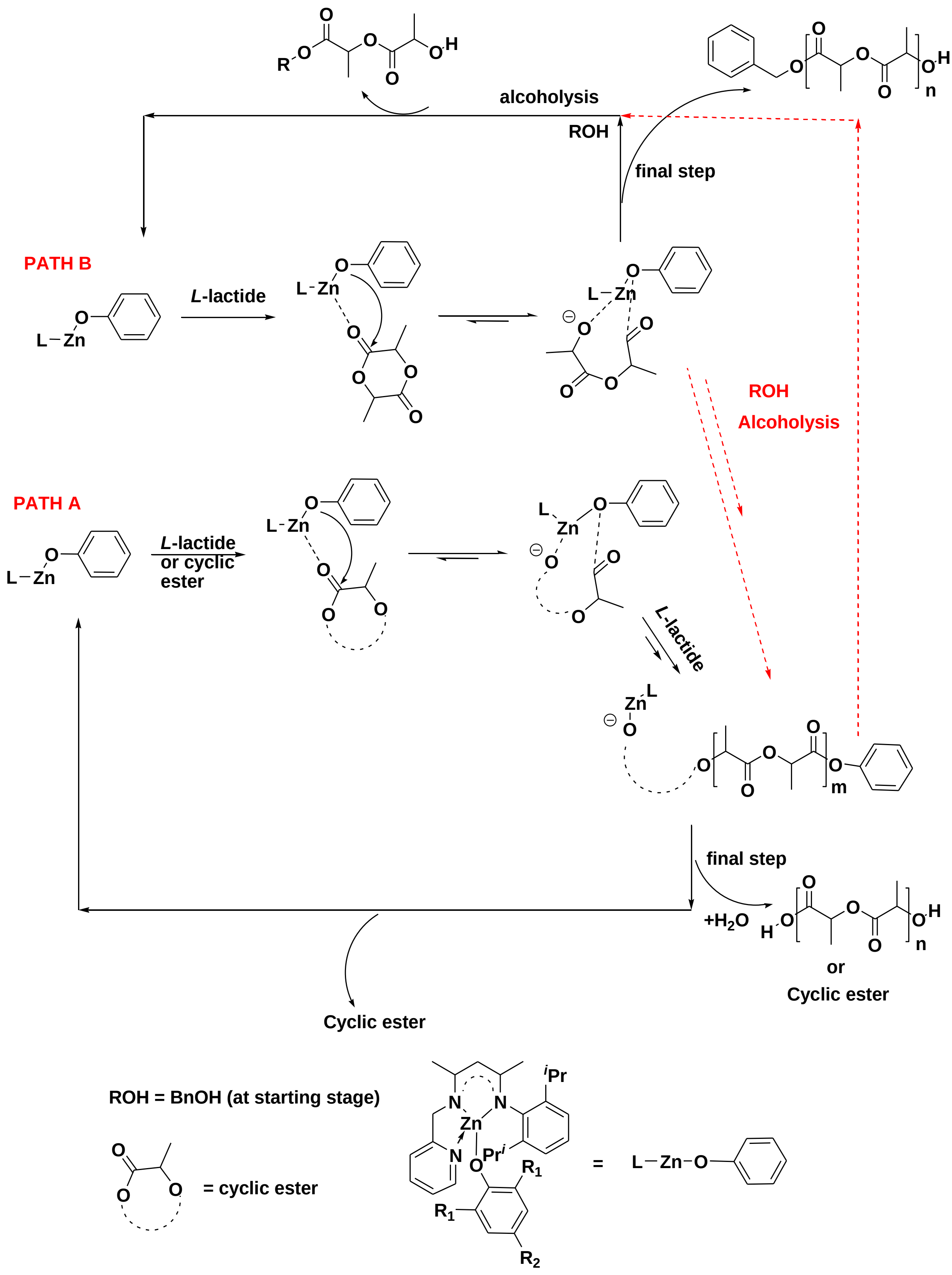
Scheme S31. Synthesis of NHC proligand.



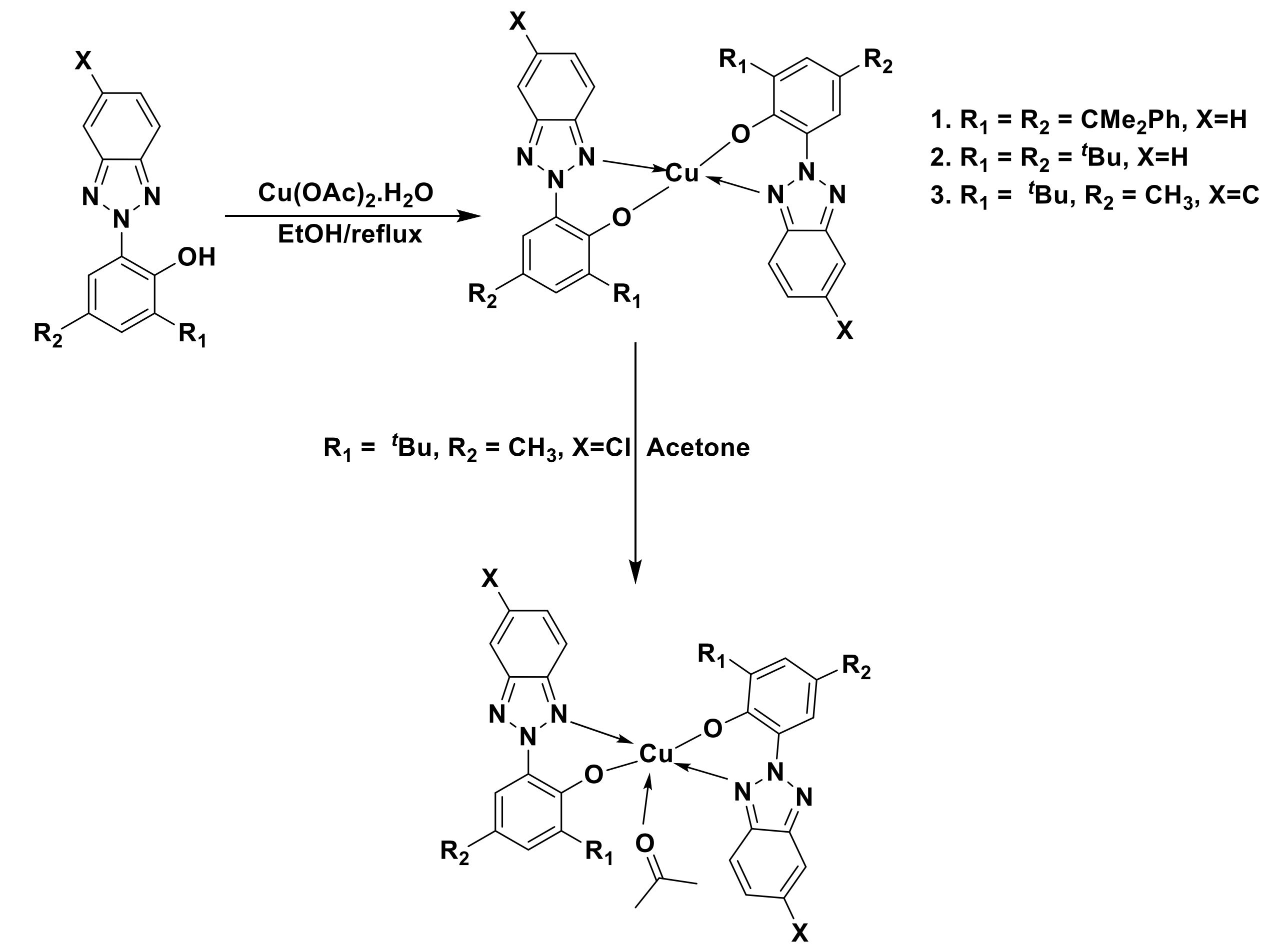
Scheme S32. Synthesis of Zr-NHC isopropoxide complex.



Scheme S33. Synthesis of zinc complex.



Scheme S34. Proposed mechanism for the ROP of lactide.



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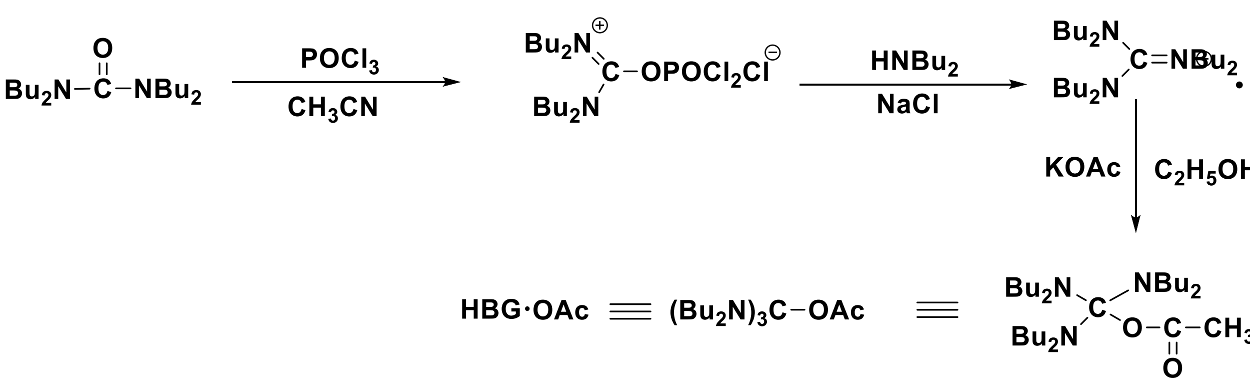
Scheme S35. Synthesis of copper complex.



Scheme S36. Synthesis of HBG·OAc