## Supporting Information

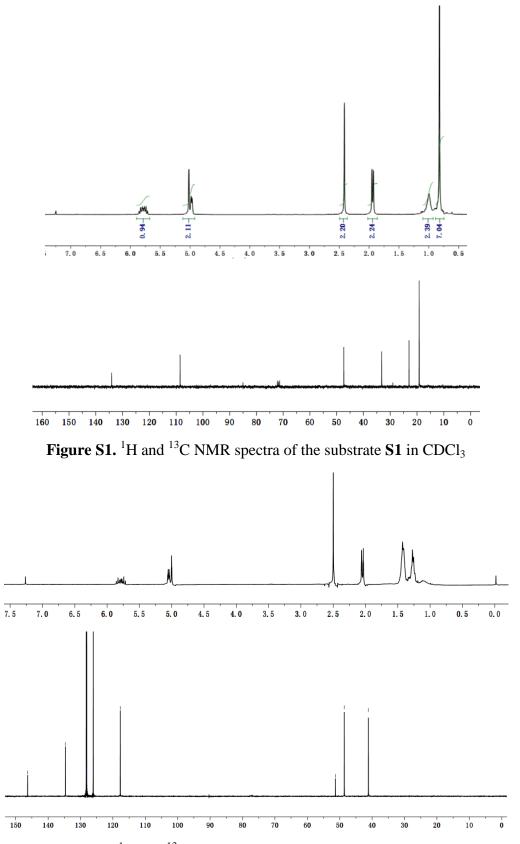
## Rare-Earth-Metal Complexes Supported by New Chiral Tetra-Azane Chelating Ligands: Synthesis, Characterization, and Catalytic Properties for Intramolecular Asymmetric Hydroamination

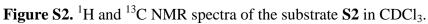
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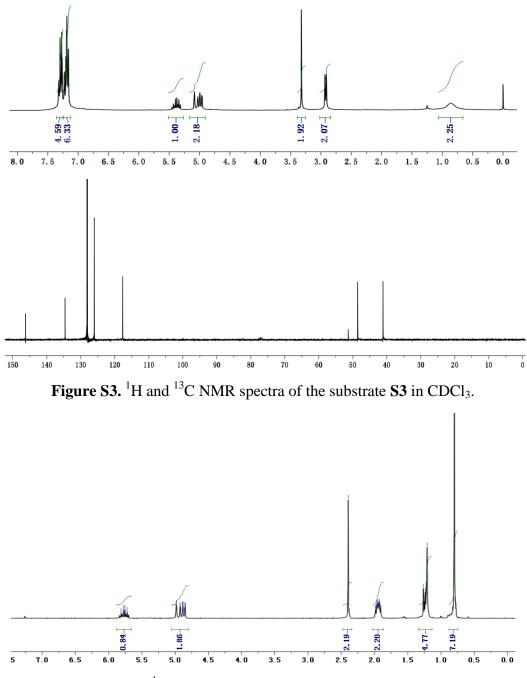
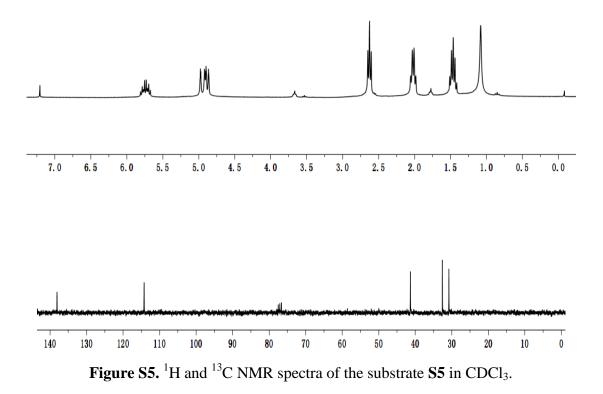


Figure S4. <sup>1</sup>H NMR spectra of the substrate S4 in CDCl<sub>3</sub>.



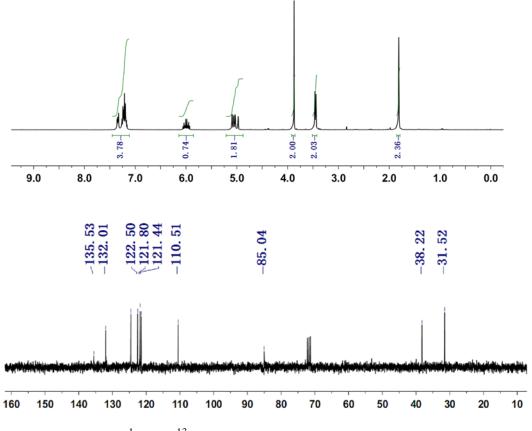
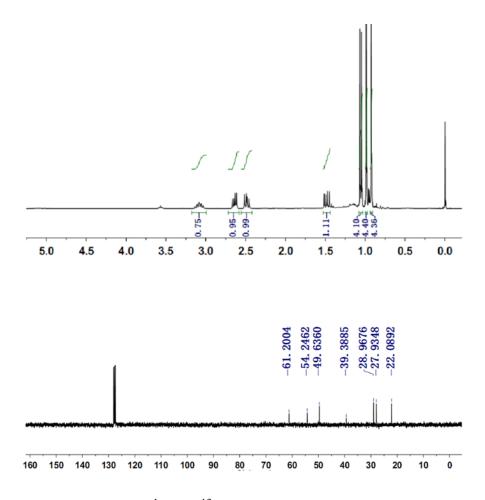


Figure S6. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the substrate S6 in CDCl<sub>3</sub>.



**Figure S7.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **P1** in  $C_6D_6$ .

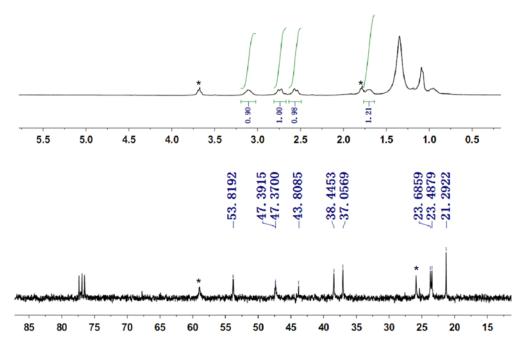


Figure S8. <sup>1</sup>H and <sup>13</sup>C NMR spectra of P2 in CDCl<sub>3</sub>.

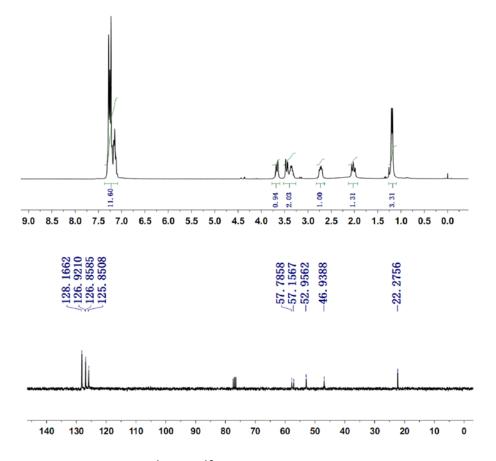
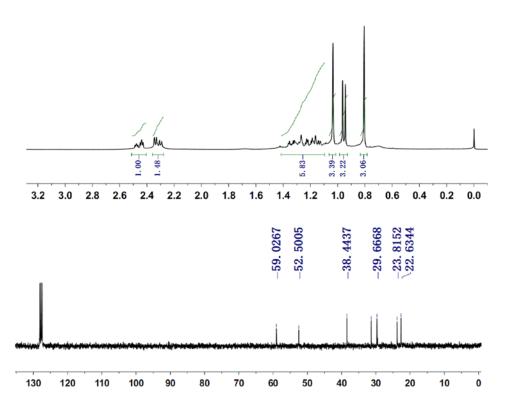
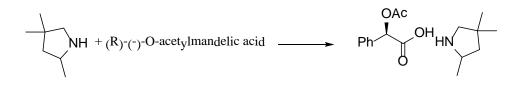


Figure S9. <sup>1</sup>H and <sup>13</sup>C NMR spectra of P3 in CDCl<sub>3</sub>



**Figure S10.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **P4** in  $C_6D_6$ .



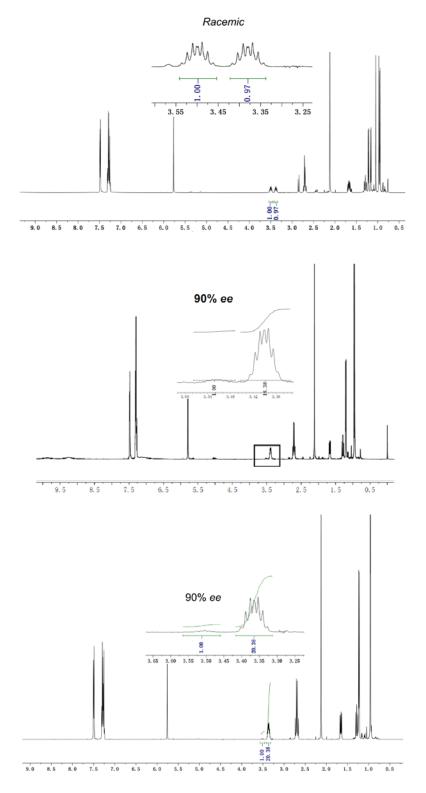


Figure S11. <sup>1</sup>H NMR spectrum of the mixture of P1 and (R)-(-)-O-acetylmandelic acid in  $CDCl_3$ .

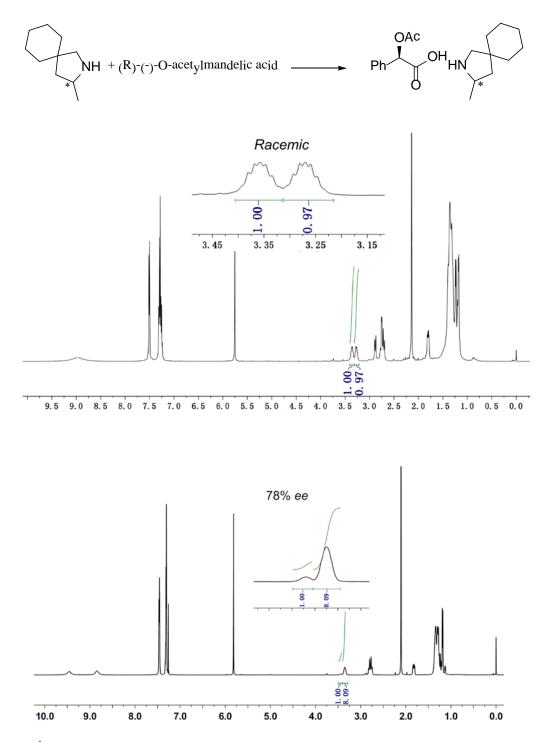


Figure S12. <sup>1</sup>H NMR spectrum of the mixture of P2 and (R)-(-)-O-acetylmandelic acid in  $CDCl_3$ .

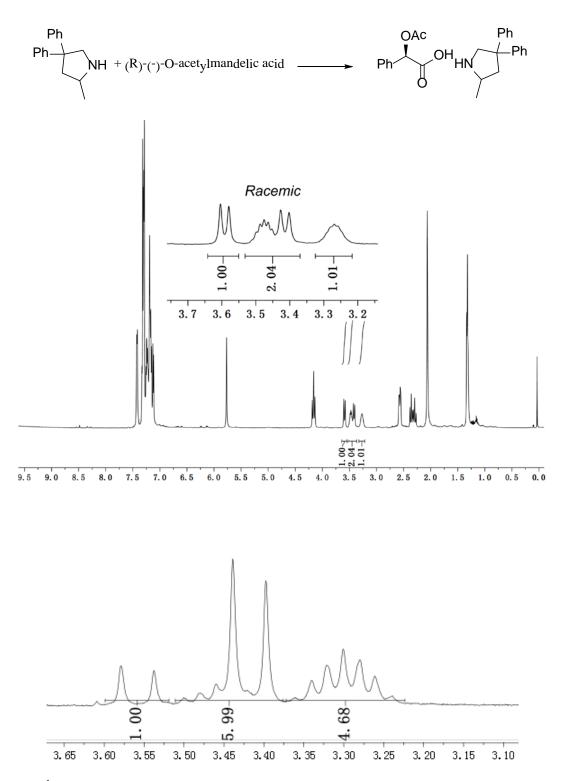


Figure S13. <sup>1</sup>H NMR spectrum of the mixture of P3 and (R)-(-)-O-acetylmandelic acid in CDCl<sub>3</sub>.

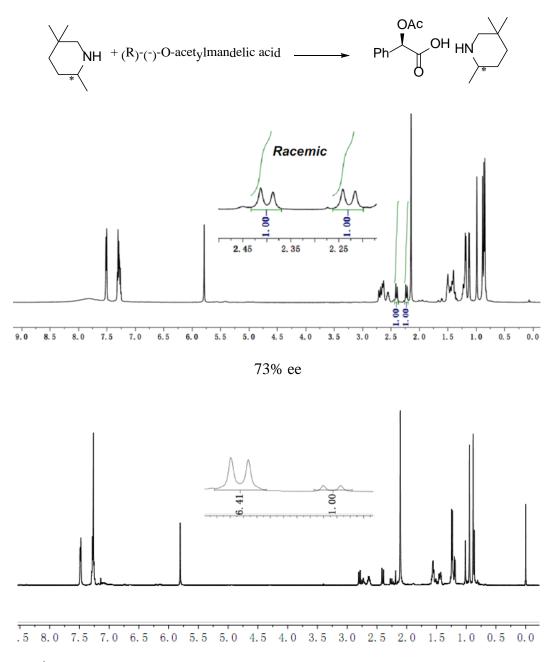


Figure S14. <sup>1</sup>H NMR spectrum of the mixture of P4 and (R)-(-)-O-acetylmandelic acid in CDCl<sub>3</sub>.

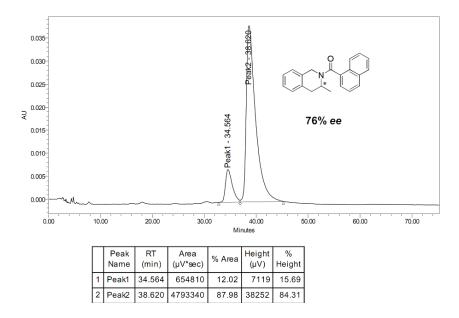


Figure S15. HPLC trace and integration data from the naphthoylamide of P6.

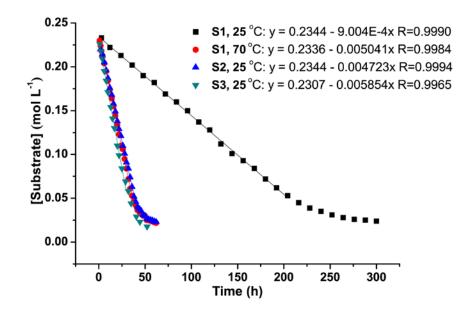
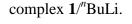


Figure S16. Time dependence of substrate concentration in the hydroamination/cyclization using



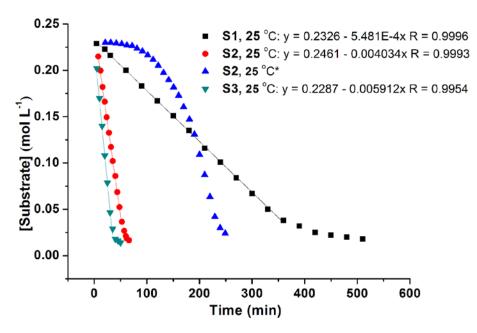


Figure S17. Time dependence of substrate concentration in the hydroamination/cyclization using complex  $2/^{n}$ BuLi: \*The substrate S2 was mixed with butyllithium first , and the complex 2 later.

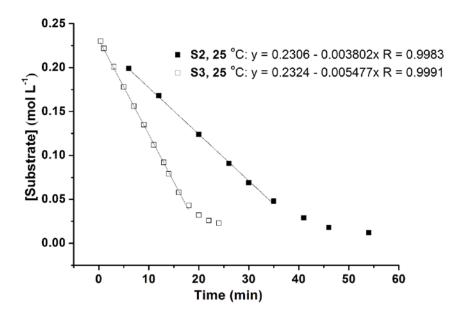


Figure S18. Time dependence of substrate concentration in the hydroamination/ cyclization using

complex  $3/^{n}$ BuLi.

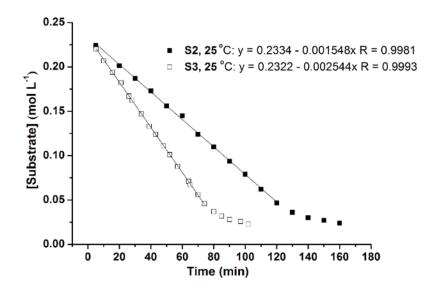


Figure S19. Time dependence of substrate concentration in the hydroamination/ cyclization using

complex  $4/^{n}$ BuLi.

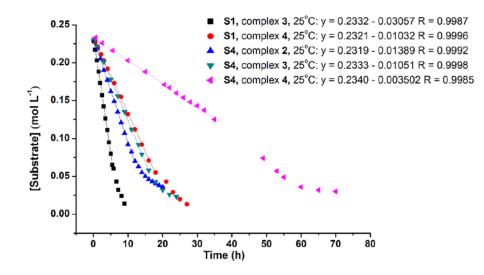


Figure S20. Time dependence of substrate concentration in the hydroamination/ cyclization.