Supporting Information

Bis(((S)-binaphthoxy)(isopropoxy)titanium) Oxide as a μ -Oxo Type Chiral Lewis Acid: Application to Catalytic Asymmetric Allylation of Aldehydes

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Synthesis of Chiral Bis-Ti(IV) Oxide (*S,S*)-1 by Method A. To a stirred solution of TiCl_4 (0.1 mmol) in CH_2Cl_2 (2 mL) was added dried $\text{Ti}(\text{OPr}^i)_4$ (88 μL , 0.3 mmol) at 0 °C under argon. The solution was allowed to warm to room temperature. After 1 h, silver(I) oxide (46.4 mg, 0.2 mmol) was added at room temperature, and the whole mixture was stirred there for 5 h under exclusion of direct light. The mixture was diluted with CH_2Cl_2 (4 mL), and treated with (*S*)-binaphthol (114.5 mg, 0.4 mmol) at room temperature for 2 h to furnish chiral bis-Ti(IV) oxide (*S,S*)-1.

Synthesis of Chiral Bis-Ti(IV) Oxide (*S,S*)-1 by Method B. To a stirred solution of TiCl_4 (0.1 mmol) in CH_2Cl_2 (2 mL) was added dried $\text{Ti}(\text{OPr}^i)_4$ (88 μL , 0.3 mmol) at 0 °C under argon. The solution was allowed to warm to room temperature. After 1 h, (*S*)-binaphthol (114.5 mg, 0.4 mmol) was added at room temperature, and the solution was stirred there for 2 h. The mixture was cooled to 0 °C, and treated with silver(I) oxide (46.4 mg, 0.2 mmol) at 0 °C. The whole mixture was allowed to warm to room temperature, and stirred there for 5 h under exclusion of direct light to furnish chiral bis-Ti(IV) oxide (*S,S*)-1, which was diluted with CH_2Cl_2 (4 mL) before use.

Representative Procedure for Asymmetric Allylation of Aldehydes (by Method A). The in-situ generated (*S,S*)-1 (0.2 mmol) [prepared by Method A] in CH_2Cl_2 (6 mL) was cooled to -15°C, and treated sequentially with hydrocinnamaldehyde (263 μL , 2.0 mmol) and allyltributyltin (682 μL , 2.2 mmol) at -15°C. The whole mixture was allowed to warm to 0°C and stirred there for 4 h. The reaction mixture was quenched with saturated NaHCO_3 , and extracted with ether. The organic extracts were dried over Na_2SO_4 . Evaporation of solvents and purification of the residue by column chromatography on silica gel (ether/hexane = 1:4 as eluent) gave (*R*)-1-phenyl-5-hexen-3-ol as a colorless oil (296.1 mg, 84% yield). The absolute configuration and enantiomeric purity of the product was determined to be *R* and 99% ee by analytical HPLC analysis [Daicel Chiralcel OD, *i*-PrOH/hexane = 1:20, Flow rate = 0.5 mL/min, t_R = 18.86 min ((*S*)-isomer), t_R = 29.17 min ((*R*)-isomer)] in comparison with the racemic and authentic samples.

Asymmetric Allylation with ((S)-Binaphthoxy)Ti=O (5) and (S)-Binaphthoxy-titanium Diisopropoxide (2). ((S)-Binaphthoxy)Ti=O (**5**)¹ and (S)-binaphthoxytitanium diisopropoxide (**2**)² were prepared independently according to the literature procedures, and then asymmetric allylation of hydrocinnamaldehyde with allyltributyltin by mixing of such **5** and **2** (each 10 mol%) at 0 °C for 4 h afforded homoallylic alcohol **4** (R = CH₂CH₂Ph) in 31% yield with 88% ee. Since the sole use of **5** gave product **4** (R = CH₂CH₂Ph) in 20% yield with 5% ee, mixing of **5** and **2** seems to partially generate bis-Ti(IV) oxide **1**. Indeed, by refluxing a mixture of **5** and **2** in CH₂Cl₂ for 3 h, we observed higher reactivity and selectivity (78% yield with 94% ee) in this allylation under similar conditions.

Asymmetric Allylation with (S)-Binaphthoxytitanium μ -Oxo Complex 6. asymmetric allylation of hydrocinnamaldehyde with allyltributyltin in the presence of (S)-binaphthoxytitanium μ -oxo complex **6** at 0 °C for 4 h afforded homoallylic alcohol **4** (R = CH₂CH₂Ph) in 14% yield with 25% ee.³

Asymmetric Allylation with Keck's Reagent. Keck's mono-Ti(IV) reagent (20 mol%) derived from Ti(OPr^{*i*})₄ (20 mol%) and (S)-binaphthol (40 mol%) was utilized for the asymmetric allylation of hydrocinnamaldehyde with allyltributyltin at 0 °C for 4 h to furnish homoallylic alcohol **4** (R = CH₂CH₂Ph) in 53% yield with 93% ee.⁴

References

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