

Supporting Information Available.

Typical example of the asymmetric amplification of the enantioselective hetero Diels-Alder reaction: To a suspension of **Yb-5** (36.4 mg, 0.03 mmol) prepared from 34% ee of (*R*)-BNPH by the method II [for the preparation of the Yb(BNP)₃ complex, see refernce 8] and 2,6-lutidine (3.2 mg, 0.03 mmol) in dichloromethane (1 ml) was added aldehyde **1a** (10.6 mg, 0.10 mmol) and diene **2** (25.8 mg, 0.15 mmol) under argon. The mixture was stirred for 20 h at room temperature, and then successively treated with three drops of trifluoroacetic acid and four drops of pyridine. The resulting mixture was directly subjected to column chromatography on silica gel to give (*R*)-**4a** (12.7 mg, 73%), the enantiomeric purity of which was determined to be 90% ee by HPLC using DAICEL CHIRALCEL OD (2-propanol/hexane=1:9, flow rate 1.0 ml/min, *t*_R 16.1 min [13.8 min for (*S*)-enantiomer]).

Determination of the optical purity of the component ligand of the complex Yb-9: To a solution of **Yb-9** (21.2 mg, 0.017 mmol) in THF (1 ml) was added a 1 M solution of LiAlH₄ in ether (170 μ l, 0.17 mmol) at 0 °C under argon. The mixture was stirred at room temperature for 46 h, and then quenched with dilute hydrochloric acid. The crude product was extracted with dichloromethane and dried over anhydrous MgSO₄. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel to give (*R*)-BINOL (13.9 mg, 93%), the optical purity of which was determined to be 98% ee by HPLC using DAICEL CHIRALPAK AD (ethanol/hexane=1:9, flow rate 0.5 ml/min, *t*_R 44.0 min [49.1 min for (*S*)-enantiomer]).