

SUPPORTING INFORMATION

Title: Catalytic Asymmetric Alkylation of Aldehydes by Using Trialkylboranes

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General

Aldehydes and titanium tetraisopropoxide were used after distillation. (*R*)-3-(3,5-Diphenylphenyl)-1,1'-bi-2-naphthol (DPP-BINOL **3**)^[1] and (*R*)-3-(3,5-diphenylphenyl)-H₈-BINOL (DPP-H₈-BINOL **4**)^[2] was prepared according to the reported procedure. Triethylborane (1M in THF) and tributylborane (1M in THF) were purchased from Aldrich and used without titration.

Ee Determination of Alkylation Products **5a–m** and **6**.

1-Naphthalen-1-yl-propan-1-ol (**5a**) (HPLC analysis using a Chiralcel OD column, 0.8 mL/min, 10% *i*-PrOH in hexane); retention times: 16.8 min (major *R*-enantiomer) and 9.9 min (minor *S*-enantiomer). 1-Phenylpropan-1-ol (**5b**) (HPLC analysis using a Chiralcel OD column, 1.0 mL/min, 3% *i*-PrOH in hexane); retention times: 13.0 min (major *R*-enantiomer) and 16.2 min (minor *S*-enantiomer). 1-*p*-Tolylpropan-1-ol (**5c**) (HPLC analysis using a Chiralcel OD column, 1.0 mL/min, 0.1% *i*-PrOH in hexane); retention times: 63.4 min (major *R*-enantiomer) and 79.8 min (minor *S*-enantiomer). 1-Biphenyl-4-yl-propan-1-ol (**5d**) (HPLC analysis using a Chiralcel AD-H column, 1.0 mL/min, 4% *i*-PrOH in hexane); retention times: 13.1 min (major *R*-enantiomer) and 11.8 min (minor *S*-enantiomer). 1-(4-Chlorophenyl)propan-1-ol (**5e**) (HPLC analysis using a Chiralcel OD column, 1.0 mL/min, 2.5% *i*-PrOH in hexane); retention times: 13.1 min (major *R*-enantiomer) and 12.3 min (minor *S*-enantiomer). 1-(4-Fluorophenyl)propan-1-ol (**5f**) (GC analysis using a BETA DEX 225 column (30 m), 1.8 kg/cm², initial temperature 100 °C for 30 min, and then 1 °C/min ramp to 170 °C), 35.8 min (major *R*-enantiomer) and 39.7 min (minor *S*-enantiomer). 1-(4-Trifluoromethylphenyl)propan-1-ol (**5g**) (GC analysis using a BETA DEX 225 column (30 m), 1.8 kg/cm², initial temperature 100 °C for 30 min, and then 1 °C/min ramp to 130 °C), 45.0 min (major *R*-enantiomer) and 47.6 min (minor *S*-enantiomer). 1-(3-Methoxyphenyl)propan-1-ol (**5h**) (HPLC analysis using a Chiralcel OD column, 1.0 mL/min, 1% *i*-PrOH in hexane); retention times: 48.5 min (major *R*-enantiomer) and 63.0 min (minor *S*-enantiomer). 1-(2-

^[1] T. Harada, K. Kanda, *Org. Lett.* **2006**, 8, 3817.

^[2] T. Ukon, T. Harada, *Tetrahedron: Asymmetry* **2007**, 18, 2499.

Chlorophenyl)propan-1-ol (**5i**) (HPLC analysis using a Chiralcel OB column, 1.0 mL/min, 1% *i*-PrOH in hexane); retention times: 9.8 min (major *R*-enantiomer) and 8.5 min (minor *S*-enantiomer). Naphthalen-2-yl-propan-1-ol (**5j**) (HPLC analysis using a Chiralcel OD column, 0.8 mL/min, 10% *i*-PrOH in hexane); retention times: 14.2 min (major *R*-enantiomer) and 12.5 min (minor *S*-enantiomer). 1-Furan-2-yl-propan-1-ol (**5k**) (HPLC analysis of the benzoate derivative using a Chiralcel AD-H column, 0.5 mL/min, 2% *i*-PrOH in hexane); retention times: 13.0 min (major *R*-enantiomer) and 15.1 min (minor *S*-enantiomer). 1-Phenyl-pent-1-en-3-ol (**5l**) (HPLC analysis using a Chiralcel OD column, 1.0 mL/min, 3% *i*-PrOH in hexane); retention times: 20.1 min (major *R*-enantiomer) and 35.3 min (minor *S*-enantiomer). 1-Phenyl-pentan-3-ol (**5m**) (HPLC analysis using a Chiralcel OD column, 1.0 mL/min, 2% *i*-PrOH in hexane); retention times: 19.8 min (major *R*-enantiomer) and 33.8 min (minor *S*-enantiomer). 1-Naphthalen-1-yl-pentan-1-ol (**6**) (HPLC analysis using a Chiralcel OD column, 1.0 mL/min, 2% *i*-PrOH in hexane); retention times: 46.1 min (major *R*-enantiomer) and 24.0 min (minor *S*-enantiomer).