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Supporting Information

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Catalytic Asymmetric Alkylation of Aldehydes with Grignard Reagents

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General

Dichloromethane was dried and distilled over CaH_2. Aldehydes and titanium tetraisopropoxide were used after distillation. (*R*)-3-(3,5-Diphenylphenyl)-1,1'-bi-2-naphthol (DPP-BINOL) was prepared according to the reported procedure.[1] Following Grignard reagents were purchased from Aldrich and used without titration; BuMgCl (2M in Et_2O), PrMgCl (2M in Et_2O), EtMgCl (2M in Et_2O and 1.6M in THF), EtMgBr (3M in Et_2O), MeMgCl (3M in THF), and PhMgBr (3M in Et_2O).

Pinacol-Coupling Byproducts

The yield of pinacol-coupling byproducts ($R^1CH(OH)CH(OH)R^1$) is summarized in ***Table S-1***.

Table S-1. Yield of Pinacol-Coupling Byproducts [a]

entry	yield (%)	entry	yield (%)	entry	yield (%)
1	4	9	6	17	[c]
2	7	10	26	18	[c]
3	7	11	9	19	[d]
4	10	12	32	20	[d]
5	31	13	5	21	[d]
6	9 [b]	14	22	22	23
7	44	15	3		
8	6	16	22		

[a] Isolated yield unless otherwise noted. The entry numbers correspond to those of Table 1.
[b] The yield was determined by 1H NMR. [c] Not observed. [d] Not determined.

Ee Determination of Product 1–5.

1-Phenylpentan-1-ol (**1a**) (HPLC analysis using a Chiralcel OD column, 1.0 mL/min, 2% *i*-PrOH in hexane); retention times: 11.8 min (major *R*-enantiomer) and 14.7 min (minor *S*-enantiomer). 1-Phenylbutan-1-ol (**1b**) (HPLC analysis using a Chiralcel OB column, 0.5 mL/min, 3% *i*-PrOH in hexane); retention times: 17.8 min (major *R*-enantiomer) and 15.7 min (minor *S*-enantiomer). 1-Phenylpropan-1-ol (**1c**) (HPLC analysis using a Chiralcel OD column, 1.0 mL/min, 3% *i*-PrOH in hexane); retention times:

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

12.5 min (major *R*-enantiomer) and 15.1 min (minor *S*-enantiomer). 1-*p*-Tolylpentan-1-ol (**1d**) (HPLC analysis using a Chiralcel OJ column, 1.0 mL/min, 0.5% *i*-PrOH in hexane); retention times: 41.6 min (major *R*-enantiomer) and 45.1 min (minor *S*-enantiomer). 1-*p*-Tolylpentan-1-ol (**1e**) (HPLC analysis using a Chiralcel OD column, 1.0 mL/min, 0.1% *i*-PrOH in hexane); retention times: 75.4 min (major *R*-enantiomer) and 86.8 min (minor *S*-enantiomer). 1-(4-Trifluoromethylphenyl)pentan-1-ol (**1f**) (GC analysis using a BETA DEX 225 column (30 m), 1.8 kg/cm^2, initial temperature 80 ºC, 1 ºC/min ramp to 170 ºC), 17.8 min (major *R*-enantiomer) and 15.7 min (minor *S*-enantiomer). 1-(3-Methoxyphenyl)pentan-1-ol (**1g**) (HPLC analysis using a Chiralcel OD column, 1.0 mL/min, 1% *i*-PrOH in hexane); retention times: 51.3 min (major *R*-enantiomer) and 55.3 min (minor *S*-enantiomer). 1-(3-Methoxyphenyl)propan-1-ol (**1h**) (HPLC analysis using a Chiralcel OD column, 1.0 mL/min, 1% *i*-PrOH in hexane); retention times: 53.0 min (major *R*-enantiomer) and 66.4 min (minor *S*-enantiomer). 1-(2-Chlorophenyl)pentan-1-ol (**1i**) (HPLC analysis using a Chiralcel OD column, 0.5 mL/min, 6% *i*-PrOH in hexane); retention times: 51.3 min (major *R*-enantiomer) and 55.3 min (minor *S*-enantiomer). 1-(2-Chlorophenyl)propan-1-ol (**1j**) (HPLC analysis using a Chiralcel OB column, 1.0 mL/min, 1% *i*-PrOH in hexane); retention times: 9.79 min (major *R*-enantiomer) and 8.45 min (minor *S*-enantiomer). 1-Naphthalen-1-yl-pentan-1-ol (**2a**) (HPLC analysis using a Chiralcel OD column, 1.0 mL/min, 2% *i*-PrOH in hexane); retention times: 30.3 min (major *R*-enantiomer) and 60.2 min (minor *S*-enantiomer). 1-Naphthalen-1-yl-propan-1-ol (**2b**) (HPLC analysis using a Chiralcel OD column, 0.8 mL/min, 9% *i*-PrOH in hexane); retention times: 21.3 min (major *R*-enantiomer) and 11.5 min (minor *S*-enantiomer). 1-Naphthalen-1-yl-ethan-1-ol (**2c**) (HPLC analysis using a Chiralcel OD column, 1.0 mL/min, 3% *i*-PrOH in hexane); retention times: 41.9 min (major *R*-enantiomer) and 27.0 min (minor *S*-enantiomer). Naphthalen-1-yl-phenyl-methanol (**2d**) (HPLC analysis using a Chiralcel OJ column, 1.0 mL/min, 2% *i*-PrOH in hexane); retention times: 17.3 min (major *R*-enantiomer) and 12.9 min (minor *S*-enantiomer). 1-Naphthalen-2-yl-pentan-1-ol (**3**) (HPLC analysis using a Chiralcel OD column, 0.8 mL/min, 9% *i*-PrOH in hexane); retention times: 14.1 min (major *R*-enantiomer) and 12.4 min (minor *S*-enantiomer). 1-Phenyl-hept-1-en-3-ol (**4a**) (HPLC analysis using a Chiralcel OB column, 0.5 mL/min, 9% *i*-PrOH in hexane); retention times: 11.8 min (major *R*-enantiomer) and 14.1 min (minor *S*-enantiomer). 2-Methyl-hept-1-en-3-ol (**4b**) (HPLC analysis of the benzoate derivative using a Chiralcel OB column, 0.5 mL/min, 0.1% *i*-PrOH in hexane); retention times: 15.0 min (major *R*-enantiomer) and 15.9 min (minor *S*-enantiomer). 1-Phenyl-pentan-3-ol (**5**) (HPLC analysis using a Chiralcel OD column, 1.0 mL/min, 2% *i*-PrOH in hexane); retention times: 17.9 min (major *R*-enantiomer) and 29.4 min (minor *S*-enantiomer).