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# Supporting Information

# Catalytic Asymmetric Aryl Transfer Reactions to Aldehydes with Grignard Reagents as Aryl Source

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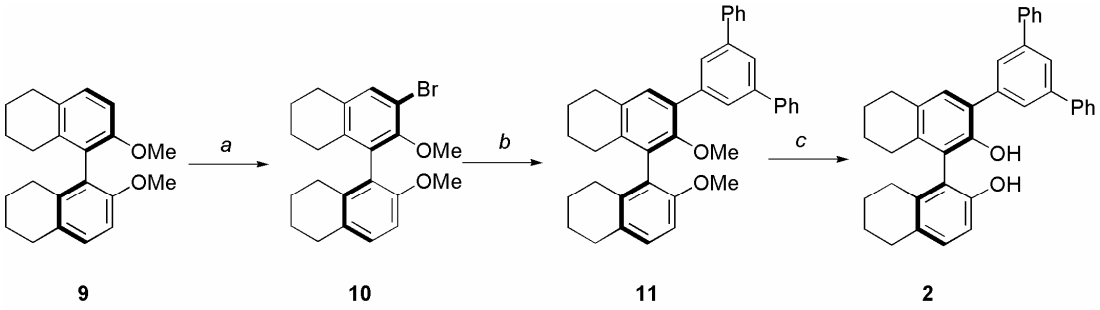
**General.** Dichloromethane was dried and distilled over $CaH_2$. $Et_2O$ was distilled from sodium benzophenone ketyl. Aldehydes and titanium tetraisopropoxide were used after distillation. Following Grignard reagents were purchased from Aldrich and used without titration; PhMgBr (3M in $Et_2O$), *p*-$MeC_6H_4MgBr$ (0.5M in $Et_2O$), *p*-$ClC_6H_4MgBr$ (1M in $Et_2O$), *p*-$FC_6H_4MgBr$ (2M in $Et_2O$), *o*-$MeOC_6H_4MgBr$ (1M in $Et_2O$), 2,4,6-$Me_3C_6H_2MgBr$ (1M in $Et_2O$), *i*PrMgCl (2M in $Et_2O$ and 2M in THF), *c*$C_5H_9MgCl$ (2.0M in $Et_2O$).




**9** **10** **11** **2**

*a* $Br_2$ (1 equiv), $CH_2Cl_2$. *b* 3,4-$Ph_2C_6H_3B(OH)_2$, $Pd(PPh_3)_4$ (5 mol%), $Ba(OH)_2{\cdot}8H_2O$, aqueous dioxane.
*c* $BBr_3$, $CH_2Cl_2$.

**(*R*)-3-Bromo-2,2'-dimethoxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl (10)**. Bromine (0.19 M in dichloromethane, 9.8 mL, 1.86 mmol) was added to a solution of (*R*)-2,2'-dimethoxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl (**9**)[1] (0.600 g, 1.86 mmol) in dichloromethane (28 mL) at 0 °C. After being stirred for 5 min, the red solution was poured into a 5% solution of $NaHSO_3$, and the mixture was extracted three times with dichloromethane. The combined organic layers were dried ($MgSO_4$) and concentrated in *vacuo*. The residue was purified by a silica gel flash chromatography (1 % ethyl acetate and 25% toluene in hexane) to give 0.496 g (66 % yield) of **10** as an amorphous solid: $^1$H NMR (500 MHz; $CDCl_3$) δ 1.58–1.73 (8H, m), 1.98–2.04 (2H, m), 2.22 (1H, m), 2.35 (1H, m), 2.71–2.83 (4H, m), 3.46 (3H, s), 3.71 (3H, s), 6.76 (1H, d, *J* = 8.4 Hz), 7.08 (1H, d, *J* = 8.4 Hz), 7.29 (1H, s); $^{13}$C NMR (125.8 MHz; $CDCl_3$) δ 22.7, 22.8, 23.0, 23.1, 26.8, 27.2, 29.3, 29.4, 107.8, 113.8, 124.8, 129.1, 129.7, 132.4, 132.7, 134.6, 136.6, 136.7, 151.9, 154.3.

**(*R*)-3-(3,5-Diphenylphenyl)-2,2'-dimethoxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl (11)**. A mixture of mono bromide **10** (0.340 g, 0.847 mmol), 3,5-diphenylphenylboronic acid (0.256 g, 0.934 mmol),[2] $Pd(PPh_3)_4$ (49 mg, 0.042 mmol), and $Ba(OH)_2{\cdot}8H_2O$ (0.294 g, 0.932 mmol) in water (2.17 mL) and 1,4-dioxane (6.23 mL) was heated under reflux for 18 h under argon atmosphere. The reaction mixture was poured into water and extracted twice with ethyl acetate. The combined organic layers were dried ($Na_2SO_4$) and concentrated in *vacuo*. The residue was purified by flash column chromatography

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(0.5 % ethyl acetate and 25% toluene in hexane) to give 0.433 g (93 % yield) of **11** as an amorphous solid: $^1$H NMR (500 MHz; $CDCl_3$) δ 1.64–1.86 (8H, m), 2.12–2.22 (2H, m), 2.36 (1H, m), 2.47 (1H, m), 2.78–2.94 (4H, m), 3.27 (3H, s), 3.76 (3H, s), 6.81 (1H, d, *J* = 8.4 Hz), 7.10 (1H, d, *J* = 8.4 Hz), 7.24 (1H, s), 7.38 (2H, t, *J* = 7.4 Hz), 7.48 (4H, t, *J* = 7.5 Hz), 7.72 (4H, dd, *J* = 1.0 and 8.0 Hz), 7.78 (1H, t, *J* = 1.7 Hz), 7.86 (2H, d, *J* = 1.7 Hz); $^{13}$C NMR (126 MHz, $CDCl_3$) 23.05, 23.10, 23.15, 23.22, 27.0, 27.4, 29.4, 29.6, 55.3, 60.4, 107.9, 124.5, 125.8, 127.0, 127.28, 127.32, 128.73, 128.76, 129.6, 130.7, 131.4, 131.6, 132.8, 136.65, 136.68, 140.2, 141.4, 141.5, 152.9, 154.5.

**(*R*)-3-(3,5-Diphenylphenyl)-2,2'-dihydroxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl** (**2**). To a solution of **11** (450 mg, 0.817 mmol) in dichloromethane (5.5 mL) at –10 ºC under argon atmosphere was added boron tribromide (0.77 mL, 8.17 mmol). The solution was stirred at this temperature for 2 h. The reaction mixture was poured into water, and extracted twice with ethyl acetate. The combined organic layers were dried ($Na_2SO_4$) and concentrated in *vacuo*. The residue was purified by a silica gel flash chromatography (20 % ethyl acetate in hexane) to give 409.1 mg (96 % yield) of **2** as an amorphous solid: $[\alpha]_D^{25}$ = +69.7 (*c* = 1.00, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 1.68–1.83 (8H, m), 2.21–2.30 (2H, m), 2.34–2.45 (2H, m), 2.78 (2H, t, *J* = 6.0 Hz), 2.85 (2H, t, *J* = 6.2 Hz), 4.71 (1H, br), 4.95 (1H, br), 6.87 (1H, d, *J* = 8.3 Hz), 7.09 (1H, d, *J* = 8.3 Hz), 7.30 (1H, s), 7.38 (2H, t, *J* = 7.4 Hz), 7.47 (4H, t, *J* = 7.5 Hz), 7.70 (4H, d, *J* = 7.2 Hz), 7.78 (1H, t, *J* = 1.6 Hz), 7.84 (2H, d, *J* = 1.6 Hz); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 22.9, 23.0 (3C), 27.14, 27.19, 29.2 (2C), 113.0, 119.1, 119.8, 125.0, 125.8, 127.2, 127.4 (2C), 128.7, 130.2, 130.4, 131.1, 131.8, 137.0, 137.1, 138.8, 141.2, 141.9, 148.3, 151.3.

**(*R*)-Naphthalen-1-ylphenylmethanol** (**3a**) (Procedure for Asymmetric Phenylation by Using Phenyllithium, Table 1, entry 16). A two-layer mixture of $MgBr_2$ in $Et_2O$ (2 mL) was prepared by the reaction of magnesium turnings (29 mg, 1.2 mmol) with 1,2-dibromoethane (1.2 mmol, 0.10 mL) under argon atmosphere. To this was added $CH_2Cl_2$ (8 mL) at room temperature. To the resulting solution of $MgBr_2$ at –78 ºC was added PhLi (0.98 M in cyclohexane and $Et_2O$) (1.22 mL, 1.2 mmol). The resulting suspension was stirred at room temperature for 15 min and then cooled again at –78 ºC. Titanium tetraisopropoxide (0.59 mL, 2.0 mmol) was added. After being stirred for 10 min at this temperature, the resulting mixture was slowly added over a period of 2 h by using a syringe pump to a $CH_2Cl_2$ (4 mL) solution of (*R*)-DPP-$H_8$-BINOL **2** (10.5 mg, 0.020 mmol), 1-naphthaldehyde (0.156 g, 1.0 mmol), and titanium tetraisopropoxide (0.30 mL, 1.0 mmol) at 0 ºC. After being stirred further for 1 h, the reaction mixture was quenched by the addition of aqueous 1N HCl and extracted three times with ethyl acetate. The organic layers were washed successively with aqueous 5% $NaHCO_3$ and with brine, dried ($MgSO_4$), and concentrated in *vacuo*. Flash chromatography (silica gel, 2–20% ethyl acetate in hexane) of the residue gave 0.199 g (85% yield) of **3a** (95% ee).

**(*R*)-3-[Hydroxy(naphthalen-1-yl)methyl]benzonitrile (8a)** (Typical Procedure for Asymmetric Arylation by Using Functionalized Grignard Reagents, Scheme 1). To a solution of 3-iodobenzonitrile

(0.344 g, 1.50 mmol) in dry $Et_2O$ (3 mL) at –20 ºC under argon atmosphere was added *c*-$C_5H_9MgCl$ (2 M in $Et_2O$) (0.825 mL, 1.65 mmol). After being stirred for 1 h at this temperature, the resulting suspension was cooled to –78 ºC and diluted with $CH_2Cl_2$ (10 mL). To the suspension at this temperature was added titanium tetraisopropoxide (0.74 mL, 2.5 mmol). After being stirred for 10 min at this temperature, the resulting mixture was slowly added over a period of 2 h by using a syringe pump to a $CH_2Cl_2$ (4 mL) solution of (*R*)-DPP-$H_8$-BINOL **2** (10.5 mg, 0.020 mmol), 1-naphthaldehyde (0.156 g, 1.0 mmol), and titanium tetraisopropoxide (0.30 mL, 1.0 mmol) at 0 ºC under argon atmosphere. After being stirred further for 1 h, the reaction mixture was quenched by the addition of aqueous 1N HCl and extracted three times with ethyl acetate. The organic layers were washed successively with aqueous 5% $NaHCO_3$ and with brine, dried ($MgSO_4$), and concentrated in *vacuo*. Flash chromatography (silica gel, 12% ethyl acetate in hexane) of the residue gave 0.235 g (94% yield) of **8a** (95% ee). **8a**: $^1$H NMR (500 MHz, $CDCl_3$) δ 2.51 (1H, br), 6.52 (1H, d, *J* = 3,7 Hz), 7.42 (1H, t, *J* = 8,0 Hz), 7.43–7.57 (5H, m), 7.64 (1H, d, *J* = 7.9 Hz), 7.75 (1H, s), 7.83–7.91 (2H, m), 8.00 (1H, d, *J* = 8.0 Hz); $^{13}$C NMR (125.8 MHz, $CDCl_3$) δ 73.5, 112.5, 118.8, 123.7, 125.30, 125.31, 125.9, 126.5, 129.0, 129.17, 129.24, 130.40, 130.42, 131.1, 131.2, 134.1, 137.8, 144.6; HRMS (EI) calcd for $C_{18}H_{13}NO$ 259.0997, found 259.1006. The ee value was determined by HPLC analysis using a Chiralcel AD-H column (1 mL/min, 9% *i*-PrOH in hexane); retention times: 36.2 min (major *R*-enantiomer) and 24.3 min (minor *S*-enantiomer). The absolute stereochemistry was assumed by analogy.

**Ee Determination of Products 3a-m, 4a,b, 5a-b, and 8b.**

**(*R*)-Naphthalen-1-ylphenylmethanol** (**3a**) (HPLC analysis using a Chiralcel OD column, 1.5 mL/min, 10% *i*-PrOH in hexane); retention times: 26.8 min (major *R*-enantiomer) and 11.4 min (minor *S*-enantiomer).[3]

**(*S*)-Phenyl-*p*-tolylmethanol** (**3b**) (HPLC analysis using a Chiralcel OD column, 0.5 mL/min, 5% *i*-PrOH in hexane); retention times: 31.9 min (major *S*-enantiomer) and 37.4 min (minor *R*-enantiomer).[4]

**(*S*)-(4-Chlorophenyl)phenylmethanol** (**3c**) (HPLC analysis using a Chiralcel OB column, 1 mL/min, 9% *i*-PrOH in hexane); retention times: 21.5 min (major *S*-enantiomer) and 15.0 min (minor *R*-enantiomer).[3]

**(*S*)-(4-Fluorophenyl)phenylmethanol** (**3d**) (HPLC analysis using a Chiralcel OB column, 0.75 mL/min, 20% *i*-PrOH in hexane); retention times: 24.9 min (major *S*-enantiomer) and 18.9 min (minor *R*-enantiomer).[5]

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**(*S*)-(2-Methoxyphenyl)phenylmethanol** (**3e**) (HPLC analysis using a Chiralcel OJ column, 1 mL/min, 10% *i*-PrOH in hexane); retention times: 21.6 min (major *S*-enantiomer) and 16.8 min (minor *R*-enantiomer).[6]

**(*S*)-Phenyl(2,4,6-trimethylphenyl)methanol** (**3f**) (HPLC analysis using a Chiralcel OD column, 0.7 mL/min, 5% *i*-PrOH in hexane); retention times: 14.7 min (major *S*-enantiomer) and 17.3 min (minor *R*-enantiomer). The absolute stereochemistry was assumed by analogy.

**(*R*)-Biphenyl-4-ylphenylmethanol** (**3g**) (HPLC analysis using a Chiralcel AD-H column, 1 mL/min, 2% *i*-PrOH in hexane); retention times: 64.6 min (major *R*-enantiomer) and 56.3 min (minor *S*-enantiomer).[4]

**(*R*)-4-(Hydroxyphenylmethyl)benzonitrile** (**3h**) (HPLC analysis using a Chiralcel OD column, 1 mL/min, 9% *i*-PrOH in hexane); retention times: 26.9 min (major *R*-enantiomer) and 32.1 min (minor *S*-enantiomer). The absolute stereochemistry was assumed by analogy.

**(*R*)-(3-Methoxyphenyl)phenylmethanol** (**3i**) (HPLC analysis using a Chiralcel OD column, 1 mL/min, 10% *i*-PrOH in hexane); retention times: 22.3 min (major *R*-enantiomer) and 15.7 min (minor *S*-enantiomer).[6]

**(*R*)-(2-Chlorophenyl)phenylmethanol** (**3j**) (HPLC analysis using a Chiralcel OJ column, 1.5 mL/min, 10% *i*-PrOH in hexane); retention times: 11.7 min (major *R*-enantiomer) and 22.2 min (minor *S*-enantiomer).[6]

**(*R*)-Naphthalen-2-ylphenylmethanol** (**3k**) (HPLC analysis using a Chiralcel OD column, 1 mL/min, 5% *i*-PrOH in hexane); retention times: 37.4 min (major *R*-enantiomer) and 30.1 min (minor *S*-enantiomer).[7]

**(*R*)-Furan-2-ylphenylmethanol** (**3*l***) (HPLC analysis using a Chiralcel OD column, 1 mL/min, 5% *i*-PrOH in hexane); retention times: 19.9 min (major *R*-enantiomer) and 16.8 min (minor *S*-enantiomer).[8]

**(*R*)-Phenylthiophen-2-yl-methanol** (**3m**) (HPLC analysis using a Chiralcel OD column, 1 mL/min, 5% *i*-PrOH in hexane); retention times: 19.1 min (major *R*-enantiomer) and 16.9 min (minor *S*-enantiomer).[9]

**(*S*)-2-Methyl-1-phenylprop-2-en-1-ol** (**4a**) (HPLC analysis using a Chiralcel OD column, 1 mL/min, 1% *i*-PrOH in hexane); retention times: 26.5 min (major *S*-enantiomer) and 29.2 min (minor *R*-enantiomer). The absolute stereochemistry was assumed by analogy.

**(*S*)-1-Phenylbut-2-en-1-ol** (**4b**) (HPLC analysis using a Chiralcel OD column, 1 mL/min, 1% *i*-PrOH in hexane); retention times: 26.5 min (major *S*-enantiomer) and 19.2 min (minor *R*-enantiomer).[10]

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**(*S*)-1-Phenylpentan-1-ol** (**5a**) (HPLC analysis using a Chiralcel OD column, 1 mL/min, 2% *i*-PrOH in hexane); retention times: 17.6 min (major *S*-enantiomer) and 15.9 min (minor *R*-enantiomer).[11]

**(*S*)-Cyclohexylphenylmethanol** (**5b**) (HPLC analysis using a Chiralcel AD-H column, 0.5 mL/min, 3% *i*-PrOH in hexane); retention times: 25.5 min (major *S*-enantiomer) and 27.4 min (minor *R*-enantiomer).[12]

**(*R*)-[3-(Hydroxynaphthalen-1-ylmethyl)phenyl]piperidin-1-ylmethanone** (**8b**) (HPLC analysis using a Chiralcel AD-H column, 1 mL/min, 10% *i*-PrOH in hexane); retention times: 67.5 min (major *R*-enantiomer) and 48.2 min (minor *S*-enantiomer). The absolute stereochemistry was assumed by analogy.

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