Supporting Information

Enantioselective Additions of Diethylzinc and Diphenylzinc to Aldehydes using 2-Dialkylaminomethyl-2'-Hydroxy-1,1'-Binaphthyls

Dong-Hyun Ko, Kyung Hoon Kim, and Deok-Chan Ha*

Department of Chemistry, Korea University, Seoul 136-701, Korea

General

IR spectra were recorded on a Bomem MB-104 spectrophotometer. Optical rotations were measured with a Rudolph Research Autopol III polarimeter. ^1H NMR spectra were recorded on a Bruker AMX 400 (400 MHz), or Varian Gemini 300 (300 MHz) with TMS as an internal reference. ^{13}C NMR spectra were recorded on a Bruker AMX 400 (100 MHz) with TMS or CDCl_3 as an internal reference. Elemental analyses were obtained from Sogang Organic Chemistry Research Center, Seoul. Chiral HPLC analysis was performed on a Jasco LC-1500 Series HPLC system with a UV detector. GC analysis was performed on a Hewlett Packard 5890 series II plus GAS Chromatograph with a FID detector.

All reactions were carried out in oven dried glassware under an argon atmosphere. Toluene (CaH_2), THF (Na, benzophenone) were dried by distillation before use. Diethylzinc was purchased from Aldrich, diphenylzinc from Strem.

Synthesis of amides (6a-f); general procedure

To a suspension of amine or dimethylamine hydrochloride (0.66 mmol) in toluene (2 ml) was added a solution of trimethylaluminum (2M solution in toluene, 0.33 ml, 0.66 mmol) at 0°C and the mixture was stirred at room temperature for 1h. Ester (**5**)¹ (150 mg, 0.33 mmol) was added and the solution was heated at reflux under argon atmosphere for 3h. The reaction mixture was cooled to room temperature, quenched with 1N HCl solution (20 ml) and the mixture was extracted with ethyl acetate (20ml x 2). The combined organic extracts were washed with brine (20 ml x 2), dried (MgSO_4), and concentrated in vacuo. The residue was purified by flash column chromatography

on silica gel with ethyl acetate/hexanes (1:2) to give the pure amide product (quantitative yield) as a white foamy solid.

(*R*)-2-*N,N*-Dimethylcarbamoyl-2'-trifluoromethanesulfonyloxy-1,1'-binaphthyl (6a)

$[\alpha]_D^{25} = -48.9$ ($c = 5.0$, CHCl_3). IR (KBr) ν 1640 (carbonyl) cm^{-1} .

^1H NMR (300 MHz, CDCl_3) δ 2.83 (s, 3H), 2.95 (s, 3H), 7.17 (d, $J = 8.4$ Hz, 1H), 7.25 (d, $J = 8.1$ Hz, 1H), 7.29-7.54 (m, 6H), 7.93 (d, $J = 7.2$ Hz, 1H), 7.95 (d, $J = 7.5$ Hz, 1H), 8.01 (d, $J = 8.4$ Hz, 1H), 8.04 (d, $J = 7.5$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 34.68, 39.02, 118.15 (q, $J_{\text{C-F}} = 318$ Hz), 118.79, 123.72, 126.92, 126.98, 127.02, 127.56, 128.06, 128.08, 128.38, 128.89, 129.16, 130.96, 132.05, 132.88, 133.24, 134.11, 135.31, 144.92, 169.61.

Anal. Calcd for $\text{C}_{24}\text{H}_{18}\text{F}_3\text{NO}_4\text{S}$: C, 60.88; H, 3.83; F, 12.04; N, 2.96; O, 13.52; S, 6.77.

Found: C, 60.82; H, 3.86; N, 2.71; S, 6.73.

(*R*)-2--*N,N*-Di-*n*-butylcarbamoyl-2'-trifluoromethanesulfonyloxy-1,1'-binaphthyl (6b)

$[\alpha]_D^{25} = +1.28$ ($c = 4.3$, CHCl_3). IR (KBr) ν 1632 (carbonyl) cm^{-1} .

^1H NMR (300 MHz, CDCl_3) δ 0.72-1.64 (m, 14H), 2.84 (br, 1H), 2.96 (br, 1H), 3.45 (br, 1H), 3.58 (br, 1H), 7.22-7.55 (m, 8H), 7.92-8.06 (m, 4H).

^{13}C NMR (100 MHz, CDCl_3) δ 13.71, 13.77, 19.75, 19.89, 28.70, 30.65, 43.21, 48.39, 118.12 (q, $J_{\text{C-F}} = 318$ Hz), 118.46, 123.16, 126.74, 126.99, 127.09, 127.52, 127.87, 128.11, 129.60, 130.80, 132.09, 132.77, 133.07, 136.13.

Anal. Calcd for $\text{C}_{30}\text{H}_{30}\text{F}_3\text{NO}_4\text{S}$: C, 64.62; H, 5.42; F, 10.22; N, 2.51; O, 11.48; S, 5.75

Found: C, 64.67; H, 5.44; N, 2.56; S, 5.60.

(R)-2-*N,N*-Dibenzylcarbamoyl-2'-trifluoromethanesulfonyloxy-1,1'-binaphthyl (6c)

$[\alpha]_D^{25} = +72.2$ ($c = 1.7$, CHCl_3). IR (KBr) ν 1639 (carbonyl) cm^{-1} .

^1H NMR (300 MHz, CDCl_3) δ 3.69 (br, 1H), 4.11 (br, 1H), 4.73 (br, 1H), 5.28 (br, 1H), 6.63-6.75 (m, 18H), 7.90-8.12 (m, 4H).

^{13}C NMR (100 MHz, CDCl_3) δ 46.47, 50.96, 118.04 (q, $J_{\text{C-F}} = 318$ Hz), 118.93, 122.82, 126.72, 126.93, 127.00, 127.17, 127.29, 127.58, 127.75, 128.13, 128.31, 128.58, 128.90, 129.50, 130.86, 132.18, 132.83, 133.27, 135.00, 136.22.

Anal. Calcd for $\text{C}_{36}\text{H}_{26}\text{F}_3\text{NO}_4\text{S}$: C, 69.11; H, 4.19; F, 9.11; N, 2.24; O, 10.23; S, 5.13. Found: C, 69.33; H, 4.29; N, 1.95; S, 5.05.

(R)-2-(Pyrrolidine-1-carbonyl)-2'-trifluoromethanesulfonyloxy-1,1'-binaphthyl (6d)

$[\alpha]_D^{25} = -56.1$ ($c = 2.05$, CHCl_3). IR (KBr) ν 1634 (carbonyl) cm^{-1} .

^1H NMR (300 MHz, CDCl_3) δ 1.78-1.89 (m, 4H), 3.27-3.50 (4H, m), 7.19 (d, $J = 8.4$ Hz, 1H), 7.23-7.56 (m, 6H), 7.61 (d, $J = 8.4$ Hz, 1H), 7.93 (d, $J = 7.5$ Hz, 1H), 7.96 (d, $J = 7.8$ Hz, 1H), 8.02 (d, $J = 9.0$ Hz, 1H), 8.05 (d, $J = 8.7$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 24.31, 26.12, 45.48, 48.79, 118.24 (q, $J_{\text{C-F}} = 318$ Hz), 118.78, 123.66, 126.95, 127.11, 127.50, 127.54, 128.10, 128.11, 128.80, 128.90, 129.16, 130.89, 132.08, 132.86, 133.39, 134.33, 136.16, 145.13, 167.90.

Anal. Calcd for $\text{C}_{26}\text{H}_{20}\text{F}_3\text{NO}_4\text{S}$: C, 62.52; H, 4.04; F, 11.41; N, 2.80; O, 12.81; S, 6.42. Found: C, 62.55; H, 4.07; N, 2.89; S, 6.35.

(R)-2-(Piperidine-1-carbonyl)-2'-trifluoromethanesulfonyloxy-1,1'-binaphthyl (6e)

$[\alpha]_D^{25} = +8.0$ ($c = 1.0$, CHCl_3). IR (KBr) ν 1635 (carbonyl) cm^{-1} .

^1H NMR (300 MHz, CDCl_3) δ 1.26-1.59 (m, 6H), 3.29 (br, 2H), 3.54 (br, 2H), 7.15 (d, $J = 8.7$ Hz, 1H), 7.26-7.54 (m, 7H), 7.92 (d, $J = 6.3$ Hz, 1H), 7.95 (d, $J = 8.1$ Hz, 1H), 8.03 (d, $J = 9.0$ Hz, 1H), 8.04 (d, $J = 8.4$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 24.50, 25.59, 26.35, 42.48, 48.31, 118.56 (q, $J_{\text{C-F}} = 318$ Hz), 118.53, 123.59, 126.88, 126.95, 127.12, 127.60, 127.96, 128.06, 128.79, 129.18, 130.97, 132.18, 132.94, 133.25, 133.59, 134.45, 135.53, 144.92, 168.25.

Anal. Calcd for $\text{C}_{27}\text{H}_{22}\text{F}_3\text{NO}_4\text{S}$: C, 63.15; H, 4.32; F, 11.10; N, 2.73; O, 12.46; S, 6.24. Found: C, 63.44; H, 4.44; N, 2.32; S, 6.12.

(R)-2-(Morpholine-4-carbonyl)-2'-trifluoromethanesulfonyl-1,1'-binaphthyl (6f)

$[\alpha]_D^{25} = -25.5$ ($c = 1.0$, CHCl_3). IR (CHCl_3) ν 1640 (carbonyl) cm^{-1} .

^1H NMR (300 MHz, CDCl_3) δ = 3.00-3.75 (8H, m), 7.19-7.57 (m, 8H), 7.96 (d, $J = 7.8$ Hz, 2H), 8.06 (d, $J = 8.4$ Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 31.74, 41.93, 47.69, 66.82, 118.18 (q, $J_{\text{C-F}} = 318$ Hz), 118.55, 123.51, 124.29, 127.05, 127.17, 127.19, 127.73, 128.13, 129.45, 131.15, 132.13, 132.91, 133.41, 134.36, 145.02, 168.42.

Anal. Calcd for $\text{C}_{26}\text{H}_{20}\text{F}_3\text{NO}_5\text{S}$: C, 60.58; H, 3.91; F, 11.06; N, 2.72; O, 15.52; S, 6.22. Found: C, 61.13; H, 4.23; N, 2.44; S, 6.08.

Synthesis of amino alcohols (3a-f); general procedure

To a solution of amide (0.26 mmol) in THF (5 ml) was added LiAlH_4 (40 mg, 1.05 mmol) in small portions at room temperature and the mixture was refluxed for 12h. After cooled to 0°C , the reaction mixture was quenched with water (20 ml) and filtered through Celite with washing by ethyl acetate. The filtrate was extracted with ethyl acetate (30 ml x 3) and combined organic extracts were washed with brine (30 ml), dried (MgSO_4), and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel with $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (9:1) to give the pure amine product as a white foamy solid.

(R)-2-(N,N-Dimethylamino)methyl-2'-hydroxy-1,1'-binaphthyl (3a)

yield; 64%, $[\alpha]_D^{25} = -208.5$ ($c = 1.75$, CHCl_3).

IR (KBr) ν 3427 (OH), 1620 and 1590 ($\text{C}=\text{C}$ aromatic) cm^{-1} .

^1H NMR (300 MHz, CDCl_3) δ 2.27 (s, 6H), 3.19 (d, $J = 12.0$ Hz, 1H), 3.74 (d, $J = 12.0$ Hz, 1H), 6.70 (d, $J = 8.1$ Hz, 1H), 6.98 (d, $J = 8.7$ Hz, 1H), 7.09 (ddd, $J = 8.4, 6.9, 1.5$ Hz, 1H), 7.17 (ddd, $J = 8.4, 6.9, 1.5$ Hz, 1H), 7.26 (ddd, $J = 8.4, 6.9, 1.5$ Hz, 1H), 7.41 (ddd, $J = 8.1, 6.6, 1.2$ Hz, 1H), 7.43 (d, $J = 9.0$ Hz, 1H), 7.50 (d, $J = 8.4$ Hz, 1H), 7.43 (d, $J = 9.0$ Hz, 1H), 7.85 (d, $J = 8.7$ Hz, 1H), 7.89 (d, $J = 8.7$ Hz, 2H), 7.93 (d, $J = 8.1$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 44.19, 63.59, 121.79, 122.63, 123.04, 125.34, 125.90, 125.94, 126.32, 127.23, 127.68, 127.78, 127.82, 128.31, 129.13, 129.65, 133.59, 133.85, 134.29, 134.38, 135.20, 154.49.

Anal. Calcd for $\text{C}_{23}\text{H}_{21}\text{NO}$: C, 84.37; H, 6.46; N, 4.28; O, 4.89. Found: C, 84.43; H, 6.55; N, 4.10.

(R)-2-(N,N-Di-*n*-butylamino)methyl-2'-hydroxy-1,1'-binaphthyl (3b)

yield; 71%, $[\alpha]_D^{25} = -42.6$ ($c = 2.8$, CHCl_3).

IR (KBr) ν 3410 (OH), 1615 and 1590 ($\text{C}=\text{C}$ aromatic) cm^{-1} .

^1H NMR (300 MHz, CDCl_3) δ 0.83 (t, $J = 7.5$ Hz, 6H), 1.17-1.43 (m, 8H), 2.32-2.42 (m, 2H), 2.60-2.69 (m, 2H), 3.37 (d, $J = 12.0$ Hz, 1H), 3.77 (d, $J = 12.0$ Hz, 1H), 6.69 (d, $J = 8.7$ Hz, 1H), 6.97 (d, $J = 8.7$ Hz, 1H), 7.09 (t, $J = 8.1$ Hz, 1H), 7.15 (t, $J = 8.1$ Hz, 1H), 7.26 (t, $J = 8.7$ Hz, 1H), 7.40 (m, 1H), 7.40 (d, $J = 9.0$ Hz, 1H), 7.51 (d, $J = 8.7$ Hz, 1H), 7.85 (d, $J = 9.3$ Hz, 2H), 7.92 (d, $J = 8.4$ Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ = 13.86, 20.67, 27.06, 52.30, 59.15, 121.96, 122.94, 123.00, 125.32, 125.83, 125.87, 126.25, 126.26, 127.46, 127.73, 127.86, 128.94, 129.11, 129.53, 133.53, 133.90, 134.42, 134.56, 135.26, 154.42.

Anal. Calcd for $\text{C}_{29}\text{H}_{33}\text{NO}$: C, 84.63; H, 8.08; N, 3.40; O, 3.89. Found: C, 84.65; H, 8.12; N, 3.42.

(R)-2-(N,N-Dibenzylamino)methyl-2'-hydroxy-1,1'-binaphthyl (3c)

yield; 62%, $[\alpha]_D^{25} = +47.4$ ($c = 1.25$, CHCl_3).

IR (KBr) ν 3414 (OH), 1619 and 1594 ($\text{C}=\text{C}$ aromatic) cm^{-1} .

^1H NMR (300 MHz, CDCl_3) δ = 3.29 (d, $J = 13.5$ Hz, 2H), 3.30 (d, $J = 13.2$ Hz, 1H), 3.64 (d, $J = 13.5$ Hz, 2H), 3.66 (d, $J = 13.2$ Hz, 1H), 6.79 (d, $J = 7.8$ Hz, 1H), 7.08 (d, $J = 9.0$ Hz, 1H), 7.12 - 7.30 (m, 14H), 7.34 (d, $J = 9.0$ Hz, 1H), 7.44 (ddd, $J = 8.1, 6.6, 1.2$ Hz, 1H), 7.85-7.92 (m, 3H), 7.99 (d, $J = 8.7$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 57.76, 65.82, 118.81, 119.45, 123.29, 125.42, 126.01, 126.33, 126.39, 126.61, 127.10, 127.97, 127.98, 128.02, 128.26, 128.55, 128.77, 128.99, 129.12, 129.18, 129.78, 131.71, 133.33, 133.84, 137.06, 137.97, 152.06.

Anal. Calcd for $\text{C}_{35}\text{H}_{29}\text{NO}$: C, 87.65; H, 6.09; N, 2.92; O, 3.34. Found: C, 87.62; H, 6.19; N, 2.73.

(R)-2-Pyrrolidinylmethyl-2'-hydroxy-1,1'-binaphthyl (3d)

yield; 79%, $[\alpha]_D^{25} = -107.0$ ($c = 1.9$, CHCl_3).

IR (KBr) ν 3410 (OH), 1617 and 1590 ($\text{C}=\text{C}$ aromatic) cm^{-1} .

^1H NMR (400 MHz, CDCl_3) δ 1.76-1.89 (m, 4H), 2.52-2.57 (m, 2H), 2.61-2.65 (m, 2H), 3.30 (d, $J = 11.7$ Hz, 1H), 4.01 (d, $J = 11.7$ Hz, 1H), 6.73 (d, $J = 8.5$ Hz, 1H), 6.99 (d, $J = 8.5$ Hz, 1H), 7.09 (ddd, $J = 8.4, 7.0, 1.4$ Hz, 1H), 7.15 (ddd, $J = 8.4, 7.0, 1.5$ Hz, 1H), 7.25 (ddd, $J = 8.0, 6.8, 1.2$ Hz, 1H), 7.39 (ddd, $J = 8.1, 6.8, 1.2$ Hz, 1H), 7.42 (d, $J = 8.9$ Hz, 1H), 7.53 (d, $J = 8.3$ Hz, 1H), 7.85 (d, $J = 7.9$ Hz, 1H), 7.87 (d, $J = 8.9$ Hz, 1H), 7.88 (d, $J = 8.3$ Hz, 1H), 7.92 (d, $J = 8.4$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 23.21, 53.26, 59.82, 121.52, 122.61, 122.98, 125.43, 125.81, 125.93, 126.29, 127.30, 127.79, 127.81, 127.82, 127.89, 129.08, 129.61, 133.57, 133.81, 134.46, 134.67, 134.79, 154.74.

Anal. Calcd for $\text{C}_{25}\text{H}_{23}\text{NO}$: C, 84.95; H, 6.56; N, 3.96; O, 4.53. Found: C, 84.95; H, 6.74; N, 3.92.

(R)-2-Piperidinomethyl-2'-hydroxy-1,1'-binaphthyl (3e)

yield; 70%, $[\alpha]_D^{25} = -100.3$ ($c = 0.75$, CHCl_3).

IR (CHCl_3) ν 3413 (OH), 1618 and 1590 ($\text{C}=\text{C}$ aromatic) cm^{-1} .

^1H NMR (400 MHz, CDCl_3) δ 1.48-1.56 (br, 4H), 1.69 (br, 2H), 2.27 (br, 2H), 2.64 (br, 2H), 3.24 (d, $J = 12.0$ Hz, 1H), 3.64 (d, $J = 12.0$ Hz, 1H), 6.69 (dd, $J = 8.6, 0.9$ Hz, 1H), 6.98 (dd, $J = 8.5, 0.9$ Hz, 1H), 7.08 (ddd, $J = 8.4, 6.9, 1.4$ Hz, 1H), 7.15 (ddd, $J = 8.2, 6.7, 1.2$ Hz, 1H), 7.25 (ddd, $J = 8.1, 6.9, 1.2$ Hz, 1H), 7.40 (ddd, $J = 8.1, 6.9, 1.2$ Hz, 1H), 7.43 (d, $J = 8.9$ Hz, 1H), 7.48 (d, $J = 8.4$ Hz, 1H), 7.84 (d, $J = 8.2$ Hz, 1H), 7.87 (d, $J = 8.7$ Hz, 1H), 7.88 (d, $J = 8.4$ Hz, 1H), 7.91 (d, $J = 8.6$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 23.86, 24.96, 53.72, 63.18, 121.99, 122.75, 122.98, 125.35, 125.84, 125.89, 126.26, 127.26, 127.37, 127.76, 127.81, 128.76, 129.14, 129.59, 133.54, 133.88, 133.92, 134.35, 135.40, 154.38.

Anal. Calcd for $\text{C}_{26}\text{H}_{25}\text{NO}$: C, 84.98; H, 6.86; N, 3.81; O, 4.35. Found: C, 84.89; H, 6.84; N, 3.45.

(R)-2-Morpholinomethyl-2'-hydroxy-1,1'-binaphthyl (3f)

yield; 79%, $[\alpha]_D^{25} = -84.8$ ($c = 1.25$, CHCl_3).

IR (CHCl_3) ν 3392 (OH), 1619 and 1592 ($\text{C}=\text{C}$ aromatic) cm^{-1} .

^1H NMR (400 MHz, CDCl_3) δ 2.36 (ddd, $J = 9.6, 6.5, 3.1$ Hz, 2H), 2.67 (m, 2H), 3.29 (d, $J = 12.0$ Hz, 1H), 3.65 (d, $J = 12.0$ Hz, 1H), 3.65 (ddd, $J = 12.0, 6.4, 3.6$, 2H), 3.78 (ddd, $J = 11.7, 6.6, 3.0$ Hz, 2H), 6.71 (dd, $J = 8.5, 0.9$ Hz, 1H), 6.99 (dd, $J = 8.5, 0.6$ Hz, 1H), 7.11 (ddd, $J = 8.4, 7.0, 1.4$ Hz, 1H), 7.18 (ddd, $J = 8.4, 7.0, 1.3$ Hz, 1H), 7.28 (ddd, $J = 8.5, 6.9, 1.2$ Hz, 1H), 7.41 (d, $J = 8.9$ Hz, 1H), 7.41 (ddd, $J = 8.1, 6.8, 1.3$ Hz, 1H), 7.51 (d, $J = 8.4$ Hz, 1H), 7.85 (d, $J = 8.1$ Hz, 1H), 7.89 (d, $J = 8.8$ Hz, 1H), 7.90 (d, $J = 8.1$ Hz, 1H), 7.93 (d, $J = 8.3$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 52.94, 62.79, 66.20, 121.52, 121.93, 125.32, 126.25, 126.14, 126.48, 127.07, 127.73, 127.83, 127.87, 128.40, 129.29, 129.80, 133.51, 133.58,

133.89, 134.23, 134.88, 153.51.

Anal. Calcd for $C_{25}H_{23}NO_2$: C, 81.27; H, 6.27; N, 3.79; O, 8.66. Found: C, 81.28; H, 6.17; N, 3.63.

General Procedure for the Addition of Et_2Zn to aldehyde

To a solution of chiral ligand **3d** (10.6 mg, 0.03 mmol) in toluene (10 ml) at room temperature was added dropwise a solution of diethylzinc (1.0 M solution in hexane, 2 ml, 2 mmol). The resulting solution was stirred at room temperature for 15 min. Aldehyde (1 mmol) was added in one portion at 0°C and the reaction mixture was stirred for 24h at room temperature. The reaction was quenched by the addition of 1M HCl solution (30 ml) and the mixture was extracted with ethyl acetate (30 ml x 2). The combined organic extracts were washed with brine (30 ml x 2), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel with ethyl acetate/hexanes (1:7) to give the pure alcohol product.

Conditions for the determination of the enantiomeric excess are listed below. All alcohols were compared with racemic samples which were prepared via Grignard reaction.

1-Phenyl-1-propanol

$[\alpha]_D^{25} = +42.4$ ($c = 2.5$, $CHCl_3$) {lit.² $[\alpha]_D^{22} = -47.6$ ($c = 6.11$, $CHCl_3$) for 98% ee (*S*) }; 94% ee by GC analysis (Chiraldex G-TA column, 50 to 100 °C at 5 °C /min, N_2 , 1.41 ml/min), $t_R = 23.37$ min for (*R*) and $t_R = 24.68$ min for (*S*).

1-(4'-Methoxyphenyl)-1-propanol

$[\alpha]_D^{25} = +34.6$ ($c = 5.1$, C_6H_6) {lit.² $[\alpha]_D^{22} = -32.1$ ($c = 1.25$, C_6H_6) for 93% ee (*S*) }; 94% ee by HPLC analysis (Chiralcel OD column, hexane:2-propanol = 97:3, 1 ml/min, 254 nm UV detector), $t_R = 12.91$ min for (*R*) and $t_R = 14.43$ min for (*S*).

1-(1'-Naphthyl)-1-propanol

$[\alpha]_{\text{D}}^{25} = +54.3$ ($c = 2.9$, CHCl_3) {lit.³ $[\alpha]_{\text{D}}^{20} = +52.6$ ($c = 2.55$, CHCl_3) for 93.5% ee (*R*) }; 96% ee by HPLC analysis (Chiralcel OD column, hexane:2-propanol = 9:1, 1 ml/min, 254 nm UV detector), $t_{\text{R}} = 12.53$ min for (*R*) and $t_{\text{R}} = 7.63$ min for (*S*).

1-(2'-Naphthyl)-1-propanol

$[\alpha]_{\text{D}}^{25} = +27.1$ ($c = 5.05$, C_6H_6) {lit.³ $[\alpha]_{\text{D}}^{20} = +27.5$ ($c = 3.80$, C_6H_6) for 96.1% ee (*R*) }; 96% ee by HPLC analysis (Chiralcel OD column, hexane:2-propanol = 95:5, 1 ml/min, 254 nm UV detector), $t_{\text{R}} = 11.10$ min for (*R*) and $t_{\text{R}} = 9.69$ min for (*S*).

1-(4'-Chlorophenyl)-1-propanol

$[\alpha]_D^{25} = +27.0$ ($c = 5.15$, C_6H_6) {lit.² $[\alpha]_D^{22} = -23.5$ ($c = 0.82$, C_6H_6) for 93% ee (*S*) };
99% ee by GC analysis (Chiraldex G-TA column, 100 to 130 °C at 5 °C /min, N_2 1.41 ml/min), $t_R = 15.71$ min for (*R*) and $t_R = 16.69$ min for (*S*).

1-(3'-Chlorophenyl)-1-propanol

$[\alpha]_D^{25} = +26.3$ ($c = 3.5$, C_6H_6) {lit.³ $[\alpha]_D^{20} = +26.6$ ($c = 2.36$, C_6H_6) for 97% ee (*R*) };
96% ee by HPLC analysis (Chiralcel OD column, hexane:2-propanol = 98:2, 0.5 ml/min, 254 nm UV detector), $t_R = 27.84$ min for (*R*) and $t_R = 25.54$ min for (*S*).

1-(2'-Chlorophenyl)-1-propanol

$[\alpha]_D^{25} = +51.7$ ($c = 3.1$, $CHCl_3$) {lit.⁴ $[\alpha]_D = +37.1$ ($c = 4$, $CHCl_3$) for 79% ee (*S*) }; 93% ee by HPLC analysis {(*R, R*)-Welk-O 1 column, hexane:2-propanol = 99:1, 0.3 ml/min, 254 nm UV detector}, $t_R = 23.30$ min for (*R*) and $t_R = 25.07$ min for (*S*).

(E)-1- Phenyl-1-penten-3-ol

$[\alpha]_D^{25} = +7.14$ ($c = 5.0$, CHCl_3) {lit.² $[\alpha]_D^{22} = -5.7$ ($c = 100$, CHCl_3) for 96% ee (*S*)};
 86% ee by HPLC analysis (Chiralcel OD column, hexane:2-propanol = 95:5, 1 ml/min, 254 nm UV detector), $t_R = 9.63$ min for (*R*) and $t_R = 14.68$ min for (*S*).

1-Phenyl-1-pentyn-3-ol

$[\alpha]_D^{25} = +7.57$ ($c = 6.5$, CHCl_3) {lit.⁵ $[\alpha]_D^{\text{RT}} = -59.32$ (neat) for 99% ee (*S*)}; 76% ee by
 HPLC analysis (Chiralcel OD column, hexane:2-propanol = 95:5, 1 ml/min, 254 nm UV
 detector), $t_R = 6.93$ min for (*R*) and $t_R = 16.49$ min for (*S*).

1-(Triisopropylsilyl)-1-pentyn-3-ol⁶

$[\alpha]_D^{25} = +4.13$ ($c = 2.3$, CHCl_3); 92% ee by ^{19}F -NMR analysis of the corresponding (*R*)-MTPA ester derivative. (300 MHz, CDCl_3)

3-Nonanol

$[\alpha]_D^{25} = -8.44$ ($c = 5.45$, CHCl_3) {lit.² $[\alpha]_D^{22} = +5.1$ ($c = 1.31$, CHCl_3) for 61% ee (*S*)}; 94% ee by GC analysis of the corresponding acetate derivative. (ChiralDEX G-TA column, 50 to 100 °C at 2 °C /min, N_2 , 1.41 ml/min) $t_R = 25.59$ min for (*R*) and $t_R = 25.17$ min for (*S*).

1-Cyclohexyl-1-propanol

$[\alpha]_D^{25} = +6.87$ ($c = 4.44$, CHCl_3) {lit.³ $[\alpha]_D^{20} = +6.35$ ($c = 3.0$, CHCl_3) for 94.8% ee

(*R*) }; 98% ee by GC analysis of the corresponding acetate derivative. (Chiraldex G-TA column, 50 to 100 °C at 5 °C /min, N₂, 1.41 ml/min) t_R = 19.99 min for (*R*) and t_R = 19.12 min for (*S*).

General Procedure for the Addition of Ph₂Zn to aldehyde

To a solution of chiral ligand **3f** (9.2 mg, 0.025 mmol) in toluene (5 ml) was added diphenylzinc (110 mg, 0.5 mmol) at room temperature and the mixture was stirred at room temperature for 15 min. Aldehyde (0.25 mmol) was added in one portion at 0°C and the reaction mixture was stirred for 1h at 0°C. The reaction was quenched by the addition of 1M HCl solution (10 ml) and the mixture was extracted with ethyl acetate (20 ml x 2). The combined organic extracts were washed with brine (20 ml x 2), dried (MgSO₄), and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel with ethyl acetate/hexanes (1:7) to give the pure alcohol product.

Conditions for the determination of the enantiomeric excess are listed below. All alcohols were compared with racemic samples which were prepared via Grignard reaction.

(4-Methoxyphenyl)phenylmethanol

$[\alpha]_D^{25} = +17.8$ (c = 2.5, C₆H₆) {lit.⁷ $[\alpha]_D^{26} = -12.8$ (c = 0.9, C₆H₆) for 68% ee (*S*) }; 98% ee by HPLC analysis (Chiralcel OJ column, hexane:2-propanol = 9:1, 1 ml/min, 254 nm UV detector), t_R = 22.66 min for (*R*) and t_R = 26.53 min for (*S*).

(4-Tolyl)phenylmethanol

$[\alpha]_D^{25} = +9.0$ ($c = 0.5$, C_6H_6) { lit.⁸ $[\alpha]_D^{22} = +8.71$ ($c = 0.4$, C_6H_6) for 84.6% ee (*R*) }; 97% ee by HPLC analysis (Chiralcel OD column, hexane:2-propanol = 98:2, 1 ml/min, 254 nm UV detector), $t_R = 26.23$ min for (*R*) and $t_R = 22.77$ min for (*S*).

(2-Naphthyl)phenylmethanol

$[\alpha]_D^{25} = +6.3$ ($c = 1.0$, C_6H_6) { lit.⁹ $[\alpha]_D = +6.22$ ($c = 0.76$, C_6H_6) for 87% ee (*R*) }; 97% ee by HPLC analysis (Chiralcel OD column, hexane:2-propanol = 95:5, 1 ml/min, 254 nm UV detector), $t_R = 28.31$ min for (*R*) and $t_R = 23.15$ min for (*S*).

(2-Chlorophenyl)phenylmethanol

$[\alpha]_D^{25} = +22.3$ ($c = 1.75$, CHCl_3) {lit.¹⁰ $[\alpha]_D^{20} = -21.51$ ($c = 1.136$, CHCl_3) for 97% ee (*S*) }; 96% ee by HPLC analysis (Chiralcel OD column, hexane:2-propanol = 95:5, 1 ml/min, 254 nm UV detector), $t_R = 11.71$ min for (*R*) and $t_R = 15.38$ min for (*S*).

(3-Chlorophenyl)phenylmethanol

$[\alpha]_D^{25} = -27.6$ ($c = 1.05$, acetone) {lit.¹¹ $[\alpha]_D^{20} = +30.3$ ($c = 1.12$, acetone) for >95% ee (*S*) }; 92% ee by HPLC analysis (Merck (*R,R*)-Welk-O 1 column, hexane:2-propanol = 99:1, 0.3 ml/min, 254 nm UV detector), $t_R = 35.41$ min for (*R*) and $t_R = 33.50$ min for (*S*).

(4-Chlorophenyl)phenylmethanol

$[\alpha]_D^{25} = -17.8$ ($c = 0.9$, CHCl_3) {lit.⁹ $[\alpha]_D = -18.36$ ($c = 0.86$, CHCl_3) for 94% ee (*R*) }; 95% ee by HPLC analysis (Chiralcel OB-H column, hexane:2-propanol = 9:1, 1 ml/min, 254 nm UV detector), $t_R = 13.43$ min for (*R*) and $t_R = 20.28$ min for (*S*).

1-Phenyl-heptan-1-ol

$[\alpha]_D^{25} = -20.0$ ($c = 0.62$, CHCl_3) {lit.⁷ $[\alpha]_D^{26} = +30.0$ ($c = 0.7$, CHCl_3) for 79% ee (*R*) };
 66% ee by HPLC analysis (Chiralcel OD column, hexane:2-propanol = 98:2, 1 ml/min, 254 nm UV detector), $t_R = 20.70$ min for (*R*) and $t_R = 24.52$ min for (*S*).

(Cyclohexyl)phenylmethanol

$[\alpha]_D^{25} = -17.3$ ($c = 1.5$, C_6H_6) {lit.¹² $[\alpha]_D^{22} = +26.8$ ($c = 3.29$, C_6H_6) for 92% ee (*R*) };
 68% ee by HPLC analysis (Chiralcel AD-H column, hexane:2-propanol = 97:3, 0.5 ml/min, 254 nm UV detector), $t_R = 23.14$ min for (*R*) and $t_R = 21.52$ min for (*S*).

1,3-Diphenyl-prop-2-en-1-ol

$[\alpha]_D^{25} = -17.55$ ($c = 1.1$, CH_2Cl_2) {lit.⁷ $[\alpha]_D^{27} = +28.1$ ($c = 1.0$, CH_2Cl_2) for 82% ee (*R*) }; 75% ee by HPLC analysis (Chiralcel OD column, hexane:2-propanol = 9:1, 1 ml/min, 254 nm UV detector), $t_R = 17.63$ min for (*R*) and $t_R = 13.38$ min for (*S*).

1-Phenyl-3-triisopropylsilylprop-2-yn-1-ol

$[\alpha]_D^{25} = +18.45$ ($c = 1.1$, CHCl_3) {lit.¹³ $[\alpha]_D^{27} = +17.8$ ($c = 1.35$, CHCl_3) for 92% ee (*S*) }; 85% ee by ^1H -NMR analysis of the corresponding (*R*)-MTPA ester derivative. (300 MHz, CDCl_3 , integration of the methoxy group signal).

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