Supporting informations for:

Highly Enantioselective Addition of Dimethylzinc to Aldehydes Catalyzed by ClCr(Salen)

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1. General Information

General: ^{1}H NMR spectra were recorded on Varian 200 MHz or Varian 300 MHz spectrometers. Chemical Shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: δ 7.27 ppm). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian 50 MHz or Varian 75 MHz spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal standard (deuterochloroform: δ 77.0 ppm). Mass spectra were performed at an ionizing voltage of 70 eV. Chromatographic purification was done with 240-400 mesh silica gel. Analytical gas chromatography (GC) was performed on a Hewlett-Packard HP 6890 gas chromatograph with a flame ionization detector and split mode capillary injection system, using a Crosslinked 5% PH ME Siloxane (30 m) column or a Megadex5 chiral (25 m) column. Analytical high performance liquid chromatograph (HPLC) was performed on a HP 1090 liquid chromatograph equipped with a variable wavelength UV detector (deuterium lamp 190-600 nm), using a Daicel Chiralcel™ OD column (0.46 cm I.D. x 25 cm) (Daicel Inc.) and AD. Column. HPLC grade isopropanol and hexane were used as the eluting solvents. Elemental analyses were carried out by using a EACE 1110 CHNOS analyzer. All the reactions were carried out under a nitrogen atmosphere in flame-dried glassware using standard inert techniques for introducing reagents and solvents. All commercially available aldehydes were purified before use.

Me_2Zn 2M in toluene was purchased by Aldrich. Commercially available ClCr(Salen) (Aldrich) was used in all the reaction. Anhydrous tBuOMe was purchased by Aldrich.

The aldehydes 2-methyl-2-phenyl propanal and 1-(3-phenyl-allyl)-cyclohexanecarboxyaldehyde, were prepared according literature.[1]

The aldehydes 2,2-dimethyl-3-phenyl-propionaldehyde and 2,2-dimethyl-5-phenyl-pent-4-enal were prepared according the literature.[2] 1-Benzyloxy-2-methyl-propanal and 1-*tert*butyl-dimethylsilyloxy-2-methyl-propanal were prepared by mono-protection of 2,2 dimethyl-1,3-propane-diol (NaH, THF, benzyl bromide or *t*butyldimethylsilylchloride) and successive Swern oxidation.

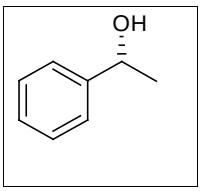
General procedure for the addition of Me_2Zn to aldehydes (diluted conditions)

To a solution of the aldehyde (0.3mmol) in anhydrous *t*BuOMe (2mL) ClCr(Salen) (2-4 mol%) was added and solution was stirred for 5 minutes. Me_2Zn (0.6mmol) was added drop wise by a syringe at RT and the resulting red-brown solution was stirred at RT for 24-48hours. The reaction was diluted with Et_2O, then quenched with water. The mixture was filtered over a glass septum then the phases were separated, and the aqueous phase was extracted with Et_2O. The organic phases were collected, dried over Na_2SO_4 and evaporated under reduced pressure to give an orange oil purified by chromatography.

General procedure for the addition of Me_2Zn to aldehydes (concentrated conditions)

To a commercially available 2M solution of Me_2Zn in toluene (0.6-0.8mmol) ClCr(Salen) (4 mol%) was added at 0°C and the mixture was stirred for 5 minutes. The aldehyde (0.3-0.4mmol) was added drop wise by syringe at 0°C. The reaction was stirred at 0°C for 5 minutes then the solution was warmed to room temperature and stirred for 24-48 hours. The reaction was diluted with Et_2O then quenched with water. The mixture was filtered other a glass septum, then the phase were separated and the aqueous phase was extracted with Et_2O. The organic phases were collected, dried over Na_2SO_4 and evaporated under reduced pressure to give an orange oil purified by chromatography.

(*R*)-1-Phenyl-ethanol



$C_8H_{10}O$ Fw = 122.16

e.e. = 97 % yield = 91 %

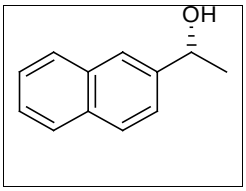
$[\alpha]_D$ = + 28.4 (c 1.2, MeOH). Lit.[3] (*R*)-1-phenylethanol $[\alpha]_D$ = + 45.2 (c 1.01, CH_2Cl_2)

^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.48 (d, 3H, J = 6.3Hz); 2.00 (brs, 1H); 4.87 (q, 1H, J = 6.3Hz); 7.36-7.23 (m, 5H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 31.9; 76.0; 126.0; 127.5; 128.4; 144.6.

HPLC analysis; column OD: from 99:1 to 95:5 in 10min., flux 0.5mL/m, hexane: *iso*propanol. TM: 20.36 min; tm: 23.94min.

***(R)*-2-Naphtyl-ethanol**



$C_{12}H_{12}O$ Fw = 172.22

e.e. = 93 % yield = 91 %

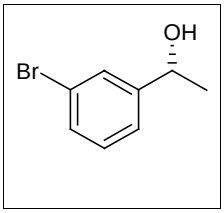
$[\alpha]_D$ = + 30.4 (c 1.4, $CHCl_3$); Lit.[4] (*R*)-2-naphtyl-ethanol $[\alpha]_D$ = + 36.3 (c 0.58, EtOH)

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.59 (d, 3H, J = 6.4Hz); 1.94 (d, 1H, J = 3.2Hz); 5.07 (dq, 1H, J = 3.2, 6.4Hz); 7.53-7.74 (m, 3H); 7.86-7.81(m, 4H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 25.08; 74.48; 123.56; 123.77; 125.75; 126.10; 127.63; 127.89; 128.26; 132.85; 133.26; 143.13.

HPLC analysis: column OD: from 99:1 to 95:5 in 10min., flux 0.5mL/m, hexane: *iso*propanol. tm: 35.14 min TM: 37.19 min.

(*R*)-1-(3'Bromophenyl)-ethanol



C_8H_9BrO Fw = 201.06

e.e. = 96 % yield = 86 %

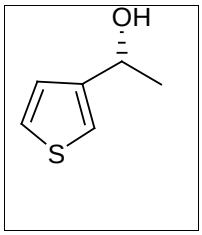
$[\alpha]_D$ = + 45.0 (c 1, $CHCl_3$); Lit.[5] (*R*)-1-(3'bromophenyl)-ethanol $[\alpha]_D$ = + 39.3 (c 0.5, CH_2Cl_2)

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.51 (d, 3H, J = 6.3Hz); 2.12 (brs, 1H); 4.91 (q, 1H, J = 6.3Hz); 7.24 (t, 1H, J = 6Hz); 7.32 (dt, 1H, J = 0.6, 7.8Hz); 7.43 (dt, 1H, J = 0.6, 6.9Hz); 7.56 (s, 1H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 25.21; 69.71; 122.56; 123.97; 128.51; 130.06; 130.42; 148.07.

HPLC analysis: column OD: from 99:1 to 95:5 in 10min., flux 0.5mL/m, hexane: *iso*propanol. tm: 20.22 min TM: 21.05 min.

(*R*)-1-Thiophen -3-yl-ethanol



C_6H_8OS Fw = 128.19

e.e. = 99 % yield = 86 %

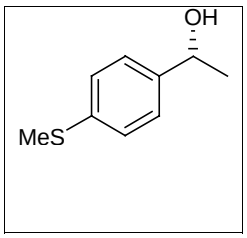
$[\alpha]_D$ = + 26.6 (c 0.9, $CHCl_3$). Lit.[6] (*S*)- 1-thiophen 3-yl-ethanol $[\alpha]_D$ = - 44.7 (c = 1.0, EtOH)

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.56 (d, 3H, J = 6.3Hz); 2.03 (brs, 1H); 5.01 (q, 1H, J = 6.3Hz); 7.13 (d, 1H, J = 5.1Hz); 7.15 (s, 1H); 7.35-7.34 (m, 1H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 24.41; 66.51; 120.15; 125.60; 126.13; 147.25.

HPLC analysis OD: from 99:1 to 95:5 in 10min., flux 0.5mL/m, hexane: *iso*propanol. TM: 22.40 min; tm: 22.80min.

(*R*)-1-(4'Methylthiophenyl)-ethanol



$C_9H_{12}OS$ Fw = 168.25

e.e. = 98 % yield = 88 %

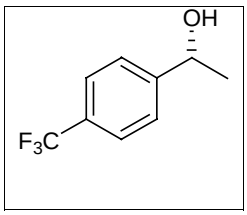
$[\alpha]_D$ = + 43.9 (c 0.98, $CHCl_3$.); Lit.[7] (*R*)-1-(4'Methylthiophenyl)-ethanol $[\alpha]_D$ = + 46.4 (c 1.7, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.50 (d, 3H, J = 6.3Hz); 2.10 (brs, 1H); 2.51 (s, 3H); 4.88 (q, 1H, J = 6.3Hz); 7.29 (AA'BB', 4H, J = 8.1Hz).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 15.93; 25.02; 69.89; 125.92; 126.74; 137.31; 142.72.

HPLC analysis: column OD: from 99:1 to 95:5 in 10min., flux 0.5mL/m, hexane: *iso*propanol. TM: 25.88 min; tm: 26.25min.

(*R*)-1-(4'Trifluoromethylphenyl)-ethanol



$C_9H_9F_3O$ Fw = 190.16

e.e. = 94 % yield = 95 %

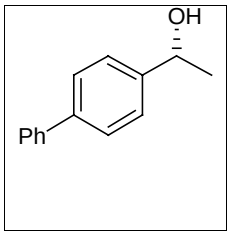
$[\alpha]_D$ = + 20.6 (c 1.4, $CHCl_3$). Lit.[8] (*R*)-1-(4'trifluoromethylphenyl)-ethanol $[\alpha]_D$ = + 27 (c 1.27, CH_2Cl_2)

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.53 (d, 3H, J = 6.3Hz); 2.1 (brs, 1H); 5.03 (q, 1H, J = 6.3Hz); 7.51 (AA'BB', 2H, J = 8.1Hz); 7.66 (AA'BB', 2H, J = 8.1Hz).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 25.34; 69.79; 122.32; 125.39; 125.44; 125.61; 149.67.

HPLC analysis: column OD, from 99:1 to 95:5 in 10min., flux 0.5mL/m, hexane: *iso*propanol. tm: 18.59; TM: 18.88 min.

(*R*)-1-Biphenyl-ethanol



$C_{14}H_{14}O$ Fw = 198.26

e.e. = 94 % yield = 89 %

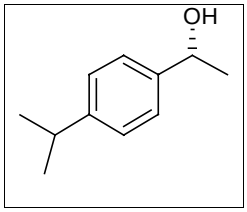
$[\alpha]_D$ = + 30.8 (c 1.3, $CHCl_3$). Lit.[9] (*S*)-1-biphenyl-ethanol $[\alpha]_D$ = - 43.7 (c 0.75, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.59 (d, 3H, J = 6.3Hz); 2.01(brs, 1H); 5.99 (q, 1H; J = 6.3Hz); 7.41 (d, 1H, J = 6.9Hz); 7.50-7.47 (m. 4H); 7.66-7.52 (m, 4H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 25.09; 70.09; 125.81; 127.02; 127.20; 128.72; 140.35; 140.78; 144.76.

HPLC analysis: column OD, 99:1 hexane: *iso*propanol (isocratic), flux 0.7mL/m. tm: 28.57; TM: 31.13.

(*R*)-1-(4'Isopropylphenyl)-ethanol



$C_{11}H_{16}O$ Fw = 164.24

e.e. = 96 % yield = 87 %

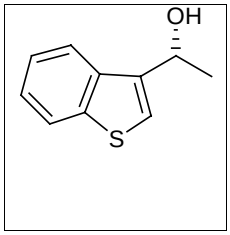
$[\alpha]_D$ = + 15.6 (c 0.90, $CHCl_3$. Lit.[7] (*R*)-1-(4'isopropylphenyl)-ethanol $[\alpha]_D$ = - 45.8 (c 3.34, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.30 (d, 6H, J = 6.9Hz); 1.54 (d, 3H; J = 6.6Hz); 1.83(brs, 1H); 2.96 (sept, 1H, J = 6.9Hz); 4.92 (q, 1H; J = 6.6Hz); 7.26 (AA'BB', 2H, J = 7.8Hz); 7.35 (AA'BB', 2H, J = 7.8Hz).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 23.98; 24.92; 26.88; 70.24; 124.40; 126.51; 143.16; 148.18.

HPLC analysis: column AD, from 99:1 to 97:3 in 16min., flux 0.5mL/m, hexane: *iso*propanol. TM: 25.88 min; tm: 27.15.

(R)-1-Benzo[b]thiophen-3-yl-ethanol



$C_{10}H_{10}OS$ Fw = 178.25

e.e. = 95 % yield = 80 %

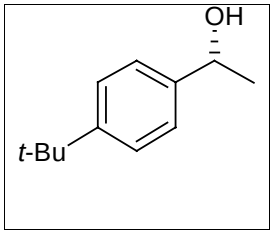
$[\alpha]_D$ = + 3.8 (c 0.79, $CHCl_3$).

^1H NMR ($CDCl_3$, 300 MHz) δ: 1.71 (d, 3H, J = 6.6Hz); 2.05 (brs, 1H); 5.31 (q, 1H, J = 6.6Hz); 7. 42 (s, 1H); 7.46-7.39 (m, 2H); 7.96-7.91 (m, 2H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 23.39; 65.73; 121.42; 121.44; 122.27; 122.89; 124.02; 124.40; 137.22; 140.68.

HPLC analysis: column AD, from 99:1 to 97:3 in 10min., flux 0.5mL/m, hexane: *iso*propanol. TM: 39.12 min; tm: 41.00.

***(R)*-1-(4-*tert*Butylphenyl*)*-ethanol**



$C_{12}H_{18}O$ Fw = 178.27

e.e. = 96 % yield = 89 %

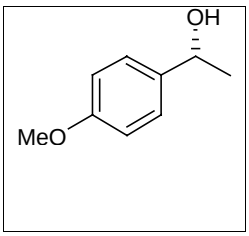
$[\alpha]_D$ = + 30.8 (c 1.3, $CHCl_3$). Lit.[7] *(S)*-1-(4-*tert*butylphenyl*)*-ethanol $[\alpha]_D$ = -38.8. (c 1.54, $CHCl_3$)

^1H NMR ($CDCl_3$, 300 MHz) δ: 1.37 (s, 9H); 1.54 (d, 3H, J = 6.6Hz); 1.84 (brs, 1H); 4.92 (q, 1H, J = 6.6Hz); 7.36 (AA'BB', 2H, J = 7.5Hz); 7.43 (AA'BB', 2H, J = 7.5Hz).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 24.89; 31.34; 34.48; 70.17; 125.15; 125.38; 142.76; 150.43.

HPLC analysis. column OD, 99:1 hexane: *iso*propanol (isocratic), flux 0.5ml/min. TM: 21.85 min; tm: 23.12 min.

(*R*)-1-(4-Methoxyphenyl)-ethanol



$C_9H_{12}O_2$ Fw = 152.19

e.e. = 92 % yield = 95 %

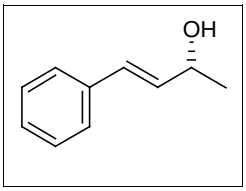
$[\alpha]_D$ = + 31.9 (c 1 0.94, $CHCl_3$). Lit[2]. (*R*)-1-(4-Methoxyphenyl)-ethanol $[\alpha]_D$ = + 39.8 (c 0.3, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.47 (d, 3H, J = 6.3Hz); 2.00 (brs, 1H); 3.80 (s, 3H); 4.85 (q, 1H, J = 6.3Hz); 6.85-6.93 (AA'BB', 2H, J = 8.6Hz); 7.26-7.36 (AA'BB', 2H, J = 8.6Hz).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 24.95; 55.23; 69.90; 113.78; 126.62; 137.95; 158.90.

HPLC analysis: column OD, 97:3 hexane: *iso*propanol (isocratic), flux 0.7ml/min. TM: 21.90 min; tm: 23.49 min .

(*R*)-*E*-4-Phenyl-but-3-en-2-ol



$C_{10}H_{12}O$ Fw = 148.20

e.e. = 89 % yield = 81 %

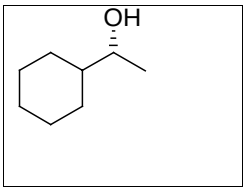
$[\alpha]_D$ = + 12 (c 1, $CHCl_3$). Lit.[10] (R)-1-*E*-4-phenyl-but-3-en-2-ol $[\alpha]_D$ = + 7.6 (c 0.83, $CHCl_3$).

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.42 (d, 3H, J = 6.6Hz); 1.91 (s, 1H); 4.53 (t, 1H; J = 6.6Hz); 6.31 (ddd, 1H, J = 1.8, 6.3, 15.9Hz); 6.62 (d, 1H, J = 15.9Hz); 7.44-7.26 (m, 5H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 23.34; 68.87; 126.40; 127.58; 128.53; 129.32; 133.50; 136.62.

HPLC analysis: column OD, 95:5 hexane: *iso*propanol (isocratic), flux 0.5ml/min. TM: 25.63 min; tm: 40.52 min.

(*R*)-1-Cyclohexylethanol



$C_8H_{16}O$ Fw = 128.21

e.e. = 82% yield = 68%

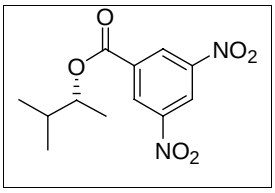
$[\alpha]_D$ = -6.15 (c 2.6, $CHCl_3$). lit.[11](S)-1-Cyclohexylethanol $[\alpha]_D$ = + 3.51 (c 3.1, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.16 (d, 3H, J = 6.3Hz); 1.87-0.90 (m, 12H); 3.55 (dq. 1H, J = 6.3,6.3Hz).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 20.36; 26.10; 26.20; 26.48; 26.32; 28.68; 45.09; 72.22.

HPLC analysis performed on the corresponding 3,5 dinitrobenzoate:[12] column AD, 99:1 hexane: *iso*propanol (isocratic), flux 0.8ml/min. tm: 36.64 min; TM: 51.31 min.

(*R*)-3-Methylbutan-2-ol



$C_{12}H_{14}N_2O_6$ Fw = 282.24

e.e. = 80% yield = 82%

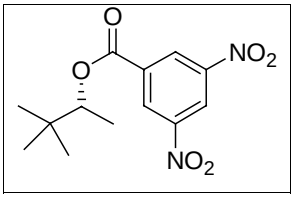
$[\alpha]_D$ = -11 (c 1.0 , $CHCl_3$).

^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.06 (d, 6H J = 6.6Hz); 1.41 (d, 3H, J = 6.6Hz); 2.05 (setp, 1H, J = 6.6Hz); 5.18-5.1 (m, 1H); 9.19 (s, 2H); 9.26 (s, 1H).

^{13}C NMR ($CDCl_3$, 50 MHz) δ:18.11; 18.05; 29.66; 32.74; 78.64; 122.15; 129.30; 134.55; 148.63; 162.03.

HPLC analysis performed on the corresponding 3,5 dinitrobenzoate:[11] column AD, 99:1 hexane: *iso*propanol (isocratic), flux 0.8ml/min. tm: 15.63 min;TM: 18.35 min.

(*R*)-3,5-Dinitro benzoic acid-1,2,2 trimethyl-propyl ester



$C_{13}H_{16}N_2O_6$ Fw = 296.27

e.e. = 97% yield = 75%

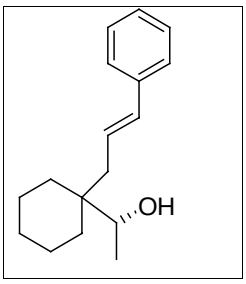
$[\alpha]_D$ = -31.3 (c 1.15, $CHCl_3$).

^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.05 (s, 3H); 1.35 (d, 1H; J = 6Hz); 5.08 (q, 1H, J = 6Hz); 9.16 (s, 2H); 9.25 (s, 1H).

^{13}C NMR ($CDCl_3$, 50 MHz) δ: 14.87; 25.69; 34.47; 80.99; 122.12; 129.22; 134.50; 191.90; 197.93.

HPLC analysis performed on the corresponding 3,5 dinitrobenzoate:[11] column OD, 90:10 hexane: *iso*propanol (isocratic), flux 0.5ml/min. TM: 22.54min; tm: 24.51 min.

(*R*)-1-[1-(3-Phenyl-allyl-)-cyclohexyl]-2-ethanol



$C_{17}H_{24}O$ Fw = 244.37

e.e. = 80% yield = 73 %

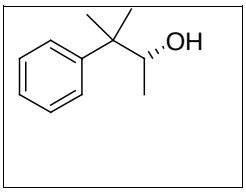
$[\alpha]_D$ = -20 (c 0.75, $CHCl_3$).

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.24 (d, 1H; J = 6.3Hz); 1.59-1.20 (m, 10H); 2.32 (dd, 1H; J = 7.2, 14.4Hz); 2.50 (dd, J = 7.214.4Hz); 3.78 (q, 1H, J = 6.3Hz); 6.51-6.32 (m, 2H); 7.42-7.23 (m, 5H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 17.21; 21.27; 21.39; 26.20; 30.55; 31.39; 35.68; 40.64; 72.88; 125.91; 126.89; 127.69; 128.45; 131.76; 137.56.

HPLC analysis: column OD, 95:5 hexane: *iso*propanol (isocratic), flux 0.5ml/min. TM: 15.55 min; tm: 21.46 min.

(*R*)-3-Methyl-3-phenyl-butan-2-ol



$C_{11}H_{16}O$ Fw = 164.24

e.e. = 73% yield = 78%

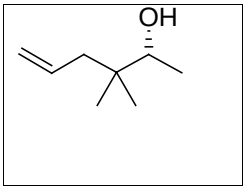
$[\alpha]_D$ = -8 (c 1.2, $CHCl_3$).

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.11 (d, 3H, J = 6.3Hz); 1.35 (s, 3H); 1.38 (s, 3H): 3.91 (q, 1H, J = 6.3Hz); 7.27 (t, 1H; J = 7.2Hz); 7.46-7.35 (m, 4H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 17.50; 22.69; 24.37; 26.85; 75.29; 126.05; 126.50; 128.19; 146.90.

HPLC analysis: column OD: from 99:1 to 97:3 in 15min., hexane: *iso*propanol, flux 0.5mL/m. tm: 14.55 min; TM: 15.20 min.

(*R*)-Dimethyl-hex-5-2-ol



$C_8H_{16}O$ Fw = 128.21

e.e. = 76% yield = 57 %

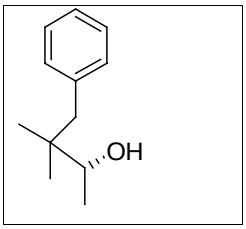
$[\alpha]_D$ = -7.2(c 1.1, $CHCl_3$).

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.98 (s, 3H); 0.93(s, 3H); 1.16 (d, 3H, J = 6Hz); 2.01 (dd, 1H, J = 6, 12Hz); 2.14 (dd, 1H; J = 9, 15Hz); 3.56 (q, 1H, J = 6Hz); 5.40-5.10 (m, 2H); 5.95-5.84 (m, 1H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 17.63; 22.12; 22.94; 43.57; 74.25; 117.07; 135.54.

HPLC analysis performed on the corresponding 3,5 dinitrobenzoate[11]: column OD, 90:10, hexane: *iso*propanol (isocratic), flux 0.5ml/min. tm: 21.54 min; TM: 22.44 min.

(*R*)-3,3-Dimethyl-4-phenyl-butan-2-ol



$C_{12}H_{18}O$ Fw = 178.27

e.e. = 79% yield = 56%

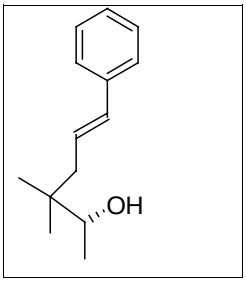
$[\alpha]_D$ = -4.66 (c 3.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.89 (s, 3H); 0.95(s, 3H); 1.26 (d, 3H, J = 6.3Hz); 2.60 (A part of AB, 1H, J = 13.2Hz); 2.78 (B part of AB, 1H, J = 13.2Hz); 3.62 (q, 1H, J = 6.3Hz); 7.42-7.20 (m, 5H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 17.79; 21.64; 22.87; 38.52; 44.34; 73.57; 125.69; 127.65; 130.60; 138.81.

HPLC analysis: column OF: from 99.5:0.5 to 85:15 in 30min., hexane: *iso*propanol, flux 0.5mL/m. tm: 15.56 min; TM: 16.04 min.

(*R*)-3,3-Dimethyl-6-phenyl-hex-5-en-2-ol



$C_{14}H_{20}O$ Fw = 204.30

e.e. = 82% yield = 49%

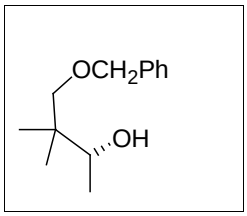
$[\alpha]_D$ = -6.50 (c 2.1, $CHCl_3$).

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.96 (s, 3H); 0.99 (s, 3H); 1.21 (d, 3H, J = 6.6Hz); 2.19 (dd, 1H; J = 7.2, 13.5Hz); 2.32 (dd, 1H, J = 7.5, 13.5Hz); 3.64 (q, 1H, J = 6.6Hz); 6.38-6.28 (m, 1H); 6.46 (d, 1H, J = 15.6Hz); 7.43-7.23 (m, 5H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 17.71; 22.19; 23.07; 38.46; 42.53; 74.16; 125.95 (x 2); 126.91; 127.07; 127.31; 128.45; 132.22; 137.62.

HPLC analysis performed on the corresponding 3,5 dinitrobenzoate[11]: column OD, from 99:1 to 80:10 in 30min., flux 0.6mL/m, hexane: *iso*propanol. tm 29.20 min; TM: 30.91 min.

(*R*)-4-(Benzyloxy)-3,3-dimethyl-butan-2-ol



$C_{12}H_{28}O_2Si$ Fw = 232.43

e.e. = 71% yield = 40%

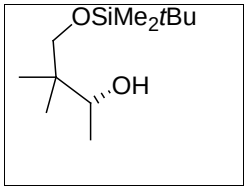
$[\alpha]_D$ = +5.0 (c 1.6, $CHCl_3$).

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.91 (s, 3H); 0.96 (s, 3H); 1.14 (d, 3H, J = 6.6Hz); 3.38 (d, 1H; J = 3.9Hz); 3.39 (AB, 2H, J = 8,7Hz); 3.73 (dq, 1H, J = 3.9, 6.6Hz); 4.56 (s, 2H); 7.42-7.30 (m, 5H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 17.71; 18.88; 22.71; 38.31; 75.58; 74.59; 80.06; 127.48; 127.60; 127.69; 18.34; 128.41; 137.87.

HPLC analysis: column OD: from 99:1 to 90:10 in 30min., hexane: *iso*propanol, flux 0.5mL/m. tm: 16.96 min; TM: 18.35 min.

(*R*)-4-(*tert*Butylmethylsilyoxy)-3,3-dimethyl-butan-2-ol



$C_{12}H_{28}O_2Si$ Fw = 232.43

e.e. = 77% yield = 65%

$[\alpha]_D$ = -1.11 (c 0.9, $CHCl_3$).

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.78 (s, 6H); 0.80 (s, 3H); 0.90 (s, 12H); 1.11 (d, 3H; J = 6.3Hz); 3.48 (AB, 2H, J = 9.6Hz); 4.70 (q, 1H, J = 6.3Hz).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: -5.83; 17.68; 18.02; 21.32; 22.17; 25.67; 38.12; 73.45; 75.01.

HPLC analysis performed on the corresponding 3,5 dinitrobenzoate[11]: column OF, from 99:1 to 97:3 in 50min., flux 0.7mL/m, hexane: *iso*propanol. TM: 29.25 min; tm: 31.08 min.

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