Supporting Information

Synthesis of Catalyst A

A mixture of (*R*)-(+)-1,1'-binaphtol (**1**) (28.6 mg, 0.1 mmol), $TiCl_2(OiPr)_2$ (**2**) 0.5M in toluene (0.2 ml, 0.1 mmol) and allyltributyltin (**3a**) (0.062 ml, 0.2 mmol) in 2 ml of dichloromethane was stirred at room temperature under anhydrous atmosphere. After 1h the initially red-brown solution became orange and the disappearance of allyltributyltin was checked by GC analysis.

Synthesis of Catalyst B

The same procedure for synthesis of **Cat A** was applied using tetrallyltin (**3b**) (0.048 ml, 0.2 mmol) instead of allyltributyltin.

Synthesis of tertiary homoallylic alcohols (5a-h).

The ketone (**4a-h**) (0.5 mmol) and tetrallyltin (**3b**) (0.180 ml, 0.75 mmol) were consecutively added to the catalyst prepared *in situ* as above described. The reaction was monitored by GC, quenched by the addition of HCl 0.1M (0.5 ml) and extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$ and then concentrated. The residue was purified by flash cromatography on silica gel column, eluing with ether / ciclohexane (15/85) to afford the correnspondingtertiary homoallylic alcohol (**5a-h**) with yields and enantiomeric excesses reported in **Tables 1** and **2**.

(*R*)- 2-phenyl-4-penten-2-ol (5a) ($C_{11}H_{14}O$).

Colorless oil. $[\alpha]_D^{25}$ = + 58.4° (c= 0.37, $CHCl_3$).

^{1}H NMR (200 MHz, $CDCl_3$): δ 1.48 (s, 3H); 1.99 (s, 1H); 1.99 (dd, *J*=13.7, 8.3 Hz, 1H); 2.62 (dd, *J*= 13.7, 6.4 Hz, 1H); 5.04 (d, *J*= 11.1 Hz, 1H); 5.08 (d, *J*= 5.06 Hz, 1H); 5.55 (dddd, *J*= 11.1, 5.6, 8.3, 6.4 Hz, 1H); 7.10-7.50 (m, 5H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ 29.87, 48.44, 73.69, 119.40, 124.73, 126.58, 128.14, 133.64, 144.89.

MS (70 eV) *m/z* (rel.int.): 146 (1), 128 (2), 122 (10), 121 (100), 105 (9), 77 (26), 51 (12).

The enantiomeric excess was determined by HPLC analysis on CHIRALCEL OD column : hexane-*i*PrOH from 100:0 to 95:5 in 20min t_r= 19.66 min (minor), t_r= 20.17 min (major).

(*S*)- 2-(2'-naphtyl)-4-penten-2-ol (5b) ($C_{15}H_{16}O$).

Pail yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.53 (s, 3H); 2.15 (s, 1H); 2.49 (dd, *J*=13.8, 8.7 Hz, 1H); 2.70 (dd, *J*=13.8, 6.3 Hz, 1H); 5.01 (d, *J*=9.9 Hz, 1H); 5.06 (d, *J*=17.0 Hz, 1H); 5.54 (dddd, *J*=17.1, 9.9, 8.7, 6.3 Hz, 1H); 7.31-7.51 (m, 3H); 7.68-7.90 (m, 4H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ 29.92, 48.28, 73.69, 119.47, 123.12, 123.47, 125.62, 125.96, 127.38, 127.81, 128.06, 132,16, 133.08, 133.50, 144.89.

MS (70 eV) *m/z* (rel. int.): 212 (3), 194 (2), 179 (6), 171 (100), 155 (24), 141 (5), 127 (39), 77 (9), 51 (5).

The enantiomeric excess was determined by HPLC analysis on CHIRALCEL OD column : hexane-*i*PrOH from 100:0 to 80:20 in 20min t_r= 18.48 min (major) t_r= 20.49 min (minor).

(*R*)- 2-(4-metoxyphenyl)-4-penten-2-ol (5b) ($C_{12}H_{16}O_2$).

Pale yellow oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ 1.54 (s, 3H); 2.46 (dd, 1H, *J*= 12.6 Hz, , *J*= 8.1 Hz); 2.67 (dd, 1H, *J*= 12.6 Hz, , *J*= 6.6 Hz); 3.82 (s, 3H); 5.12 (d, 1H, *J*= 11.1 Hz); 5.13 (d, 1H, *J*=15.5 Hz); 5.65 (dddd, 1H, *J*=15.5, 11.1, 8.1, 6.6 Hz)**;** 6.88 (d, 2H, *J*= 8.8 Hz); 7.37 (d, 2H, *J*= 8.8 Hz).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ 29.91, 48.52, 55.22, 73.33, 113.43, 119.26, 125.94, 133.82, 139.84.

MS (70 eV) *m/z* (rel. int): 174 (2), 151 (100), 135 (24), 107 (4), 77 (13).

The enantiomeric excess was determined by HPLC analysis on CHIRALCEL OD column : hexane-*i*PrOH from 100:0 to 95:5 in 20 min t_r= 22.68 min(major), t_r= 23.39 min (minor).

(*R*)- 2-(4-methylphenyl)-4-penten-2-ol (5d) ($C_{12}H_{16}O$).

Colorless oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ 1.56 (s, 3H); 2.05 (s, 1H); 2.36 (s, 3H,); 2.50 (dd, 1H, *J*= 13.6, 8.2 Hz); 2.70 (dd, 1H, *J*= 13.6, 5.4 Hz); 5.13 (d, 1H, *J*= 10.3 Hz); 5.14 (d, 1H, *J*=15.7 Hz); 5.81 (dddd, 1H, *J*= 15.7, 10.3, 8.2, 5.4 Hz)**;** 7.17 (d, 2H, *J*= 8.1 Hz); 7.35 (d, 2H, *J*= 8.1 Hz).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ 20.93,29.95, 48.42, 73.50, 119.33, 124.68, 128.85, 133.81.

MS (70 eV) *m/z* (rel.int.): 158 (8), 143 (20), 135 (100), 128 (20), 119 (20), 115 (15), 105 (8), 91 (30), 77 (10), 65 (18).

The enantiomeric excess was determined by HPLC analysis on the hydroboration oxidation product on CHIRALCEL OD column : hexane-*i*PrOH (92:8) t_r= 21.99 min (minor), t_r= 22.96 min (major).

(*R*)- 2-(*p*nitrophenyl)-4-penten-2-ol (5e) ($C_{11}H_{14}O_3N$).

Pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.58 (s, 3H); 2.16 (s, 1H); 2.54 (dd, 1H, *J*= 14.4, 7.8 Hz); 2.69 (dd, 1H, *J*= 14.4, 6.6 Hz); 5.13 (d, 1H, *J*= 10.3 Hz); 5.14 (d, 1H, *J*=15.7 Hz); 5.81 (dddd, 1H, *J*= 15.7, 10.3, 8.2, 5.4 Hz); 7.17 (d, 2H, *J*= 8.1 Hz); 7.35 (d, 2H, *J*= 8.1 Hz).

MS (70 eV) *m/z* (rel. int.): 166 (100), 150 (8), 105 (15), 77 (13), 65 (8), 51 (5).

The enantiomeric excess was determined by HPLC analysis on the hydroboration oxidation product on CHIRALCEL OD column : hexane-*i*PrOH (92:8) t_r= 32.63 min (minor), t_r= 42.56 min (major) .

(*S*) -1-allyl-1,2,3,4-tetrahydro-naphtalen-1-ol (5f) ($C_{13}H_{16}O$)

Pale yellow oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ 1.70-2.20 (m, 4H); 2.62 (d, *J*= 6.9 Hz, 2H); 2.70-2.90 (m, 2H); 5.15 (d, *J*=11.8 Hz, 2H); 5.68-5.98 (m, 1H); 7.05 (m, 3H); 7.50-7.65 (m, 1H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ 19.69, 29.74, 36.08, 47.03, 71.94, 118.57, 126.22, 126.35, 127.13, 128.85, 134.03, 136.77, 141.86.

MS (70 eV) *m/z* (rel. int.): 170 (1), 147 (100), 129 (25), 115 (11), 91 (45).

The enantiomeric excess was determined by HPLC analysis on CHIRALCEL OD column : hexane-iPrOH from 100: 0 to 80:20 in 40 min t_r= 18.03 min (minor), t_r= 18.36 min (major).

(*R*)-1-phenyl-3-hydroxy-3-methyl-1,5-hexandiene (5g) ($C_{13}H_{16}O$)

Colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.37 (s, 3H); 1.78 (s, 1H); 2.34 (dd, *J*= 13.5, 8.1 Hz, 1H); 2.43 (dd, *J*= 12.6, 8.1 Hz, 1H); 5.14 (d, *J*= 16.5 Hz, 1H); 5.15 (d, *J*=10.5 Hz 1H); 5.82 (dddd, 1H, *J*=16.5, 13.5, 12.6, 10.5 Hz); 6.22 (d, 1H, *J*= 16.2 Hz); 6.52 (d, 1H, *J*=16.2 Hz); 7.17- 7.39 (m, 5H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ 27.96, 46.32, 72.30, 119.20, 126.32, 127.31, 128.46, 133.47, 136.12, 136.81.

MS (70 eV) *m/z* (rel. int.): 188 (1), 170 (3), 156 (5), 147 (100), 129 (35), 115 (10), 103 (12), 91 (10), 77 (12).

The enantiomeric excess was determined by GC analysis MEGADEX 5 column : 100 °C for 2 min than 100-180°C at 3°C/min t_r= 27.45 min (minor) t_r= 27.79 min (major).

(*S*)-4-methyl-1-decen-4-ol (5h) ($C_{11}H_{22}O$)

Pale yellow oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ 0.82 (m, 3H); 1.10 (s, 3H); 1.75-1.42 (m, 11H); 2.16 (d, *J*= 7.5 Hz, 2H); 5.05 (d, *J*= 16.5 Hz, 1H); 5.07 (d, *J*= 10.7 Hz, 1H); 5.96 (ddd, *J*=16.5, 10.7, 7.5 Hz, 1H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ 14.05, 22.60, 23.78, 26.68, 29.83, 31.82, 41.85, 46.25, 72.15, 118.45, 134.13.

MS (70 eV) *m/z* (rel.int.): 155 (1), 129 (90), 113 (10), 85 (50), 69 (100), 55 (50).

The enantiomeric excess was determined by GC analysis on MEGADEX 5 column: 100-180°C at 5°C/min t_r= 5.89 min (minor) t_r= 6.13 min (major).