**Enantioselective Synthesis of Homoallylic alcohols**
***Via* a Chiral In(III)- PYBOX Complex**

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**Supporting Information**

**General**

Experiments involving moisture and/or air sensitive components were performed in oven-dried glassware. Commercial solvents and reagents were used without further purification with the following exceptions: Hexane, dichloromethane, ethyl acetate were fractionally distilled. Aldehydes were distilled before used. Azeotropic drying of starting materials or reagents was performed by the addition of the stated amount of anhydrous tetrahydrofuran, ensued by azeotropic removal of tetrahydrofuran with traces of moisture in vacuo followed by subsequent purging with nitrogen.
Analytical thin layer chromatography (TLC) was performed using Merck 60 $F_{254}$ precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate, followed by heating on a hot plate.
Flash chromatography was performed using Merck silica gel 60 with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use.
Infrared spectra were recorded on a Bio-Rad FTS 165 FTIR spectrometer. Liquid samples were examined as film between NaCl salt plates.
Proton nuclear magnetic resonance spectra ($^1$H NMR) were recorded on a Bruker Avance DPX 300 and Bruker AMX 500 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for 1H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.2600, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); ddd (doublets of doublets of doublet); dddd (doublets of doublets of doublets of doublet); dt (doublets of triplet); or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a J value in Hz. Carbon nuclear magnetic resonance spectra ($^{13}$C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of

chloroform-d (δ 77.03, triplet). The proportion of diastereomers and geometric isomers was determined from the integration of $^{1}H$ NMR and $^{13}C$ NMR spectra.
Mass spectral analyses were carried out on a VG 7035 micromass mass spectrophotometer at a source temperature of 200 ºC and at an ion current of 70 eV. Mass spectral data were reported in units of mass to charge (m/z) and % intensity.

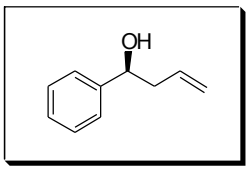
**Experimental Section**

**Representative procedure for asymmetric allylation of aldehydes : Preparation of (*R*)-1-phenylbut-3-en-1-ol**

To an oven dried 5mL round-bottom flask equipped with a magnetic stirring bar was added $In(OTf)_3$ (16.9 mg, 0.03 mmol, 0.2 equiv.) and 4Å molecular sieve (120 mg). The solid was azeotropically dried with anhydrous tetrahydrofuran twice (2 mL x 2) prior to the addition of 1 mL of dichloromethane. PYBOX (**1**) (13 mg, 0.033 mmol, 0.22 equiv.) was added and the mixture was stirred under nitrogen at room temperature for 2 hours to afford a white suspension. A mixture of benzaldehyde (15 ul, 0.15 mmol, 1 equiv.) and TMSCl (23 ul, 0.18 mmol, 1.2 equiv.) in dichloromethane (0.2 mL) was added to the resulting suspension and stirred for 10 minutes. The mixture was then cooled to -60 $^{0}C$ for 15 minutes followed by addition of allyltributylstannane (57 ul, 0.18 mmol, 1.2 equiv.). The reaction mixture was stirred at -60 $^{0}C$ for 30 hours, then was treated with 2mL saturated sodium bicarbonate solution at room temperature for 30 min., extracted with dichloromethane (3 x 10 mL), washed with brine, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The residual crude product was purified via silica gel chromatography to afford the homoallylic alcohol as colorless oil (65% yield).

**Characterization of tertiary homoallylic alcohols in Table 1**

**(*S*)-1-phenylbut-3-en-1-ol**




**Selectivity**: 87 % *ee*
**Opt. Rot.**: $[\alpha]_D^{25}$ -40.6 (c = 1.02 in $CH_2Cl_2$)
$R_f$ = 0.38 (4:1 hexane/ethyl acetate)

$^1$H NMR (300 MHz, $CDCl_3$): δ 7.37-7.27 (m, 5H), 5.89-5.75 (m, 1H), 5.20-5.13 (m, 2H), 4.75 (t, *J* = 5.6 Hz, 1H), 2.54-2.49 (m, 2H), 2.20 (br, 1H)

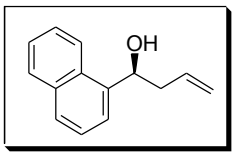
$^{13}$C NMR (75.4 MHz, $CDCl_3$): δ 143.9, 134.5, 128.4, 127.6, 125.8, 118.4, 73.3, 43.8

FTIR (neat): 3468, 2932, 1707, 1642, 1494, 1452, 1051, 999, 916, 758, 701 $cm^{-1}$.

HRMS Calcd for $C_{10}H_{12}0$ [$M^+$]: 148.0888. Found: 148.0899.

The enantiomeric excess was determined by HPLC analysis employing a Daicel Chiracel OD column (Hexane: *i*-propanol 98:2, 1.0 mL/min: $t_1$ =10.35 min for *R* enantiomer, $t_2$ = 13.86 min for *S* enantiomer).

**(*S*)-1-Naphthalen-1-yl-but-3-en-1-ol**




**Selectivity**: 90 % *ee*
**Opt. Rot.**: $[\alpha]_D^{25}$ -60.4 (c = 1.22 in $CH_2Cl_2$)
$R_f$ = 0.62 (4:1 hexane/ethyl acetate)

$^1$H NMR (300 MHz, $CDCl_3$): δ 8.10-7.46(m, 7H), 6.01-5.87(m, 1H), 5.55-5.52(m, 1H), 5.29-5.17(m, 2H), 2.82-2.73(m, 1H), 2.66-2.56(m, 1H), 2.22(br, 1H)

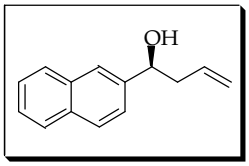
$^{13}$C NMR (75.4 MHz, $CDCl_3$): δ 139.4, 134.7, 133.7, 130.2, 128.9, 127.9, 125.9, 125.5, 125.4, 122.9, 122.8, 118.3, 69.9, 42.8

FTIR (neat): 3399$cm^{-1}$.

HRMS Calcd for $C_{14}H_{14}0$ [$M^+$]: 198.1047. Found: 198.1053.

The enantiomeric excess was determined by HPLC analysis employing a Daicel Chiracel OD-H column (Hexane: *i*-propanol 98:2, 1 mL/min: $t_1$ = 18.42min for *S* enantiomer , $t_2$ = 22.52min for *R* enantiomer).

**(*S*)-1-Naphthalen-2-yl-but-3-en-1-ol**




**Selectivity**: 86 % *ee*
**Opt. Rot.**: $[\alpha]_D^{25}$ -29.8 (c = 1.22 in $CH_2Cl_2$)
$R_f$ = 0.40 (4:1 hexane/ethyl acetate)

$^1H$ NMR (300 MHz, $CDCl_3$): δ 7.81-7.85 (m, 4H), 7.45-7.50 (m, 3H), 5.77-5.91 (m, 1H), 5.13-5.22 (m, 2H), 4.91 (t, *J* = 6.4 Hz, 1H), 2.53-2.68 (m, 2H), 2.14 (br, 1H)

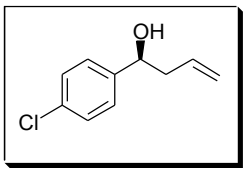
$^{13}C$ NMR (75.4 MHz, $CDCl_3$): δ 141.2, 134.3, 133.2, 132.9, 128.1, 127.9, 127.6, 126.0, 125.7, 124.4, 123.9, 118.4, 73.3, 43.6

FTIR (neat): 3380$cm^{-1}$.

HRMS Calcd for $C_{14}H_{14}0$ [$M^+$]: 198.1047. Found: 198.1054.

The enantiomeric excess was determined by HPLC analysis employing a Daicel Chiracel OD-H column (Hexane: *i*-propanol 98:2, 1 mL/min: $t_1$ = 40.11min for *S* enantiomer , $t_2$ = 46.68min for *R* enantiomer).

**(*S*)-1-(4-chlorophenyl)but-3-en-1-ol**




**Selectivity**: 93 % *ee*
**Opt. Rot.**: $[\alpha]_D^{25}$ -34.7 (c = 0.98 in $CH_2Cl_2$)
$R_f$ = 0.5 (4:1 hexane/ethyl acetate)

$^1$H NMR (300 MHz, $CDCl_3$): δ 7.31 (d, J= 2.7Hz, 2H), 7.12 (d, J = 2.8Hz, 2H), 5.84-5.70 (m, 1H), 5.19-5.11 (m, 2H), 4.70-4.65 (m, 1H), 2.55-2.37 (m, 2H), 2.11(br, 1H).

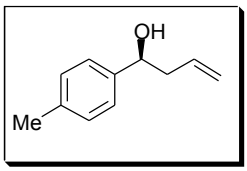
$^{13}$C NMR (75.4 MHz, $CDCl_3$): δ 146.88, 134.21, 133.84, 129.58, 127.51, 125.94, 123.88, 118.74, 72.45, 43.64.

FTIR (neat): 3367, 2905, 1573, 1432, 1196 $cm^{-1}$.

HRMS Calcd for $C_{10}H_{11}ClO$ [$M^+$]: 182.0498. Found: 182.0502.

The enantiomeric excess was determined by HPLC analysis employing a Daicel Chiracel ASH column (Hexane: *i*-propanol 98:2, 1 mL/min: $t_1$ =8.72min for the *R* enantiomer, $t_2$ =9.34 min for the *S* enantiomer).

**(*S*)-1-(4-methylphenyl)but-3-en-1-ol**




**Selectivity**: 83 % *ee*
**Opt. Rot.**: $[\alpha]_D^{25}$ -28.7 (c = 1.49 in $CH_2Cl_2$)
$R_f$ = 0.61 (4:1 hexane/ethyl acetate)

$^1$H NMR (300 MHz, $CDCl_3$): δ 7.27 (d, J= 7.6 Hz, 2H), 7.18(d, J = 7.6 Hz, 2H), 5.83-5.68 (m, 1H), 5.20-5.18 (m, 2H), 4.71-4.66 (m, 1H), 2.56-2.38 (m, 2H), 2.34(s, 3H), 2.08(br, 1H).

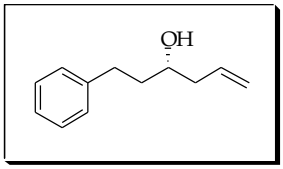
$^{13}$C NMR (75.4 MHz, $CDCl_3$): δ 140.8, 138.2, 134.4, 128.7, 125.8, 118.9, 74.2, 43.6, 21.6.

FTIR (neat): 3389 $cm^{-1}$.

HRMS Calcd for $C_{10}H_{14}O$ [$M^+$]: 162.1045. Found: 162.1049.

The enantiomeric excess was determined by HPLC analysis employing a Daicel Chiracel ASH column (Hexane: *i*-propanol 99:1, 1 mL/min: $t_1$ =8.87min for the *R* enantiomer, $t_2$ =10.92 min for the *S* enantiomer).

**(*R*)-1-phenylhex-5-en-3-ol**




**Selectivity**: 60% *ee*
**Opt. Rot.**: $[\alpha]_D^{25}$ +11.2 (c = 1.26 in $CH_2Cl_2$)
$R_f$ = 0.49 (4:1 hexane/ethyl acetate)

$^1H$ NMR (300 MHz, $CDCl_3$): δ 7.31-7.16 (m, 5H), 5.89-5.75 (m, 1H), 5.17-5.12 (m, 2H), 3.68 (m, 1H), 2.74 (m, 2H), 2.36-2.14 (m, 2H), 1.81-1.76 (m, 2H)

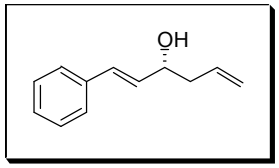
$^{13}C$ NMR (75.4 MHz, $CDCl_3$): δ 142.0, 134.6, 128.4, 125.8, 118.2, 70.0, 42.0, 38.4, 32.0.

FTIR (neat): 3377, 2928, 1495 $cm^{-1}$.

HRMS Calcd for $C_{12}H_{16}0$ [$M^+$]: 176.1201. Found: 176.1199.

The enantiomeric excess was determined by HPLC analysis employing a Daicel Chiracel OD column (Hexane: *i*-propanol 99:1, 1.0 mL/min: $t_1$ = 13.18 min for *S* enantiomer, $t_2$ = 21.46 min for *R* enantiomer). It has been established that the *S* enantiomer elutes first.

**(*S*)-1-phenylhexa-1,5-dien-3-ol**




**Selectivity**: 67 % *ee*
**Opt. Rot.**: $[\alpha]_D^{25}$ -9.82 (c = 1.64 in $CH_2Cl_2$)
$R_f$ = 0.40 (4:1 hexane/ethyl acetate)

$^1$H NMR (300 MHz, $CDCl_3$): δ 7.21-7.40 (m, 5H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.25 (dd, *J* = 15.9, 6.3 Hz, 1H), 5.79-5.93 (m, 1H), 5.15-5.21 (m, 2H), 4.35-4.37 (m, 1H), 2.33-2.48 (m, 2H), 1.80 (br, 1H)

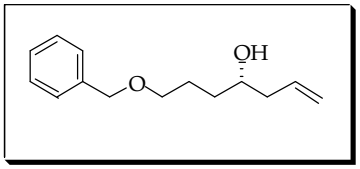
$^{13}$C NMR (75.4 MHz, $CDCl_3$): δ 136.6, 134.0, 131.5, 130.3, 128.5, 127.6, 126.4, 118.4, 71.6, 42.0.

FTIR (neat): 3414 $cm^{-1}$.

HRMS Calcd for $C_{12}H_{14}O$ [$M^+$]: 174.1045. Found: 176.1040.

**The enantiomeric excess was determined by HPLC analysis employing a Daicel Chiracel ODH column (Hexane: *i*-propanol 98:2, 1.0 mL/min: $t_1$ = 16.03 min for *R* enantiomer, $t_2$ = 26.53 min for *S* enantiomer). It has been established that the *R* enantiomer elutes first.**

**(*R*)-7-(benzyloxy)hept-1-en-4-ol**




**Selectivity**: 63 % *ee*
**Opt. Rot.**: $[\alpha]_D^{25}$+5.44 (c = 0.96 in $CH_2Cl_2$)
$R_f$ = 0.38 (4:1 hexane/ethyl acetate)

$^1$H NMR (300 MHz, $CDCl_3$): δ 7.39-7.28 (m, 5H), 5.90-5.77 (m, 1H), 5.17-5.09 (m, 2H), 4.52 (s, 2H), 3.71-3.61 (m, 1H), 3.52 (t, *J* = 5.9 Hz, 2H), 2.32-2.13 (m, 2H), 1.78-1.63 (m, 2H), 1.53-1.41 (m, 2H)

$^{13}$C NMR (75.4 MHz, $CDCl_3$): δ 138.2, 135.0, 128.4, 127.7, 127.6, 117.7, 73.0, 70.6, 70.4, 42.0, 34.0, 26.2

FTIR (neat): 3451, 2928, 2862, 1641, 1452, 1097, 1026, 998, 915, 740, 699 $cm^{-1}$.

HRMS Calcd for $C_{14}H_{20}O_2$ [$M^+$]: 220.1463. Found: 220.1465.

The enantiomeric excess was determined by HPLC analysis employing a Daicel Chiracel OB column (Hexane: *i*-propanol 99:1, 1.0 mL/min: $t_1$ =21.24min for the *R* enantiomer, $t_2$ =28.05 min for the *S* enantiomer).