Graphical Abstract

In the presence of 20mol% of chiral catalytic complex prepared from In(OTf)_3 and chiral PYBOX, allytributylstananne reacted with achiral ketones to afford the corresponding homoallylic alcohols in moderate to high enantioselectivities (54–95% ee), which constitutes the first example of enantioselective allylation of ketones catalyzed by chiral In(III)-PYBOX complex.
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 F254 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 (1H NMR) were recorded on a Bruker Avance DPX 300 and Bruker AMX 500 spectrophotometer (CDCl3 as solvent). Chemical shifts for 1H NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe4 (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 (13C NMR) are reported as δ in units of parts per million (ppm) downfield from SiMe4 (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 °C 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 ketones:**

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 (5) (19.9 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 acetophenone (18 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 0 °C for 15 minutes followed by addition of allyltributylstannane (57 ul, 0.18 mmol, 1.2 equiv.). The reaction mixture was stirred at 0 °C for 70 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$_2$SO$_4$, filtered and concentrated in vacuo. The residual crude product was purified via silica gel chromatography to afford the homoallylic alcohol as colorless oil (62% yield).

**Characterization of tertiary homoallylic alcohols in Table 2**

(R)-2-Phenyl-4-penten-2-ol

![](image)

$^1$H NMR (300 MHz, CDCl3): δ 7.21-7.48 (m, 5H), 5.57-5.72 (m, 1H), 5.10-5.18(m, 2H), 2.70 (dd, J = 13.9, 6.3 Hz, 1H), 2.51 (dd, J = 13.6, 8.0Hz, 1H), 2.08 (s, 1H), 1.56 (s, 3H)

$^{13}$C NMR (75.4 MHz, CDCl3): δ 147.6, 133.6, 128.1, 126.6, 124.7, 119.4, 73.6, 48.4, 29.8

FTIR (neat): 3415, 3075, 2974, 1640, 1445, 914, 766, 700 cm$^{-1}$.

HRMS Calcd for C$_{12}$H$_{16}$O [M - H$_2$O]: 144.0939 Found: 144.0934

The enantiomeric excess was determined by HPLC analysis employing a Daicel Chiracel OJ column (Hexane : i-propanol 98:2, 1.0 mL/min: $t_1$ = 7.76 min for S enantiomer, $t_2$ = 10.39 min for R enantiomer).
(R)-2-(4-methylPhenyl)-4-penten-2-ol

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\begin{align*}
1^1\text{H NMR (300 MHz, CDCl}_3\text{): } & \delta 7.36 (d, J=8.2, 2H), 7.15(d, J=8.2, 2H), 5.56-5.71 (m, 1H), \\
& 5.16-5.09(m, 2H), 2.71 (dd, J = 13.8, 5.8 Hz, 1H), 2.50 (dd, J = 13.6, 8.0Hz, 1H), 2.34(s, 3H), \\
& 2.08 (s, 1H), 1.56 (s, 3H)
\end{align*}
\]

\[
\begin{align*}
1^3\text{C NMR (75.4 MHz, CDCl}_3\text{): } & \delta 147.6, 133.6, 128.1, 126.6, 124.7, 119.4, 73.6, 48.4, 29.8, 20.8 \\
\text{FTIR (neat): } & 3415, 3075, 2974, 1640, 1445, 914, 766, 700 \text{ cm}^{-1}.
\end{align*}
\]

HRMS Calcd for C\textsubscript{12}H\textsubscript{16}O [M - H\textsubscript{2}O]: 158.1096 Found: 158.1093

The enantiomeric excess was determined by HPLC analysis employing a Daicel Chiracel ODH column (Hexane: i-propanol 99:1, 0.5 mL/min: \(t_1 = 14.04\) min for \textit{S} enantiomer, \(t_2 = 16.88\) min for \textit{R} enantiomer).

(S)-3-Methyl-1-phenyl-5-hexen-3-ol

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\begin{align*}
1^1\text{H NMR (300 MHz, CDCl}_3\text{): } & \delta 7.19 – 7.31 (m, 5H), 5.82-5.96 (m, 1H), 5.12-5.19 (m, 2H), \\
& 2.68-2.74 (m, 2H), 2.30 (d, J = 7.2, 2H), 1.75-1.81 (m, 2H), 1.26 (s, 3H), \\
1^3\text{C NMR (75.4 MHz, CDCl}_3\text{): } & \delta 142.5, 133.8, 128.4, 128.3, 125.8, 118.9, 72.1, 46.5, 43.7, 30.3, \\
& 26.8.
\end{align*}
\]

FTIR (neat): 3429, 3415, 2977, 1640, 912, 742, 699 cm\textsuperscript{-1}.

HRMS Calcd for C\textsubscript{12}H\textsubscript{16}O [M – H\textsubscript{2}O]: 172.1252. Found: 172.1252

The enantiomeric excess was determined by HPLC analysis employing a Daicel Chiracel ODH column (Hexane: i-propanol 99:1, 0.5 mL/min: \(t_1 = 31.03\) min for \textit{R} enantiomer, \(t_2 = 35.52\) min for \textit{S} enantiomer).
(R)-3-Methyl-1-phenyl-hexa-1,5-dien-3-ol

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\begin{align*}
\text{\textsuperscript{1}H NMR (300 MHz, CDCl3): } & \delta 7.19 – 7.40 (m, 5H), 6.60 (d, J = 16.1 Hz, 1H), 6.30 (d, J = 16.0 Hz, 1H), 5.77-5.91 (m, 1H), 5.14-5.19 (m, 2H), 2.45 (dd, J = 13.6, 6.4 Hz, 1H), 2.36 (dd, J = 13.6, 8.0 Hz, 1H), 1.77 (s, 1H), 1.39 (s, 3H). \\
\text{\textsuperscript{13}C NMR (75.4 MHz, CDCl3): } & \delta 137.0, 136.3, 133.6, 128.6, 127.5, 127.4, 126.4, 119.3, 72.4, 47.4, 28.0. \\
\text{FTIR (neat): } & 3410, 3078, 1640, 970, 916, 748, 693 \text{ cm}^{-1}. \\
\text{HRMS Calcd for C}_{13}\text{H}_{16}\text{O [M – H}_{2}\text{O}: } & 170.1095. \text{ Found: 170.1091}
\end{align*}
\]

The enantiomeric excess was determined by HPLC analysis employing a Daicel Chiracel ODH column (Hexane: \textit{i}-propanol 99:1, 0.5 mL/min: \(t_1 = \) 37.87 min for \(R\) enantiomer, \(t_2 = \) 44.59 min for \(S\) enantiomer).

(R)-1-Allyl-indan-1-ol

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\begin{align*}
\text{\textsuperscript{1}H NMR (300 MHz, CDCl3): } & \delta 7.31 – 7.36 (m, 1H), 7.21 – 7.29 (m, 3H), 5.80-5.93 (m, 1H), 5.14-5.20 (m, 2H), 3.00 (ddd, J = 16.0, 8.7, 4.5, 1H), 2.77-2.87 (m, 1H), 2.64 (dd, J = 13.8, 7.3 1H), 2.52 (dd, J = 13.6, 7.0, 1H), 2.29-2.38 (m, 1H), 2.19 (bs, 1H), 2.03-2.12 (m, 1H). \\
\text{\textsuperscript{13}C NMR (75.4 MHz, CDCl3): } & \delta 147.0, 143.0, 133.8, 128.2, 126.6, 124.9, 122.9, 118.7, 82.7, 45.0, 39.6, 29.4 \\
\text{FTIR (neat): } & 3402, 1640, 996, 914, 760 \text{ cm}^{-1}. \\
\text{HRMS Calcd for C}_{12}\text{H}_{14}\text{O [M – H}_{2}\text{O]: } & 156.0939. \text{ Found 156.0934}
\end{align*}
\]

The enantiomeric excess was determined by HPLC analysis employing a Daicel Chiracel ODH column (Hexane: \textit{i}-propanol 99:1, 1.0 mL/min: \(t_1 = \) 9.63 min for \(S\) enantiomer, \(t_2 = \) 12.39 min for \(R\) enantiomer).
(R)-1-Allyl-5-methyl-indan-1-ol

![Image](image_url)

$^1$H NMR (300 MHz, CDCl₃): $\delta$ 7.08 – 7.15 (m, 3H), 5.79-5.93 (m, 1H), 5.15-5.21 (m, 2H), 2.95 (ddd, $J$ = 16.0, 8.7, 4.5, 1H), 2.72-2.82 (m, 1H), 2.64 (dd, $J$ = 13.6, 7.7, 1H), 2.50 (dd, $J$ = 13.6, 7.0, 1H), 2.36 (s, 3H), 2.28-2.35 (m, 1H), 2.02-2.11 (m, 1H).

$^{13}$C NMR (75.4 MHz, CDCl₃): $\delta$ 147.2, 140.0, 136.3, 133.9, 129.2, 124.7, 123.4, 118.8, 82.7, 45.0, 39.9, 29.0, 21.4.

FTIR (neat): 3294, 3079, 3015, 2844, 1638, 1491, 996, 913, 812 cm$^{-1}$.

HRMS Calcd for C$_{13}$H$_{18}$O [M – H$_2$O]: 170.1095 Found : 170.1091

The enantiomeric excess was determined by HPLC analysis employing a Daicel Chiracel OD column (Hexane: $i$-propanol 99:1, 1.0 mL/min: $t_1$ = 7.18 min for $S$ enantiomer, $t_2$ = 11.03 min for $R$ enantiomer).

(R)-1-allyl-1,2,3,4-tetrahydro-naphtalen-1-ol

![Image](image_url)

$^1$H NMR (300 MHz, CDCl₃): $\delta$ 7.14-7.07 (m, 4H), 5.92-5.79 (m, 1H), 5.20-5.14 (m, 2H), 2.99-2.48 (m, 4H), 2.46-2.36 (m, 3H), 2.11-2.04 (m, 1H).

$^{13}$C NMR (75.4 MHz, CDCl₃): $\delta$ 147.16, 139.98, 136.34, 133.85, 129.18, 124.66, 123.36, 118.80, 82.67, 44.96, 39.92, 29.00, 21.36

FTIR (neat): 3394, 3082, 2844, 16701, 1512, 998, 909, 818 cm$^{-1}$.

HRMS Calcd for C$_{13}$H$_{16}$O [M – H$_2$O]: 170.1096 Found : 170.1092

The enantiomeric excess was determined by HPLC analysis employing a Daicel Chiracel OD column (Hexane: $i$-propanol 99:1, 1.0 mL/min: $t_1$ = 8.31 min for $R$ enantiomer, $t_2$ = 10.13 min for $S$ enantiomer).