Supporting Information

General

Experiments involving moisture and/or air sensitive components were performed under a positive pressure of nitrogen in flame-dried glassware equipped with a rubber septum inlet. Dried solvents and liquid reagents were transferred by over dried syringes cooled in a desiccator. Moisture in non volatile reagents were removed by the addition of dry THF followed by azeotropic removal of the solvent in vacuo.

Commercial solvents and reagents were used without further purification with the following exceptions: Hexane, dichloromethane, ethyl acetate were fractionally distilled; dry dichloromethane were distilled from calcium hydride under nitrogen. Dry THF was obtained by distillation from a deep blue solution resulting from benzophenone and sodium. All Lewis acids were heated at 100 °C under reduced pressure for two hours before used.

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. 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 a slurry and equilibrated with the appropriate solvent 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) and carbon nuclear magnetic resonance spectra (\(^{13}\)C NMR) were recorded on a Bruker DPX 300 spectrophotometer (internal reference SiMe\(_4\) and CDCl\(_3\) as solvent). Chemical shifts for \(^1\)H and \(^{13}\)C NMR spectra are reported as \(\delta\) in units of parts per million (ppm) downfield from SiMe\(_4\) (\(\delta\) 0.0) and relative to the signal of chloroform-\(d\) (\(\delta\) 77.03) respectively. Multiplicities are 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 \(n\)H. The proportion of diastereomers 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/e) and % intensity.

Experimental procedures

A representative procedure for preparation of α-adduct linear homoallylic alcohols (4a)

A mixture of 2,2-Dimethyl-5-hepten-3-ol 1 (0.1776 g, 1.25 mmol) in 1mL of CH₂Cl₂ was added to a round bottom flask containing In(OTf)₃ (0.028 g, 0.05 mmol) and 1 mL of CH₂Cl₂. Following that, 3-Phenylpropanal 2a (0.056 g, 0.5 mmol) in 1 mL of CH₂Cl₂ was slowly added to the reaction mixture in 10 to 15 minutes at room temperature. The reaction mixture was stirred for 2 hours at ambient temperature. Ether was added to dilute the reaction mixture followed by 1 M HCl to quench the reaction. The reaction mixture was extracted with ether. The combined organic layer was washed with brine, and dried over anhydrous magnesium sulphate, filtered and the solvent was removed in vacuo. The crude
product was purified by column chromatography to afford 1-Phenyl-hept-5-en-3-ol 4a as colorless oil in 69% yield.

\[
\text{Ph} \quad \text{OH} \quad \text{Ph}
\]

1-Phenyl-hept-5-en-3-ol

\[ R_f : 0.34 \text{ (4:1 hexane/ethyl acetate).} \]

\[ \text{H NMR (300 MHz, CDCl}_3\text{) } E \text{ isomer: } \delta 7.31-7.16 \text{ (m, 5H), 5.57 (dq, } J = 15.3, 6.3 \text{ Hz, 1H), 5.47-5.37 \text{ (m, 1H), 3.61 (br m, 1H), 2.86-2.63 \text{ (m, 2H), 2.29-2.05(m, 2H), 1.81-1.58 \text{ (m, 2H), 1.69 (d, } J = 5.94 \text{ Hz)}} \]

\[ \text{C NMR (75.4 MHz, CDCl}_3\text{) } E \text{ isomer: } \delta 142.2, 129.2, 128.5, 128.4, 126.9, 125.8, 70.2, 40.9, 38.4, 32.1, 18.1 \]

\[ \text{FTIR (KBr salt plate): } \nu 3568, 3412, 3083, 3064, 3028, 3001, 2963, 2932, 2868, 1640, 1545, 1000, 914, 748, 700 \text{ cm}^{-1}. \]

\[ \text{HRMS (EI) Calcd for C}_{13}\text{H}_{16} \text{ [M-H}_2\text{O]}^+: 172.1252. \text{ Found: 172.1259} \]

\[ [\alpha]_D = +6.4, \text{ (c = 1.75, MeOH)} \]

HPLC analysis employing a Daicel Chiralcel OD column (n-hexane : i-propanol 99: 1; 1.0 ml/min): \( t = 19.97 \)

\[
\text{Ph} \quad \text{OH} \quad \text{Ph}
\]

1-Phenyl-hex-4-en-2-ol
$R_f$ 0.44 (4:1 hexane/ethyl acetate).

$^1$H NMR (300 MHz, CDCl$_3$) E isomer: $\delta$ 7.36-7.23 (m, 5H), 5.60 (ddd, $J = 15.3$, 6.3, 5.6 Hz, 1H), 5.51 (dq, $J = 15.3$, 7.7 Hz, 1H), 3.86 (dddd, $J = 7.7$, 6.90, 5.6, 4.9 Hz, 1H), 2.82 (dd, $J = 13.9$, 4.9 Hz, 1H), 2.75 (dd, $J = 13.9$, 7.7 Hz, 1H), 2.29 (dt, $J = 13.9$, 6.9 Hz, 1H), 2.16 (dt, $J = 13.9$, 6.9 Hz, 1H), 1.73 (d, $J = 6.9$ Hz, 3H)

$^{13}$C NMR (75.4 MHz, CDCl$_3$) E isomer: $\delta$ 138.6, 129.4, 129.0, 128.5, 127.0, 126.4, 72.0, 43.3, 40.0, 18.1

FTIR (KBr Salt Plate): ν 3562, 3407, 3027, 2933, 2917, 2732, 1602, 1496, 1454, 1080, 1031, 742 cm$^{-1}$.

HRMS Calcd for [C$_{12}$H$_{16}$O$^+$. Found: 176.1206. 

[$\alpha$] = +5.25, (c = 1.56, MeOH)

HPLC analysis employing a Daicel Chiralcel OD column (n-hexane : i-propanol 99: 1; 1.0 ml/min): $t = 8.90$ min

Non-7-ene-1,5-diol

$R_f$ 0.14 (1:1 hexane/ethyl acetate).

$^1$H NMR (300 MHz, CDCl$_3$) E isomer: $\delta$ 5.55 (dt, $J = 14.6$, 6.3, 1H), 5.42 (ddq, $J = 14.6$, 6.3, 1.4, 1H), 3.66 (t, $J = 6.3$ Hz, 2H), 3.62-3.56 (m, 1H), 2.23 (dddd, $J = 11.1$, 7.7, 6.3, 1.4 Hz, 1H), 2.06 (ddd, $J = 11.1$, 7.7, 6.9 Hz, 1H), 1.70 (d, $J = 6.3$ Hz, 3H), 1.60-1.40 (m, 6H).
\[^{13}\text{C}\] NMR (75.4 MHz, CDCl\(_3\)) \text{ } \text{E isomer: } \delta 129.0, 127.0, 70.7, 62.7, 40.6, 36.2, 32.5, 21.7, 17.9

\[^{19}\text{F}\] NMR (282.2 MHz, CDCl\(_3\)) \text{ } \text{E isomer: } \delta 4.27, 3.92

\text{FTIR (KBr salt Plate): } \nu 3345, 3026, 2934, 2863, 1695, 1646, 1449, 1373, 1340, 1256, 1063, 1026, 963, 917 \text{ cm}^{-1}.

[\alpha] = + 13.0, \ (c = 0.36, \text{MeOH})

\begin{align*}
\text{TBDPSO} & \quad \text{OH} \\
\text{1-}(\text{tert-Butyl-diphenyl-silanyloxy})-\text{oct-6-en-4-ol} \\
\text{Rf: } & 0.39 \ (4:1 \text{ hexane/ethyl acetate}).
\end{align*}

\[^{1}\text{H}\] NMR (300 MHz, CDCl\(_3\)) \text{ } \text{E isomer: } \delta 7.69-7.67 \text{ (m, 4H), } 7.46-7.36 \text{ (m, 6H), } 5.62-5.39 \text{ (m, 2H), } 3.71 \text{ (t, } J = 6.3 \text{ Hz, 2H),} \\
3.66-3.58 \text{ (m, 1H), } 2.29-2.06 \text{ (m, 3H), } 1.80-1.40 \text{ (m, 4H),} \\
1.70 \text{ (dd, } J = 5.91, 1.05 \text{ Hz, 3H), } 1.07 \text{ (s, 9H)}

\[^{13}\text{C}\] NMR (75.4 MHz, CDCl\(_3\)) \text{ } \text{E isomer: } \delta 135.6, 133.9, 129.6, 128.7, 127.6, 127.2, 70.9, 64.1, 40.7, 33.4, 28.8, 26.9, 19.2, 18.1

\[^{19}\text{F}\] NMR (282.2 MHz, CDCl\(_3\)) \text{ } \text{E isomer: } \delta 4.16

\text{FTIR (KBr salt plate): } \nu 3427, 2960, 2932, 2858, 2636, 1428, 1112, 969, 823, 740, 701 \text{ cm}^{-1}.

[\alpha] = - 7.7, \ (c = 0.72, \text{MeOH})

\text{MS (ESI) Calcd for } [\text{C}_{24}\text{H}_{34}\text{O}_2\text{SiNa}]^+: 405.2. \text{ Found: } 405.2.
2,2-Dimethyl-hept-5-en-3-ol

$R_f$: 0.47 (4:1 hexane/ethyl acetate).

$^1$H NMR (300 MHz, CDCl$_3$) E isomer: $\delta$ 5.69-5.31 (m, 2H), 3.17 (dd, $J = 10.4, 2.0, 1H$), 2.36-2.19 (m, 2H), 1.70 (d, $J = 6.4, 3H$), 0.90 (s, 9H)

$^{13}$C NMR (75.4 MHz, CDCl$_3$) E isomer: $\delta$ 128.8, 128.3, 78.3, 35.2, 34.4, 25.7, 17.9.

$^{19}$F NMR (282.2 MHz, CDCl$_3$) E isomer: $\delta$ 4.33

FTIR (KBr Salt Plate): $\nu$ 3406.4, 3081.2, 2974.0, 2246.3, 1637.6, 1453.9, 1021.3, 912.8, 701.3.

$[\alpha] = +11.4, \ (c = 5.19, \text{MeOH})$


6-Cyclohexyl-3-methyl-2-phenethyl-tetrahydro-pyran-4-ol

$R_f$: 0.38 (4:1 hexane/ethyl acetate).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.25–7.15 (m, 5H), 3.27 (dt, $J = 10.3, 4.6$ Hz, 1H), 3.03–2.95 (m, 1H), 2.93–2.80 (m, 2H), 2.78–2.59 (m, 1H), 2.12–1.88 (m, 3H), 1.79–1.62 (m, 8H),
1.27-1.18 (m, 5H), 1.03-0.99 (m, 1H), 0.91 (d, J = 6.6 Hz, 3H).

$^{13}$C NMR (75.4 MHz, CDCl$_3$): $\delta$ 142.6, 128.6, 128.3, 125.7, 125.7, 79.7, 79.5, 74.2, 44.3, 42.9, 38.6, 34.9, 31.8, 29.4, 29.0, 26.6, 26.2, 26.1, 12.8.

FTIR (NaCl Salt Plate): ν 3649, 3589, 3530, 3455, 3427, 1631, 455, 430.

HRMS Calcd for [C$_{20}$H$_{30}$O$_2$]$^+$: 302.2246. Found: 302.2239

6-Isopropyl-3-methyl-2-phenethyl-tetrahydro-pyran-4-ol

$R_f$: 0.30 (4:1 hexane/ethyl acetate).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.31-7.15 (m, 5H), 3.28 (dt, $J$ = 10.5, 4.5 Hz, 1H), 2.99-2.92 (m, 2H), 2.87 (dt, $J$ = 2.6, 9.6 Hz, 1H), 2.72-2.59 (m, 1H), 2.05-1.88 (m, 2H), 1.82-1.65 (m, 2H), 1.39-1.16 (m, 2H), 1.03 (d, $J$ = 6.6 Hz, 3H), 0.92 (d, $J$ = 6.6 Hz, 6H).

$^{13}$C NMR (75.4 MHz, CDCl$_3$): $\delta$ 142.7, 128.6, 128.3, 125.7, 80.5, 79.5, 74.2, 44.2, 38.5, 34.9, 33.3, 31.8, 19.0, 18.8, 12.8, 5.1.

FTIR (NaCl Salt Plate): ν 3630, 3568, 3475, 3423, 2958, 2874, 1456, 1152, 1008, 747, 699.

3-Methyl-6-octyl-2-phenethyl-tetrahydro-pyran-4-ol

\(R_f\) : 0.33 (4:1 hexane/ethyl acetate).

\(^1\text{H NMR (300 MHz, CDCl}_3\):} \(\delta\) 7.31-7.15 (m, 5H), 3.30-3.22 (m, 2H), 2.87 (dt, \(J = 2.8, 9.8\) Hz, 1H), 2.82-2.59 (m, 2H), 2.03-1.88 (m, 12H), 1.83-1.28 (m, 1H), 0.92 (d, \(J = 6.6\) Hz, 3H), 0.86 (t, \(J = 7.1\) Hz, 3H).

\(^{13}\text{C NMR (75.4 MHz, CDCl}_3\):} \(\delta\) 142.6, 128.6, 128.4, 125.8, 79.6, 75.3, 73.9, 44.2, 41.6, 36.2, 35.6, 34.8, 31.9, 31.8, 29.7, 29.4, 25.8, 22.7, 14.3, 5.1.

\(\text{FTIR (NaCl Salt Plate):} \nu\) 3566, 2930, 2089, 1684, 1606, 1496, 1374, 735, 699, 429.


3-Methyl-2-phenethyl-6-phenyl-tetrahydro-pyran-4-ol

\(R_f\) : 0.33 (4:1 hexane/ethyl acetate).
$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.42-7.16 (m, 10H), 4.41 (dd, $J = 1.7$, 11.5 Hz, 1H), 3.52-3.46 (m, 1H), 3.14 (dt, $J = 2.8$, 9.4 Hz, 1H), 2.95-2.70 (m, 3H), 2.27 (ddd, $J = 2.1$, 4.5, 12.5 Hz, 1H), 2.09-1.98 (m, 2H), 1.46-1.37 (m, 1H), 1.01 (d, $J = 6.6$ Hz, 3H).

$^{13}$C NMR (75.4 MHz, CDCl$_3$): $\delta$ 142.6, 142.4, 128.6, 128.4, 127.4, 125.9, 125.8, 125.7, 80.2, 76.9, 74.0, 43.7, 43.0, 34.8, 31.6, 12.9.

FTIR (NaCl Salt Plate) ν 3657, 3630, 1685, 1638, 1497, 1453, 699, 414.


6-tert-Butyl-3-methyl-2-phenethyl-tetrahydro-pyran-4-ol

$R_f$: 0.24 (4:1 hexane/ethyl acetate).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.28-7.15 (m, 5H), 3.33-3.24 (m, 1H), 2.94-2.87 (m, 2H), 2.86 (dt, $J = 3.3$, 9.6 Hz, 1H), 2.66 (dt, $J = 1.7$, 7.4 Hz, 1H), 1.99-1.89 (m, 2H), 1.76-1.64 (m, 1H), 1.32-1.13 (m, 2H), 0.95 (s, 9H), 0.92 (d, $J = 6.6$ Hz, 3H).

$^{13}$C NMR (75.4 MHz, CDCl$_3$): $\delta$ 142.9, 128.6, 128.3, 125.7, 82.7, 79.6, 74.7, 44.1, 35.6, 35.0, 34.2, 32.4, 26.2, 12.9.
FTIR (NaCl Salt Plate): ν 3648, 3629, 3477, 3383, 2954, 698, 458, 431.