Supporting Information

Catalytic Enantioselective Grignard-Nozaki-Hiyama Methallylation from the Alcohol Oxidation Level: Chloride Compensates for π-Complex Instability

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Electronic Supplementary Material (ESI) for Chemical Communications

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I. General Methods

All reactions were run under an atmosphere of nitrogen. Tetrahydrofuran was dried over sodium metal benzophenone and distilled immediately prior to use. Dichloromethane was dried over CaCl₂ and distilled immediately prior to use. Commercially available methallyl chloride (Sigma-Aldrich) and allyl acetate (Acros) were purified by distillation prior to use. [Ir(cod)₂Cl] was used as received from Strem Chemicals. Tribasic potassium phosphate (Sigma-Aldrich) was flame dried under vacuum before use. Cesium carbonate was purchased from Alfa Aesar and used directly without further purification. Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates (DC-Fertigplatten Kieselgel 60 F₂₅₄). Infrared spectra were recorded on a Perkin-Elmer 1600 spectrometer. High-resolution mass spectra (HRMS) were obtained on a Karatos MS9 and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion (M+1 or M+Na). ¹H Nuclear magnetic resonance spectra were recorded using a 400 MHz and spectrometer. Coupling constants are reported in Hertz (Hz). For CDCl₃ solutions and chemical shifts are reported as parts per million (ppm) relative to residual CHCl₃ δ(H) (7.26 ppm). ¹³C Nuclear magnetic resonance spectra were recorded using a 100 MHz spectrometer. For CDCl₃ solutions and chemical shifts are reported as parts per million (ppm) relative to residual CDCl₃ δ(C) (77.0 ppm).
II. Experimental Details and Spectral Data

II.a. Synthesis of Catalyst of (R)-I

To a mixture of [Ir(cod)Cl]₂ (134.3 mg, 0.20 mmol, 100 mol%), (R)-Cl,MeO-BIPHEP (260.6 mg, 0.40 mmol, 200 mol%), Cs₂CO₃ (260.6 mg, 0.80 mmol, 400 mol%), 4-Cl-3-NO₂BzOH (161.2 mg, 0.89 mmol, 400 mol%) and allyl acetate (100.1 mg, 1.0 mmol, 500 mol%) in a sealed tube under an atmosphere of nitrogen was added THF (4.0 mL, 0.05 M). The reaction mixture was stirred for 30 min at ambient temperature and heated for 1.5 hr at 80 °C, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered with the aid of THF (10 mL). The filtrate was concentrated *in vacuo* and the residue was subjected to flash column chromatography (dichloromethane:ether, 3:1). The residue obtained upon chromatographic isolation was dissolved in THF (2 mL) and hexane (50 mL) was added. The resulting yellow precipitate was collected by filtration and dried under vacuum to provide (R)-I (344.0 mg, 0.320 mmol) in 80% yield.
II.b. Experimental Details for Methallylation from Alcohol Oxidation Level

(S)-2-Methyldodec-1-en-4-ol (3a)

To a resealable pressure tube equipped with a magnetic stir bar was added (R)-I (10.7 mg, 0.01 mmol, 5 mol%) and potassium phosphate (42.4 mg, 0.20 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. THF (0.2 mL, 1.0 M), alcohol 1a (28.5 mg, 0.20 mmol, 100 mol%) and β-methallyl chloride (54.3 mg, 0.60 mmol, 300 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was placed in an oil bath at 50 °C and was allowed to stir for 24 hr. The reaction mixture was concentrated in vacuo. The residue was subjected to column chromatography (SiO\textsubscript{2}; ethyl acetate: hexanes, 1:40 to 1:20) to provide the title compound 3a (31.7 mg, 0.160 mmol) as a colorless oil in 80% yield.

\textbf{TLC (SiO\textsubscript{2})}: R\textsubscript{f} = 0.38 (ethyl acetate: hexanes, 1:9).

\([\alpha]D\textsuperscript{25} = -8.0 (c = 1, \text{CH}_2\text{Cl}_2), \text{literature value for }\text{ent }3a, +11.2 (c = 3.02, \text{CCl}_4)^1\]

\textbf{1H NMR} (400 MHz, CDCl\textsubscript{3}): δ 4.90-4.87 (m, 1H), 4.81-4.78 (m, 1H), 3.75-3.68 (m, 1H), 2.21 (dd J = 13.5, 3.3 Hz, 1H), 2.08 (ddd, J = 13.7, 9.4, 0.7 Hz, 1H), 1.76 (s 3H), 1.68 (d, J = 1.7, 1H), 1.46-1.27 (m, 14H), 0.88 (t, J = 6.9 Hz, 3H).

\textbf{13C NMR} (100 MHz, CDCl\textsubscript{3}): δ 142.9, 113.4, 68.6, 46.2, 37.1, 31.9, 29.7, 29.6, 29.3, 25.7, 22.7, 22.4, 14.1

\textbf{FTIR} (neat): 3315, 2921, 2859, 2367, 2331, 1842, 1739, 1647, 1563, 1534, 1456, 1375, 1261, 1230, 1216, 1072, 1018, 887, 867, 846, 804, 758, 750, 721, 703, 669, 655 cm\textsuperscript{-1}.

\textbf{HPLC}: Enantiomeric excess was determined by HPLC analysis of the 4-nitrobenzoate derivative of the product, (Chiralcel OD-H-OD-H column, hexanes:i-PrOH = 99.5:0.5, 1 mL/min, 254 nm), \(t\textsubscript{major} = 35.8 \text{ min } t\textsubscript{minor} = 41.9 \text{ min} ;\ ee = 95\%.

\textsuperscript{1}The optical rotation of compound 3a correspond with the reported \textit{ent}-compound.

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(R)-1-(Benzyloxy)-5-methylhex-5-en-3-ol (3b)

To a resealable pressure tube equipped with a magnetic stir bar was added (R)-I (10.7 mg, 0.01 mmol, 5 mol%) and potassium phosphate (42.4 mg, 0.20 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. THF (0.2 mL, 1.0 M), alcohol 1b (33.2 mg, 0.20 mmol, 100 mol%) and β-methallyl chloride (54.3 mg, 0.60 mmol, 300 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was placed in an oil bath at 50 °C and was allowed to stir for 24 hr. The reaction mixture was concentrated *in vacuo*. The residue was subjected to column chromatography (SiO$_2$; ethyl acetate: hexanes, 1:10 to 1:5) to provide the title compound 3b$^2$ (30.4 mg, 0.138 mmol) as a colorless oil in 69% yield.

**TLC (SiO$_2$):** $R_f = 0.35$ (ethyl acetate: hexanes, 1:4).

$[\alpha]_D^{25} = -2.0$ (c = 1, CH$_2$Cl$_2$), literature value -3.39$^o$ (c = 0.5, CHCl$_3$).$^2$

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.37-7.27 (m, 5H), 4.85-4.84 (m, 1H), 4.78-4.77 (m, 1H), 4.53 (s, 2H), 4.01-3.94 (m, 1H), 3.75-3.70 (m, 1H), 3.68-3.63 (m, 1H) 2.73 (d, $J = 2.5$ Hz, OH), 2.24-2.14 (m, 2H), 1.82-1.70 (m, 2H), 1.75 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 142.7, 138.0, 128.4, 127.7, 127.6, 113.1, 73.3, 68.7, 68.2, 46.0, 36.2, 22.5.

**FTIR** (neat): 3441, 3066, 3025, 2920, 2859, 2347, 2335, 1722, 1495, 1453, 1365, 1275, 1205, 1166, 1028, 891, 736, 697, 668 cm$^{-1}$.

**HPLC:** (Chiralcel AS-H column, hexanes:i-PrOH = 95:05, 0.5 mL/min, 254 nm), $t_{\text{minor}} = 8.7$ min, $t_{\text{major}} = 9.5$ min; ee = 96%.

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$^2$The spectral data and optical rotation of the product 3b correspond with the reported compound.

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(R)-1-(4-methoxybenzyloxy)-2,2,5-trimethylhex-5-en-3-ol (3c)

To a resealable pressure tube equipped with a magnetic stir bar was added (R)-I (10.7 mg, 0.01 mmol, 5 mol%) and potassium phosphate (42.4 mg, 0.20 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. THF (0.2 mL, 1.0 M), alcohol 1c (44.9 mg, 0.20 mmol, 100 mol%) and β-methallyl chloride (54.3 mg, 0.60 mmol, 300 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was placed in an oil bath at 50 °C and was allowed to stir for 24 hr. The reaction mixture was concentrated in vacuo. The residue was subjected to column chromatography (SiO2; ethyl acetate: hexanes, 1:10 to 1:5) to provide the title compound 3c (50.1 mg, 0.180 mmol) as a colorless oil in 90% yield.

**TLC (SiO2):** Rf = 0.31 (ethyl acetate: hexanes, 1:10).

[ α ]D25 = +2.0 (c = 1, CH2Cl2).

**1H NMR** (400 MHz, CDCl3): δ 7.25-7.22 (m, 2H), 6.89-6.85 (m, 2H), 4.86-4.84 (m, 1H), 4.80-4.78 (m, 1H), 4.44 (s, 2H), 2.94 (s, 3H), 3.64-3.60 (m, 1H), 3.35 (d, J = 8.86, 1H), 3.27 (d, J = 8.86, 1H), 3.47 (d, J = 3.47, 1H), 2.17 (d, J = 13.7 Hz, 1H), 2.03 (ddd, J = 13.72, 10.66, 0.47 Hz, 1H), 1.77 (s, 3H), 0.92 (s, 3H), 0.91 (s, 3H).

**13C NMR** (100 MHz, CDCl3): δ 159.1, 143.8, 130.2, 129.1, 113.7, 112.6, 78.9, 74.9, 73.2, 55.3, 40.3, 38.3, 22.5, 22.3, 19.7.

**FTIR** (neat): 3484, 3068, 2958, 2935, 2857, 1646, 1612, 1586, 1513, 1465, 1439, 1362, 1301, 1247, 1207, 1173, 1088, 1036, 889, 820, 756 cm⁻¹.


**HPLC:** (Chiralcel OD-H column, hexanes:i-PrOH = 95:5, 0.5 mL/min, 220 nm), t_minor = 13.2 min, t_major = 13.8 min; ee = 94%.
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(R)-1-Cyclohexyl-3-methylbut-3-en-1-ol (3d)

To a resealable pressure tube equipped with a magnetic stir bar was added (R)-I (10.7 mg, 0.01 mmol, 5 mol%) and potassium phosphate (42.4 mg, 0.20 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. THF (0.2 mL, 1.0 M), alcohol 1d (22.8 mg, 0.20 mmol, 100 mol%) and β-methallyl chloride (54.3 mg, 0.60 mmol, 300 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was placed in an oil bath at 50 °C and was allowed to stir for 24 hr. The reaction mixture was concentrated in vacuo. The residue was subjected to column chromatography (SiO2; ethyl acetate: hexanes, 1:20 to 1:10) to provide the title compound 3d (24.3 mg, 0.144 mmol) as a colorless oil in 72% yield.

**TLC (SiO2):** Rf = 0.45 (ethyl acetate: hexanes, 1:10).

\[ \alpha \] = -5.0° (c = 1, CH2Cl2), literature value for ent 3d, +2.0 (c = 1.4, CCl4).4

1H NMR (400 MHz, CDCl3):  δ 4.90-4.88 (m, 1H), 4.81-4.80 (m, 1H), 3.50-3.45 (m, 1H), 2.24 (ddd, J = 13.6, 20.0, 0.4 Hz, 1H) 2.06 (ddd, J = 13.6, 10, 0.4 Hz, 1H), 1.89-1.84 (m, 1H), 1.71-1.64 (m, 3H), 1.40-1.30 (m, 1H), 1.28-0.99 (m, 5H).

13C NMR (100 MHz, CDCl3): δ 143.3, 113.5, 72.4, 43.4, 43.0, 29.0, 28.2, 26.6, 26.3, 26.2, 22.2.

FTIR (neat): 3422, 3074, 2978, 2852, 1644, 1449, 1396, 1374, 1259, 1173, 1142, 1100, 1086, 1060, 1044, 986, 953, 864, 842 cm⁻¹.

**HPLC:** Enantiomeric excess was determined by HPLC analysis of the 4-nitrobenzoate derivative of the product, (Chiralcel AS-H column, hexanes:i-PrOH = 99:01, 0.5 mL/min, 254 nm), t_major = 9.1 min, t_minor = 10.1 min; ee = 92%.

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3The spectral data of the product 3a correspond with the reported compound.


4The optical rotation of the product 3a corresponds with the reported ent-compound.

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(R)-(E)-5-Methyl-1-phenylhexa-1,5-dien-3-ol (3e)

To a resealable pressure tube equipped with a magnetic stir bar was added (R)-I (10.7 mg, 0.01 mmol, 5 mol%) and potassium phosphate (42.4 mg, 0.20 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. THF (0.2 mL, 1.0 M), alcohol 1e (26.8 mg, 0.20 mmol, 100 mol%), β-methallyl chloride (54.3 mg, 0.60 mmol, 300 mol%), and isopropanol (31 µL, 0.40 mmol, 200 mol %) were added and the rubber septum was quickly replaced with a screw cap. The mixture was placed in an oil bath at 50 °C and was allowed to stir for 24 hr. The reaction mixture was concentrated \textit{in vacuo}. The residue was subjected to column chromatography (SiO$_2$; ethyl acetate: hexanes, 1:12 to 1:7) provided the oxidized product 4e (4.5 mg, 0.024 mmol) as a colorless oil in 12% yield and the title compound 3e$^5$ (30.1 mg, 0.160 mmol) as a colorless oil in 80% yield.

**TLC (SiO$_2$):** $R_f = 0.31$ (ethyl acetate: hexanes, 1:4).

$[\alpha]_D^{25} = +24.0$ (c = 1, CH$_2$Cl$_2$), literature value $+19.0$ (c = 1.44, CH$_2$Cl$_2$).$^5$

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.4-7.22 (m, 5H), 6.64 (dd, $J = 15.9$, 1.2 Hz, 1H), 6.24 (dd, $J = 15.9$, 6.3 Hz, 1H), 4.94-4.86 (m, 2H), 4.47-4.42 (m, 1H), 2.39-2.29 (m, 2H), 1.87 (bs, 1H), 1.81 (t, $J = 1.1$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 142.0, 136.7, 131.7, 130.1, 128.5, 127.6, 126.4, 114.1, 69.9, 46.2, 22.5.

**FTIR** (neat): 3371, 3076, 3026, 2931, 1647, 1599, 1494, 1448, 1274, 1099, 1070, 1046, 965, 891, 747, 740 cm$^{-1}$.

**HPLC:** (Chiralcel OD-H column, hexanes:i-PrOH = 90:10, 1 mL/min, 254 nm), $t_{\text{major}} = 7.1$ min, $t_{\text{minor}} = 12.0$ min; ee = 94%.

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$^5$The spectral data of the product 3e and optical rotation correspond to the reported compound.

(R)-(E)-2,6,10-trimethylundeca-1,5,9-trien-4-ol (3f)

To a resealable pressure tube equipped with a magnetic stir bar was added (R)-I (10.7 mg, 0.01 mmol, 5 mol%) and potassium phosphate (42.4 mg, 0.20 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. THF (0.2 mL, 1.0 M), alcohol 1f (30.9 mg, 0.20 mmol, 100 mol%), β-methallyl chloride (54.3 mg, 0.60 mmol, 300 mol%), and isopropanol (31 μL, 0.40 mmol, 200 mol %) were added and the rubber septum was quickly replaced with a screw cap. The mixture was placed in an oil bath at 50 °C and was allowed to stir for 24 hr. The reaction mixture was concentrated in vacuo. The residue was subjected to column chromatography (SiO2; ethyl acetate: hexanes, 1:40 to 1:20) to provide the title compound 3f (33.3 mg, 0.160 mmol) as a colorless oil in 80% yield.

TLC (SiO2): Rf = 0.40 (ethyl acetate: hexanes, 1:10).

\[ [\alpha]_D^{25} = +13.0 \ (c = 1, \ CH_2Cl_2), \ literature \ value \ +19.2 \ (c = 6.5, \ CH_2Cl_2).^{6} \]

\[ ^1H \ NMR \ (400 \ MHz, \ CDCl_3): \ \delta \ 5.19 \ (dq, \ J = 8.4, \ 1.3 \ Hz, \ 1H), \ 5.11-5.06 \ (m, \ 1H), \ 4.88-4.80 \ (m, \ 2H), \ 4.51 \ (dt, \ J = 8.5, \ 4.8 \ Hz, \ 1H), \ 4.45 \ (ddd, \ J = 13.7, \ 8.6, \ 0.9, \ 1H), \ 2.19-2.14 \ (m, \ 1H), \ 2.13-1.99 \ (m, \ 4H), \ 1.78 \ (t, \ J = 0.9, \ 3H), \ 1.70 \ (d, \ J = 1.4 \ Hz, \ 3H), \ 1.68 \ (d, \ J = 1.1 \ Hz, \ 3H), \ 1.60 \ (s, \ 3H), \]

\[ ^13C \ NMR \ (100 \ MHz, \ CDCl_3): \ \delta \ 142.4, \ 138.6, \ 131.6, \ 127.1, \ 123.9, \ 66.0, \ 46.2, \ 39.5, \ 26.3, \ 25.7, \ 22.5, \ 17.7, \ 16.6. \]

\[ \text{FTIR (neat):} \ 3362, \ 3074, \ 2967, \ 2916, \ 2855, \ 2322, \ 1647, \ 1442, \ 1375, \ 1261, \ 1201, \ 1139, \ 1105, \ 1046, \ 1008, \ 979, \ 887 \ \text{cm}^{-1}. \]

**HPLC:** Enantiomeric excess was determined by HPLC analysis of the 4-nitrobenzoate derivative of the product, (Chiralcel OJ-H/AS-H column, hexanes:i-PrOH = 99:1, 0.4 mL/min, 254 nm), \( t_{\text{major}} = 22.6 \ \text{min}, \ t_{\text{minor}} = 24.2 \ \text{min}; \ \text{ee} = 94\%.

---

6The spectral data and optical rotation of the product 3f correspond to the reported compound.

## Electronic Supplementary Material (ESI) for Chemical Communications

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### Chromatograms

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(R)-1-(4-Bromophenyl)-3-methylbut-3-en-1-ol (3g)

To a resealable pressure tube equipped with a magnetic stir bar was added alcohol 1g (37.4 mg, 0.20 mmol, 100 mol%), (R)-I (10.7 mg, 0.01 mmol, 5 mol%) and potassium phosphate (42.4 mg, 0.20 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. THF (0.2 mL, 1.0 M) and β-methallyl chloride (54.3 mg, 0.60 mmol, 300 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was placed in an oil bath at 50 °C and was allowed to stir for 24 hr. The reaction mixture was concentrated in vacuo. The residue was subjected to column chromatography (SiO2; ethyl acetate: hexanes, 1:10 to 1:5) provided the oxidized product 4g (6.7 mg, 0.028 mmol) as white solid in 14% yield and the title compound 3g \(^7\) (40.0 mg, 0.166 mmol) as white solid in 83% yield.

**TLC (SiO\(_2\))**: R\(_f\) = 0.30 (ethyl acetate: hexanes, 1:5).

**m.p.**: 72-73 °C.

\([\alpha]_D^{25}\) = +45.0° (c = 1, CH\(_2\)Cl\(_2\)).

**\(^1\)H NMR** (400 MHz, CDCl\(_3\)): \(\delta\) 7.47 (d, \(J = 8.8\) Hz, 2H), 7.25 (d, \(J = 8.8\) Hz 2H), 4.94-4.93 (m, 1H), 4.85-4.84 (m, 1H), 4.78-4.75 (m, 1H), 2.39-2.36 (m, 2H), 2.18 (d, \(J = 2.4\) Hz, 1H), 1.79 (s, 3H).

**\(^{13}\)C NMR** (100 MHz, CDCl\(_3\)): \(\delta\) 143.0, 142.0, 131.5, 127.5, 121.2, 114.5, 70.7, 48.4, 22.3.

**FTIR** (neat): 3358, 3075, 2976, 2934, 1900, 1803, 1648, 1592, 1488, 1472, 1406, 1373, 1336, 1304, 1202, 1169, 1046, 1008, 902, 874, 822, 803, 718 cm\(^{-1}\).

**HPLC**: (Chiralcel OJ-H column, hexanes:i-PrOH = 95:05, 1 mL/min, 254 nm), \(t_{\text{minor}}\) = 8.7 min, \(t_{\text{major}}\) = 9.5 min; ee = 96%.

---

\(^7\)The spectral data of the product 3g corresponds to the reported compound.

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(R)-1-(benzo[d][1,3]dioxol-5-yl)-3-methylbut-3-en-1-ol (3h)

To a resealable pressure tube equipped with a magnetic stir bar was added alcohol 1h (30.4 mg, 0.20 mmol, 100 mol%), (R)-I (10.7 mg, 0.01 mmol, 5 mol%) and potassium phosphate (42.4 mg, 0.20 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. THF (0.2 mL, 1.0 M) and β-methallyl chloride (54.3 mg, 0.60 mmol, 300 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was placed in an oil bath at 50 °C and was allowed to stir for 24 hr. The reaction mixture was concentrated in vacuo. The residue was subjected to column chromatography (SiO₂; ethyl acetate: hexanes, 1:20 to 1:10) provided the oxidized product 4h (2.0 mg, 0.010 mmol) as a colorless oil in 5% yield and the title compound 3h⁸ (32.2 mg, 0.156 mmol) as a colorless oil in 78% yield.

TLC (SiO₂): Rf = 0.28 (ethyl acetate: hexanes, 1:4).

[α]D²5 = +50.0 (c = 1, CH₂Cl₂).

¹H NMR (400 MHz, CDCl₃): δ 6.90 (dt, J = 1.69, 0.44 Hz, 1H), 6.82 (ddd, J = 8.0, 1.7, 0.57 Hz, 1H), 6.77 (dd, J = 8.0, 0.32 Hz, 1H), 5.95 (s, 2H), 4.93-4.83 (m, 2H), 4.73 (dd, J = 8.4, 5.1, 1H), 2.44-2.34 (m, 2H), 2.07 (bs, 1H), 1.79 (t, J = 1.0, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 147.7, 146.8, 142.3, 138.1, 119.1, 114.1, 108.0, 106.3, 101.0, 71.2, 48.3, 22.3

FTIR (neat): 3408, 3076, 2897, 1726, 1646, 1609, 1503, 1487, 1442, 1376, 1187, 1124, 1094, 1209, 1186, 1124, 1094, 1010, 932, 896, 810, 783, 750, 727 cm⁻¹.

HPLC: (Chiralcel OJ-H column, hexanes:i-PrOH = 95:5, 1 mL/min, 280 nm), t_minor = 15.3 min, t_major = 16.6 min; ee = 94%.

---

⁸The spectral data of the product 3h corresponds to the reported compound.

(R)-1-(benzo[b]thiophen-2-yl)-3-methylbut-3-en-1-ol (3i)

To a resealable pressure tube equipped with a magnetic stir bar was added alcohol 1i (32.8 mg, 0.20 mmol, 100 mol%), (R)-I (10.7 mg, 0.01 mmol, 5 mol%) and potassium phosphate (42.4 mg, 0.20 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. THF (0.2 mL, 1.0 M) and β-methallyl chloride (54.3 mg, 0.60 mmol, 300 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was placed in an oil bath at 50 °C and was allowed to stir for 24 hr. The reaction mixture was concentrated \textit{in vacuo}. The residue was subjected to column chromatography (SiO$_2$; ethyl acetate: hexanes, 1:20 to 1:10) to provide the oxidized product 4i (2.2 mg, 0.010 mmol) as a white solid in 5% yield and the title compound 3i (38.0 mg, 0.174 mmol) as a white solid in 87% yield.

\textbf{TLC (SiO$_2$):} $R_f = 0.25$ (ethyl acetate: hexanes, 1:4).

\textbf{m.p.:} 78-80 °C.

\([\alpha]_D^{25} = +36.1$ (c = 1, CH$_2$Cl$_2$).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.83-7.81 (m, 1H), 7.73-7.71 (m, 1H), 7.36-7.28 (m, 2H), 7.22 (t, $J = 0.74$, 1H), 5.16 (t, $J = 6.76$, 1H), 4.97-4.90 (m, 2H), 2.65-2.57 (m, 2H), 2.32 (bs, 1H), 1.12 (t, $J = 1.1$ Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 148.6, 141.5, 139.5, 139.2, 124.2, 124.1, 123.4, 122.4, 120.0, 114.7, 68.1, 47.9, 22.4

FTIR (neat): 3556, 3069, 2966, 2937, 1643, 1457, 1438, 1376, 1326, 1275, 1261, 1155, 1118, 1054, 973, 946, 899, 876, 845, 831, 754, 728, 669 cm$^{-1}$.

HRMS (CI) Calcd. for C$_{13}$H$_{14}$OS $[M]^+$: 218.0766, Found: 218.0765.

HPLC: (Chiralcel OJ-H column, hexanes:i-PrOH = 95:5, 1 mL/min, 254 nm), $t_{\text{minor}} = 19.8$ min, $t_{\text{major}} = 26.0$ min; ee = 96%.
II.c. Experimental Details for Methallylation from Aldehyde Oxidation Level

(S)-2-Methyldodec-1-en-4-ol (3a)

To a resealable pressure tube equipped with a magnetic stir bar was added (R)-1 (10.7 mg, 0.01 mmol, 5 mol%) and potassium phosphate (42.4 mg, 0.20 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. THF (0.2 mL, 1.0 M), aldehyde 2a (28.4 mg, 0.20 mmol, 100 mol%), β-methallyl chloride (54.3 mg, 0.60 mmol, 300 mol%), and isopropanol (31 μL, 0.40 mmol, 200 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was placed in an oil bath at 50 °C and was allowed to stir for 24 hr. The reaction mixture was concentrated in vacuo. The residue was subjected to column chromatography (SiO₂; ethyl acetate: hexanes, 1:40 to 1:20) to provide the title compound 3a (29.8 mg, 0.150 mmol) as a colorless oil in 75% yield.

**HPLC:** Enantiomeric excess was determined by HPLC analysis of the 4-nitrobenzoate derivative of the product, (Chiralcel OD-H-OD-H column, hexanes:i-PrOH = 99.5:0.5, 1 mL/min, 254 nm), \( t_{\text{major}} = 36.2 \text{ min} \ t_{\text{minor}} = 42.3 \text{ min} \); ee = 97%.
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(R)-1-(benzyloxy)-5-methylhex-5-en-3-ol (3b)

To a resealable pressure tube equipped with a magnetic stir bar was added (R)-I (10.7 mg, 0.01 mmol, 5 mol%) and potassium phosphate (42.4 mg, 0.20 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. THF (0.2 mL, 1.0 M), aldehyde 2b (32.8 mg, 0.20 mmol, 100 mol%), β-methallyl chloride (54.3 mg, 0.60 mmol, 300 mol%) and isopropanol (31 μL, 0.40 mmol, 200 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was placed in an oil bath at 50 °C and was allowed to stir for 24 hr. The reaction mixture was concentrated *in vacuo*. The residue was subjected to column chromatography (SiO2; ethyl acetate: hexanes, 1:9 to 1:5) to provide the title compound 3b (24.2 mg, 0.110 mmol) as a colorless oil in 55% yield.

**HPLC**: (Chiralcel AS-H column, hexanes:i-PrOH = 95:05, 0.5 mL/min, 254 nm), $t_{\text{minor}} = 10.0$ min, $t_{\text{major}} = 11.0$ min; ee = 97%.
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(R)-1-(4-Methoxybenzyloxy)-2,2,5-trimethylhex-5-en-3-ol (3c)

To a resealable pressure tube equipped with a magnetic stir bar was added (R)-I (10.7 mg, 0.01 mmol, 5 mol%) and potassium phosphate (42.4 mg, 0.20 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. THF (0.2 mL, 1.0 M), aldehyde 2c (44.5 mg, 0.20 mmol, 100 mol%), β-methallyl chloride (54.3 mg, 0.60 mmol, 300 mol%), and isopropanol (31 μL, 0.40 mmol, 200 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was placed in an oil bath at 50 °C and was allowed to stir for 24 hr. The reaction mixture was concentrated in vacuo. The residue was subjected to column chromatography (SiO₂; ethyl acetate: hexanes, 1:10 to 1:5) to provide the title compound 3c (50.7 mg, 0.182 mmol) as a colorless oil in 91% yield.

**HPLC**: (Chiralcel OD-H column, hexanes:i-PrOH = 95:5, 0.5 mL/min, 220 nm), tₘᵢₙᵢᵣₒᵣ = 12.0 min, tₘₐᵢⱼᵣₒᵣ = 12.6 min; ee = 97%.
(R)-1-Cyclohexyl-3-methylbut-3-en-1-ol (3d)

To a resealable pressure tube equipped with a magnetic stir bar was added (R)-I (10.7 mg, 0.01 mmol, 5 mol%) and potassium phosphate (42.4 mg, 0.20 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. THF (0.2 mL, 1.0 M), aldehyde 2d (22.4 mg, 0.20 mmol, 100 mol%), β-methallyl chloride (54.3 mg, 0.60 mmol, 300 mol%) and isopropanol (31 μL, 0.40 mmol, 200 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was placed in an oil bath at 50 °C and was allowed to stir for 24 hr. The reaction mixture was concentrated in vacuo. The residue was subjected to column chromatography (SiO₂; ethyl acetate: hexanes, 1:20) to provide the title compound 3d (24.9 mg, 0.148 mmol) as a colorless oil in 74% yield.

**HPLC:** Enantiomeric excess was determined by HPLC analysis of the 4-nitrobenzoate derivative of the product, (Chiralcel AS-H column, hexanes:i-PrOH = 99:01, 0.5 mL/min, 254 nm), t_{major} = 8.9 min, t_{minor} = 9.7 min; ee = 91%.
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(R)-(E)-5-Methyl-1-phenylhexa-1,5-dien-3-ol (3e)

To a resealable pressure tube equipped with a magnetic stir bar was added (R)-I (10.7 mg, 0.01 mmol, 5 mol%) and potassium phosphate (42.4 mg, 0.20 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. THF (0.2 mL, 1.0 M), aldehyde 2e (26.4 mg, 0.20 mmol, 100 mol%), β-methallyl chloride (54.3 mg, 0.60 mmol, 300 mol%), and isopropanol (62 μL, 0.80 mmol, 400 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was placed in an oil bath at 50 °C and was allowed to stir for 24 hr. The reaction mixture was concentrated in vacuo. The residue was subjected to column chromatography (SiO₂; ethyl acetate: hexanes, 1:12 to 1:7) provided the oxidized product 4e (4.8 mg, 0.026 mmol) as a colorless oil in 13% yield and the title compound 3e (30.9 mg, 0.164 mmol) as a colorless oil in 82% yield.

**HPLC**: (Chiralcel OD-H column, hexanes:i-PrOH = 90:10, 1 mL/min, 254 nm), t_major = 7.1 min, t_minor = 12.0 min; ee = 95%.
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(R)-(E)-2,6,10-Trimethylundeca-1,5,9-trien-4-ol (3f)

To a resealable pressure tube equipped with a magnetic stir bar was added (R)-I (10.7 mg, 0.01 mmol, 5 mol%) and potassium phosphate (42.4 mg, 0.20 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. THF (0.2 mL, 1.0 M), aldehyde 2f (30.4 mg, 0.20 mmol, 100 mol%), β-methallyl chloride (54.3 mg, 0.60 mmol, 300 mol%), and isopropanol (62 μL, 0.80 mmol, 400 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was placed in an oil bath at 50 °C and was allowed to stir for 24 hr. The reaction mixture was concentrated in vacuo. The residue was subjected to column chromatography (SiO₂; ethyl acetate: hexanes, 1:40 to 1:20) provided the oxidized product 4f (2.5 mg, 0.012 mmol) as a colorless oil in 6% yield and the title compound 3f (31.3 mg, 0.150 mmol) as a colorless oil in 75% yield.

**HPLC:** Enantiomeric excess was determined by HPLC analysis of the 4-nitrobenzoate derivative of the product, (Chiralcel OJ-H/AS-H column, hexanes:i-PrOH = 99:1, 0.4 mL/min, 254 nm), t_major = 25.0 min, t_minor = 27.0 min; ee = 93%.
(R)-1-(4-Bromophenyl)-3-methylbut-3-en-1-ol (3g)

To a resealable pressure tube equipped with a magnetic stir bar was added aldehyde 2g (37.0 mg, 0.20 mmol, 100 mol%), (R)-I (10.7 mg, 0.01 mmol, 5 mol%) and potassium phosphate (42.4 mg, 0.20 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. THF (0.2 mL, 1.0 M), β-methallyl chloride (54.3 mg, 0.60 mmol, 300 mol%) and isopropanol (31 μL, 0.40 mmol, 200 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was placed in an oil bath at 50 °C and was allowed to stir for 24 hr. The reaction mixture was concentrated in vacuo. The residue was subjected to column chromatography (SiO2; ethyl acetate: hexanes, 1:10 to 1:5) provided the oxidized product 4g (3.8 mg, 0.016 mmol) as white solid in 14% yield and the title compound 3g (43.5 mg, 0.180 mmol) as white solid in 83% yield.

**HPLC**: (Chiralcel OJ-H column, hexanes:i-PrOH = 95:05, 1 mL/min, 254 nm), t_{minor} = 8.7 min, t_{major} = 9.5 min; ee = 95%.
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(R)-1-(Benzo[d][1,3]dioxol-5-yl)-3-methylbut-3-en-1-ol (3h)

To a resealable pressure tube equipped with a magnetic stir bar was added aldehyde 2h (30.0 mg, 0.20 mmol, 100 mol%), (R)-I (10.7 mg, 0.01 mmol, 5 mol%) and potassium phosphate (42.4 mg, 0.20 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. THF (0.2 mL, 1.0 M), β-methallyl chloride (54.3 mg, 0.60 mmol, 300 mol%), and isopropanol (31 µL, 0.40 mmol, 200 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was placed in an oil bath at 50 °C and was allowed to stir for 24 hr. The reaction mixture was concentrated in vacuo. The residue was subjected to column chromatography (SiO2; ethyl acetate: hexanes, 1:20 to 1:10) provided the oxidized product 4h (4.0 mg, 0.020 mmol) as a colorless oil in 10% yield and the title compound 3h (35.1 mg, 0.170 mmol) as a colorless oil in 85% yield.

HPLC: (Chiralcel OJ-H column, hexanes:i-PrOH = 95:5, 1 mL/min, 280 nm), t_{minor} = 14.3 min, t_{major} = 15.6 min; ee = 96%.
### Table 1

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(R)-1-(Benzo[b]thiophen-2-yl)-3-methylbut-3-en-1-ol (3i)

To a resealable pressure tube equipped with a magnetic stir bar was added aldehyde 2i (32.4 mg, 0.20 mmol, 100 mol%), (R)-I (10.7 mg, 0.01 mmol, 5 mol%) and potassium phosphate (42.4 mg, 0.20 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. THF (0.2 mL, 1.0 M), β-methallyl chloride (54.3 mg, 0.60 mmol, 300 mol%), and isopropanol (31 μL, 0.40 mmol, 200 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was placed in an oil bath at 50 °C and was allowed to stir for 24 hr. The reaction mixture was concentrated in vacuo. The residue was subjected to column chromatography (SiO₂; ethyl acetate: hexanes, 1:20 to 1:10) provided the oxidized product 4i (2.2 mg, 0.010 mmol) as white solid in 5% yield and the title compound 3i (39.7 mg, 0.182 mmol) as a white solid in 91% yield.

**HPLC:** (Chiralcel OJ-H column, hexanes:i-PrOH = 95:5, 1 mL/min, 254 nm), t_{minor} = 19.8 min, t_{major} = 26.3 min; ee = 96%.
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II.d. Experimental Details for the bis(Methallylation) of Propanediol

(4R,6R)-2,8-dimethylnona-1,8-diene-4,6-diol (6)

To a resealable pressure tube equipped with a magnetic stir bar was added (R)-I (32.2 mg, 0.03 mmol, 10 mol%) and potassium phosphate (127.4 mg, 0.60 mmol, 200 mol%). The tube was sealed with a rubber septum and purged with nitrogen. THF (0.6 mL, 0.5 M), alcohol 5 (22.8 mg, 0.30 mmol, 100 mol%) and β-methallyl chloride (135.8 mg, 1.50 mmol, 500 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was placed in an oil bath at 50 °C and was allowed to stir for 24 hr. The reaction mixture was concentrated in vacuo. The residue was subjected to column chromatography (SiO₂; ethyl acetate: hexanes, 1:5 to 1:3) to provide the title compound 6 (36.5 mg, 0.198 mmol) as a white solid in 66% yield.

TLC (SiO₂): Rf = 0.20 (ethyl acetate: hexanes, 1:4).

m.p.: 75-76 °C.

[α]D²⁵ = -24.0° (c = 1, CH₂Cl₂).

¹H NMR (400 MHz, CDCl₃): δ 4.89-4.87 (m, 2H), 4.80-4.79 (m, 2H), 4.14-4.07 (m, 2H), 2.52 (s, 2H), 2.27-2.16 (m, 4H), 1.77 (s, 6H), 1.62 (t, J = 6.0 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 142.5, 113.5, 113.5, 66.0, 46.1, 42.3, 22.4.

FTIR (neat): 3370, 3293, 3075, 2968, 2939, 1778, 1651, 1438, 1397, 1371, 1325, 1292, 1244, 1212, 1183, 1100, 1062, 1038, 989, 974 cm⁻¹.


HPLC: Enantiomeric excess was determined by HPLC analysis of the bis-4-nitrobenzoate derivative of the product, (Chiralcel OD-H column, hexanes/i-PrOH = 95:05, 1 mL/min, 254 nm), tminor = 12.7 min, tmeso = 12.8 and tmajor = 20.7 min; ee = 99%.
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(4R,6R)-2,2-Dimethyl-4,6-bis(2-methylallyl)-1,3-dioxane (7)

To a stirred solution of diol 6 (33 mg, 0.179 mmol, 100 mol%) in dichloromethane (1.8 mL, 0.1 M) was added 2,2-dimethoxypropane (278 mg, 2.685 mmol, 1500 mol%) and pyridinium p-toluenesulfonate (4.5 mg, 0.018 mmol, 10 mol%). The reaction mixture was stirred for 2 hr at ambient temperature at which point TLC analysis revealed complete conversion. The reaction mixture was treated with saturated NaHCO$_3$ aq. (4 mL) and extracted with dichloromethane (5 mL x 3). The combined organic extracts were dried with (MgSO$_4$), filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO$_2$: ethyl acetate:hexanes, 1:20 with 0.1% TEA) to provide the acetonide 7 (30.4 g, 0.135 mmol) as a colorless oil in 76% yield.

**TLC (SiO$_2$):** $R_f = 0.50$ (ethyl acetate: hexanes, 1:20).

[α]$_D^{25}$ = -28.0° (c = 1, CH$_2$Cl$_2$).

**$^1$H NMR** (400 MHz, CDCl$_3$): δ 4.79-4.78 (m, 2H), 4.75-4.74 (m, 2H), 4.03-3.96 (m, 2H), 2.31-2.25 (m, 2H), 2.15-2.10 (m, 2H), 1.74 (s, 6H), 1.60 (t, 2H), 1.37 (s, 6H).

**$^{13}$C NMR** (100 MHz, CDCl$_3$): δ 142.3, 112.1, 100.3, 65.0, 44.0, 38.1, 24.8, 22.8.

**FTIR** (neat): 3075, 2986, 2937, 1650, 1443, 1376, 1230, 1166, 1114, 1025, 987, 939, 821 cm$^{-1}$.

**HRMS** (Cl) Calcd. for C$_{14}$H$_{24}$O$_2$ [M]$^+$: 225.1855, Found: 225.1856.
1,1′-((4S,6S)-2,2-dimethyl-1,3-dioxane-4,6-diyl)dipropan-2-one (8)

To a stirred solution of acetonide 7 (39 mg, 0.174 mmol, 100 mol%) in dichloromethane (3.5 mL, 0.05 M) was bubbled ozone at -78 °C for around 5 min until a blue color persisted. O₂ was bubbled for 2 min followed by argon for 10 min. Triphenylphosphine (183 mg, 0.696 mmol, 400 mol%) was added and the reaction mixture was slowly warmed to ambient temperature overnight. The reaction mixture was concentrated in vacuo and residue was purified by column chromatography (SiO₂: ethyl acetate:hexanes, 1:2 with 0.1% TEA) to give the diketone 8 (26.0 mg, 0.114 mmol) as a colorless oil in 65% yield.

**TLC (SiO₂)**: Rf = 0.35 (ethyl acetate: hexanes, 1:2).

\[ \alpha \]D 25 = -37.0° (c = 1, CH₂Cl₂).

**1H NMR** (400 MHz, CDCl₃): δ 4.27 (ddd, , J = 15.6, 7.6, 4.8 Hz, 2H), 2.75-2.69 (m, 2H), 2.50-2.45 (m, 2H), 2.17 (s, 6H), 1.68 (t, , J = 7.6 Hz, 2H), 1.33 (s, 6H).

**13C NMR** (100 MHz, CDCl₃): δ 206.6, 100.7, 62.8, 49.4, 37.7, 30.8, 24.5.

**FTIR** (neat): 3753, 3504, 2988, 2937, 2854, 2370, 2331, 1698, 1423, 1380, 1367, 1306, 1223, 1170, 1121, 1092, 1032, 1011, 930 cm⁻¹.

**e. Absolute Stereochemical determination**

The absolute stereochemistry was determined by single crystal x-ray analysis of product 3g and was found to be $R$, see figure 1. In addition, as described above, the correlation of numerous methallylation products is consistent with this assignment.

**Figure 1.** View of 3g showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.