Supporting Information

Redox-Triggered C-C Coupling of Alcohols and Vinyl Epoxides: Diastereo- and Enantioselective Formation of All-Carbon Quaternary Centers via tert-(Hydroxy)-Prenylation

Jiajie Feng, Victoria J. Garza and Michael J. Krische

University of Texas at Austin, Department of Chemistry and Biochemistry, Austin, TX 78712, USA

Table of Contents:

General Information .................................................................................................................................... S2
Spectroscopy, Spectrometry, and Data Collection ...................................................................................... S2
General Procedures for Preparation of Iridium Complexes 1a-IVb ................................................................. S3
Detailed Procedures and Spectral Data for tert-(Hydroxy)-Prenylation of Alcohols (1a-1j) and Aldehydes (2a-2i): ........................................................................................................................................................ S5
Synthesis of Myrcene Oxide 3c .................................................................................................................. S45
Detailed Procedures and Spectral Data for Couplings between 4-Bromobenzyl Alcohol (1a) and Other Vinyl Epoxides: Butadiene Monoxide (3b) and Myrcene Oxide (3c): ......................................................... S47
Crystallographic Material for 4a-acetonide ................................................................................................... S52
**General Information**

All reactions were run under an atmosphere of argon. Sealed tubes (13x100 mm) were purchased from Fischer Scientific (catalog number 14-959-35C) and were flame dried followed by cooling in a desiccator. Tetrahydrofuran, toluene, and dioxanes were distilled from sodium-benzophenone immediately prior to use. Ethyl Acetate was dried over potassium carbonate and distilled immediately prior to use. Anhydrous solvents were transferred by oven-dried syringes. Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates (Dynanmic Absorbents F254). Visualization was accomplished with UV light followed by dipping in p-anisaldehyde stain solution then heating. Purification of reactions was carried out by flash chromatography using Silacycle silica gel (40-63 μm, unless indicated specifically). Potassium phosphate was purchased through Acros Organics, flame dried prior to use, and stored in a desiccator. All alcohol substrates were purchased from commercially available sources and purified prior to use. Cyclohexylacetaldehyde 2i and geranial 2d were prepared through known procedures with NMR spectra comparable to that in the literature. All other aldehydes were used from commercially available sources, and purified via distillation in a Hickman still or column chromatography prior to use.

**Spectroscopy, Spectrometry, and Data Collection**

Infrared spectra were recorded on a Perkin-Elmer 1600 spectrometer. Low-resolution mass spectra (LRMS) were obtained on a Karatos MS9 and are reported as m/z (relative intensity). High-resolution mass spectra (HRMS) were obtained on an Agilent Technologies 6530 Accurate Mass Q-TOF LC/MS instrument and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion (M, M+H, or M-H), or a suitable fragment ion. $^1$H nuclear magnetic resonance spectra were recorded using a 400 MHz spectrometer. Coupling constants are reported in Hertz (Hz) for CDCl$_3$ solutions, and chemical shifts are reported as parts per million (ppm) relative to residual CHCl$_3$ δ$_H$ (7.26 ppm). $^{13}$C nuclear magnetic resonance spectra were recorded using a 100 MHz spectrometer for CDCl$_3$ solutions, and chemical shifts are reported as parts per million (ppm) relative to residual CDCl$_3$ δ$_C$ (77.0 ppm). $^{31}$P nuclear magnetic resonance spectra were recorded using a 162 MHz spectrometer for CDCl$_3$ solutions. The products formed through C-C coupling from the alcohol and aldehyde oxidation levels are identical in all respects outside of diastereomeric ratios and enantiomeric excess. Melting points were taken on a Stuart SMP3 melting point apparatus.

---

1 Valente, C.; Organ, M. G. *Chem. Eur. J.* 2008, 14, 8239

2 Wilson, M. S., Woo, J. C. S.; Dake, G. R. *J. Org. Chem.* 2006, 11, 4237.
General Procedures for Preparation of Iridium Complexes Ia-IVb

A sealed tube equipped with a magnetic stir bar was added Cs₂CO₃ (169 mg, 0.52 mmol, 200 mol%), corresponding benzoic acid (0.52 mmol, 200 mol%), bidentate phosphine ligand (0.26 mmol, 100 mol%), and [Ir(cod)Cl]₂ (87.3 mg, 0.13 mmol, 50 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (2.6 mL, 0.1 M) and allyl acetate (0.070 mL, 0.65 mmol, 250 mol%) were added by syringe. The resulted mixture was allowed to stir at room temperature for 30 min, and was allowed to stir at 80 °C for another 90 min. The reaction was allowed to reach ambient temperature, and the mixture was filtered through a celite plug and washed by DCM (50 mL) until all yellow residue was dissolved. The combined filtrate was concentrated in vacuo and subjected to column chromatography (SiO₂: DCM:THF, 15:1). The obtained gum-like product was dissolved in THF (0.6 mL), and precipitated upon rapid addition of HPLC grade hexanes (6 mL). The product was filtered and washed by small amount of HPLC grade hexanes, followed by removal of trace amount of solvent in vacuo.

(R)-Ir-Ia: 3-nitrobenzoic acid (87 mg) and (R)-SEGPHOS (159 mg) was used. The title complex was obtained as light yellow powder in 63% yield (166 mg).

(R)-Ir-Ib: 4-cyano-3-nitrobenzoic acid (100 mg) and (R)-SEGPHOS (159 mg) was used. The title complex was obtained as yellow powder in 62% yield (167 mg).

(R)-Ir-IIa: 3-nitrobenzoic acid (87 mg) and (R)-DM-SEGPHOS (188 mg) was used. The title complex was obtained as yellow powder in 47% yield (110 mg).

(R)-Ir-IIb: 4-cyano-3-nitrobenzoic acid (100 mg) and (R)-DM-SEGPHOS (188 mg) was used. The title complex was obtained as bright yellow powder in 82% yield (243 mg).

(R)-Ir-IIIa: 3-nitrobenzoic acid (87 mg) and (R)-BINAP (162 mg) was used. After chromatography purification, the title complex was obtained as light yellow powder in 83% yield (221 mg) without any further precipitation.

(R)-Ir-IIIb: 4-cyano-3-nitrobenzoic acid (100 mg) and (R)-BINAP (162 mg) was used. The title complex was obtained as yellow powder in 63% yield (171 mg).

(R)-Ir-IVA: 3-nitrobenzoic acid (87 mg) and (R)-TolBINAP (176 mg) was used. The title complex was obtained as yellow powder in 73% yield (205 mg).
(R)-Ir-IVb

Following the general procedure, 4-cyano-3-nitrobenzoic acid (100 mg) and (R)-TolBINAP (176 mg) was used. The title complex was obtained as yellow powder in 70% yield (202 mg).

$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ -7.14* (d, $J = 21.2$ Hz, 0.3H), -13.68 (d, $J = 22.7$ Hz, 1H), -14.56* (d, $J = 21.2$ Hz, 0.3H), -16.64 (d, $J = 22.7$ Hz, 1H).

HRMS (ESI) Calcd. for C$_{59}$H$_{47}$IrN$_2$O$_4$P$_2$Na [M+Na]$^+$: 1125.2537, Found: 1125.2525.

MP 228.3-229.9 °C (decomposition)
Detailed Procedures and Spectral Data for tert-(Hydroxy)-Prenylation of Alcohols (1a-1j) and Aldehydes (2a-2i):

(1S,2S)-1-(4-bromophenyl)-2-methyl-2-vinylpropane-1,3-diol (4a)

![Chemical structure of (1S,2S)-1-(4-bromophenyl)-2-methyl-2-vinylpropane-1,3-diol (4a)]

**Detailed Procedures**

*From alcohol oxidation level:* An oven-dried pressure tube equipped with a magnetic stir bar was charged with K$_3$PO$_4$ (2.2 mg, 0.01 mmol, 5 mol%), (R)-Ir-IVb (11.0 mg, 0.01 mmol, 5 mol%), and 4-bromobenzyl alcohol (37.4 mg, 0.2 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.4 mL, 0.5 M) and isoprene monoxide (59 µL, 0.6 mmol, 300 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 45˚C for 1 day. The reaction was allowed to reach ambient temperature and concentrated *in vacuo*. The residue was subjected to column chromatography (SiO$_2$: hexanes:ethyl acetate, 5:1) to furnish the title compound as a white solid (49.5 mg, *anti*:syn > 20:1) in 91% yield.

*From aldehyde oxidation level:* An oven-dried pressure tube equipped with a magnetic stir bar was charged with K$_3$PO$_4$ (2.2 mg, 0.01 mmol, 5 mol%), (R)-Ir-IVb (11.0 mg, 0.01 mmol, 5 mol%), and 4-bromobenzaldehyde (37.0 mg, 0.2 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.4 mL, 0.5 M), 2-propanol (46 µL, 0.6 mmol, 300 mol%) and isoprene monoxide (59 µL, 0.6 mmol, 300 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 45˚C for 1 day. The reaction was allowed to reach ambient temperature and concentrated *in vacuo*. The residue was subjected to column chromatography (SiO$_2$: hexanes:ethyl acetate, 5:1) to furnish the title compound as a white solid (46.9 mg, *anti*:syn = 10:1) in 87% yield.

**$^1$H NMR** (400 MHz, CDCl$_3$) δ 7.42 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.02 (dd, *J* = 17.7, 11.0 Hz, 1H), 5.22 (dd, *J* = 11.0, 1.1 Hz, 1H), 5.01 (dd, *J* = 17.7, 1.2 Hz, 1H), 4.65 (s, 1H), 3.60 (d, *J* = 10.7 Hz, 1H), 3.52 (d, *J* = 10.7 Hz, 1H), 3.28 (br, 1H), 2.62 (br, 1H), 0.87 (s, 3H).

**$^{13}$C NMR** (100 MHz, CDCl$_3$) δ 139.7, 139.1, 130.8, 129.4, 121.5, 116.6, 79.2, 69.8, 46.3, 17.6.

**LRMS** (ESI) Calcd. for C$_{12}$H$_{15}$BrO$_2$Na [M+Na]$^+$: 293.0, Found: 293.0.

**FTIR** (neat): 3343, 2926, 1637, 1592, 1486, 1404, 1200, 1104, 1070, 1036, 1009, 921, 826, 755, 698 cm$^{-1}$.

**MP** 51.1-51.7 °C

**HPLC** (Chiralcel OD-H column, hexanes:i-PrOH = 90:10, 0.50 mL/min, 230 nm), *anti*:syn = 40:1, ee = 94% from 4-bromobenzyl alcohol, ee = 94% from 4-bromobenzaldehyde.
### From Alcohol Oxidation Level

| Peak Ret Time | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area [%] |
|---------------|------|-------------|--------------|--------------|----------|
| 1             | VV   | 0.3739      | 5373.34814   | 223.97386    | 4.8940   |
| 2             | VV   | 0.4869      | 4.85357e4    | 1595.49243   | 44.2062  |
| 3             | VB   | 0.5048      | 4.99210e4    | 1570.89380   | 45.4679  |
| 4             | BB   | 0.4736      | 5963.83789   | 195.68607    | 5.4319   |

---

| Peak Ret Time | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area [%] |
|---------------|------|-------------|--------------|--------------|----------|
| 1             | MM   | 0.4320      | 2004.05054   | 77.31152     | 2.6874   |
| 2             | MM   | 0.6576      | 7.12945e4    | 1807.01978   | 95.6034  |
| 3             | MM   | 0.5602      | 1274.59680   | 37.91838     | 1.7092   |
From Aldehyde Oxidation Level

| Peak | Time  | Type | Area     | Height  | Width | Start | End   |
|------|-------|------|----------|---------|-------|-------|-------|
| 1    | 17.183| VV   | 2589.09790| 101.23418| 0.3984| 16.715| 17.536|
| 2    | 18.055| VB   | 6.55493e4 | 1783.26868| 0.5968| 17.536| 19.244|
| 3    | 19.983| BB   | 5596.25928 | 177.88858 | 0.4830| 19.270| 20.864|
(1S,2S)-1-(benzo[d][1,3]dioxol-5-yl)-2-methyl-2-vinylpropane-1,3-diol (4b)

**Detailed Procedures**

*From alcohol oxidation level:* An oven-dried pressure tube equipped with a magnetic stir bar was charged with K$_3$PO$_4$ (2.2 mg, 0.01 mmol, 5 mol%), (R)-Ir-IVb (11.0 mg, 0.01 mmol, 5 mol%), and piperonyl alcohol (30.4 mg, 0.2 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.2 mL, 1 M) and isoprene monoxide (59 µL, 0.6 mmol, 300 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 45 °C for 1 day. The reaction was allowed to reach ambient temperature and concentrated in vacuo. The residue was subjected to column chromatography (SiO$_2$: hexanes:ethyl acetate, 4:1) to furnish the title compound as a colorless oil (42.1 mg, *anti*:syn > 20:1) in 89% yield.

*From aldehyde oxidation level:* An oven-dried pressure tube equipped with a magnetic stir bar was charged with K$_3$PO$_4$ (2.2 mg, 0.01 mmol, 5 mol%), (R)-Ir-IVb (11.0 mg, 0.01 mmol, 5 mol%), and piperonal (30.0 mg, 0.2 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.2 mL, 1 M), 2-propanol (46 µL, 0.6 mmol, 300 mol%), and isoprene monoxide (59 µL, 0.6 mmol, 300 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 45 °C for 1 day. The reaction was allowed to reach ambient temperature and concentrated in vacuo. The residue was subjected to column chromatography (SiO$_2$: hexanes:ethyl acetate, 4:1) to furnish the title compound as a colorless oil (42.5 mg, *anti*:syn > 20:1) in 90% yield.

**1H NMR** (400 MHz, CDCl$_3$) $\delta$ 6.84 (s, 1H), 6.75 (d, $J = 0.5$ Hz, 2H), 6.07 (dd, $J = 17.8$, 11.0 Hz, 1H), 5.96-5.93 (m, 2H), 5.25 (dd, $J = 11.0$, 1.3 Hz, 1H), 5.07 (dd, $J = 17.8$, 1.3 Hz, 1H), 4.64 (s, 1H), 3.62 (d, $J = 10.7$ Hz, 1H), 3.56 (d, $J = 10.7$ Hz, 1H), 2.81 (br, 1H), 2.35 (br, 1H), 0.91 (s, 3H).

**13C NMR** (100 MHz, CDCl$_3$) $\delta$ 147.1, 146.9, 139.6, 134.7, 121.1, 116.3, 108.2, 107.4, 100.9, 79.8, 69.9, 46.5, 17.7.

**LRMS** (ESI) Calcd. for C$_{13}$H$_{16}$O$_4$Na [M+Na]$^+$: 259.1, Found: 259.1.

**FTIR** (neat): 3362, 2922, 1739, 1504, 1487, 1442, 1372, 1241, 1124, 1094, 1038, 929, 866, 816, 757 cm$^{-1}$.

**HPLC** (Chiralcel OJ-H column, hexanes:i-PrOH = 95:5, 0.50 mL/min, 280 nm), *anti*:syn = 60:1, ee = 91% from piperonyl alcohol, *anti*:syn = 50:1, ee = 90% from piperonal.
From Alcohol Oxidation Level

| #  | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area [%] |
|----|---------------|------|-------------|--------------|--------------|----------|
| 1  | 53.625        | BV   | 0.9198      | 3254.34741   | 53.49318     | 9.1137   |
| 2  | 55.171        | VV   | 0.9244      | 3139.77246   | 51.27665     | 8.7928   |
| 3  | 57.471        | VB   | 1.0593      | 1.46131e4    | 210.66290    | 40.9235  |
| 4  | 63.683        | BB   | 1.1709      | 1.47012e4    | 191.22240    | 41.1700  |
From Aldehyde Oxidation Level

| # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %   |
|---|--------------|------|-------------|--------------|-------------|---------|
| 1 | 55.486       | BV   | 0.7324      | 286.49448    | 5.60444     | 1.7399  |
| 2 | 58.236       | VB   | 1.0328      | 1.54241e4    | 229.30447   | 93.6717 |
| 3 | 73.997       | BB   | 0.9421      | 755.52783    | 10.06055    | 4.5884  |
(1R,2S)-1-(furan-2-yl)-2-methyl-2-vinylpropane-1,3-diol (4c)

**Detailed Procedures**

*From alcohol oxidation level:* An oven-dried pressure tube equipped with a magnetic stir bar was charged with K$_3$PO$_4$ (2.2 mg, 0.01 mmol, 5 mol%), (R)-Ir-IVb (11.0 mg, 0.01 mmol, 5 mol%), and furfuryl alcohol (19.6 mg, 0.2 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.4 mL, 0.5 M) and isoprene monoxide (59 µL, 0.6 mmol, 300 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 45 °C for 1 day. The reaction was allowed to reach ambient temperature and concentrated in vacuo. The residue was subjected to column chromatography (SiO$_2$: hexanes:ethyl acetate, 5:1) to furnish the title compound as a colorless oil (33.3 mg, anti: syn > 20:1) in 91% yield.

*From aldehyde oxidation level:* An oven-dried pressure tube equipped with a magnetic stir bar was charged with K$_3$PO$_4$ (2.2 mg, 0.01 mmol, 5 mol%), (R)-Ir-IVb (11.0 mg, 0.01 mmol, 5 mol%), and furfural (19.2 mg, 0.2 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.6 mL, 0.33 M), 2-propanol (46 µL, 0.6 mmol, 300 mol%), and isoprene monoxide (59 µL, 0.6 mmol, 300 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 45 °C for 1 day. The reaction was allowed to reach ambient temperature and concentrated in vacuo. The residue was subjected to column chromatography (SiO$_2$: hexanes:ethyl acetate, 5:1) to furnish the title compound as a colorless oil (33.1 mg, anti: syn = 5:1) in 91% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.37 (dd, $J$ = 1.8, 0.8 Hz, 1H), 6.34 (dd, $J$ = 3.1, 2.0 Hz, 1H), 6.30-6.26 (m, 1H), 6.04 (dd, $J$ = 17.7, 11.0 Hz, 1H), 5.26 (dd, $J$ = 11.0, 1.1 Hz, 1H), 5.15 (dd, $J$ = 17.8, 1.1 Hz, 1H), 4.74 (s, 1H), 3.71 (d, $J$ = 10.8 Hz, 1H), 3.56 (d, $J$ = 10.9 Hz, 1H), 2.88 (br, 1H), 2.27 (br, 1H), 1.02 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.4, 141.7, 139.6 116.1, 110.2, 107.7, 73.6, 69.3, 46.4, 17.8.

LRMS (ESI) Calcd. for C$_{10}$H$_{14}$O$_3$Na [M+Na]$^+$: 205.1, Found: 205.1.

FTIR (neat): 3363, 2923, 1637, 1503, 1459, 1416, 1259, 1148, 1007, 921, 884, 813, 734, 669 cm$^{-1}$.

HPLC (two connected Chiralcel OC-H columns, hexanes:i-PrOH = 88:12, 0.20 mL/min, 210 nm), anti: syn = 30:1, ee = 91% from furfuryl alcohol, ee = 94% from furfural.
From Alcohol Oxidation Level
From Aldehyde Oxidation Level

| #  | RetTime | Type | Width | Area    | Height | Area      | %    |
|----|---------|------|-------|---------|--------|-----------|------|
| 1  | 74.729  | BV   | 0.9818| 1.17614e5 | 1498.28320 | 75.3427 |
| 2  | 76.789  | VB   | 1.1783| 3.63492e4 | 462.78833  | 23.2852 |
| 3  | 85.848  | MM   | 1.5995| 2141.89429 | 22.31884  | 1.3721  |
(2S,3S,E)-2,5,9-trimethyl-2-vinyldeca-4,8-diene-1,3-diol (4d)

**Detailed Procedures**

**From alcohol oxidation level**: An oven-dried pressure tube equipped with a magnetic stir bar was charged with K$_3$PO$_4$ (2.2 mg, 0.01 mmol, 5 mol%), (R)-Ir-IVb (11.0 mg, 0.01 mmol, 5 mol%), and geraniol (30.9 mg, 0.2 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.6 mL, 0.3 M) and isoprene monoxide (79 µL, 0.8 mmol, 400 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 45 °C for 1 day. The reaction was allowed to reach ambient temperature and concentrated in vacuo. The residue was subjected to column chromatography (SiO$_2$: chloroform:methanol, 150:1) to furnish the title compound as a colorless oil (35.0 mg, anti:syn > 20:1) in 73% yield.

**From aldehyde oxidation level**: An oven-dried pressure tube equipped with a magnetic stir bar was charged with K$_3$PO$_4$ (2.2 mg, 0.01 mmol, 5 mol%), (R)-Ir-IVb (11.0 mg, 0.01 mmol, 5 mol%), and geranial (30.4 mg, 0.2 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.4 mL, 0.5 M), 2-propanol (46 µL, 0.6 mmol, 300 mol%), and isoprene monoxide (59 µL, 0.6 mmol, 300 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 45 °C for 1 day. The reaction was allowed to reach ambient temperature and concentrated in vacuo. The residue was subjected to column chromatography (SiO$_2$: chloroform:methanol, 50:1) to furnish the title compound as a colorless oil (36.7 mg, anti:syn = 20:1) in 77% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.03 (dd, $J = 17.7, 11.0$ Hz, 1H), 5.26 (dd, $J = 11.0, 1.4$ Hz, 1H), 5.21 (dd, $J = 9.4, 1.2$ Hz, 1H), 5.16 (dd, $J = 17.7, 1.4$ Hz, 1H), 5.06 (dd, $J = 6.9, 4.1$, 1.3 Hz, 1H), 4.35 (d, $J = 9.4$ Hz, 1H), 3.64 (d, $J = 10.7$ Hz, 1H), 3.56 (d, $J = 10.8$ Hz, 1H), 2.38 (br, 1H), 2.25-1.86 (m, 5H), 1.69 (d, $J = 1.4$ Hz, 3H), 1.68 (d, $J = 1.0$ Hz, 3H), 1.60 (s, 3H), 0.95 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.3, 139.8, 131.7, 123.9, 123.9, 116.0, 73.8, 69.9, 46.1, 39.8, 26.2, 25.7, 17.7, 17.2, 16.8.

LRMS (ESI) Calcd. C$_{15}$H$_{26}$O$_2$Na for [M+Na]$^+$: 261.2, Found: 261.2.

FTIR (neat): 3340, 2966, 2922, 1669, 1637, 1439, 1415, 1377, 1260, 1097, 1035, 1009, 916, 818, 756, 668 cm$^{-1}$.

HPLC Diastereomeric ratio and enantiomeric excess was determined by HPLC analysis of the 1-benzoate of product (Chiralcel OD-H column, hexanes:i-PrOH = 99:1, 0.20 mL/min, 210 nm), anti:syn = 30:1, ee = 91% from geraniol, ee = 94% from geranial.
### From Alcohol Oxidation Level

| Peak | RetTime | Type | Width  | Area     | Height | Area   | %     |
|------|---------|------|--------|----------|--------|--------|-------|
| #    | [min]   | [min]| [mAU*s]| [mAU]    | %      |        |       |
| 1    | 41.946  | BB   | 0.7982 | 3878.34546 | 75.89896 | 6.1285 |
| 2    | 54.315  | BV   | 1.3010 | 2.76214e4  | 303.16302 | 43.6467 |
| 3    | 58.485  | VV   | 1.2532 | 2.77584e4  | 342.62363 | 43.8632 |
| 4    | 61.739  | VB   | 1.1138 | 4025.89600 | 53.87474 | 6.3616 |

### Diagram

**From Alcohol Oxidation Level**

| Peak | RetTime | Type | Width  | Area     | Height | Area   | %     |
|------|---------|------|--------|----------|--------|--------|-------|
| #    | [min]   | [min]| [mAU*s]| [mAU]    | %      |        |       |
| 1    | 42.173  | BB   | 0.5652 | 141.35085 | 3.39873 | 0.2727 |
| 2    | 54.239  | BB   | 1.0403 | 4.80523e4 | 718.49957 | 92.6957 |
| 3    | 58.361  | BB   | 1.1394 | 2178.22876 | 24.16941 | 4.2019 |
| 4    | 63.462  | BB   | 0.9835 | 1466.89954 | 19.06814 | 2.8297 |
## From Aldehyde Oxidation Level

![Graph showing aldehyde oxidation level](image)

| Peak | RetTime | Type | Width  | Area       | Height     | Area %   |
|------|---------|------|--------|------------|------------|----------|
| 1    | 40.799  | MM   | 0.8599 | 2.05757e4 | 398.80432  | 9.0374   |
| 2    | 52.176  | MM   | 1.4991 | 1.99822e5 | 2221.62500 | 87.7664  |
| 3    | 56.739  | MM   | 1.2249 | 7276.98828| 99.01257  | 3.1962   |
(2S,3S)-2,5-dimethyl-2-vinylhex-4-ene-1,3-diol (4e)

Detailed Procedures

From alcohol oxidation level: An oven-dried pressure tube equipped with a magnetic stir bar was charged with K$_3$PO$_4$ (2.2 mg, 0.01 mmol, 5 mol%), (R)-Ir-IVb (11.0 mg, 0.01 mmol, 5 mol%), and prenol (17.2 mg, 0.2 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.2 mL, 1 M) and isoprene monoxide (79 µL, 0.8 mmol, 400 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 45 °C for 1 day. The reaction was allowed to reach ambient temperature and concentrated in vacuo. The residue was subjected to column chromatography (SiO$_2$: hexanes:ethyl acetate, 5:1) to furnish the title compound as a white solid (29.1 mg, anti:syn > 20:1) in 85% yield.

From aldehyde oxidation level: An oven-dried pressure tube equipped with a magnetic stir bar was charged with K$_3$PO$_4$ (2.2 mg, 0.01 mmol, 5 mol%), (R)-Ir-IVb (11.0 mg, 0.01 mmol, 5 mol%), and prenal (16.8 mg, 0.2 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.4 mL, 0.5 M), 2-propanol (46 µL, 0.6 mmol, 300 mol%), and isoprene monoxide (59 µL, 0.6 mmol, 300 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 45 °C for 1 day. The reaction was allowed to reach ambient temperature and concentrated in vacuo. The residue was subjected to column chromatography (SiO$_2$: hexanes:ethyl acetate, 5:1) to furnish the title compound as a white solid (27.6 mg, anti:syn = 20:1) in 81% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.04 (dd, $J = 17.8, 11.0$ Hz, 1H), 5.26 (dd, $J = 11.0, 1.4$ Hz, 1H), 5.22 (dq, $J = 9.4, 1.4$ Hz, 1H), 5.16 (dd, $J = 17.8, 1.4$ Hz, 1H), 4.34 (d, $J = 9.4$ Hz, 1H), 3.64 (d, $J = 10.7$ Hz, 1H), 3.56 (d, $J = 10.7$ Hz, 1H), 2.52 (br, 1H), 2.14 (br, 1H), 1.75 (d, $J = 1.3$ Hz, 3H), 1.70 (d, $J = 1.3$ Hz, 3H), 0.95 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 139.8, 137.1, 123.9, 116.0, 73.9, 69.9, 46.0, 26.0, 18.4, 17.3.

LRMS (ESI) Calcd. C$_{10}$H$_{18}$O$_2$Na for [M+Na]$^+$: 193.1, Found: 193.1.

FTIR (neat): 3361, 2969, 2923, 1675, 1637, 1445, 1416, 1376, 1005, 915, 846, 681 cm$^{-1}$.

MP 39.8-41.0 °C

HPLC Diastereomeric ratio and enantiomeric excess was determined by HPLC analysis of the 1-benzoate of product (two connected Chiralpak AD-H columns, hexanes:i-ProOH = 95:5, 0.20 mL/min, 210 nm), anti:syn > 99:1, ee = 93% from prenol, ee = 86% from prenal.
### From Alcohol Oxidation Level

| # | RetTime | Type | Width [min] | Area [mAU*s]       | Height [mAU] | Area [%] |
|---|---------|------|-------------|--------------------|--------------|----------|
| 1 | 94.556  | BV   | 1.1457      | 1.45915e4          | 193.95432    | 7.5084   |
| 2 | 96.541  | VB   | 1.6253      | 8.29694e4          | 760.21350    | 42.6943  |
| 3 | 104.758 | BB   | 1.6311      | 1.84827e4          | 167.79832    | 9.5108   |
| 4 | 112.571 | BB   | 1.8968      | 7.82903e4          | 609.39807    | 40.2865  |
From Aldehyde Oxidation Level

| # | RetTime | Type | Width | Area    | Height | Area %  |
|---|---------|------|-------|---------|--------|--------|
| 1 | 83.835  | BB   | 1.2388| 7536.07959 | 89.82337 | 78.5005 |
| 2 | 90.379  | BB   | 0.8929| 402.28818  | 5.31590  | 4.1905  |
| 3 | 105.492 | BB   | 1.3433| 1661.66968 | 14.58324 | 17.3090 |
(2S,3S,E)-2-methyl-5-phenyl-2-vinylpent-4-ene-1,3-diol (4f)

**Detailed Procedures**

*From alcohol oxidation level:* An oven-dried pressure tube equipped with a magnetic stir bar was charged with K$_3$PO$_4$ (2.2 mg, 0.01 mmol, 5 mol%), (R)-Ir-IVb (11.0 mg, 0.01 mmol, 5 mol%), and cinnamyl alcohol (26.8 mg, 0.2 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.6 mL, 0.3 M) and isoprene monoxide (59 µL, 0.6 mmol, 300 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 45 °C for 1 day. The reaction was allowed to reach ambient temperature and concentrated *in vacuo*. The residue was subjected to column chromatography (SiO$_2$: hexanes:ethyl acetate, 5:1) to furnish the title compound as a white solid (37.2 mg, *anti*:syn > 20:1) in 85% yield.

*From aldehyde oxidation level:* An oven-dried pressure tube equipped with a magnetic stir bar was charged with K$_3$PO$_4$ (2.2 mg, 0.01 mmol, 5 mol%), (R)-Ir-IVb (11.0 mg, 0.01 mmol, 5 mol%), and cinnamaldehyde (26.4 mg, 0.2 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (2.0 mL, 0.1 M) 2-propanol (46 µL, 0.6 mmol, 300 mol%), and isoprene monoxide (59 µL, 0.6 mmol, 300 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 45 °C for 1 day. The reaction was allowed to reach ambient temperature and concentrated *in vacuo*. The residue was subjected to column chromatography (SiO$_2$: hexanes:ethyl acetate, 5:1) to furnish the title compound as a white solid (33.2 mg, *anti*:syn = 10:1) in 76% yield.

**1H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.43-7.20 (m, 5H), 6.59 (d, $J = 15.8$ Hz, 1H), 6.23 (dd, $J = 15.9, 7.5$ Hz, 1H), 6.07 (dd, $J = 17.8, 11.0$ Hz, 1H), 5.28 (dd, $J = 11.0, 1.3$ Hz, 1H), 5.17 (dd, $J = 17.8, 1.3$ Hz, 1H), 4.25 (d, $J = 7.4$ Hz, 1H), 3.71 (d, $J = 10.8$ Hz, 1H), 3.61 (d, $J = 10.7$ Hz, 1H), 2.69 (br, 1H), 2.51 (br, 1H), 1.05 (d, $J = 8.4$ Hz, 3H).

**13C NMR** (100 MHz, CDCl$_3$) $\delta$ 139.7, 136.6, 132.6, 128.6, 128.4, 127.8, 126.6, 116.1, 78.8, 69.8, 45.8, 18.1.

**LRMS** (ESI) Calcd. C$_{14}$H$_{18}$O$_2$Na for [M+Na]$^+$: 241.1, Found: 241.1.

**FTIR** (neat): 3357, 3081, 3025, 2965, 2926, 2875, 1637, 1494, 1449, 1416, 1300, 1156, 1095, 1070, 1028, 967, 919, 836, 757, 741, 692 cm$^{-1}$.

**MP** 87.0-87.6 °C

**HPLC** (two connected Chiralcel OJ-H columns, hexanes:i-PrOH = 92:8, 0.50 mL/min, 230 nm), *anti*:syn = 40:1, ee = 93% from cinnamyl alcohol, ee = 91% from cinnamaldehyde.
### From Alcohol Oxidation Level

| # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area [%] |
|---|---------------|------|-------------|--------------|--------------|----------|
| 1 | 49.245        | VV   | 0.5703      | 2.8901*10^4  | 765.79352    | 11.6025  |
| 2 | 50.181        | VV   | 0.6663      | 2.9384*10^4  | 669.12909    | 11.7967  |
| 3 | 52.199        | VB   | 0.7797      | 9.4803*10^4  | 1832.00684   | 38.0594  |
| 4 | 54.894        | BB   | 0.8895      | 9.6003*10^4  | 1578.56946   | 38.5413  |

---

| # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area [%] |
|---|---------------|------|-------------|--------------|--------------|----------|
| 1 | 50.196        | BV   | 0.4991      | 612.76685    | 18.66265     | 0.3878   |
| 2 | 51.035        | VB   | 0.6355      | 3380.96704   | 81.23939     | 2.1398   |
| 3 | 53.418        | BV   | 0.6328      | 5530.77246   | 135.33653    | 3.5004   |
| 4 | 55.220        | VB   | 0.9970      | 1.4848*10^5  | 1988.94861   | 93.9720  |
From Aldehyde Oxidation Level
(2S,3S)-2-methyl-2-vinlynonane-1,3-diol (4g)

**Detailed Procedures**

*From alcohol oxidation level:* An oven-dried pressure tube equipped with a magnetic stir bar was charged with K$_3$PO$_4$ (2.2 mg, 0.01 mmol, 5 mol%), (R)-Ir-IVb (11.0 mg, 0.01 mmol, 5 mol%), and 1-heptanol (23.2 mg, 0.2 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.4 mL, 0.5 M) and isoprene monoxide (79 μL, 0.8 mmol, 400 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 60 °C for 1 day. The reaction was allowed to reach ambient temperature and concentrated *in vacuo*. The residue was subjected to column chromatography (SiO$_2$: hexanes:ethyl acetate, 6:1) to furnish the title compound as a white solid (30.3 mg, anti:syn > 20:1) in 74% yield.

*From aldehyde oxidation level:* An oven-dried pressure tube equipped with a magnetic stir bar was charged with K$_3$PO$_4$ (2.2 mg, 0.01 mmol, 5 mol%), (R)-Ir-IVb (11.0 mg, 0.01 mmol, 5 mol%), and heptanal (22.8 mg, 0.2 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.4 mL, 0.5 M) 2-propanol (46 μL, 0.6 mmol, 300 mol%), and isoprene monoxide (59 μL, 0.6 mmol, 300 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 60 °C for 1 day. The reaction was allowed to reach ambient temperature and concentrated *in vacuo*. The residue was subjected to column chromatography (SiO$_2$: hexanes:ethyl acetate, 6:1) to furnish the title compound as a white solid (29.2 mg, anti:syn = 12:1) in 73% yield.

**1H NMR** (400 MHz, CDCl$_3$) δ 5.96 (dd, $J = 17.8$, 11.1 Hz, 1H), 5.23 (dd, $J = 11.1$, 1.3 Hz, 1H), 5.13 (dd, $J = 17.8$, 1.3 Hz, 1H), 3.69 (d, $J = 10.7$ Hz, 1H), 3.60-3.51 (m, 2H), 2.48 (br, 1H), 2.42 (br, 1H), 1.60-1.40 (m, 2H), 1.40-1.21 (m, 8H), 1.01 (s, 3H), 0.88 (t, $J = 6.8$ Hz, 3H).

**13C NMR** (100 MHz, CDCl$_3$) δ 140.2, 115.6, 77.8, 70.0, 45.6, 32.0, 31.8, 29.3, 26.5, 22.6, 18.2, 14.1.

**LRMS** (CI) Calcd. C$_{12}$H$_{25}$O$_2$ for [M+H]$^+$: 201, Found: 201.

**FTIR** (neat): 3348, 2955, 2927, 2857, 1459, 1417, 1377, 1028, 963, 915, 679 cm$^{-1}$.

**MP** 53.6-54.3 °C

**HPLC** Diastereomeric ratio and enantiomeric excess was determined by HPLC analysis of the 1-benzoate of product (Chiralcel OD-H column, hexanes:i-PrOH = 98:2, 0.25 mL/min, 254 nm), anti:syn = 40:1, ee = 93% from 1-heptanol, ee = 93% from heptanal.
From Alcohol Oxidation Level
From Aldehyde Oxidation Level

| # | Ret Time | Type | Width | Area | Height | Area % |
|---|----------|------|-------|------|--------|-------|
| 1 | 23.327   | MM   | 0.7276| 1644.37085| 37.66661| 96.7509|
| 2 | 25.910   | MM   | 1.1734| 17.41916 | 2.47408e-1| 1.0249 |
| 3 | 43.439   | MM   | 1.3668| 37.80240 | 4.60965e-1| 2.2242 |
(2S,3S)-2-methyl-5-phenyl-2-vinylpentane-1,3-diol (4h)

Detailed Procedures

From alcohol oxidation level: An oven-dried pressure tube equipped with a magnetic stir bar was charged with K$_3$PO$_4$ (2.2 mg, 0.01 mmol, 5 mol%), (R)-Ir-IVb (11.0 mg, 0.01 mmol, 5 mol%), and 3-phenyl-1-propanol (27.2 mg, 0.2 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.4 mL, 0.5 M) and isoprene monoxide (59 µL, 0.6 mmol, 300 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 60 °C for 1 day. The reaction was allowed to reach ambient temperature and concentrated in vacuo. The residue was subjected to column chromatography (SiO$_2$: hexanes:ethyl acetate, 5:1) to furnish the title compound as a white solid (33.7 mg, anti:syn > 20:1) in 76% yield.

From aldehyde oxidation level: An oven-dried pressure tube equipped with a magnetic stir bar was charged with K$_3$PO$_4$ (2.2 mg, 0.01 mmol, 5 mol%), (R)-Ir-IVb (11.0 mg, 0.01 mmol, 5 mol%), and 3-phenylpropionaldehyde (26.8 mg, 0.2 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.4 mL, 0.5 M), 2-propanol (46 µL, 0.6 mmol, 300 mol%), and isoprene monoxide (59 µL, 0.6 mmol, 300 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 60 °C for 1 day. The reaction was allowed to reach ambient temperature and concentrated in vacuo. The residue was subjected to column chromatography (SiO$_2$: hexanes:ethyl acetate, 5:1) to furnish the title compound as a white solid (40.0 mg, anti:syn = 5:1) in 91% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.35–7.12 (m, 5H), 5.95 (dd, $J = 17.8$, 11.1 Hz, 1H), 5.22 (dd, $J = 11.1$, 1.2 Hz, 1H), 5.10 (dd, $J = 17.8$, 1.3 Hz, 1H), 3.69 (d, $J = 10.7$ Hz, 1H), 3.61-3.52 (m, 2H), 2.96-2.87 (m, 1H), 2.62 (ddd, $J = 13.7$, 9.6, 6.8 Hz, 1H), 2.79-2.38 (m, 2H), 1.86-1.75 (m, 1H), 1.74-1.58 (m, 1H), 1.00 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 142.2, 140.0, 128.5, 128.4, 125.9, 115.8, 77.1, 69.9, 45.5, 33.9, 32.8, 18.3.

LRMS (ESI) Calcd. C$_{14}$H$_{20}$O$_2$Na for [M+Na]$^+$: 243.2, Found: 243.1.

FTIR (neat): 3326, 2923, 1496, 1454, 1417, 1313, 1155, 1071, 1029, 918, 748, 699, 669 cm$^{-1}$.

MP 72.1-73.4 °C

HPLC (two connected Chiralcel OJ-H columns, hexanes:i-PrOH = 98:2, 0.50 mL/min, 210 nm), anti:syn = 30:1, ee = 93% from 3-phenyl-1-propanol, ee = 85% from 3-phenylpropionaldehyde.
From Alcohol Oxidation Level

| # | RetTime | Type | Width  | Area      | Height | Area %  |
|---|---------|------|--------|-----------|--------|---------|
| 1 | 160.020 | BB   | 1.6347 | 1.08077e4 | 78.87156 | 8.3340  |
| 2 | 186.058 | BV   | 1.6558 | 1.09341e4 | 77.69662 | 8.4315  |
| 3 | 191.048 | VB   | 2.5492 | 5.44213e4 | 279.30661 | 41.9652 |
| 4 | 201.188 | BB   | 2.7592 | 5.35188e4 | 227.44640 | 41.2693 |

| # | RetTime | Type | Width  | Area      | Height | Area %  |
|---|---------|------|--------|-----------|--------|---------|
| 1 | 180.055 | MM   | 2.4549 | 1053.76868 | 7.15417 | 3.2073  |
| 2 | 185.545 | MM   | 2.3959 | 1006.25250 | 6.99975 | 3.0626  |
| 3 | 193.176 | MM   | 3.0734 | 3.07957e4  | 166.99921 | 93.7301 |
### From Aldehyde Oxidation Level

![Graph showing aldehyde oxidation level with peaks and areas](image)

| Peak | RetTime | Type | Width | Area    | Height | Area % |
|------|---------|------|-------|---------|--------|--------|
| 1    | 196.154 | MM   | 2.2134| 7877.12500 | 59.31392 | 13.8838 |
| 2    | 202.192 | MM   | 2.4781| 3694.45679 | 24.84729 | 6.5116  |
| 3    | 209.675 | MM   | 3.4103| 4.51647e4  | 220.72470| 79.6046 |
(2S,3S)-4-cyclohexyl-2-methyl-2-vinylbutane-1,3-diol (4i)

**Detailed Procedures**

**From alcohol oxidation level:** An oven-dried pressure tube equipped with a magnetic stir bar was charged with K$_3$PO$_4$ (2.2 mg, 0.01 mmol, 5 mol%), (R)-Ir-IVb (11.0 mg, 0.01 mmol, 5 mol%), and 2-cyclohexyl-1-ethanol (25.6 mg, 0.2 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.4 mL, 0.5 M) and isoprene monoxide (79 µL, 0.8 mmol, 400 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 60 °C for 1 day. The reaction was allowed to reach ambient temperature and concentrated in vacuo. The residue was subjected to column chromatography (SiO$_2$: hexanes:ethyl acetate, 6:1) to furnish the title compound as a white solid (32.3 mg, anti:syn > 20:1) in 76% yield.

**From aldehyde oxidation level:** An oven-dried pressure tube equipped with a magnetic stir bar was charged with K$_3$PO$_4$ (2.2 mg, 0.01 mmol, 5 mol%), (R)-Ir-IVb (11.0 mg, 0.01 mmol, 5 mol%), and cyclohexylacetaldehyde (25.2 mg, 0.2 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.4 mL, 0.5 M), 2-propanol (46 µL, 0.6 mmol, 300 mol%), and isoprene monoxide (59 µL, 0.8 mmol, 300 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 70 °C for 1 day. The reaction was allowed to reach ambient temperature and concentrated in vacuo. The residue was subjected to column chromatography (SiO$_2$: hexanes:ethyl acetate, 6:1) to furnish the title compound as a white solid (27.4 mg, anti:syn = 20:1) in 65% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.95 (dd, $J = 17.8$, 11.1 Hz, 1H), 5.23 (dd, $J = 11.1$, 1.3 Hz, 1H), 5.12 (dd, $J = 17.8$, 1.3 Hz, 1H), 3.72-3.65 (m, 2H), 3.57 (d, $J = 10.7$ Hz, 1H), 2.40 (br, 1H), 2.30 (br, 1H), 1.84 (d, $J = 12.7$ Hz, 1H), 1.75-1.59 (m, 4H), 1.55-1.40 (m, 1H), 1.35-1.11 (m, 5H), 1.04-0.89 (m, 4H), 0.86-0.73 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.2, 115.7, 74.8, 70.0, 45.5, 39.8, 34.8, 34.0, 32.2, 26.6, 26.4, 26.1, 18.2.

LRMS (ESI) Calcd. C$_{13}$H$_{24}$O$_2$Na for [M+Na]$^+$: 235.2, Found: 235.2.

FTIR (neat): 3289, 2922, 2854, 1457, 1444, 1418, 1263, 1200, 1129, 1069, 1051, 1033, 992, 953, 916, 834, 759, 685 cm$^{-1}$.

MP 96.0-96.8 °C

HPLC Diastereomeric ratio and enantiomeric excess was determined by HPLC analysis of the 1-benzoate of product (two connected Chiralcel OC-H columns, hexanes:i-PrOH = 98:2, 0.50 mL/min, 230 nm), anti:syn = 30:1, ee = 99% from 2-cyclohexyl-1-ethanol, ee = 95% from cyclohexylacetaldehyde.
### From Alcohol Oxidation Level

| Peak RetTime | Type | Width  | Area      | Height     | Area % |
|--------------|------|--------|-----------|------------|--------|
| 1            | 38.564 BB | 1.1697 | 5.35729e4 | 699.39789 | 40.6564 |
| 2            | 46.378 BB | 1.3130 | 1.31294e4 | 116.01938 | 9.9638  |
| 3            | 51.389 BV  | 1.7017 | 5.04832e4 | 427.49615 | 38.3116 |
| 4            | 54.851 VB  | 1.6986 | 1.45846e4 | 122.35559 | 11.0682 |

---

**From Alcohol Oxidation Level**

| Peak RetTime | Type | Width  | Area      | Height     | Area % |
|--------------|------|--------|-----------|------------|--------|
| 1            | 40.137 BB | 1.3499 | 1.24632e5 | 1312.45300 | 96.3233 |
| 2            | 50.102 VB  | 1.3678 | 2722.18823 | 25.49278  | 2.1039  |
| 3            | 54.014 BB  | 0.7880 | 400.06882 | 6.01470   | 0.3092  |
| 4            | 57.795 BB  | 1.3488 | 1634.99207 | 14.41982  | 1.2636  |
**From Aldehyde Oxidation Level**

![Graph showing aldehyde oxidation level](image)

| Peak | RetTime | Type | Width | Area   | Height | Area Percent |
|------|---------|------|-------|--------|--------|--------------|
| #    | [min]   |      | [min] | [mAU*s] | [mAU]  |              |
| 1    | 38.324  | MM   | 1.4002| 4.57392e4| 544.42340 | 93.3408      |
| 2    | 46.954  | MM   | 1.9818| 2092.56323 | 17.59784   | 4.2703       |
| 3    | 54.783  | MM   | 2.2931| 1170.60303 | 8.50797    | 2.3889       |
**(2S,3S,5S)-2-methyl-2-vinylhexane-1,3,5-triol (4j)**

**Detailed Procedures**

An oven-dried pressure tube equipped with a magnetic stir bar was charged with K$_3$PO$_4$ (2.2 mg, 0.01 mmol, 5 mol%), (R)-Ir-IVb (11.0 mg, 0.01 mmol, 5 mol%), and (S)-butane-1,3-diol (18.0 mg, 0.2 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.2 mL, 1.0 M) and isoprene monoxide (79 µL, 0.8 mmol, 400 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 60 °C for 2 day. The reaction was allowed to reach ambient temperature and concentrated in vacuo. The residue was subjected to column chromatography (SiO$_2$: DCM:i-PrOH, 10:1) to furnish the title compound (4j) as a colorless oil (20.9 mg) in 60% yield. The (2R,3R)-diastereomer (iso-4j) was obtained as a colorless oil (1.0 mg) in 3% yield.

**$^1$H NMR** (400 MHz, CDCl$_3$) δ 6.00 (dd, $J = 17.8, 11.1$ Hz, 1H), 5.23 (dd, $J = 11.1, 1.3$ Hz, 1H), 5.11 (dd, $J = 17.8, 1.3$ Hz, 1H), 4.14 (br, 1H), 4.10-3.99 (m, 1H), 3.86 (dd, $J = 10.5, 2.0$ Hz, 1H), 3.71 (d, $J = 10.6$ Hz, 1H), 3.58 (d, $J = 10.7$ Hz, 1H), 3.23 (br, 1H), 2.83 (br, 1H), 1.58 (dt, $J = 14.4, 2.3$ Hz, 1H), 1.55-1.43 (m, 1H), 1.22 (d, $J = 6.2$ Hz, 3H), 1.02 (s, 3H).

**$^{13}$C NMR** (100 MHz, CDCl$_3$) 140.0, 115.4, 79.2, 70.1, 69.5, 45.0, 39.2, 24.3, 18.4.

**LRMS** (ESI) Calcd. C$_9$H$_{18}$O$_3$Na for [M+Na]$^+$: 197.1, Found: 197.1.

**FTIR** (neat): 3343, 2967, 2920, 2879, 1457, 1417, 1375, 1317, 1161, 1121, 1073, 1031, 982, 917, 836, 680 cm$^{-1}$. 
**Detailed Procedures**

An oven-dried pressure tube equipped with a magnetic stir bar was charged with K$_3$PO$_4$ (2.2 mg, 0.01 mmol, 5 mol%), (S)-Ir-$\text{IVb}$ (11.0 mg, 0.01 mmol, 5 mol%), and (S)-butane-1,3-diol (18.0 mg, 0.2 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.2 mL, 1.0 M) and isoprene monoxide (79 µL, 0.8 mmol, 400 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 60 °C for 2 day. The reaction was allowed to reach ambient temperature and concentrated \textit{in vacuo}. The residue was subjected to column chromatography (SiO$_2$: DCM:i-PrOH, 10:1) to furnish the title compound (iso-$\text{4j}$) as a colorless oil (23.0 mg) in 66% yield. The (2$S,3S$)-diastereomer (4j) was obtained as a colorless oil (1.3 mg) in 4% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 6.01 (dd, $J = 17.8$, 11.1 Hz, 1H), 5.23 (dd, $J = 11.0$, 1.2 Hz, 1H), 5.12 (dd, $J = 17.8$, 1.2 Hz, 1H), 4.23-4.07 (m, 1H), 3.97 (d, $J = 10.1$ Hz, 1H), 3.70 (d, $J = 10.7$ Hz, 1H), 3.66-3.50 (m, 2H), 3.14 (br, 1H), 2.84 (br, 1H), 1.68-1.55 (m, 1H), 1.49 (ddd, $J = 14.9$, 7.9, 1.8 Hz, 1H), 1.25 (d, $J = 6.2$ Hz, 3H), 0.99 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 140.0, 115.5, 73.7, 70.0, 65.5, 45.1, 39.1, 23.2, 18.0.

LRMS (ESI) Calcd. C$_9$H$_{18}$O$_3$Na for [M+Na]$^+$: 197.1, Found: 197.1.

FTIR (neat): 3345, 2966, 2925, 1457, 1417, 1374, 1127, 1084, 1029, 984, 916, 855, 835, 811, 680 cm$^{-1}$. 

(2$R,3R,5S$)-2-methyl-2-vinylhexane-1,3,5-triol (iso-4j)
Synthesis of Myrcene Oxide 3c\textsuperscript{3}

6-methyl-2-vinylhept-5-ene-1,2-diol (X1)

A solution of potassium permanganate (7.9 g, 50 mmol, 100 mol%) and benzyltri-\textit{n}-butylammonium chloride (15.6 g, 50 mmol, 100 mol%) in DCM (500 mL) was stirred at ambient temperature for 3 h. It was then cooled to -5 °C, and myrcene (15.4 mL, 90 mmol, 180 mol%) was added to the solution. The resulted mixture was stirred at this temperature overnight. Aqueous NaOH solution (1.5 M, 160 mL), NaHSO\textsubscript{3} solution (0.6 M, 200 mL), and H\textsubscript{2}SO\textsubscript{4} solution (1.0 M, 250 mL) was added in sequence to quench the reaction. The organic phase was separated and the aqueous phase was extracted with DCM (3 × 100 mL). The combined organic phases were washed with saturated NaHCO\textsubscript{3} solution (100 mL), and dried over anhydrous magnesium sulfate. The excessive myrcene was removed by a short plug of silica gel (hexanes:ethyl acetate, 5:1). The more polar residue was collected and subjected to column chromatography (SiO\textsubscript{2}: hexanes:Et\textsubscript{2}O, 2:1) to furnish the title compound as a colorless oil (0.95 g) in 11% yield.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 5.80 (dd, J = 17.4, 10.8 Hz, 1H), 5.34 (dd, J = 17.3, 1.4 Hz, 2H), 5.26 (dd, J = 10.8, 1.4 Hz, 1H), 5.10 (tq, J = 7.4, 1.4 Hz, 1H), 3.53-3.42 (m, 2H), 2.36 (br, 1H), 2.12-1.93 (m, 2H), 1.67 (d, J = 1.2 Hz, 3H), 1.65-1.57 (m, 4H), 1.50 (ddd, J = 13.8, 10.4, 5.5 Hz, 1H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 140.6, 132.2, 124.1, 115.2, 76.2, 68.8, 36.7, 25.7, 22.0, 17.7.

2-hydroxy-6-methyl-2-vinylhept-5-en-1-yl 4-methylbenzenesulfonate (X2)

A solution of X1 (0.95 g, 5.6 mmol, 100 mol%) in pyridine (7.5 mL) was cooled to 0 °C and TsCl (1.28 g, 6.7 mmol, 120 mmol%) was added. The resulted mixture was stirred at 0 °C for 5 h. Aqueous HCl solution (1.2 M, 5 mL) was then added, and the mixture was extracted with Et\textsubscript{2}O (3 × 10 mL). The combined organic phase was washed with HCl (0.1 M, 10 mL) and brine (10 mL). It was dried over anhydrous sodium sulfate and concentrated \textit{in vacuo}. The residue was subjected to column chromatography (SiO\textsubscript{2}: hexanes:ethyl acetate, 7:1) to furnish the title compound as a colorless oil (1.50 g) in 83% yield.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.81-7.76 (m, 2H), 7.35 (d, J = 8.6 Hz, 2H), 5.73 (dd, J = 17.3, 10.8 Hz, 1H), 5.33 (dd, J = 17.3, 1.1 Hz, 1H), 5.23 (dd, J = 10.8, 1.1 Hz, 1H), 5.05 (tq, J = 7.2, 1.3 Hz, 1H), 3.89 (s, 2H), 2.45 (s, 3H), 2.10 (s, 1H), 2.07-1.89 (m, 2H), 1.68-1.58 (m, 4H), 1.56 (s, 3H), 1.49 (ddd, J = 13.9, 10.4, 5.6 Hz, 1H).

\textsuperscript{3} (a) Fauchet, V.; Arreguy-San Miguel, B.; Taran, M.; Delmond, B. \textit{Synth. Commun.} 1993, 23, 2503. (b) Löbermann, F.; Weisheit, L.; Trauner, D. \textit{Org. Lett.} 2013, 15, 4324.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.77 (dd, $J$ = 17.4, 10.8 Hz, 1H), 5.35 (dd, $J$ = 17.4, 1.3 Hz, 1H), 5.22 (dd, $J$ = 10.8, 1.3 Hz, 1H), 5.11 (tq, $J$ = 7.1, 1.4 Hz, 1H), 2.82 (d, $J$ = 5.3 Hz, 1H), 2.67 (d, $J$ = 5.3 Hz, 1H), 2.10 (dd, $J$ = 15.6, 7.6 Hz, 2H), 1.80-1.66 (m, 5H), 1.60 (s, 3H).

$^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.5, 132.1, 123.5, 116.5, 58.5, 55.1, 33.6, 25.7, 23.7, 17.7.

$^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.0, 138.7, 132.6, 132.6, 129.9, 128.0, 123.6, 116.0, 75.2, 74.3, 36.7, 25.7, 21.7, 21.7, 17.7.

2-(4-methylpent-3-en-1-yl)-2-vinyloxirane (3c)

A solution of X2 (1.57 g, 4.8 mmol, 100 mol%) in Et$_2$O was cooled to 0 °C and KOH powder (0.54 g, 9.6 mmol, 200 mol%) was added. The resulted slurry was vigorously stirred at 0 °C for 3 h. The reaction mixture was then filtered through a short plug of celite and washed with excessive Et$_2$O. The filtrate was carefully concentrated in vacuo (185 mbar, 0 °C). The residue was subjected to column chromatography (SiO$_2^4$: pentane:Et$_2$O, 200:1) to furnish the title compound (3c) as a colorless oil (0.63 g) in 83% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.77 (dd, $J$ = 17.4, 10.8 Hz, 1H), 5.35 (dd, $J$ = 17.4, 1.3 Hz, 1H), 5.22 (dd, $J$ = 10.8, 1.3 Hz, 1H), 5.11 (tq, $J$ = 7.1, 1.4 Hz, 1H), 2.82 (d, $J$ = 5.3 Hz, 1H), 2.67 (d, $J$ = 5.3 Hz, 1H), 2.10 (dd, $J$ = 15.6, 7.6 Hz, 2H), 1.80-1.66 (m, 5H), 1.60 (s, 3H).

$^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.5, 132.1, 123.5, 116.5, 58.5, 55.1, 33.6, 25.7, 23.7, 17.7.

---

4 Sorbent standard silica gel (40-63 µm).
Detailed Procedures and Spectral Data for Couplings between 4-Bromobenzyl Alcohol (1a) and Other Vinyl Epoxides: Butadiene Monoxide (3b) and Myrcene Oxide (3c):

(1R,2S)-1-(4-bromophenyl)-2-vinylpropane-1,3-diol (5a)

Detailed Procedures

An oven-dried pressure tube equipped with a magnetic stir bar was charged with K$_3$PO$_4$ (2.2 mg, 0.01 mmol, 5 mol%), (R)-Ir-Ib (10.3 mg, 0.01 mmol, 5 mol%), and 4-bromobenzyl alcohol (37.4 mg, 0.2 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.4 mL, 0.5 M) and butadiene monoxide (32 µL, 0.4 mmol, 200 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 60 °C for 1 day. The reaction was allowed to reach ambient temperature and concentrated in vacuo. The residue was subjected to column chromatography (SiO$_2$: DCM:ethyl acetate, 10:1) to furnish the title compound as a yellow oil (32.3 mg, anti:syn = 5:1) in 63% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 (d, $J$ = 8.4 Hz, 2H), 7.21 (d, $J$ = 8.4 Hz, 2H), 5.78 (ddd, $J$ = 17.2, 10.8, 8.4 Hz, 1H), 5.24 (dd, $J$ = 10.8, 1.6 Hz, 1H), 5.13 (dd, $J$ = 17.2, 1.6 Hz, 1H), 4.84 (d, $J$ = 5.2 Hz, 1H), 3.66 (m, 2H), 2.73 (br, 1H), 2.58-2.51 (m, 1H), 1.90 (br, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 141.1, 134.5, 131.3, 128.1, 121.4, 119.9, 74.3, 63.8, 53.1.

HPLC (two connected Chiralcel OC-H columns, hexanes:i-PrOH = 90:10, 0.50 mL/min, 230 nm), anti:syn = 5:1, ee = 94%.

The spectroscopic properties of this compound were consistent with the data available in the literature.$^5$

---

$^5$ Zhang, Y. J.; Yang, J. H.; Kim, S. H.; Krische, M. J. J. Am. Chem. Soc. 2010, 132, 4562.
Peak RetTime Type Width Area Height Area
#  [min]  [min]  [mAU*s]  [mAU]  %
1  31.070  VV  0.5718  5.27088e4  1464.98840  43.5267
2  32.945  VV  0.6643  5.41713e4  1294.19458  44.7344
3  34.347  VV  0.5530  7082.66064  198.15199  5.8488
4  35.376  MF  0.6306  7132.60547  188.50462  5.8901

Peak RetTime Type Width Area Height Area
#  [min]  [min]  [mAU*s]  [mAU]  %
1  31.332  VV  0.6642  1289.96228  28.06549  2.3364
2  33.206  MF  0.6804  4.57839e4  1121.45105  82.9228
3  34.293  FM  0.3785  779.22272  34.31005  1.4113
4  35.570  VV  0.5953  7359.58105  190.23361  13.3295
(1S,2S)-1-(4-bromophenyl)-2-(4-methylpent-3-en-1-yl)-2-vinylpropane-1,3-diol (5b)

**Detailed Procedures**

An oven-dried pressure tube equipped with a magnetic stir bar was charged with K$_3$PO$_4$ (1.1 mg, 0.005 mmol, 5 mol%), (R)-Ir-IVb (5.5 mg, 0.005 mmol, 5 mol%), and 4-bromobenzyl alcohol (18.7 mg, 0.1 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.1 mL, 1.0 M) and myrcene oxide 3e (60.9 mg, 0.4 mmol, 400 mol%) were added by syringe. The reaction vessel was sealed and the reaction mixture was allowed to stir at 45 °C for 2 day. The reaction was allowed to reach ambient temperature and concentrated in vacuo. The residue was subjected to column chromatography (SiO$_2$: DCM:i-PrOH, 200:1) to furnish the title compound as a colorless oil (32.0 mg, anti:syn > 20:1) in 94% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.46-7.40 (m, 2H), 7.23-7.15 (m, 2H), 5.62 (dd, $J$ = 18.0, 11.3 Hz, 1H), 5.21 (dd, $J$ = 11.3, 1.0 Hz, 1H), 5.07 (ddq, $J$ = 8.4, 5.6, 1.3 Hz, 1H), 4.89 (dd, $J$ = 18.0, 1.0 Hz, 1H), 4.71 (s, 1H), 3.86 (d, $J$ = 11.0 Hz, 1H), 3.64 (d, $J$ = 11.0 Hz, 1H), 3.09 (br, 1H), 2.31 (br, 1H), 1.95 (dd, $J$ = 16.0, 7.5 Hz, 2H), 1.73-1.63 (m, 4H), 1.58 (s, 3H), 1.37-1.28 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 139.8, 138.2, 131.8, 130.7, 129.6, 124.3, 121.4, 116.5, 79.2, 64.6, 48.2, 32.5, 25.7, 22.3, 17.7.

LRMS (ESI) Calcd. for C$_{17}$H$_{23}$BrO$_2$Na [M+Na]$^+$: 361.1, Found: 361.1.

FTIR (neat): 3347, 2969, 2924, 1487, 1448, 1404, 1376, 1072, 1037, 1010, 919, 836, 760, 670 cm$^{-1}$.

HPLC (two connected Chiralcel OC-H column, hexanes:i-PrOH = 98:2, 0.75 mL/min, 230 nm), anti:syn = 40:1, ee = 87%.
Crystallographic Material for 4a-acetonide

X-ray Experimental for C₁₅H₁₉O₂Br (4a-acetonide)

Crystals grew as colorless prisms by slow evaporation from n-hexanes. The data crystal had approximate dimensions; 0.35 x 0.13 x 0.05 mm. The data were collected on a Rigaku AFC12 diffractometer with a Saturn 724+ CCD using a graphite monochromator with MoKα radiation (λ = 0.71073Å). A total of 1192 frames of data were collected using ω-scans with a scan range of 0.5° and a counting time of 45 seconds per frame. The data were collected at 100 K using a Rigaku XStream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using the Rigaku Americas Corporation’s Crystal Clear version 1.40. The structure was solved by direct methods using SIR97 and refined by full-matrix least-squares on F² with anisotropic displacement parameters for the non-H atoms using SHELXL-97. Structure analysis was aided by use of the programs PLATON98 and WinGX. The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

The absolute configuration of 4a-acetonide was determined by the method of Flack. The Flack x-parameter refined to 0.016(8). The assignment was corroborated by use of the Hooft y-parameter, which refined to 0.020(6).

The function, Σw(|F₀|² - |Fc|²)², was minimized, where w = 1/[σ(FO)² + (0.0234*P)² + (0.1828*P)] and P = ([FO]² + 2|Fc|²)/3. Rw(F²) refined to 0.0512, with R(F) equal to 0.0201 and a goodness of fit, S, =

---

6 CrystalClear 1.40 (2008). Rigaku Americas Corporation, the Woodlands, TX.
7 Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. J. Appl. Cryst. 1999, 32, 115.
8 Sheldrick, G. M. Acta Cryst. 2008, A64, 112.
9 Spek, A. L. (1998). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, the Netherlands.
10 Farrugia, L. J. J. Appl. Cryst. 1999, 32, 837.
11 Flack, H. D. Acta Cryst. 1983, A39, 876.
12 Hooft, R. W. W.; Straver, L. H.; Spek, A. L. J. Appl. Cryst. 2008, 41, 96.
Definitions used for calculating $R(F)$, $R_w(F^2)$ and the goodness of fit, $S$, are given below.\(^{13}\) The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).\(^{14}\) All figures were generated using SHELXTL/PC.\(^{15}\) Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

\[^{13}\] $R_w(F^2) = \left\{ \sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|)^4 \right\}^{1/2}$ where $w$ is the weight given each reflection. $R(F) = \sum (|F_o| - |F_c|) / \sum |F_o|$ for reflections with $F_o > 4(\sigma(F_o))$. $S = \left[ \sum w(|F_o|^2 - |F_c|^2)^2 / (n - p) \right]^{1/2}$, where $n$ is the number of reflections and $p$ is the number of refined parameters.

\[^{14}\] Wilson, A. J. C. *International Tables for X-ray Crystallography*; Kluwer Academic Press: Boston, 1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4.

\[^{15}\] Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.
Table 1. Crystal data and structure refinement for 4a-acetonide.

| Property                                              | Value                                      |
|-------------------------------------------------------|--------------------------------------------|
| Empirical formula                                     | C_{15}H_{19}BrO_{2}                        |
| Formula weight                                        | 311.21                                     |
| Temperature                                           | 100(2) K                                   |
| Wavelength                                            | 0.71073 Å                                  |
| Crystal system                                        | orthorhombic                               |
| Space group                                           | P 2 1 2 1 2 1                              |
| Unit cell dimensions                                  | a = 7.051(3) Å, b = 12.646(5) Å, c = 16.338(5) Å |
|                                                       | a = 90°, b = 90°, g = 90°                  |
| Volume                                                | 1456.9(9) Å                                |
| Z                                                     | 4                                          |
| Density (calculated)                                  | 1.419 Mg/m³                                |
| Absorption coefficient                                | 2.814 mm⁻¹                                 |
| F(000)                                                | 640                                        |
| Crystal size                                          | 0.350 x 0.130 x 0.050 mm                   |
| Theta range for data collection                       | 3.147 to 27.460°                           |
| Index ranges                                          | -9 <= h <= 9, -16 <= k <= 15, -21 <= l <= 21 |
| Reflections collected                                 | 19873                                      |
| Independent reflections                               | 3327 [R(int) = 0.0445]                     |
| Completeness to theta = 25.242°                      | 99.8%                                      |
| Absorption correction                                 | Semi-empirical from equivalents            |
| Max. and min. transmission                            | 1.00 and 0.770                             |
| Refinement method                                     | Full-matrix least-squares on F²            |
| Data / restraints / parameters                        | 3327 / 0 / 167                             |
| Goodness-of-fit on F²                                  | 1.082                                      |
| Final R indices [I>2sigma(I)]                         | R1 = 0.0201, wR2 = 0.0508                  |
| R indices (all data)                                  | R1 = 0.0209, wR2 = 0.0512                  |
| Absolute structure parameter                          | 0.016(8)                                  |
| Extinction coefficient                                | n/a                                        |
| Largest diff. peak and hole                           | 0.223 and -0.216 e Å⁻³                     |
Table 2. Atomic coordinates ($x \times 10^4$) and equivalent isotropic displacement parameters ($\AA^2 \times 10^3$) for 4a-acetonide. U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|      | x    | y    | z    | U(eq) |
|------|------|------|------|-------|
| C1   | 6572(4) | 4143(2) | 1332(1) | 19(1) |
| C2   | 8152(3) | 5825(2) | 1200(1) | 16(1) |
| C3   | 9329(3) | 5616(2) | 1990(1) | 18(1) |
| C4   | 9483(3) | 4403(2) | 2053(1) | 21(1) |
| C5   | 4593(3) | 3739(2) | 1508(2) | 26(1) |
| C6   | 7389(4) | 3632(2) | 565(2)  | 28(1) |
| C7   | 7697(3) | 6980(2) | 1063(1) | 16(1) |
| C8   | 6091(3) | 7444(2) | 1413(1) | 18(1) |
| C9   | 5729(3) | 8518(2) | 1313(1) | 20(1) |
| C10  | 7005(3) | 9117(2) | 864(1)  | 20(1) |
| C11  | 8585(4) | 8684(2) | 498(1)  | 22(1) |
| C12  | 8925(3) | 7604(2) | 603(1)  | 20(1) |
| C13  | 8300(3) | 6025(2) | 2736(1) | 22(1) |
| C14  | 8987(4) | 6708(2) | 3269(2) | 30(1) |
| C15  | 11319(3) | 6071(2) | 1898(2) | 25(1) |
| Br1  | 6540(1) | 10594(1) | 740(1)  | 28(1) |
| O1   | 6386(2) | 5263(1) | 1236(1) | 18(1) |
| O2   | 7659(2) | 3906(1) | 2044(1) | 20(1) |
Table 3. Bond lengths [Å] and angles [°] for 4a-acetonide.

| Bond                  | Length  | Bond                  | Length  |
|-----------------------|---------|-----------------------|---------|
| C1-O2                 | 1.425(3)| C6-H6C                | 0.98    |
| C1-O1                 | 1.432(2)| C7-C12                | 1.392(3)|
| C1-C5                 | 1.513(3)| C7-C8                 | 1.398(3)|
| C1-C6                 | 1.523(3)| C8-C9                 | 1.390(3)|
| C2-O1                 | 1.434(2)| C8-H8                 | 0.95    |
| C2-C7                 | 1.512(3)| C9-C10                | 1.386(3)|
| C2-C3                 | 1.557(3)| C9-H9                 | 0.95    |
| C2-H2                 | 1.00    | C10-C11               | 1.378(3)|
| C3-C13                | 1.510(3)| C10-Br1               | 1.907(2)|
| C3-C15                | 1.523(3)| C11-C12               | 1.397(3)|
| C3-C4                 | 1.542(3)| C11-H11               | 0.95    |
| C4-O2                 | 1.432(3)| C12-H12               | 0.95    |
| C4-H4A                | 0.99    | C13-C14               | 1.320(3)|
| C4-H4B                | 0.99    | C13-H13               | 0.95    |
| C5-H5A                | 0.98    | C14-H14A              | 0.95    |
| C5-H5B                | 0.98    | C14-H14B              | 0.95    |
| C5-H5C                | 0.98    | C15-H15A              | 0.98    |
| C6-H6A                | 0.98    | C15-H15B              | 0.98    |
| C6-H6B                | 0.98    | C15-H15C              | 0.98    |
| O2-C1-O1              | 110.33(17)| C13-C3-C15            | 113.13(19)|
| O2-C1-C5              | 105.68(17)| C13-C3-C4            | 108.68(18)|
| O1-C1-C5              | 105.71(19)| C15-C3-C4            | 108.51(17)|
| O2-C1-C6              | 112.3(2)| C13-C3-C2             | 110.76(17)|
| O1-C1-C6              | 111.36(17)| C15-C3-C2            | 110.24(17)|
| C5-C1-C6              | 111.17(19)| C4-C3-C2            | 105.17(17)|
| O1-C2-C7              | 107.48(16)| O2-C4-C3            | 111.93(16)|
| O1-C2-C3              | 110.13(16)| O2-C4-H4A         | 109.2    |
| C7-C2-C3              | 113.55(17)| C3-C4-H4A         | 109.2    |
| O1-C2-H2              | 108.5    | O2-C4-H4B            | 109.2    |
| C7-C2-H2              | 108.5    | C3-C4-H4B            | 109.2    |
| C3-C2-H2              | 108.5    | H4A-C4-H4B          | 107.9    |
| Bond                        | Angle   | Bond                        | Angle   |
|-----------------------------|---------|-----------------------------|---------|
| C1-C5-H5A                   | 109.5   | C11-C10-Br1                 | 118.81(16) |
| C1-C5-H5B                   | 109.5   | C9-C10-Br1                  | 118.71(17) |
| H5A-C5-H5B                  | 109.5   | C10-C11-C12                 | 118.3(2) |
| C1-C5-H5C                   | 109.5   | C10-C11-H11                 | 120.8 |
| H5A-C5-H5C                  | 109.5   | C12-C11-H11                 | 120.8 |
| H5B-C5-H5C                  | 109.5   | C7-C12-C11                  | 120.9(2) |
| C1-C6-H6A                   | 109.5   | C7-C12-H12                  | 119.6 |
| C1-C6-H6B                   | 109.5   | C11-C12-H12                 | 119.6 |
| H6A-C6-H6B                  | 109.5   | C14-C13-C3                  | 125.5(2) |
| C1-C6-H6C                   | 109.5   | C14-C13-H13                 | 117.3 |
| H6A-C6-H6C                  | 109.5   | C3-C13-H13                  | 117.3 |
| H6B-C6-H6C                  | 109.5   | C13-C14-H14A                | 120.0 |
| C12-C7-C8                   | 119.1(2) | C13-C14-H14B                | 120.0 |
| C12-C7-C2                   | 119.71(19) | H14A-C14-H14B               | 120.0 |
| C8-C7-C2                    | 121.15(19) | C3-C15-H15A                | 109.5 |
| C9-C8-C7                    | 120.7(2) | C3-C15-H15B                 | 109.5 |
| C9-C8-H8                    | 119.6    | H15A-C15-H15B               | 109.5 |
| C7-C8-H8                    | 119.6    | C3-C15-H15C                 | 109.5 |
| C10-C9-C8                   | 118.5(2) | H15A-C15-H15C               | 109.5 |
| C10-C9-H9                   | 120.8    | H15B-C15-H15C               | 109.5 |
| C8-C9-H9                    | 120.8    | C1-O1-C2                    | 114.55(17) |
| C11-C10-C9                  | 122.5(2) | C1-O2-C4                    | 113.51(16) |
Table 4. Anisotropic displacement parameters (Å² x 10³) for 4a-acetonide. The anisotropic displacement factor exponent takes the form: -2\(p^2\) [h²a*²U₁₁ + ... + 2hka*b*U₁₂]

|     | U₁₁   | U₂₂   | U₃₃   | U₁₂   | U₁₃   | U₂₃   |
|-----|-------|-------|-------|-------|-------|-------|
| C1  | 20(1) | 15(1) | 21(1) | 3(1)  | 0(1)  | -1(1) |
| C2  | 16(1) | 16(1) | 17(1) | 0(1)  | 2(1)  | -1(1) |
| C3  | 18(1) | 17(1) | 20(1) | 2(1)  | -1(1) | 1(1)  |
| C4  | 14(1) | 18(1) | 31(1) | 3(1)  | -2(1) | 1(1)  |
| C5  | 20(1) | 26(1) | 31(1) | 9(1)  | -2(1) | -5(1) |
| C6  | 37(1) | 18(1) | 28(1) | -2(1) | 6(1)  | -5(1) |
| C7  | 19(1) | 16(1) | 13(1) | 0(1)  | -1(1) | -1(1) |
| C8  | 19(1) | 20(1) | 16(1) | 2(1)  | 1(1)  | 1(1)  |
| C9  | 21(1) | 22(1) | 17(1) | -1(1) | -4(1) | 3(1)  |
| C10 | 26(1) | 15(1) | 19(1) | 0(1)  | -8(1) | 0(1)  |
| C11 | 26(1) | 20(1) | 21(1) | 4(1)  | 1(1)  | -5(1) |
| C12 | 22(1) | 20(1) | 18(1) | 0(1)  | 5(1)  | 0(1)  |
| C13 | 21(1) | 24(1) | 19(1) | 4(1)  | -2(1) | 3(1)  |
| C14 | 36(1) | 28(1) | 24(1) | -1(1) | -7(1) | 10(1) |
| C15 | 18(1) | 21(1) | 36(1) | 1(1)  | -1(1) | 0(1)  |
| Br1 | 35(1) | 14(1) | 35(1) | 1(1)  | -13(1)| 2(1)  |
| O1  | 17(1) | 16(1) | 20(1) | 2(1)  | -1(1) | -2(1) |
| O2  | 18(1) | 19(1) | 24(1) | 6(1)  | -1(1) | -1(1) |
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for 4a-acetonide.

|    | x    | y    | z    | U(eq) |
|----|------|------|------|-------|
| H2 | 8888 | 5560 | 719  | 20    |
| H4A| 10246| 4133 | 1589 | 25    |
| H4B| 10149| 4215 | 2566 | 25    |
| H5A| 4641 | 2976 | 1613 | 39    |
| H5B| 3775 | 3877 | 1035 | 39    |
| H5C| 4082 | 4102 | 1990 | 39    |
| H6A| 8687 | 3885 | 479  | 42    |
| H6B| 6605 | 3820 | 92   | 42    |
| H6C| 7400 | 2862 | 632  | 42    |
| H8 | 5237 | 7022 | 1722 | 22    |
| H9 | 4632 | 8833 | 1547 | 24    |
| H11| 9421 | 9109 | 183  | 27    |
| H12| 10010| 7292 | 357  | 24    |
| H13| 7052 | 5769 | 2828 | 26    |
| H14A|10230|6984|3199|36|
| H14B| 8240|6924|3723|36|
| H15A|11250|6844|1885|37|
| H15B|11886|5813|1389|37|
| H15C|12100|5847|2363|37|

Table 6. Torsion angles [°] for 4a-acetonide.

| Torsion Angle | Value 1 | Value 2 | Value 3 |
|---------------|---------|---------|---------|
| O1-C2-C3-C13  | -62.6(2)| C9-C10-C11-C12 | -1.5(3) |
| C7-C2-C3-C13  | 57.9(2) | Br1-C10-C11-C12 | 179.15(17) |
| O1-C2-C3-C15  | 171.38(17) | C8-C7-C12-C11 | 0.9(3) |
| C7-C2-C3-C15  | -68.0(2) | C2-C7-C12-C11 | -177.0(2) |
| O1-C2-C3-C4   | 54.6(2) | C10-C11-C12-C7 | 0.2(3) |
| C7-C2-C3-C4   | 175.18(17) | C15-C3-C13-C14 | 0.3(3) |
| C13-C3-C4-O2  | 63.4(2) | C4-C3-C13-C14 | 120.9(2) |
| C15-C3-C4-O2  | -173.18(17) | C2-C3-C13-C14 | -124.1(2) |
| C2-C3-C4-O2   | -55.2(2) | O2-C1-O1-C2 | 56.3(2) |
| O1-C2-C7-C12  | -146.97(19) | C5-C1-O1-C2 | 170.15(17) |
| C3-C2-C7-C12  | 91.0(2) | C6-C1-O1-C2 | -69.0(2) |
| O1-C2-C7-C8   | 35.2(3) | C7-C2-O1-C1 | 177.67(16) |
| C3-C2-C7-C8   | -86.9(2) | C3-C2-O1-C1 | -58.2(2) |
| C12-C7-C8-C9  | -0.7(3) | O1-C1-O2-C4 | -55.3(2) |
| C2-C7-C8-C9   | 177.14(19) | C5-C1-O2-C4 | -169.07(17) |
| C7-C8-C9-C10  | -0.5(3) | C6-C1-O2-C4 | 69.6(2) |
| C8-C9-C10-C11 | 1.7(3) | C3-C4-O2-C1 | 58.0(2) |
| C8-C9-C10-Br1 | -179.02(16) | | |
**Figure 1.** View of 4a-acetonide showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.