Experimental and Supporting Information

Stereoselective 4-Benzyloxybut-2-enylation of Aldehydes via an Allyl-Transfer Reaction from a Chiral Allyl Donor

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1. General Methods. Infrared spectra were recorded on a Nicolet Series II Magna-IR system 550 spectrometer. $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were measured on a JEOL JNMX 400 spectrometer. High-resolution mass spectra were obtained with a JEOL JMS-700 mass spectrometer. Elemental analyses were obtained on a Perkin-Elmer PE-2400 Series II CHN analyzer. Optical rotations were obtained on a JASCO DIP-370 polarimeter. The enantiomeric excess (ee) was determined by HPLC analysis. HPLC was performed on a Shimadzu HPLC system consisting of the following: pump, LC-6A; detector, SPD-6A; chromatopac, C-R3A, measured at 254 nm; column, DAICEL CHIRALPAK AD-H (0.46 cm x 25 cmL); eluent, hexane/Pr$i$OH = 40/1; flow rate, 0.3 mL/min. The operation of HPLC was carried out at room temperature (15-27 °C; without control of the column temperature). Dichloromethane was dried over calcium hydride and distilled. tert-Butyl hydroperoxide (TBHP) was dried azeotropically by well dried molecular sieves (3Å) using Dean Stark’s apparatus, after separation (removal) of water layer which was formed by addition of dichloromethane into a commercially available 70% aqueous TBHP. Tetrahydrofuran (THF) and diethyl ether were distilled from benzophenone ketyl. Molecular sieves were dried under reduced pressure after heating in electric wave oven for 1 min (repeated three times). All other chemical reagents were used as supplied without further purification.

2. Sharpless Asymmetric Epoxidation of 3-Methylbut-2-ene-1-ol (7) to 8.

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\text{7} & \quad \text{7} \quad \text{7}
\end{align*}
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Asymmetric epoxidation of 3-methylbut-2-ene-1-ol 7 was performed using a slightly modified version of the procedure reported by Sharpless et al. (Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. J. Am. Chem. Soc. 1987, 109, 5765-5780.)

To a stirred suspension of dried 4Å molecular sieves (powder, 0.45 g) in CH$_2$Cl$_2$ (30 mL) was added Ti(OPr$i$)$_4$ (443 µL, 1.5 mmol), (+)-diethyl tartrate (309 µL, 1.8 mmol), and tert-butyl hydroperoxide (3.4 mL of 4.5 M solution in CH$_2$Cl$_2$) at –40 °C. After stirring for 30 min, 3-methylbut-2-en-1-ol 7 (1.5 mL, 15 mmol) was added to the reaction mixture. The resulting mixture was stirred for 2 h at –40 °C. Quenching of the reaction was accomplished by slow addition of trimethylphosphite (3.6 mL, 30 mmol) at –40 °C, and then the temperature was slowly raised to -20 °C to ensure the decomposition of excess tert-butyl hydroperoxide. To the reaction mixture was added triethylamine (2.5 mL, 18 mmol) and benzoyl chloride (2.1 g, 15 mmol, in 15 mL of CH$_2$Cl$_2$ solution) successively at -20 °C, and then stirring of the resulting mixture was maintained for 2 h at 0 °C. After filtration through a pad of celite, the filtrate was washed with 10% aqueous tartaric acid, saturated aqueous NaHCO$_3$ solution, and brine. Concentration of the filtrate gave the crude product (2 g), which was sufficient for a next step.

Benzoyloxy Epoxide 8 (Colorless oil); $R_f = 0.5$ (hexane/EtOAc = 3/1); [α]$_D^{22}$ = -22.2 (c 1.00, CHCl$_3$); IR (neat): 3065, 2995, 2361, 2341, 1918, 1843, 1718, 1684, 1653, 1559, 1541, 1456, 1381, 1273, 1175, 1070, 874, 754, 687, 616 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.1 (d, $J = 7.6$ Hz, 2H), 7.6 (t, $J = 7.6$ Hz, 1H), 7.45
3. Reaction of 8 with Vinylmagnesium Chloride to 9.

Reaction of benzoyloxy epoxide 8 with vinylmagnesium chloride was performed according to the procedure reported by Roush et al. (Roush, W. R.; Adam, M. A.; Walts, A. E.; Harris, D. J. J. Am. Chem. Soc. 1986, 108, 3422-3434.)

To a mixture of CuBr•Me2S (2.9 g, 14.0 mmol) and Me2S (2.1 mL) in Et2O (21 mL) was added vinylmagnesium chloride (41 mL of 1.38 M solution in THF, 56.6 mmol) and 8 (1.44 g, 7.0 mmol, 6.0 mL of ether) at -25 °C. The reaction mixture was stirred at -25 °C for 5 h, and then stirred at room temperature overnight. The resulting reaction mixture was poured into a pH 8.5 aqueous NH4Cl/NaOH solution at 0 °C and extracted twice with EtOAc. The combined extract was dried over MgSO4 and concentrated in vacuo. The crude product was purified by column chromatography on silica gel to give the pure product (0.65 g, 71%).

3-methyl-2-vinylbutane-1,3-diol (9) (yellow oil); Rf = 0.5 (hexane/EtOAc = 1/1); IR (neat): 3319, 3077, 2979, 2932, 2888, 1640, 1466, 1420, 1380, 1366, 1269, 1238, 1177, 1120, 1068, 1028, 1000, 945, 916, 866, 814, 795 cm⁻¹; ¹H NMR (400 MHz, CDCl3) δ 5.7 (m, 1H), 5.2 m, 2H), 3.9 (A of AB JAB = 8 Hz, 1H), 3.85 (B of AB JAB = 7.6 Hz, 1H), 3.74 (C of CD JCD = 5.2 Hz, 1H), 3.71 (D of CD JCD = 5.2 Hz, 1H), 1.234 (s, 3H), 1.224 (s, 3H); ¹³C NMR (100 MHz, CDCl3) δ 25.7, 29.5, 55.7, 63.8, 73.1, 118.7, 135.7.

Optical purity was determined to be 89% ee by HPLC analysis [column, Daicel CHIRALPAK AD-H (0.46 cm x 25 cmL); eluent, hexane/PrOH (40/1); flow rate, 0.3 mL/min]. The isomers of (R)-9 and (S)-9 were detected at 28.6 and 30.1 min in the ratio of 76.7/4.63, respectively, whereas those of the racemate were detected at 28.4 and 29.8 min in the ratio of 30.9/31.1, respectively.

4. Conversion of Diol (9) to 3-Benzoyloxymethyl-2-methylpent-4-en-2-ol [(R)-10].

To a THF (22 mL) suspension of sodium hydride (ca. 360 mg, 9.0 mmol), prepared from 1.0 g of NaH (60% dispersion in mineral oil) by washing with dry hexane, was slowly added diol 9 (586 g, 4.5 mmol) at 0 °C. The resulting solution was stirred for 30 min, and then benzyl bromide (0.8 mL, 6.8 mmol) was added at 0 °C. After stirring overnight at 20 °C, to the reaction mixture was added saturated aqueous
NH₄Cl solution (3 mL) at 0 °C. After the usual workup, the extract was dried over MgSO₄ and concentrated in vacuo. The residual oil was purified by column chromatography on silica gel to give the pure desired product (878 mg, 89%).

3-Benzylxymethyl-2-methylpent-4-en-2-ol [(R)-10] (colorless oil); Rₛ = 0.5 (hexane/EtOAc = 3/1); [α]D²⁵⁻⁵⁰.₄ (c 1.00, CHCl₃); IR (neat) 3453, 3067, 3031, 2974, 2929, 2866, 1642, 1454, 1364, 1207, 1175, 1096, 1028, 996, 949, 915, 868, 791, 737, 698 cm⁻¹; ¹H NMR (400 MHz) δ 7.3 (m, 5H), 5.72 (ddd, J = 16.4, 10.8, 9.2 Hz, 1H), 5.13 (d, J = 10.8 Hz, 1H), 5.11 (d, J = 8.4, 2.0 Hz, 1H), 4.52 (s, 2H), 3.65 (m, 2H), 2.44 (m, 1H), 1.175 (s, 3H), 1.168 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 26, 29, 54, 71.96, 72.05, 73.5, 118.0, 127.6, 127.7, 128.3, 136, 137; Anal. Calcd for C₁₄H₂₀O₂: C, 76.33; H, 9.15. Found: C, 76.38; H, 8.96.

Optical purity was determined to be 90% ee by HPLC analysis [column, Daicel CHIRALPAK AD-H (0.46 cm φ x 25 cmL); eluent, hexane/PrOH (40/1); flow rate, 0.3 mL/min]. The retention time of (R)-10 and (S)-10 were detected at 38.3 and 40.4 min, in the ratio of 95.2/4.79, respectively, whereas those of the racemate were detected at 38.5 and 40.5 min, in the ratio of 50.0/50.0, respectively.

5-1.

5-1-1. Allyl-Transfer Reaction of Chiral Allyl Donor [(R)-10] with 3-Phenylpropanal (2a).

To a solution of 3-phenylpropanal 2a (44 µL, 0.3 mmol) and (R)-10 (66 mg, 0.3 mmol) in dichloromethane (1.5 mL) was added trifluoromethanesulfonic acid (5.3 µL, 0.06 mmol). After stirring for 30 h at 10 °C, the resulting mixture was washed with saturated sodium bicarbonate (2 mL), dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give 11a (82%, 73 mg) as a colorless oil. The enantiomeric purity of E isomers of 11a was determined to be 90% ee by HPLC analysis [column, CHIRALPAK AD-H (0.46 cm φ x 25 cmL); eluent, hexane/EtOH = 40/1; flow rate, 0.3 mL/min; retention time]. Isomers of 11a were detected at 87.4, 96.9, and 106.0 min, in a ratio of 4.35/90.78/4.87 (ZR/ES/ER), respectively, whereas four isomers, derived from the reaction of racemic allyl donor with 3-phenylpropanal at room temperature (reaction temperature was not controlled for authentic sample) were detected at 82.6, 85.2, 93.1, 100.5 in a ratio of 3.4/3.4/46.6/46.6, and were identified as ZR/ZS/ES/ER, resp.

(5E,3S)-7-Benzoyloxy-1-1-phenyleth-5-en-3-ol (11a): [α]D²⁵⁺⁵-9.30 (c 1.00, CHCl₃); IR (neat) 3418, 3026, 2927, 2857, 1605, 1495, 1454, 1363, 1093, 1055, 1028, 973, 742, 699 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.34 (m, 4H), 7.27 (m, 3H), 7.19 (m, 3H), 5.72 (m, 2H), 4.50 (s, 2H), 4.00 (d, J = 4.4 Hz, 2H), 3.66 (m, 1H), 2.80 (m, 1H), 2.67 (m, 1H), 2.31 (m, 1H), 2.21 (m, 1H), 1.78 (m, 2H); ¹³C (100 MHz, CDCl₃) δ 32, 39, 41, 70.1, 70.5, 72.1, 126, 127, 127.7, 128.37, 128.40, 129.8, 130.0, 138, 142 ; Anal. Calcd for C₂₀H₂₄O₂: C, 81.04; H, 8.16. Found: C, 81.05; H, 8.46; HRMS (EI) m/z Calcd for C₂₀H₂₄O₂ 296.1776, found 297.1768.
5-1-2. Determination of the Configuration of 11a [(E)-11a and (Z)-11a]

![Chemical Structure]

The optical purity of (E)-11a (entry 1 in Table 1) was determined to be 86% ee by HPLC analysis. The isomers of ZR, ES, and ER were detected at 93.0, 104.1, 114.1 min, in a ratio of 4.79/87.0/6.36, respectively. The mixture was converted to the corresponding 3-benzyloxy-5-phenylpentan-1-ol via benzylation of the hydroxyl group of 11a and osmium-catalyzed oxidation of the double bond followed by reduction of the resulting aldehyde with NaBH₄. Since the product had [α]D²⁵ 20.0, and its HPLC analysis [CHIRALCEL OD (0.46 cm x 25 cm L) with a mixed solvent, hexane/PrOH = 20/1, as eluent under a flow rate of 0.3 mL/min] showed the retention times of the major isomer and the minor isomer at 74.5 and 82.5 min, respectively. The configuration of the major isomer of 11a was determined to be S by comparison with that of the R configurational authentic sample ([α]D²⁵ -25.8, retention time: 82.5 min) which was derived from >99% ee of (R)-1-phenylhex-5-en-3-ol.⁴⁺⁻¹

The configuration of the Z isomer, detected at a retention time 93.0 min, was determined to be R as follows. The product 11a (a mixture of three HPLC detectable isomers) was treated with Pd/C (10%) under hydrogen in methanol to give (R)-7-benzyloxy-1-phenylthioheptan-3-ol in 85% yield with 77.6% ee by HPLC analysis [CHIRALPAK AD-H (0.46 cm x 25 cm L) with a mixed solvent, hexane/PrOH = 40/1, as eluent under a flow rate of 0.3 mL/min]. The major isomer and the minor isomer were detected at the retention times of 107 and 124 min in a ratio of 88.8/11.2. This shows that the configuration of the Z isomer, which was detected at 93.0 min by HPLC analysis, should be R, and not the same configuration as major isomer of (E)-11a which has 86% ee.

5-2

![Chemical Structure]

(5E,3R)-7-Benzyloxy-1-phenylthiohept-5-en-3-ol (11b): [α]D²⁵ -21.0 (c 1.00, CHCl₃); IR (neat) 3423, 3036, 2926, 2855, 1579, 1481, 1439, 1363, 1091, 1059, 1032, 973, 907, 738, 667 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.34 (m, 5H), 7.30 (m, 4H), 7.17 (m, 1H), 5.71 (m, 2H), 4.50 (s, 2H), 3.99 (d, J = 2.4 Hz, 2H), 3.82 (m, 1H), 3.11 (ddd, J = 13.2, 7.2, 6.4 Hz, 1H), 3.01 (dt, J = 13.2, 7.2 Hz, 1H), 2.24 (m, 2H), 1.78 (m, 3H); ¹³C (100 MHz, CDCl₃) δ 30, 36, 41, 69.6, 70.5, 72, 126, 127.6, 127.7, 128.30, 128.8, 129.0, 129.4, 130.2, 136, 138; Anal. Calcd for C₂₀H₂₀O₂S: C, 73.13; H, 7.36. Found: C, 72.92; H, 7.48.

S5
The enantiomeric purity was determined to be 90% by HPLC analysis [column, CHIRALPAK AD-H (0.46 cmφ x 25 cmL); eluent, hexane/PrOH = 20/1; flow rate, 0.3 mL/min]. The products were detected at retention times of 83.0, 86.1, and 96.5 min, in a ratio of 8.5/87.1/4.4. Four isomers, derived from the racemic allyl donor, were detected at 74.1, 79.1, 81.5, and 90.8 in a ratio of 4.5/4.6/45.4/45.5.

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\text{11c 90% ee of } E \quad (E/Z = 26)
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\((2E,5S)-1,10\text{-Dibenzylxoyde-2-en-5-ol (11c)}: \left[\alpha\right]_D^{25}2.00 \text{ (c 1.00, CHCl}_3\); \ IR (neat) 3426, 3036, 2933, 2856, 1500, 1454, 1362, 1100, 1028, 974, 737, 698 cm\(^{-1}\); \ H NMR (400 MHz, CDCl\(_3\)) \delta 7.34 (m, 8H), 7.30 (m, 2H), 5.71 (m, 2H), 4.50 (s, 2H), 4.49 (s, 2H), 3.99 (d, \(J = 4.4 \text{ Hz}, 2H\)), 3.61 (m, 1H), 3.46 (t, \(J = 6.6 \text{ Hz}, 2H\)), 2.27 (m, 1H), 1.21 (m, 1H), 1.6 (m, 2H), 1.4 (m, 6H); \(^{13}\text{C} \text{ (100 MHz, CDCl}_3\)) \delta 25, 26, 30, 37, 40, 70.3, 70.6, 70.8, 72, 73, 127.3, 127.5, 127.6, 127.7, 128.2, 129.6, 130.1, 138.2, 138.5; Anal. Calcd for C\(_{23}\)H\(_{30}\)O\(_3\): C, 78.22; H, 8.75. Found: C, 77.94; H, 9.05.

The enantiomeric purity was determined to be 90.0% ee by HPLC analysis [column, CHIRALPAK AD-H (0.46 cmφ x 25 cmL); eluent, hexane/PrOH = 20/1; flow rate, 0.3 mL/min; retention time]. Three isomers were detected at 74.4, 79.0 and 83.1 min in a ratio of 3.51/91.74/4.75. Four isomers, derived from the corresponding racemic allyl donor via an allyl-transfer reaction with 6-benzyloxyhexanal, were detected at 72.7, 74.2, 79.1, and 82.8 min in a ratio of 2.84/2.70/46.65/46.64, respectively.

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\text{11d 90% ee of } E \quad (E/Z = 35)
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\((2E,5S)-1\text{-Benzyloxyde-2-en-5-ol (11d)}: \left[\alpha\right]_D^{25}8.40 \text{ (c 1.00, CHCl}_3\); \ IR (neat) 3386, 2930, 2858, 1728, 1500, 1454, 1368, 1273, 1100, 1070, 1028, 973, 737, 698 cm\(^{-1}\); \ H NMR (400 MHz, CDCl\(_3\)) \delta 7.34 (m, 4H), 7.28 (m, 1H), 5.72 (m, 2H), 4.51 (s, 2H), 4.01 (d, \(J = 4.8 \text{ Hz}, 2H\)), 3.65 (m, 1H), 2.30 (m, 1H), 2.16 (m, 1H), 1.2-1.6 (m, 8H), 0.89 (t, \(J = 6.8 \text{ Hz}\)); \(^{13}\text{C} \text{ (100 MHz, CDCl}_3\)) \delta 14, 23, 25, 32, 37, 40, 70.6, 71.0, 72, 127.5, 127.7, 128.3, 129.8, 130.1, 138; Anal. Calcd for C\(_1\)H\(_{26}\)O\(_2\): C, 78.82; H, 9.99. Found: C, 77.81; H, 9.80.

The enantiomeric purity of the \(E\) isomer was determined to be 90.0% ee by HPLC analysis [column, CHIRALPAK AD-H (0.46 cmφ x 25 cmL); eluent, hexane/PrOH = 40/1; flow rate, 0.3 mL/min]. The products were detected at retention times of 57.6, 60.6, and 65.0 min in a ratio of 2.64/91.96/5.40. Four isomers derived from the racemic allyl donor were detected at 52.4, 53.3, 56.7, and 60.5 min in a ratio of 2.27/2.27/46.9/48.6.
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\begin{align*}
&\text{O} \\
\text{OBn} \\
\text{E/Z} = 28)
\end{align*}
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(\textbf{2E,5S})-\textbf{1-Benzoxypentadeca-2,14-dien-5-ol (11e)}: \([\alpha]_D^{25} = 2.00 \) (c 1, CHCl\textsubscript{3}); IR (neat) 3386, 2927, 2854, 2387, 1721, 1642, 1453, 1358, 1068, 971, 909, 739, 697 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (400 MHz) \(\delta\) 7.34 (m, 4H), 7.29 (m, 1H), 5.81 (m, 1H), 5.73 (m, 2H), 4.96 (m, 2H), 4.51 (s, 2H), 4.01 (d, \(J = 4.8\) Hz, 2H), 3.64 (m, 1H), 2.30 (dt, \(J = 13.2, 4.4\) Hz), 2.16 (dq, \(J = 13.2, 6.8\) Hz, 1H), 2.04 (q, \(J = 14.8, 6.8\) Hz, 2H), 1.2-1.5 (m, 14H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 26, 29.0, 29.2, 29.5, 29.6, 29.7, 34, 37, 40, 70.6, 70.9, 72, 114, 127.5, 127.7, 128, 129.7, 130.2, 138, 139. Anal. Calcd for C\textsubscript{22}H\textsubscript{34}O\textsubscript{2}: C, 79.94; H, 10.37. Found: C, 79.86; H, 10.39.

The enantiomeric purity was determined to be 90% ee by HPLC analysis [column, CHIRALPAK AD-H (0.46 cm φ x 25 cmL); eluent, hexane/Pr\textsubscript{i}OH = 40/1; flow rate, 0.3 mL/min]. The products were detected at retention times of 50.3, 53.1, 61.0 min in a ratio of 3.28(ZR)/92.27(ES)/4.45(ER). The mixture derived from the racemic allyl donor was detected at retention times of 50.9, 53.8, 60.9 min in a ratio of 3.4(ZR)/50.6(ES, ZS)/46.0(ER).

5-6

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\text{OBn} \\
\text{E/Z} = 20)
\end{align*}
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(\textbf{5E,3S})-\textbf{7-Benzoxo-2,2-dimethylhept-5-en-3-ol (11f)}: \([\alpha]_D^{25} = 14.4 \) (c 1.00, CHCl\textsubscript{3}); IR (neat) 3438, 3036, 2954, 2867, 1479, 1454, 1363, 1069, 1009, 973, 737, 698 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.34 (m, 4H), 7.28 (m, 1H), 5.75 (m, 2H), 4.51 (s, 2H), 4.01 (d, \(J = 6.0\) Hz, 2H), 3.26 (dd, \(J = 10.6, 2.4\) Hz, 1H), 2.35 (m, 1H), 2.00 (ddd, \(J = 13.6, 10.8, 7.6\) Hz, 1H), 0.92 (s, 9H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 26, 34.8, 35.0, 71, 72, 79, 127.5, 127.7, 127.8, 128.3, 129.4, 132, 138. Anal. Calcd for C\textsubscript{16}H\textsubscript{24}O\textsubscript{2}: C, 77.38; H, 9.74. Found: C, 77.60; H, 9.72.

The E/Z ratio and enantiomeric purity of the E isomers were determined to be >20 and >90% ee by HPLC analysis [column, CHIRALPAK AD-H (0.46 cm φ x 25 cmL); eluent, hexane/Pr\textsubscript{i}OH = 40/1; flow rate, 0.3 mL/min]. The products were detected at retention times of 39.8, 44.9, 47.1 min in a ratio of 91.1(ER)/4.3(ES)/4.6(ZS). The corresponding four isomers, derived from racemate, were detected at 40.1, 45.0, 47.3 min in a ratio of 49.8(ER, ZR)/46.4(ES)/3.8(ZS).

6. \textbf{Removal (Deprotection) of Benzyl Group in Benzyl Allyl Ether by Ca in Liq. NH\textsubscript{3}.}

[Diagram of reaction]

Freshly powdered Ca (32 mg, 0.8 mmol) was dissolved in liq. ammonia (2 mL) at -78°C under an
argon atmosphere. To the blue solution of Ca in NH₃ was added a solution of benzyl ether (30 mg, 0.1
mmol) in THF (0.5 mL). The cooling bath was removed, and the deep blue colored reaction mixture was
warmed to -33 °C and stirred for 4 h. After solid NH₄Cl (54 mg, 10 equiv.) and ether (3 mL) were added to
the reaction mixture, the remaining ammonia was allowed to evaporate overnight. After the organic solvent
was removed under reduced pressure, saturated aqueous NH₄Cl was added to the residue. The aqueous
phase was extracted with ethyl acetate, and then the combined extract was washed with saturated aqueous
NH₄Cl, 10% aqueous NaHCO₃, and brine, dried over anhydrous MgSO₄, and concentrated under reduced
pressure. The residue was purified by chromatography on silica gel to obtain diol (19 mg, 92%) as a
colorless wax: Rf 0.05 (AcOEt/hexane = 1/2); ¹H NMR (CDCl₃, 400 MHz) δ 1.76-1.82 (m, 2H), 2.14 (br s,
2H), 2.14-2.21 (m, 1H), 2.27-2.33 (m, 1H), 2.64-2.71 (m, 1H), 2.76-2.84 (m, 1H), 3.64-3.69 (m, 1H), 4.10
(d, J = 4.4 Hz, 2H), 5.66-5.78 (m, 2H), 7.17-7.30 (m, 5H); ¹³C NMR (CDCl₃, 100 MHz) δ 32.1, 38.5, 40.4,
63.3, 70.2, 125.8, 128.3, 132.5, 141.9.

7. References for Preparation of 4-benzyloxyalk-2-enylstannanes.
(4-alkoxyalk-2-enyl)trialkylstannanes 4³ᵇ⁻ᵈ were prepared as shown in (1) and (2) below.

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\begin{align*}
\text{Br} & \quad \text{Me}_3\text{Sn} \quad \xrightarrow{\text{Bu}_3\text{SnH}} \quad \text{Me}_3\text{Sn} \\
\text{OBn} & \quad \text{SnMe}_3 \\
\text{SMe} & \quad \text{OBn} \quad \text{SnBu}_3 \\
\end{align*}
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The synthesis by radical reaction using tributyltinhydride, as shown in (2), was reported by Ueno et. al.;

8. Copies of ¹H and ¹³C NMR (10, 11a, 11b, 11c, and 11f)

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\begin{align*}
\text{HO} & \quad \text{OBn} \\
(R)-\text{10} (90\% \text{ ee})
\end{align*}
\]
11a 90% ee of $E$  \( (E/Z = 35) \)
PhS\text{OH} \quad 11b \ 90\% \ ee \ of \ E \quad (E/Z \ = \ 10)
$\text{OH}$

\[
\begin{align*}
\text{OH} & \quad \text{OBn} \\
11f \quad 90\% \text{ ee of } E & \quad (E/Z = 20)
\end{align*}
\]