SUPPORTING INFORMATION

De Novo Synthesis of \( \alpha-L\)-fucose, \( \alpha-L\)-6-deoxy-allopyranoside and its 3,4-dideoxy Sugar Congeners via Wharton Rearrangement

Hua-Yu Leo Wang and George A. O’Doherty

Department of Chemistry and Chemical Biology, Northeastern University, Boston, MA, 02115,

'To whom correspondence should be addressed. g.o’doherty@neu.edu

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Section A: General Methods

Air- and/or moisture-sensitive reactions were carried out under an atmosphere of argon or nitrogen using oven-dried glassware and standard syringe/septa techniques. Diethyl ether, tetrahydrofuran, methylene chloride and methanol were dried by passing through an activated alumina column under argon gas pressure. Hexanes refer to the petroleum fraction bp 40-60 °C. Commercial reagents were used without purification unless otherwise noted. Flash chromatography was performed using the indicated solvent system on silica gel standard grade 60 (230-400 mesh). Analytical thin-layer chromatography was performed with pre-coated glass-backed plates (60, F254) and visualized by UV irradiation (254 nm) or by staining with KMnO₄ stain or anisaldehyde stain (465 mL of 95% EtOH, 17 mL conc. H₂SO₄, 5 mL acetic acid, and 13 mL anisaldehyde). Rₓ values are obtained by elution in the specified solvent ratio (v/v). Optical rotations were obtained using a digital polarimeter in the solvent specified. ¹H and ¹³C NMR spectra were recorded on both 600 and 400 MHz spectrometer. Chemical shifts are reported relative to CDCl₃ (δ 7.26 ppm) for ¹H and CDCl₃ (δ 77.23 ppm) for ¹³C or CD₃OD (δ 4.81 ppm) for ¹H and CD₃OD (δ 49.15 ppm) for ¹³C. Multiplicities are reported using the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad) resonance. IR spectra were recorded on a Bruker FT-IR spectrometer; thin film was formed in CH₂Cl₂ solution. Melting points were determined with electrothermal apparatus and are uncorrected.
Section B: Synthetic Procedures

(2S, 6S)-tert-butyl-5,6-dihydro-6-methyl-5-oxo-2H-pyran-2-yl carbonate (α-11 and β-11)\(^1\)

\[\text{BocO} \quad \text{BocO}\]

To a 500 mL Erlenmeyer flask of HCO\(_2\)Na (37.1 g, 0.545 mol) in deionized H\(_2\)O (272 ml) was added furan ketone 10 (15 g, 0.136 mol) and CH\(_2\)Cl\(_2\) (2 mL). After degassed (3 times) and addition of small quantity of NaHCO\(_3\) to adjust the basicity, surfactant Cetyltrimethylammonium Bromide (5 g, 10 mol%) was added and stirred for 5 minutes. Followed by adding Noyori asymmetric catalyst (\(\text{R}\)-Ru(η\(_6\)-mesitylene)-(S,S)-TsDPEN (85 mg, 0.1 mol%) and the resulting solution was stirred at room temperature for 24 h. The reaction mixture was diluted with water (200 mL) and extracted with EtOAc (3 x 300 mL). The combined organic layers were washed with saturated NaHCO\(_3\), dried over Na\(_2\)SO\(_4\), and concentrated under reduced pressure. The resulting crude enantiomeric mixture of furan alcohols were further dissolved in 228 mL of THF/H\(_2\)O (3:1) and cooled to 0 °C. Solid NaHCO\(_3\) (23 g, 0.273 mol), NaOAc•3H\(_2\)O (18.6 g, 0.136 mol), and NBS (24.2 g, 0.136 mol) were added to the solution and the mixture was stirred for 1 h at 0 °C. The reaction was quenched with saturated NaHCO\(_3\) (200 mL), extracted (3 x 300 mL) with Et\(_2\)O, dried over Na\(_2\)SO\(_4\), and concentrated under reduced pressure. The crude mixture was further dissolved in CH\(_2\)Cl\(_2\) (200 mL) and the solution was cooled to −78 °C. Catalytic amount of DMAP (1.22 g 7 mol%) was added to the reaction mixture, followed by adding (Boc)\(_2\)O (59.5 g, 0.273 mol) in CH\(_2\)Cl\(_2\) (70 ml) and allowed the resulting solution to stir for 12 h at −78 to −30 °C. The reaction was quenched with saturated NaHCO\(_3\), extracted with Et\(_2\)O (3x), dried over Na\(_2\)SO\(_4\), and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography with elution of 6% Et\(_2\)O in hexane to give two diastereomers of Boc-protected pyranone α-11 (15 g, 65.7 mmol, 48%) and β-11 (5 g, 21.9 mmol, 16%) in 3:1. Boc-pyranone α-11, \(R_f\) (20% Et\(_2\)O in hexane) = 0.58; \([\alpha]^{25}_D = +98 \ (c \ 1.0, \text{CH}_2\text{Cl}_2)\); IR (thin film, cm\(^{-1}\)) \(\nu\) 2984, 2942, 1752, 1703, 1371, 1273, 1254, 1153, 938, 838; \(^1\)H NMR (600 MHz; CDCl\(_3\)) \(\delta\) 6.78 (1H, dd, \(J_{2,3}\) 10.2, \(J_{2,1}\) 3.6, 2-H), 6.22 (1H, d, \(J_{1,2}\) 3.6, 1-H), 6.09 (1H, d, \(J_{3,2}\) 10.2, 3-H), 4.53 (1H, q, \(J_{5,5-\text{Me}}\) 6.6, 5-H), 1.40 (9H, s, OCOOC(CH\(_3\)_3)), 1.28 (3H, d, \(J_{5-\text{Me}}\) 6.6, 5-CH\(_3\)); \(^{13}\)C NMR (150 MHz; CDCl\(_3\)) \(\delta\) 195.5, 151.7, 140.9, 128.2, 89.1, 83.3, 72.0, 27.5, 15.1; HRMS: Calculated for [C\(_{11}\)H\(_{16}\)O\(_5\)Na\(^+\)]: 251.0890, Found: 251.0883.

A CH$_2$Cl$_2$ solution (35.0 mL) of Boc-pyranone $\alpha$-11 (2.78 g, 12.2 mmol) and benzyl alcohol (1.98 g, 18.3 mmol) was cooled to 0 °C. A CH$_2$Cl$_2$ (5.0 mL) solution of Pd$_2$(dba)$_3$•CHCl$_3$ (315.2 mg, 2.5 mol%) and PPh$_3$ (319.1 mg, 10 mol%) was added dropwise to the reaction mixture via dry cannula at 0 °C. The resulting solution was stirred at 0 °C for 8 hours. The reaction mixture was concentrated under reduced pressure and directly loaded onto silica gel flash column to obtain $\alpha$-benzyl-pyranone 9 (2.55 g, 11.7 mmol, 96%) as a yellow gel with elution of 5% EtOAc in hexane; $R_f$ (30% EtOAc in hexanes) = 0.70; $[\alpha]^{25}_D = + 46.0$ (c 1.11, CH$_2$Cl$_2$); IR (thin film, cm$^{-1}$) v 2985, 2939, 2873, 1697, 1231, 1022, 953; $^1$H NMR (270 MHz; CDCl$_3$) δ 7.32–7.38 (5H, m, Ph), 6.85 (1H, dd, $J_{2,3}$ 10.2, $J_{2,1}$ 3.6, 2-H), 6.11 (1H, d, $J_{3,2}$ 10.2, 3-H), 5.28 (1H, d, $J_{1,2}$ 3.6, 1-H), 4.86 (1H, d, $J_{AB}$ 11.4, PhCH$_2$), 4.70 (1H, d, $J_{AB}$ 11.4, PhCH$_2$), 4.57 (1H, q, $J_{5,5\text{-Me}}$ 6.7, 5-H), 1.36 (3H, d, $J_{5,5\text{-Me}}$ 6.7 Hz, 5-CH$_3$); $^{13}$C NMR (67.5 MHz; CDCl$_3$) δ 197.0, 143.5, 137.2, 126.6, 128.2, 128.1, 127.5, 92.4, 70.8, 70.5, 15.3; ESIHRMS Calcd for [C$_{13}$H$_{14}$O$_3$+Na]$^+$: 241.0835, found 241.0843.

To a solution of $\alpha$-benzyl-pyranone 9 (2.55 g, 11.7 mmol) in methanol (39.0 mL) at 0 °C was added dropwise 35% aqueous hydrogen peroxide (1.09 g, 29.0 mmol), followed by addition of aqueous sodium hydroxide (1.17 mL, 0.5 M). The reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was diluted with Et$_2$O (10 mL) and was quenched with 10 mL of saturated aqueous NaHCO$_3$, extracted with Et$_2$O (3 x 20 mL), dried with Na$_2$SO$_4$, and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 5% EtOAc in hexane to give epoxide ketone 8 (2.47 g, 10.5 mmol, 90%) as a yellow oil; $R_f$ (20% EtOAc in hexanes) = 0.5; $[\alpha]^{20}_D = -59.3$ (c 1.0, MeOH); IR (thin film, cm$^{-1}$) v 3034, 2937, 1726, 1455, 1369, 1256, 1146, 1060, 996, 859, 699; $^1$H NMR (270 MHz; CDCl$_3$): δ 7.36 (5H, m, Ph), 5.30 (1H, d, $J_{1,2}$ 1.2 Hz, 1-H), 4.80 (1H, d, $J_{AB}$ 11.6, PhCH$_2$), 4.64 (1H, d, $J_{AB}$ 11.6, PhCH$_2$), 4.17 (1H, q, $J_{5,5\text{-Me}}$ 6.9, 5-H), 3.59 (1H,

dd, \(J_{2,3} 4.0, J_{2,1} 1.2, 2-H\)), 3.46 (1H, d, \(J_{3,2} 4.0, 3-H\)), 1.38 (3H, d, \(J_{5,Me,5} 6.9\) Hz, 5-CH3); \(^{13}\text{C}\) NMR (67.5 MHz; CDCl3): \(\delta 203.1, 136.6, 128.7, 128.4, 128.2, 93.3, 93.2, 72.0, 70.8, 53.8, 53.1\); HRMS Calcd for [C\textsubscript{13}H\textsubscript{14}O\textsubscript{4}+Na]\(^{+}\): 257.0784, Found 257.0784.

\((2R,3R,6S)-2-\text{(benzyloxy)}-6\text{-methyl}-3,6\text{-dihydro}-2\text{H}-\text{pyran}-3\text{-ol (7)}\)

A solution of epoxide ketone 8 (1.35 g, 5.76 mmol) in methanol (20 mL) was cooled to 0 °C, and N\textsubscript{2}H\textsubscript{4}•H\textsubscript{2}O (1.41 mL, 29.5 mmol) was added dropwise to the reaction mixture. After reaction mixture stirring at 0 °C for 30 minutes, AcOH (0.66 mL) was added dropwise and stirred until TLC showed complete conversion to allylic alcohol. The reaction mixture was then diluted with CH\textsubscript{2}Cl\textsubscript{2} and quenched with 20 mL of saturated aqueous NaHCO\textsubscript{3} at 0 °C. The mixture was extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 x), dried over MgSO\textsubscript{4}. The compound was then filtered and concentrated under reduced pressure. The crude product was purified via silica gel flash chromatography eluting with 15% EtOAc in hexane to give allylic alcohol 7 (850 mg, 3.86 mmol, 67%) as a colorless oil; \([\alpha]^{25}_D = -179.5\) (c 1.0, CH\textsubscript{2}Cl\textsubscript{2}); IR (thin film, cm\(^{-1}\)) \(\nu 3417, 3066, 3033, 2931, 2870, 1051, 1005, 735, 699\); \(^{1}\text{H}\) NMR (600MHz; CDCl3) \(\delta 7.35 – 7.28\) (5H, m, Ph), 5.90 (1H, dddd, \(J_{3,4} 10.8, J_{3,2} 4.8, J_{3,5} 1.8, J_{3,1} 1.2, 3-H\)), 5.86 (1H, dd, \(J_{3,4} 10.8, J_{4,5} 1.2, 4-H\)), 4.91 (1H, s, 1-H), 4.80 (1H, d, \(J_{AB} 12.0, \text{PhCH}_2\)), 4.61 (1H, d, \(J_{AB} 12.0, \text{PhCH}_2\)), 4.35 (1H, ddq, \(J_{5,5-Me} 7.2, J_{5,4} 3.6, J_{5,3} 1.8, 5-H\)), 3.83 (1H, m, 2-H), 1.78 (1H, br, OH), 1.30 (3H, d, \(J_{5,Me,5} 7.2, 5-\text{CH}_3\)); \(^{13}\text{C}\) NMR (150 MHz; CDCl3) \(\delta 137.74, 134.54, 128.67(3H), 128.16(2H), 128.04, 123.95, 99.66, 70.09, 64.50, 64.27, 20.62\); ESIHRMS Calcd. for [C\textsubscript{13}H\textsubscript{16}O\textsubscript{3}Na\(^{+}\)]: 243.09917, found: 243.09901.

\((2R,3R,4S,5R,6S)-2-\text{(benzyloxy)}-6\text{-methyltetrahydro}-2\text{H}-\text{pyran}-3,4,5\text{-triol (3)}\)

To a t-BuOH/acetone (1.5 mL, 1:1 (v/v)) solution of allylic alcohol 7 (66.3 mg, 0.30 mmol) at 0°C was added a solution of N-methylmorpholine-N-oxide/water (50% w/v, 0.3 mL). Crystalline OsO\textsubscript{4} (3.0 mg, 4 mol %) was added rapidly and the reaction mixture was stirred at 0°C until TLC showed complete conversion. The reaction mixture was then concentrated under reduced pressure and directly loaded onto

silica gel flash chromatography to obtain $\alpha$-6-deoxy-altrose 3 (69 mg, 0.27 mmol, 92%) as a colorless oil with elution of 75% EtOAc in hexane; $R_f = 0.42$ (EtOAc); $[\alpha]^{23}_D = -112.5$ (c 1.0, MeOH); IR (thin film, cm$^{-1}$) ν 3384, 2930, 1455, 1375, 1259, 1127, 1061, 1014, 970, 852, 737, 698; $^1$H NMR (600MHz; CDCl$_3$) δ 7.38 – 7.32 (5H, m, Ph), 4.79 (1H, s, 1H), 4.74 (1H, d, $J_{AB}$ 12.0, PhCH$_2$), 4.54 (1H, d, $J_{AB}$ 12.0, PhCH$_2$), 3.96 (1H, m, 2H), 3.88 (1H, ddd, $J_{3,3,3,4}$, 9.6, 3.6, $J_{3,2}$ 3.6, 3-H), 3.80 (1H, dq, $J_{5,4}$ 9.6, $J_{5,5$,Me} 6.6, 5-H), 3.51 (1H, ddd, $J_{4,5}$ 9.6, $J_{4,4$,OH} 9.6, $J_{4,3}$ 3.6, 4-H), 3.37 (1H, d, $J_{5,OH,3}$ 9.6, 3-OH), 2.68 (1H, d, $J_{4,OH,4}$ 9.6, 4-OH), 2.52 (1H, d, $J_{2,OH,2}$ 6.0, 2-OH), 1.34 (3H, d, $J_{5$,Me,5} 6.6, 5-CH$_3$); $^{13}$C NMR (150 MHz; CDCl$_3$) δ 136.52, 128.86(2C), 128.52, 128.40(2C), 99.03, 70.94, 70.05, 69.86, 69.68, 65.82, 17.77; ESIHRMS Calcd. for [C$_{13}$H$_{18}$O$_5$Na$^+$]: 277.1046, found: 277.1047.

(2R,3R,6S)-2-(benzyloxy)-6-methyltetrahydro-2H-pyran-3-ol (12)

To a N-methylmorpholine (NMM) (0.5 ml, 0.3M) solution of allylic alcohol 7 (34 mg, 0.154 mmol) at 0 °C was added o-nitrobenzenesulfonyl hydrazine (NBSH) (200 mg, 0.921 mmol) and Et$_3$N (62.8 mg, 0.616 mmol). The resulting mixture was raised to room temperature and stirred for 12 hours. Additional NBSH (100 mg, 0.462 mmol) was added to the reaction mixture and stirred for another 12 hours. The reaction was diluted with EtOAc and quenched with saturated aqueous NaHCO$_3$. The mixture was extracted with EtOAc. The organic extract was washed with water and saturated brine solution, then dried over with Na$_2$SO$_4$ and concentrated under reduced pressure. The crude product was purified via silica gel flash chromatography eluting with 10% EtOAc in hexane to give 3,4-dideoxy rhamnose 12 (29 mg, 0.130 mmol, 85%); $R_f$ (30% EtOAc in hexane) = 0.27; $[\alpha]^{23}_D = -102.7$ (c 1.0, CH$_2$Cl$_2$); IR (thin film, cm$^{-1}$) ν 3420, 2970, 2931, 2878, 1124, 1039, 1028, 1005, 973, 735, 698; $^1$H NMR (600MHz; CDCl$_3$) δ 7.36 – 7.28 (5H, m, Ph), 4.76 (1H, d, $J_{AB}$ 12.0, PhCH$_2$), 4.73 (1H, s, 1H), 4.53 (1H, d, $J_{AB}$ 12.0, PhCH$_2$), 3.95 (1H, ddq, $J_{5,5,Me}$ 9.6, $J_{5,4}$ 2.4, 5-H), 3.67 (1H, dd, $J_{2,3}$ 4.8, $J_{2,2,3}$ 3.0, 2-H), 2.04 (1H, dddd, $J_{4,4}$ 13.8, $J_{4,5}$ 13.8, $J_{4,3}$ 4.8, $J_{4,3}$ 3.0, 4-H), 1.95 (1H, br, OH), 1.73 (1H, dddd, $J_{3,3}$ 13.8, $J_{3,4}$ 4.2, $J_{3,4}$ 3.0, $J_{3,2}$ 1.2, 3-H), 1.59 (1H, dddd, $J_{4,4}$ 13.8, $J_{4,3}$ 13.8, $J_{4,3}$ 4.2, $J_{4,5}$ 3.6, 4-H), 1.46 (1H, dddd, $J_{3,3}$ 13.8, $J_{3,4}$ 9.6, $J_{3,2}$ 4.8, $J_{3,3}$ 3.0, 3-H), 1.18 (3H, d, $J_{5,Me,5}$ 6.6, 5-CH$_3$); $^{13}$C NMR (150 MHz; CDCl$_3$) δ 138.04, 128.63(2C), 128.03(2C), 127.91, 99.39, 69.06, 65.89, 65.21, 27.16, 25.72, 21.68; ESIHRMS Calcd. for [C$_{13}$H$_{18}$O$_5$Na$^+$]: 245.11482, found: 245.11462.
(2R,6S)-2-(benzyloxy)-6-methyl-2H-pyr-3(6H)-one (I)

A solution of allylic alcohol 7 (750 mg, 3.40 mmol) in CH₂Cl₂ (34 mL) was added activated MnO₂ (2.4 g, 27.6 mmol). The reaction mixture was stirred under reflux at 50 °C for 12 hours. More MnO₂ (2.4 g, 27.6 mmol) was added until TLC showed complete conversion. The mixture was then cooled down to room temperature and filtered through a pad of celite. The filtrate was concentrated under reduced pressure to give enone I (565 mg, 2.59 mmol, 76%) as a yellow oil; Purification was performed on silica gel flash chromatography to obtain enone with elution of 5% EtOAc in hexane; Rf (5% EtOAc in hexane) = 0.30; [α]²⁳_D = −84.1 (c 0.45, CH₂Cl₂), (lit. [⁴] [α] = −116 (c 3.39, CHCl₃)); ¹H NMR (400MHz; CDCl₃) δ 7.38-7.28 (5H, m, Ph), 6.90 (1H, dd, J₃,₄ 10.4, J₃,₅ 1.2, 3-H), 6.08 (1H, d, J₄,₃ 10.4, J₄,₅ 2.4, 4-H), 4.92 (1H, s, 1-H), 4.82 (1H, d, JAB 11.6, PhCH₂), 4.72 (1H, d, JAB 11.6, PhCH₂), 4.66 (1H, ddq, J₅,₅-Me 6.4, J₅,₄ 2.4, J₅,₃ 1.2, 5-H), 1.38 (3H, d, J₅,Me₅ 6.4, 5-CH₃); ¹³C NMR (100 MHz; CDCl₃) δ 189.13, 152.52(2C), 137.04, 128.73(2C), 128.28(2C), 124.39, 97.20, 71.02, 64.71, 20.30.

(2R,6S)-2-(benzyloxy)-6-methyl-3,6-dihydro-2H-pyr-3-ol (17)

A solution of enone I (390 mg, 1.79 mmol) in CH₂Cl₂ (3.6 mL) was added CeCl₃/MeOH (3.6 mL, 0.4M) and cooled to −78 °C. NaBH₄ (101 mg, 2.68 mmol) was added to the reaction mixture and stirred for 2 hours. The reaction mixture was diluted with Et₂O at 0 °C and quenched the reaction by addition of saturated aqueous NaHCO₃. The mixture was extracted with Et₂O and dried over MgSO₄. The organic extract was then filtered and concentrated under reduced pressure. The crude product was purified via silica gel flash chromatography eluting with 7% EtOAc in hexane to give allylic alcohol 17 (393 mg, 1.79 mmol, quantitative yield) as white solid; mp 64 – 65 °C; Rf (10% EtOAc in hexane) = 0.43; [α]⁰⁹_D = −50.8 (c 1.10, CH₂Cl₂); IR (thin film, cm⁻¹) ν 3331, 3066, 3032, 2930, 2895, 2869, 1497, 1454, 1043, 719; ¹H NMR (400MHz; CDCl₃) δ 7.42-7.28 (5H, m, Ph), 5.71 (1H, d, J₄,₃ 10.2, 4-H), 5.66 (1H, dd, J₃,₄ 10.2, J₃,₂ 1.6, 3-H), 5.07 (1H, d, J₁,₂ 4.4, 1-H), 4.85 (1H, d, JAB 12.0, PhCH₂), 4.63 (1H, d, JAB 12.0, PhCH₂), 4.30 – 4.19 (2H, m, 2-H & 5-H), 2.24 (1H, d, JOH₂ 11.2, OH), 1.24 (3H, d, J₅,Me₅ 6.8, 5-CH₃); ¹³C NMR (100 MHz; CDCl₃) δ 137.60, 131.62, 128.76(2C), 128.20(3C), 126.05, 96.37, 70.17, 64.49, 64.35, 20.87.

⁴ Spectral data was confirmed with literature reported by K. Tatsuta and T. Hirabayashi, J. Antibiot. 2004, 57, 291-297.
4-Dimethylaminopyridine (DMAP) (13.3 mg, 0.109 mmol) was added to a solution of allylic alcohol 17 (24.2 mg, 0.109 mmol) in CH₂Cl₂ (0.4 mL) under argon at room temperature. The resulting suspension was stirred until DMAP completely dissolved and added dropwise of pivaloyl chloride (26.5 mg, 0.220 mmol). The reaction mixture was stirred until TLC showed complete conversion, and quenched with water and extracted with CH₂Cl₂. The organic extract was washed with 1N HCl, then saturated aqueous NaHCO₃, and dried over MgSO₄. The crude product was concentrated under reduced pressure and purified via silica gel flash chromatography eluting with 3% EtOAc in petroleum ether to give pivalate ester II (27.5 mg, 0.09 mmol, 83%) as a colorless gel; Rf (5% EtOAc in petroleum ether) = 0.25; [α]₂¹°D = –86.7 (c 1.4, CH₂Cl₂); IR (thin film, cm⁻¹) ν 2972, 2938, 2880, 1728, 1159, 1049; ¹H NMR (400 MHz; CDCl₃) δ 7.36 – 7.27 (5H, m, Ph), 5.83 (1H, dd, J₄,3 10.4, J₄,5 2.0, J₄,2 1.6, 4-H), 5.58 (1H, d, J₃,4 10.4, J₃,2 1.2, 3-H), 5.28 (1H, m, 2-H), 5.23 (1H, d, J₁,2 4.4, 1-H), 4.79 (1H, d, J₉,12 12.4, PhCH₂), 4.61 (1H, d, J₉,12 12.4, PhCH₂), 4.35 (1H, m, 5-H), 1.27 (3H, d, J₅-Me 5.6, 5-CH₃), 1.19 (9H, s, OCOC(CH₃)₂). ¹³C NMR (100 MHz; CDCl₃) δ 178.28, 137.67, 133.32, 128.52(2C), 128.32(2C), 127.99, 121.71, 94.05, 69.85, 66.60, 64.38, 38.86, 27.33(3C), 20.72.

(((2R,6S)-2-(benzyloxy)-6-methyl-3,6-dihydro-2H-pyran-3-yl)oxy)(tert-butyl)dimethylsilane (III)

4-Dimethylaminopyridine (DMAP) (13.3 mg, 0.109 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (68.5 mg, 0.45 mmol) was added to a solution of allylic alcohol 17 (33 mg, 0.150 mmol) in acetonitrile (0.5 mL) under argon at room temperature. The resulting suspension was stirred until DMAP completely dissolved and added tert-butyldimethylsilyl chloride (TBSCI) (70 mg, 0.46 mmol). The reaction mixture was stirred at rt until TLC showed complete conversion, and quenched with water and extracted with CH₂Cl₂. The organic extract was washed with 1N HCl, saturated aqueous NaHCO₃, and dried over MgSO₄. The crude product was concentrated under reduced pressure and purified via silica gel flash chromatography eluting with 2% EtOAc in petroleum ether to give allylic tert-butyl silyl-ether III (41 mg, 0.12 mmol, 82%) as a colorless gel; Rf (5% EtOAc in petroleum ether) = 0.25; [α]₂³°D = –35.0 (c 1.77, CH₂Cl₂); IR (thin film, cm⁻¹) ν 2954, 2929, 2894, 2857, 1254, 1111, 1026, 877, 836, 776, 698; ¹H NMR (400 MHz; CDCl₃) δ 7.42 – 7.24 (5H, m, Ph), 5.68 (1H, d, J₄,3 10.4, 4-H), 5.57 (1H,
dd, J_{3,4} 10.4, J_{3,2} 1.2, 3-H), 4.85 (1H, d, J_{1,2} 4.4, 1-H), 4.81 (1H, d, J_{AB} 12.4, PhCH_2), 4.66 (1H, d, J_{AB} 12.4, PhCH_2), 4.38 (1H, m, 2-H), 4.30 (1H, m, 5-H), 1.23 (3H, d, J_{5-Me} 7.6, 5-Me), 0.88 (9H, s, OSi(CH_3)_3), 0.007 (3H, s, OSiC(CH_3)) – 0.001 (3H, s, OSiCCH_3); ^{13}C NMR (100 MHz; CDCl_3) δ 137.91, 131.18, 128.45(3C), 127.81, 126.22(2C), 96.07, 69.20, 65.77, 64.54, 26.07(3C), 20.81, 18.47, –4.47, –4.74.

(2R,3S,6S)-2-(benzyloxy)-6-methyltetrahydro-2H-pyran-3-ol (20)

To a N-methylmorpholine (NMM) (1.1 ml, 0.2M) solution of allylic alcohol 17 (50 mg, 0.227 mmol) at 0 ºC was added o-nitrobenzenesulfonyl hydrazine (NBSH) (296 mg, 1.36 mmol) and Et_3N (46 mg, 0.454 mmol). The resulting mixture was raised to room temperature and stirred for 12 hours. Additional NBSH (250 mg, 1.15 mmol) was added to the reaction mixture and stirred for another 12 hours. The reaction mixture was then diluted with EtOAc and quenched with saturated aqueous NaHCO_3. The organic extract in EtOAc was washed with water and saturated brine solution, and dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified via silica gel flash chromatography eluting with 8% EtOAc in hexane to give 3,4,6-dideoxy glucose 20 (48 mg, 0.216 mmol, 96%) as a colorless gel; R_f (10% EtOAc in hexane) = 0.15; [α]_D^{21} = –98.4 (c 1.11, CH_2Cl_2); IR (thin film, cm^{-1}) ν 3448, 2969, 2933, 2873, 1089, 1039, 697; ^{1}H NMR (400 MHz; CDCl_3) δ 7.39 – 7.29 (5H, m, Ph), 4.88 (1H, d, J_{1,2} 3.6, 1-H), 4.79 (1H, d, J_{AB} 12.0, PhCH_2), 4.53 (1H, d, J_{AB} 12.0, PhCH_2), 3.85 (1H, dqd, J_{5,4} 12.8, J_{5,5-Me} 6.4, J_{5,4} 2.4, 5-H), 3.64 (1H, dddd, J_{2,OH} 10.8, J_{2,3} 4.8, J_{2,3} 3.6, J_{2,1} 3.6, 2-H), 1.91 – 1.83 (2H, m, 3-H & OH), 1.79 – 1.66 (2H, m, 3-H & 4-H), 1.44 – 1.33 (1H, m, 4-H), 1.15 (3H, d, J_{5-Me} 6.4, 5-CH_3); ^{13}C NMR (100 MHz; CDCl_3) δ 138.00, 128.68(2C), 128.12(2C), 128.02, 98.12, 69.39, 68.36, 64.87, 32.34, 28.0, 21.12.

Reaction Conditions for OsO_4 Dihydroxylation:

Method A – Upjohn condition in t-BuOH

To a t-BuOH/acetone (1.7 mL, 1:1 (v/v)) solution of allylic alcohol 17 (110 mg, 0.50 mmol) at 0 ºC was added a solution of N-methylmorpholine-N-oxide/water (50% w/v, 0.5 mL). Crystalline OsO_4 (1.3 mg, 1 mol %) was added rapidly and the reaction mixture was stirred at 0 ºC until TLC showed complete conversion. The reaction mixture was then concentrated under reduced pressure and directly loaded onto silica gel flash chromatography. Elution of 55% EtOAc in petroleum ether to obtain 6-deoxy-allose 5
(40 mg, 0.157 mmol, 32%) as a colorless gel, and 80% EtOAc in petroleum ether to obtain fucose 6 (80 mg, 0.315 mmol, 63%) as a white solid; mp 164.5 – 165.2 °C (lit. 5 166 – 167 °C).

**Method B – Upjohn condition in CH$_2$Cl$_2$**

To a CH$_2$Cl$_2$ (0.5 mL, 0.1M) solution of allylic alcohol 17 (10.6 mg, 0.048 mmol) at 0 °C was added a solution of N-methylmorpholine-N-oxide/water (50% w/v, 0.05 mL). Crystalline OsO$_4$ (0.5 mg, 4 mol %) was added rapidly and the reaction mixture was stirred at 0 °C until TLC showed complete conversion. The reaction mixture was then concentrated under reduced pressure and directly loaded onto silica gel flash chromatography with elution mentioned above to obtain 6-deoxy-allose 5 and fucose 6 accordingly (10.2 mg, 84% combined yield).

**Method C – Sharpless condition**

A reaction tube is charged with K$_2$OsO$_2$(OH)$_4$ (1.47 mg, 4 mol%), Ligand (see table below, 20 mol%), K$_3$Fe(CN)$_6$ (100 mg, 0.30 mmol), K$_2$CO$_3$ (42 mg, 0.30 mmol), and MeSONH$_2$ (10 mg, 0.11 mmol). This freshly prepared AD-mix was stirred in t-BuOH/H$_2$O (1.0 mL, 1:1 (v/v), 0.05M) at room temperature until a clear biphasic solution is observed. The mixture was then cooled to 0 °C and added allylic alcohol solid 17 (22 mg, 0.100 mmol). The reaction mixture was stirred vigorously at 0 °C until TLC showed complete conversion. The reaction was quenched at 0 °C by addition of solid Na$_2$SO$_3$, and stirred the mixture at room temperature for an hour. The mixture was extracted with EtOAc, dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The diastereomeric ratio, based on crude material, of 6-deoxy-allose 5 and fucose 6 was analyzed by 400MHz NMR spectroscopy with the comparison of anomeric proton H$_1$. Purification was performed on silica gel flash chromatography with elution mentioned above to obtain 6-deoxy-allose 5 and fucose 6 accordingly.

**Method D – Sharpless condition at –78 °C**

A reaction tube is charged with or without Ligand (see table above, 50 mol%), and N-methylmorpholine-N-oxide/water (70% w/v, 0.05 mL)$^7$ dissolved in CH$_2$Cl$_2$ (1 mL). Cooled the tube to –78 °C and allowed to stir for 5 minutes. OsO$_4$ (2.5 mg, 20 mol%) solution in CH$_2$Cl$_2$ (1 mL) was added to the reaction at –78 °C. Followed by the addition of solid allylic alcohol 17 (11 mg, 0.050 mmol). The reaction mixture was stirred at –78 °C until TLC showed complete conversion. The reaction was quenched at 0 °C by addition of solid Na$_2$SO$_3$, and stirred the mixture at room temperature for an

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$^7$ N-methylmorpholine-N-oxide/water (70% w/v) was prepared by diluting N-methylmorpholine-N-oxide/water (90% w/v, 10 mg/µL NMO/H$_2$O) in the reaction mixture with 50% N-methylmorpholine-N-oxide/water.
hour. The mixture was extracted with EtOAc, dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The diastereomeric ratio, based on crude material, of 6-deoxy-allose 5 and fucose 6 was analyzed by 400MHz NMR spectroscopy with the comparison of anomeric proton H$_1$. Purification was performed on silica gel flash chromatography with elution mentioned above to obtain 6-deoxy-allose 5 and fucose 6 accordingly.

**Method E – Donohoe condition**

A reaction tube is charged with allylic alcohol 17 (11 mg, 0.05 mmol) in CH$_2$Cl$_2$ (1 mL) and cooled to –78 ºC. Tetramethylethylenediamine (TMEDA) (8 mg, 0.068 mmol) was added to the mixture, followed by addition of OsO$_4$ (15.3 mg, 0.06 mmol) solution in CH$_2$Cl$_2$ (0.5 mL). The reaction mixture was stirred at –78 ºC until TLC showed complete conversion to the corresponding osmate ester (R$_f$ = 0). The reaction was quenched at 0 ºC by addition of ethylenediamine (~ 1 mL), and stirred the mixture at room temperature for 24 hours. The mixture was then washed with water and extracted with EtOAc, dried over Na$_2$SO$_4$ and concentrated under reduced pressure. Alternative work up procedure can also be followed by removal of solvent under the reduced pressure, and added methanol (~ 5 mL) and conc. HCl (~ 5 drops). The mixture was stirred at room temperature for 2 hours, and extract with EtOAc. The organic extract in EtOAc was then washed with cold saturated aqueous NaHCO$_3$, saturated brine and dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The diastereomeric ratio, based on crude material, of 6-deoxy-allose 5 and fucose 6 was analyzed by 400MHz NMR spectroscopy with comparison of anomeric proton H$_1$. Purification was performed on silica gel flash chromatography with elution mentioned above to obtain 6-deoxy-allose 5 and fucose 6 accordingly.

(2R,3S,4S,5R,6S)-2-(benzyloxy)-6-methyltetrahydro-2H-pyran-3,4,5-triol (5)

[Chemical structure image]

Colorless gel; R$_f$ (70% EtOAc in hexane) = 0.26; [α]$^2_{D}^{23}$ = –93.8 (c 3.26, MeOH); IR (thin film, cm$^{-1}$) ν 3424, 2973, 2930, 1454, 1035; $^1$H NMR (400 MHz; CD$_3$OD) δ 7.43 – 7.24 (5H, m, Ph), 4.83 (1H, d, $J_{1,2}$ 3.6, 1-H), 4.73 (1H, d, $J_{AB}$ 12.0, PhCH$_2$), 4.57 (1H, d, $J_{AB}$ 12.0, PhCH$_2$), 3.95 (1H, dd, $J_{3,2}$ 3.2, $J_{3,4}$ 3.2, 3-H), 3.82 (1H, dq, $J_{5,4}$ 9.6, $J_{5,5-Me}$ 6.4, 5-H), 3.61 (1H, dd, $J_{2,1}$ 3.6, $J_{2,1}$ 3.6, 2-H), 3.14 (1H, dd, $J_{4,5}$ 9.6, $J_{4,3}$ 3.2, 4-H), 1.21 (3H, d, $J_{5-Me,5}$ 6.4, 5-CH$_3$); $^{13}$C NMR (100 MHz; CD$_3$OD) δ 139.00, 129.58(2C), 129.35(2C), 129.00, 99.83, 74.05, 73.56, 71.11, 69.82, 64.52, 17.82.


S12
(2R,3S,4R,5S,6S)-2-(benzylxylo)-6-methyltetrahydro-2H-pyran-3,4,5-triol (6)

White solid, mp 164.5 – 165.2 °C (lit., 9 166 – 167 °C); $R_f$ (70% EtOAc in hexane) = 0.12; $[\alpha]_D^{23} = -182.5$ (c 0.4, MeOH) (lit., 9 $[\alpha]_D^{23} = -184$ (MeOH)); IR (thin film, cm$^{-1}$) ν 3384, 2933, 2907, 1166, 1078, 1038; $^1$H NMR (400MHz; CD$_3$OD) δ 7.40-7.25 (5H, m, Ph), 4.85 (1H, d, $J_{1,2}$ 3.2, 1-H), 4.68 (1H, d, $J_{AB}$ 12.0, PhCH$_2$), 4.55 (1H, d, $J_{AB}$ 12.0, PhCH$_2$), 3.94 (1H, q, $J_{5,5\text{-Me}}$ 6.4, 5-H), 3.78 (1H, dd, $J_{3,2}$ 9.6, $J_{3,4}$ 3.2, 3-H), 3.75 (1H, dd, $J_{2,3}$ 9.6, $J_{2,1}$ 3.2, 2-H), 3.65 (1H, dd, $J_{4,3}$ 3.2, $J_{4,5}$ 3.2, 4-H), 1.18 (3H, d, $J_{5\text{-Me}}$ 6.4, 5-CH$_3$); $^{13}$C NMR (100 MHz; CD$_3$OD) δ 139.38, 129.47(2C), 129.32(2C), 128.83, 99.89, 73.80, 71.78, 70.70, 70.14, 67.87, 16.73.

(2R,3S,4S,5R,6S)-2-(benzylxylo)-4,5-dihydroxy-6-methyltetrahydro-2H-pyran-3-yl pivalate (IV)

Colorless oil; $R_f$ (30% EtOAc in hexane) = 0.25; $[\alpha]_D^{23} = -82.7$ (c 0.68, CH$_2$Cl$_2$); IR (thin film, cm$^{-1}$) ν 3504, 2972, 2935, 2878, 1733, 1157, 1108, 1041; $^1$H NMR (400 MHz; CDCl$_3$) δ 7.39 – 7.30 (5H, m, Ph), 5.01 (1H, d, $J_{1,2}$ 4.0, 1-H), 4.76 (1H, d, $J_{AB}$ 12.0, PhCH$_2$), 4.75 (1H, dd, $J_{2,1}$ 3.6, $J_{2,3}$ 3.6, 2-H), 4.54 (1H, d, $J_{AB}$ 12.0, PhCH$_2$), 4.11 (1H, ddd, $J_{3,\text{OH}}$ 9.6, $J_{3,2}$ 3.2, $J_{3,4}$ 3.2, 3-H), 3.76 (1H, dd, $J_{4,3}$ 9.6, $J_{5,5\text{-Me}}$ 6.4, 5-H), 3.46 (1H, d, $J_{\text{OH,3}}$ 9.6, 3-OH), 3.23 (1H, dd, $J_{4,\text{OH}}$ 10.4, $J_{4,5}$ 9.6, $J_{4,3}$ 3.6, 4-H), 2.55 (1H, d, $J_{\text{OH,4}}$ 10.4, 4-OH), 1.35 (3H, d, $J_{5\text{-Me}}$ 6.4, 5-CH$_3$), 1.23 (9H, s, OCOC(CH$_3$)$_3$); $^{13}$C NMR (100 MHz; CDCl$_3$) δ 177.77, 128.84(2C), 128.50(2C), 128.16(2C), 96.36, 72.53, 70.25, 70.00, 69.30, 64.61, 39.15, 27.30(3C), 17.47.

(2R,3S,4R,5S,6S)-2-(benzylxylo)-4,5-dihydroxy-6-methyltetrahydro-2H-pyran-3-yl pivalate (V)

Colorless oil; $R_f$ (30% EtOAc in hexane) = 0.10; $[\alpha]_D^{23} = -123.5$ (c 2.8, CH$_2$Cl$_2$); IR (thin film, cm$^{-1}$) ν 3465, 2973, 2934, 2875, 1725, 1288, 1165, 1046; $^1$H NMR (400 MHz; CDCl$_3$) δ 7.37 – 7.27 (5H, m, Ph), 5.04 (1H, d, $J_{1,2}$ 3.6, 1-H), 4.94 (1H, dd, $J_{2,3}$ 10.4, $J_{2,1}$ 3.6, 2-H), 4.69 (1H, d, $J_{AB}$ 12.0, PhCH$_2$),

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4.51 (1H, d, J_{AB} 12.0, PhCH₂), 4.09 (1H, m, 3-H), 4.06 (1H, q, J_{5,5-Me} 6.4, 5-H), 3.81 (1H, m, 4-H), 2.72 (1H, d, J_{OH,3} 6.8, 3-OH), 2.53 (1H, d, J_{OH,4} 4.4, 4-OH), 1.29 (3H, d, J_{5-Me,5} 6.4, 5-CH₃), 1.21 (9H, s, OCOC(CH₃)₃); ¹³C NMR (100 MHz; CDCl₃) δ 179.38, 137.55, 128.60(2C), 128.02, 127.99(2C), 95.87, 72.60, 71.74, 69.72, 69.16, 65.87, 39.14, 27.29(3C), 16.31.

(2S,3R,4S,5S,6R)-6-(benzoxyl)-5-((tert-butyldimethylsilyloxy)-2-methyltetrahydro-2H-pyran-3,4-diol (VI)

![Structure of (VI)](image_url)

Colorless oil; Rᵣ (30% EtOAc/hexanes) = 0.5; [α]^{24}_D = −46.1 (c 0.38, CH₂Cl₂); IR (thin film, cm⁻¹) ν 3514, 2954, 2928, 2856, 1104, 1051; ¹H NMR (400 MHz; CDCl₃) δ 7.38 – 7.30 (5H, m, Ph), 4.76 (1H, d, J_{AB} 12.0, PhCH₂), 4.75 (1H, d, J_{1,2} 4.4, 1-H), 4.56 (1H, d, J_{AB} 12.0, PhCH₂), 3.97 (1H, ddd, J_{3,OH} 7.2, J_{3,2} 3.6, J_{3,4} 3.6, 3-H), 3.79 (1H, dq, J_{5,4} 9.6, J_{5,5-Me} 6.4, 5-H), 3.73 (1H, dd, J_{2,1} 3.6, J_{2,3} 3.6, 2-H), 3.40 (1H, d, J_{OH,3} 7.2, 3-OH), 3.15 (1H, ddd, J_{4,4-OH} 10.4, J_{4,5} 9.6, J_{4,3} 3.6, 4-H), 2.57 (1H, d, J_{OH,4} 10.4, 4-OH), 1.31 (3H, d, J_{5-Me,5} 6.4, 5-CH₃), 0.91 (9H, s, OSiC(CH₃)₃), 0.08 (3H, s, OSi(CH₃)₃), 0.04 (3H, s, OSiCH₃); ¹³C NMR (100 MHz; CDCl₃) δ 137.12, 128.68(2C), 128.16, 128.08(2C), 98.70, 98.66, 72.97, 72.37, 70.08, 69.53, 64.31, 29.93, 25.93(3C), 18.35, 17.55, −4.58.

(2S,3S,4R,5S,6R)-6-(benzoxyl)-5-((tert-butyldimethylsilyloxy)-2-methyltetrahydro-2H-pyran-3,4-diol (VII)

![Structure of (VII)](image_url)

Colorless oil; Rᵣ(30% EtOAc in hexane) = 0.28; [α]^{24}_D = −107.5 (c 3.56, CH₂Cl₂); IR (thin film, cm⁻¹) ν 3453, 2951, 2928, 2897, 2856, 1251, 1129, 1096, 1026, 874, 836, 778; ¹H NMR (400 MHz; CDCl₃) δ 7.38 – 7.27 (5H, m, Ph), 4.82 (1H, d, J_{1,2} 3.2, 1-H), 4.70 (1H, d, J_{AB} 12.0, PhCH₂), 4.53 (1H, d, J_{AB} 12.0, PhCH₂), 4.02 (1H, q, J_{5,5-Me} 6.8, 5-H), 3.96 (1H, ddd, J_{3,2} 9.6, J_{3,4} 2.8, J_{3,OH} 2.8, 3-H), 3.92 (1H, dd, J_{2,3} 9.6, J_{2,1} 3.2, 2-H), 3.83 (1H, m, 4-H), 2.39 (1H, s, 4-OH), 2.33 (d, J_{OH,3} 2.8, 3-OH), 1.29 (3H, d, J_{5-Me,5} 6.8, 5-CH₃), 0.89 (9H, s, OSiC(CH₃)₃), 0.06 (3H, s, OSi(CH₃)₃), -0.00 (3H, s, OSiCH₃); ¹³C NMR (100 MHz; CDCl₃) δ 137.54, 128.55(2C), 128.43(2C), 128.00, 98.16, 71.92, 70.76, 70.64, 69.58, 66.05, 25.98(3C), 18.32, 16.30, −4.22, -4.56.
(2R,3R,6S)-2-(benzyloxy)-6-methyl-3,6-dihydro-2H-pyran-3-yl tert-butyl carbonate (14):

4-Dimethylaminopyridine (DMAP) (17 mg, 0.139 mmol) was added to a solution of allylic alcohol 7 (610 mg, 2.77 mmol) in CH₂Cl₂ (8.0 mL) under argon at 0 °C. The resulting suspension was stirred until DMAP completely dissolved and added dropwise of (Boc)₂O (906.5 mg, 4.15 mmol) solution in CH₂Cl₂ (1.5 mL). The reaction mixture was stirred at room temperature until TLC showed complete conversion (~ 2 hours). The mixture was diluted with Et₂O and quenched with saturated NaHCO₃ solution at 0 ºC. The resulting organic extract in Et₂O was subsequently washed with saturated aqueous NH₄Cl, saturated NaHCO₃, saturated brine solution and dried over MgSO₄. The crude product was concentrated under reduced pressure and purified via silica gel chromatography eluting with 5% EtOAc in hexane to give tert-butyl carbonate 14 (880 mg, 2.75 mmol, 99%) as colorless gel; R_f (10% EtOAc in hexane) = 0.57; [α]²⁵_D = –180.4 (c 1.34, CH₂Cl₂); IR (thin film, cm⁻¹) ν 3089, 3065, 2980, 2934, 1737, 1274, 1255, 1163; ¹H NMR (400 MHz; CDCl₃) δ 7.38 – 7.26 (5H, m, Ph), 5.99 (1H, d, J₄,₃ 10.4, 4-H), 5.86 (1H, dddd, J₃,₄ 10.4, J₃,₂ 5.2, J₃,₁ 1.6, 3-H), 5.02 (1H, s, 1-H), 4.80 (1H, d, J₂,₂ 1.6, J₂,₁ 2-H), 4.63 (1H, d, J₃,₂ 12.0, PhCH₂), 4.34 (1H, m, 5-H), 1.48 (9H, s, OCOOC(CH₃)₃), 1.31 (3H, d, J₃,Me₅ 6.8, 5-CH₃); ¹³C NMR (100 MHz; CDCl₃) δ 153.08, 137.54, 136.66, 128.57(2C), 128.03(2C), 127.94, 119.36, 97.13, 82.65, 70.02, 67.97, 63.82, 27.91(3C), 27.56, 20.28.

(2S,3S,4R,5S,6R)-6-(benzyloxy)-5-((tert-butoxycarbonyl)oxy)-4-iodo-2-methyltetrahydro-2H-pyran-3-yl acetate (15)

N-Iodosuccinimide (NIS) (155 mg, 0.687 mmol) was added to a solution of allylic tert-butyl carbonate 14 (110 mg, 0.344 mmol) in AcOH (1.15 mL) at room temperature. The reaction mixture was stirred at rt until TLC showed complete conversion. The mixture was diluted with EtOAc and quenched with saturated NaHCO₃ solution at 0 °C. The resulting organic extract in EtOAc was subsequently washed with saturated aqueous Na₂S₂O₃, saturated brine solution and dried over Na₂SO₄. The crude product was concentrated under reduced pressure and purified via silica gel chromatography eluting with 5% EtOAc in hexane to give iodo-acetate 15 (135 mg, 0.27 mmol, 78%) as colorless gel; R_f (5% EtOAc in hexane)
\[ [\alpha]_{20}^{D} = -42.1 \ (c \ 0.58, \ \text{CH}_2\text{Cl}_2); \ IR \ (\text{thin film, cm}^{-1}) \ \nu 2982, 2933, 1747, 1371, 1277, 1221, 1122, 1046; \ \ ^1H \ NMR \ (400 \ MHz; \ \text{CDCl}_3) \ \delta 7.39 - 7.31 \ (5H, \ m, \ \text{Ph}), 5.15 \ (1H, \ dd, \ J_{4,5} 9.6, \ J_{4,3} 9.6, \ 4-H), 5.04 \ (1H, \ dd, \ J_{2,3} 2.4, \ J_{2,1} 2.0, \ 2-H), 4.82 \ (1H, \ s, \ 1-H), 4.70 \ (1H, \ d, \ J_{\text{AB}} 12.0, \ \text{PhCH}_2), 4.54 \ (1H, \ dd, \ J_{3,4} 9.6, \ J_{3,2} 2.4, \ 3-H), 4.53 \ (1H, \ d, \ J_{\text{AB}} 12.0, \ \text{PhCH}_2), 3.87 \ (1H, \ dq, \ J_{5,4} 9.6, \ J_{5,5-Me} 6.8, \ 5-H), 2.11 \ (3H, \ s, \ \text{OCOCH}_3), 1.51 \ (9H, \ s, \ \text{OCOOC(CH}_3)_3), 1.20 \ (1H, \ d, \ J_{5-Me} 6.4, \ 5-\text{CH}_3); \ ^{13}C \ NMR \ (100 \ MHz; \ \text{CDCl}_3) \ \delta 170.02, 153.25, 137.23, 129.08(2C), 128.66, 128.53(2C), 96.55, 83.65, 76.57, 73.92, 70.28, 68.89, 28.29(3C), 26.63, 21.55, 18.61.

**\((2S,3S,4S,5S,6R)-6-(\text{benzyloxy})-5\text{-hydroxy-4-iodo-2-methyltetrahydro-2H-pyran-3-yl acetate (13)}**

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\(_{N}\)-Iodosuccinimide (NIS) (204 mg, 0.905 mmol) was added to a solution of allylic alcohol 7 (133 mg, 0.60 mmol) in AcOH (2.0 mL) at room temperature. The reaction mixture was stirred at rt until TLC showed complete conversion (~ 1 hour). The mixture was diluted with EtOAc and quenched with saturated NaHCO\(_3\) solution at 0 ºC. The resulting organic extract in EtOAc was subsequently washed with saturated aqueous Na\(_2\)S\(_2\)O\(_3\), saturated brine solution and dried over Na\(_2\)SO\(_4\). The crude product was concentrated under reduced pressure and purified via silica gel chromatography eluting with 10% EtOAc in hexane to give iodo-acetate 13 (180 mg, 0.44 mmol, 73%) as colorless gel; \( R_f \) (50% EtOAc in hexane) = 0.68; [\(\alpha\)]\(_{23}^{D}\) = -50.0 (c 0.90, CH\(_2\)Cl\(_2\)); IR (thin film, cm\(^{-1}\)) \(\nu 3485, 2972, 2938, 1738, 1375, 1223, 1123, 1044; \ ^1H \ NMR \ (400 MHz; \ \text{CDCl}_3) \ \delta 7.39 - 7.31 \ (5H, \ m, \ \text{Ph}), 5.19 \ (1H, \ dd, \ J_{4,5} 9.6, \ J_{4,3} 9.6, \ 4-H), 4.86 \ (1H, \ s, \ 1-H), 4.71 \ (1H, \ d, \ J_{\text{AB}} 12.0, \ \text{PhCH}_2), 4.57 \ (1H, \ dd, \ J_{3,4} 9.6, \ J_{3,2} 2.4, \ 3-H), 4.53 \ (1H, \ d, \ J_{\text{AB}} 12.0, \ \text{PhCH}_2), 4.05 \ (1H, \ d, \ J_{2,3} 2.4, \ J_{2,1} 2.0, \ 2-H), 3.90 \ (1H, \ dq, \ J_{5,4} 9.6, \ J_{5,5-Me} 6.4, \ 5-H), 2.38 \ (1H, \ d, \ J_{\text{OH,2}} 4.4, \ \text{OH}), 2.11 \ (3H, \ s, \ \text{OCOCH}_3), 1.21 \ (3H, \ d, \ J_{5-Me} 6.4, \ 5-\text{CH}_3); \ ^{13}C \ NMR \ (100 MHz; \ \text{CDCl}_3) \ \delta 169.77, 137.00, 128.79(2C), 128.36, 128.28(2C), 97.20, 73.58, 73.50, 69.63, 68.74, 34.85, 21.25, 18.34.

**\((2S,3R,5R,6R)-6-(\text{benzyloxy})-5\text{-hydroxy-2-methyltetrahydro-2H-pyran-3-yl acetate (VIII)}**

\[ \begin{align*}
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A solution of iodo-acetate 13 (138 mg, 0.340 mmol) in toluene (3.5 mL) at 0 ºC was added tris(trimethylsilyl)silane (TTMSS) (170 mg, 0.680 mmol) and solid AIBN (28 mg, 0.17 mmol) in one portion. The system was repeatedly froze/thawed three times at –78 ºC under vacuum and refilled with Ar gas. The resulting mixture was then heated to 75 ºC until TLC showed complete conversion (~ 40
minutes). The reaction mixture was cooled to room temperature and directly loaded onto silica gel column. Elution with 15% EtOAc in petroleum ether to obtain 4-acetyl-ascarylose VIII (83 mg, 0.296 mmol, 87%) as colorless gel; $R_f$ (30% EtOAc/petroleum ether) = 0.24; [$\alpha]^D_{23} = -97.8$ (c 5.05, CH$_2$Cl$_2$); IR (thin film, cm$^{-1}$) ν 3432, 2978, 2935, 2906, 1735, 1242, 1037, 700; $^1$H NMR (400 MHz; CDCl$_3$) δ 7.38 – 7.28 (5H, m, Ph), 4.85 (1H, ddd, $J_{4,5}$ 9.6, $J_{4,3}$ 9.6, $J_{4,4}$ 4.8, 4-H), 4.75 (1H, d, $J_{AB}$ 12.0, PhCH$_2$), 4.71 (1H, s, 1-H), 4.53 (1H, d, $J_{AB}$ 12.0, PhCH$_2$), 3.92 – 3.85 (2H, m, 5-H & 2-H), 3.70 (1H, dq, $J_{5,4}$ 9.6, $J_{5,5}$ 6.4, 5-H), 3.63 (1H, m, 4-H), 2.09 (1H, ddd, $J_{3,3}$ 13.2, $J_{3,4}$ 3.6, 3-H), 1.88 (1H, ddd, $J_{3,3}$ 13.2, $J_{3,4}$ 13.2, $J_{3,6}$ 2.8, 3-H), 1.62 (1H, s, OH), 1.54 (1H, s, OH), 1.30 (1H, d, $J_{5,6}$ 6.4, 5-Me); $^{13}$C NMR (100 MHz; CDCl$_3$) δ 170.52, 137.58, 128.62(2C), 128.09(2C), 128.01, 98.43, 70.32, 69.32, 68.30, 67.23, 32.07, 21.32, 17.80.

(2R,3R,5R,6S)-2-(benzyloxy)-6-methyltetrahydro-2H-pyran-3,5-diol (4)$^{10}$

A solution of acetate VIII (32.4 mg, 0.116 mmol) in MeOH (0.6 mL) was added K$_2$CO$_3$ (32 mg, 0.231 mmol) at room temperature. The reaction mixture was stirred for 30 minutes at room temperature and cooled to 0 ºC after TLC showed complete hydrolysis. The mixture was diluted with Et$_2$O and added 1N HCl (~1 mL) dropwise to quench the reaction. The mixture was extracted with Et$_2$O (3x), and washed the organic extract with saturated aqueous NaHCO$_3$, and saturated brine solution. The extract was then dried over MgSO$_4$, filtered and concentrated under the reduced pressure. The compound was purified via silica gel chromatography with elution of 45% EtOAc in hexane to obtain α-ascarylose 4 (26 mg, 0.109 mmol, 95%) as colorless oil. $R_f$ (70% EtOAc in hexane) = 0.27; [$\alpha]^{21}_{D} = -51.8$ (c 0.94, MeOH); IR (thin film, cm$^{-1}$) ν 3405, 2935, 1718, 1686, 1256, 1123, 1080, 995; $^1$H NMR (400 MHz; CDCl$_3$) δ 7.38 – 7.28 (5H, m, Ph), 4.75 (1H, d, $J_{AB}$ 11.6, PhCH$_2$), 4.68 (1H, s, 1-H), 4.53 (1H, d, $J_{AB}$ 11.6, PhCH$_2$), 3.91 (1H, m, 2-H), 3.70 (1H, dq, $J_{5,4}$ 9.6, $J_{5,5}$ 6.4, 5-H), 3.63 (1H, m, 4-H), 2.09 (1H, ddd, $J_{3,3}$ 13.2, $J_{3,4}$ 3.6, $J_{3,6}$ 3.6, 3-H), 1.88 (1H, ddd, $J_{3,3}$ 13.2, $J_{3,4}$ 13.2, $J_{3,6}$ 2.8, 3-H), 1.62 (1H, s, OH), 1.54 (1H, s, OH), 1.30 (1H, d, $J_{5,6}$ 6.4, 5-Me); $^{13}$C NMR (100 MHz; CDCl$_3$) δ 170.52, 137.58, 128.62(2C), 128.09(2C), 128.01, 98.43, 70.32, 69.32, 68.30, 67.23, 32.07, 21.32, 17.80.

**Alternative approach to α-ascarylose 4.** To a round-bottom flask was added 2-Boc 4-acetyl 3-iodide rhamnose 15 (22 mg, 0.043 mmol), anhydrous THF (0.4 mL), and LiAlH$_4$ (7 mg, 0.184 mmol) at 0 ºC. $^{10}$ Spectrum for ascarylose 4 is identical to our previous reported data: M. Shan, Y. Xing and G. A. O’Doherty, *J. Org. Chem.* 2009, 74, 5961-5966.
The reaction mixture was stirred for 1 hour at 0 ºC. Water was added dropwise to quench the reaction, and the mixture was extracted with Et<sub>2</sub>O. The organic layer was washed with saturated brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography to give obtain α-ascarylose 4 (8.5 mg, 0.036 mmol, 82%) as colorless oil.

(2R,3S,4R,5R,6S)-2-(benzylxy)-3-hydroxy-5-iodo-6-methyltetrahydro-2H-pyranyl-4-yl acetate (18)

N-Iodosuccinimide (NIS) (65 mg, 0.289 mmol) was added to a solution of allylic alcohol 17 (40.6 mg, 0.184 mmol) in AcOH (1.0 mL) at room temperature. The reaction mixture was stirred at rt until TLC showed complete conversion (~ 2 hours). The mixture was diluted with EtOAc and quenched with saturated NaHCO<sub>3</sub> solution at 0 ºC. The resulting organic extract in EtOAc was subsequently washed with saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, saturated brine solution and dried over Na<sub>2</sub>SO<sub>4</sub>. The crude product was concentrated under reduced pressure and purified via silica gel flash chromatography eluting with 10% EtOAc in petroleum ether to give iodoacetate 18 (55 mg, 0.135 mmol, 74%) as white solid; mp 89 – 90 ºC; Rf (30% EtOAc in petroleum ether) = 0.48; [α]<sup>23</sup> <sub>D</sub> = −140.8 (c 3.17, CH<sub>2</sub>Cl<sub>2</sub>); IR (thin film, cm<sup>−1</sup>) ν 2971, 2940, 1744, 1455, 1399, 1229, 1042; <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>) δ 7.37–7.29 (5H, m, Ph), 5.31 (1H, dd, J<sub>3,2</sub> 3.6, J<sub>3,3</sub> 3.6, 3-H), 4.96 (1H, d, J<sub>1,2</sub> 3.6, 1-H), 4.81 (1H, d, J<sub>AB</sub> 12.0, PhCH<sub>2</sub>), 4.58 (1H, d, J<sub>AB</sub> 12.0, PhCH<sub>2</sub>), 4.46 (1H, ddd, J<sub>2,2</sub>-OH 11.0, J<sub>2,1</sub> 3.6, J<sub>2,3</sub> 3.6, 2-H), 4.28 (1H, dd, J<sub>4,3</sub> 2.8, J<sub>4,4</sub> 2.0, 4-H), 3.30 (1H, dq, J<sub>5,5-Me</sub> 6.4, J<sub>5,4</sub> 2.0, 5-H), 2.48 (1H, d, J<sub>OH</sub> 11.0, OH), 2.13 (3H, s, OCOCH<sub>3</sub>), 1.10 (3H, d, J<sub>6-Me</sub> 7.0, 6-H); <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>) δ 170.30, 137.79, 128.65(2C), 127.99, 127.50(2C), 97.61, 74.31, 70.07, 63.17, 60.77, 35.49, 22.74, 21.20.

(2R,3S,4S,6S)-2-(benzylxy)-3-hydroxy-6-methyltetrahydro-2H-pyran-4-yl acetate (VIII)

A solution of iodoacetate 18 (260 mg, 0.640 mmol) in anhydrous toluene (6.4 mL) at 0 ºC was added tris(trimethylsilyl)silane (TTMSS) (318 mg, 1.28 mmol) and solid AIBN (53 mg, 0.32 mmol) in one portion. The system was repeatedly froze/thawed three times at −78 ºC under vacuum and refilled with Ar gas. The resulting mixture was then heated to 75 ºC until TLC showed complete conversion (~ 30 minutes). The reaction mixture was cooled to room temperature and directly loaded onto silica gel column. Elution with 13% EtOAc in hexane to obtain 3-acetyl-4,6-dideoxy-allose VIII (166 mg, 0.592
mmol, 93%) as colorless gel; Rf (30% EtOAc in hexane) = 0.17; [α]_{D}^{22} = -63.1 (c 5.04, CH₂Cl₂); IR (thin film, cm⁻¹) v 3437, 2972, 2918, 1734, 1238, 1130, 1042, 735, 697; ¹H NMR (400 MHz; CDCl₃) δ 7.40 – 7.27 (5H, m, Ph), 5.17 (1H, ddd, J₃,₂ 3.6, J₃,₄ 3.6, J₅,₄ 2.4, 3-H), 4.95 (1H, d, J₁,₂ 4.4, 1-H), 4.86 (1H, d, J₁,₂ 12.0, PhCH₂), 4.52 (1H, d, J₁,₂ 12.0, PhCH₂), 4.09 (1H, ddd, J₅,₄ 13.2, J₅,₅-Me 6.4, J₅,₅ 2.4, 5-H), 3.73 (1H, ddd, J₂,OH 10.0, J₂,₁ 3.6, J₂,₃ 3.6, 2-H), 2.58 (1H, d, J₀H₂ 10.0, OH), 2.10 (3H, s, OCOCH₃), 1.96 (1H, ddd, J₄,₄ 14.4, J₄,₅ 2.4, J₄,₃ 2.4, 4-H), 1.61 (1H, ddd, J₄,₄ 14.4, J₄,₅ 13.2, J₄,₃ 3.6, 4-H), 1.14 (3H, d, J₅,₅-Me 6.4, 5-CH₃); ¹³C NMR (100 MHz; CDCl₃) δ 171.00, 138.26, 128.51(2C), 127.72, 127.25(2C), 97.64, 69.90, 69.46, 67.04, 59.88, 36.39, 21.44, 20.59.

(2R,3S,4S,6S)-2-(benzoyloxy)-6-methyltetrahydro-2H-pyran-3,4-diol (19)

A solution of acetate VIII (45.8 mg, 0.163 mmol) in MeOH (0.80 mL) was added K₂CO₃ (45 mg, 0.326 mmol) at room temperature. The reaction mixture was stirred for 30 minutes at room temperature and cooled to 0 °C after TLC showed complete hydrolysis. The mixture was diluted with Et₂O and added 1N HCl (~1 mL) dropwise to quench the reaction. The reaction mixture was extracted with Et₂O (3x), and washed the organic extract with saturated aqueous NaHCO₃, saturated brine solution and dried over MgSO₄. The compound was then filtered and concentrated under reduced pressure. The crude product was purified via silica gel flash chromatography with elution of 30% EtOAc in hexane to give 4,6-dideoxy-allose 19 (37 mg, 0.155 mmol, 95%) as colorless oil. Rf (50% EtOAc in hexane) = 0.28; [α]_{D}^{21} = -80.1 (c 1.78, CH₂Cl₂); IR (thin film, cm⁻¹) v 3492, 2971, 2931, 1096, 1050, 740, 699; ¹H NMR (400 MHz; CDCl₃) δ 7.39 – 7.30 (5H, m, Ph), 4.97 (1H, d, J₁,₂ 3.6, 1-H), 4.78 (1H, d, J₁,₂ 12.0, PhCH₂), 4.54 (1H, d, J₁,₂ 12.0, PhCH₂), 4.08 (1H, ddd, J₅,₄ 12.8, J₅,₅-Me 6.4, J₅,₅ 2.4, 5-H), 3.99 (1H, m, 3-H), 3.60 (1H, m, 2-H), 3.13 (1H, br, 3-OH), 2.71 (1H, br, 2-OH), 1.97 (1H, ddd, J₄,₄ 14.4, J₄,₅ 3.2, J₄,₃ 2.8, 4-H), 1.62 (ddd, J₄,₄ 14.4, J₄,₅ 12.8, J₄,₃ 2.8, 4-H), 1.21 (3H, d, J₅,₅-Me 6.4, 5-CH₃); ¹³C NMR (100 MHz; CDCl₃) δ 137.00, 128.83(2C), 128.37, 128.24(2C), 99.93, 70.50, 68.91, 68.24, 59.34, 39.80, 20.79.

Alternative approach to 4,6-dideoxy-allose 19. To a round-bottom flask was added 3-acetyl 4-iodide allose 18 (17 mg, 0.040 mmol), anhydrous THF (0.4 mL), and LiAlH₄ (4 mg, 0.105 mmol) at 0 °C. The reaction mixture was stirred for 1 hour at 0 °C. Water was added dropwise to quench the reaction, and the mixture was extracted with Et₂O. The organic layer was washed with saturated brine, dried over Na₂SO₄, and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography to give obtain α-4,6-dideoxy allose 19 (8.8 mg, 0.037 mmol, 88%) as colorless oil.
Undesired S2' nucleophilic substitution of allylic alcohol 7 under Mitsunobu reaction:

(2S,3R,6R)-6-(benzylxy)-2-methyl-3,6-dihydro-2H-pyran-3-yl 4-nitrobenzoate (Xa) and
(2S,3S,6R)-6-(benzylxy)-2-methyl-3,6-dihydro-2H-pyran-3-yl 4-nitrobenzoate (Xb)

A THF (4.5 mL) solution of allylic alcohol 7 (147 mg, 0.667 mmol) at 0 ºC were added triphenylphosphine (PPh3) (262.2 mg, 1.00 mmol) and p-nitrobenzoic acid (223 mg, 1.33 mmol). Diisopropyl azodicarboxylate (DIAD) (202.4 mg, 1.00 mmol) in THF (1.0 mL) was added dropwise to the mixture, and the reaction mixture was slowly warm up to room temperature and stirred for 12 hours. The reaction was diluted with Et2O, quenched with saturated aqueous NaHCO₃, and extract with Et2O. The compound was dried over MgSO₄ and concentrated under reduced pressure. The crude products were purified and separated using silica gel flash chromatography eluting with 6% EtOAc in petroleum ether to obtain 1st isomer Xa (100 mg, 0.270 mmol, 41%) as colorless oil and 7% EtOAc in petroleum ether to obtain 2nd isomer Xb (75 mg, 0.203 mmol, 30%) as yellow solid, mp 103.5 – 104.7 ºC. Xa: Rf (20% EtOAc in petroleum ether) = 0.73; [α]²²ₒ = −76.8 (c 2.34, CH₂Cl₂); IR (thin film, cm⁻¹) ν 3056, 3032, 2930, 2934, 1725, 1527, 1262, 1102, 1047, 1015, 719; ¹H NMR (400 MHz; CDCl₃) δ 8.32 – 8.27 (2H, m, PNB), 8.22 – 8.18 (2H, m, PNB), 7.41 – 7.29 (5H, m, Ph), 5.97 (1H, d, J₂,₃ 10.4, 2-H), 5.92 (1H, d, J₃,₂ 10.4, J₃,₅ 2.4, J₃,₄ 1.6, 3-H), 5.37 (dd, J₄,₅ 9.6, J₄,₃ 1.6, 4-H), 5.13 (1H, s, 1-H), 4.82 (1H, d, J₉,₈ 2.34, CH₃), 13C NMR (100 MHz; CDCl₃) δ 164.38, 150.89, 137.96, 135.34, 131.11, 131.04, 129.27, 128.70, 128.28, 128.07, 123.79, 93.87, 72.59, 70.59, 65.08, 29.04, 18.24; Xb: Rf (20% EtOAc in petroleum ether) = 0.64; [α]²²ₒ = −151.5 (c 0.97, CH₂Cl₂); IR (thin film, cm⁻¹) ν 3057, 3032, 2984, 2936, 1720, 1528, 1344, 1269, 1101, 1023, 719; ¹H NMR (400 MHz; CDCl₃) δ 8.29 (2H, d, J₉,₈ 147.90, PNB), 8.24 (2H, d, J₉,₈ 19.0, PNB), 7.42 – 7.28 (5H, m, Ph), 6.21 (1H, dd, J₅,₂ 10.4, J₅,₃ 5.2, 3-H), 6.11 (1H, dd, J₂,₃ 10.4, J₂,₂ 2.4, 2-H), 5.19 (1H, d, J₁,₂ 2.4, 1-H), 5.17 (1H, dd, J₄,₃ 5.2, J₄,₅ 2.0, 4-H), 4.81 (1H, d, J₉,₈ 2.34, CH₃), 4.66 (1H, d, J₉,₈ 11.6, PhCH₂), 4.39 (1H, qd, J₅,₅-Me 6.8, J₅,₄ 2.0, 5-H), 1.26 (3H, d, J₅-Me 6.8, 5-CH₃), 13C NMR (100 MHz; CDCl₃) δ 164.55, 150.87, 138.00, 135.52, 131.47, 131.15, 128.75, 128.30, 128.11, 125.64, 123.82, 94.74, 70.38, 66.89, 65.03, 16.42.
### Table 1. Screening of different ligands.

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### Table 2. Optimization of OsO$_4$ Dihydroxylation.

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*a* Diastereomeric ratio are based on crude NMR analysis in the comparison of anomeric H$_1$. *b* Combined yield after flash column purification.
LW-DIG-221-allylic-OH-1H

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(600 MHz, CDCl₃)
LW-01G-221-allylic-OH-13C
Pulse Sequence: 52pul

(150 MHz, CDCl₃)

7
PW-011-224-altrose-13C

Pulse Sequence: s2pul

(150 MHz, CDCl₃)
LW-DIG-225-a-L-C3-C4-dideoxy-rhamnose-1H

Archive directory: /export/home/vmnrs/data
Sample directory:
File: PROTON
Pulse sequence: s2pul

12

(600 MHz, CDCl₃)
400 MHz, CDCl₃
$^{1}H$ NMR spectrum of compound I in CDCl$_3$ at 100 MHz.
17

400 MHz, CDCl$_3$

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100 MHz, CDCl₃
400 MHz, CDCl₃
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III

400 MHz, CDCl₃

[Chemical structure diagram]
100 MHz, CDCl₃
400 MHz, CDCl$_3$
$\text{H}_2\text{C}$

$\text{O}$

$\text{H}_2\text{C}$

$\text{O}$

$\text{OH}$

100 MHz, CDCl$_3$
400 MHz, CD$_3$OD
100 MHz, CD$_3$OD
Chemical structure of compound 6 with the following 1H NMR spectrum:

400 MHz, CD$_3$OD
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6

100 MHz, CD$_3$OD
100 MHz, CDCl₃
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400 MHz, CDCl₃
$\text{VI}$

400 MHz, CDCl$_3$
VII

400 MHz, CDCl$_3$
VII

100 MHz, CDCl$_3$
14

400 MHz, CDCl$_3$
100 MHz, CDCl$_3$
100 MHz, CDCl$_3$
400 MHz, CDCl$_3$
100 MHz, CDCl$_3$
400 MHz, CDCl₃
VIII

100 MHz, CDCl₃
400 MHz, CDCl₃
100 MHz, CDCl$_3$
$\text{18}$

$400 \text{ MHz, } \text{CDCl}_3$
100 MHz, CDCl₃
VIII

100 MHz, CDCl$_3$
19

400 MHz, CDCl$_3$
19

100 MHz, CDCl₃

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Xa

400 MHz, CDCl₃
$\textbf{Xa}$

100 MHz, CDCl$_3$
$Xb$

$400$ MHz, CDCl$_3$
100 MHz, CDCl$_3$

Xb

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