Electronic Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

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

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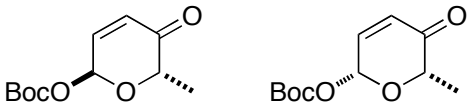
Section A: General Methods

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 $^{\circ}$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 $KMnO_4$ stain or anisaldehyde stain (465 mL of 95% EtOH, 17 mL conc. H_2SO_4, 5 mL acetic acid, and 13 mL anisaldehyde). R_f values are obtained by elution in the specified solvent ratio (v/v). Optical rotations were obtained using a digital polarimeter in the solvent specified. ^{1}H and ^{13}C NMR spectra were recorded on both 600 and 400 MHz spectrometer. Chemical shifts are reported relative to $CDCl_3$ (δ 7.26 ppm) for ^{1}H and $CDCl_3$ (δ 77.23 ppm) for ^{13}C or CD_3OD (δ 4.81 ppm) for ^{1}H and CD_3OD (δ 49.15 ppm) for ^{13}C. 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 CH_2Cl_2 solution. Melting points were determined with electrothermal apparatus and are uncorrected.

Section B: Synthetic Procedures

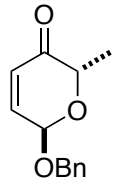
(2*S*, 6*S*)-*tert*-butyl -5,6-dihydro-6-methyl-5-oxo-2*H*-pyran-2-yl carbonate (α-11 and β-11)[1]



To a 500 mL Erlenmeyer flask of HCO_2Na (37.1 g, 0.545 mol) in deionized H_2O (272 ml) was added furan ketone **10** (15 g, 0.136 mol) and CH_2Cl_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 (*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_2SO_4, and concentrated under reduced pressure. The resulting crude enantiomeric mixture of furan alcohols were further dissolved in 228 mL of THF/H_2O (3:1) and cooled to 0 ºC. Solid $NaHCO_3$ (23 g, 0.273 mol), NaOAc•$3H_2O$ (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 ºC. The reaction was quenched with saturated $NaHCO_3$ (200 mL), extracted (3 x 300 mL) with Et_2O, dried over Na_2SO_4, and concentrated under reduced pressure. The crude mixture was further dissolved in CH_2Cl_2 (200 mL) and the solution was cooled to –78 ºC. Catalytic amount of DMAP (1.22 g 7 mol%) was added to the reaction mixture, followed by adding $(Boc)_2O$ (59.5 g, 0.273 mol) in CH_2Cl_2 (70 ml) and allowed the resulting solution to stir for 12 h at –78 to –30 ºC. The reaction was quenched with saturated $NaHCO_3$, extracted with Et_2O (3x), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography with elution of 6% Et_2O 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**, *Rf* (20% Et_2O in hexane) = 0.58; $[\alpha]^{25}_D$ = + 98 (*c* 1.0, CH_2Cl_2); IR (thin film, cm-1) ν 2984, 2942, 1752, 1703, 1371, 1273, 1254, 1153, 938, 838; ^{1}H NMR (600 MHz; $CDCl_3$) δ 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, $J_{5\text{-Me},5}$ 6.6, 5-CH_3); ^{13}C NMR (150 MHz; $CDCl_3$) δ 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.

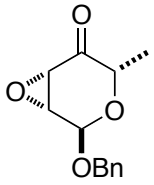
[1] Spectral data for the intermediates 2-methyl furan alcohol and pyranyl alcohols matches the previously reported compound, see: M. Zhou and G. A. O'Doherty, *J. Org. Chem.* **2007**, *72,* 2485-2493; H. Guo and G. A. O'Doherty, *J. Org. Chem.* **2008**, *73,* 5211-5220; M. Shan, Y. Xing and G. A. O'Doherty, *J. Org. Chem.* **2009**, *74*, 5961-5966.

(2*S*,6*R*)-6-(benzyloxy)-2-methyl-2*H*-pyran-3(6*H*)-one (9)[2]



A CH_2Cl_2 solution (35.0 mL) of Boc-pyranone **α-11** (2.78 g, 12.2 mmol) and benzyl alcohol (1.98 g, 18.3 mmol) was cooled to 0 ºC. A CH_2Cl_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 ºC. The resulting solution was stirred at 0 ºC for 8 hours. The reaction mixture was concentrated under reduced pressure and directly loaded onto silica gel flash column to obtain α-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_2Cl_2); IR (thin film, cm^{-1}) ν 2985, 2939, 2873, 1697, 1231, 1022, 953; ^1H 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, $J_{5\text{-Me},5}$ 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.

(1*R*,2*R*,4*S*,6*S*)-2-(benzyloxy)-4-methyl-3,7-dioxabicyclo[4.1.0]heptan-5-one (8)[2]

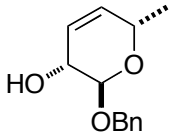


To a solution of α-benzyl-pyranone **9** (2.55 g, 11.7 mmol) in methanol (39.0 mL) at 0 ºC was added dropwise 35% aqueous hydrogen peroxide (1.09 g, 29.0 mmol), followed by addition of aqueous sodium hydroxide (1.17 mL, 0.5 M). The reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was diluted with Et_2O (10 mL) and was quenched with 10 mL of saturated aqueous $NaHCO_3$, extracted with Et_2O (3 x 20 mL), dried with Na_2SO_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}) ν 3034, 2937, 1726, 1455, 1369, 1256, 1146, 1060, 996, 859, 699; ^1H 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,

[2] Spectrum for a-benzyl-enone **9** and epoxide-keton **8** are identical to our previous reported data: M. Shan, Y. Xing and G. A. O'Doherty, *J. Org. Chem.* **2009**, *74*, 5961-5966.

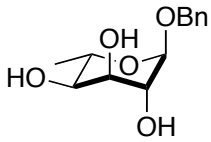
dd, $J_{2,3}$ 4.0, $J_{2,1}$ 1.2, 2-H), 3.46 (1H, d, $J_{3,2}$ 4.0, 3-H), 1.38 (3H, d, $J_{5\text{-Me},5}$ 6.9 Hz, 5-CH_3); ^{13}C NMR (67.5 MHz; $CDCl_3$): δ 203.1, 136.6, 128.7, 128.4, 128.2, 93.3, 93.2, 72.0, 70.8, 53.8, 53.1; HRMS Calcd for $[C_{13}H_{14}O_4+Na]^+$: 257.0784, Found 257.0784.

(2*R*,3*R*,6*S*)-2-(benzyloxy)-6-methyl-3,6-dihydro-2*H*-pyran-3-ol (7)



A solution of epoxide ketone **8** (1.35 g, 5.76 mmol) in methanol (20 mL) was cooled to 0 ºC, and N_2H_4•H_2O (1.41 mL, 29.5 mmol) was added dropwise to the reaction mixture. After reaction mixture stirring at 0 ºC 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_2Cl_2 and quenched with 20 mL of saturated aqueous $NaHCO_3$ at 0 ºC. The mixture was extracted with CH_2Cl_2 (3 x), dried over $MgSO_4$. 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; R_f (30% EtOAc in hexanes) = 0.27; $[\alpha]^{25}_D$ = –179.5 (*c* 1.0, CH_2Cl_2); IR (thin film, cm^{-1}) ν 3417, 3066, 3033, 2931, 2870, 1051, 1005, 735, 699; ^{1}H NMR (600MHz; $CDCl_3$) δ 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, $J_{4,3}$ 10.8, $J_{4,5}$ 1.2, 4-H), 4.91 (1H, s, 1-H), 4.80 (1H, d, J_{AB} 12.0, $PhCH_2$), 4.61 (1H, d, J_{AB} 12.0, $PhCH_2$), 4.35 (1H, ddq, $J_{5,5\text{-Me}}$ 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, $J_{5\text{-Me},5}$ 7.2, 5-CH_3); ^{13}C NMR (150 MHz; $CDCl_3$) δ 137.74, 134.54, 128.67(2C), 128.16(2C), 128.04, 123.95, 99.66, 70.09, 64.50, 64.27, 20.62; ESIHRMS Calcd. for $[C_{13}H_{16}O_3Na^+]$: 243.09917, found: 243.09901.

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

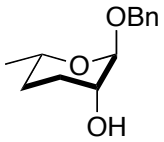


To a *t*-BuOH/acetone (1.5 mL, 1:1 (v/v)) solution of allylic alcohol **7** (66.3 mg, 0.30 mmol) at 0 ºC was added a solution of *N*-methylmorpholine-*N*-oxide/water (50% w/v, 0.3 mL). Crystalline OsO_4 (3.0 mg, 4 mol %) was added rapidly and the reaction mixture was stirred at 0 ºC until TLC showed complete conversion. The reaction mixture was then concentrated under reduced pressure and directly loaded onto

[3] Spectrum for 6-deoxy altrose **3** is identical to our previous reported data: M. Shan, Y. Xing and G. A. O'Doherty, *J. Org. Chem*. **2009**, *74*, 5961-5966.

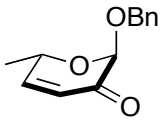
silica gel flash chromatography to obtain α-6-deoxy-altrose **3** (69 mg, 0.27 mmol, 92%) as a colorless oil with elution of 75% EtOAc in hexane; R_f = 0.42 (EtOAc); $[\alpha]^{23}_D$ = –112.5 (*c* 1.0, MeOH); IR (thin film, cm^{-1}) ν 3384, 2930, 1455, 1375, 1259, 1127, 1061, 1014, 970, 852, 737, 698; ^{1}H NMR (600MHz; $CDCl_3$) δ 7.38 – 7.32 (5H, m. Ph), 4.79 (1H, s, 1-H), 4.74 (1H, d, J_{AB} 12.0, $PhCH_2$), 4.54 (1H, d, J_{AB} 12.0, $PhCH_2$), 3.96 (1H, m, 2-H), 3.88 (1H, ddd, $J_{3,3\text{-OH}}$ 9.6, $J_{3,4}$ 3.6, $J_{3,2}$ 3.6, 3-H), 3.80 (1H, dq, $J_{5,4}$ 9.6, $J_{5,5\text{-Me}}$ 6.6, 5-H), 3.51 (1H, ddd, $J_{4,5}$ 9.6, $J_{4,4\text{-OH}}$ 9.6, $J_{4,3}$ 3.6, 4-H), 3.37 (1H, d, $J_{3\text{-OH},3}$ 9.6, 3-OH), 2.68 (1H, d, $J_{4\text{-OH},4}$ 9.6, 4-OH), 2.52 (1H, d, $J_{2\text{-OH},2}$ 6.0, 2-OH), 1.34 (3H, d, $J_{5\text{-Me},5}$ 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.

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



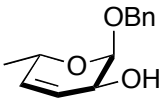
To a *N*-methylmorpholine (NMM) (0.5 ml, 0.3M) solution of allylic alcohol **7** (34 mg, 0.154 mmol) at 0 ºC was added *o*-nitrobenzenesulfonyl hydrazine (NBSH) (200 mg, 0.921 mmol) and Et_3N (62.8 mg, 0.616 mmol). The resulting mixture was raised to room temperature and stirred for 12 hours. Additional 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_2SO_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_2Cl_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, 1-H), 4.53 (1H, d, J_{AB} 12.0, $PhCH_2$), 3.95 (1H, ddq, $J_{5,4}$ 9.6, $J_{5,5\text{-Me}}$ 6.6, $J_{5,4}$ 2.4, 5-H), 3.67 (1H, dd, $J_{2,3}$ 4.8, $J_{2,3}$ 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, ddddd, $J_{3,3}$ 13.8, $J_{3,4}$ 9.6, $J_{3,4}$ 6.6, $J_{3,2}$ 4.8, $J_{3,5}$ 3.0, 3-H), 1.18 (3H, d, $J_{5\text{-Me},5}$ 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 [$C_{13}H_{18}O_3$+Na^+]: 245.11482, found: 245.11462.

(2*R*,6*S*)-2-(benzyloxy)-6-methyl-2*H*-pyran-3(6*H*)-one (I)



A solution of allylic alcohol **7** (750 mg, 3.40 mmol) in CH_2Cl_2 (34 mL) was added activated MnO_2 (2.4 g, 27.6 mmol). The reaction mixture was stirred under reflux at 50 ºC for 12 hours. More MnO_2 (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; R_f (5% EtOAc in hexane) = 0.30; $[\alpha]^{23}_D$ = –84.1 (*c* 0.45, CH_2Cl_2), (lit.[4] [α] = –116 (*c* 3.39, $CHCl_3$)); ^{1}H NMR (400MHz; $CDCl_3$) δ 7.38-7.28 (5H, m, Ph), 6.90 (1H, dd, $J_{3,4}$ 10.4, $J_{3,5}$ 1.2, 3-H), 6.08 (1H, d, $J_{4,3}$ 10.4, $J_{4,5}$ 2.4, 4-H), 4.92 (1H, s, 1-H), 4.82 (1H, d, J_{AB} 11.6, $PhCH_2$), 4.72 (1H, d, J_{AB} 11.6, $PhCH_2$), 4.66 (1H, ddq, $J_{5,5\text{-Me}}$ 6.4, $J_{5,4}$ 2.4, $J_{5,3}$ 1.2, 5-H), 1.38 (3H, d, $J_{5\text{-Me},5}$ 6.4, 5-CH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 189.13, 152.52(2C), 137.04, 128.73(2C), 128.28(2C), 124.39, 97.20, 71.02, 64.71, 20.30.

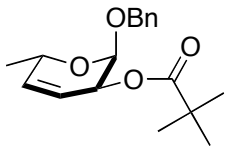
(2*R*,6*S*)-2-(benzyloxy)-6-methyl-3,6-dihydro-2H-pyran-3-ol (17)



A solution of enone **I** (390 mg, 1.79 mmol) in CH_2Cl_2 (3.6 mL) was added $CeCl_3$/MeOH (3.6 mL, 0.4M) and cooled to –78 ºC. $NaBH_4$ (101 mg, 2.68 mmol) was added to the reaction mixture and stirred for 2 hours. The reaction mixture was diluted with Et_2O at 0 ºC and quenched the reaction by addition of saturated aqueous $NaHCO_3$. The mixture was extracted with Et_2O and dried over $MgSO_4$. 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 ºC; R_f (10% EtOAc in hexane) = 0.43; $[\alpha]^{19}_D$ = –50.8 (*c* 1.10, CH_2Cl_2); IR (thin film, cm^{-1}) ν 3331, 3066, 3032, 2930, 2895, 2869, 1497, 1454, 1043, 719; ^{1}H NMR (400MHz; $CDCl_3$) δ 7.42-7.28 (5H, m, Ph), 5.71 (1H, d, $J_{4,3}$ 10.2, 4-H), 5.66 (1H, dd, $J_{3,4}$ 10.2, $J_{3,2}$ 1.6, 3-H), 5.07 (1H, d, $J_{1,2}$ 4.4, 1-H), 4.85 (1H, d, J_{AB} 12.0, $PhCH_2$), 4.63 (1H, d, J_{AB} 12.0, $PhCH_2$), 4.30 – 4.19 (2H, m, 2-H & 5-H), 2.24 (1H, d, $J_{OH,2}$ 11.2, OH), 1.24 (3H, d, $J_{5\text{-Me},5}$ 6.8, 5-CH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 137.60, 131.62, 128.76(2C), 128.20(3C), 126.05, 96.37, 70.17, 64.49, 64.35, 20.87.

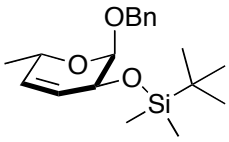
[4] Spectral data was confirmed with literature reported by K. Tatsuta and T. Hirabayashi, *J. Antibiot.* **2004**, *57*, 291-297.

(2*R*,6*S*)-2-(benzyloxy)-6-methyl-3,6-dihydro-2H-pyran-3-yl pivalate (II)



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 CH_2Cl_2 (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 CH_2Cl_2. The organic extract was washed with 1N HCl, then saturated aqueous $NaHCO_3$, and dried over $MgSO_4$. 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; R_f (5% EtOAc in petroleum ether) = 0.25; $[\alpha]^{21}_D$ = –86.7 (*c* 1.4, CH_2Cl_2); IR (thin film, cm^{-1}) ν 2972, 2938, 2880, 1728, 1159, 1049; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.36 – 7.27 (5H, m, Ph), 5.83 (1H, dd, $J_{4,3}$ 10.4, $J_{4,5}$ 2.0, $J_{4,2}$ 1.6, 4-H), 5.58 (1H, d, $J_{3,4}$ 10.4, $J_{3,2}$ 1.2, 3-H), 5.28 (1H, m, 2-H), 5.23 (1H, d, $J_{1,2}$ 4.4, 1-H), 4.79 (1H, d, J_{AB} 12.4, $PhCH_2$), 4.61 (1H, d, J_{AB} 12.4, $PhCH_2$), 4.35 (1H, m, 5-H), 1.27 (3H, d, $J_{5\text{-}Me,5}$ 6.4, 5-CH_3), 1.19 (9H, s, $OCOC(CH_3)_3$). ^{13}C NMR (100 MHz; $CDCl_3$) 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.

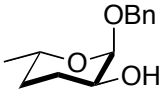
(((2*R*,6*S*)-2-(benzyloxy)-6-methyl-3,6-dihydro-2H-pyran-3-yl)oxy)(tert-butyl)dimethylsilane (III)



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 (TBSCl) (70 mg, 0.46 mmol). The reaction mixture was stirred at rt until TLC showed complete conversion, and quenched with water and extracted with CH_2Cl_2. The organic extract was washed with 1N HCl, saturated aqueous $NaHCO_3$, and dried over $MgSO_4$. 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 *t*-butyl silyl-ether **III** (41 mg, 0.12 mmol, 82%) as a colorless gel; R_f (5% EtOAc in petroleum ether) = 0.25; $[\alpha]^{23}_D$ = –35.0 (*c* 1.77, CH_2Cl_2); IR (thin film, cm^{-1}) ν 2954, 2929, 2894, 2857, 1254, 1111, 1026, 877, 836, 776, 698; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.42 – 7.24 (5H, m, Ph), 5.68 (1H, d, $J_{4,3}$ 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, $J_{5\text{-}Me,5}$ 7.6, 5-CH_3), 0.88 (9H, s, $OSiC(CH_3)_3$), 0.007 (3H, s, $OSiCCH_3$), –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.

(2*R*,3*S*,6*S*)-2-(benzyloxy)-6-methyltetrahydro-2*H*-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; $[\alpha]^{21}_D$= –98.4 (*c* 1.11, CH_2Cl_2); IR (thin film, cm^{-1}) ν 3448, 2969, 2933, 2873, 1089, 1039, 697; ^1H 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, $J_{5,5\text{-}Me}$ 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, $J_{5\text{-}Me,5}$ 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 ºC (lit. [5] 166 – 167 ºC).

Method B – Upjohn condition in CH_2Cl_2

To a CH_2Cl_2 (0.5 mL, 0.1M) solution of allylic alcohol **17** (10.6 mg, 0.048 mmol) at 0 ºC 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 ºC 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[6]

A reaction tube is charged with $K_2OsO_2(OH)_4$ (1.47 mg, 4 mol%), **Ligand** (see table below, 20 mol%), $K_3Fe(CN)_6$ (100 mg, 0.30 mmol), K_2CO_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_2O (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 ºC and added allylic alcohol solid **17** (22 mg, 0.100 mmol). The reaction mixture was stirred vigorously at 0ºC until TLC showed complete conversion. The reaction was quenched at 0 ºC by addition of solid Na_2SO_3, and stirred the mixture at room temperature for an hour. The mixture was extracted with EtOAc, dried over Na_2SO_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 ºC

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_2Cl_2 (1 mL). Cooled the tube to –78 ºC and allowed to stir for 5 minutes. OsO_4 (2.5 mg, 20 mol%) solution in CH_2Cl_2 (1 mL) was added to the reaction at –78 ºC. Followed by the addition of solid allylic alcohol **17** (11 mg, 0.050 mmol). The reaction mixture was stirred at –78 ºC until TLC showed complete conversion. The reaction was quenched at 0 ºC by addition of solid Na_2SO_3, and stirred the mixture at room temperature for an

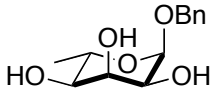
[5] R. G. Schweiger, *J. Chem. Eng. Data*. **1964**, *9*, 408-410.
[6] H. C. Kolb, M. S. VanNieuwenhze and K. B. Sharpless, *Chem. Rev.* **1994**, *94*, 2483-2547.
[7] *N*-methylmorpholine-*N*-oxide/water (70% w/v) was prepared by diluting *N*-methylmorpholine-*N*-oxide/water (90% w/v, 10 mg/μL NMO/H_2O) in the reaction mixture with 50% *N*-methylmorpholine-*N*-oxide/water.

hour. The mixture was extracted with EtOAc, dried over Na_2SO_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[8]

A reaction tube is charged with allylic alcohol **17** (11 mg, 0.05 mmol) in CH_2Cl_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_2Cl_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_2SO_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_2SO_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.

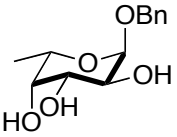
(2*R*,3*S*,4*S*,5*R*,6*S*)-2-(benzyloxy)-6-methyltetrahydro-2H-pyran-3,4,5-triol (5)



Colorless gel; R_f (70% EtOAc in hexane) = 0.26; $[\alpha]^{23}_D$ = –93.8 (*c* 3.26, MeOH); IR (thin film, cm^{-1}) ν 3424, 2973, 2930, 1454, 1035; ^{1}H NMR (400 MHz; CD_3OD) 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, $J_{5,5\text{-Me}}$ 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, $J_{5\text{-Me},5}$ 6.4, 5-CH_3); ^{13}C NMR (100 MHz; CD_3OD) 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.

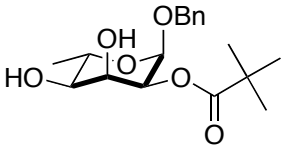
[8] T. J. Donohoe, K. Blades, P. R. Moore, M. J. Waring, J. J. G. Winter, M. Helliwell, N. J. Newcombe and G. Stemp, *J. Org. Chem*. **2002**, *67*, 7946-7956.

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



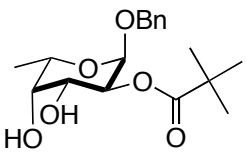
White solid, mp 164.5 – 165.2 ºC (lit., [9] 166 – 167 ºC); R_f (70% EtOAc in hexane) = 0.12; $[\alpha]^{23}_D$= –182.5 (*c* 0.4, MeOH) (lit., [9] $[\alpha]^{20}_D$= –184 (MeOH)); IR (thin film, cm^{-1}) ν 3384, 2933, 2907, 1166, 1078, 1038; ^{1}H NMR (400MHz; CD_3OD) δ 7.40-7.25 (5H, m, Ph), 4.85 (1H, 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, $J_{5\text{-Me},5}$ 6.4, 5-CH_3); ^{13}C NMR (100 MHz; CD_3OD) 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.

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



Colorless oil; R_f (30% EtOAc in hexane) = 0.25; $[\alpha]^{23}_D$= –82.7 (*c* 0.68, CH_2Cl_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, $J_{3,OH}$ 9.6, $J_{3,2}$ 3.2, $J_{3,4}$ 3.2, 3-H), 3.76 (1H, dq, $J_{5,4}$ 9.6, $J_{5,5\text{-Me}}$ 6.4, 5-H), 3.46 (1H, d, $J_{OH,3}$ 9.6, 3-OH), 3.23 (1H, ddd, $J_{4,OH}$ 10.4, $J_{4,5}$ 9.6, $J_{4,3}$ 3.6, 4-H), 2.55 (1H, d, $J_{OH,4}$ 10.4, 4-OH), 1.35 (3H, d, $J_{5\text{-Me},5}$ 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.

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

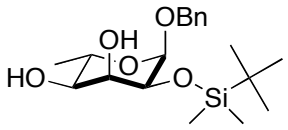


Colorless oil; R_f (30% EtOAc in hexane) = 0.10; $[\alpha]^{23}_D$= –123.5 (*c* 2.8, CH_2Cl_2); IR (thin film, cm^{-1}) ν 3465, 2973, 2934, 2875, 1725, 1288, 1165, 1046; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.37 – 7.27 (5H, m, Ph), 5.04 (1H, d, $J_{1,2}$ 3.6, 1-H), 4.94 (1H, dd, $J_{2,3}$ 10.4, $J_{2,1}$ 3.6, 2-H), 4.69 (1H, d, J_{AB} 12.0, $PhCH_2$),

[9] R. G. Schweiger, *J. Chem. Eng. Data*. **1964**, *9*, 408-410.

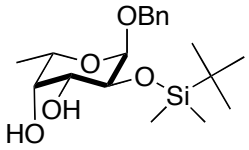
4.51 (1H, d, J_{AB} 12.0, $PhCH_2$), 4.09 (1H, m, 3-H), 4.06 (1H, q, $J_{5,5\text{-Me}}$ 6.4, 5-H), 3.81 (1H, m, 4-H), 2.72 (1H, d, $J_{OH,3}$ 6.8, 3-OH), 2.53 (1H, d, $J_{OH,4}$ 4.4, 4-OH), 1.29 (3H, d, $J_{5\text{-Me},5}$ 6.4, 5-CH_3), 1.21 (9H, s, $OCOC(CH_3)_3$); ^{13}C NMR (100 MHz; $CDCl_3$) δ 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.

(2*S*,3*R*,4*S*,5*S*,6*R*)-6-(benzyloxy)-5-((tert-butyldimethylsilyl)oxy)-2-methyltetrahydro-2H-pyran-3,4-diol (VI)



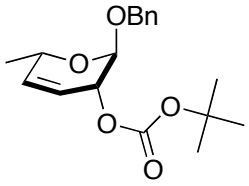
Colorless oil; R_f (30% EtOAc/hexanes) = 0.5; $[\alpha]^{24}_D$= –46.1 (*c* 0.38, CH_2Cl_2); IR (thin film, cm^{-1}) ν 3514, 2954, 2928, 2856, 1104, 1051; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.38 – 7.30 (5H, m, Ph), 4.76 (1H, d, J_{AB} 12.0, $PhCH_2$), 4.75 (1H, d, $J_{1,2}$ 4.4, 1-H), 4.56 (1H, d, J_{AB} 12.0, $PhCH_2$), 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, $J_{5,5\text{-Me}}$ 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, $J_{4,4\text{-OH}}$ 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, $J_{5\text{-Me},5}$ 6.4, 5-CH_3), 0.91 (9H, s, $OSiC(CH_3)_3$), 0.08 (3H, s, $OSiCH_3$), 0.04 (3H, s, $OSiCH_3$); ^{13}C NMR (100 MHz; $CDCl_3$) 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.

(2*S*,3*S*,4*R*,5*S*,6*R*)-6-(benzyloxy)-5-((tert-butyldimethylsilyl)oxy)-2-methyltetrahydro-2H-pyran-3,4-diol (VII)



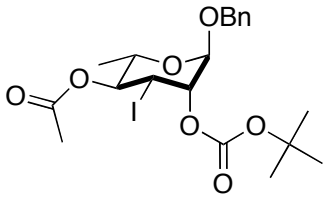
Colorless oil; R_f(30% EtOAc in hexane) = 0.28; $[\alpha]^{24}_D$= –107.5 (*c* 3.56, CH_2Cl_2); IR (thin film, cm^{-1}) ν 3453, 2951, 2928, 2897, 2856, 1251, 1129, 1096, 1026, 874, 836, 778; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.38 – 7.27 (5H, m, Ph), 4.82 (1H, d, $J_{1,2}$ 3.2, 1-H), 4.70 (1H, d, J_{AB} 12.0, $PhCH_2$), 4.53 (1H, d, J_{AB} 12.0, $PhCH_2$), 4.02 (1H, q, $J_{5,5\text{-Me}}$ 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, $J_{5\text{-Me},5}$ 6.8, 5-CH_3), 0.89 (9H, s, $OSiC(CH_3)_3$), 0.06 (3H, s, $OSiCH_3$), -0.00 (3H, s, $OSiCH_3$); ^{13}C NMR (100 MHz; $CDCl_3$) 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.

(2*R*,3*R*,6*S*)-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 CH_2Cl_2 (8.0 mL) under argon at 0 ºC. The resulting suspension was stirred until DMAP completely dissolved and added dropwise of $(Boc)_2O$ (906.5 mg, 4.15 mmol) solution in CH_2Cl_2 (1.5 mL). The reaction mixture was stirred at room temperature until TLC showed complete conversion (~ 2 hours). The mixture was diluted with Et_2O and quenched with saturated $NaHCO_3$ solution at 0 ºC. The resulting organic extract in Et_2O was subsequently washed with saturated aqueous NH_4Cl, saturated $NaHCO_3$, saturated brine solution and dried over $MgSO_4$. 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; $[\alpha]^{25}_D = -180.4$ (*c* 1.34, CH_2Cl_2); IR (thin film, cm^{-1}) ν 3089, 3065, 2980, 2934, 1737, 1274, 1255, 1163; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.38 – 7.26 (5H, m, Ph), 5.99 (1H, d, $J_{4,3}$ 10.4, 4-H), 5.86 (1H, dddd, $J_{3,4}$ 10.4, $J_{3,5}$ 5.2, $J_{3,2}$ 2.0, $J_{3,1}$ 1.6, 3-H), 5.02 (1H, s, 1-H), 4.80 (1H, d, J_{AB} 12.0, $PhCH_2$), 4.79 (1H, d, $J_{2,1}$ 1.6, 2-H), 4.63 (1H, d, J_{AB} 12.0, $PhCH_2$), 4.34 (1H, m, 5-H), 1.48 (9H, s, $OCOOC(CH_3)_3$), 1.31 (3H, d, $J_{5\text{-Me},5}$ 6.8, 5-CH_3); ^{13}C NMR (100 MHz; $CDCl_3$) 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.

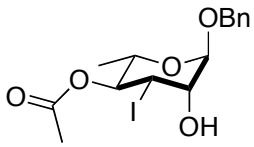
(2*S*,3*S*,4*R*,5*S*,6*R*)-6-(benzyloxy)-5-((tert-butoxycarbonyl)oxy)-4-iodo-2-methyltetrahydro-2H-pyran-3-yl acetate (15)



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 $NaHCO_3$ solution at 0 ºC. The resulting organic extract in EtOAc was subsequently washed with saturated aqueous $Na_2S_2O_3$, saturated brine solution and dried over Na_2SO_4. 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)

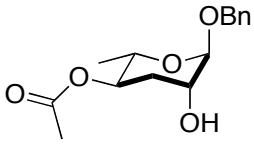
= 0.15; $[\alpha]^{20}_D$ = –42.1 (*c* 0.58, CH_2Cl_2); IR (thin film, cm^{-1}) ν 2982, 2933, 1747, 1371, 1277, 1221, 1122, 1046; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.39 – 7.31 (5H, m, Ph), 5.15 (1H, dd, $J_{4,5}$ 9.6, $J_{4,3}$ 9.6, 4-H), 5.04 (1H, dd, $J_{2,3}$ 2.4, $J_{2,1}$ 2.0, 2-H), 4.82 (1H, s, 1-H), 4.70 (1H, d, J_{AB} 12.0, $PhCH_2$), 4.54 (1H, dd, $J_{3,4}$ 9.6, $J_{3,2}$ 2.4, 3-H), 4.53 (1H, d, J_{AB} 12.0, $PhCH_2$), 3.87 (1H, dq, $J_{5,4}$ 9.6, $J_{5,5\text{-Me}}$ 6.8, 5-H), 2.11 (3H, s, $OCOCH_3$), 1.51 (9H, s, $OCOOC(CH_3)_3$), 1.20 (1H, d, $J_{5\text{-Me},5}$ 6.8, 5-CH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 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.

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



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 $Na_2S_2O_3$, saturated brine solution and dried over Na_2SO_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_2Cl_2); IR (thin film, cm^{-1}) ν 3485, 2972, 2938, 1738, 1375, 1223, 1123, 1044; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.39 – 7.31 (5H, m, 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_{AB} 12.0, $PhCH_2$), 4.57 (1H, dd, $J_{3,4}$ 9.6, $J_{3,2}$ 2.4, 3-H), 4.53 (1H, d, J_{AB} 12.0, $PhCH_2$), 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, $J_{5,5\text{-Me}}$ 6.4, 5-H), 2.38 (1H, d, $J_{OH,2}$ 4.4, OH), 2.11 (3H, s, $OCOCH_3$), 1.21 (3H, d, $J_{5\text{-Me},5}$ 6.4, 5-CH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 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.

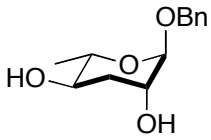
(2*S*,3*R*,5*R*,6*R*)-6-(benzyloxy)-5-hydroxy-2-methyltetrahydro-2H-pyran-3-yl acetate (VIII)



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; $[\alpha]^{23}_D$= –97.8 (*c* 5.05, CH_2Cl_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, $J_{4,3}$ 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), 2.48 (1H, br, OH), 2.14 (1H, ddd, $J_{3,3}$ 13.2, $J_{3,4}$ 4.8, $J_{3,2}$ 3.6, 3-H), 2.04 (3H, s, $OCOCH_3$), 1.93 (1H, ddd, $J_{3,3}$ 13.2, $J_{3,4}$ 9.6, $J_{3,2}$ 2.8, 3-H), 1.20 (3H, d, $J_{5\text{-Me},5}$ 6.4, 5-H); ^{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.

(2*R*,3*R*,5*R*,6*S*)-2-(benzyloxy)-6-methyltetrahydro-2H-pyran-3,5-diol (4)[10]



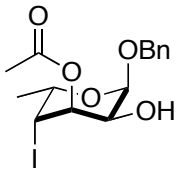
A solution of acetate **VIII** (32.4 mg, 0.116 mmol) in MeOH (0.6 mL) was added K_2CO_3 (32 mg, 0.231 mmol) at room temperature. The reaction mixture was stirred for 30 minutes at room temperature and cooled to 0 ºC after TLC showed complete hydrolysis. The mixture was diluted with Et_2O and added 1N HCl (~1 mL) dropwise to quench the reaction. The mixture was extracted with Et_2O (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, $J_{5,5\text{-Me}}$ 6.4, 5-H), 3.63 (1H, m, 4-H), 2.09 (1H, ddd, $J_{3,3}$ 13.2, $J_{3,4}$ 3.6, $J_{3,2}$ 3.6, 3-H), 1.88 (1H, ddd, $J_{3,3}$ 13.2, $J_{3,4}$ 13.2, $J_{3,2}$ 2.8, 3-H), 1.62 (1H, s, OH), 1.54 (1H, s, OH), 1.30 (1H, d, $J_{5\text{-Me},5}$ 6.4, 5-Me); ^{13}C NMR (100 MHz; $CDCl_3$) δ 137.61, 128.67(2C), 128.15(2C), 128.06, 98.38, 70.04, 69.21, 68.94, 68.26, 35.39, 17.91; HRMS calcd for $[C_{13}H_{18}O_4+H]^+$ 239.0202, found 239.0204.

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.

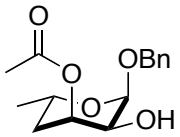
The reaction mixture was stirred for 1 hour at 0 ºC. Water was added dropwise to quench the reaction, and the mixture was extracted with Et_2O. The organic layer was washed with saturated brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography to give obtain α-ascarylose **4** (8.5 mg, 0.036 mmol, 82%) as colorless oil.

(2*R*,3*S*,4*R*,5*R*,6*S*)-2-(benzyloxy)-3-hydroxy-5-iodo-6-methyltetrahydro-2H-pyran-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 $NaHCO_3$ solution at 0 ºC. The resulting organic extract in EtOAc was subsequently washed with saturated aqueous $Na_2S_2O_3$, saturated brine solution and dried over Na_2SO_4. The crude product was concentrated under reduced pressure and purified via silica gel flash chromatography eluting with 10% EtOAc in petroleum ether to give iodo-acetate **18** (55 mg, 0.135 mmol, 74%) as white solid; mp 89 – 90 ºC; *Rf* (30% EtOAc in petroleum ether) = 0.48; $[\alpha]^{23}_D$= –140.8 (*c* 3.17, CH_2Cl_2); IR (thin film, cm^{-1}) ν 2971, 2940, 1744, 1455, 1399, 1229, 1042; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.37 – 7.29 (5H, m, Ph), 5.31 (1H, dd, $J_{3,2}$ 3.6, $J_{3,4}$ 3.6, 3-H), 4.96 (1H, d, $J_{1,2}$ 3.6, 1-H), 4.81 (1H, d, J_{AB} 12.0, $PhCH_2$), 4.58 (1H, d, J_{AB} 12.0, $PhCH_2$), 4.46 (1H, ddd, $J_{2,2\text{-OH}}$ 11.0, $J_{2,1}$ 3.6, $J_{2,3}$ 3.6, 2-H), 4.28 (1H, dd, $J_{4,3}$ 2.8, $J_{4,5}$ 2.0, 4-H), 3.30 (1H, dq, $J_{5,5\text{-Me}}$ 6.4, $J_{5,4}$ 2.0, 5-H), 2.48 (1H, d, $J_{OH,2}$ 11.0, OH), 2.13 (3H, s, $OCOCH_3$), 1.10 (3H, d, $J_{5\text{-Me},5}$ 6.4, 5-CH_3); ^{13}C NMR (100 MHz; $CDCl_3$) 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.

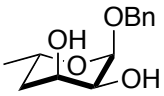
(2*R*,3*S*,4*S*,6*S*)-2-(benzyloxy)-3-hydroxy-6-methyltetrahydro-2H-pyran-4-yl acetate (VIIII)



A solution of iodo-acetate **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 **VIIII** (166 mg, 0.592

mmol, 93%) as colorless gel; *Rf* (30% EtOAc in hexane) = 0.17; $[\alpha]^{22}_{D}$= –63.1 (*c* 5.04, CH_2Cl_2); IR (thin film, cm^{-1}) ν 3437, 2972, 2918, 1734, 1238, 1130, 1042, 735, 697; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.40 – 7.27 (5H, m, Ph), 5.17 (1H, ddd, $J_{3,2}$ 3.6, $J_{3,4}$ 3.6, $J_{3,4}$ 2.4, 3-H), 4.95 (1H, d, $J_{1,2}$ 4.4, 1-H), 4.86 (1H, d, J_{AB} 12.0, $PhCH_2$), 4.52 (1H, d, J_{AB} 12.0, $PhCH_2$), 4.09 (1H, ddd, $J_{5,4}$ 13.2, $J_{5,5\text{-Me}}$ 6.4, $J_{5,4}$ 2.4, 5-H), 3.73 (1H, ddd, $J_{2,OH}$ 10.0, $J_{2,1}$ 3.6, $J_{2,3}$ 3.6, 2-H), 2.58 (1H, d, $J_{OH,2}$ 10.0, OH), 2.10 (3H, s, $OCOCH_3$), 1.96 (1H, ddd, $J_{4,4}$ 14.4, $J_{4,5}$ 2.4, $J_{4,3}$ 2.4, 4-H), 1.61 (1H, ddd, $J_{4,4}$ 14.4, $J_{4,5}$ 13.2, $J_{4,3,}$ 3.6, 4-H), 1.14 (3H, d, $J_{5\text{-Me},5}$ 6.4, 5-CH_3); ^{13}C NMR (100 MHz; $CDCl_3$) 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.

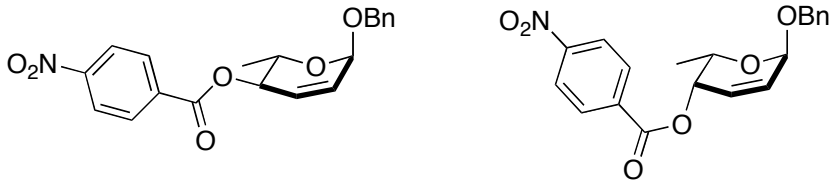
(2*R*,3*S*,4*S*,6*S*)-2-(benzyloxy)-6-methyltetrahydro-2H-pyran-3,4-diol (19)



A solution of acetate **VIIII** (45.8 mg, 0.163 mmol) in MeOH (0.80 mL) was added K_2CO_3 (45 mg, 0.326 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_2O and added 1N HCl (~1 mL) dropwise to quench the reaction. The reaction mixture was extracted with Et_2O (3x), and washed the organic extract with saturated aqueous $NaHCO_3$, saturated brine solution and dried over $MgSO_4$. 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; $[\alpha]^{21}_{D}$= –80.1 (*c* 1.78, CH_2Cl_2); IR (thin film, cm^{-1}) ν 3492, 2971, 2931, 1096, 1050, 740, 699; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.39 – 7.30 (5H, m, Ph), 4.97 (1H, d, $J_{1,2}$ 3.6, 1-H), 4.78 (1H, d, J_{AB} 12.0, $PhCH_2$), 4.54 (1H, d, J_{AB} 12.0, $PhCH_2$), 4.08 (1H, ddd, $J_{5,4}$ 12.8, $J_{5,5\text{-Me}}$ 6.4, $J_{5,4}$ 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, $J_{4,4}$ 14.4, $J_{4,5}$ 3.2, $J_{4,3}$ 2.8, 4-H), 1.62 (ddd, $J_{4,4}$ 14.4, $J_{4,5}$ 12.8, $J_{4,3}$ 2.8, 4-H), 1.21 (3H, d, $J_{5\text{-Me},5}$ 6.4, 5-CH_3); ^{13}C NMR (100 MHz; $CDCl_3$) 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 $LiAlH_4$ (4 mg, 0.105 mmol) at 0 ºC. 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_2O. The organic layer was washed with saturated brine, dried over Na_2SO_4, 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 S_N2' nucleophilic substitution of allylic alcohol 7 under Mitsunobu reaction: (2*S*,3*R*,6*R*)-6-(benzyloxy)-2-methyl-3,6-dihydro-2H-pyran-3-yl 4-nitrobenzoate (Xa) and (2*S*,3*S*,6*R*)-6-(benzyloxy)-2-methyl-3,6-dihydro-2H-pyran-3-yl 4-nitrobenzoate (Xb)

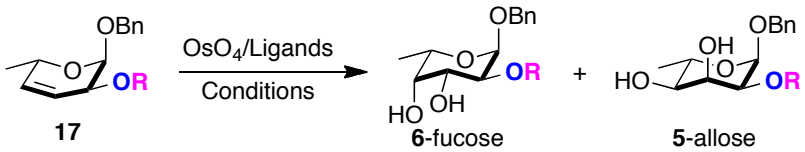


A THF (4.5 mL) solution of allylic alcohol **7** (147 mg, 0.667 mmol) at 0 ºC were added triphenylphosphine (PPh_3) (262.2 mg, 1.00 mmol) and *p*-nitrobenzoic acid (223 mg, 1.33 mmol). Diisopropyl azodicarboxylate (DIAD) (202.4 mg, 1.00 mmol) in THF (1.0 mL) was added dropwise to the mixture, and the reaction mixture was slowly warm up to room temperature and stirred for 12 hours. The reaction was diluted with Et_2O, quenched with saturated aqueous $NaHCO_3$, and extract with Et_2O. The compound was dried over $MgSO_4$ 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; $[\alpha]^{22}_D$= –76.8 (*c* 2.34, CH_2Cl_2); IR (thin film, cm^{-1}) ν 3056, 3032, 2930, 2934, 1725, 1527, 1262, 1102, 1047, 1015, 719; ^{1}H NMR (400 MHz; $CDCl_3$) 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, $J_{2,3}$ 10.4, 2-H), 5.92 (1H, d, $J_{3,2}$ 10.4, $J_{3,5}$ 2.4, $J_{3,4}$ 1.6, 3-H), 5.37 (dd, $J_{4,5}$ 9.6, $J_{4,3}$ 1.6, 4-H), 5.13 (1H, s, 1-H), 4.82 (1H, d, J_{AB} 12.0, $PhCH_2$), 4.65 (1H, d, J_{AB} 12.0, $PhCH_2$), 4.21 (1H, dq, $J_{5,4}$ 9.6, $J_{5,5\text{-Me}}$ 6.4, 5-H), 1.27 (3H, d, $J_{5\text{-Me},5}$ 6.4, 5-CH_3); ^{13}C NMR (100 MHz; $CDCl_3$) 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; $[\alpha]^{22}_D$= –151.5 (*c* 0.97, CH_2Cl_2); IR (thin film, cm^{-1}) ν 3057, 3032, 2984, 2936, 1720, 1528, 1344, 1269, 1101, 1023, 719; ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.29 (2H, d, J_{HCCH} 9.0, PNB), 8.24 (2H, d, J_{HCCH} 9.0, PNB), 7.42 – 7.28 (5H, m, Ph), 6.21 (1H, dd, $J_{3,2}$ 10.4, $J_{3,4}$ 5.2, 3-H), 6.11 (1H, dd, $J_{2,3}$ 10.4, $J_{2,1}$ 2.4, 2-H), 5.19 (1H, d, $J_{1,2}$ 2.4, 1-H), 5.17 (1H, dd, $J_{4,3}$ 5.2, $J_{4,5}$ 2.0, 4-H), 4.81 (1H, d, J_{AB} 11.6, $PhCH_2$), 4.66 (1H, d, J_{AB} 11.6, $PhCH_2$), 4.39 (1H, qd, $J_{5,5\text{-Me}}$ 6.8, $J_{5,4}$ 2.0, 5-H), 1.26 (3H, d, $J_{5\text{-Me},5}$ 6.8, 5-CH_3); ^{13}C NMR (100 MHz; $CDCl_3$) 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.

Ligand	MW	Ligand	MW	Ligand	MW
DHQ	363	$(DHQD)_2PHAL$	779	$(DHQD)_2DPP$	933
DHQD	363	$(DHQD)_2AQN$	857	(DHQD)PHN	502
$(DHQ)_2PHAL$	779	$(DHQD)_2Pyr$	881	(DHQ)-4-Me-Quin	468

Table 2. Optimization of OsO_4 Dihydroxylation.



17 **6**-fucose **5**-allose

A = 1% OsO_4, 1 M NMO/H_2O (1:1), 0.3 M *t*-BuOH/Acetone, 0 ºC
B = 4% OsO_4, 1 M NMO/H_2O (1:1), 0.3 M CH_2Cl_2, 0 ºC
C = 4% $K_2OsO_2(OH)_4$, 10% **Ligand**, 3 eq $K_3Fe(CN)_6$, 3 eq K_2CO_3, 3 eq $MeSO_2NH_2$, 0.05 M *t*-BuOH/H_2O (1:1), 0 ºC
D = 20% OsO_4, NMO/H_2O (70% w/v), 50% **Ligand** or w/o ligand, 0.03 M CH_2Cl_2, –78 ºC
E = 1 eq OsO_4, 1.5 eq TMEDA, 0.05 M CH_2Cl_2, –78 ºC

Entry	R	Condition	Ligand	ratio (**6** : **5**) [a]	Yield (%) [b]
1	—H	**A**	———	2 : 1	95
2	—H	**B**	———	1 : 3	84
3	—H	**D**	———	1 : 4	80
4	—H	**E**	———	2 : 1	65
5	—H	**C**	$(DHQ)_2PHAL$	1 : 1.5	94
6	—H	**C**	$(DHQD)_2PHAL$	1 : 1.2	89
7	—H	**C**	$(DHQD)_2AQN$	1 : 1	85
8	—H	**C**	$(DHQD)_2Pyr$	1 : 3	88
9	—H	**C**	$(DHQD)_2DPP$	1 : 5	97
10	—H	**D**	DHQ	1 : 6	88
11	—H	**D**	DHQD	1 : 1	82
12	—H	**D**	$(DHQ)_2PHAL$	1 : 4	85
13	—H	**D**	$(DHQD)_2PHAL$	1 : 2	88
14	—H	**D**	$(DHQD)_2AQN$	1 : 3	82
15	—H	**D**	$(DHQD)_2Pyr$	1 : 4	78
16	—H	**D**	$(DHQD)_2DPP$	<1 : 10	92
17	—H	**D**	(DHQD)PHN	1 : 2.7	87
18	—H	**D**	(DHQ)4-Me-2-Quin	1 : 2.6	83
19	—Piv	**A**	———	5 : 1	90
20	—TBS	**A**	———	7 : 1	95

[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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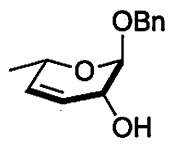

(600 MHz, $CDCl_3$)

7

LW-DIG-221-allylic-OH-13C

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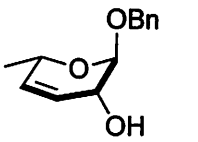

(150 MHz, $CDCl_3$)

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LW-DIG-224-altrose-1H

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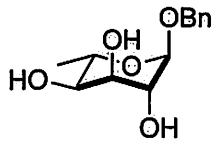

(600 MHz, $CDCl_3$)

3

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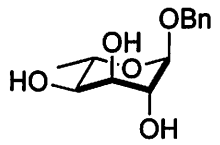

(150 MHz, $CDCl_3$)

3

LW-DIG-225-a-L-C3-C4-dideoxy-rhamnose-1H

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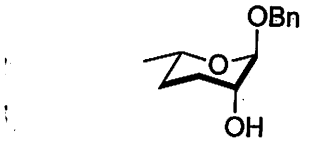
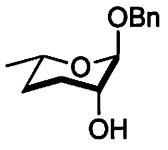


(600 MHz, $CDCl_3$)

12

LW-DIG-225-a-L-C3-C4-dideoxy-rhamnose-13C

Pulse Sequence: s2pul



(150 MHz, $CDCl_3$)

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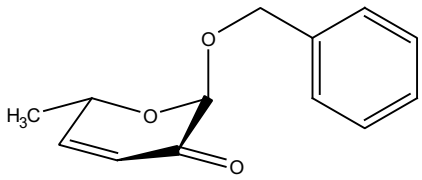

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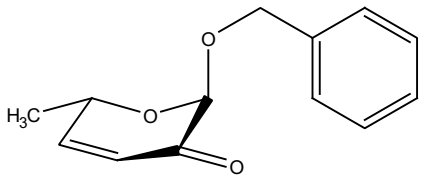

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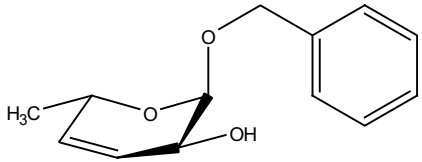

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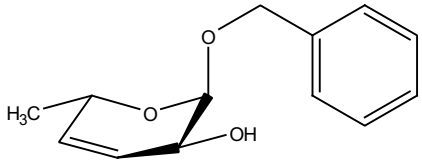

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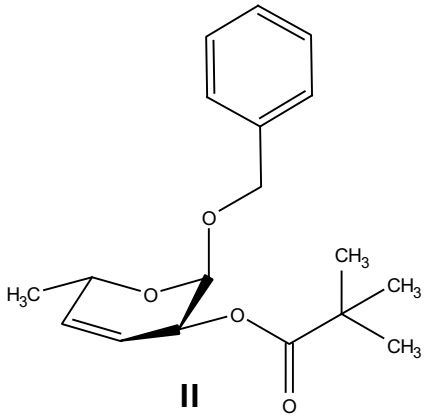

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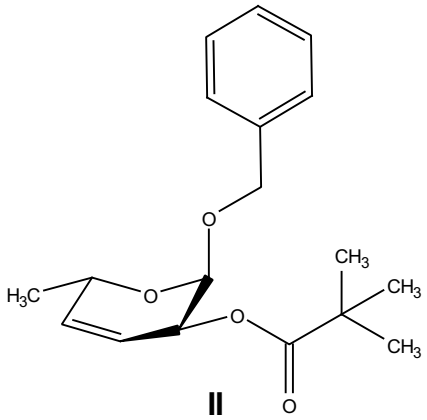

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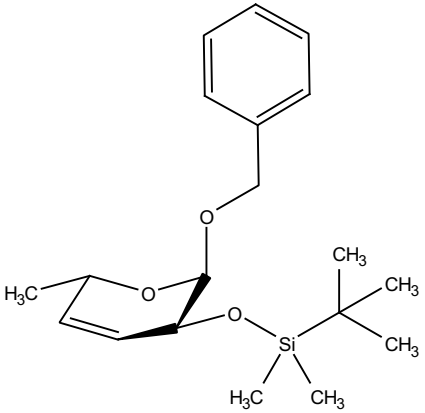

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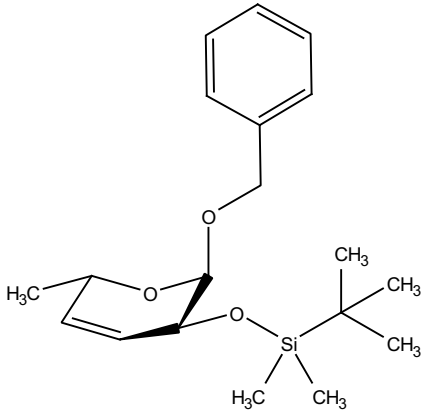

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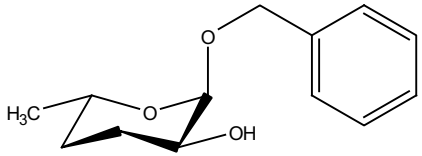

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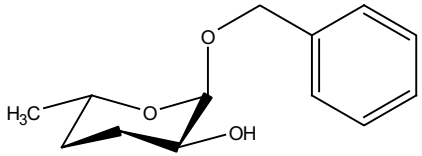

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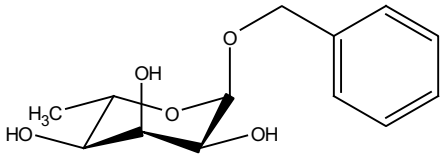

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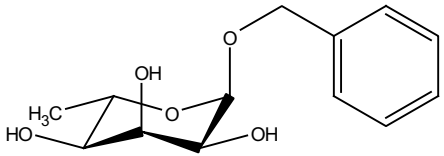

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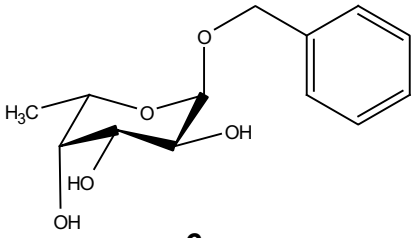

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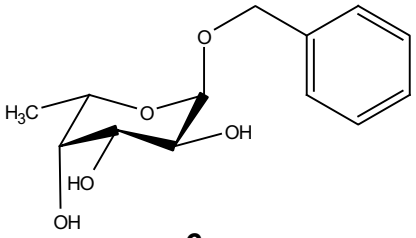

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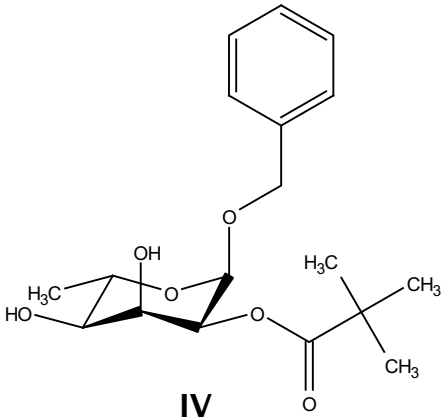

IV

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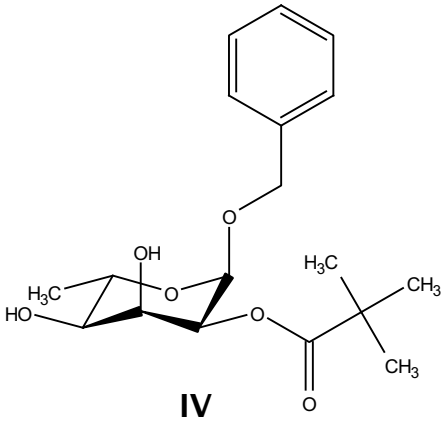

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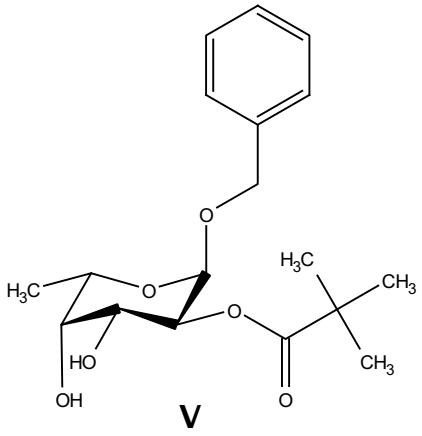

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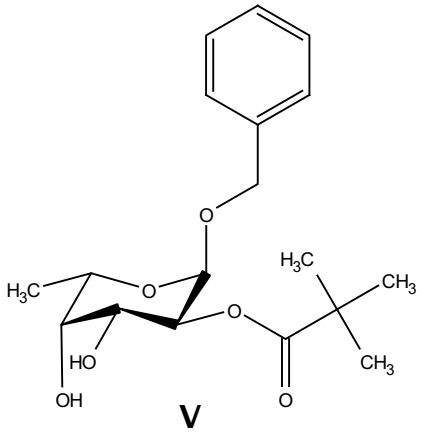

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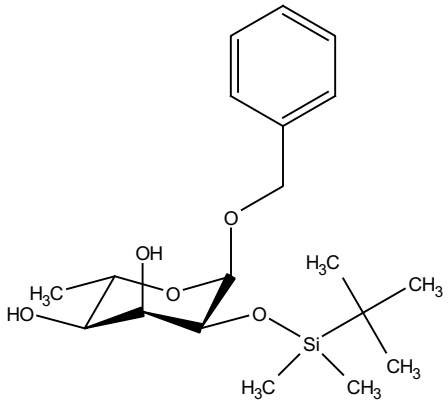

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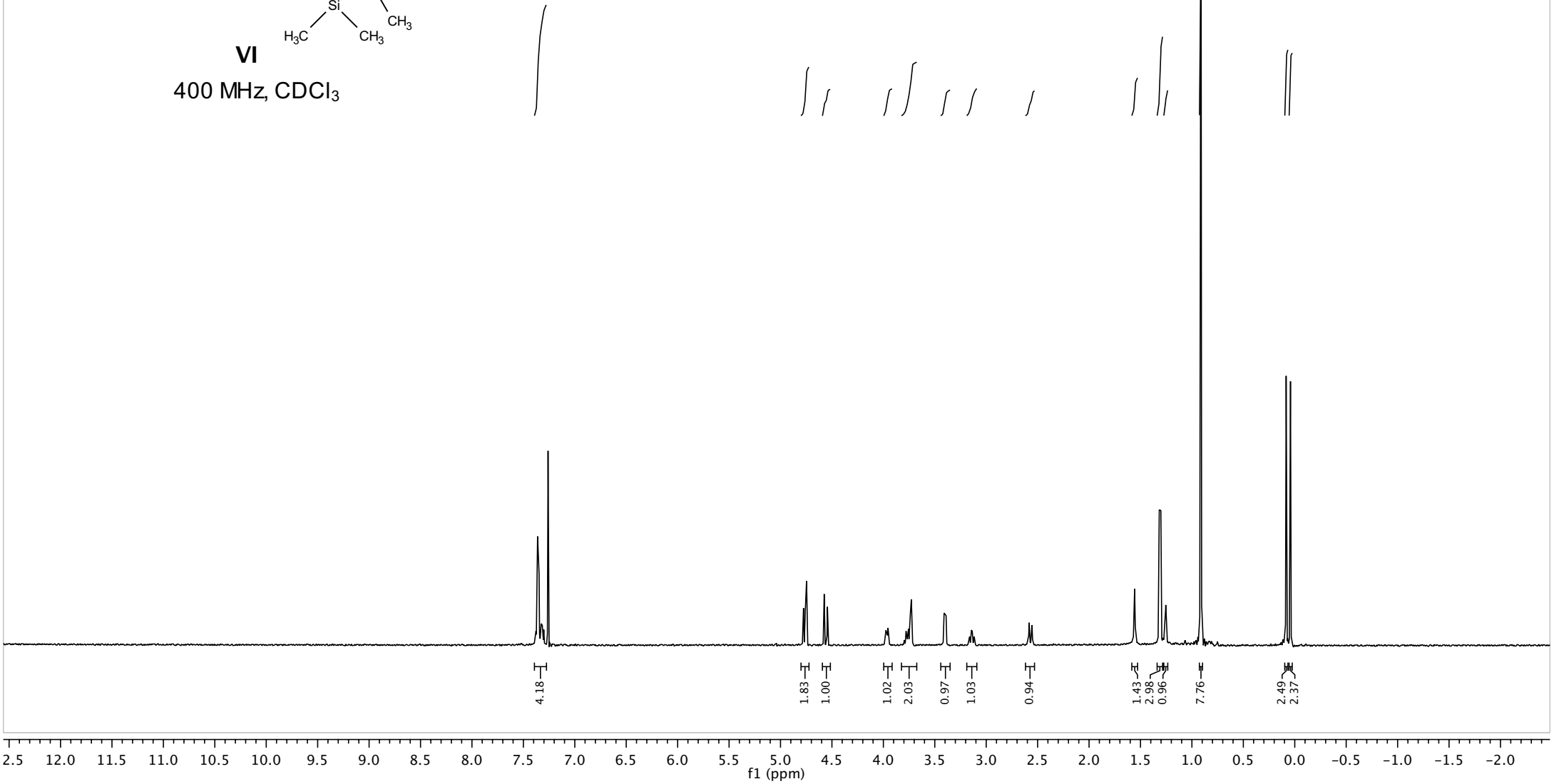

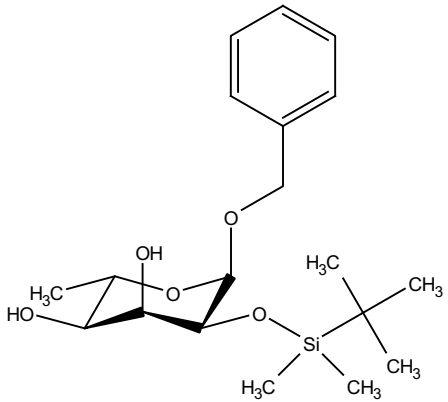

VI

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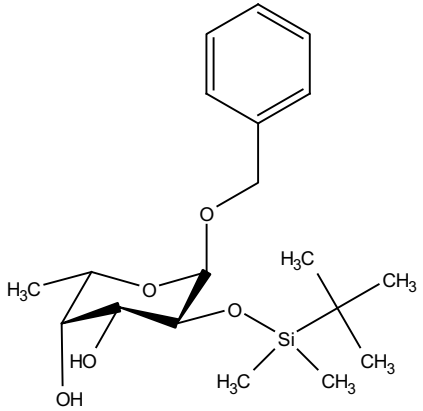
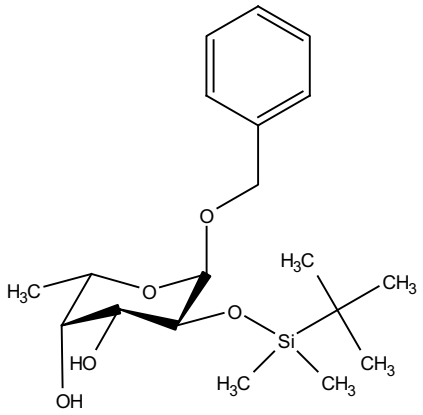


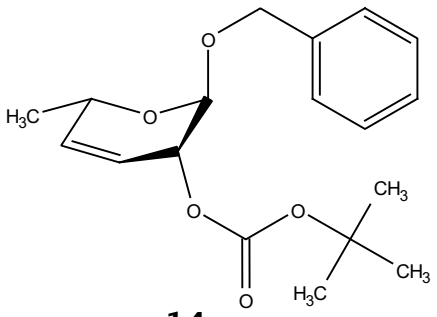
VII

400 MHz, $CDCl_3$



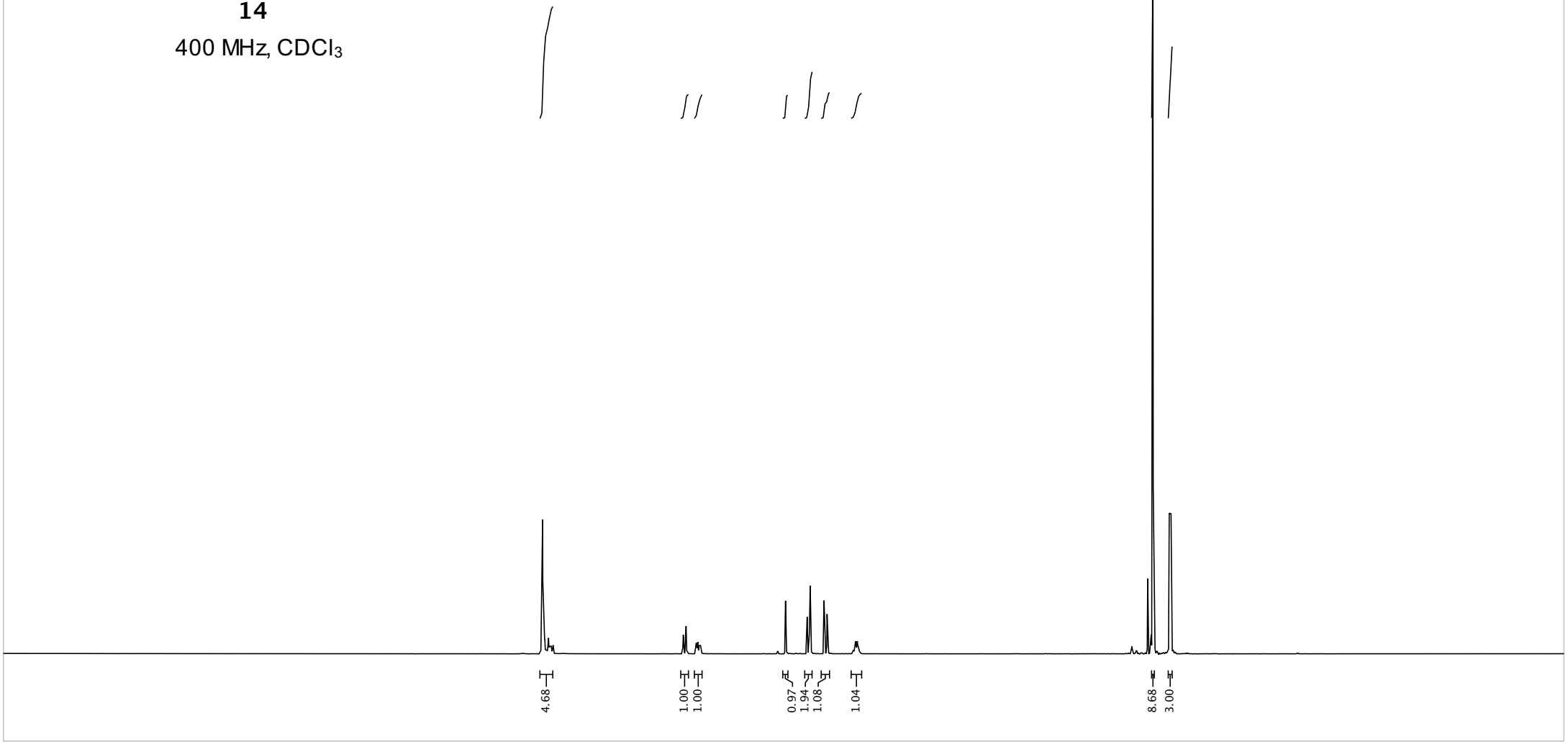
VII

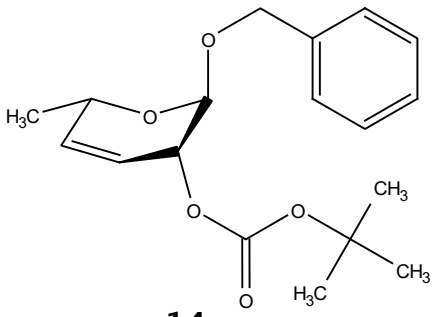
100 MHz, $CDCl_3$



14

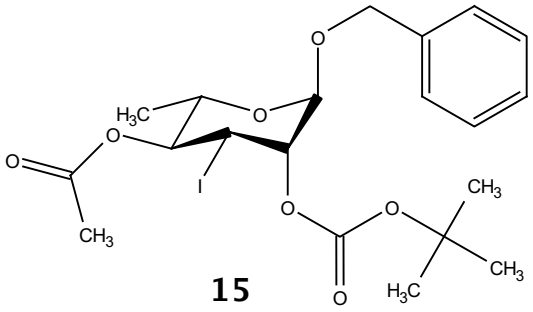
400 MHz, $CDCl_3$





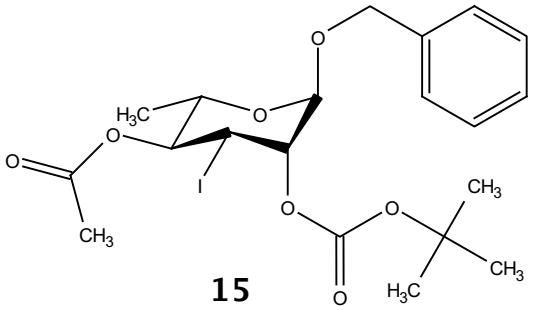
14

100 MHz, $CDCl_3$



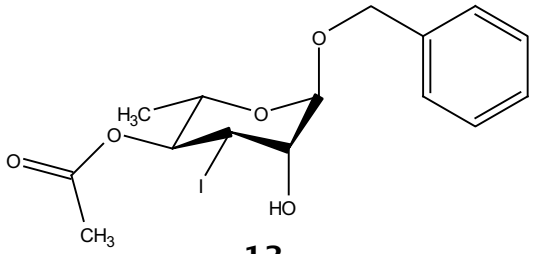
15

400 MHz, $CDCl_3$



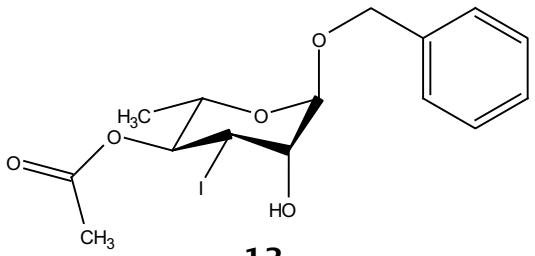
15

100 MHz, $CDCl_3$



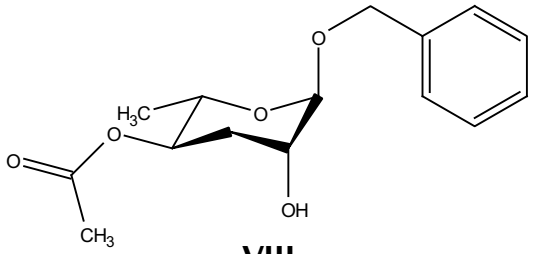
13

400 MHz, $CDCl_3$



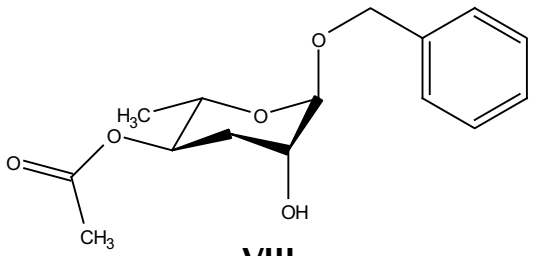
13

100 MHz, $CDCl_3$



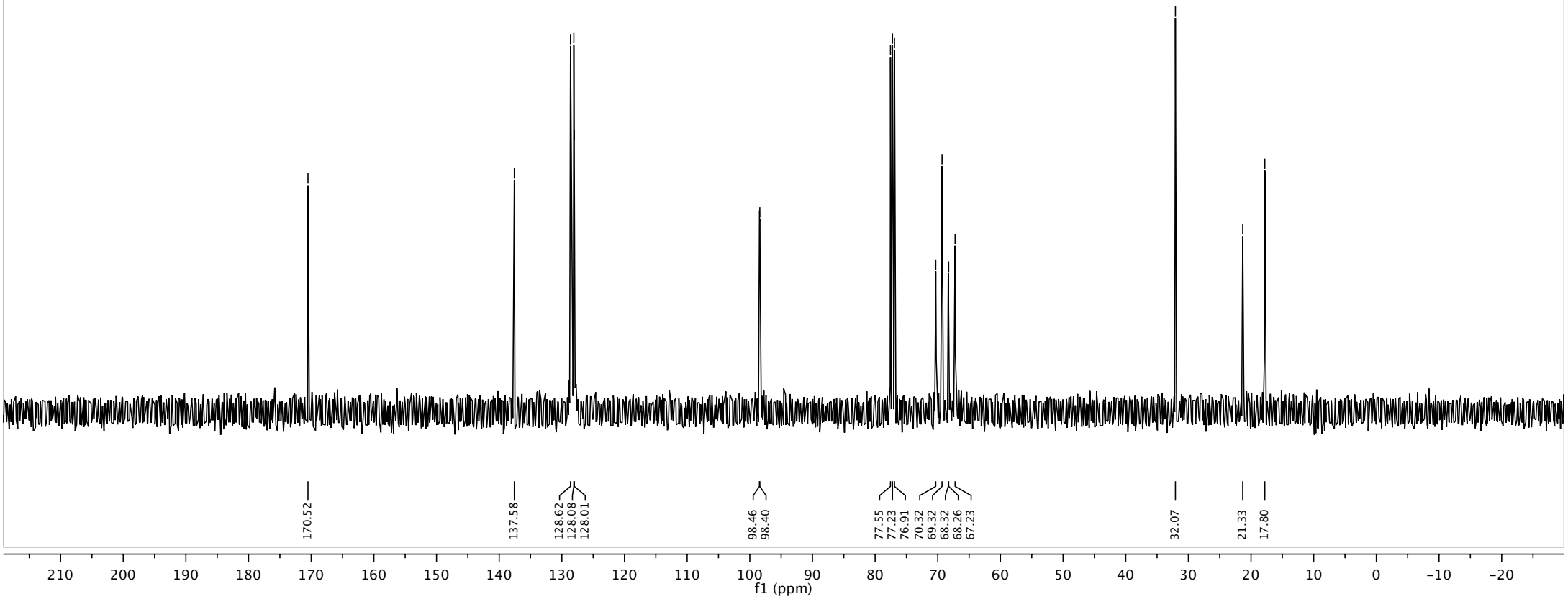
VIII

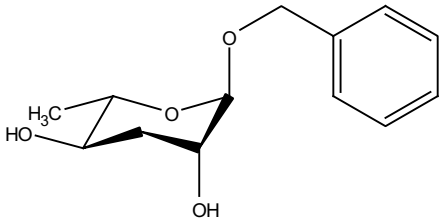
400 MHz, $CDCl_3$



VIII

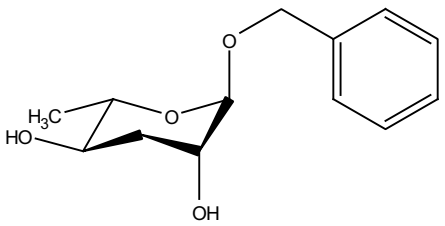
100 MHz, $CDCl_3$





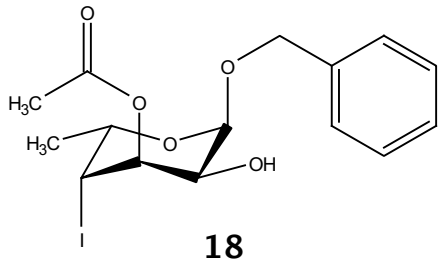
4

400 MHz, $CDCl_3$



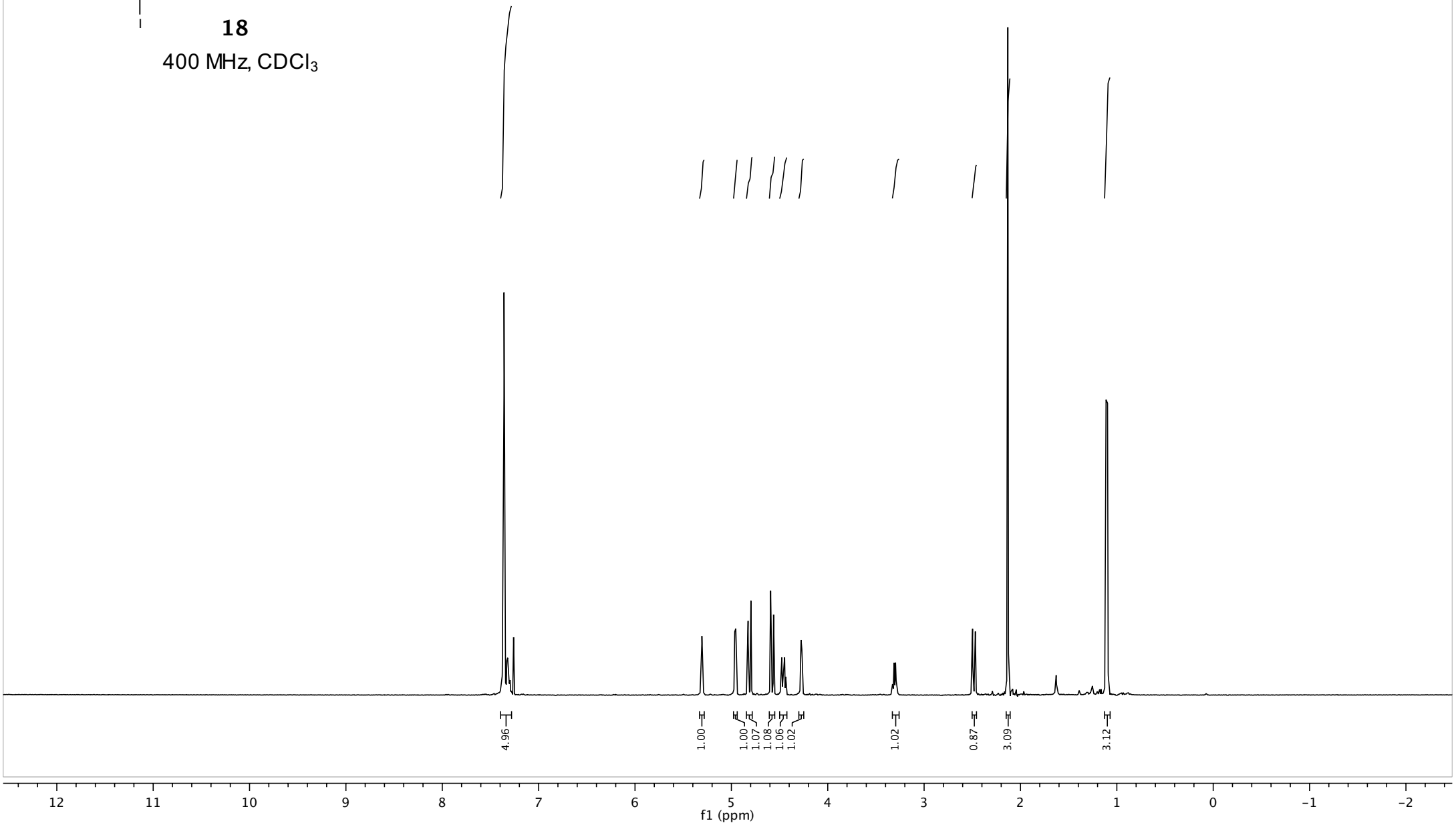
4

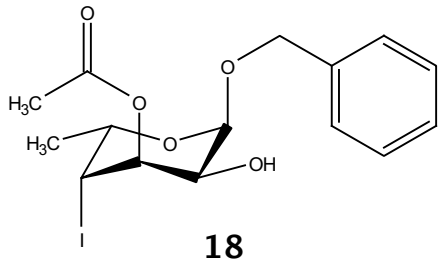
100 MHz, $CDCl_3$



18

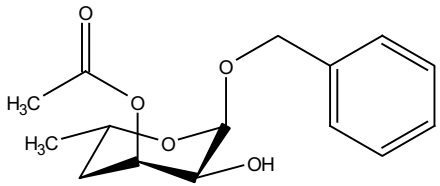
400 MHz, $CDCl_3$





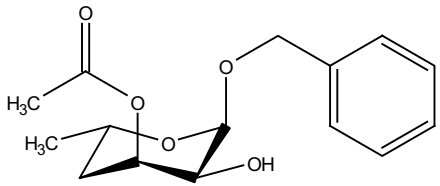
18

100 MHz, $CDCl_3$



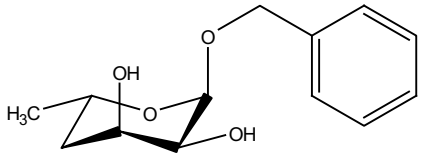
VIIII

400 MHz, $CDCl_3$



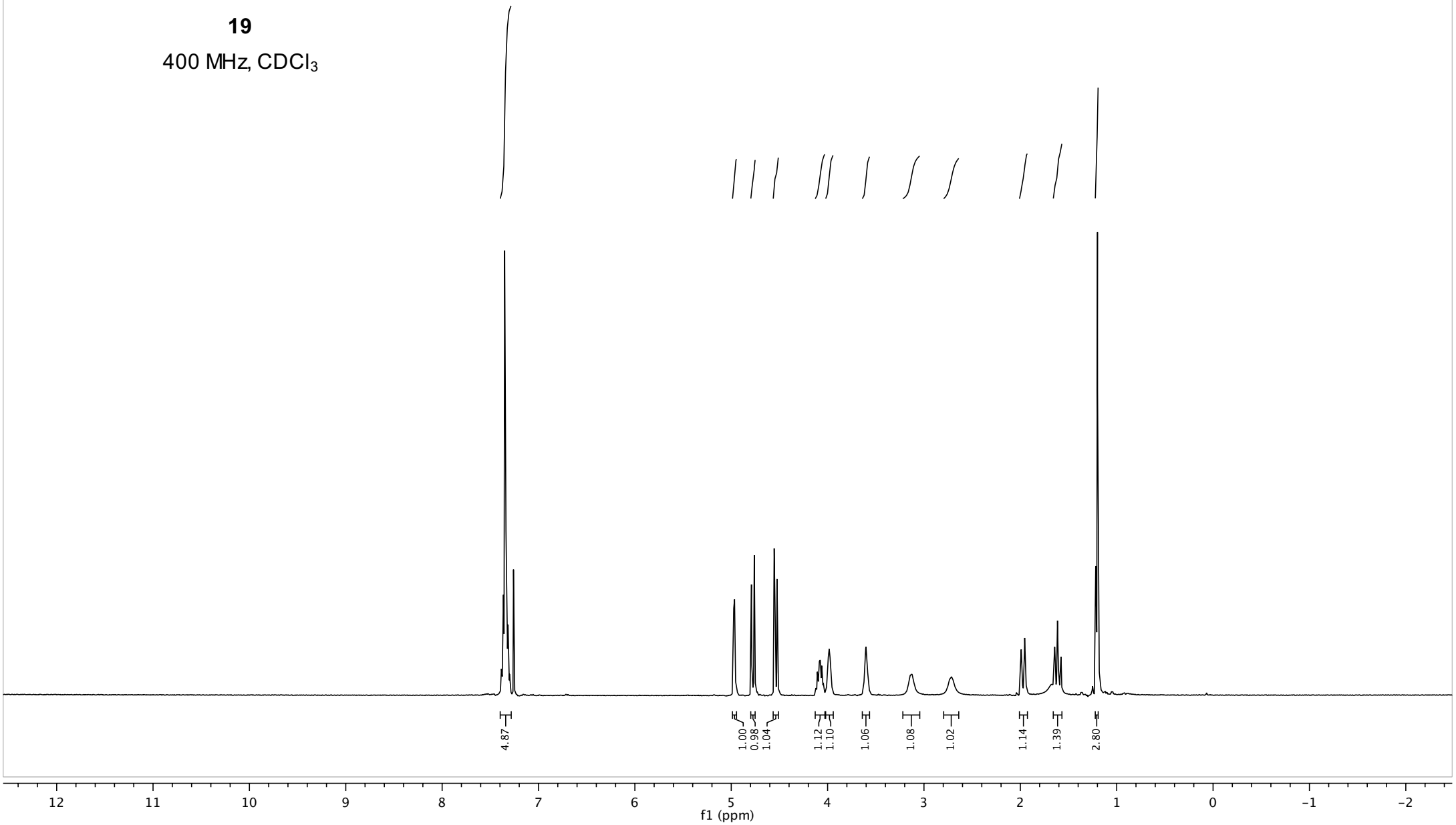
VIIII

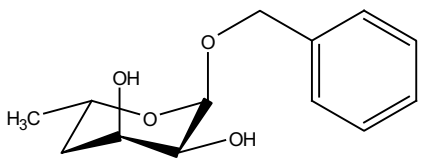
100 MHz, $CDCl_3$



19

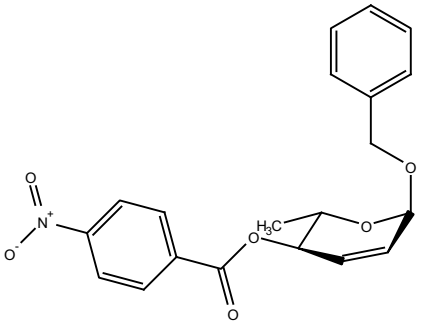
400 MHz, $CDCl_3$





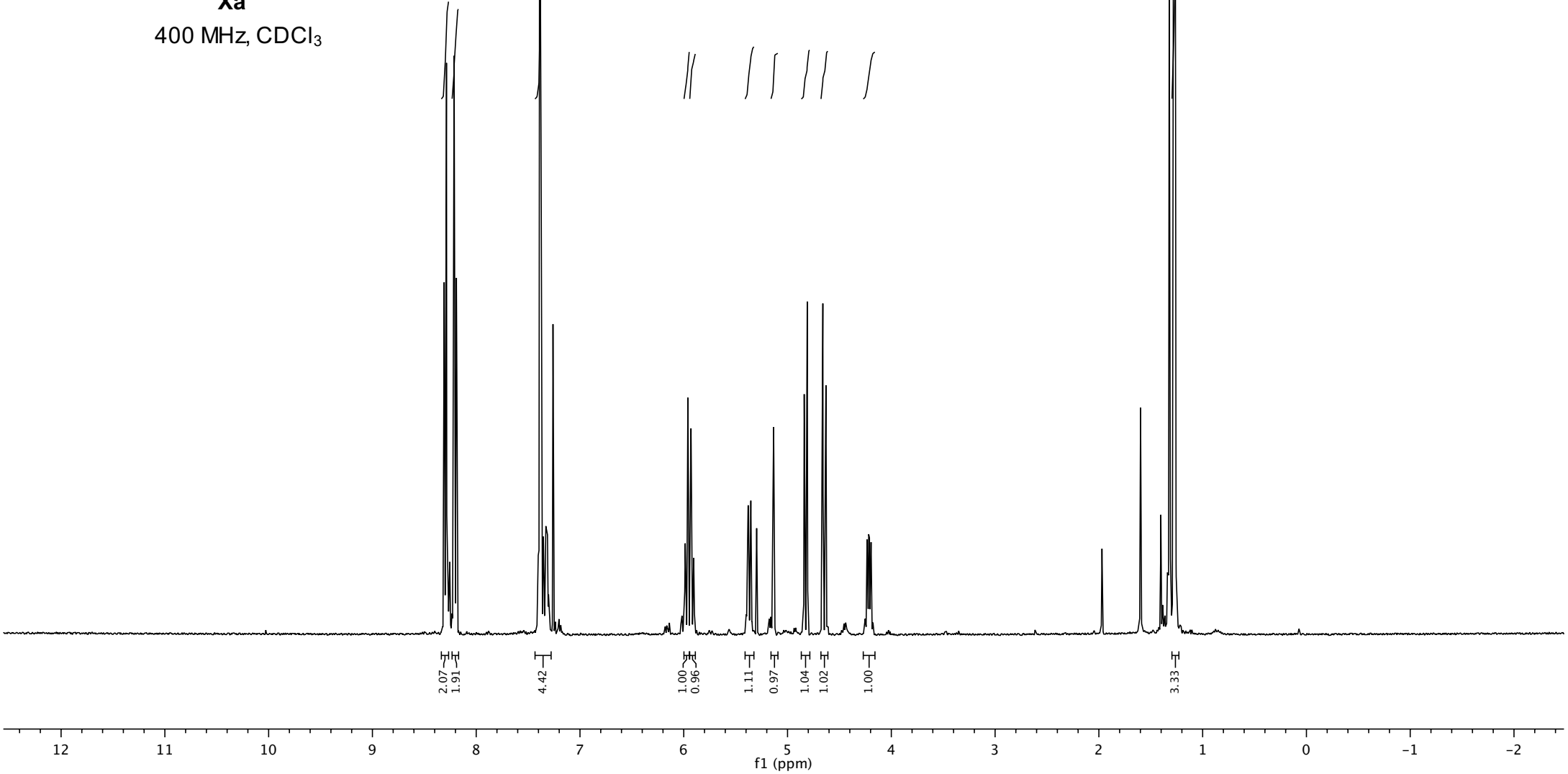
19

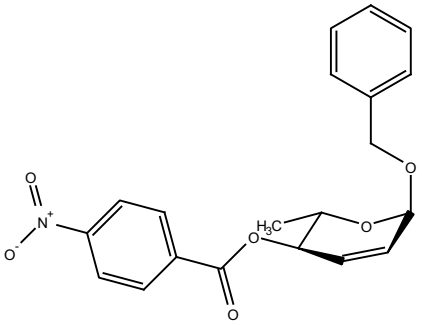
100 MHz, $CDCl_3$



Xa

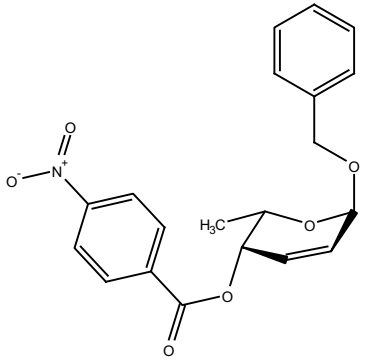
400 MHz, $CDCl_3$





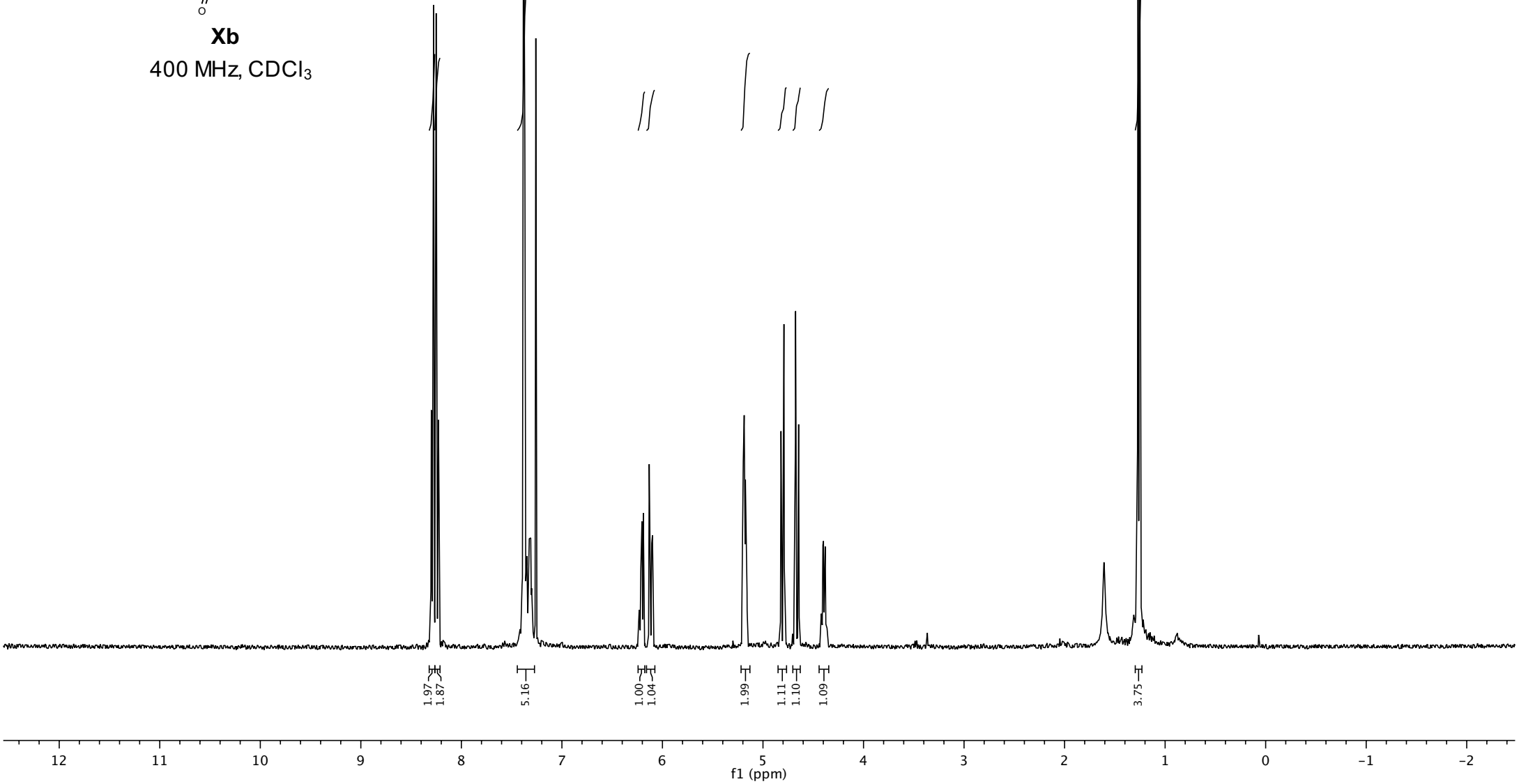
Xa

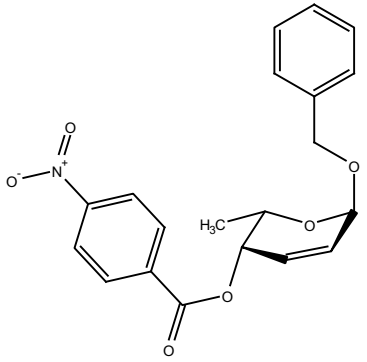
100 MHz, $CDCl_3$



Xb

400 MHz, $CDCl_3$





Xb

100 MHz, $CDCl_3$