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Supplementary Material for:

Synthesis of Carbon-Linked Glycopeptides Through Catalytic Asymmetric Hydrogenation

Sheryl D. Debenham, John S. Debenham, Mark J. Burk, and Eric J. Toone*

Paul M. Gross Chemical Laboratory, Department of Chemistry
Duke University, Durham, NC 27708

General experimental: All reactions were conducted under an inert argon atmosphere. THF and toluene were distilled from sodium benzophenone ketyl. Dichloromethane was distilled from calcium hydride. Methanol, ethanol and isopropanol were distilled from magnesium. Solutions of compounds in organic solvents were dried over sodium sulfate prior to rotary evaporation. TLC plates were Kieselgel 60 F254 (Merck Art. 5554). Carbohydrate compounds were visualized on the TLC plate by charring with H_2SO_4/EtOH/H_2O (1:10:10). Flash column chromatography was done with silica gel 60 (230-400 mesh, Merck). ^1H and ^{13}C NMR spectra were recorded on a Varian Inova-400 spectrometer. Abbreviations for NMR data are as follows: s= singlet, bs= broad singlet, d= doublet, bd= broad doublet, m= multiplet, dd= doublet of doublets, t= triplet, bt= broad triplet. Coupling constants are reported in Hertz and chemical shifts are in ppm on the delta scale . ^1H and ^{13}C chemical shifts are reported relative to internal tetramethylsilane (0.00 ppm). Although not technically correct, compounds are named as derivatives as the corresponding *O*-glycosides for ease of identification.

General procedure for preparation of enamide esters: To methyl α-(dimethoxyphosphoryl)-*N*-*t*-butyloxycarbonylglycinate (435.0 mg, 1.1 eq) in dry THF (2 mL) at -78°C was added tetramethylguanidine (184 μL, 1.1 eq). The solution was allowed to stir for 10 min at -78°C. Following addition of the appropriate *C*-glycosyl aldehyde (500.0 mg, 1.334 mmol), the reaction stirred for 1 h at rt. The solution was diluted with 100 mL EtOAc and washed with 1N HCl and subsequently satd $NaHCO_3$. The reaction mixture was concentrated and the compound purified *via* chromatography eluding with 1:1 EtOAc/hexanes to afford the enamide ester.

Methyl 4-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-2-ene-2-(*N*-*t*-butyloxycarbonyl)butenoate (1): Yield, 85%; ^1H NMR (400 MHz, $CDCl_3$) δ 6.58-

6.54 (bt, J=7.2 Hz, 1H), 6.20 (bs, 1H), 5.34-5.30 (m, 2H), 5.12-5.08 (dd, J=5.6, 9.2 Hz, 1H), 4.99-4.94 (t, J=8.8 Hz, 1H), 4.37-4.31 (m, 1H), 4.28-4.23 (dd, J=6.0, 12.2 Hz, 1H), 4.08-4.04 (dd, J=2.8, 12.2 Hz, 1H), 3.90-3.86, (m, 1H), 3.78 (s, 3H), 2.77-2.69 (m, 1H), 2.08 (s, 3H), 2.05 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.65, 170.05, 169.85, 169.57, 129.78, 71.25, 70.09, 69.96, 69.34, 68.52, 62.16, 52.49, 28.16, 25.81, 20.65. Anal. Calcd for $C_{24}H_{35}NO_{13}$: C, 52.84; H, 6.47; N, 2.57. Found: C, 52.72; H, 6.54; N, 2.51.

Methyl 4-(2,3,4,6-Tetra-*O*-acetyl-α-D-galacopyranosyl)-2-ene-2-(*N*-*t*-butyloxycarbonyl)butenoate (2). Yield, 79%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.45-6.42 (bt, J=6.8 Hz, 1H), 6.24 (bs, 1H), 5.32-5.31 (t, J=2.8 Hz, 1H), 5.19-5.09 (m, 2H), 4.28-4.19 (m, 2H), 3.95-3.91 (dd, J=4.4, 11.4 Hz, 1H), 4.06-3.98 (m, 1H), 3.67 (s, 3H), 2.60-2.48 (m, 1H), 2.37-2.26 (m, 1H), 2.01 (s, 3H), 1.97 (s, 3H), 1.94 (s, 3H), 1.93 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.40, 169.78, 169.59, 169.55, 152.97, 133.80, 130.09, 129.26, 128.72, 127.86, 80.54, 73.38, 68.68, 68.16, 67.66, 67.11, 61.07, 57.15, 52.19, 29.02, 27.95, 25.95, 20.52, 20.39. Anal. Calcd for $C_{24}H_{35}NO_{13}\bullet H_2O$: C, 51.15; H, 6.62; N, 2.45. Found: C, 51.03; H, 6.39; N, 2.49.

Methyl 4-(2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl)-2-ene-2-(*N*-*t*-butyloxycarbonyl)butenoate (3): Yield, 88%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.56-6.53 (bt, J=6.4 Hz, 1H), 6.32 (bs, 1H), 5.29-5.26 (dd, J=3.6, 7.8 Hz, 1H), 5.20-5.10 (m, 2H), 4.50-4.45 (dd, J=7.6, 12.2 Hz, 1H), 4.15-4.05 (m, 2H), 3.98-3.93 (m, 1H), 3.78 (s, 3H), 2.70-2.62 (m, 1H), 2.56-2.49 (m, 1H), 2.10 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.51, 169.87, 169.58, 169.49, 164.76, 153.01, 129.27, 80.73, 71.93, 71.33, 69.73, 68.23, 67.15, 61.61, 52.30, 28.53, 28.04, 20.72, 20.67, 20.58, 20.51. Anal. Calcd for $C_{24}H_{35}NO_{13}\bullet H_2O$: C, 51.15; H, 6.62; N, 2.45. Found: C, 51.38; H, 6.26; N, 2.41.

General procedure for hydrogenation of a *C*-glycosyl enamide ester: In a dry box, [(COD)Rh-((*R,R*)-*n*-Pr-DuPHOS)]$^+$OTf$^-$ catalyst precursor (1 mg, 0.0014 mmol) and enamide ester (50.0 mg) were dissolved in deoxygenated anhydrous MeOH (3 mL) in a Fischer-Porter tube. The reaction vessel was brought outside the dry box and pressurized

with 90 psi of H_2 after five vacuum/H_2 cycles. Reactions stirred at rt for 48 h. The vessel was then depressurized and the mixture filtered through a short plug of silica gel to remove the catalyst and concentrated. The samples were then dissolved in $CDCl_3$ analyzed by ^1H NMR (400 MHz) to determine diastereostereomeric excess.

Methyl (2*R*)-4-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-2-(*N*-*t*-butyloxycarbonyl)butanoate: ^1H NMR (400 MHz, $CDCl_3$) δ 5.29-5.25 (t, J=8.8 Hz, 1H), 5.18-5.12 (m, 1H), 5.10-5.06 (dd, J=5.6, 9.4 Hz, 1H), 4.98-4.94 (t, J=8.8 Hz, 1H), 4.33 (m, 1H), 4.26-4.21 (dd, J=5.8, 9.4 Hz, 1H), 4.20-4.13 (m, 1H), 4.12-1.08 (dd, J=2.7, 12.3 Hz, 1H), 3.81-3.78 (m, 1H), 3.76 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.98-1.77 (m, 1H), 1.64-1.50 (m, 1H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.52, 169.91, 169.48, 169.39, 155.32, 76.94, 75.53, 74.14, 71.66, 70.13, 70.12, 68.66, 68.50, 62.22, 53.10, 52.79, 52.31, 52.17, 28.18, 28.03, 21.38, 20.57, 20.53. Anal. Calcd for $C_{24}H_{37}NO_{13}$: C, 52.65; H, 6.81; N, 2.56. Found: C, 52.71; H, 6.68; N, 2.60.

Methyl (2*S*)-4-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-2-(*N*-*t*-butyloxycarbonyl)butanoate: yield, 95% ^1H NMR (400 MHz, $CDCl_3$) δ 5.27-5.25 (t, J=9.2 Hz, 1H), 5.16-5.09 (m, 1H), 5.06-5.02 (dd, J=5.8, 9.6 Hz, 1H), 4.96-4.91 (t, J=9.2 Hz, 1H), 4.37-4.33 (m, 1H), 4.25-4.21 (dd, J=5.5, 11.9 Hz, 1H), 4.12-4.08 (m, 2H), 3.81-3.78 (m, 1H), 3.76 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.90-1.75 (m, 1H), 1.58-1.50 (m, 1H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.59, 170.02, 169.57, 169.48, 75.65, 74.21, 72.31, 71.51, 70.24, 70.15, 68.82, 68.60, 62.26, 62.10, 53.10, 52.41, 52.28, 28.49, 28.24, 28.12, 27.70, 21.41, 20.66, 20.61. HRMS (Fab) calcd for MH^+ $C_{24}H_{37}NO_{13}$ 548.2343, Found 548.2349.

Methyl (2*R*)-4-(2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl)-2-(*N*-*t*-butyloxycarbonyl)butanoate (4): ^1H NMR (400 MHz, $CDCl_3$) δ 5.41-5.40 (t, J=2.8 Hz, 1H), 5.28-5.24 (dd, J=5.2, 9.2 Hz, 1H), 5.17-5.14 (dd, J=3.6, 9.2 Hz, 1H), 4.34-4.20 (m, 3H), 4.11-4.07 (dd, J=4.8, 11.8 Hz, 1H), 4.02 (3.99, J=m Hz, 2H), 3.76 (s, 3H), 2.13 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.79-1.68 (m, 1H), 1.57-1.49 (m, 1H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.59, 170.06, 169.91, 169.78, 155.47, 80.10, 71.18, 68.27, 68.17, 67.96, 67.44, 61.48, 52.88, 52.41, 28.56,

28.28, 21.81, 20.77, 20.68, 20.65. Anal. Calcd for $C_{24}H_{37}NO_{13}$: C, 52.65; H, 6.81; N, 2.56. Found: C, 52.59; H, 6.84; N, 2.56.

Methyl (2*S*)-4-(2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl)-2-(*N*-*t*-butyloxycarbonyl)butanoate: yield, 86%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.42-5.40 (t, J=2.9 Hz, 1H), 5.27-5.23 (dd, J=5.1, 9.3 Hz, 1H), 5.19-5.16 (dd, J=3.2, 9.4 Hz, 1H), 4.33-4.26 (m, 1H), 4.24-4.13 (m, 2H), 4.12-4.08 (m, 1H), 4.05-4.01 (m, 1H), 3.75 (s, 3H), 2.12 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 1.71-1.67 (m, 1H), 1.59-1.51 (m, 1H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.75, 170.41, 169.95, 169.71, 155.25, 77.10, 74.05, 72.00, 71.70, 68.84, 67.80, 67.60, 67.40, 53.10, 52.80, 52.29, 28.75, 28.19, 27.59, 26.96, 21.84, 20.67, 20.61, 20.56. HRMS (Fab) calcd for MH^+ $C_{24}H_{37}NO_{13}$ 548.2343, Found 548.2365.

Methyl (2*R*)-4-(2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl)-2-(*N*-*t*-butyloxycarbonyl)butanoate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23-5.21 (m, 2H), 5.18-5.08 (m, 2H), 4.38-4.34 (m, 1H), 4.13-4.11 (m, 1H), 3.97-3.95 (m, 1H), 3.86-3.83 (m, 1H), 3.76 (s, 3H), 2.11 (s, 3H), 2.01 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 1.88-1.79 (m, 1H), 1.77-1.67 (m, 1H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.56, 170.64, 170.15, 169.63, 73.52, 71.80, 70.62, 70.38, 69.92, 69.30, 68.71, 67.13, 62.27, 61.61, 52.45, 35.76, 35.49, 28.58, 28.29, 24.64, 20.92, 20.72. Anal. Calcd for $C_{24}H_{37}NO_{13}\bullet H_2O$: C, 50.97; H, 6.95; N, 2.48. Found: C, 50.50; H, 6.55; N, 2.37.

Methyl (2*S*)-4-(2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl)-2-(*N*-*t*-butyloxycarbonyl)butanoate. yield, 75% ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24-5.13 (m, 4H), 4.37-4.33 (m, 2H), 4.13-4.10 (m, 2H), 3.95-3.92 (m, 1H), 3.88-3.79 (m, 1H), 3.76 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.87-1.73 (m, 1H), 1.71-1.61 (m, 1H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.63, 170.86, 169.86, 169.62, 72.38, 71.81, 70.50, 69.92, 69.30, 68.77, 68.12, 67.26, 66.92, 62.17, 61.62, 53.07, 52.49, 52.09, 35.49, 28.66, 28.29, 24.59, 20.92, 20.72. HRMS (Fab) calcd for MH^+ $C_{24}H_{37}NO_{13}$ 548.2343, Found 548.2339.