A New Method for the Stereoselective Synthesis of α - and β -Glycosylamines Using the Burgess Reagent

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Supporting Information

Experimental Data for Compounds

General Procedures. All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Dry tetrahydrofuran (THF), benzene, and methylene chloride (CH_2Cl_2) were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Yields refer to chromatographically and spectroscopically (^1H NMR) homogeneous materials, unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and an ethanolic solution of phosphomolybdic acid and cerium sulfate, and heat as developing agents. E. Merck silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography. NMR spectra were recorded on Bruker DRX-600, DRX-500, AMX-500 or AMX-400 instruments and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, quin = quintuplet, sext = sextet, sep = septet, br = broad, app = apparent, AB = AB quartet. IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. Electrospray ionization (ESI) mass spectrometry (MS) experiments were

performed on an API 100 Perkin Elmer SCIEX single quadrupole mass spectrometer at 4000V emitter voltage. High-resolution mass spectra (HRMS) were recorded on a VG ZAB-ZSE mass spectrometer using MALDI (matrix-assisted laser-desorption ionization).

General procedure for the synthesis of Burgess-type reagents. To a solution of chlorosulfonylisocyanate (8.71 mL, 100 mmol, 1.0 equiv) in CH₂Cl₂ (25 mL) at 0 °C was added a solution of the appropriate alcohol (105 mmol, 1.05 equiv) in CH₂Cl₂ (25 mL) over the course of 30 minutes. Once the addition was complete, the reaction contents were concentrated directly to give the desired sulfamoyl chloride intermediate as a white solid. Pressing forward without any additional purification steps, a solution of the newly-formed sulfamoyl chloride (20.0 mmol, 1.0 equiv) in benzene (40 mL) was added dropwise to a solution of Et₃N (6.27 mL, 45 mmol, 2.25 equiv) in benzene (25 mL) at 25 °C. After the addition was complete (~1 hour), the triethylammonium hydrochloride precipitate was removed by filtration, and the filtrate was concentrated to give **1**, **2**, or **3** as clear oils which solidified upon standing.

Alloc-protected Burgess-type reagent 2: *R*_f = 0.04 (silica gel, EtOAc); IR (film) $\nu_{\max}$ 2995, 2948, 1693, 1457, 1332, 1161, 1098, 970, 859, 788, 714, 597, 548 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 5.91 (m, 1 H), 5.30 (d, *J* = 16.2 Hz, 1 H), 5.18 (d, *J* = 10.3 Hz, 1 H), 4.54 (s, 2 H), 3.45 (q, *J* = 7.4 Hz, 6 H), 1.39 (t, *J* = 7.0 Hz, 9 H); ¹³C NMR (125 MHz, CDCl₃) δ 157.2, 132.5, 117.9, 66.6, 50.5, 9.3; MS (ESI) calcd for C₁₀H₂₁N₂O₄S⁺ [*M* + *H*⁺] 265, found 265.

Troc-protected Burgess-type reagent 3: *R*_f = 0.03 (silica gel, EtOAc); IR (film) $\nu_{\max}$ 2950, 1702, 1457, 1368, 1339, 1254, 1111, 1059, 857, 816, 716, 605, 548 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.75 (s, 2 H), 3.48 (q, *J* = 7.4 Hz, 6 H), 1.43 (t, *J* = 7.3 Hz, 9 H); ¹³C NMR (100 MHz, CDCl₃) δ 156.0, 95.4, 75.3, 50.7, 9.3; MS (ESI) calcd for C₉H₁₈Cl₃N₂O₄S⁺ [*M* + *H*⁺] 355, found 355.

3,4,6-Tri-*O*-benzyl-D-glucopyranose 12. 4-Methylmorpholine *N*-oxide (0.351 g, 3.0 mmol, 3.0 equiv) and osmium tetroxide (0.641 mL, 2.5 wt % in *t*-BuOH, 0.05 mmol, 0.05 equiv) were added sequentially at 25 °C to a solution of 3,4,6-tri-*O*-benzyl-D-glucal (0.417 g, 1.0 mmol,

1.0 equiv) in THF/*t*-BuOH/H₂O (7:3:1, 5 mL), and the resulting orange solution was stirred for 12 hours at 25 °C. Upon completion, the reaction contents were then diluted with water (10 mL), treated with Na₂SO₃ (0.630 g, 5.0 mmol, 5.0 equiv), and allowed to stir for an additional 2 hours at 25 °C. Once this operation was complete, the reaction mixture was poured into water (10 mL) and extracted with EtOAc (3 × 25 mL). The combined organic layers were then washed with water (2 × 15 mL), dried (MgSO₄), and concentrated. The resultant light yellow solid was purified by flash column chromatography (silica gel, EtOAc/hexanes, 1:1) to give diol **12** (0.414 g, 92%) as an amorphous white solid. **12**: *R_f* = 0.13 (silica gel, EtOAc/hexanes, 1:1); IR (film) ν_{max} 3410, 2938, 1452, 1390, 1190, 1080, 886, 590 cm⁻¹; ¹H NMR (500 MHz, CDCl₃, 1:1 mixture of anomers) δ 7.38–7.10 (m, 30 H), 5.18 (d, *J* = 4.8 Hz, 1 H), 4.81 (s, 2 H), 4.75 (d, *J* = 13.9 Hz, 2 H), 4.54–4.49 (m, 3 H), 4.47 (app t, *J* = 5.5 Hz, 3 H), 4.43 (d, *J* = 3.3 Hz, 1 H), 4.01 (t, *J* = 6.4 Hz, 1 H), 3.98 (dd, *J* = 6.2 Hz, 1 H), 3.74 (app t, *J* = 11.4 Hz, 1 H), 3.63–3.58 (m, 3 H), 3.51–3.46 (m, 2 H); ¹³C NMR (125 MHz, CDCl₃, 1:1 mixture of anomers) δ 138.5, 138.4, 138.0, 137.8, 137.6, 128.5, 128.4, 128.0, 127.9, 127.8, 127.7, 96.7, 92.3, 84.3, 82.5, 77.6, 77.5, 75.5, 75.3, 74.8, 73.4, 72.7, 70.4, 68.7; HRMS (MALDI-FTMS) calcd for C₂₇H₃₀O₆Na⁺ [*M* + Na⁺] 473.1934, found 473.1925.

3,4-Di-*O*-benzyl-L-rhamnopyranose 16. 4-*O*-Benzyl-L-rhamnal (0.220 g, 1.0 mmol, 1.0 equiv) was dissolved in DMF (5 mL) and treated with NaH (0.400 g, 60% dispersion in mineral oil, 2.0 mmol, 2.0 equiv) at 25 °C. After stirring the resultant solution for 5 minutes at 25 °C, the reaction contents were cooled to 0 °C and benzyl bromide (0.238 mL, 2.0 mmol, 2.0 equiv) added dropwise over the course of 10 minutes. The reaction mixture was then warmed to 25 °C over the course of 30 minutes. Upon completion, the reaction mixture was poured into 1 N aqueous HCl (10 mL) and extracted with Et₂O (3 × 25 mL). The combined organic layers were then washed with water (2 × 15 mL), dried (MgSO₄), and concentrated. The resultant light yellow solid was purified by flash column chromatography (silica gel, Et₂O) to give the desired di-*O*-benzylated-L-rhamnal intermediate (0.292 g, 94%) as an amorphous white solid. This compound was then dihydroxylated in a manner similar to the preparation of **12** to give diol **16**

(0.314 g, 91% yield) as a white amorphous solid. **16**: R_f = 0.40 (silica gel, EtOAc/hexanes, 1:1); IR (film) $\nu_{\max}$ 3388, 2870, 1645, 1453, 1363, 1091, 994, 734, 694 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3 , 1:1 mixture of anomers) δ 7.40–7.32 (m, 20 H), 5.34 (d, J = 3.0 Hz, 1 H), 4.98 (d, J = 2.6 Hz, 1 H), 4.95 (d, J = 2.6 Hz, 1 H), 4.77 (br d, J = 8.4 Hz, 1 H), 4.71–4.62 (m, 5 H), 4.04 (m, 2 H), 3.64 (ddd, J = 13.1, 8.5, 4.8 Hz, 1 H), 3.40 (dd, J = 9.6, 6.3 Hz, 1 H), 3.21 (br s, 1 H), 3.15 (dt, J = 8.7, 3.7 Hz, 1 H), 2.60 (br s), 2.43 (ddd, J = 12.5, 5.2, 2.2 Hz, 1 H), 2.32 (ddd, J = 13.2, 5.2, 1.5 Hz, 1 H), 1.74 (m, 1 H), 1.43 (m, 1 H), 1.35 (d, J = 6.3 Hz, 3 H), 1.28 (d, J = 6.3 Hz, 3 H); ^{13}C NMR (125 MHz, CDCl_3 , 1:1 mixture of anomers) δ 138.6, 138.5, 138.3, 138.2, 128.4 (3 C), 128.3, 128.0 (2 C), 127.7 (2 C), 127.6 (2 C), 93.8, 92.0, 84.3, 83.4, 78.9, 76.8, 75.2 (2 C), 71.8 (2 C), 71.5, 71.4, 67.4, 38.3, 37.7, 18.2 (2 C); MS (ESI) calcd for $\text{C}_{20}\text{H}_{22}\text{O}_4^+$ [$\text{M} - \text{H}_2\text{O}^+$] 327, found 327.

3,4,6-Tri-*O*-benzyl-D-galactopyranose 18. 3,4,6-Tri-*O*-benzyl- β -D-galactal (0.417 g, 1.0 mmol, 1.0 equiv) was dihydroxylated in a manner similar to the preparation of **12** to give diol **18** (0.379 g, 91% yield) as a white amorphous solid. **18**: R_f = 0.13 (silica gel, EtOAc/hexanes, 1:1); IR (film) $\nu_{\max}$ 3401, 2919, 2861, 1455, 1361, 1085, 738, 691 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.41–7.26 (m, 15 H), 5.31 (d, J = 3.5 Hz, 1 H), 4.87 (dd, J = 11.8, 3.5 Hz, 1 H), 4.70 (m, 2 H), 4.61–4.39 (m, 4 H), 4.14 (dd, J = 10.0, 3.8 Hz, 1 H), 3.88 (m, 1 H), 3.73 (dd, J = 10.0, 2.6 Hz, 1 H), 3.61–3.50 (m, 3 H), 3.41 (m, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.3, 138.0, 137.6, 128.5, 128.4, 128.2, 128.0 (2 C), 127.8, 127.7, 92.6, 79.0, 74.5, 73.8, 73.4, 72.3, 69.6, 69.2, 68.9; HRMS (MALDI-FTMS) calcd for $\text{C}_{27}\text{H}_{30}\text{O}_6\text{Na}^+$ [$\text{M} + \text{Na}^+$] 473.1934, found 473.1921.

3,5-Di-*O*-TBS-D-ribofuranose 22. The requisite D-ribose glycal intermediate was prepared from thymidine following the procedure of Larsen and co-workers.¹ The resultant product was then dihydroxylated in a manner similar to the preparation of **12** to give diol **22** (0.378 g, 88% yield) as a white amorphous solid. **22**: R_f = 0.35 (silica gel, EtOAc/hexanes, 1:2); IR (film) $\nu_{\max}$ 3425, 2930, 2858, 1471, 1391, 1255, 1095, 937, 779 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 1:1 mixture of anomers) δ 5.24 (d, J = 6.8 Hz, 1 H), 5.13 (d, J = 10.6 Hz, 1 H), 4.24 (br

d, $J = 8.5$ Hz, 1 H), 4.18 (app t, $J = 2.6$ Hz, 1 H), 4.09–4.06 (m, 2 H), 3.91 (br d, $J = 11.1$ Hz, 1 H), 3.86–3.81 (m, 2 H), 3.77 (dd, $J = 8.6, 2.6$ Hz, 1 H), 3.71 (d, $J = 1.8$ Hz, 1 H), 3.63 (dd, $J = 10.8, 2.0$ Hz, 1 H), 0.89 (s, 9 H), 0.87 (s, 9 H), 0.84 (s, 9 H), 0.82 (s, 9 H), 0.10 (s, 6 H), 0.07–0.04 (m, 18 H); ^{13}C NMR (100 MHz, CDCl_3 , 1:1 mixture of anomers) δ 104.1, 97.6, 87.1, 84.8, 78.8, 78.5, 77.3, 69.9, 65.7, 63.5, 63.1, 25.7, 25.5, 17.7, 15.1, –4.7, –5.0, –5.1, –5.6, –5.7, –5.8; HRMS (MALDI-FTMS) calcd for $\text{C}_{17}\text{H}_{38}\text{O}_5\text{Si}_2\text{Na}^+$ [$\text{M} + \text{Na}^+$] 401.2150, found 401.2147.

General procedure for the synthesis of sulfamidates on carbohydrates. The appropriate carbohydrate diol (0.5 mmol, 1.0 equiv) was dissolved in THF/ CH_2Cl_2 (4:1, 5 mL) and the desired Burgess-type reagent (**1**, **2** or **3**, 1.25 mmol, 2.5 equiv) was added at 25 °C in a single portion. The resultant solution was immediately warmed to reflux (using a preheated oil bath) and stirred for 6 hours. Upon completion, the reaction contents were cooled to 25 °C, poured into saturated aqueous NH_4Cl (25 mL), and extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were then washed with water (50 mL), dried (MgSO_4), and concentrated. The resultant yellow residue was purified by flash column chromatography (silica gel) in an appropriate solvent system to give the desired product in high purity.

13: $R_f = 0.68$ (silica gel, EtOAc/hexanes, 1:1); IR (film) ν_{max} 3037, 2866, 1753, 1444, 1385, 1312, 1196, 1094, 842, 741, 699, 665 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.39–7.29 (m, 13 H), 7.21 (m, 2 H), 6.02 (d, $J = 4.8$ Hz, 1 H), 4.90 (t, $J = 4.0$ Hz, 1 H), 4.60 (s, 2 H), 4.47 (AB, $J = 11.8$ Hz, $\nu_{\text{ab}} = 88.6$ Hz, 2 H), 4.44 (AB, $J = 11.9$ Hz, $\nu_{\text{ab}} = 88.6$ Hz, 2 H), 4.09 (t, $J = 3.5$ Hz, 1 H), 3.96 (dd, $J = 11.4, 2.6$ Hz, 1 H), 3.94 (s, 3 H), 3.92 (dd, $J = 9.2, 3.5$ Hz, 1 H), 3.68 (dd, $J = 11.0, 2.2$ Hz, 1 H), 3.61 (dd, $J = 10.9, 3.5$ Hz, 1 H); ^{13}C NMR (150 MHz, CDCl_3) δ 149.8, 137.8, 137.3, 136.6, 128.7, 128.5, 128.4, 128.3, 128.1, 128.0 (2 C), 127.8, 127.7, 81.6, 75.5, 73.3, 73.1, 72.9, 72.4, 68.9, 54.9; HRMS (MALDI-FTMS) calcd for $\text{C}_{29}\text{H}_{31}\text{NO}_9\text{SNa}^+$ [$\text{M} + \text{Na}^+$] 592.1612, found 592.1608.

14: $R_f = 0.67$ (silica gel, EtOAc/hexanes, 1:1); IR (film) ν_{max} 3363, 2923, 1763, 1453, 1390, 1294, 1199, 1092, 847, 738, 699 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.30–7.20 (m, 15 H), 6.09 (d, $J = 5.2$ Hz, 1 H), 4.95 (d, $J = 4.4$ Hz, 1 H), 4.90 (AB, $J = 12.1$ Hz, $\nu_{\text{ab}} = 48.4$ Hz, 2

H), 4.62 (s, 2 H), 4.45 (AB, $J = 11.7$ Hz, $v_{ab} = 101.2$ Hz, 2 H), 4.43 (AB, $J = 11.8$ Hz, $v_{ab} = 44.8$ Hz, 2 H), 4.12 (t, $J = 3.7$ Hz, 1 H), 3.99 (dt, $J = 9.2, 2.6$ Hz, 1 H), 3.93 (dd, $J = 9.2, 3.3$ Hz, 1 H), 3.68 (dd, $J = 11.0, 2.2$ Hz, 1 H), 3.61 (dd, $J = 11.0, 3.3$ Hz, 1 H); ^{13}C NMR (125 MHz, CDCl_3) δ 148.1, 137.8, 137.3, 136.6, 128.7, 128.5, 128.4, 128.1, 128.0, 127.8, 127.7, 93.6, 81.8, 76.0, 75.4, 73.4, 73.3, 72.9, 72.8, 72.5, 68.8; HRMS (MALDI-FTMS) calcd for $\text{C}_{30}\text{H}_{30}\text{Cl}_3\text{NO}_9\text{SNa}^+$ [$\text{M} + \text{Na}^+$] 708.0599, found 708.0611.

15: $R_f = 0.68$ (silica gel, EtOAc/hexanes, 1:1); IR (film) v_{max} 3398, 2865, 1746, 1453, 1376, 1300, 1284, 1197, 1088, 1028 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.36–7.29 (m, 13 H), 7.20–7.18 (m, 2 H), 6.02 (d, $J = 4.8$ Hz, 1 H), 5.93 (m, 1 H), 5.42 (dd, $J = 17.0, 1.1$ Hz, 1 H), 5.30 (m, 1 H), 4.88 (dt, $J = 8.1, 0.7$ Hz, 1 H), 4.79 (ABX, $J = 16.1, 5.5$ Hz, $v_{ab} = 21.6$ Hz, 2 H), 4.60 (s, 2 H), 4.53 (AB, $J = 12.1$ Hz, $v_{ab} = 21.3$ Hz, 2 H), 4.38 (AB, $J = 12.1$ Hz, $v_{ab} = 22.4$ Hz, 2 H), 4.08 (t, $J = 3.7$ Hz, 1 H), 3.95 (td, $J = 7.4, 2.8$ Hz, 1 H), 3.89 (dd, $J = 7.4, 3.7$ Hz, 1 H), 3.67 (dd, $J = 9.3, 2.2$ Hz, 1 H), 3.59 (dd, $J = 9.1, 3.7$ Hz, 1 H); ^{13}C NMR (125 MHz, CDCl_3) δ 149.1, 137.9, 137.4, 136.7, 31.4, 130.4, 128.7, 128.5, 128.4 (2 C), 128.1 (2 C), 127.9, 127.7, 119.6, 119.2, 81.6, 77.4, 75.6, 73.5, 73.4, 72.9, 72.8, 72.4, 69.0, 68.5, 66.8; HRMS (MALDI-FTMS) calcd for $\text{C}_{31}\text{H}_{33}\text{NO}_9\text{SNa}^+$ [$\text{M} + \text{Na}^+$] 618.1768, found 618.1773.

17: $R_f = 0.60$ (silica gel, EtOAc/hexanes, 1:1); IR (film) v_{max} 3248, 1752, 1636, 1494, 1444, 1381, 1314, 1196, 1146, 1077, 1001, 740 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.41–7.29 (m, 8 H), 7.27–7.25 (m, 2 H), 5.88 (d, $J = 5.3$ Hz, 1 H), 4.90 (ddd, $J = 6.2, 3.5, 1.2$ Hz, 1 H), 4.57 (AB, $J = 10.8$ Hz, $v_{ab} = 11.8$ Hz, 2 H), 4.44 (AB, $J = 12.0$ Hz, $v_{ab} = 34.9$ Hz, 2 H), 4.02 (dd, $J = 3.2, 2.0$ Hz, 1 H), 3.98 (m, 1 H), 3.95 (s, 3 H), 3.36 (ddd, $J = 8.8, 1.8, 1.2$ Hz, 1 H), 1.28 (d, $J = 6.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.0, 137.3, 136.5, 128.8, 128.5 (2 C), 128.1, 128.0 (3 C), 81.5, 80.5, 75.2, 74.4, 72.6, 72.4, 67.9, 54.9, 19.3; HRMS (MALDI-FTMS) calcd for $\text{C}_{22}\text{H}_{25}\text{NO}_8\text{SNa}^+$ [$\text{M} + \text{Na}^+$] 486.1193, found 486.1202.

19: $R_f = 0.66$ (silica gel, EtOAc/hexanes, 1:1); IR (film) v_{max} 2961, 1755, 1443, 1384, 1320, 1290, 1190, 1061, 991, 855, 732, 697 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.39–7.25 (m, 15 H), 5.89 (d, $J = 4.0$ Hz, 1 H), 5.02 (dd, $J = 5.2, 3.5$ Hz, 1 H), 4.75 (AB, $J = 11.0$ Hz, $v_{ab} =$

160.4 Hz, 2 H), 4.73 (AB, $J = 11.9$ Hz, $v_{ab} = 68.8$ Hz, 2 H), 4.53 (AB, $J = 11.9$ Hz, $v_{ab} = 31.1$ Hz, 2 H), 4.20 (m, 1 H), 4.15 (dd, $J = 4.0, 1.7$ Hz, 1 H), 4.03 (dd, $J = 5.3, 1.8$ Hz, 1 H), 3.92 (s, 3 H), 3.71 (dd, $J = 9.7, 7.4$ Hz, 1 H), 3.65 (dd, $J = 9.7, 6.5$ Hz, 1 H); ^{13}C NMR (150 MHz, CDCl_3) δ 149.5, 137.7, 137.4, 136.8, 128.6, 128.4, 128.2, 128.1, 128.0, 127.8 (2 C), 127.6, 84.1, 80.3, 78.7, 75.4, 75.3, 73.7, 72.1, 66.9, 54.9; HRMS (MALDI-FTMS) calcd for $\text{C}_{29}\text{H}_{31}\text{NO}_9\text{SNa}^+$ [$\text{M} + \text{Na}^+$] 592.1612, found 592.1633.

21: $R_f = 0.33$ (silica gel, EtOAc/hexanes, 1:2); IR (film) ν_{max} 2978, 1746, 1437, 1412, 1294, 1249, 1187, 1073, 1023, 973, 861, 797, 609 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.98 (d, $J = 3.8$ Hz, 1 H), 5.13 (d, $J = 2.4$ Hz, 1 H), 4.72 (dd, $J = 15.0, 2.9$ Hz, 1 H), 4.71 (d, $J = 3.5$ Hz, 1 H), 4.36 (q, $J = 2.6$ Hz, 1 H), 4.09 (dd, $J = 15.0, 2.6$ Hz, 1 H), 3.86 (s, 3 H), 1.49 (s, 3 H), 1.33 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.9, 113.0, 104.9, 87.3, 82.5, 70.6, 54.9, 48.2, 26.5, 26.1; HRMS (MALDI-FTMS) calcd for $\text{C}_{10}\text{H}_{15}\text{NO}_8\text{SNa}^+$ [$\text{M} + \text{Na}^+$] 332.0411, found 332.0418.

23: $R_f = 0.68$ (silica gel, EtOAc/hexanes, 1:2); IR (film) ν_{max} 2954, 2858, 1759, 1442, 1392, 1313, 1257, 1196, 1098, 1011, 838, 806, 781 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.12 (d, $J = 4.4$ Hz, 1 H), 4.93 (d, $J = 4.1$ Hz, 1 H), 4.61 (s, 1 H), 4.12 (ddd, $J = 8.5, 5.2, 1.9$ Hz, 1 H), 3.96 (s, 3 H), 3.77 (dd, $J = 10.7, 5.5$ Hz, 1 H), 3.71 (dd, $J = 10.6, 8.8$ Hz, 1 H), 0.90 (s, 18 H), 0.14 (d, $J = 5.5$ Hz, 6 H), 0.07 (d, $J = 2.6$ Hz, 6 H); ^{13}C NMR (125 MHz, CDCl_3) δ 149.8, 88.8, 87.7, 86.2, 74.3, 61.7, 55.0, 25.8, 25.5, 18.3, 17.9, -4.9, -5.0, -5.5 (2 C); HRMS (MALDI-FTMS) calcd for $\text{C}_{19}\text{H}_{40}\text{NO}_8\text{Si}_2\text{S}^+$ [$\text{M} + \text{H}^+$] 498.2008, found 498.2015.

Scheme S1. X-ray crystallographic proof of sulfamidate stereochemistry.

2-Azido-3,4,6-tri-*O*-benzyl-D-glucopyranose 24. NaN₃ (0.033 g, 0.50 mmol, 5.0 equiv) was added in a single portion to a solution of glucose-derived sulfamidate **13** (0.057 g, 0.10 mmol, 1.0 equiv) in THF/CH₂Cl₂ (4:1, 1 mL) at 25 °C. The resulting clear solution was then warmed to 60 °C and stirred for 5 hours. Upon completion, the reaction contents were diluted with Et₂O (5 mL), treated with 10% aqueous H₂SO₄ (1 mL), and allowed to stir for an additional 30 minutes at 25 °C. Once this operation was complete, the reaction mixture was poured into water (10 mL) and extracted with Et₂O (3 × 25 mL). The combined organic layers were then washed with water (2 × 15 mL), dried (MgSO₄), and concentrated. The resultant light yellow solid was purified by flash column chromatography (silica gel, Et₂O/hexanes, 1:1) to give the azide-opened tri-benzylated glucose derivative **24** (0.049 g, 92%) as an amorphous white solid. **24**: R_f = 0.47 (silica gel, EtOAc/hexanes, 1:1); IR (film) ν_{max} 3318, 2924, 2106, 1732, 1532, 1454, 1357, 1243, 1098, 1027, 738, 699 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.26–7.15 (m, 15 H), 5.42 (br s, 1 H), 5.27 (br m, 1 H), 4.65–4.47 (m, 5 H), 3.82 (m, 2 H), 3.74 (m, 2 H), 3.68 (s, 3 H); ¹³C NMR (125 MHz, CDCl₃) δ 155.7, 138.0, 137.6, 137.1, 128.6, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 78.3, 73.8, 73.2, 72.8, 68.2, 60.0, 52.7, 53.4; HRMS (MALDI-FTMS) calcd for C₃₄H₃₈NO₅⁺ [M + H⁺] 555.2214, found 555.2217.

Allylated sulfamidate 25. Et₂NH (0.354 mL, 6.71 mmol, 40 equiv) was added to a solution of sulfamidate **23** (0.100 g, 0.167 mmol, 1.0 equiv) in CH₃CN/H₂O (1:1, 3 mL) at 25 °C. After stirring this mixture for 5 minutes at 25 °C, Pd(OAc)₂ (0.002 g, 0.017 mmol, 0.1 equiv) and TPPTS (0.019 g, 0.033 mmol, 0.2 equiv) were added sequentially, providing a yellow solution which was stirred for an additional 30 minutes at 25 °C. Upon completion, the reaction contents were poured into water (5 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were then dried (MgSO₄) and concentrated to give the desired deprotected sulfamidate (0.075 g, 87% yield) as a white oil.² Pressing forward without any additional purification steps, this material (0.075 g, 0.146 mmol, 1.0 equiv) was dissolved in DMSO (2 mL) and treated with NaH (0.029 g, 60% dispersion in mineral oil, 0.730 mmol, 5.0 equiv) at 25 °C. After stirring the resultant reaction mixture for 10 minutes at 25 °C, allyl bromide (0.051 mL,

0.584 mmol, 4.0 equiv) was added in a single portion; the reaction mixture was then stirred for an additional 15 minutes at 25 °C. Upon completion, the reaction contents were poured into water (5 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were then washed with water (2 × 15 mL), dried (MgSO₄), and concentrated. The resultant light yellow oil was purified by flash column chromatography (silica gel, EtOAc/hexanes, 1:3→1:1) to give the allylated sulfamidate **25** (0.067 g, 73% yield over two steps) as an amorphous white solid. **25**: *R_f* = 0.64 (silica gel, EtOAc/hexanes, 1:1); IR (film) ν_{max} 2890, 1452, 1352, 1193, 1114, 1052, 988, 741, 694, 606 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.30–7.24 (m, 15 H), 5.87 (m, 1 H), 5.35 (d, *J* = 17.1 Hz, 1 H), 5.29 (s, 1 H), 5.28 (d, *J* = 16.7 Hz, 1 H), 4.95 (dd, *J* = 7.4, 5.3 Hz, 1 H), 4.75 (AB, *J* = 11.0 Hz, ν_{ab} = 185.9 Hz, 2 H), 4.73 (AB, *J* = 11.8 Hz, ν_{ab} = 76.7 Hz, 2 H), 4.43 (AB, *J* = 11.8 Hz, ν_{ab} = 26.3 Hz, 2 H), 4.12 (dd, *J* = 7.4, 2.6 Hz, 1 H), 4.04 (t, *J* = 5.3 Hz, 1 H), 4.00 (app s, 1 H), 3.79 (dd, *J* = 14.5, 5.7 Hz, 1 H), 3.73 (dd, *J* = 14.5, 7.9 Hz, 1 H), 3.52 (AB, *J* = 9.6 Hz, ν_{ab} = 16.2 Hz, 2 H); ¹³C NMR (150 MHz, CDCl₃) δ 137.8, 137.6, 137.4, 130.4, 128.5 (2 C), 128.4, 128.2, 128.0 (2 C), 127.9, 127.7 (2 C), 121.1, 84.3, 82.2, 78.5, 74.9, 73.5 (2 C), 72.8, 72.4, 67.7, 47.0; HRMS (MALDI-FTMS) calcd for C₃₀H₃₃NO₇SN⁺ [M + Na⁺] 574.1870, found 574.1866.

2,3,4-Tri-*O*-benzyl-D-fucose (30). Concentrated H₂SO₄ (1 mL) was added to a solution of D-fucose (1.64 g, 10.0 mmol, 1.0 equiv) in MeOH (30 mL) at 25 °C, and the resultant mixture was stirred for 5 hours. Upon completion, the reaction contents were neutralized by the addition of 3 N aqueous NaOH (monitored using standard pH paper) and concentrated directly. The resulting white solid was then taken up in EtOAc (50 mL), filtered through a short silica gel, and concentrated to give 1-*O*-methyl-D-fucose (1.78 g, 100% yield) as a white solid. Pressing forward without any additional purification steps, this newly-formed material (1.78 g, 10.0 mmol, 1.0 equiv) was dissolved in DMF (10 mL) and treated with NaH (3.60 g, 60% dispersion in mineral oil, 90.0 mmol, 9.0 equiv) at 25 °C. After stirring the resultant solution for 5 minutes at 25 °C, the reaction contents were cooled to 0 °C and benzyl bromide (5.95 mL, 50.0 mmol, 5.0 equiv) added dropwise over the course of 10 minutes. The reaction mixture was then

warmed to 25 °C over the course of 4 hours. Upon completion, the reaction mixture was poured into 1 N aqueous HCl (25 mL) and extracted with Et₂O (3 × 25 mL). The combined organic layers were then washed with water (2 × 15 mL), dried (MgSO₄), and concentrated. The resultant light yellow solid was purified by flash column chromatography (silica gel, Et₂O/hexanes, 1:3→1:1) to give the desired tri-*O*-benzylated D-fucose intermediate (3.7 g, 82%) as an amorphous white solid. Finally, a portion of this newly-formed product (0.452 g, 1.0 mmol, 1.0 equiv) was dissolved 6 M aqueous HCl/concentrated HCl (1:1, 5 mL) at 25 °C. The resultant mixture was then warmed to 60 °C and stirred for 12 hours. Upon completion, the reaction contents were concentrated directly. The resultant yellow oil was purified by flash column chromatography (silica gel, Et₂O/hexanes, 1:1) to give the desired D-fucose-derived starting material **30** (0.297 g, 68%) as an amorphous white solid. **30**: *R*_f = 0.54 (silica gel, EtOAc/hexanes, 1:1); IR (film) ν_{max} 3416, 3031, 2867, 1453, 1364, 1208, 1098, 740, 698 cm⁻¹; ¹H NMR (500 MHz, CDCl₃, 1:1 mixture of anomers) δ 7.48–7.34 (m, 30 H), 5.55 (s, 1 H), 5.41 (dd, *J* = 9.5, 4.4 Hz, 1 H), 4.83–4.49 (m, 11 H), 4.35 (app t, *J* = 5.2 Hz, 1 H), 4.30 (br d, *J* = 11.4 Hz, 1 H), 4.25 (app t, *J* = 5.2 Hz, 1 H), 4.13 (dd, *J* = 5.5, 4.8 Hz, 1 H), 4.10 (dd, *J* = 2.2, 1.1 Hz, 1 H), 4.05 (dd, *J* = 5.2, 2.2 Hz, 1 H), 3.99 (dd, *J* = 4.8, 3.0 Hz, 1 H), 3.78 (m, 1 H), 3.63 (dd, *J* = 6.3, 3.0 Hz, 1 H), 3.55 (br s, 1 H), 3.48 (m, 1 H), 1.38 (d, *J* = 4.6 Hz, 3 H), 1.28 (d, *J* = 4.8 Hz, 3 H); ¹³C NMR (125 MHz, CDCl₃, 1:1 mixture of anomers) δ 138.5, 137.7, 137.5, 137.4 (2 C), 137.3, 128.4 (2 C), 128.3 (2 C), 128.2, 128.0, 127.9 (2 C), 127.8 (3 C), 127.7, 127.5, 127.4, 126.9, 100.7, 96.0, 87.3, 85.2, 84.5, 84.4, 82.8, 82.2, 74.0, 73.9, 71.9 (2 C), 71.8, 71.6, 71.2, 71.1, 65.1; MS (ESI) calcd for C₂₇H₃₀O₉Cl⁻ [*M* + Cl⁻] 470, found 470.

2,3,4,6-Tetra-*O*-methyl-D-mannose (32). D-Mannose (1.80 g, 10.0 mmol) was converted into **32** in a manner similar to the preparation of **30** by substituting methyl iodide for benzyl bromide, ultimately providing compound **32** (0.146 g, 62% yield) as a white amorphous solid. **32**: *R*_f = 0.15 (silica gel, EtOAc/hexanes, 1:2); IR (film) ν_{max} 3402, 2932, 2828, 1644, 1453, 1193, 1109, 1030, 958, 792 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 5.25 (s, 1 H), 4.62 (br s, 1 H), 3.86 (td, *J* = 7.3, 1.8 Hz, 1 H), 3.59–3.51 (m, 4 H), 3.45 (s, 3 H), 3.44 (s, 3 H), 3.43 (s, 3 H),

3.32 (s, 3 H), 3.26 (t, $J = 9.2$ Hz, 1 H); ^{13}C NMR (125 MHz, CDCl_3) δ 91.5, 80.8, 74.5, 77.1, 72.7, 70.3, 60.6, 59.1, 58.8, 57.6; HRMS (MALDI-FTMS) calcd for $\text{C}_{10}\text{H}_{20}\text{O}_6\text{Na}^+$ [$\text{M} + \text{Na}^+$] 259.1152, found 259.1152.

2,3,5-Tri-*O*-benzyl-L-arabinofuranose 34. Lactol **34** was prepared from L-arabinose using the sequence established by Tejima and Fletcher.³ **34**: $R_f = 0.51$ (silica gel, EtOAc/hexanes, 1:1); IR (film) ν_{max} 3418, 3030, 2866, 1495, 1454, 1365, 1264, 1208, 1099, 1028, 738, 698 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3 , 1:1 mixture of anomers) δ 7.36–7.26 (m, 30 H), 5.40 (s, 1 H), 5.34 (d, $J = 3.7$ Hz, 1 H), 4.66 (d, $J = 9.5$ Hz, 1 H), 4.61–4.52 (m, 10 H), 4.48–4.45 (m, 2 H), 4.17 (t, $J = 4.0$ Hz, 1 H), 4.09 (q, $J = 3.7$ Hz, 1 H), 4.02 (t, $J = 4.0$ Hz, 1 H), 3.98 (d, $J = 1.5$ Hz, 1 H), 3.94 (m, 1 H), 3.61–3.50 (m, 4 H); ^{13}C NMR (125 MHz, CDCl_3 , 1:1 mixture of anomers) δ 138.0, 137.4, 137.3, 137.2 (2 C), 128.6, 128.5 (4 C), 128.4 (2 C), 128.3, 128.0 (2 C), 127.9 (2 C), 127.8 (2 C), 127.7 (2 C), 127.6, 101.1, 96.2, 86.3, 84.0, 82.6, 82.0, 81.8, 80.5, 76.8, 73.5, 73.3, 72.2, 72.0 (2 C), 71.7, 70.4, 70.1; HRMS (MALDI-FTMS) calcd for $\text{C}_{26}\text{H}_{28}\text{O}_5\text{Na}^+$ [$\text{M} + \text{Na}^+$] 443.1829, found 443.1809.

Furanose 36. The requisite lactol intermediate was prepared from D-ribose following the procedure of Kaskar and co-workers.⁴ **36**: $R_f = 0.51$ (silica gel, EtOAc/hexanes, 1:2); IR (film) ν_{max} 3416, 2934, 2858, 1469, 1381, 1257, 1211, 1075, 1004, 939, 838, 779 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.24 (d, $J = 11.4$ Hz, 1 H), 4.74 (d, $J = 11.7$ Hz, 1 H), 4.66 (d, $J = 5.9$ Hz, 1 H), 4.47 (d, $J = 5.9$ Hz, 1 H), 4.31 (s, 1 H), 3.75–3.72 (m, 2 H), 1.45 (s, 3 H), 1.29 (s, 3 H), 0.90 (s, 9 H), 0.11 (s, 3 H), 0.10 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 111.9, 103.3, 87.5, 86.8, 81.7, 64.7, 26.4, 25.7, 24.8, 18.1 –5.7; HRMS (MALDI-FTMS) calcd for $\text{C}_{14}\text{H}_{28}\text{O}_5\text{SiNa}^+$ [$\text{M} + \text{Na}^+$] 327.1598, found 327.1592.

General procedure for the synthesis of β -disposed glycosylamines. The lactol starting material (0.5 mmol, 1.0 equiv) was dissolved in THF/ CH_2Cl_2 (4:1, 5 mL) and the desired Burgess-type reagent (**1**, **2**, or **3**, 0.75 mmol, 1.5 equiv) was added at 25 °C in a single portion. The resultant solution was immediately warmed to reflux (using a preheated oil bath) and stirred for 6 hours. Upon completion, the reaction contents were cooled to 25 °C, poured into saturated

aqueous NH_4Cl (25 mL), and extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were then washed with water (50 mL), dried (MgSO_4), and concentrated. The resultant yellow residue was purified by flash column chromatography (silica gel) in an appropriate solvent system to give the desired product in high purity.

CO_2Me -protected 2,3,4,6-tetra-*O*-methyl- β -D-glucosylamine (27): $R_f = 0.13$ (silica gel, EtOAc/hexanes, 1:1); IR (film) ν_{max} 3329, 2937, 2836, 1712, 1544, 1450, 1278, 1158, 1099, 989, 945, 647 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.30 (d, $J = 8.8$ Hz, 1 H), 4.75 (t, $J = 8.4$ Hz, 1 H), 3.68 (br s, 3 H), 3.62 (s, 3 H), 3.58–3.53 (m, 2 H), 3.52 (s, 3 H), 3.51 (s, 3 H), 3.41 (s, 3 H), 3.30 (m, 1 H), 3.22 (d, $J = 6.7$ Hz, 2 H), 2.91 (br m, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.1, 99.5, 87.2, 82.8, 81.6, 78.9, 75.8, 70.5, 60.8, 60.3, 59.1, 52.4; HRMS (MALDI-FTMS) calcd for $\text{C}_{12}\text{H}_{23}\text{NO}_7\text{Na}^+$ [$\text{M} + \text{Na}^+$] 316.1367, found 316.1363.

Figure S1. X-ray crystal structure of compound 27.

Alloc-protected 2,3,4,6-tetra-*O*-benzyl- β -D-glucosylamine (29): $R_f = 0.64$ (silica gel, EtOAc/hexanes, 1:1); IR (film) ν_{max} 3331, 3030, 2867, 1703, 1537, 1453, 1360, 1280, 1071, 735, 697 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.45–7.32 (m, 18 H), 7.19–7.17 (m, 2 H), 5.93 (ddd, $J = 22.7, 10.9, 5.7$ Hz, 1 H), 5.32 (d, $J = 17.1$ Hz, 1 H), 5.23 (d, $J = 10.1$ Hz, 1 H), 5.07 (d, $J = 10.1$ Hz, 1 H), 4.92 (m, 1 H), 4.91 (AB, $J = 11.0$ Hz, $\nu_{\text{ab}} = 18.8$ Hz, 2 H), 4.82 (d, $J = 10.9$ Hz, 2 H), 4.72 (d, $J = 11.0$ Hz, 1 H), 4.64–4.60 (m, 3 H), 4.53 (d, $J = 10.5$ Hz, 1 H), 4.47 (d, $J = 12.3$ Hz, 1 H), 3.73 (m, 4 H), 3.52 (d, $J = 7.9$ Hz, 1 H), 3.38 (t, $J = 8.3$ Hz, 1 H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.3, 138.3, 138.0, 137.7, 132.4, 128.5, 128.4 (3 C), 128.3 (3 C), 128.2, 128.0, 127.8,

127.7, 127.6, 117.8, 85.9, 81.6, 80.1, 77.4, 76.1, 75.6, 74.9, 74.7, 73.5, 68.1; HRMS (MALDI-FTMS) calcd for $C_{38}H_{41}NO_7Na^+$ $[M + Na^+]$ 646.2775, found 646.2766.

CO₂Me-protected 2,3,4-tri-*O*-benzyl- β -D-fucosylamine (31): $R_f = 0.70$ (silica gel, EtOAc/hexanes, 1:1); IR (film) ν_{max} 3326, 2927, 1730, 1504, 1453, 1351, 1067, 736, 697 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.31 (m, 15 H), 5.81 (br d, $J = 6.4$ Hz, 1 H), 5.76 (br s, 1 H), 4.69 (AB, $J = 9.4$ Hz, $\nu_{ab} = 21.4$ Hz, 2 H), 4.67 (m, 1 H), 4.57 (m, 3 H), 4.24 (dd, $J = 4.7, 2.6$ Hz, 1 H), 4.04 (d, $J = 1.5$ Hz, 1 H), 3.98 (br s, 1 H), 3.80 (m, 1 H), 3.77 (br s, 3 H), 1.20 (d, $J = 4.9$ Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 138.6, 137.2, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8 (2 C), 127.6, 127.4, 86.1, 85.3 (2 C), 82.4, 74.1, 71.8, 71.4, 52.3, 15.7; HRMS (MALDI-FTMS) calcd for $C_{29}H_{33}NO_6Na^+$ $[M + Na^+]$ 514.2200, found 514.2191.

Alloc-protected 2,3,4,6-tetra-*O*-methyl- β -D-mannosylamine (33): $R_f = 0.38$ (silica gel, EtOAc); IR (film) ν_{max} 3332, 2934, 1726, 1529, 1450, 1305, 1237, 1100 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 5.90 (ddd, $J = 23.1, 10.7, 4.8$ Hz, 1 H), 5.52 (br s, 1 H), 5.32 (d, $J = 17.2$ Hz, 1 H), 5.22 (d, $J = 10.3$ Hz, 1 H), 4.60 (s, 2 H), 3.63–3.48 (m, 15 H), 3.45–3.42 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 132.7, 118.7, 80.4, 77.1, 76.4, 73.3, 71.6, 66.5, 59.7, 58.8, 58.3, 51.5; HRMS (MALDI-FTMS) calcd for $C_{14}H_{25}NO_7Na^+$ $[M + Na^+]$ 342.1523, found 342.1522.

CO₂Me-protected 2,3,5-tri-*O*-benzyl- β -L-arabinofuranosylamine 35: $R_f = 0.63$ (silica gel, EtOAc/hexanes, 1:1); IR (film) ν_{max} 3317, 3030, 2865, 1732, 1498, 1454, 1363, 1238, 1058, 739, 698 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.27 (m, 15 H), 5.88 (br d, $J = 9.4$ Hz, 1 H), 5.76 (br d, $J = 10.0$ Hz, 1 H), 4.61–4.45 (m, 6 H), 4.38 (app t, $J = 5.6$ Hz, 1 H), 4.02 (s, 1 H), 3.93 (s, 1 H), 3.70 (br s, 3 H), 3.64 (dd, $J = 9.4, 5.9$ Hz, 1 H), 3.52 (app t, $J = 8.8$ Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 137.9, 137.1, 128.4 (2 C), 128.3, 128.2, 127.9, 127.8, 127.7, 127.6 (2 C), 85.5, 84.9, 82.7, 82.1, 73.2, 71.6, 71.4, 70.0, 52.2; HRMS (MALDI-FTMS) calcd for $C_{28}H_{31}NO_6Na^+$ $[M + Na^+]$ 500.2043, found 500.2033.

CO₂Me-protected ribosylamine 37: $R_f = 0.67$ (silica gel, EtOAc/hexanes, 1:2); IR (film) ν_{max} 3347, 2933, 1737, 1509, 1461, 1377, 1251, 1082, 931, 837, 779 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 6.27 (br d, $J = 11.8$ Hz, 1 H), 5.68 (br d, $J = 10.0$ Hz, 1 H), 4.72 (d, $J = 5.9$ Hz, 1

H), 4.50 (d, $J = 6.2$ Hz, 1 H), 4.29 (s, 1 H), 3.77 (m, 1 H), 3.71 (m, 3 H), 3.66 (br s, 3 H), 1.51 (s, 3 H), 1.33 (s, 3 H), 0.94 (s, 9 H), 0.13 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.8, 112.2, 89.0, 86.6, 86.0, 82.1, 79.4, 65.0, 51.8, 25.7, 24.8, 18.1; HRMS (MALDI-FTMS) calcd for $\text{C}_{16}\text{H}_{31}\text{NO}_6\text{SiNa}^+ [\text{M} + \text{Na}^+]$ 384.1813, found 384.1814.

2,3,4,6-Tetra-*O*-benzyl- β -D-glucosylamine. Et_2NH (0.179 mL, 3.40 mmol, 40 equiv) was added to a solution of intermediate **29** (0.053 g, 0.085 mmol, 1.0 equiv) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1, 2 mL) at 25 °C. After stirring this mixture for 5 minutes at 25 °C, $\text{Pd}(\text{OAc})_2$ (0.002 g, 0.009 mmol, 0.1 equiv) and TPPTS (0.010 g, 0.017 mmol, 0.2 equiv) were added sequentially, providing a yellow solution which was stirred for an additional 30 minutes at 25 °C. Upon completion, the reaction contents were poured into water (5 mL), and extracted with EtOAc (3 $\times$ 10 mL). The combined organic layers were then dried (MgSO_4) and concentrated to give 2,3,4,6-tetra-*O*-benzyl- β -D-glucosylamine (0.043 g, 95% yield)² as an amorphous white solid: R_f = 0.48 (silica gel, EtOAc/hexanes, 1:1); IR (film) ν_{max} 3352, 3030, 2862, 1453, 1351, 1122, 1094, 1086, 1027, 750, 698 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.48–7.21 (m, 20 H), 5.08 (d, $J = 13.2$ Hz, 1 H), 5.03 (d, $J = 13.1$ Hz, 1 H), 4.94–4.86 (m, 3 H), 4.65 (AB, $J = 14.3$ Hz, $\nu_{\text{ab}} = 37.4$ Hz, 2 H), 4.58 (m, 1 H), 4.20 (d, $J = 9.9$ Hz, 1 H), 3.85–3.80 (m, 5 H), 3.56 (dd, $J = 11.5$, 3.3 Hz, 1 H), 3.30 (t, $J = 10.4$ Hz, 1 H), 1.97 (br s, 2 H); ^{13}C NMR (150 MHz, CDCl_3) δ 138.6, 138.3, 138.0, 137.9, 128.7, 128.4 (2 C), 128.3, 128.2, 127.9, 127.8 (2 C), 127.7 (2 C), 127.6, 86.2, 85.8, 83.4, 78.1, 75.7, 75.6, 75.0, 74.9, 73.5, 68.9; HRMS (MALDI-FTMS) calcd for $\text{C}_{34}\text{H}_{38}\text{NO}_5^+ [\text{M} + \text{H}^+]$ 540.2744, found 540.2750.⁵

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