Supporting Information

Intramolecular Hydrogen Abstraction Reaction Promoted by *N*-Radicals in Carbohydrates. Synthesis of Chiral 7-Oxa-2-azabicyclo[2.2.1]heptane and 8-Oxa-6-azabicyclo[3.2.1]octane Ring Systems

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Contents: Detailed experimental procedures, and spectral and analytical data for compounds: **2**, **3**, **5**, **6**, **8-10**, **12-14**, **16**, and **18-23**.

Methyl 3,6-Anhydro-7-azido-2,7-dideoxy-4,5-*O*-isopropylidene-D-*altro*-heptonate (2). To a solution of compound **1**¹ (398 mg, 1.62 mmol) in dry toluene (15 mL), were added Ph₃P (847 mg, 3.23 mmol), ZnN₆•2Py² (373 mg, 1.21 mmol), and DIAD (0.64 mL, 3.23 mmol). The mixture was stirred at rt for 27 h under nitrogen, poured into water and extracted with EtOAc. The organic layer was dried (Na₂SO₄) and concentrated in vacuo. Column chromatography of the residue (hexanes–EtOAc, 80:20) gave compound **2** (352 mg, 1.3 mmol, 80.5%) as a colorless oil: [α]_D +21 (*c* = 1.82); IR 2988, 2940, 2102, 1738, 1383, 1273 cm⁻¹; ¹H NMR 1.31 (3H, s), 1.46 (3H, s), 2.71 (1H, dd, *J* = 6.8, 16.5 Hz), 2.76 (1H, dd, *J* = 6.8, 16.5 Hz), 3.26 (1H, dd, *J* = 4.9, 12.9 Hz), 3.39 (1H, dd, *J* = 6.4, 13.1 Hz), 3.69 (3H, s), 4.18 (1H, dd, *J* = 5.7, 5.7 Hz), 4.38 (1H, ddd, *J* = 4.1, 6.9, 6.9 Hz), 4.61 (1H, dd, *J* = 1.5, 6.1 Hz), 4.77 (1H, dd, *J* = 4.0, 6.1 Hz); ¹³C NMR 14.9 (CH₃), 26.1 (CH₃), 34.2 (CH₂), 51.5 (CH₂), 51.7 (CH₃), 77.3 (CH), 81.2 (CH), 82.6 (CH), 83.2 (CH), 112.9 (C), 171.3 (C); MS (EI) *m/z* (rel intensity) 272 (M⁺ +

H, 3), 256 (90), 240 (27), 215 (52); HRMS calcd for $C_{11}H_{18}N_3O_5$ 272.1246329, found 272.126366. Anal. Calcd for $C_{11}H_{17}N_3O_5$: C, 48.70; H, 6.32; N, 15.49. Found: C, 49.01; H, 6.51; N, 15.12.

Methyl 3,6-Anhydro-2,7-dideoxy-7-[(diphenoxyphosphoryl)amino]-4,5-O-isopropylidene-D-*altro*-heptonate (3). To a solution of compound **2** (121 mg, 0.446 mmol) in dry EtOAc (5 mL) was added Pd/C (5%) (30 mg, 25%) and the degassed mixture was stirred under hydrogen, at room temperature and atmospheric pressure, for 1 h. The reaction mixture was filtered through Celite and the solvent evaporated in vacuo to give the crude amine which was dissolved in dry CH_2Cl_2 (5 mL) and treated with TEA (250 μ L, 1.78 mmol) and diphenylchlorophosphate (180 μ L, 0.89 mmol). The mixture was stirred at rt for 1.5 h under nitrogen, poured into a dilute hydrochloric acid (5%) solution, and extracted with $CHCl_3$. The organic layer was washed with an aqueous saturated solution of $NaHCO_3$ and concentrated in vacuo. Column chromatography of the residue (hexanes–EtOAc, 60:40) afforded the title compound **3** (140 mg, 0.29 mmol, 65%) as a colorless oil: $[\alpha]_D^{25} +17.5$ ($c = 0.61$); IR 3223, 3068, 2992, 2952, 1738, 1591, 1488 cm^{-1} ; 1H NMR 1.25 (3H, s), 1.43 (3H, s), 2.64 (1H, dd, $J = 6.9, 16.7$ Hz), 2.72 (1H, dd, $J = 6.7, 16.7$ Hz), 3.04 (1H, m), 3.13 (1H, m), 3.66 (3H, s), 4.02 (1H, dd, $J = 5.1, 8.8$ Hz), 4.18 (1H, ddd, $J = 4.0, 6.8, 6.8$ Hz), 4.19 (1H, d, $J = 6.2$ Hz), 4.63 (1H, dd, $J = 4.0, 6.1$ Hz), 7.1–7.3 (10H, m); ^{13}C NMR 24.8 (CH_3), 26.0 (CH_3), 33.9 (CH_2), 41.2 (CH_2), 51.7 (CH_3), 76.2 (CH), 80.9 (CH), 82.8 (CH), 83.0 (CH, $^3J_{CP} = 6.1$ Hz), 112.9 (C), 120.1 ($4 \times CH$), 125.0 ($2 \times CH$), 129.7 ($4 \times CH$), 159.4 ($2 \times C$), 171.3 (C); MS (EI) m/z (rel intensity) 478 ($M^+ + H$, 5), 462 (27), 446 (13), 419 (6), 388 (10), 262 (100); HRMS calcd for $C_{23}H_{29}NO_8P$ 478.1630634, found 478.159203. Anal. Calcd for $C_{23}H_{28}NO_8P$: C, 57.86; H, 5.91; N, 2.93. Found: C, 57.52; H, 6.02; N, 3.3.

4,7-Anhydro-8-azido-1,2,3,8-tetradecoxy-5,6-*O*-oxomethylene-D-*altro*-oct-1-enitol

(5). To a solution of compound **4**³ (387 mg, 1.93 mmol) in dry pyridine (5 mL), was added under nitrogen at 0 °C mesyl chloride (442 mg, 3.86 mmol). The mixture was stirred at rt for 20 min, poured into an aqueous solution of hydrochloric acid (5%) and extracted with EtOAc. The organic layer was washed with a saturated solution of NaHCO₃, dried over Na₂SO₄ and concentrated in vacuo. To the crude mesylate in dry DMF (5 mL) was added NaN₃ (627 mg, 9.66 mmol). After stirring under an atmosphere of nitrogen at 80 °C for 30 min, the mixture was poured into brine and extracted with EtOAc. The organic layer was dried over Na₂SO₄ and concentrated in vacuo. Column chromatography (*n*-hexane–EtOAc, 80:20) of the residue afforded compound **5** (430 mg, 1.91 mmol, 98.8%) as a colorless oil: $[\alpha]_D -9.8$ ($c = 1.25$); IR 2921, 2105, 1799, 1166, 1086 cm⁻¹; ¹H NMR 2.49 (2H, m), 3.49 (1H, dd, $J = 4.4, 13.1$ Hz), 3.58 (1H, dd, $J = 4.8, 13.1$ Hz), 4.20 (1H, ddd, $J = 3.1, 7.0, 7.0$ Hz), 4.42 (1H, dd, $J = 4.8, 4.8$ Hz), 5.08 (1H, dd, $J = 7.5, 7.5$ Hz), 5.10 (1H, d, $J = 6.8$ Hz), 5.15 (1H, d, $J = 10.2$ Hz), 5.23 (1H, dd, $J = 1.4, 17.4$ Hz), 5.82 (1H, m); ¹³C NMR 32.3 (CH₂), 51.0 (CH₂), 80.3 (2 × CH), 80.9 (CH), 81.2 (CH), 117.8 (CH₂), 131.6 (CH), 153.0 (C); MS (EI) m/z (rel intensity) 226 (M⁺ + H, <1), 197 (4), 184 (6); HRMS calcd for C₉H₁₂N₃O₄ 226.0827712, found 226.083309. Anal. Calcd for C₉H₁₁N₃O₄: C, 48.00; H, 4.92; N, 18.66. Found: C, 48.36; H, 4.80; N, 18.30.

4,7-Anhydro-1,2,3,8-tetradecoxy-8-[(diphenoxyphosphoryl)amino]-5,6-*O*-

oxomethylene-D-*altro*-octitol (6). To a solution of compound **5** (380 mg, 1.69 mmol) in dry EtOAc (15 mL) was added Pd/C (5%) (114 mg, 30%) and the degassed mixture was stirred under hydrogen, at room temperature and atmospheric pressure, for 2.5 h. The reaction mixture was filtered through Celite and the solvent evaporated in vacuo to give the crude amine which was dissolved in dry CH₂Cl₂ (15 mL) and treated with TEA (684

mg, 6.75 mmol) and diphenylchlorophosphate (908 mg, 3.37 mmol). The mixture was stirred at rt for 1.5 h under nitrogen, poured into a dilute hydrochloric acid (5%) solution, and extracted with CHCl₃. The organic layer was washed with an aqueous saturated solution of NaHCO₃ and concentrated in vacuo. Column chromatography (*n*-hexane–EtOAc, 50:50) of the residue gave the title compound **6** (297 mg, 0.69 mmol, 40.9%) as a colorless oil: $[\alpha]_D^{+10}$ (*c* = 0.59); IR 3236, 3069, 2958, 1738, 1488, 1193 cm⁻¹; ¹H NMR 0.88 (3H, t, *J* = 7.4 Hz), 1.33 (2H, m), 1.57 (2H, m), 3.06 (2H, m), 3.81 (1H, ddd, *J* = 3.6, 6.9, 6.8 Hz), 4.14 (1H, dd, *J* = 7.1, 7.1 Hz), 4.49 (1H, ddd, *J* = 6.4, 6.4, 12.2 Hz), 4.78 (1H, dd, *J* = 3.8, 6.9 Hz), 4.92 (1H, d, *J* = 7.1 Hz), 7.16 (2H, dd, *J* = 7.4, 7.4 Hz), 7.20 (4H, dd, *J* = 2.3, 7.9 Hz), 7.31 (4H, dd, *J* = 7.9, 7.9 Hz); ¹³C NMR 13.2 (CH₃), 18.2 (CH₂), 29.5 (CH₂), 40.0 (CH₂), 79.3 (CH), 80.3 (CH), 81.1 (CH), 81.7 (CH, ³*J*_{CP} = 6.1 Hz), 119.4 (4 × CH), 124.5 (2 × CH), 129.1 (4 × CH), 149.7 (2 × C), 153.5 (C); MS (EI) *m/z* (rel intensity) 433 (*M*⁺, 1), 389 (1), 371 (4), 340 (5), 262 (100); HRMS calcd for C₂₁H₂₄NO₇P 433.1290263, found 433.133263. Anal. Calcd for C₂₁H₂₄NO₇P: C, 58.20; H, 5.58; N, 3.23. Found: C, 58.41; H, 5.86; N, 3.27.

3,6-Anhydro-7-azido-7-deoxy-1,2:4,5-di-*O*-isopropylidene-D-glycero-D-manno-heptitol (8). To a solution of compound **7**⁴ (250 mg, 0.91 mmol) in dry toluene (10 mL) were added Ph₃P (477 mg, 1.82 mmol), ZnN₆•2Py² (210 mg, 0.68 mmol), and DIAD (360 μL, 1.82 mmol). The mixture was stirred at rt for 15 h under nitrogen, poured into water and extracted with EtOAc. The organic layer was dried (Na₂SO₄) and concentrated in vacuo. Column chromatography of the residue (hexanes–EtOAc, 90:10→85:15) gave compound **8** (165 mg, 0.55 mmol, 60%) as a crystalline solid: mp 58–60 °C (from *n*-pentane–EtOAc); $[\alpha]_D^{+10}$ (*c* = 0.3); IR 2987, 2936, 2102, 1725, 1377, 1264, 1214, 1068 cm⁻¹; ¹H NMR 1.32 (3H, s), 1.34 (3H, s), 1.42 (3H, s), 1.47 (3H, s), 3.20 (1H, dd, *J* = 4.7, 12.9 Hz), 3.39 (1H, dd, *J* = 6.9, 12.9 Hz), 3.91 (1H, dd, *J*

= 3.7, 7.5 Hz), 4.02 (1H, dd, J = 4.7, 8.6 Hz), 4.07 (1H, dd, J = 6.4, 9.0 Hz), 4.20 (1H, dd, J = 5.6, 5.6 Hz), 4.35 (1H, dd, J = 6.9, 11.6 Hz), 4.60 (1H, d, J = 6.0 Hz), 4.78 (1H, dd, J = 3.9, 6.0 Hz); ^{13}C NMR (50.3 MHz) 24.7 (CH₃), 25.1 (CH₃), 26.2 (CH₃), 26.8 (CH₃), 51.4 (CH₂), 66.7 (CH₂), 73.4 (CH), 80.9 (CH), 81.7 (CH), 83.2 (CH), 83.6 (CH), 109.2 (C), 113.1 (C); MS (EI) m/z (rel intensity) 284 ($\text{M}^+ - \text{Me}$, 100); HRMS calcd for C₁₂H₁₈N₃O₅ 284.1246329, found 284.125595. Anal. Calcd for C₁₃H₂₁N₃O₅: C, 52.16; H, 7.07; N, 14.04. Found: C, 51.93; H, 7.35; N, 13.68.

3,6-Anhydro-7-deoxy-7-[(diphenoxyphosphoryl)amino]-1,2:4,5-di-*O*-isopropylidene-D-glycero-D-manno-heptitol (9). To a solution of compound **8** (226 mg, 0.75 mmol) in dry EtOAc (8 mL) was added Pd/C (5%) (68 mg, 30%) and the degassed mixture was stirred under hydrogen, at room temperature and atmospheric pressure, for 1.5 h. The reaction mixture was filtered through Celite and the solvent evaporated in vacuo to give the crude amine which was dissolved in dry CH₂Cl₂ (10 mL) and treated with TEA (430 μL , 3.02 mmol) and diphenylchlorophosphate (320 μL , 1.51 mmol). The mixture was stirred at rt for 1 h under nitrogen, poured into a dilute hydrochloric acid (5%) solution, and extracted with CHCl₃. The organic layer was washed with an aqueous saturated solution of NaHCO₃ and concentrated in vacuo. Column chromatography of the residue (hexanes–EtOAc, 60:40) afforded the title compound **9** (350 mg, 0.69 mmol, 91%) as a solid: mp 134.2–135 °C (from *n*-hexane–EtOAc); $[\alpha]_{\text{D}} +9.5$ (c = 0.35); IR 3236, 3068, 2986, 2937, 1592, 1489 cm⁻¹; ^1H NMR (C₆D₆) 1.17 (3H, s), 1.38 (3H, s), 1.44 (3H, s), 1.53 (3H, s), 2.89 (2H, ddd, J = 6.9, 6.9, 10.5 Hz), 3.84 (1H, dd, J = 3.8, 6.8 Hz), 4.07 (1H, ddd, J = 6.4, 6.4, 12.3 Hz), 4.14 (1H, dd, J = 6.6, 8.7 Hz), 4.24 (1H, dd, J = 5.9, 16.9 Hz), 4.25 (1H, dd, J = 7.2, 7.2 Hz), 4.37 (1H, dd, J = 3.8, 5.9 Hz), 4.59 (1H, dd, J = 6.3, 12.7 Hz), 6.93 (2H, dd, J = 7.2, 14.4 Hz), 7.12 (4H, dd, J = 8.7, 16.3 Hz), 7.45 (4H, dd, J = 2.5, 8.1 Hz); ^{13}C NMR (C₆D₆)

24.8 (CH₃), 25.6 (CH₃), 26.4 (CH₃), 27.1 (CH₃), 41.9 (CH₂), 67.2 (CH₂), 73.9 (CH), 81.2 (CH), 81.5 (CH), 83.2 (CH), 84.5 (CH, ³J_{CP} = 5.7 Hz), 108.9 (C), 112.4 (C), 120.7 (4 × CH), 125.0 (2 × CH), 129.9 (4 × CH), 151.5 (2 × C); MS (EI) *m/z* (rel intensity) 506 (M⁺ + H, 3), 490 (19), 432 (25), 262 (100); HRMS calcd for C₂₅H₃₃NO₈P 506.1943618, found 506.197502. Anal. Calcd for C₂₅H₃₂NO₈P: C, 59.40; H, 6.38; N, 2.77. Found: C, 59.39; H, 6.24; N, 2.80.

3,6-Anhydro-7-[(tert-butoxycarbonyl)amino]-7-deoxy-1,2:4,5-di-*O*-isopropylidene-D-glycero-D-manno-heptitol (10). To a solution of compound **8** (118 mg, 0.39 mmol) in dry EtOAc (6 mL) was added Pd/C (5%) (35 mg, 30%) and di-*tert*-butyldicarbonate (127 mg, 0.58 mmol), and the degassed mixture was stirred under hydrogen, at room temperature and atmospheric pressure, for 5 h. The reaction mixture was filtered through Celite and the solvent evaporated in vacuo. The residue was purified by column chromatography (*n*-hexane–EtOAc, 70:30) to give compound **10** (131 mg, 0.35 mmol, 90%) as a colorless oil: [α]_D +11 (*c* = 0.23, CCl₄); IR 3367, 2983, 1715, 1257 cm⁻¹; ¹H NMR 1.33 (3H, s), 1.37 (3H, s), 1.44 (12H, s), 1.48 (3H, s), 3.06 (1H, ddd, *J* = 4.5, 9.0, 13.6 Hz), 3.25 (1H, dd, *J* = 7.0, 13.5 Hz), 3.83 (1H, dd, *J* = 3.8, 6.5 Hz), 4.03 (1H, dd, *J* = 4.6, 8.7 Hz), 4.07 (1H, m), 4.08 (1H, m), 4.38 (1H, ddd, *J* = 4.7, 6.5, 6.5 Hz), 4.57 (1H, d, *J* = 6.1 Hz), 4.77 (1H, dd, *J* = 3.8, 6.0 Hz); ¹³C NMR 24.8 (CH₃), 25.1 (CH₃), 26.1 (CH₃), 26.9 (CH₃), 28.3 (3 × CH₃), 40.1 (CH₂), 66.8 (CH₂), 73.4 (CH), 77.1 (C) 80.6 (CH), 80.7 (CH), 83.1 (CH), 83.6 (CH), 109.2 (C), 112.8 (C), 155.5 (C); MS (EI) *m/z* (rel intensity) 358 (M⁺ – Me, 9), 302 (14), 244 (43); HRMS calc for C₁₇H₂₈NO₇ 358.1865607, found 358.186111. Anal. Calcd for C₁₈H₃₁NO₇: C, 57.89; H, 8.37; N, 3.75. Found: C, 57.99; H, 8.42; N, 3.77.

2,6-Anhydro-1-[[bis(benzyloxy)phosphoryl]amino]-7-*O*-(*tert*-butyldimethyl)silyl-1,3,4,5-tetradecoxy-D-threo-heptitol (12). To a solution of

compound 7-*O*-acetyl-2,6-anhydro-3,4,5-trideoxy-D-*threo*-heptonitrile⁵ (140 mg, 0.76 mmol) in MeOH (5 mL) was added Na₂CO₃ (121 mg, 1.15 mmol). After stirring at rt for 3 h, CH₂Cl₂ (10 mL) was added and the mixture filtered and concentrated under reduced pressure. The crude alcohol (87 mg) was dissolved in dry DMF (5 mL) containing imidazole (78 mg, 1.146 mmol) and *tert*-butyldimethylsilyl chloride (137 mg, 0.92 mmol). The mixture was stirred at rt for 30 min, poured into ice-water, and extracted with EtOAc. The organic layer was washed with water, dried over Na₂SO₄, and concentrated in vacuo. Column chromatography (hexanes–EtOAc, 85:15) of the residue afforded the corresponding silyl ether **11** (129 mg, 0.50 mmol, 70%) as a colorless oil, which was added to a suspension of LAH (77 mg, 2.02 mmol) in dry THF (10 mL) at rt under nitrogen. The mixture was stirred at reflux temperature for 30 min. The excess hydride was destroyed by adding a saturated aqueous solution of Na₂SO₄, and the white salts were separated by filtration. Concentration under reduced pressure gave the crude amine as a colorless oil which was dissolved in dry CHCl₃ (2 mL) and treated with TEA (255 mg, 2.53 mmol) and a freshly prepared solution of dibenzylchlorophosphate in benzene (8 mL, 1.02 mmol, 0.12 M). The mixture was stirred at rt for 1.5 h under nitrogen, poured into an aqueous hydrochloric acid solution (10%), and extracted with EtOAc. The organic layer was washed with an aqueous saturated solution of NaHCO₃, dried (Na₂SO₄), and concentrated in vacuo. Column chromatography (hexanes–EtOAc, 60:40→50:50) of the residue afforded compound **12** (150 mg, 0.29 mmol, 54%) as a colorless oil: [α]_D +7.5 (*c* = 0.32); IR 3244, 3034, 2929, 1456, 1380, 1257, 998 cm⁻¹; ¹H NMR (200 MHz) 0.02 (6H, s), 0.87 (9H, s), 1.23–1.55 (6H, m), 2.81 (1H, m), 3.03 (1H, m), 3.54 (1H, m), 3.58 (1H, m), 5.06 (4H, m), 7.30 (10H, br s); ¹³C NMR (50.3 MHz) –5.3 (CH₃), –5.4 (CH₃), 18.2 (CH₂), 18.5 (C), 25.8 (3 × CH₃), 26.1 (CH₂), 27.1 (CH₂), 43.2 (CH₂), 64.4 (CH₂), 67.2 (CH₂, ²*J*_{CP} = 5.2 Hz), 67.8

(CH₂, $^2J_{CP}$ = 5.2 Hz), 71.3 (CH, $^3J_{CP}$ = 7.3 Hz), 71.6 (CH), 127.7 (4 × CH), 128.2 (2 × CH), 128.4 (2 × CH), 128.6 (2 × CH), 136.5 (2 × C); MS (EI) m/z (rel intensity) 519 (M⁺, <1), 504 (<1), 486 (<1), 462 (11), 91 (100); HRMS calcd for C₂₇H₄₂NO₅PSi 519.2569699, found 519.253769. Anal. Calcd for C₂₇H₄₂NO₅PSi: C, 62.40; H, 8.15; N, 2.70; Found: C, 62.57; H, 8.42; N, 2.63.

2,6-Anhydro-3,4-dideoxy-5,7-di-*O*-methyl-D-arabino-heptonitrile (13). To a suspension of NaH (202 mg, 8.4 mmol) in dry DMF (40 mL) was added 2,6-anhydro-3,4-dideoxy-D-arabino-heptonitrile^{5c,6} (440 mg, 2.8 mmol) in DMF (10 mL) and the mixture stirred at 0 °C under nitrogen until all hydrogen evolution had ceased. Then an excess of methyl iodide (1.75 mL, 28 mmol) was added dropwise and stirring continued at room temperature for 2 h. Excess reagent was destroyed by slow addition of MeOH and the solution poured into water and extracted with EtOAc. The organic extracts were dried over Na₂SO₄ and concentrated in vacuo. Column chromatography (hexanes–EtOAc, 80:20) of the residue afforded **13** (430 mg, 2.32 mmol, 83%) as a colorless oil: $[\alpha]_D +103.5$ (c = 0.54); IR 2935, 2830, 1455, 1105 cm⁻¹; ¹H NMR 1.65 (1H, m), 1.94 (2H, m), 2.25 (1H, ddd, J = 4.1, 8.1, 12.5 Hz), 3.20 (1H, dddd, J = 4.7, 4.7, 4.7, 10.9 Hz), 3.34 (3H, s), 3.36 (3H, s), 3.56 (1H, m), 3.63 (2H, m), 4.78 (1H, dd, J = 3.4, 3.4 Hz); ¹³C NMR 24.9 (CH₂), 27.7 (CH₂), 56.6 (CH₃), 59.2 (CH₃), 64.2 (CH), 71.0 (CH₂), 73.2 (CH), 76.8 (CH), 117.0 (C); MS (EI) m/z (rel intensity) 185 (M⁺, 5), 170 (1), 153 (4), 140 (6), 58 (100); HRMS calcd for C₉H₁₅NO₃ 185.1051845, found 185.102406. Anal. Calcd for C₉H₁₅NO₃: C, 58.36; H, 8.16; N, 7.56. Found: C, 58.35; H, 7.89; N, 7.36.

2,6-Anhydro-1,3,4-trideoxy-1-[(diphenoxyphosphoryl)amino]-5,7-di-*O*-methyl-D-arabino-heptitol (14). A suspension of LAH (55 mg, 1.47 mmol) in dry THF (5 mL) was stirred at room temperature as a solution of compound **13** (136 mg, 0.73 mmol) in

THF (5 mL) was added. The reaction mixture was kept at this temperature for 1 h. The excess hydride was destroyed by adding a saturated aqueous solution of Na₂SO₄, and the white salts were separated by filtration. Concentration under reduced pressure gave the crude amine (142 mg) as a colorless oil which was dissolved in dry CH₂Cl₂ (5 mL) and treated with TEA (410 µL, 2.94 mmol) and diphenylchlorophosphate (310 µL, 1.47 mmol). The mixture was stirred at rt for 1.5 h under nitrogen, poured into a dilute hydrochloric acid (5%) solution, and extracted with CHCl₃. The organic layer was washed with an aqueous saturated solution of NaHCO₃ and concentrated in vacuo. Column chromatography (hexanes–EtOAc, 1:1) of the residue afforded compound **14** (221 mg, 0.52 mmol, 71%) as a colorless oil: [α]_D +34 (*c* = 0.93); IR 3238, 3067, 2935, 1590, 1489, 1194 cm⁻¹; ¹H NMR 1.51 (1H, m), 1.58 (1H, m), 1.69 (1H, m), 1.79 (1H, m), 3.09 (1H, m), 3.18 (2H, m), 3.31 (3H, s), 3.32 (3H, s), 3.41 (1H, dd, *J* = 4.7, 10.0 Hz), 3.46 (1H, dd, *J* = 5.4, 9.9 Hz), 3.67 (1H, m), 3.70 (1H, dd, *J* = 5.2, 10.3 Hz), 7.14 (4H, dd, *J* = 7.1, 7.1 Hz), 7.22 (2H, d, *J* = 8.6 Hz), 7.30 (4H, dd, *J* = 7.8, 7.8 Hz); ¹³C NMR 23.1 (CH₂), 23.5 (CH₂), 43.9 (CH₂), 56.3 (CH₃), 59.1 (CH₃), 71.1 (CH, ³*J*_{CP} = 6.2 Hz), 71.4 (CH₂), 73.3 (CH), 74.0 (CH), 120.1 (4 × CH), 124.8 (2 × CH), 129.6 (4 × CH), 150.7 (2 × C); MS (EI) *m/z* (rel intensity) 422 (*M*⁺ + H, 33), 389 (16), 357 (24), 263 (100); HRMS calcd for C₂₁N₂₈NO₆P 421.1654106, found 421.163956. Anal. Calcd for C₂₁H₂₈NO₆P: C, 59.85; H, 6.70; N, 3.32. Found: C, 59.91; H, 6.55; N, 3.41.

2,6-Anhydro-7-deoxy-7-[(diphenoxyphosphoryl)amino]-1,3,4,5-tetra-*O*-methyl-D-glycero-L-gulo-heptitol (16). To a suspension of LAH (300 mg, 7.91 mmol) in dry THF (10 mL) was added compound **15**⁷ (485 mg, 1.98 mmol) at rt under nitrogen. The mixture was stirred at reflux temperature for 30 min. The excess hydride was destroyed by adding a saturated aqueous solution of Na₂SO₄, and the white salts were separated by filtration. Concentration under reduced pressure gave the crude amine as a colorless oil

which was dissolved in dry CH_2Cl_2 (10 mL) and treated with TEA (1.1 mL, 7.91 mmol) and diphenylchlorophosphate (0.82 mL, 3.95 mmol). The mixture was stirred at rt for 1.5 h under nitrogen, poured into an aqueous hydrochloric acid solution (10%), and extracted with EtOAc. The organic layer was washed with an aqueous saturated solution of NaHCO_3 , dried (Na_2SO_4), and concentrated in vacuo. Column chromatography (hexanes–EtOAc, 50:50) of the residue afforded compound **16** (495 mg, 1.03 mmol, 52%) as a colorless oil: $[\alpha]_{\text{D}} +41$ ($c = 0.64$); IR 3236, 2936, 1591, 1488, 1102 cm^{-1} ; ^1H NMR 3.12 (1H, dd, $J = 9.1, 9.1$ Hz), 3.21 (1H, dd, $J = 8.7, 8.7$ Hz), 3.30 (2H, m), 3.33 (2H, m), 3.35 (3H, s), 3.39 (3H, s), 3.46 (2H, d, $J = 3.5$ Hz), 3.49 (3H, s), 3.57 (3H, s), 4.01 (1H, ddd, $J = 5.2, 5.2, 5.2$ Hz); ^{13}C NMR 37.4 (CH_2), 59.0 (CH_3), 59.2 (CH_3), 60.3 (CH_3), 60.6 (CH_3), 71.2 (CH_2), 71.4 (CH), 73.2 (CH), 79.2 (CH), 80.7 (CH), 83.5 (CH), 120.2 ($4 \times \text{CH}$), 124.9 ($2 \times \text{CH}$), 129.7 ($4 \times \text{CH}$), 150.7 ($2 \times \text{C}$); MS (EI) m/z (rel intensity) 481 (M^+ , 1), 436 (<1), 417 (3); HRMS calcd for $\text{C}_{23}\text{H}_{32}\text{NO}_8\text{P}$ 481.1865372, found 481.190155. Anal. Calcd for $\text{C}_{23}\text{H}_{32}\text{NO}_8\text{P}$: C, 57.37; H, 6.70; N, 2.91. Found: C, 57.62; H, 6.56; N, 2.78.

2,6-Anhydro-7-azido-7-deoxy-1,3,4,5-tetra-*O*-methyl-D-glycero-D-manno-heptitol (18). To a solution of compound **17**³ (310 mg, 1.24 mmol) in dry toluene (15 mL) were added Ph_3P (650 mg, 2.48 mmol), $\text{ZnN}_6 \bullet 2\text{Py}^2$ (381 mg, 1.24 mmol) and DIAD (501 mg, 2.48 mmol). The mixture was stirred at rt for 30 h under nitrogen, filtered through Celite and concentrated in vacuo. Column chromatography (hexanes–EtOAc, 60:40) of the residue gave compound **18** (223 mg, 0.81 mmol, 65 %) as a colorless oil: $[\alpha]_{\text{D}} +41.5$ ($c = 1.08$); IR 2984, 2934, 2826, 2100, 1455, 1287, 1198, 1120 cm^{-1} ; ^1H NMR 3.39 (3H, s), 3.41 (3H, s), 3.44 (3H, s), 3.46 (2H, dd, $J = 4.0, 10.8$ Hz), 3.48 (1H, m), 3.50 (3H, s), 3.52 (1H, dd, $J = 3.6, 4.5$ Hz), 3.59 (1H, dd, $J = 5.4, 10.2$ Hz), 3.68 (1H, dd, $J = 3.6, 3.6$ Hz), 3.69 (1H, dd, $J = 6.0, 10.2$ Hz), 3.96 (1H, m), 3.97

(1H, m); ^{13}C NMR 51.3 (CH₂), 57.0 (CH₃), 58.2 (CH₃), 58.4 (CH₃), 59.1 (CH₃), 69.6 (CH), 70.4 (CH₂), 73.3 (CH), 75.2 (CH), 75.7 (CH), 76.1 (CH); MS (EI) m/z (rel intensity) 275 (M⁺, 1), 262 (2), 247 (3), 232 (3), 219 (27); HRMS calcd for C₁₁H₂₁N₃O₅ 275.1481067, found 275.149635. Anal. Calcd for C₁₁H₂₁N₃O₅: C, 47.99; H, 7.69; N, 15.27. Found: C, 47.88; H, 8.03; N, 14.93.

2,6-Anhydro-7-deoxy-7-[(diphenoxyphosphoryl)amino]-1,3,4,5-tetra-*O*-methyl-D-glycero-D-manno-heptitol (19). To a suspension of LAH (82 mg, 2.18 mmol) in dry THF (8 mL) was added compound **18** (150 mg, 0.54 mmol) at rt under nitrogen. The mixture was refluxed for 30 min. The excess hydride was destroyed by adding a saturated aqueous solution of Na₂SO₄, and the white salts were separated by filtration. Concentration under reduced pressure gave the crude amine (210 mg) as a colorless oil which was dissolved in dry CH₂Cl₂ (7 mL) and treated with TEA (300 μL , 2.18 mmol) and diphenylchlorophosphate (230 μL , 1.09 mmol). The mixture was stirred at rt for 2 h under nitrogen, poured into a dilute hydrochloric acid (5%) solution, and extracted with EtOAc. The organic layer was washed with an aqueous saturated solution of NaHCO₃ and concentrated in vacuo. Column chromatography (hexanes–EtOAc, 50:50 $\rightarrow$ 25:75) of the residue afforded compound **19** (166 mg, 0.34 mmol, 62.5%) as a colorless oil: $[\alpha]_{\text{D}} +19.5$ ($c = 0.66$); IR 3242, 3070, 2932, 2826, 1591, 1487, 1455, 1193, 1114, 1025 cm⁻¹; ^1H NMR 3.26 (1H, dd, $J = 7.6, 13.2$ Hz), 3.30 (3H, s), 3.32 (3H, s), 3.34 (1H, m), 3.40 (1H, dd, $J = 3.5, 7.3$ Hz), 3.41 (3H, s), 3.44 (1H, m), 3.45 (3H, s), 3.46 (1H, dd, $J = 5.1, 10.2$ Hz), 3.60 (1H, dd, $J = 7.1, 10.2$ Hz), 3.62 (1H, dd, $J = 4.5, 4.5$ Hz), 3.81 (1H, ddd, $J = 4.0, 7.2, 7.2$ Hz), 3.85 (1H, ddd, $J = 4.7, 4.7, 7.0$ Hz), 7.12–7.32 (10H, m); ^{13}C NMR 41.3 (CH₂), 56.1 (CH₃), 57.6 (2 $\times$ CH₃), 58.3 (CH₃), 68.9 (CH, $^3J_{\text{CP}} = 6.1$ Hz), 69.7 (CH₂), 72.5 (CH), 74.6 (CH), 75.1 (CH), 75.4 (CH), 119.5 (4 $\times$ CH), 124.1 (2 $\times$ CH), 128.9 (4 $\times$ CH), 150.0 (2 $\times$ C); MS (EI) m/z (rel intensity) 482 (M⁺ + H, 1), 417

(18), 385 (63); HRMS calcd for $C_{23}H_{33}NO_8P$ 482.1943618, found 482.201019. Anal. Calcd for $C_{23}H_{32}NO_8P$: C, 57.37; H, 6.70; N, 2.91. Found: C, 57.46; H, 6.83; N, 2.97.

2,6-Anhydro-7-deoxy-3,4,5-tri-*O*-methyl-L-glycero-L-talo-heptonitrile (20- α) and 2,6-Anhydro-7-deoxy-3,4,5-tri-*O*-methyl-L-glycero-L-galacto-heptonitrile (20- β). To a solution of 1-*O*-acetyl-6-deoxy-2,3,4-tri-*O*-methyl-L-mannopyranose⁸ (568 mg, 2.29 mmol) in dry MeCN (15 mL) were added trimethylsilyl cyanide (1.22 mL, 9.15 mmol) and $BF_3 \cdot OEt_2$ (280 μ L, 2.29 mmol) at 0 °C under nitrogen. The mixture was stirred at rt for 30 min, poured into ice-water and extracted with EtOAc. The organic layer was dried (Na_2SO_4) and concentrated in vacuo. Column chromatography (hexanes–EtOAc, 75:25) of the residue gave compound **20- α** (187 mg, 0.87 mmol, 38%) and compound **20- β** (204 mg, 0.95 mmol, 41.5%). Compound **20- α** : crystalline solid; mp 87.5–88 °C (from *n*-hexane–EtOAc); $[\alpha]_D^{+34}$ ($c = 0.31$); IR 2937, 1106 cm^{-1} ; 1H NMR 1.32 (3H, d, $J = 6.1$ Hz), 3.12 (1H, m), 3.14 (1H, m), 3.18 (1H, m), 3.51 (3H, s), 3.53 (3H, s), 3.71 (3H, s), 3.80 (1H, dd, $J = 1.2, 2.5$ Hz), 4.18 (1H, d, $J = 1.2$ Hz); ^{13}C NMR 17.9 (CH_3), 58.4 (CH_3), 61.4 (CH_3), 61.9 (CH_3), 67.3 (CH), 76.9 (CH), 77.1 (CH), 81.2 (CH), 84.5 (CH), 116.2 (C); MS (EI) m/z (rel intensity) 215 (M^+ , 1), 188 (1), 170 (1); HRMS calcd for $C_{10}H_{17}NO_4$ 215.1157478, found 215.114498. Anal. Calcd for $C_{10}H_{17}NO_4$: C, 55.80; H, 7.96; N, 6.51. Found: C, 55.74; H, 8.32; N, 6.59. Compound **20- β** : colorless oil; $[\alpha]_D^{-19}$ ($c = 0.5$); IR 2938, 1121 cm^{-1} ; 1H NMR 1.32 (3H, d, $J = 6.1$ Hz), 3.12 (1H, dd, $J = 9.4, 9.4$ Hz), 3.48 (3H, s), 3.52 (1H, dd, $J = 2.8, 9.4$ Hz), 3.52 (3H, s), 3.53 (3H, s), 3.64 (1H, dt, $J = 6.1, 9.4$ Hz), 3.76 (1H, dd, $J = 2.8, 2.8$ Hz), 4.82 (1H, d, $J = 1.9$ Hz); ^{13}C NMR 17.6 (CH_3), 58.1 (CH_3), 58.6 (CH_3), 61.0 (CH_3), 64.2 (CH), 73.6 (CH), 77.4 (CH), 81.1 (CH), 81.3 (CH), 115.6 (C); MS (EI) m/z (rel intensity) 215 (M^+ , <1), 170 (1); HRMS calcd for $C_{10}H_{17}NO_4$ 215.1157478, found 215.110516. Anal. Calcd for $C_{10}H_{17}NO_4$: C, 55.80; H, 7.96; N, 6.51. Found: C, 55.48; H, 8.31; N, 6.90.

2,6-Anhydro-1,7-dideoxy-7-[(diphenoxyphosphoryl)amino]-3,4,5-tri-*O*-methyl-L-glycero-L-manno-heptitol (21). To a suspension of LAH (72 mg, 1.9 mmol) in dry THF (8 mL) was added compound **20-β** (204 mg, 0.95 mmol) at rt under nitrogen. The mixture was refluxed for 45 min. The excess hydride was destroyed by adding a saturated aqueous solution of Na₂SO₄, and the white salts were separated by filtration. Concentration under reduced pressure gave the crude amine (210 mg) as a colorless oil which was dissolved in dry CH₂Cl₂ (15 mL) and treated with TEA (0.53 mL, 3.8 mmol) and diphenylchlorophosphate (390 μL, 1.9 mmol). The mixture was stirred at rt for 1.5 h under nitrogen, poured into a dilute hydrochloric acid (5%) solution, and extracted with EtOAc. The organic layer was washed with an aqueous saturated solution of NaHCO₃ and concentrated in vacuo. Column chromatography (hexanes–EtOAc, 50:50 → 25:75) of the residue afforded compound **21** (247 mg, 0.55 mmol, 58%) as a crystalline solid: mp 75.5–76.5 °C (from *n*-hexane–EtOAc); [α]_D –20.5 (*c* = 0.39); IR 3236, 2929, 1727, 1593, 1195 cm^{–1}; ¹H NMR 1.25 (3H, d, *J* = 7.2 Hz), 3.21 (1H, m), 3.29 (1H, m), 3.31 (3H, s), 3.41 (3H, s), 3.44 (3H, s), 3.21 (1H, dd, *J* = 4.9, 4.9 Hz), 3.35 (1H, dd, *J* = 3.4, 6.9 Hz), 3.55 (1H, dd, *J* = 3.1, 5.4 Hz), 3.77 (1H, ddd, *J* = 6.7, 6.7, 10.8 Hz), 3.85 (1H, ddd, *J* = 4.2, 7.3, 7.3 Hz), 7.13 (2H, dd, *J* = 7.2, 7.2 Hz), 7.23 (4H, d, *J* = 9.0 Hz), 7.30 (4H, dd, *J* = 7.6, 7.6 Hz); ¹³C NMR 16.7 (CH₃), 41.9 (CH₂), 57.0 (CH₃), 58.1 (CH₃), 58.7 (CH₃), 69.2 (CH, ³*J*_{CP} = 7.0 Hz), 70.0 (CH), 76.1 (CH), 77.0 (CH), 79.8 (CH), 120.2 (2 × CH), 124.8 (4 × CH), 129.6 (4 × CH), 150.7 (2 × C); MS (EI) *m/z* (rel intensity) 452 (*M*⁺ + H, 21), 419 (1), 387 (35); HRMS calcd for C₂₂H₃₁NO₇P 452.1837985, found 452.18605. Anal. Calcd for C₂₂H₃₀NO₇P: C, 58.53; H, 6.70; N, 3.10. Found: C, 58.84; H, 6.57; N, 3.11.

2,6-Anhydro-7-[[*(benzyloxy)carbonyl*]amino]-1,7-dideoxy-3,4,5-tri-*O*-methyl-L-glycero-L-manno-heptitol (22). To a suspension of LAH (167 mg, 4.42 mmol) in dry

THF (7 mL) was added compound **20-β** (317 mg, 1.47 mmol) at rt under nitrogen. The mixture was stirred at reflux temperature for 1 h. The excess hydride was destroyed by adding a saturated aqueous solution of Na₂SO₄, and the white salts were separated by filtration. Concentration under reduced pressure gave the crude amine as a colorless oil which was dissolved in dry THF (17 mL) and treated with TEA (2 mL) and dibenzyl dicarbonate (1.08 mL, 4.42 mmol). The mixture was stirred at rt for 1.5 h under nitrogen, poured into water, and extracted with EtOAc. The organic layer was washed with an aqueous saturated solution of NaHCO₃, dried (Na₂SO₄), and concentrated in vacuo. Column chromatography (hexanes–EtOAc, 50:50) of the residue afforded compound **22** (294 mg, 0.83 mmol, 56.5%) as a colorless oil: $[\alpha]_D -16$ ($c = 0.96$); IR 3334, 3033, 2976, 2934, 2826, 1722, 1538, 1455, 1257, 1118 cm⁻¹; ¹H NMR 1.29 (3H, d, $J = 6.6$ Hz), 3.21 (1H, dd, $J = 5.9, 5.9$ Hz), 3.33 (1H, m), 3.36 (1H, m), 3.39 (3H, s), 3.45 (3H, s), 3.45 (1H, m), 3.46 (1H, s), 3.54 (1H, dd, $J = 5.9, 6.1$ Hz), 3.73 (1H, dq, $J = 5.8, 6.1$ Hz), 3.93 (1H, ddd, $J = 4.5, 4.5, 8.2$ Hz), 5.09 (2H, br s), 5.14 (1H, s), 7.26–7.34 (5H, m); ¹³C NMR 17.2 (CH₃), 40.9 (CH₂), 57.5 (CH₃), 58.1 (CH₃), 59.2 (CH₃), 66.7 (CH₂), 69.9 (2 × CH), 76.5 (CH), 78.2 (CH), 80.4 (CH), 128.1 (3 × CH), 128.5 (2 × CH), 136.5 (C), 156.3 (C); MS (EI) m/z (rel intensity) 353 (M⁺, 2), 321 (1), 289 (14), 91 (100); HRMS calcd for C₁₈H₂₇NO₆ 353.183822, found 353.180244. Anal. Calcd for C₁₈H₂₇NO₆: C, 61.17; H, 7.70; N, 3.96. Found: C, 61.04; H, 7.69; N, 3.92.

2,6-Anhydro-7-[(tert-butoxycarbonyl)amino]-1,7-dideoxy-3,4,5-tri-*O*-methyl-L-glycero-L-manno-heptitol (23). To a suspension of LAH (217 mg, 5.73 mmol) in dry THF (8 mL) was added compound **20-β** (411 mg, 1.91 mmol) at rt under nitrogen. The mixture was stirred at rt for 1 h. The excess hydride was destroyed by adding a saturated aqueous solution of Na₂SO₄, and the white salts were separated by filtration. Concentration under reduced pressure gave the crude amine as a colorless oil which was

dissolved in dry DMF (15 mL) and treated with di-*tert*-butyl dicarbonate (1.67 g, 7.64 mmol). The mixture was stirred at rt for 1.5 h under nitrogen, poured into water, and extracted with EtOAc. The organic layer was washed with an aqueous saturated solution of NaHCO₃, dried (Na₂SO₄), and concentrated in vacuo. Column chromatography (hexanes–EtOAc, 50:50) of the residue afforded compound **23** (300 mg, 0.94 mmol, 49%) as a colorless oil: [α]_D –10 (*c* = 0.42); IR 3349, 2976, 2933, 1713, 1519, 1455, 1366, 1251, 1172 cm^{–1}; ¹H NMR 1.31 (3H, d, *J* = 6.6 Hz), 1.43 (9H, s), 3.20 (1H, dd, *J* = 6.3, 6.3 Hz), 3.27 (1H, dd, *J* = 4.5, 8.6 Hz), 3.39 (1H, m), 3.40 (1H, dd, *J* = 3.8, 5.6 Hz), 3.41 (3H, s), 3.47 (3H, s), 3.47 (3H, s), 3.51 (1H, dd, *J* = 3.3, 6.6 Hz), 3.69 (1H, dq, *J* = 6.2, 6.6 Hz), 3.93 (1H, ddd, *J* = 5.6, 8.5, 8.5 Hz), 4.83 (1H, s, NH); ¹³C NMR 17.4 (CH₃), 28.2 (3 × CH₃), 40.2 (CH₂), 57.7 (CH₃), 58.0 (CH₃), 59.4 (CH₃), 69.8 (CH), 70.7 (CH), 76.7 (CH), 78.8 (CH), 80.3 (C), 80.7 (CH), 155.8 (C); MS (EI) *m/z* (rel intensity) 319 (M⁺, 1), 287 (1), 230 (40), 101 (100); HRMS calcd for C₁₅H₂₉NO₆ 319.1994712, found 319.200768. Anal. Calcd for C₁₅H₂₉NO₆: C, 56.40; H, 9.15; N, 4.39. Found: C, 56.35; H, 9.32; N, 4.29.

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