Supporting Information
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**Experimental Section**

Melting points were determined using a Kofler Thermogerate apparatus and are uncorrected. Specific rotations were recorded on a JASCO DIP-370 optical polarimeter. Nuclear magnetic resonance spectra were recorded on a Varian Mercury plus 200 spectrometer. Mass spectra were obtained on a Hewlett Packard 5988A mass spectrometer. Thin layer chromatography (TLC) was performed using Merck GF-254 type 60 silica gel and ethyl acetate/hexane mixtures as eluants; the TLC spots were visualized with Hanessian mixture. Column chromatography was carried out using Merck type 9385 silica gel.

**Synthesis of β-nitroamines 4:** To a solution of the corresponding aldehyde (0.50 mmol) in dry THF (1 mL), Ti(OEt)$_4$ (1.00 mmol) was added, followed by SnCl$_2$ (1.00 mmol) and $p$-anisidine (0.45 mmol). After 1 hour, bromonitromethane (0.50 mmol) was added. The reaction mixture was stirring at room temperature over a period of 4 hours. The excess of Ti(OEt)$_4$ was decomposed by the slow addition of a solution of brine. The resulting suspension was filtered through a pad of Celite®, washed with ethyl acetate and the resulting solution was taken to a separating funnel. Organic layer was separated, washed with aqueous 1M HCl, H$_2$O, aqueous saturated solution of HNaCO$_3$ and brine, dried over Na$_2$SO$_4$ and concentrated under vacuum. The residue was purified by flash column chromatography in mixtures of ethyl acetate and hexane to yield β-nitroamines 4.

**4-Methoxy-N-(2-nitro-1-phenylethyl)benzenamine (4a):** Brown oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.61–7.24 (m, 5 H), 6.73 (d, $J = 9.0$ Hz, 2 H), 6.58 (d, $J = 9.0$ Hz, 2 H), 6.23 (d, $J = 7.4$ Hz, 1 H), 5.09 (t, $J = 6.7$ Hz, 1 H), 4.69 (d, $J = 6.7$ Hz, 2 H), 3.71 (s, 3 H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 153.1 (C), 139.6 (C), 137.9 (C), 129.2 (2 x CH), 128.5 (CH), 126.4 (2 x CH), 115.6 (2 x CH), 114.8 (2 x CH), 80.0 (CH$_2$), 57.7 (CH), 55.6 (CH$_3$); MS (ESI$^+$) $m/z$ (%) 273 ([M + H]$^+$, 4), 213 (7), 124 (7); HRMS (ESI$^+$) calc. for [C$_{15}$H$_{17}$N$_2$O$_3$]$^+$ [M + H]$^+$ 273.1239, found 273.1233; IR (neat): 3375, 1554, 1511, 1378, 1243 cm$^{-1}$; $R_f$ = 0.23 (hexane/AcOEt 3:1).

**4-[1-(4-Methoxyphenylamino)-2-nitroethyl]benzonitrile (4b):** Brown oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.68 (d, $J = 8.3$ Hz, 2 H), 7.53 (d, $J = 8.3$ Hz, 2 H), 6.73 (d, $J = 9.0$ Hz, 2 H), 6.53 (d, $J = 9.0$ Hz, 2 H), 5.12 (t, $J = 6.4$ Hz, 1 H), 4.71 (d, $J = 6.4$ Hz, 2 H), 3.71 (s, 3 H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 153.4 (C), 143.3 (C), 138.7 (C), 133.0 (2 x CH), 129.3 (C), 127.4 (2 x CH), 118.1 (C), 115.7 (2 x CH), 114.9 (2 x CH), 79.5 (CH$_2$), 57.3 (CH), 55.6 (CH$_3$); MS (ESI$^+$) $m/z$ (%) 320 ([M+Na]$^+$, 100), 298 ([M+H]$^+$, 64), 212 (60), 186 (24); HRMS (ESI$^+$) calc. for [C$_{16}$H$_{16}$N$_3$O$_3$]$^+$ [M+H]$^+$ 298.1192, found 298.1192; IR (neat): 3388, 2230, 1556, 1512, 1378, 1240, cm$^{-1}$; $R_f$ = 0.20 (hexane/AcOEt 3:1).

**N-(1-Cyclohexyl-2-nitroethyl)-4-methoxybenzenamine (4c):** Brown oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 6.76 (d, $J = 9.0$ Hz, 2 H), 6.65 (d, $J = 9.0$ Hz, 2 H), 4.72 (dd, $J = 12.3, 5.2$ Hz,
1H), 4.46 (dd, J = 12.3, 7.4 Hz, 1H), 4.08–4.04 (m, 1H, 1H), 3.73 (s, 3H, 2.73 (s, 11H); 13C NMR (75 MHz, CDCl3): δ 152.7 (C), 141.0 (C), 115.0 (2 x CH), 114.9 (2 x CH), 75.7 (CH2), 60.9 (CH), 55.7 (CH3), 43.0 (CH), 34.7 (2 x CH2), 25.2 (CH2), 21.6 (2 x CH2); MS (ESI+) m/z (%) 279 ([M + H]+, 6), 234 (19), 216 (100), 214 (28); HRMS (ESI+) calc. for [C15H23N2O3]+ [M + H]+ 279.1709, found 279.1703; Rf = 0.22 (hexane/EtOAc 3:1).

4-Methoxy-N-(3-methyl-1-nitrobutan-2-yl)benzenamine (4d): Brown oil; 1H NMR (300 MHz, CDCl3): δ 6.79 (d, J = 7.2 Hz, 2H), 6.64 (d, J = 7.2 Hz, 2H), 4.48 (d, J = 5.9 Hz, 1H), 4.12 (q, J = 7.1 Hz, 1H), 3.89–3.74 (m, 2H), 3.70 (s, 3H), 1.29–1.23 (m, 1H), 1.03 (apparent t, J = 7.0 Hz, 6H); 13C NMR (75 MHz, CDCl3): δ 152.8 (C), 140.3 (C), 115.2 (2 x CH), 115.0 (2 x CH), 76.5 (CH2), 58.9 (CH), 55.7 (CH3), 30.4 (CH), 19.0 (CH3), 18.1 (CH3); MS (ESI+) m/z (%) 239 ([M+H]+, 100), 232 (29), 208 (20), 176 (24); HRMS (ESI+) calc. for [C12H19N2O3]+ [M + H]+ 239.1396, found 239.1390; Rf = 0.53 (hexane/EtOAc 3:1).

4-Methoxy-N-(1-nitrononan-2-yl)benzenamine (4e): Brown oil; 1H NMR (300 MHz, CDCl3): δ 6.80 (d, J = 8.5 Hz, 2H), 6.64 (d, J = 8.5 Hz, 2H), 4.51 (dd, J = 11.5, 4.9 Hz, 1H), 4.41 (dd, J = 11.5, 5.7 Hz, 1H), 3.98–3.87 (m, 1H), 3.75 (s, 3H), 1.71–1.27 (m, 12H), 0.88 (t, J = 6.2 Hz, 3H); 13C NMR (75 MHz, CDCl3): δ 152.9 (C), 139.9 (C), 115.3 (2 x CH), 115.0 (2 x CH), 78.0 (CH2), 55.6 (CH3), 53.5 (CH), 32.8 (CH2), 31.6 (CH2), 29.2 (CH2), 28.9 (CH2), 25.8 (CH2), 22.5 (CH3), 13.9 (CH3); MS (ESI+) m/z (%) 295 ([M + H]+, 100), 234 (5), 201 (4); HRMS (ESI+) calc. for [C16H27N2O3]+ [M + H]+ 295.2022, found 295.2016; IR (neat): 3380, 1550, 1513, 1381, 1243 cm−1; Rf = 0.48 (hexane/EtOAc 5:1).

4-Methoxy-N-(4-methyl-1-nitropentan-2-yl)benzenamine (4f): Brown oil; 1H NMR (300 MHz, CDCl3): δ 6.76 (d, J = 9.1 Hz, 2H), 6.75 (d, J = 9.0 Hz, 2H), 6.65 (d, J = 9.0 Hz, 2H), 6.64 (d, J = 9.0 Hz, 2H), 4.70 (dd, J = 12.5, 1.7 Hz, 1H), 4.67 (dd, J = 12.3, 2.0 Hz, 1H), 4.45 (dd, J = 12.5, 1.8 Hz, 1H), 4.43 (dd, J = 12.3, 2.7 Hz, 1H), 4.15–4.05 (m, 2H, 1H), 3.72 (s, 6H), 1.74–1.48 (m, 2H), 1.28–1.23 (m, 4H), 1.20 (d, J = 4.3 Hz, 6H), 0.95 (t, J = 7.2 Hz, 3H), 0.88 (t, J = 7.5 Hz, 3H); 13C NMR (75 MHz, CDCl3): δ 152.6 (2 x C), 140.9 (C), 140.7 (C), 114.9 (4 x CH), 114.8 (4 x CH), 76.1 (CH2), 75.9 (CH2), 75.1 (CH), 74.7 (CH), 55.6 (2 x CH3), 32.1 (CH), 32.0 (CH), 23.3 (CH2), 23.0 (CH2), 8.0 (2 x CH3), 7.7 (2 x CH3); MS (ESI+) m/z (%) 275 [M + Na]+, 100), 270 [M + NH4]+, 47), 253 [M + H]+, 12), 209 (6), 206 (4); HRMS (ESI+) calc. for [C13H21N2O3]+ [M + H]+ 253.1552, found 253.1548; Rf = 0.53 (hexane/EtOAc 1:1).

4-Methoxy-N-(1-nitro-3-phenylpropan-2-yl)aniline (4g): Brown oil; 1H NMR (300 MHz, CDCl3): δ 7.41–7.26 (m, 5H, Ar), 6.68 (d, J = 7.2 Hz, 2H, Ar), 6.62 (d, J = 7.2 Hz, 2H, Ar), 4.38–4.31 (m, 1H, Ar), 3.75 (s, 3H, OCH3), 3.57–3.51 (m, 1H), 2.94–2.71 (m, 2H); 13C NMR (75 MHz, CDCl3): δ 152.9 (C), 139.9 (C), 138.5 (C), 129.2 (CH), 128.8 (CH), 128.7 (CH), 128.6 (CH), 128.1 (CH), 125.3 (CH), 115.6 (2 x CH), 114.5 (2 x CH), 80.7 (CH2), 55.7 (CH3), 47.9 (CH), 38.4 (CH2); MS (ESI+) m/z (%) 387 ([M+H]+, 100), 270 [M + NH4]+, 47), 253 [M + H]+, 12), 209 (6), 206 (4); HRMS (ESI+) calc. for [C16H27N2O3]+ [M + H]+ 295.2022, found 295.2016; IR (neat): 3380, 1550, 1513, 1381, 1243 cm−1; Rf = 0.48 (hexane/EtOAc 5:1).
for [C₁₆H₁₉N₂O₃]⁺ [M+H]⁺ 387.1390, found 387.1372; IR (neat): 3402, 1554, 1512, 1382, 1242 cm⁻¹; Rf = 0.53 (hexane/EtOAc 3:1).

**Ethyl 2-[(4-methoxyphenyl)amino]-3-nitropropanoate (4h):** Brown oil; ¹H NMR (300 MHz, CDCl₃): δ 6.75 (d, J = 9.1 Hz, 2 H), 6.66 (d, J = 9.0 Hz, 2 H), 4.78–4.75 (m, 2 H), 4.64–4.61 (m, 1 H), 4.39–4.29 (m, 2 H), 3.74 (s, 3 H), 1.33 (t, J = 7.1 Hz, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 170.4 (C=O), 152.5 (C), 139.6 (C), 116.3 (2 x CH), 116.2 (2 x CH), 76.9 (CH₂), 67.5 (CH), 62.4 (CH₂), 55.4 (CH), 13.8 (CH₃); MS (ESI⁺) m/z (%) 291 [M + Na]⁺, 100), 259 (11), 106 (4); IR (neat): 3410, 1714, 1555, 1513, 1380, 1247 cm⁻¹; Rf = 0.33 (hexane/EtOAc 1:4).

**4-Methoxy-N-(2-nitroethyl)aniline (4i):** Orange oil; ¹H NMR (300 MHz, CDCl₃): δ 6.81 (d, J = 8.9 Hz, 2 H, Ar), 6.61 (d, J = 7.2 Hz, 2 H, Ar), 4.59–4.32 (m, 2 H), 3.86–3.76 (m, 5 H); ¹³C NMR (75 MHz, CDCl₃): 153.0 (C), 140.0 (C), 115.0 (2 x CH), 114.8 (2 x CH), 74.3 (CH₂), 55.7 (OCH₃), 42.3 (CH₂); MS (ESI⁺) m/z (%) 197 ([M+H]⁺, 100), 180 (21), 90 (12); IR (neat): 3400, 1558, 1375 cm⁻¹; Rf = 0.48 (hexane/EtOAc 3:1).

**1-O-tert-Butyldimethylsilyl-5,6-deoxy-2,3-di-O-isopropylidene-5-p-methoxyphenylamino-6-nitro-D-D-mannofuranose and L-gulofuranose (4j):** Orange oil; [D]₂₆ +7.5º (c 1.4 in CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 6.78 (d, J = 8.7 Hz, 4 H, Ar), 6.71 (d, J = 8.7 Hz, 4 H, Ar), 5.64 (d, J = 1.7 Hz, 2 H), 5.33 (s, 1 H), 5.30 (s, 1 H), 4.82–4.65 (m, 4 H), 4.60–4.53 (m, 4 H), 4.50–4.32 (m, 2 H), 4.17 (dd, J = 7.5, 2.4 Hz, 1 H), 4.10 (dd, J = 7.1, 1.7 Hz, 1 H), 3.72 (s, 3 H, OCH₃), 3.71 (s, 3 H, OCH₃), 1.50 (s, 3 H, CH₃), 1.48 (s, 3 H, CH₃), 1.29, (s, 6 H, 2x CH₃), 0.89 (s, 9 H, 3 x CH₃), 0.88 (s, 9 H, 3 x CH₃), 0.12 (s, 3 H, CH₃), 0.11 (s, 3 H, CH₃), 0.09 (s, 3 H, CH₃), 0.08 (s, 3 H, CH₃); ¹³C NMR (125 MHz, CDCl₃): major isomer D-manno (anti): δ 153.1 (C), 139.3 (C), 116.5 (2 x CH), 114.6 (2 x CH), 112.2 (C), 101.0 (CH), 86.6 (CH), 79.4 (CH), 75.2 (CH₂), 55.2 (OCH₃), 52.5 (CH), 25.7 (CH₃), 25.3 (3 x CH₃), 24.3 (CH₃), 17.5 (C), –4.8 (CH₃), –5.8 (CH₃), minor isomer L-gulo (syn): δ 152.8 (C), 139.7 (C), 116.5 (2 x CH), 115.2 (CH), 114.6 (2 x CH), 112.4 (C), 101.0 (CH), 79.0 (CH), 78.0 (CH), 76.1 (CH₂), 55.2 (OCH₃), 53.0 (CH), 25.5 (CH₃), 25.3 (3 x CH₃), 23.9 (CH₃), 17.5 (C), –4.7 (CH₃), –5.7 (CH₃); MS (ESI⁺) m/z (%) 491 ([M+Na]⁺, 2), 469 ([M+H]⁺, 100), 408 (13), 337 (9); HRMS (ESI⁺) calc. for [C₂₂H₃₇N₂O₇Si]⁺ [M+Na]⁺ found 469.2370; Rf = 0.53 (hexane/EtOAc 3:1).

**3-O-Benzyl-5,6-dideoxy-1,2-O-isopropylidene-5-p-methoxyphenylamino-6-nitro-α-D-glucofuranose (4k):** Yellow oil; [α]₂⁰⁰ +7.5º (c 1.4 in CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 7.34–7.12 (m, 5 H), 6.54 (d, J = 9.0 Hz, 2 H), 6.34 (d, J = 9.0 Hz, 2 H), 5.83 (d, J = 3.6 Hz, 1 H), 4.67 (dd, J = 13.1, 3.9 Hz, 1 H), 4.59–4.44 (m, 3 H), 4.42–4.38 (m, 1 H), 4.24–4.17 (m, 3 H), 4.02 (d, J = 3.1 Hz, 1 H), 3.73 (s, 3 H), 1.47 (s, 3 H); ¹³C NMR (125 MHz, CDCl₃): δ 153.3 (C), 139.3 (C), 136.9 (C), 128.4 (2 x CH), 128.0 (CH), 127.9 (2 x CH), 116.3 (2 x CH), 114.9 (2 x CH), 112.1 (C), 104.9 (CH), 81.9 (CH), 81.2 (CH), 79.9 (CH), 75.8 (CH₂), 72.1 (CH₂), 55.6 (CH₃), 51.9 (CH), 26.7 (CH₃), 26.2 (CH₂); MS (ESI⁺) m/z (%) 445 ([M + H]⁺,
100), 444 (1), 316 (5), 289 (1), 288 (21); HRMS (ESI⁺) calc. for [C_{23}H_{29}N_{2}O_{7}]⁺ [M + H]⁺ 445.1975, found 445.1969; \( R_f = 0.28 \) (hexane/AcOEt 3:1).

6,7-Dideoxy-1,2:3,4-di-O-isopropylidene-6-p-methoxyphenylamino-7-nitro-glycero-β-D-galacto-heptose (41): Orange oil; [\( \beta \rceil_{D}^{20} = +12.1^\circ \) (c 0.7 in CHCl₃); \(^1\)H NMR (300 MHz, CDCl₃):
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&\delta 6.80–6.65 (m, 8 H), 5.59 (d, J = 3.1 Hz, 1 H), 5.56 (d, J = 3.1 Hz, 1 H), 4.87 (dd, J = 8.0, 2.3 Hz, 1 H), 4.81 (dd, J = 7.8, 3.0 Hz, 1 H), 4.67 (dd, J = 7.9, 4.4 Hz, 1 H), 4.61–4.57 (m, 3 H), 4.44–4.40 (m, 1 H), 4.38 (dd, J = 4.9, 1.1 Hz, 1 H); 4.35 (dd, J = 4.8, 1.1 Hz, 1 H), 4.32 (dd, J = 3.0, 1.4 Hz, 1 H), 4.29 (dd, J = 3.0, 1.4 Hz, 1 H), 4.28–4.27 (m, 2 H), 4.12 (dd, J = 3.4, 1.0 Hz, 1 H), 3.95 (dd, J = 3.6, 1.0 Hz, 1 H), 3.74 (s, 6 H), 1.46 (s, 8 H), 1.33–1.32 (m, 13 H), 1.29 (s, 4 H); 13C NMR (75 MHz, CDCl₃): major isomer D-glycero (anti) \( \delta \) 153.5 (C), 139.8 (C), 117.0 (2 x CH), 114.9 (2 x CH), 109.4 (C), 108.8 (C), 96.3 (CH), 75.1 (CH₂), 71.1 (CH), 70.9 (CH), 70.7 (CH), 67.0 (CH), 55.6 (CH₂), 54.6 (CH), 25.8 (CH₃), 25.7 (CH₃), 24.8 (CH₃), 24.0 (CH₃), minor isomer L-glycero (syn): \( \delta \) 153.0 (C), 139.9 (C), 115.1 (2 x CH), 115.0 (2 x CH), 109.6 (C), 108.9 (C), 96.5 (CH), 76.0 (CH₂), 70.9 (2 x CH), 70.4 (CH), 65.4 (CH), 55.6 (CH₂), 54.8 (CH), 25.8 (2 x CH₃), 24.8 (CH₃), 24.0 (CH₃); MS (ESI⁺) \( m/z \) (%): 447 ([M + Na]+, 5), 424 ([M + H]+, 100), 386 (22), 364 (26); HRMS (ESI⁺) calc. for [C_{20}H_{29}N_{2}O_{8}]⁺ [M + H]⁺ 425.1924 found 425.1918; \( R_f = 0.46 \) (hexane/AcOEt 3:1).