**SUPPORTING INFO**

**Synthesis of alkylated sugar amino acids:**
conformationally restricted L-Xaa-L-Ser/Thr mimics

Martijn D.P. Risseeuw¹, Jaroslaw Mazurek², Arjan van Langenvelde³,
Gijsbert A van der Marel¹, Herman S. Overkleeft¹, Mark Overhand¹*

¹Leiden Institute of Chemistry, Department of Bioorganic Synthesis
PO box 9502, 2300 RA, Leiden, The Netherlands. overhand@chem.leidenuniv.nl
²Avantium Technologies, Zekeringstraat 29, 1014BV, Amsterdam, The Netherlands

All reactions described were performed under an argon atmosphere and at ambient temperature unless stated otherwise. Dichloromethane was distilled from P₂O₅ and THF was distilled from LiAlH₄ prior to use. Grignard reagents were purchased from Aldrich in 1.0-3.0 m stock solutions in THF or diethyl ether. All other reagents were purchased from Sigma-Aldrich or Acros and were used as received. Reactions were monitored by TLC analysis using TLC aluminium sheets (Merk, Silica gel 60, F₂₅₄) with detection by spraying with a solution of (NH₄)₆Mo₇O₂₄·4H₂O (25 g/L) and (NH₄)₄Ce(SO₄)₂·2H₂O (10 g/L) in H₂SO₄ (10 %) followed by charring. Column chromatography was performed on 60Å silica gel (40-63 μm). High resolution spectra were recorded with a Finnigan LTQ Orbitrap Mass spectrometer. ¹H- and ¹³C-APT-NMR spectra were recorded with a Bruker DMX-400 (400/100 MHz) spectrometer. Chemical shifts are given in ppm (δ) relative to tetramethylsilane as an internal standard (¹H NMR) or CDCl₃ (¹³C NMR). Coupling constants are given in Hz. All presented ¹³C-APT spectra are proton decoupled. Optical rotations were measured with a Propol automatic polarimeter (λ= 589 nm) and IR (ATR-IR) spectra were recorded with a Shimadzu FTIR-8300 spectrometer. Melting points are given uncorrected and were determined on a Stuart Scientific SMP3 melting point apparatus. Throughout this paper the atoms in all compounds are numbered according to the scheme below.

**Figure 1**

![Scheme](image)

**Compound 9:** Aldehyde 3 (1.10 g, 2.0 mmol) and S-tert-butane sulfinamide (276 mg, 2.20 mmol) were taken up in 15 mL dry CH₂Cl₂ and placed under an argon atmosphere. To this solution, Ti(OiPr)₄ (1.3 mL, 4.4 mmol) was added and the mixture was stirred for 4 h at room temperature. Concentration in vacuo followed by silica gel chromatography of the residue (0 → 20% EtOAc in light petroleum) yielded sulfinimine 9 (945 mg, 1.44 mmol 72%) as a colorless oil.
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$^1$H NMR (400 MHz, CDCl$_3$) δ 1.13 (s, 9 H, tBu), 3.52-3.58 (m, 1 H, H$_2$), 3.65-3.78 (m, 3 H, H$_1$, H$_3$, H$_5$), 3.79-3.84 (m, 1 H, H$_4$), 4.14-4.19 (m, 1 H, H$_6$), 7.13-7.30 (m, 20 H, 4×CH$_2$Ph), 8.17 (d, 1 H, J = 4 Hz, -CH=N-).

$^{13}$C NMR (100 MHz, CDCl$_3$) 22.08 (CMe$_3$), 56.77 (CMe$_3$), 68.42 (C$^1$), 77.24 (CH$_2$Ph), 74.44 (CH$_2$Ph), 75.34 (CH$_2$Ph), 77.74 (C$^3$), 78.86 (C$^6$), 79.29 (C$^5$ + C$^4$), 127.19, 127.26, 127.32, 127.39, 127.43, 127.49, 127.54, 127.90, 127.98, 128.07, 128.10, 128.14, 128.17, 128.22, 128.30, 129.18, 129.32, 129.39, 129.43, 129.49, 129.54, 137.29, 137.67, 137.85, 137.98, 164.51 (-CH=N-);

IR neat (cm$^{-1}$): 695.8, 734.6, 910.0, 1069.7, 1270.6, 1453.8, 1591.9, 1724.1, 2869.8, 3031.1, 3064.4, 3290.5.

$[^\alpha]_D^{20}$ + 45.6 (c 1.0, CHCl$_3$) HRMS: calcd for C$_{39}$H$_{46}$O$_6$NS ([M+H$^+$]) 656.30404, found 656.30450

**Compound 7:** Imine 9 (660 mg, 1.0 mmol) was coevaporated twice with toluene (10 mL) and dissolved in freshly distilled CH$_2$Cl$_2$ 60 mL and placed under an argon atmosphere. After cooling of the solution to -78°C MeMgBr (1.0 mL, 3.0 M in Et$_2$O) was added dropwise. After stirring for 80 minutes at -78 °C the reaction was quenched by the addition of sat. aq. NH$_4$Cl and the temperature was allowed to rise to RT. The reaction mixture was extracted twice with diethyl ether and the combined organic phases were washed with a saturated aqueous solution of NaHCO$_3$, water, dried (Na$_2$SO$_4$), and concentrated in vacuo.

The crude sulfonamide was taken up in 100 mL methanol and 1.25 mL HCl in 1,4-dioxane (4.0 m) was added. The methanolic mixture was stirred for half an hour and concentrated and coevaporated with methanol (2 × 20 mL). The crude hydrochloride was dissolved in 100 mL of CH$_2$Cl$_2$ and 1,4-dioxane (1:1 v/v) and DIPEA (3.0 mmol, 530 μL) and FmocOSu (1.5 mmol, 508 mg). Stirring was continued for 2.5 hr after which the reaction mixture was diluted with CH$_2$Cl$_2$ and water (100 mL each). The organic phase was separated and washed with 10% aq. citric acid, satd. aq. NaHCO$_3$, and water (100 mL each). The organic layer was dried on Na$_2$SO$_4$, concentrated in vacuo and purified silica gel column chromatography (10% Æ 20% EtOAc in light petroleum v/v) yielding 592 mg (0.75mmol, 75 %) of the title compound as a pale yellow sirup.

$^1$H NMR (400 MHz, CDCl$_3$) δ 1.26 (d, 1 H, J = 6.8 Hz, H$_8$), 3.20 (d, 1 H, J = 9.6 Hz, H$_6$), 3.40-3.48 (m, 2 H, H$_2$ and H$_5$), 3.61 (t, 1 H, J = 9.4 Hz), 3.69-3.74 (m, 3 H, H$_1$ and H$_4$), 4.21 (t, 1 H, J = 6.8 Hz, CH$_2^{Fmoc}$), 4.28-4.33 (m, 1 H, H$_7$), 4.44, (dd, 2 H, J = 7.2 Hz, CH$_2^{Fmoc}$), 4.55, (dd, 2 H, J = 4.0Hz, J = 12 Hz CH$_2$Ph), 4.62 (t, 2 H, J= 10 Hz, CH$_2$Ph), 4.82 (dd, 2 H J = 10.8, J = 8.8, CH$_2$Ph), 4.94 (s, 2 H, CH$_2$Ph), 5.25, (d, 1 H, J = 10 Hz, NH$_2$), 7.15-7.39 (m, 24 H, ArBn and ArFmoc), 7.59, (dd, 2 H, J = 3.2 Hz, J = 7.6 Hz, Ar$_{Fmoc}$), 7.72, (d, 2 H, J = 7.6 Hz, Ar$_{Fmoc}$), $^{13}$C NMR (100 MHz, CDCl$_3$) δ 19.05, 45.35, 47.28, 66.36, 68.91, 73.20, 74.92, 75.40, 78.13, 78.44, 78.64, 80.69, 87.02, 119.86, 124.93, 126.97, 127.46, 127.55, 127.61, 127.69, 127.81, 128.32, 128.36, 128.50, 137.87, 137.97, 138.47, 141.20, 143.83, 143.90, 155.84; IR neat (cm$^{-1}$): 621.0, 698.2, 729.0, 905.2, 995.2, 1026.1, 1211.2, 1450.4, 1500.5, 1716.5, 2341.4; $[^\alpha]_D^{20}$ + 16.2 (c 1.0, CHCl$_3$), HRMS: calcd for C$_{51}$H$_{55}$O$_7$N$_2$ ([M+H]) 807.40038, found 807.40118

**Compound 12a.** Aldehyde 3 (2.31g, 4.18 mmol) was coevaporated thrice with toluene (25 mL) dissolved in 40 mL freshly distilled THF and placed under an argon atmosphere. The solution was cooled to -78°C and 12.6 mL phenylmagnesium bromide (1.0 M in THF 3.0 eq.) was added over 30 minutes. The reaction was stirred for another 3 hours and poured into 100 mL of NH$_4$Cl (sat. aq.) and diluted with 100 mL diethyl ether. The organic layer was washed with water (2× 100 mL) and saturated aqueous NaCl (100 mL). The organic fractions were dried on Na$_2$SO$_4$ and concentrated in vacuo.

Chromatography of the residue on silica gel (0-20 % EtOAc in light petroleum) yields the title compound (1.74g, 2.76 mmol, 66%) as a colorless syrup.
In an oven dried flask, 1.8 mL of a 3.0 M solution of methyl magnesium bromide in diethylether, was placed under an argon atmosphere, diluted with 3.5 mL freshly distilled THF and cooled on ice to 0°C. Aldehyde 3 (0.98 g, 1.77 mmol) was coevaporated twice with toluene (20 mL), taken up in 5 mL freshly distilled THF and added dropwise to the precooled Grignard reagent. The reaction was stirred for 3 hrs at 0°C, diluted with 20 mL of ether after which 30 mL of sat. aq. NH₄Cl was added. The organic layer was separated and the aqueous layer was extracted once with 20 mL of ether. The organic layers were combined and extracted with sat. aq NaCl, was dried on Na₂SO₄ and concentrated in vacuo.

Chromatography of the residue on silica gel (10-25% EtOAc in light petroleum, shallow gradient) yields 512 mg (0.90 mmol, 51%) of the R-alcohol 12b as a colorless oil. Further elution allows the isolation of the S-isomer (222mg, 0.39 mmol, 22%) whose physical data were in agreement with earlier published data.¹ H NMR (400 MHz, CDCl₃) δ 1.31 (d, 3 H, J = 6.5 Hz, H8), 3.11 (m, 1 H, H6), 3.61 (m, 1 H, H5), 4.50-4.95 (m, 8 H, 4×CH₂Ph), 7.13-7.34 (m, 20 H, ArBn); ¹³C NMR (100 MHz, CDCl₃) δ 20.31 (C8), 65.25 (C7), 69.16 (C1), 73.32 (C8), 74.42 (C7), 74.92 (C8), 75.07 (C8), 75.09 (C8), 75.38 (C8), 78.20 (C8), 78.33 (C8), 78.64 (C8), 81.33 (C8), 87.04 (C8), 127.52, 127.59, 127.61, 127.65, 127.84, 127.87, 128.30, 128.36, 128.38, 128.93, 130.08, 138.12, 138.55; IR neat (cm⁻¹): 694.3, 1049.2, 1091.6, 1454.2, 1496.7, 1732.0, 2032.8, 2160.1, 2869.9, 2923.9, 3031.9. [α]D²⁰ + 16.0 (c 1.0, CHCl₃), HRMS: calcd for C₃₆H₄₄O₆N ([M+NH₄]) 614.34784, found 614.34784

**Compound 12c.** Aldehyde 3 (1.33g, 2.40 mmol) was transformed into alcohol 12c analogously to the synthesis of compound 12b but by using 3.6 mL isopropylmagnesium chloride (2.0 M in diethyl ether). Before addition of the aldehyde, the concentration of the Grignard reagent was adjusted to ~1 M by the addition of 3.6 mL THF. Workup and chromatography on silica (10-25% EtOAc in light petroleum) yielded 516 mg (0.87 mmol, 36%) of the title compound as an oil.¹ H NMR (400 MHz, CDCl₃) δ 0.89 (d, 3 H, J = 6.4 Hz, Me), 1.05 (d, 3 H, J = 6.8 Hz, Me), 1.88 (m, 1H, CH(Me)₂), 3.37 (d, 2 H, J = 8.4, H6 H7), 3.44 (m, 1H, H2), 3.59 (t, 1 H, J = 9.6 Hz, H3), 3.66-3.80 (m, 4 H, H1, H4, H5), 4.44-4.92 (m 8 H, 4×CH₂Ph), 7.09-7.33 (m, 20 H, 4×CH₂Ph)¹³C NMR (100 MHz, CDCl₃) δ 19.18 (Me), 19.56 (Me), 31.48 (C8), 69.16 (C8), 73.32 (CH₃Ph), 74.42 (C8), 74.92 (C8), 75.07 (CH₂Ph), 75.48 (CH₂Ph), 78.19 (C3), 78.28 (C1 and C5), 78.73 (C8), 87.20 (C8), 127.52, 127.59, 127.61, 127.66, 127.84, 128.03, 128.16, 128.36, 138.12, 138.62; IR neat (cm⁻¹) :694.3, 1049.2, 1091.6, 1454.2, 1496.7, 1732.0, 2032.8, 2160.1, 2869.9, 2923.9, 3031.9. [α]D²⁰ + 15.2 (c 1.0, CHCl₃), HRMS: calcd for C₃₆H₄₄O₆N ([M+NH₄]) 648.33215, found 648.33215

**Compound 12d.** Aldehyde 3 (1.22g, 2.20 mmol) was transformed into alcohol 12c analogously to the synthesis of compound 12b but by using 3.3 mL isobutylmagnesium bromide (2.0 M in diethyl ether). Before addition of the aldehyde, the concentration of the Grignard reagent was adjusted to ~1 M by the
addition of 3.3 mL THF. Workup and chromatography on silica (10-25% EtOAc in light petroleum) yielded 645 mg (1.06 mmol, 48%) of the title compound as a white solid. 

$^1$H NMR (400 MHz, CDCl$_3$) δ 0.91 (d, 3 H, J = 6.4 Hz, Me), 0.93 (d, 3 H, J = 6.8 Hz, Me), 1.23-1.30 (m, 1 H, H8a), 1.62-1.70 (m, 1 H, H8b), 1.74-1.84 (m, 1 H, H9), 3.13 (d, 1 H, J = 8.0 Hz, H1), 3.45 (dd, 1 H, J =9.4, 2.4Hz, H2), 3.59 (t, 1 H, J = 8.8 Hz, H3), 3.66-3.77 (m, 4 H, H1, H4, H5), 3.90 (dd, 1 H, J = 9.0, 3.8 Hz, H7), 4.51-4.60, 4.73-4.76, 4.82-4.96 (m, 8 H, 4 × CH$_2$Ph), 7.11-7.42 (m, 20 H, 4 × CH$_2$Ph), 13C NMR (100 MHz, CDCl$_3$) δ 21.95(Me), 23.38(Me), 24.59 (C9), 43.39 (C8), 67.12 (C7), 69.19 (C1), 73.32 (CH$_2$Ph), 74.98 (CH$_2$Ph), 75.23 (CH$_2$Ph), 75.46 (CH$_2$Ph), 78.33 (C3, C5), 78.82 (C2), 80.74 (C6), 87.15 (C4), 127.59, 127.62, 127.72, 127.79, 127.91, 128.04, 128.33, 128.38, 128.45, 138.12, 138.20, 138.65, IR neat (cm$^{-1}$): 698.2, 736.8, 952.8, 1049.2, 1207.4, 1365.5, 1978.8, 2954.7. 

$\alpha$D$_{20}$ + 24.0 (c 1.0, CHCl$_3$), mp: 102°C (Ethanol) HRMS: calcd for C$_{39}$H$_{50}$O$_6$N ([M+NH$_4$]) 628.36326, found 628.36346

**Compound 13a.** Hydrazoic acid solution (CAUTION: HN$_3$ is volatile, highly toxic and explosive!): Sodium azide (4.0 g, 61.5 mmol) was dissolved in 10 mL water. Toluene (50 mL) was added and the resulting biphasic system was cooled on ice to 0°C. Under vigorous stirring, 8 mL concentrated sulfuric acid was added dropwise. After 30 minutes of stirring, the organic layer was separated and stored on anhydrous Na$_2$SO$_4$.

Alcohol 12a (568 mg, 0.90 mmol) was coevaporated twice with toluene 20 mL and taken up in 10 mL toluene. DEAD, (0.85 mL, ~40% in toluene, ± 1.85 mmol) and triphenylphosphine (475 mg, 1.81 mmol) were added. Finally 4.0 mL of the hydrazoic acid solution was added. The reaction was stirred for 1hr at room temperature during which the color shifted from bright yellow to cloudy white. The reaction mixture was concentrated in vacuo. Column chromatography (0–10% EtOAc in light petroleum) allowed isolation of the product (442 mg, 0.70 mmol, 78%) as a pale yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 3.22 (t, 1 H, J = 9.2 Hz, H5), 3.51 (m, 1 H, H2), 3.65 (t, 1 H, J = 9.6 Hz, H3), 3.75 (t, 1 H, J = 8.8 Hz), 3.84 (m, 2 H, H1), 3.88, (dd, 1 H, J = 10 Hz, 2.8 Hz), 4.30-4.34, 4.55-4.65, 4.76-4.82, 4.90-4.93 (m, 8H, 4 × CH$_2$Ph), 4.68 (d, 1 H, J = 2.8 Hz, H7), 7.06-7.48, (m, 25 H, 4 × Ph), 13C NMR (100 MHz, CDCl$_3$) δ 64.27 (C 7), 68.80 (C 1), 71.31 (CH$_2$Ph), 74.18 (CH$_2$Ph), 74.86 (CH$_2$Ph), 75.33 (CH$_3$Ph), 78.03 (C3), 78.51 (C5), 78.96 (C1), 80.88 (C6), 88.20 (C4), 127.21, 127.23, 127.33, 127.43, 127.51, 127.59, 127.64, 127.74, 128.22, 128.21, 128.29, 128.54, 128.45, 138.12, 138.20, 138.65, IR neat (cm$^{-1}$): 536.1, 696.1, 730.7, 908.7, 1094.9, 1361.0, 1454.0, 1497.0, 20.97.7, 2865.9, 3030.8. $\alpha$D$_{20}$ + 28.2 (c 2.0, CHCl$_3$) HRMS: calcd for C$_{41}$H$_{45}$O$_5$N$_4$ ([M+NH$_4$]) 673.33845, found 673.33887

**Compound 13b.** Alcohol 12b (723mg, 1.27 mmol) was transformed into its corresponding azide according to the procedure described for compound 13a. Column chromatography (0–10% EtOAc in light petroleum) yielded the title compound (603 mg, 1.06 mmol, 83%) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.16 (d, 3 H, J = 7.0 Hz, Me), 3.41 (t, 1 H, J = 8.5 Hz, H5), 3.45-3.47 (m, 1 H, H2), 3.50 (dd, 1 H, J = 9.5 Hz, J = 1.3 Hz, H6), 3.57 (m, 1 H, H7), 3.67 (t, 1 H, J = 9 Hz, H3), 3.71-3.79 (m, 3 H, H1, H4), 4.53-4.97 (m, 8 H, 4 × CH$_2$Ph), 7.20-7.33 (m, 20 H, 4 × CH$_2$Ph), 13C NMR (100 MHz, CDCl$_3$) δ 12.36 (Me), 56.21 (C1), 68.84 (C7), 73.49 (CH$_2$Ph), 74.57 (CH$_2$Ph), 74.98 (CH$_2$Ph), 75.54 (CH$_3$Ph), 77.94 (C4), 78.25 (C5), 79.15 (C6), 80.81 (C8), 87.42 (C4), 127.45, 127.49, 127.60, 127.64, 127.74, 127.88, 127.95, 128.06, 128.29, 128.39, 128.43, 128.49, 137.68, 138.03, 138.35, IR neat (cm$^{-1}$): 694.3, 732.9, 1002.9, 1091.6, 1454.2, 1542.9, 2102.3, 2858.3, 3031.9. $\alpha$D$_{20}$ + 6.0 (c 1.0, CHCl$_3$) HRMS: calcd for C$_{36}$H$_{43}$O$_5$N$_4$ ([M+NH$_4$]) 611.32280, found 611.32281
Compound 13c. Alcohol 12c (943 mg, 1.58 mmol) was transformed into its corresponding azide according to the procedure described for compound 13a except with 72 hr stirring after the addition of the hydrazoic acid solution. Column chromatography (0-10 % EtOAc in light petroleum) yielded the title compound (473 mg, 0.76 mmol, 48%) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.96 (d, 3 H, J = 6.8 Hz, Me), 1.02 (d, 3 H, J = 6.8 Hz, Me), 1.93 (m, 1 H, CHMe$_2$), 3.34 (dd, 1 H, J = 8.4 Hz, H7), 3.46 (m, 1 H, H2), 3.59-3.68 (m, 2 H, H3, H6), 3.69-3.75 (m, 4 H, H1, H4, H5), 4.54-4.94 (m, 8 H, 4 × CH$_2$Ph), $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 20.32 (Me), 20.65 (Me), 29.84 (C8), 69.33 (C1), 71.34 (C4), 73.47 (CH$_2$Ph), 74.59 (CH$_2$Ph), 74.96 (CH$_2$Ph), 75.57 (CH$_2$Ph), 76.37 (C5), 78.67 (C6), 79.16 (C2), 87.54 (C6), 127.43, 127.46, 127.49, 127.56, 127.75, 127.90, 128.32, 128.34, 128.40, 130.08, 138.12, 138.42, IR neat (cm$^{-1}$): 694.3, 910.3, 1056.4, 1261.5, 1302.8, 1454.2, 1496.7, 1869.9. [\alpha]$_D^{20}$ -19.4 (c 1.0, CHCl$_3$), HRMS: calcd for C$_{38}$H$_{47}$O$_5$N$_4$ ([M+NH$_4$]) 639.35410 found 639.35443

Compound 13d. Alcohol 12d (1.62 g, 2.65 mmol) was transformed into its corresponding azide according to the procedure described for compound 13a. Column chromatography (0 $\rightarrow$ 10 % EtOAc in light petroleum) yielded the title compound (1.55 g, 2.44 mmol, 92%) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.88 (d, 3 H, J = 6.4 Hz, Me), 0.95 (d, 3 H, J = Hz, Me), 1.21-1.28 (m, 1 H, H8 a), 1.75-1.88 (m, 2 H, H8b, H9), 3.45-3.49 (m, 1 H, H2), 3.51-3.62 (m, 3 H, H2), 3.63-3.69 (t, 1 H, J = 9.4 Hz, H3), 3.71-3.79 (m, 3 H, H4, H1) 4.55-4.66, 4.80-4.97 (m, 8H, 4 × CH$_2$Ph), $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.25 (Me), 23.55 (Me), 36.62 (C8), 60.01 (C7), 68.99 (C1), 74.49 (CH$_2$Ph), 74.79 (CH$_2$Ph), 74.99 (CH$_2$Ph), 75.50 (CH$_2$Ph), 78.30 (C3), 78.36 (C5), 79.24 (C2), 81.54 (C6), 87.42 (C4), 127.49, 127.60, 127.77, 127.83, 127.91, 128.30, 128.40, 128.41, 128.45, 137.75, 138.03, 138.07, 138.41, IR neat (cm$^{-1}$): 694.3, 732.9, 1056.4, 1454.2, 1496.7, 2102.3, 2866.0 [\alpha]$_D^{20}$ – 2.2 (c 1.0, CHCl$_3$), HRMS: calcd for C$_{39}$H$_{49}$O$_5$N$_4$ ([M+NH$_4$]) 653.36975 found 653.37006

Compound 14a. Azide 13a (1.22 g, 1.86 mmol) is taken up in 30 mL Ac$_2$O/AcOH (2:1 v/v). ZnCl$_2$ (5.0 g, 37.2 mmol, 20 eq.) is added and the reaction is stirred for 5 hr at room temperature. The color of the reaction slowly turned dark green during this time. The reaction mixture is poured into 30 mL water and diluted with 50 mL diethylether. The ether layer is washed water (2× 50 mL), sat aq Na$_2$CO$_3$ (2× 50 mL), dried on Na$_2$SO$_4$ and concentrated in vacuo. The residue is taken up in 50 mL methanol and the pH is adjusted to ± 10 by the addition of sodium methoxide (30% w/w solution in methanol) and stirred o/n at room temperature. The pH is adjusted to 7 by the addition of amberlyte IR120H resin, the solution is filtered and concentrated in vacuo. Residual benzyl alcohol was removed by twofold coevaporation with water 20 mL. The residue was coevaporated once with toluene and purified by silica gel chromatography (0-20% EtOAc in light petroleum) to yield the title compound (770 mg, 1.36 mmol, 73 %) as a viscous oil which solidified upon standing.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.06 (s, 1 H, OH), (3.21 (t, 1 H, J = 9.6 Hz, H5), 3.43-3.46 (m, 2 H, H2, H3), 3.73 (d, 1 H, J = 1.14 Hz, H1$'$), 3.77 (t, 1 H, J = 8.4 Hz, H4), 3.90 (dd, 1 H, J = 10.2 Hz, J = 2.4 Hz, H6), 4.35-4.37 and 4.62-4.63 (m, 2 H, CH$_2$Ph), 4.71 (d, 1 H, J = 2.4 Hz, H7), 4.77-4.92 (m, 4 H, 2×CH$_2$Ph), 7.16-7.38 (m, 20 H, 3×CH$_2$Ph, Ph), $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 62.01 (C1), 64.45 (C4$'$), 74.18 (CH$_2$Ph), 75.00 (CH$_2$Ph), 75.40 (CH$_2$Ph), 78.05 (C5), 78.35 (C5$'$), 79.35 (C5$''$), 80.88 (C8), 87.08 (C8$'$), 127.23, 127.45, 127.62, 127.68, 127.76, 127.82, 127.86, 128.36, 128.39, 128.42, 128.53, 128.66, 129.06, 134.75, 137.65,
Compound 14b. Azide 13b (660 mg, 1.11 mmol) was debenzylated at the primary position using the procedure described for compound 14a. Column chromatography (0-20 % EtOAc in light petroleum) yielded the title compound (332 mg, 0.66 mmol, 78%) as a colorless oil. 1H NMR (400 MHz, CDCl3) δ 1.10 (d, 3 H, J = 7.2 Hz, Me), 2.30 (s, 1 H, OH), 3.44-3.40 (m, 2 H, H2, H3), 3.49-3.56 (m, 3 H, H5, H6, H7), 3.64 (dd, 1 H, J = 11.6 Hz, J = 4.4, H1a), 3.73 (t, 1 H, J = 9.2 Hz, H4), 3.85 (d, 1 H, J = 10.8 Hz, H1b), 4.57-4.67, 4.81-4.95 (m, 6 H, 3×CH2Ph), 7.22-7.32 (m, 15 H, 3×CH2Ph). 13C NMR (100 MHz, CDCl3) δ 12.03(Me), 56.18 (C7), 61.77 (C1), 74.30 (CH2Ph), 74.78 (CH2Ph), 75.29 (CH2Ph), 77.62 (C3), 77.98 (C5), 79.15 (C2), 80.74 (C6), 81.64 (C7), 127.39, 127.44, 127.64, 127.69, 127.74, 127.82, 127.99, 128.23, 128.27, 137.45, 137.69, 138.10, IR neat (cm−1): 694.3, 910.3, 1060.8, 1149.5, 1234.4, 1357.8, 1454.2, 2103.3. [α]D20 + 2.8 (c 1.0, CHCl3), HRMS: calcd for C29H37O5N4 ([M+NH4]+) 521.27585 found 521.27588

Compound 14c. Azide 13c (156 mg, 0.25 mmol) was debenzylated at the primary position using the procedure described for compound 14a. Column chromatography (0-20 % EtOAc in light petroleum) yielded the title compound (89 mg, 0.17 mmol, 68%) as a colorless oil. 1H NMR (600 MHz, CDCl3) δ 0.95 (d, 3 H, J = 6.6 Hz, Me), 1.00 (d, 3 H, J = 6.6 Hz, Me), 1.89 (m, 1 H, CHMe2), 3.34 (d, 1 H, J = 8.4 Hz, H7), 3.37 (m, 1 H, H2), 3.63 (m, 1 H, H3), 3.70 (dd, 1 H, J = 11.4 Hz, J = 3.6 Hz, H1a), 3.75-3.78 (m, 3 H, H4,H5,H6), 3.86 (dd, 1 H, J = 12 Hz, J = 1.8 Hz, H1b), 3.67-3.71, 4.84-4.88, 7.21-7.33 (m, 15 H, 3×CH2Ph). 13C NMR (150 MHz, CDCl3) δ 20.48 (Me), 20.61 (Me), 29.60 (CHMe2), 61.87 (C1), 71.68 (C7), 74.59 (CH-Ph), 75.04 (CH-Ph), 75.58 (CH2-Ph), 77.76 (C3), 78.35 (C5), 79.03 (C7), 79.23 (C6), 87.23 (C8), 127.31, 127.54, 127.62, 127.87, 127.91, 128.32, 128.40, 128.45, 137.38, 137.94, 138.22 IR neat (cm−1): 695.2, 750.6, 1027.8, 1087.4, 1261.5, 1261.5, 1454.0, 1497.8, 1733.6, 2097.5, 2873.3. [α]D20 - 47.6 (c 1.0, CHCl3), HRMS: calcd for C31H41O5N4 ([M+NH4]+) 549.30731 found 549.30751

Compound 14d. Azide 13d (1.02g, 1.61 mmol) was debenzylated at the primary position using the procedure described for compound 14a. Column chromatography (0-20 % EtOAc in light petroleum) yielded the title compound (712 mg, 1.30 mmol, 81%) as a colorless oil. 1H NMR (400 MHz, CDCl3) δ 0.85 (d, 3 H, J = 6.4 Hz, Me), 0.94 (d, 3 H, J = 6.4 Hz, Me), 1.21 (m, 1 H, H8a), 1.78 (m, 2H, H8b, H9), 2.14 (s, 1 H, OH), 3.40 (m, 1 H, H2), 3.48-3.57 (m 3 H, H3, H5, H7), 3.62-3.78 (m, 2 H, H1b, H6), 3.75 (t, 1 H, H4), 3.86 (d, 1 H, J = 10.7 Hz, H1b), 4.92-4.68, 4.82-4.97 (m, 6 H, 3×CH-Ph), 7.12-7.31 (m, 15 H, 3×CH2-Ph). 13C NMR (100 MHz, CDCl3) δ 21.07(Me), 23.34(Me), 24.91 (C8), 36.12, (C9), 59.93 (C7), 61.92 (C1), 74.62 (CH2-Ph), 74.89 (CH-Ph), 75.35 (CH2-Ph), 78.05 (C3), 78.20 (C5), 79.34 (C7), 81.64 (C6), 87.10 (C4), 127.26, 127.49, 127.58, 127.73, 127.80, 128.28, 128.31, 137.54, 137.69, 138.17, IR neat (cm−1): 698.2, 729.0, 1064.6, 1353.9, 1662.5, 2106.1. [α]D20 - 5.6 (c 1.0, CHCl3), HRMS: calcd for C32H42O5N4 ([M+NH4]+) 563.32280 found 563.32300

Compound 15a. Azido alcohol 14a (634 mg, 1.12 mmol) was taken up in 5 mL CH2Cl2 and 2.5 mL water. The biphasic mixture was stirred vigorously and iodobenzene diacetate (BAIB, 0.91 g, 2.80 mmol) and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, 35 mg, 0.224 mmol) were added. Stirring was continued for 1 hr after which the reaction was quenched with 20 mL sat. aq. Na2S2O4 and diluted with 30 mL CH2Cl2.
The organic layer was separated and the aqueous phase was acidified with 1 M HCl to pH 2 and extracted twice with CH$_2$Cl$_2$. The combined organic layers were dried on Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by column chromatography (0-15 % MeOH in CH$_2$Cl$_2$) to yield the title compound (580 mg, 1.00 mmol, 89%) as a pale yellow oil.

1H NMR (400 MHz, CDCl$_3$) $\delta$ 3.16 (dd, 1 H, J = 9.2, J = 8.4 Hz, H5), 3.64 (dd, 1 H, J = 17.7 Hz, J = 8.8 Hz, H3), 3.68 (dd, 1 H, J = 16.8 Hz, J = 8.8 Hz, H4), 3.83 (dd, 1 H, J = 10 Hz, J = 2.8, H6), 3.98 (d, 2 H, J = 8.8 Hz, H2), 3.25-2.28 and 4.54-4.80 (m, 7 H, 3×CH$_2$Ph, H7), 7.10-7.35 (20 H, 3×CH$_2$Ph, Ph), 13C NMR (100 MHz, CDCl$_3$) $\delta$ 64.58 (C 7), 74.15 (C H$_2$Ph), 74.95 (C H$_2$Ph), 75.30 (C H$_2$Ph), 77.50 (C 2), 77.81 (C 5), 79.27 (C$^3$), 80.56 (C$^4$), 85.61 (C$^5$), 127.38, 127.59, 127.80, 127.84, 128.03, 128.49, 128.70, 128.88, 129.42, 134.30, 137.73, 137.79, 173.06 (C 1). IR neat (cm$^{-1}$): 694.3, 1026.1, 1087.8, 1249.8, 1357.8, 1454.2, 1496.7, 1724.2, 1978.8, 2098.4. $[\alpha]_D^{20} - 0.2$ (c 1.0, CHCl$_3$), HRMS: calcd for C$_{34}$H$_{37}$O$_6$N$_4$ ([M+NH$_4$]) 597.27076 found 597.27100

**Compound 15b.** Azido alcohol 14b (514 mg, 1.02 mmol) was oxidized to azido acid 15b according to the protocol described for compound 15a. Column chromatography (0-15 % MeOH in CH$_2$Cl$_2$) yielded the title compound (482 mg, 0.93 mmol, 91%) as an off white solid.

1H NMR (400 MHz, CDCl$_3$) $\delta$ 1.15 (d, 3 H, J = 6.8 Hz, Me), 3.46, (dd, 1 H, J = 9.6 Hz, J = 8.0 Hz, H5), 3.56 (dd, 1 H, J = 10 Hz, J = 2.0 Hz, H6), 3.63 (dq, 1 H, J = 6.8 Hz, J = 2.0 Hz, H7), 3.70-3.80 (m, 2 H, H3, H4), 3.98 (d, 1 H, J = 8.8 Hz, H2), 4.58-3.92 (m, 6 H, 3×CH$_2$Ph), 7.23-7.36 (m, 15 H, 3×CH$_2$Ph), 13C NMR (100 MHz, CDCl$_3$) $\delta$ 12.34 (Me), 56.19 (C 7), 74.45 (C H$_2$Ph), 74.83 (C H$_2$Ph), 75.45 (C H$_2$Ph), 77.14 (C$^3$), 77.67 (C 2), 79.33 (C 3), 80.72 (C$^6$), 98.05 (C$^4$), 127.62, 127.69, 127.83, 127.97, 128.02, 128.29, 128.37, 128.43, 137.30, 137.87, 173.42 (C 1). IR neat (cm$^{-1}$): 462.1, 696.7, 752.7, 1026.3, 1083.8, 1149.3, 1251.3, 1363.3, 1497.7, 1740.6, 2109.6. $[\alpha]_D^{20} + 21.6$ (c 1.0, CHCl$_3$), mp: 133°C (from hexane), HRMS: calcd for C$_{29}$H$_{35}$O$_6$N$_4$ ([M+NH$_4$]) 535.25511 found 535.25513

**Compound 15c.** Azido alcohol 14c (89 mg, 0.17 mmol) was oxidized to azido acid 15c according to the protocol described for compound 15a. Column chromatography (0-15 % MeOH in CH$_2$Cl$_2$) yielded the title compound (71 mg, 0.13 mmol, 76%) as an oil.

1H NMR (400 MHz, CDCl$_3$) $\delta$ 0.95 (d, 3 H, J = 6.5 Hz, Me), 1.00 (d, 3 H, J = 6.5 Hz, Me), 1.24 (m, 1 H, H8 a), 1.73-1.82 (m, 2 H, H8b, CH(Me)$_2$), 3.57-3.63 (m, 2 H, H5, H7), 3.68 (dd, 1 H, J = 9.6 Hz, J = 1.6 Hz, H6), 3.77 (dd, 1 H, J = 16.4 Hz, J = 8.8 Hz, H4), 3.80 (dd, 1 H, J = 17.2 Hz, J = 8.8 Hz, H3), 3.99 (d, 1 H, J =
Compound 16. Compound 13b (422 mg, 0.71 mmol) was taken up in 8 mL THF and 2 mL water and cooled on ice. Me₃P (3.5 mL, 1 M in Toluene) was added to the reaction was stirred for 4 hr. The solvents were removed and the residue was coevaporated twice with toluene. The crude amine was taken up in 70 mL CH₂Cl₂/1,4 dioxane (1:1 v/v) and DIPEA ( 2.10 mmol, 370 μL) and FmocCl (1.05 mmol, 272 mg) was added. Stirring was continued for 2.5 hr after which the reaction mixture was diluted with CH₂Cl₂ and water (50 mL each). The organic phase was separated and washed with 10% aq. citric acid, satd. aq. NaHCO₃, and water (50 mL each). The organic layer was dried on Na₂SO₄, concentrated in vacuo and purified silica gel column chromatography (10% → 20% EtOAc in light petroleum v/v) yielding 411mg (0.52 mmol 73%) of the title compound as an off white wax. The compound exists as a 5:1 mixture of rotamers. Major rotamer: ¹H NMR (400 MHz, CDCl₃) δ 1.02 (d, 3 H, J = 6.8 Hz, Me), 3.35-3.45 (m, 3 H, H₂, H₅, H₆), 3.60 (t, 1 H, J = 9.2 Hz, H₃), 3.68-3.73 (m, 3 H, H₁, H₄), 4.17, (m, 1 H, J = 7.2 Hz, -OCH₂CH₂Fmoc), 4.40 (d, 2 H, J = 7.2 Hz, -OCH₂CH₂Fmoc), 4.52-4.70 and 4.81-4.94 (m, 8 H, 4×CH₂Ph), 5.22 (d, 1 H, J = 9.2 Hz, 7.19-7.40 (m, 24 H, 4×CH₂Ph, ArFmoc), 7.59 (d, 2 H, J = 7.6 Hz, ArFmoc), 7.75 (d, 2 H, J = 7.6 Hz, ArFmoc), 13C NMR (100 MHz, CDCl₃) δ 14.03 (Me), 46.38 (C7), 47.27 (OCH₂CH₂Fmoc), 66.49 (OCH₂CH₂Fmoc), 73.30 (CH₂Ph), 74.42 (CH₂Ph), 74.99 (CH₂Ph), 75.48 (CH₂Ph), 78.03 (C5), 78.40 (C3), 78.89 (C²), 80.63 (C⁶), 87.27 (C⁴), 119.80, 119.89, 125.00, 125.04, 126.98, 127.40, 127.53, 127.59, 127.61, 127.74, 127.82, 127.85, 128.05, 128.20, 128.34, 128.39, 128.41, 128.43, 137.79, 137.89, 138.03, 138.19, 138.39, 141.24, 143.94, 144.03, 155.53 (COFmoc), IR neat (cm⁻¹): 694.1, 734.2, 911.7, 1037.8, 1093.5, 1256.9, 1452.1, 1553.9, 1680.3, 2846.4, 3031.7, 3302.8. [α]D 20 + 2.0 (c 1.0, CHCl₃) , HRMS: calcd for C₅₁H₅₅O₇N₂ ([M+NH₄]+) 807.40038, found 807.40137

Compound 17. Compound 13a (607 mg, 0.93 mmol) was taken up in 20 mL dry methanol. To this solution Lindlars Catalyst (Pd/CaCO₃/Pb 120 mg, 20 % by wt.) and di-tert-butyl dicarbonate (250 mg, 1.15 mmol) were added. Hydrogen gas was bubbled through the reaction mixture until TLC indicated full conversion into a more polar product (6 hr). the reaction was filtered concentrated in vacuo and the residue was purified by silica gel column chromatography (10% → 35% EtOAc in light petroleum v/v) yielding 577 mg (0.79 mmol 85 %) of the title compound as an colorless syrup. The compound exists as a 3.5:1 mixture of rotamers. (¹H NMR): ¹H NMR (400 MHz, CDCl₃) δ 1.34 (minor) and 1.40 (major) (s, 9 H, CMe₃), 3.06 (t, 1 H, J = 7.2 Hz, H₅), 3.47-3.55 (m, 2 H, H₂, H₃), 3.73-3.83 (m, 4 H, H₁, H₄, H₆), 4.33-4.96 (mm, 8 H, 4×CH₂Ph), 4.96 (m, H₇ minor rotamer), 5.11 (dd, J = 7.2 Hz, J = 2.4 Hz ,H₇ major rotamer.), 5.57 (d, J = 6.8 Hz, NH minor rotamer), 5.71 (d, J = 7.2 Hz), 7.18-7.44 (m, 25 H, 4×CH₂Ph, Ph), ¹³C NMR (100 MHz, CDCl₃) δ 28.28 (CMe₃), 54.35 (C7), 68.96 (C1), 73.11 (CH₂Ph), 73.97 (CH₂Ph), 74.91 (CH₂Ph), 75.29 (CH₂Ph), 78.26 (C3 and C5), 78.75 (C2), 79.21 (CMe₃), 80.73 (C6), 87.33 (C4), 126.97, 127.23, 127.29, 127.41, 127.48, 127.67, 127.74, 127.91, 128.09, 138.301, 128.33, 128.10, 137.881, 138.066, 138.186, 138.23, 138.84, 154.73 (C=O), IR neat (cm⁻¹): 649.8, 733.3, 1094.9, 1158.1, 1364.7,
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1454.0, 1489.8, 1713.8, 2865.9, 3444.2, [α]_D^20 + 22.0 (c 1.0, CHCl₃) , MS: (M+H) 730.6, [M+H-Boc], 630.4

**Compound 18.** Compound 17 (577 mg, 0.79 mmol) was taken up in 20 mL methanol. To the solution 10 % Pd/C was added. Hydrogen gas was bubbled through for 4 hours after which the reaction was filtered and concentrated *in vacuo*. The residue was taken up in 10 mL trifluoroacetic acid and the solution was stirred for 30 minutes. Concentration of the acidic mixture yielded the product (207 mg, 0.77 mmol 97%) as an oil which solidified over time. ¹H NMR (400 MHz, D₂O) δ 2.69 (t, 1 H, J = 9.6 Hz, H5), 2.93 (t, 1 H, J = 9.6 Hz, H3), 3.32-3.37 (m, 2H, H2, H4), 3.54 (dd, 1 H, J = 12.0 Hz, J = 7.6 Hz, H1a), 3.70 (dd, 1 H, J = 9.6 Hz, J = 2.8 Hz, H6), 3.82 (d, 1 H, J = 11.6 Hz, H1b), 4.62 (d, 1 H, J = 2.4 Hz, H7), 7.33-7.38 (m, 5 H, Ph) ¹³C NMR (100 MHz, D₂O) δ 54.93 (C7), 61.55 (C1), 69.64 (C3), 69.99 (C5), 77.03 (C6), 77.18 (C2), 79.87 (C4), 128.75, 128.79, 129.51, 131.43 IR neat (cm⁻¹): 628.4, 699.0, 799.8, 987.9, 1185.5, 1318.3, 1463.8, 1656.4, 3042.2, [α]_D^20 + 20.0 (c 1.0, H₂O) lit.² [α]_D^20 + 20.8 (c 1.0, H₂O), ESI- MS: (M+H) 270.1, [M+Na], 292.0
