

Electronic Supplementary Information

Direct Deprotected Glycosyl-Asparagine Ligation.

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and Benjamin G. Davis^{a*}

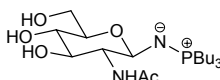
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Aza-Ylid intermediate 1

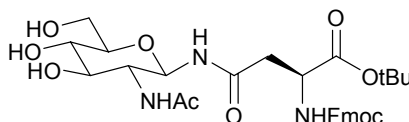


Tributyl phosphine (17 μ L, 0.7 mmol) was added to 2-*N*-acetylamido-2-deoxy- β -D-glucopyranosyl azide (17 mg, 0.7 mmol) in d_3 -acetonitrile (1 mL). After 45 min, nmr revealed complete conversion to the aza-ylid intermediate **1**; δ_H (400 MHz, d_3 -MeCN) 0.94 (9H, t, J 7.2 Hz, 3 x CH₃), 1.36-1.53 (12H, m, 6 x CH₂), 1.61-1.81 (6H, m, 3 x CH₂), 1.91 (3H, s, Ac), 3.19-3.22 (1H, m, H-5), 3.33 (1H, at, J 8.8 Hz, H-2), 3.43 (1H, at, J 9.0 Hz, H-4), 3.50 (1H, at, J 9.5 Hz, H-3), 3.66-3.74 (2H, m, H-6, H-6'), 4.41 (1H, dd, $J_{1,2}$ 8.2 Hz, $J_{H,P}$ 21.1 Hz, H-1); δ_P (250 MHz, d_3 -MeCN) 37.4;ⁱ m/z (ESI⁺) 421 (M+H⁺, 100%); HRMS (ESI⁺) calcd. for C₂₀H₄₂N₂O₅P (M+H⁺) 421.2831. Found 421.2835.

General method for synthesis of *N*-linked glycoamino acids:

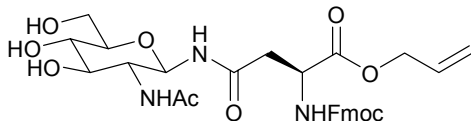
Amino acid (1 equiv) 1-hydroxybenzotriazole (1 equiv) and 1,3-dicyclohexylcarbodiimide (1 equiv) were stirred in anhydrous acetonitrile (1.5 mL) under an atmosphere of argon. After 30 min the azide sugar (1.1 equiv) and tributyl phosphine (1.1 equiv) were added and the reaction mixture stirred for a further 16 h. The reaction mixture was concentrated *in vacuo* and the residue was purified by flash column chromatography (ethyl acetate then water:isopropanol:ethyl acetate, 1:2:5) to afford the glycoamino acid.

N*- α -9-Fluorenylmethoxycarbonyl-*N*- β -(2-*N*-acetylamido-2-deoxy- β -D-glucopyranosyl)-L-asparagine *tert*-butyl ester **2*



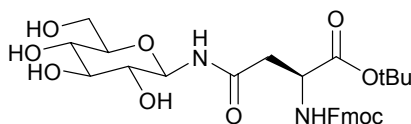
Yield 87%; m.p. 178.5-180.5 °C [Ref 182-184 °C]ⁱⁱ; $[\alpha]_D^{21} +2.0$ (*c*, 0.5 in MeOH); $\nu_{\max}$ (KBr) 3323 (br, N-H, O-H), 1750, 1703, 1661, 1627 (s, C=O) cm^{-1} ; δ_{H} (500 MHz, CD_3OD) 1.48 (9H, s, 3 x CH_3), 1.93 (3H, s, Ac), 2.68 (1H, dd, $J_{\alpha\text{H},\text{CH}}$ 7.2 Hz, $J_{\text{CH},\text{CH}'}$ 15.7 Hz, $\text{CHH}'\text{C}\alpha\text{H}$), 2.73 (1H, dd, $J_{\alpha\text{H},\text{CH}'}$ 5.0 Hz, $\text{CHH}'\text{C}\alpha\text{H}$), 3.45-3.49 (2H, m, H-4, H-5), 3.68 (1H, dd, $J_{5,6}$ 2.7 Hz, $J_{6,6'}$ 11.4 Hz, H-6), 3.77 (1H, at, J 9.9 Hz, H-2), 3.85 (1H, d, J 11.7 Hz, H-6'), 4.24 (1H, at, J 6.6 Hz, $\text{CHH}'\text{Fmoc}$), 4.32 (1H, at, J 7.0 Hz, CH_{Fmoc}), 4.44 (1H, at, J 3.5 Hz, $\text{CHH}'\text{Fmoc}$), 4.97 (1H, d, J 9.7 Hz, H-1), 7.33 (2H, at, J 7.3 Hz, Ar-H_{3Fmoc}), 7.41 (2H, at, J 7.3 Hz, Ar-H_{4Fmoc}), 7.68 (2H, d, J 7.4 Hz, Ar-H_{2Fmoc}), 7.81 (2H, d, J 7.5 Hz, Ar-H_{5Fmoc}); δ_{C} (100 MHz, CD_3OD) 21.9 (q, CH_3), 27.2 (q, $\text{C}(\underline{\text{C}}\text{H}_3)_3$), 37.6 (d, $\alpha\text{C}\underline{\text{C}}\text{H}_2$), 48.7 (d, CH_{Fmoc}), 51.7 (d, $\alpha\text{-C}$), 55.1 (d, C-2), 61.7 (t, C-6), 67.0 (t, CH_2Fmoc), 70.8 (d, C-5), 75.3 (d, C-3), 78.7 (d, C-4), 79.4 (d, C-1), 82.1 (s, $\underline{\text{C}}(\text{CH}_3)_3$), 119.9 (d, Ar-C_{5Fmoc}), 125.2 (d, Ar-C_{2Fmoc}), 127.2 (d, Ar-C_{3Fmoc}), 127.8 (d, Ar-C_{4Fmoc}), 141.6, 144.2 (2 x s, Ar-C), 171.0, 171.7, 173.5 (3 x s, s x C=O); m/z (ESI) 612 (M-H^+ , 100 %); HRMS (ESI) calcd. for $\text{C}_{31}\text{H}_{38}\text{N}_3\text{O}_{10}$ (M-H^+) 612.2557. Found 612.2542.

N*- α -9-Fluorenylmethoxycarbonyl-*N*- β -(2-*N*-acetylamido-2-deoxy- β -D-glucopyranosyl)-L-asparagine allyl ester **3*



Yield 62 %; amorphous solid; $[\alpha]_D^{23} +5.0$ (*c*, 0.5 in MeOH); $\nu_{\max}$ (KBr) 3363 (br, N-H, O-H), 1750, 1668 (s, C=O) cm^{-1} ; δ_{H} (500 MHz, d_6 -DMSO) 1.77 (3H, s, CH_3), 2.52 (1H, dd, $J_{\text{CH},\alpha\text{H}}$ 7.0 Hz, $J_{\text{CH},\text{CH}'}$ 16.1 Hz, CHH'), 2.65 (1H, dd, $J_{\text{CH},'\alpha\text{H}}$ 5.8 Hz, CHH'), 3.06-3.12 (2H, m, H-4, H-5), 3.23-3.27 (1H, m, H-6), 3.43-3.45 (1H, m, H-3), 3.53 (1H, dd, J 9.6 Hz, J 19.1 Hz, H-2), 3.66 (1H, ad, J 10.9 Hz, H-6'), 4.21-4.34 (3H, m, CH_{Fmoc} , $\text{CH}_2_{\text{Fmoc}}$), 4.46 (1H, dd, J 6.8 Hz, J 14.3 Hz, αH), 4.53-4.57 (2H, m, $\text{CH}_2\text{-CH}$), 4.82 (1H, at, J 9.4 Hz, H-1), 4.97, 5.01 (2H, 2 x s, 2 x OH), 5.19 (1H, d, J 10.5 Hz, $\text{CHH}'\text{=CH}$), 5.30 (1H, d, J 17.3 Hz, $\text{CHH}'\text{=CH}$), 5.88 (1H, ddd, J 5.1 Hz, J 10.3 Hz, J 22.1 Hz, CH=CH_2), 7.33 (2H, t, J 7.3 Hz, Ar-H3), 7.43 (2H, t, J 7.4 Hz, Ar-H4), 7.65 (1H, d, J 8.3 Hz, $\text{NH}\alpha\text{H}$), 7.71 (2H, d, J 7.4 Hz, Ar-H2), 7.78 (1H, d, J 8.9 Hz, NH-Ac), 7.90 (2H, d, J 7.5 Hz, Ar-H5), 8.25 (1H, d, J 9.1 Hz, NH-H1); δ_{C} (125 MHz, d_6 -DMSO) 22.7 (q, CH_3), 39.8 (t, $\text{CH}_2\alpha\text{C}$), 46.6 (d, CH_{Fmoc}), 50.2 (d, αC), 54.5 (d, C-2), 60.9 (t, C-6), 64.9 (t, $\text{CH}_2\text{-CH=CH}_2$), 65.8 (t, $\text{CH}_2_{\text{Fmoc}}$), 70.5 (d, C-4), 74.5 (d, C-3), 78.7 (d, C-5), 78.9 (d, C-1), 117.9 (t, $\text{CH}_2\text{=CH}$), 120.1 (d, Ar-C5), 125.2 (d, Ar-C2), 127.1 (d, Ar-C3), 127.6 (d, Ar-C4), 132.4 (d, CH=CH_2), 140.7, 143.7 (2 x s, Ar-C), 155.8, 169.2, 169.9, 171.1 (4 x s, 4 x C=O); m/z (ESI^+) 620 ($\text{M}+\text{Na}^+$, 100 %); HRMS (ESI^+) calcd. for $\text{C}_{30}\text{H}_{35}\text{N}_3\text{O}_{10}\text{Na}$ ($\text{M}+\text{Na}^+$) 620.2220. Found 620.2216.

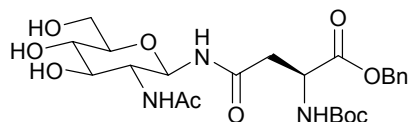
N*- α -9-Fluorenylmethoxycarbonyl-*N*- β -(β -D-glucopyranosyl)-L-asparagine *tert*-butyl ester **4*



Yield 50 %; $[\alpha]_D^{23} +3.7$ (*c*, 1.0 in MeOH); δ_{H} (400MHz, CD_3OD) 1.47 (9H, s, 3 x CH_3), 2.80 (2H, dd, J 2.9 Hz, J 6.5 Hz, $\text{CH}_2\alpha\text{H}$), 3.27 (1H, at, J 9.1 Hz, H-2), 3.20-3.34 (2H, m, H-4, H-5), 3.43 (1H, at, J 8.7 Hz, H-3), 3.67 (1H, dd, $J_{5,6}$ 5.1 Hz, $J_{6,6'}$ 11.9 Hz, H-6), 3.85

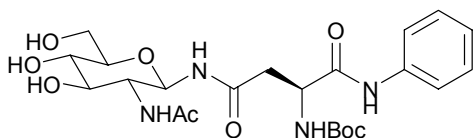
(1H, dd, $J_{5,6'}$ 2.1 Hz, H-6'), 4.24 (1H, at, J 7.0 Hz, CH_{Fmoc}), 4.28-4.40 (2H, m, CH_{2Fmoc}), 4.49 (1H, at, J 5.7 Hz, α H), 4.90 (1H, d, $J_{1,2}$ 9.7 Hz, H-1), 7.33 (2H, at, J 7.4 Hz, Ar-H_{3Fmoc}), 7.40 (2H, at, J 7.3 Hz, Ar-H_{4Fmoc}), 7.68 (2H, d, J 7.3 Hz, Ar-H_{2Fmoc}), 7.80 (2H, d, J 7.5 Hz, Ar-H_{5Fmoc}); δ_C (100 MHz, CD₃OD), 26.9 (q, CH₃), 37.1 (t, CH₂ α C), 47.0 (d, CH_{Fmoc}), 51.2 (d, α C), 61.3 (t, C-6), 66.8 (t, CH_{2Fmoc}), 70.0 (d, C-5), 72.5 (d, C-2), 77.6 (d, C-3), 78.2 (d, C-4), 79.6 (d, C-1), 82.7 (s, C(CH₃)₃), 119.6 (d, Ar-C_{5Fmoc}), 124.9 (d, Ar-C_{2Fmoc}), 126.8 (d, Ar-C_{3Fmoc}), 127.4 (d, Ar-C_{4Fmoc}), 141.2, 143.8 (2 x s, Ar-C), 157.0, 170.7, 171.8 (3 x s, C=O); m/z (ESI⁺) 595 (M+Na⁺, 100 %).ⁱⁱⁱ

N*- α -[(1,1-Dimethylethoxy)carbonyl]-*N*- β -(2-*N*-acetylamido-2-deoxy- β -D-glucopyranosyl)-L-asparagine benzyl ester **5*



Yield 62 %, m.p. 100.3-101.8 °C; $[\alpha]_D^{25} + 29.0$ (c , 1.0 in MeOH); $\nu_{\max}$ (KBr) 3363 (br, N-H, O-H), 1668, 1652, (s, C=O) cm⁻¹; δ_H (400 MHz, CD₃OD) 1.42 (9H, s, C(CH₃)₃), 1.97 (3H, s, NHAc), 2.72 (2H, d, J 5.2 Hz, α CHCH₂), 3.33-3.35 (1H, m, H-4), 3.47 (1H, dd, J 4.8 Hz, J 8.7 Hz, H-3), 3.65-3.85 (4H, m, H-2, H-5, H-6, H-6'), 4.56 (1H, $J_{\alpha H, CH}$ 5.3 Hz, $J_{\alpha H, CH'}$ 7.2 Hz, α H), 4.97 (1H, d, $J_{1,2}$ 9.6 Hz, H-1), 5.16 (2H, s, CH₂Ph), 7.30-7.37 (5H, m, 5 x Ar-H); δ_C (100 MHz, CD₃OD) 23.4 (q, NHC(O)CH₃), 29.1 (q, C(CH₃)₃), 38.9 (t, CH₂ α CH), 52.3 (d, α -C), 56.5 (d, C-2), 63.1 (t, C-6), 68.5 (t, CH₂Ph), 72.2 (d, C-4), 76.7 (d, C-3), 80.2 (d, C-5), 80.7 (d, C-1), 112.8 (s, C(CH₃)₃), 130.3 (d, 5 x Ar-C), 137.6 (s, Ar-C), 158.3 (s, OC(O)N), 170.3, 173.5, 174.9 (3 x s, C=O); m/z (ESI⁺) 526 (M+H⁺, 100 %); HRMS (ESI⁺) calcd. for C₂₄H₃₆N₃O₁₀ (M+H⁺) 526.2401. Found 526.2404.

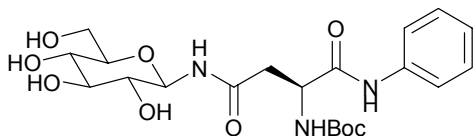
N*- α -[(1,1-Dimethylethoxy)carbonyl]-*N*- β -(2-*N*-acetylamido-2-deoxy- β -D-glucopyranosyl)-L-asparagine anilide **6*



Yield 53 %, m.p. 207-209 °C; $[\alpha]_D^{19} + 7.4$ (c, 1.0 in CHCl_3); ν_{max} (KBr) 3414 (br, N-H, O-H), 1692, 1667, 1628 (s, C=O) cm^{-1} ; δ_{H} (CD_3OD , 400 MHz) 1.47 (9H, s, $\text{C}(\text{CH}_3)_3$), 1.98 (3H, s, CH_3), 2.66 (1H, dd, $J_{\text{CH},\alpha\text{H}}$ 6.9 Hz, $J_{\text{CH},\text{CH}'}$ 15.8 Hz, CHH'), 2.75 (1H, dd, $J_{\text{CH}',\alpha\text{H}}$ 5.5 Hz, CHH'), 3.35-3.37 (2H, m, H-4, H-5), 3.46-3.51 (1H, m, H-3), 3.65-3.70 (1H, m, H-6), 3.75 (1H, at, J 9.9 Hz, H-2), 3.84 (1H, d, J 11.6 Hz, H-6'), 4.58-4.60 (1H, bm, αH), 5.00 (1H, d, J 9.7 Hz, H-1), 7.11 (1H, t, J 7.4 Hz, *p*-Ar-H), 7.32 (2H, t, J 7.7 Hz, *m*-Ar-H), 7.56 (2H, d, J 7.9 Hz, *o*-Ar-H); δ_{C} (CD_3OD , 100 MHz) 21.9 (q, CH_3), 27.7 (q, $\text{C}(\text{CH}_3)_3$), 33.7 (t, $\text{CH}_2\alpha\text{C}$), 48.7 (d, αC), 55.2 (d, C-2), 61.8 (t, C-6), 71.0 (d, C-5), 75.3 (d, C-3), 78.7 (d, C-4), 79.4 (d, C-1), 117.7 (s, $\text{C}(\text{CH}_3)_3$), 120.7 (d, *o*-Ar-C), 124.5 (d, *p*-Ar-C), 128.8 (d, *m*-Ar-C), 138.4 (s, Ar-C), 159.0, 171.0, 173.7 (2 x s, C=O); m/z (ESI) 509 (M-H^+ , 100); HRMS (ESI⁺) calcd. for $\text{C}_{23}\text{H}_{35}\text{N}_4\text{O}_9$ (M-H^+) 511.2404. Found 511.2425.

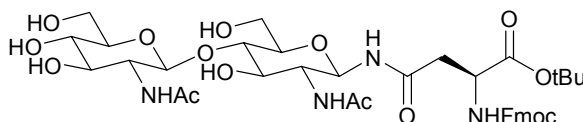
***N*- α -[(1,1-Dimethylethoxy)carbonyl]-*N*- β -(β -D-glucopyranosyl)-L-asparagine anilide**

7



Yield 47 %, clear oil; $[\alpha]_D^{21} + 4.8$ (c, 0.5 in MeOH); ν_{max} (thin film) 3423 (br, N-H, O-H), 1637 (s, C=O) cm^{-1} ; δ_{H} (400 MHz, CD_3OD) 1.47 (9H, s, 3 x CH_3), 2.73-2.81 (2H, m, CH_2), 3.28 (1H, at, J 9.2 Hz, H-2), 3.32-3.38 (2H, m, H-4, H-5), 3.43 (1H, at, J 8.7 Hz, H-3), 3.64 (1H, dd, $J_{5,6}$ 5.2 Hz, $J_{6,6'}$ 11.9 Hz, H-6), 3.83 (1H, dd, $J_{5,6'}$ 2.1 Hz, H-6'), 4.58-4.61 (1H, m, αH), 4.92 (1H, d, $J_{1,2}$ 9.4 Hz, H-1), 7.12 (1H, t, J 7.4 Hz, *p*-Ar-H), 7.32 (2H, t, J 7.8 Hz, *m*-Ar-H), 7.56 (2H, d, J 7.9 Hz, *o*-Ar-H); δ_{C} (100 MHz, CD_3OD) 27.7 (q, $\text{C}(\text{CH}_3)_3$), 37.9 (t, CH_2), 52.4 (d, αC), 61.7 (t, C-6), 70.4, 78.6 (2 x d, C-4, C-5), 73.0 (d, C-2), 77.7 (d, C-3), 80.0 (d, C-1), 120.7 (d, *o*-Ar-C), 124.5 (d, *p*-Ar-C), 128.8 (d, *m*-Ar-C), 138.4 (s, $\text{C}(\text{CH}_3)_3$), 143.5 (s, Ar-C), 156.7, 171.2, 172.2 (3 x s, C=O); m/z (ESI⁺) 492 ($\text{M}+\text{Na}^+$, 100%); HRMS (ESI⁺) calcd. for $\text{C}_{21}\text{H}_{31}\text{N}_3\text{O}_9\text{Na}$ ($\text{M}+\text{Na}^+$) 492.1958. Found 492.1952.

N*- α -9-Fluorenylmethoxycarbonyl-*N*- β -(2-*N*-Acetylamido-4-*O*-(2-*N*-acetylamido-2-deoxy- β -D-glucopyranosyl)-2-deoxy- β -D-glucopyranosyl)-L-asparagine *tert*-butyl ester **8*



Yield 61 %; $[\alpha]_{\text{D}}^{23} +2.0$ (*c*, 1.0 in DMSO); δ_{H} (500 MHz, d_6 -DMSO) 1.40 (9H, s, 3 x CH_3), 1.79, 1.84 (6H, 2 x s, 2 x Ac), 2.46 (1H, dd, $J_{\text{CH},\alpha\text{H}}$ 1.7 Hz, $J_{\text{CH},\text{CH}'}$ 16.2 Hz, $\text{CHH}'\alpha\text{H}$), 2.60 (1H, dd, $J_{\text{CH}',\alpha\text{H}}$ 5.5 Hz, $\text{CHH}'\alpha\text{H}$), 3.04-3.76 (12H, bm, H-2a, H-2b, H-3a, H-3b, H-4a, H-4b, H-5a, H-5b, H-6a, H-6b, H-6'a, H-6'b), 4.20-4.24 (1H, m, CH_{Fmoc}), 4.30-4.33 (3H, m, $\text{CH}_2_{\text{Fmoc}}$, αH), 4.43 (1H, d, $J_{1,2}$ 8.7 Hz, H-1b), 4.82-4.87 (1H, m, H-1a), 7.33-7.35 (2H, m, Ar-H3), 7.41-7.44 (2H, m, Ar-H4), 7.48 (1H, d, J 8.2 Hz, $\text{NH}\alpha\text{H}$), 7.63 (2H, d, J 8.6 Hz, Ar-H2), 7.72 (2H, d, J 7.3 Hz, Ar-H5), 7.79 (1H, d, J 8.1 Hz, NH-H2b), 7.85 (1H, d, J 7.5 Hz, NH -H2a), 8.24 (1H, d, J 9.0 Hz, N-H $_{[\text{N-link}]}$); δ_{C} (100MHz, d_6 -DMSO) 23.5 (q, CH_3), 28.1 (q, $\text{C}(\text{CH}_3)_3$), 40.3 (t, $\text{CH}_2\alpha\text{C}$), 46.6 (d, CH_{Fmoc}), 50.9 (d, αC), 55.0, 56.6 (2 x d, C-2a, C-2b), 60.9, 62.2 (2 x t, C-6a, C-6b), 66.3 (t, $\text{CH}_2_{\text{Fmoc}}$), 71.9, 73.8, 75.3, 78.1, 78.4, 82.8 (6 x d, C-3a, C-3b, C-4a, C-4b, C-5a, C-5b), 79.7 (d, C-1a), 81.3 (s, $\text{C}(\text{CH}_3)_3$), 103.4 (d, C-1b), 118.1 (d, Ar-C5), 125.9 (d, Ar-C2), 127.8 (d, Ar-C3), 128.4 (d, Ar-C4), 141.6, 144.5 (2 x s, 2 x Ar-C), 196.6, 170.5, 170.7 (3 x s, C=O); m/z (ESI $^{+}$) 839 (M+Na $^{+}$, 100%); HRMS (ESI $^{+}$) calcd. for $\text{C}_{39}\text{H}_{52}\text{N}_4\text{O}_{15}\text{Na}$ (M+Na $^{+}$) 839.3327. Found 839.3320.

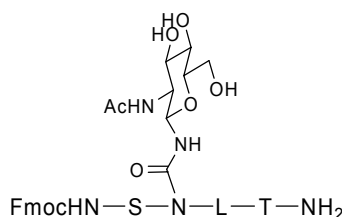
Solid phase peptide synthesis

This was carried out manually on a rink amide resin. Amino acids were coupled using HOBt, PyBOP, DIEA in DMF. Piperidine (20 % in DMF) was used to remove Fmoc protecting groups. Double coupling was required for the coupling of *N*-linked glycoamino acids and the two adjacent amino acids and HATU was used as an alternative coupling agent for these steps also. TFA/TIS/H $_2$ O was used to cleave the glycopeptides from the resin.

Staudinger Ligation on tetrapeptide

Peptide (1 equiv, typically 10 mg), 1-hydroxybenzotriazole (1.5 equiv) and 1,3-dicyclohexylcarbodiimide (1.5 equiv) were stirred in anhydrous DMF (1.5 mL) under an atmosphere of argon. After 30 min the azide sugar (2 equiv) and tributyl phosphine (2 equiv) were added and the reaction mixture stirred for a further 72 h. The reaction mixture was concentrated *in vacuo* and the residue was purified by reverse phase HPLC. The absorbance of the starting peptide and glycopeptide were assumed identical in the calculation of percentage conversion.

Tetramer glycopeptide 12



δ_{H} (500 MHz, d_6 -DMSO) 0.79 (3H, d, J 6.4 Hz, CH_3 -L), 0.84 (3H, d, J 6.6 Hz, CH_3 -L), 1.03 (3H, d, J 5.7 Hz, CH_3 -T), 1.48 (2H, t, J 6.8, β - CH_2 -L), 1.58 (1H, d, J 6.7 Hz, γCH -L), 1.81 (3H, s, Ac), 2.44 (1H, dd, $J_{\text{CH},\alpha\text{H}}$ 6.1 Hz, $J_{\text{CH},\text{CH}'}$ 16.5 Hz, CHH' -N), 2.69 (1H, dd, $J_{\text{CH}',\alpha\text{H}}$ 6.3 Hz, CHH' -N), 3.03-3.07 (1H, m, H-4), 3.11-3.13 (1H, m H-5), 3.33-3.34 (1H, m, H-3), 3.40 (1H, m, H-6), 3.51-3.53 (1H, m, H-2), 3.58 (2H, s, βCH_2 -S), 3.66-3.67 (1H, m, H-6'), 3.51-3.66 (3H, m, αH -T, βCH_2 -T), 4.12 (1H, d, J 6.8 Hz, αH -S), 4.21-4.29 (4H, m, αH -L, CH_{Fmoc} , CH_2Fmoc), 4.58 (1H, d, J 6.6Hz, αH -N), 4.79 (1H, at, J 9.6 Hz, H-1), 4.87 (1H, bs, OH-T), 5.09 (2H, bs, 3-OH, 4-OH), 5.18 (1H, bs, 6-OH), 7.34 (2H, t, J 7.9 hz, Ar-H), 7.43 (3H, t, J 7.4 Hz, Ar-H, NH-S), 7.58 (1H, d, J 7.9 Hz, NH-T), 7.74 (2H, d, J 3.6 Hz, Ar-H), 7.85 (1H, d, J 8.3 Hz, NHAc), 7.99 (2H, d, J 8.1 Hz, NH-L), 8.29 (1H, d, J 8.5 Hz, NH-N link), 8.33 (1H, d, J 7.0 Hz, NH-N); m/z (ESI^+) 858 ($\text{M}+\text{H}^+$, 100%); HRMS (ESI^+) calcd. for $\text{C}_{40}\text{H}_{55}\text{N}_7\text{O}_{14}\text{Na}$ ($\text{M}+\text{Na}^+$) 880.3699. Found 880.3698.

ⁱ I. Bosch, A. Gonzalez, F. Urpi, J. Vilarrasa, *J. Org. Chem.*, 1996, **61**, 5638; D. Sikora, T. Gajda, *Tetrahedron*, 2000, **56**, 3755.

ⁱⁱ M. Bejugam, S. L. Flitsch, *Org. Lett.*, 2004, **6**, 4001.

ⁱⁱⁱ L. Urge, E. Kollat, M. Hollosi, I. Laczko, K. Wroblewski, J. Thurin, L. Otvos Jr, *Tett. Lett.*, 1991, **32**, 3445.