

Ph₂SO-Tf₂O: a Powerful Promotor System in Chemoselective Glycosylations Using Thioglycosides

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General Procedures. Dichloromethane was refluxed with P₂O₅ and distilled before use. All reactions were performed under argon atmosphere. 1-Bezenesulfinyl piperidine (BSP) and tri-*tert*-butylpyrimidine (TTBP) were synthesized as described by Crich *et al.*¹ Traces of water from the donor and acceptor glycosides, diphenylsulfoxide (Acros), BSP and TTBP were removed by repeated coevaporation with toluene and dichloroethane. Molecular sieves (3Å) were flame dried before use. Trifluoromethanesulfonic anhydride (Acros) was used as received. ¹H and ¹³C NMR spectra were recorded with a Bruker DPX 300 (300 and 75.1 MHz) or a Bruker AV 400 (400 and 100 MHz). ¹H NMR chemical shifts () in CDCl₃ are reported relative to tetramethylsilane. Mass spectra were recorded on a PE/SCIEX API 165 equipped with an Electrospray Interface (Perkin-Elmer). Optical rotations were recorded on a Propol automatic polarimeter in CHCl₃.

General procedure for the Ph₂SO/Tf₂O mediated glycosylations:

Synthesis of **9** / :

To a solution of mannosazide **3a** (1.0 equiv), Ph₂SO (2.8 equiv), TTBP (3.0 equiv) in dichloromethane (4 mL) was added at -60°C trifluoromethanesulfonic anhydride (1.4 equiv). The reaction mixture was stirred for 5 min, after which a solution of the acceptor (**6**, 1.5 equiv) in dichloromethane (2 mL) was added. The mixture was stirred at -60°C for

1 h, after which it was slowly warmed to room temperature and quenched by the addition of saturated aqueous NaHCO₃. The organic layer was washed with brine, dried (MgSO₄), filtered and concentrated. The glycosides were isolated by silica gel chromatography (ethyl acetate/ petroleum ether).

Methyl 2,3,4-Tri-*O*-acetyl-6-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy- -*D*-mannopyranosyl)- -*D*-glucopyranoside (9): [α]²⁵_D +6.8 (*c* = 1.16, CHCl₃); *R*_f 0.37 (50 % EtOAc in PE); ¹H-NMR (400 MHz, CDCl₃): δ = 7.55-7.36 (m, 10H_{arom}), 5.57 (s, 1H, CHPh), 5.49 (t, 1H, *J* = 9.8 Hz, H-3), 4.82 (m, 5H, H-4, H-1, H-2, CH₂Bn), 4.57 (s, 1H, H-1'), 4.29 (dd, 1H, *J* = 10.4, 4.8 Hz, H-6'), 4.09 (m, 1H, H-5), 4.08 (dd, 1H, *J* = 10.6, 3.5 Hz, H-6), 4.00 (t, 1H, *J* = 10.0 Hz, H-6'), 3.87 (t, 1H, *J* = 10.2 Hz, H-4'), 3.73 (dd, 1H, *J* = 9.5, 3.7 Hz, H-6), 3.52 (dd, 1H, *J* = 10.6, 7.1 Hz, H-3'), 4.43 (d, 1H, *J* = 10.5 Hz, H-2'), 3.38 (s, 3H), 3.34 (m, 1H, H-5'), 2.05 (s, 3H), 2.03 (s, 3H), 1.99 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃): δ = 170.1, 169.9, 169.6, 137.7, 137.2, 129.1, 129.0, 128.5, 128.2, 127.7, 125.9, 125.3, 125.2, 101.5, 100.7, 96.6, 78.3, 76.0, 72.9, 70.8, 69.9, 68.8, 68.7, 67.6, 55.3, 20.6; ES-MS: *m/z* = 708.3 [M + Na]⁺.

Methyl 2,3,4-Tri-*O*-acetyl-6-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy- -*D*-mannopyranosyl)- -*D*-glucopyranoside (9): [α]²⁵_D -1.8 (*c* = 0.54, CHCl₃); *R*_f 0.48 (50 % EtOAc in PE); ¹H-NMR (400 MHz, CDCl₃): δ = 7.55-7.36 (m, 10H_{arom}), 5.60 (s, 1H, CHPh), 5.46 (t, 1H, *J* = 9.7 Hz, H-3), 5.08 (t, 1H, *J* = 9.7 Hz, H-4), 4.90 (m, 3H, H-1, H-2, CHH Bn), 4.80 (s, 1H, H-1'), 4.74 (d, 1H, *J* = 8 Hz, CHH Bn), 4.19 (dd, 1H, *J* = 10.1, 4.5 Hz, H-6'), 4.10 (m, 2H, H-5, H-6), 3.92 (m, 2H, H-4', H-6'), 3.81 (t, 1H, *J* = 10.4 Hz, H-6), 3.78 (m, 2H, H-3', H-5'), 3.49 (d, 1H, *J* = 11.3 Hz, H-2'), 3.35 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃): δ = 171.4, 170.8, 139.1, 137.2, 128.9, 128.8.0, 128.3, 128.2, 127.9, 126.3, 125.9, 125.6, 100.8, 99.9, 96.4, 78.2, 76.3, 72.7, 71.1, 70.0, 69.3, 69.0, 67.9, 55.1, 20.7; ES-MS: *m/z* = 708.4 [M + Na]⁺.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy- -*D*-mannopyranosyl)- -*D*-glucopyranoside (10): R_f 0.67 (25% EtOAc in PE); $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 7.37-7.24 (m, 25 H_{arom}), 5.55 (s, 1H, CHPh), 5.03-4.57 (m, 8H, CH_2 Bn), 4.55 (d, 1H, J = 3.8 Hz, H-1), 4.26 (dd, 1H, J = 10.5, 5.0 Hz, H-6'), 4.18 (s, 1H, H-1'), 4.05 (t, 1H, J = 8.5 Hz, H-3), 3.85 (m, 2H, H-6, H-4'), 3.80 (t, 1H, J = 10.4 Hz, H-6'), 3.75 (m, 1H, H-5), 3.70 (d, 1H, J = 2.9 Hz, H-2'), 3.59 (dd, 1H, J = 11.3, 6.1 Hz, H-3'), 3.49 (m, 2H, H-2, H-6), 3.52 (t, 1H, J = 8.6 Hz, H-4), 3.33 (s, 3H, OCH_3), 3.32 (m, 1H, H-5'); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ = 138.7, 138.5, 138.1, 137.3, 129.0, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 126.0, 101.5, 100.3, 97.9, 82.1, 79.9, 78.5, 75.7, 74.6, 73.4, 72.9, 69.5, 68.5, 68.4, 67.3, 63.5, 55.2; ES-MS: m/z = 852.3 $[\text{M} + \text{Na}]^+$.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy- -*D*-mannopyranosyl)- -*D*-glucopyranoside (10): R_f 0.67 (25% EtOAc in PE); $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 7.38-7.24 (m, 25 H_{arom}), 5.54 (s, 1H, CHPh), 5.03-4.59 (m, 8H, CH_2 Bn), 4.55 (d, 1H, J = 3.8 Hz, H-1), 4.27 (dd, 1H, J = 10.5, 5.0 Hz, H-6'), 4.23 (s, 1H, H-1'), 4.08 (t, 1H, J = 8.5 Hz, H-3), 3.83 (m, 2H, H-6, H-4'), 3.81 (t, 1H, J = 10.4 Hz, H-6'), 3.76 (m, 1H, H-5), 3.72 (d, 1H, J = 2.9 Hz, H-2'), 3.59 (dd, 1H, J = 11.3, 6.1 Hz, H-3'), 3.49 (m, 2H, H-2, H-6), 3.53 (t, 1H, J = 8.6 Hz, H-4), 3.59 (m, 1H, H-5'), 3.34 (s, 3H, OCH_3); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ = 138.5, 137.9, 137.8, 137.6, 136.5, 132.2, 129.3, 128.8, 128.7, 127.5, 125.9, 125.2, 125.0, 101.5, 99.3, 97.8, 82.0, 79.8, 78.4, 77.4, 75.7, 75.0, 74.9, 74.5, 73.3, 73.2, 67.1, 66.2, 63.9, 62.5, 55.1; ES-MS: m/z = 852.3 $[\text{M} + \text{Na}]^+$.

3-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy- -*D*-mannopyranosyl)-1,2:5,6-di-*O*-isopropylidene- -*D*-glucofuranose (11): R_f 0.45 (50 % EtOAc in PE); $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 7.50-7.33 (m, 10 H_{arom}), 5.94 (d, 1H, J = 3.8 Hz, H-1), 5.59 (s, 1H, CHPh), 4.91 (d, 1H, J = 10.2 Hz, CHH Bn), 4.73 (d, 1H, J = 10.2 Hz, CHH Bn), 4.68 (d, 1H, J = 1 Hz, H-1'), 4.50 (d, 1H, J = 3.8 Hz, H-2), 4.37 (m, 1H, H-5), 4.33 (m, 2H, H-

4, H-3), 4.27 (dd, 1H, $J = 10.2, 4.5$ Hz, H-6'), 4.18 (t, 1H, $J = 6.4$ Hz, H-6), 4.07 (m, 2H, H-4', H-6), 3.90 (d, 1H, $J = 3.5$ Hz, H-2'), 3.86 (t, 1H, $J = 10.2$ Hz, H-6'), 3.77 (dd, 1H, $J = 9.5, 3.8$ Hz, H-3'), 3.33 (m, 1H, H-5'), 1.50 (s, 3H), 1.45 (s, 3H), 1.38 (s, 3H), 1.32 (s, 3H); ^{13}C -NMR (100 MHz, CDCl_3): $\delta = 137.7, 137.1, 129.0, 128.5, 128.3, 127.9, 127.7, 126.0, 112.0, 108.6, 105.0, 101.5, 98.1, 82.6, 80.4, 80.3, 78.4, 76.4, 73.1, 73.0, 68.3, 67.5, 66.0, 63.5, 26.7, 26.5, 26.3, 25.5$; ES-MS: $m/z = 748.2$ $[\text{M} + \text{Na}]^+$.

3-O-(2-azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy- β -D-mannopyranosyl)-1,2:5,6-di-O-isopropylidene- β -D-glucofuranose (11): R_f 0.56 (50 % EtOAc in PE); ^1H -NMR (400 MHz, CDCl_3): $\delta = 7.46\text{--}7.31$ (m, 10H_{arom}), 5.86 (d, 1H, $J = 3.8$ Hz, H-1), 5.64 (s, 1H, CHPh), 5.07 (s, 1H, H-1'), 4.89 (d, 1H, $J = 10.2$ Hz, CHH Bn), 4.74 (d, 1H, $J = 10.2$ Hz, CHH Bn), 4.54 (d, 1H, $J = 3.8$ Hz, H-2), 4.41 (m, 1H, H-5), 4.38 (m, 2H, H-4, H-3), 4.33 (dd, 1H, $J = 10.2, 4.5$ Hz, H-6'), 4.18 (t, 1H, $J = 6.4$ Hz, H-6), 4.09 (m, 5H, H-4', H-6, H-2', H-6', H-5'), 3.82 (dd, 1H, $J = 9.5, 3.8$ Hz, H-3'), 1.49 (s, 3H), 1.46 (s, 3H), 1.39 (s, 3H), 1.31 (s, 3H); ^{13}C -NMR (100 MHz, CDCl_3): $\delta = 137.8, 137.0, 129.0, 128.5, 128.4, 128.0, 127.8, 126.2, 112.1, 108.4, 105.2, 100.6, 98.0, 82.4, 80.6, 80.2, 78.4, 76.4, 73.2, 73.2, 68.6, 67.7, 66.3, 63.5, 26.7, 26.5, 26.3, 25.5$; ES-MS: $m/z = 748.2$ $[\text{M} + \text{Na}]^+$.

Methyl 2,3,4-Tri-O-acetyl-6-O-(2-azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy- β -D-glucopyranosyl)- β -D-glucopyranoside (12): R_f 0.34 (50 % EtOAc in PE); ^1H -NMR (400 MHz, CDCl_3): $\delta = 7.47\text{--}7.32$ (m, 10H_{arom}), 5.56 (s, 1H, CHPh), 5.50 (t, 1H, $J = 9.4$ Hz, H-3), 5.03 (t, 1H, $J = 10$ Hz, H-4), 4.97 (d, 1H, $J = 3.6$ Hz, H-1), 4.90 (d, 1H, $J = 11.2$ Hz, CHH Bn), 4.87 (dd, 1H, $J = 10.2, 3.6$ Hz, H-2), 4.79 (d, 1H, $J = 11.2$ Hz, CHH Bn), 4.38 (d, 1H, $J = 8.0$ Hz, H-1'), 4.33 (dd, 1H, $J = 10.5, 5.0$ Hz, H-6'), 4.01 (m, 1H, H-5), 3.93 (dd, 1H, $J = 11.2, 2.1$ Hz, H-6), 3.78 (t, 1H, $J = 10.3$ Hz, H-6'), 3.69 (t, 1H, $J = 9.2$ Hz, H-4'), 3.62 (dd, 1H, $J = 11.2, 6.3$ Hz, H-6), 3.56 (t, 1H, $J = 9.4$ Hz, H-3'), 3.44 (m, 5H, OCH_3 , H-2', H-5'); ^{13}C -NMR (100 MHz, CDCl_3): $\delta = 170.1, 169.7, 137.8, 137.0, 129.0, 128.3, 128.2, 128.1, 127.8, 125.9, 102.8, 101.3, 96.6, 81.4, 79.0, 74.9, 70.8, 70.1, 69.1, 68.7, 68.5, 68.3, 66.4, 66.2, 55.4, 20.7$; ES-MS: $m/z = 708.3$ $[\text{M} + \text{Na}]^+$.

Methyl 2,3,4-Tri-O-acetyl-6-O-(2-azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy- β -D-glucopyranosyl)- β -D-glucopyranoside (12): R_f 0.44 (50 % EtOAc in PE); $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 7.47-7.32 (m, 10H_{arom}), 5.59 (s, 1H, CHPh), 5.47 (t, 1H, J = 9.4 Hz, H-3), 5.07 (t, 1H, J = 10.1 Hz, H-4), 4.92 (m, 3H, H-1, CHH Bn , H-2), 4.78 (d, 1H, J = 11.2 Hz, CHH Bn), 4.48 (d, 1H, J = 3.9 Hz, H-1'), 4.37 (dd, 1H, J = 10.5, 5.0 Hz, H-6'), 4.09 (m, 1H, H-5), 3.98 (dd, 1H, J = 11.3, 2.0 Hz, H-6), 3.82 (t, 1H, J = 10.3 Hz, H-6'), 3.75 (t, 1H, J = 9.2 Hz, H-4'), 3.69 (dd, 1H, J = 11.2, 6.3 Hz, H-6), 3.54 (m, 2H, H-3', H-5'), 3.47 (m, 4H, OCH_3 , H-2'); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ = 170.1, 169.8, 138.0, 137.5, 129.8, 128.4, 128.3, 128.1, 127.6, 126.1, 101.3, 99.6, 96.6, 81.6, 79.6, 75.3, 71.4, 70.4, 69.3, 69.0, 68.8, 68.3, 66.6, 66.3, 55.5, 20.8; ES-MS: m/z = 708.3 $[\text{M} + \text{Na}]^+$.

Methyl 2,3,4-Tri-O-benzyl-6-O-(2-azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy- β -D-glucopyranosyl)- β -D-glucopyranoside (13): R_f 0.60 (25% EtOAc in PE); $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 7.36-7.27 (m, 25H_{arom}), 5.52 (s, 1H, CHPh), 5.05-4.65 (m, 8H, $\text{CH}_2 \text{ Bn}$), 4.62 (d, 1H, J = 3.9 Hz, H-1), 4.27 (dd, 1H, J = 11.0, 5.8 Hz, H-6'), 4.22 (d, 1H, J = 7.7 Hz, H-1'), 4.04 (t, 1H, J = 9.2 Hz, H-6), 4.00 (t, 1H, J = 7.5 Hz, H-3), 3.79 (m, 4H, H-6', H-5, H-4', H-6), 3.61 (t, 1H, J = 7.6 Hz, H-4), 3.51 (m, 3H, H-2, H-3', H-2'), 3.37 (s, 3H), 3.30 (m, 1H, H-5'); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ = 138.7, 138.4, 138.1, 137.1, 132.2, 130.9, 127.9, 127.7, 125.9, 125.3, 124.7, 102.3, 101.2, 98.2, 82.0, 81.4, 79.7, 79.2, 76.9, 76.5, 75.7, 74.8, 73.4, 69.5, 69.2, 68.8, 68.6, 66.2, 55.2; ES-MS: m/z = 852.3 $[\text{M} + \text{Na}]^+$.

Methyl 2,3,4-Tri-O-benzyl-6-O-(2-azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy- β -D-glucopyranosyl)- β -D-glucopyranoside (13): R_f 0.60 (25% EtOAc in PE); $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 7.36-7.27 (m, 25H_{arom}), 5.53 (s, 1H, CHPh), 5.05-4.65 (m, 8H, $\text{CH}_2 \text{ Bn}$), 4.62 (d, 1H, J = 3.9 Hz, H-1), 4.25 (m, 2H, H-6', H-1), 4.06 (t, 1H, J = 9.2 Hz, H-6), 3.98 (t, 1H, J = 7.5 Hz, H-3), 3.76 (m, 4H, H-6', H-5, H-4', H-6), 3.60 (t, 1H, J = 7.6 Hz, H-4), 3.51 (m, 4H, H-2, H-5', H-3', H-2'), 3.36 (s, 3H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ = 138.6, 138.4, 138.1, 137.3, 132.0, 131.1, 127.8, 127.7, 126.0, 125.3, 124.8,

101.3, 100.9, 98.1, 82.1, 81.5, 80.0, 79.6, 76.9, 76.7, 75.5, 75.2, 73.6, 70.1, 69.6, 68.9, 68.8, 66.1, 55.0; ES-MS: m/z = 852.3 $[M + Na]^+$.

3-O-(2-azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy- -D-glucopyranosyl)-1,2:5,6-di-O-isopropylidene- -D-glucofuranose (14): R_f 0.36 (50 % EtOAc in PE); 1H -NMR (400 MHz, $CDCl_3$): δ = 7.45-7.31 (m, 10 H_{arom}), 5.96 (d, 1H, J = 3.8 Hz, H-1), 5.59 (s, 1H, $CHPh$), 4.97 (d, 1H, J = 10.2, CHH Bn), 4.89 (d, 1H, J = 7.6 Hz, H-1'), 4.77 (d, 1H, J = 10.2 Hz, CHH Bn), 4.60 (d, 1H, J = 2.7 Hz, H-3), 4.36 (m, 3H, H-3', H-6', H-5), 4.07 (t, 1H, J = 6.4 Hz, H-4), 3.81 (m, 3H, H-6, H-4', H-5'), 3.58 (m, 2H, H-6', H-6), 3.39 (dd, 1H, J = 10.1, 7.6 Hz, H-2); 3.51 (dd, 1H, J = 10.0, 3.8 Hz, H-2'), 1.52 (s, 3H), 1.47 (s, 3H), 1.39 (s, 3H), 1.34 (s, 3H); ^{13}C -NMR (100 MHz, $CDCl_3$): δ = 139.9, 136.9, 128.3, 128.2, 127.5, 127.3, 111.6, 110.1, 104.4, 101.5, 94.6, 85.3, 82.2, 79.6, 78.7, 74.5, 72.6, 69.1, 67.5, 61.6, 61.4, 27.2, 25.6; ES-MS: m/z = 748.2 $[M + Na]^+$.

3-O-(2-azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy- -D-glucopyranosyl)-1,2:5,6-di-O-isopropylidene- -D-glucofuranose (14): R_f 0.43 (50 % EtOAc in PE); 1H -NMR (400 MHz, $CDCl_3$): δ = 7.45-7.31 (m, 10 H_{arom}), 5.92 (d, 1H, J = 3.8 Hz, H-1), 5.62 (s, 1H, $CHPh$), 5.25 (d, 1H, J = 4.2 Hz, H-1'), 4.98 (d, 1H, J = 10.2, CHH Bn), 4.79 (d, 1H, J = 10.2 Hz, CHH Bn), 4.57 (d, 1H, J = 3.8 Hz, H-2), 4.42 (m, 1H, H-5), 4.38 (dd, 1H, J = 10.1, 4.8 Hz, H-6'), 4.28 (d, 1H, J = 2.7 Hz, H-3), 4.15 (m, 2H, H-4, H-3'), 4.01 (t, 1H, J = 6.3 Hz, H-6), 3.85 (m, 1H, H-5'), 3.79 (m, 3H, H-6, H-6', H-4'), 3.51 (dd, 1H, J = 10.0, 3.8 Hz, H-2'), 1.49 (s, 3H), 1.45 (s, 3H), 1.37 (s, 3H), 1.31 (s, 3H); ^{13}C -NMR (100 MHz, $CDCl_3$): δ = 139.8, 136.7, 128.3, 128.2, 127.6, 127.5, 111.5, 109.7, 104.4, 101.6, 93.2, 85.1, 83.1, 79.8, 78.1, 74.9, 72.7, 69.6, 67.5, 62.6, 61.6, 27.2, 25.6; ES-MS: m/z = 748.2 $[M + Na]^+$.

Methyl 2,3,4-tri-O-acetyl-6-O-(4-O-benzyl-2,3-O-carbonyl- -L-rhamnopyranosyl)- -D-glucopyranoside (15): 1H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.32 (m, 5H, H_{arom}), 5.47 (t, 1H, J = 9.7 Hz, H-3), 5.09 (t, 1H, J = 9.9 Hz, H-4), 4.99 (s, 1H, H-1'), 4.91 (d, 1H, J = 3.6 Hz, H-1), 4.86-4.82 (m, 2H, H-2/H-3'), 4.68 (d, 1H, J = 7.2 Hz, H-2'), 4.72

(AB, 2H, CH₂ Bn), 3.91 (m, 1H, H-5), 3.79 (dd, 1H, $J = 6.2$ Hz, $J = 9.8$ Hz, H-5'), 3.76 (dd, 1H, $J = 1.6$ Hz, $J = 12.4$ Hz, H-6), 3.51 (dd, 1H, $J = 4.6$ Hz, $J = 11.4$ Hz, H-6), 3.39 (s, 3H, OMe), 3.30 (dd, 1H, $J = 6.8$ Hz, $J = 9.8$ Hz, H-4'), 2.06, 2.03, 2.00 (3 s, 3 CH₃ Ac), 1.29 (d, 3H, $J = 6.2$ Hz, H-6'). ¹³C NMR (400 MHz, CDCl₃): 170.0, 169.9, 169.5, 153.2, 136.9, 129.0-125.2, 96.7, 95.5, 79.6, 79.3, 76.2, 70.7, 70.0, 68.0, 67.6, 63.7, 73.3, 63.7, 55.4, 20.5, 17.5. ES-MS: $m/z = 583$ [M+H]⁺, 605 [M+Na]⁺.

Methyl 2,3,4-tri-*O*-acetyl-6-*O*-(4-*O*-benzyl-2,3-*O*-carbonyl- -L-rhamnopyranosyl)- -D-glucopyranoside (15): ¹H NMR (400 MHz, CDCl₃): 7.19-7.05 (m, 5H, H_{arom}), 5.45 (t, 1H, $J = 9.5$ Hz, H-3), 5.11 (t, 1H, $J = 9.8$ Hz, H-4), 4.89 (d, 1H, $J = 3.7$ Hz, H-1), 4.89-4.83 (m, 2H, H-2, H-3'), 4.76 (d, 1H, $J = 7.2$ Hz, H-2'), 4.71 (AB, 2H, CH₂ Bn), 4.76 (d, 1H, $J = 3.5$ Hz, H-1'), 3.90-3.81, 3.64-3.55 (2 m, 4H, H-5, H-5', 2x H-6), 3.51 (dd, 1H, $J = 6.7$ Hz, $J = 9.8$ Hz, H-4'), 3.41 (s, 3H, OMe), 2.06, 2.03, 2.00 (3 s, 3 CH₃ Ac), 1.32 (d, 3H, $J = 6.2$ Hz, H-6'). ¹³C NMR (100 MHz, CDCl₃): 170.8, 170.1, 154.9, 136.7, 128.9-125.8, 97.0, 95.6, 80.0, 79.4, 74.8, 70.6, 70.3, 68.4, 68.1, 66.8, 72.8, 65.5, 55.4, 20.7, 18.2. ES-MS: $m/z = 605$ [M+Na]⁺.

Methyl 2,3,4-tri-*O*-acetyl-6-*O*-(4-*O*-benzoyl-2,3-*O*-carbonyl- -L-rhamnopyranosyl)- -D-glucopyranoside (16): ¹H NMR (400 MHz, CDCl₃): 8.08-8.06, 7.63-7.46 (2 m, 5H, H_{arom}), 5.50 (t, 1H, $J = 9.8$ Hz, H-3), 5.19-5.15 (m, 2H, H-4, H-4'), 5.07 (s, 1H, H-1), 4.96 (t, 1H, $J = 7.1$ Hz, H-3'), 4.93 (d, 1H, $J = 3.4$ Hz, H-1), 4.87 (dd, 1H, $J = 3.6$ Hz, $J = 10.2$ Hz, H-2), 4.77 (d, 1H, $J = 7.1$ Hz, H-2'), 4.01 (dd, 1H, $J = 3.1$ Hz, $J = 6.4$ Hz, H-5'), 3.94 (m, 1H, H-5), 3.84 (dd, 1H, $J = 1.7$ Hz, $J = 11.4$ Hz, H-6), 3.57 (dd, 1H, $J = 4.1$ Hz, $J = 11.5$ Hz, H-6), 3.41 (s, 3H, OMe), 2.09, 2.05, 2.02 (3 s, 3 CH₃ Ac), 1.29 (d, 3H, $J = 6.4$ Hz, H-6'). ¹³C NMR (100 MHz, CDCl₃): 170.2, 169.9, 169.5, 165.0, 153.5, 133.6-128.5, 128.8, 96.7, 95.9, 76.2, 75.8, 72.8, 70.7, 69.9, 68.2, 67.9, 63.6, 65.9, 55.5, 20.6, 17.2. ES-MS: $m/z = 619$ [M+Na]⁺.

Methyl 2,3,4-tri-*O*-acetyl-6-*O*-(4-*O*-benzoyl-2,3-*O*-carbonyl- -L-rhamnopyranosyl)- -D-glucopyranoside (16): ¹H NMR (400 MHz, CDCl₃): 7.19-7.05 (m, 5H, H_{arom}),

5.45 (t, 1H, $J = 9.5$ Hz, H-3), 5.11 (t, 1H, $J = 9.8$ Hz, H-4), 4.89 (d, 1H, $J = 3.7$ Hz, H-1), 4.89-4.83 (m, 2H, H-2, H-3), 4.76 (d, 1H, $J = 7.2$ Hz, H-2'), 4.71 (AB, 2H, CH₂ Bn), 4.76 (d, 1H, $J = 3.5$ Hz, H-1'), 3.90-3.81, 3.64-3.55 (2 m, 4H, H-5/H-5', 2x H-6), 3.51 (dd, 1H, $J = 6.7$ Hz, $J = 9.8$ Hz, H-4'), 3.41 (s, 3H, OMe), 2.06, 2.03, 2.00 (3 s, 3 3H, 3 CH₃ Ac), 1.32 (d, 3H, $J = 6.2$ Hz, H-6'). ¹³C NMR (100 MHz, CDCl₃): 170.8, 170.1, 154.9, 136.7, 128.9-125.8, 97.0, 95.6, 80.0, 79.4, 74.8, 70.6, 70.3, 68.4, 68.1, 66.8, 72.8, 65.5, 55.4, 20.7, 18.2. ES-MS: $m/z = 605$ [M+Na]⁺.

General procedure for chemoselective BSP/Tf₂O mediated glycosylations:

Synthesis of trisaccharide **20**:

To a solution of thio galactoside **17** (254 mg, 0.40 mmol), BSP (92 mg, 0.44 mmol), TTBP (212 mg, 0.85 mmol) in dichloromethane (6 mL) was added at -60°C trifluoromethanesulfonic anhydride (72 μ L, 0.41 mmol). The reaction mixture was stirred for 5 min, after which a solution of the acceptor **18** (170 mg, 0.44 mmol) in dichloromethane (2 mL) was added. The mixture was stirred at -60°C for 1 h, after which it was slowly warmed to -10°C and quenched by the addition of triethylphosphite (71 μ L, 0.41 mmol) followed by saturated aqueous NaHCO₃. Standard work-up and purification by silica gel chromatography (ethyl acetate/ petroleum ether) gave the thio disaccharide **19** (73 % yield). Disaccharide **19** was condensed with acceptor **6** as described above for the synthesis of **9**, to provide trisaccharide **20** (64% yield).

Phenyl 3-O-(2,3,4,6-tetra-O-benzyl- -D-galactopyranosyl)-2-azido-4,6-O-benzylidene-2-deoxy-1-thio- -D-mannopyranoside (19): R_f 0.80 (25% EtOAc in PE). ¹H NMR (400 MHz, CDCl₃): δ 7.38-7.03 (m, 30H, H_{arom}), 5.47 (d, 1H, $J = 3.3$ Hz, H-1'), 5.45 (s, 1H, CHPh), 5.41 (bs, 1H, H-1), 4.91 (d, 1H, $J = 11.8$ Hz, CHH Bn), 4.87 (d, 1H, $J = 13.1$ Hz, CHH Bn), 4.69 (d, 1H, $J = 11.9$ Hz, CHH Bn), 4.59 (d, 1H, $J = 12.6$ Hz, CHH Bn), 4.56 (d, 1H, $J = 11.8$ Hz, CHH Bn), 4.53 (d, 1H, $J = 11.8$ Hz, CHH Bn), 4.45 (m, 3H, H-3, CHH Bn, CHH Bn), 4.35 (m, 2H, H-2, H-5), 4.21 (t, 1H, $J = 9.6$ Hz, H-4), 4.14 (dd, 1H, $J = 4.8$ Hz, $J = 10.3$ Hz, H-6), 4.00 (m, 3H, H-2', H-3', H-5'), 3.87 (bs, 1H,

H-4'), 3.79 (t, 1H, $J = 10.3$ Hz, H-6), 3.59 (dd, 1H, $J = 6.8$ Hz, $J = 9.8$ Hz, H-6'), 3.46 (dd, 1H, $J = 5.4$ Hz, $J = 9.8$ Hz, H-6'); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 138.8, 138.43, 138.38, 137.9, 137.0, 132.9, 131.7, 129.23, 129.15, 128.3, 127.9, 127.8, 127.6, 127.54, 127.51, 127.4, 127.0, 126.3, 102.2, 98.3, 87.0, 79.1, 78.0, 75.3, 74.5, 73.6, 73.5, 73.3, 71.0, 70.0, 69.7, 68.3, 64.9$; ES-MS: m/z 930.4 $[\text{M} + \text{Na}]^+$.

Methyl 6-O-[3-O-(2,3,4,6-tetra-O-benzyl- β -D-galactopyranosyl)-2-azido-4,6-O-benzylidene-2-deoxy- β -D-mannopyranosyl]-2,3,4-tri-O-acetyl- β -D-glucopyranoside (20): R_f 0.50 (50% EtOAc in PE). $[\alpha]_D^{25} + 9.2$ ($c = 0.60$, CHCl_3); ^1H NMR (400 MHz, CDCl_3): $\delta = 7.35\text{--}7.01$ (m, 25H, H_{arom}), 5.49 (dd, 1H, $J = 9.3$ Hz, $J = 9.9$ Hz, H-3), 5.41 (bs, 2H, H-1", CHPh), 4.95 (dd, 1H, $J = 9.3$ Hz, $J = 10.3$ Hz, H-4), 4.90 (d, 1H, $J = 4.0$ Hz, H-1), 4.89 (d, 1H, CHH Bn), 4.88 (d, 1H, CHH Bn), 4.86 (dd, 1H, $J = 4.4$ Hz, $J = 6.5$ Hz, H-2), 4.70 (d, 1H, CHH Bn), 4.57 (d, 1H, CHH Bn), 4.55 (bs, 1H, H-1'), 4.52 (d, 2H, $J = 11.7$ Hz, CHH Bn , CHH Bn), 4.42 (d, 1H, $J = 13.0$ Hz, CHH Bn), 4.42 (d, 1H, $J = 11.6$ Hz, CHH Bn), 4.26 (dd, 1H, $J = 4.9$ Hz, $J = 10.5$ Hz, H-6'), 4.17 (dd, 1H, $J = 1.3$ Hz, $J = 3.4$ Hz, H-2'), 4.08 (m, 1H, H-3'), 4.07 (m, 1H, H-4'), 4.01 (m, 1H, H-5), 3.98 (m, 3H, H-2", H-3", H-5"), 3.94 (dd, 1H, $J = 2.0$ Hz, $J = 10.8$ Hz, H-6), 3.88 (bs, 1H, H-4"), 3.81 (t, 1H, $J = 10.4$ Hz, H-6'), 3.54 (dd, 1H, $J = 6.8$ Hz, $J = 9.6$ Hz, H-6"), 3.50 (dd, 1H, $J = 7.6$ Hz, $J = 11.1$ Hz, H-6), 3.44 (dd, 1H, $J = 5.6$ Hz, $J = 9.7$ Hz, H-6"), 3.38 (s, 3H, OMe), 3.34 (m, 1H, H-5'), 2.07 (s, 3H), 2.01 (s, 3H), 1.97 (2, 3H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 170.1, 170.0, 169.9, 138.8, 138.4, 138.0, 137.0, 129.3, 128.4, 128.3, 128.2, 128.0, 127.8, 127.6, 127.5, 127.4, 127.1, 126.2, 102.1, 100.5, 98.4, 96.4, 78.2, 78.1, 75.3, 75.1, 74.6, 74.5, 73.6, 73.5, 71.1, 70.9, 70.5, 70.0, 69.5, 69.1, 68.8, 68.4, 68.1, 67.3, 64.3, 55.3, 20.7, 20.6$; ES-MS: m/z 1141.9 $[\text{M} + \text{Na}]^+$.

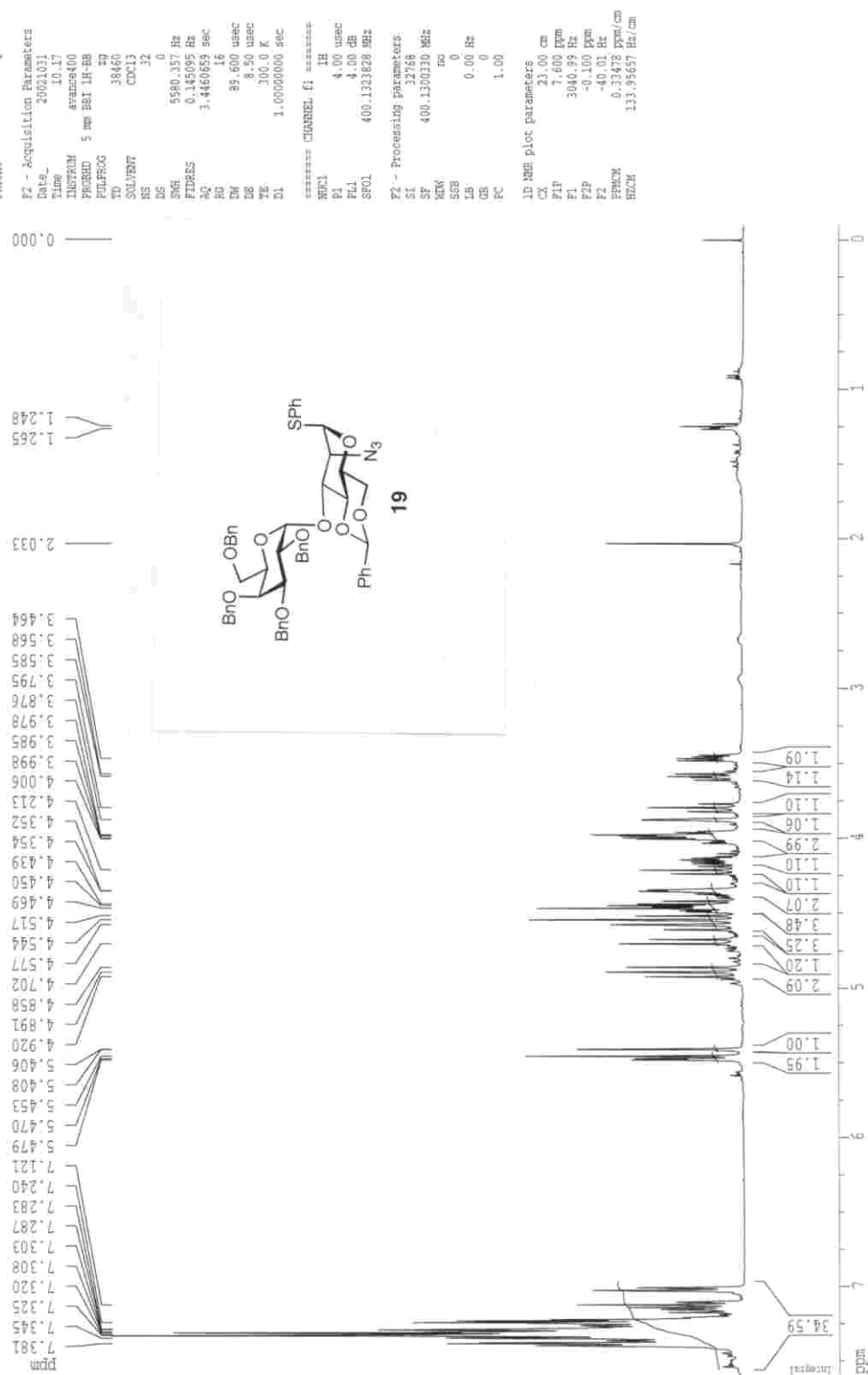
Phenyl 3-O-(2,3,4,6-tetra-O-benzoyl- β -D-galactopyranosyl)-2-azido-4,6-O-benzylidene-2-deoxy-1-thio- β -D-glucopyranoside (24): Thiodisaccharide **24** (123 mg, 0.13 mmol) was synthesized as described for **19**, from phenyl 2,3,4,5-O-benzoyl-1-thio-

galactopyranoside **22** (275 mg, 0.40 mmol) and phenyl 2-azido-4,6-*O*-benzylidene-2-deoxy-1-thio-glucopyranoside **23** (77 mg, 0.20 mmol). R_f 0.50 (25% EtOAc in PE). ^1H NMR (400 MHz, CDCl_3): δ = 8.04-7.02 (m, 30H, H_{arom}), 5.93 (d, 1H, J = 2.7 Hz, H-4'), 5.82 (dd, 1H, J = 8.1 Hz, J = 10.4 Hz, H-2'), 5.58 (s, 1H, CHPh), 5.57 (dd, 1H, J = 3.4 Hz, J = 10.6 Hz, H-3'), 5.10 (d, 1H, J = 8.1 Hz, H-1'), 4.42 (d, 1H, J = 10.1 Hz, H-1), 4.30 (m, 3H, H-6, H-6', H-6''), 4.02 (t, 1H, J = 7.3 Hz, H-5'), 3.80 (t, 1H, J = 9.1 Hz, H-3), 3.78 (t, 1H, J = 9.1, H-6), 3.70 (t, 1H, J = 9.3 Hz, H-4), 3.41 (m, 2H, H-2, H-5); ^{13}C NMR (100 MHz, CDCl_3): δ = 165.6, 165.5, 165.4, 165.2, 136.8, 133.9, 133.4, 133.1, 130.2, 129.9, 129.7, 129.6, 129.4, 129.3, 129.2, 129.1, 129.0, 128.8, 128.5, 128.2, 125.9, 101.4, 87.0, 81.3, 79.2, 71.7, 71.4, 70.5, 70.3, 68.4, 67.8, 64.3, 64.3, 61.2; ES-MS: m/z 986.5 $[\text{M} + \text{Na}]^+$.

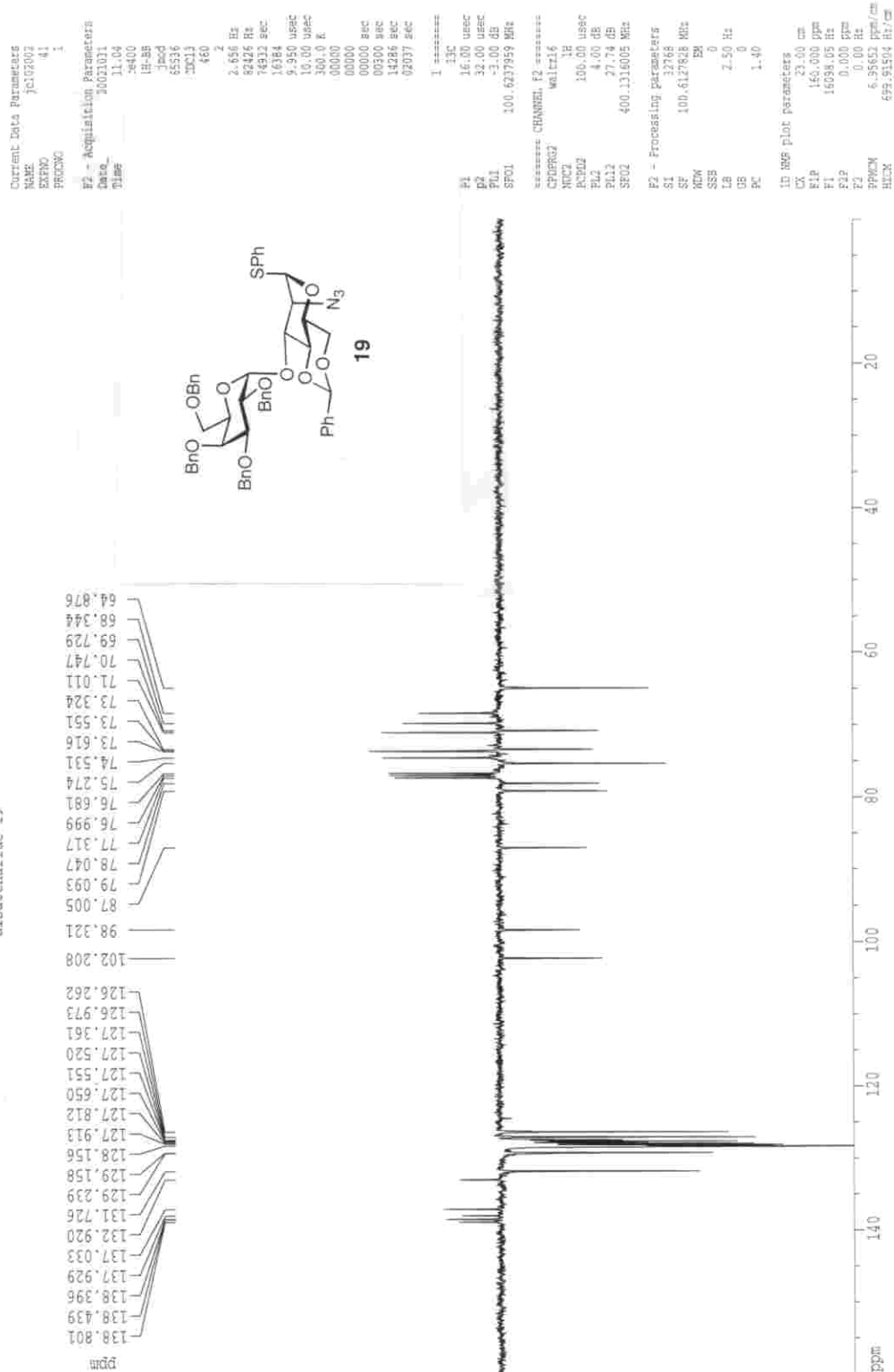
Methyl 6-*O*-[3-*O*-(2,3,4,6-tetra-*O*-benzoyl- β -D-galactopyranosyl)-2-azido-4,6-*O*-benzylidene-2-deoxy- β -D-glucopyranosyl]-2,3,4-tri-*O*-benzyl- β -D-glucopyranoside (25): Trisaccharide **25** was synthesized as described for **20**. R_f 0.55 (33% EtOAc in PE). ^1H NMR (400 MHz, CDCl_3): δ = 8.07-7.18 (m, 40H, H_{arom}), 5.94 (bd, 1H, J = 3.5 Hz, H-4), 5.83 (dd, 1H, J = 8.0 Hz, J = 10.4 Hz, H-2''), 5.58 (dd, 1H, J = 10.5 Hz, J = 3.4 Hz, H-3''), 5.57 (s, 1H, CHPh), 5.06 (d, 1H, J = 8.0 Hz, H-1''), 4.97 (d, 1H, J = 11.0 Hz, CHH Bn), 4.87 (d, 1H, J = 11.0 Hz, CHH Bn), 4.80 (d, 1H, J = 11.0 Hz, CHH Bn), 4.76 (d, 1H, J = 11.0 Hz, CHH Bn), 4.63 (d, 1H, J = 11.0 Hz, CHH Bn), 4.46 (d, 1H, J = 3.5 Hz, H-1), 4.50 (d, 1H, J = 11.0 Hz, CHH Bn), 4.41 (dd, 1H, J = 5.8, J = 11.1 Hz, H-6''), 4.31 (m, 1H, H-6''), 4.28 (m, 1H, H-6'), 4.20 (d, 1H, J = 8.1 Hz, H-1'), 4.09 (t, 1H, J = 7.2 Hz, H-5''), 4.02 (dd, 1H, J = 1.8 Hz, J = 10.8 Hz, H-6), 3.97 (t, 1H, J = 9.2 Hz, H-3), 3.78 (m, 1H, H-6'), 3.75 (m, 1H, H-5), 3.70 (m, 1H, H-4'), 3.68 (m, 1H, H-3), 3.65 (dd, 1H, J = 4.4 Hz, J = 10.9 Hz, H-6), 3.50 (dd, 1H, J = 7.4 Hz, J = 11.0 Hz, H-2), 3.44 (t, 2H, J = 9.1 Hz, H-2', H-4), 3.31 (s, 3H, OMe), 3.29 (m, 1H, H-5'); ^{13}C NMR (100 MHz, CDCl_3): δ = 165.7, 165.6, 165.5, 165.3, 138.8, 138.3, 138.1, 137.0, 133.5, 133.2, 130.0, 129.5, 129.4, 129.1, 128.8, 128.6, 128.3, 128.2, 128.1, 127.9, 127.7, 127.6, 126.0, 125.9, 102.8, 101.9,

101.3, 98.1, 82.0, 79.8, 79.5, 79.3, 75.6, 74.7, 73.4, 71.7, 71.3, 70.2, 69.7, 68.7, 68.4, 67.8, 66.5, 65.8, 61.3, 55.2; ES-MS: m/z 1340.5 $[M + Na]^+$.

disaccharide 19



disaccharide 19

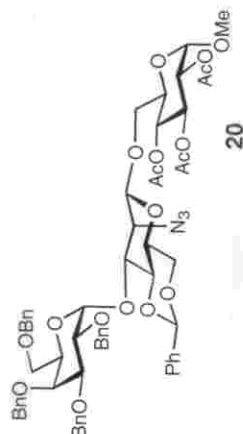


trisaccharide 20

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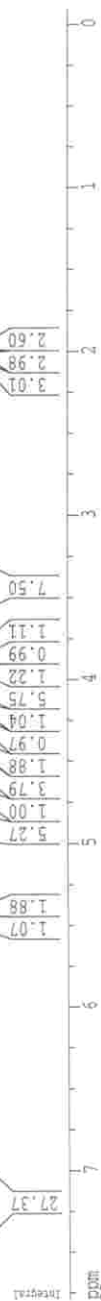
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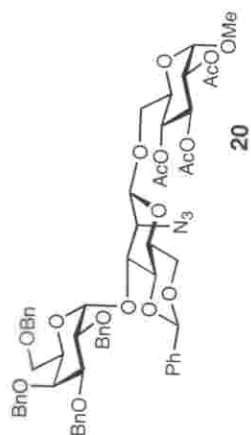


trisaccharide 20

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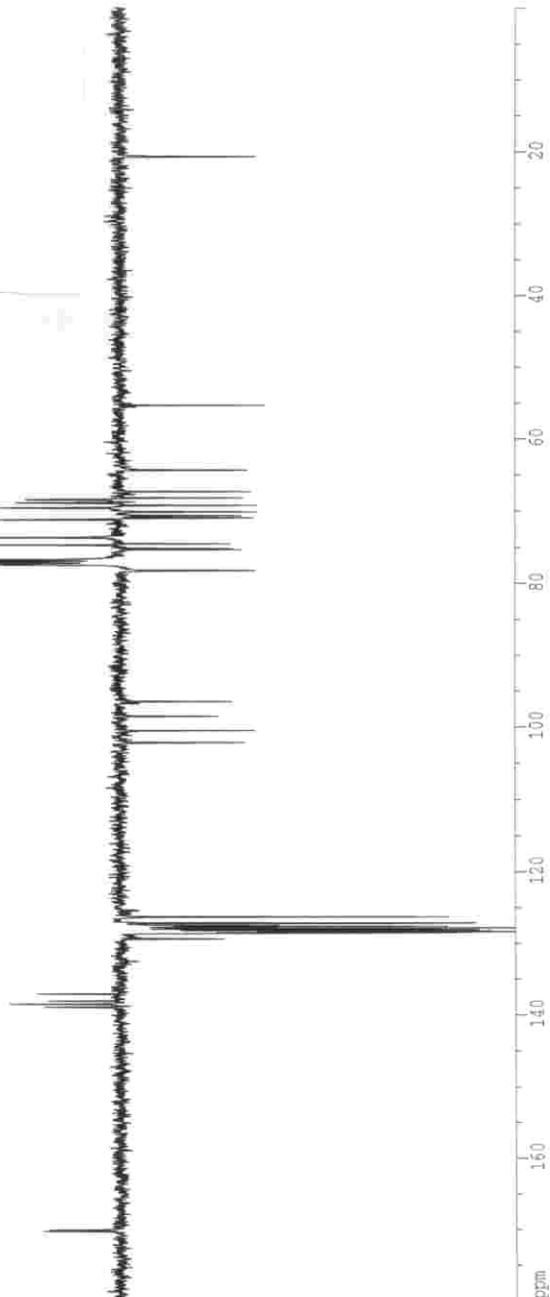
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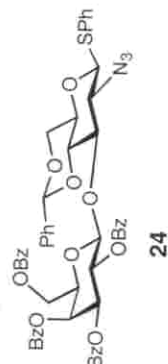
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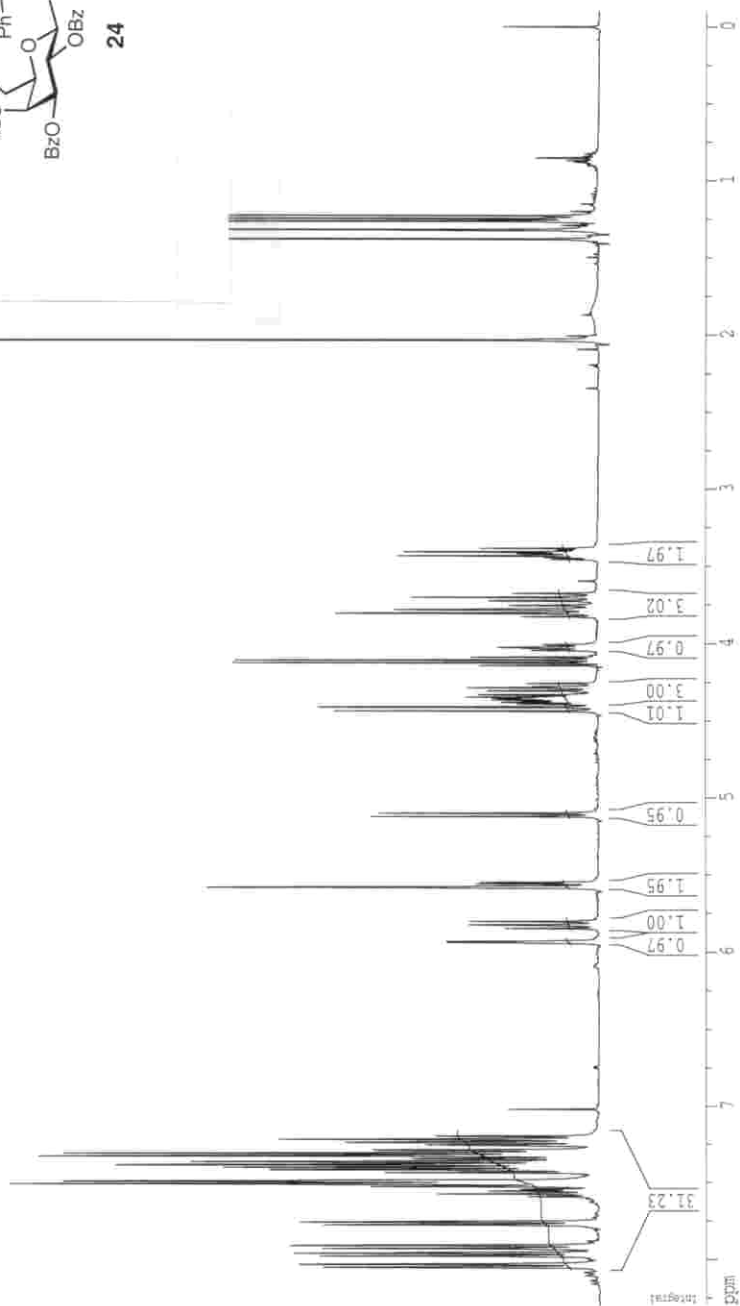
disaccharide 24

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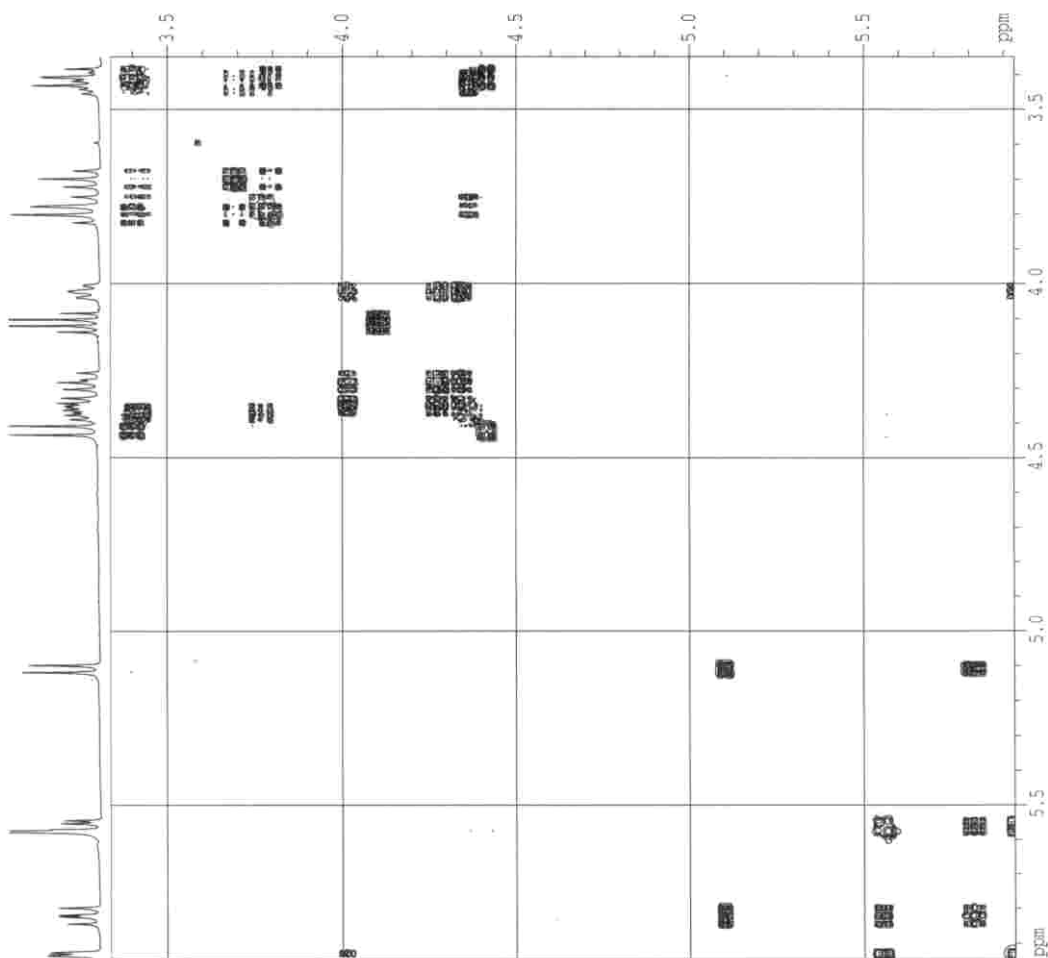
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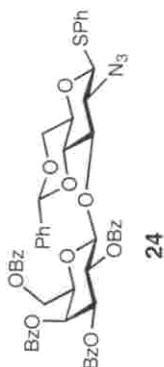
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disaccharide 24



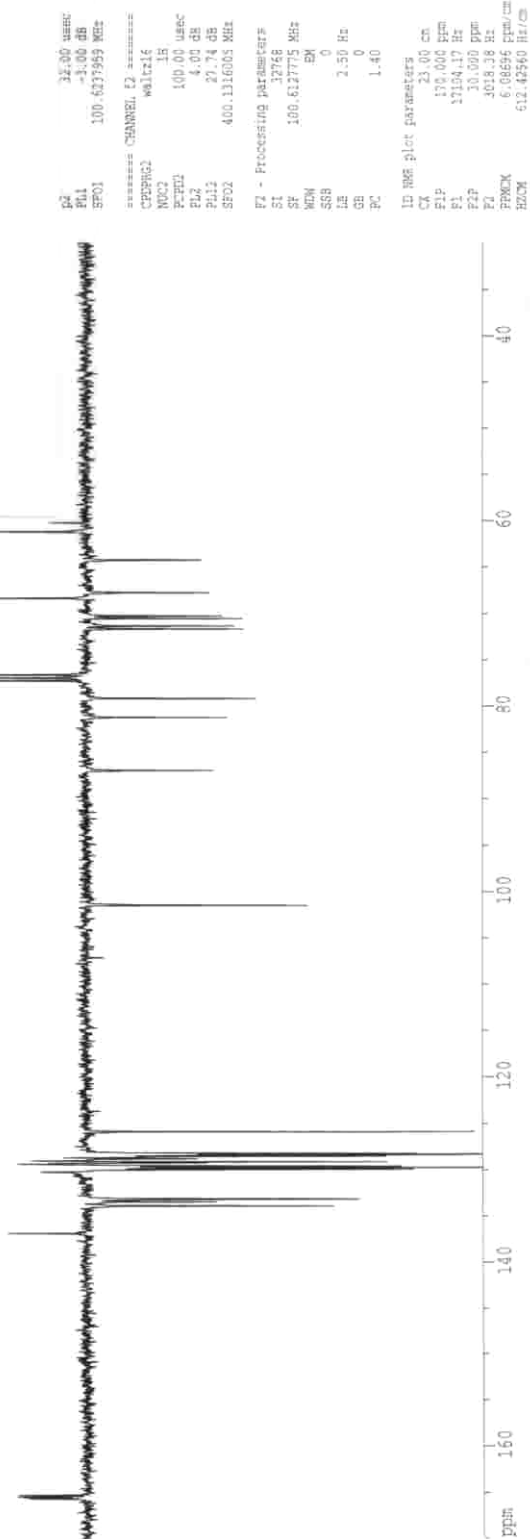
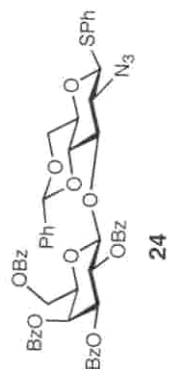
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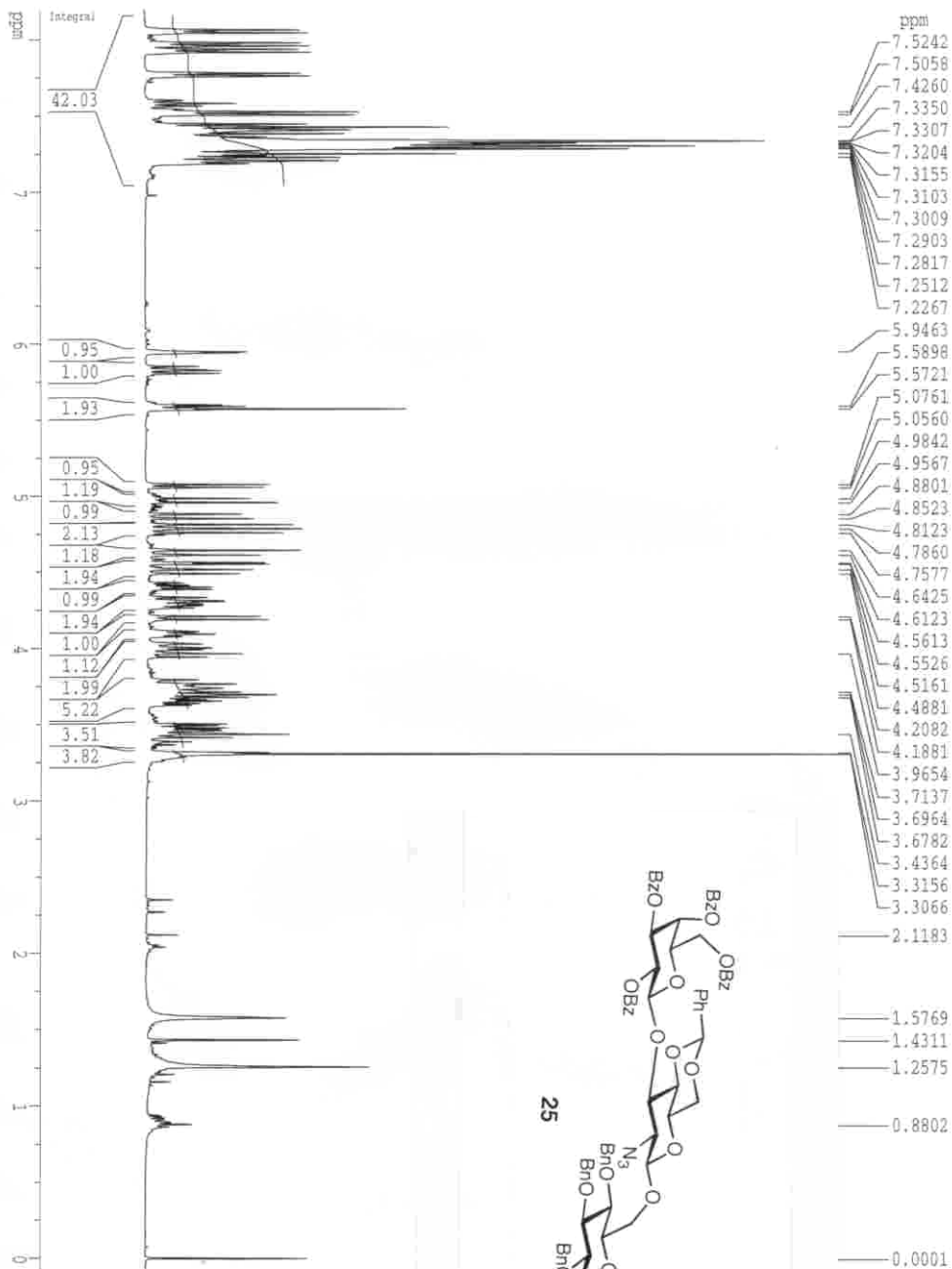
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 Time : 12.15
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 PRGNAME : 3 no 80 12-80
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disaccharide 24

Current Data Parameters
 NAME 3-072002
 EXPNO 43
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20020718
 Time 13:10
 INSTRUM avance400
 PROCNO 5
 PULPROG zgpg30
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 SI 32768
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 WDW EM
 SSF 0
 LB 2.50 Hz
 GB 0
 PC 1.40
 ID NMR plot parameters
 CX 23.00 cm
 FIP 170.000 ppm
 FI 37194.17 Hz
 F2 30.000 ppm
 F2 3618.38 Hz
 F2 6.06596 ppm/cm
 HZCM 612.42560 Hz/cm



trisaccharide 25



Current Data Parameters
NAME jco82002
EXPNO 52
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080515
Time 12.46
INSTRUM spect
PROBHD 5 mm BBI 1H-13C
PULPROG zgpg30
TD 32768
SOLVENT DMSO-d6
NS 409
DS 4

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92.800 usec
8.50 usec
100.0 K
1.00000000 sec

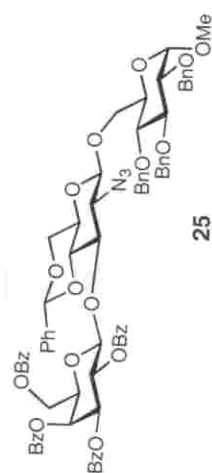
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Channel Parameters
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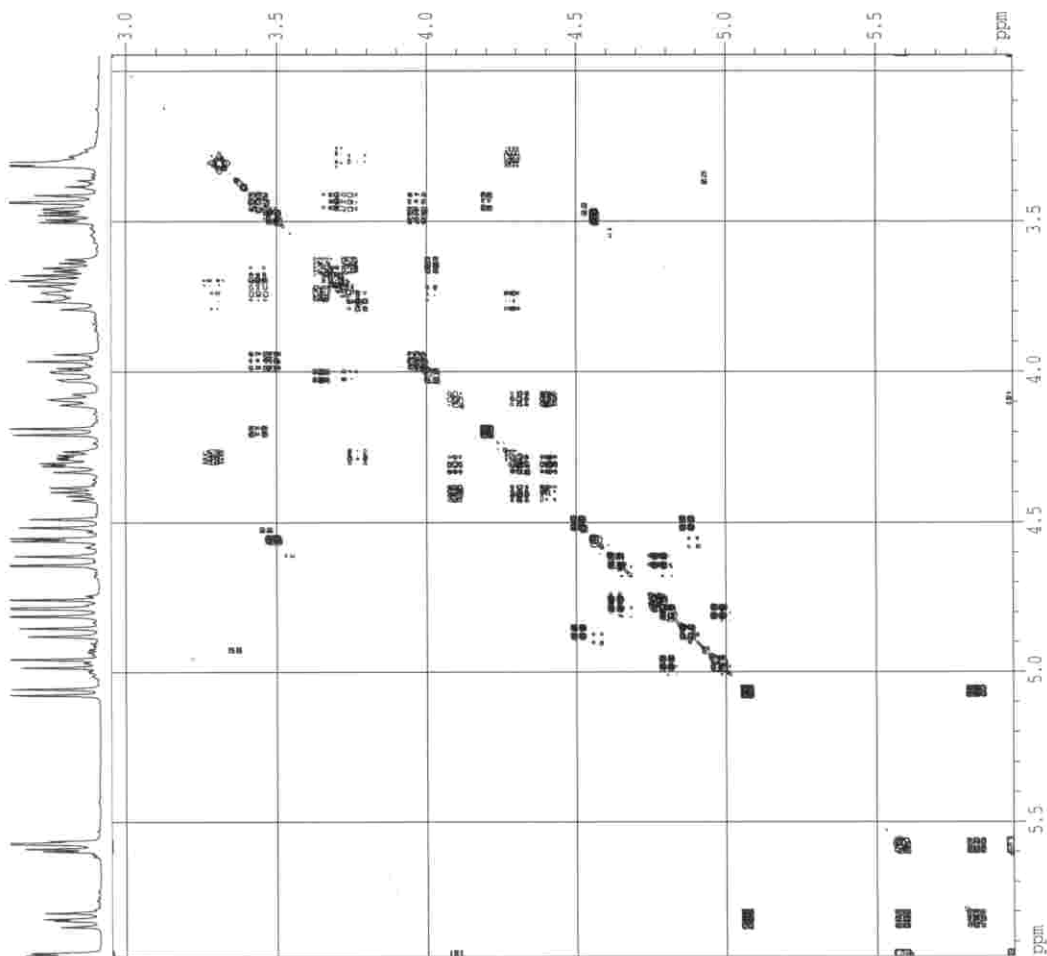
NO 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CY 33.00 cm
VLP 8.200 ppm
F1 3281.07 Hz
F2 -40.100 ppm
F2 40.01 Hz
F2FREQ 0.56957 ppm/cm
H2CH 144.35476 Hz/cm

trisaccharide 25



25

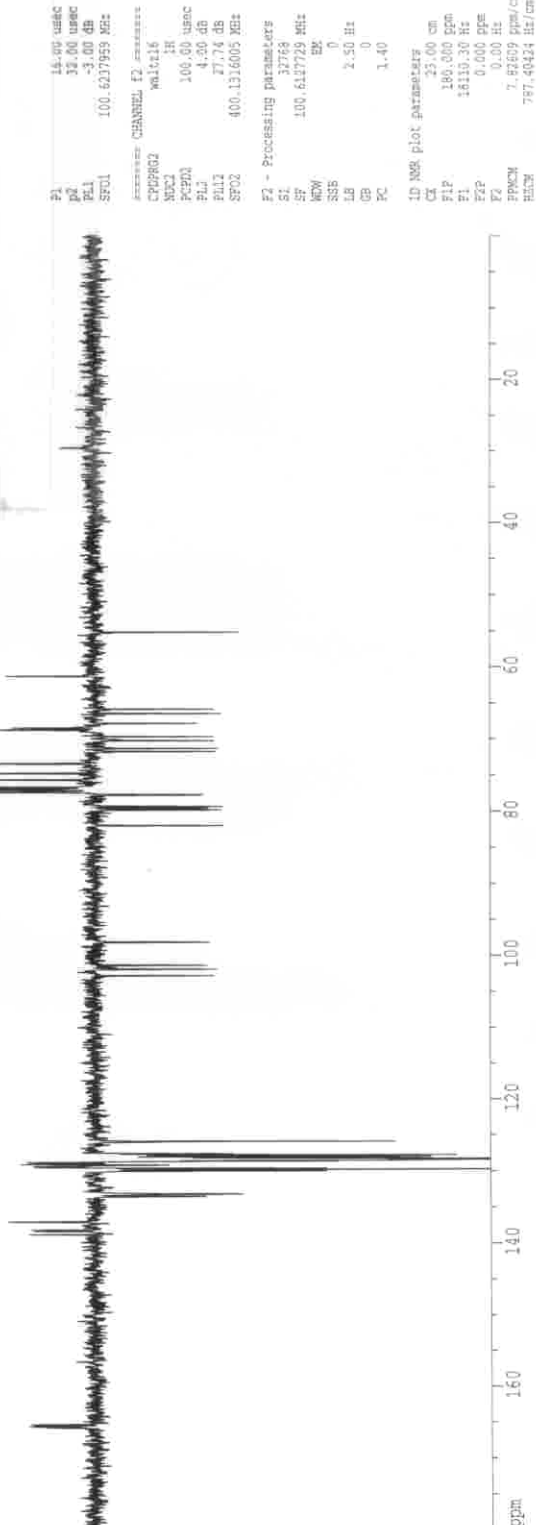
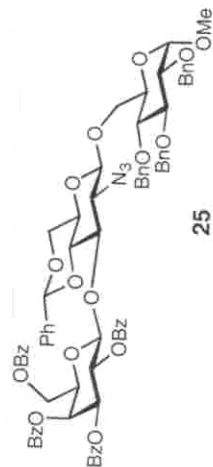


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trisaccharide 25

Current Data Parameters
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Time 15:53
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PROBHD 5 mm BBI 1H-55
PULPROG zgpg30

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References:

- (1) BSP: Crich, D., Smith, M., *J. Am. Chem. Soc.* **2001**, 123, 9015-9020.
- (2) TTBP: Crich, D., Smith, M., Yao, Q., Picione, J. *Synthesis* **2001**, 323-326.