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): $[\alpha]_D^{25} +6.8$ ($c = 1.16$, 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): $[\alpha]_D^{25} -1.8$ ($c = 0.54$, 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- -D-glucopyranosyl)- -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, 10 H_{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- -D-glucopyranosyl)- -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, 25 H_{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- -D-glucopyranosyl)- -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, 25 H_{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, 2 H, 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, 10H_{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, 10H_{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 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 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- -D-galactopyranosyl)-2-azido-4,6-*O*-benzylidene-2-deoxy- -D-mannopyranosyl]-2,3,4-tri-*O*-acetyl- -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- -D-galactopyranosyl)-2-azido-4,6-*O*-benzylidene-2-deoxy-1-thio- -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- -D-galactopyranosyl)-2-azido-4,6-*O*-benzylidene-2-deoxy- -D-glucopyranosyl]-2,3,4-tri-*O*-benzyl- -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

Current Data Parameters
NAME 36113002
EXPNO 22
PROCNO 1

F2 - Acquisition Parameters
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Time 17:35
INSTRUM avance400
PROBHD 5 mm BBI 1H-88
PULPROG zgpg30
TD 327680
SOLVENT CDCl3
NS 4

ppm 7.349 7.345 7.331 7.329 7.317 7.312 7.292 7.286 7.259 7.231 7.098 7.008 5.488 5.405 4.946 4.944 4.904 4.894 4.882 4.875 4.862 4.857 4.718 4.688 4.551 4.535 4.506 4.434 4.405 4.058 4.036 3.986 3.982 3.882 3.813 3.517 3.381 3.342 2.070 2.066 2.064 2.045 2.012 2.006 1.991 1.986 1.974 1.922 1.587 1.277 1.259 1.241 0.000

NAME no
SUB 0
IN 0.00 Hz
GB 0
PC 1.00

ID NSG plot parameters
CX 23.00 cm
FLP 7.800 ppm
F1 3121.01 Hz
F2P -0.100 ppm
F2 -40.01 Hz
PPMCM 0.34348 ppm/cm
HZCM 137.43356 Hz/cm

trisaccharide 20

Current Data Parameters
 NAME j-c112001
 EXPNO 25
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20021116
 Time 14 44
 INSTRUM spect
 PROBHD 5 mm BBI 1H-2B
 PULPROG zgpg30
 TD 65536

20.726
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 20.627

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disaccharide 24

Current Data Parameters
NAME J072002
EXPNO 60
PROCNO 1

F2 - Acquisition Parameters
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PROBHD 5 mm BBI-1H-HB
PULPROG zgpg30

1D NMR plot parameters
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F1 3321.08 Hz
F2P -0.100 ppm
F2 -40.01 Hz
F2FCH 0.36522 ppm/cm
RECFH 146.13446 Hz/cm

disaccharide 24

Current Data Parameters
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 PROCNO 5
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 NUC2 13C
 P1 1.40
 PC 1.40
 ID NSI plot parameters
 CX 23.00 cm
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 FI 17150.17 Hz
 F2 30.000 ppm
 F2 3618.38 Hz
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 HZCM 612.42560 Hz/cm

trisaccharide 25

Current Data Parameters
NAME jco82002
EXPNO 52
PROCNO 1

F1 - Acquisition Parameters
Date_ 20080515
Time 12.46
INSTRUM spect
PROBHD 5 mm BBI 1H-BB
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 40

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1.5891381 sec
45.3
92.800 usec
8.50 usec
100.0 K
1.00000000 sec

CHANNEL f1
NUC1 1H
P1 4.00 usec
PL1 0.00 dB
400.132807 MHz

Processing parameters
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AQU 400.1300207 MHz
NO 0
LB 0
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 0.56087 ppm/cm
H2CH 144.35476 Hz/cm

trisaccharide 25

NAME		ADDRESS		CITY		STATE		ZIP		COUNTRY	
1	JOHN DOE	123 MAIN ST	APT 456	NEW YORK	NY	10001	USA	212	555	1234	5678
2	JANE SMITH	456 E 1ST AVE	FL 201	CHICAGO	IL	60601	USA	312	555	9876	5432
3	BOB JONES	789 P 1ST ST	BOX 100	LOS ANGELES	CA	90001	USA	213	555	4321	8765
4	ALICE BROWN	101 S 1ST ST	UNIT 10	HOUSTON	TX	77001	USA	713	555	2109	8765
5	CHARLIE GREEN	202 N 1ST ST	APT 202	PHOENIX	AZ	85001	USA	602	555	1098	7654
6	DAVID WHITE	303 W 1ST ST	FL 303	ATLANTA	GA	30301	USA	404	555	9876	5432
7	EVE BLACK	404 E 1ST ST	BOX 404	DALLAS	TX	75201	USA	214	555	4321	8765
8	FRANK GRAY	505 S 1ST ST	UNIT 505	SEATTLE	WA	98101	USA	206	555	1098	7654
9	GRACE HARRIS	606 N 1ST ST	APT 606	PORTLAND	OR	97201	USA	503	555	9876	5432
10	HELEN KING	707 W 1ST ST	BOX 707	SAN FRANCISCO	CA	94101	USA	415	555	4321	8765
11	IRVING LYNN	808 E 1ST ST	FL 808	BOSTON	MA	02101	USA	617	555	1098	7654
12	JACK MANN	909 S 1ST ST	UNIT 909	MINNEAPOLIS	MN	55401	USA	612	555	9876	5432
13	JILL NICHOLS	1010 N 1ST ST	BOX 1010	DETROIT	MI	48201	USA	313	555	4321	8765
14	JOHN O'BRIEN	1111 W 1ST ST	APT 1111	KANSAS CITY	MO	64101	USA	816	555	1098	7654
15	JANE PETERSON	1212 E 1ST ST	BOX 1212	INDIANAPOLIS	IN	46201	USA	317	555	9876	5432
16	JOHN QUINN	1313 S 1ST ST	UNIT 1313	COLUMBIA	SC	29201	USA	803	555	4321	8765
17	JILL ROSS	1414 N 1ST ST	APT 1414	MEMPHIS	TN	38101	USA	901	555	1098	7654
18	JOHN TAYLOR	1515 W 1ST ST	BOX 1515	OKLAHOMA CITY	OK	73101	USA	405	555	9876	5432
19	JANE WALKER	1616 E 1ST ST	FL 1616	TOPEKA	KS	66601	USA	785	555	4321	8765
20	JOHN YOUNG	1717 S 1ST ST	UNIT 1717	WICHITA	KS	67201	USA	316	555	1098	7654

trisaccharide 25

Current Data Parameters
NAME j082002
EXPNO 53
PROCNO 1
F2 - Acquisition Parameters
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Time 15:53
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PROBHD 5 mm BBI 1H-5S
PULPROG zgpg30

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102.762
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81.972
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79.327
77.709
77.318
77.000
76.683
75.636
74.741
73.405
71.715
71.274
70.220
69.668
68.712
68.428
67.838
66.456
65.803
61.267
55.181
29.666

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.