"A novel sulfonamidoglycosylation of glycals"

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Supporting Information

3,4,6-Tri-*O*-benzyl-2-deoxy-β–D-galactopyranosyl p-toluenesulfonamide (**3a**) mp 107-107.5 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.95 (q, 1H, *J* = 11.4 Hz, H-2a), 2.10 (brd, 1 H, *J* = 11.4 Hz, H-2e),2.30 (s, 3H, CH_3Ph), 3.15 (dd, 1H, *J*=5.3 Hz, *J*=9.1, H-6), 3.35 (dd, 1H, *J*=7.3 Hz, *J*=9.1 Hz, H-6), 3.45 (t, 1H, *J*= 6.1 Hz, H-4), 3.60 (brd, 1H, *J*=10.5 Hz, H-3), 3.80 (brs, 1 H, H-5), 4.30 (s, 2H, $PhCH_2O$), 4.55 (d, 1H, *J*=11.5 Hz, $PhCH_2O$), 4.60 (s, 2H, $PhCH_2O$), 4.80 (td, 1H, *J*=2.5 Hz, *J*=10.5 Hz, H-1), 4.90 (d, 1H, *J*=11.5 Hz, $PhCH_2O$), 5.45 (d, 1H, *J*= 10.5 Hz, NH), 7.1 (d, 2H, *J*=8.6 Hz, CH_3Ph), 7.2-7.4 (m, 15H, 3Ph), 7.75 (d, 2H, *J*=8.6 Hz, CH_3Ph). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3 (CH_3-Ph), 32.7 (C-2), 68.3 (C-6), 70.3 ($PhCH_2O$), 71.6 (C-5), 73.2 ($PhCH_2O$), 74.5 ($PhCH_2O$), 75.1 (C-3), 76.5 (C-4), 81.1 (C-1), 126.3-129.5 (Ph), 137.7-138.6 (Ph). HRMS (FAB): calcd. for $C_{34}H_{37}NO_6SNa$: 610.2239, found 610.2238.

3,4,6-Tri-*O*-benzyl-2-deoxy-β–D-galactopyranosyl benzylsulfonamide (**3b**) mp 126-127 ^{o}C ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.94 (q, 1H, *J* = 12 Hz, H-2a), 2.04 (brd, 1 H, *J* = 12 Hz, H-2e), 3.58 (dd, 1H, *J*=5.8 Hz, *J*=8.2, H-6), 3.60 (brd, 1H, *J*=6.0 Hz, H-3), 3.62 (t, 1H, *J*=5.9 Hz,, H-4), 3.68 (dd, 1H, *J*= 5.8 Hz, *J*= 8.2 Hz H-6), 3.83 (brs, 1 H, H-5), 4.37 (s, 2H, $PhCH_2SO_2$), 4.45 (s, 2H, $PhCH_2O$), 4.57 (s, 2H, $PhCH_2O$), 4.62 (d, 1H, *J*=11.6 Hz, $PhCH_2O$), 4.73 (td, 1H, *J*=2.2 Hz, *J*=10.7 Hz, H-1), 4.93 (d, 1H, *J*=11.6 Hz, $PhCH_2O$), 5.11 (d, 1H, *J*= 10.7 Hz, NH), 7.2-7.4 (m, 20H, 4Ph). ^{13}C NMR (125 MHz, $CDCl_3$) δ 32.3 (C-2), 61.2 ($PhCH_2SO_2$), 69.3 (C-6), 70.5 ($PhCH_2O$), 71.7 (C-5), 73.5 ($PhCH_2O$), 74.4 ($PhCH_2O$), 75.2 (C-3), 77.3 (C-4), 81.1 (C-1), 127.4-128.7 (Ph), 130.9 (Ph), 131.1 (Ph). HRMS (FAB): calcd. for $C_{34}H_{37}NO_6SNa$: 610.2239, found 610.2234.

3,4,6-Tri-*O*-benzyl-2-deoxy-β–D-galactopyranosyl ethanesulfonamide (**3e**) mp 92-93 ^{o}C ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32 (t, 3H, *J*=7.4 Hz, CH_3), 2.0 (q, 1H, *J* = 11.9 Hz, H-2a), 2.06 (brd, 1 H, *J* = 11.9 Hz, H-2e), 3.14 (q, 2H, *J*=7.4 Hz, CH_2SO_2), 3.56 (m, 4H, H-3, H-4, 2 x H-6), 3.82 (brs, 1 H, H-5), 4.44 (s, 2H, $PhCH_2O$), 4.65 (m, 4H, H-1, 3 x $PhCH_2O$), 4.93 (d, 1H, *J*=11.5 Hz, $PhCH_2O$), 5.42 (d, 1H, *J*= 10.5 Hz, NH), 7.2-7.4 (m, 15H, 3Ph). ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.9 (CH_3), 32.5 (C-2), 49.7 (CH_2SO_2) 69.2 (C-6), 70.4 ($PhCH_2O$), 71.5 (C-5), 73.3 ($PhCH_2O$), 74.5 ($PhCH_2O$), 75.2 (C-3), 77.4 (C-4), 80.8 (C-1), 127.2-129 (Ph), 130.9 (Ph), 131.1 (Ph). HRMS (FAB): calcd. for $C_{29}H_{35}NO_6SNa$: 548.2083, found 548.2080.

3,4,6-Tri-*O*-benzyl-2-deoxy-β–D-galactopyranosyl *N*-methyl-p-toluenesulfonamide (**3f**) oil ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.95 (brd, 1 H, *J* = 11.7 Hz, H-2e), 2.26 (q, 1H, *J* = 11.7 Hz, H-2a), 2.32 (s, 3H, CH_3), 2.75 (s, 3H, CH_3-N), 3.33 (dd, 1H, *J*=5.7 Hz, *J*=9.1, H-6), 3.45 (dd, 1H, *J*= 7.1 Hz, *J*= 9.1 Hz H-6), 3.57 (t, 1H, *J*=6.3 Hz, H-4), 3.68 (ddd, 1H, *J*=2.8 Hz, *J*=4.4 Hz, *J*=11.7 Hz, H-3), 3.82 (brs, 1 H, H-5), 4.42 (s, 2H, $PhCH_2O$), 4.56 (d, 1H, *J*=11.6 Hz, $PhCH_2O$), 4.62 (s, 2H, $PhCH_2O$), 4.93 (d, 1H, *J*=11.3 Hz, $PhCH_2O$), 5.27

(dd, *J*=2.2 Hz, *J*=11.1 Hz, C-1), 7.09 (d, 2H, *J*=8.3 Hz, CH_3Ph), 7.2-7.4 (m, 15H, 3Ph), 7.72 (d, 2H, *J*=8.3 Hz, CH_3Ph). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.38 (CH_3Ph), 28.7 (CH_3N), 32.7 (C-2), 68.6 (C-6), 70.4 ($PhCH_2O$), 71.7 (C-5), 73.2 ($PhCH_2O$), 74.2 ($PhCH_2O$), 75.2 (C-3), 77.6 (C-4), 83.4 (C-1), 126.3-129.5 (Ph), 137.7-139.2 (Ph). HRMS (FAB): calcd. for $C_{35}H_{39}NO_6SNa$: 624.2396, found 624.2394.

3,4,6-Tri-*O*-benzyl-2-deoxy-β–D-glucopyranosyl p-toluenesulfonamide (**4a**) oil. ^1H NMR (500 MHz, $CDCl_3$) δ 1.98 (q, 1H, *J* = 11.6 Hz, H-2a), 2.15 (brd, 1 H, *J* = 11.6 Hz, H-2e), 2.32 (s, 3H, CH_3Ph), 3.05 (dd, 1H, *J*=2.9 Hz, *J*=10.5, H-6), 3.15 (t, 1H, *J*= 7.4 Hz, H-4), 3.41 (dd, 1H, *J*=8.3 Hz, *J*=10.5 Hz, H-6), 3.62 (brd, 1H, *J*=10.6 Hz, H-3), 3.84 (brs, 1 H, H-5), 4.35 (s, 2H, $PhCH_2O$), 4.46 (d, 1H, *J*=11.6 Hz, $PhCH_2O$), 4.56 (s, 2H, $PhCH_2O$), 4.85 (td, 1H, *J*=2.7 Hz, *J*=10.6 Hz, H-1), 4.85 (d, 1H, *J*=11.6 Hz, $PhCH_2O$), 5.75 (d, 1H, *J*= 10.6 Hz, NH), 7.14 (d, 2H, *J*=8.5 Hz, CH_3Ph), 7.2-7.4 (m, 15H, 3Ph), 7.74 (d, 2H, *J*=8.5 Hz, CH_3Ph). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4 (CH_3-Ph), 32.6 (C-2), 67.7 (C-6), 71.6 (C-5), 73.3 ($PhCH_2O$), 73.3 ($PhCH_2O$), 74.5 ($PhCH_2O$), 74.7 (C-3), 77.4 (C-4), 83.1 (C-1), 126.4-129.5 (Ph), 137.8-138.6 (Ph). HRMS (FAB): calcd. for $C_{34}H_{37}NO_6SNa$: 610.2239, found 610.2235.