

Supporting Information

Sulfo-Protected Hexosamine Monosaccharides: Potentially Versatile Building Blocks for Glycosaminoglycan Synthesis

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Dimethylthexylsilyl 2-azido-3-O-benzoyl-4-O-chloroacetyl-2-deoxy-6-O-trifluoroethylsulfonato- β -D-glucopyranoside 6

¹H NMR (400MHz, CDCl₃) : δ = 8.03-7.46 (m, 5 H, Ar_H), 5.31 (dd, $J_{2,3}$ = 10.1, $J_{3,4}$ = 9.5 Hz, 1 H, H-3), 5.22 (t, $J_{4,5}$ = 9.5 Hz, 1 H, H-4), 4.76 (d, $J_{1,2}$ = 7.6 Hz, 1 H, H-1), 4.55 (dd, 2 H, CH₂CF₃), 4.42 (dd, $J_{5,6a}$ = 2.7, $J_{6a,6b}$ = 10.9 Hz, 1 H, H-6a), 4.36 (dd, $J_{5,6b}$ = 5.1 Hz, 1 H, H-6b), 3.97-3.88 (m, 3 H, CH₂Cl, H-5), 3.61 (dd, 1 H, H-2), 1.67 (m, 1 H, CH(CH₃)₂), 0.92-0.91 (m, 12 H, CH(CH₃)₂ and C(CH₃)₂), 0.24, 0.23 (2s, 6 H, (CH₃)₂Si). ¹³C NMR (300MHz, CDCl₃) : δ = 169.391, 165.457, 133.728, 129.813, 128.557, 128.537, 126.997, 123.322, 119.646, 115.970, 97.016, 77.983, 70.987, 70.604, 69.761, 67.626, 67.128, 66.620, 66.140, 66.106, 40.052, 33.778, 24.691, 19.743, 19.611, 18.346, 18.239, -2.509, -3.460. HRMS calcd. for C₂₅H₃₅N₃O₁₀F₃NaSiS₂ 712.1351; found 712.1356.

Dimethylthexylsilyl 2-azido-2-deoxy-3,6-O-trifluoroethylsulfonato- β -D-glucopyranoside 7

¹H NMR (400MHz, CDCl₃) : δ = 4.70-4.62 (m, 3 H, H-1, CH₂CF₃), 4.61-4.49 (m, 4 H, H-6a, H-6b, CH₂CF₃), 4.43 (t, $J_{2,3}$ = 10.2, $J_{3,4}$ = 8.8 Hz, 1 H, H-3), 3.83 (dd, $J_{4,5}$ = 9.7, $J_{4,OH-4}$ = 4.6 Hz, 1 H, H-4), 3.60 (ddd, $J_{5,6a}$ = 2.3, $J_{5,6b}$ = 4.7 Hz, 1 H, H-5), 3.46 (dd, $J_{1,2}$ = 7.5 Hz, 1 H, H-2), 3.12 (d, 1 H, OH-4), 1.68 (m, 1 H, CH(CH₃)₂), 0.91-0.89 (m, 12 H, CH(CH₃)₂ and C(CH₃)₂), 0.23, 0.21 (2s, 6 H, (CH₃)₂Si). ¹³C NMR (300MHz, CDCl₃) : δ = 126.992, 123.315, 123.298, 119.639, 119.622, 115.962, 96.792, 87.109, 72.321, 71.713, 68.119, 67.965, 67.940, 67.632, 67.608, 67.122, 67.095, 66.611, 66.581, 66.100, 33.730, 24.693, 19.705, 19.531, 18.329, 18.201, -2.591, -3.493. HRMS calcd. for C₁₈H₃₁N₃O₁₁F₆NaSiS₂ 694.0964; found 694.0971.

Dimethylthexylsilyl 2-azido-3-O-benzyl-2-deoxy-6-O-trifluoroethylsulfonato-4-O-p-methoxybenzyl β -D-glucopyranoside 12

¹H NMR (400MHz, CDCl₃) : δ = 7.40-6.87 (m, 10 H, Ar_H), 4.87 (Abq, 2 H, CH₂Ph), 4.80 (0.5 ABq, 1 H, CH₂Ph), 4.54-4.43 (m, 4 H, 0.5 ABq, CH₂CF₃, H-1), 4.36 (dd, 1 H, $J_{5,6a}$ = 1.8, $J_{6a,6b}$ = 10.5 Hz, H-6a), 4.22 (dd, $J_{5,6b}$ = 5.1 Hz, 1 H, H-6b), 3.49-3.39 (m, 3 H, H-3, H-4, H-2), 3.21 (m, 1 H, H-5), 1.66 (m, 1 H, CH(CH₃)₂), 0.90-0.89 (m, 12 H, CH(CH₃)₂ and C(CH₃)₂), 0.20, 0.18 (2s, 6 H, (CH₃)₂Si). ¹³C NMR (400MHz, CDCl₃) : δ = 159.692, 137.734, 129.974, 129.132, 128.478, 128.301, 127.944, 127.929, 127.789, 127.670, 122.915, 120.151, 117.398, 114.047, 96.938, 82.865, 75.778, 75.504, 74.621, 72.374, 68.662, 67.199, 66.818, 66.436,

66.053, 55.171, 33.832, 24.721, 19.825, 19.699, 18.394, 18.290, -2.302, -3.347. HRMS calcd. for $C_{31}H_{44}N_3O_9F_3NaSiS$ 742.2417; found 742.2430.

4-Methoxyphenyl 4,6-O-benzylidene-2-deoxy-2-dimethylmaleimido-3-O-trifluoroethylsulfonato- β -D-glucopyranoside 17

1H NMR (400MHz, $CDCl_3$) : δ = 7.53-6.79 (m, 9 H, Ar_H), 5.73 (d, $J_{1,2}$ = 8.3 Hz, 1 H, H-1), 5.57 (s, 1 H, CH), 5.40 (dd, $J_{2,3}$ = 10.2, $J_{3,4}$ = 9.8 Hz, 1 H, H-3), 4.46 (dd, 1 H, H-2), 4.45 (dd, $J_{5,6a}$ = 4.7, $J_{6a,6b}$ = 11.0 Hz, 1 H, H-6a), 4.29-4.07 (m, 2 H, CH_2CF_3), 3.91-3.86 (m, 2 H, H-4, H-6b), 3.80-3.74 (m, 4 H, H-5, OCH_3), 1.99 (s, 6 H, CH_3). ^{13}C NMR (400MHz, $CDCl_3$) : δ = 155.878, 150.183, 137.747, 135.789, 129.902, 128.610, 126.167, 122.898, 118.681, 114.558, 102.508, 97.968, 80.158, 78.589, 68.471, 67.359, 66.851, 68.536, 55.606, 54.496, 8.792. MS (ES) m/z = 665.5 [M^+ + Na]

Dimethylthexylsilyl 3-O-benzoyl-4-O-chloroacetyl -2-deoxy-2-dimethylmaleimido-6-O-trifluoroethylsulfonato- β -D-glucopyranoside 19

1H NMR (400MHz, $CDCl_3$) : δ = 7.90-7.40 (m, 5 H, Ar_H), 5.97 (dd, $J_{2,3}$ = 10.9, $J_{3,4}$ = 9.0 Hz, 1 H, H-3), 5.54 (d, $J_{1,2}$ = 8.9 Hz, 1 H, H-1), 5.29 (dd, $J_{4,5}$ = 10.1 Hz, 1 H, H-4), 4.56 (m, 2 H, CH_2CF_3), 4.45 (dd, $J_{5,6a}$ = 2.8, $J_{6a,6b}$ = 10.8 Hz, 1 H, H-6a), 4.40 (dd, $J_{5,6b}$ = 5.1 Hz, 1 H, H-6b), 4.23 (dd, 1 H, H-2), 4.08 (ddd, 1 H, H-5), 3.94 (ABq, 2 H, CH_2Cl), 1.89 (s, 6 H, CH_3), 1.51 (m, 1 H, $CH(CH_3)_2$), 0.79-0.73 (m, 12 H, $CH(CH_3)_2$ and $C(CH_3)_2$), 0.16, 0.06 (2s, 6 H, $(CH_3)_2Si$). ^{13}C NMR (400MHz, $CDCl_3$) : δ = 166.350, 165.514, 137.417, 133.614, 129.831, 128.532, 126.995, 123.335, 119.662, 115.942, 93.375, 71.190, 70.660, 70.632, 70.552, 67.704, 67.195, 66.685, 66.174, 40.132, 33.931, 19.782, 19.607, 18.354, 18.251, 8.618, -2.127, -3.920. HRMS calcd. for $C_{31}H_{41}NO_{12}F_3NaSiS$ 794.1657; found 794.1674.

Dimethylthexylsilyl 2-azido-3-O-benzoyl-6-O-benzyl-2-deoxy-4-O-trifluoroethylsulfonato β -D-galactopyranoside 26

1H NMR (400MHz, $CDCl_3$) : δ = 8.11-7.31 (m, 10 H, Ar_H), 5.35 (d, $J_{3,4}$ = 2.6, $J_{4,5}$ < 1 Hz, 1 H, H-4), 5.05 (dd, $J_{2,3}$ = 11.0 Hz, 1 H, H-3), 4.65 (d, $J_{1,2}$ = 7.6 Hz, 1 H, H-1), 4.54 (Abq, 2 H, CH_2Ph), 4.47 (dd, 2 H, CH_2CF_3), 3.89 (t, $J_{5,6a}$ = $J_{5,6b}$ = 6.7 Hz, 1 H, H-5), 3.76 (dd, 1 H, H-2), 3.68 (m, 2 H, H-6a, H-6b), 1.68 (m, 1 H, $CH(CH_3)_2$), 0.93-0.91 (m, 12 H, $CH(CH_3)_2$ and $C(CH_3)_2$), 0.23, 0.22 (2s, 6 H, $(CH_3)_2Si$). ^{13}C NMR (400MHz, $CDCl_3$) : δ = 165.453, 137.258, 133.739, 129.982, 128.684, 128.541, 128.477, 127.960, 127.825, 122.85, 120.087, 97.345 (C-1), 80.337, 73.623 (CH_2), 71.626, 71.005, 67.606, 67.223, 67.158 (C-6), 66.841, 66.458, 63.433 (C-2), 33.894, 24.851, 19.945, 19.825, 18.483, 18.387, -2.086, -3.227. HRMS calcd. for $C_{30}H_{40}N_3O_9F_3NaSiS$ 726.2104; found 726.2106.

Dimethylthexylsilyl 2-azido-3-O-benzoyl-4-O-benzyl-2-deoxy-6-O-trifluoroethylsulfonato β -D-galactopyranoside 27

1H NMR (400MHz, $CDCl_3$) : δ = 8.13-7.22 (m, 10 H, Ar_H), 4.97 (dd, $J_{2,3}$ = 10.9, $J_{3,4}$ = 3.1 Hz, 1 H, H-3), 4.78 (0.5 Abq, 1 H, CH_2Ph), 4.60 (d, $J_{1,2}$ = 7.6 Hz, 1 H, H-1), 4.45 (dd, 2 H, CH_2CF_3), 4.42 (0.5 Abq, 1 H, CH_2Ph), 4.35 (dd, $J_{5,6a}$ = 7.5, $J_{6a,6b}$ = 10.4 Hz, 1 H, H-6a), 4.06 (dd, $J_{5,6b}$ = 4.5 Hz, 1 H, H-6b), 4.01 (dd, $J_{4,5}$ = 1 Hz, 1 H, H-4), 3.93 (dd, 1 H, H-2), 3.82 (m, 1 H, H-5), 1.68 (m, 1 H, $CH(CH_3)_2$), 0.92-0.90 (m, 12 H, $CH(CH_3)_2$ and $C(CH_3)_2$), 0.23, 0.21 (2s, 6 H, $(CH_3)_2Si$). ^{13}C NMR (400MHz, $CDCl_3$) : δ = 165.716, 133.782, 130.946, 129.916, 129.840, 129.683, 128.867, 128.703, 128.614, 128.508, 128.463, 128.397, 128.305, 128.115, 127.719, 125.636, 122.876, 120.117, 117.358, 97.238, 77.316, 76.999, 76.681, 75.004, 73.995, 72.391, 72.194, 71.744, 66.909, 66.526, 63.679, 33.850, 24.815, 19.894, 19.768, 18.458, 18.358, -2.151, -3.346. HRMS calcd. for $C_{30}H_{40}N_3O_9F_3NaSiS$ 726.2104; found 726.2084.

Dimethylthexylsilyl 2-azido-3-*O*-benzoyl-2-deoxy-4,6-*O*-trifluoroethylsulfonato β -D-galactopyranoside 28

^1H NMR (400MHz, CDCl_3) : δ = 8.10-7.47 (m, 5 H, Ar_H), 5.25 (d, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1 Hz, 1 H, H-4), 5.04 (dd, $J_{2,3}$ = 10.6, 1 H, H-3), 4.69 (d, $J_{1,2}$ = 7.6 Hz, 1 H, H-1), 4.58-4.22 (m, 6 H, 2 CH_2CF_3 , H-6a, H-6b), 4.09 (t, $J_{5,6a} = J_{5,6b} = 6.4$ Hz, 1 H, H-5), 3.79 (dd, 1 H, H-2), 1.69 (m, 1 H, $\text{CH}(\text{CH}_3)_2$), 0.94-0.92 (m, 12 H, $\text{CH}(\text{CH}_3)_2$ and $\text{C}(\text{CH}_3)_2$), 0.25, 0.24 (2s, 6 H, $(\text{CH}_3)_2\text{Si}$).

^{13}C NMR (300MHz, CDCl_3) : δ = 165.572, 134.040, 129.897, 128.678, 128.288, 126.911, 126.735, 123.057, 119.569, 119.368, 115.879, 115.690, 97.281, 78.877, 70.682, 70.138, 68.084, 67.795, 67.565, 67.279, 67.051, 66.766, 66.537, 66.257, 62.946, 33.846, 24.794, 19.838, 19.710, 18.430, 18.326, -2.304, -3.398. HRMS calcd. for $\text{C}_{25}\text{H}_{35}\text{N}_3\text{O}_{12}\text{F}_6\text{NaSi}_2$ 798.1233; found 798.1252.