SUPPLEMENTARY MATERIAL TO

Synthesis of 1,3-divalent glycoconjugates with diverse structure and functionalization

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ANALYTICAL AND SPECTRAL DATA FOR SYNTHESIZED COMPOUNDS

Compound **5**. Yield: 90%, Physical State: syrup, $[\alpha]_D$: +5.6˚ (c = 0.4, MeOH, 25 ^oC), ^1H NMR (500 MHz, $CDCl_3$): 5.04 (t, 1H, *J* = 10.0 Hz, H-4), 4.93 (t, 1H, *J* = 9.0 Hz, H-2), 4.52 (d, 1H, *J* = 9.0 Hz, H-1), 4.25-4.14 (m, 4H, -C$\underline{H}_2$-C-, H-6a & H-6b), 3.80 (t, 1H, *J* = 9.5 Hz, H-3), 3.73-3.72 (m, 1H, H-5), 2.46 (t, 1H, alkyne C-H) 2.14, 2.11, 2.10 (3s, 9H, 3 x -COC$\underline{H}_3$) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.7, 169.2, 169.0 (3 x –$\underline{C}OCH_3$), 87.9, 79.2, 78.8, 74.9, 74.2, 71.9, 69.0, 61.9, 59.4, 20.8, 20.7 ppm; ESI-MS HRMS: observed 392.1050 for $[M+Na]^+$ calculated 392.1070 for $C_{15}H_{19}N_3O_8Na$.

Compound **6**. Yield: 80%, Physical State: syrup, $[\alpha]_D$: +42.7˚ (c = 0.2, $CHCl_3$, 25 ^oC), ^1H NMR (400 MHz, $CDCl_3$): δ 5.06 (d, 1H, *J* = 3.6 Hz, H-1), 4.99 (t, 1H, *J* = 10.0 Hz, H-4), 4.77-4.74 (dd, 1H, H-2), 4.32-4.28 (dq, 2H, -C$\underline{H}_2$-C-), 4.24-4.19 (dd, 1H, H-6a), 4.09-4.05 (dd, 1H, H-6b), 4.00 (t, 1H, *J* = 9.6 Hz, H-3), 3.95-3.91 (m, 1H, H-5), 3.65-3.62 (t, 2H, -O-C$\underline{H}_2$-), 2.43 (t, 1H, alkyne C-H), 2.11 (x 2), 2.08 (3s, 9H, 3 x -COC$\underline{H}_3$), 1.61-1.54 (m, 2H, -O-CH_2-C$\underline{H}_2$-), 1.30-1.26 (bs, 18H, 9 x -C$\underline{H}_2$-), 0.88 (t, 3H, -CH_2C$\underline{H}_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 170.0, 169.5 (3 x –$\underline{C}OCH_3$), 95.6, 79.8, 76.5, 74.2, 73.5, 69.2, 68.5, 67.5, 63.0, 62.3, 59.7, 32.7, 31.9, 31.8, 29.7, 29.6, 29.4, 29.3, 29.2, 29.0, 26.0, 25.7, 22.7, 22.6, 20.9, 20.7, 14.0 ppm; ESI-MS HRMS: observed 535.2864 for $[M+Na]^+$ calculated 535.2883 for $C_{27}H_{44}O_9Na$.

Compound **7**. Yield: 90%, Physical State: solid, M.p.: 68-72 ^oC, $[\alpha]_D$: +99.1˚ (c = 0.8, $CHCl_3$, 25 ^oC), ^1H NMR (500 MHz, $CDCl_3$): δ 5.00 (t, 1H, *J* = 10.0 Hz, H-4), 4.95 (d, 1H, *J* = 9.0 Hz, H-1), 4.82-4.80 (dd, 1H, H-2), 4.32-4.27 (dq, 2H, -C$\underline{H}_2$-C-), 4.24-4.20 (dd, 1H, H-6a), 4.11-4.08 (dd, 1H, H-6b), 4.02 (t, 1H, *J* = 9.5 Hz, H-3), 3.92-3.88 (m, 1H, H-5), 3.39 (s, 3H, OC$\underline{H}_3$), 2.43 (t, 1H, alkyne C-$\underline{H}$), 2.14, 2.10, 2.09 (3s, 9H, 3 x -COC$\underline{H}_3$) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.8, 170.1, 169.5 (3 x –$\underline{C}OCH_3$), 96.9, 79.8, 76.3, 74.4, 73.3, 69.4, 67.6, 62.3, 59.8, 55.4, 21.0, 20.8 ppm; ESI-MS HRMS: observed 381.1173 for $[M+Na]^+$ calculated 381.1162 for $C_{16}H_{22}O_9Na$.

Compound **10**. Yield: 70%, Physical State: White Solid, M.p.: 121-123 ^{o}C, $[\alpha]_D$: +87.9˚ (c = 0.3, $CHCl_3$, 25 ^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.87 (d, 1H, *J* = 8.8 Hz, N<u>H</u>), 5.09-5.03 (m, 2H, H-1 & H-4), 4.37-4.17 (m, 6H, 2 x -C<u>H</u>$_2$-C-, H-2 & H-6a), 4.11-4.06 (m, 1H, H-6b), 3.95-3.91 (m, 1H, H-5), 3.85 (t, 1H, *J* = 9.6 Hz, H-3), 2.51-2.49 (m, 1H, alkyne C-<u>H</u>), 2.09, 2.03 (2s, 9H, 3 x -COC<u>H</u>$_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 170.1, 169.3 (3 x –<u>C</u>OCH$_3$), 96.6, 80.3, 78.5, 76.4, 75.4, 74.8, 70.1, 68.6, 62.1, 59.1, 55.2, 51.9, 23.4, 21.0, 20.8 ppm; ESI-MS HRMS: observed 382.1500 for $[M+H]^+$ calculated 382.1502 for $C_{18}H_{24}NO_8$.

Compound **11**. Yield: 70%, Physical State: syrup, $[\alpha]_D$: +64.9˚ (c = 0.4, $CHCl_3$, 25 ^{o}C), ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.77 (d, 1H, *J* = 9.0 Hz, N<u>H</u>), 5.03 (t, 1H, *J* = 9.0 Hz, H-4), 4.85 (d, 1H, *J* = 3.0 Hz, H-1), 4.33-4.16 (m, 4H, -C<u>H</u>$_2$-C-, H-2 & H-6a), 4.08-4.06 (dd, 1H, H-6b), 3.89-3.86 (m, 1H, H-5), 3.83 (t, 1H, *J* = 9.5 Hz, H-3), 3.68-3.65 (m, 1H, O-C<u>H</u>$_2$-CH$_2$-), 3.47-3.42 (m, 1H, O-C<u>H</u>$_2$-CH$_2$-), 2.50 (t, 1H, alkyne C-H), 2.09, 2.08, 2.04 (3s, 9H, 3 x -COC<u>H</u>$_3$), 1.62-1.59 (m, 2H, O-CH$_2$-C<u>H</u>$_2$-), 1.32-1.26 (m, 14H, 7 x C<u>H</u>$_2$-), 0.88 (t, 3H, C<u>H</u>$_3$) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.8, 169.9, 169.4 (3 x –<u>C</u>OCH$_3$), 97.4, 80.4, 76.8, 74.6, 70.3, 68.4, 68.1, 62.4, 59.0, 52.2, 31.9, 29.6 (x 2), 29.5, 29.4, 29.3, 26.2, 23.4, 22.7, 20.9, 20.8, 14.1 ppm; ESI-MS HRMS: observed 484.2925 for $[M+H]^+$ calculated 484.2910 for $C_{25}H_{42}NO_8$.

Compound **13**. Yield: 60%, Physical State: syrup, $[\alpha]_D$: -34.3˚ (c = 1.0, $CHCl_3$, 25 ^{o}C), ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.94 (d, 1H, *J* = 7.5 Hz, N<u>H</u>), 5.17 (d, 1H, *J* = 8.0 Hz, H-1) 4.95 (t, 1H, *J* = 9.5 Hz, H-4), 4.41-4.30 (m, 2H, -OC<u>H</u>$_2$-), 4.27-4.19 (dd, 1H, H-6a), 4.10-4.07 (dd, 1H, H-6b), 3.69-3.66 (m, 1H, H-5), 3.59-3.49 (m, 2H, O-C<u>H</u>$_2$-), 3.27-3.24 (m, 1H, H-2), 2.46 (t, 1H, alkyne C<u>H</u>), 2.07, 2.00 (2s, 9H, 3 xCOC<u>H</u>$_3$), 1.46 (t, 2H, O-CH$_2$-C<u>H</u>$_2$), 1.24 (s, 14H, 7 x -C<u>H</u>$_2$), 0.87 (t, 3H, *J* = 6.5 Hz, -C<u>H</u>$_3$) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.9, 170.8, 169.6 (<u>C</u>OCH$_3$), 90.6, 78.7, 75.1, 72.4, 72.0, 70.5, 62.4, 57.7, 56.2, 32.0, 31.9, 30.4, 29.8, 29.7, 29.6, 29.5, 29.4 (x 2), 26.1, 23.7, 22.7, 21.0, 14.2 ppm; ESI-MS HRMS: observed 484.2921 for $[M+H]^+$ calculated 484.2910 for $C_{25}H_{42}NO_8$.

Compound **14**. Yield: 50%, Physical State: syrup, $[\alpha]_D$: -34.4˚ (c = 1.2, $CHCl_3$, 25 ^{o}C), ^{1}H NMR (500 MHz, $CDCl_3$): 5.52 (d, 1H, *J* = 7.0 Hz, N<u>H</u>), 4.88 (s, 1H, H-1), 4.36-4.32 (m, 2H, H-3, H-5), 4.30-4.29 (d, 1H, H-2), 4.03-4.01 (d, 2H, H-6a & H-6b), 3.80-3.79 (d, 1H, *J* = 4.0 Hz, H-3), 3.71-3.66 (m, 2H, O-C<u>H</u>$_2$-), 3.44-3.36 (m, 2H, O-C<u>H</u>$_2$-), 1.98 (s, 3H, COC<u>H</u>$_3$), 1.57-1.51 (m, 4H, O-CH$_2$-C<u>H</u>$_2$), 1.43, 1.35 (2s, 6H, 2 x C<u>H</u>$_3$), 1.29 (s, 28H, 14 x -C<u>H</u>$_2$), 0.88 (t, 6H, *J* = 6.5 Hz , 2 x C<u>H</u>$_3$) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.6 (<u>C</u>OCH$_3$), 108.4, 107.1, 82.5, 74.6, 70.1, 68.6, 66.4, 59.5, 32.0, 29.9, 29.8, 29.7 (x 2), 29.6 (x 2), 29.5, 26.7, 26.2, 25.4, 23.4, 22.8, 14.2 ppm; ESI-MS HRMS: observed 564.4221 for $[M+Na]^+$ calculated 564.4240 for $C_{31}H_{59}NO_6Na$.