Supplementary Material (ESI) for Chemical Communications

ELECTRONIC SUPPORTING INFORMATION

Carbohydrate triazoles and isoxazoles as inhbitors of galectins-1 and -3†

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Materials and methods:

All reactions involving water-sensitive chemicals were carried out in flame-dried glassware with magnetic stirring under a nitrogen atmosphere. Anhydrous DCM was distilled from CaH_2 and anhydrous THF were distilled from Na/K prior to use. All non-aqueous reactions were carried out under anhydrous conditions within an nitrogen atmosphere in distilled solvents. All other solvents and reagents were used as received. TLC was performed on aluminium plates with detection by UV or by coloration with a molybdate solution. Column chromatography were performed on silica gel (230-400 mesh) with the indicated eluent. ^{1}H and ^{13}C NMR spectra were recorded at 300 (75) MHz with a Variant apparatus. Chemical shifts (ppm) are reported relative to $CHCl_3$ or D_2O or CD_3OD as internal standard. Optical rotations were measured on a Polarimeter JASCO P-1000, melting point on a Fisher-Johns Melting Point Apparatus and ESI-MS analyses were carried out on a MICROMASS Quattro LC.

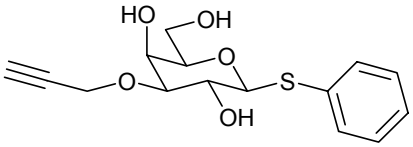
General procedure for triazole synthesis:

Carbohydrate containing alkyne (0.302 mmol) dissolved in THF (0.1 M) and CuI (0.03 mmol), DIPEA (0.606 mmol) and azide (0.332 mmol) were added and stirred, at room temperature. The green solution was stirred until disappearance of the starting material (maximum 3 hours) and then evaporated under reduced pressure, dissolved with ethyl acetate and filtered through a pad of celite. The organic solution was washed with aqueous HCl (10%), dried over sodium sulfate, filtered, evaporated under reduced pressure and purified using flash chromatography with a mixture of ethyl acetate and hexane as eluent (or DCM and MeOH).

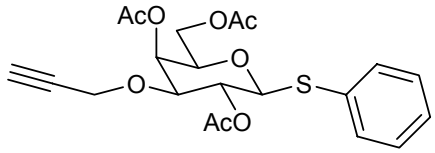
General procedure for de-*O*-acetylation:

The acetyls protected glycoside (0.1 mmol) was dissolved into methanol (2 mL), to which was added a catalytic amount of sodium methoxide. The solution was stirred at room temperature until disappearance of the starting material (usually less than 3 hours). After neutralization of sodium methoxide with Amberlite IR-120 (H^+) resin, the solution was filtered and removal of the methanol under reduced pressure afforded the fully deprotected glycoside.

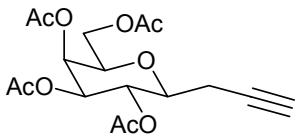
Spectroscopic data:



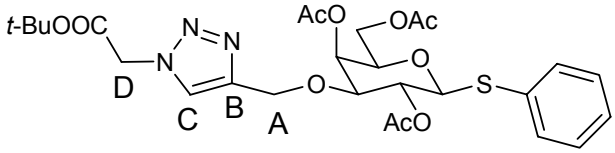
Phenyl 3-*O*-propynyl-1-thio-β-D-galactopyranoside **3**: Phenyl 1-thio-β-D-galactopyranoside **2** (0.354g, 1.29 mmol) was dissolved in MeOH (8 mL) and the mixture was heated under reflux for 2 hours, then concentrated to dryness under reduced pressure. The residue was diluted with benzene (8 mL), Bu_4NI (0.29 g, 0.79 mmol) and propargyl bromide (1.07 mL, 9.6 mmol) were added to the mixture. The reaction was stirred at 60°C for 20 hours, then filtered throught a celica path. The resulting organic solution was concentrated under reduced pressure and purified by flash silica gel column chromatography to afforded **3** (0.314g, 78 %) as a yellow oil; $[\alpha]^{20}_D$ -33.9 (c 0.26 in MeOH); ^{1}H NMR (300 MHz, CD_3OD): δ 7.42-7.39 (2H, m, H_{AR}), 7.28-7.19 (3H, m, H_{AR}), 4.62 (1H, d, *J* = 7.9 Hz, H-1), 4.19 (2H, s, $\underline{CH_2}CCH$), 4.08 (1H, dd, *J* = 1.3 Hz, H-4), 3.61-3.47 (5H, m, H-2, H-3, H-5, H-6a, H-6b), 2.73 (1H, t, J = 1.4 Hz, $CH_2C\underline{CH}$); ^{13}C NMR (75 MHz, CD_3OD): δ 132.61, 131.34, 129.46, 128.05 (4 C_{AR}), 88.08 (C-1), 81.03 (C-3), 79.52 ($CH_2\underline{C}CH$), 78.86 ($CH_2C\underline{CH}$), 76.20 (C-5), 68.08 (C-4), 65.27 (C-2), 61.04 (C-6), 56.52 ($O\underline{CH_2}CCH$); ESI-MS calcd for $C_{15}H_{18}O_5S$ + (Na^+): 333.1; found: 333.3.



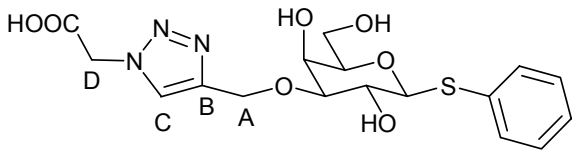
Phenyl 2,4,6-tri-*O*-acetyl-3-*O*-propynyl-1-thio-β-D-galactopyranoside **4** : To a mixture of **3** (1g, 2.29 mmol) dissolved in pyridine (25 mL) at 0°C was added dropwise acetic anhydride (5 mL) and the mixture was stirred over night at room temperature. At the morning, pieces of ice and ethyl acetate is added to the mixture and the aqueous layer is washed with ethyl acetate. The combine organic layer were washed with a solution of $NaHCO_3$, brine, water, dried over Na_2SO_4, filtered, concentrated under reduced pressure and purified by flash silica gel column chromatography to afforded **4** (0.949g, 95%) as white solid; $[\alpha]^{20}_D$ +36.0 (c 0.11 in DCM); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54-7.50 (2H, m, H_{AR}), 7.32-7.27 (3H, m, H_{AR}), 5.43 (1H, dd, J = 3.3 Hz, H-4), 5.11 (1H, dd, J = 9.6 Hz, H-2), 4.70 (1H, d, J = 9.89 Hz, H-1), 4.19-4.16 (4H, m, H-3, H-6a, $\underline{CH_2}CCH$), 3.91-3.83 (2H, m, H-5, H-6b), 2.44 (1H, t, J = 0.5 Hz, $CH_2C\underline{CH}$), 2.14, 2.11, 2.07 (9H, 3s, $CO\underline{CH_3}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.71, 170.61, 169.81 (3 $\underline{CO}CH_3$), 133.10, 132.64, 129.05, 128.18 (6 C_{AR}), 86.76 (C-1), 79.24 ($OCH_2C\underline{CH}$), 76.91 (C-3), 75.43 ($OCH_2\underline{C}CH$), 74.79 (C-5), 68.60 (C-4), 65.94 (C-2), 62.43 (C-6), 56.71 ($O\underline{CH_2}CCH$), 21.24, 20.98, 20.96 (3 $CO\underline{CH_3}$); ESI-MS calcd for $C_{21}H_{24}O_8S$ + (Na^+): 459.1; found: 459.3.



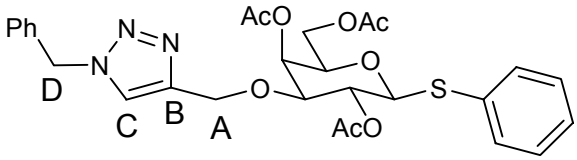
Propynyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside **6**: A solution of **5** (0.111g, 0.3 mmol) in MeOH (10 mL) was cooled at -78°C. The solution was degassed by bubbling with nitrogen. O_3 was then passed through the solution with vigorous stirring. After 30 minutes TLC showed disappearance of the starting material. Dry nitrogen was passed through the cold solution in order to remove the excess of O_3. Me_2S (0.5 mL) was added and stirred 30 minutes at -78°C and 1 hour at room temperature. After evaporation, the resulting crude was dissolved in MeOH (10 mL) and Na_2CO_3 (0.6 mmol) was added at 0°C. Ohira's reagent (0.5 mmol) dissolved in 1 mL of MeOH was added to the mixture and was stirred over night at room temperature. The solution was then concentrated, ether was added and the organic solution was washed with water, dried over sodium sulfate and concentrated under reduce pressure. To the resulting crude material Ac_2O (3 mL), pyridine (3 mL) and DMAP (10 mg) were added. The reaction mixture was stirred 20 hours at room temperature and the resulting solution was concentrated and purified by flash silica gel column chromatography using a mixture of hexanne: ethyl acetate (2:1) to afforded 6 (0.095g, 86%) as a white solid; R_f: 0.5 (hexane: AcOEt, 1:3); $[\alpha]^{20}_D$ +13.4 (c 0.1 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.51 (1H, d, *J* = 3.3 Hz, H-7), 5.20 (1H, t, *J* = 9.9 Hz, H-5), 5.04 (1H, dd, *J*=3.6, 10.2 Hz, H-6), 4.18-4.06 (2H, m, H-9), 3.91 (1H, t, *J* = 6.6 Hz, H-8), 3.60 (1H, m, H-4), 2.52 (2H, m, H-3), 2.16 (3H, s, $\underline{CH_3}CO$), 2.12 (1H, m, H-1), 2.06 (3H, s, $\underline{CH_3}CO$), 2.05, (3H, s, $\underline{CH_3}CO$), 1.99 (3H, s, $\underline{CH_3}CO$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.43, 170.25, 170.17, 169.79 (4 $CH_3\underline{CO}$), 79.24 (C-2), 76.42, 74.20, 71.87, 70.14, 69.06, 67.49, 61.48 (C-6), 22.48 (C-3), 20.85, 20.66, 20.58, 20.58 (4 $\underline{CH_3}CO$).



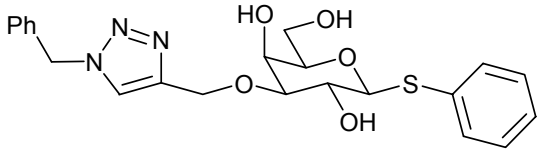
Phenyl 2,4,6-tri-*O*-acetyl-3-*O*-[2-(1-*tert*-butoxyacetyl-1*H*-1,2,3-triazol-4-yl)methyl]-1-thio-β-D-galactopyranoside **14-OAc** was isolated as a white solid (92 %); mp 85 °C; $[\alpha]^{20}_D$ +43.3 (c 0.12 in DCM); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 (1H, s, $H_{triazole}$), 7.49-7.46 (2H, m, H_{AR}), 7.29-7.26 (3H, m, H_{AR}), 5.45 (1H, dd, J = 3.3 Hz, H-4), 5.10 (1H, dd, J = 9.8 Hz, H-2), 5.02 (2H, s, $CO\underline{CH_2}N$), 4.69 (1H, d, J = 9.3 Hz, H-1), 4.62 (2H, m, $O\underline{CH_2}C$), 4.16-4.12 (2H, m, H-6a, H-6b), 3.85 (1H, ddd, J = 6.0 Hz, H-5), 3.74 (1H, dd, J = 3.5, 9.6 Hz, H-3), 2.09, 2.04, 2.02 (9H, 3s, $CO\underline{CH_3}$), 1.46 (9H, s, $C(\underline{CH_3})_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.37, 170.28, 169.58 (3 $\underline{CO}CH_3$), 165.04 ($\underline{CO}OC(CH_3)_3$), 132.85 (C-B), 132.15, 128.71, 127.77 (6 C_{AR}), 124.33 (C-C), 86.44, 83.75 (C-1), 77.71 (C-3), 74.46 (C-5), 68.65 (C-4), 66.38 (C-2), 62.94, 62.03 (C-A, C-6), 51.35 (C-D),27.94, 27.85 ($C(\underline{CH_3})_3$), 20.77, 20.63 (3 $CO\underline{CH_3}$); ESI-MS calcd for $C_{27}H_{35}N_3O_{10}S$ + (Na^+): 616.2; found: 616.3.



Phenyl 2,4,6-tri-*O*-acetyl-3-*O*-[2-(1-*tert*-butoxyacetyl-1*H*-1,2,3-triazol-4-yl)methyl]-1-thio-β-D-galactopyranoside **14** was obtained as a white solid (quant.); mp 102 °C; $[\alpha]^{20}_{D}$ +0.649 (c 0.11 in MeOH); ^{1}H NMR (300 MHz, CD_3OD): δ 7.93 (1H, s, $H_{triazole}$), 7.43-7.39 (2H, m, H_{AR}), 7.27-7.21 (3H, m, H_{AR}), 5.12 (2H, s, C-D), 4.62 (1H, d, *J* = 7.7 Hz, H-1), 4.03 (2H, m, C-A), 3.65-3.44 (6H, m, H-2, H-3, H-4, H-5, H-6a, H-6b); ^{13}C NMR (75 MHz, CD_3OD): δ 171.21 (COOH), 132.53 (C-B), 131.36, 129.42, 128.02 (6 C_{AR}) 126.53 (C-C), 87.99 (C-1), 81.58 (C-3), 78.91 (C-5), 68.24 (C-4), 65.40 (C-2), 61.71, 61.05 (C-6, C-A), 51.55 (C-D); ESI-MS calcd for $C_{17}H_{21}N_3O_7S$ + (Na^+): 434.1; found: 434.3.

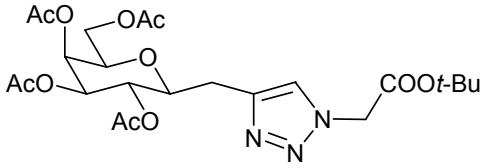


Phenyl 2,4,6-tri-*O*-acetyl-3-*O*-[2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]-1-thio-β-D-galactopyranoside **15-OAc** was isolated as a yellow oli (97 %); mp 79.5 °C; $[\alpha]^{20}_{D}$ + 42.4 (c 0.34 in DCM); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 1H, s, $H_{triazole}$), 7.49-7.40 (1H, m, H_{AR}), 7.39-7.34 (3H, m, H_{AR}), 7.31-7.28 (6H, m, H_{AR}), 5.51 (2H, m, PhCH_2N), 5.43 (1H, dd, *J* = 2.7 Hz, H-4), 5.07 (1H, dd, *J* = 9.9 Hz, H-2), 4.65 (2H, m, OCH_2C), 4.62 (1H, d, *J* = 10.1 Hz, H-1), 4.18-4.11 (2H, m, H-6a, H-6b), 3.85 (1H, ddd, *J* = 6.8 Hz, H-5), 3.73 (1H, dd, *J* = 3.2, 9.6 Hz, H-3), 2.17, 2.07, 2.06 (9H, 3s, COCH_3);^{13}C NMR (75 MHz, $CDCl_3$): δ 170.04, 169.91, 169.13 (3 $COCH_3$), 144.61 (C-B), 134.25, 132.60, 131.78, 128.77, 128.48, 128.44, 127.80, 127.52 (12 C_{AR}), 122.56 (C-C), 86.03 (C-1), 77.39 (C-3), 74.18 (C-5), 68.35 (C-4), 66.03 (C-2), 62.59, 61.78 (C-A, C-6), 53.74 (C-D), 20.37, 20.32 (3 $COCH_3$); ESI-MS calcd for $C_{28}H_{31}N_3O_8S$ + (Na^+): 592.2; found: 592.3.

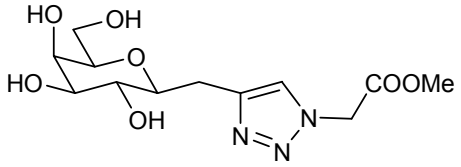


Phenyl 3-*O*-[2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]-1-thio-β-D-galactopyranoside **15** was obtained as a white solid (quant.); 109-110 °C; $[\alpha]^{20}_{D}$ +6.38 (c 0.13 in MeOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (1H, s, $H_{triazole}$), 7.43-7.41 (2H, m, H_{AR}), 7.27-7.22 (8H, m, H_{AR}), 5.49 (2H, s, PhCH_2N), 4.60 (3H, m, H-1, OCH_2C), 3.96 (1H, dd, J = 3.0 Hz, H-

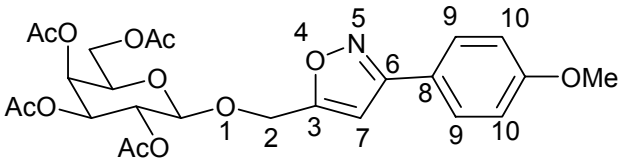
4), 3.60-3.54 (4H, m, H-2, H-5, H-6a, H-6b), 3.46 (1H, dd, J = 3.5, 9.6 Hz, H-3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.37 (C-B), 129.42, 129.24, 128.86, 128.13, 128.03 (12 C_{AR}), 125.39 (C-C), 88.03 (C-1), 81.53 (C-3), 78.86 (C-5), 68.19 (C-4), 65.44 (C-2), 61.76, 61.00 (C-6, C-A), 54.00 (C-D); ESI-MS calcd for $C_{22}H_{25}N_3O_5S$ + (Na^+): 466.1; found: 466.3.



tert-Butyl 2-{4-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosylmethyl)-[1,2,3]triazole-2-yl} acetate **16-OAc** (94%); R_f: 0.5 (AcOEt); $[\alpha]^{20}_D$ +13.2 (c 0.1 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 (1H, s, H-1), 5.40 (1H, d, *J* = 3.3 Hz, H-7), 5.15 (1H, t, *J* = 9.9 Hz, H-5), 4.99 (3H, m, H-1', H-6), 4.11-4.03 (2H, m, H-9), 3.82 (1H, t, *J* = 6.6 Hz, H-8), 3.68 (1H, td, *J* = 9.3, 2.8 Hz, H-4), 3.05 (1H, dd, *J* = 14.4, 2.7 Hz), 2.87 (1H, dd, *J* = 15.4, 9.3 Hz), 2.12 (3H, s, $\underline{CH_3}CO$), 2.02 (3H, s, $\underline{CH_3}CO$), 1.98 (3H, s, $\underline{CH_3}CO$), 1.94 (3H, s, $\underline{CH_3}CO$), 1.44 (9H, s, *t*-Bu); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.25, 170.12, 170.03, 169.86 (4 $CH_3\underline{CO}$), 165.17, 143.61 (C-1'), 123.94 (C-2'), 83.55, 77.18, 74.08, 71.88, 69.05, 67.94 (C-6), 61.59, 51.31, 28.52, 27.83 (t-Bu), 20.68, 20.57, 20.53, 20.48 (4 $\underline{CH_3}CO$).

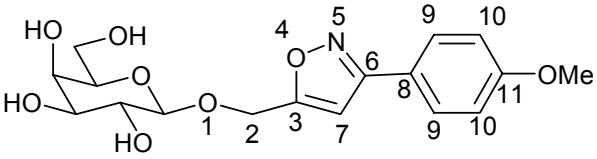


Methyl 2-{4-(β-D-galactopyranosyl)-[1,2,3]triazole-2-yl-methyl} acetate **16** (quant.); ESI-MS calcd for $C_{25}H_{29}NO_{12}$ + (Na^+): 340.1; found: 340.3.

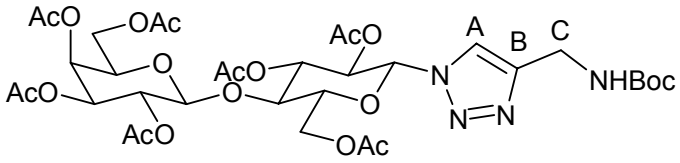


5-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyloxymethyl)-3-(*p*-methoxyphenyl)-isoxazole **18-OAc** was obtained as a white solid (61%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72 (2H, d, *J* = 8.51 Hz, H-9'), 6.96 (2H, d, *J* = 8.79 Hz, H-10'), 6.51 (1H, s, H-7'), 5.39

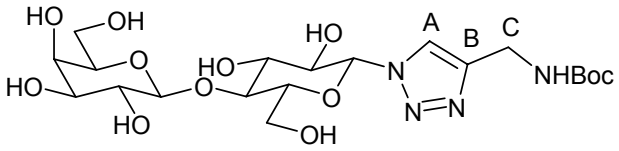
(1H, dd, J = 2.75 Hz, H-4), 5.26 (1H, dd, *J* = 7.97, 10.44 Hz, H-2), 5.02 (1H, dd, *J* = 3.57, 10.44 Hz, H-3), 4.85 (2H, dd, *J* = 13.74, 41.48 Hz, H-2'), 4.63 (1H, d, *J* = 7.97 Hz, H-1), 4.20-4.09 (2H, m, H-6a, H-6b), 3.95 (1H, ddd, *J* = 6.59 Hz, H-5), 3.84 (3H, s, OMe), 2.15 (3H, s, $\underline{CH_3}CO$), 2.03 (3H, s, $\underline{CH_3}CO$), 1.97 (3H, s, $\underline{CH_3}CO$), 1.86 (3H, s, $\underline{CH_3}CO$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.34, 170.13, 169.99, 169.45 (4 $CH_3\underline{CO}$), 168.03 (C-6'), 161.94 (C-11'), 161.02 (C-3'), 128.10 (C-9'), 121.06 (C-8'), 114.28 (C-10'), 101.28 (C-7), 100.31 (C-1), 70.89 (C-5), 70.63 (C-3), 68.45 (C-4), 66.86 (C-2), 61.58 (C-6), 61.18 (C-2'), 55.26 (OMe), 20.64, 20.58, 20.56, 20.47 (4 $\underline{CH_3}CO$); ESI-MS calcd for $C_{25}H_{29}NO_{12}$ + (Na^+): 558.2; found: 558.3.



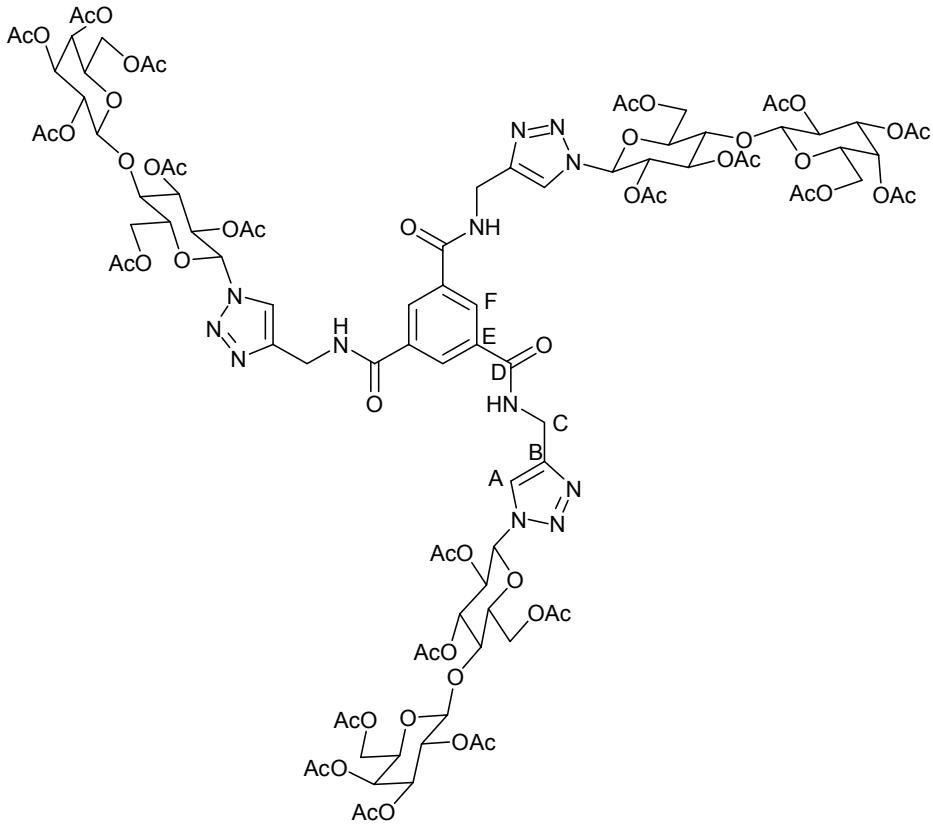
5-(β-D-Galactopyranosyloxymethyl)-3-(p-methoxyphenyl)-isoxazole **18** was obtained as white solid (quant.); mp 134-135 °C; $[\alpha]^{20}_D$ -14.9 (c 0.5 in H_2O); ^1H NMR (300 MHz, $CDCl_3$): δ 7.67 (2H, d, *J* = 8.79 Hz, H-9'), 6.93 (2H, d, *J* = 8.79 Hz, H-10'), 6.77 (1H, s, H-7'), 4.29 (1H, d, *J* = 7.42 Hz, H-1), 3.76 (3H, s, OMe), 3.75-3.61 (2H, m, H-2, H-4), 3.53-3.37 (5H, m, H-2', H-3, H-5, H-6a, H-6b); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.11 (C-6'), 163.52 (C-11'), 162.79 (C-3'), 129.26 (C-9'), 122.49 (C-8'), 115.45 (C-10'), 104.34 (C-7'), 102.48 (C-1), 76.96 (C-5), 74.88 (C-3), 72.41, 70.32, (C-2, C-4), 62.58, 62.36 (C-6, C-2'), 55.84 (OMe); ESI-MS calcd for $C_{17}H_{21}NO_8$ + (Na^+): 390.1; found: 390.3.



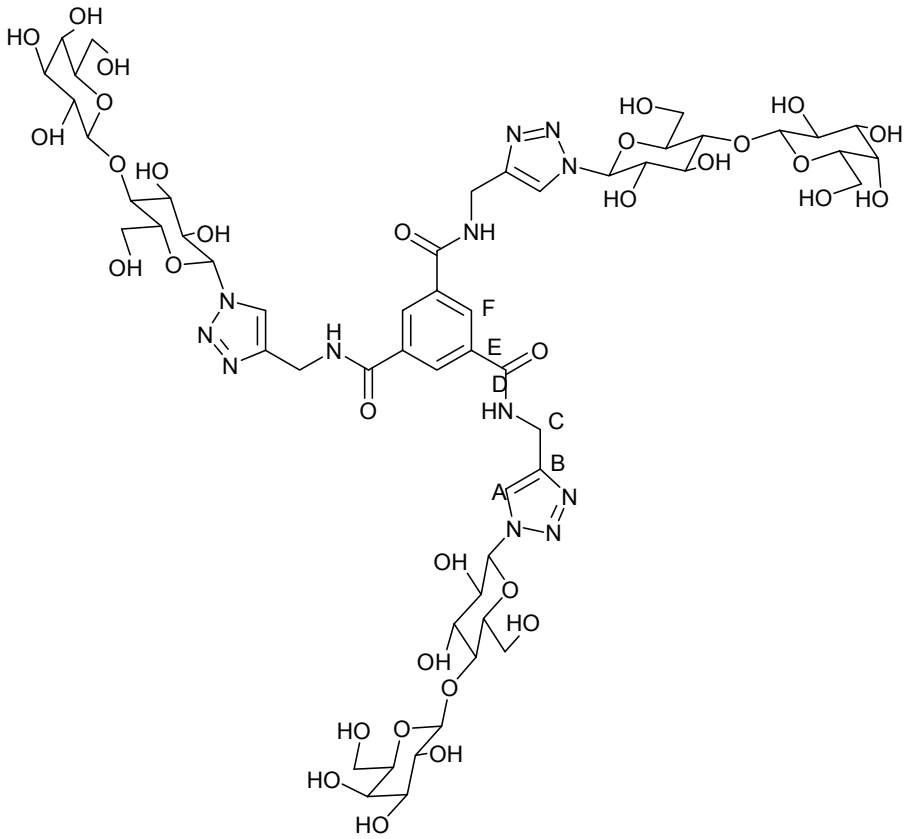
4-(*tert*-Butoxycarbonyl)aminomethyl-1-(2,2',3,3',4',6,6'-hepta-*O*-acetyl-β-D-lactosyl)-[1,2,3]triazole **19-OAc** was isolated as a white solid (98%); mp 176-177 °C; $[\alpha]^{20}_D$ -12.3 (c 1 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.65 (1H, s, H-A), 5.76 (1H, m, NH), 5.36-5.24 (3H, m, H-2, H-3, H-4'), 5.09 (1H, dd, *J* = 7.96, 10.44 Hz, H-2'), 4.93 (1H, dd, *J* = 3.57, 10.44 Hz, H-3'), 4.49-4.42 (3H, m, H-1, H-1', H-6a), 4.41-4.36 (2H, m, H-C), 4.15-4.03 (3H, m, H-6a', H-6b, H-6b'), 3.92-3.84 (3H, m, H-4, H-5, H-5'), 2.13, 2.07, 2.05, 2.03, 2.02, 1.94, 1.84 (21H, 7s, $\underline{CH_3}CO$), 1.41 (9H, s, *t*-Bu); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.33, 170.17, 170.07, 170.01, 169.47, 169.03 (7 $CH_3\underline{CO}$), 155.71 ($N\underline{CO}OC(CH_3)_3$), 146.01 (C-B), 120.42 (C-A), 101.07 (C-1'), 85.47 (C-1), 79.77 ($NCOO\underline{C}(CH_3)_3$), 75.82 (C-4), 75.54 (C-3), 72.55 (C-5), 70.86 (C-3'), 70.79 (C-5'), 70.43 (C-2), 68.98 (C-2'), 66.54 (C-4'), 61.66 (C-6), 60.78 (C-6'), 36.00 (C-C), 28.30 ($NCOOC(\underline{CH_3})_3$), 20.74, 20.66, 20.63, 20.59, 20.57, 20.46, 20.18 (7 $\underline{CH_3}CO$); ESI-MS calcd for $C_{34}H_{48}N_4O_{19}$ + (H^+): 817.3; found: 817.4.



4-(*tert*-Butoxycarbonyl)aminomethyl-1-(β-D-lactosyl)-[1,2,3]triazole **19** was obtained as a white solid (quant.); mp 169 °C; ^{1}H NMR (300 MHz, CD_3OD): δ 7.98 (1H, s, H-A), 5.57 (1H, d, J = 9.06 Hz, H-1), 4.37 (1H, s, H –1'), 4.27 (2H, s, H-C), 3.92-3.34 (12H, m, H-2, H-2', H-3, H-3', H-4, H-4', H-5, H-5', H-6, H-6'), 1.39 (9H, s, *t*-Bu). ESI-MS calcd for $C_{37}H_{55}N_5O_{20}$ + (Na^+): 545.2; found: 545.4.



Compound **20-OAc** was isolated as a white solid (88%); mp 114-115 °C; $[\alpha]^{20}_{D}$ -20.5 (c 1 in $CHCl_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.31, 170.08, 169.98, 169.56, 169.47, 169.06 (21 $CH_3\underline{CO}$), 166.24 (<u>CO</u>NH), 146.11 (C-B), 134.71 (C-F), 128.50 (C-A), 212.44 (C-E), 100.99 (C-1'), 85.42 (C-1), 77.20 (C-4), 75.85 (C-3), 75.48 (C-5), 72.76 (C-3'), 70.88 (C-5'), 70.64 (C-2), 69.08 (C-2'), 66.58 (C-4'), 61.92 (C-6), 60.70 (C-6'), 35.71 (C-C), 20.70, 20.59, 20.46, 20.19 (21 $\underline{CH_3}CO$); ESI-MS calcd for $C_{30}H_{40}N_4O_{18}$ + (Na^+): 767.2; found: 767.2.



Compound **20** was isolated as a white solid (0.95%); mp 200 ^{o}C; ^{1}H NMR (300 MHz, D_2O): δ 8.22 (3H, s, $H_{triazole}$), 8.04 (3H, s, H_{AR}), 5.52 (3H, d, *J* = 9.06 Hz, NH), 4.531 (6H, s, CH_2), 4.28 (3H, d, *J* = 6.59 Hz, H-1'), 3.83-3.39 (36H, m); ^{13}C NMR (75 MHz, D_2O): δ 168.16 (CONH), 144.92 (C-B), 134.32 (C-F), 129.29 (C-A), 123.38 (C-E), 103.06 (C-1'), 87.43 (C-1), 77.83 (C-4), 77.54 (C-3), 75.53 (C-5), 74.65 (C-2), 72.65 (C-3'), 72.11 (C-5'), 71.09 (C-2'), 68.71 (C-4'), 61.20 (C-6'), 59.91 (C-6), 35.21 (C-C).