CHEMBIOCHEM

Supporting Information

Rapid Screening of Lectins for Multivalency Effects with a Glycodendrimer Microarray

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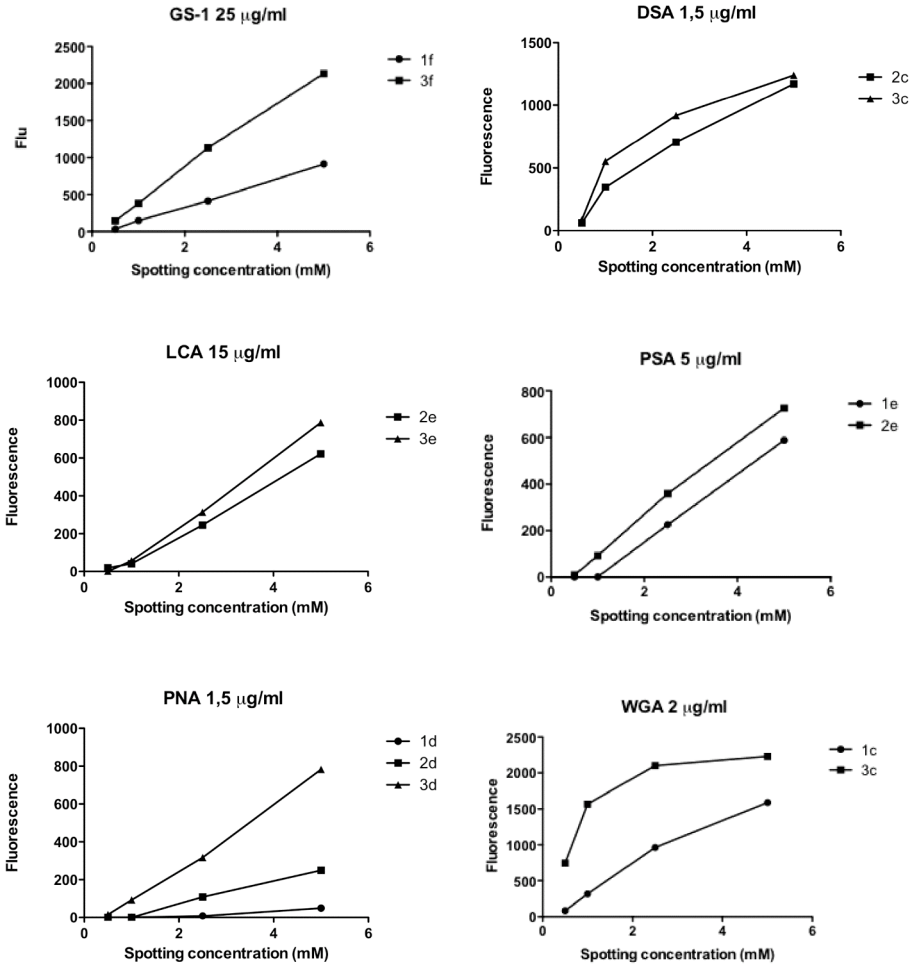
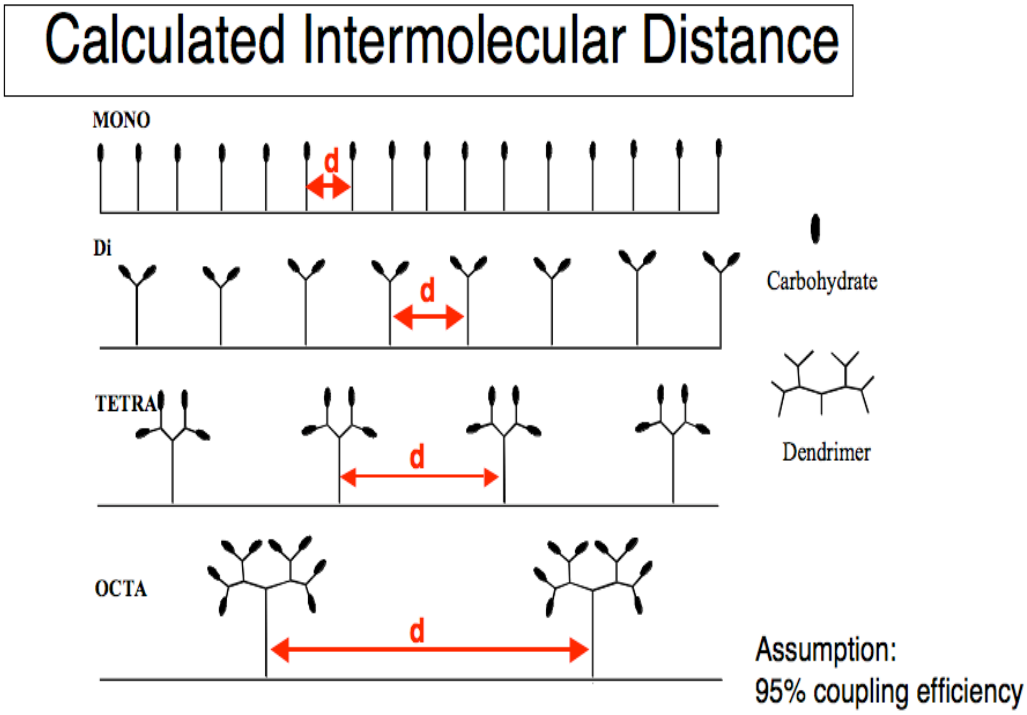
Spotting concentration

The observed signals of binding experiments of the various lectins versus the spotting concentration show a linear correlation in most cases. Below several cases are shown of lectins that give visible binding signals at all spotting concentrations. Notable exceptions are the WGA binding to the tetravalent **3c** and the DSA binding to the di- and tetravalent **2c** and **3c**. In these cases the graph curves downward, indicating relatively less binding at higher spotting concentrations. The origin of this we don't yet fully understand but could be caused by steric crowding. In no case did we observe any upward curves for the monovalent compounds, which could have been an indication of intermolecular chelation, where the monovalent ligands are so close to each other at high spotting concentration that chelation, and thus stronger binding becomes possible. Such intramolecular chelation is theoretically a possibility, as can be deduced from the calculations below for high spotting concentrations along with a very high coupling yield of the ligands to the chip. However, the data indicate that this is not happening.



Estimated distance between spotted compounds

Below are the results of the calculation of intermolecular distance between spotted compounds as a function of the concentration of the spotting solution (0.5 and 5 mM with respect to the carbohydrate concentration) and based on the assumption that the coupling efficiency is 95%. See ref. 13 for details. The spotting concentrations are corrected for valency, so in the case of a 5 mM carbohydrate spotting concentration the monovalent compound is present at 5 mM, the divalent at 2.5 mM, the tetravalent at 1.25 mM and the octavalent at 0.625 mM.

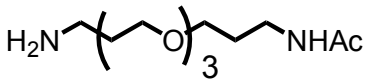


compound	Low: spotting conc. sugars (0.5 mM)	Calcd. Dist. (Å)	High spotting conc. sugars (5 mM)	Calcd. Dist. (Å)
MONO	0.5	87	5	28
Di	0.25	124	2.5	39
TETRA	0.125	175	1.25	55
OCTA	0.0625	247	0.625	78

Spotting with a ‘dummy’ spacer

Due to the large surface area of the aluminium oxide chips, a ‘dummy’ spacer that contains no sugar was previously found not to be necessary,[1] since many maleimides are available on the surface. This is in agreement with the linear correlation between spotting concentration and observed binding signal. Nevertheless the experiment was repeated here and the results are shown below. There is no significant difference between experiments spotted with or without the ‘dummy’ spacer.

The ‘dummy’ spacer, i.e. the spacer with a functional amino group for attachment to the chip, but with a sugar attached:



With ‘dummy’ spacer

Spotting concentrations:

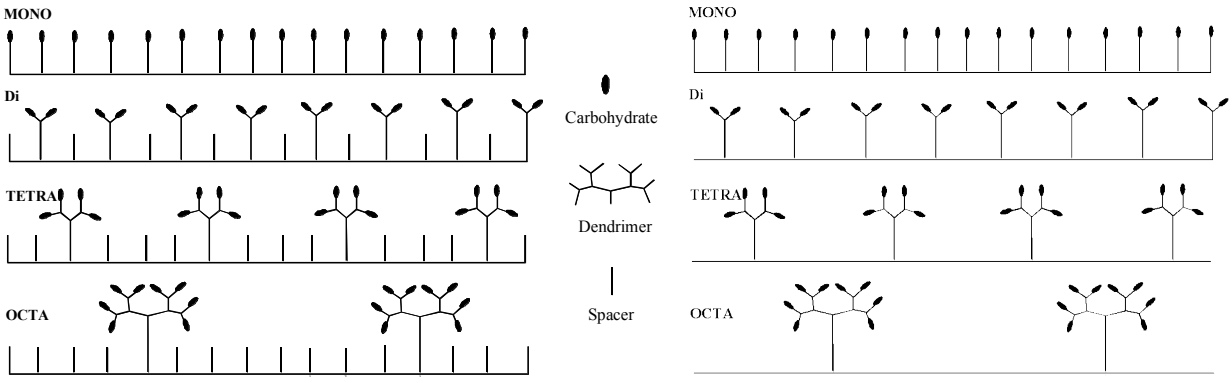
- Mono (**1d**, **1e**) : 2.5 mM + dummy: 0 mM
- Di (**2d, 2e**): 1.25 mM + dummy: 1.25 mM
- Tetra (**3d, 3e**): 0.625 mM + dummy: 1.875 mM
- Octa (**4e**): 0.3125 mM + dummy: 2.1875 mM

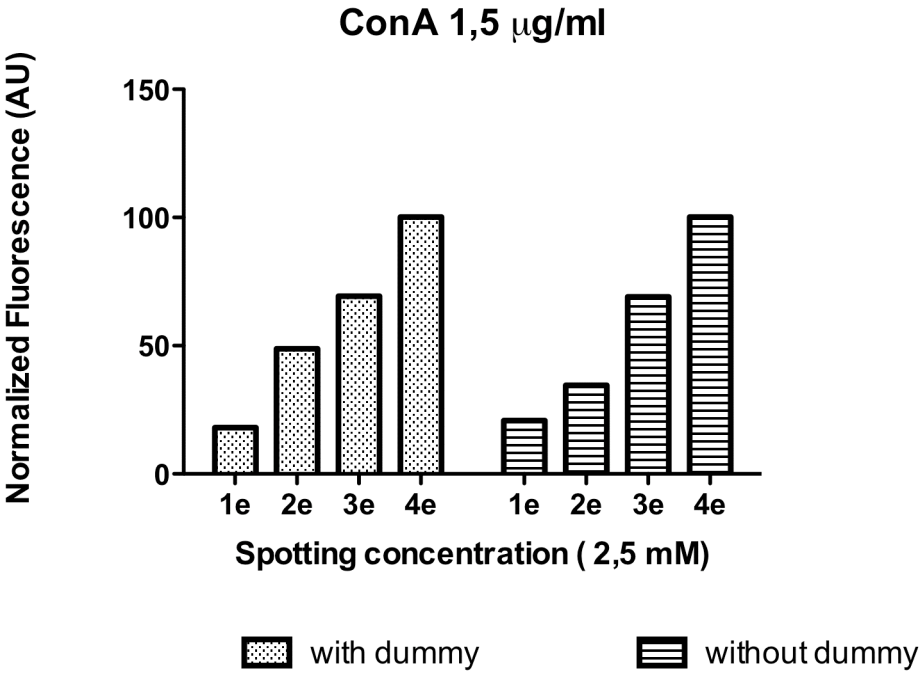
Without ‘dummy’ spacer

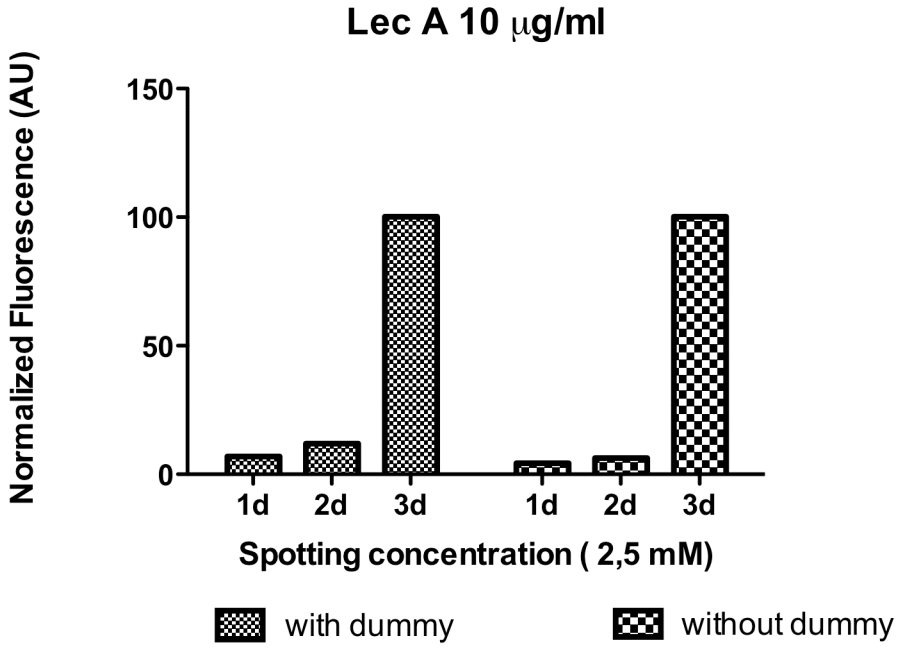
Spotting concentrations:

- Mono (**1d**, **1e**): 2.5 mM
- Di (**2d, 2e**): 1.25 mM
- Tetra (**3d, 3e**): 0.625 mM
- Octa (**4e**): 0.3125 mM

Schematic situation on the chip:

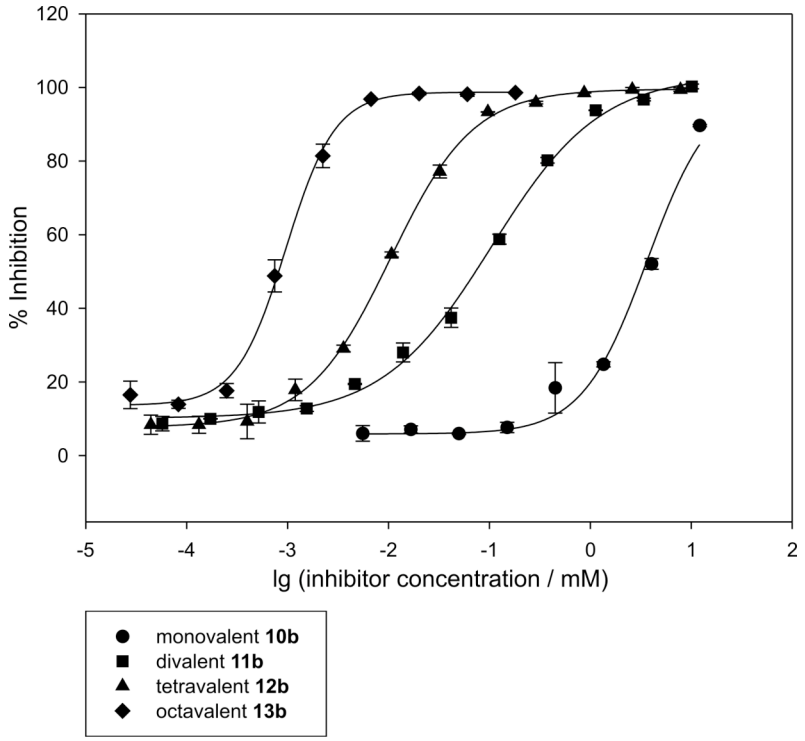



ConA 1,5 μg/ml
Normalized Fluorescence (AU)
150
100
50
0
1e
2e
3e
4e
1e
2e
3e
4e
Spotting concentration (2,5 mM)
with dummy
without dummy


Lec A 10 μg/ml
Normalized Fluorescence (AU)
150
100
50
0
1d
2d
3d
1d
2d
3d
Spotting concentration (2,5 mM)
with dummy
without dummy

ELLA with WGA

Enzyme-linked lectin assays (ELLA) were carried out as previously described.[2] Briefly, microtiter plates with covalently immobilized GlcNAc as reference ligand were incubated with mixtures of horseradish peroxidase (HRP)-labeled WGA (1 mg mL^{-1}) and synthetic WGA ligands **10-13b** in varying concentrations. After incubation, the plates were washed and remaining labeled WGA bound to the reference ligand was quantified by a HRP-catalyzed color reaction using 2,2'-azinobis(3-ethyl-benzo-thiazoline-6-sulfonic acid) diammonium salt (ABTS) as substrate. Dose-response curves for inhibition of the binding of HRP-labeled WGA to immobilized GlcNAc are shown in the figure below. From these curves the concentrations that reduce the binding of labeled WGA to the microtiter plates by 50% (IC_{50} values) were determined as a measure of potency of the synthesized inhibitors (Table 1).

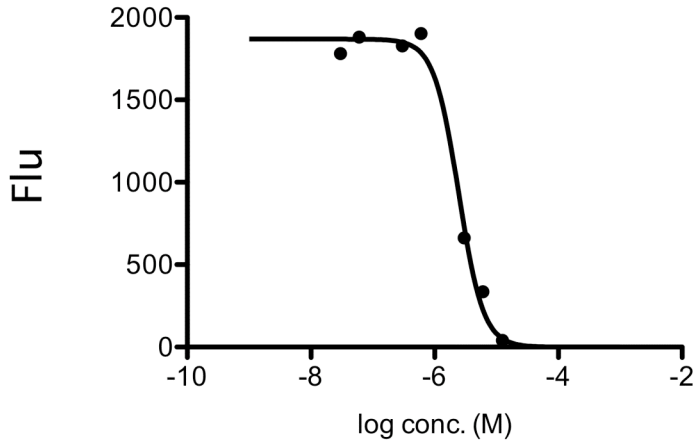


Dose-response curves for inhibition of the binding of HRP-labeled WGA to covalently modified microtiter plates by synthetic ligands **10-13b**

Inhibition of LecA by soluble glycodendrimers

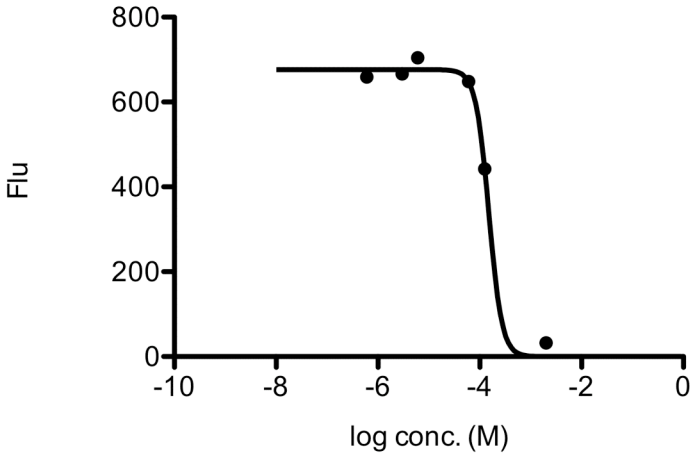
Exemplary inhibition curves and curve fitting of lecA binding to the spots of **1d** on the chip. The IC_{50}'s obtained for binding and inhibition to spots of **2d** and **3d** gave similar values and results were averaged.

Inhibition by tetravalent **3d:**



	flu
log(inhibitor) vs. response -- Variable slope	
Best-fit values	
Bottom	= 0.0
Top	1869
LogIC50	-5.612
HillSlope	-2.186
IC50	2.444e-006
Span	= 1869
Std. Error	
Top	56.28
LogIC50	0.05472
HillSlope	0.5357
95% Confidence Intervals	
Top	1712 to 2025
LogIC50	-5.764 to -5.460
HillSlope	-3.673 to -0.6989
IC50	1.723e-006 to 3.468e-006
Goodness of Fit	
Degrees of Freedom	4
R^2	0.9907
Absolute Sum of Squares	37775
Sy.x	97.18
Constraints	
Bottom	Bottom = 0.0
Number of points	
Analyzed	7

Inhibition by monovalent **1d:**



	flu
log(inhibitor) vs. response -- Variable slope	
Best-fit values	
Bottom	= 0.0
Top	676.5
LogIC50	-3.821
HillSlope	-3.372
IC50	0.0001509
Span	= 676.5
Std. Error	
Top	15.61
LogIC50	0.04366
HillSlope	1.499
95% Confidence Intervals	
Top	626.8 to 726.1
LogIC50	-3.960 to -3.682
HillSlope	-8.143 to 1.399
IC50	0.0001096 to 0.0002078
Goodness of Fit	
Degrees of Freedom	3
R^2	0.9935
Absolute Sum of Squares	2190
Sy.x	27.02
Constraints	
Bottom	Bottom = 0.0
Number of points	
Analyzed	6

Synthesis

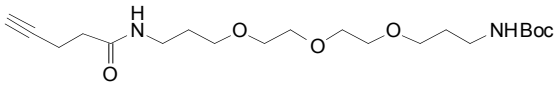
General: Unless stated otherwise, chemicals were obtained from commercial sources and were used without further purification. Solvents were purchased from Biosolve (Valkenswaard, The Netherlands). Microwave reactions were carried out in a dedicated microwave oven, that is, the Biotage Initiator (Uppsala, Sweden). The microwave power was limited by temperature control once the desired temperature was reached. A sealed vessel of 2–5 mL was used. Analytical HPLC runs were performed on a Shimadzu automated HPLC system with a reversed-phase column (Alltech, Adsorbosphere C8, 90 M, 5 mm, 250L4.6 mm, Deerfield, IL, USA) that was equipped with an evaporative light-scattering detector (PLELS 1000, Polymer Laboratories, Amherst, MA, USA) and a UV/Vis detector that was operating at 220 and 254 nm. Preparative HPLC runs were performed on a Applied Biosystems workstation. Elution was effected by using a linear gradient of 5% MeCN/0.1% TFA in H_2O to 5% H_2O/0.1% TFA in MeCN or by a gradient of 5% MeOH/0.1% TFA in H_2O to 5% H_2O/0.1% TFA in MeOH. ^1H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) were performed on a Varian G-300 spectrometer.

General "click" conditions:

Alkyne dendrimer, sugar azide (1.5 equiv/alkyne), $CuSO_4$ (0.15 equiv/alkyne) and sodium ascorbate (0.3 equiv/alkyne) were dissolved in an appropriate volume of 1% H_2O in DMF. The mixture was heated under microwave irradiation to 80 ^oC for 20 min. The mixture was concentrated *in vacuo* and the product was isolated by silica gel chromatography. Compounds **1e–4e** were synthesized according to previously publications.[1]

General deprotection procedure:

Dendrimers were dissolved in MeOH. Catalytic NaOMe was added, and the reaction was stirred until TLC showed full deacetylation. The mixture was neutralized with Dowex H^+, filtered and concentrated *in vacuo*. The residue was stirred in 5% H_2O in TFA for 1 h. Solvents were evaporated and the product was purified by preparative HPLC and lyophilized from H_2O/MeCN.



Precursor of 1f: A solution of 1-*N*-*tert*-Butoxycarbonyl-4,7,10-trioxa-1,13-tridecanediamine[3] (160 mg, 0.5 mmol) was dissolved in CH_2Cl_2. Pentynoic acid (73.5 mg, 0.75 mmol) and $^iPr_2EtN$ (0.09 mL, 0.5 mmol) were added together with BOP (331.7 mg, 0.75 mmol) to the reaction mixture and stirred for 18 h. Crude product was taken up in EtOAc (100 mL) and washed twice with H_2O (50 mL) and with brine (50 mL). The organic phase was dried over Na_2SO_4, filtered and concentrated. The product was isolated by silica gel chromatography (130 mg, 65%). ^1H NMR (300 MHz, $CDCl_3$): δ = 6.3 (1H, s, NH), 4.9 (1H, s, NH), 3.6 (12H, m, OCH_2), 3.3 (2H, q, *J* = 6.0 Hz, $OCH_2CH_2CH_2NH$), 3.2 (2H, q, *J* = 6.0 Hz, $OCH_2CH_2CH_2NH$), 2.5 (2H, m, $C(O)CH_2CH_2CCH$), 2.3 (2H, t, *J* = 7.1 Hz,

CH_2CH_2CCH), 1.9 (1H, q, *J* = 3.0 Hz, CH_2CH_2CCH), 1.7 (4H, q, *J* = 6.0 Hz, $OCH_2CH_2CH_2NH$), 1.4 (9H, s, $NHC(O)OC(CH_3)_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.4, (C(O)NH), 156.4 ($NHC(O)C(CH_3)_3$), 83.3 (*C*CH), 79.2 ($NHC(O)OC(CH_3)_3$), 70.5, 70.2, 69.8, 69.4, 69.3 (4 x CH_2CH_2O and CCH), 38.4, 37.7 (2 x CH_2NH), 35.4 ($C(O)CH_2$), 29.8, 29.1 (2 x $OCH_2CH_2CH_2NH$), 28.6 ($NHC(O)OC(CH_3)_3$). ESMS for $C_{20}H_{36}N_2O_6$ (M: 400.26, $[M+Na]^+$: 423.25): found $[M+Na]^+$ 423.5.

Galabiose derivative (1f): A "click" reaction of **1a**[i] and the galabiose derivative **9** was performed according to the general procedure. Protected galabiose derivative was isolated by silica gel chromatography (EtOAc/MeOH, 1/0 → 4/1) (125 mg, 90%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.4 (1H, s, $CH_{triazole}$), 6.4 (1H, s, NH), 5.59 (1H, d, *J* = 2.7 Hz, H-4'), 5.4 (1H, dd, $J_{3',4'}$ = 3.3 Hz, $J_{2',3'}$ = 7.7 Hz), 5.3 – 5.2 (2H, m, H-2, H-2'), 5.0 (2H, d, *J* = 3.5 Hz, H-1'), 4.8 (1H, dd, $J_{3,4}$ = 2.7 Hz, $J_{2,3}$ = 8.2 Hz, H-3), 4.5 – 4.4 (5H, m), 4.2 – 4.0 (4H, m), 3.9 – 3.8 (2H, m, H-5, H-5'), 3.7 – 3.5 (13H, m), 3.3 (2H, dd, *J* = 7.4 Hz, 6.3 Hz, $OCH_2CH_2CH_2N_{triazole}$), 3.2 (2H, q, *J* = 6.3 Hz, $CH_2CH_2NHC(O)OC(CH_3)_3$), 3.0 (2H, t, *J* = 7.4 Hz, $OCH_2CH_2CH_2N_{triazole}$), 2.6 (2H, t, *J* = 6.3 Hz, $OCH_2CH_2CH_2N_{triazole}$), 2.1 – 1.9 (21H, m, 6 x $C(O)CH_3$, $NHC(O)CH_3$), 1.7 – 1.4 (6H, m, $OCH_2CH_2CH_2NH$), 2.6 (9H, s, $NHC(O)OC(CH_3)_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 172.0, 170.9, 170.7, 170.4, 170.2, 169.5 ($C(O)CH_3$), 156.3 (C(O)NH), 146.8 ($NHC(O)C(CH_3)_3$), 122.0 ($CH_2C_{triazole}$), 101.3 (C-1), 99.8 (C-1'), 79.1, 72.9, 72.2, 70.7, 70.4, 70.1, 69.7, 68.9, (C-2, C-2', C-3, C-3', C-4, C-4', C-5, C-5') 68.1, 67.6, 67.4 (OCH_2) 66.0 (CH_2O_{gal}), 62.2, 60.7 (C-6, C-6'), 46.8 ($CH_2N_{triazole}$), 38.7 ($CH_2NHC(O)OC(CH_3)_3$), 38.0 ($C(O)NHCH_2$), 35.9, 30.5, 29.9, 29.2 ($OCH_2CH_2CH_2NH$, $OCH_2CH_2CH_2N_{triazole}$), 28.7 ($NHC(O)OC(CH_3)_3$), 21.7, 21.2, 20.9 ($C(O)CH_3$). ESMS for $C_{49}H_{77}N_5O_{24}$ (M: 1119.5, $[M+Na]^+$: 1142.49): found $[M+H]^+$ 1120.5, $[M+Na]^+$ 1142.4. Deprotection reaction was performed by the general procedure. Deprotected galabiose derivative was isolated by preparative HPLC (36.3 mg, 95%). ^1H NMR (300 MHz, D_2O): δ = 7.7 (1H, s, $CH_{triazole}$), 4.8 (1H, s, H-1'), 4.71 (2H, m, $CH_2N_{triazole}$), 4.7 – 4.6 (15H, m), 4.5 (1H, s, H-1), 4.4 (2H, t, *J* = 6.3 Hz, OCH_2CH_2), 4.3 (2H, q, *J* = 8.0 Hz, OCH_2CH_2), 3.9 (2H, s, NH_2), 3.8 – 3.6 (5H, m), 3.6 – 3.4 (15H, m), 3.3 (2H, t, *J* = 6.0 Hz, CH_2NH_3), 3.0 (2H, t, *J* = 6.8 Hz, $OCH_2CH_2CH_2NH_2$), 2.9 (2H, t, *J* = 6.8 Hz, $CH_2CH_2C(O)NH$), 2.8 (2H, t, *J* = 6.8 Hz, $OCH_2CH_2CH_2NH_2$), 2.5 (2H, t, *J* = 7.1 Hz, $CH_2CH_2C(O)NH$), 2.0 (2H, t, *J* = 6.0 Hz, $OCH_2CH_2CH_2N_{triazole}$), 1.8 (2H, t, *J* = 6.3 Hz, $OCH_2CH_2CH_2NH_2$), 1.5 (2H, t, *J* = 6.3 Hz, $OCH_2CH_2CH_2NH$). ^{13}C NMR (from HSQC, D_2O): δ = 105.4 (C-1), 103.3 (C-1'), 79.7, 77.8, 75.3, 73.6, 73.2, 72.9, 71.9, 71.7, 71.5, 71.4, 71.0, 70.9, 70.6, (C-2, C-2', C-3, C-3', C-4, C-4', C-5, C-5', OCH_2), 69.2, 69.0 (OCH_2), 62.9 (CH_2O_{gal}), 62.2, (C-6, C-6'), 49.4 ($CH_2N_{triazole}$), 40.3, 38.6 (CH_2NH_3), 37.4 ($C(O)NHCH_2$), 32.3, 30.2, 28.7, 23.5 ($OCH_2CH_2CH_2NH$, $OCH_2CH_2CH_2N_{triazole}$). ESMS for $C_{30}H_{55}N_5O_{15}$ (M: 728.5, $[M+Na]^+$: 751.49): found $[M+Na]^+$ 750.5.

Tetravalent galabiose dendrimer (3f): A "click" reaction of **3a**[i] and the galabiose derivative **9** was performed according to the general procedure. Protected tetravalent galabiose dendrimer was isolated by silica gel chromatography (EtOAc/MeOH, 1/0 → 4/1) (95.8 mg, 65%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.4 (4H, s, $CH_{triazole}$), 7.2 (2H, s, C(O)NH), 6.9 (2H, s, CH_{arom}), 6.9 (4H, s, CH_{arom}), 6.6 (1H, s, CH_{arom}), 6.4 (2H, s, CH_{arom}), 5.6 (4H, d, $J_{3,4}$ = 2.6 Hz, H-4'), 5.4 (4H, dd, $J_{3',4'}$ = 2.6 Hz, $J_{2',3'}$ = 10.8 Hz, H-3'), 5.2 (8H, td, $J_{4,5}$ = 4.0 Hz, $J_{5,6}$ = 7.8 Hz, H-5, H-5'), 4.9 (4H, d, $J_{1',2'}$ = 3.6 Hz, H-1'), 4.8 (8H, dd, *J* = 2.6 Hz, 7.8 Hz, H-6), 4.5 – 4.2 (20H, m), 4.2 – 4.0 (20H, m, CH), 3.9 – 3.8 (8H, m), 3.7 – 3.6 (12H, m), 3.6 – 3.5 (18H, m, CH), 3.5 – 2.6 (24H, m, $C(O)CH_3$), 2.0 (8H, m, $OCH_2CH_2CH_2NH$),

1.4 (9H, s, NHC(O)OC(CH_3)$_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 170.9, 170.7, 170.4, 170.3, 169.6 (*C*(O)CH_3), 160.1 (C(O)NH), 159.9 (C_{arom}-3'5'), 143.0 ($C_{triazole}$-4), 136.6 (C_{arom}-1'), 106.4 (C_{arom}-2,6), 101.3 (C-1), 99.7 (C-1'), 72.9, 72.2, 70.5, 68.9, 68.8, 68.1, 67.6, 67.4, 67.1, 66.0 (C-2, C-2', C-3, C-3', C-4, C-4', C-5, C-5', OCH_2), 62.1, 60.8 (C-6, C-6'), 39.0, (*C*H_2NHC(O)) 31.1, 29.8 (OCH_2*C*H_2CH_2NH, OCH_2*C*$H_2CH_2N_{triazole}$), 28.6 (OCH_2*C*H_2CH_2NH, OCH_2*C*$H_2CH_2N_{triazole}$), 21.2, 20.9 (C(O)*C*H_3). Deprotection reaction was performed by the general procedure. Deprotected tetravalent galabiose dendrimer was isolated by preparative HPLC (30 mg, 83%). ^{1}H NMR (300 MHz, D_2O): δ = 7.52 (4H, s, $CH_{triazole}$), 6.77 (2H, s, CH_{arom}-2',6'), 6.63 (4H, s, CH_{arom}-2,6), 6.42 (2H, s, CH_{arom}-4'), 4.81 (4H, d, $J_{3,4}$ = 3.0 Hz, H-1'), 4.21 – 4.07 (16H, m, H-2, H-2', $OCH_2C_{triazole}$), 3.87 – 3.78 (8H, m), 3.75 (4H, m), 3.71 – 3.67 (10H, m), 3.56 (12H, d, *J* = 6.0 Hz), 3.52 – 3.46 (15H, m), 3.41 – 3.36 (10H, m), 3.29 – 3.21 (6H, m), 2.95 (2H, t, *J* = 6.9 Hz, *C*H_2NH_2), 2.80 (8H, t, *J* = 6.0 Hz, O*C*$H_2CH_2CH_2N_{triazole}$), 2.44 (8H, t, *J* = 6.6 Hz, OCH_2*C*$H_2CH_2N_{triazole}$), 1.81 – 1.69 (12H, m, OCH_2*C*H_2CH_2NH). ^{13}C NMR (from HSQC, D_2O): δ = 126.9 ($C_{triazole}$-5), 109.5, 109.1, 108.4 (C_{arom}), 106.2, 103.4 (C-1), 80.3, 80.0, 77.8, 75.0, 73.1, 71.9, 70.3, 70.0, 69.4, 69.1, (C-2, C-2', C-3, C-3', C-4, C-4', C-5, C-5', OCH_2), 63.4, 63.1, 62.8, 62.5 (C-6, C-6') 49.1, ($CH_2N_{triazole}$), 42.2, 41.9, 40.6, 40.0, (*C*H_2NHC(O)), 37.8, 32.5, 30.9, 29.0, 23.4 (OCH_2*C*H_2CH_2NH, OCH_2*C*$H_2CH_2N_{triazole}$). MALDI-TOF for $C_{123}H_{190}N_{20}O_{60}$ (M: 2908.92, $[M+Na]^+$: 2930.91): found $[M+Na]^+$ 2930.3.

Galactose derivative (1d): A "click" reaction of **1a**^{i} and the galactose derivative **7** was performed according to the general procedure. Protected galactose derivative was isolated by silica gel chromatography (CH_2Cl_2/MeOH, 19/1 → 9/1) (44 mg, quant.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (1H, s, $CH_{triazole}$), 7.49 (1H, d, CH_{arom}-6), 7.37 – 7.29 (2H, m, CH_{arom}-2,5), 7.17 (1H, bs, C(O)NH), 7.12 – 7.08 (1H, m, CH_{arom}-4), 5.39 (1H, dd, H-4, $J_{3,4}$ = 3.6 Hz, $J_{4,5}$ = 1.2 Hz), 5.25 – 5.18 (3H, m, H-2, $OCH_2C_{triazole}$), 5.02 (1H, dd, H-3, $J_{2,3}$ = 10.8 Hz, $J_{3,4}$ = 3.6 Hz), 4.98 (1H, bs, N*H*C(O)OC(CH_3)$_3$), 4.46 (1H, d, H-1, $J_{1,2}$ = 8.1 Hz), 4.55 – 4.37 and 3.90 – 3.86 (2 x 1H, 2 x m, CH_2O_{gal}), 4.15 (2H, dd, H-6, $J_{5,6}$ = 2.1 Hz, $J_{6a,6b}$ = 6.9 Hz), 3.93 – 3.90 (1H, m, H-5), 3.67 – 3.44 (16H, m, $CH_2N_{triazole}$, *C*H_2NHC(O), CH_2O), 3.22 – 3.16 (2H, m, *C*H_2NHC(O)OC(CH_3)$_3$), 2.21 – 2.09 (2H, m, OCH_2*C*$H_2CH_2N_{triazole}$), 2.16, 2.09, 2.03 and 1.99 (4 x 3H, 4 x s, C(O)CH_3), 1.94 – 1.86 and 1.75 – 1.67 (2 x 2H, 2 x m, OCH_2*C*H_2CH_2NH) and 1.43 (9H, s, NHC(O)OC(CH_3)$_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 170.3, 170.1 and 169.6 (*C*(O)CH_3), 166.8 (C(O)NH), 158.3 (C_{arom}-3), 156.0 (NH*C*(O)C(CH_3)$_3$), 143.7 ($C_{triazole}$-4), 136.4 (C_{arom}-1), 129.5 (C_{arom}-5), 123.2 ($C_{triazole}$-5), 119.3 (C_{arom}-6), 117.9 (C_{arom}-4), 113.4 (C_{arom}-2), 101.1 (C-1), 78.9 (NHC(O)O*C*(CH_3)$_3$), 70.7, 68.7 and 66.9 (C-2, C-3, C-4, C-5), 70.4, 70.0 and 69.4 (OCH_2), 65.6 (CH_2O_{gal}), 62.0 (O*C*$H_2C_{triazole}$), 61.2 (C-6), 46.7 ($CH_2N_{triazole}$), 38.8 (*C*H_2NHC(O)OC(CH_3)$_3$), 38.5 (*C*H_2NHC(O)), 30.1, 29.6 and 28.8 (OCH_2*C*H_2CH_2NH, OCH_2*C*$H_2CH_2N_{triazole}$), 28.4 (NHC(O)OC(*C*H_3)$_3$), 20.8 and 20.6 (C(O)*C*H_3). Deprotection was performed according to the general procedure. Deprotected galactose derivative was isolated by preparative HPLC (12 mg, 48%). ^{1}H NMR (300 MHz, D_2O): δ = 7.66 (1H, s, $CH_{triazole}$), 7.49 (1H, d, CH_{arom}-6), 7.37 – 7.29 (2H, m, CH_{arom}-2,5), 7.17 (1H, bs, C(O)NH), 7.12 – 7.08 (1H, m, CH_{arom}-4), 5.39 (1H, dd, H-4, $J_{3,4}$ = 3.6 Hz, $J_{4,5}$ = 1.2 Hz), 5.25 – 5.18 (3H, m, H-2, $OCH_2C_{triazole}$), 5.02 (1H, dd, H-3, $J_{2,3}$ = 10.8 Hz, $J_{3,4}$ = 3.6 Hz), 4.46 (1H, d, H-1, $J_{1,2}$ = 8.1 Hz), 4.55 – 4.37 and 3.90 – 3.86 (2 x 1H, 2 x m, CH_2O_{gal}), 4.15 (2H, dd, H-6, $J_{5,6}$ = 2.1 Hz, $J_{6a,6b}$ = 6.9 Hz), 3.93 – 3.90 (1H, m, H-5), 3.67 – 3.44 (16H, m, $CH_2N_{triazole}$, *C*H_2NHC(O), CH_2O), 3.22 – 3.16 (2H, m, *C*H_2NHC(O)OC(CH_3)$_3$), 2.21 – 2.09 (2H, m, OCH_2*C*$H_2CH_2N_{triazole}$), 1.94 – 1.86 and 1.75 – 1.67 (2 x 2H, 2 x m, OCH_2*C*H_2CH_2NH). ^{13}C NMR (75.5 MHz, D_2O:Acetone): δ = 216.1 (acetone

residual peak), 170.6 (C(O)NH), 158.2 (C_{arom}-3), 143.8 ($C_{triazole}$-4), 136.1 (C_{arom}-1), 130.8 (C_{arom}-5), 121.1 ($C_{triazole}$-5), 119.7 (C_{arom}-6), 119.5 (C_{arom}-4), 114.7 (C_{arom}-2), 103.5 (C-1), 75.8, 73.4 and 71.4 (C-2, C-3, C-4, C-5), 70.3, 70.0 and 69.4 (OCH_2), 66.8 (CH_2O_{gal}), 62.2 ($OCH_2C_{triazole}$), 61.5 (C-6), 47.7 ($CH_2N_{triazole}$), 38.3 (CH_2NH_3), 37.9 ($CH_2NHC(O)$), 30.9 (acetone residual peak), 30.1, 28.9 and 27.1 ($OCH_2CH_2CH_2NH$, $OCH_2CH_2CH_2N_{triazole}$). MALDI-TOF for $C_{29}H_{47}N_5O_{11}$ (M: 641.7): found $[M+H]^+$ 642.7.

Divalent galactose dendrimer (2d): A "click" reaction of **2a**^{i} and the galactose derivative **7** was performed according to the general procedure. Protected divalent galactose dendrimer was isolated by silica gel chromatography (CH_2Cl_2/MeOH, 19/1 → 9/1) (58 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (2H, s, $CH_{triazole}$), 7.15 (1H, bs, C(O)NH), 7.06 (2H, d, CH_{arom}-2,6), 6.75 (1H, t, CH_{arom}-4), 5.40 (2H, d, $J_{3,4}$ = 3.3 Hz, H-4), 5.24 – 5.18 (7H, m, H-2, $CH_2C_{triazole}$, $NHC(O)OC(CH_3)_3$), 5.03 (2H, dd, $J_{2,3}$ = 10.5 Hz, $J_{3,4}$ = 3.6 Hz, H-3), 4.47 (2H, d, $J_{1,2}$ = 8.1 Hz, H-1), 4.55 – 4.38 and 3.95 – 3.87 (2 x 2H, 2 x m, CH_2O_{gal}), 4.15 (4H, dd, $J_{5,6}$ = 2.7 Hz, $J_{6a,6b}$ = 6.9 Hz, H-6), 3.95 – 3.88 (2H, m, H-5), 3.64 – 3.44 (18H, m, $CH_2N_{triazole}$, $CH_2NHC(O)$), CH_2O), 3.22 – 3.16 (2H, m, $CH_2NHC(O)OC(CH_3)_3$), 2.23 – 2.13 (4H, m, $OCH_2CH_2CH_2N_{triazole}$), 2.16, 2.09, 2.03 and 1.99 (4 x 6H, 4 x s, $C(O)CH_3$), 1.93 – 1.85 and 1.75 – 1.66 (2 x 2H, 2 x m, $OCH_2CH_2CH_2NH$) and 1.42 (9H, s, $NHC(O)OC(CH_3)_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 170.3, 170.1, 170.0 and 169.5 ($C(O)CH_3$), 166.7 (C(O)NH), 159.3 (C_{arom}-3,5), 156.0 ($NHC(O)C(CH_3)_3$), 137.2 (C_{arom}-1), 106.3 (C_{arom}-2,6), 104.8 (C_{arom}-4), 101.1 (C-1), 78.8 ($NHC(O)C(CH_3)_3$), 70.7, 68.7 and 66.9 (C-2, C-3, C-4, C-5), 70.3, 70.2, 70.0 and 69.3 (OCH_2), 65.6 (CH_2O_{gal}), 62.0 ($OCH_2C_{triazole}$), 61.2 (C-6), 46.7 ($CH_2N_{triazole}$), 38.5 ($CH_2NHC(O)OC(CH_3)_3$), 30.1, 29.5 and 28.9 ($OCH_2CH_2CH_2NH$, $OCH_2CH_2CH_2N_{triazole}$), 28.3 ($NHC(O)OC(CH_3)_3$), 20.8 and 20.6 ($C(O)CH_3$). Deprotection was performed according to the general procedure. Deprotected divalent galactose dendrimer was isolated by preparative HPLC (23 mg, 76%). ^{1}H NMR (300 MHz, D_2O): δ = 8.11 (2H, s, $CH_{triazole}$), 6.99 (2H, d, CH_{arom}-2,6), 6.82 (1H, t, CH_{arom}-4), 5.22 (4H, s, $CH_2C_{triazole}$), 4.55 (1H, t), 4.24 (2H, d, $J_{1,2}$ = 7.8 Hz, H-1), 3.90 (2H, d, $J_{3,4}$ = 2.7 Hz, H-4), 3.88 – 3.78 (2H, m), 3.76 – 3.70 (4H, m), 3.65 – 3.40 (20H, m), 3.08 (2H, t, CH_2NH_3), 2.22 – 2.17 (4H, m, $OCH_2CH_2CH_2N_{triazole}$) and 1.93 – 1.85 (4H, m, $OCH_2CH_2CH_2NH$). ^{13}C NMR (75.5 MHz, D_2O): δ = 169.8 (C(O)NH), 159.4 (C_{arom}-3,5), 143.5 ($C_{triazole}$-4), 136.8 (C_{arom}-1), 108.0 (C_{arom}-2,6), 106.5 (C_{arom}-4), 103.5 (C-1), 75.7, 73.4, 71.4 and 69.2 (C-2, C-3, C-4, C-5), 70.0, 69.5 and 68.9 (OCH_2), 66.8 (CH_2O_{gal}), 62.2 ($OCH_2C_{triazole}$), 61.6 (C-6), 47.8 ($CH_2N_{triazole}$), 38.3 and 38.1 (CH_2NH, CH_2NH_3), 30.2, 28.9 and 27.1 ($OCH_2CH_2CH_2NH$, $OCH_2CH_2CH_2N_{triazole}$). MALDI-TOF for $C_{41}H_{66}N_8O_{18}$ (M: 958.4): found $[M+H]^+$ 959.6.

Tetravalent galactose dendrimer (3d): A "click" reaction of **3a**^{i} and the galactose derivative **7** was performed according to the general procedure. Protected tetravalent galactose dendrimer was isolated by silica gel chromatography (CH_2Cl_2/MeOH, 19/1 → 9/1) (60 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69 (4H, s, $CH_{triazole}$), 7.25 (3H, bs, C(O)NH), 7.07 (4H, s, CH_{arom}-2',6'), 6.98 (2H, s, CH_{arom}-2,6), 6.74 (1H, s, CH_{arom}-4'), 6.63 (1H, s, CH_{arom}-4), 5.39 (4H, d, $J_{3,4}$ = 3.0 Hz, H-4) 5.23 – 5.17 (12H, m, H-2, $OCH_2C_{triazole}$), 5.03 (4H, dd, $J_{2,3}$ = 10.5 Hz, $J_{3,4}$ = 3.3 Hz, H-3), 4.47 (4H, d, $J_{1,2}$ = 8.1 Hz, H-1), 4.55 – 4.38 and 3.90 – 3.84 (2 x 4H, 2 x m, CH_2O_{gal}), 4.20 – 4.09 (12H, m, H-6, OCH_2CH_2NH), 3.95 – 3.90 (4H, m, H-5), 3.84 – 3.76 (4H, m, OCH_2CH_2NH), 3.62 – 3.41 (18H, m, $CH_2N_{triazole}$, $CH_2NHC(O)$, CH_2O), 3.18 – 3.12 (2H, m, $CH_2NHC(O)OC(CH_3)_3$), 2.24 – 2.05 (8H, m, $OCH_2CH_2CH_2N_{triazole}$), 2.16, 2.09, 2.02 and 1.98 (4 x 12H, 4 x s, $C(O)CH_3$), 1.89 – 1.85 and 1.70 – 1.65 (2 x 2H, 2 x

m, $OCH_2CH_2CH_2NH$) and 1.40 (9H, s, $NHC(O)OC(CH_3)_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 170.4, 170.2 and 170.0 ($C(O)CH_3$), 167.2 and 166.8 (C(O)NH), 159.6 (C_{arom}-3,5), 159.3 (C_{arom}-3',5'), 156.0 ($NHC(O)C(CH_3)_3$), 137.2 (C_{arom}-1), 136.6 (C_{arom}-1'), 106.4 (C_{arom}-2',6'), 106.1 (C_{arom}-2,6), 105.2 (C_{arom}-4,4'), 101.1 (C-1), 70.7, 70.6, 68.8 and 67.0 (C-2, C-3, C-4, C-5), 70.2, 70.1, 70.0 and 69.2 (OCH_2), 65.6 (CH_2O_{gal}), 62.0 ($OCH_2C_{triazole}$), 61.2 (C-6), 46.7 ($CH_2N_{triazole}$), 39.4 and 38.5 ($CH_2NHC(O)$), 30.1, 29.6 and 28.9 ($OCH_2CH_2CH_2NH$, $OCH_2CH_2CH_2N_{triazole}$), 28.3 ($NHC(O)OC(CH_3)_3$), 20.8, 20.6 and 20.5 ($C(O)CH_3$). Deprotection was performed according to the general procedure. Deprotected tetravalent galactose dendrimer was isolated by preparative HPLC (30.6 mg, quant.). ^1H NMR (300 MHz, D_2O): δ = 7.69 (4H, s, $CH_{triazole}$), 7.25 (3H, bs, C(O)NH), 7.07 (4H, s, CH_{arom}-2',6'), 6.98 (2H, s, CH_{arom}-2,6), 6.74 (1H, s, CH_{arom}-4'), 6.63 (1H, s, CH_{arom}-4), 5.39 (4H, d, $J_{3,4}$ = 3.0 Hz, H-4), 5.23 – 5.17 (12H, m, H-2, $OCH_2C_{triazole}$), 5.03 (4H, dd, $J_{2,3}$ = 10.5 Hz, $J_{3,4}$ = 3.3 Hz, H-3), 4.47 (4H, d, $J_{1,2}$ = 8.1 Hz, H-1), 4.55 – 4.38 and 3.90 – 3.84 (2 x 4H, 2 x m, CH_2O_{gal}), 4.20 – 4.09 (12H, m, H-6, OCH_2CH_2NH), 3.95 – 3.90 (4H, m, H-5), 3.84 – 3.76 (4H, m, OCH_2CH_2NH), 3.62 – 3.41 (18H, m, $CH_2N_{triazole}$, $CH_2NHC(O)$, CH_2O), 3.18 – 3.12 (2H, m, CH_2NH_3), 2.24 – 2.05 (8H, m, $OCH_2CH_2CH_2N_{triazole}$), 1.89 – 1.85 and 1.70 – 1.65 (2 x 2H, 2 x m, $OCH_2CH_2CH_2NH$). ^{13}C NMR (75.5 MHz, D_2O): δ = 169.2 and 169.0 (C(O)NH), 160.0 (C_{arom}-3,5), 159.3 (C_{arom}-3',5'), 143.3 ($C_{triazole}$-4), 136.1 (C_{arom}-1'), 107.1 and 105.6 (C_{arom}), 103.5 (C-1), 75.7, 73.4, 71.4 and 69.2 (C-2, C-3, C-4, C-5), 70.0 and 68.9 (OCH_2), 66.7 (CH_2O_{gal}), 62.0 ($OCH_2C_{triazole}$), 61.5 (C-6), 47.7 ($CH_2N_{triazole}$), 38.3 and 37.7 ($CH_2NHC(O)$), 30.3 and 27.1 ($OCH_2CH_2CH_2NH$, $OCH_2CH_2CH_2N_{triazole}$). MALDI-TOF for $C_{83}H_{122}N_{16}O_{36}$ (M: 1919.9): found $[M+H]^+$ 1920.6.

GlcNAc derivative (1c): A "click" reaction of **1a**^{i} and the GlcNAc derivative **6** was performed according to the general procedure. Protected GlcNAc derivative was isolated by silica gel chromatography (CH_2Cl_2/MeOH, 19/1 → 9/1) (52 mg, quant.). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.70 (1H, s, $CH_{triazole}$), 7.47 – 7.09 (4H, m, $CH_{arom,}$ C(O)NH), 6.60 (1H, bd, $NHC(O)CH_3$), 5.26 – 5.19 (3H, m, $OCH_2C_{triazole}$, H-3), 5.05 (1H, t, J = 9.6 Hz, H-4), 5.0 (1H, bs, $NHC(O)C(CH_3)_3$), 4.52 (1H, d, $J_{1,2}$ = 8.4 Hz, H-1), 4.53 – 4.37 and 3.90 – 3.83 (2 x 1H, 2 x m, CH_2O_{GlcNAc}), 4.24 (1H, dd, $J_{5,6a}$ = 4.5 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.14 (1H, dd, $J_{5,6b}$ = 2.1 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6b), 3.68 – 3.57 (14H, m), 3.50 – 3.46 (2H, m), 3.26 – 3.16 (2H, m, $CH_2NHC(O)C(CH_3)_3$), 2.24 – 2.08 (2H, m, $OCH_2CH_2CH_2N_{triazole}$), 2.06, 2.02, 2.02 and 1.95 (4 x 3H, 4 x s, $C(O)CH_3$), 1.93 – 1.80 and 1.75 – 1.64 (2 x 2H, 2 x m, $OCH_2CH_2CH_2NH$) and 1.43 (9H, s, $NHC(O)OC(CH_3)_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 170.6 and 169.3 ($C(O)CH_3$), 167.0 (C(O)NH), 158.2 (C_{arom}-3), 156.0 ($NHC(O)C(CH_3)_3$), 136.4 (C_{arom}-1), 129.6 (C_{arom}-5), 119.3 (C_{arom}-6), 118.5 (C_{arom}-4), 113.2 (C_{arom}-2), 101.1 (C-1), 78.9 ($NHC(O)C(CH_3)_3$), 72.7, 71.7 and 68.5 (C-3, C-4, C-5), 70.3, 70.0 and 69.4 (OCH_2), 65.3 (CH_2O_{GlcNAc}), 61.9 ($OCH_2C_{triazole}$, C-6), 54.1 (C-2), 46.5 ($CH_2N_{triazole}$), 38.9 ($CH_2NHC(O)C(CH_3)_3$), 38.4 ($CH_2NHC(O)$), 29.9, 29.6 and 28.8 ($OCH_2CH_2CH_2NH$, $OCH_2CH_2CH_2N_{triazole}$), 28.4 ($NHC(O)OC(CH_3)_3$), 23.2 and 20.6 ($C(O)CH_3$). ESMS for $C_{42}H_{64}N_6O_{16}$ (M: 908.4, $[M+Na]^+$: 931.43): found $[M+H]^+$ 909.2, $[M+Na]^+$: 931,4. Deprotection was performed according to the general procedure. Deprotected GlcNAc derivative was isolated by preparative HPLC (25 mg, 70%). ^{13}C NMR (75.5 MHz, D_2O): δ = 175.8 and 170.6 (C(O)NH), 158.1 (C_{arom}-3), 143.8 ($C_{triazole}$-4), 136.0 (C_{arom}-1), 130.9 (C_{arom}-5), 125.9 ($C_{triazole}$-5), 121.0 (C_{arom}-6), 119.5 (C_{arom}-4), 114.7 (C_{arom}-2), 101.8 (C-1), 76.5, 74.4 and 70.5 (C-3, C-4, C-5), 70.0, 69.4 and 68.9 (OCH_2), 66.8 (CH_2O_{GlcNAc}), 62.1 ($OCH_2C_{triazole}$), 61.4 (C-6), 56.2 (C-2), 47.6 ($CH_2N_{triazole}$), 38.3 (CH_2NH_3), 38.0 ($CH_2NHC(O)$), 30.0, 28.9 and 27.4 ($OCH_2CH_2CH_2NH$, $OCH_2CH_2CH_2N_{triazole}$) and 22.8 ($C(O)CH_3$). MALDI-TOF for $C_{31}H_{50}N_6O_{11}$ (M: 682.3): found $[M+H]^+$ 683.4.

Divalent GlcNAc dendrimer (2c): A "click" reaction of **2a**^{i} and the GlcNAc derivative **6** was performed according to the general procedure. Protected divalent GlcNAc dendrimer was isolated by silica gel chromatography (EtOAc/MeOH, 19/1 → 4/1) (34 mg, 49%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69 (2H, s, $CH_{triazole}$), 7.34 (1H, bs, C(O)NH), 7.02 (2H, d, CH_{arom}-2,6), 6.74 (1H, t, CH_{arom}-4), 6.43 (2H, bd, N*H*C(O)C$(CH_3)_3$), 5.25 – 5.18 (6H, m, $OCH_2C_{triazole}$, H-3), 5.06 (4H, t, *J* = 9.6 Hz, H-4), 4.52 (2H, d, $J_{1,2}$ = 8.4 Hz, H-1), 4.60 – 4.38 and 3.92 – 3.82 (2 x 2H, 2 x m, CH_2O_{GlcNAc}), 4.23 (2H, dd, $J_{5,6a}$ = 4.8 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.14 (2H, dd, $J_{5,6b}$ = 2.7 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6b), 4.06 – 3.97 (2H, m, H-2), 3.89 – 3.43 (18H, m, $CH_2N_{triazole}$, C*H*$_2$NH(CO), CH_2O), 3.30 – 3.23 (2H, m, H-5), 3.22 – 3.15 (2H, m, C*H*$_2$NHC(O)OC$(CH_3)_3$), 2.21 – 2.10 (4H, m, $OCH_2CH_2CH_2N_{triazole}$), 2.07, 2.03, 2.02 and 1.96 (4 x 6H, 4 x s, C(O)CH_3), 1.92 – 1.88 and 1.75 – 1.66 (2 x 2H, 2 x m, $OCH_2CH_2CH_2NH$) and 1.42 (9H, s, NHC(O)OC$(CH_3)_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 170.7 and 169.3 (*C*(O)CH_3), 167.0 (C(O)NH), 159.3 (C_{arom}-3,5), 143.3 ($C_{triazole}$-4), 137.3 (C_{arom}-1), 106.5 (C_{arom}-2,6), 101.2 (C-1), 72.6, 71.7 and 68.5 (C-3, C-4, C-5), 70.3 and 69.3 (OCH_2), 65.4 (CH_2O_{GlcNAc}), 62.0 ($OCH_2C_{triazole}$, C-6), 54.2 (C-2), 46.6 ($CH_2N_{triazole}$), 38.8 (*C*H_2NHC(O)C$(CH_3)_3$), 30.0 and 29.6 ($OCH_2CH_2CH_2NH$, $OCH_2CH_2CH_2N_{triazole}$), 28.4 (NHC(O)OC(*C*$H_3)_3$), 23.2 and 20.7 (C(O)*C*H_3). ESMS for $C_{62}H_{92}N_{10}O_{26}$ (M: 1392.6, $[M+Na]^+$: 1415.61): found $[M+H]^+$ 1393.4, $[M+Na]^+$ 1415.58. Deprotection was performed according to the general procedure. Deprotected divalent GlcNAc dendrimer was isolated by preparative HPLC (20 mg, 72%). ^{1}H NMR (300 MHz, D_2O): δ = 7.9 (s, $2H_{triazole}$), 6.88 (d, *J* = 2.2 Hz, $2H_{arom}$), 6.73 (s, $1H_{arom}$), 5.13 (4H, s, $CH_2C_{triazole}$), 4.34 (4H, t, *J* = 6.8 Hz, H-6), 4.28 (2H, d, *J* = 8.2 Hz, H-1), 3.78 – 3.27 (28H, m), 2.95 (2H, t, *J* = 7.1 Hz, C*H*$_2$NH$_2$), 2.09 (6H, s, NHCO*CH*$_3$), 2.03 (2H, t, *J* = 5.5 Hz, $OCH_2CH_2CH_2NH$), 1.89 (4H, s, $OCH_2CH_2CH_2N_{triazole}$), 1.77 (2H, q, *J* = 6.5 Hz, $OCH_2CH_2CH_2NH_2$). ^{13}C NMR (75.5 MHz, D_2O): δ = 216.1 (acetone residual peak), 169.8 (C(O)NH), 158.9 (C_{arom}-3,5), 125.5 ($C_{triazole}$-5), 101.3 (C-1), 76.1 – 73.9 (C-3, C-4, C-5), 70.0, 69.5 and 68.9 (OCH_2), 66.3 (CH_2O_{GlcNAc}), 61.7 ($OCH_2C_{triazole}$), 60.8 (C-6), 55.7 (C-2), 47.2 ($CH_2N_{triazole}$), 38.7 and 37.8 (CH_2NH, CH_2NH_3), 30.9 (acetone residual peak), 29.8, 26.6 and 22.3 ($OCH_2CH_2CH_2NH$, $OCH_2CH_2CH_2N_{triazole}$). MALDI-TOF for $C_{45}H_{72}N_{10}O_{18}$ (M: 1040.5): found $[M+H]^+$ 1041.4.

Tetravalent GlcNAc dendrimer (3c): A "click" reaction of **3a**^{i} and the GlcNAc derivative **6** was performed according to the general procedure. Protected tetravalent GlcNAc dendrimer was isolated by silica gel chromatography (CH_2Cl_2/MeOH, 19/1 → 9/1) (110 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (4H, bs, $CH_{triazole}$), 7.01 (4H, bs, CH_{arom}-2',6'), 6.91 (2H, s, CH_{arom}-2,6), 6.63 (1H, s, CH_{arom}-4'), 6.55 (1H, s, CH_{arom}-4), 5.25 (4H, t, H-3), 5.16 – 5.0 (12H, s, $OCH_2C_{triazole}$, H-4), 4.62 (4H, d, $J_{1,2}$ = 7.8 Hz, H-1), 4.54 – 4.30 (8H, m), 4.24 (4H, bd, H-6a), 4.15 – 3.90 (12H, m), 3.90 – 3.20 (30H), 3.20 – 3.10 (2H, m, C*H*$_2$NHC(O)OC$(CH_3)_3$), 2.20 – 1.85 (10H, m, $OCH_2CH_2CH_2N_{triazole}$, $OCH_2CH_2CH_2NH$), 2.05, 2.0, 2.0 and 1.93 (4 x 12H, 4 x s, C(O)CH_3), 1.75 – 1.65 (2H, m, $OCH_2CH_2CH_2NH$) and 1.40 (9H, s, NHC(O)OC(C*H*$_3)_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 170.7 and 169.4 (*C*(O)CH_3), 167.6 and 167.0 (C(O)NH), 159.7 (C_{arom}-3,5), 159.2 (C_{arom}-3',5'), 156.1 (NH*C*(O)C$(CH_3)_3$), 143.0 ($C_{triazole}$-4), 137.1 (C_{arom}-1), 136.6 (C_{arom}-1'), 124.0 ($C_{triazole}$-5), 106.5 (C_{arom}-2',6'), 106.1 (C_{arom}-2,6), 104.3 (C_{arom}-4'), 101.0 (C-1), 78.9 (NHC(O)*C*$(CH_3)_3$), 72.6, 71.6 and 68.6 (C-3, C-4, C-5), 70.3, 70.0 and 69.3 (OCH_2), 66.7 (CH_2O_{GlcNAc}), 62.0 ($OCH_2C_{triazole}$), 61.7 (C-6), 54.2 (C-2), 46.7 ($CH_2N_{triazole}$), 39.6 and 38.3 (*C*H_2NHC(O), 29.9 and 29.6 ($OCH_2CH_2CH_2NH$, $OCH_2CH_2CH_2N_{triazole}$), 28.4 (NHC(O)OC(*C*$H_3)_3$), 23.2 and 20.7 (C(O)*C*H_3). Deprotection was

performed according to the general procedure. Deprotected tetravalent GlcNAc dendrimer was isolated by preparative HPLC (35 mg, 65%). ^{1}H NMR (300 MHz, CD_3OD): δ = 8.03 (4H, s, $CH_{triazole}$), 7.01 (3H, bs, C(O)NH), 6.94 (4H, s, CH_{arom}-2',6'), 6.80 (2H, s, CH_{arom}-2,6), 6.73 (1H, s, CH_{arom}-4'), 5.12 (8H, s, $OCH_2C_{triazole}$), 4.43 (8H, bs), 4.30 (4H, d, $J_{1,2}$ = 8.2 Hz, H-1), 4.14 (4H, bs), 3.80 (4H, t, *J* = 10.0 Hz), 3.73 (8H, t, *J* = 6.0 Hz, H-6), 3.62 (2 x 4H, 2 x m, CH_2O_{GlcNAc}), 3.39 – 3.36 (4H, m, CH_2O), 3.26 – 3.22 (20H, m, $CH_2N_{triazole}$, C*H*$_2$NH(CO), CH_2O), 3.04 – 3.02 (2H, m, C*H*$_2$$NH_3$), 2.07 – 2.05 (8H, m, $OCH_2CH_2CH_2N_{triazole}$), 1.89 – 1.85 and 1.72 – 1.66 (2 x 2H, 2 x m, $OCH_2CH_2CH_2NH$). ^{13}C NMR (75.5 MHz, D_2O): δ = 170.0 (C(O)NH), 161.7 (C_{arom}-3,5), 160.9 (C_{arom}-3',5'), 137.7 (C_{arom}-1), 112.2 ($C_{triazole}$-5), 107.9 (C_{arom}-2',6'), 102.7 (C-1), 77.9, 75.9, 72.1, 66.5, 62.7, (C-2, C-3, C-4, C-5, C-6, OCH_2, CH_2O_{GlcNAc}, O*C*$H_2C_{triazole}$), 57.3 ($CH_2N_{triazole}$), 38.1 (*C*H_2NHC(O)), 31.3 and 23.2 ($OCH_2CH_2CH_2NH$, $OCH_2CH_2CH_2N_{triazole}$). MALDI-TOF for $C_{91}H_{134}N_{20}O_{36}$ (M: 2082.93, $[M+Na]^+$: 2105.92): found $[M+Na]^+$ 2110.6.

Octavalent GlcNAc dendrimer (4c): A "click" reaction of **4a**^{i} and the GlcNAc derivative **6** was performed according to the general procedure. Protected octavalent GlcNAc dendrimer was isolated by silica gel chromatography (CH_2Cl_2/MeOH, 19/1 → 4/1) (38 mg, 48%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (8H, bs, $CH_{triazole}$), 7.14 (bs, C(O)NH), 6.99 (8H, bs, CH_{arom}-2'',6''), 6.85 (6H, bs, CH_{arom}-2,6,2',6'), 6.56 (4H, bs, CH_{arom}-4''), 5.30 – 5.23 (8H, m), 5.07 – 5.01 (24H, m), 4.67 (8H, bs), 4.60 – 3.25 (100H, m), 3.18 – 3.12 (2H, m, C*H*$_2$NHC(O)OC(CH_3)$_3$), 2.20 – 1.65 (116H, m) and 1.40 (9H, s, NHC(O)OC(C*H*$_3$)$_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 170.9, 170.7 and 169.5 (*C*(O)CH_3), 167.5 (C(O)NH), 159.5 (C_{arom}-3',5'), 159.1 (C_{arom}-3'',5''), 143.1 ($C_{triazole}$-4), 136.4 (C_{arom}-1''), 106.4 (C_{arom}-2'',6''), 100.9 (C-1), 72.6, 71.6 and 68.7 (C-3, C-4, C-5), 70.3 and 70.0 (OCH_2), 65.5 (CH_2O_{GlcNAc}), 62.0 (O*C*$H_2C_{triazole}$), 61.7 (C-6), 54.2 (C-2), 46.9 ($CH_2N_{triazole}$), 39.5 (*C*H_2NHC(O)), 29.9 ($OCH_2CH_2CH_2NH$, $OCH_2CH_2CH_2N_{triazole}$), 28.4 (NHC(O)OC(*C*$H_3$)$_3$), 23.7 and 20.7 (C(O)*C*H_3). Deprotection was performed according to the general procedure. Deprotected octavalent GlcNAc dendrimer was isolated by preparative HPLC (20 mg, 45%). ^{1}H NMR (300 MHz, D_2O): δ = 8.01 (8H, s, $CH_{triazole}$), 6.99 (8H, s, CH_{arom}-2'',6''), 6.87 (8H, s, CH_{arom}-2,6), 6.81 (4H, s, CH_{arom}-2',6'), 6.66 (4H, s, CH_{arom}-4''), 6.61 (1H, s, CH_{arom}-4), 6.51 (2H, s, CH_{arom}-4'), 5.07 (16H, bs, $OCH_2C_{triazole}$), 4.88 – 4.66 (32H, m), 4.41 (16H, bs, H-2, H-3), 4.30 (8H, d, $J_{1,2}$ = 8.2 Hz, H-1), 4.16 – 4.07 (16H, bs, CH_2O_{GlcNAc}), 3.83 (12H, m, C(O)NHC*H*$_2$), 3.48 – 3.25 (40H, m), 3.06 (8H, m, 2 x OCH_2), 2.10 – 1.93 (16H, m, $OCH_2CH_2CH_2N_{triazole}$). ^{13}C NMR (from HSQC, 500 MHz, CD_3OD): δ = 126.1 ($C_{triazole}$-5), 107.9 (C_{arom}-6), 107.5 (C_{arom}-4), 106.5 (C_{arom}-2), 102.8 (C-1), 77.9, 75.9 and 71.9 (C-3, C-4, C-5), 70.8 and 69.9 (OCH_2), 67.6 (CH_2O_{GlcNAc}), 66.4 (O*C*$H_2C_{triazole}$), 62.6 (C-6), 57.1 (C-2), 47.9 ($CH_2N_{triazole}$), 40.4 (CH_2NH_3), 33.6 (*C*H_2NHC(O)), 33.6 and 31.1 ($OCH_2CH_2CH_2NH$, $OCH_2CH_2CH_2N_{triazole}$) and 22.8 (NHC(O)*C*$H_3$). MALDI-TOF for $C_{183}H_{258}N_{40}O_{72}$ (M: 4167.7): found $[M+H]^+$ 4168.9.

GlcNAc derivative (10b): A "click" reaction of **10a**^{i} and the GlcNAc derivative **6** was performed according to the general procedure. Protected GlcNAc derivative was isolated by silica gel chromatography (CH_2Cl_2/MeOH, 19/1 → 4/1) (32 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77 (1H, s, $CH_{triazole}$), 7.65 (2H, m, NH, CH_{arom}), 7.36 (1H, t, *J* = 7.9 Hz, CH_{arom}), 7.21 (1H, m, CH_{arom}), 6.77 (1H, d, *J* = 8.5 Hz, CH_{arom}), 5.23 (3H, m, OCH_2, H-4), 5.06 (1H, t, *J* = 9.6 Hz, H-3), 4.64 (1H, d, *J* = 8.2 Hz, H-1), 4.25 (4H, m, H-2, H-5, CH_2), 4.01 (2H, m, CH_2), 3.91 (3H, s, C(O)OC*H*$_3$), 3.71 (2H, m, CH_2), 3.41 (2H, m, CH_2), 2.14 (12H, m, NHC(O)C*H*$_3$, C(O)CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 170.4,

170.3, 169.1 (3 x O*C*(O)CH_3), 166.5 (NH*C*(O)CH_3), 167.1 (*C*(O)OCH_3), 157.9 ($C_{arom}OCH_2$), 143.2 ($C_{triazole}$), 131.26 ($C_{arom}C(O)OCH_3$), 129.7 ($C_{triazole}$), 123.4, 122.3, 119.7, 114.8 (CH_{arom}), 100.8 (C-1), 72.3, 71.6, 68.4 (C-3, C-4, C-5), 65.3, 61.8 (CH_2O, $NCH_2CH_2CH_2$), 53.9 (C-2), 51.9 (C(O)O*C*H_3), 46.5 ($NCH_2CH_2CH_2$), 29.8 ($NCH_2CH_2CH_2$), 23.0 (NHC(O)*C*H_3), 20.5, 20.4, 20.4 (3 x OC(O)*C*H_3). MALDI-TOF for $C_{28}H_{36}N_4O_{12}$ (M: 620.605, $[M+Na]^+$: 643.59): found $[M+Na]^+$ 643.1. Deprotection was performed according to the general procedure. Deprotected GlcNAc derivative was isolated by preparative HPLC (13 mg, 40%). ^{1}H NMR (300 MHz, CD_3OD): δ = 8.07 (1H, s, $CH_{triazole}$), 7.76 (2H, s, CH_{arom}), 7.33 (1H, m, CH_{arom}), 7.21 (1H, m, CH_{arom}), 5.42 (1H, s, H-4), 5.16 (2H, s, OCH_2), 4.46 (2H, t, *J* = 4.1 Hz, H-6), 4.31 (1H, d, *J* = 8.2 Hz, H-1), 3.83 (5H, m, CH_2, C(O)OCH_3), 3.63 (3H, m, H-2, H-3, H-5), 3.40 (2H, m, CH_2), 3.27 (6H, m, CH_2), 1.94 (3H, NHC(O)C*H*$_3$). ^{13}C NMR (75.5 MHz, CD_3OD): δ = 168.4 (*C*(O)OCH_3), 161.2 (NH*C*(O)CH_3), 132.9 (C_{arom}), 131.0 (CH_{arom}), 123.6 (CH_{arom}), 121.2 ($CH_{triazole}$), 120.9 (CH_{arom}), 116.6 (CH_{arom}), 102.9 (C-1), 78.7 (C-3), 76.2 (C-4), 72.2 (C-5), 66.7 (CH_2), 62.9 (CH_2), 62.7 (C-6), 57.5 (C-2), 52.9 (CH_3), 31.6 (CH_2). ESMS for $C_{22}H_{30}N_4O_9$ (M: 494.20, $[M+Na]^+$: 517.19): found $[M+Na]^+$ 517.2.

Divalent GlcNAc dendrimer (11b): A "click" reaction of **11a**^{i} and the GlcNAc derivative **6** was performed according to the general procedure. Protected divalent GlcNAc dendrimer was isolated by silica gel chromatography (CH_2Cl_2/MeOH, 19/1 → 4/1) (38 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (2H, s, 2 x $CH_{triazole}$), 7.28 (2H, s, 2 x NH), 6.83 (1H, s, CH_{arom}), 6.66 (2H, m, 2x CH_{arom}), 5.20 (6H, m, 2x $C_{arom}OCH_2$, 2 x H-4), 5.06 (2H, t, *J* = 9.3 Hz, 2 x H-3), 4.60 (2H, d, *J* = 7.9 Hz, 2 x H-1), 3.91 (3H, s, C(O)OC*H*$_3$), 2.07 (28H, m, 2 x NHCOC*H*$_3$, 6 x C(O)CH_3, 2 x CH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.3, 171.3, 171.4 (3 x *C*(O)CH_3), 170.0 (NH*C*(O)CH_3), 167.1 (*C*(O)OCH_3), 159.8 ($C_{arom}OCH_2$), 143.9 ($C_{arom}C(O)OCH_3$), 132.8 ($C_{triazole}$), 124.5 ($C_{triazole}$), 109.3 107.6 (2 x C_{arom}), 101.8 (C-1), 73.2, 72.3, 69.2 (C-3, C-4, C-5), 66.1, 62.6 (CH_2O, $NCH_2CH_2CH_2$, C-6), 54.8 (C-2), 53.0 (C(O)O*C*H_3), 47.3 ($NCH_2CH_2CH_2$), 30.6 ($NCH_2CH_2CH_2$), 23.8 (NHC(O)*C*H_3), 20.6, 20.5, 20.5 (3 x OC(O)*C*H_3). MALDI-TOF for $C_{48}H_{64}N_8O_{22}$ (M: 1105.06, $[M+Na]^+$: 1128,05): found $[M+Na]^+$ 1127.37. Deprotected divalent GlcNAc dendrimer was isolated by preparative HPLC (10 mg, 35%). ^{1}H NMR (300 MHz, D_2O): δ = 8.01 (2H, s, 2 x $CH_{triazole}$), 7.09 (2H, s, 2 x CH_{arom}), 6.75 (1H, s, CH_{arom}), 5.12 (4H, s, 2 x $C_{arom}OCH_2$), 4.43 (2H, m, 2 x H-1), 2.09 (4H, m, 2 x CH_2), 2.03 (6H, s, 2 x NHCOC*H*$_3$). ^{13}C NMR (75.5 MHz, D_2O): δ = 174.7 (NH*C*(O)CH_3), 168.1 (*C*(O)OCH_3), 158.7 ($C_{arom}OCH_2$), 131.7 ($C_{triazole}$), 109.2 (C_{arom}), 101.4 (C-1), 76.1, 73.9, 70.1 (C-3, C-4, C-5), 66.3, 61.6, 60.9 (CH_2O, $NCH_2CH_2CH_2$, C-6), 55.8 (C-2), 53.0 (C(O)O*C*H_3), 47.2 ($NCH_2CH_2CH_2$), 29.6 ($NCH_2CH_2CH_2$), 22.4 (NHC(O)*C*H_3). HRMS for $C_{36}H_{52}N_8O_{16}$ (M: 853.84, $[M+Na]^+$: 875.83): found $[M+Na]^+$ 875.3.

Tetravalent GlcNAc dendrimer (12b): A "click" reaction of **12a**^{i} and the GlcNAc derivative **6** was performed according to the general procedure. Protected tetravalent GlcNAc dendrimer was isolated by silica gel chromatography (CH_2Cl_2/MeOH, 19/1 → 4/1) (40 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (4H, s, 4 x $CH_{triazole}$), 7.06 (10H, m, 4 x NH, 6 x CH_{arom}), 6.64 (3H, s, 3 x CH_{arom}), 5.25 (4H, m, 4 x H-4), 5.04 (12H, m, 4 x H-3, 4 x $C_{arom}OCH_2$), 4.63 (4H, d, *J* = 8.2 Hz, 4 x H-1), 3.84 (3H, s, C(O)OCH_3), 2.01 (56H, m, 4 x NHCOC*H*$_3$, 12 x OC(O)CH_3, 4 x CH_2). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.6, 171.4 (3 x O*C*(O)CH_3), 170.1 (NH*C*(O)CH_3), 168.3 (N*C*(O)C_{arom}), 167.2 (*C*(O)OCH_3), 160.2 ($C_{arom}OCH_2CH_2$), 159.9 ($C_{arom}OCH_2C_{triazole}$), 143.8 ($C_{arom}C(O)OCH_3$), 137.2 ($C_{triazole}$), 132.7 ($OCH_2CH_2N$), 115.3 ($OCH_2CH_2N$), 107.2 ($C_{arom}$), 101.6 (C-1), 73.3, 72.3, 69.3 (C-3, C-4, C-5), 66.1,

62.7, 62.4 (CH_2O, $NCH_2CH_2\mathit{C}H_2$, C-6), 54.8 (C-2), 53.0 (C(O)O$\mathit{C}H_3$), 47.4 (N$\mathit{C}H_2CH_2CH_2$), 30.6 ($NCH_2\mathit{C}H_2CH_2$), 23.8 (NHC(O)$\mathit{C}H_3$), 21.4, 21.3, 21.2 (3 x OC(O)$\mathit{C}H_3$). MS for $C_{106}H_{138}N_{18}O_{46}$ (M: 2398.90, $[M+Na]^+$: 2422.89): found $[M+Na]^+$ 2422.94. Deprotected tetravalent GlcNAc dendrimer was isolated by preparative HPLC (26 mg, 75%). ^{1}H NMR (300 MHz, D_2O): δ = 7.89 (4H, s, 4 x $CH_{triazole}$), 6.82 (4H, s, 4 x CH_{arom}), 6.70 (2H, s, 2 x CH_{arom}), 6.52 (2H, s, 2 x CH_{arom}), 6.36 (1H, s, CH_{arom}), 4.41 (4H, m, 4 x H-1), 1.99 (20H, s, 4 x NHC(O)CH_3, 4 x CH_2). ^{13}C NMR (75.5 MHz, D_2O): δ = 178.3 (NHC(O)CH_3), 172.8 (C(O)OCH_3), 162.9 ($\mathit{C}_{arom}OCH_2$), 120.0 (OCH_2CH_2N), 105.3 (C-1), 80.0, 77,9, 74.0 (C-3, C-4, C-5), 70.2, 64.9 (CH_2O, $NCH_2CH_2\mathit{C}H_2$, C-6), 59.7 (C-2), 53.0 (C(O)O$\mathit{C}H_3$), 51.1 (N$\mathit{C}H_2CH_2CH_2$), 33.7 ($NCH_2\mathit{C}H_2CH_2$), 26.4 (NHC(O)$\mathit{C}H_3$).HRMS for $C_{82}H_{114}N_{18}O_{34}$ (M: 1895.88, $[M+Na]^+$: 1918.87): found $[M+Na]^+$ 1918.3.

Octavalent GlcNAc dendrimer (13b): A "click" reaction of **13a**^{i} and the GlcNAc derivative **6** was performed according to the general procedure. Protected octavalent GlcNAc dendrimer was isolated by silica gel chromatography (CH_2Cl_2/MeOH, 19/1 → 4/1) (60 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.07 (8H, s, 8 x NH), 7.76 (8H, s, 8 x $CH_{triazole}$), 7.0 (8H, s, 8 x CH_{arom}), 6.85 (4H, s, 4 x CH_{arom}), 6.55 (4H, s, 4 x CH_{arom}), 6.36 (2H, s, 2 x CH_{arom}), 2.03 (112H, m, 8 x NHC(O)CH_3, 24x OC(O)CH_3, 8 x CH_2). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 171.8, 171.1, 170.4 (3 x OC(O)CH_3), 168.3 (NHC(O)CH_3), 160.3, 159.9 (2 x NC(O)C_{arom}), 101.7 (C-1), 73.3, 72.4, 69.4 (C-3, C-4, C-5), 62.7, 61.1 ($NCH_2CH_2\mathit{C}H_2$, C-6), 54.9 (C-2), 53.0 (C(O)OCH_3), 50.6 (N$\mathit{C}H_2CH_2CH_2$), 30.7 ($NCH_2\mathit{C}H_2CH_2$), 23.9 (NHC(O)$\mathit{C}H_3$), 21.4, 21.4, 21.3 (3 x OC(O)$\mathit{C}H_3$). MS for $C_{222}H_{286}N_{38}O_{94}$ (M: 4987.88, $[M+Na]^+$: 5010,87): found $[M+Na]^+$ 5012.38. Deprotected octavalent GlcNAc dendrimer (**13b**) was isolated by preparative HPLC (29 mg, 78%). ^{1}H NMR (300 MHz, D_2O): δ = 7.89 (8H, s, 8 x $CH_{triazole}$), 6.81 (8H, s, 8 x CH_{arom}), 6.51 (4H, s, 4 x CH_{arom}), 1.99 (40H, s, 8 x NHC(O)CH_3, 8 x CH_2). HRMS for $C_{174}H_{238}N_{38}O_{70}$ (M: 3981.96, $[M+Na]^+$: 4004.95): found $[M+Na]^+$ 4003.398.

Glucose derivative (1b): A "click" reaction of **1a**^{i} and the glucose derivative **5** was performed according to the general procedure. Protected glucose derivative was isolated by silica gel chromatography (CH_2Cl_2/MeOH, 19/1 → 9/1) (41 mg, quant.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 (1H, s, $CH_{triazole}$), 7.49 (1H, s, CH_{arom}-6), 7.37 – 7.28 (2H, m, CH_{arom}-2,5), 7.16 (1H, bs, C(O)NH), 7.12 – 7.08 (1H, m, CH_{arom}-4), 5.24 (2H, s, $OCH_2C_{triazole}$), 5.21 (1H, t, H-4, J = 9.9 Hz), 5.08 (1H, t, J = 9.6 Hz, H-3), 5.01 (1H, dd, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 4.50 (1H, d, $J_{1,2}$ = 7.5 Hz, H-1), 4.53 – 4.37 and 3.90 – 3.82 (2 x 1H, 2 x m, CH_2O_{glc}), 4.26 (1H, dd, $J_{5,6a}$ = 4.5 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.14 (1H, dd, $J_{5,6b}$ = 2.4 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6b), 3.73 – 3.45 (17H, m, H-5, $CH_2N_{triazole}$, CH_2NHC(O), CH_2O), 3.22 – 3.16 (2H, m, CH_2NHC(O)OC$(CH_3)_3$), 2.24 – 2.08 (2H, m, $OCH_2C\mathit{H}_2CH_2N_{triazole}$), 2.07, 2.06, 2.03 and 2.01 (4 x 3H, 4 x s, C(O)CH_3), 1.94 – 1.86 and 1.75 – 1.67 (2 x 2H, 2 x m, $OCH_2C\mathit{H}_2CH_2NH$) and 1.43 (9H, s, NHC(O)OC(C$\mathit{H}_3)_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 170.6, 170.1 and 169.4 (C(O)CH_3), 166.9 (C(O)NH), 158.3 (C_{arom}-3), 156.0 (NHC(O)C$(CH_3)_3$), 136.4 (C_{arom}-1), 129.5 (C_{arom}-5), 119.4 (C_{arom}-6), 118.0 (C_{arom}-4), 113.4 (C_{arom}-2), 100.7 (C-1), 72.7, 71.8, 71.2 and 68.2 (C-2, C-3, C-4, C-5), 70.4, 70.1 and 69.4 (OCH_2), 65.7 (CH_2O_{glc}), 62.0 (O$\mathit{C}H_2C_{triazole}$), 61.7 (C-6), 46.7 ($CH_2N_{triazole}$), 38.8 ($\mathit{C}H_2$NHC(O)OC$(CH_3)_3$), 38.5 ($\mathit{C}H_2$NHC(O)), 30.1, 29.6 and 28.8 ($OCH_2\mathit{C}H_2CH_2NH$, $OCH_2\mathit{C}H_2CH_2N_{triazole}$), 28.4 (NHC(O)OC($\mathit{C}H_3)_3$), 20.7 and 20.5 (C(O)$\mathit{C}H_3$). Deprotection was performed according to the general procedure. Deprotected glucose derivative was isolated by preparative HPLC (18 mg, 74%). ^{1}H

NMR (300 MHz, D_2O): δ = 7.67 (1H, s, $CH_{triazole}$), 7.49 (1H, s, CH_{arom}-6), 7.37 – 7.28 (2H, m, CH_{arom}-2,5), 7.16 (1H, bs, C(O)NH), 7.12 – 7.08 (1H, m, CH_{arom}-4), 5.24 (2H, s, $OCH_2C_{triazole}$), 5.21 (1H, t, *J* = 9.9 Hz, H-4), 5.08 (1H, t, *J* = 9.6 Hz, H-3), 5.01 (1H, dd, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 4.50 (1H, d, $J_{1,2}$ = 7.5 Hz, H-1), 4.53 – 4.37 and 3.90 – 3.82 (2 x 1H, 2 x m, CH_2O_{glc}), 4.26 (1H, dd, $J_{5,6a}$ = 4.5 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.14 (1H, dd, $J_{5,6b}$ = 2.4 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6b), 3.73 – 3.45 (17H, m, H-5, $CH_2N_{triazole}$, C*H*$_2$NHC(O), CH_2O), 3.22 – 3.16 (2H, m, C*H*$_2$$NH_3$), 2.24 – 2.08 (2H, m, $OCH_2CH_2CH_2N_{triazole}$), 1.94 – 1.86 and 1.75 – 1.67 (2 x 2H, 2 x m, $OCH_2CH_2CH_2NH$). ^{13}C NMR (75.5 MHz, CD_3OD): δ = 170.0 (C(O)NH), 160.0 (C_{arom}-3), 137.4 (C_{arom}-1), 131.0 (C_{arom}-5), 126.4 ($CH_{triazole}$), 121.2 (C_{arom}-6), 119.4 (C_{arom}-4), 115.1 (C_{arom}-2), 104.6 (C-1), 78.2, 75.3, 71.8 and 71.6 (C-2, C-3, C-4, C-5), 70.6 and 70.2 (OCH_2), 67.0 (CH_2O_{glc}), 62.9 ($OCH_2C_{triazole}$), 62.7 (C-6), 40.4 (CH_2NH_3), 38.8 (*C*H_2NHC(O)), 31.7, 30.7 and 28.3 ($OCH_2CH_2CH_2NH$, $OCH_2CH_2CH_2N_{triazole}$). MALDI-TOF for $C_{29}H_{47}N_5O_{11}$ (M: 641.7): found $[M+H]^+$ 642.6.

Divalent glucose dendrimer (2b): A "click" reaction of **2a**^{i} and the glucose derivative **5** was performed according to the general procedure. Protected divalent glucose dendrimer was isolated by silica gel chromatography (CH_2Cl_2/MeOH, 19/1 → 9/1) (66.7 mg, quant.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69 (2H, s, $CH_{triazole}$), 7.15 (1H, bs, C(O)NH), 7.06 (2H, d, CH_{arom}-2,6), 6.76 (1H, t, CH_{arom}-4), 5.21 (2H, t, *J* = 9.3 Hz, H-4), 5.20 (4H, s, $OCH_2C_{triazole}$), 5.09 (2H, t, *J* = 9.6 Hz, H-3), 5.01 (2H, dd, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 4.51 (2H, d, $J_{1,2}$ = 8.1 Hz, H-1), 4.53 – 4.38 and 3.92 – 3.82 (2 x 2H, 2 x m, CH_2O_{glc}), 4.27 (2H, dd, $J_{5,6a}$ = 4.8 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.14 (2H, dd, $J_{5,6b}$ = 2.4 Hz, $J_{6a,6b}$ = 12.6 Hz, H-6b), 3.74 – 3.68 (2H, m, H-5), 3.64 – 3.44 (18H, m, $CH_2N_{triazole}$, C*H*$_2$NH(CO), CH_2O), 3.22 – 3.15 (2H, m, C*H*$_2$NHC(O)OC$(CH_3)_3$), 2.23 – 2.13 (4H, m, $OCH_2CH_2CH_2N_{triazole}$), 2.08, 2.07, 2.03 and 2.01 (4 x 6H, 4 x s, C(O)CH_3), 1.93 – 1.85 and 1.75 – 1.66 (2 x 2H, 2 x m, $OCH_2CH_2CH_2NH$) and 1.42 (9H, s, NHC(O)OC(C*H*$_3$)$_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 170.5, 170.1 and 169.3 (*C*(O)CH_3), 166.7 (C(O)NH), 159.3 (C_{arom}-3,5), 156.0 (NH*C*(O)C$(CH_3)_3$), 137.2 (C_{arom}-1), 106.3 (C_{arom}-2,6), 104.7 (C_{arom}-4), 100.6 (C-1), 78.8 (NHC(O)*C*$(CH_3)_3$), 72.6, 71.7, 71.1 and 68.2 (C-2, C-3, C-4, C-5), 70.3, 70.0 and 69.3 (OCH_2), 65.7 (CH_2O_{glc}), 62.0 ($OCH_2C_{triazole}$), 61.8 (C-6), 46.6 ($CH_2N_{triazole}$), 38.5 (*C*H_2NHC(O)OC$(CH_3)_3$), 30.0, 29.5 and 28.9 ($OCH_2CH_2CH_2NH$, $OCH_2CH_2CH_2N_{triazole}$), 28.3 (NHC(O)OC(*C*$H_3$)$_3$), 20.6 and 20.5 (C(O)*C*H_3). Deprotection was performed according to the general procedure. Deprotected divalent glucose dendrimer was isolated by preparative HPLC (38 mg, quant.). ^{1}H NMR (300 MHz, D_2O): δ = 8.21 (2H, s, $CH_{triazole}$), 7.10 (2H, d, CH_{arom}-2,6), 6.89 (1H, s, CH_{arom}-4), 5.29 (4H, s, $OCH_2C_{triazole}$), 4.90 (1H, bs), 4.65 (4H, t, *J* = 7.7 Hz, H-6), 4.44 (2H, d, $J_{1,2}$ = 7.8 Hz, H-1), 3.94 – 3.47 (28H, m), 3.37 (2H, t, *J* = 7.9 Hz, C*H*$_2$NH), 3.21 (2H, t, *J* = 6.8 Hz, (C*H*$_2$$NH_3$), 2.22 – 2.17 (4H, m, $OCH_2CH_2CH_2N_{triazole}$) and 1.93 – 1.85 (4H, m, $OCH_2CH_2CH_2NH$). ^{13}C NMR (75.5 MHz, D_2O): δ = 169.6 (C(O)NH), 159.4 (C_{arom}-3,5), 143.5 ($C_{triazole}$-4), 136.8 (C_{arom}-1), 108.0 (C_{arom}-2,6), 106.5 (C_{arom}-4), 103.5 (C-1), 75.7, 73.4, 71.4 and 69.2 (C-2, C-3, C-4, C-5), 70.0, 69.5 and 68.9 (OCH_2), 66.8 (CH_2O_{glc}), 62.2 ($OCH_2C_{triazole}$), 61.6 (C-6), 47.8 ($CH_2N_{triazole}$), 38.3 and 38.1 (CH_2NH), 30.2, 28.9 and 27.1 ($OCH_2CH_2CH_2NH$, $OCH_2CH_2CH_2N_{triazole}$). MALDI-TOF for $C_{41}H_{66}N_8O_{18}$ (M: 958.4): found $[M+H]^+$ 959.6.

Tetravalent glucose dendrimer (3b): A "click" reaction of **3a**^{i} and the glucose derivative **5** was performed according to the general procedure. Protected tetravalent glucose dendrimer was isolated by silica gel chromatography (CH_2Cl_2/MeOH, 19/1 → 9/1) (61 mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 (4H, s, $CH_{triazole}$),

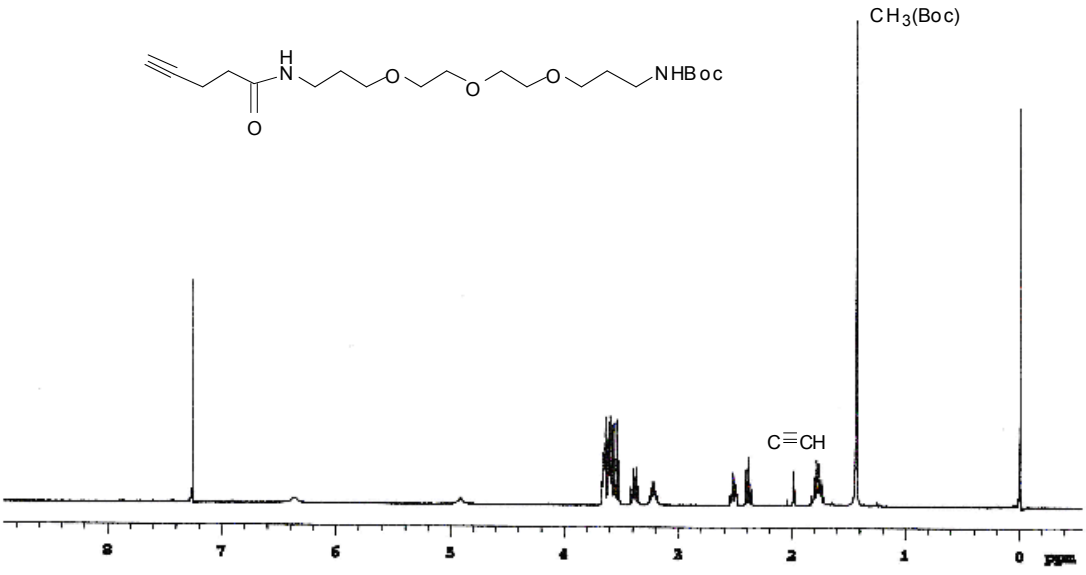
7.20 (3H, bs, C(O)NH), 7.05 (4H, s, CH_{arom}-2',6'), 6.98 (2H, s, CH_{arom}-2,6), 6.74 (1H, s, CH_{arom}-4'), 6.63 (1H, s, CH_{arom}-4), 5.21 (4H, t, *J* = 9.3 Hz, H-4), 5.16 (8H, s, $OCH_2C_{triazole}$), 5.08 (4H, t, *J* = 9.6 Hz, H-3), 5.0 (4H, dd, $J_{1,2}$ = 8.1 Hz, $J_{2,3}$ = 9.3 Hz, H-2), 4.51 (4H, d, $J_{1,2}$ = 8.1 Hz, H-1), 4.50 – 4.36 and 3.90 – 3.76 (2 x 4H, 2 x m, CH_2O_{glc}), 4.26 (4H, dd, $J_{5,6a}$ = 4.8 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.16 – 4.11 (8H, m, H-6b, OCH_2CH_2NH), 3.74 – 3.69 (4H, m, H-5), 3.61 – 3.41 (20H, m, $CH_2N_{triazole}$, $CH_2NH(CO)$, CH_2O), 3.20 – 3.10 (2H, m, $CH_2NHC(O)OC(CH_3)_3$), 2.26– 2.08 (8H, m, $OCH_2CH_2CH_2N_{triazole}$), 2.07, 2.06, 2.02 and 2.01 (4 x 12H, 4 x s, $C(O)CH_3$), 1.89 – 1.85 and 1.72 – 1.66 (2 x 2H, 2 x m, $OCH_2CH_2CH_2NH$) and 1.41 (9H, s, $NHC(O)OC(CH_3)_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 170.6, 170.1 and 169.4 ($C(O)CH_3$), 167.2 and 166.7 (C(O)NH), 159.6 (C_{arom}-3,5), 159.3 (C_{arom}-3',5'), 156.0 ($NHC(O)C(CH_3)_3$), 143.2 ($C_{triazole}$-4), 137.1 (C_{arom}-1), 136.6 (C_{arom}-1'), 123.5 ($C_{triazole}$-5), 106.4 (C_{arom}-2',6'), 106.1 (C_{arom}-2,6), 105.1 (C_{arom}-4'), 104.3 (C_{arom}-4), 100.6 (C-1), 78.8 ($NHC(O)C(CH_3)_3$), 71.7, 71.2, 70.6 and 68.2 (C-2, C-3, C-4, C-5), 70.2 and 69.3 (OCH_2), 65.7 (CH_2O_{glc}), 62.0 ($OCH_2C_{triazole}$), 61.7 (C-6), 46.7 ($CH_2N_{triazole}$), 39.4 and 38.5 ($CH_2NHC(O)$, 30.0, 29.5 and 28.9 ($OCH_2CH_2CH_2NH$, $OCH_2CH_2CH_2N_{triazole}$), 28.3 ($NHC(O)OC(CH_3)_3$), 20.6 and 20.5 ($C(O)CH_3$). Deprotection was performed according to the general procedure. Deprotected tetravalent glucose dendrimer was isolated by preparative HPLC (31 mg, 83%). ^{1}H NMR (300 MHz, D_2O): δ = 7.70 (4H, s, $CH_{triazole}$), 7.20 (3H, bs, C(O)NH), 7.05 (4H, s, CH_{arom}-2',6'), 6.98 (2H, s, CH_{arom}-2,6), 6.74 (1H, s, CH_{arom}-4'), 6.63 (1H, s, CH_{arom}-4), 5.21 (4H, t, *J* = 9.3 Hz, H-4), 5.16 (8H, s, $OCH_2C_{triazole}$), 5.08 (4H, t, *J* = 9.6 Hz, H-3), 5.0 (4H, dd, $J_{1,2}$ = 8.1 Hz, $J_{2,3}$ = 9.3 Hz, H-2), 4.51 (4H, d, $J_{1,2}$ = 8.1 Hz, H-1), 4.50 – 4.36 and 3.90 – 3.76 (2 x 4H, 2 x m, CH_2O_{glc}), 4.26 (4H, dd, $J_{5,6a}$ = 4.8 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.16 – 4.11 (8H, m, H-6b, OCH_2CH_2NH), 3.74 – 3.69 (4H, m, H-5), 3.61 – 3.41 (20H, m, $CH_2N_{triazole}$, $CH_2NH(CO)$, CH_2O), 3.20 – 3.10 (2H, m, CH_2NH_3), 2.26 – 2.08 (8H, m, $OCH_2CH_2CH_2N_{triazole}$), 1.89 – 1.85 and 1.72 – 1.66 (2 x 2H, 2 x m, $OCH_2CH_2CH_2NH$). ^{13}C NMR (75.5 MHz, D_2O): δ = 169.2 and 169.0 (C(O)NH), 160.1 (C_{arom}-3,5), 159.3 (C_{arom}-3',5'), 143.4 ($C_{triazole}$-4), 136.3 (C_{arom}-1), 136.1 (C_{arom}-1'), 125.8 ($C_{triazole}$-5), 107.1 (C_{arom}-2',6'), 106.3 and 105.5 (C_{arom}), 102.9 (C-1), 76.6, 76.4, 73.8 and 71.6 (C-2, C-3, C-4, C-5), 70.0, 69.2 and 68.9 (OCH_2), 66.9 (CH_2O_{glc}), 61.8 ($OCH_2C_{triazole}$), 61.4 (C-6), 47.8 ($CH_2N_{triazole}$), 38.3 ($CH_2NHC(O)$), 30.3, 29.1 and 27.1 ($OCH_2CH_2CH_2NH$, $OCH_2CH_2CH_2N_{triazole}$). MALDI-TOF for $C_{83}H_{122}N_{16}O_{36}$ (M: 1919.9): found $[M+H]^+$ 1920.6.

Octavalent glucose dendrimer (4b): A "click" reaction of **4a**^{i} and the glucose derivative **5** was performed according to the general procedure. Protected octavalent glucose dendrimer was isolated by silica gel chromatography (CH_2Cl_2/MeOH, 19/1 → 9/1) (37.8 mg, 48%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71 (8H, s, $CH_{triazole}$), 7.05 (8H, s, CH_{arom}-2'',6''), 6.89 (2H, s, CH_{arom}-2,6), 6.86 (4H, s, CH_{arom}-2',6'), 6.66 (4H, s, CH_{arom}-4''), 6.57 (1H, s, CH_{arom}-4), 6.46 (2H, s, CH_{arom}-4'), 5.20 (8H, t, *J* = 9.3 Hz, H-4), 5.10 – 4.96 (32H, m, $OCH_2C_{triazole}$, H-3, H-2), 4.51 (4H, d, $J_{1,2}$ = 8.1 Hz, H-1), 4.50 – 4.35 and 3.90 – 3.78 (2 x 8H, 2 x m, CH_2O_{glc}), 4.26 (8H, dd, $J_{5,6a}$ = 4.5 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.12 (8H, dd, $J_{5,6b}$ = 2.1 Hz, $J_{6a,6b}$ = 12.5 Hz, H-6b), 4.02 (12H, m, OCH_2CH_2NH), 3.76 – 3.40 (40H, m), 3.18 – 3.12 (2H, m, $CH_2NHC(O)OC(CH_3)_3$), 2.15 – 2.05 (16H, m, $OCH_2CH_2CH_2N_{triazole}$), 2.06, 2.05, 2.02 and 2.0 (4 x 24H, 4 x s, $C(O)CH_3$) and 1.39 (9H, s, $NHC(O)OC(CH_3)_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 170.6, 170.1 and 169.5 ($C(O)CH_3$), 167.5 (C(O)NH), 159.7 (C_{arom}-3,5), 159.5 (C_{arom}-3',5'), 159.3 (C_{arom}-3'',5''), 143.3 ($C_{triazole}$-4), 136.5 (C_{arom}-1''), 106.4 (C_{arom}-2'',6''), 105.2 (C_{arom}-4''), 100.6 (C-1), 72.7, 71.8, 71.2 and 68.3 (C-2, C-3, C-4, C-5), 70.3 (OCH_2), 65.8 (CH_2O_{glc}), 61.8 ($OCH_2C_{triazole}$, C-6), 46.8 ($CH_2N_{triazole}$), 39.5 ($CH_2NHC(O)$), 30.1 ($OCH_2CH_2CH_2NH$, $OCH_2CH_2CH_2N_{triazole}$), 28.4 ($NHC(O)OC(CH_3)_3$), 20.7 and 20.5 ($C(O)CH_3$). Deprotection was

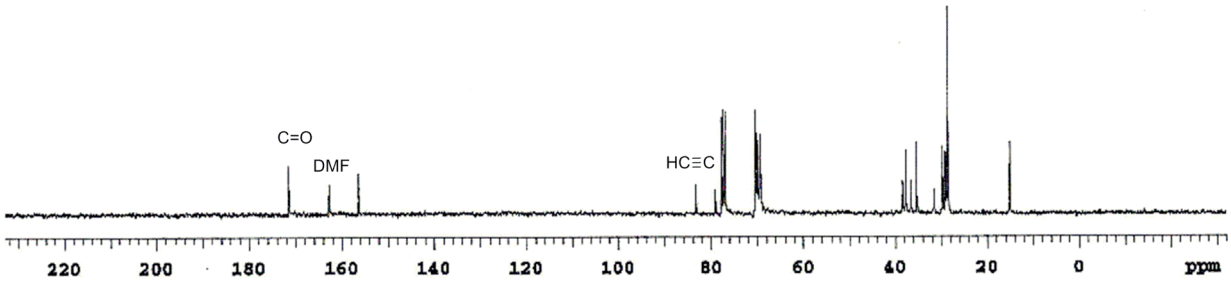
performed according to the general procedure. Deprotected octavalent glucose dendrimer was isolated by preparative HPLC (13 mg, 58%). ^{1}H NMR (300 MHz, D_2O): δ = 7.71 (8H, s, $CH_{triazole}$), 7.05 (8H, s, CH_{arom}-2'',6''), 6.89 (2H, s, CH_{arom}-2,6), 6.86 (4H, s, CH_{arom}-2',6'), 6.66 (4H, s, CH_{arom}-4''), 6.57 (1H, s, CH_{arom}-4), 6.46 (2H, s, CH_{arom}-4'), 5.20 (8H, t, J = 9.3 Hz, H-4), 5.10 – 4.96 (32H, m, $OCH_2C_{triazole}$, H-3, H-2), 4.51 (4H, d, $J_{1,2}$ = 8.1 Hz, H-1), 4.50 – 4.35 and 3.90 – 3.78 (2 x 8H, 2 x m, CH_2O_{glc}), 4.26 (8H, dd, $J_{5,6a}$ = 4.5 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.12 (8H, dd, $J_{5,6b}$ = 2.1 Hz, $J_{6a,6b}$ = 12.5 Hz, H-6b), 4.02 (12H, m, OCH_2CH_2NH), 3.76 – 3.40 (40H, m), 3.18 – 3.12 (2H, m, CH_2NH_3) and 2.15 – 2.05 (16H, m, $OCH_2CH_2CH_2N_{triazole}$). MALDI-TOF for $C_{167}H_{234}N_{32}O_{72}$ (M: 3839.6): found $[M+H]^+$ 3865.6.

Precursor of **1f**:

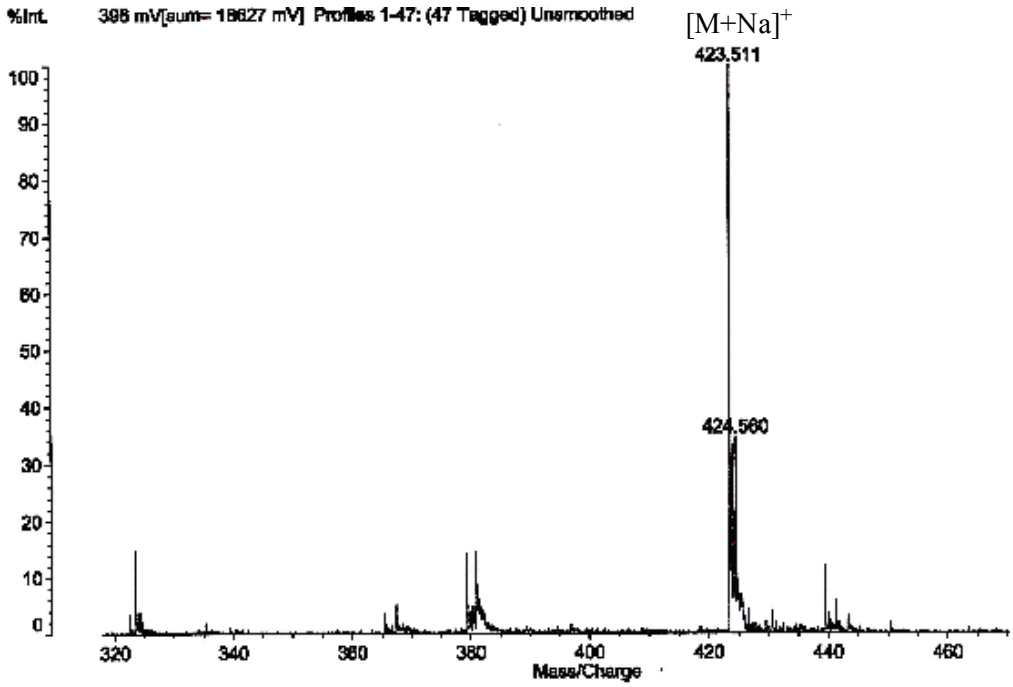
^{1}H NMR (300 MHz, $CDCl_3$):



^{13}C NMR (75.5 MHz, $CDCl_3$):

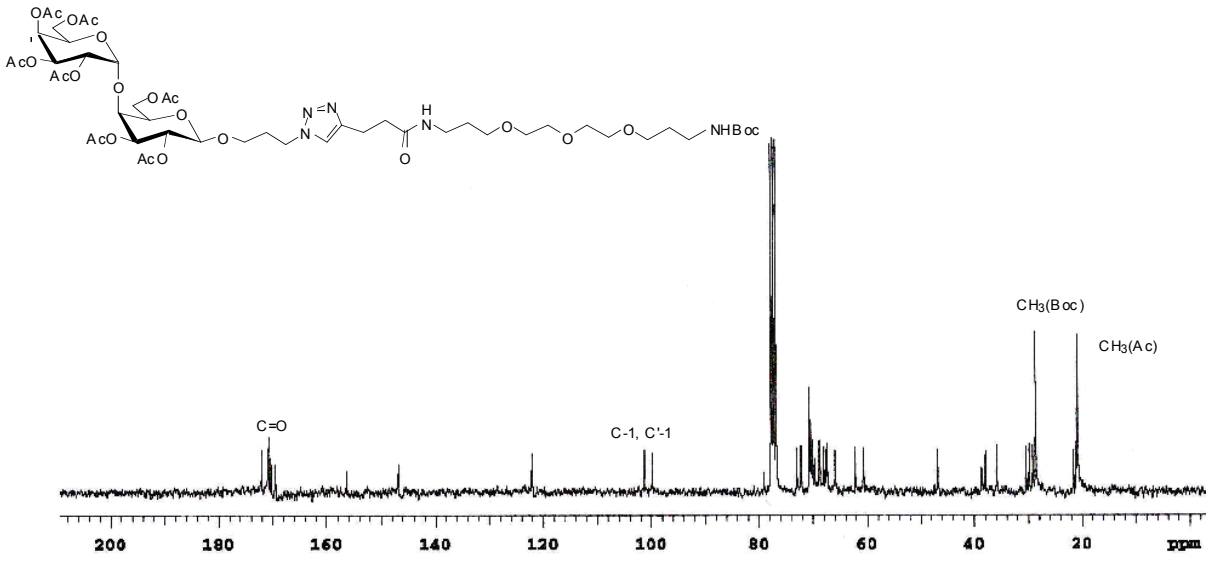


Electrospray Shizmadu LCMS-QP8000 (Mass Scan ES+):

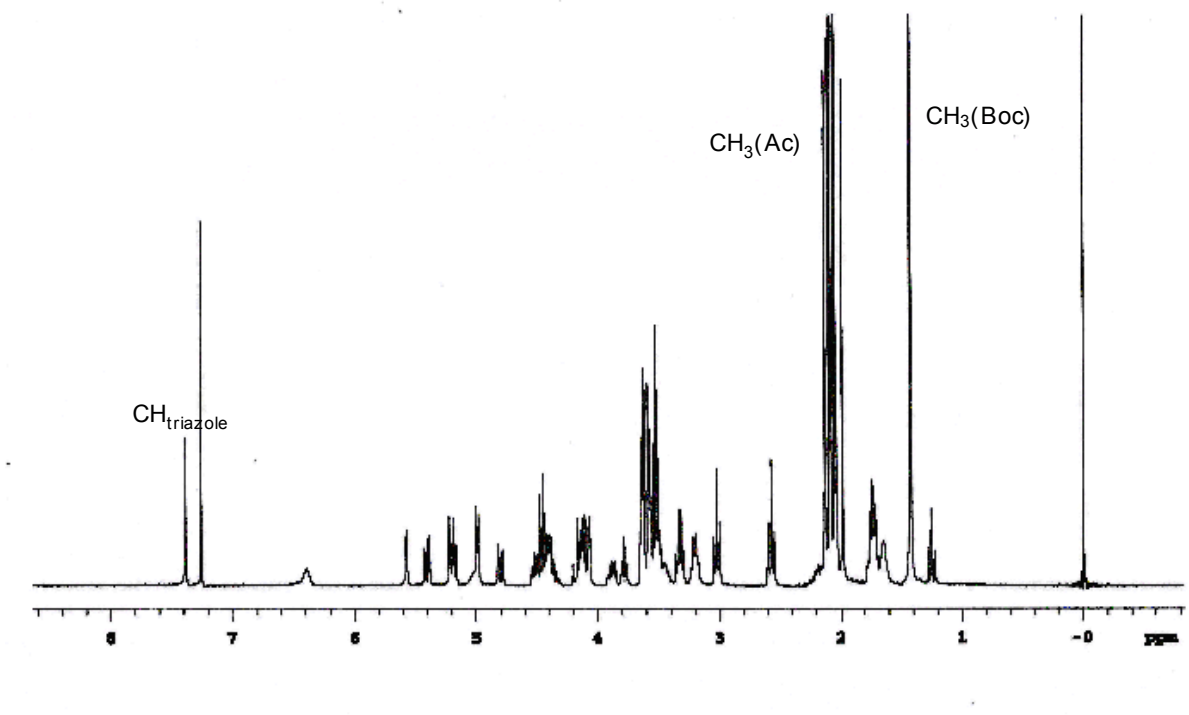


Galabiose derivative (**1f**):

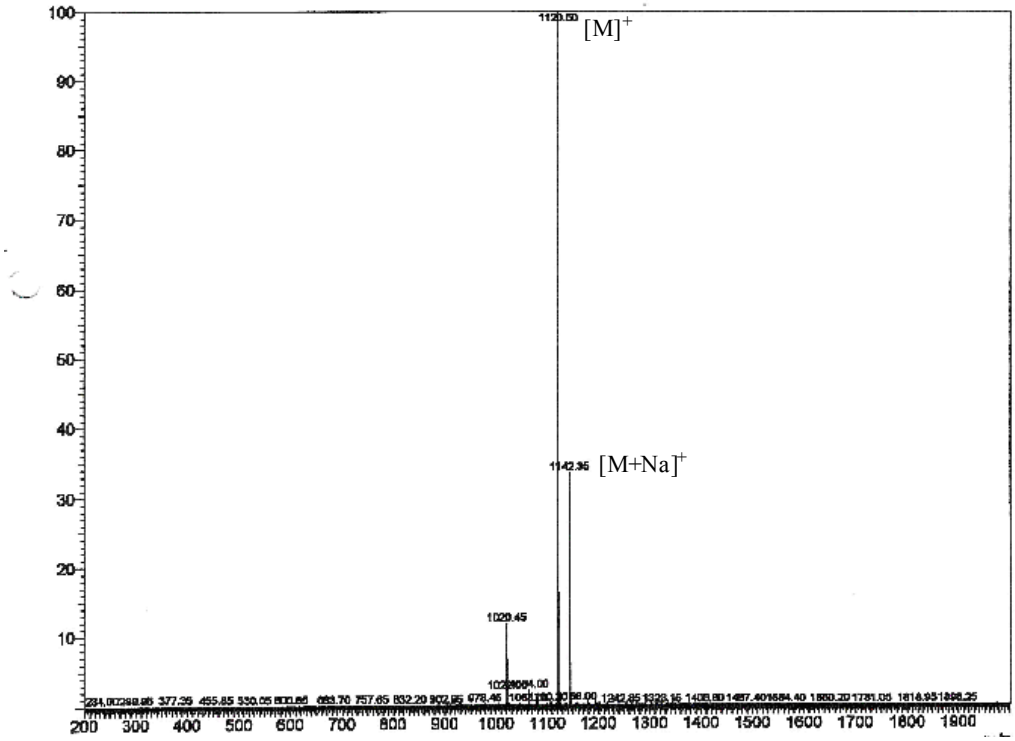
^{13}C NMR (75.5 MHz, $CDCl_3$):



^{1}H NMR (300 MHz, $CDCl_3$):

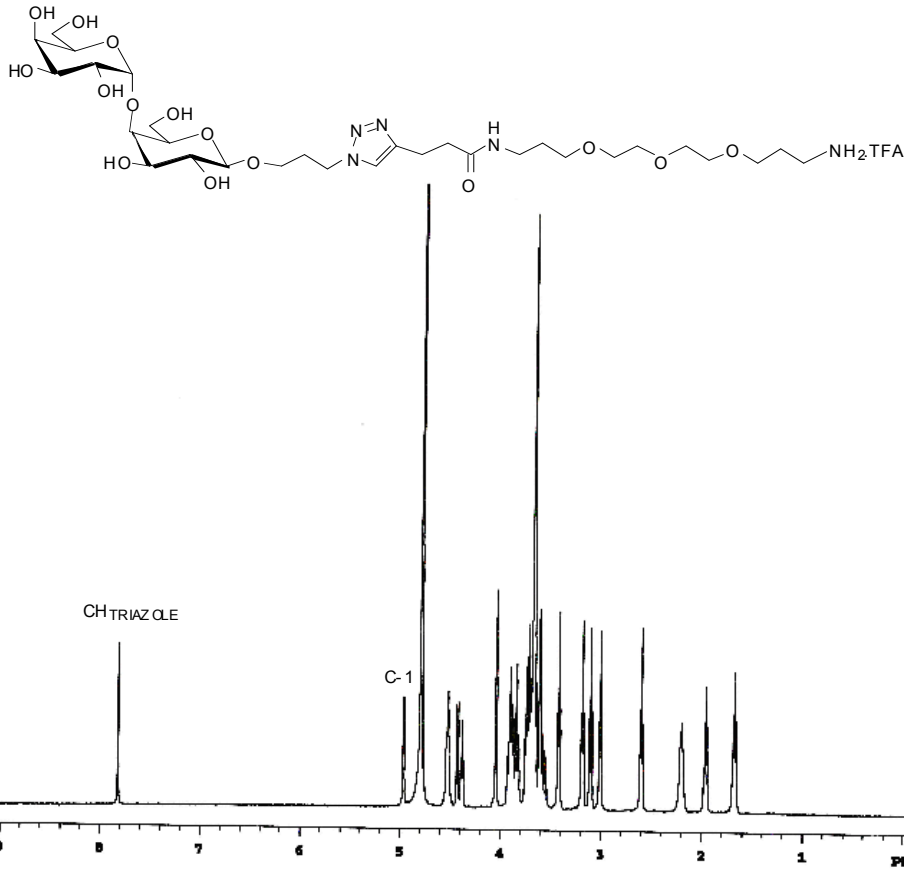


Electrospray Shizmadu LCMS-QP8000 (Mass Scan ES+):

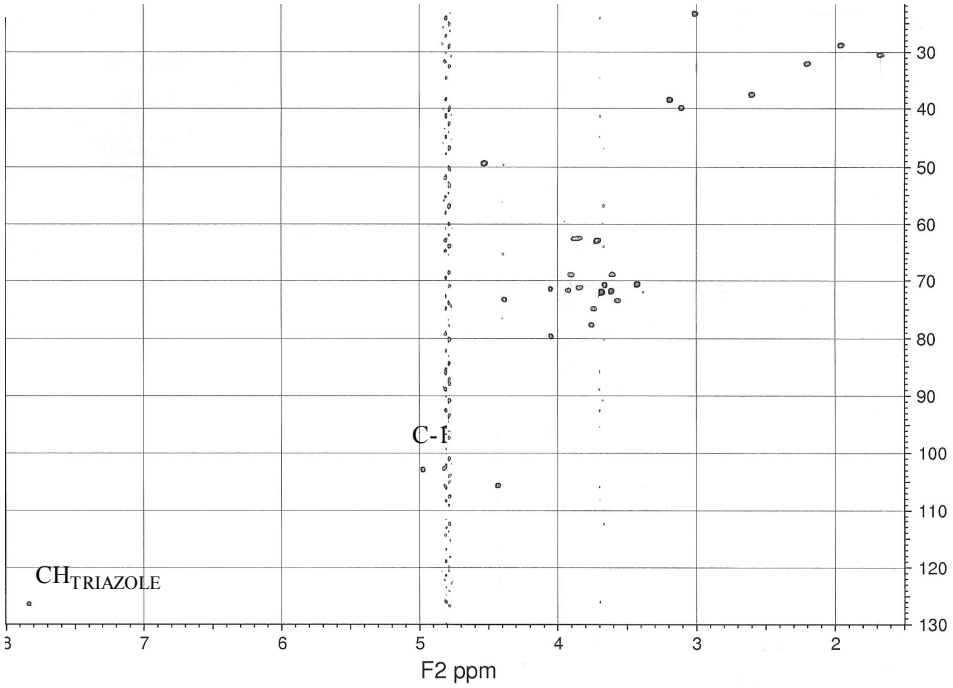


Galabiose derivative deprotected (**1f**):

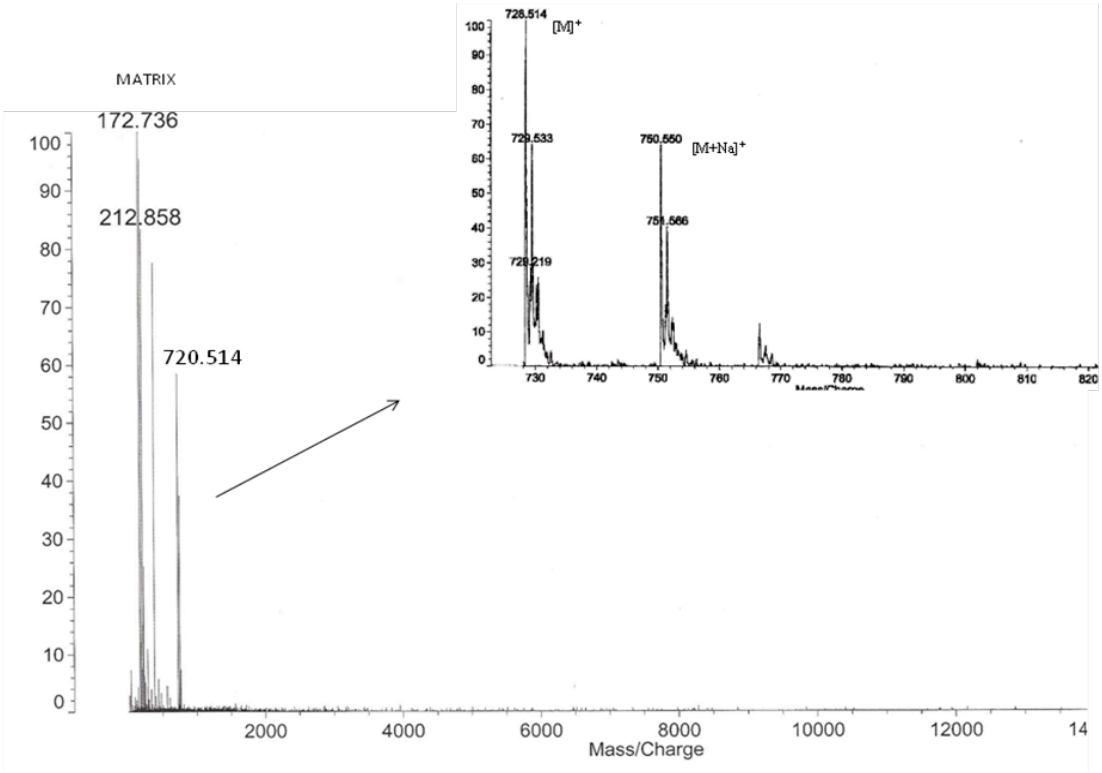
^{1}H NMR (300 MHz, D_2O):



HSQC NMR (500 MHz, D_2O):

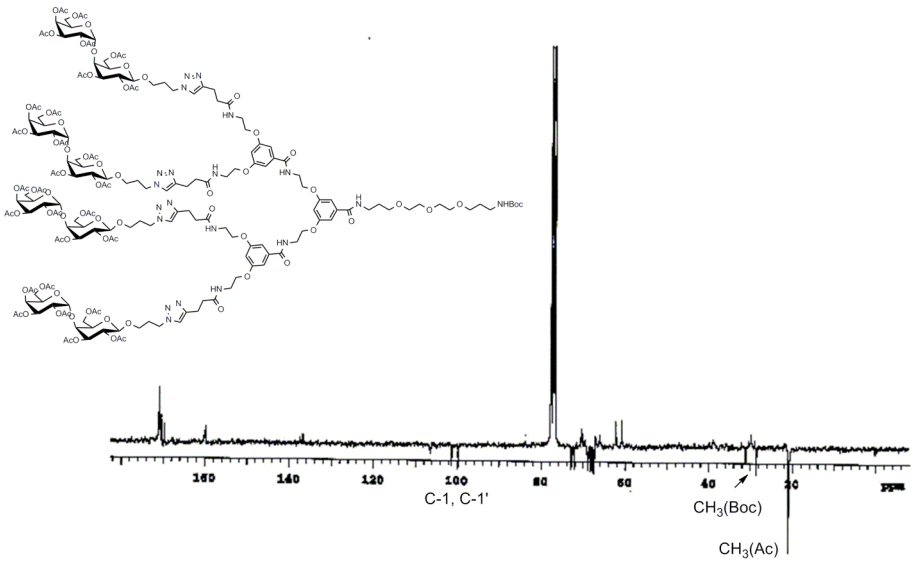


Electrospray Shizmadu LCMS-QP8000 (Mass Scan ES+):

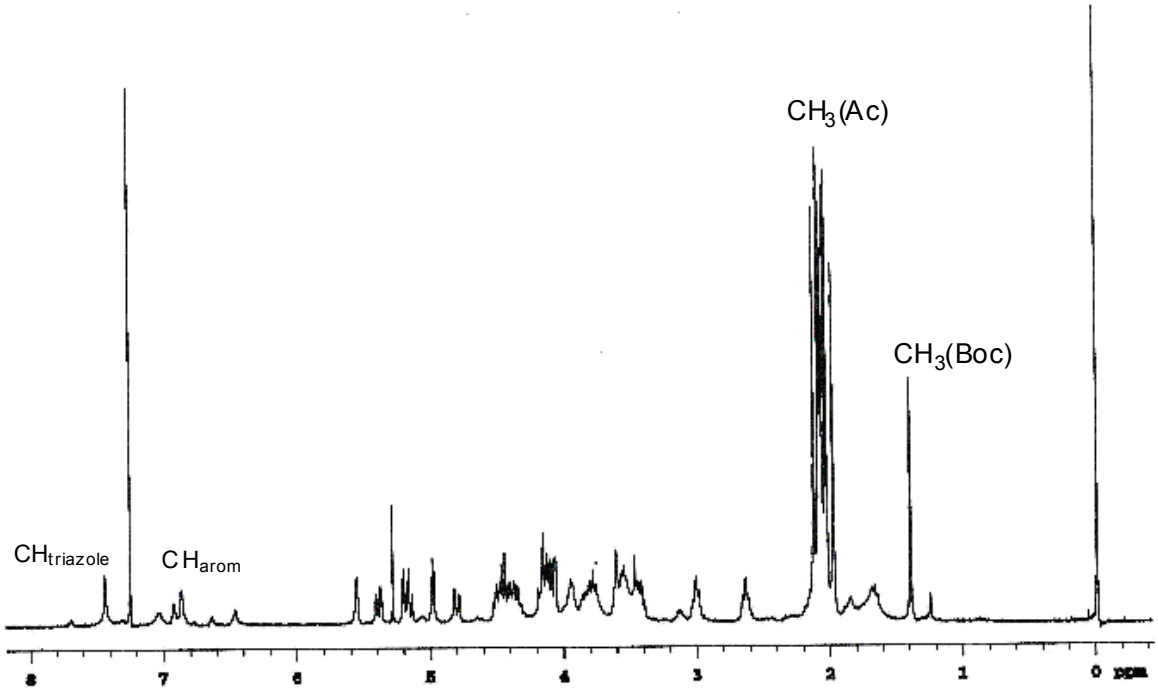


Tetravalent galabiose dendrimer (**3f**):

^{13}C NMR (75.5 MHz, $CDCl_3$):

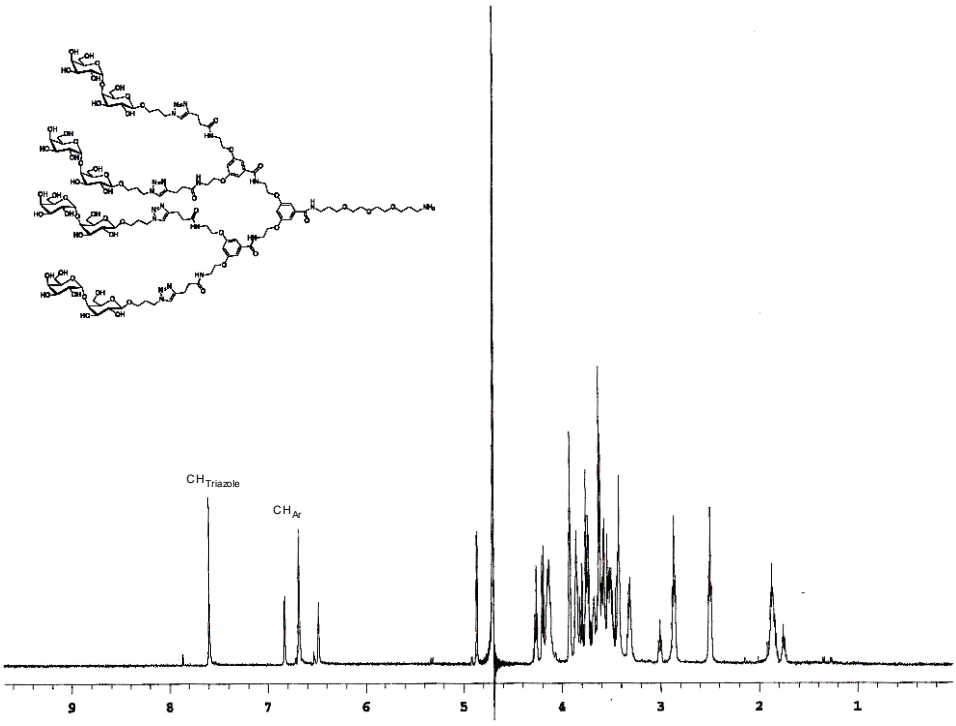


^{1}H NMR (300 MHz, $CDCl_3$):

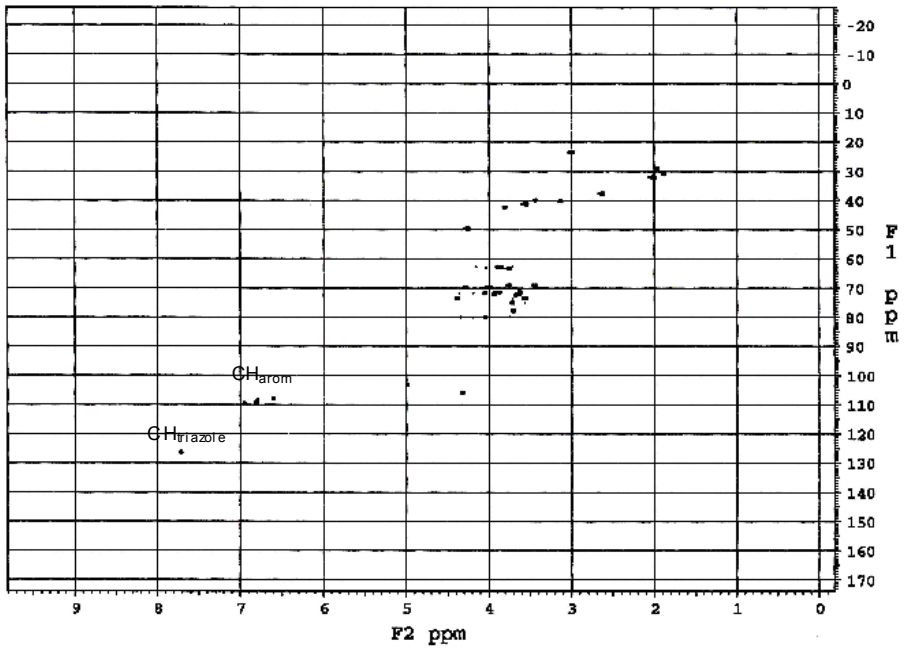


Tetravalent galabiose dendrimer deprotected (**3f**):

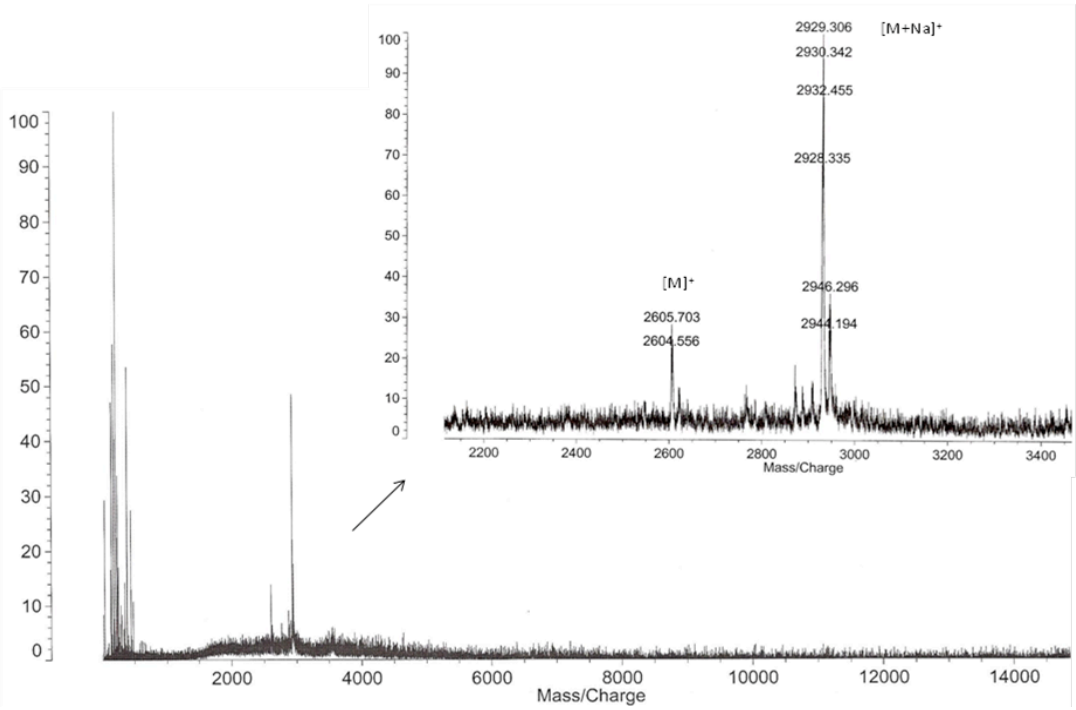
^{1}H NMR (300 MHz, D_2O):



HSQC NMR (500 MHz, D_2O):

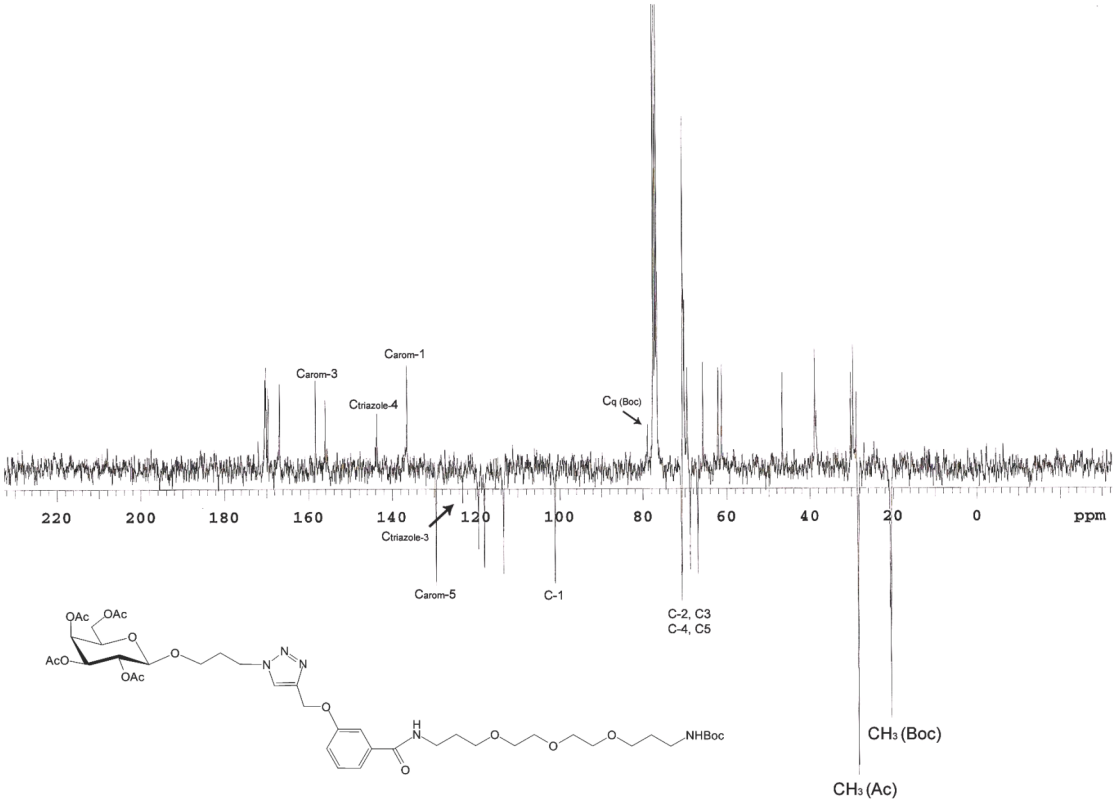


MALDI-TOF (MATRIX: α-Cyano-4-hydroxycinnamic acid):

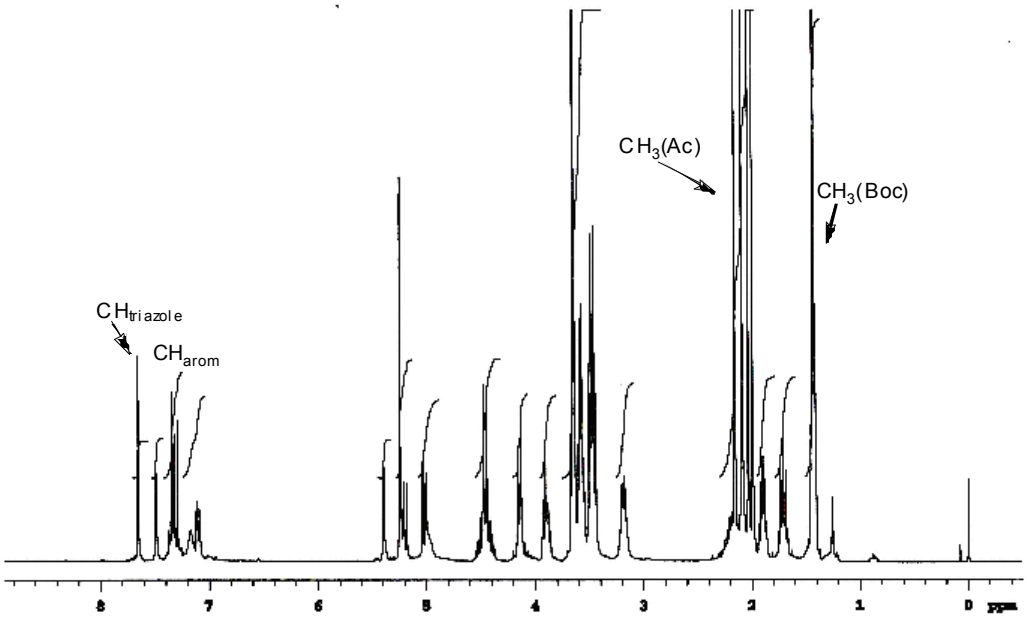


Galactose dendrimer (**1d**):

^{13}C NMR – APT (75.5 MHz, $CDCl_3$):

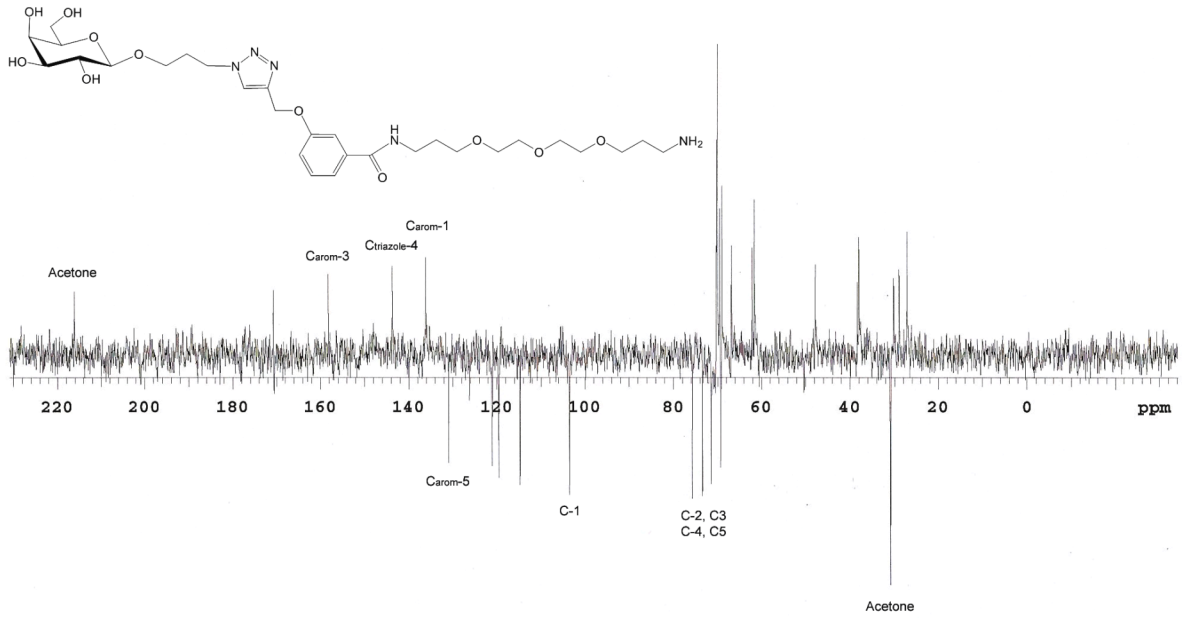


^{1}H NMR (300 MHz, $CDCl_3$):

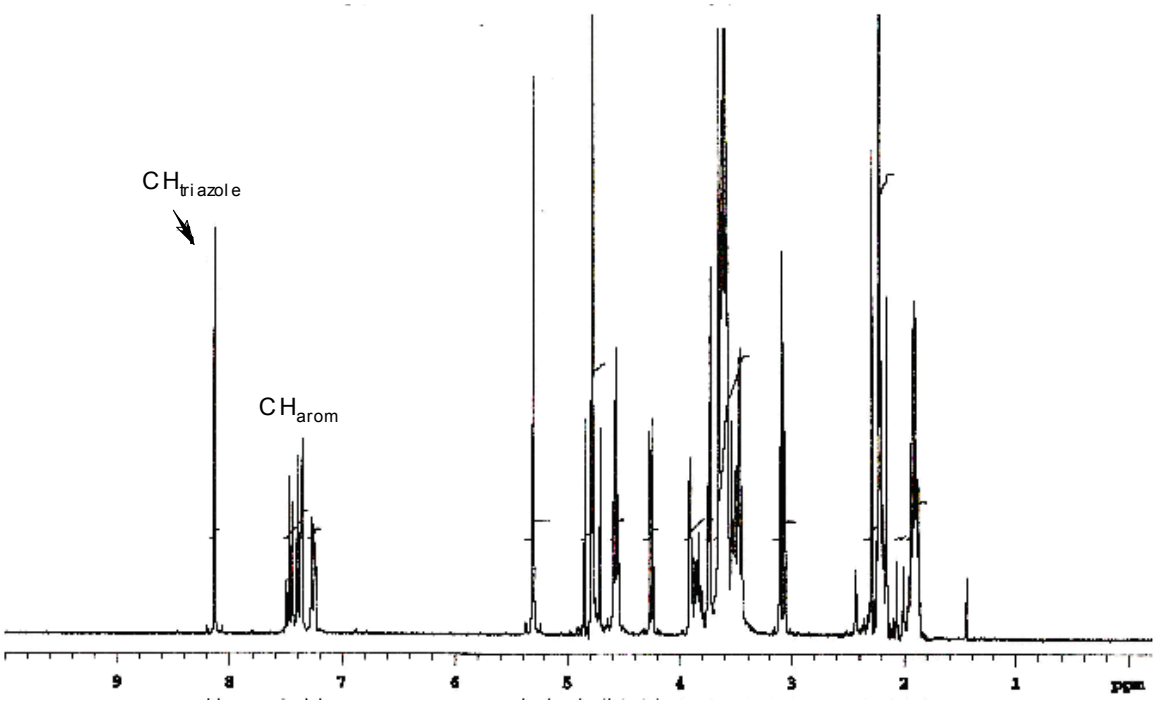


Galactose dendrimer deprotected (**1d**):

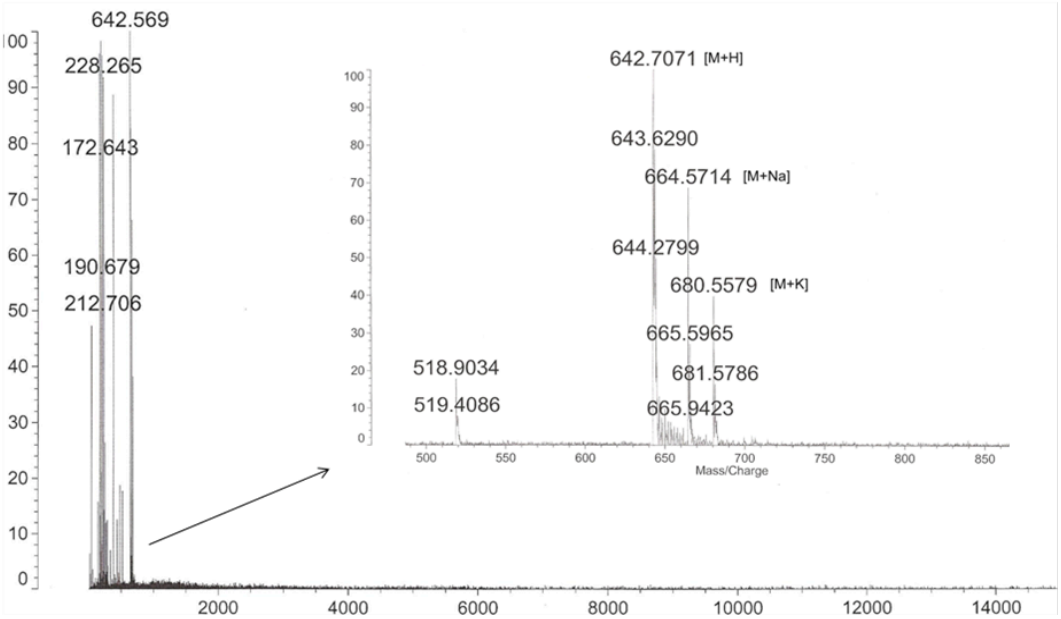
^{13}C NMR – APT (75.5 MHz, D_2O:Acetone 99:0.1):



^{1}H NMR (300 MHz, D_2O:Acetone 99:0.1):

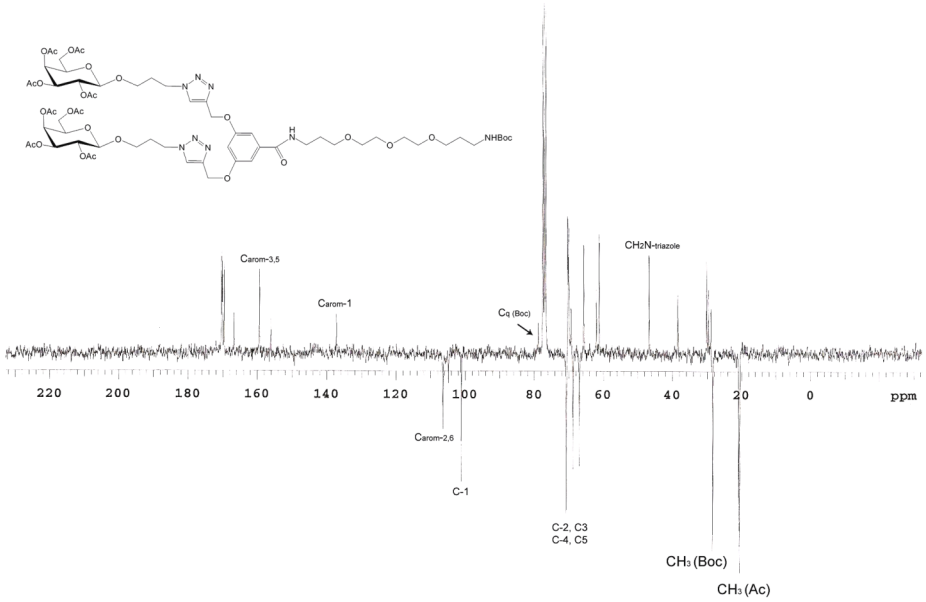


MALDI-TOF (MATRIX: α-Cyano-4-hydroxycinnamic acid):

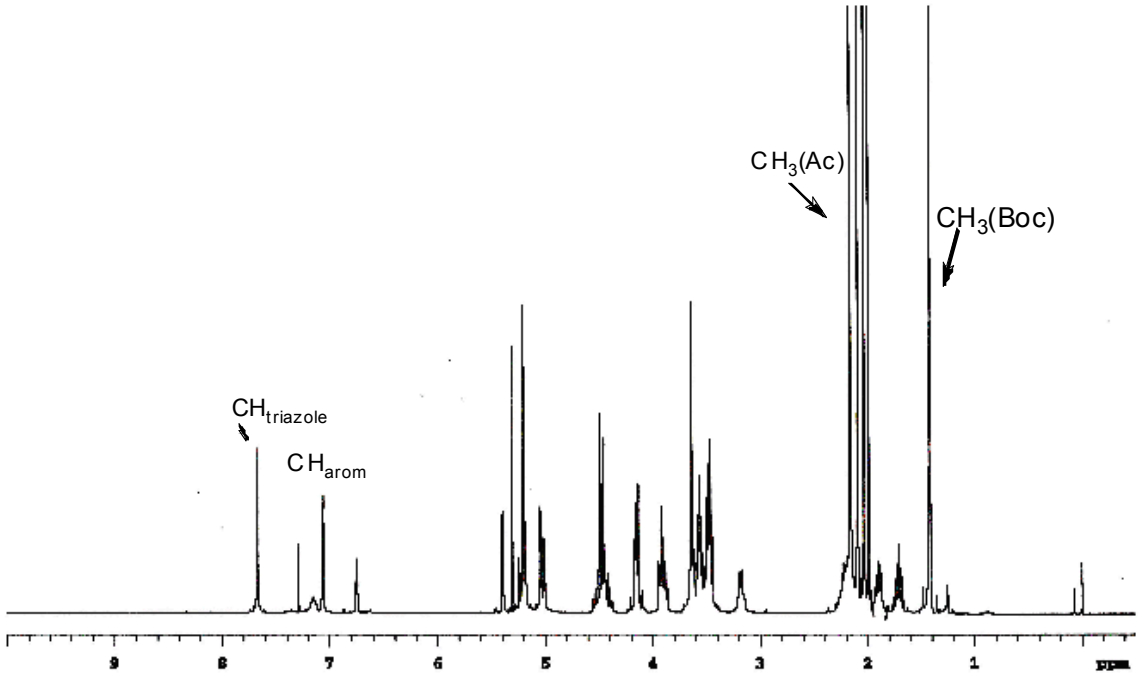


Divalent galactose dendrimer (**2d**):

^{13}C NMR – APT (75.5 MHz, $CDCl_3$):

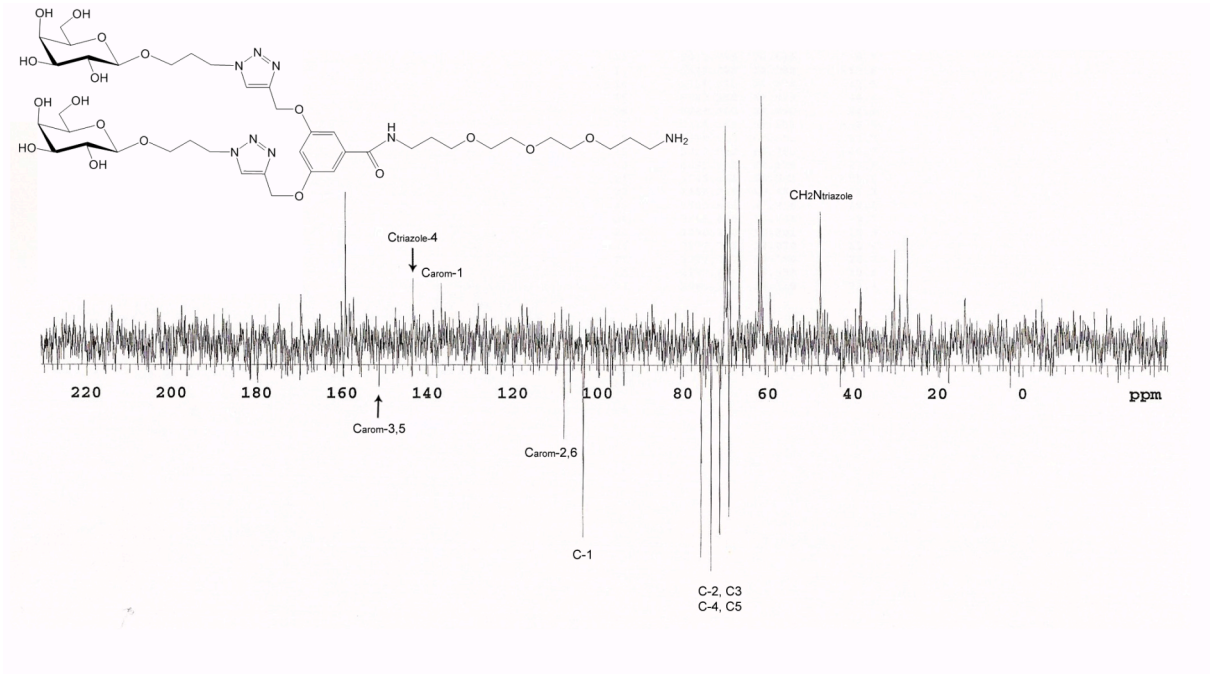


^{1}H NMR (300 MHz, $CDCl_3$):

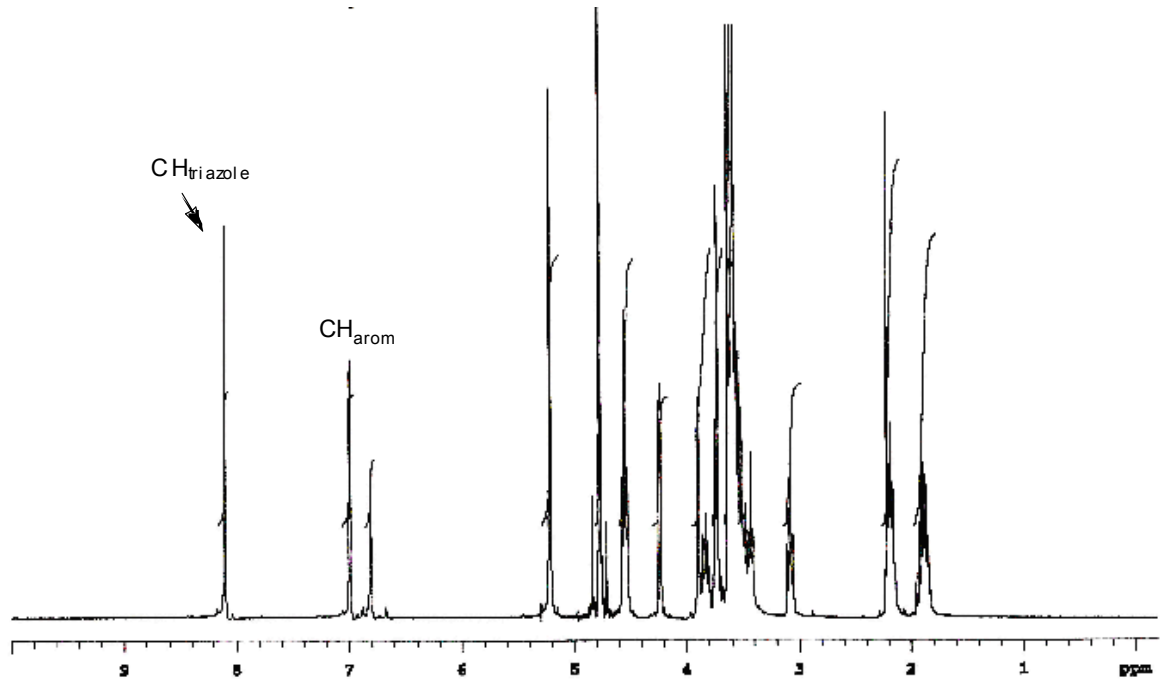


Divalent galactose dendrimer deprotected (**2d**):

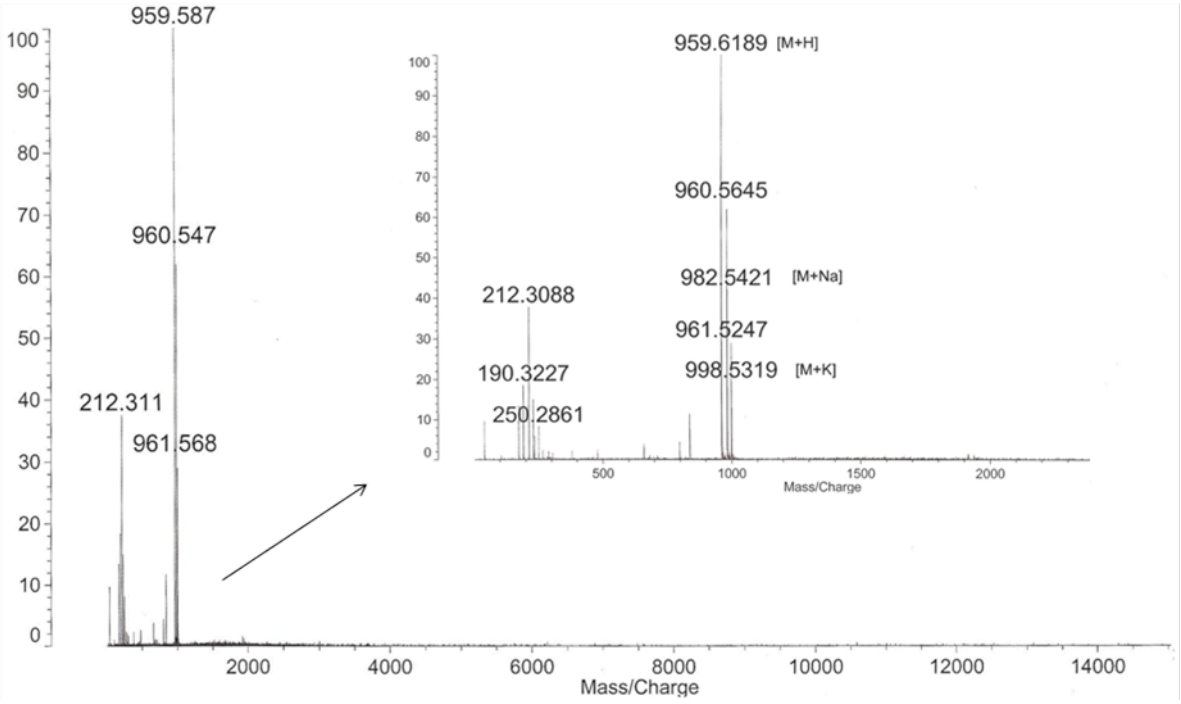
^{13}C NMR – APT (75.5 MHz, D_2O:Acetone 99:0.1):



^{1}H NMR (300 MHz, D_2O:Acetone 99:0.1):

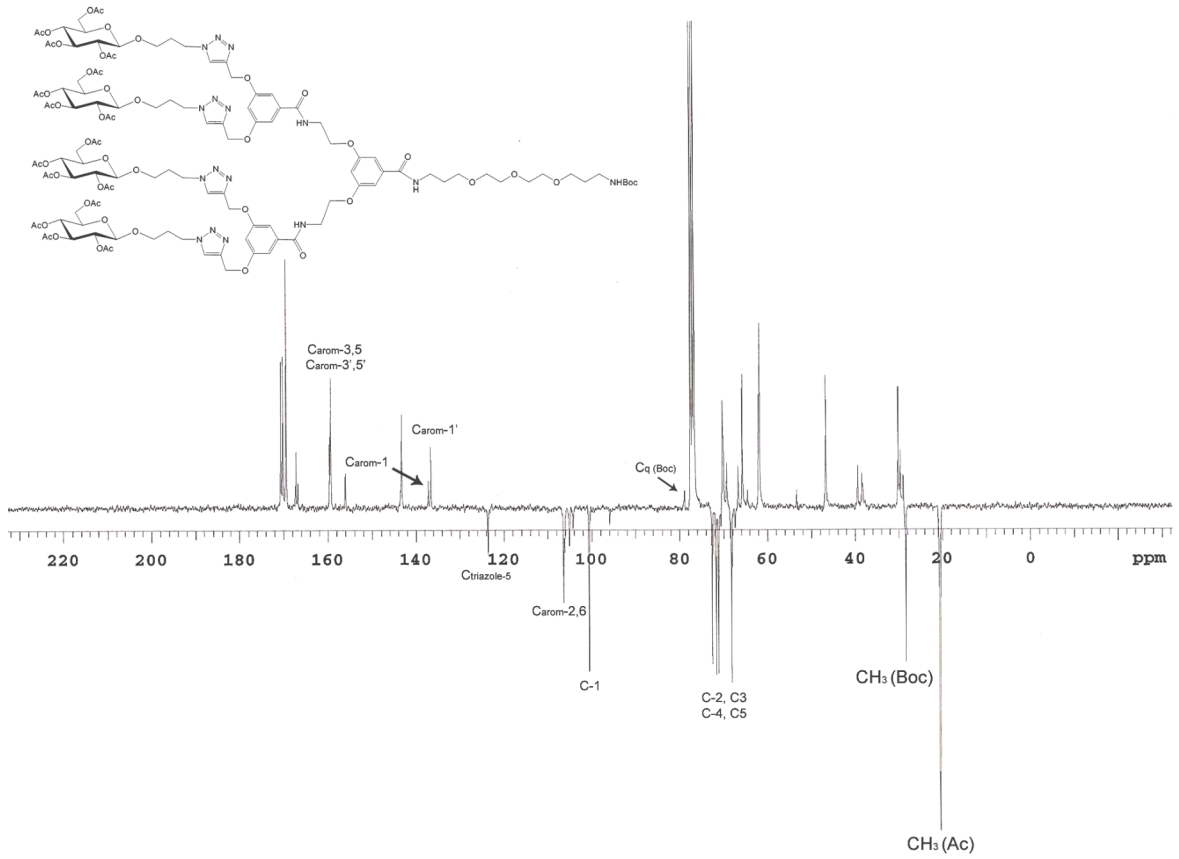


MALDI-TOF (MATRIX: α-Cyano-4-hydroxycinnamic acid):

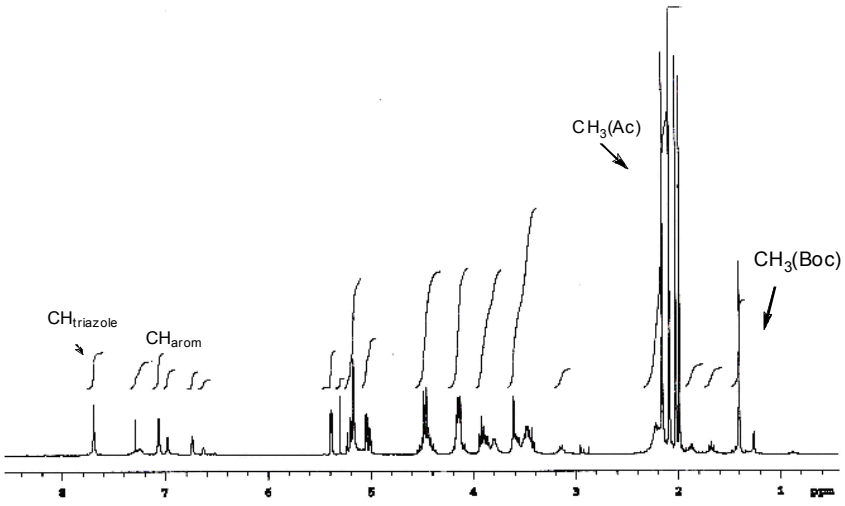


Tetravalent galactose dendrimer (**3d**):

^{13}C NMR – APT (75.5 MHz, $CDCl_3$):

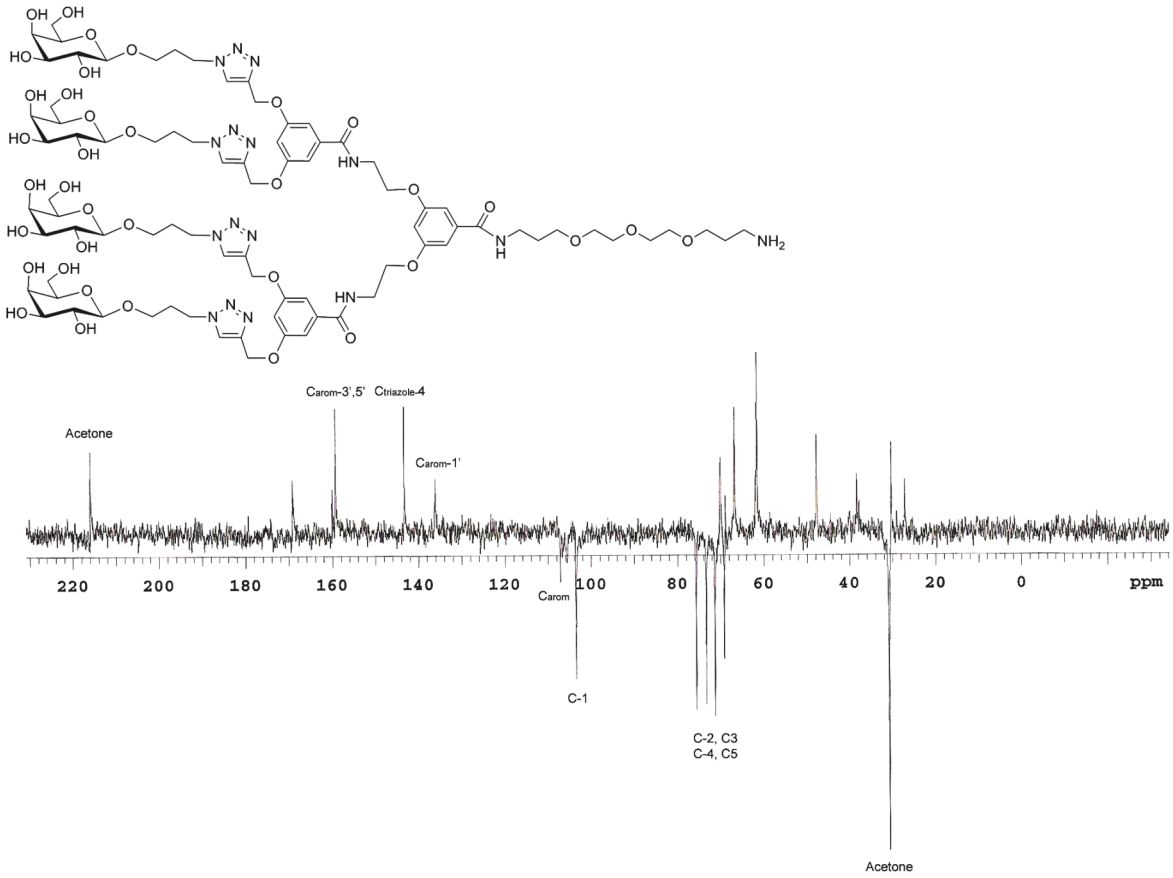


^{1}H NMR (300 MHz, $CDCl_3$):

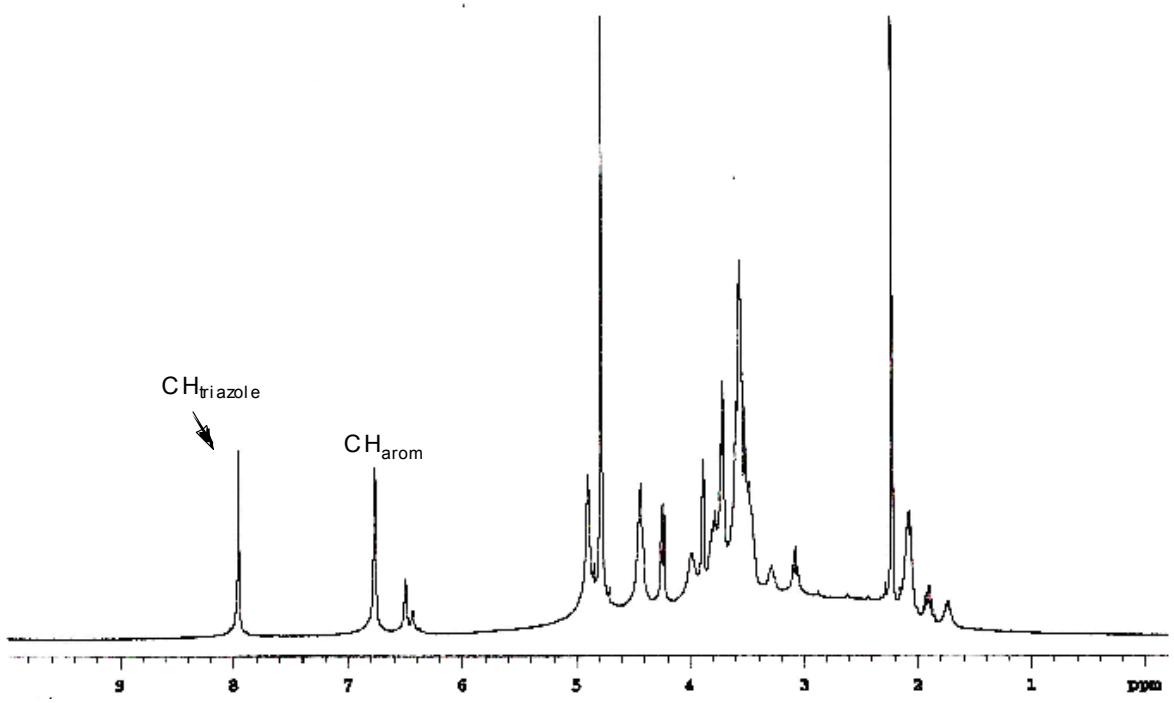


Tetravalent galactose dendrimer deprotected (**3d**):

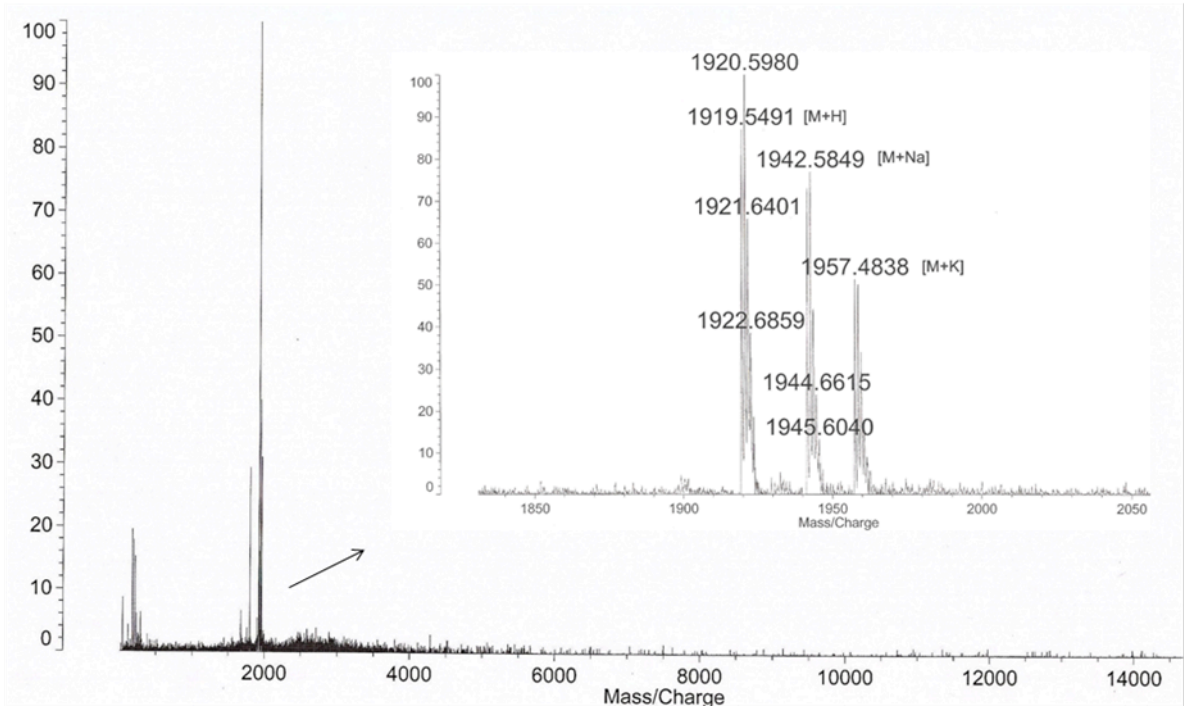
^{13}C NMR – APT (75.5 MHz, D_2O:Acetone 99:0.1):



^{1}H NMR (300 MHz, D_2O:Acetone 99:0.1):

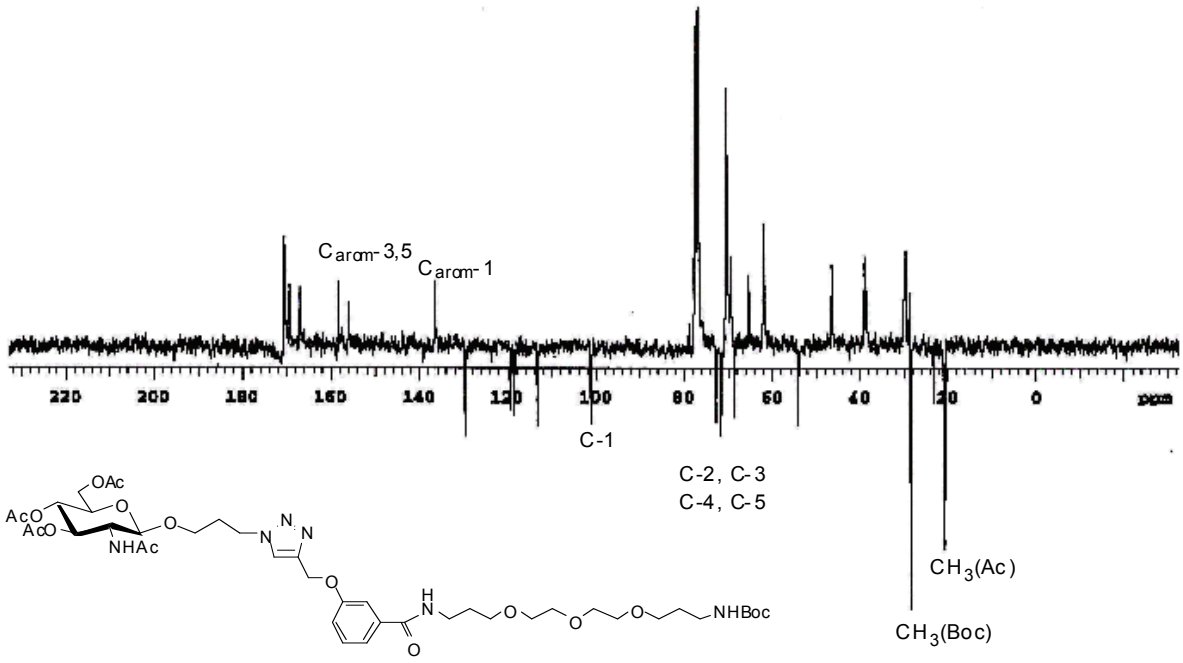


MALDI-TOF (MATRIX: α-Cyano-4-hydroxycinnamic acid):

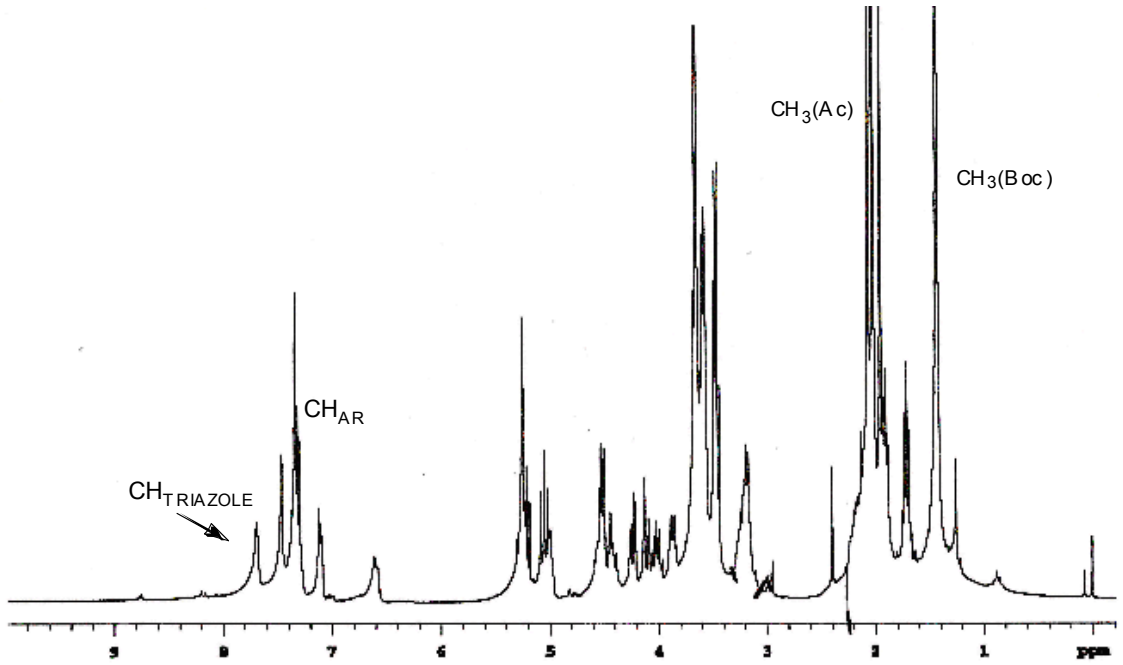


GlcNAc derivative (**1c**):

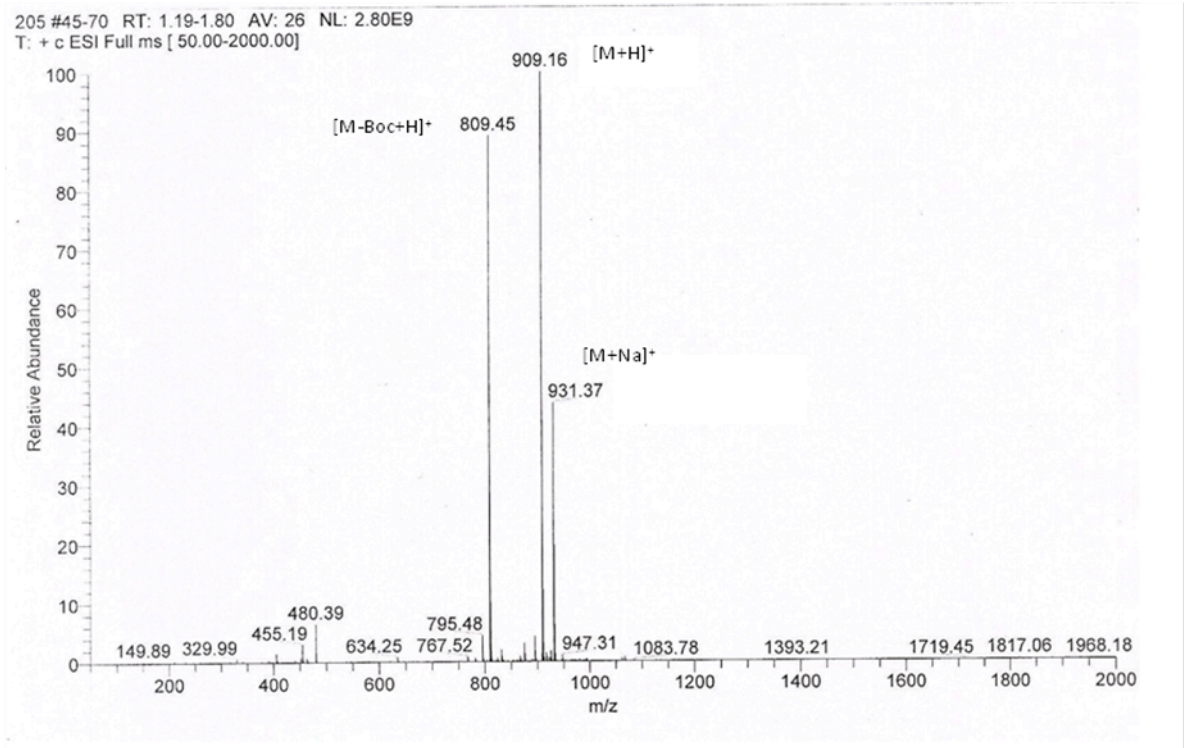
^{13}C NMR – APT (75.5 MHz, $CDCl_3$):



^{1}H NMR (300 MHz, $CDCl_3$):

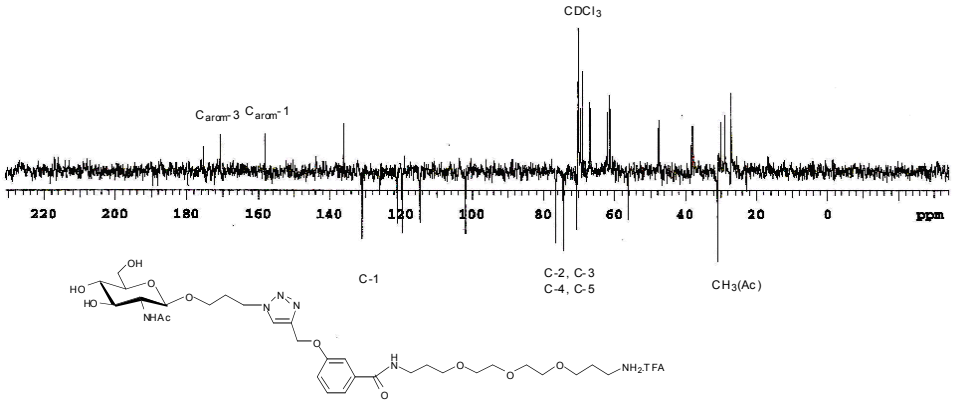


Electrospray Shizmadu LCMS-QP8000 (Mass Scan ES+):

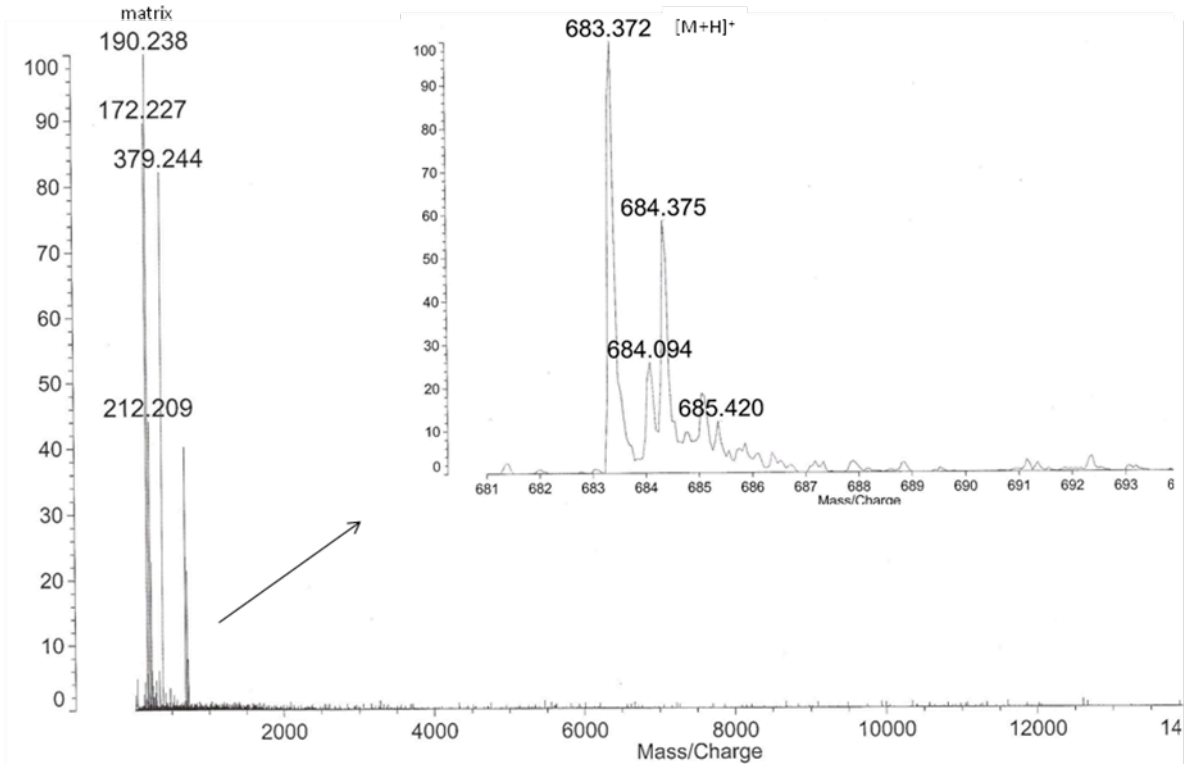


GlcNAc derivative deprotected (**1c**):

^{13}C NMR – APT (75.5 MHz, D_2O:Acetone 99:0.1):

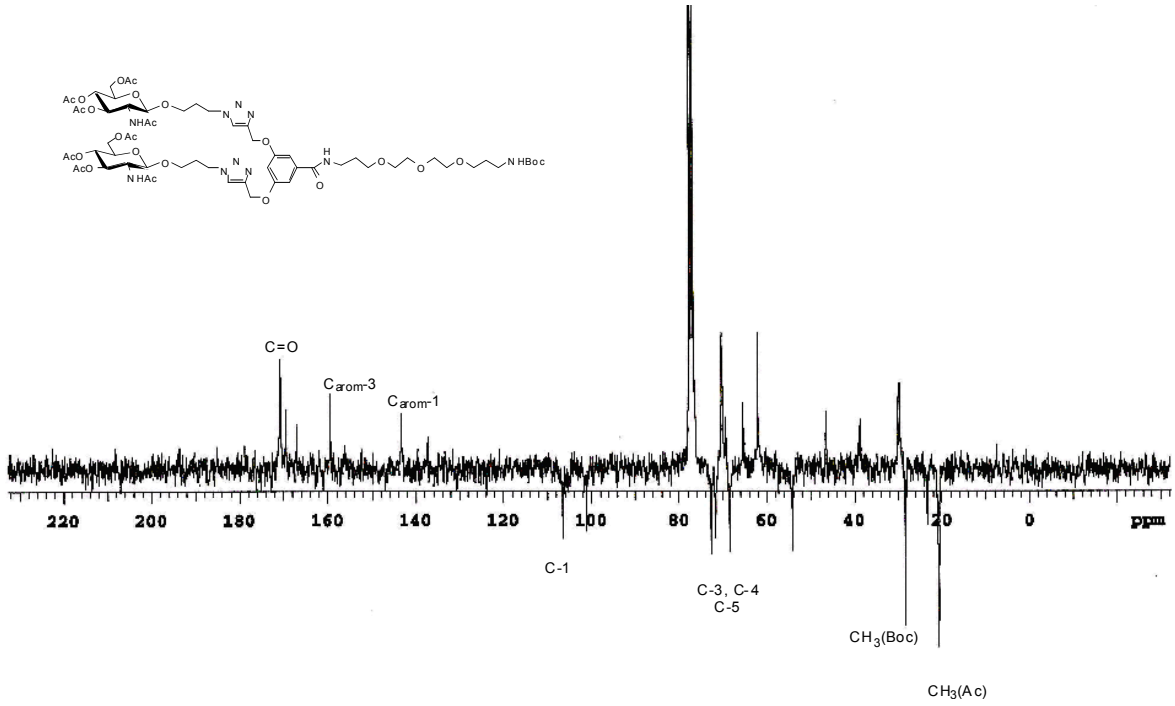


MALDI-TOF (MATRIX: α-Cyano-4-hydroxycinnamic acid):

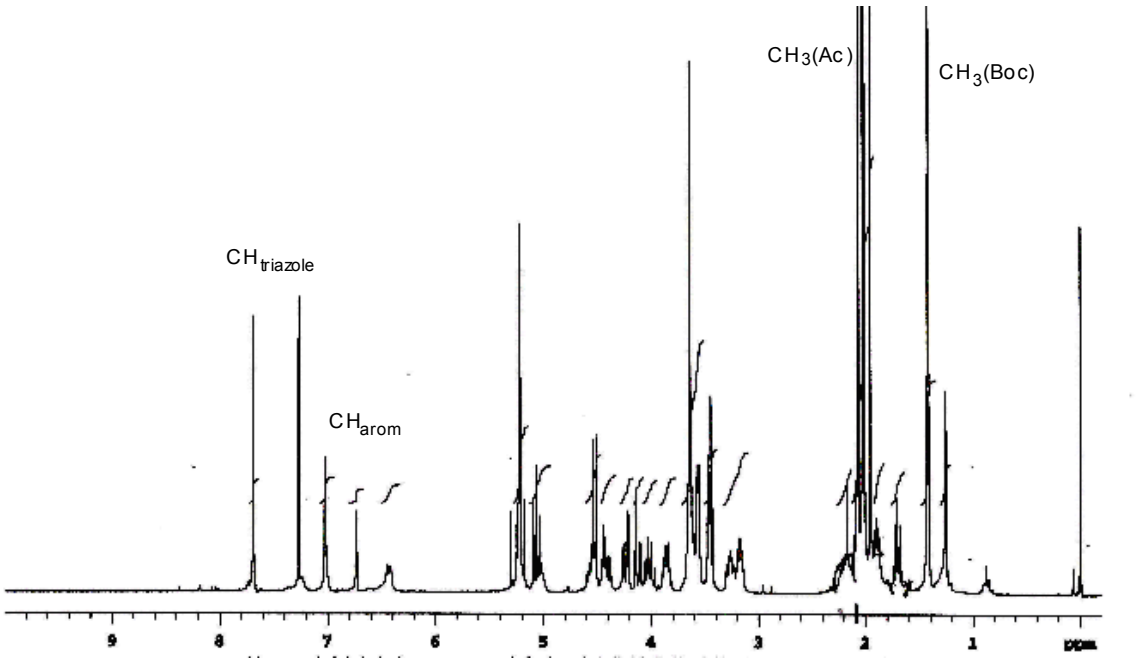


Divalent GlcNAc dendrimer (**2c**):

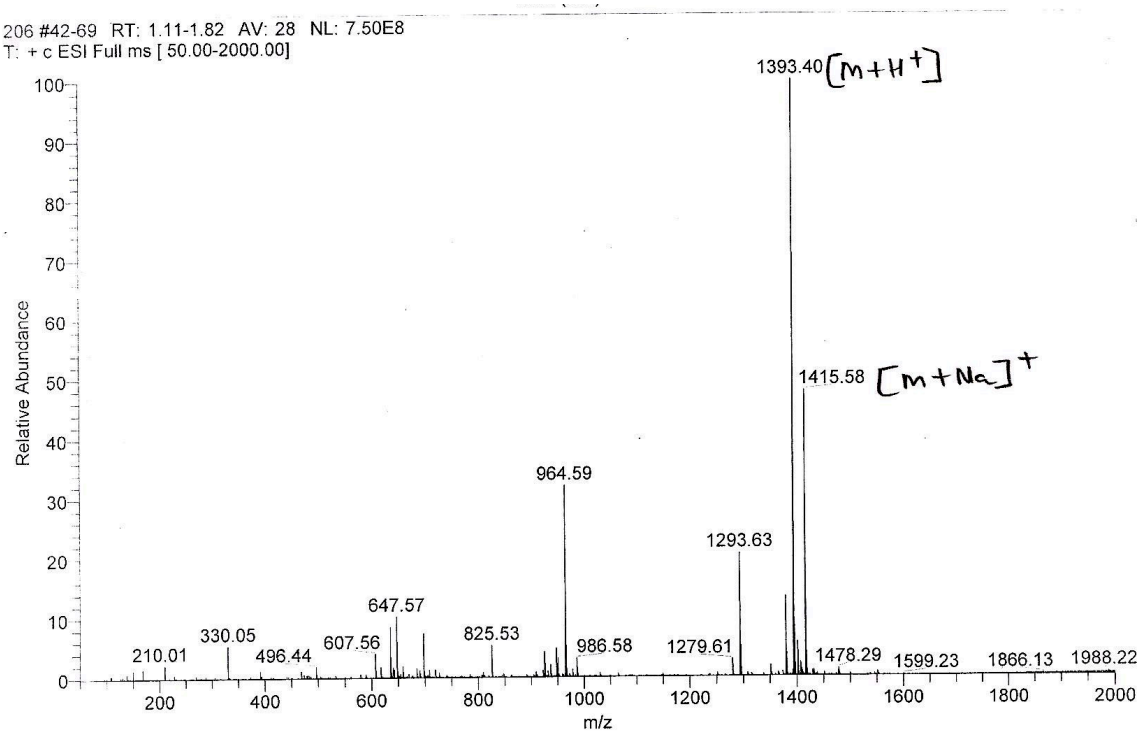
^{13}C NMR – APT (75.5 MHz, $CDCl_3$):



^{1}H NMR (300 MHz, $CDCl_3$):

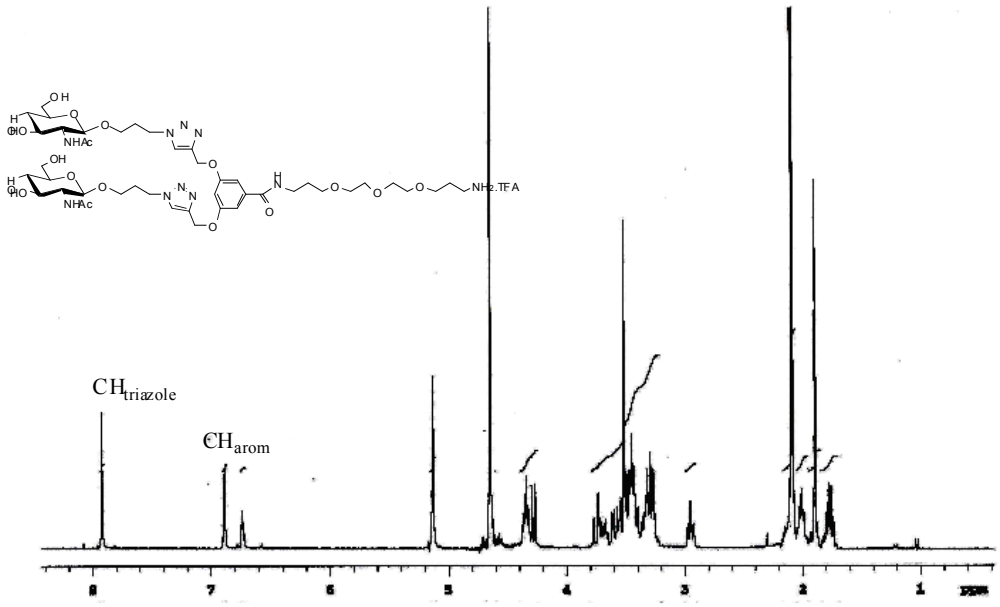


Electrospray Shizmadu LCMS-QP8000 (Mass Scan ES+):

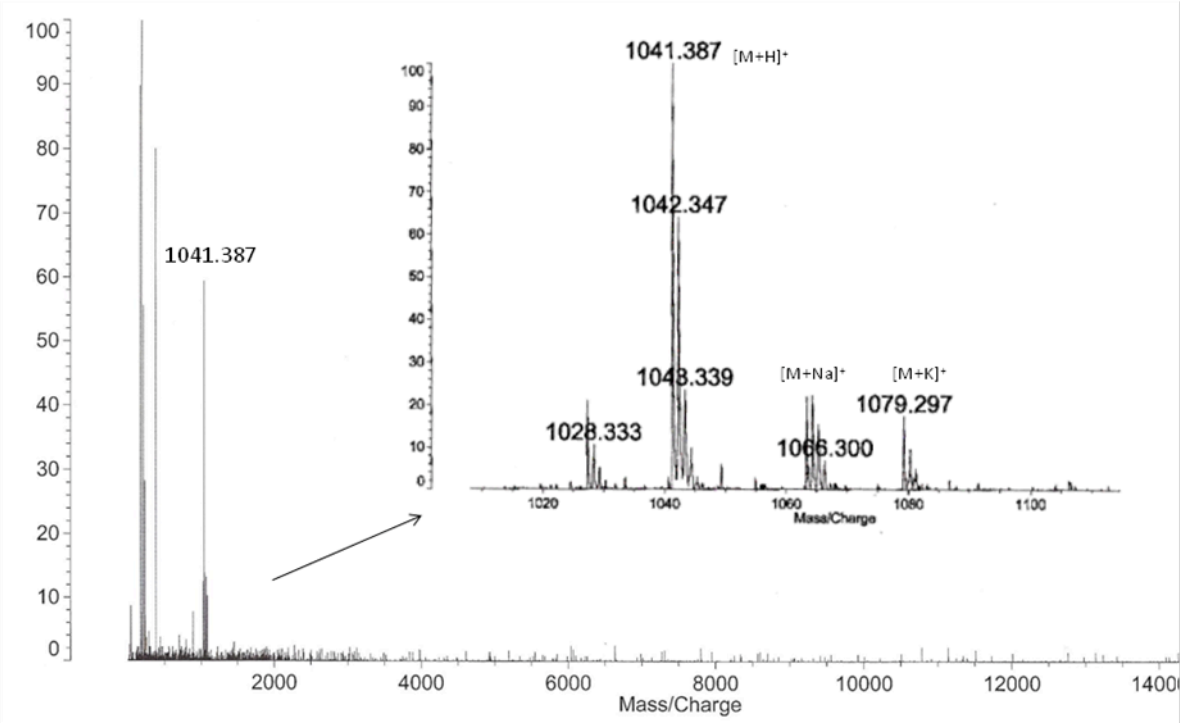


Divalent GlcNAc dendrimer deprotected (**2c**):

^{1}H NMR (300 MHz, D_2O: Acetone 99:0.1):

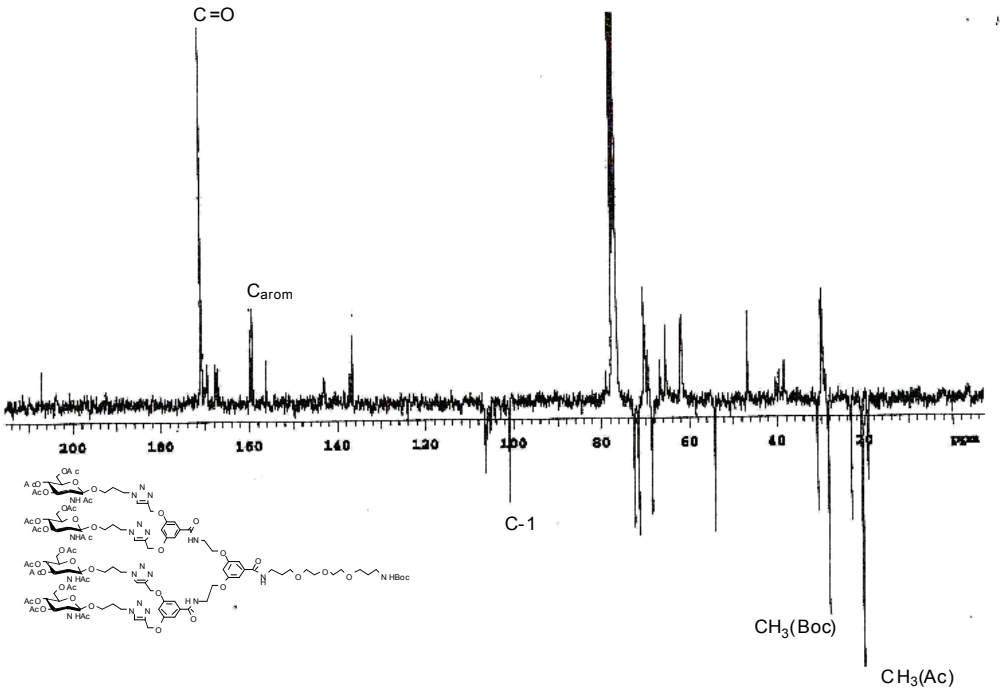


MALDI-TOF (MATRIX: α-Cyano-4-hydroxycinnamic acid):

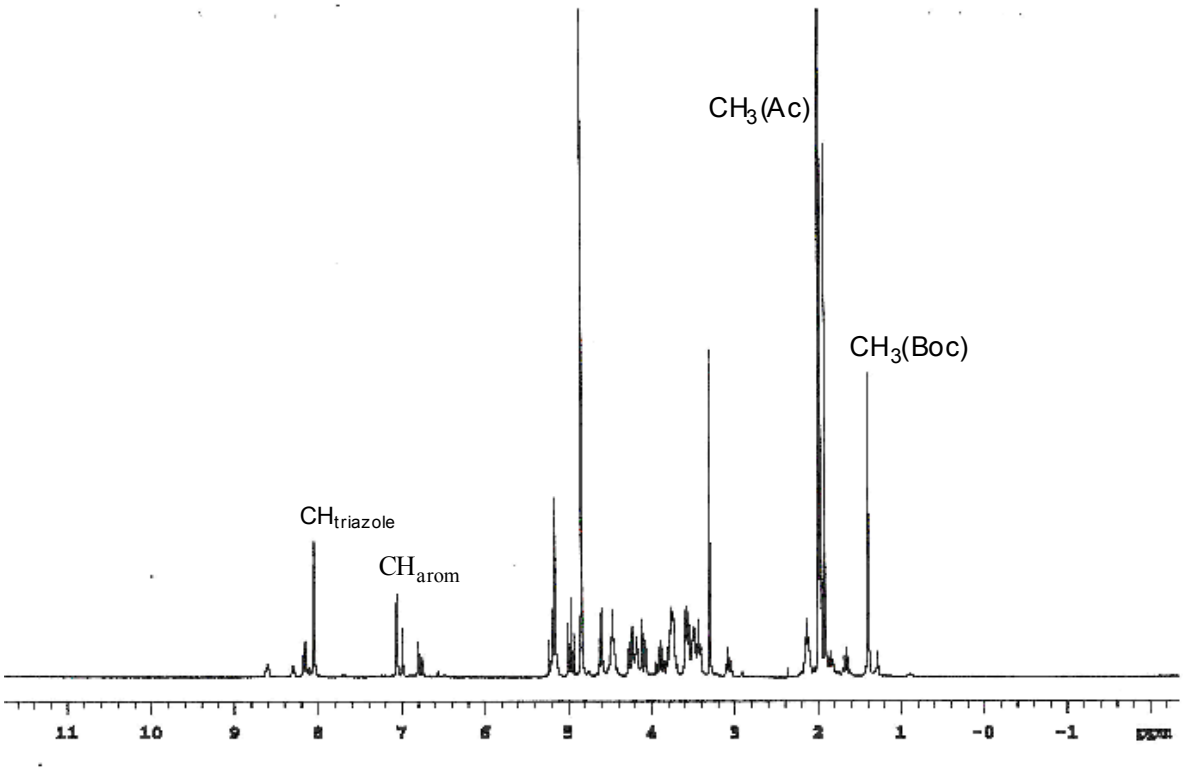


Tetravalent GlcNAc dendrimer (**3c**).

^{13}C NMR – APT (75.5 MHz, CD_3OD):

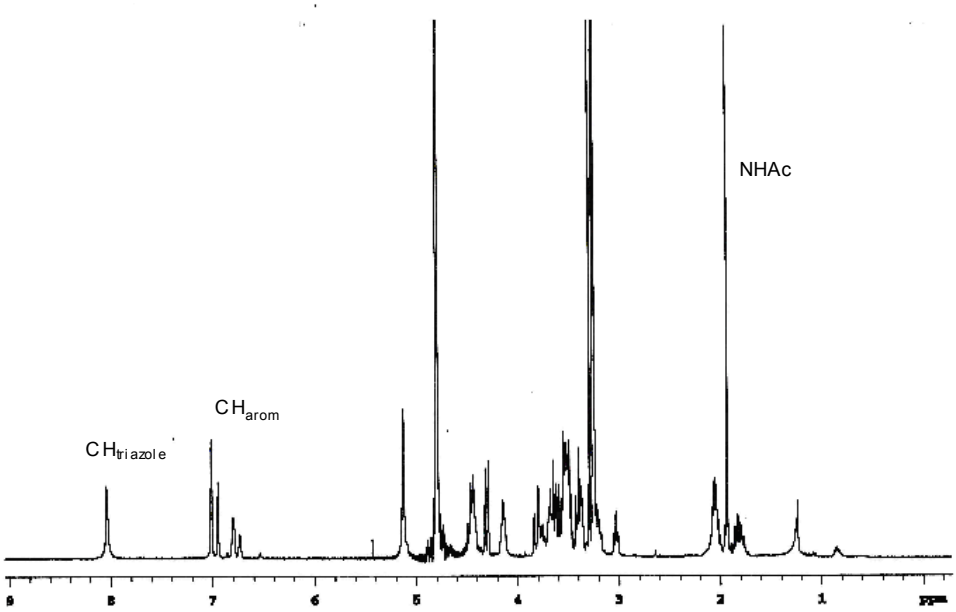


^{1}H NMR (300 MHz, CD_3OD):

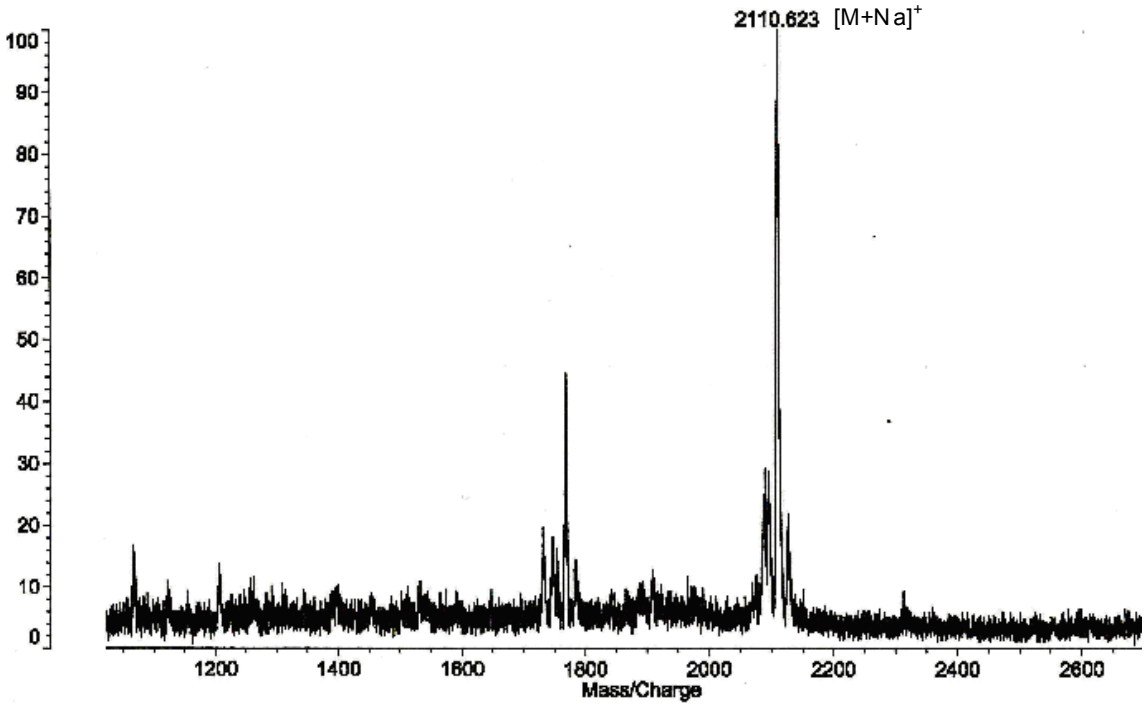


Tetravalent GlcNAc dendrimer deprotected (**3c**):

^{1}H NMR (300 MHz, D_2O:Acetone 99:0.1):

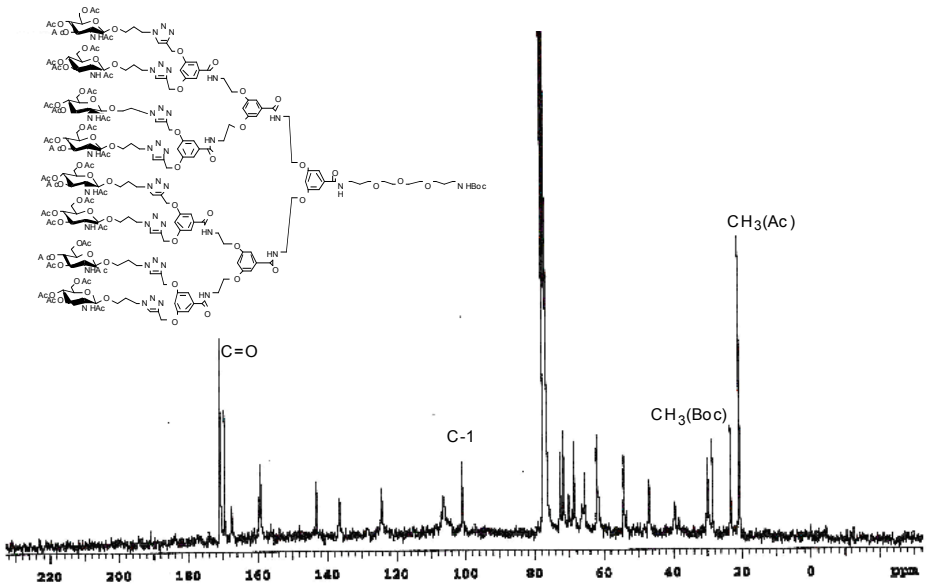


MALDI-TOF (MATRIX: α-Cyano-4-hydroxycinnamic acid):

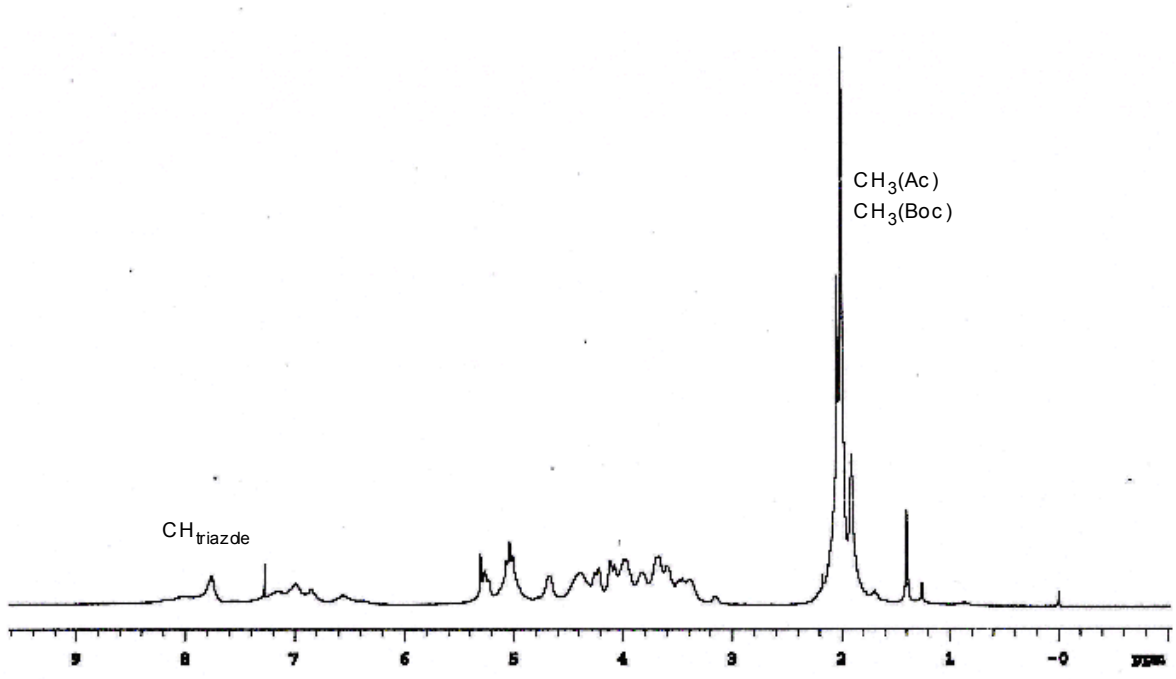


Octavalent GlcNAc dendrimer (**4c**):

^{13}C NMR (75.5 MHz, CD_3OD):

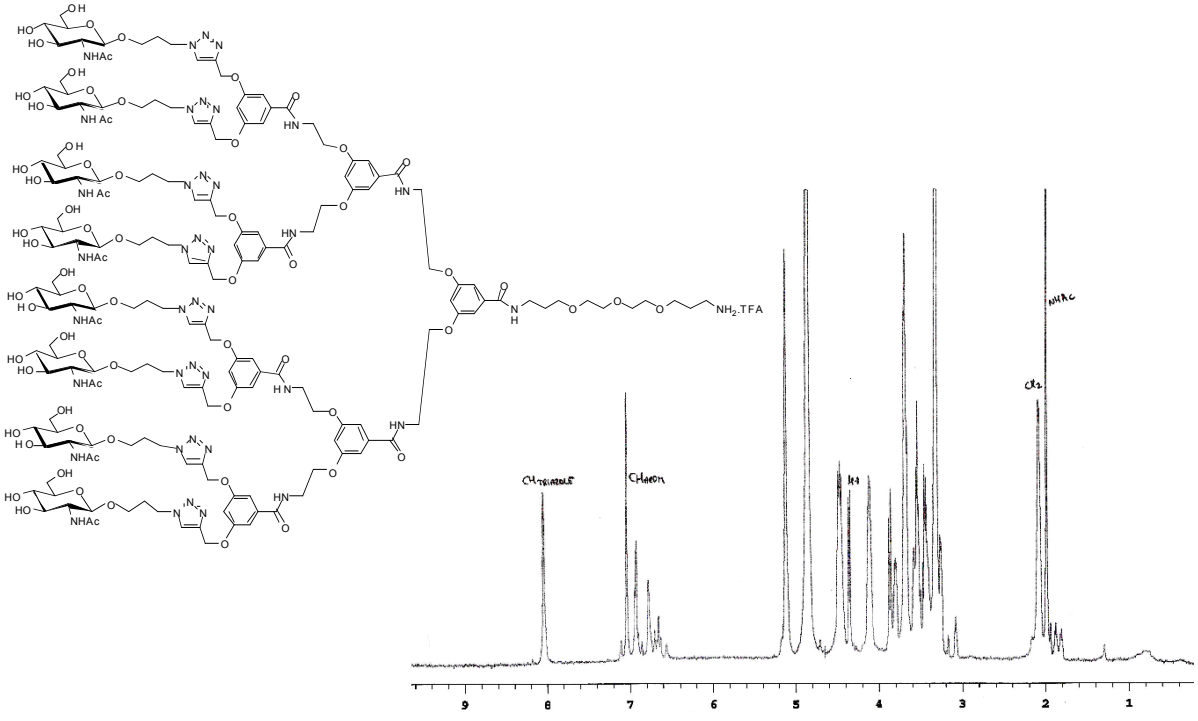


^{1}H NMR (300 MHz, CD_3OD):

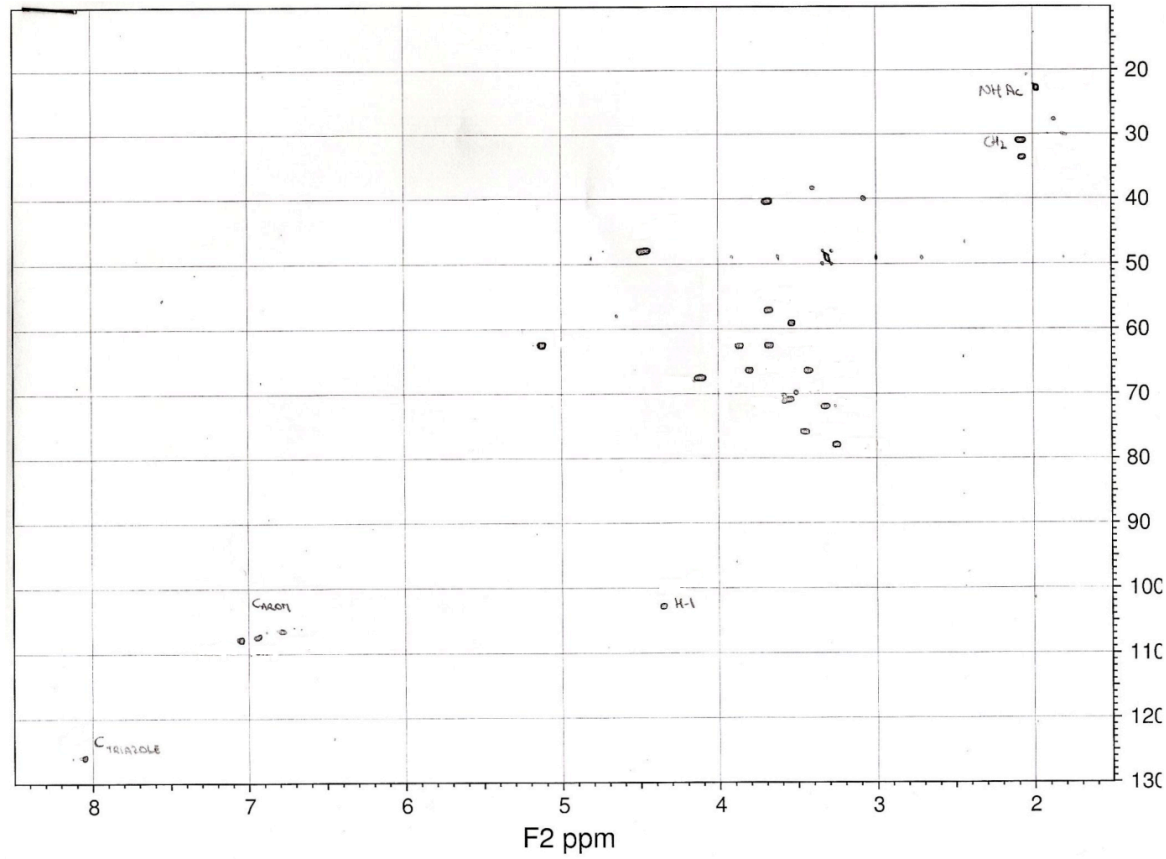


Octavalent GlcNAc dendrimer deprotected (**4c**):

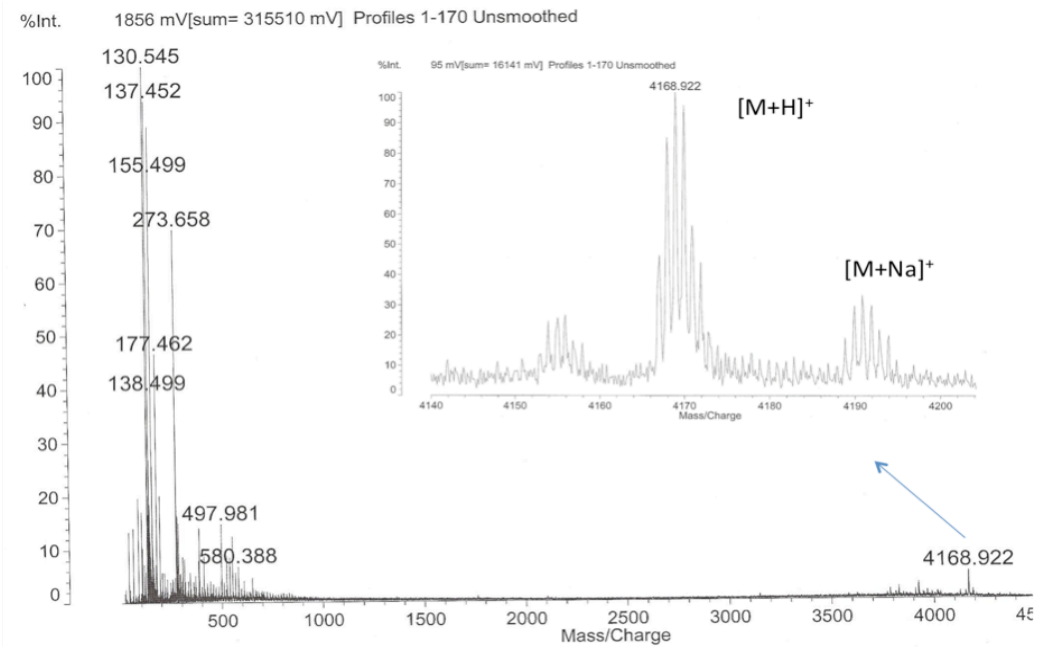
^{1}H NMR (500 MHz, CD_3OD):



HSQC NMR (500 MHz, CD_3OD):

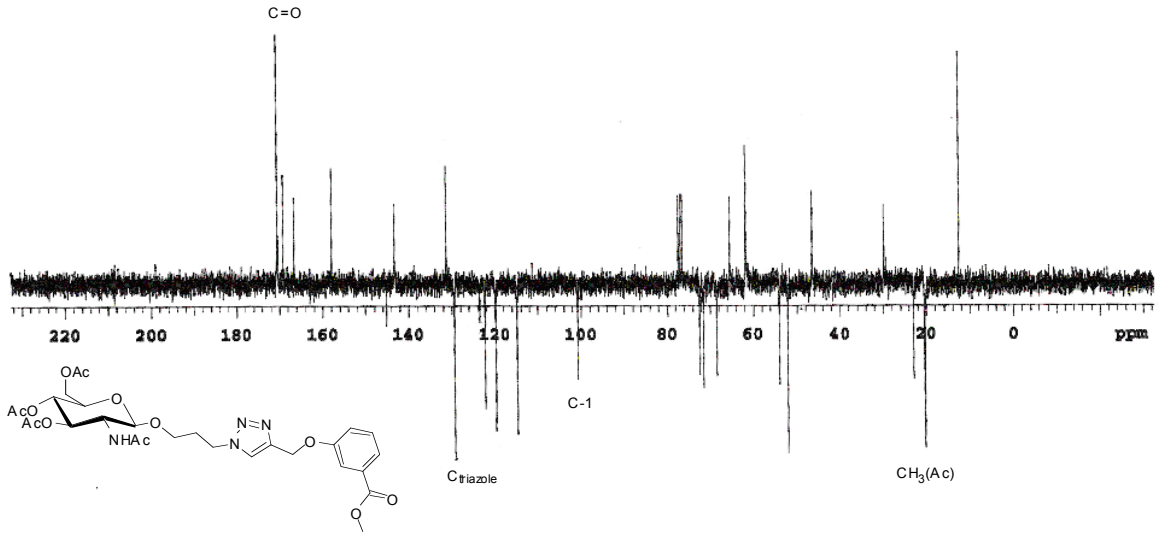


MALDI-TOF (MATRIX: α-Cyano-4-hydroxycinnamic acid):

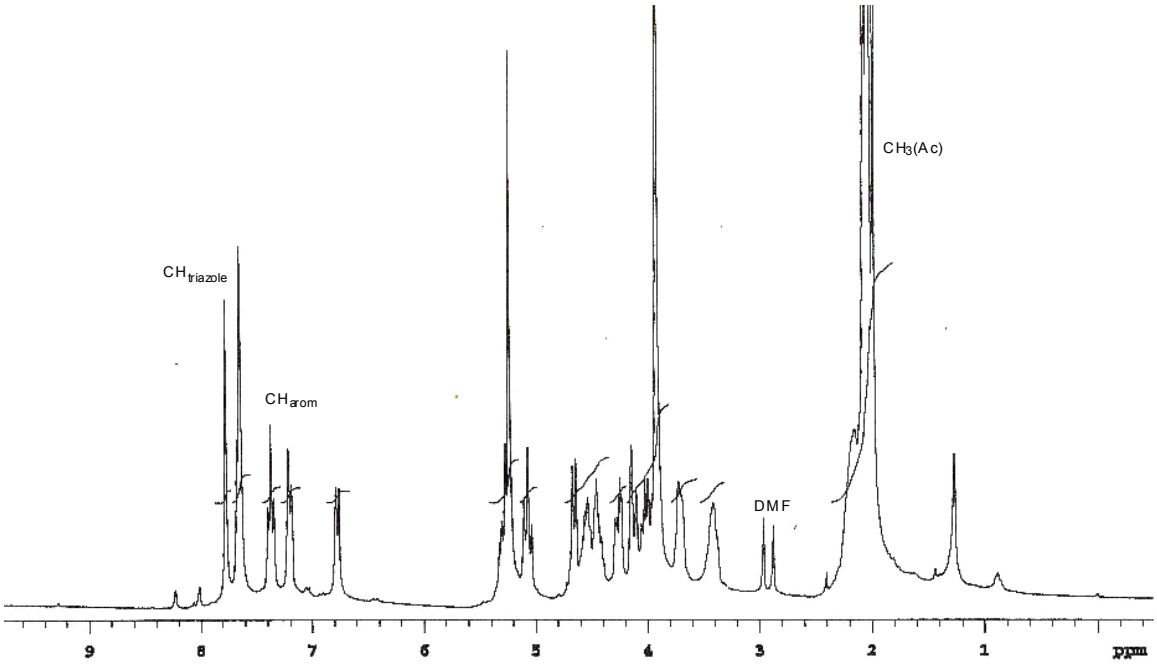


GlcNAc derivative (**10b**):

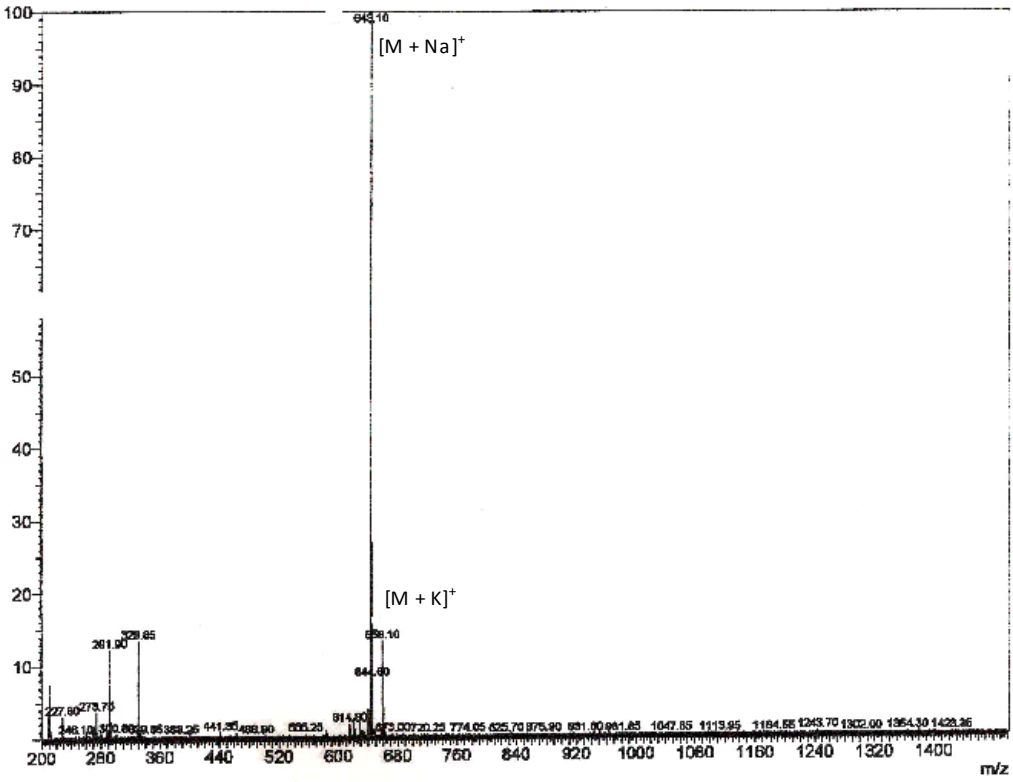
^{13}C NMR – APT (75.5 MHz, $CDCl_3$):



^{1}H NMR (300 MHz, $CDCl_3$):

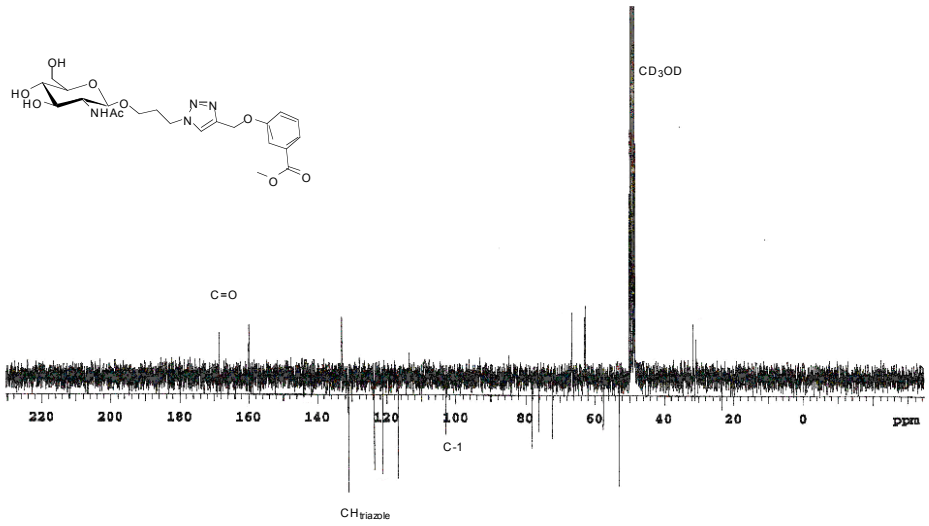


Electrospray Shizmadu LCMS-QP8000 (Mass Scan ES+):

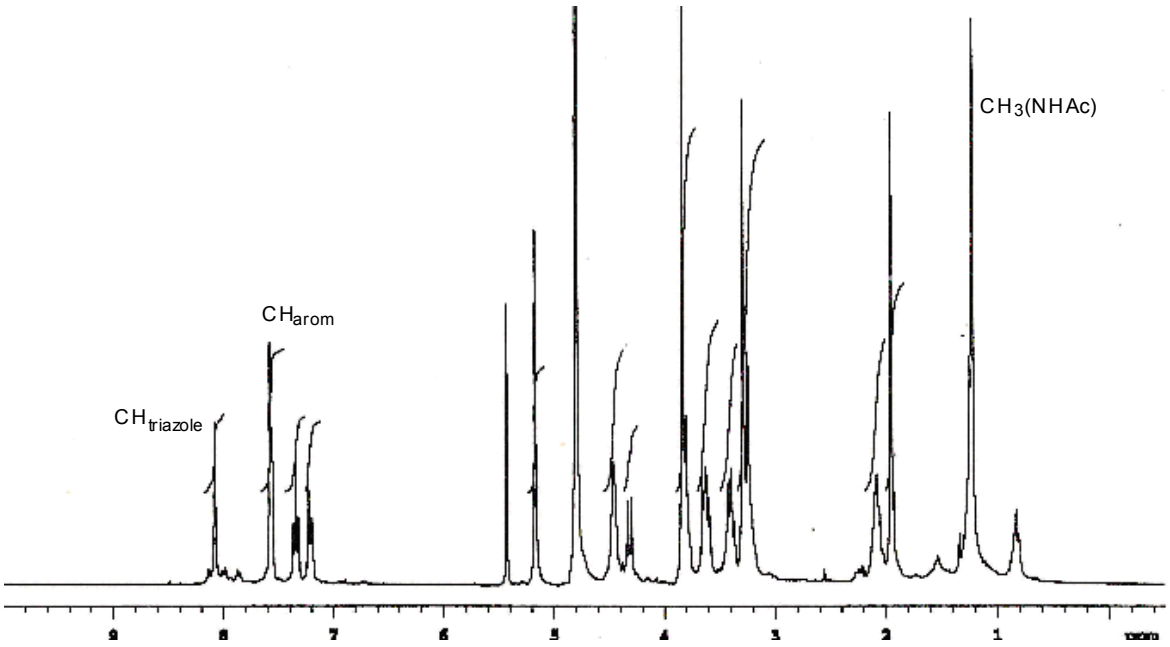


GlcNAc derivative deprotected (**10b**):

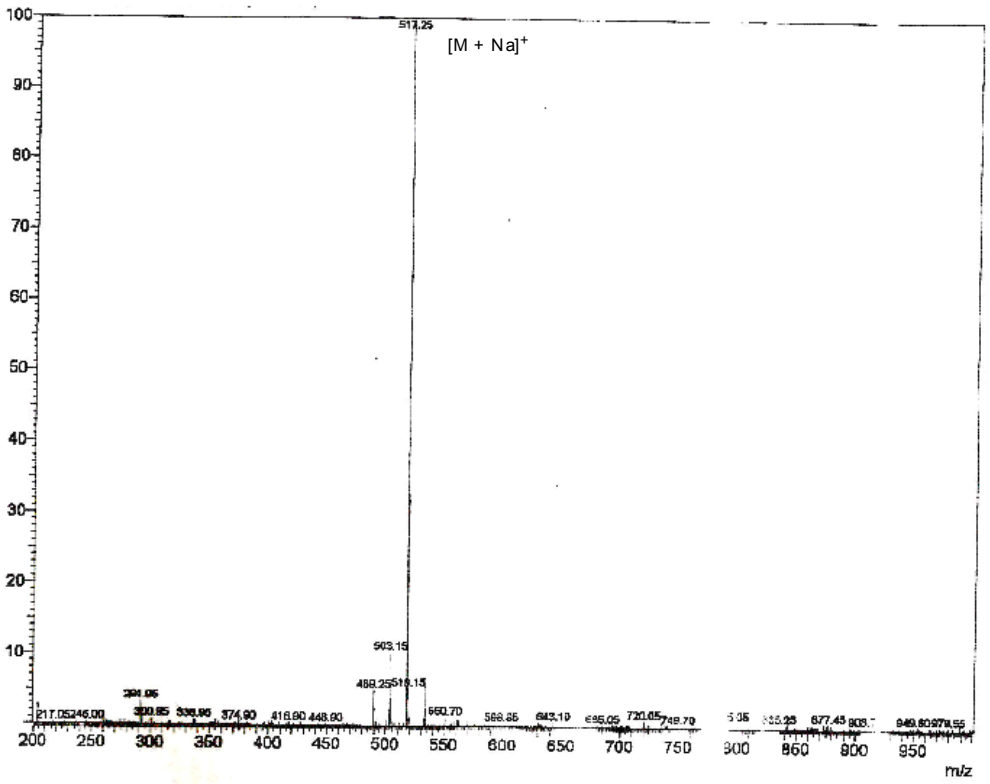
^{13}C NMR – APT (75.5 MHz, CD_3OD):



^{1}H NMR (300 MHz, CD_3OD):

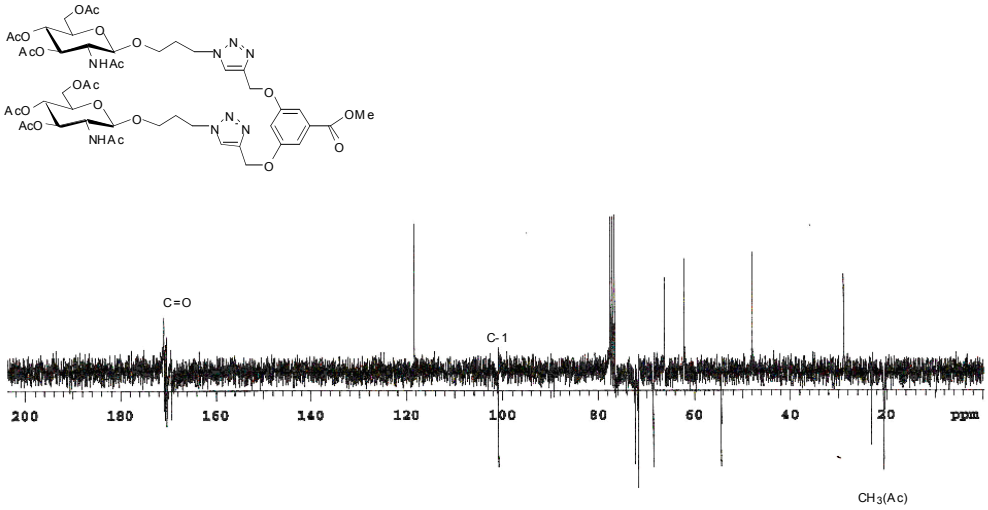


Electrospray Shizmadu LCMS-QP8000 (Mass Scan ES+):

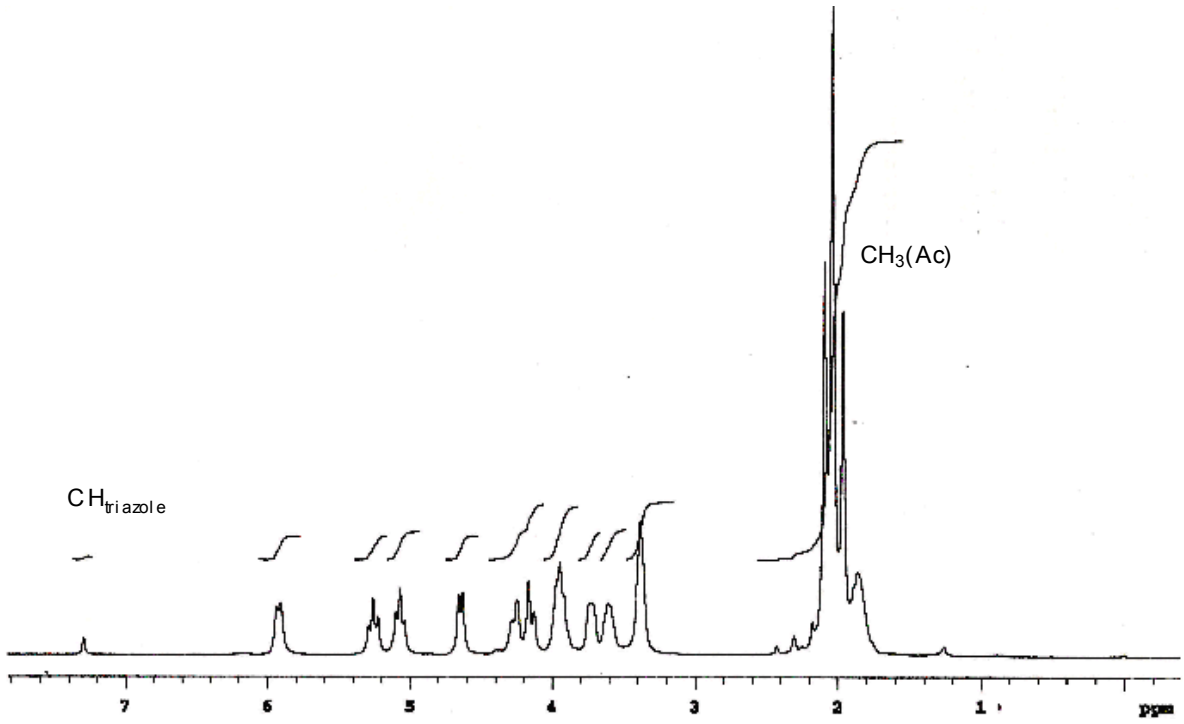


Divalent GlcNAc dendrimer (**11b**):

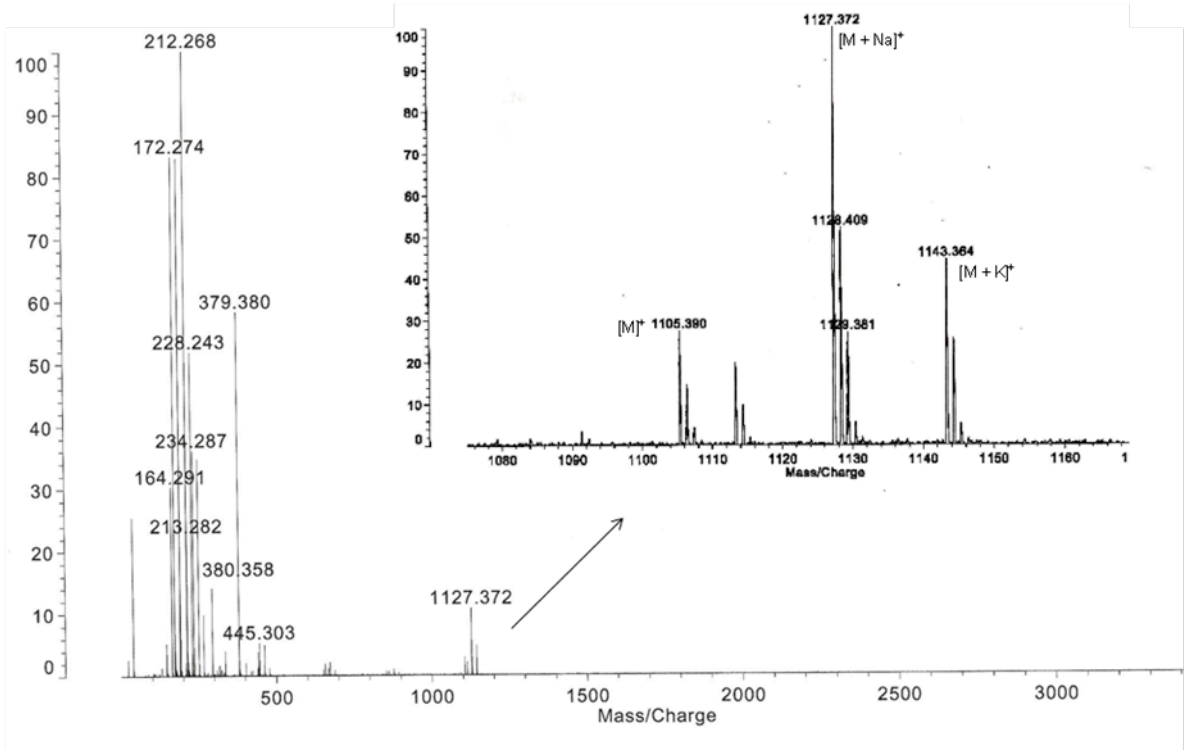
^{13}C NMR – APT (75.5 MHz, $CDCl_3$):



^{1}H NMR (300 MHz, $CDCl_3$):

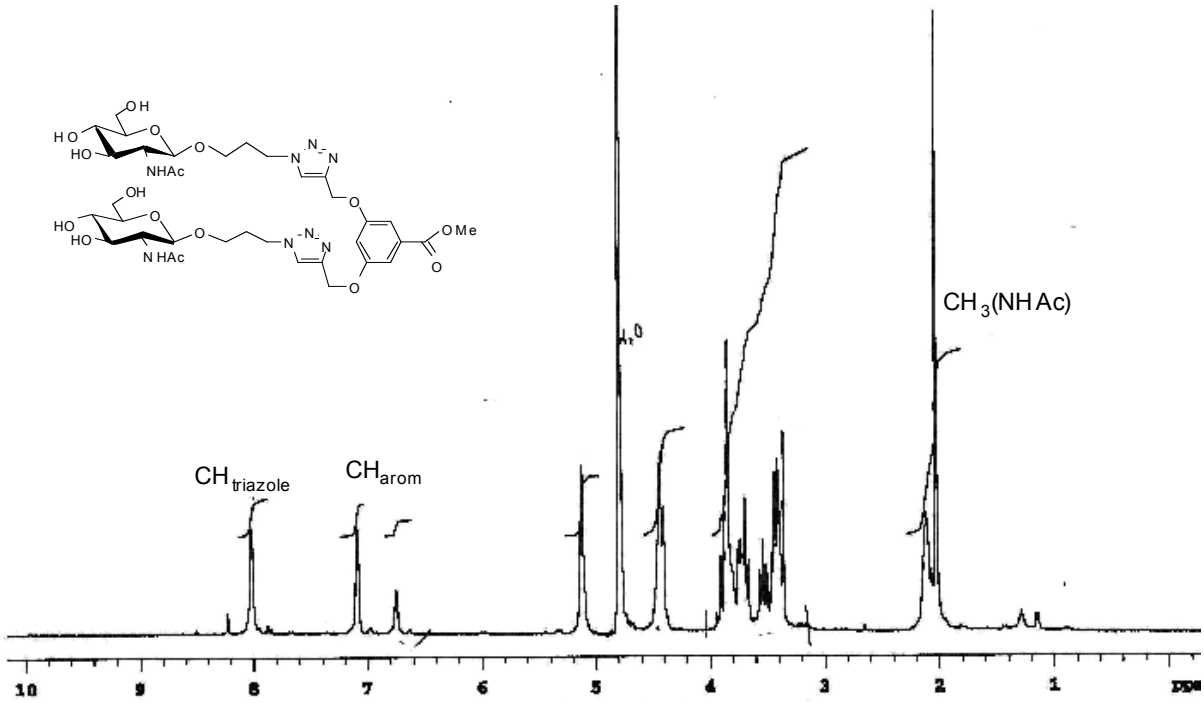


MALDI-TOF (MATRIX: α-Cyano-4-hydroxycinnamic acid):

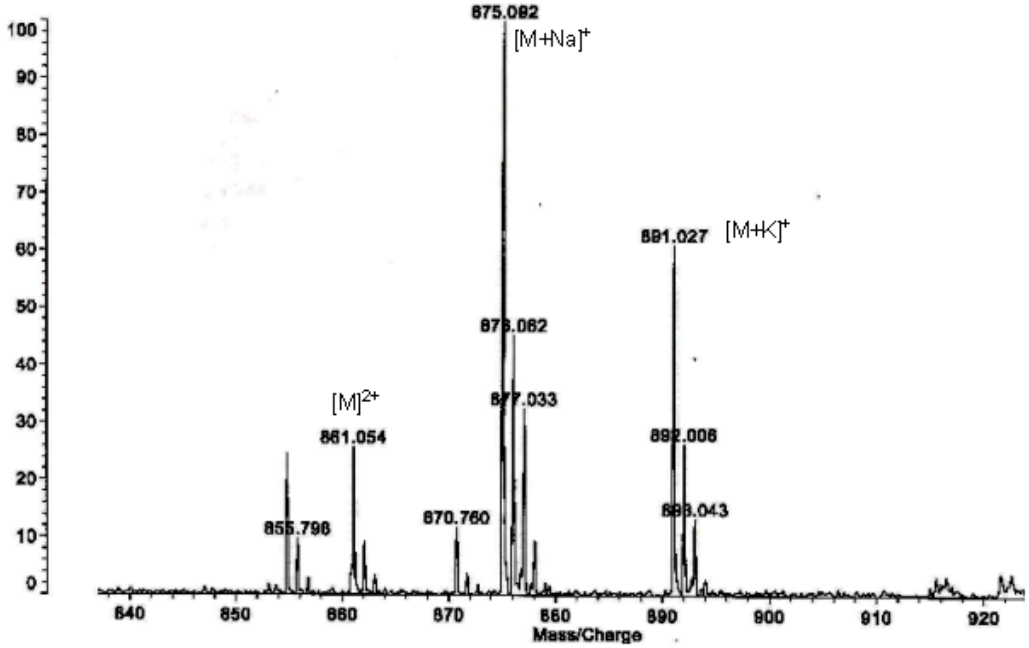


Divalent GlcNAc dendrimer deprotected (**11b**):

^{1}H NMR (300 MHz, D_2O):

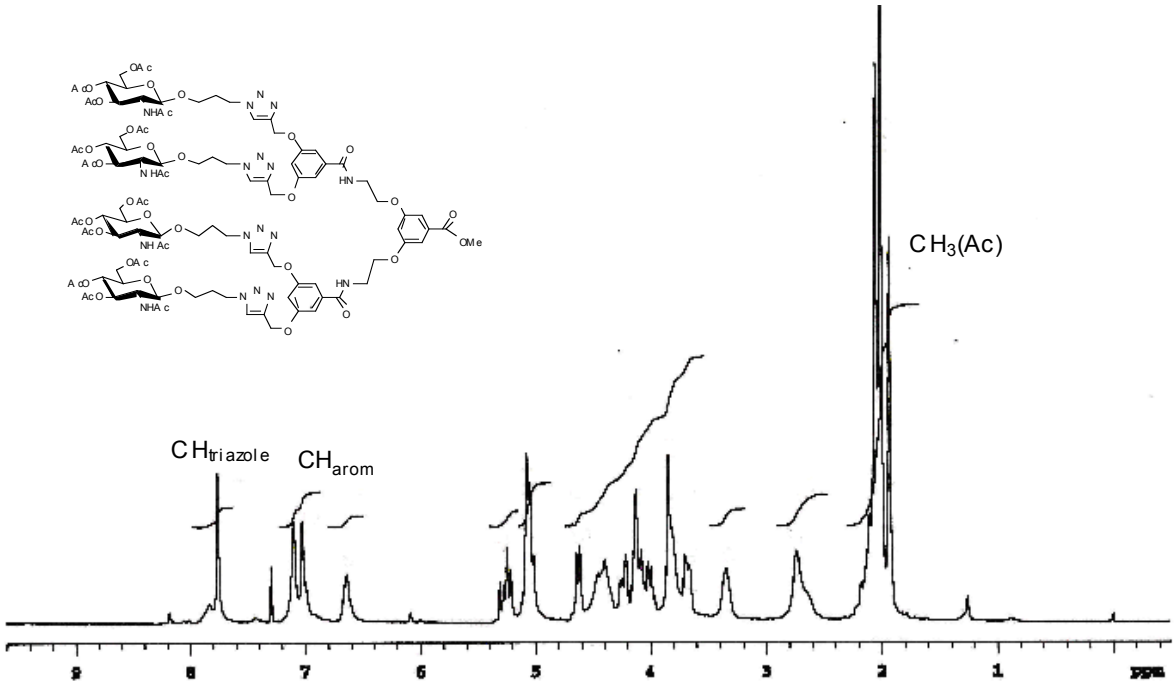


MALDI-TOF (MATRIX: α-Cyano-4-hydroxycinnamic acid):

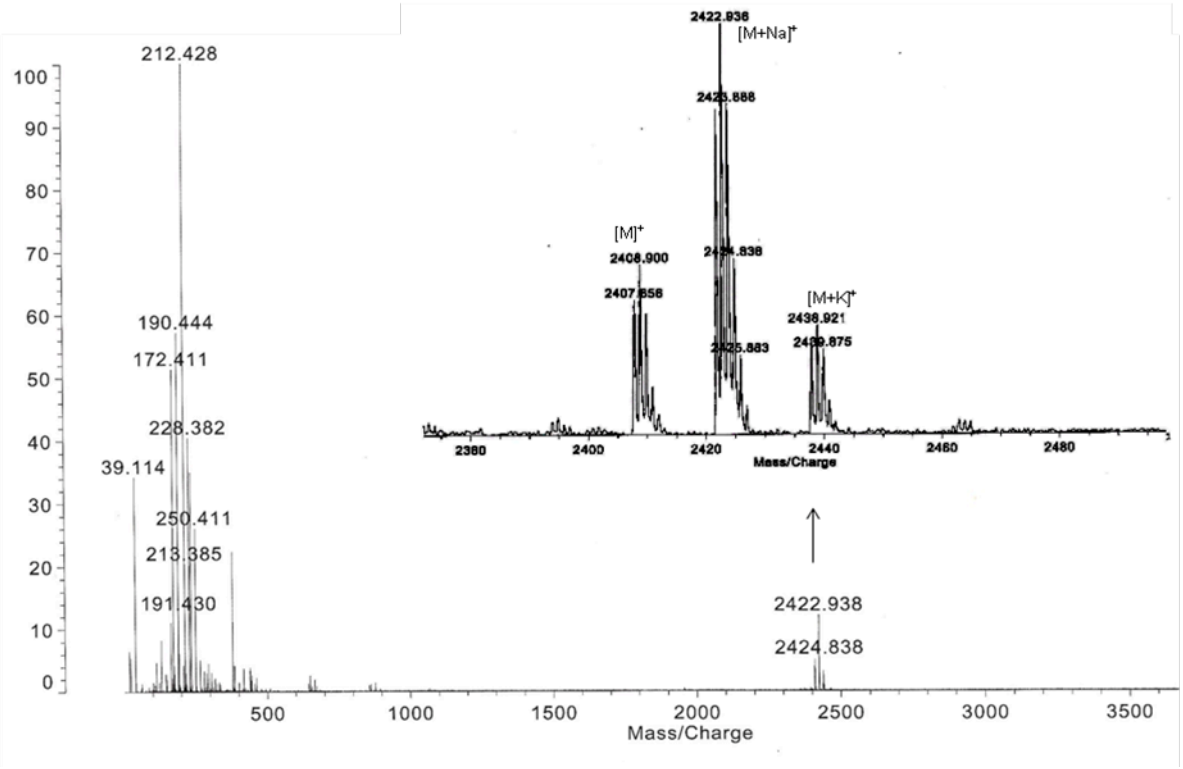


Tetravalent GlcNAc dendrimer (**12b**):

^{1}H NMR (300 MHz, $CDCl_3$):

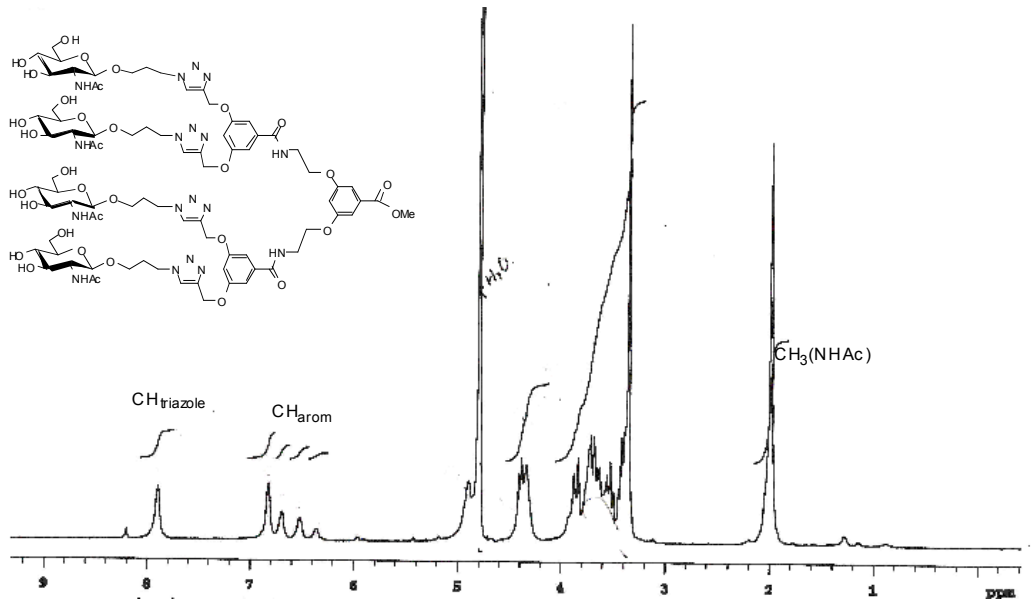


MALDI-TOF (MATRIX: α-Cyano-4-hydroxycinnamic acid):

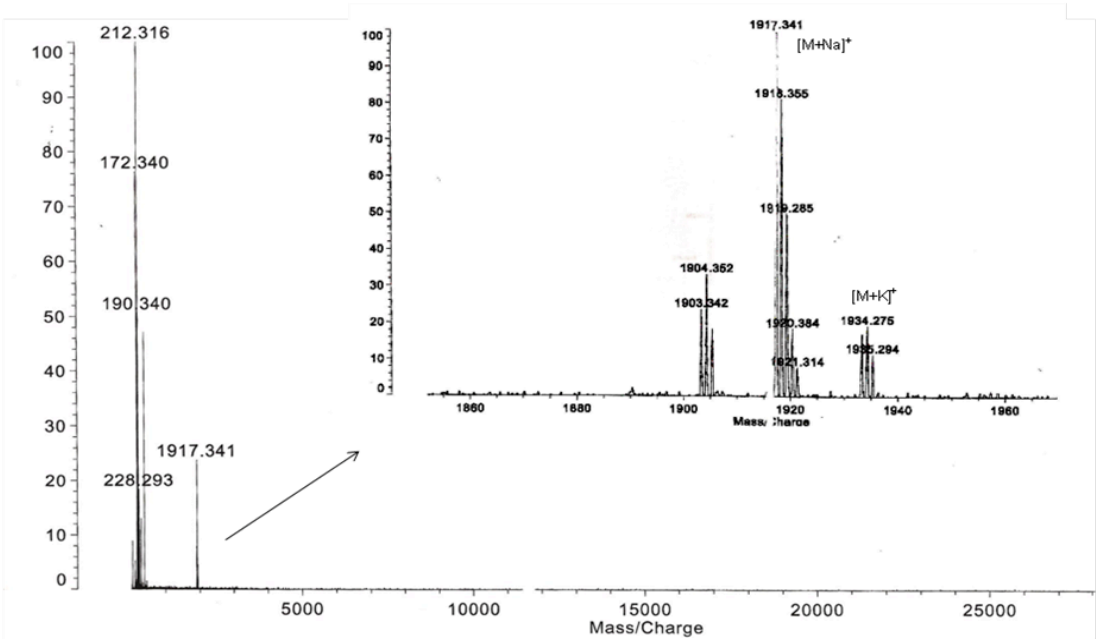


Tetravalent GlcNAc dendrimer deprotected (**12b**):

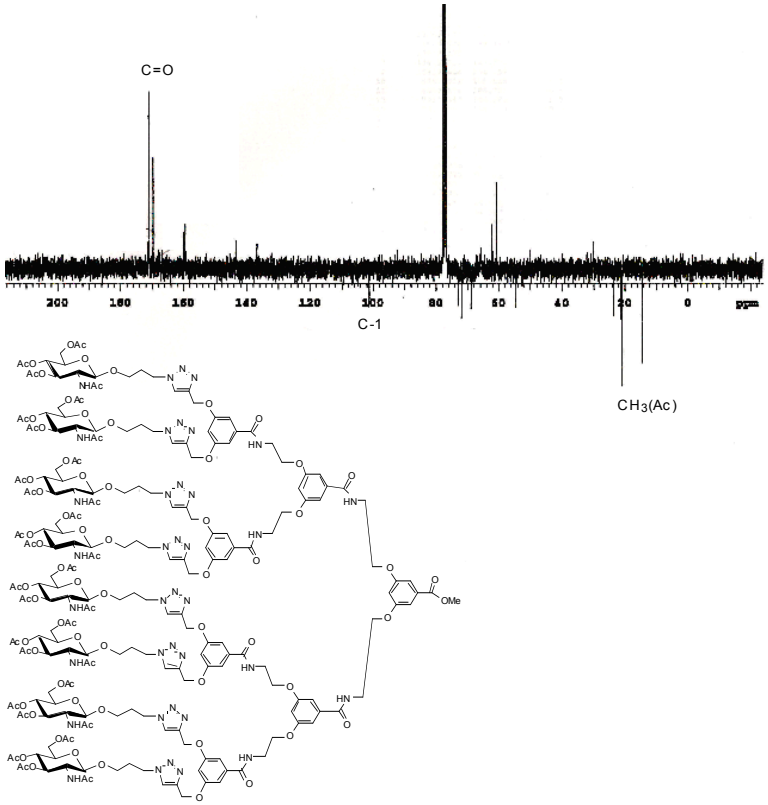
^{1}H NMR (300 MHz, D_2O):



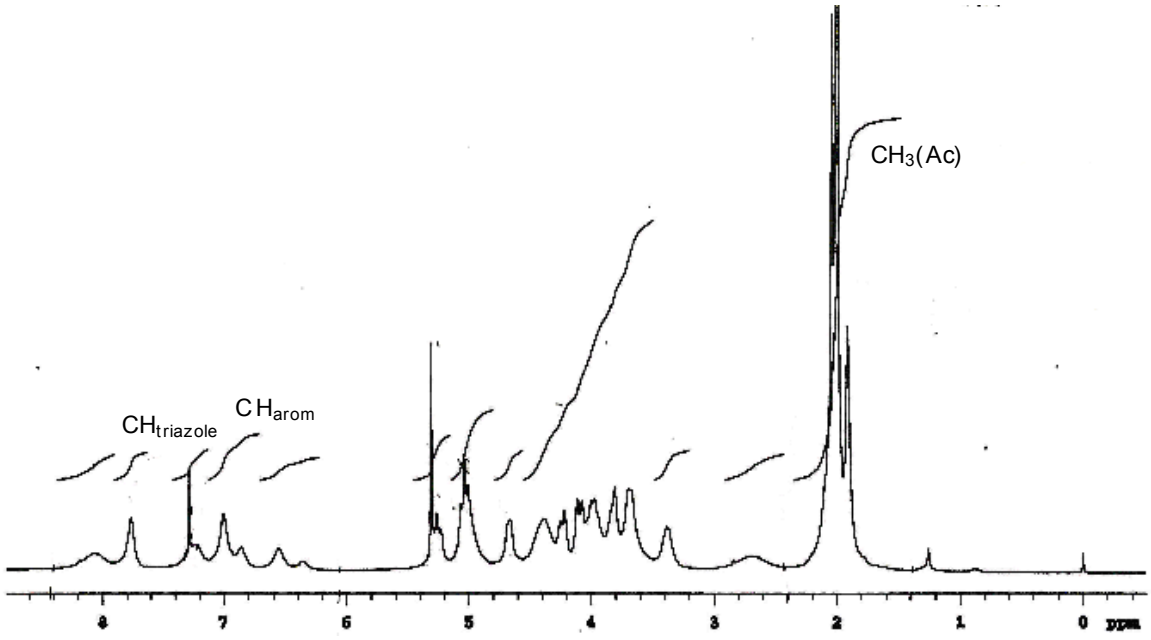
MALDI-TOF (MATRIX: α-Cyano-4-hydroxycinnamic acid):



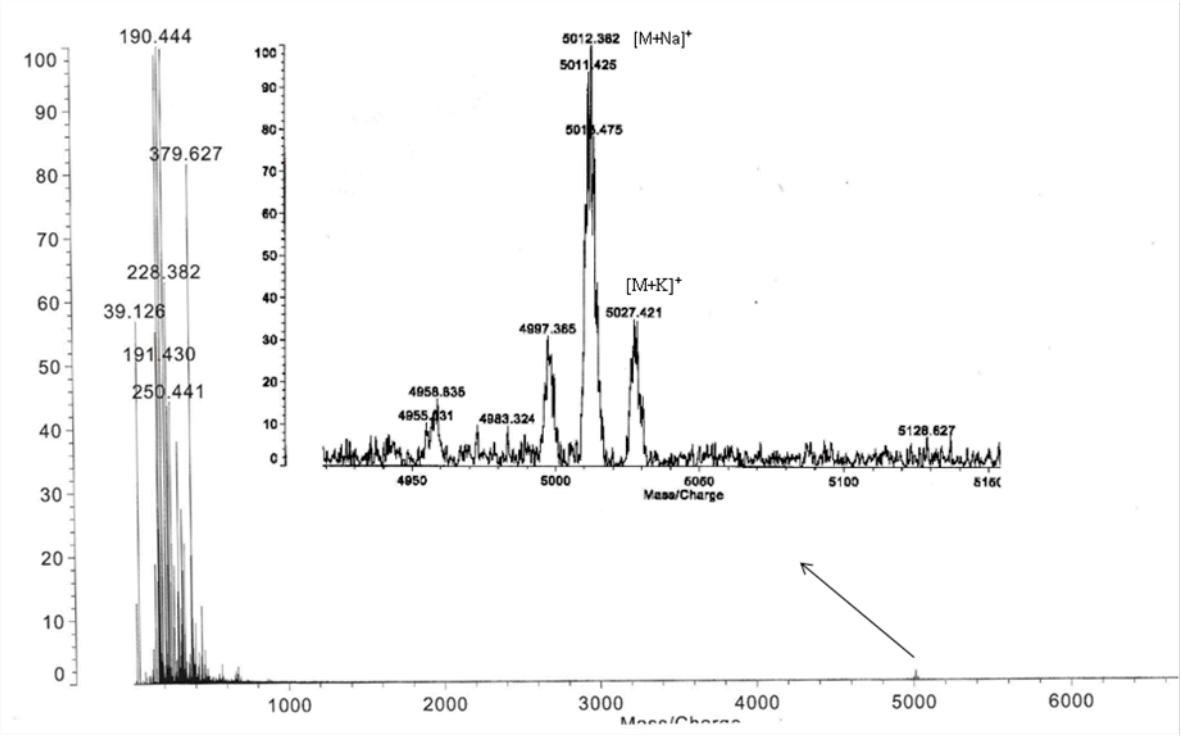
Octavalent GlcNAc dendrimer (**13b**):
^{13}C NMR – APT (75.5 MHz, $CDCl_3$):



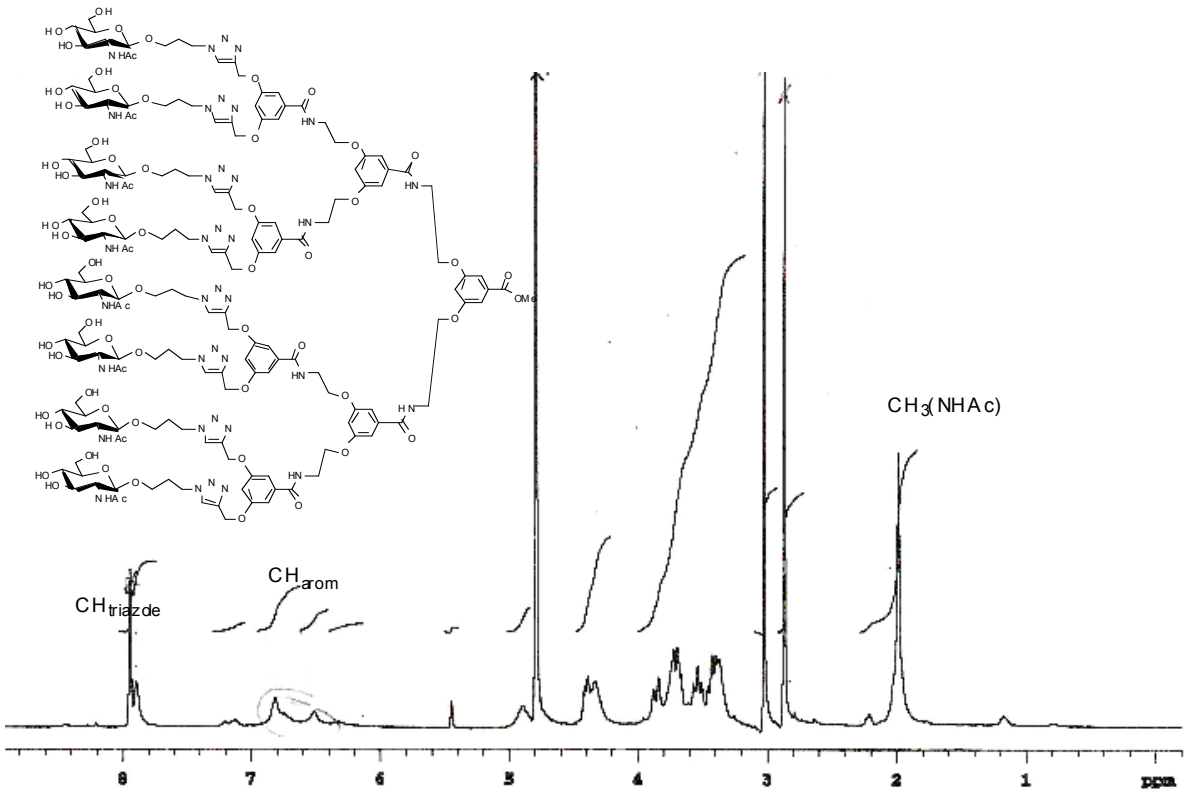
^{1}H NMR (300 MHz, $CDCl_3$):



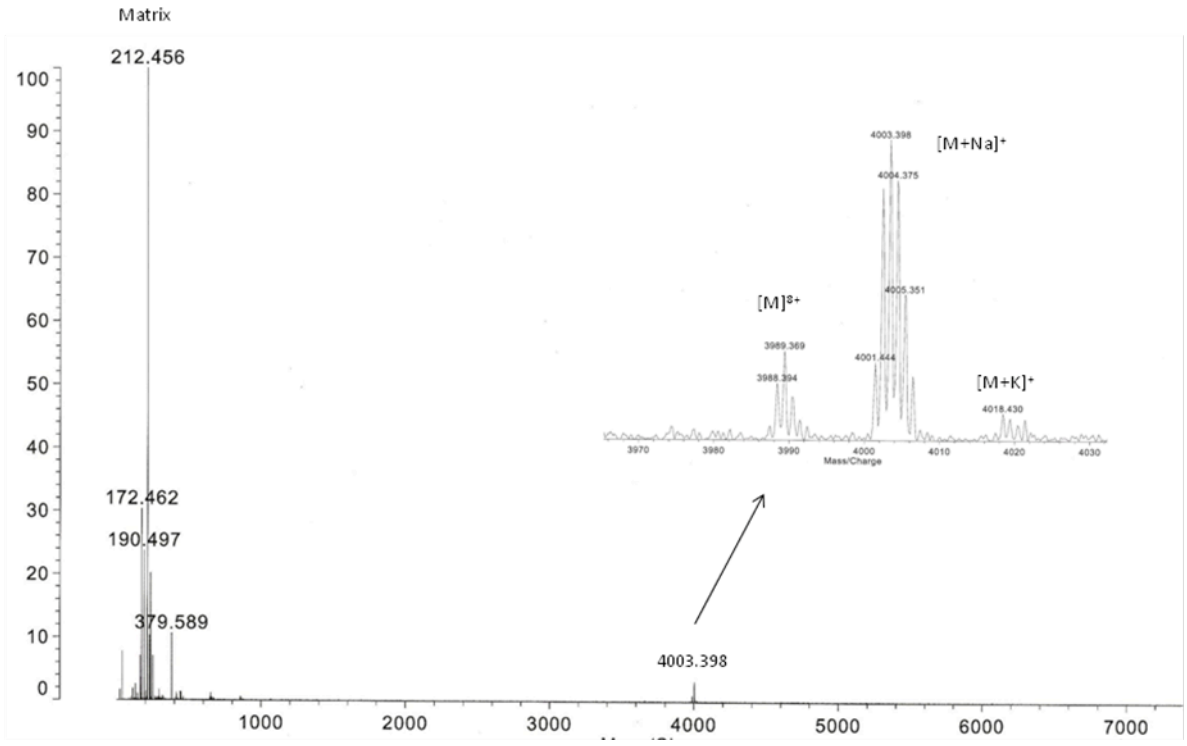
MALDI-TOF (MATRIX: α-Cyano-4-hydroxycinnamic acid):



Octavalent GlcNAc dendrimer deprotected (**13b**):
^{1}H NMR (300 MHz, D_2O):

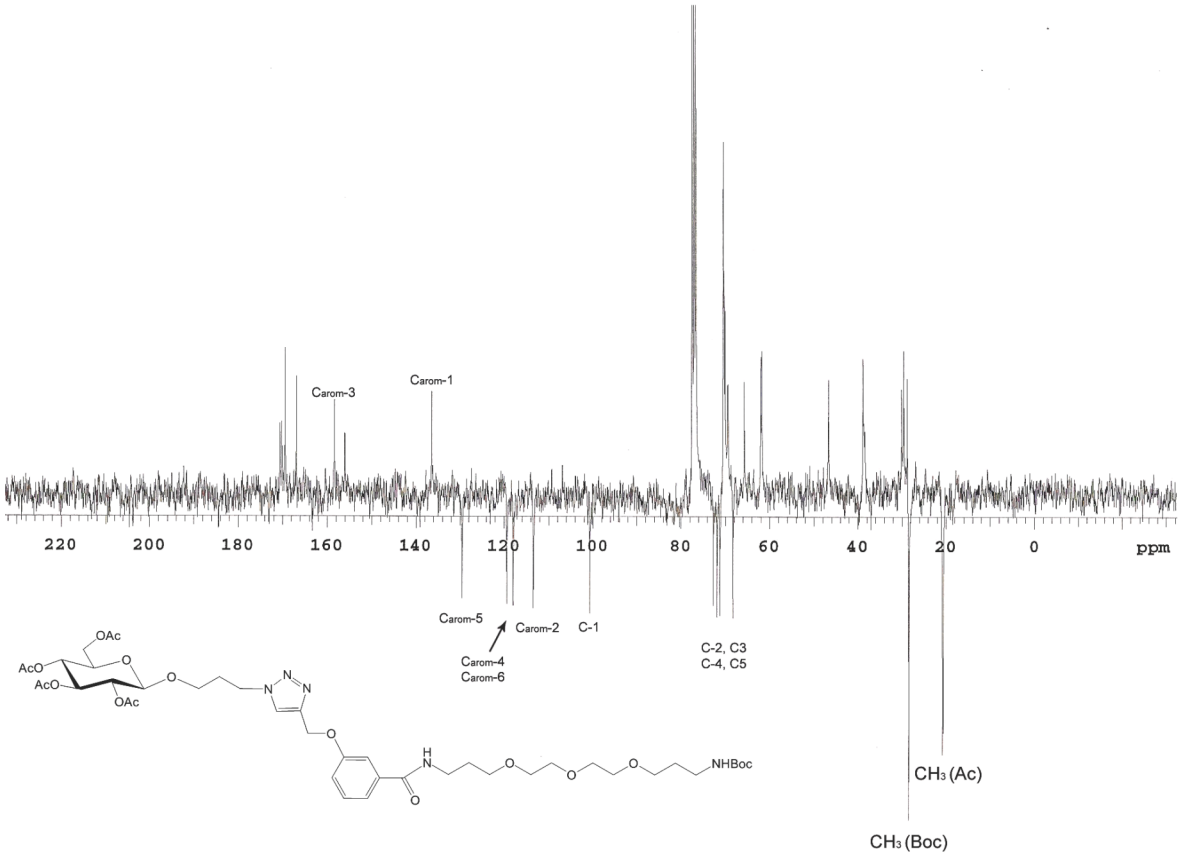


MALDI-TOF (MATRIX: α-Cyano-4-hydroxycinnamic acid):

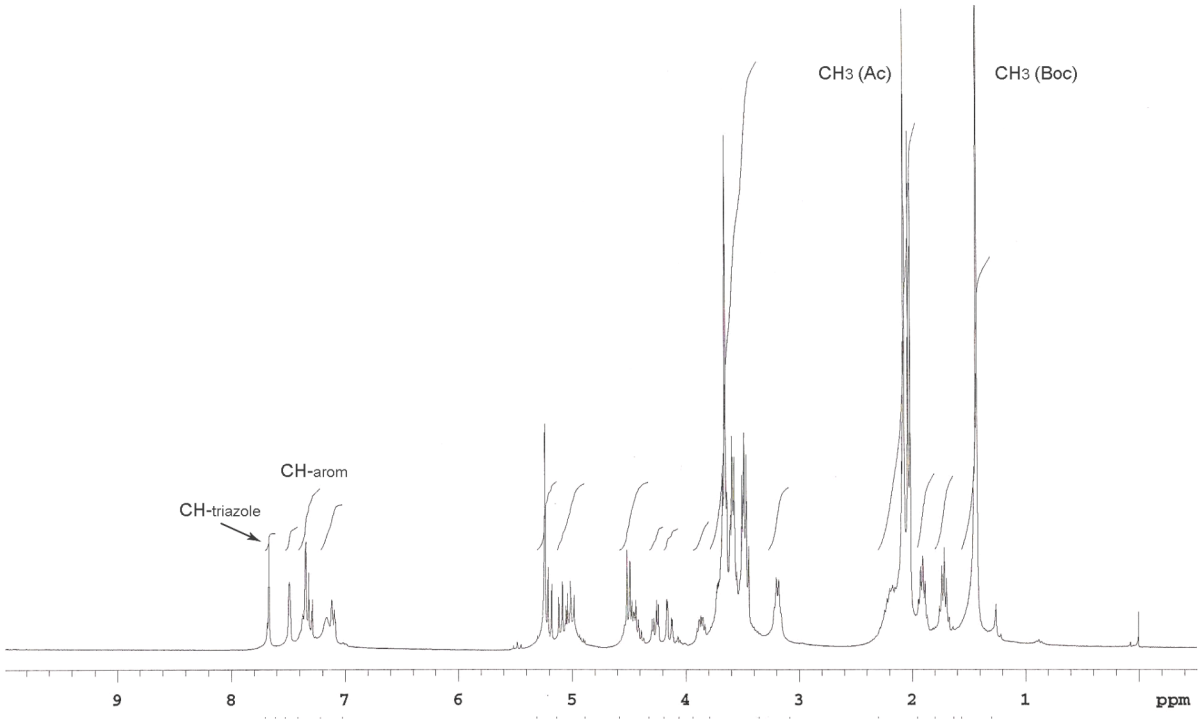


Glucose derivative (**1b**):

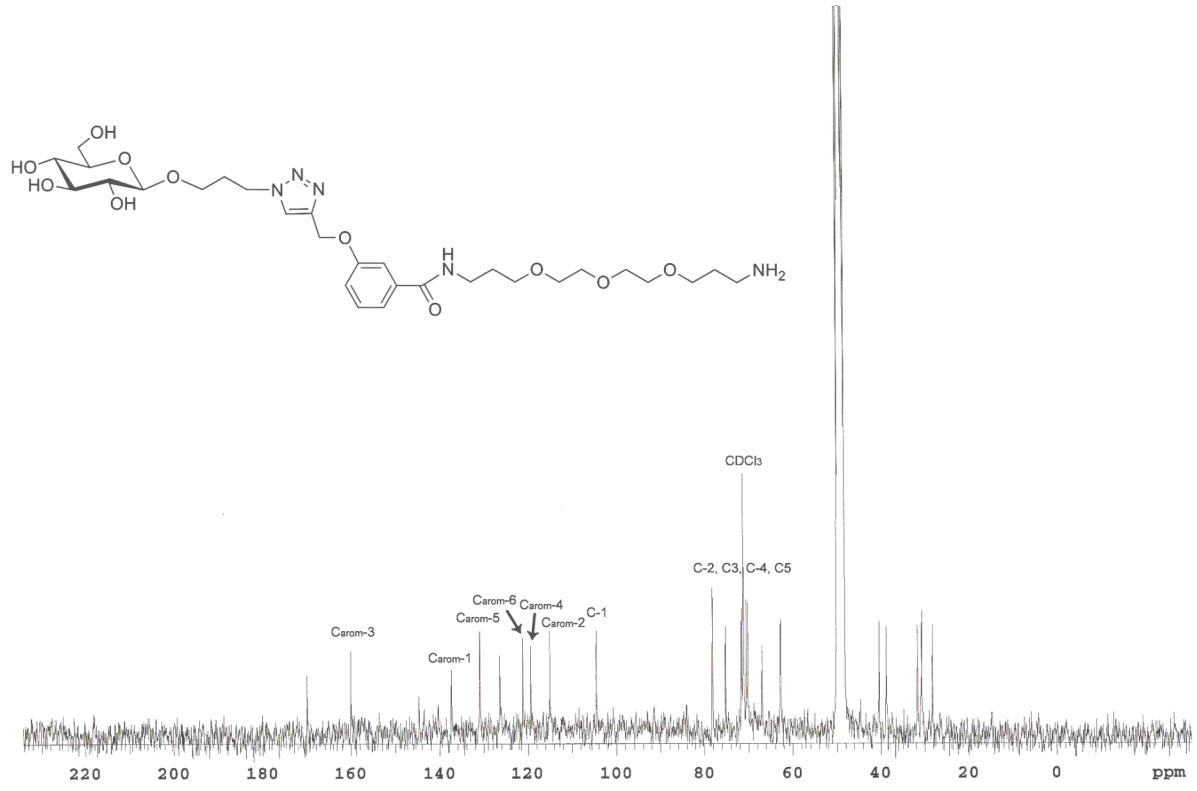
^{13}C NMR – ATP (75.5 MHz, $CDCl_3$):



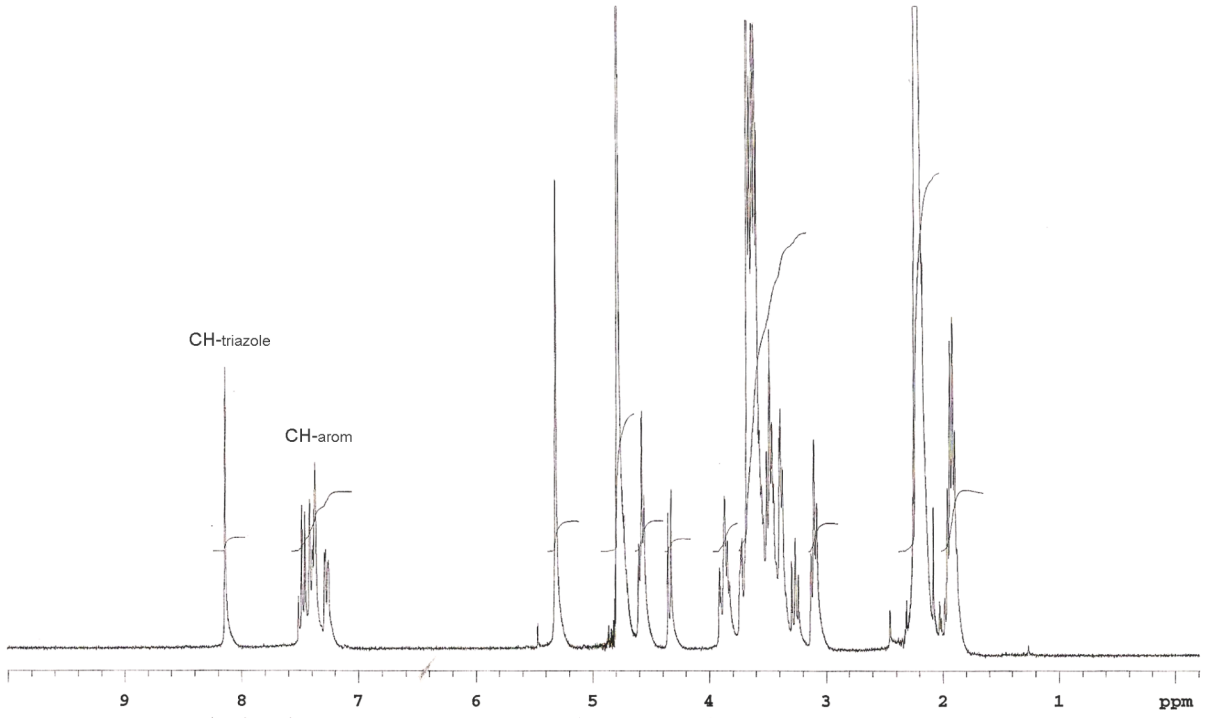
^{1}H NMR (300 MHz, $CDCl_3$):



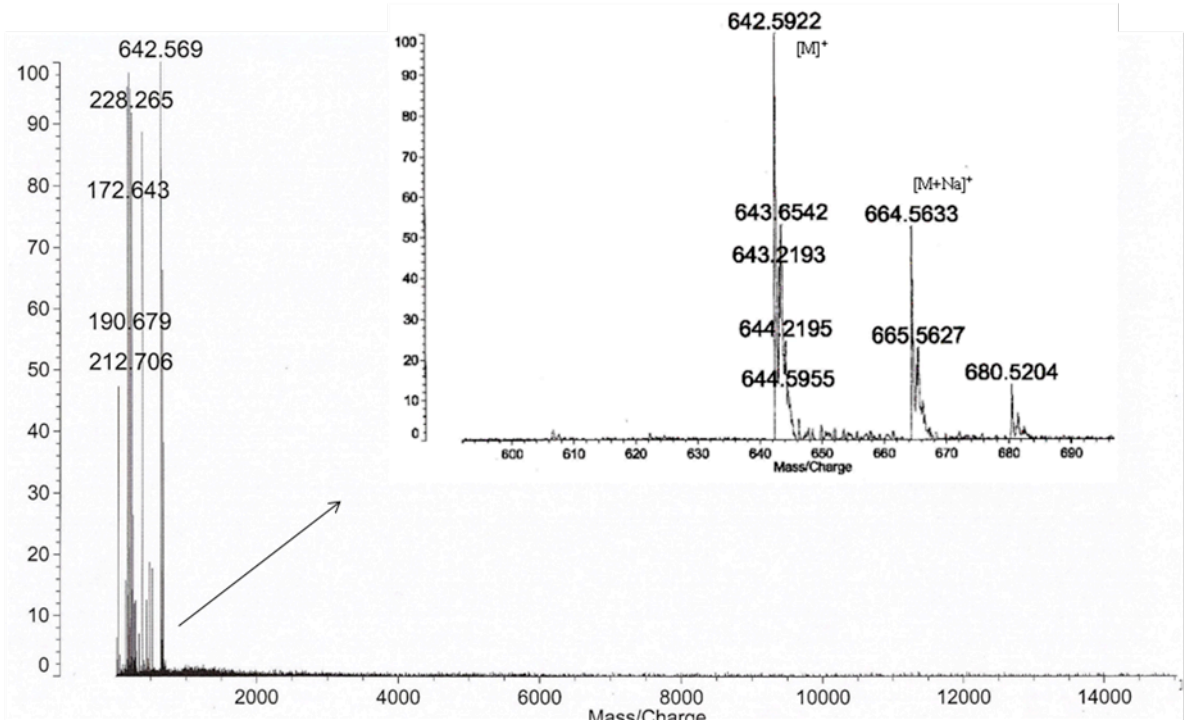
Glucose derivative deprotected (**1b**):
^{13}C NMR (75.5 MHz, D_2O:Acetone 99:0.1):



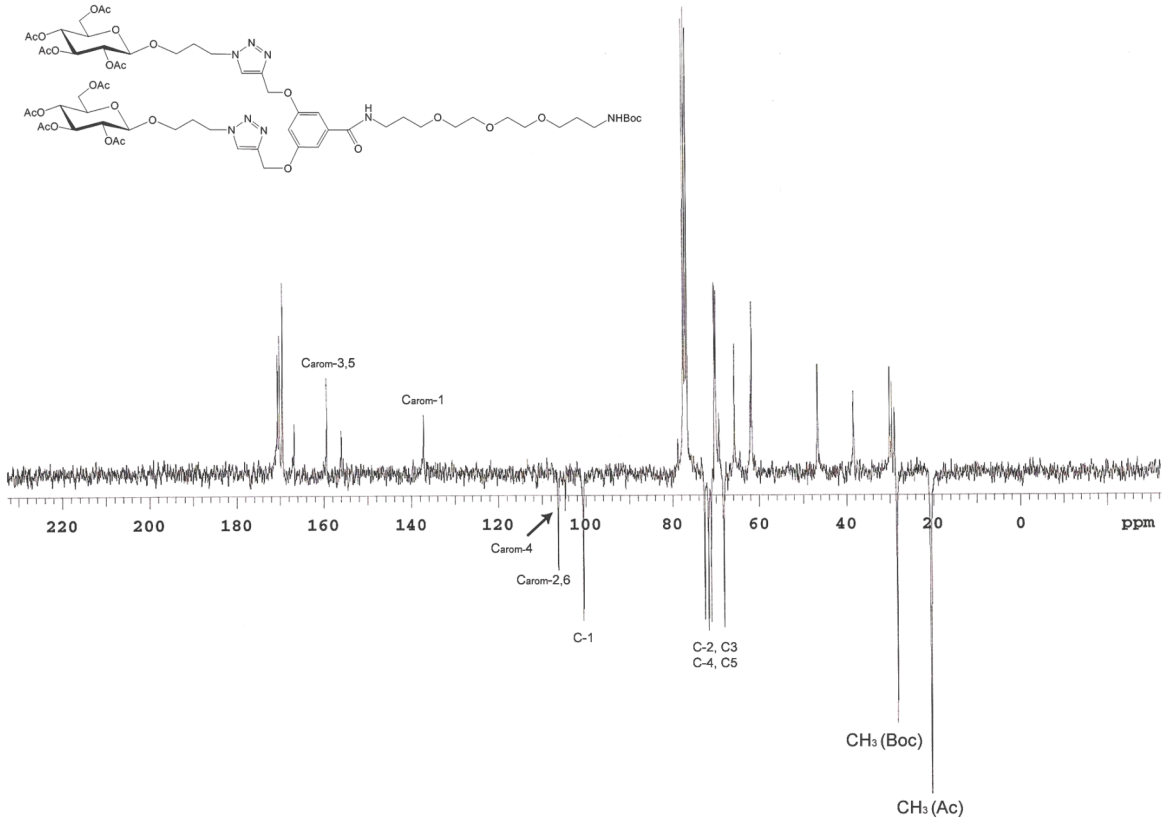
^{1}H NMR (300 MHz, D_2O:Acetone 99:0.1):



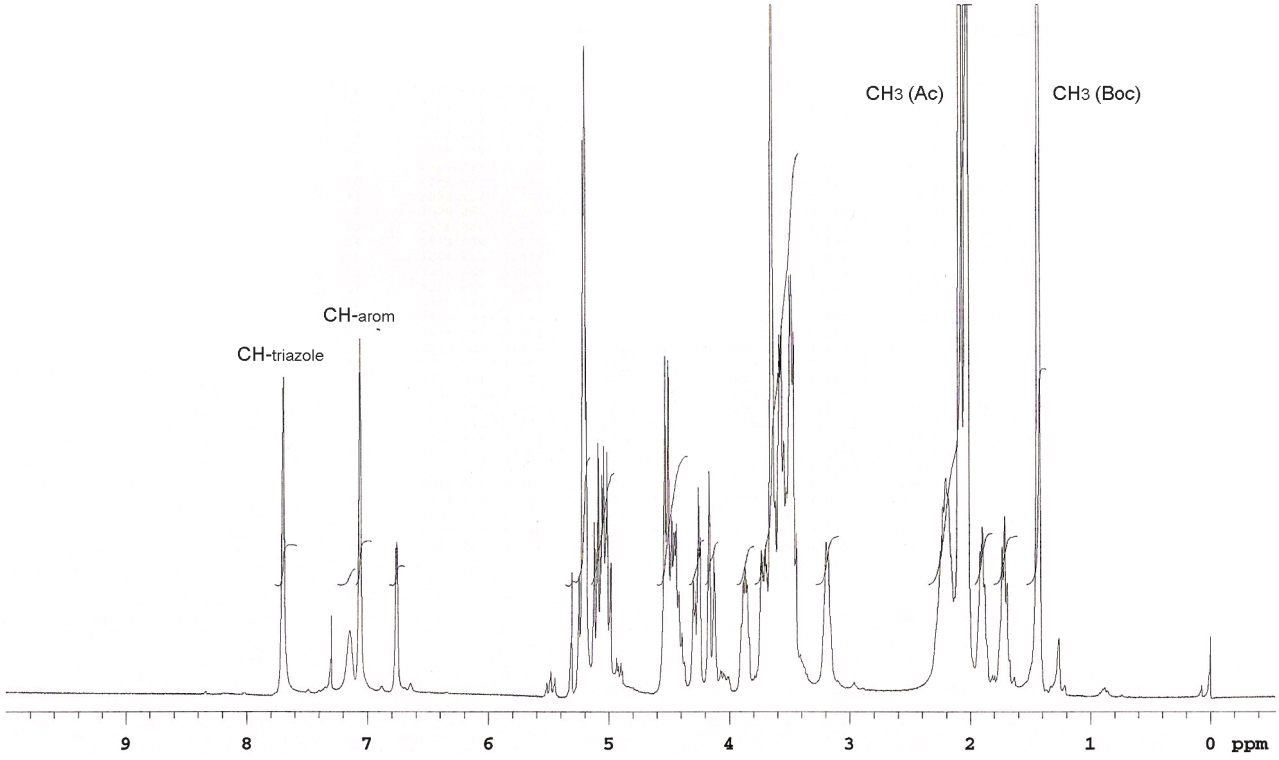
MALDI-TOF (MATRIX: α-Cyano-4-hydroxycinnamic acid):



Divalent glucose dendrimer (**2b**):
^{13}C NMR – ATP (75.5 MHz, $CDCl_3$):

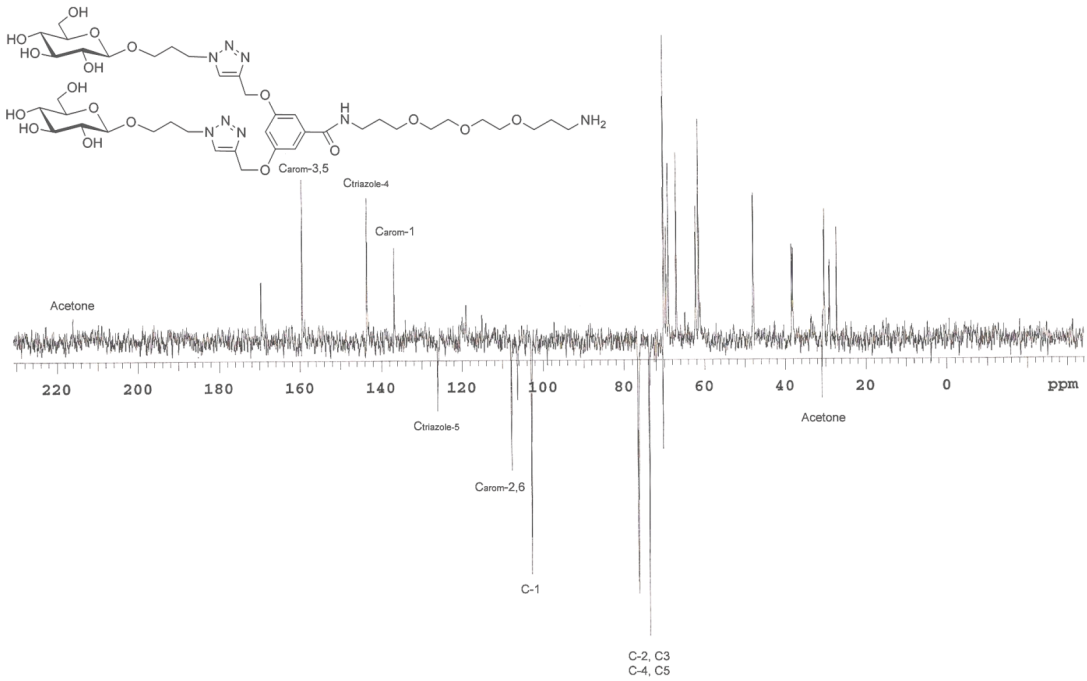


^{1}H NMR (300 MHz, $CDCl_3$):

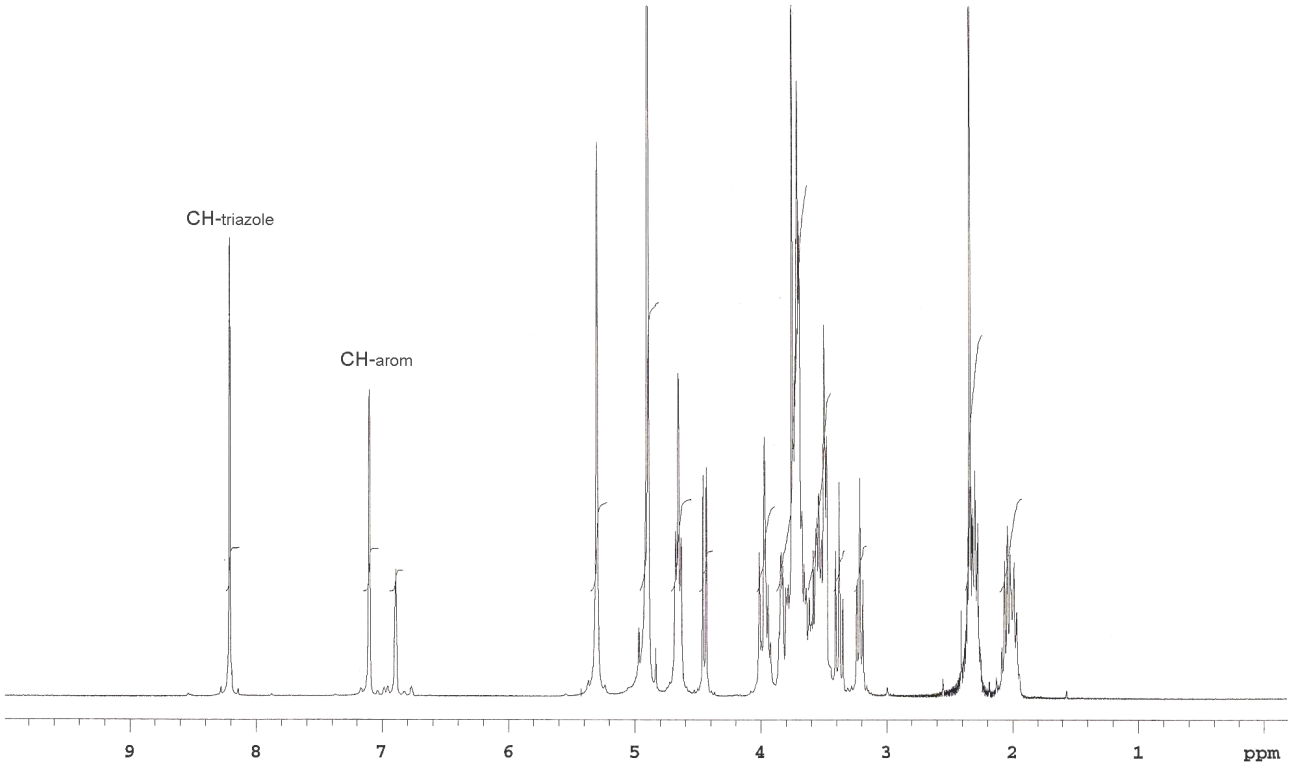


Divalent glucose dendrimer deprotected (**2b**):

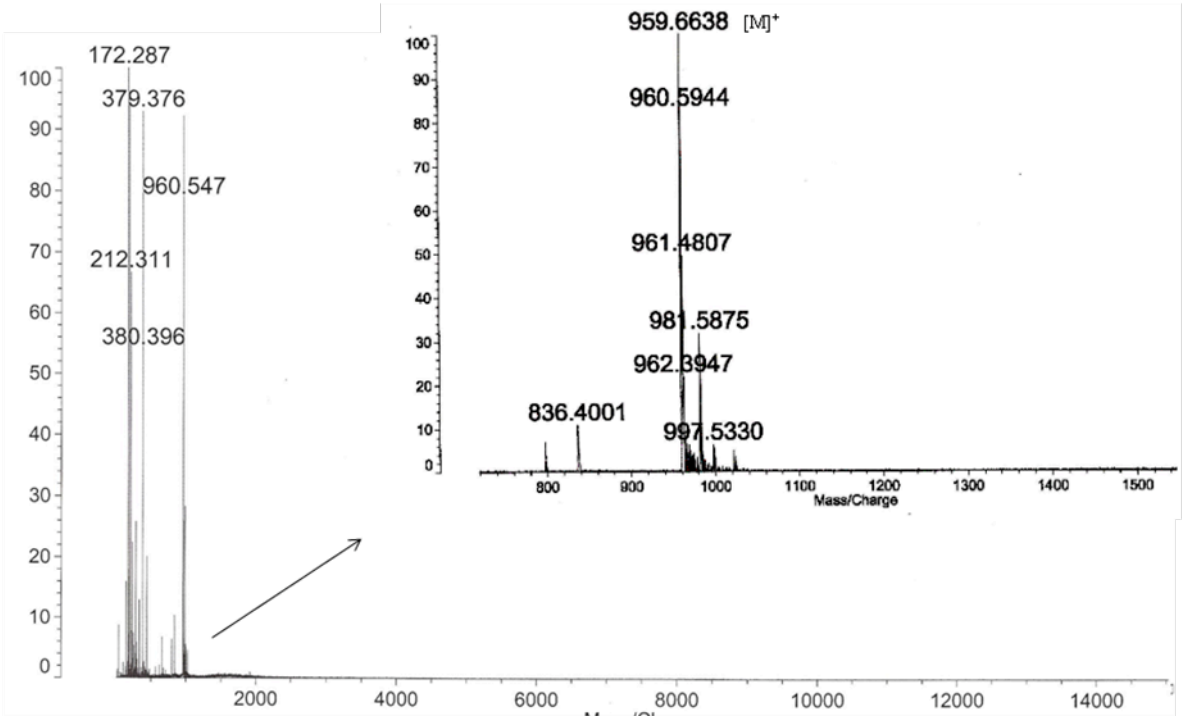
^{13}C NMR – ATP (75.5 MHz, D_2O:Acetone 99:0.1):



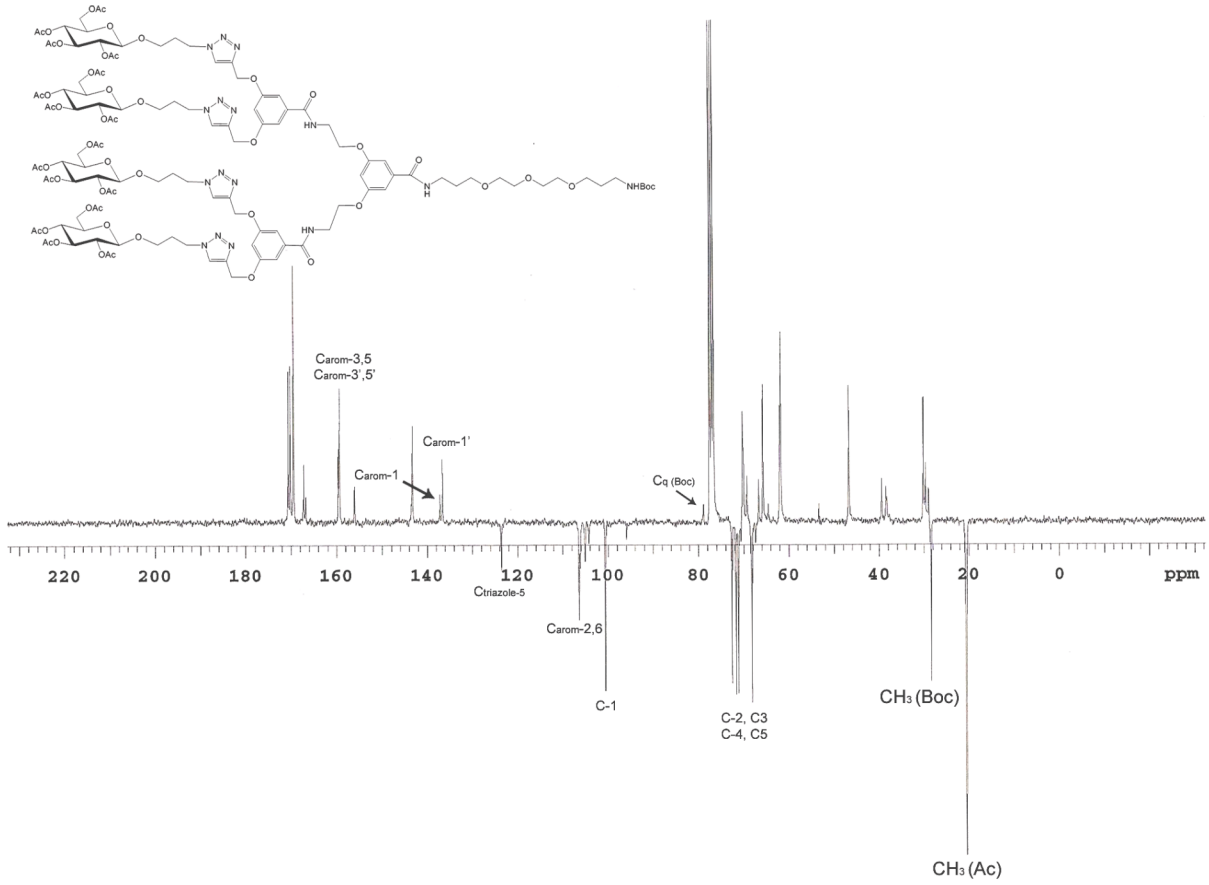
^{1}H NMR (300 MHz, D_2O:Acetone 99:0.1):



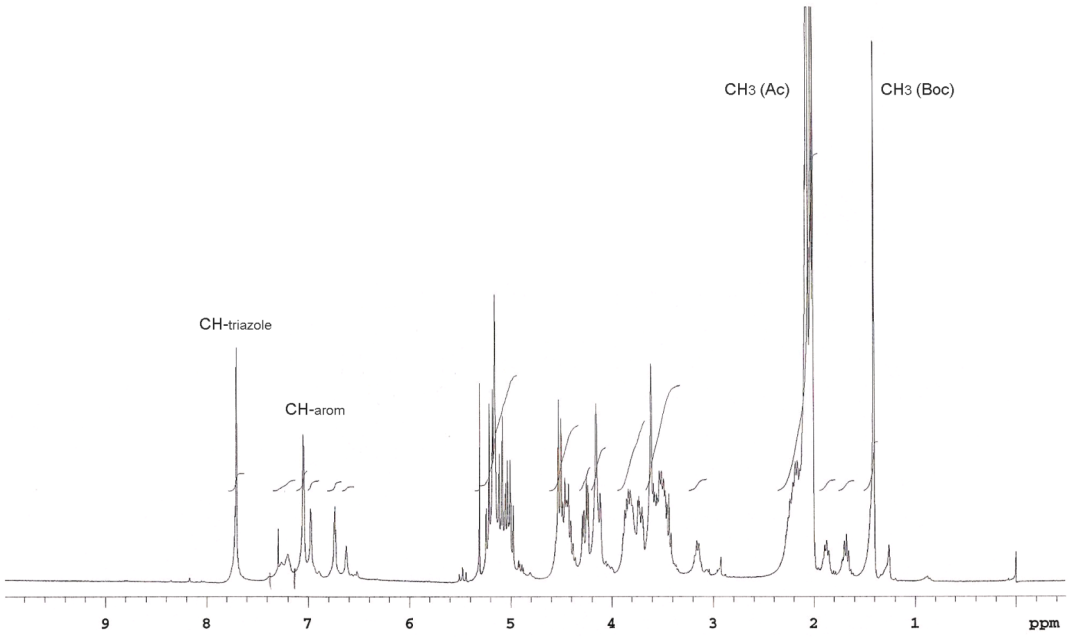
MALDI-TOF (MATRIX :α-Cyano-4-hydroxycinnamic acid):



Tetravalent glucose dendrimer (**3b**):
^{13}C NMR – APT (75.5 MHz, $CDCl_3$):

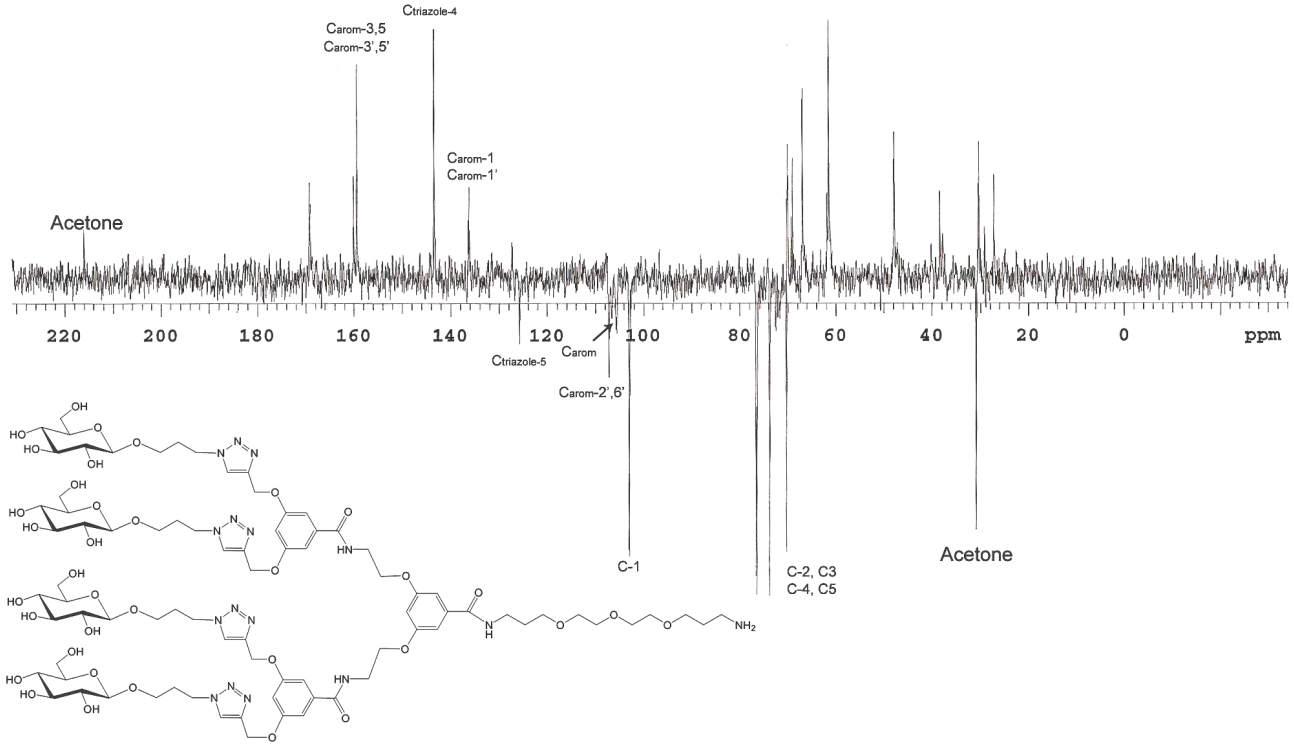


^{1}H NMR (300 MHz, $CDCl_3$):

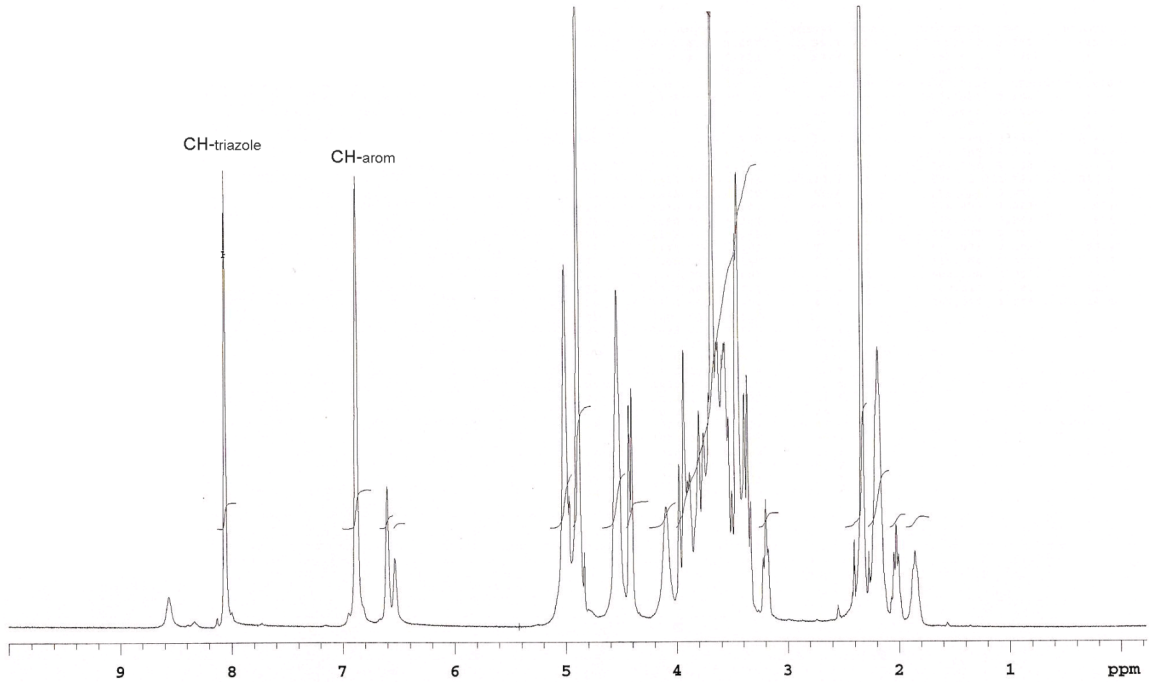


Tetravalent glucose dendrimer deprotected (**3b**):

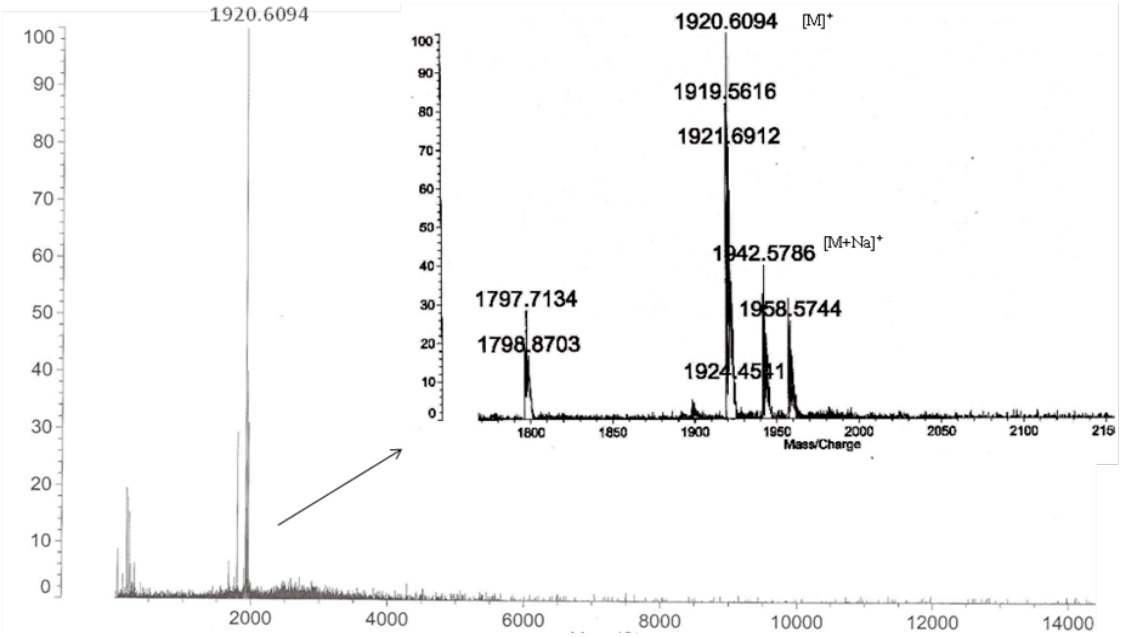
^{13}C NMR – APT (75.5 MHz, D_2O:Acetone 99:0.1):



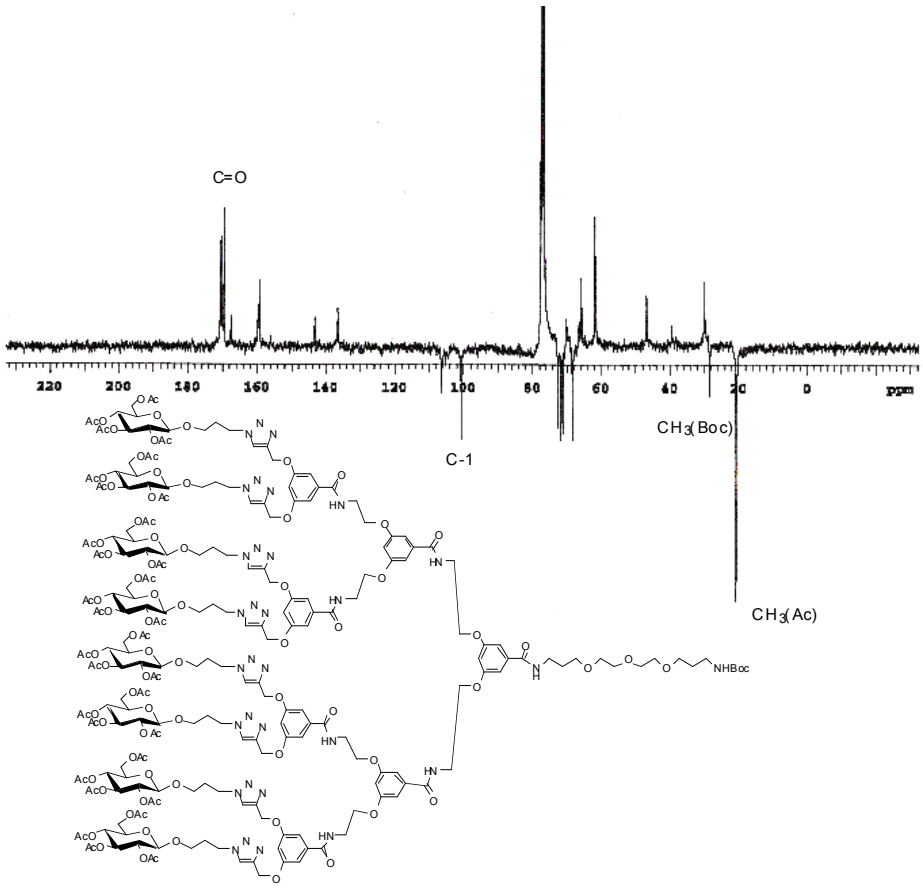
^{1}H NMR (300 MHz, D_2O:Acetone 99:0.1):



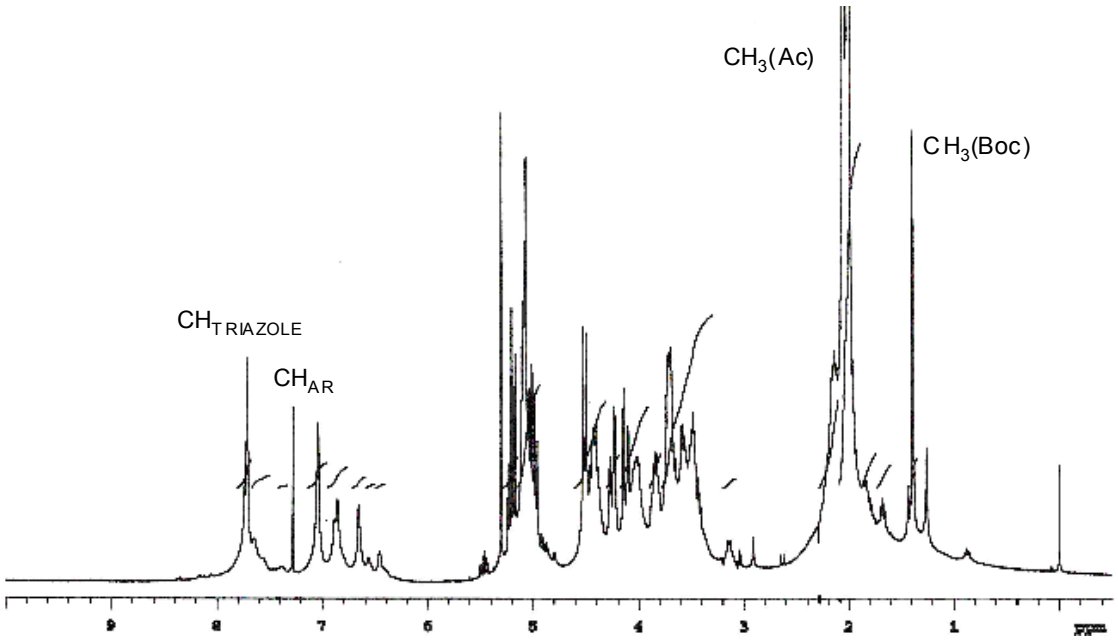
MALDI-TOF (MATRIX: α-Cyano-4-hydroxycinnamic acid):



Octavalent glucose dendrimer (**4b**):
^{13}C NMR (75.5 MHz, $CDCl_3$):

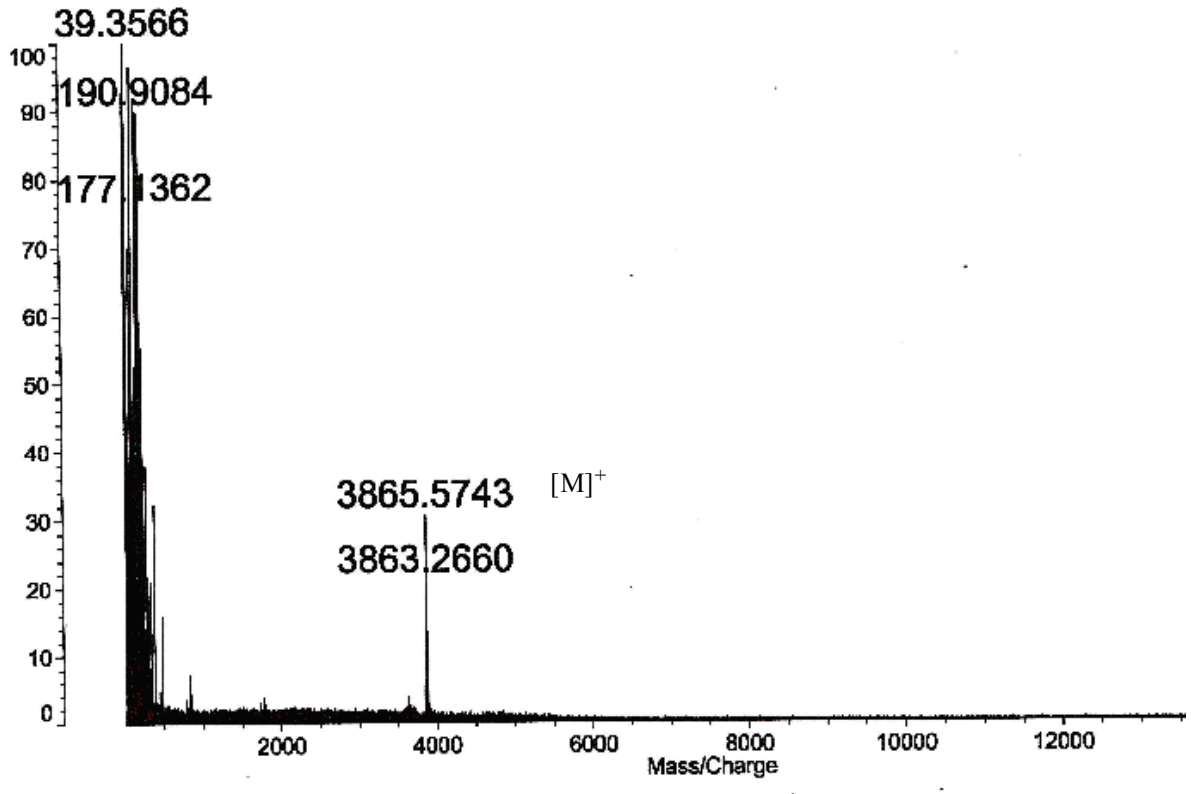


^{1}H NMR (300 MHz, $CDCl_3$):



Octavalent glucose dendrimer deprotected (**4b**):

MALDI-TOF (MATRIX :α-Cyano-4-hydroxycinnamic acid):



[1] H. M. Branderhorst, R. Ruijtenbeek, R. M. J. Liskamp, R. J. Pieters, *ChemBioChem*, **2008**, 9, 1836-1844.

[2] C. Maierhofer, K. Rohmer, V. Wittmann, *Bioorg. Med. Chem.* **2007**, *15*, 7661-7676.

[3] R. Autar, A. S. Khan, M. Schad, J. Hacker, R. M. J. Liskamp, R. J. Pieters, *ChemBioChem,* **2003**, 4, 1317-1325.