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ELECTRONIC SUPPORTING INFORMATION

Multifaceted Glycodendrimers With Programmable Bioactivity Through Convergent, Divergent, and Accelerated Approaches Using Polyfunctional Cyclotriphosphazenes

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Contents

1. Materials and methods

All reactions in organic medium were performed in standard oven dried glassware under an inert atmosphere of nitrogen using freshly distilled solvents. CH_2Cl_2 was distilled from CaH_2 and DMF from ninhydrin, and kept over molecular sieves. Solvents and reagents were deoxygenated when necessary by purging with nitrogen. Water used for lyophilization of final dendrimers was nanopure grade, purified through Barnstead NANOPure II Filter with Barnstead MegOhm-CM Sybron meter. All reagents were used as supplied without prior purification unless otherwise stated, and obtained from Sigma-Aldrich Chemical Co. Ltd.

LecA (*Pseudomonas aeruginosa* lectin-I) was purchased from Sigma-Aldrich (L9895-1MG, Lot 051M4011V).

Reactions were monitored by analytical thin-layer chromatography using silica gel 60 F254 precoated plates (E. Merck) and compounds were visualized by 254 nm light, a mixture of Iodine/silica gel and/or mixture of Ceric Ammonium Molybdate solution (100 ml H_2SO_4, 900 ml H_2O, 25g $(NH_4)_6Mo_7O_{24}H_2O$, 10g $Ce(SO_4)_2$) and subsequent development by gentle warming with a heat-gun. Purifications were performed by flash column chromatography using silica gel from Silicycle (60 Å, 40-63 µm) with the indicated eluent.

^1H NMR and ^{13}C NMR spectra were recorded at 300 or 600 MHz and 75 or 150 MHz, respectively, on a Bruker spectrometer (300 MHz) and Varian spectrometer (600 MHz). All NMR spectra were measured at 25℃ in indicated deuterated solvents. Proton and carbon chemical shifts (δ) are reported in ppm and coupling constants (J) are reported in Hertz (Hz). The resonance multiplicities in the ^1H NMR spectra are described as "s" (singlet), "d" (doublet), "t" (triplet), "quint" (quintuplet) and "m" (multiplet) and broad resonances are indicated by "br". Residual protic solvent of $CDCl_3$ (^1H, δ 7.27 ppm; ^{13}C, δ 77.0 ppm (central resonance of the triplet)), D_2O (^1H, δ4.79 ppm and 30.9 ppm for CH_3 of Acetone for ^{13}C spectra of de-*O*-acetylated compounds), MeOD (^1H, δ3.31 ppm and ^{13}C, δ 49.0 ppm. 2D Homonuclear correlation ^1H-^1H COSY and Heteronuclear correlation ^1H-^{13}C HETCOR experiments were used to confirm NMR peak assignments. *Characteristic signals of protected and deprotected peripheric lactosides at the glycodendrimers' periphery were assigned in comparison with corresponding monovalent reference previously described.*[1] 2D Gel Permeation Chromatography (GPC) was performed using THF or $CHCl_3/Et_3N$ (1%) as the eluent, at 40°C with a 1 mL/min flow rate on a Viscotek VE 2001 GPCmax (SEC System) with Wyatt DSP/Dawn EOS and refractive index RI/LS system as detectors. 2 PLGel mixed B LS (10 µm, 300×7.5 mm) and LS-MALLS detection with performances verified with polystyrene 100 kDa and 2000 kDa were used to determine the number-average molecular weight (M_n) and polydispersity index (M_W/M_n). Calculations were performed with Zimm Plot (model). Fourier transform infrared (FTIR) spectra were obtained with Thermo-scientific, Nicolet model 6700 equipped with ATR. The absorptions are given in wavenumbers (cm^{-1}). The intensity of the bands is described as s (strong), m (medium) or w (weak). Melting points were measured on a Electrothermal MEL-TEMP apparatus and are uncorrected.

Accurate mass measurements (HRMS) were performed on a LC-MSD-TOF instrument from Agilent Technologies in positive electrospray mode. Low-resolution mass spectra were performed on the same apparatus or on a LCQ

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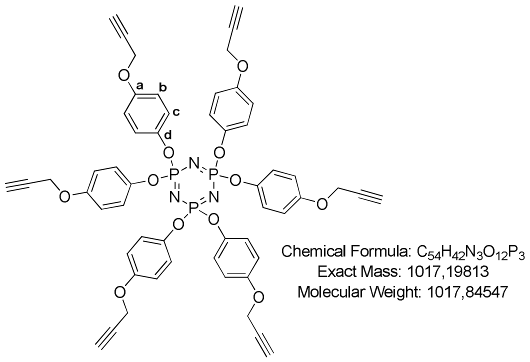
[1] V. Percec *et al.*, *J. Am. Chem. Soc.*, **2013**, *135*, 9055-9077.

Advantage ion trap instrument from Thermo Fisher Scientific in positive electrospray mode (Mass Spectrometry Laboratory (Université de Montréal), or Plateforme analytique pour molécules organiques (Université du Québec à Montréal), Québec, Canada). Either protonated molecular ions $[M{+}nH]^{n+}$ or adducts $[M{+}nX]^{n+}$ (X = Na, K, NH_4) were used for empirical formula confirmation. MALDI-TOF analyses were performed in either reflectron or linear mode on an Ultraflextreme TOF/TOF instrument from Bruker Daltonics. Mass spectra were acquired over the appropriate mass range for every particular sample. Each mass spectrum represents the sum of minimum 1000 laser shots. Samples were solubilized in either dichloromethane or water to an approximate final concentration of 6 mg/mL. Dithranol and DHB at 10 mg/mL in methanol containing 0.1 % TFA were used as matrices while NaTFA at 2 mg/mL in methanol was used as ionizing agent. A mixture of 20 uL matrix, 20 uL sample and 10 uL ionizing agent was prepared in a 600 uL Eppendorf tube. Aliquots of 1 uL of the above solution were applied on the MALDI plate and allowed to dry. All solvents for Mass Analyses (Water, Dichlorometane, Methanol and Acetonitrile) were HPLC grade, from de J.T. Baker (Phillipsburg, NJ). Sodium trifluoroacetate (NaTFA), dithranol andtrifluoroacetic (TFA) acid were from Sigma (St Louis, MO) while DHB was from Bruker Daltonics (Billerica, MA).

2. Synthetic protocols, Characterization, NMR, IR spectra, Mass, GPC, DLS traces

Hexapropargylated cyclotriphosphazene 1



Chemical Formula: $C_{54}H_{42}N_3O_{12}P_3$
Exact Mass: 1017,19813
Molecular Weight: 1017,84547

Hexachlorophosphazene $N_3P_3Cl_6$ (freshly recrystallized from Hexanes, 29.3 mg, 84.4 µmol, 1.0 eq.) and 4-propargyloxyphenol **4**[2] (150.0 mg, 1.010 mmol, 12.0 eq.) were dissolved in 4 mL of anhydrous THF. Under nitrogen atmosphere, Cs_2CO_3 (620.0 mg, 1.900 mmol, 22.5 eq.) was added and the mixture was stirred at reflux temperature (66℃) for 18 hours. The solution was filtered and washed with DCM. The filtrate was concentrated under reduced pressure. Column chromatography on silica (EtOAc/Hexanes 10:90 to 70:30) afforded the desired compound **1** (71.1 mg, 69.9 µmol, **83%**) as a white solid.

Crystallization conditions: 130 mg of amorphous **1** (white solid) are dissolved in a $Et_2O/EtOH_{abs.}$ mixture (5 mL/1.5 mL) at room temperature and 6 mL of Hexanes are added. The mixture containing the resulting white precipitate was refluxing at 75°C for 30 minutes (total dissolution was observed at 65°C). After gentle cooling, colorless plates were obtained at room temperature.

$\mathbf{R_f}$ = 0.23, EtOAc/Hexanes 35:65.
m.p. = 64°C (recryst. from $Et_2O/EtOH_{abs}$/Hexanes (5:1.5:6)).
^{1}**H NMR** (300 MHz, $CDCl_3$, δ ppm): 6.81 (dd, 24H, J = 9.0 Hz, CH_b, CH_c), 4.65 (d, 12H, J = 2.4 Hz; $OCH_2C{\equiv}CH$), 2.54 (t, 6H, J = 2.4 Hz; $OCH_2C{\equiv}CH$).
^{13}**C NMR** (75 MHz, $CDCl_3$, δ ppm): 154.5 (C_a), 144.8 (C_d), 121.8 (C_c), 115.5 (C_b), 78.5 ($C{\equiv}CH$), 75.7 ($C{\equiv}CH$), 56.1 (OCH_2).
^{31}**P NMR** (122 MHz, $CDCl_3$, δ ppm): 9.9 (s, 3P).
m/z (MALDI-MS) for $C_{54}H_{42}N_3O_{12}P_3$ = 1017.9; found 1017.2
(ESI$^+$-HRMS) 1018.20541 $[M+H]^+$; found 1018.20476; 1040.18735 $[M+Na]^+$; found 1040.18735.

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[2] M. Srinivasan, S. Sankararaman, H. Hopf, I. Dix and P.G. Jones, *J. Org. Chem.*, 2001, **66**, 4299−4303.

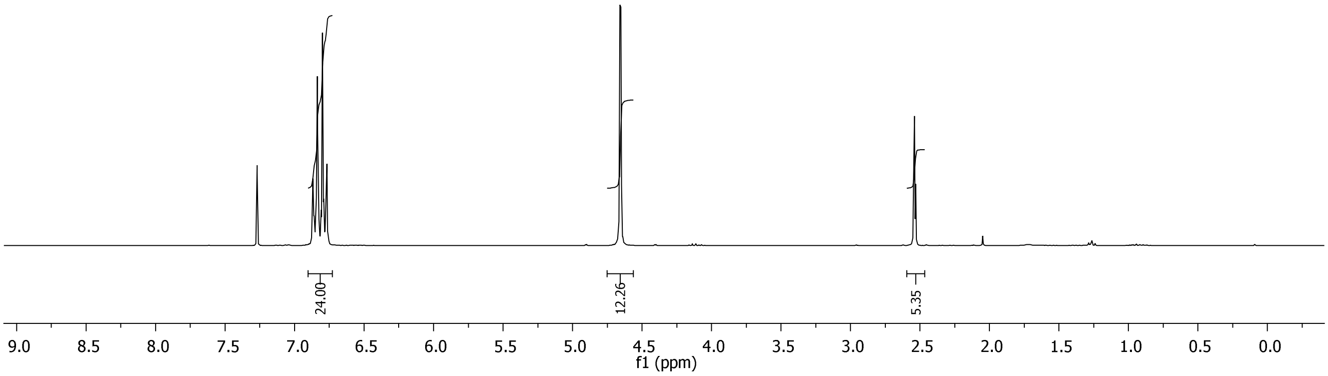


Figure S1. ^{1}H NMR spectrum of compound **1** ($CDCl_3$, 300MHz)

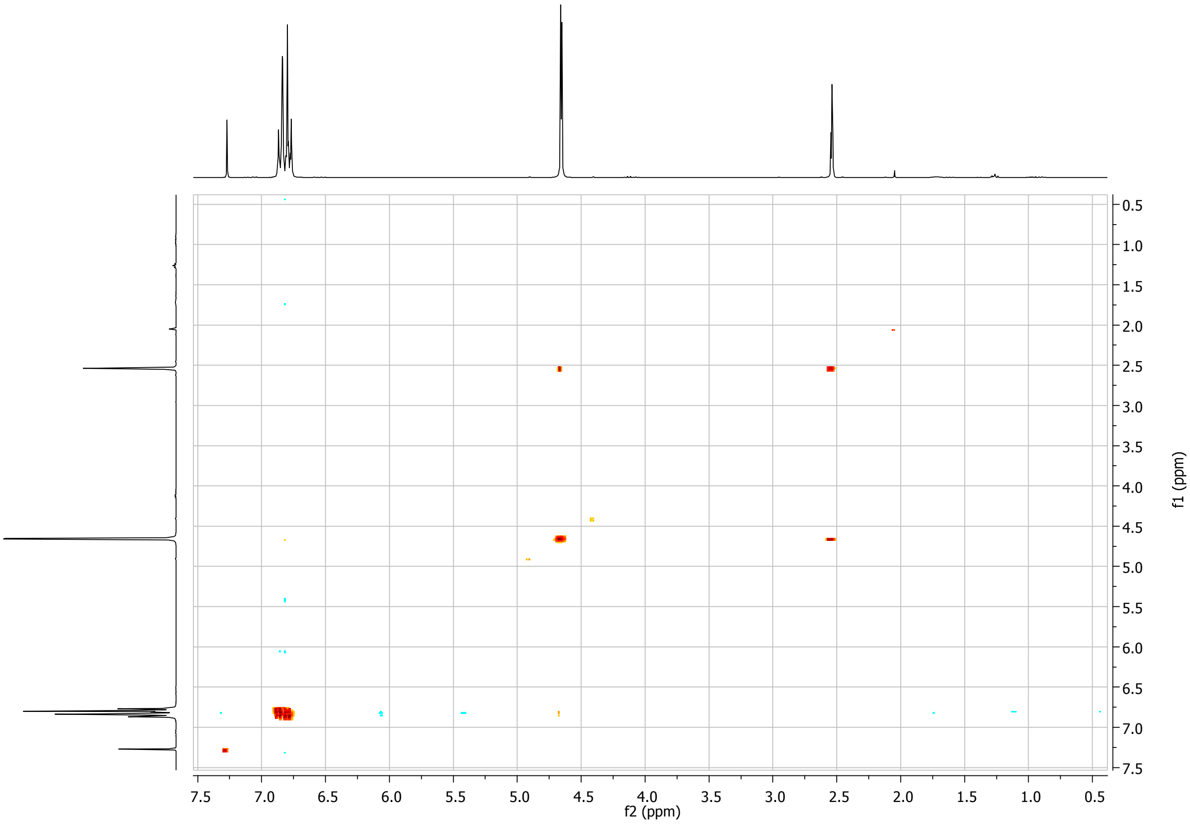


Figure S2. gCOSY spectrum of compound **1**

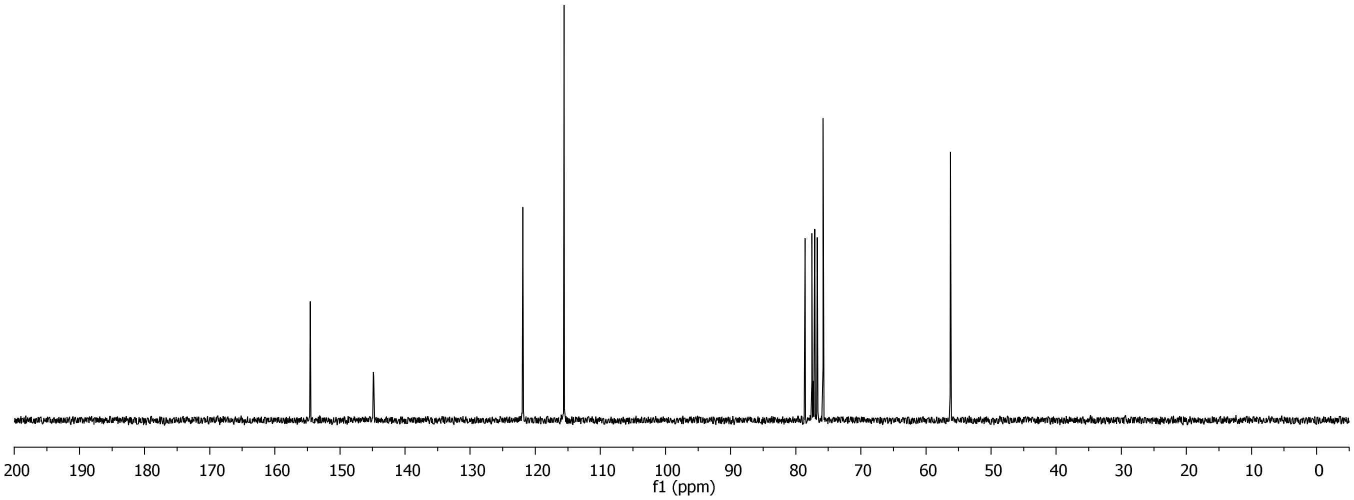


Figure S3. ^{13}C NMR spectrum of compound **1** ($CDCl_3$, 75MHz)

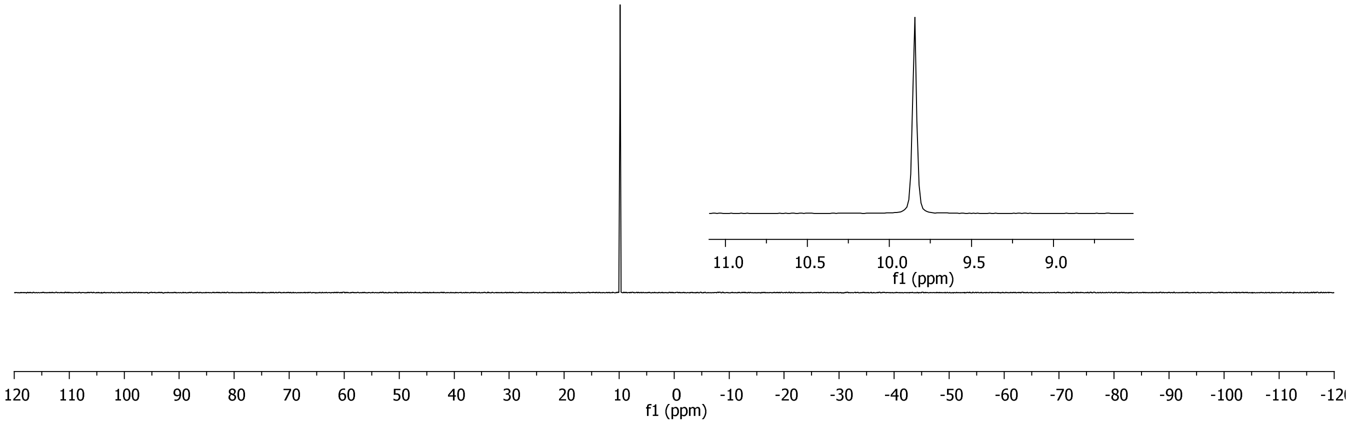
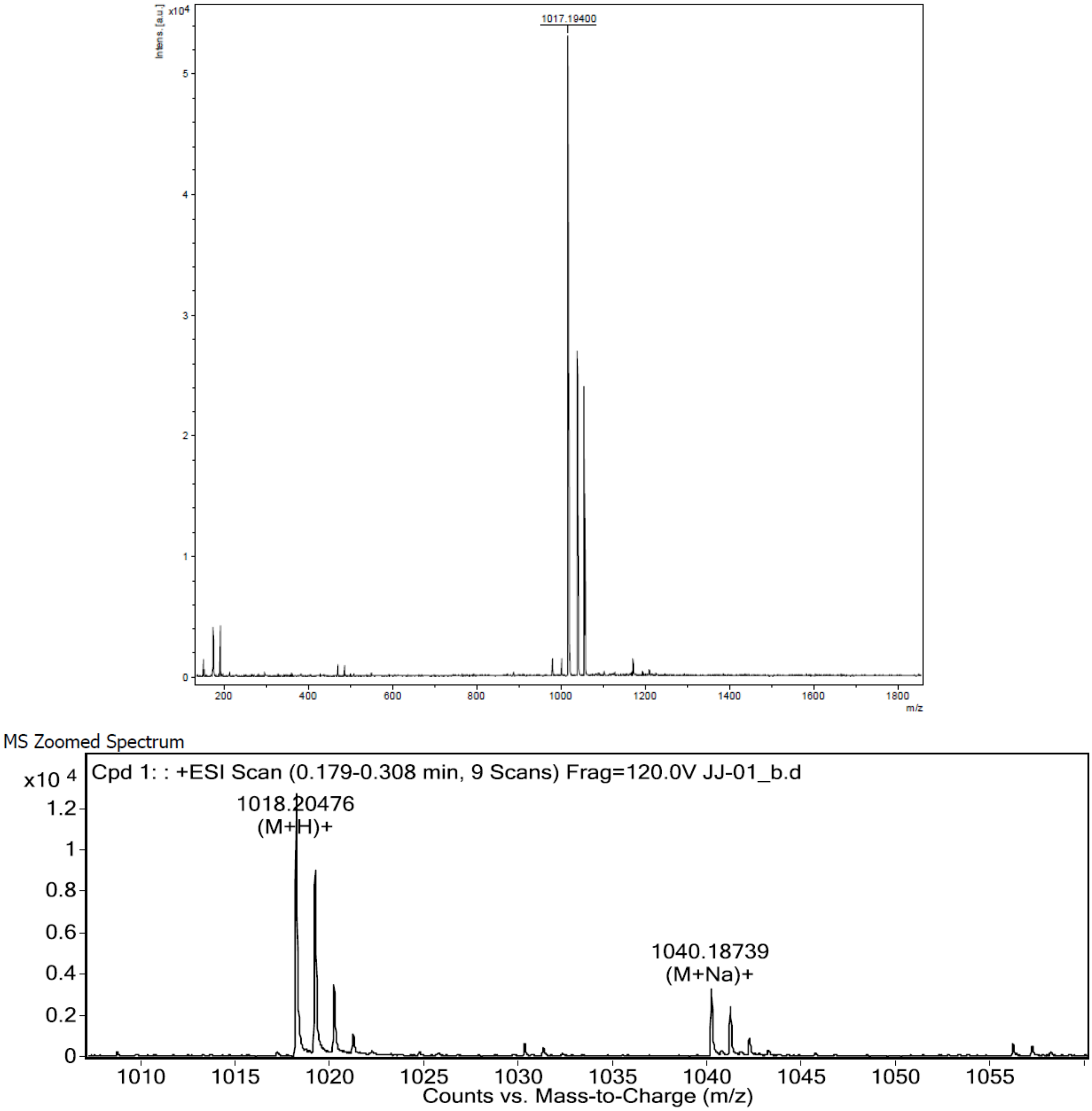


Figure S4. ^{31}P NMR spectrum of compound **1** ($CDCl_3$, 122MHz)

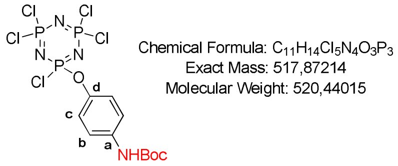


MS Spectrum Peak List

Ion	Ion Formula	Abund	*Expe. m/z*	*Calc. m/z*	Diff(ppm)
(M+H)+	$C_{54}H_{43}N_3O_{12}P_3$	12710	1018.20476	1018.20541	-0.64
(M+Na)+	$C_{54}H_{42}N_3NaO_{12}P_3$	3279	1040.18739	1040.18735	0.03

Figure S5. Mass spectrometry of compound **1** (*up*: MALDI-TOF MS and *bottom*: ESI$^+$-HRMS)

Compound 3



Chemical Formula: $C_{11}H_{14}Cl_5N_4O_3P_3$
Exact Mass: 517,87214
Molecular Weight: 520,44015

Hexachlorophosphazene (freshly recrystallized from Hexanes, 1.200 g, 3.450 mmol, 2.0 eq.) and *N*Boc-protected *p*-aminophenol derivative **2**[3] (361.0 mg, 1.725 mmol, 1.0 eq.) were dissolved in 125 mL of anhydrous THF. Under nitrogen atmosphere, Cs_2CO_3 (2.810 g, 8.630 mmol, 5.0 eq.) was added and the mixture was stirred at reflux temperature (66℃) for 24 hours. The solution was filtered and washed with DCM. The filtrate was concentrated under reduced pressure. Column chromatography on silica (DCM/Hexanes 10:90 to 70:30) afforded the desired compound **3** (538.0 mg, 1.034 mmol, **60%**) as a colorless oil.

$\mathbf{R_f}$ = 0.61, EtOAc/Hexanes 20:80.

^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.40 (d, 2H, *J* = 9.0 Hz, C*H$_b$*), 7.18 (d, 2H, *J* = 9.0 Hz, C*H$_c$*), 6.62 (br s, 1H, N*H*), 1.52 (s, 9H, C*H*$_3$).

^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 152.5 (*C*=O), 144.4 (*C*$_d$, d, $J_{P\text{-}C}$ = 10.4 Hz), 137.0 (*C*$_a$, d, $J_{P\text{-}C}$ = 2.7 Hz), 121.8 (*C*$_b$, d, $J_{P\text{-}C}$ = 5.0 Hz), 119.5 (*C*$_c$), 80.9 (*C*$_q$), 28.3 (CH_3).

^{31}P NMR (122 MHz, $CDCl_3$, δ ppm): 22.4 (d, 2P, ^2J(P,P) = 59.3 Hz, *P*Cl_2), 12.8 (t, 1P, ^2J(P,P) = 59.3 Hz, Cl-*P*-O).

m/z (ESI$^+$-HRMS) for $C_{11}H_{14}Cl_5N_4O_3P_3$ = 540.8614 [*M*+Na]$^+$; found 540.8628.

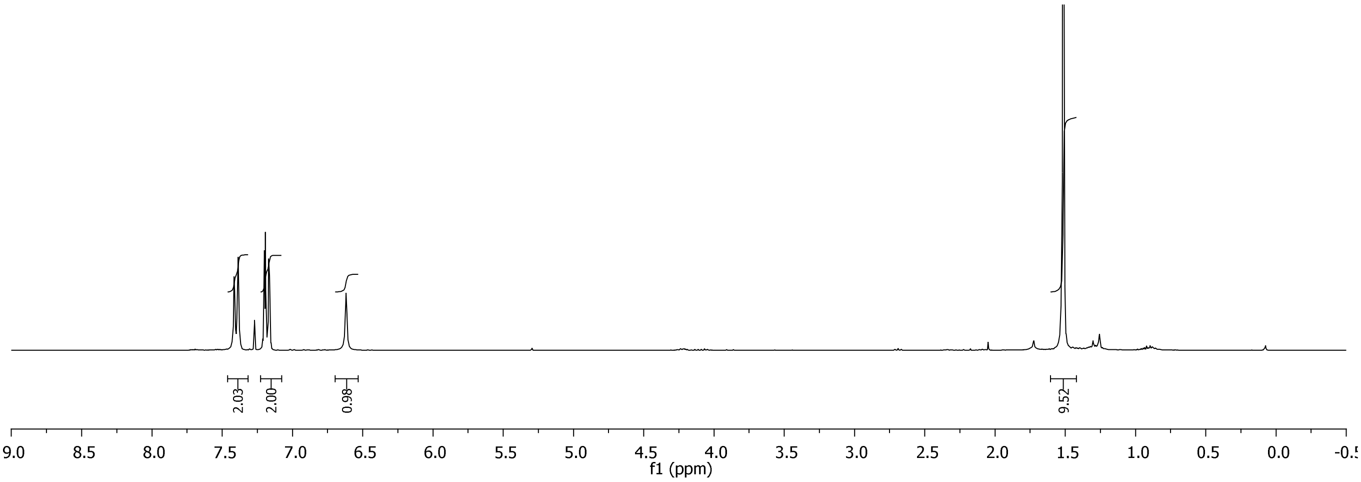


Figure S6. ^{1}H NMR spectrum of compound **3** ($CDCl_3$, 300MHz)

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[3] N. Jain, Y. Arntz, V. Goldschmidt, G. Duportail, Y. Mely and A. S. Klymchenko, *Bioconjugate Chem.*, 2010, **21**, 2110−2118.

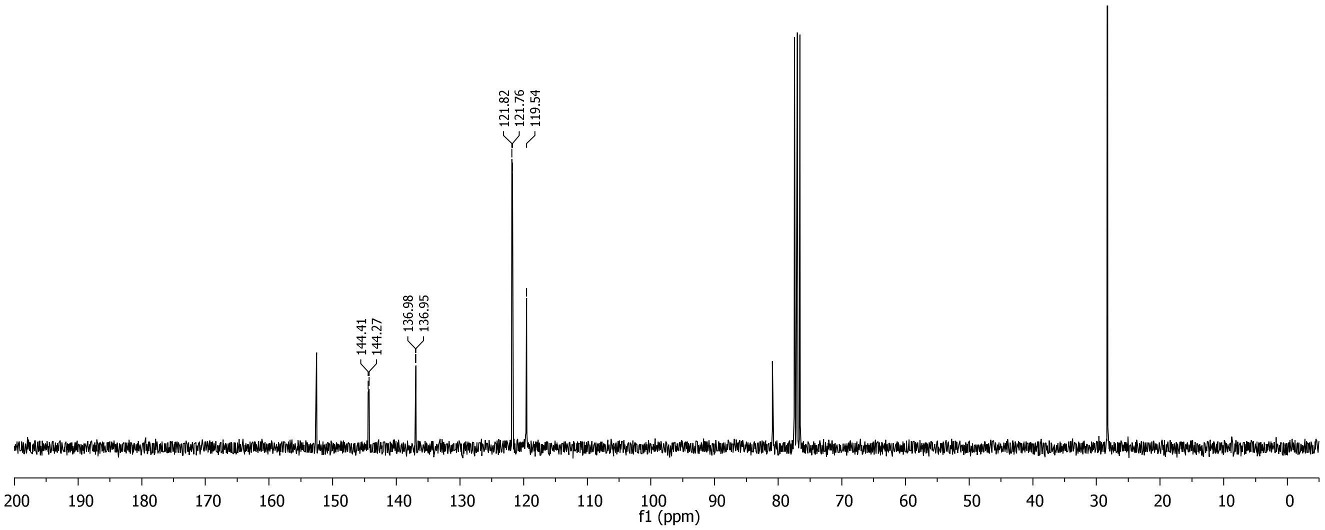


Figure S7. ^{13}C NMR spectrum of compound **3** ($CDCl_3$, 75MHz)

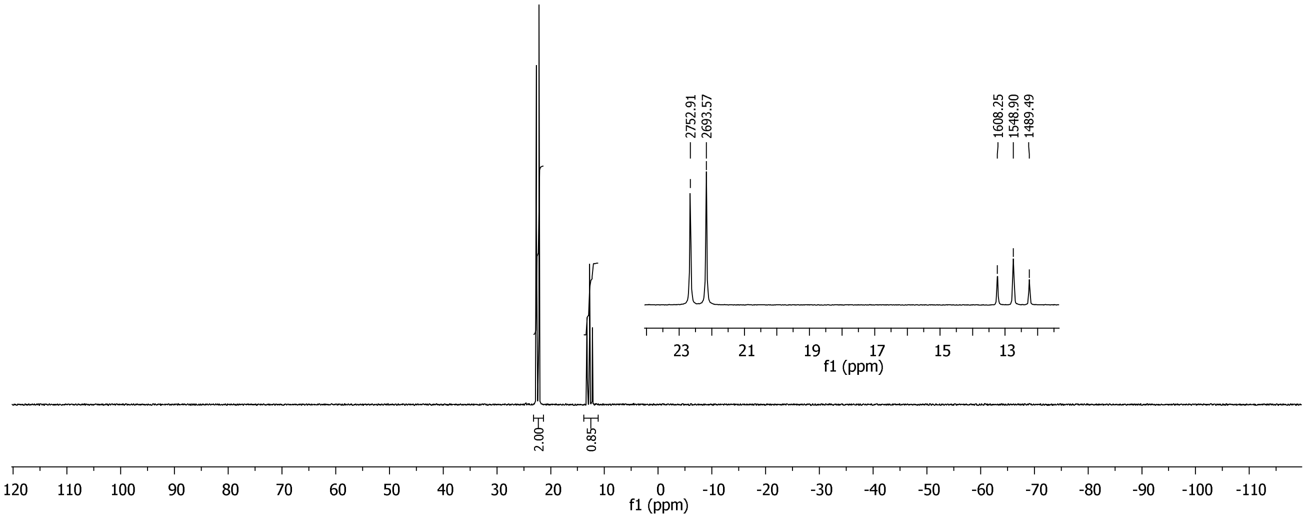
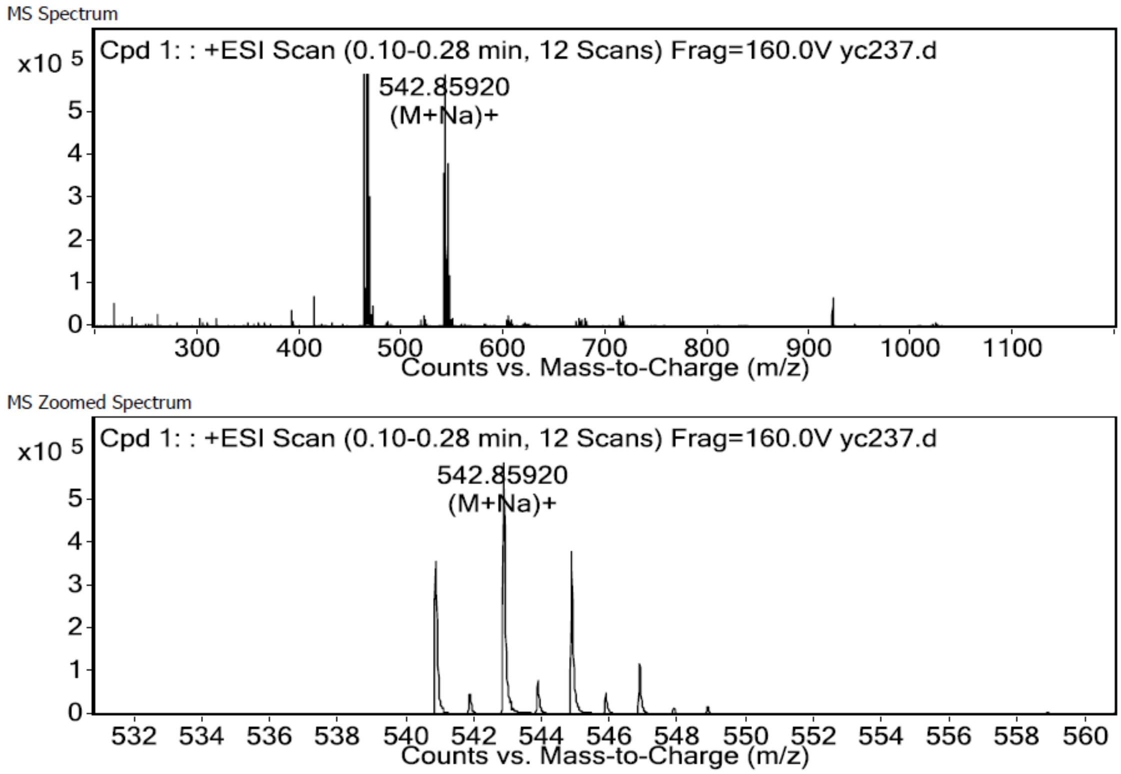


Figure S8. ^{31}P NMR spectrum of compound **3** ($CDCl_3$, 75MHz)

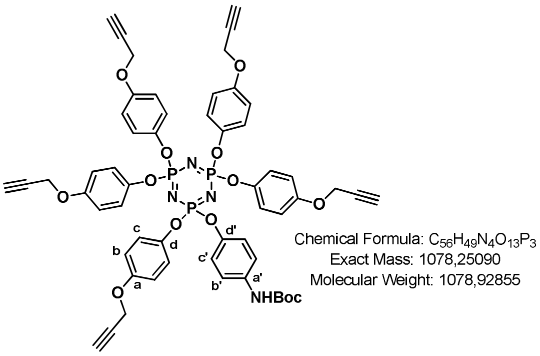


MS Spectrum Peak List

Ion	**Ion Formula**	**Abund**	***Expe. m/z***	***Calc. m/z***	**Diff(ppm)**
(M+Na)+	C11H14Cl5N4NaO3P3	366441.2	540.86277	540.86136	2.61

Figure S9. ESI$^+$-HRMS spectrum of compound **3**

Compound 5



Chemical Formula: $C_{56}H_{49}N_4O_{13}P_3$
Exact Mass: 1078,25090
Molecular Weight: 1078,92855

Monofunctionalized derivative **3** (50.0 mg, 0.0961 mmol, 1.0 eq.) and 4-propargyloxyphenol **4** (113.9 mg, 0.7690 mmol, 8.0 eq.) were dissolved in 8 mL of anhydrous THF. Under nitrogen atmosphere, Cs_2CO_3 (1.50 g, 4.81 mmol, 48.0 eq.) was added and the mixture was stirred at reflux temperature (66℃) for 6 hours. The solution was filtered and washed with DCM. The filtrate was concentrated under reduced pressure. Column chromatography on silica (EtOAc/Hexanes 10:90 to 35:65) afforded the desired compound **5** (88.0 mg, 0.0816 mmol, **87%**) as a colorless oil.

R_f = 0.36, EtOAc/Hexanes 35:65.

^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.18 (d, 2H, *J* = 9.0 Hz, C$H_{b'}$), 6.87-6.76 (m, 22H, CH_b, CH_c, C$H_{c'}$), 6.54 (br s, 1H, N*H*), 4.65 (t_{app}, 10H, OCH_2C≡CH), 2.55 (t_{app}, 5H, C≡C*H*), 1.52 (s, 9H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 154.4 (C_a), 152.6 (*C*=O), 145.8 ($C_{d'}$), 144.7 (C_d), 135.1 ($C_{a'}$), 121.8 (C_c), 121.3 ($C_{b'}$), 119.5 ($C_{c'}$), 115.4 (C_b), 80.5 (C_q), 78.5 (*C*≡CH), 78.4 (*C*≡CH), 75.7 (C≡*C*H), 56.1 (O*C*H_2), 28.3 (*C*H_3).

^{31}P NMR (122 MHz, $CDCl_3$, δ ppm): 9.81 (s_{app}, 3P).

m/z (ESI$^+$-HRMS) for $C_{56}H_{49}N_4O_{13}P_3$ = 1079.2582 [*M*+H]$^+$; found 1079.2556.

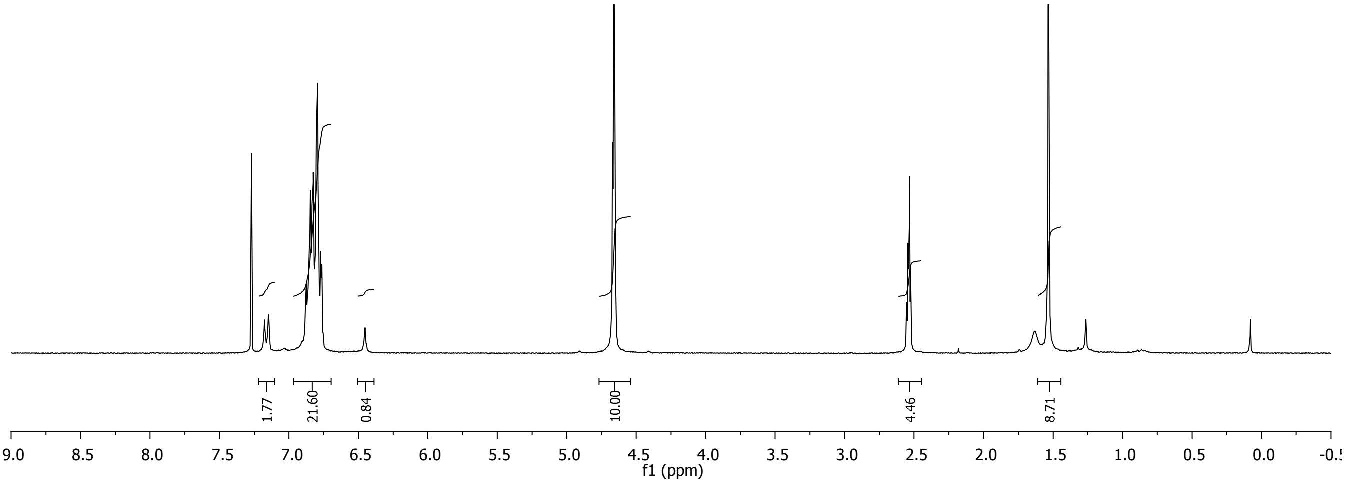


Figure S10. ^{1}H NMR spectrum of compound **5** ($CDCl_3$, 300MHz)

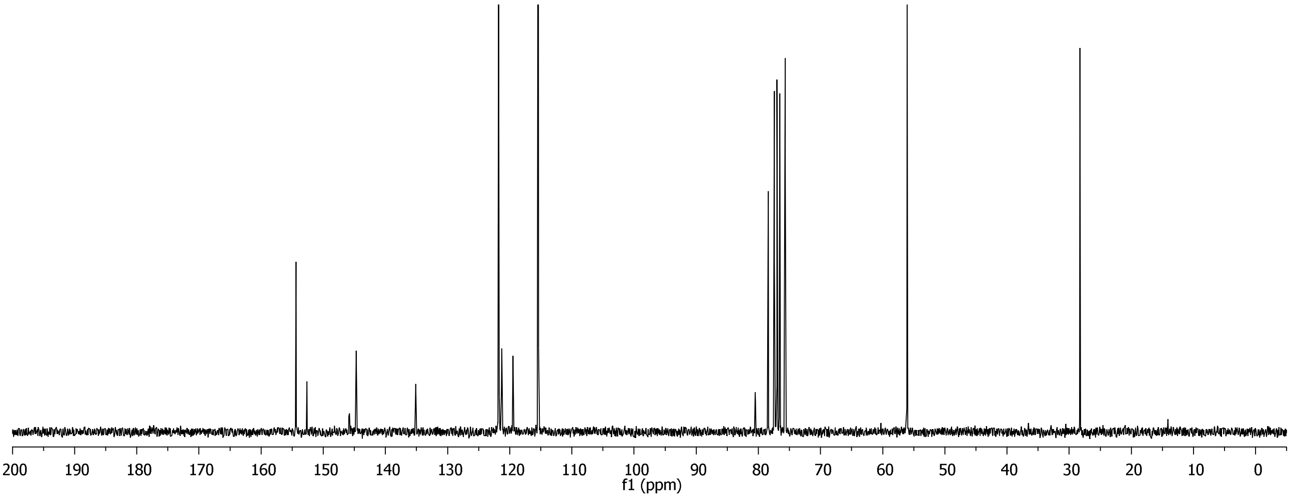


Figure S11. ^{13}C NMR spectrum of compound **5** ($CDCl_3$, 75MHz)

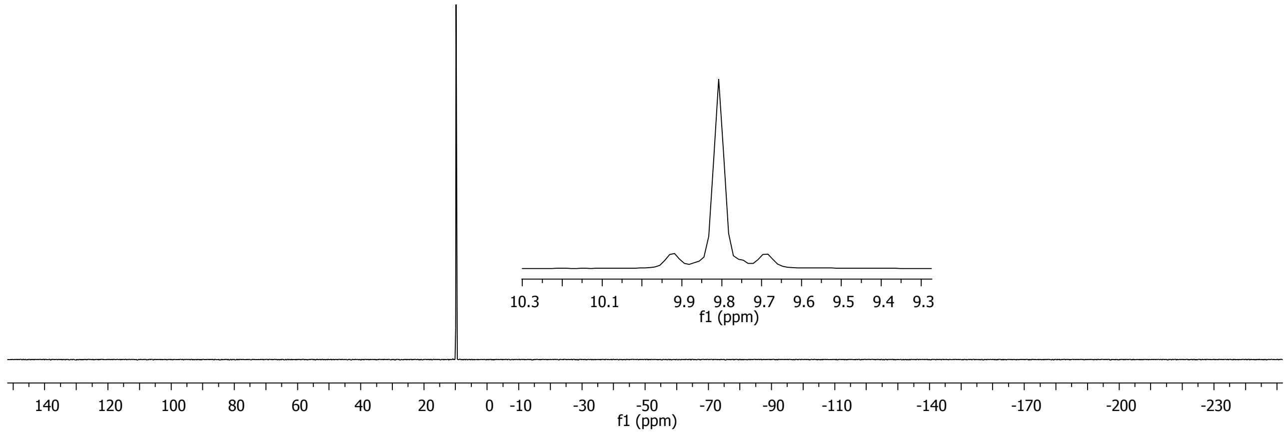
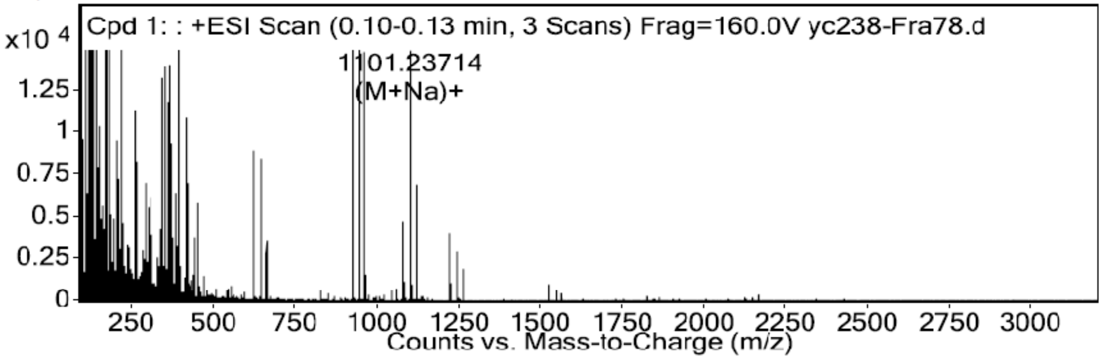
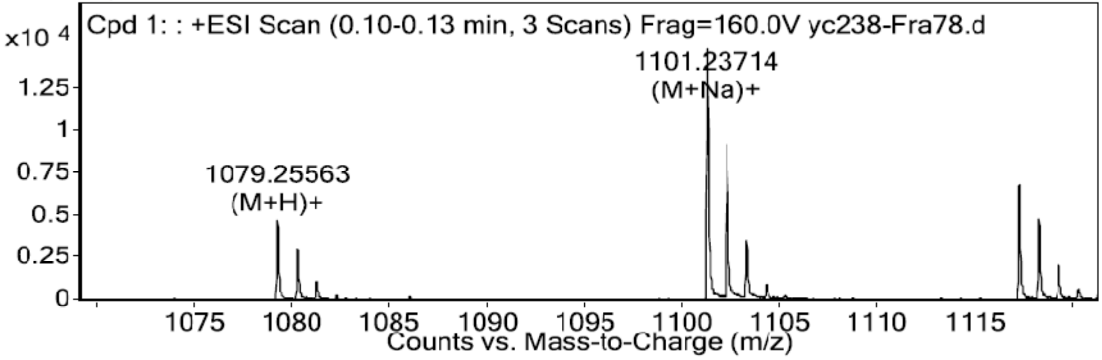


Figure S12. ^{31}P NMR spectrum of compound **5** ($CDCl_3$, 122MHz)

MS Spectrum



MS Zoomed Spectrum

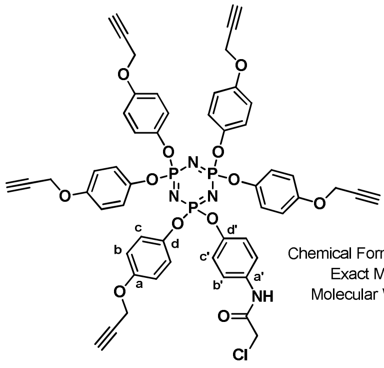


MS Spectrum Peak List

Ion	Ion Formula	Abund	*Expe. m/z*	*Calc. m/z*	Diff(ppm)
(M+H)+	C56H50N4O13P3	4746.7	1079.25563	1079.25817	-2.36
(M+Na)+	C56H49N4NaO13P3	14869.2	1101.23714	1101.24012	-2.7

Figure S13. ESI$^+$-HRMS spectrum of compound **5**

Compound 6



Chemical Formula: $C_{53}H_{42}ClN_4O_{12}P_3$
Exact Mass: 1054,17006
Molecular Weight: 1055,29447

Dissymetric hexasubstitued protected phosphazene derivative **5** (158.0 mg, 0.1460 mmol, 1.0 eq.) was dissolved in 3.5 mL of anhydrous DCM under nitrogen atmosphere and at 0^{o}C was added dropwise 550 µL of trifluoroacetic acid (TFA) over a 30 minutes period. After stirring 3 hours at rt, the solvent was removed under reduced pressure and coevaporated with toluene. The residue was dissolved in 3 mL of anhydrous DCM and, under nitrogen atmosphere, was added 100 µL of DIPEA (74.7 mg, 0.578 mmol, 4.0 eq.). At 0^{o}C was added dropwise chloroacetylchoride[*] (34.5 µL, 49.0 mg, 0.433 mmol, 3.0 eq.) in 1 mL of anhydrous DCM over a 15 minutes period. After stiring at rt for 18 hours, the solvent was removed under reduced pressure and the residue was dissolved in 25 mL of EtOAc and washed with HCl 1M (2×20 mL), NH_4Cl (20 mL), then water (10 mL). The organic phase was dried over Na_2SO_4, and concentrated under reduced pressure. Column chromatography on silica (EtOAc/Hexanes 20:80 to 45:55) afforded the desired compound **6** (112.0 mg, 0.1061 mmol, **72%**) as a yellowish oil.

R_f = 0.39, EtOAc/Hexanes 50:50.
^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 8.24 (br s, 1H, N*H*), 7.33 (d, 2H, *J* = 9.0 Hz, C$H_{b'}$), 6.88-6.76 (m, 22H, CH_b, CH_c, C$H_{c'}$), 4.65 (t_{app}, 10H, OCH_2C≡CH), 4.19 (s, 2H, CH_2Cl), 2.55 (t_{app}, 5H, C≡C*H*).
^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 163.7 (*C*=O), 154.4 (C_a), 147.3 ($C_{d'}$), 144.7 (C_d), 133.4 ($C_{a'}$), 121.7 (C_c), 121.5 ($C_{b'}$), 121.2 ($C_{c'}$), 115.4 (C_b), 78.5 (*C*≡CH), 78.4 (*C*≡CH), 75.7 (C≡*C*H), 56.1 (O*C*H_2), 42.8 (*C*H_2Cl).
^{31}P NMR (122 MHz, $CDCl_3$, δ ppm): 9.69 (s_{app}, 3P).
m/z (ESI^{+}-HRMS) for $C_{53}H_{42}ClN_4O_{12}P_3$ = 1055.1773 [*M*+H]$^{+}$; found 1055.1758.

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[*] *The use of bromoacetylchloride at this step provides a mixture of halogenated (Cl/Br) derivatives after the same steps of purification.*

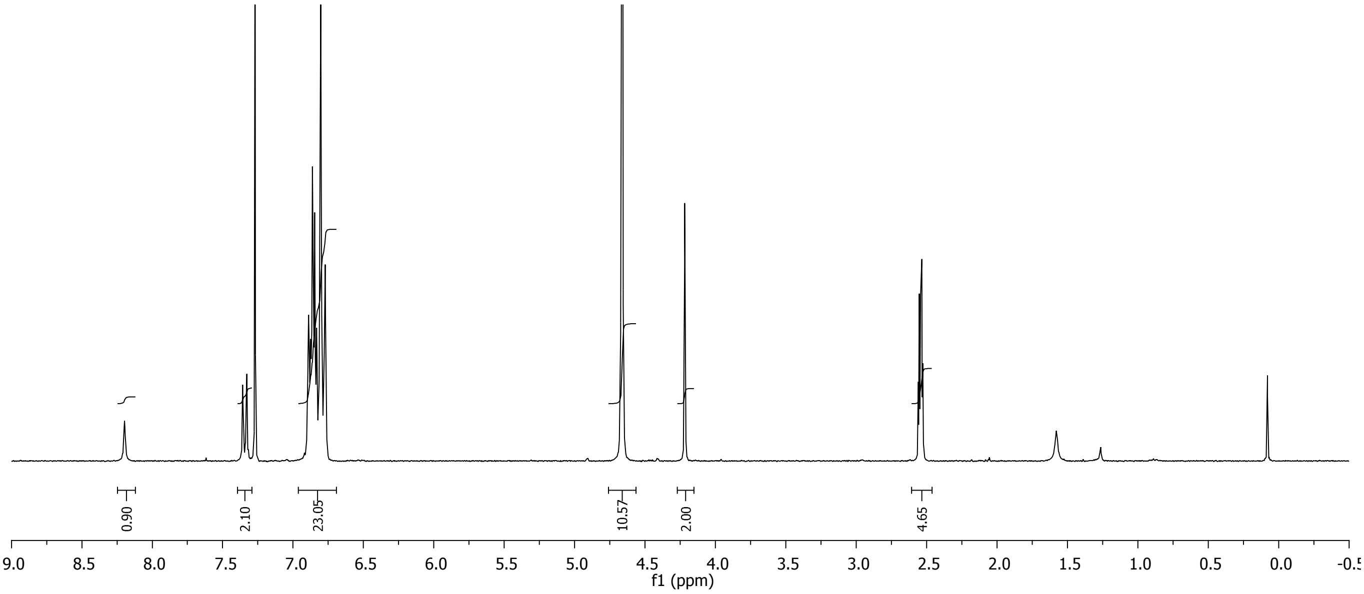


Figure S14. ^{1}H NMR spectrum of compound **6** ($CDCl_3$, 300MHz)

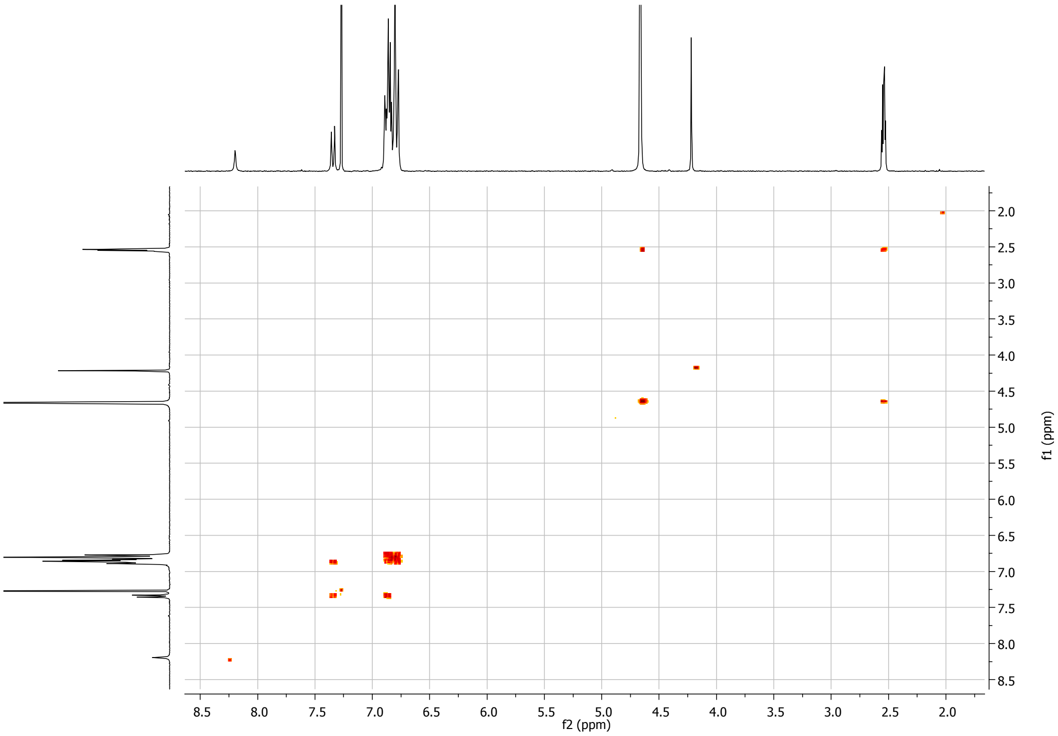


Figure S15. gCOSY spectrum of compound **6**

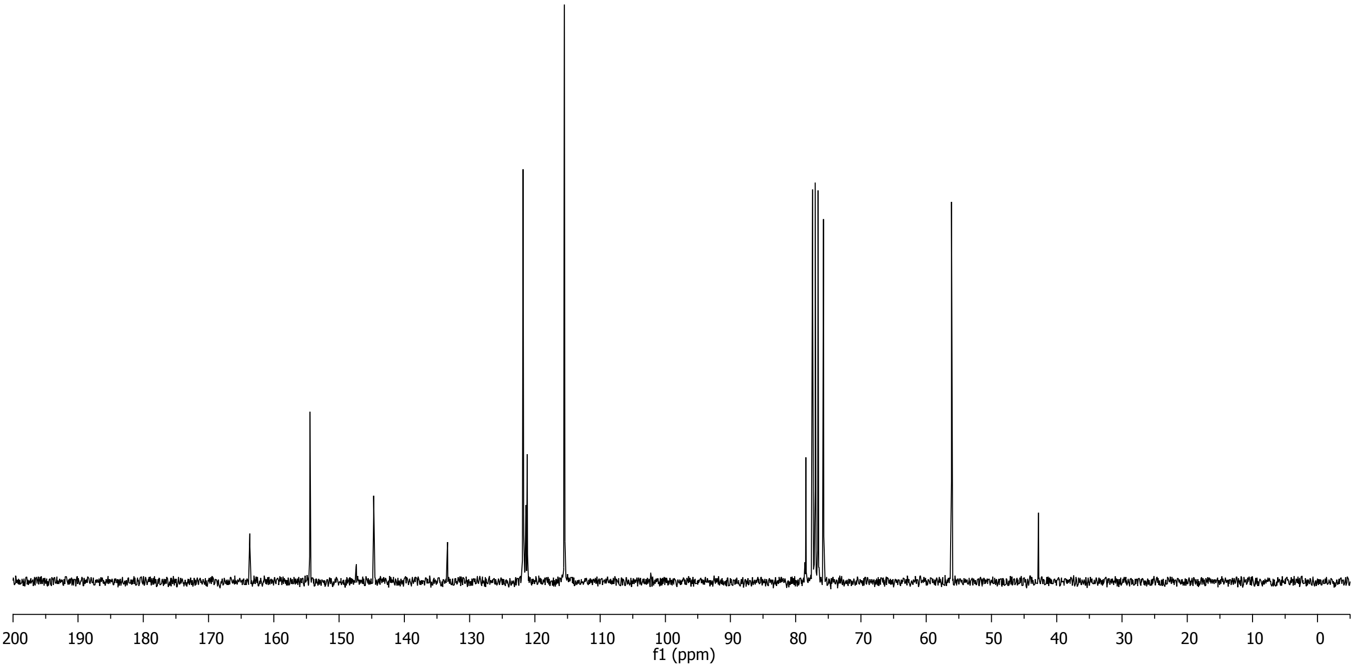


Figure S16. ^{13}C NMR spectrum of compound **6** ($CDCl_3$, 75MHz)

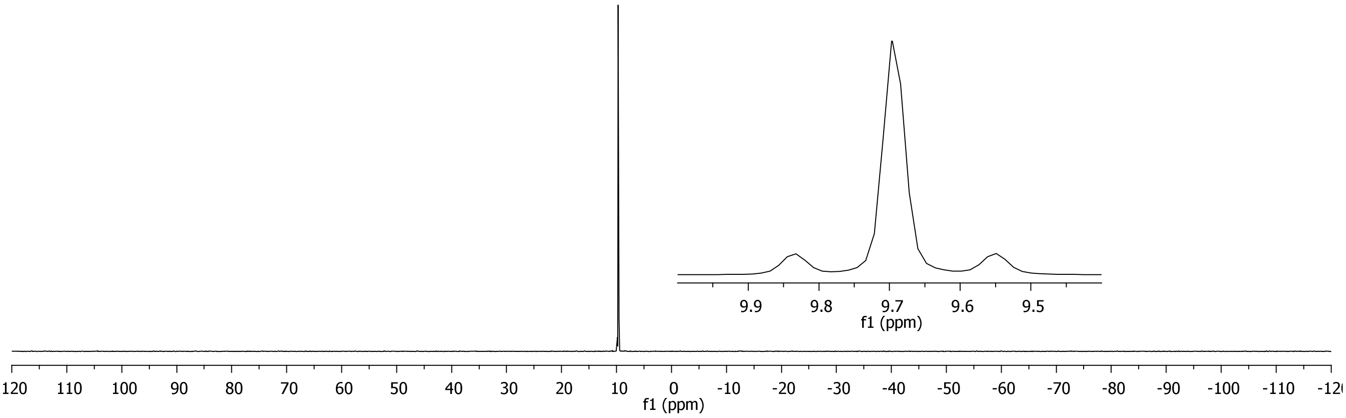
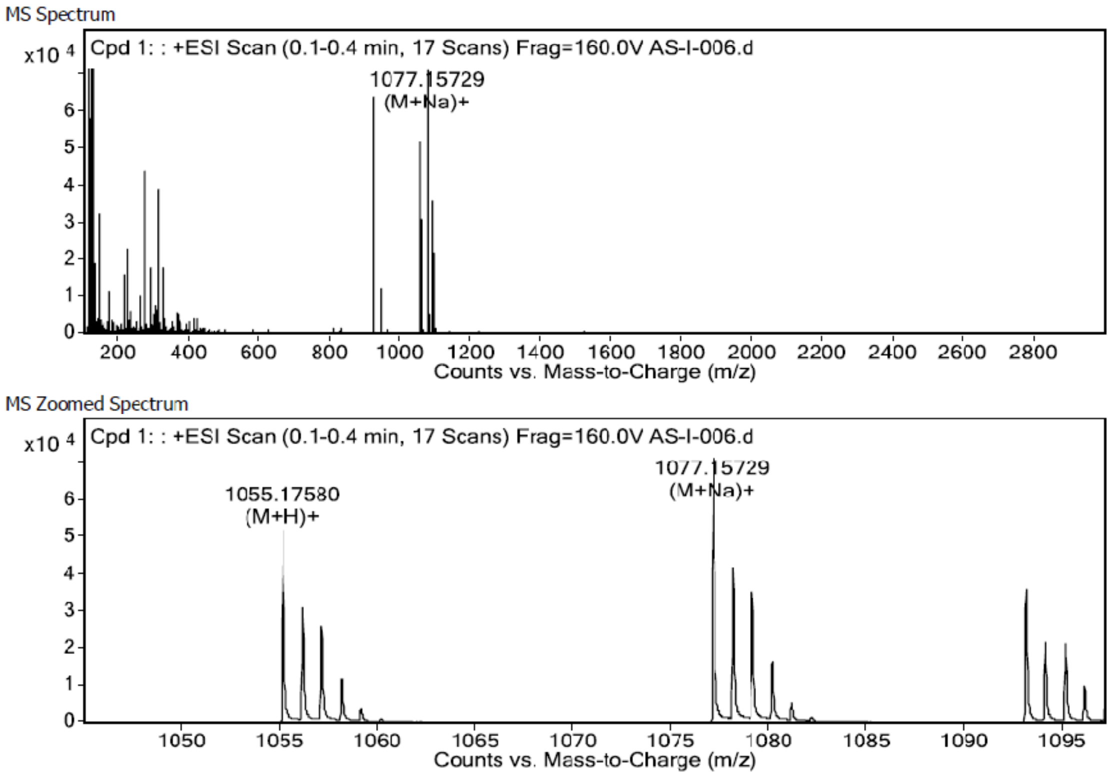


Figure S17. ^{31}P NMR spectrum of compound **6** ($CDCl_3$, 122MHz)



MS Spectrum Peak List

Ion	Ion Formula	Abund	*Expe. m/z*	*Calc. m/z*	Diff(ppm)
(M+H)+	C53H43ClN4O12P3	52261.9	1055.1758	1055.17734	-1.46
(M+Na)+	C53H42ClN4NaO12P3	71751.9	1077.15729	1077.15928	-1.85

Figure S18. ESI$^+$-HRMS spectrum of compound **6**

<u>Mixture Br/Cl (ratio of ~ 20:80) with the use of bromoacetylchloride:</u>

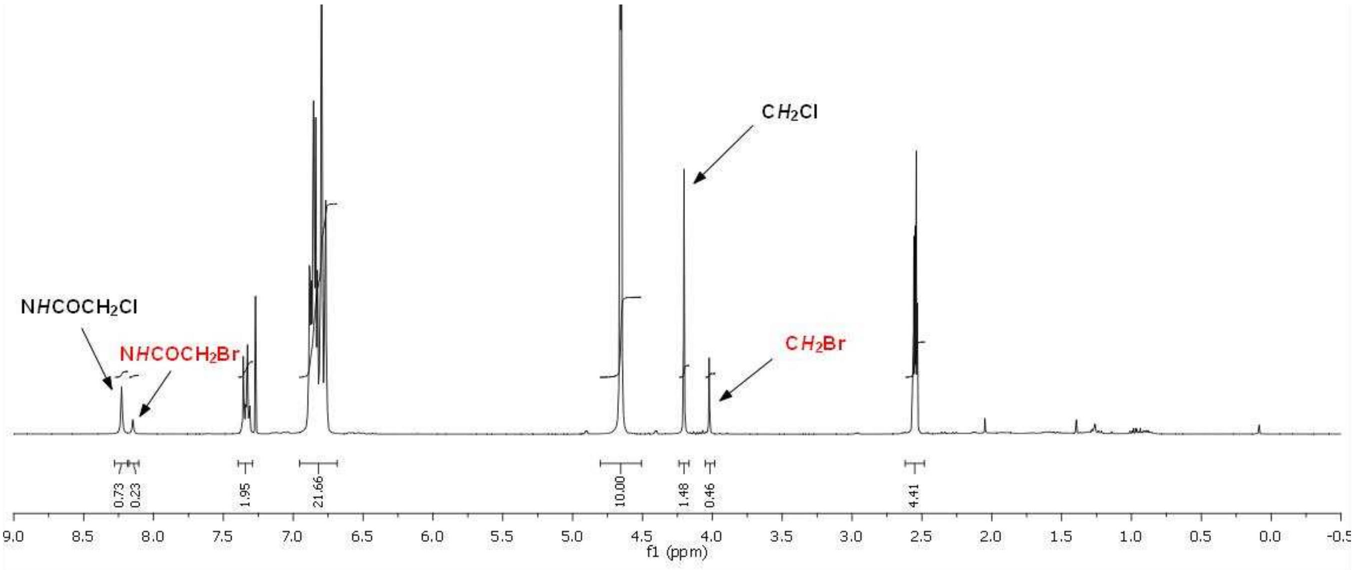


Figure S19. ^{1}H NMR spectrum of the Cl/Br mixture of compound **6** (CDCl$_3$, 300MHz)

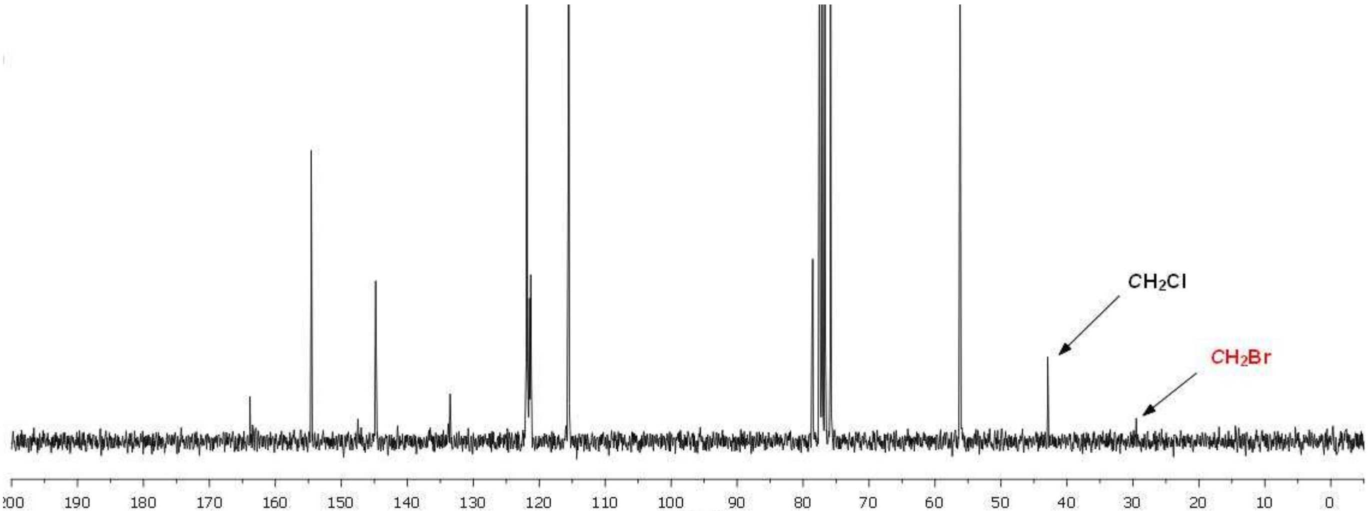
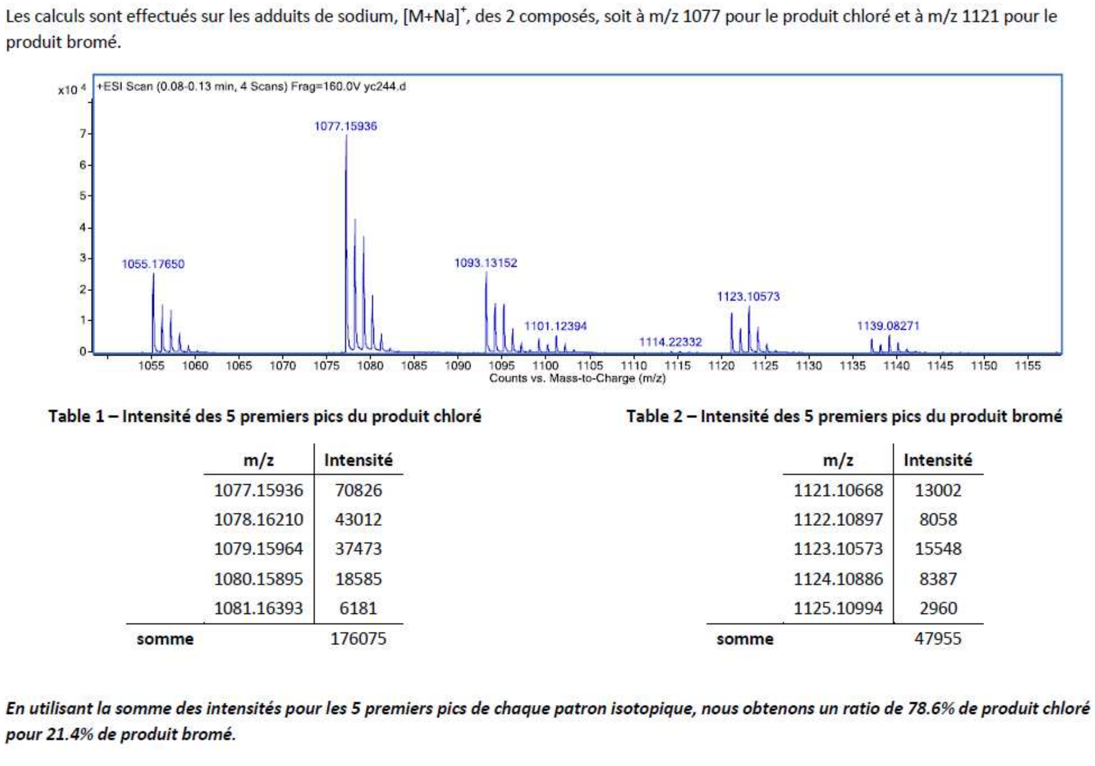


Figure S20. ^{13}C NMR spectrum of the Cl/Br mixture of compound **6** ($CDCl_3$, 75MHz)



Les calculs sont effectués sur les adduits de sodium, $[M+Na]^+$, des 2 composés, soit à m/z 1077 pour le produit chloré et à m/z 1121 pour le produit bromé.

Table 1 – Intensité des 5 premiers pics du produit chloré

	m/z	Intensité
	1077.15936	70826
	1078.16210	43012
	1079.15964	37473
	1080.15895	18585
	1081.16393	6181
somme		176075

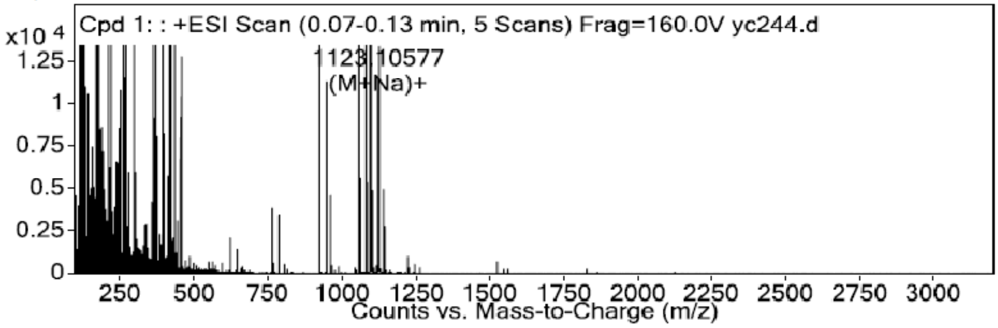
Table 2 – Intensité des 5 premiers pics du produit bromé

	m/z	Intensité
	1121.10668	13002
	1122.10897	8058
	1123.10573	15548
	1124.10886	8387
	1125.10994	2960
somme		47955

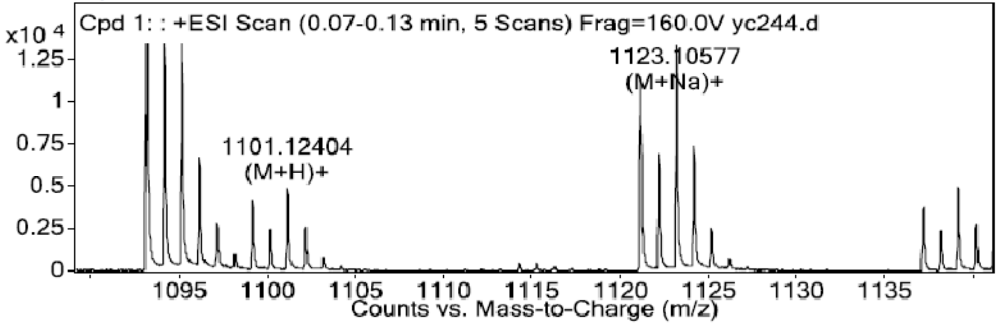
En utilisant la somme des intensités pour les 5 premiers pics de chaque patron isotopique, nous obtenons un ratio de 78.6% de produit chloré pour 21.4% de produit bromé.

Figure S21. Calculation of Cl/Br ratio from ESI$^+$-HRMS of compound **6** when using bromoacetyl chloride as reactant

MS Spectrum



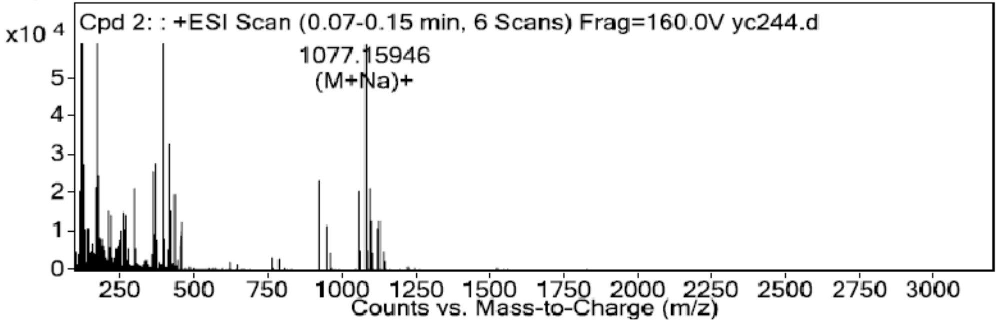
MS Zoomed Spectrum



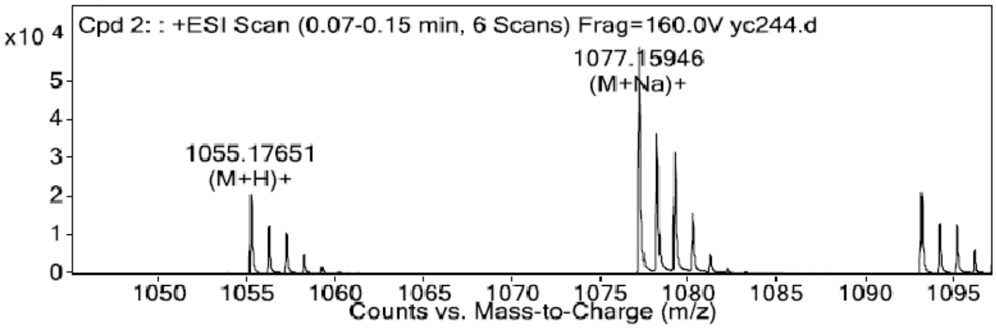
MS Spectrum Peak List

Ion	Ion Formula	Abund	*Expe. m/z*	*Calc. m/z*	Diff(ppm)
(M+H)+	C53H43BrN4O12P3	4266.3	1099.12593	1099.12682	0.81
(M+Na)+	C53H42BrN4NaO12P3	11561.4	1121.10677	1121.10877	1.78

MS Spectrum



MS Zoomed Spectrum

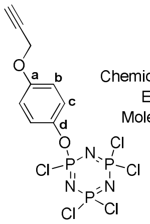


MS Spectrum Peak List

Ion	Ion Formula	Abund	*Expe. m/z*	*Calc. m/z*	Diff(ppm)
(M+H)+	C53H43ClN4O12P3	20767.8	1055.17651	1055.17734	-0.78
(M+Na)+	C53H42ClN4NaO12P3	59549.3	1077.15946	1077.15928	0.16

Figure S22. ESI$^+$-HRMS spectrum of compound **6** when using bromoacetyl chloride as reactant

Compound 7



Chemical Formula: $C_9H_7Cl_5N_3O_2P_3$
Exact Mass: 456,81937
Molecular Weight: 459,35707

Hexachlorophosphazene (freshly recrystallized from Hexanes, 518.6 mg, 1.490 mmol, 2.0 eq.) and 4-propargyloxyphenol **4** (110.5 mg, 0.745 mmol, 1.0 eq.) were dissolved in 50 mL of anhydrous THF. Under nitrogen atmosphere, Cs_2CO_3 (2.42 g, 7.44 mmol, 10.0 eq.) was added and the mixture was stirred at reflux temperature (66℃) for 22 hours. The solution was filtered and washed with DCM. The filtrate was concentrated under reduced pressure. Column chromatography on silica (DCM/Hexanes 20:80 to 75:25) afforded the desired compound **7** (243.6 mg, 0.530 mmol, **71%**) as a colorless oil.

R_f = 0.66, EtOAc/Hexanes 20:80.

^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.15-7.11 (m, 2H, C*H$_b$*), 6.93-6.89 (m, 2H, C*H$_c$*), 4.61 (d, *J* = 2.4 Hz, 2H, OC*H$_2$*C≡C), 2.46 (t, 1H, *J* = 2.4 Hz, C≡C*H*).

^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 155.8 (C_a, d, $J_{P\text{-}C}$ = 2.6 Hz), 143.3 (C_d, d, $J_{P\text{-}C}$ = 10.5 Hz), 122.4 (C_c, d, $J_{P\text{-}C}$ = 5.0 Hz), 116.0 (C_b, d, $J_{P\text{-}C}$ = 2.2 Hz), 78.1 (*C*≡CH), 76.0 (C≡*C*H), 56.3 (O*C*H$_2$C≡C).

^{31}P NMR (122 MHz, $CDCl_3$, δ ppm): 22.4 (d, 2P, ^2J(P,P) = 59.2 Hz, *P*Cl$_2$), 12.9 (t, 1P, ^2J(P,P) = 59.3 Hz, Cl-*P*-O).

m/z (ESI$^+$-HRMS) for $C_9H_7Cl_5N_3O_2P_3$ = 457.8267 [*M*+H]$^+$; found 457.8280, 479.8086 [*M*+Na]$^+$, found 479.8093.

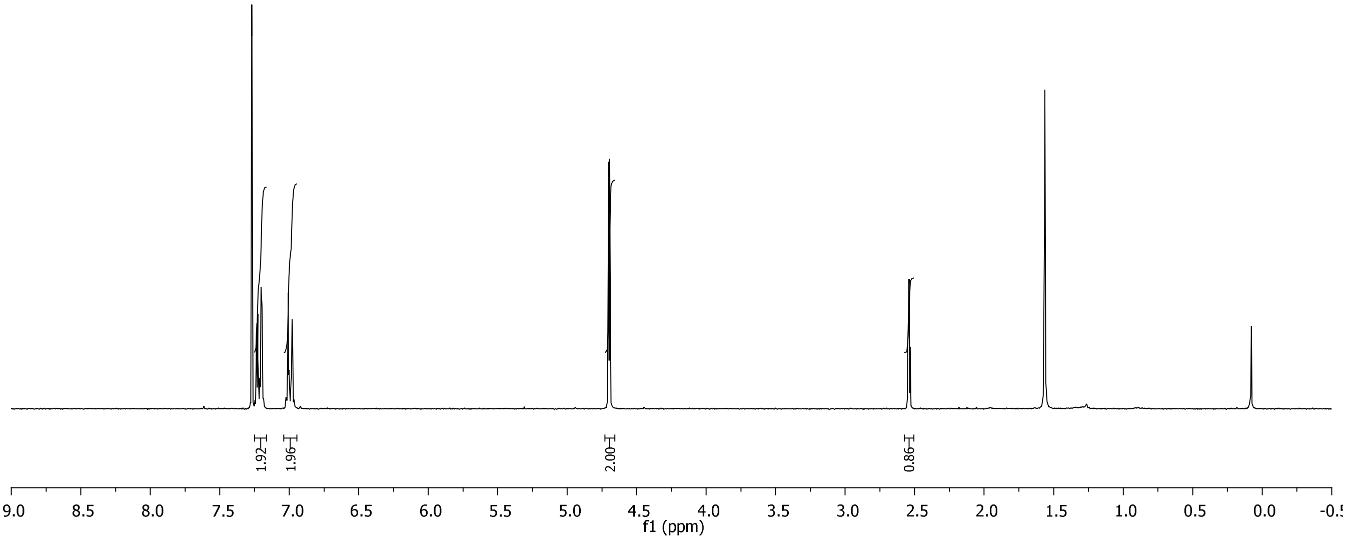


Figure S23. ^{1}H NMR spectrum of compound **7** ($CDCl_3$, 300MHz)

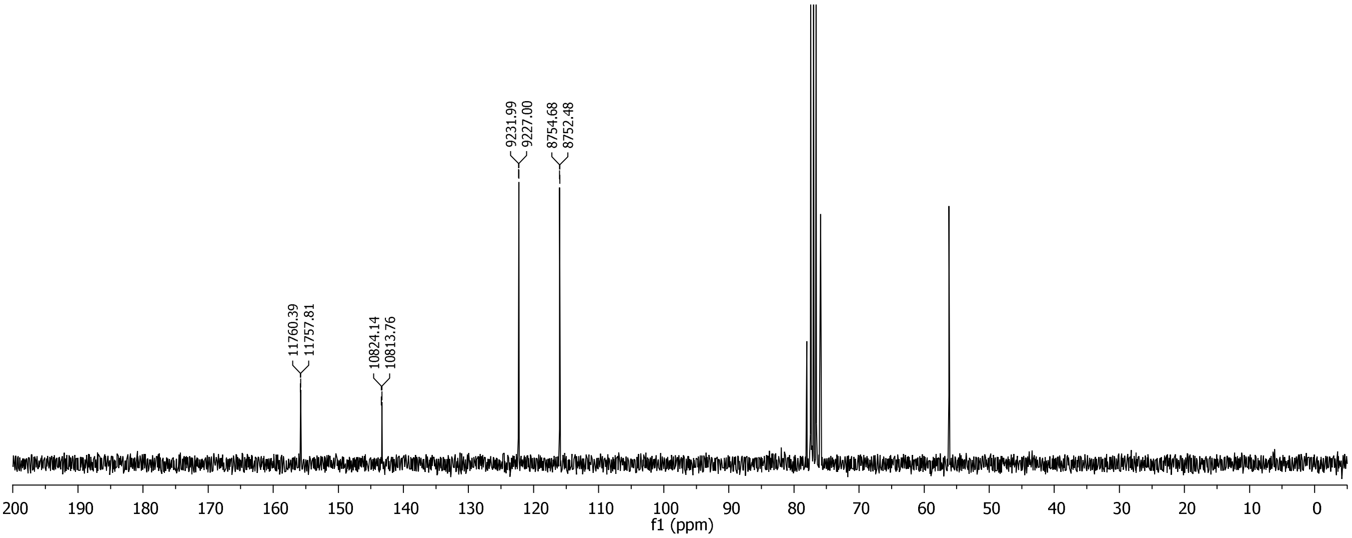


Figure S24. ^{13}C NMR spectrum of compound **7** ($CDCl_3$, 75MHz)

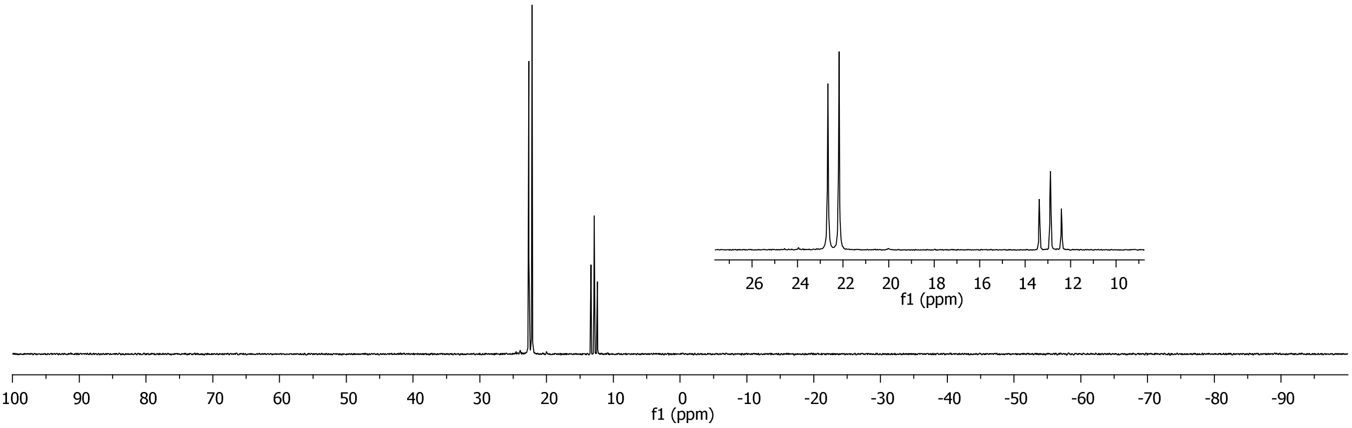
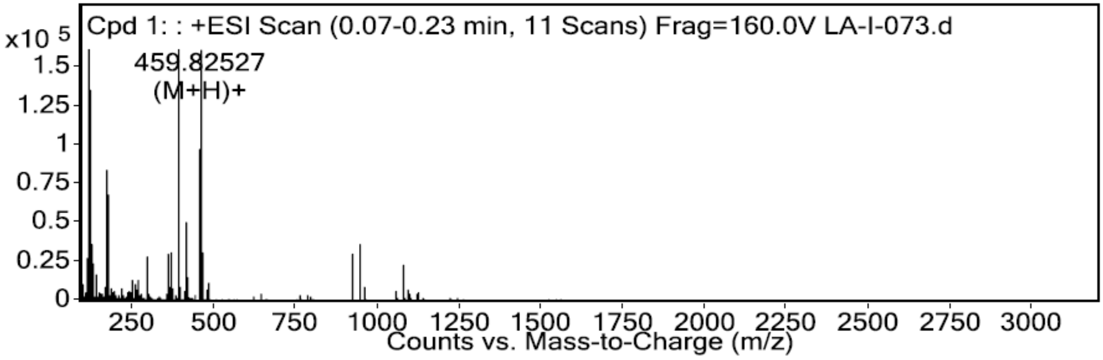
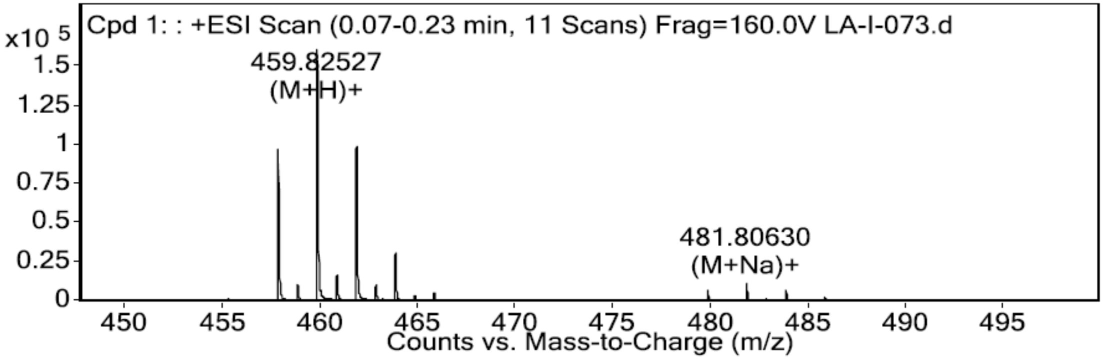


Figure S25. ^{31}P NMR spectrum of compound **7** ($CDCl_3$, 122MHz)

MS Spectrum



MS Zoomed Spectrum

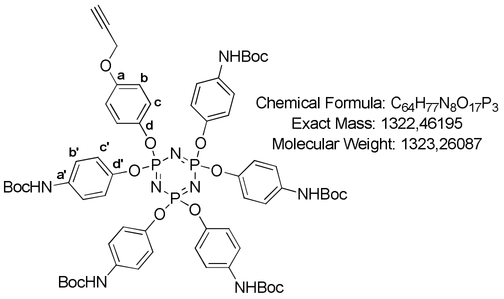


MS Spectrum Peak List

Ion	Ion Formula	Abund	*Expe. m/z*	*Calc. m/z*	Diff(ppm)
(M+H)+	C9H8Cl5N3O2P3	97981.9	457.82802	457.82665	3
(M+Na)+	C9H7Cl5N3NaO2P3	7116.5	479.80927	479.8086	1.4

Figure S26. ESI$^+$-HRMS spectrum of compound **7**

Compound 8



The monofunctionalized derivative **7** (74.7 mg, 0.163 mmol, 1.0 eq.) and protected *p*-aminophenol derivative **2** (278.0 mg, 1.329 mmol, 8.1 eq.) were dissolved in 10 mL of anhydrous THF. Under nitrogen atmosphere, Cs_2CO_3 (2.13 g, 6.53 mmol, 40.0 eq.) was added and the mixture was stirred at reflux temperature (66℃) for 18 hours. The solution was filtered and washed with DCM. The filtrate was concentrated under reduced pressure. Column chromatography on silica (EtOAc/Hexanes 5:95 to 35:65) afforded the desired compound **8** (180.0 mg, 0.136 mmol, **83%**) as an off-white foam.

R$_f$ = 0.42, EtOAc/Hexanes 4:6.

^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.07-7.00 (m, 10H, C*H*$_{b'}$), 6.82-6.64 (m, 19H, C*H*$_b$, C*H*$_c$, C*H*$_{c'}$, N*H*), 4.58 (d, *J* = 2.4 Hz, 2H, OC*H*$_2$C≡CH), 2.46 (t, 1H, *J* = 2.4 Hz, C≡C*H*), 1.46 (s, 27H, C*H*$_3$), 1.45 (s, 18H, C*H*$_3$).

^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 154.6 (*C*$_a$), 153.3 (*C*=O), 153.1 (*C*=O), 146.0 (*C*$_{d'}$), 144.8 (*C*$_d$), 135.1 (*C*$_{a'}$), 135.0 (*C*$_{a'}$), 122.0 (*C*$_c$), 121.3 (*C*$_{c'}$), 121.2 (*C*$_{c'}$), 120.7 (*C*$_{b'}$), 120.3 (*C*$_{b'}$), 115.5 (*C*$_b$), 80.5 (*C*$_q$), 78.7 (*C*≡CH), 75.7 (C≡*C*H), 56.2 (O*C*H$_2$), 28.5 (*C*H$_3$), 28.5 (*C*H$_3$).

^{31}P NMR (122 MHz, $CDCl_3$, δ ppm): 9.9 (t, ^2J = 9.3 Hz, 3P).

m/z (ESI$^+$-HRMS) for $C_{64}H_{77}N_8O_{17}P_3$ = 1323.4692 [*M*+H]$^+$; found 1323.4664, 1345.4512 [*M*+Na]$^+$, found 1345.4484.

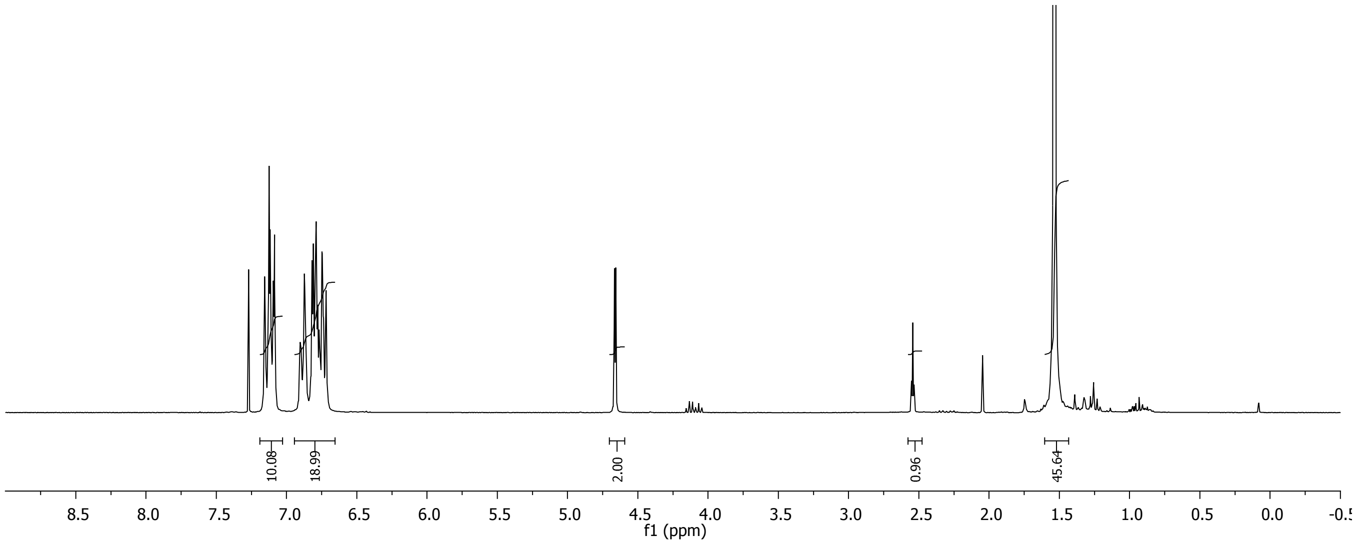


Figure S27. ^{1}H NMR spectrum of compound **8** ($CDCl_3$, 300MHz)

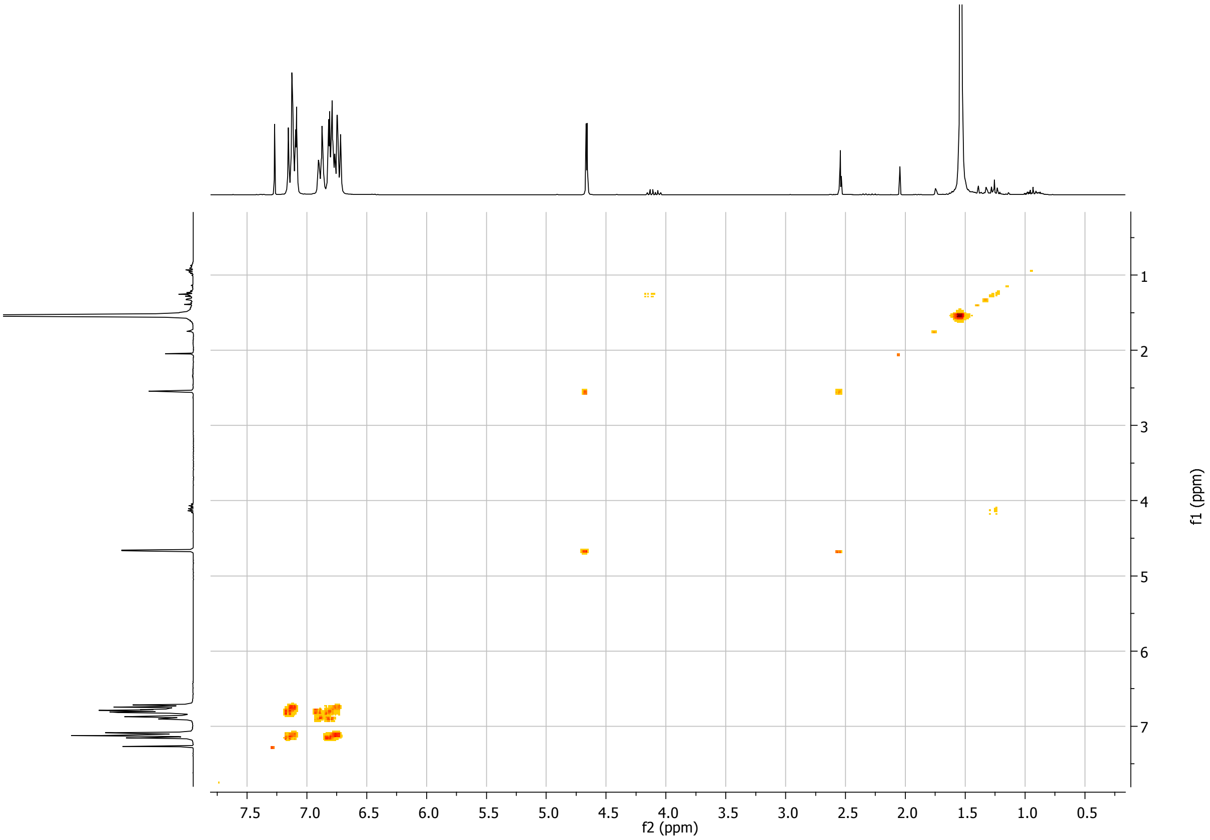


Figure S28. gCOSY spectrum of compound **8**

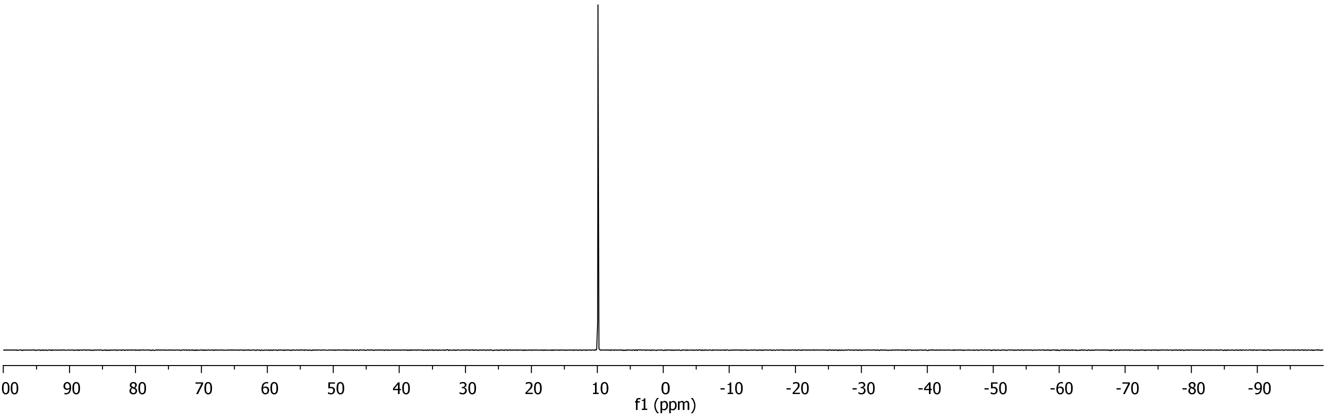


Figure S29. ^{31}P NMR spectrum of compound **8** ($CDCl_3$, 122MHz)

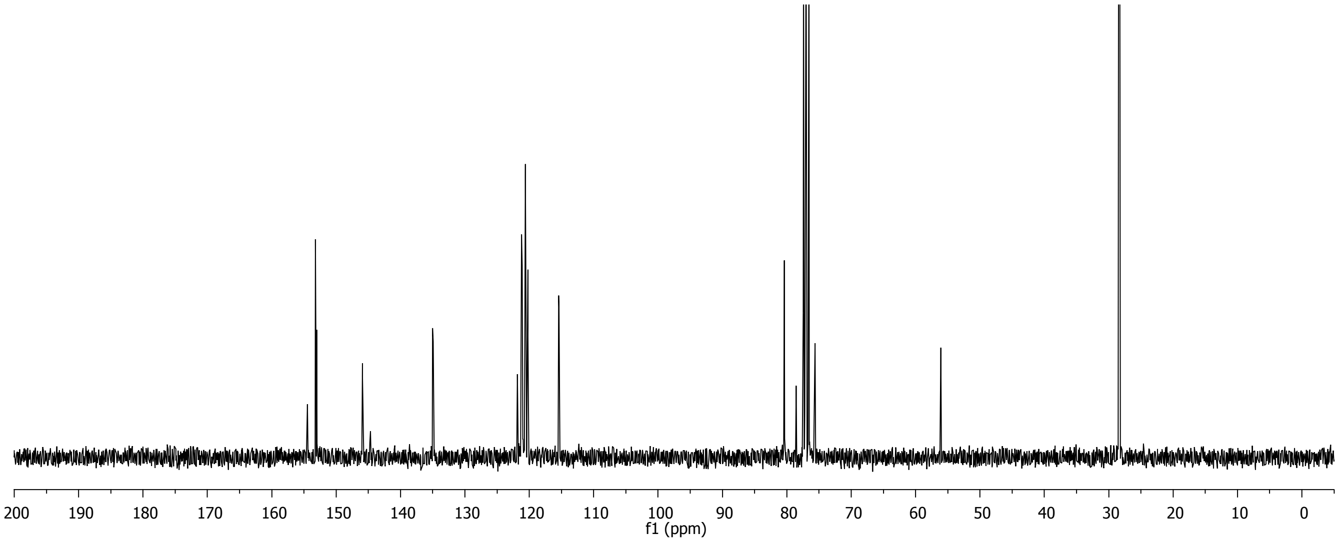
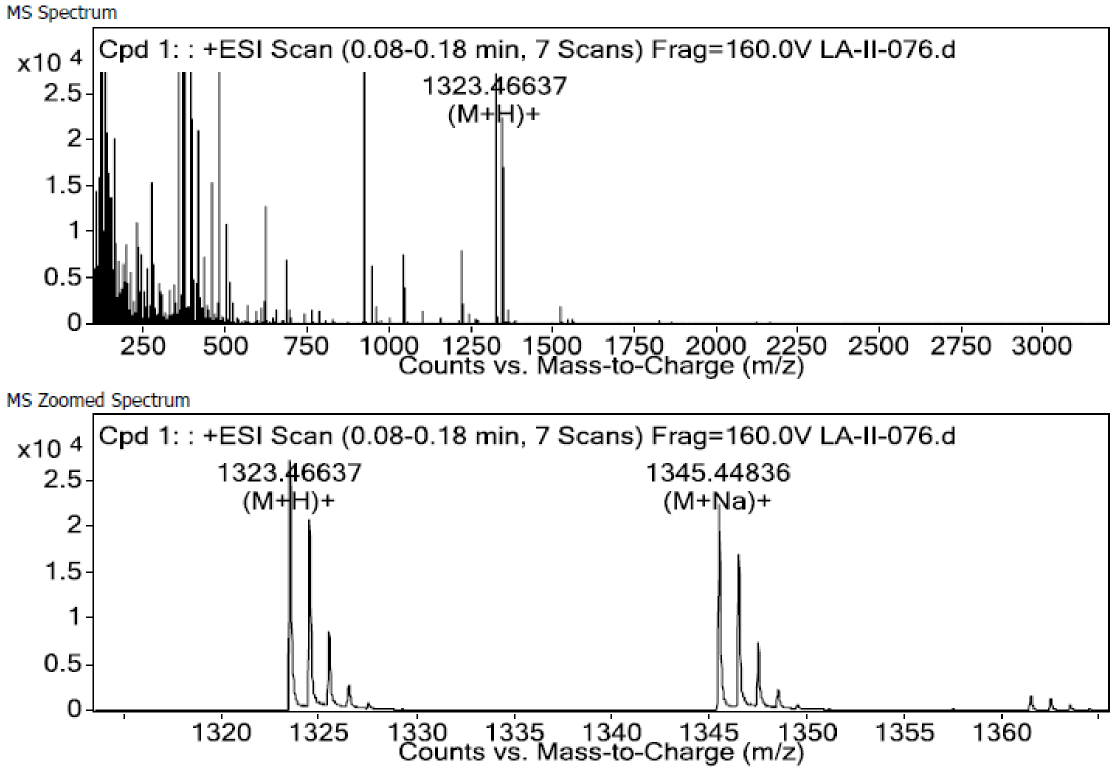


Figure S30. ^{13}C NMR spectrum of compound **8** ($CDCl_3$, 75MHz)

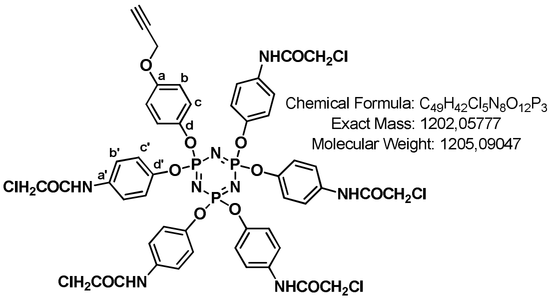


MS Spectrum Peak List

Ion	Ion Formula	Abund	*Expe. m/z*	*Calc. m/z*	Diff(ppm)
(M+H)+	C64H78N8O17P3	27308	1323.46637	1323.46923	-2.16
(M+Na)+	C64H77N8NaO17P3	22442.4	1345.44836	1345.45117	-2.09

Figure S31. ESI$^+$-HRMS spectrum of compound **8**

Compound 9



Dissymetric hexasubstitued protected phosphazene derivative **8** (100.5 mg, 0.076 mmol, 1.0 eq.) was dissolved in 5 mL of anhydrous DCM under nitrogen atmosphere and at 0^{o}C. Trifluoroacetic acid (TFA, 3 mL) was added dropwise over a 35 minutes period. After stirring 5 hours at rt, the solvent was removed under reduced pressure and co-evaporated with toluene. The residue was dissolved in 2 mL of anhydrous DCM and, under nitrogen atmosphere was added 159 µL of DIPEA (117.8 mg, 0.911 mmol, 12.0 eq.). At 0^{o}C was added dropwise chloroacetylchoride (60.4 µL, 85.8 mg, 0.760 mmol, 10.0 eq.) in 1.5 mL of anhydrous DCM over a 2 hours period. After stiring at rt for 13 hours, the solvent was removed under reduced pressure and the residue was dissolved in 25 mL of EtOAc and washed with HCl 1M (2×20 mL), NH_4Cl (20 mL), then water (10 mL). The organic phase was dried over Na_2SO_4, and concentrated under reduced pressure. Column chromatography on silica (EtOAc/Hexanes 40:60 to 100:0) afforded the desired compound **9** (44.0 mg, 0.0370 mmol, **48%**).

R$_f$ = 0.56, DCM/MeOH 10:90.

^{1}H NMR (300 MHz, MeOD, δ ppm): 7.46-7.37 (dd, 10H, *J* = 11.2 Hz, *J* = 9.0 Hz, C$H_{b'}$), 6.90-6.78 (m, 14H, CH_b, CH_c, C$H_{c'}$), 4.69 (d, 2H, *J* = 2.4 Hz, OCH_2C≡CH), 4.25 (2×s, 10H, CH_2Cl), 2.95 (t, *J* = 2.4 Hz, 1H, C≡C*H*).

^{13}C NMR (75 MHz, MeOD, δ ppm): 167.4 (*C*=O), 156.4 (C_a), 148.1 ($C_{d'}$), 148.0 (C_d), 136.5 ($C_{a'}$), 122.8 (C_c), 122.9 ($C_{b'}$), 122.7 ($C_{b'}$), 122.4 ($C_{c'}$), 122.4 ($C_{c'}$), 116.8 (C_b), 79.9 (*C*≡CH), 77.1 (C≡*C*H), 57.2 (O*C*H_2), 44.3 (*C*H_2Cl), 44.2 (*C*H_2Cl).

^{31}P NMR (122 MHz, MeOD, δ ppm): 9.6 (t, ^2J = 17.9 Hz, 3P).

m/z (ESI$^+$-HRMS) for $C_{49}H_{42}Cl_5N_8O_{12}P_3$ = 624.0181 [*M*+2Na]$^{2+}$, found 624.0190, 1225.0470 [*M*+Na]$^+$; found 1225.0463.

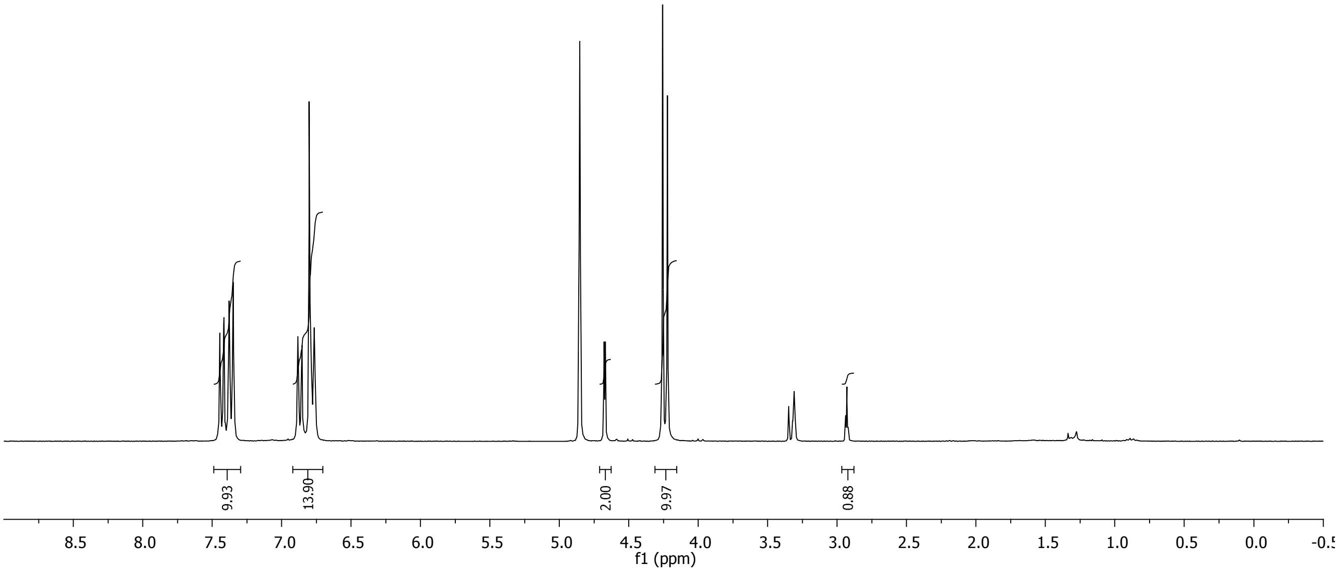


Figure S32. ^{1}H NMR spectrum of compound **9** (CD_3OD, 300MHz)

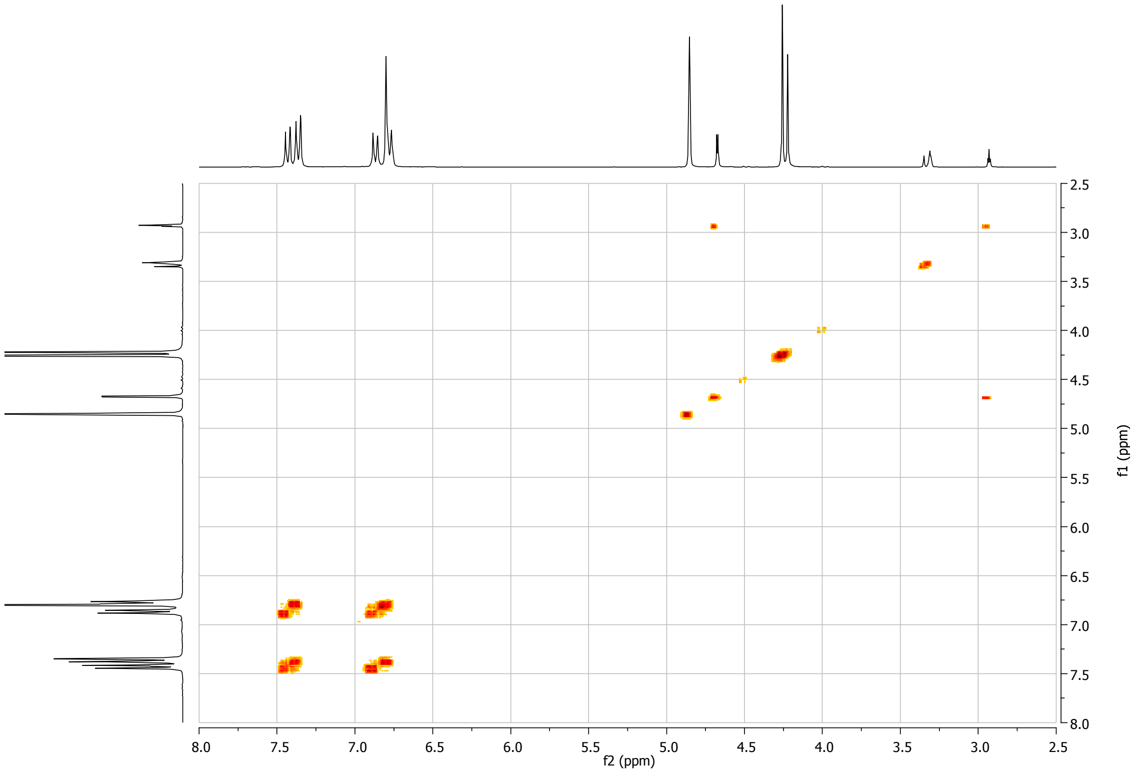


Figure S33. gCOSY spectrum of compound **9**

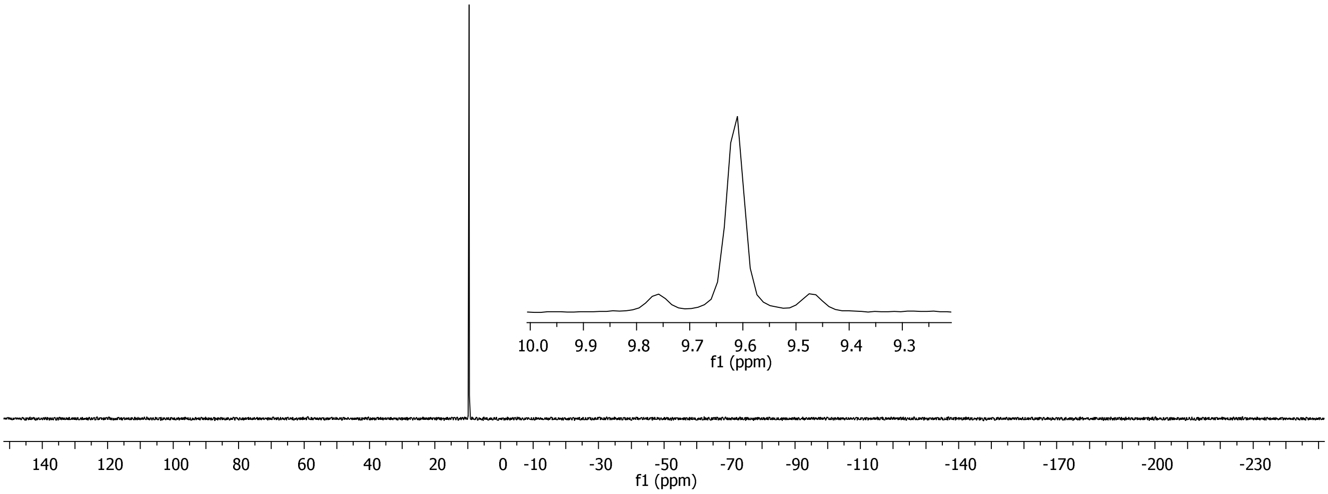


Figure S34. ^{31}P NMR spectrum of compound **9** (CD_3OD, 122MHz)

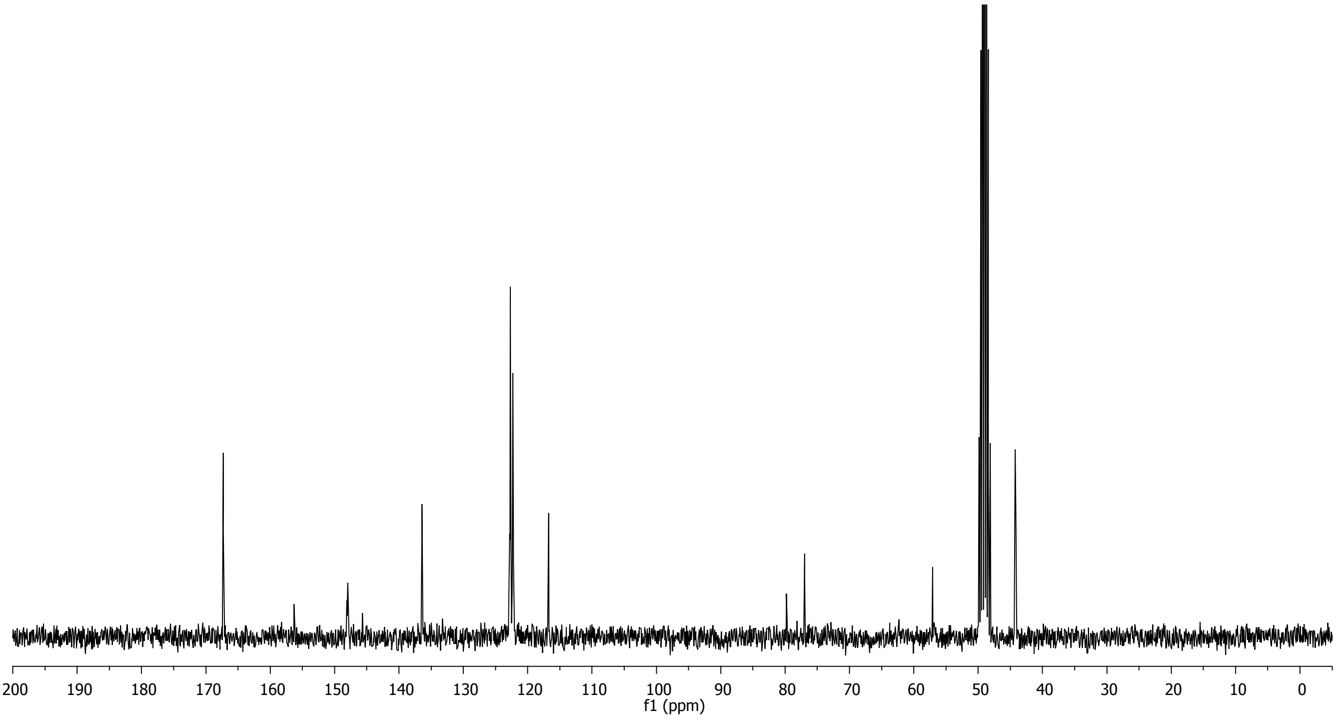
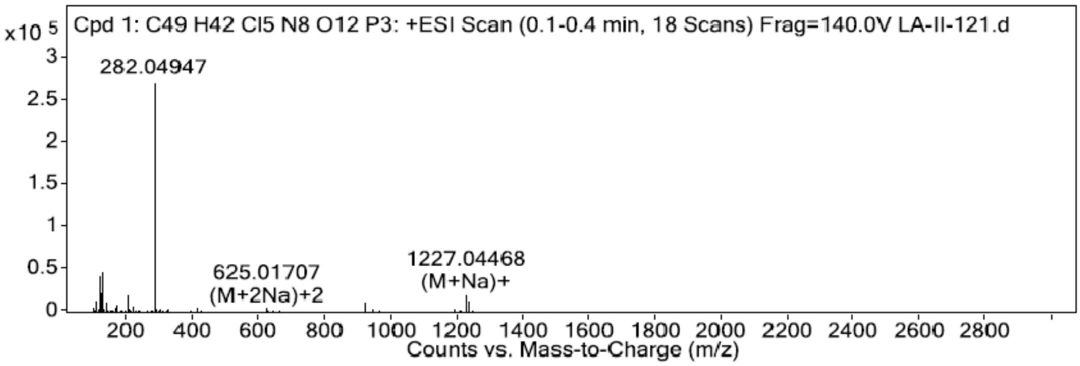
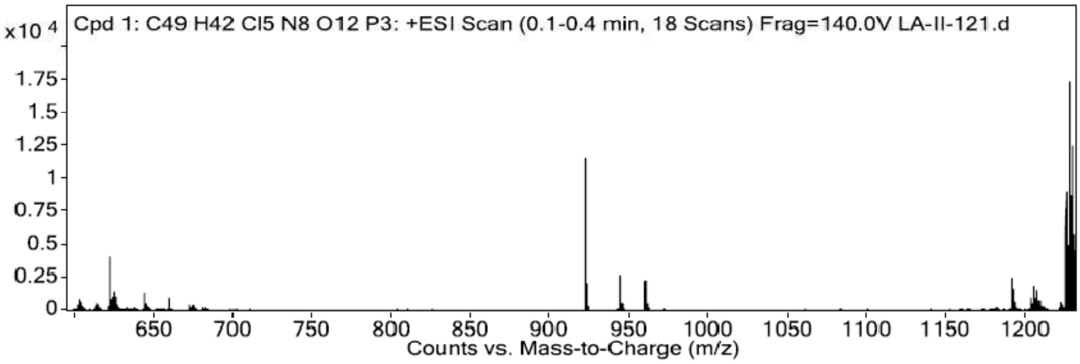


Figure S35. ^{13}C NMR spectrum of compound **9** (CD_3OD, 75MHz)

MS Spectrum



MS Zoomed Spectrum

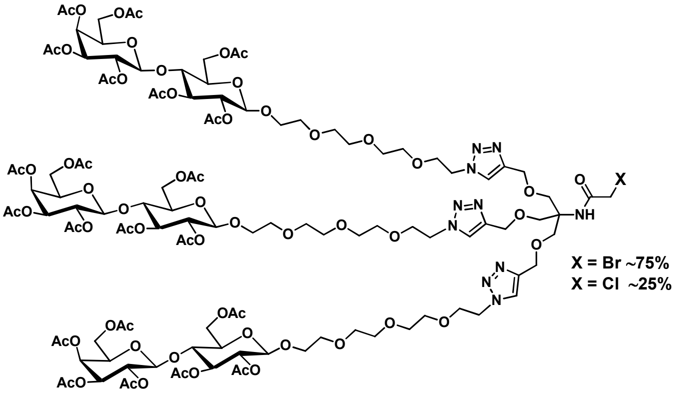


MS Spectrum Peak List

Ion	Formula	Abund	Observed m/z	Calc m/z	Diff(ppm)
(M+2Na)+2	C49H42Cl5N8Na2O12P3	1074.44	624.01899	624.0181	0.89
(M+Na)+	C49H42Cl5N8NaO12P3	9275.75	1225.04633	1225.04699	-0.66

Figure S36. ESI^{+}-HRMS spectrum of compound **9**

Trivalent dendron 12



To a stirring solution of **10**[1] (570 mg, 680 mmol, 3.45 eq.) and tripropargylated synthon **11**[4] (70.0 mg, 197 mmol, 1.00 eq.) in dry THF (6 mL) were added 6 mL of H_2O and a mixture of $CuSO_4{\cdot}5H_2O$ (44.7 mg, 179 mmol, 0.90 eq.) and Sodium ascorbate (35.5 mg, 179 mmol, 0.90 eq.). After stirring for 3 hours at 50°C in a 20 mL vial, the reaction was left stirring overnight at room temperature. EtOAc (50 mL) was added and the solution was washed successively with a saturated aqueous solution of NH_4Cl (3×25 mL), water (2×20 mL) and brine (1×10 mL). The organic phase was then dried over $MgSO_4$ and concentrated under reduced pressure. Column chromatography on silica (DCM/MeOH 98:2 to 94:6) afforded the desired compound **12** (300 mg, 108 mmol, **55%**) as a colorless oil.

R_f = 0.17, DCM/MeOH 95:5
^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 7.71 (s, 3H, H_{triazole}), 7.05 (br s, 1H, NHCOCH_2Br), 6.80 (br s, 1H, NHCOCH_2Cl), 5.33 (d$_{\text{app}}$, 3H, $H_{4\text{gal}}$), 5.17 (dd, $^3J_{4,3}$ = 9.4 Hz, $^3J_{3,2}$ = 9.1 Hz, 3H, $H_{3\text{glc}}$), 5.10 (dd, $^3J_{2,1}$ = 10.5 Hz, $^3J_{3,2}$ = 8.0 Hz, 3H, $H_{2\text{gal}}$), 4.97 (dd, $^3J_{2,3}$ = 7.0 Hz, $^3J_{3,4}$ = 3.4 Hz, 3H, $H_{3\text{gal}}$), 4.88 (dd, $^3J_{2,1}$ = 9.4 Hz, $^3J_{3,2}$ = 8.0 Hz, 3H, $H_{2\text{glc}}$), 4.57-4.47 (m, 21H, C_qCH_2O, OCH_2CH_2N, $H_{1\text{glc}}$, $H_{6\text{aglc}}$, $H_{1\text{gal}}$), 4.12-4.08 (m, 9H, $H_{6\text{bglc}}$, $H_{6\text{agal}}$, $H_{6\text{bgal}}$), 3.89-3.57 (m, 59H, CH_2Br/Cl, OCH_2CH_2N, OCH_2, $H_{4\text{glc}}$, $H_{5\text{gal}}$, $H_{5\text{glc}}$), 2.18-1.97 (m, 63H, $COCH_3$).
^{13}C NMR (150 MHz, $CDCl_3$, δ ppm): 170.3, 170.3, 170.1, 170.0, 169.7, 169.6, 169.0 (7×s, $COCH_3$), 166.7 (CO), 144.4 ($C_{triazole}$=CH), 123.7 (C=$C_{triazole}$H), 101.0 ($C_{1\text{gal}}$), 100.5 ($C_{1\text{glc}}$), 76.2 ($C_{4\text{glc}}$), 72.7 ($C_{3\text{glc}}$), 72.5 ($C_{5\text{glc}}$), 71.5 ($C_{2\text{glc}}$), 70.9 ($C_{3\text{gal}}$), 70.6 ($C_{5\text{gal}}$), 70.5, 70.4, 70.2, 69.4 (OCH$_2$), 69.0 ($C_{2\text{gal}}$), 69.0 (OCH$_2$), 68.6 ($C_q CH_2O$), 66.5 ($C_{4\text{gal}}$), 64.6 (OCH$_2$C=C), 61.9 ($C_{6\text{glc}}$), 60.7 ($C_{6\text{gal}}$), 60.2 (C_q), 50.2 ($N_{\text{triazole}}CH_2$), 42.3 (CH_2Cl), 29.8 (CH_2Br), 20.8, 20.8, 20.7, 20.6, 20.6, 20.6, 20.5 (7×s, COCH$_3$).
m/z (ESI$^+$ HRMS) for $C_{117}H_{171}BrN_{10}O_{67}$ = 1434.4805 $[M+2H]^{2+}$, found 1434.4843, 1456.4624 $[M+2Na]^{2+}$, found 1456.4624.

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[4] Y. M. Chabre, C. Contino-Pépin, V. Placide, T. C. Shiao and R. Roy, *J. Org. Chem.*, 2008, **73**, 5602−5605.

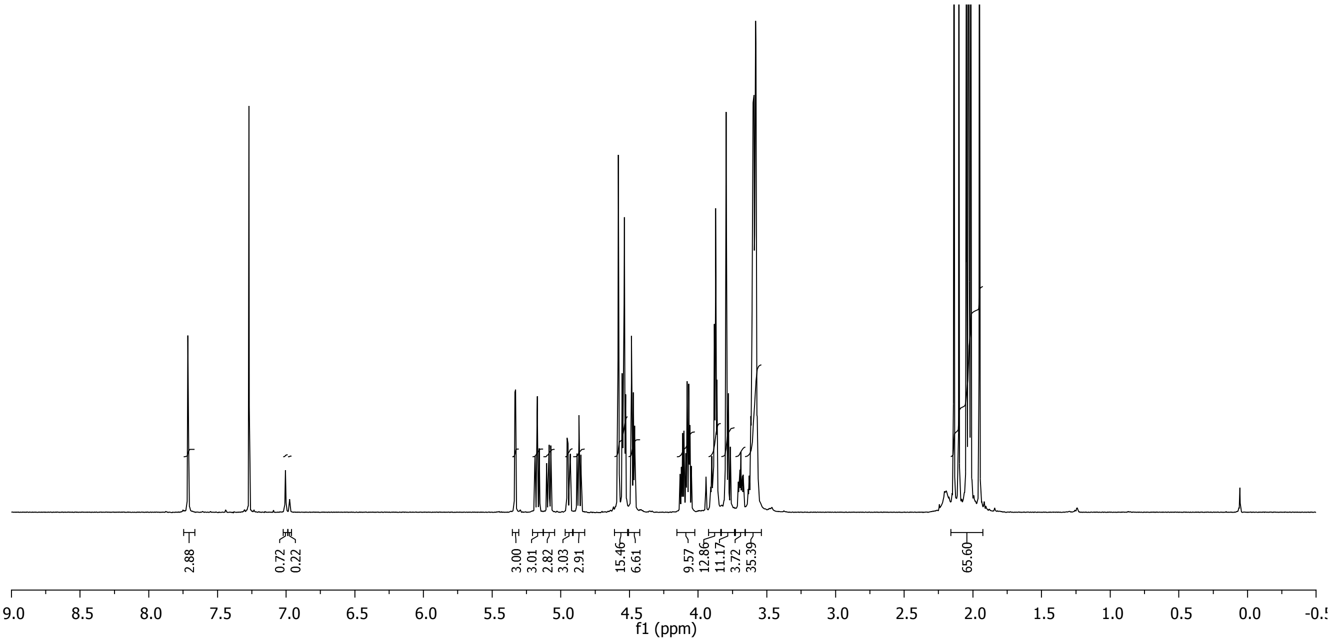


Figure S37. ^{1}H NMR spectrum of compound **12** ($CDCl_3$, 600MHz)

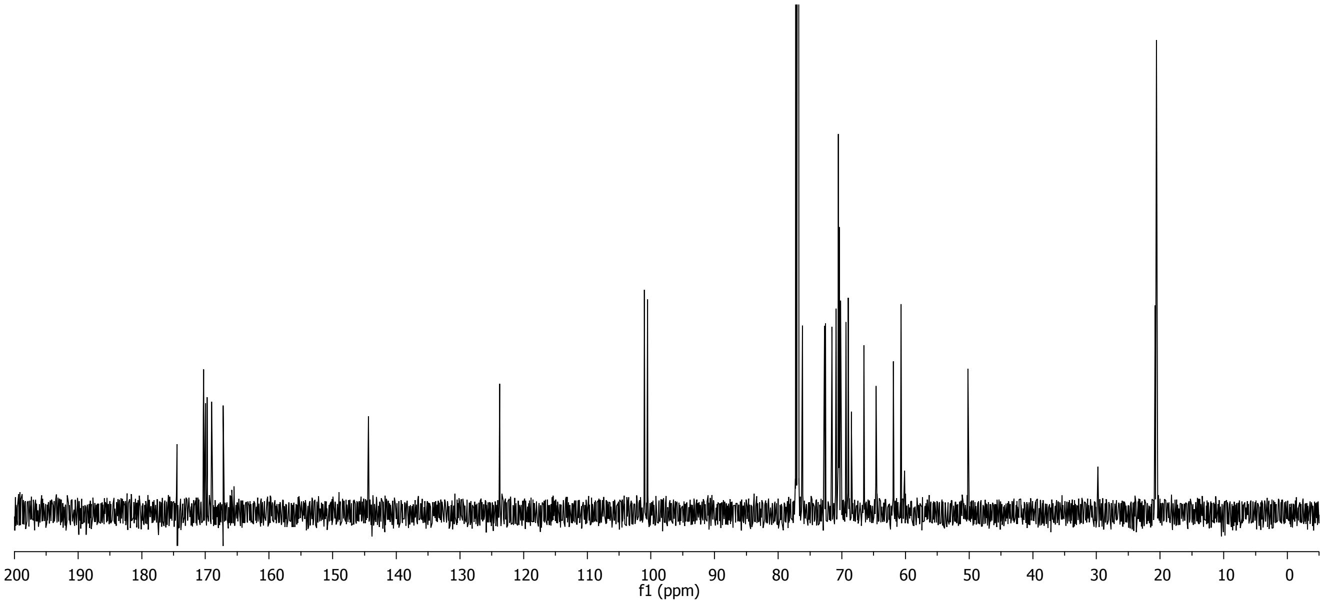
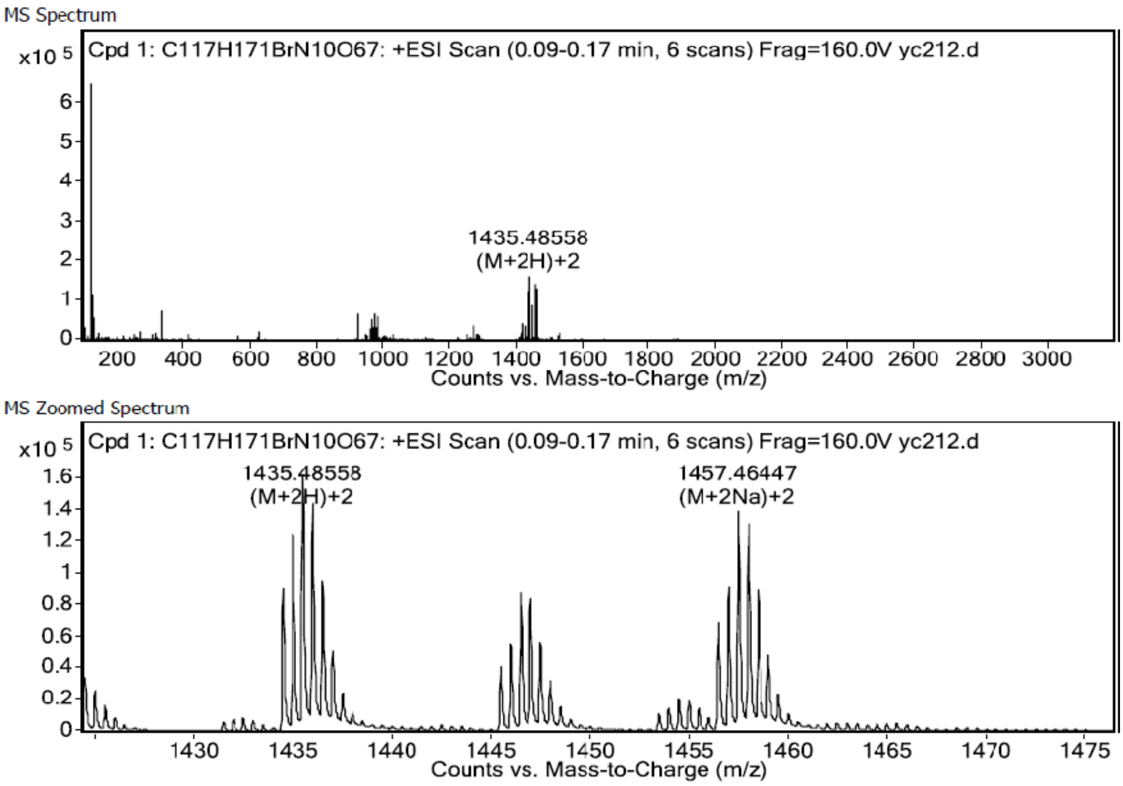


Figure S38. ^{13}C NMR spectrum of compound **12** ($CDCl_3$, 150MHz)

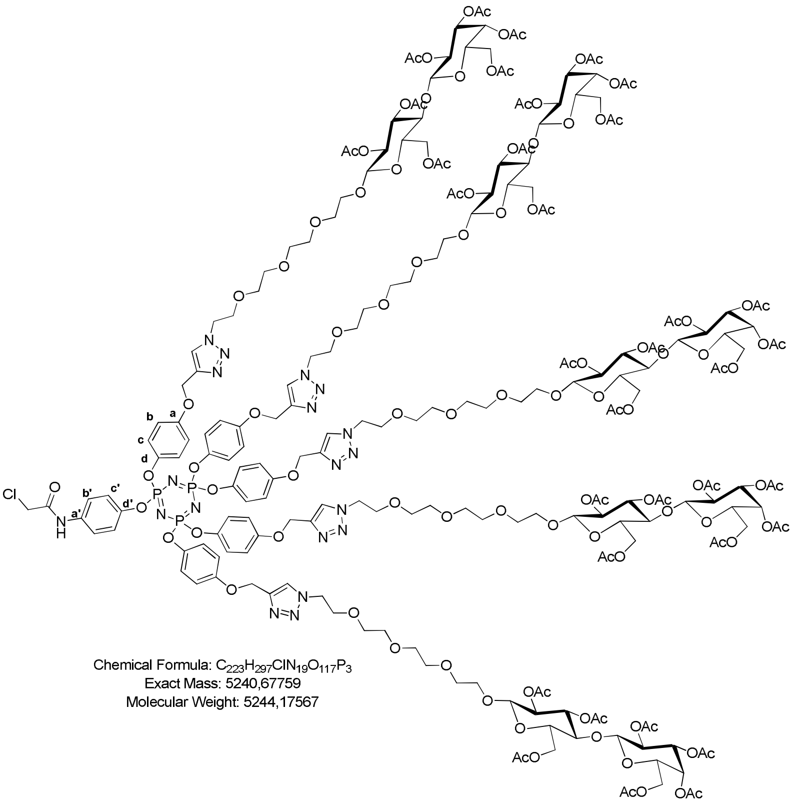


MS Spectrum Peak List

Ion	Ion Formula	Abund	*Expe. m/z*	*Calc. m/z*	Diff(ppm)
(M+2H)+2	C117 H173 Br N10 O67	91472	1434.48427	1434.4805	2.63
(M+2Na)+2	C117 H171 Br N10 Na2 O67	68812	1456.46235	1456.46244	-0.06

Figure S39. ESI$^+$-HRMS spectrum of compound **12**

Pentavalent dendron 13



Chemical Formula: $C_{223}H_{297}ClN_{19}O_{117}P_3$
Exact Mass: 5240,67759
Molecular Weight: 5244,17567

To a solution of pentapropargylated cyclotriphosphazene derivative **6** (55.8 mg, 0.053 mmol, 1.0 eq.) in a 1:1 mixture of H_2O/THF_{anh} (8 mL), were added azido derivative **10** (456.7 mg, 0.545 mmol, 10.0 eq.), $CuSO_4 \cdot 5H_2O$ (102.8 mg, 0.412 mmol, 7.8 eq.) and sodium ascorbate (83.5 mg, 0.421 mmol, 8.0 eq.). While stirring, the mixture was first heated at 50℃ for 3 hours in a 20 mL vial and at room temperature for additional 18 hours. Ethyl acetate (30 mL) was added and the solution was poured into a separatory funnel containing ethyl acetate (20 mL), washed with saturated aqueous NH_4Cl (2×20 mL), water (20 mL) and brine (10 mL). Organics were collected, dried over Na_2SO_4 and concentrated to dryness *in vacuo* with rotary evaporator. Purification by flash chromatography (SiO_2, DCM/MeOH 100:0 to 90:10) afforded desired multivalent compound **13** (230.5 mg, 0.044 mmol, **83%**).

R_f = 0.59, DCM/MeOH 90:10

^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 9.43 (s, 1H, NH), 7.88 (s, 2H, H_{triazole}), 7.82 (2×s, 3H, H_{triazole}), 7.34 (d, ^3J = 8.6 Hz, 2H, C$H_{b'}$), 6.91-6.75 (m, 20H, CH_b, CH_c), 6.57 (d, ^3J = 8.6 Hz, 2H, C$H_{c'}$), 5.31 (d_{app}, 5H, $H_{4\text{gal}}$), 5.16-5.05 (m, 20H, $H_{3\text{glc}}$, C_qCH_2O, $H_{2\text{gal}}$), 4.92 (dd, $^3J_{2,3}$ = 2.3 Hz, $^3J_{3,4}$ = 3.5 Hz, 5H, $H_{3\text{gal}}$), 4.84 (t_{app}, 6H, $H_{2\text{glc}}$), 4.53-4.45 (m, 25H, CH_2N, $H_{1\text{glc}}$, $H_{6\text{aglc}}$, $H_{1\text{gal}}$), 4.22 (s, 2H CH_2Cl), 4.11-4.03 (m, 15H, $H_{6\text{bglc}}$, $H_{6\text{agal}}$, $H_{6\text{bgal}}$), 3.87-3.54 (m, 80H, $H_{5\text{gal}}$, $H_{5\text{glc}}$, $H_{4\text{glc}}$, OCH_2), 2.14-1.93 (m, 105H, COCH_3).

^{13}C NMR (150 MHz, $CDCl_3$, δ ppm): 170.2, 170.2, 170.0, 169.9, 169.6, 169.5, 169.0 (7×s, COCH$_3$), 164.6 (C=O), 155.2 + 155.2 (C_a), 146.6 ($C_{d'}$), 144.4 ($C_{triazole}$=CH), 144.1 (C_d), 143.5 ($C_{triazole}$=CH), 143.3 ($C_{triazole}$=CH), 134.5 ($C_{a'}$), 124.4 ($C_{triazole}$=CH), 124.0 ($C_{triazole}$=CH), 121.8 (C_c), 121.8 (C_c), 121.7($C_{b'}$), 121.0 ($C_{c'}$), 120.8 (C_c), 115.2 (C_b), 115.0 (C_b), 100.9 (C_{1gal}), 100.4 (C_{1glc}), 76.1 (C_{4glc}), 72.7 (C_{3glc}), 72.5 (C_{5glc}), 72.5 (C_{2glc}), 71.5 (C_{3gal}), 70.8 (C_{5gal}), 70.5, 70.5, 70.4, 70.3, 70.3, 70.1, 70.1, 69.2, 69.2 (OCH$_2$), 68.9 (C_{2gal}), 68.9 (OCH$_2$), 66.5 (C_{4gal}), 62.2 (OCH$_2$C=C), 61.9 (C_{6glc}), 61.7 (C_{6gal}), 60.6, 50.2 (NCH$_2$), 50.1 (NCH$_2$), 43.4 (CH$_2$Cl), 20.7, 20.7, 20.6, 20.5, 20.5, 20.5, 20.4 (7×s, COCH$_3$).

^{31}P NMR (122 MHz, CDCl$_3$, δ ppm): 10.2-9.4 (m, 3P).

IR (neat, *v* cm^{-1}) 2878 (m), 1743 (s), 1501 (m), 1367 (m), 1216 (s), 1042 (m), 833 (w).

m/z (ESI$^+$-HRMS) for $C_{223}H_{297}ClN_{19}O_{117}P_3$= 1747.8998 [*M*+3H]$^{3+}$; found 1747.8958, 1769.8818 [*M*+3Na]$^{3+}$, found 1769.8798.

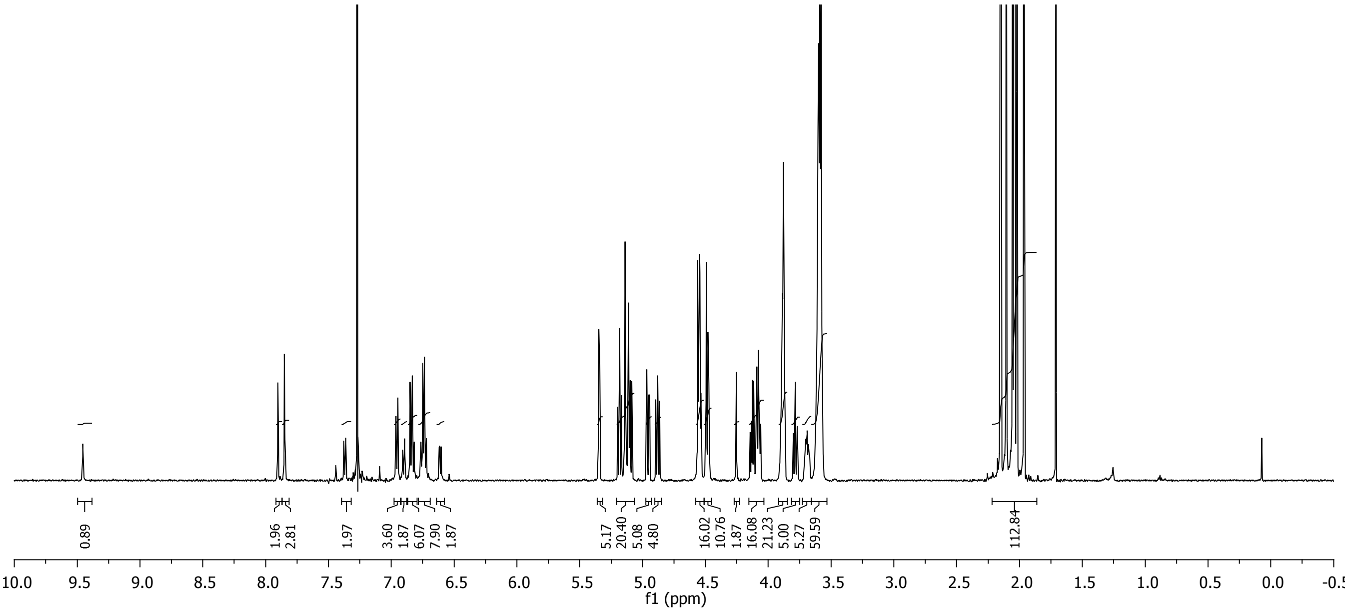


Figure S40. ^{1}H NMR spectrum of compound **13** (CDCl$_3$, 600MHz)

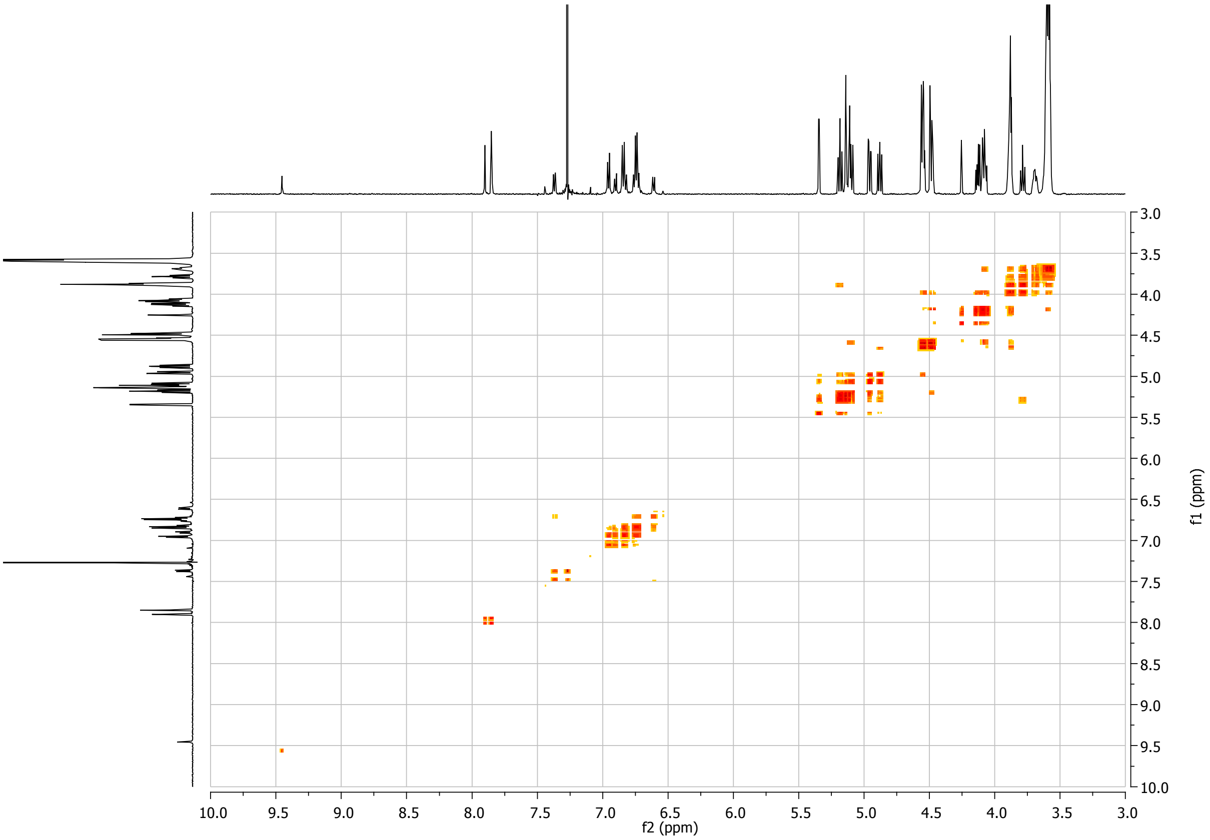


Figure S41. gCOSY spectrum of compound **13**

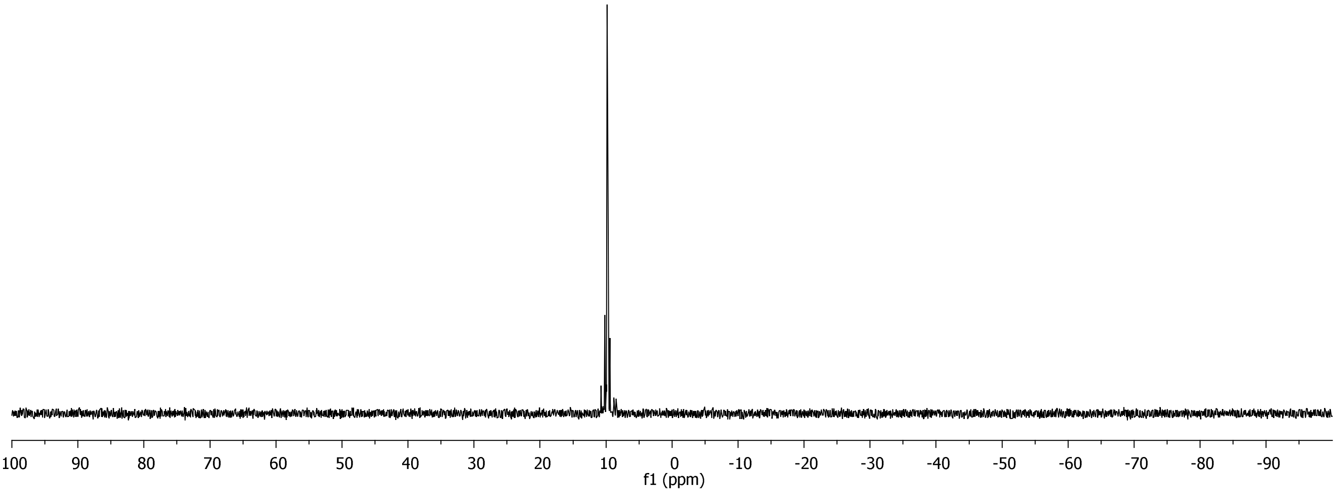


Figure S42. ^{31}P NMR spectrum of compound **13** ($CDCl_3$, 122MHz)

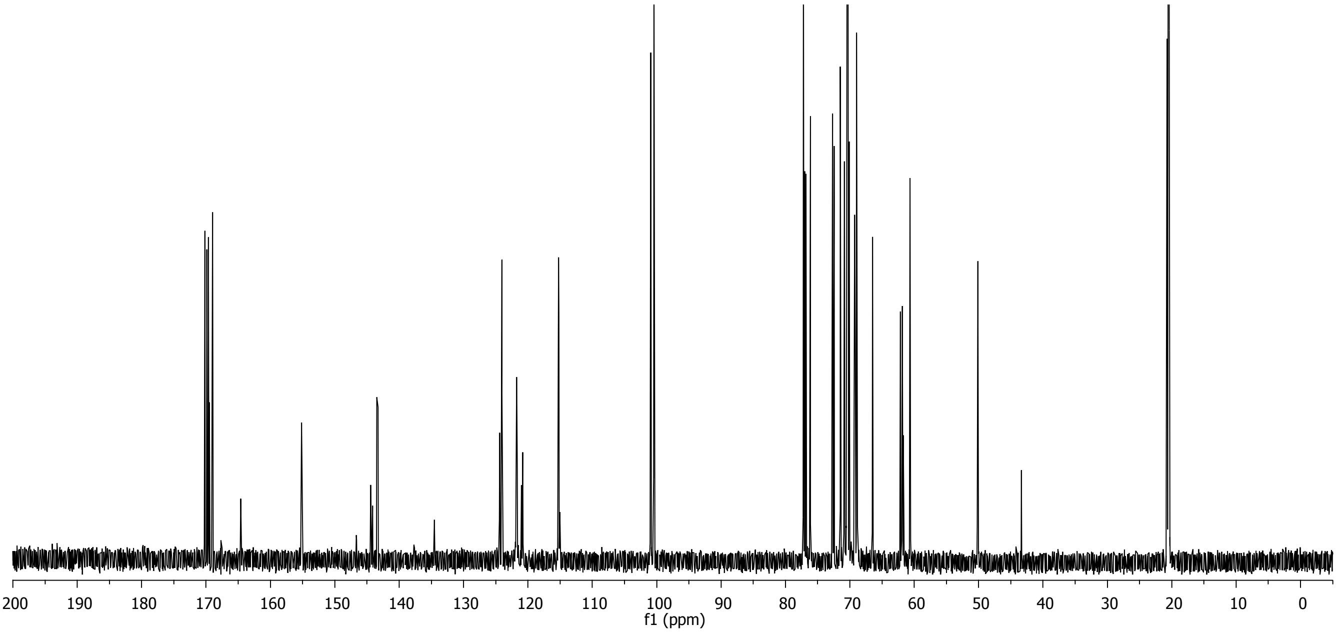


Figure S43. ^{13}C NMR spectrum of compound **13** ($CDCl_3$, 150MHz)

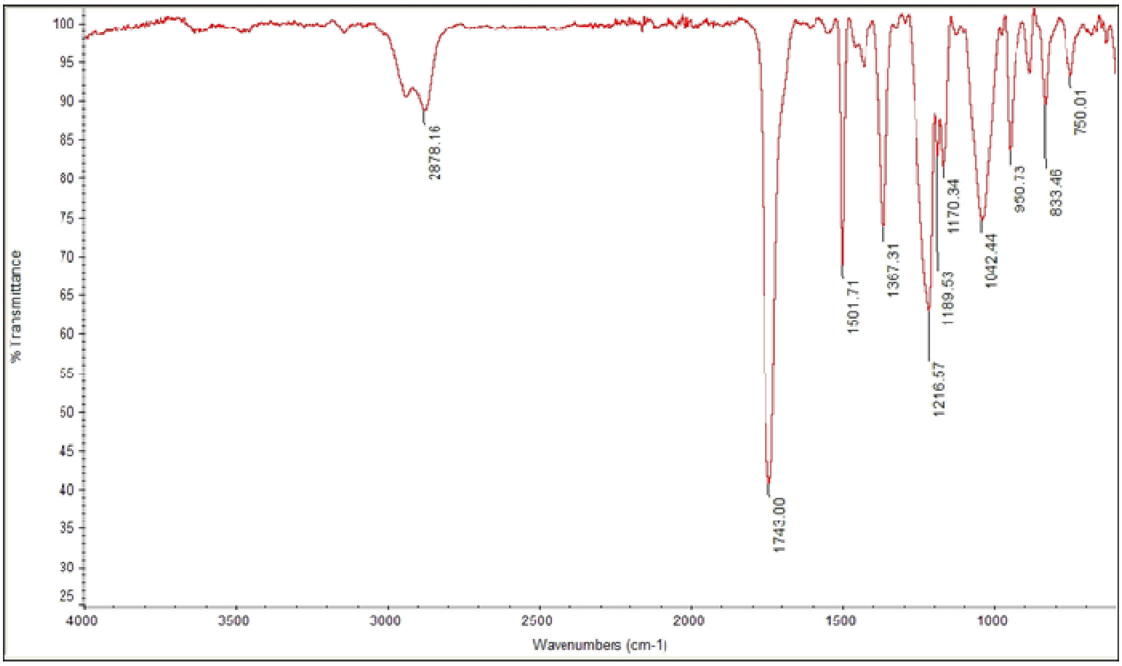
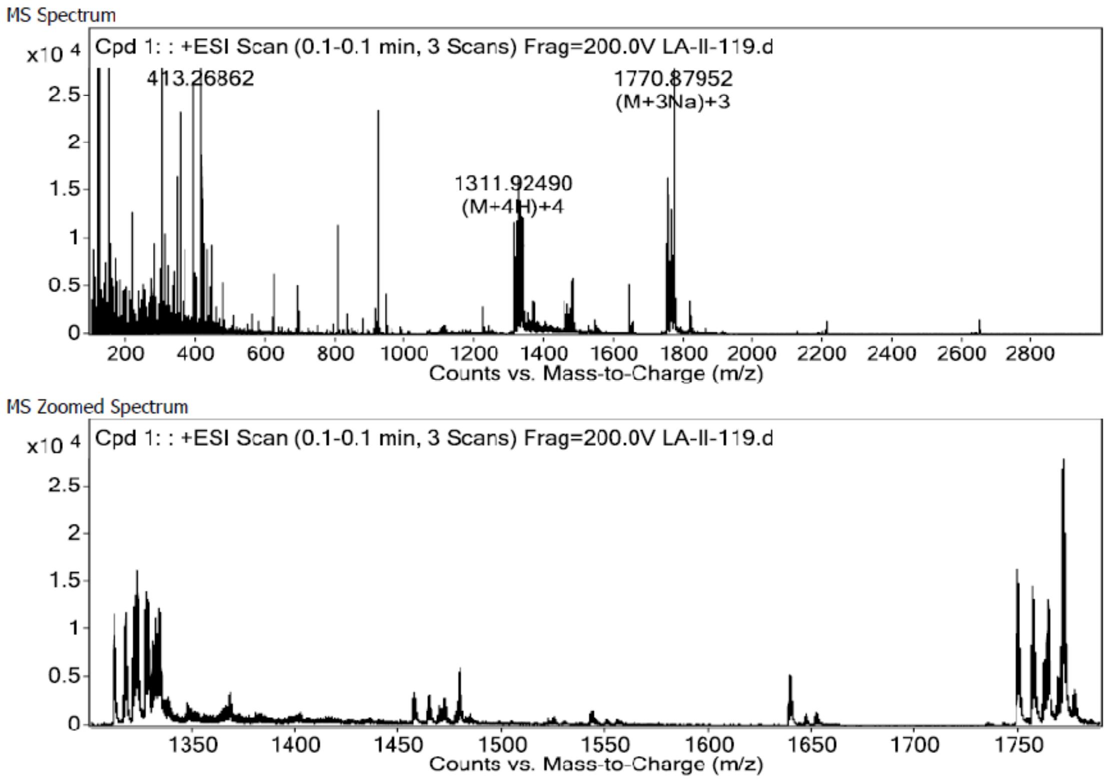


Figure S44. FT-IR spectrum of compound **13**

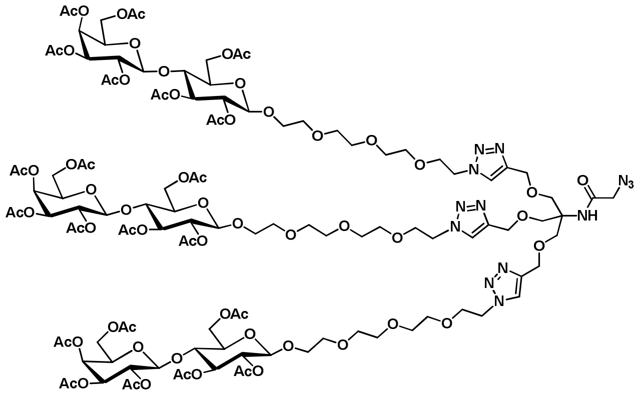


MS Spectrum Peak List

Ion	Ion Formula	Abund	*Expe. m/z*	*Calc. m/z*	Diff(ppm)
(M+4H)+4	C223H301ClN19O117P3	2878.5	1311.18078	1311.17667	3.13
(M+3H)+3	C223H300ClN19O117P3	3627.3	1747.89583	1747.89981	-2.27
(M+3Na)+3	C223H297ClN19Na3O117P3	8407.5	1769.87979	1769.88175	-1.11

Figure S45. ESI$^+$-HRMS spectrum of compound **13**

Trivalent dendron 14



To a stirring solution of **12** (443.9 mg, 0.155 mmol, 1.0 eq) in dry DMF (6 mL) under a nitrogen atmosphere were added sodium azide (25.1 mg, 0.386 mmol, 2.5 eq.) and sodium iodide (2.3 mg, 0.015 mmol, 0.1 eq.). After stirring overnight at 70^{o}C, the solvent was removed and EtOAC was added, then the solution was washed successively with water (4×50 mL) and brine (3×25 mL). The organic phase was then dried over Na_2SO_4 and concentrated under reduced pressure. Column chromatography on silica (EtOAc/Acetone 90:10 to 30:70) afforded the desired compound **27** (339.1 mg, 0.120 mmol, **77%**) as a colorless oil.

R$_f$ = 0.30, DCM/MeOH 94:6

^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 7.70 (s, 3H, H_{triazole}), 6.80 (br s, 1H, NH), 5.33 (d_{app}, 3H, H_{4gal}), 5.17 (dd, $^3J_{4,3}$ = 9.4 Hz, $^3J_{3,2}$ = 9.1 Hz, 3H, H_{3glc}), 5.10 (dd, $^3J_{2,1}$ = 10.5 Hz, $^3J_{3,2}$ = 8.0 Hz, 3H, H_{2gal}), 4.97 (dd, $^3J_{2,3}$ = 7.0 Hz, $^3J_{3,4}$ = 3.4 Hz, 3H, H_{3gal}), 4.88 (dd, $^3J_{2,1}$ = 9.4 Hz, $^3J_{3,2}$ = 8.0 Hz, 3H, H_{2glc}), 4.57-4.47 (m, 21H, C_qCH_2O, OCH_2CH_2N, H_{1glc}, H_{6aglc}, H_{1gal}), 4.12-4.08 (m, 9H, H_{6bglc}, H_{6agal}, H_{6bgal}), 3.89-3.57 (m, 59H, CH_2N_3, OCH_2CH_2N, OCH_2, H_{4glc}, H_{5gal}, H_{5glc}), 2.18-1.97 (m, 63H, $COCH_3$).

^{13}C NMR (150 MHz, $CDCl_3$, δ ppm): 170.3, 170.3, 170.1, 170.0, 169.7, 169.6, 169.0 (7×s, COCH$_3$), 166.7 (CO), 144.4 ($C_{triazole}$=CH), 123.7 (C=$C_{triazole}$H), 101.0 (C_{1gal}), 100.5 (C_{1glc}), 76.2 (C_{4glc}), 72.7 (C_{3glc}), 72.5 (C_{5glc}), 71.5 (C_{2glc}), 70.9 (C_{3gal}), 70.6 (C_{5gal}), 70.5, 70.4, 70.2, 69.4 (OCH_2), 69.0 (C_{2gal}), 69.0 (OCH_2), 68.6 (C_qCH_2O), 66.5 (C_{4gal}), 64.6 (OCH_2C=C), 61.9 (C_{6glc}), 60.7 (C_{6gal}), 60.0 (C_q), 52.6 (CH_2N_3), 50.2 ($N_{\text{triazole}}CH_2$), 20.8, 20.8, 20.7, 20.6, 20.6, 20.6, 20.5 (7×s, COCH$_3$).

m/z (ESI$^+$ HRMS) for $C_{117}H_{171}N_{13}O_{67}$ = 1416.0259 $[M+2H]^{2+}$, found 1416.0296, 1438.0079 $[M+2Na]^{2+}$, found 1438.0117.

GPC measurements (THF): M_w = 1776 ; M_n = 1671 , PDI (M_w/M_n) = 1.063

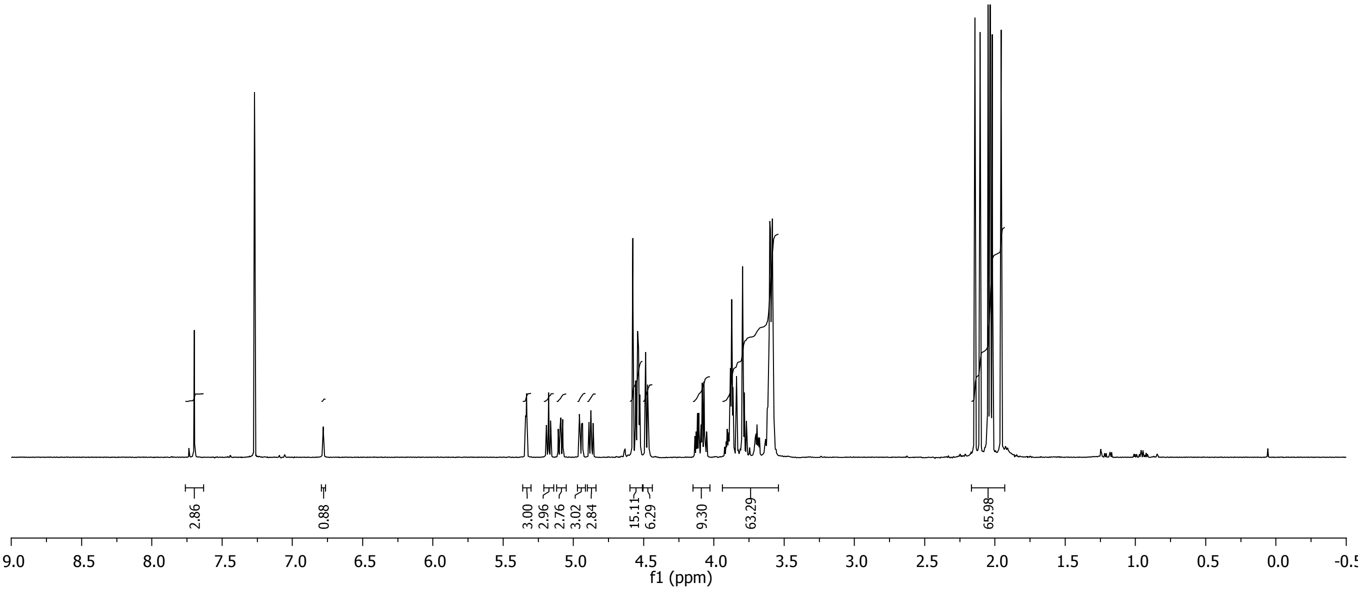


Figure S46. ^{1}H NMR spectrum of compound **14** ($CDCl_3$, 600MHz)

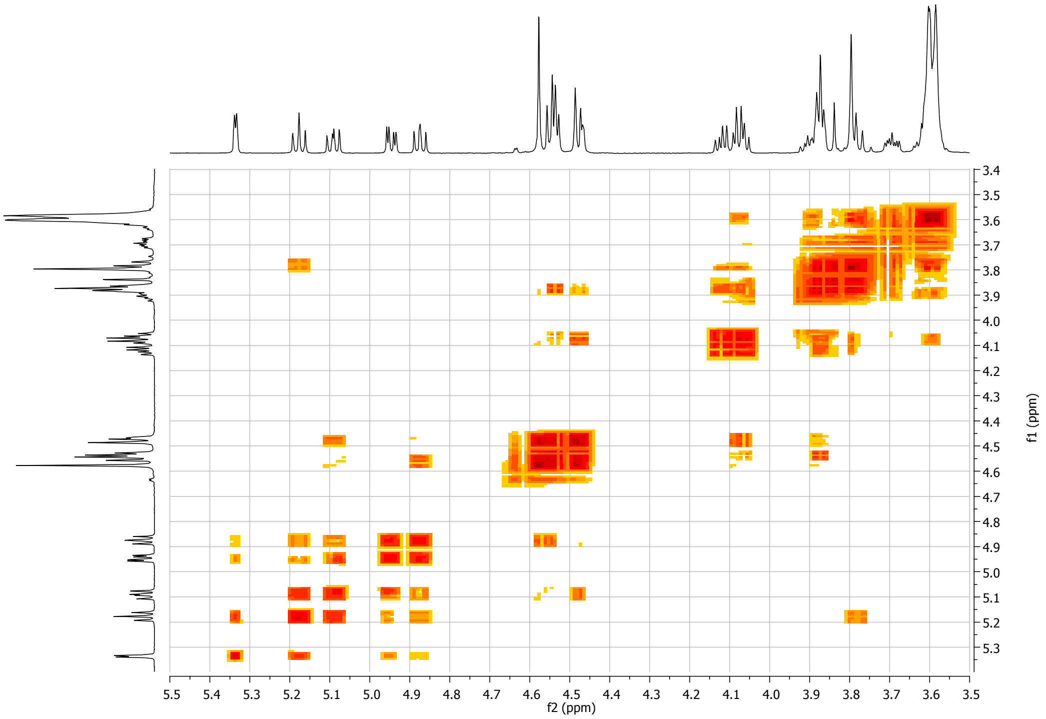


Figure S47. gCOSY spectrum of compound **14**

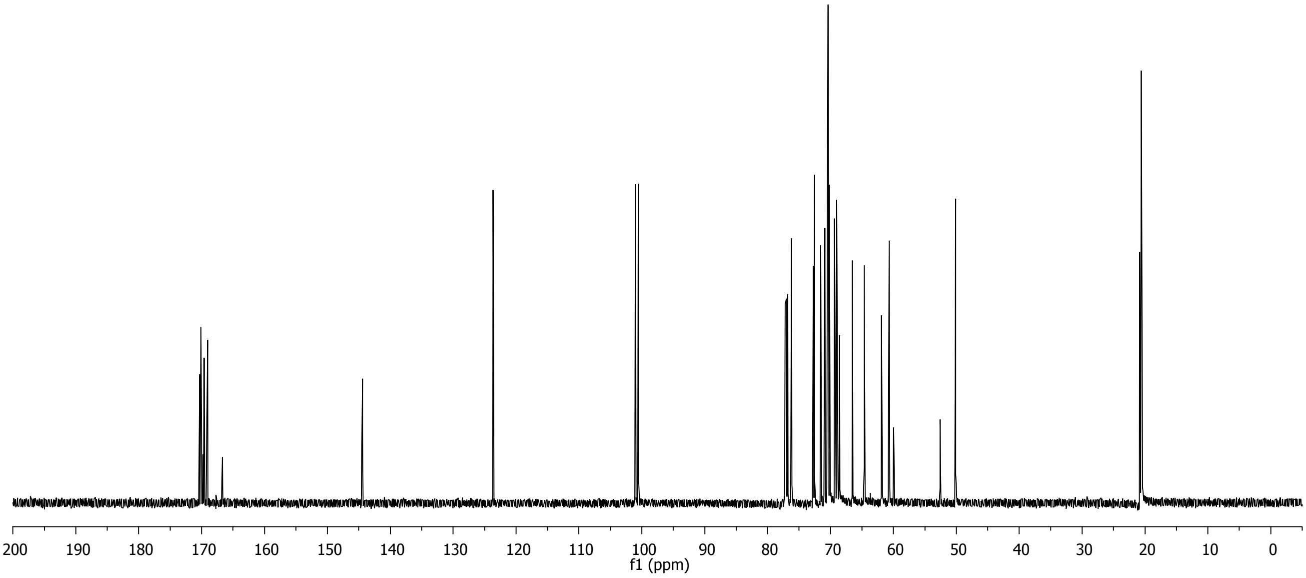
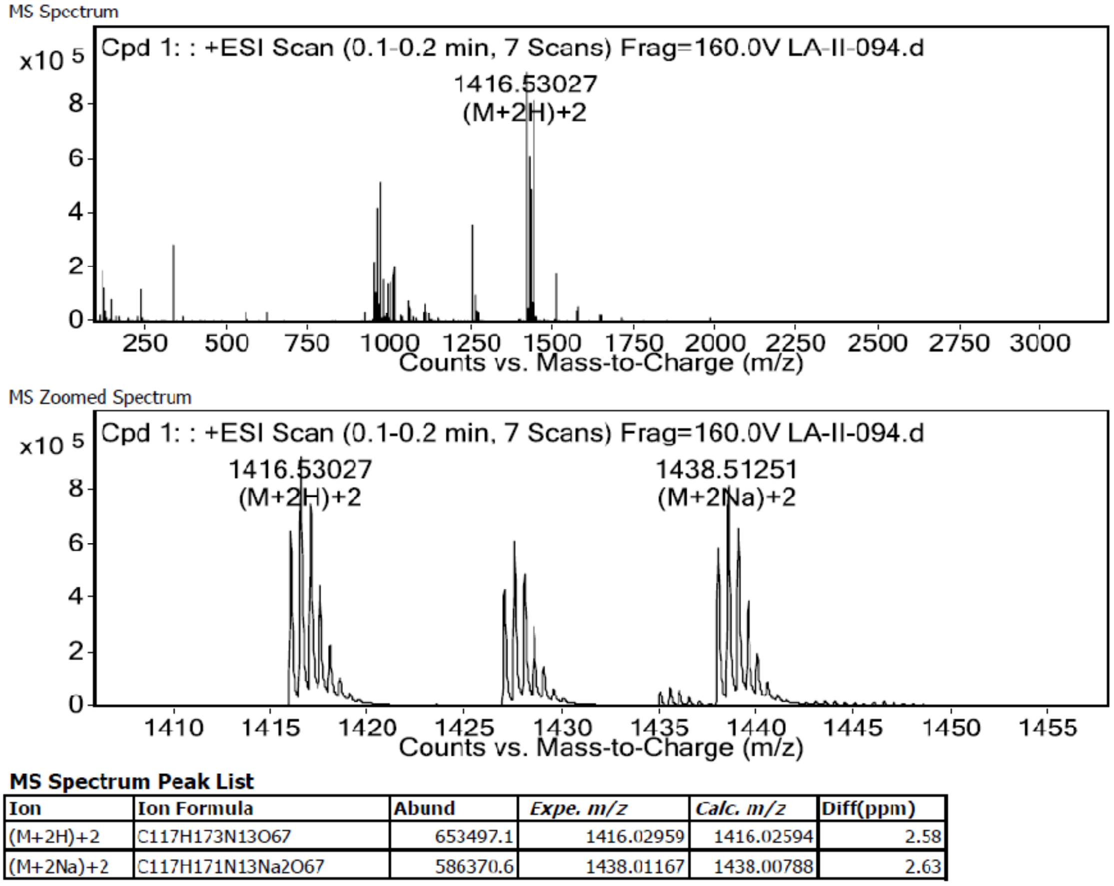


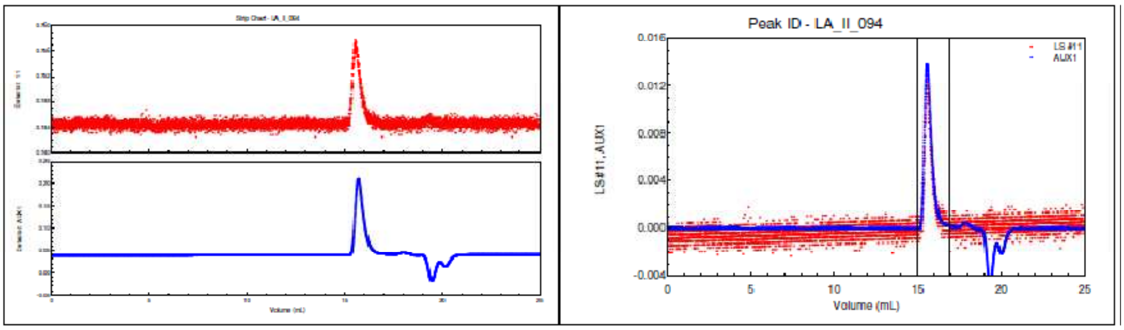
Figure S48. ^{13}C NMR spectrum of compound **14** ($CDCl_3$, 150MHz)

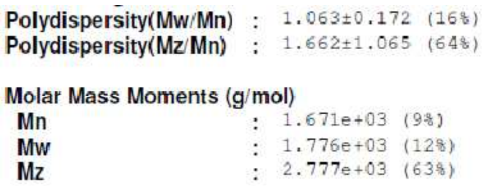


MS Spectrum Peak List

Ion	Ion Formula	Abund	*Expe. m/z*	*Calc. m/z*	Diff(ppm)
(M+2H)+2	C117H173N13O67	653497.1	1416.02959	1416.02594	2.58
(M+2Na)+2	C117H171N13Na2O67	586370.6	1438.01167	1438.00788	2.63

Figure S49. ESI$^+$-HRMS spectrum of compound **14**

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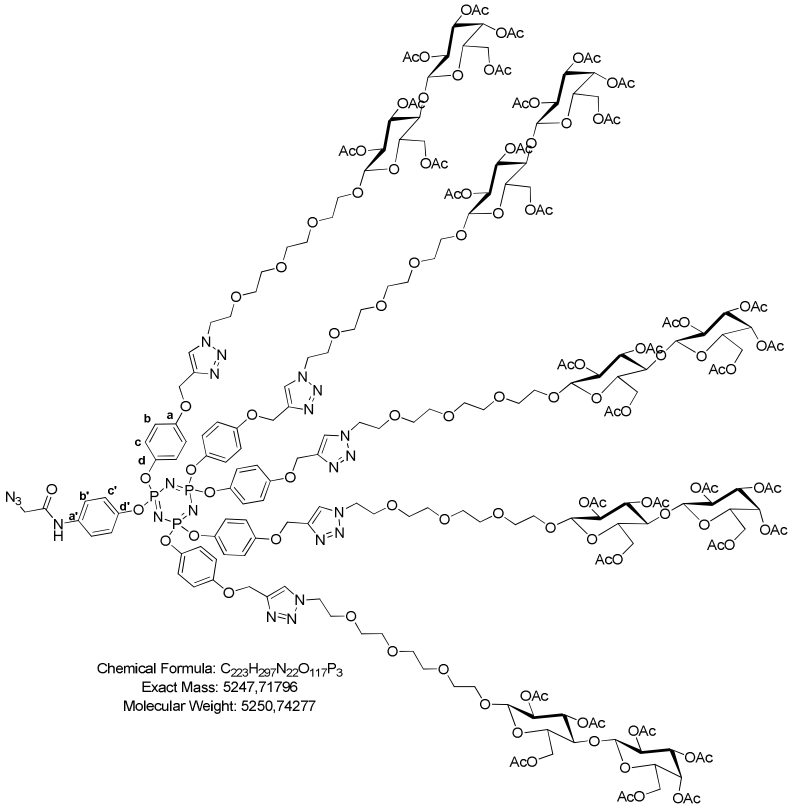
Polydispersity(Mw/Mn)  :  1.063±0.172 (16%)
Polydispersity(Mz/Mn)  :  1.662±1.065 (64%)

Molar Mass Moments (g/mol)
 Mn                    :  1.671e+03 (9%)
 Mw                    :  1.776e+03 (12%)
 Mz                    :  2.777e+03 (63%)
```

Figure S50. GPC trace (in THF) of compound **14**

Pentavalent dendron 15



To a stirring solution of **13** (224.7 mg, 0.043 mmol, 1.0 eq) in dry DMF (3 mL) under a nitrogen atmosphere were added sodium azide (8.4 mg, 0.129 mmol, 3.0 eq.) and sodium iodide (1.3 mg, 0.009 mmol, 0.2 eq.). After stirring overnight (15 h) at 70°C, the solvent was removed and EtOAc was added, then the solution was washed successively with water (4×50 mL) and brine (3×25 mL). The organic phase was then dried over Na_2SO_4 and concentrated under reduced pressure. Column chromatography on silica (DCM/MeOH 99:1 to 90:10) afforded the desired compound **15** (209.8 mg, 0.040 mmol, **93%**) as a colorless oil.

$\mathbf{R_f}$ = 0.59, DCM/MeOH 90:10

^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 9.43 (s, 1H, N*H*), 7.88 (s, 2H, H_{triazole}), 7.82 (2×s, 3H, H_{triazole}), 7.32 (d, ^3J = 8.6 Hz, 2H, C$H_{b'}$), 6.91-6.75 (m, 20H, CH_b, CH_c), 6.53 (d, ^3J = 8.6 Hz, 2H, C$H_{c'}$), 5.30 (d_{app}, 5H, $H_{4\text{gal}}$), 5.16-5.04 (m, 20H, $H_{3\text{glc}}$, C_qCH_2O, $H_{2\text{gal}}$), 4.91 (dd, $^3J_{2,3}$ = 2.3 Hz, $^3J_{3,4}$ = 3.5 Hz, 5H, $H_{3\text{gal}}$), 4.84 (t_{app}, 5H, $H_{2\text{glc}}$), 4.53-4.45 (m, 25H, CH_2N, $H_{1\text{glc}}$, $H_{6\text{aglc}}$, $H_{1\text{gal}}$), 4.10-4.02 (m, 17H, CH_2N_3, $H_{6\text{bglc}}$, $H_{6\text{agal}}$, $H_{6\text{bgal}}$), 3.86-3.54 (m, 85H, $H_{5\text{gal}}$, $H_{5\text{glc}}$, $H_{4\text{glc}}$, OCH_2), 2.17-1.92 (m, 105H, $COCH_3$).

^{13}C NMR (150 MHz, $CDCl_3$, δ ppm): 170.2, 170.2, 170.0, 169.9, 169.6, 169.5, 169.0 (7×s, $COCH_3$), 165.8 (*C*=O), 155.2 + 155.2 (C_a), 146.6 ($C_{d'}$), 144.5 (C_d), 144.4 (C_d), 143.5 ($C_{triazole}$), 143.3 ($C_{triazole}$), 134.5 ($C_{a'}$), 124.4 (CH_{triazole}), 124.0 (CH_{triazole}), 121.9 (C_c), 121.8 (C_c), 121.7 ($C_{b'}$), 121.6 ($C_{c'}$), 120.9 ($C_{c'}$), 120.9 ($C_{c'}$), 120.7 ($C_{c'}$), 115.2 (C_b), 115.0 (C_b), 100.9 ($C_{1\text{gal}}$), 100.4 ($C_{1\text{glc}}$), 76.1 ($C_{4\text{glc}}$), 72.6 ($C_{3\text{glc}}$), 72.5 ($C_{5\text{glc}}$), 72.4 ($C_{2\text{glc}}$), 71.5 ($C_{3\text{gal}}$), 70.8 ($C_{5\text{gal}}$), 70.5, 70.4, 70.4, 70.3, 70.3, 70.3, 70.1, 70.1, 69.2, 69.2 (OCH$_2$), 68.9 (C_{2gal}), 68.9 (OCH$_2$), 66.5 (C_{4gal}), 62.1 (OCH$_2$C=C), 61.8 (C_{6glc}), 61.6 (C_{6gal}), 60.6, 52.3 (CH$_2$N$_3$), 50.2 (NCH$_2$), 50.1 (NCH$_2$), 20.7, 20.7, 20.6, 20.5, 20.5, 20.4 (COCH$_3$).

^{31}P NMR (122 MHz, CDCl$_3$, δ ppm): 10.3-9.4 (m, 3P).

IR (neat, *v* cm^{-1}) 2882 (m), 2113 (w, N$_3$), 1740 (s), 1502 (m), 1366 (m), 1216 (s), 1041 (m), 833 (w)

m/z (ESI$^+$-HRMS) for $C_{223}H_{297}N_{22}O_{117}P_3$= 1750.2466 [$M$+3H]$^{3+}$; found 1750.2448, 1772.2285 [M+3Na]$^{3+}$, found 1772.2226.

NMR diffusion studies (CDCl$_3$): D = 3.10×10^{-10} m^2/s; d_s = 2.6 nm

GPC measurements (THF): M_w = 5462 ; M_n = 5367 , PDI (M_w/M_n) = 1.018
(CHCl$_3$/Et$_3$N (1%)): M_w = 4784 ; M_n = 4609 , PDI (M_w/M_n) = 1.038

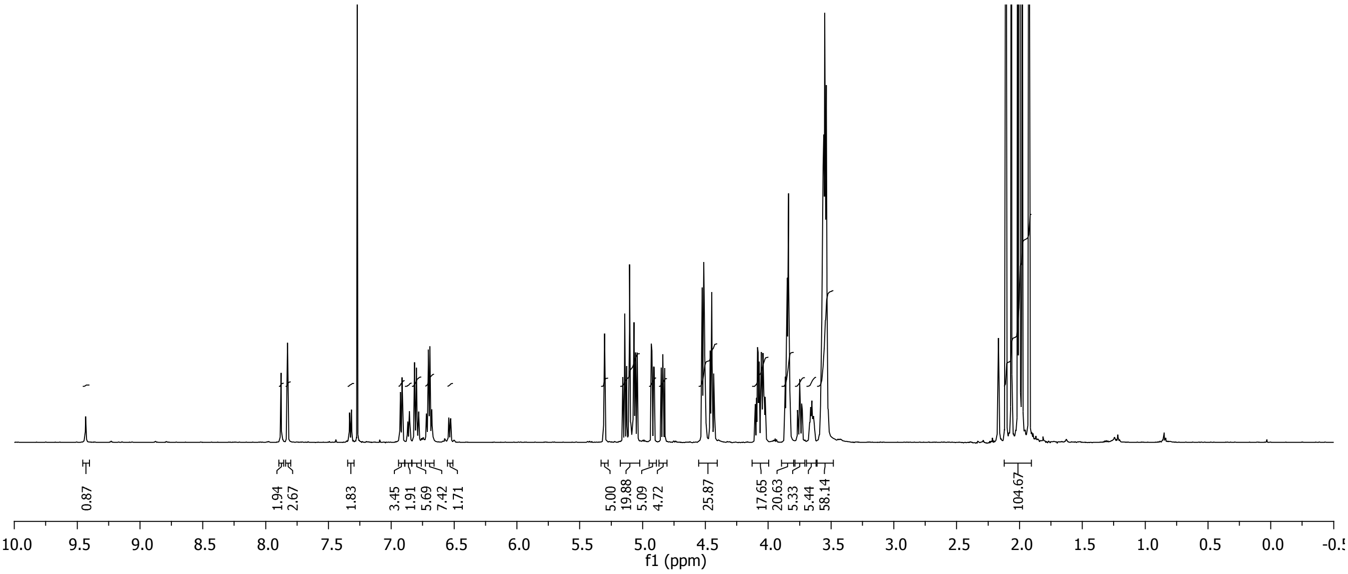


Figure S51. ^{1}H NMR spectrum of compound **15** (CDCl$_3$, 600MHz)

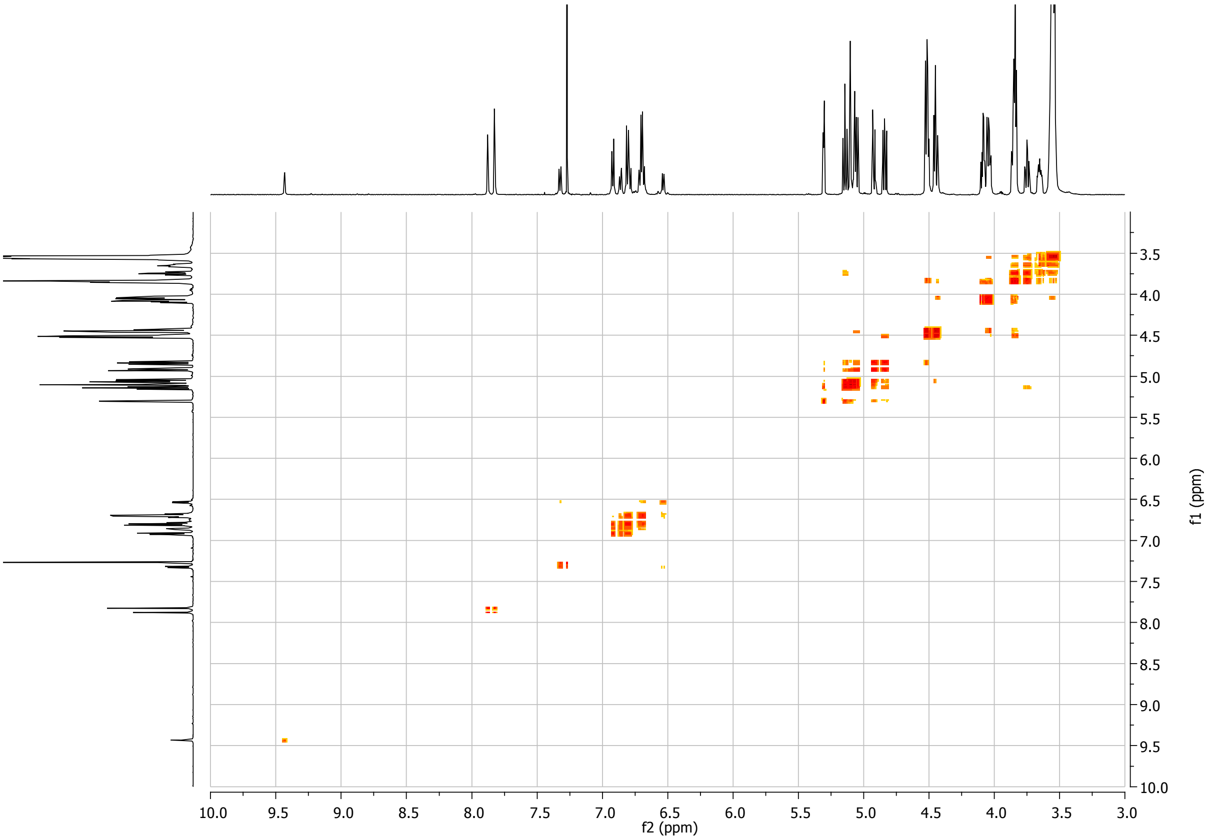


Figure S52. gCOSY spectrum of compound **15**

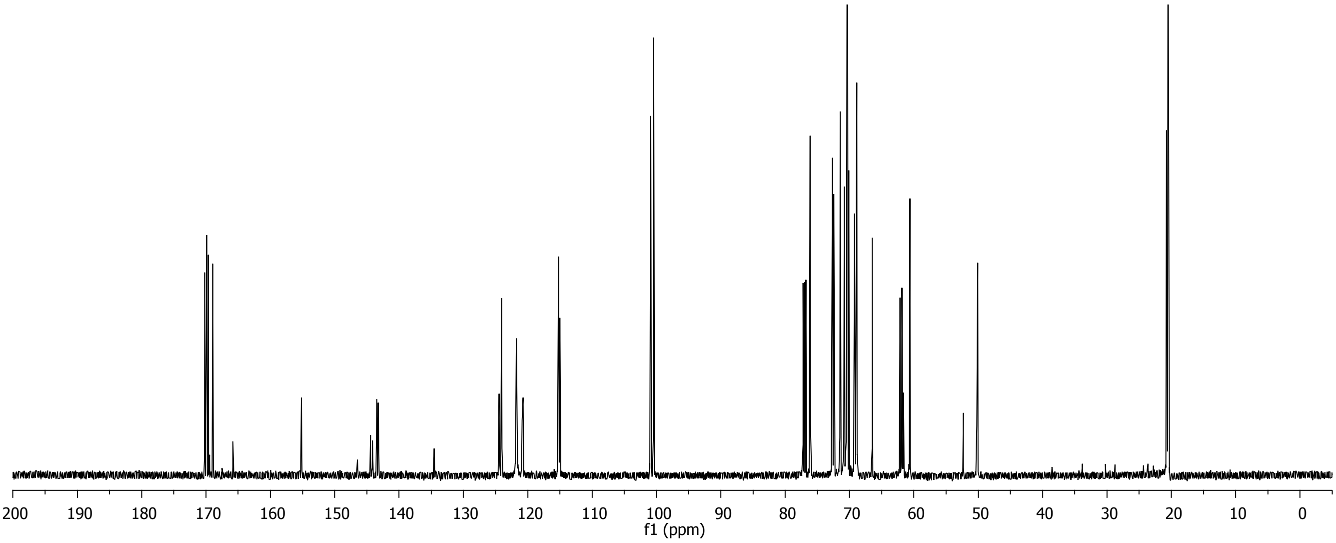


Figure S53. ^{13}C NMR spectrum of compound **15** ($CDCl_3$, 150MHz)

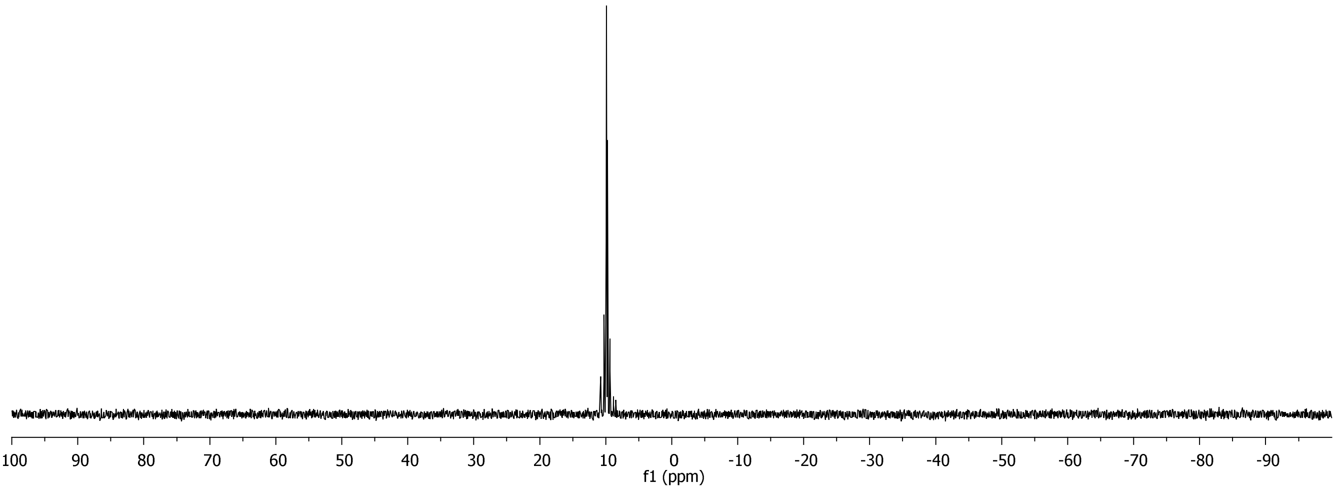


Figure S54. ^{31}P NMR spectrum of compound **15** ($CDCl_3$, 122MHz)

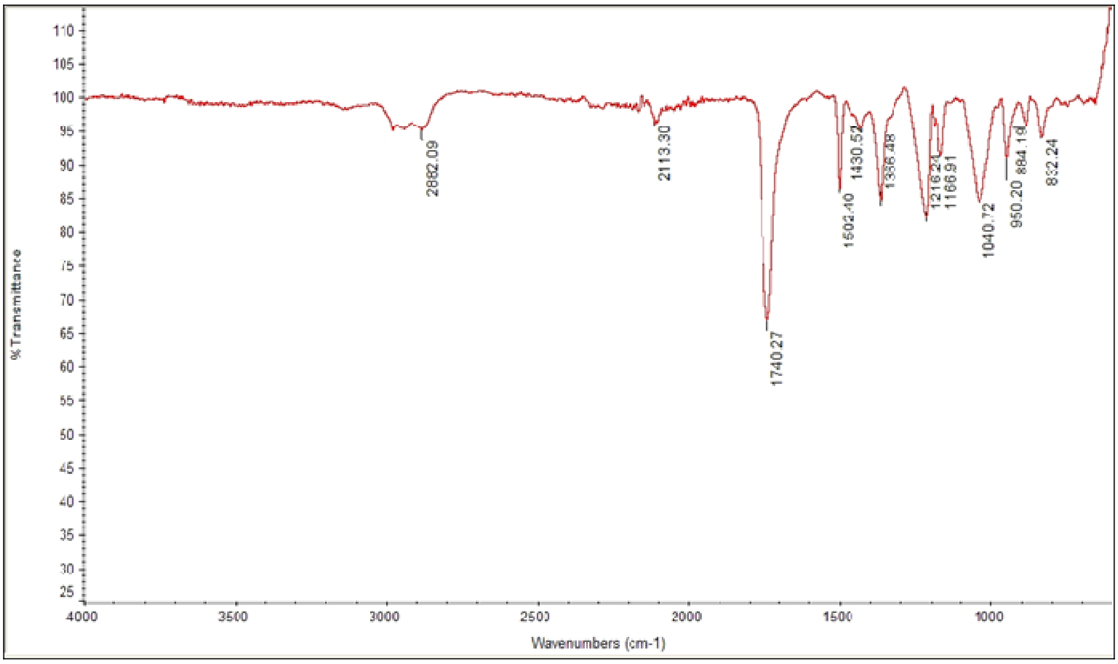
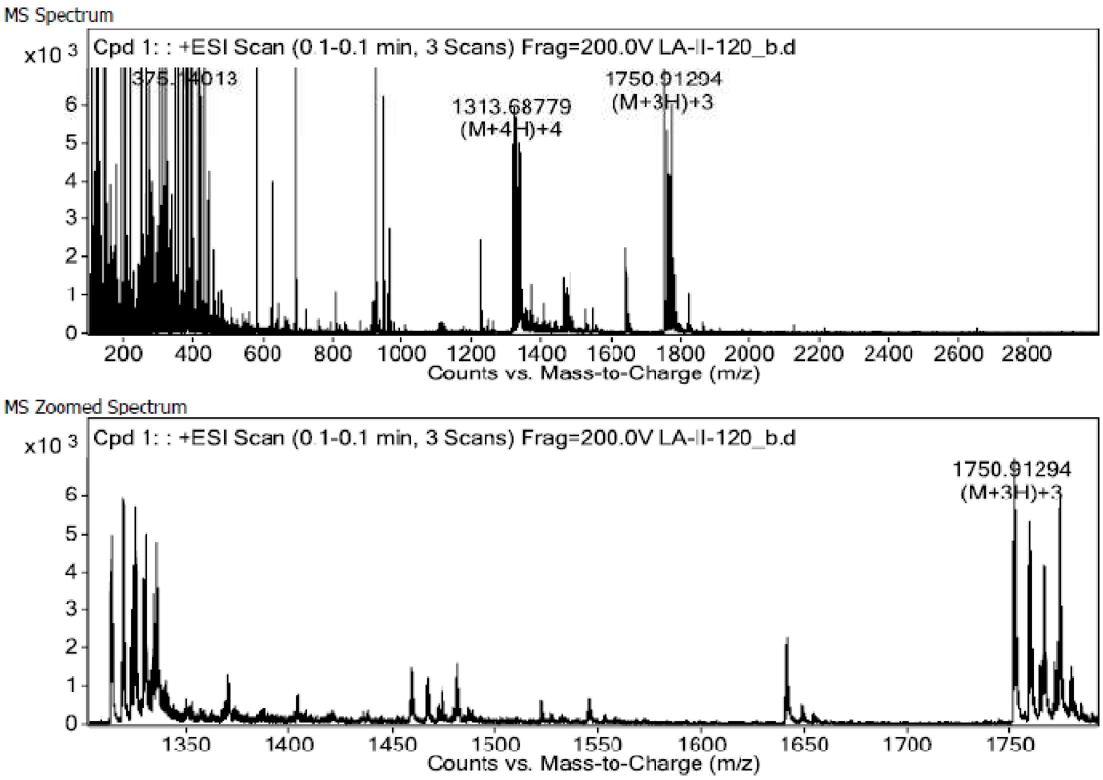


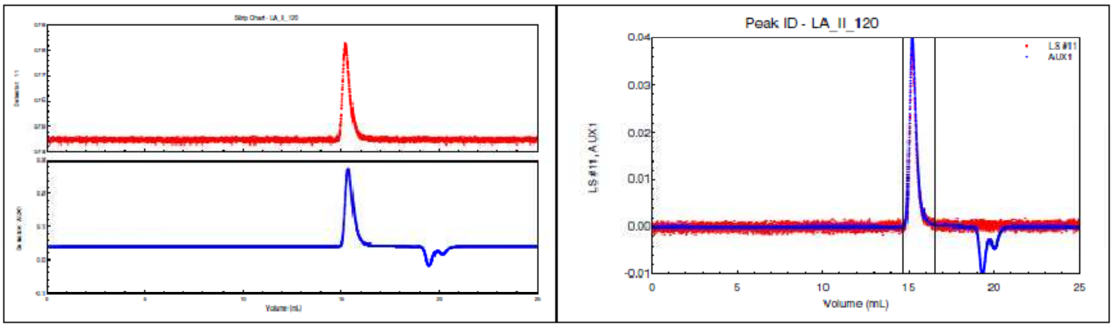
Figure S55. FT-IR spectrum of compound **15**



MS Spectrum Peak List

Ion	Ion Formula	Abund	*Expe. m/z*	*Calc. m/z*	Diff(ppm)
(M+4H)+4	C223H301N22O117P3	1451	1312.9432	1312.93677	4.9
(M+3H)+3	C223H300N22O117P3	1844	1750.24482	1750.2466	-1.02
(M+3Na)+3	C223H297N22Na3O117P3	2213.2	1772.22261	1772.22854	-3.34

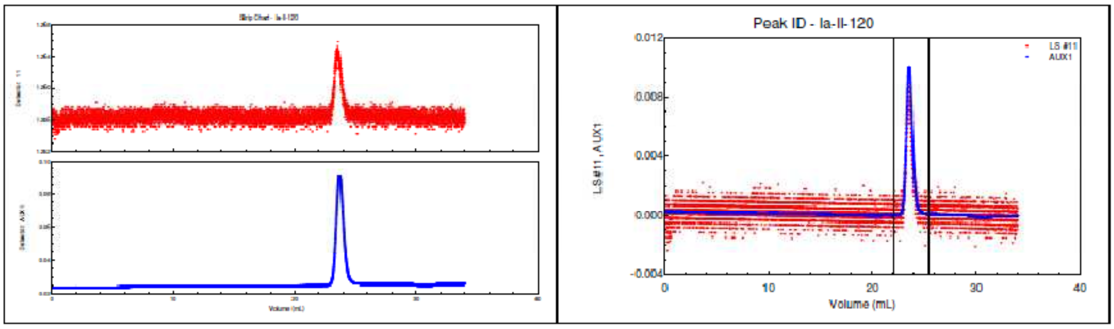
Figure S56. ESI$^+$-HRMS spectrum of compound **15**

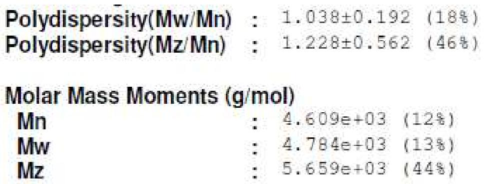


Polydispersity(Mw/Mn) : 1.018±0.145 (14%)
Polydispersity(Mz/Mn) : 1.098±0.342 (31%)

Molar Mass Moments (g/mol)
Mn : 5.367e+03 (9%)
Mw : 5.462e+03 (10%)
Mz : 5.895e+03 (29%)

Figure S57. GPC trace (in THF) of compound **15**



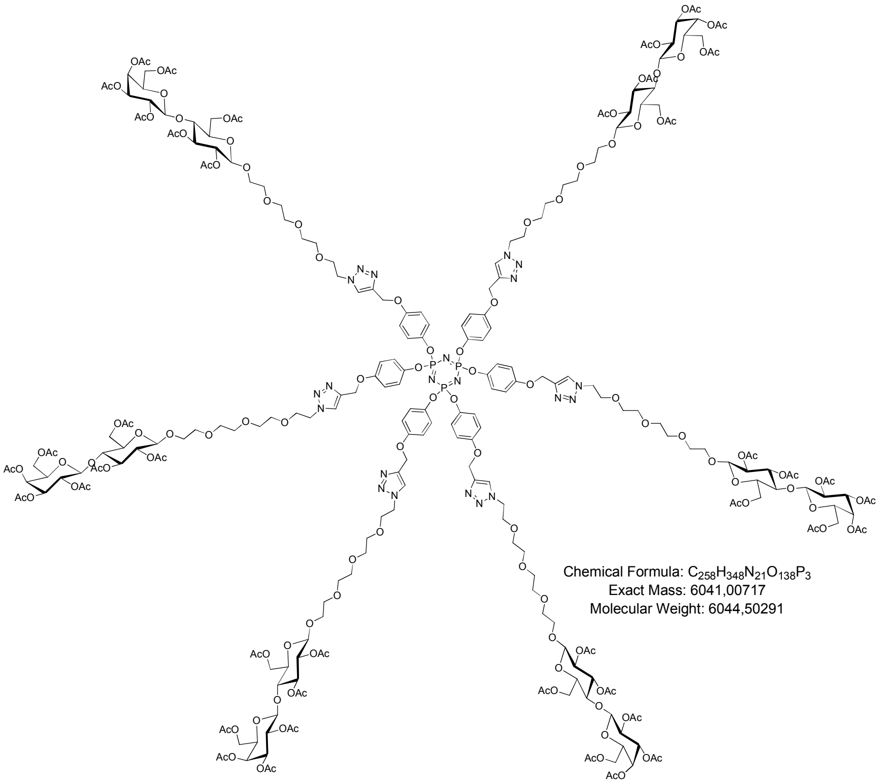


```
Polydispersity(Mw/Mn)  :  1.038±0.192 (18%)
Polydispersity(Mz/Mn)  :  1.228±0.562 (46%)

Molar Mass Moments (g/mol)
  Mn                   :  4.609e+03 (12%)
  Mw                   :  4.784e+03 (13%)
  Mz                   :  5.659e+03 (44%)
```

Figure S58. GPC trace (in $CHCl_3/Et_3N$ (1%)) of compound **15**

Protected hexavalent glycocluster 16



Chemical Formula: $C_{258}H_{348}N_{21}O_{138}P_3$
Exact Mass: 6041,00717
Molecular Weight: 6044,50291

To a solution of propargylated derivative **1** (13.5 mg, 0.013 mmol, 1.0 eq.) in a 1:1 mixture of H_2O/THF (5 mL), were added azido derivative **10** (95.6 mg, 0.114 mmol, 8.8 eq.), $CuSO_4 \cdot 5H_2O$ (26.9 mg, 0.101 mmol, 7.8 eq.) and sodium ascorbate (22.1 mg, 0.111 mmol, 8.6 eq.). While stirring, the mixture was first heated at 50℃ for 3 hours in a 20 mL vial and at room temperature for additional 18 hours. Ethyl acetate (15 mL) was added and the solution was poured into a separatory funnel containing ethyl acetate (10 mL), washed with saturated aqueous NH_4Cl (2×10 mL), water (10 mL) and brine (5 mL). Organics were collected, dried over Na_2SO_4 and concentrated to dryness with rotary evaporator. Purification by flash chromatography (SiO_2, DCM/MeOH 99:1 to 96:4) afforded desired multivalent compound **16** (67 mg, 0.011 mmol, **84%**).

R_f = 0.42, DCM/MeOH 95:5.

^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 7.82 (s, 6H, H_{triazole}), 6.79 (d, ^3J = 8.9 Hz, 12H, CH_b), 6.75 (d, ^3J = 8.9 Hz, 12H, CH_c), 5.30 (d_{app}, 6H, $H_{4\text{gal}}$), 5.14 (dd, $^3J_{4,3}$ = 9.4 Hz, $^3J_{3,2}$ = 9.1 Hz, 3H, $H_{3\text{glc}}$), 5.09-5.04 (m, 18H, C_qCH_2O, $H_{2\text{gal}}$), 4.91 (dd, $^3J_{2,3}$ = 7.1 Hz, $^3J_{3,4}$ = 3.3 Hz, 6H, $H_{3\text{gal}}$), 4.84 (t_{app}, 6H, $H_{2\text{glc}}$), 4.53-4.43 (m, 30H, CH_2N, $H_{1\text{glc}}$, $H_{6\text{aglc}}$, $H_{1\text{gal}}$), 4.08-4.03 (m, 18H, $H_{6\text{bglc}}$, $H_{6\text{agal}}$, $H_{6\text{bgal}}$), 3.86-3.83 (m, 24H, OCH_2CH_2N, $LacOCH_2$), 3.75 (t_{app}, 6H, $H_{4\text{glc}}$), 3.60-3.53 (m, 72H, OCH_2, $H_{5\text{gal}}$, $H_{5\text{glc}}$), 2.11-1.92 (7×s, 126H, $COCH_3$).

^{13}C NMR (150 MHz, $CDCl_3$, δ ppm): 170.5, 170.5, 170.3, 170.2, 170.0, 169.8, 169.3 (7s, $COCH_3$), 155.5 (C_a), 144.7 (C_d), 143.7 ($C_{triazole}$=CH), 124.4 (C_{triazole}=CH), 122.0 (C_c), 115.5 (C_b), 101.2 ($C_{1\text{gal}}$), 100.8 ($C_{1\text{glc}}$), 76.5 ($C_{4\text{glc}}$), 73.0 ($C_{3\text{glc}}$), 72.8 ($C_{5\text{glc}}$), 71.8 ($C_{2\text{glc}}$), 71.2 ($C_{3\text{gal}}$), 70.8 ($C_{5\text{gal}}$), 70.8, 70.7, 70.6, 70.4, 69.6 (OCH_2), 69.3 ($C_{2\text{gal}}$), 69.2 (OCH_2), 66.8 (C_{4gal}), 62.4 (OCH$_2$C=C), 62.2 (C_{6glc}), 61.0 (C_{6gal}), 50.4 (NCH$_2$), 21.1, 21.0, 20.9, 20.8, 20.8, 20.8, 20.7 (7×s, COCH$_3$).

^{31}P NMR (122 MHz, CDCl$_3$, δ ppm): 9.7 (s, 3P).

m/z (ESI$^+$-HRMS) for $C_{258}H_{348}N_{21}O_{138}P_3$ = 1511.5099 [*M*+4H]$^{4+}$; found 1511.5123, 1533.2410 [*M*+4Na]$^{4+}$, found 1533.2391.

NMR diffusion studies (CDCl$_3$): $D = 2.76\times10^{-10}$ m^2/s; d_s = 2.9 nm.

GPC measurements (THF): M_w = 6882 ; M_n = 6764 , PDI (M_w/M_n) = 1.017.

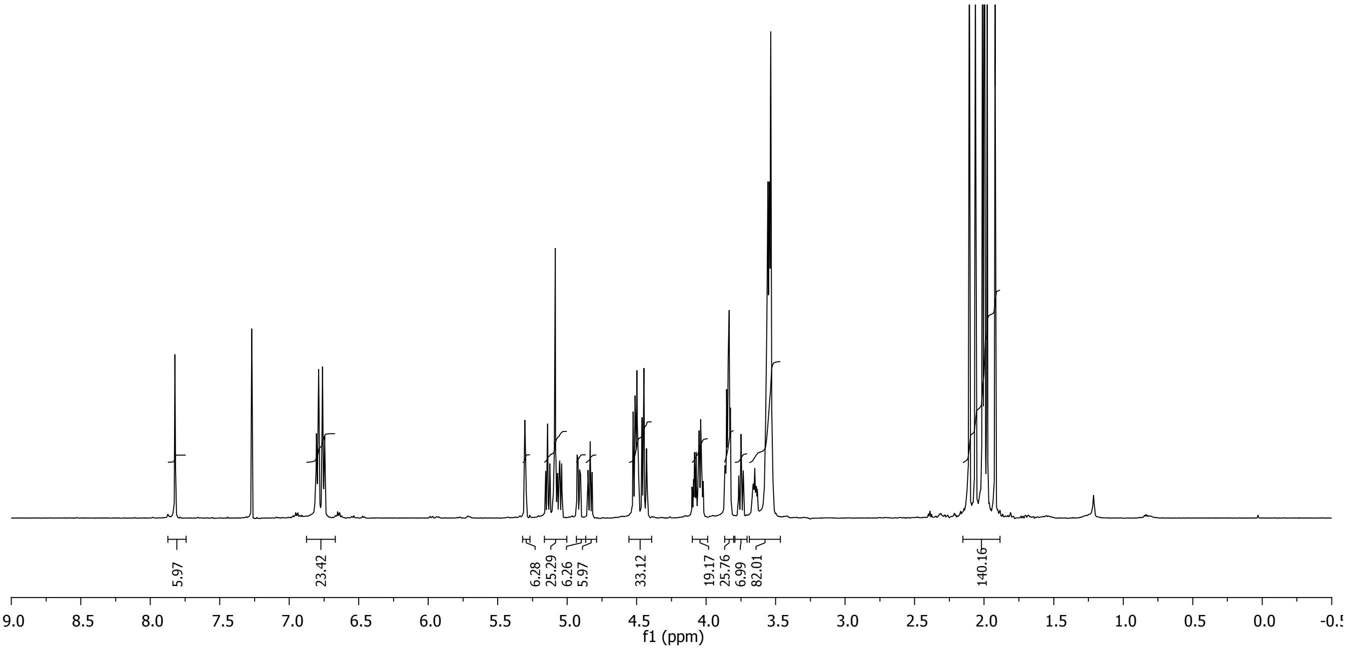


Figure S59. ^{1}H NMR spectrum of compound **16** (CDCl$_3$, 600MHz)

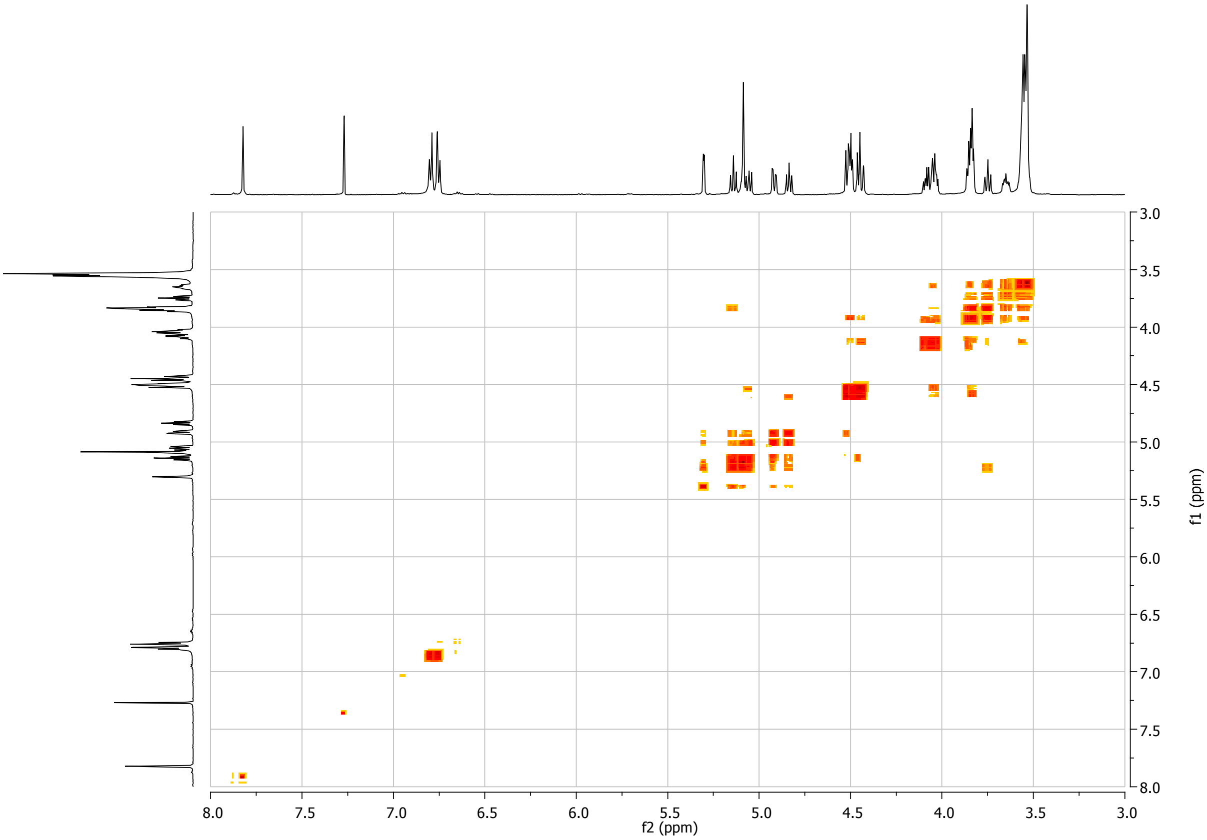


Figure S60. gCOSY spectrum of compound **16**

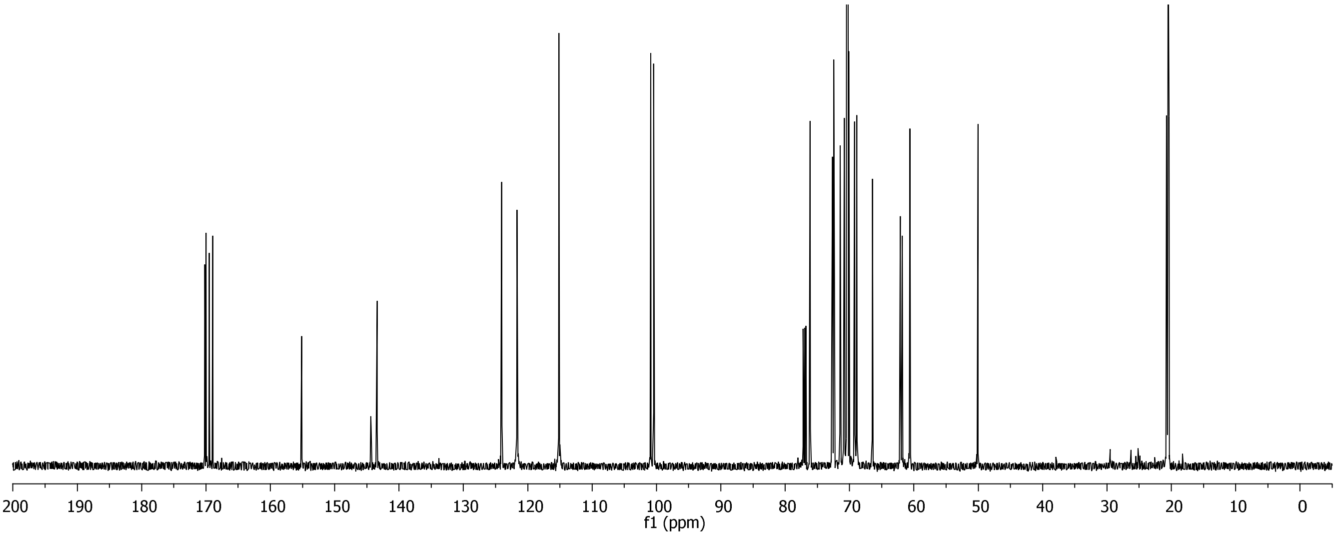


Figure S61. ^{13}C NMR spectrum of compound **16** ($CDCl_3$, 150MHz)

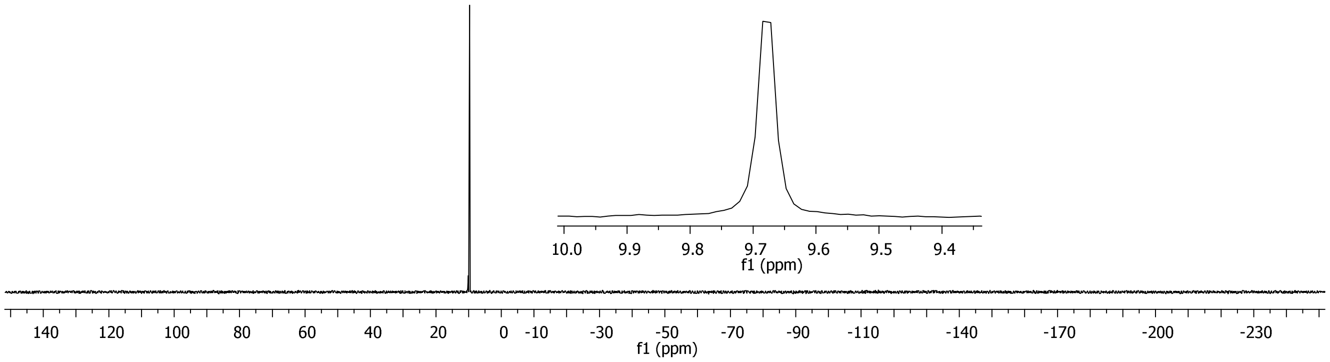
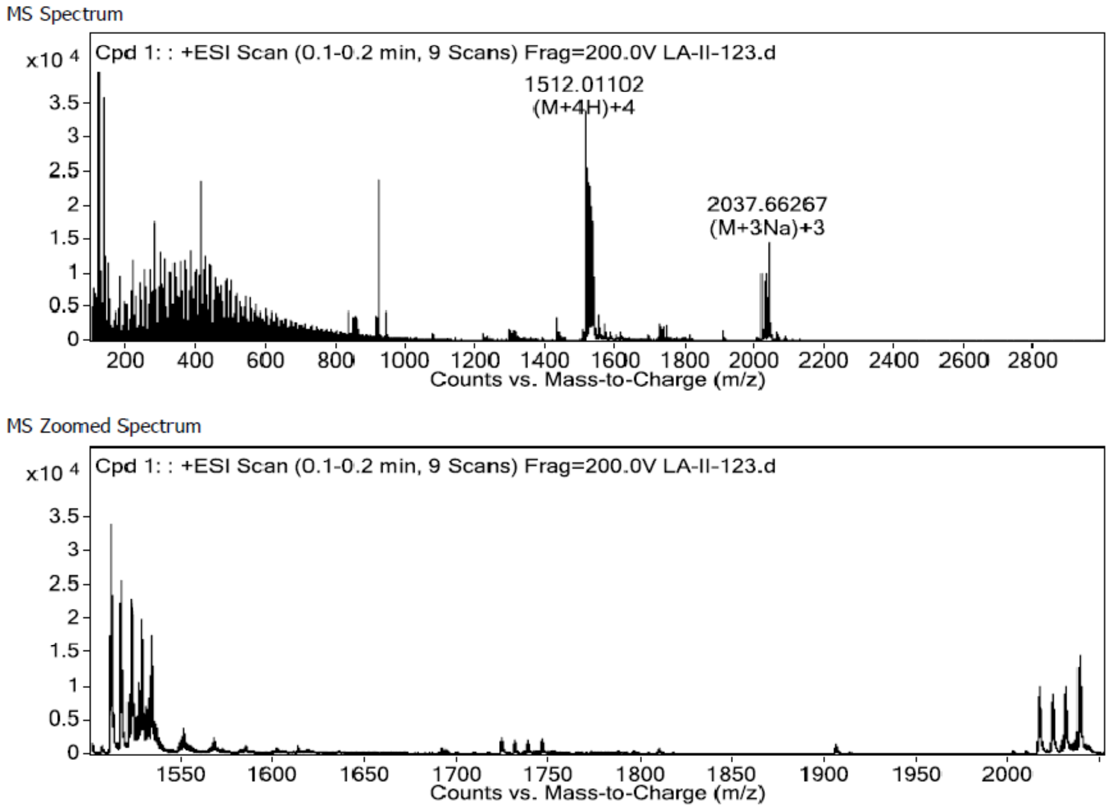


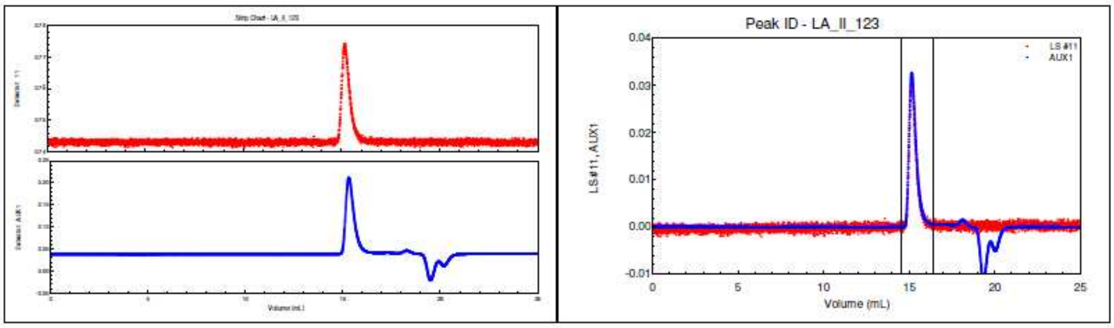
Figure S62. ^{31}P NMR spectrum of compound **16** ($CDCl_3$, 122MHz)



MS Spectrum Peak List

Ion	Formula	Abund	Observed m/z	Calc m/z	Diff(ppm)
(M+4H)+4	C258H352N21O138P3	17753.4	1511.51226	1511.50988	-2.38
(M+4Na)+4	C258H348N21Na4O138P3	7228.1	1533.23912	1533.24101	1.89
(M+3Na)+3	C258H348N21Na3O138P3	3659.9	2036.6626	2036.65828	-4.33

Figure S63. ESI^{+}-HRMS spectrum of compound **16**

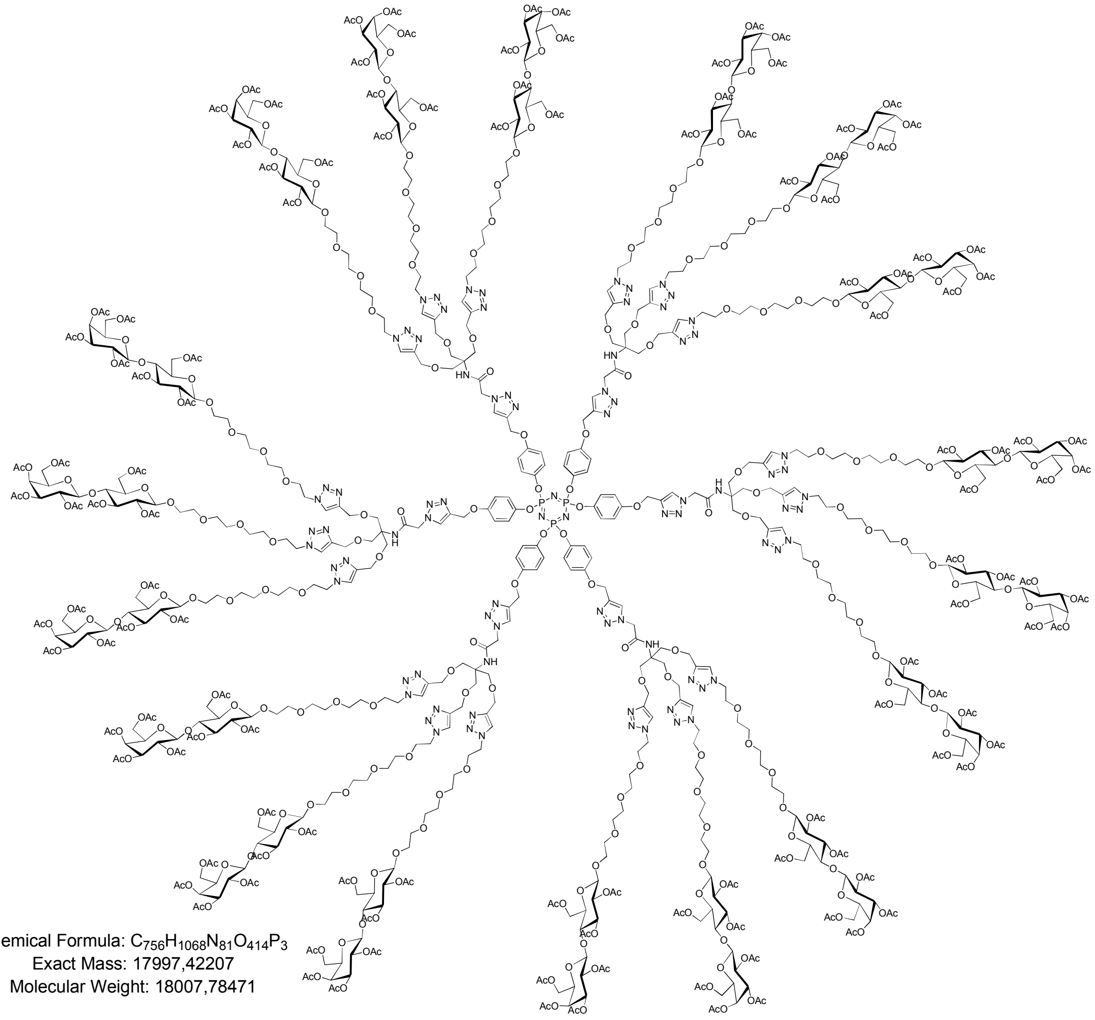


```
Polydispersity(Mw/Mn)  :  1.017±0.144 (14%)
Polydispersity(Mz/Mn)  :  1.241±0.576 (46%)

Molar Mass Moments (g/mol)
 Mn                    :  6.764e+03 (9%)
 Mw                    :  6.882e+03 (10%)
 Mz                    :  8.392e+03 (45%)
```

Figure S64. GPC trace (in THF) of compound **16**

Protected octadecavalent dendrimer 17



Chemical Formula: $C_{756}H_{1068}N_{81}O_{414}P_3$
Exact Mass: 17997,42207
Molecular Weight: 18007,78471

To a solution of hexapropargylated cyclotriphosphazene derivative **1** (6.91 mg, 6.79 μmol, 1.0 eq.) in a 1:1 mixture of H_2O/THF_{anh} (5 mL), were added azido derivative **14** (150 mg, 53.0 μmol, 7.8 eq.), $CuSO_4 \cdot 5H_2O$ (13.2 mg, 53.0 μmol, 7.8 eq.) and sodium ascorbate (10.4 mg, 53.0 μmol, 7.8 eq.). While stirring, the mixture was first heated at 50℃ for 3 hours in a 20 mL vial and at room temperature for additional 18 hours. Ethyl acetate (30 mL) was added and the solution was poured into a separatory funnel containing ethyl acetate (20 mL), washed with saturated aqueous NH_4Cl (2×20 mL), water (20 mL) and brine (10 mL). Organics were collected, dried over Na_2SO_4 and concentrated to dryness *in vacuo* with rotary evaporator. Purification by flash chromatography (SiO_2, DCM/MeOH 100:0 to 90:10) afforded desired multivalent compound **17** (79.0 mg, 4.39 μmol, **65%**).

$\mathbf{R_f}$ = 0.28, DCM/MeOH 92:8

^{1}**H NMR** (600 MHz, $CDCl_3$, δ ppm): 7.89 (s, 6H, $H_{\text{int-triazole}}$), 7.68 (s, 18H, $H_{\text{ext-triazole}}$), 6.88-6.69 (m, 24H, $CH_{b'}$, CH_b, CH_c, $CH_{c'}$ + *NH not visible*), 5.30 (d_{app}, 18H, H_{4gal}), 5.14 (t_{app}, 18H, H_{3glc}) 5.07-5.02 (m, 30H, C_qCH_2O, H_{2gal}), 4.91 (dd, $^{3}J_{2,3}$ = 3.4 Hz, $^{3}J_{3,4}$ = 7.0 Hz, 18H, H_{3gal}), 4.83 (t_{app}, 18H, H_{2glc}), 4.54-4.43 (m, 126H, C_qCH_2O, OCH_2CH_2N, H_{1glc}, H_{6aglc}, H_{1gal}), 4.10-4.02 (m, 54H, H_{6bglc}, H_{6agal}, H_{6bgal}), 3.86-3.53 (m, 354H, NHCOCH_2N$_{\mathrm{triazole}}$, OCH_2CH$_2$N, H_{5gal}, H_{5glc}, H_{4glc}, OCH_2, HNC$_q$CH_2O), 2.11-1.92 (m, 378H, COCH_3).

^{13}C NMR (150 MHz, CDCl$_3$, δ ppm): 170.2, 170.2, 170.0, 169.9, 169.6, 169.5, 168.9 (7×s, COCH$_3$), 165.1 (CO), 155.2 (C_a), 144.2 (C_d), 144.2 ($C_{triazole}$=CH), 143.3 ($C_{triazole}$=CH), 125.2 (C$_{\mathrm{triazole}}$=CH), 123.7 (C$_{\mathrm{triazole}}$=CH), 121.6 (C_c), 115.1 (C_b), 100.9 (C_{1gal}), 100.4 (C_{1glc}), 76.1 (C_{4glc}), 72.6 (C_{3glc}), 72.5 (C_{5glc}), 71.4 (C_{2glc}), 70.8 (C_{3gal}), 70.5 (C_{5gal}), 70.4, 70.3, 70.2, 70.2, 70.0, 69.2 (OCH$_2$), 68.9 (C_{2gal}), 68.9 (OCH$_2$), 68.4 (C$_q$CH$_2$O), 66.5 (C_{4gal}), 64.4 (OCH$_2$C=C), 62.0 (C_{6glc}), 61.8 (C_q), 60.6 (C_{6gal}), 60.3 (NCH$_2$), 52.5 (HNCOCH$_2$N$_{\mathrm{triazole}}$), 49.9 (OCH$_2$), 20.7, 20.7, 20.6, 20.5, 20.5, 20.4 (7×s, COCH$_3$).

^{31}P NMR (122 MHz, CDCl$_3$, δ ppm): 10.0-9.6 (m, 3P).

m/z (ESI$^+$-MS) for $C_{756}H_{1068}N_{81}O_{414}P_3$= 18008.6 [$M$+H]$^+$; found 18008.5 (after deconvolution).

NMR diffusion studies (CDCl$_3$): $D = 1.48\times10^{-10}$ m^2/s; d_s = 5.5 nm.

GPC measurements (THF): M_w = 23790 ; M_n = 23540 , PDI (M_w/M_n) = 1.011
(CHCl$_3$/Et$_3$N (1%)): M_w = 21740 ; M_n = 21350 , PDI (M_w/M_n) = 1.018.

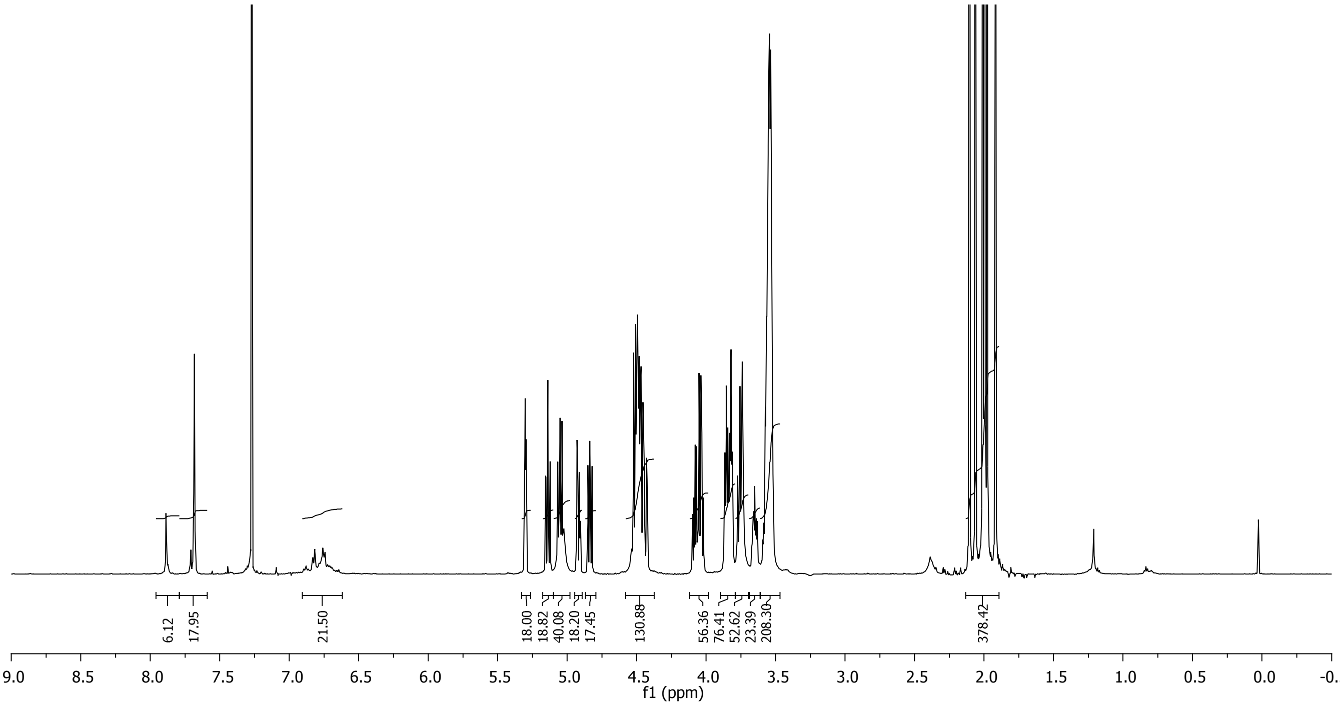


Figure S65. ^{1}H NMR spectrum of compound **17** (CDCl$_3$, 600MHz)

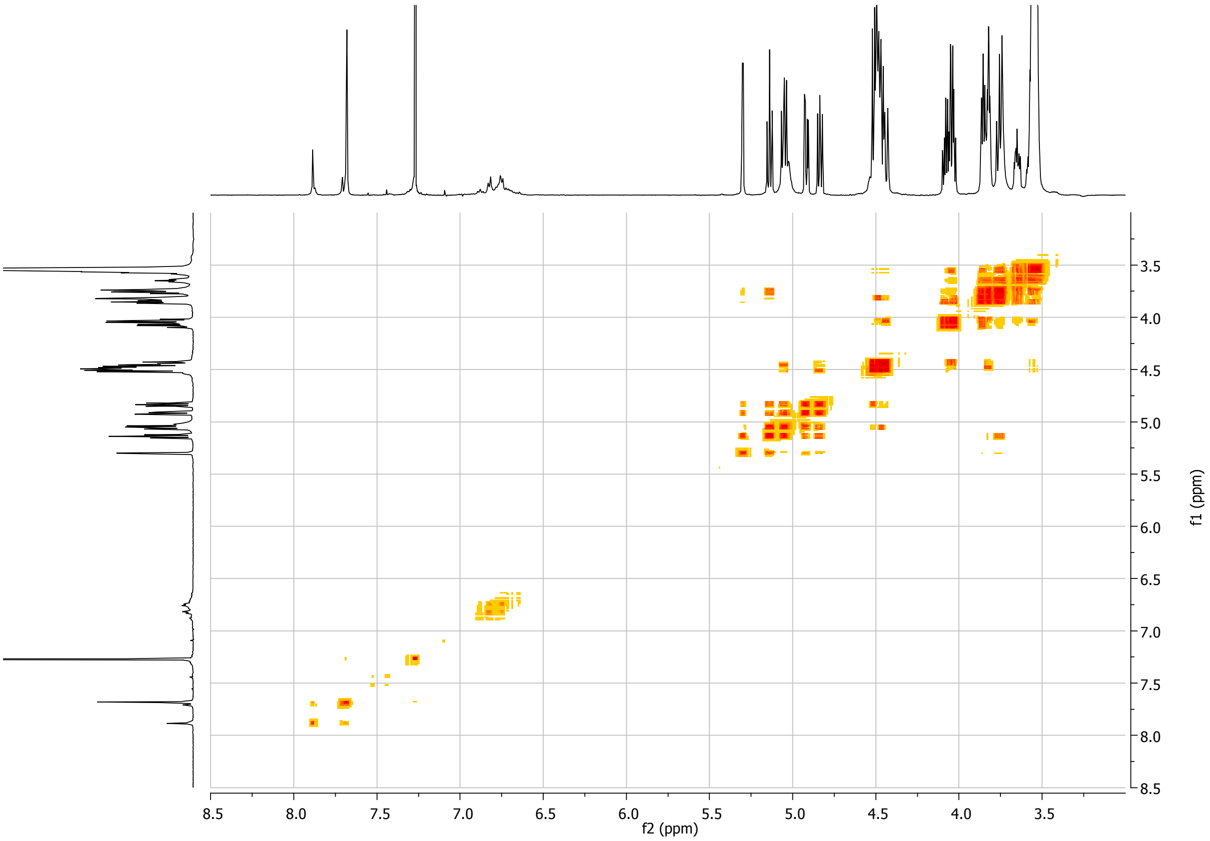


Figure S66. gCOSY spectrum of compound **17**

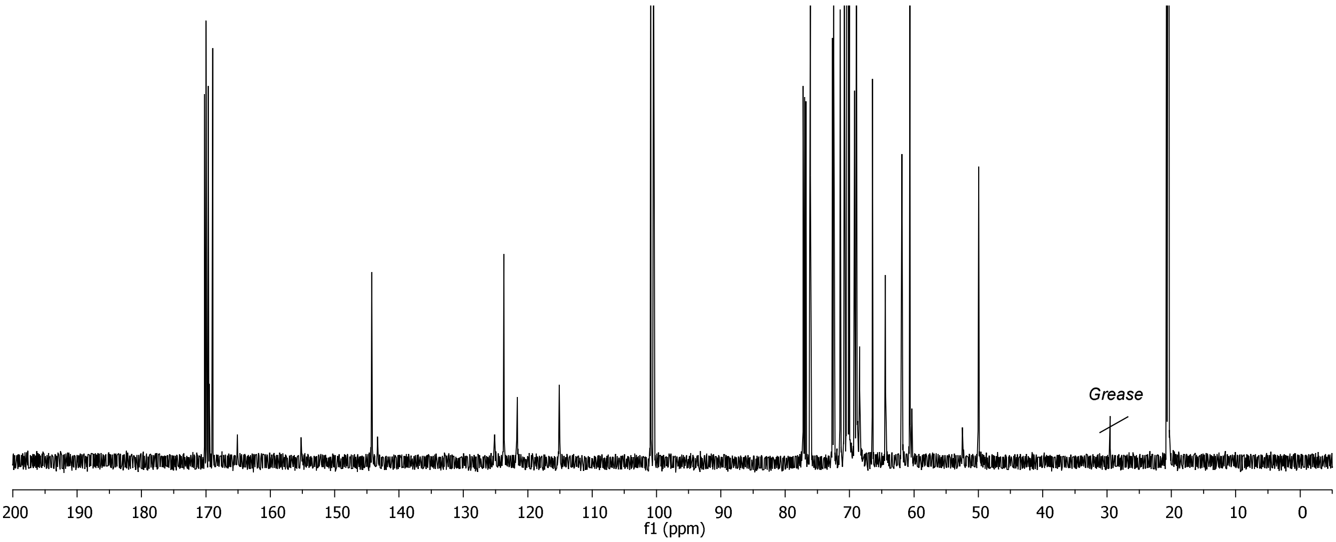


Figure S67. ^{13}C NMR spectrum of compound **17** ($CDCl_3$, 150MHz)

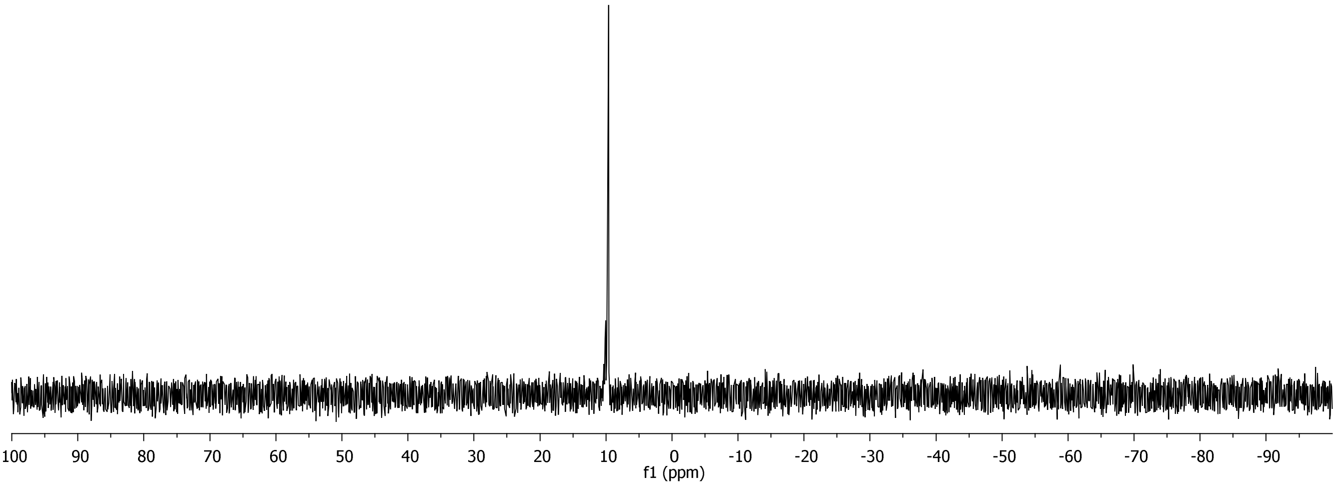
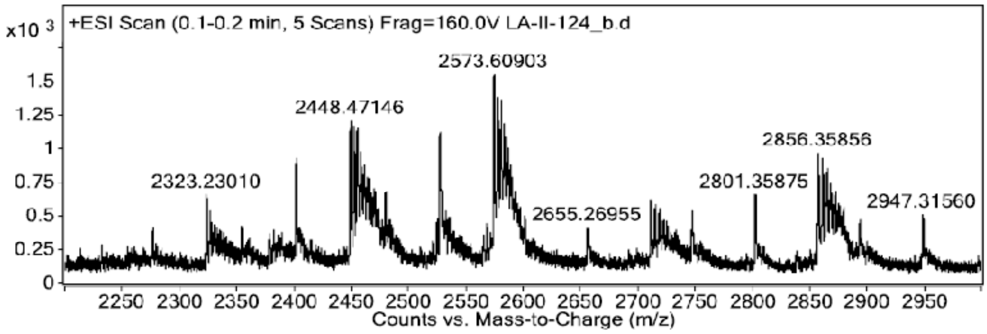
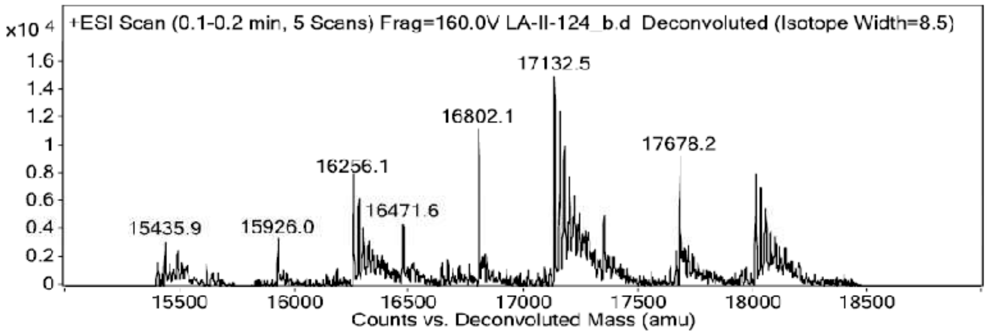


Figure S68. ^{31}P NMR spectrum of compound **17** ($CDCl_3$, 122MHz)





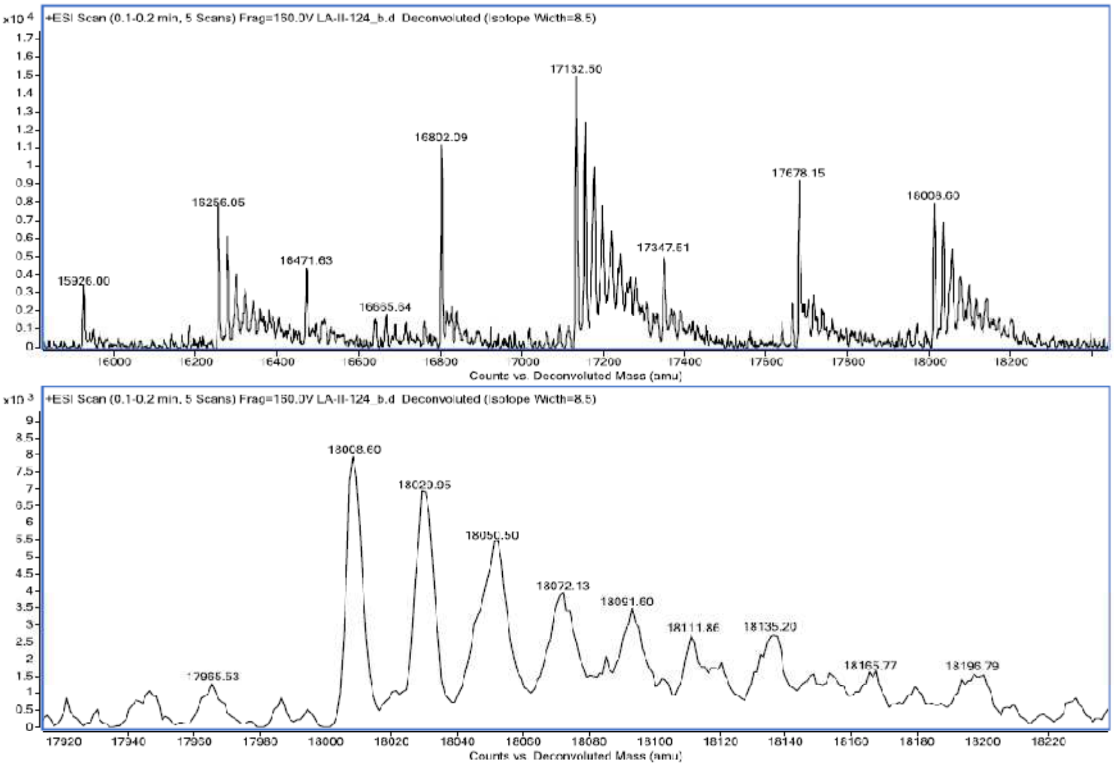
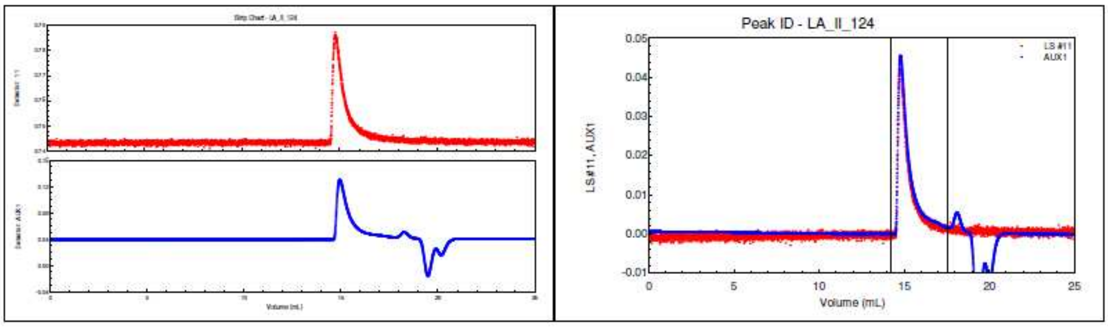


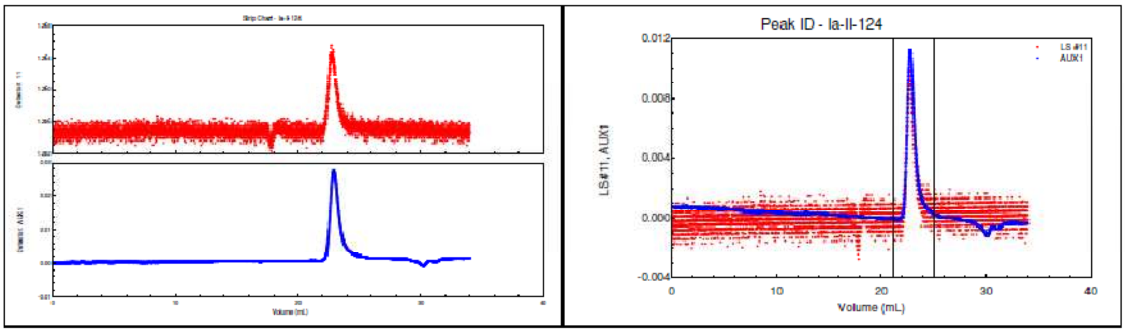
Figure S69. ESI^{+}-MS (deconvolution) spectrum of compound **17**



Polydispersity(Mw/Mn) : 1.011±0.128 (13%)
Polydispersity(Mz/Mn) : 1.021±0.226 (22%)

Molar Mass Moments (g/mol)
Mn : 2.354e+04 (8%)
Mw : 2.379e+04 (8%)
Mz : 2.403e+04 (20%)

Figure S70. GPC trace of compound **17**

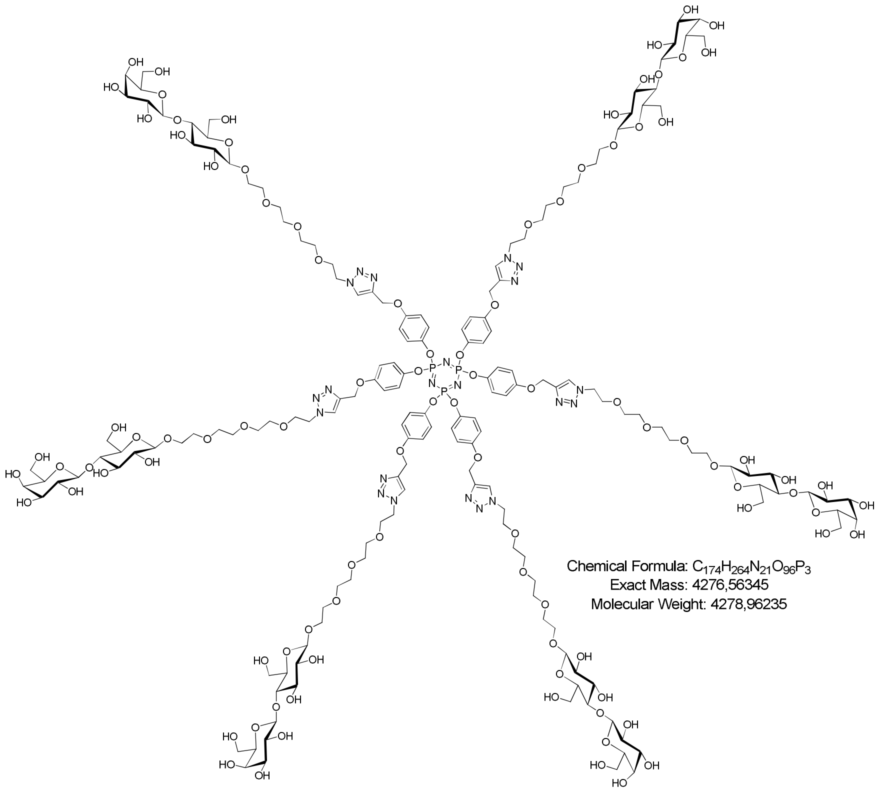


Polydispersity(Mw/Mn) : 1.018±0.184 (18%)
Polydispersity(Mz/Mn) : 1.041±0.331 (32%)

Molar Mass Moments (g/mol)
Mn : 2.135e+04 (12%)
Mw : 2.174e+04 (12%)
Mz : 2.222e+04 (28%)

Figure S71. GPC trace (in $CHCl_3/Et_3N$ (1%)) of compound **17**

Hydroxylated hexavalent glycocluster 18



Acetylated compound **16** (43.0 mg, 7.11 µmol) was dissolved in a dry mixture of MeOH/DCM (5 mL, 4:1) and a solution of sodium methoxide (1M in MeOH, 5 µL every 20 minutes until precipitation) was added. An additional 100 µL was then injected and the heterogeneous reaction mixture was stirred at room temperature for 24 h.. The solvent was then removed with a Pasteur pipette and another dry mixture of MeOH/DCM (5 mL, 4:1) is added to the residual oil. A vigorous agitation is maintained for an additional 15 min. period. After removal of the solvents with a Pasteur pipette, 2 mL of dry MeOH were added to the viscous residue under agitation. After 15 min., the MeOH was removed and the residue was dissolved in 3 mL of H_2O, and the pH was adjusted to 7 with addition of ion-exchange resin (Amberlite IR 120 H^+). After filtration, the solvent was removed under *vacuum* with rotary evaporator, lyophilized to yield the fully deprotected hexamer **18** as a white solid (25.0 mg, 5.84 µmol) in an 82% yield.

^{1}**H NMR** (600 MHz, D_2O, δ ppm): 7.99 (s, 6H, H_{triazole}), 6.73 (br s, 24H, $\mathrm{C}H_{\mathrm{ar}}$), 5.03 (br s, 12H, $\mathrm{C_qC}H_2\mathrm{O}$), 4.51 (br s, 12H, $\mathrm{C}H_2\mathrm{N}$), 4.46-4.43 (m, 12H, $H_{1\mathrm{glc}}$, $H_{1\mathrm{gal}}$), 3.98-3.84 (m, 18H, $\mathrm{O}CH_2\mathrm{CH_2N}$, $\mathrm{LacOCH}H\mathrm{CH_2}$), 3.82-3.47 (m, 132H, $H_{3\mathrm{glc}}$, $H_{2\mathrm{gal}}$, $H_{3\mathrm{gal}}$, $H_{6\mathrm{bglc}}$, $H_{4\mathrm{gal}}$, $H_{6\mathrm{agal}}$, $H_{6\mathrm{bgal}}$, $H_{6\mathrm{aglc}}$, $H_{5\mathrm{gal}}$, $H_{5\mathrm{glc}}$, $H_{4\mathrm{glc}}$, $\mathrm{LacOCH}H\mathrm{CH_2}$, $\mathrm{OC}H_2$), 3.33 (t_{app}, 6H, $H_{2\mathrm{glc}}$).
^{13}**C NMR** (150 MHz, $CDCl_3$, δ ppm): 155.6 (C_{a}), 144.6 (C_{d}), 143.7 ($C_{triazole}$=CH), 125.9 ($\mathrm{C_{triazole}}$=CH), 122.4 (C_{c}), 116.3 (C_{b}), 103.7 ($C_{1\mathrm{gal}}$), 102.8 ($C_{1\mathrm{glc}}$), 79.1 ($C_{4\mathrm{glc}}$), 76.0 ($C_{3\mathrm{glc}}$), 75.4 ($C_{5\mathrm{glc}}$), 75.0 ($C_{5\mathrm{gal}}$), 73.5 ($C_{2\mathrm{glc}}$), 73.2 ($C_{3\mathrm{gal}}$), 71.6 ($C_{2\mathrm{gal}}$), 70.3, 70.2, 70.2, 69.4, ($\mathrm{O}C\mathrm{H_2}$), 69.3 ($C_{4\mathrm{gal}}$), 69.2 ($\mathrm{O}C\mathrm{H_2}$), 62.0 ($\mathrm{O}C\mathrm{H_2C{=}C}$), 61.7 ($C_{6\mathrm{glc}}$), 60.8 ($C_{6\mathrm{gal}}$), 50.7 ($\mathrm{N}C\mathrm{H_2}$).
^{31}**P NMR** (122 MHz, D_2O, δ ppm): 10.2 (s, 3P).

m/z (ESI$^+$-HRMS) for $C_{174}H_{264}N_{21}O_{96}P_3$ = 1070.1481 [M+4H]$^{4+}$, found 1070.1473; 2139.2890 [M+2H]$^{2+}$, found 2139.2886.

NMR diffusion studies (D_2O): $D = 1.10\times10^{-10}$ m^2/s; d_s = 3.6 nm.

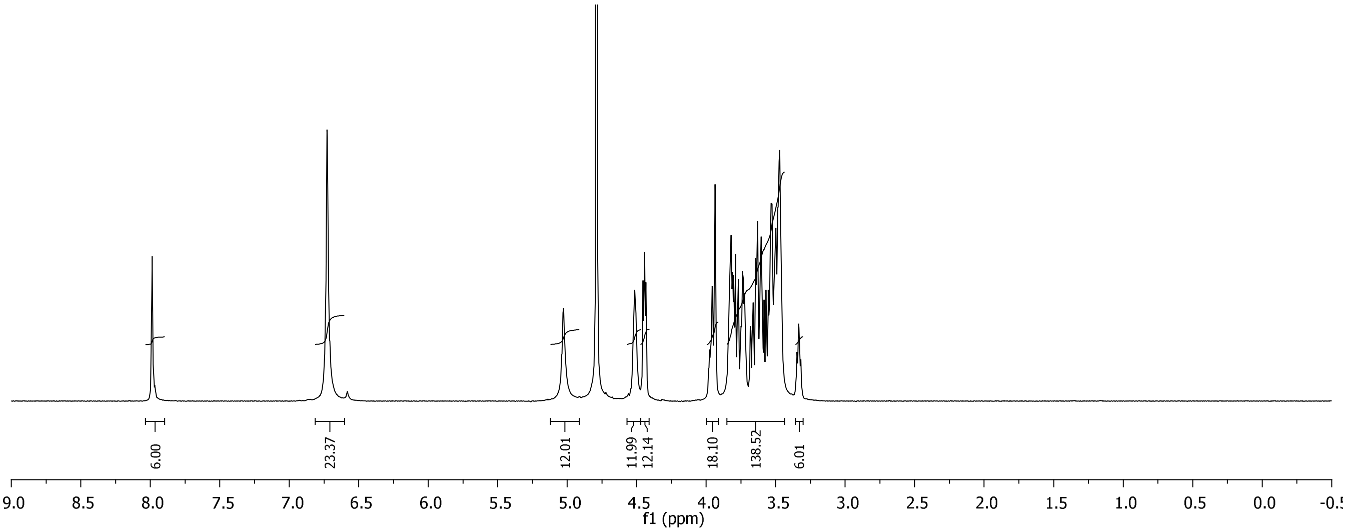


Figure S72. ^{1}H NMR spectrum of compound **18** (D_2O, 600MHz)

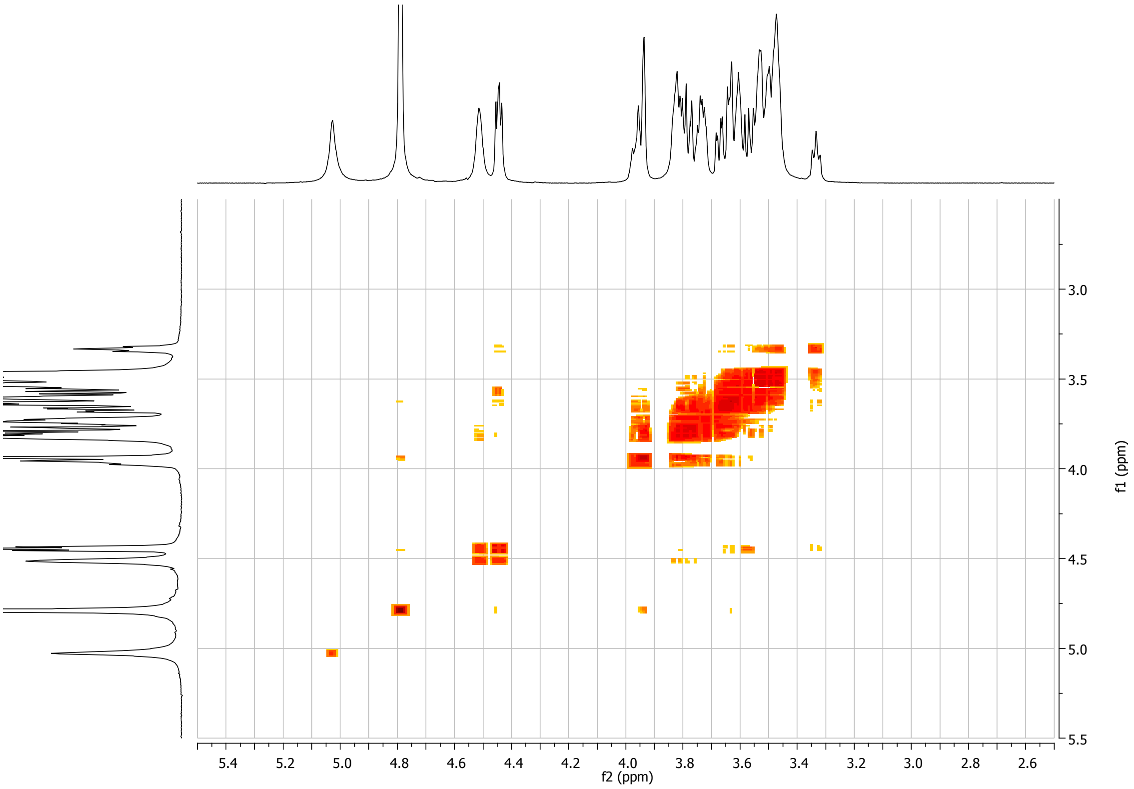


Figure S73. gCOSY spectrum of compound **18**

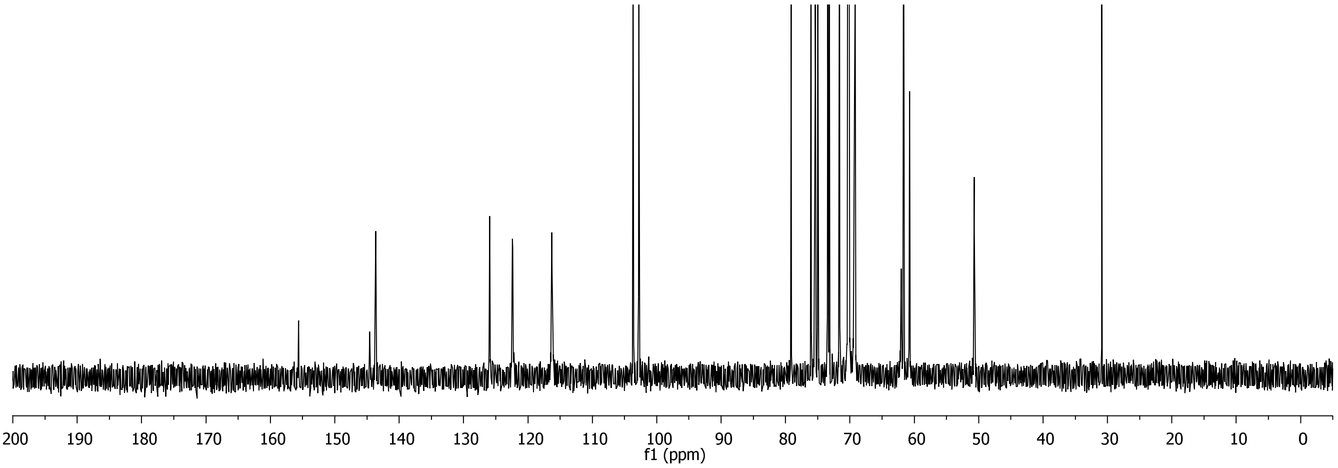


Figure S74. ^{13}C NMR spectrum of compound **18** (D_2O, 150MHz, acetone as reference)

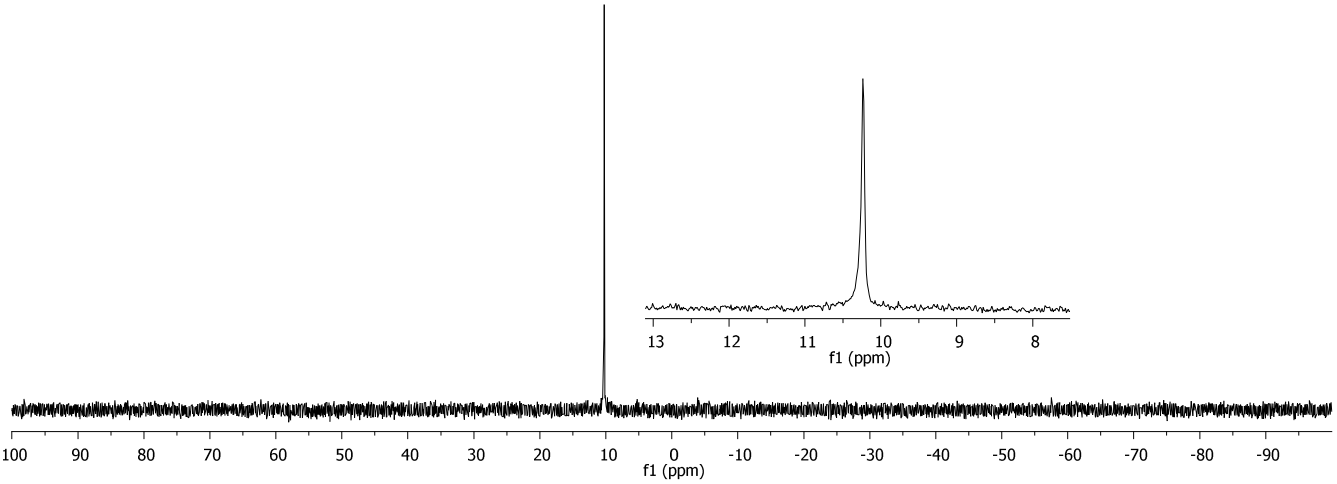
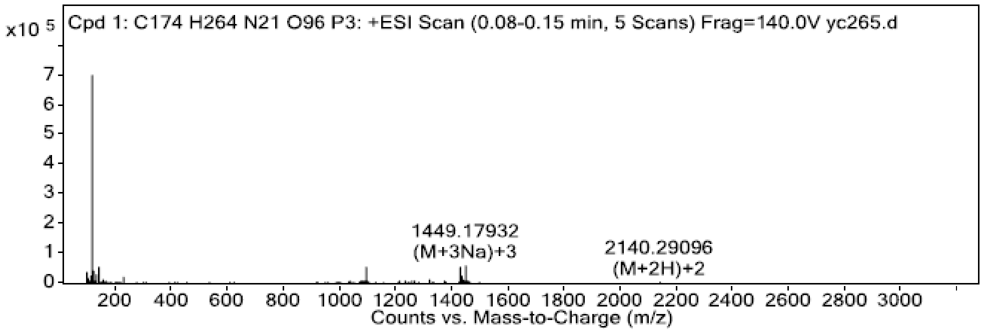
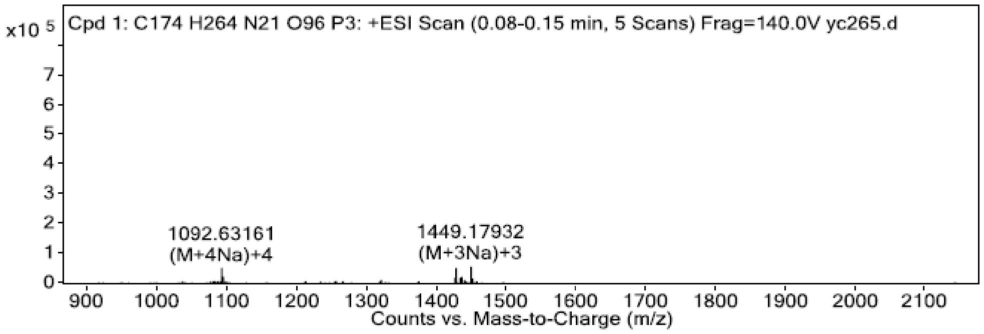


Figure S75. ^{31}P NMR spectrum of compound **18** (D_2O, 122MHz)

MS Spectrum



MS Zoomed Spectrum

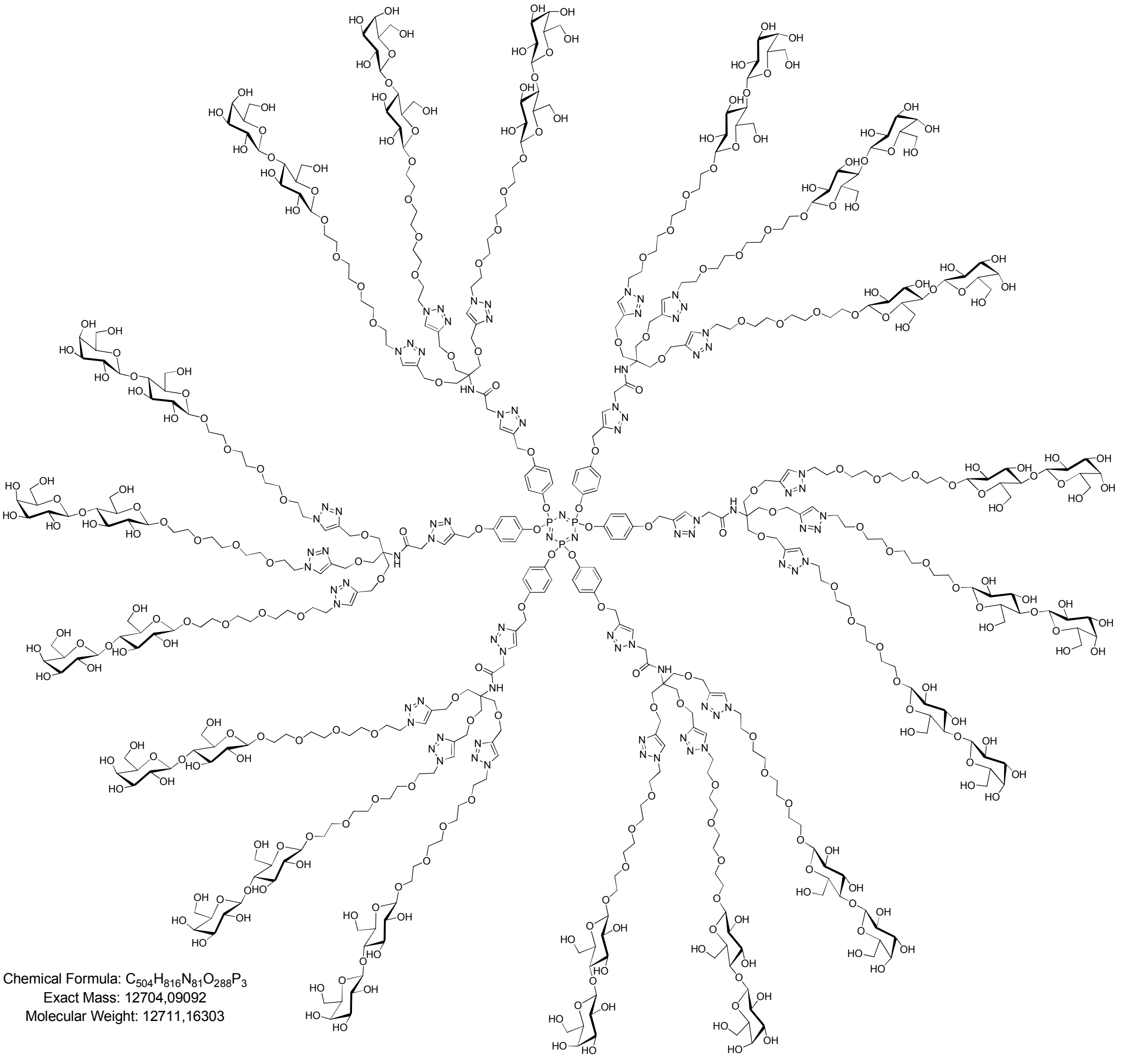


MS Spectrum Peak List

Ion	Formula	Abund	Observed m/z	Calc m/z	Diff (ppm)
(M+5Na)+5	C174H264N21Na5O96P3	963.12	878.30523	878.30191	3.78
(M+4H)+4	C174H268N21O96P3	2430.45	1070.14729	1070.14814	-0.79
(M+4Na)+4	C174H264N21Na4O96P3	22308.58	1092.12983	1092.13008	-0.23
(M+3H)+3	C174H267N21O96P3	21826.74	1426.5281	1426.52843	-0.23
(M+3Na)+3	C174H264N21Na3O96P3	26206.53	1448.50953	1448.51037	-0.58
(M+2H)+2	C174H266N21O96P3	1185.92	2139.28859	2139.289	-0.19
(M+2Na)+2	C174H264N21Na2O96P3	859.67	2161.26644	2161.27095	-2.08

Figure S76. ESI$^+$-HRMS spectrum of compound **18**

Hydroxylated octadecavalent glycodendrimer 19



Chemical Formula: $C_{504}H_{816}N_{81}O_{288}P_3$
Exact Mass: 12704,09092
Molecular Weight: 12711,16303

Acetylated compound **17** (60.0 mg, 3.33 µmol) was dissolved in a dry mixture of MeOH/DCM (5 mL, 4:1) and a solution of sodium methoxide (1M in MeOH, 5 µL every 20 minutes until precipitation) was added. An additional 100 µL was then injected and the heterogeneous reaction mixture was stirred at room temperature for 18 hours. The solvent was then removed with a Pasteur pipette and another dry mixture of MeOH/DCM (5 mL, 4:1) is added to the residual oil. A vigorous agitation is maintained for an additional 15 min. period. After removal of the solvents with a Pasteur pipette, 2 mL of dry MeOH were added to the viscous residue under agitation. After 15 min., the MeOH was removed and the residue was dissolved in 3 mL of H_2O, and the pH was adjusted to 7 with addition of ion-exchange resin (Amberlite IR 120 H^+). After filtration, the solvent was removed under *vacuum* with rotary evaporator, lyophilized to yield the fully deprotected derivative **19** as a white solid (39.0 mg, 3.07 µmol, **90%**).

^{1}**H NMR** (600 MHz, D_2O, δ ppm): 8.06-7.96 (m, 24H, H_{triazole}), 6.84-6.77 (m, 24H, CH_{ar}), 5.20-5.14 (m, 24H, NHCOCH_2N, C_qCH_2O), 4.57-4.50 (m, 72H, CH_2N, $C_{\text{q-triazole}}$CH_2O), 4.49-4.44 (m, 36H, H_{1glc}, H_{1gal}), 4.02-3.55 (m, 486, OCH_2CH_2N, H_{3glc}, H_{2gal}, H_{3gal}, H_{6bglc}, H_{6agal}, H_{6bgal}, H_{6aglc}, H_{5gal}, H_{5glc}, H_{4glc}, H_{4gal}, LacOCH_2CH_2, OCH_2, NHC$_q$$CH_2$O), 3.22 (t$_{app}$, 18H, H_{2glc}).

^{13}C NMR (150 MHz, CDCl$_3$, δ ppm): 167.1 (*C*ONH), 156.6 (C_a), 144.6 (C_d), 143.7 ($C_{triazole}$=CH), 127.0 (C$_{triazole}$=*C*H), 125.9 (C$_{triazole}$=*C*H), 122.4 (C_c), 116.3 (C_b), 103.6 (C_{1gal}), 102.8 (C_{1glc}), 79.1 (C_{4glc}), 76.0 (C_{3glc}), 75.4 (C_{5glc}), 75.0 (C_{5gal}), 73.5 (C_{2glc}), 73.2 (C_{3gal}), 71.6 (C_{2gal}), 70.3, 70.2, 70.2, 70.2, 70.1 (OCH_2), 69.3 (C_{4gal}), 69.2 (OCH_2), 68.1 (C$_q$$CH_2$O), 64.2 (O$CH_2$C=C), 62.0 ($C_q$), 61.7 ($C_{6glc}$), 60.9 ($C_{6gal}$), 60.8 (O$CH_2$), 52.9 (N$_{triazole}$$CH_2$CO), 50.6 ($CH_2$N).

^{31}P NMR (122 MHz, D$_2$O, δ ppm): 10.2 (s, 3P).

m/z (ESI$^+$-HRMS) for $C_{504}H_{816}N_{81}O_{288}P_3$ = 12712.2, found 12711.7 ([*M*+H]$^+$, after deconvolution).

NMR diffusion studies (D$_2$O): $D = 0.67\times10^{-10}$ m^2/s; d_s = 5.9 nm.

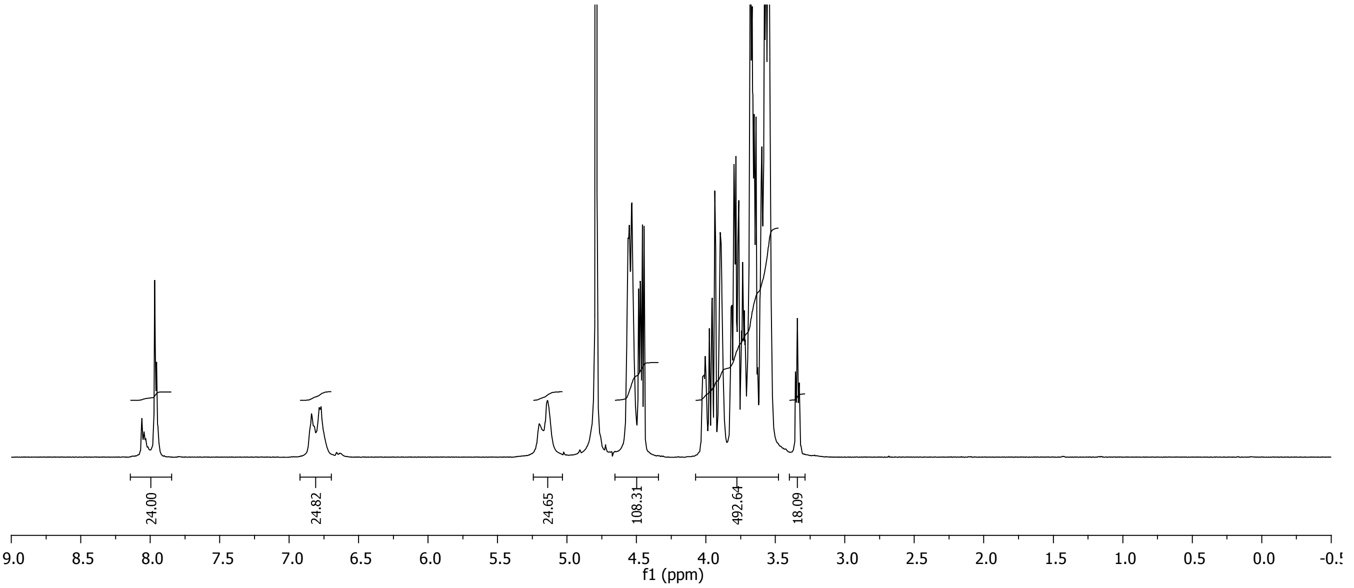


Figure S77. ^{1}H NMR spectrum of compound **19** (D$_2$O, 600MHz)

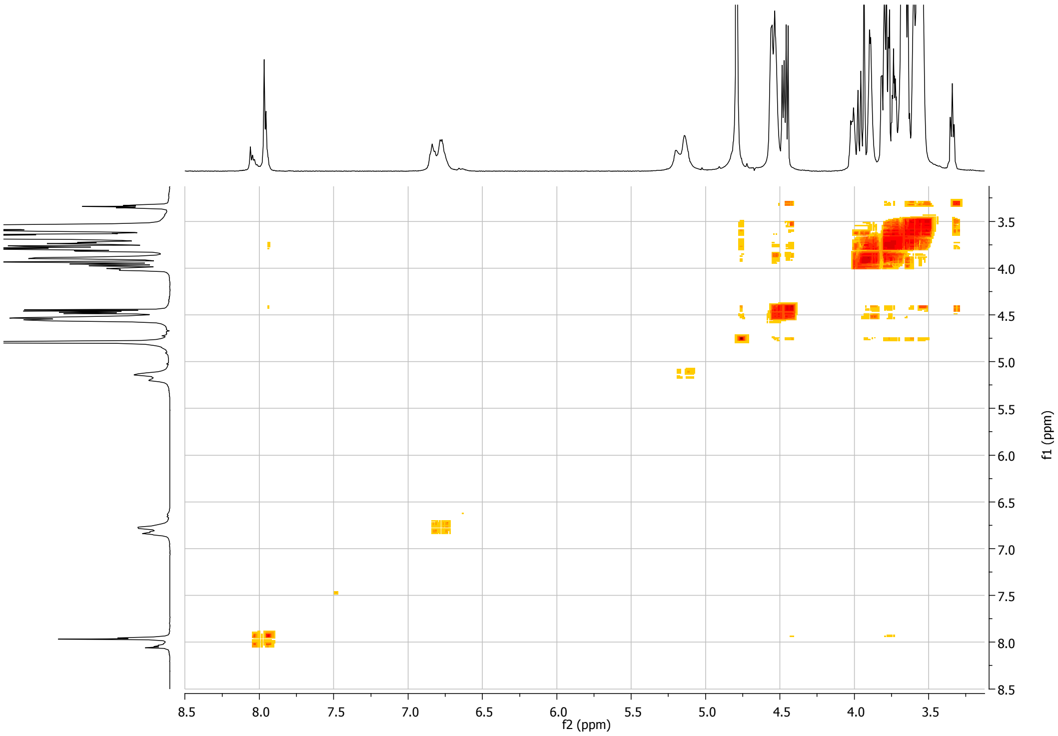


Figure S78. gCOSY spectrum of compound **19**

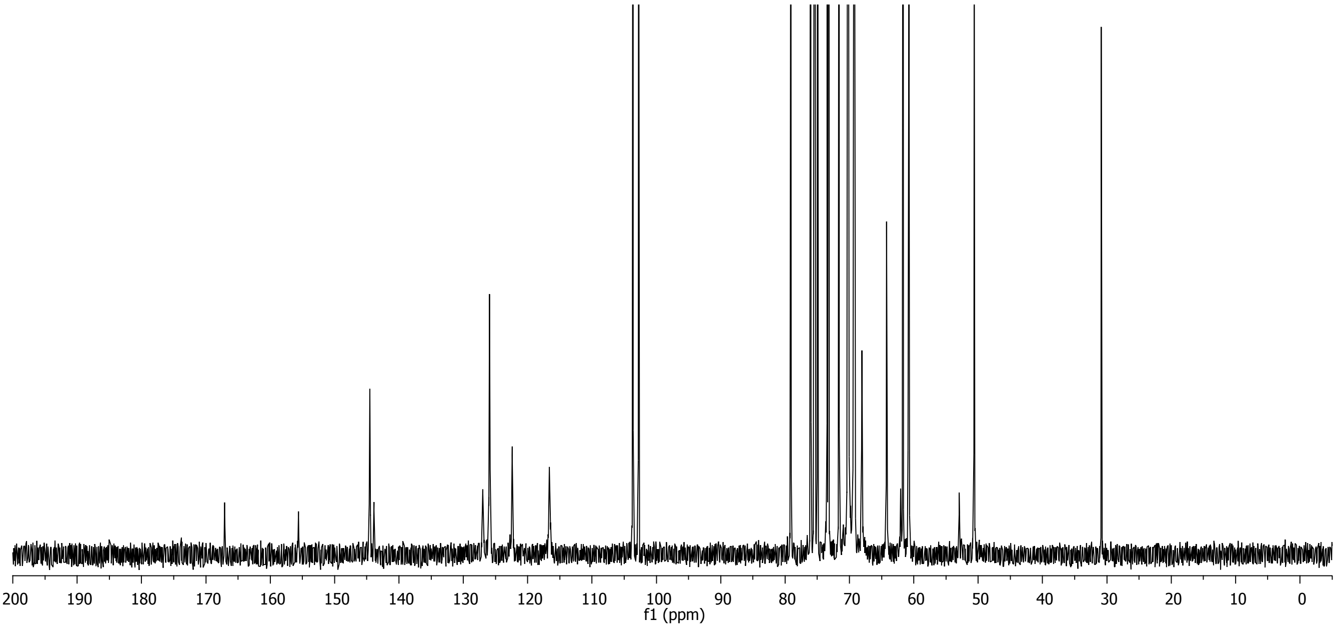


Figure S79. ^{13}C NMR spectrum of compound **19** (D_2O, 150MHz, acetone as reference)

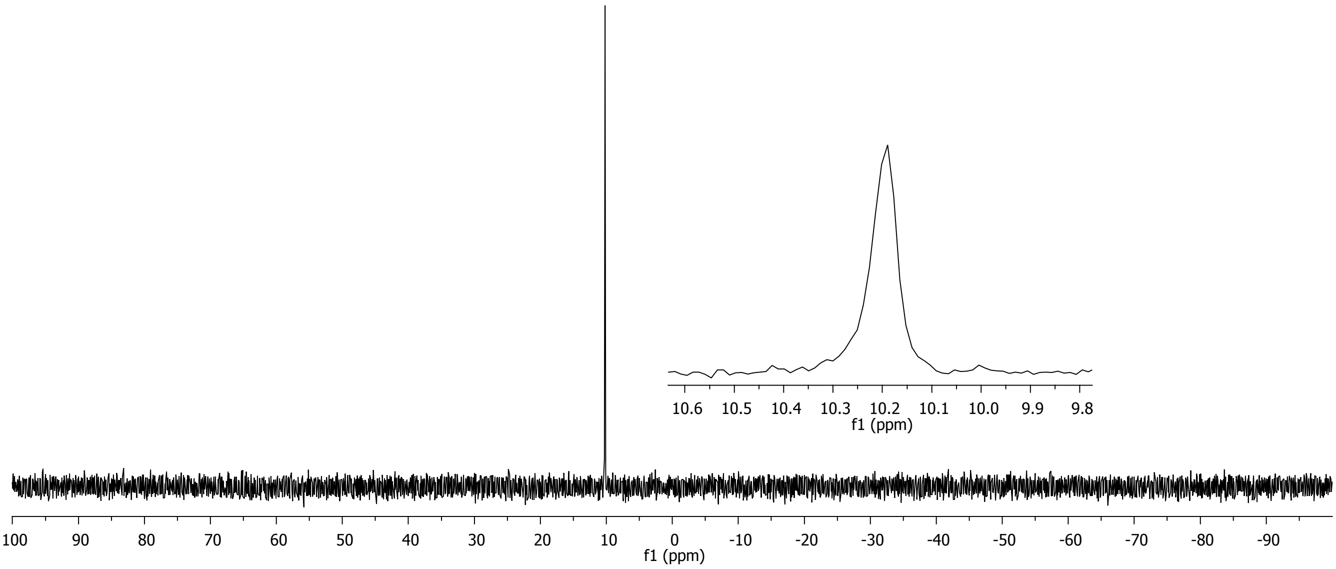


Figure S80. ^{31}P NMR spectrum of compound **19** (D_2O, 122MHz)

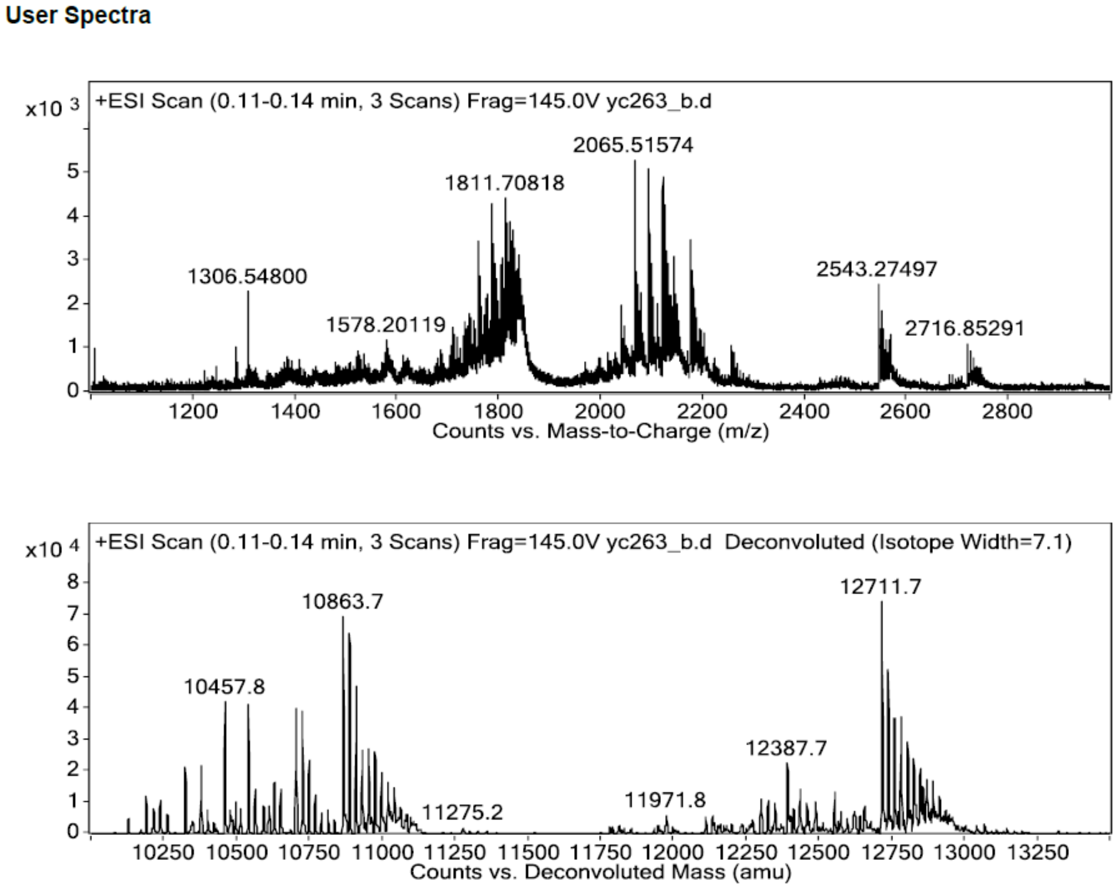
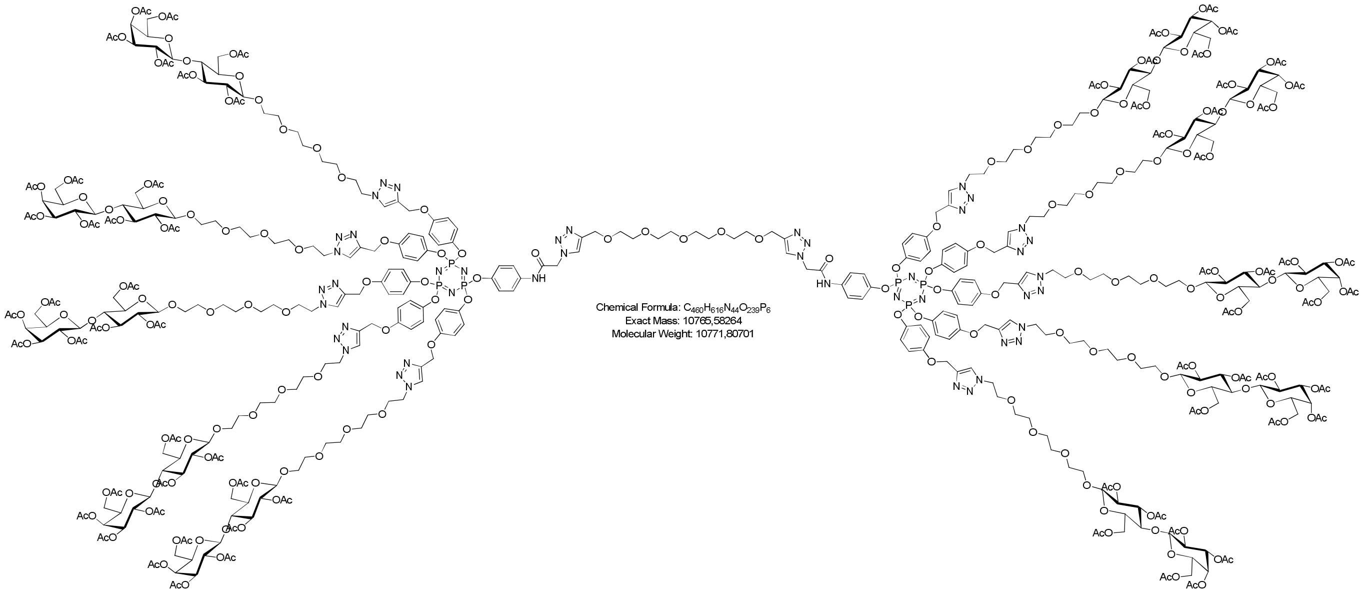


Figure S81. ESI$^+$-MS spectrum (deconvolution) of compound **19**

Protected dumbbell-shape decavalent glycocluster 21


Chemical Formula: $C_{460}H_{616}N_{44}O_{239}P_6$
Exact Mass: 10765,58264
Molecular Weight: 10771,80701

To a solution of known dipropargylated tretra(ethylene)glycol **20**[5] (1.52 mg, 5.63 µmol, 1.0 eq.) in a 1:1 mixture of H_2O/THF_{anh} (4 mL), were added azido dendron derivative **15** (65.0 mg, 12.4 µmol, 2.2 eq.), $CuSO_4{\cdot}5H_2O$ (8.4 mg, 33.0 µmol, 6.0 eq.) and sodium ascorbate (6.7 mg, 33.0 µmol, 6.0 eq.). While stirring, the mixture was first heated at 50℃ for 3 hours in a 20 mL vial and at room temperature for additional 18 hours. Ethyl acetate (15 mL) was added and the solution was poured into a separatory funnel containing ethyl acetate (10 mL), washed with saturated aqueous NH_4Cl (2×10 mL), water (10 mL) and brine (5 mL). Organics were collected, dried over Na_2SO_4 and concentrated to dryness *in vacuo* with rotary evaporator. Purification by flash chromatography (SiO_2, DCM/MeOH 100:0 to 85:15) afforded desired multivalent compound **21** (44.0 mg, 4.08 µmol, **73%**) as a yellowish foam.

$\mathbf{R_f}$ = 0.50, DCM/MeOH 90:10.
^{1}**H NMR** (600 MHz, $CDCl_3$, δ ppm): 10.12 (s, 2H, NH), 7.89 (s, 3H, H_{triazole}), 7.85-7.80 (2×s, 9H, H_{triazole}), 7.33 (d, ^3J = 8.6 Hz, 4H, C$H_{b'}$), 6.96-6.69 (m, 40H, CH_b, CH_c), 6.53 (d, ^3J = 8.6 Hz, 4H, C$H_{c'}$), 5.40 (br s, 4H, NCH_2CO), 5.30 (d_{app}, 10H, $H_{4\text{gal}}$), 5.18-5.07 (m, 40H, $H_{3\text{glc}}$, C_qCH_2O, $H_{2\text{gal}}$), 4.94 (dd, $^3J_{2,3}$ = 2.3 Hz, $^3J_{3,4}$ = 3.5 Hz, 10H, $H_{3\text{gal}}$), 4.84 (t_{app}, 10H, $H_{2\text{glc}}$), 4.64 (br s, 4H, $C_{\text{q-triazole}}$CH_2O), 4.55-4.46 (m, 50H, CH_2N, $H_{1\text{glc}}$, $H_{6\text{aglc}}$, $H_{1\text{gal}}$), 4.13-4.05 (m, 30H, $H_{6\text{bglc}}$, $H_{6\text{agal}}$, $H_{6\text{bgal}}$), 3.86-3.54 (m, 186H, $H_{5\text{gal}}$, $H_{5\text{glc}}$, $H_{4\text{glc}}$, OCH_2), 2.17-1.92 (7×s, 210H, COCH_3).
^{13}**C NMR** (75 MHz, $CDCl_3$, δ ppm): 170.2, 170.2, 170.0, 169.9, 169.6, 169.5, 169.0 (7×s, COCH$_3$), 164.0 (C=O), 155.3 + 155.2 (C_a), 146.6 ($C_{d'}$), 144.5 (C_d), 144.4 (C_d), 143.8 ($C_{triazole}$=CH), 143.5 ($C_{triazole}$=CH), 143.3 ($C_{triazole}$=CH), 134.5 ($C_{a'}$), 124.7 (CH$_{\text{triazole}}$), 124.7 (CH$_{\text{triazole}}$), 124.0 (CH$_{\text{triazole}}$), 121.9 (C_c), 121.8 (C_c), 121.7 ($C_{b'}$), 121.6 ($C_{c'}$), 120.9 ($C_{c'}$), 120.9 ($C_{c'}$), 120.7 ($C_{c'}$), 115.3 (C_b), 115.1 (C_b), 100.9 ($C_{1\text{gal}}$), 100.4 ($C_{1\text{glc}}$), 76.2 ($C_{4\text{glc}}$), 72.7 ($C_{3\text{glc}}$), 72.6 ($C_{5\text{glc}}$), 72.5 ($C_{2\text{glc}}$), 71.5 ($C_{3\text{gal}}$), 70.8 ($C_{5\text{gal}}$), 70.6, 70.5, 70.5, 70.4, 70.4, 70.3, 70.3, 70.3, 70.2, 70.1, 70.1, 69.4, 69.2, 69.2 (OCH$_2$),

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[5] X. Sheng, T. C. Mauldin and M. R. Kessler, *J. Polym. Sci.: Part A: Polym. Chem.*, 2010, **48**, 4093−4102.

68.9 ($C_{2\text{gal}}$), 68.9 (OCH_2), 66.5 ($C_{4\text{gal}}$), 64.3 ($C_{\text{q-triazole}}CH_2OCH_2$), 62.1 ($OCH_2C{=}C$), 61.8 ($C_{6\text{glc}}$), 61.6 ($C_{6\text{gal}}$), 60.6, 52.4 ($NHCOCH_2N_{\text{triazole}}$), 50.2 ($NCH_2$), 50.1 ($NCH_2$), 20.8, 20.7, 20.6, 20.5, 20.5, 20.4 (7×s, $COCH_3$).

^{31}P NMR (122 MHz, $CDCl_3$, δ ppm): 10.8-9.4 (m, 6P).

m/z (ESI$^+$-MS) for $C_{460}H_{616}N_{44}O_{239}P_6$= 10772.8 $[M{+}H]^+$; found 10772.5 (After deconvolution).

NMR diffusion studies ($CDCl_3$): $D = 2.47\times10^{-10}$ m^2/s; $d_s = 3.3$ nm.

GPC measurements (THF): $M_w = 14710$; $M_n = 13860$, PDI (M_w/M_n) = 1.061
($CHCl_3/Et_3N$ (1%)): $M_w = 10410$; $M_n = 10180$, PDI (M_w/M_n) = 1.023

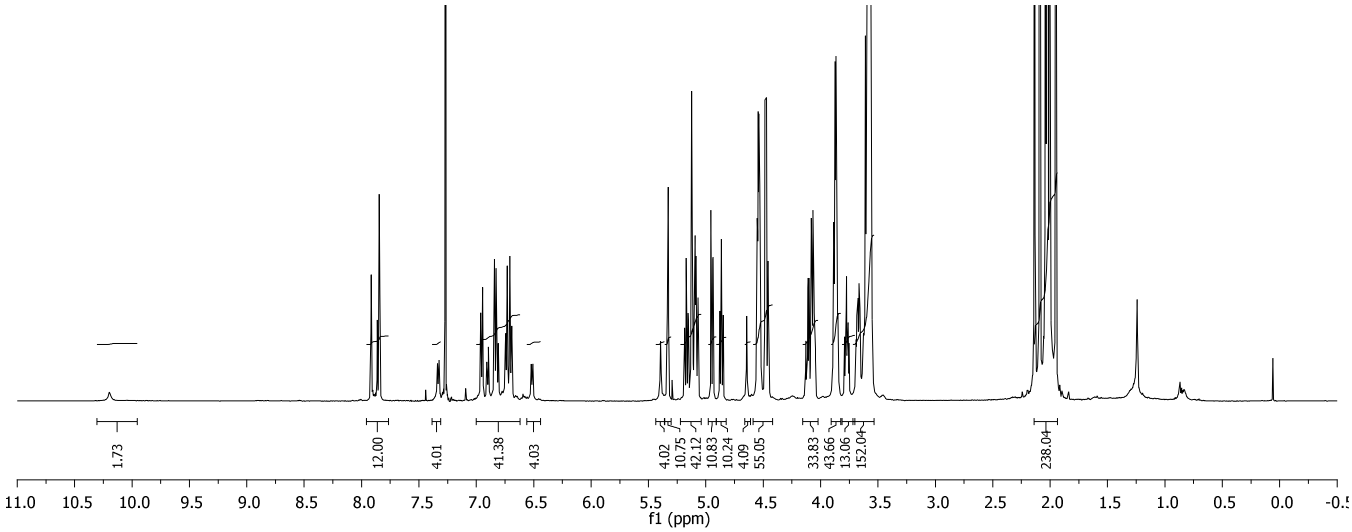


Figure S82. ^{1}H NMR spectrum of compound **21** ($CDCl_3$, 600MHz)

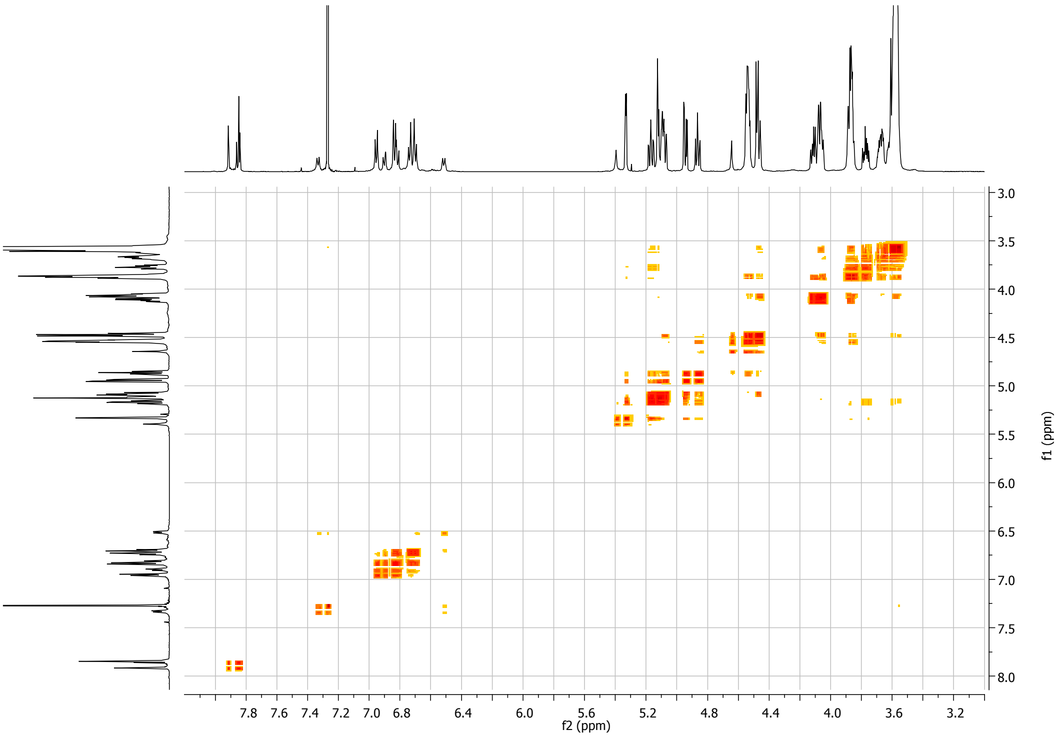


Figure S83. gCOSY spectrum of compound **21**

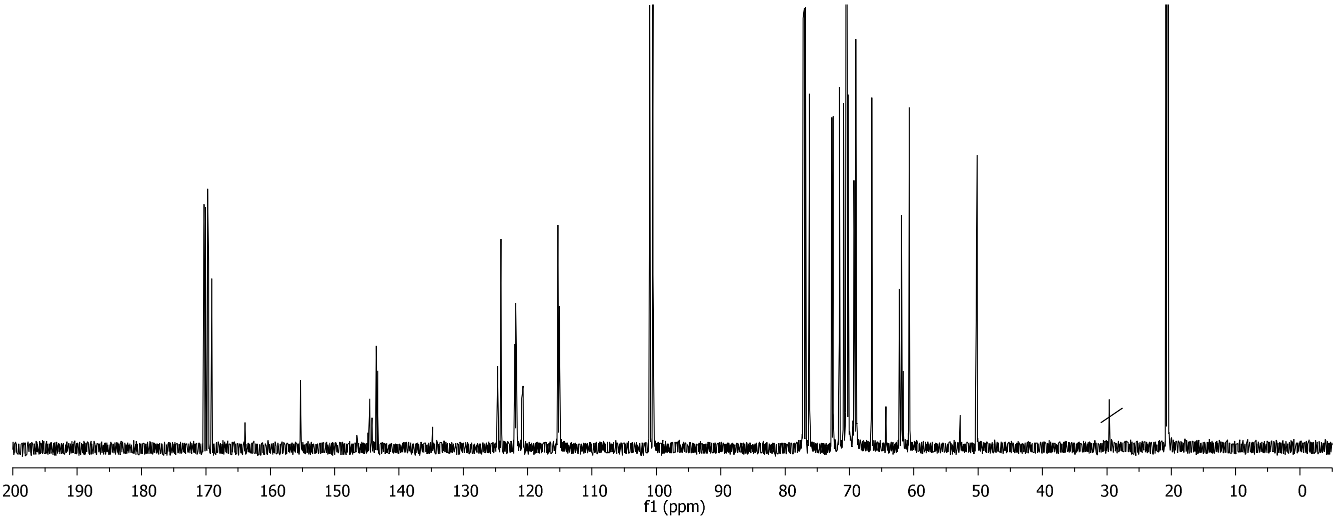


Figure S84. ^{13}C NMR spectrum of compound **21** ($CDCl_3$, 150MHz)

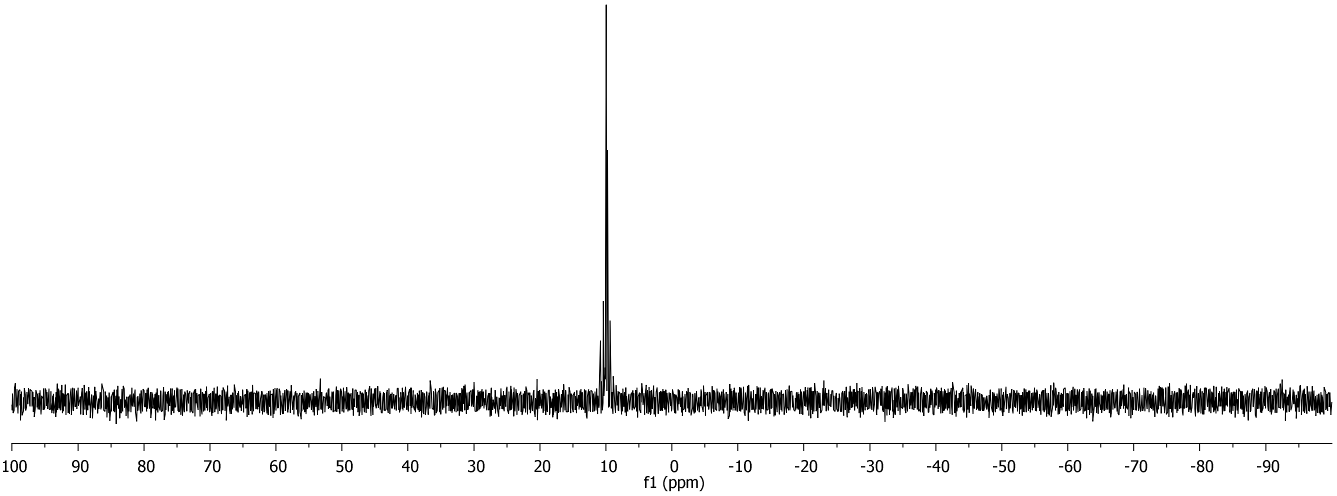


Figure S85. ^{31}P NMR spectrum of compound **21** ($CDCl_3$, 122MHz)

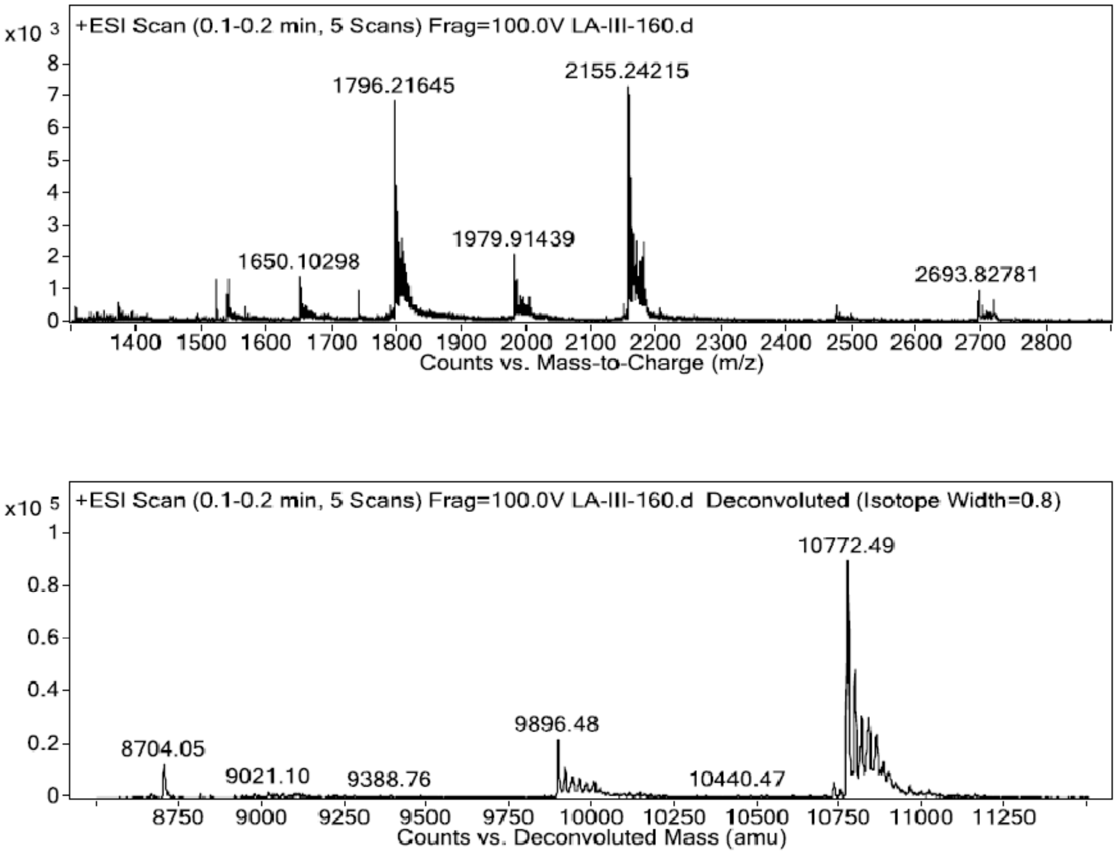
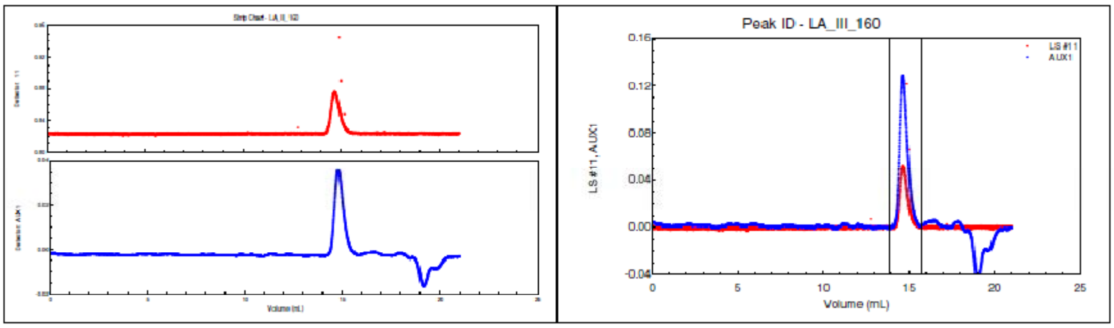
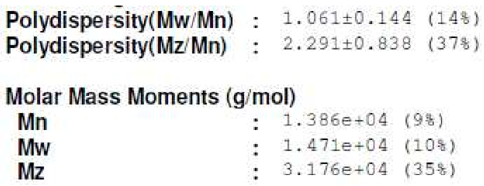


Figure S86. ESI$^+$-MS spectrum (deconvolution) of compound **21**

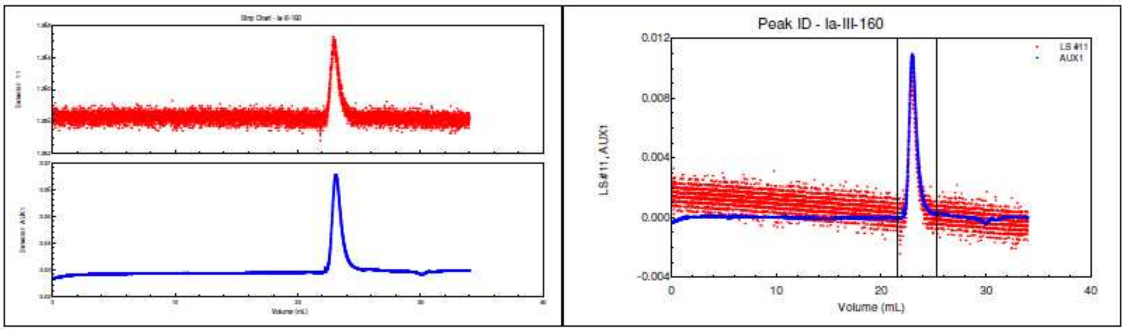




```
Polydispersity(Mw/Mn)  :  1.061±0.144 (14%)
Polydispersity(Mz/Mn)  :  2.291±0.838 (37%)

Molar Mass Moments (g/mol)
 Mn                    :  1.386e+04 (9%)
 Mw                    :  1.471e+04 (10%)
 Mz                    :  3.176e+04 (35%)
```

Figure S87. GPC trace (in THF) for compound **21**

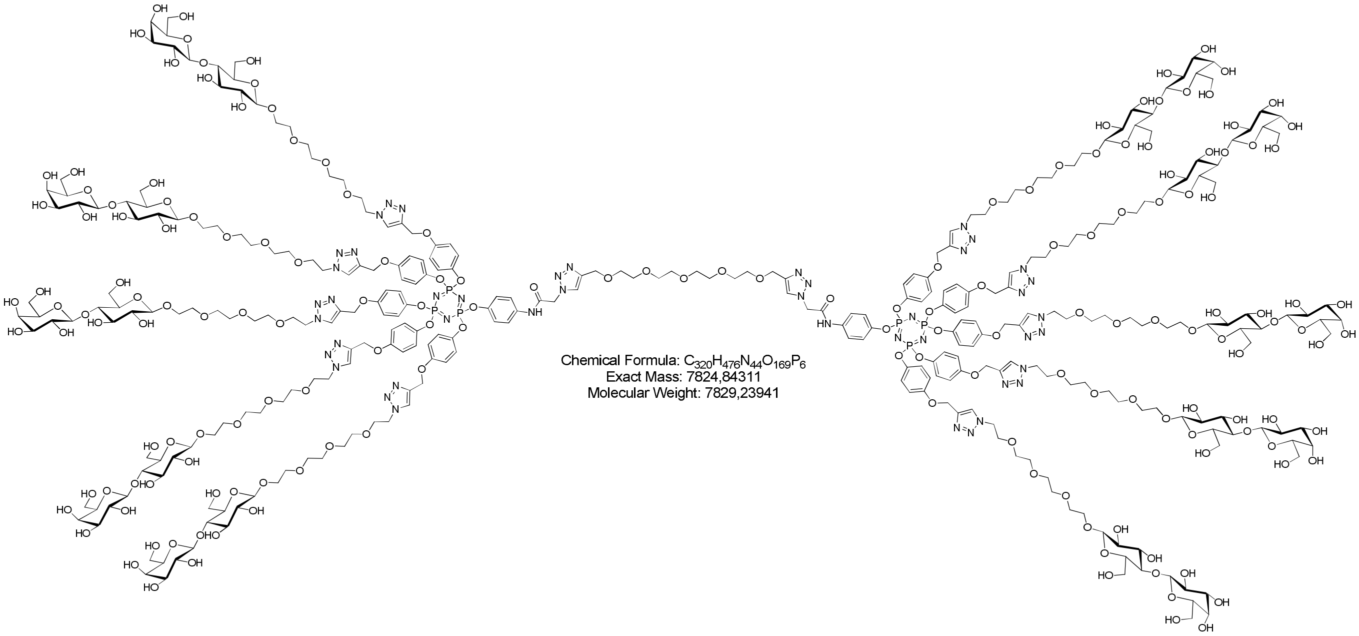


```
Polydispersity(Mw/Mn)  :  1.023±0.187 (18%)
Polydispersity(Mz/Mn)  :  1.051±0.333 (32%)

Molar Mass Moments (g/mol)
 Mn                    :  1.018e+04 (13%)
 Mw                    :  1.041e+04 (12%)
 Mz                    :  1.070e+04 (28%)
```

Figure S88. GPC trace (in $CHCl_3/Et_3N$ (1%)) for compound **21**

Hydroxylated dumbbell-shape decavalent glycocluster 22



Chemical Formula: $C_{320}H_{476}N_{44}O_{169}P_6$
Exact Mass: 7824,84311
Molecular Weight: 7829,23941

Acetylated compound **21** (28.0 mg, 2.60 µmol) was dissolved in a dry mixture of MeOH/DCM (5 mL, 4:1) and a solution of sodium methoxide (1M in MeOH, 5 µL every 20 minutes until precipitation) was added. An additional 100 µL was then injected and the heterogeneous reaction mixture was stirred at room temperature for 18 hours. The solvent was then removed with a Pasteur pipette and another dry mixture of MeOH/DCM (5 mL, 4:1) is added to the residual oil. A vigorous agitation is maintained for an additional 15 min. period. After removal of the solvents with a Pasteur pipette, 2 mL of dry MeOH were added to the viscous residue under agitation. After 15 min., the MeOH was removed and the residue was dissolved in 3 mL of H_2O, and the pH was adjusted to 7 with addition of ion-exchange resin (Amberlite IR 120 H^+). After filtration, the solvent was removed under *vacuum* with rotary evaporator, lyophilized to yield the fully deprotected derivative **22** as an off-white solid (18.5 mg, 2.55 µmol, **98%**).

^{1}H NMR (600 MHz, D_2O, δ ppm): 7.99 (s, 12H, H_{triazole}), 7.28 (br s, 4H, $CH_{b'}$), 6.75-6.50 (m, 44H, CH_{ar}), 5.29 (br s, 4H, NCH_2CO), 4.96 (br s, 20H, C_qCH_2O), 4.53-4.39 (m, 44H, $N_{\text{triazole}}CH_2CH_2$, $C_{\text{q-triazole}}CH_2O$, $H_{1\text{glc}}$, $H_{1\text{gal}}$), 3.90 (m, 30H, OCH_2CH_2N, $\text{LacOCH}H\text{CH}_2$), 3.82-3.47 (m, 236H, $H_{3\text{glc}}$, $H_{2\text{gal}}$, $H_{3\text{gal}}$, $H_{6\text{bglc}}$, $H_{4\text{gal}}$, $H_{6\text{agal}}$, $H_{6\text{bgal}}$, $H_{6\text{aglc}}$, $H_{5\text{gal}}$, $H_{5\text{glc}}$, $H_{4\text{glc}}$, $\text{LacOCH}H\text{CH}_2$, OCH_2), 3.33 (t_{app}, 10H, $H_{2\text{glc}}$).

^{13}C NMR (75 MHz, D_2O, δ ppm): 165.3 (C=O), 156.3 (C_a), 144.8 ($C_{d'}$), 144.5 (C_d), 143.7 ($C_{triazole}$=CH), 143.7 ($C_{triazole}$=CH), 126.8 ($C_{a'}$), 125.9 (C_{triazole}=CH), 122.4 (C_{triazole}=CH), 121.8 ($C_c + C_{b'} + C_{c'}$), 116.2 (C_b), 115.1 (C_b), 103.7 ($C_{1\text{gal}}$), 102.8 ($C_{1\text{glc}}$), 79.1 ($C_{4\text{glc}}$), 76.0 ($C_{3\text{glc}}$), 75.4 ($C_{5\text{glc}}$), 75.0 ($C_{5\text{gal}}$), 73.5 ($C_{2\text{glc}}$), 73.2 ($C_{3\text{gal}}$), 71.6 ($C_{2\text{gal}}$), 70.3, 70.2, 70.0, 69.4, (OCH_2), 69.3 ($C_{4\text{gal}}$), 69.2 (OCH_2), 63.8 ($C_{\text{q-triazole}}CH_2OCH_2$), 62.0 ($OCH_2C$=C), 61.7 ($C_{6\text{glc}}$), 60.7 ($C_{6\text{gal}}$), 53.2 ($N_{\text{triazole}}CH_2CO$), 50.7 ($NCH_2$).

^{31}P NMR (122 MHz, D_2O, δ ppm): 10.2 (s, 6P).

m/z (ESI^+-MS) for $C_{320}H_{476}N_{44}O_{169}P_3$ = 7830.3 $[M\text{+H}]^+$, found 7829.9 (After deconvolution).

NMR diffusion studies (D_2O): $D = 0.75\times10^{-10}$ m^2/s; d_s = 5.3 nm.

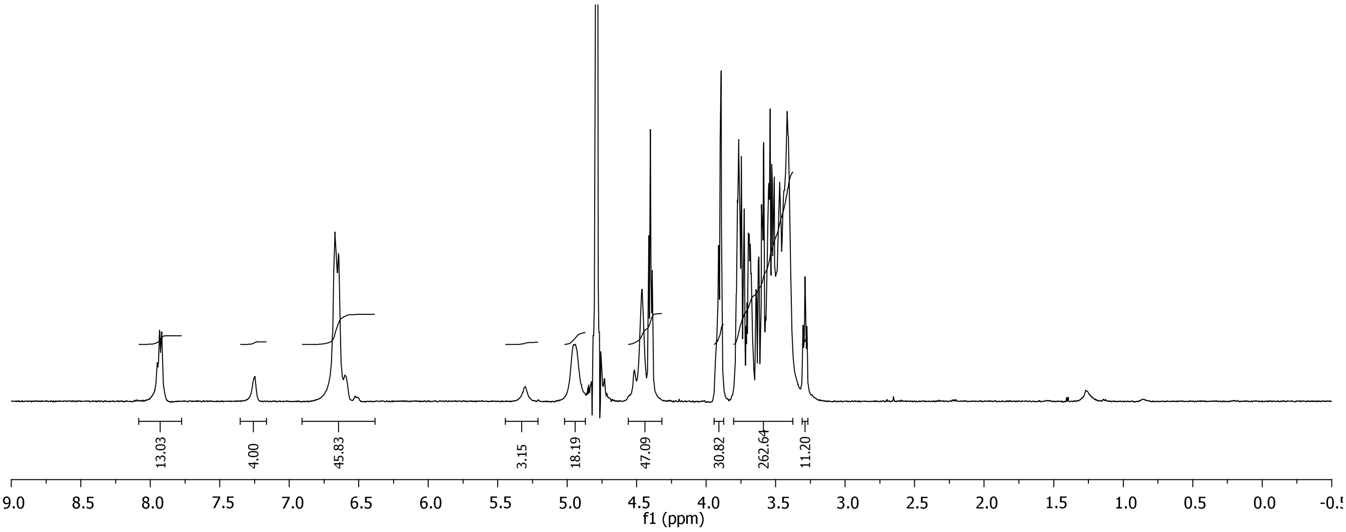


Figure S89. ^{1}H NMR spectrum of compound **22** (D_2O, 600MHz)

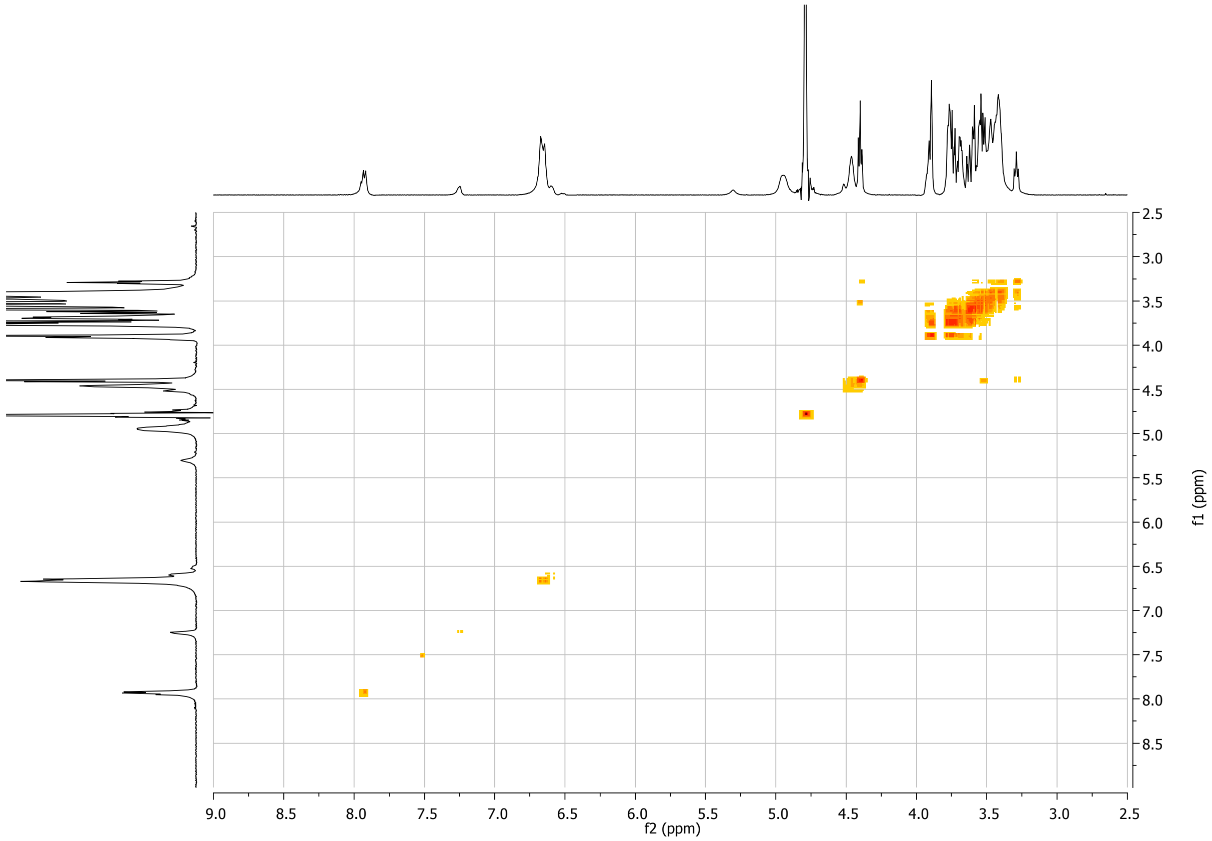


Figure S90. gCOSY spectrum of compound **22**

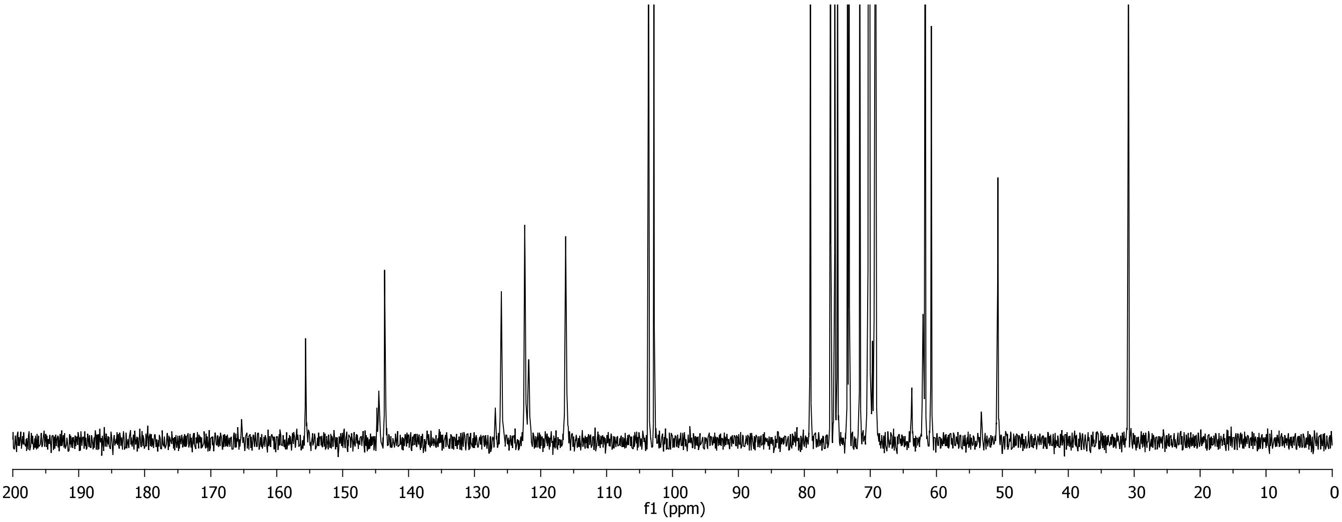


Figure S91. ^{13}C NMR spectrum of compound **22** (D_2O, 75MHz, acetone as reference)

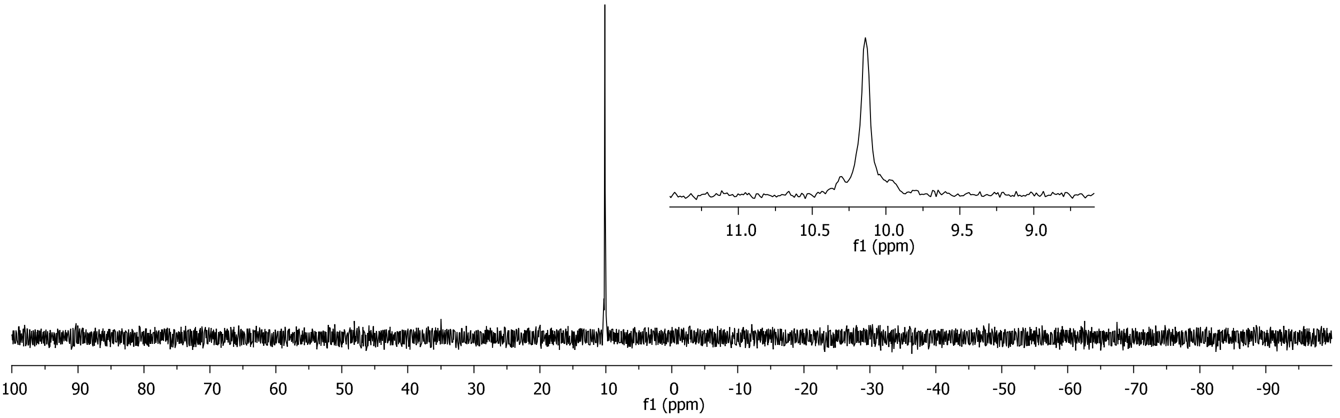


Figure S92. ^{31}P NMR spectrum of compound **22** (D_2O, 122MHz)

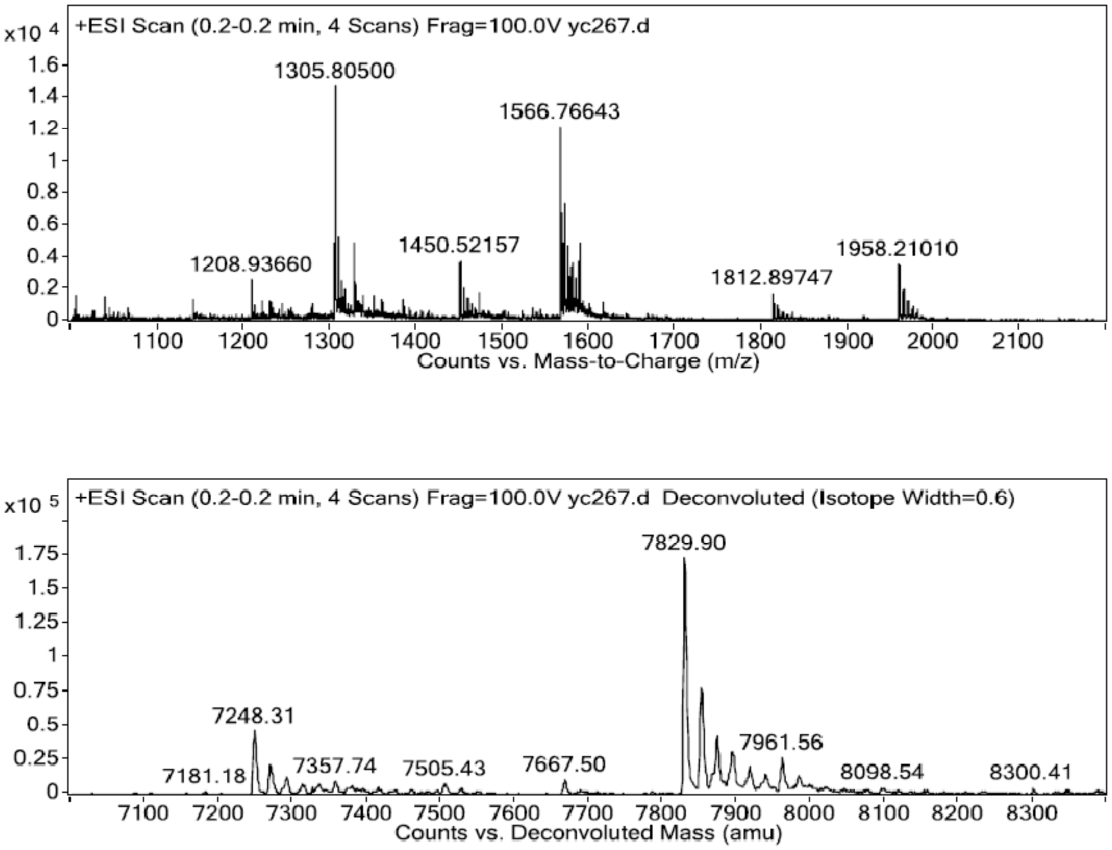
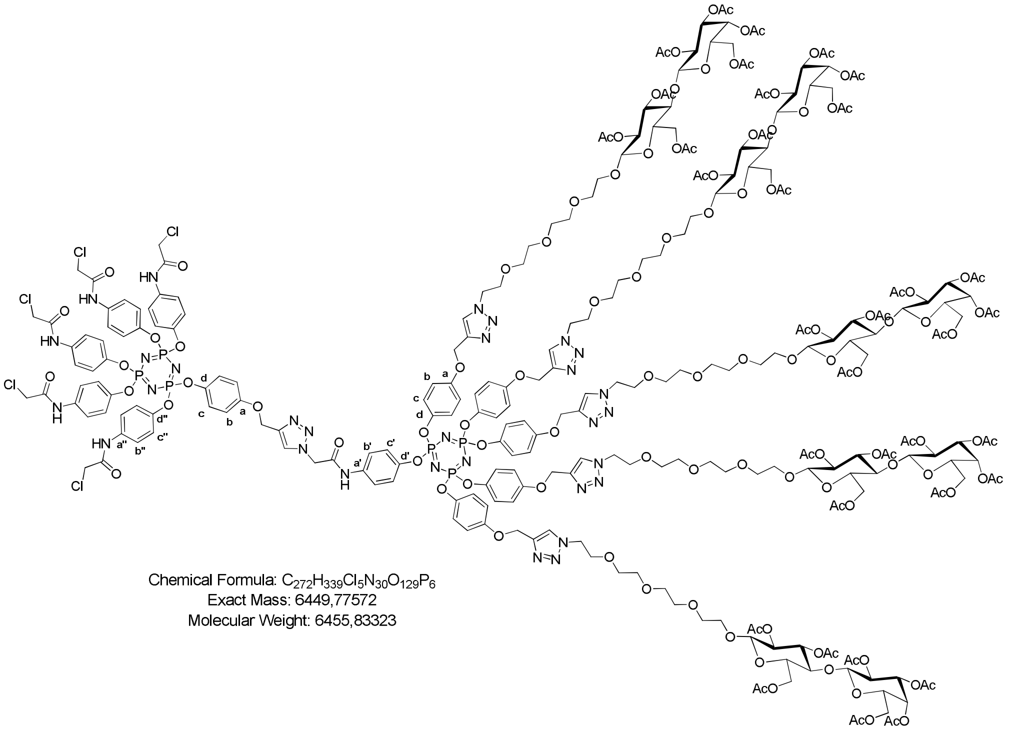


Figure S93. ESI$^+$-MS spectrum (deconvolution) of compound **22**

Heteromultifunctional Janus-type glycocluster 23



Chemical Formula: $C_{272}H_{339}Cl_5N_{30}O_{129}P_6$
Exact Mass: 6449,77572
Molecular Weight: 6455,83323

To a solution of propargylated derivative **9** (11.4 mg, 9.46 µmol, 1.1 eq.) in a 1:1 mixture of H_2O/THF_{anh} (4 mL), were added azido dendron **15** (45.0 mg, 8.57 µmol, 1.0 eq.), $CuSO_4{\cdot}5H_2O$ (23.0 mg, 92.0 µmol, 11.1 eq.) and sodium ascorbate (11.9 mg, 92.0 µmol, 11.1 eq.). While stirring, the mixture was first heated at 50℃ for 3 hours in a 20 mL vial and at room temperature for additional 18 hours. Ethyl acetate (15 mL) was added and the solution was poured into a separatory funnel containing ethyl acetate (10 mL), washed with saturated aqueous NH_4Cl (2×10 mL), water (10 mL) and brine (5 mL). Organics were collected, dried over Na_2SO_4 and concentrated to dryness *in vacuo* with rotary evaporator. Purification by flash chromatography (SiO_2, DCM/MeOH 100:0 to 85:15) afforded desired multivalent compound **23** (40 mg, 6.2 µmol, **72%**) as an off-white foam

R_f = 0.29, DCM/MeOH 94:6.

^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 10.24 (s, 1H, NH_{core}), 8.96 (s, 2H, NH_{ext}), 8.60 (s, 2H, NH_{ext}), 8.59 (s, 1H, NH_{ext}), 8.05 (s, 1H, $H_{triazole\ int}$), 7.90 (s; 2H, $H_{triazole\ ext}$), 7.85 (s, 1H, $H_{triazole\ ext}$), 7.84 (s, 2H, $H_{triazole\ ext}$), 7.32 (d, 2H, C$H_{b'}$, ^3J = 8.6 Hz), 7.23 (m, 10H, C$H_{b''}$), 6.98 (d, 2H, C$H_{c'}$), 6.91-6.44 (m, 34H, CH_b, CH_c, C$H_{c''}$), 5.46 (s, 2H, $N_{triazole}CH_2$CONH), 5.33 (br s, 5H, H_{4gal}), 5.18-5.08 (m, 22H, H_{3glc}, $C_{q\ triazole}CH_2O$, H_{2gal}), 4.94 (d_{app}, 5H, H_{3gal}), 4.86 (m, 5H, H_{2glc}), 4.55-4.46 (m, 25H, CH_2N, H_{1glc}, H_{6aglc}, H_{1gal}), 4.22 (s, 6H; CH_2Cl), 4.18 (s, 4H; CH_2Cl), 4.11-4.06 (m, 15H, H_{6bglc}, H_{6agal}, H_{6bgal}), 3.87-3.57 (m, 85H, H_{5gal}, H_{5glc}, H_{4glc}, OCH_2), 2.13-1.95 (m, 105H, COCH_3).

^{13}C NMR (150 MHz, $CDCl_3$, δ ppm): 170.3, 170.2, 170.0, 169.9, 169.6, 169.5, 169.0 (7×s, *C*OCH$_3$), 164.6 (*C*ONH), 164.5 (*C*ONH), 163.8 (*C*=O), 155.3 ($C_{a''}$), 155.2 + 155.2 (C_a), 147.0 ($C_{d''}$), 146.8 ($C_{d'}$), 144.5 (C_d), 144.5 ($C_{d''}$), 144.2 (C_d), 143.8 ($C_{triazole\ int}$=CH), 143.7 ($C_{triazole}$=CH), 143.2 ($C_{triazole}$=CH), 134.6 ($C_{a''}$), 134.5 ($C_{a'}$), 124.7 ($C_{triazole\ int}$=*C*H), 124.4 ($C_{triazole}$=*C*H), 124.0 ($C_{triazole}$=*C*H), 122.0 ($C_{b''}$), 121.9 ($C_{b''}$),121.9 (C_c), 121.8 (C_c), 121.7 ($C_{b'}$), 121.6 ($C_{c'}$), 121.2

($C_{c'}$), 121.1 ($C_{c'}$), 120.9 ($C_{c'}$), 120.4 ($C_{c''}$), 120.3 ($C_{c''}$), 115.3 (C_b), 115.2 (C_b), 115.0 (C_b), 100.9 (C_{1gal}), 100.4 (C_{1glc}), 76.1 (C_{4glc}), 72.6 (C_{3glc}), 72.5 (C_{5glc}), 72.4 (C_{2glc}), 71.5 (C_{3gal}), 70.8 (C_{5gal}), 70.5, 70.4, 70.4, 70.3, 70.3, 70.3, 70.1, 70.1, 69.2, 69.2 (OCH$_2$), 68.9 (C_{2gal}), 68.9 (OCH$_2$), 66.5 (C_{4gal}), 62.1 (OCH$_2$C=C), 61.8 (C_{6glc}), 61.6 (C_{6gal}), 60.6 (OCH$_2$), 52.9 (N$_{triazole}$$CH_2$CONH), 50.3 (N$CH_2$), 50.2 (N$CH_2$), 43.2 ($CH_2$Cl), 43.1 ($CH_2$Cl), 20.7, 20.7, 20.6, 20.5, 20.5, 20.4 (7×s, COCH$_3$).

^{31}P NMR (122 MHz, CDCl$_3$, δ ppm): 10.9-8.5 (m, 6P, *P*-O).

m/z (ESI$^+$-HRMS) for $C_{272}H_{339}Cl_5N_{30}O_{129}P_6$= 1636.6848 [$M$+4Na]$^{4+}$; found 1636.6855, 2151.9342 [M+3Na]$^{3+}$, found 2151.9363.

GPC measurements (THF): M_w = 7981 ; M_n = 7889 , PDI (M_w/M_n) = 1.012.

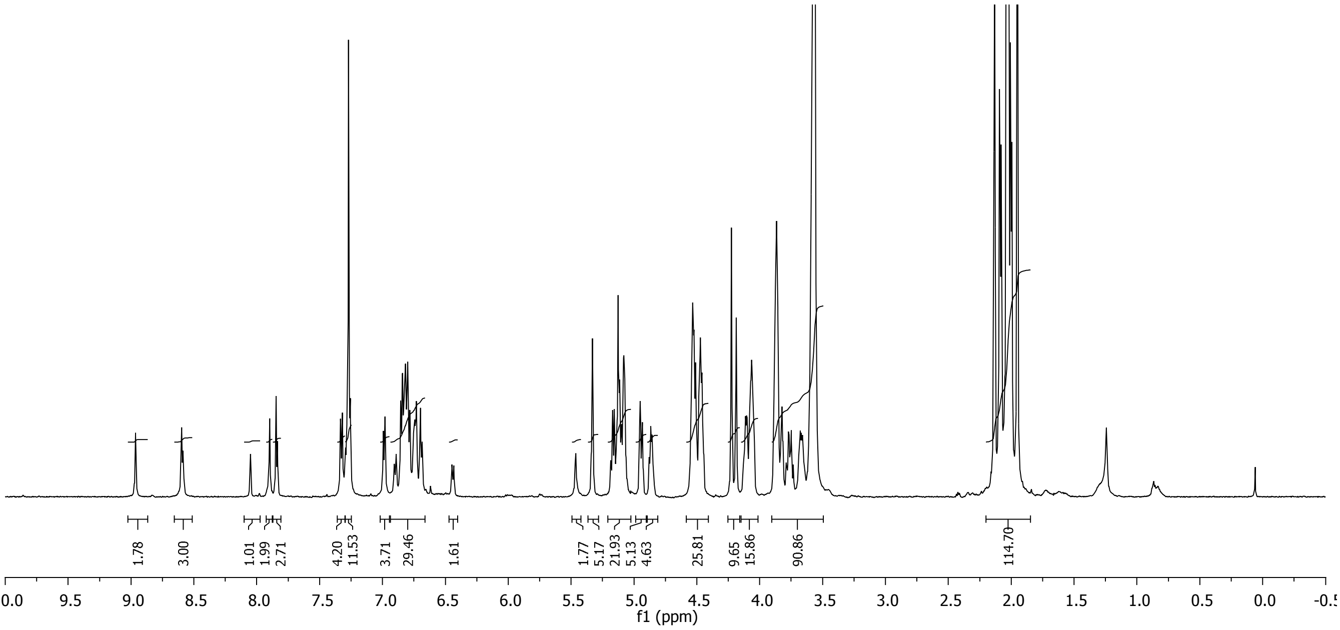


Figure S94. ^{1}H NMR spectrum of compound **23** (CDCl$_3$, 600MHz)

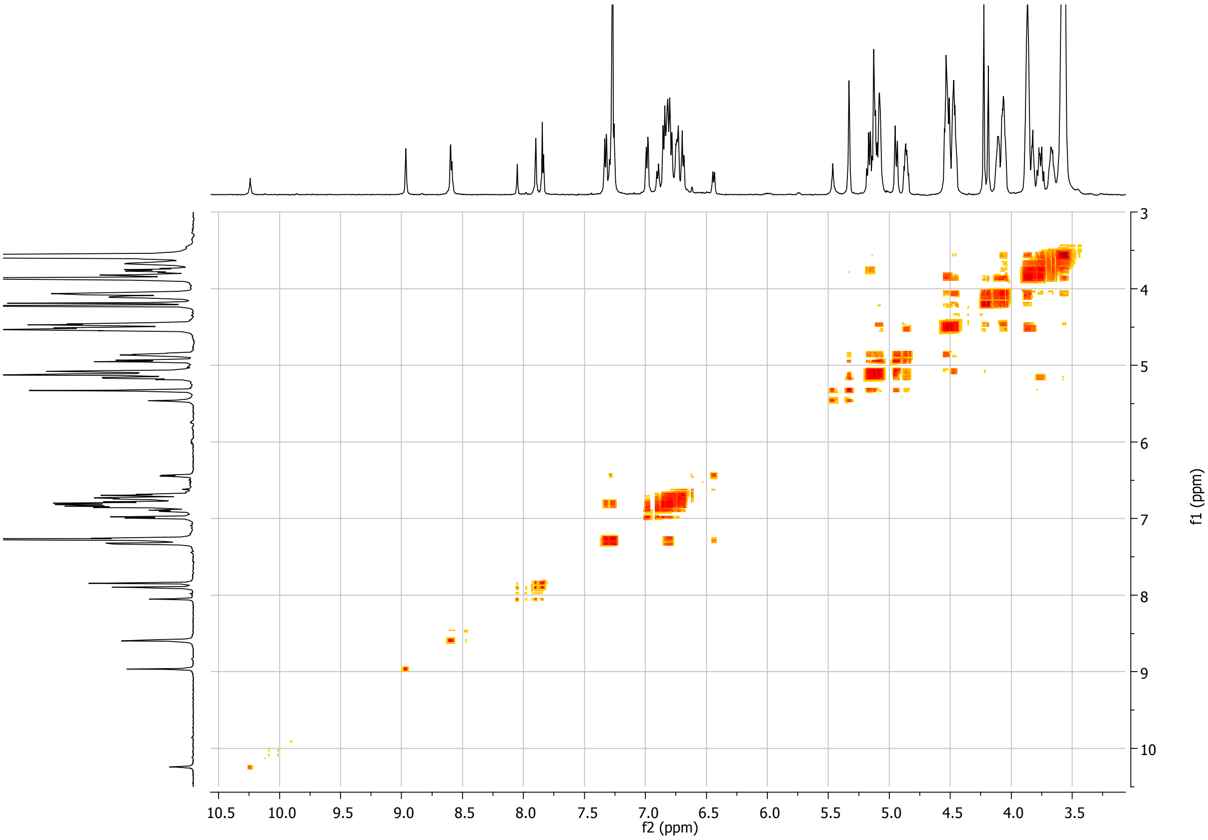


Figure S95. gCOSY spectrum of compound **23**

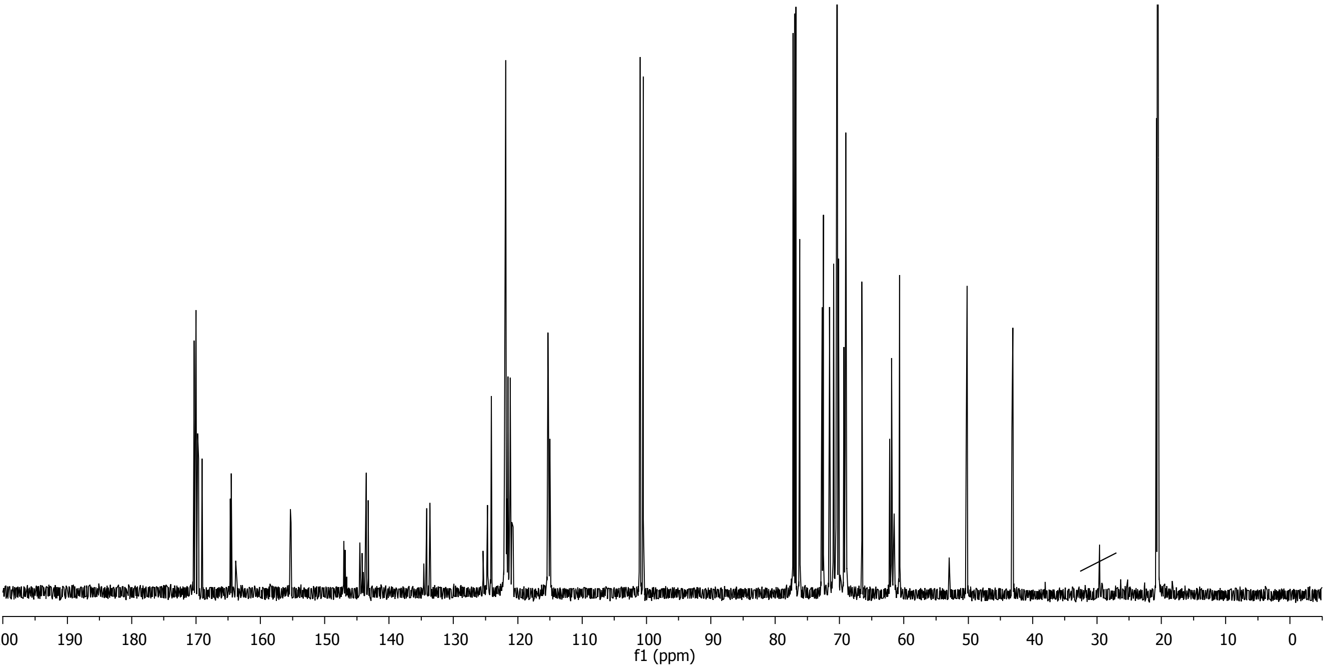


Figure S96. ^{13}C NMR spectrum of compound **23** (CDCl$_3$, 150MHz)

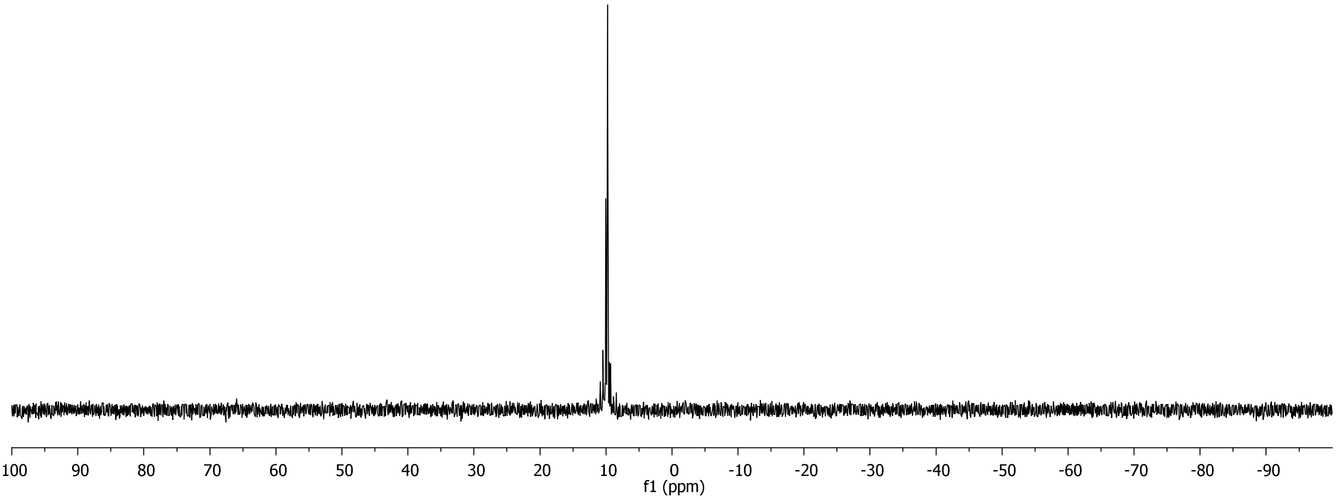
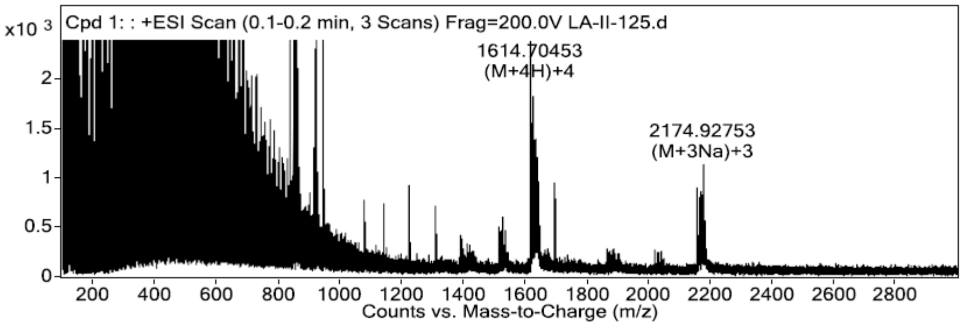
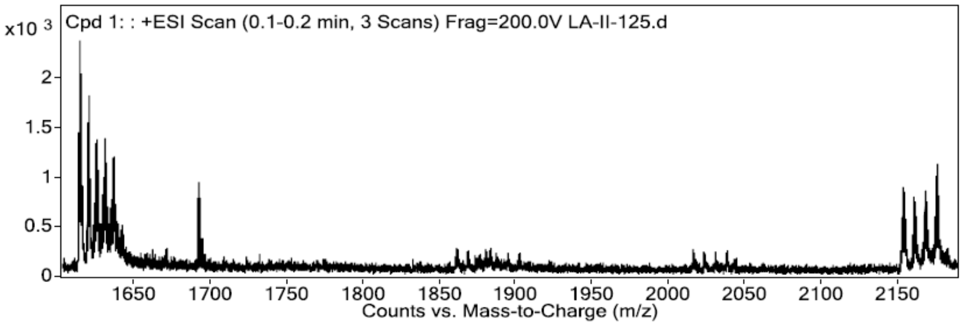


Figure S97. ^{31}P NMR spectrum of compound **23** ($CDCl_3$, 122MHz)

MS Spectrum



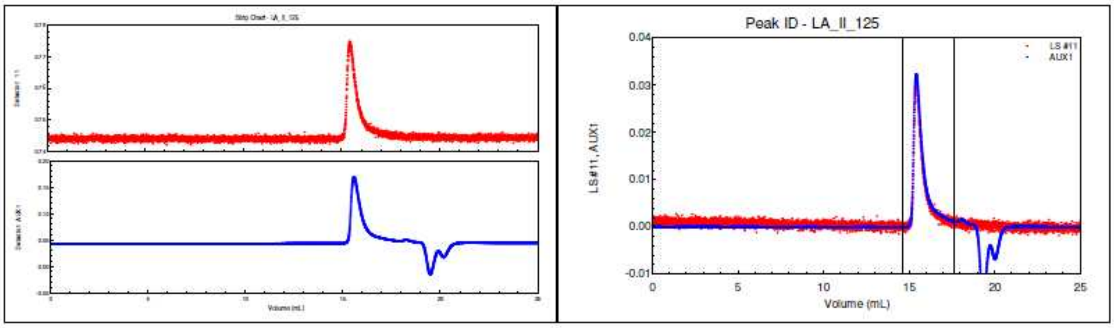
MS Zoomed Spectrum

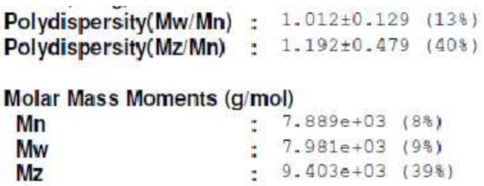


MS Spectrum Peak List

Ion	Formula	Abund	Observed m/z	Calc m/z	Diff(ppm)
(M+4Na)+4	C272H339Cl5N30Na4O129P6	1052.5	1636.68549	1636.68481	0.68
(M+3H)+3	C272H342Cl5N30O129P6	576.1	2151.93629	2151.93423	2.07
(M+3Na)+3	C272H339Cl5N30Na3O129P6	849.8	2173.91742	2173.91617	1.25

Figure S98. ESI^{+}-HRMS spectrum of compound **23**



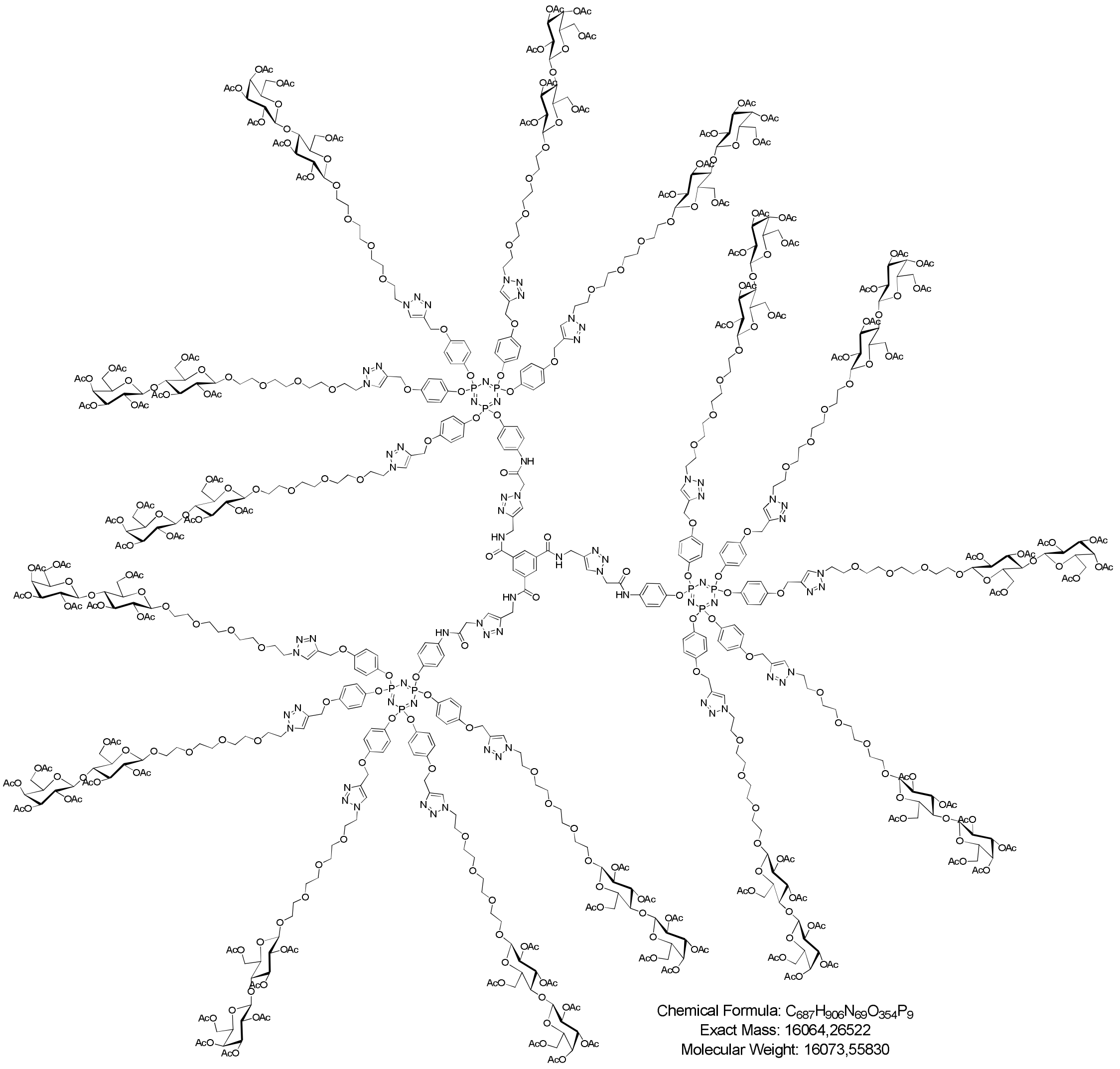


```
Polydispersity(Mw/Mn)  :  1.012±0.129 (13%)
Polydispersity(Mz/Mn)  :  1.192±0.479 (40%)

Molar Mass Moments (g/mol)
 Mn                    :  7.889e+03 (8%)
 Mw                    :  7.981e+03 (9%)
 Mz                    :  9.403e+03 (39%)
```

Figure S99. GPC trace (in THF) for compound **23**

Protected pentadecavalent glycodendrimer 25



Chemical Formula: $C_{687}H_{906}N_{69}O_{354}P_9$
Exact Mass: 16064,26522
Molecular Weight: 16073,55830

To a solution of known tripropargylated core **24**[6] (1.27 mg, 3.91 µmol, 1.0 eq.) in a 1:1 mixture of $H_2O/THF_{anh.}$ (4 mL), were added azido dendron derivative **15** (80 mg, 0.015 mmol, 3.9 eq.), $CuSO_4 \cdot 5H_2O$ (7.8 mg, 0.031 mmol, 8.0 eq.) and sodium ascorbate (6.2 mg, 0.031 mmol, 8.0 eq.). While stirring, the mixture was first heated at 50℃ for 3 hours in a 20 mL vial and at room temperature for additional 18 hours. Ethyl acetate (15 mL) was added and the solution was poured into a separatory funnel containing ethyl acetate (10 mL), washed with saturated aqueous NH_4Cl (2×10 mL), water (10 mL) and brine (5 mL). Organics were collected, dried over Na_2SO_4 and concentrated to dryness under vacuum with rotary evaporator. Purification by flash chromatography (SiO_2, DCM/MeOH 100:0 to 85:15) afforded desired multivalent compound **25** (54 mg, 3.4 µmol, **86%**) as a white foam.

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[6] Y. M. Chabre, D. Giguère, B. Blanchard, J. Rodrigue, S. Rocheleau, M. Neault, S. Rauthu, A. Papadopoulos, A. A. Arnold, A. Imberty and R. Roy, *Chem. Eur. J.*, 2011, **17**, 6545−6562.

R_f = 0.38, DCM/MeOH 93:7.

^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 10.1 (br s, 3H, N*H*), 8.49 (br s, 3H, N*H*), 7.98 (s, 3H, CH_{core}), 7.91-7.83 (m, 18H, $H_{triazole}$), 7.36-7.30 (m, 6H, C$H_{b'}$), 6.97-6.48 (m, 66H, CH_b, CH_c, C$H_{c'}$), 5.40 (br s, 6H, $N_{triazole}CH_2CONH$), 5.32 (d_{app}, 15H, H_{4gal}), 5.20-5.04 (m, 60H, H_{3glc}, C_qCH_2O, H_{2gal}), 4.93 (dd, $^3J_{2,3}$ = 3.3 Hz, $^3J_{3,4}$ = 7.1 Hz, 15H, H_{3gal}), 4.87-4.82 (m, 15H, H_{2glc}), 4.63 (br s, 6H, $CONHCH_2C_q$), 4.54-4.42 (m, 75H, CH_2N, H_{1glc}, H_{6aglc}, H_{1gal}), 4.12-4.04 (m, 45H, H_{6bglc}, H_{6agal}, H_{6bgal}), 3.86-3.54 (m, 255H, H_{5gal}, H_{5glc}, H_{4glc}, OCH_2), 2.11-1.92 (m, 315H, $COCH_3$).

^{13}C NMR (150 MHz, $CDCl_3$, δ ppm): 170.4, 170.3, 170.2, 170.1, 169.9, 169.7, 169.5 (7×s, $COCH_3$), 165.0 (NHC=O_{core}),163.9 (NHC=O), 155.3 (C_a), 155.3 (C_a), 146.5 ($C_{d'}$), 144.4 (C_d), 144.1 (C_d), 143.5 ($C_{triazole}$=CH), 143.3 ($C_{triazole}$=CH), 133.8 ($C_{q\text{-}core}$), 129.1 (CH_{core}), 124.7 ($C_{triazole}$=CH), 124.5 ($C_{a'}$), 124.1 ($C_{triazole}$=CH), 121.8 (C_c), 120.9 ($C_{c'}$), 120.7 ($C_{b'}$), 115.2 (C_b), 115.1 (C_b), 101.0 (C_{1gal}), 100.5 (C_{1glc}), 76.2 (C_{4glc}), 72.7 (C_{3glc}), 72.5 (C_{5glc}), 71.5 (C_{2glc}), 70.9 (C_{3gal}), 70.5 (C_{5gal}), 70.5, 70.4, 70.4, 70.3, 70.2, 70.1, 70.1, 69.3, 69.1, 69.0 (OCH_2), 68.9 (C_{2gal}), 68.9 (OCH_2), 66.5 (C_{4gal}), 62.1 (OCH_2C=C), 61.9 (C_{6glc}), 61.6 (OCH_2), 60.7 (C_{6gal}),, 52.7 ($N_{triazole}CH_2CONH$), 50.2 (NCH_2), 50.1 (NCH_2), 35.8 ($C_{core}CONHCH_2C_{triazole}$), 29.6, 20.8, 20.7, 20.6, 20.5, 20.5, 20.4 (7×s, $COCH_3$).

^{31}P NMR (122 MHz, $CDCl_3$, δ ppm): 10.9-9.5 (m, 9P).

m/z (ESI$^+$-MS) for $C_{687}H_{906}N_{69}O_{354}P_9$= 16074.6 [$M$+H]$^+$; found 16074.1 (After deconvolution).

NMR diffusion studies ($CDCl_3$): $D = 1.65\times10^{-10}$ m^2/s; d_s = 5.1 nm.

GPC measurements (THF): M_w = 18970 ; M_n = 18820 , PDI (M_w/M_n) = 1.008.

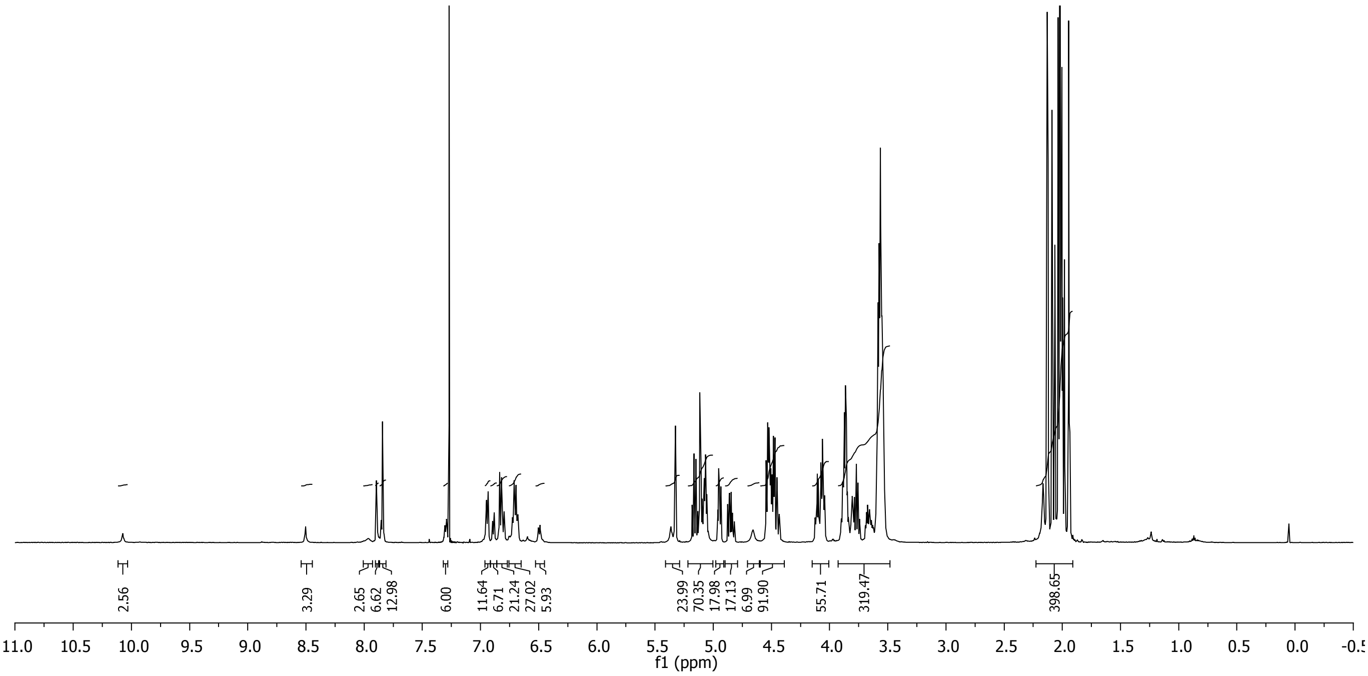


Figure S100. ^{1}H NMR spectrum of compound **25** ($CDCl_3$, 600MHz)

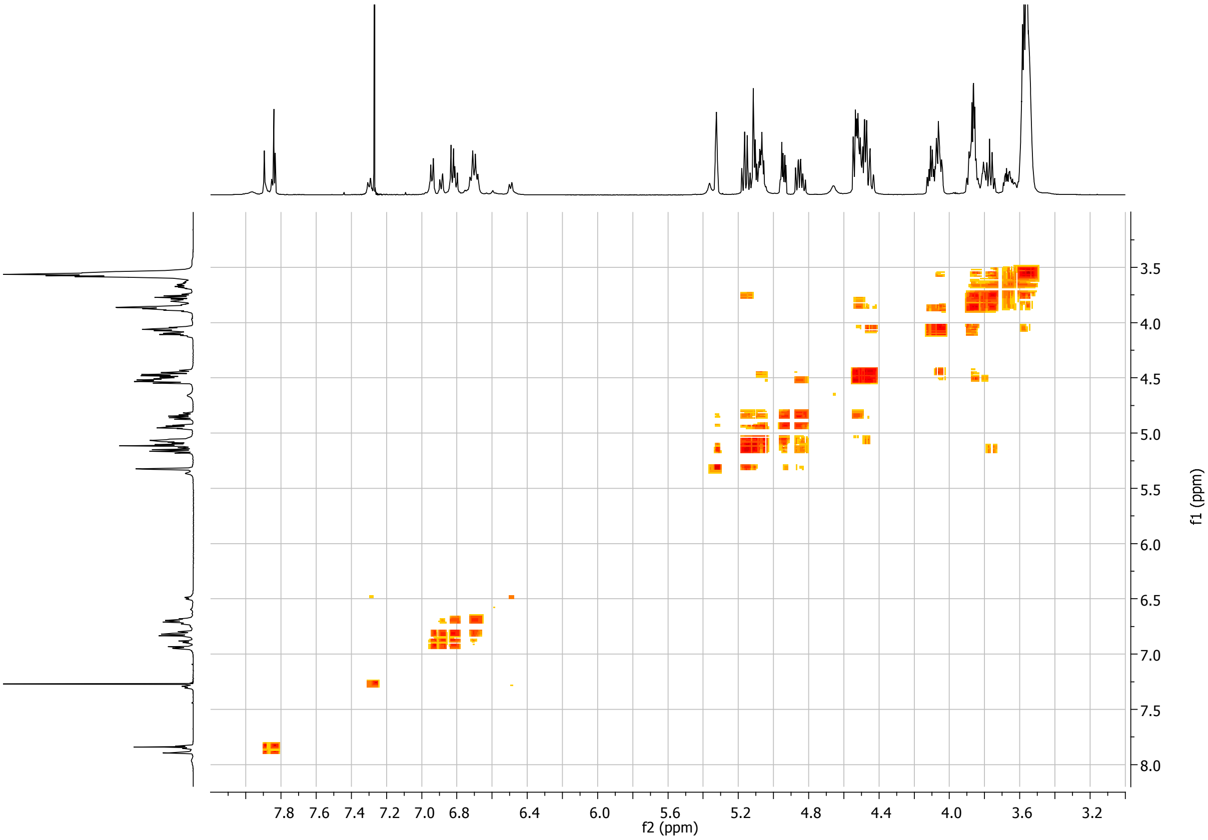


Figure S101. gCOSY spectrum of compound **25**

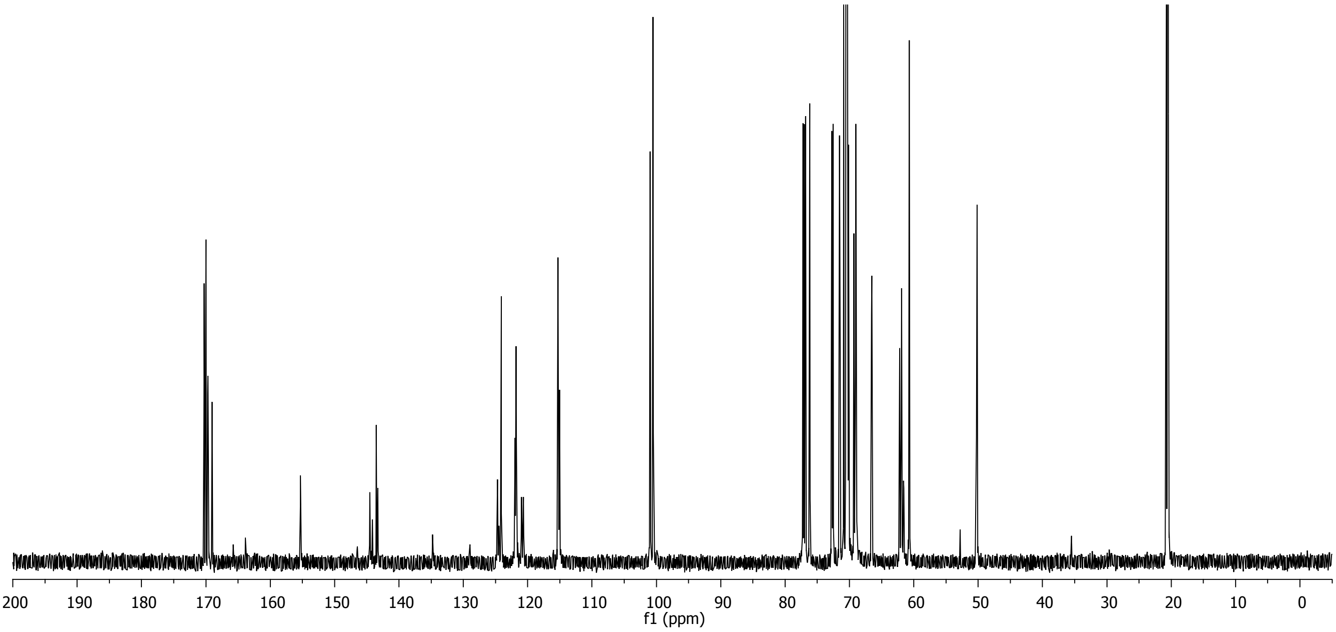


Figure S102. ^{13}C NMR spectrum of compound **25** ($CDCl_3$, 150MHz)

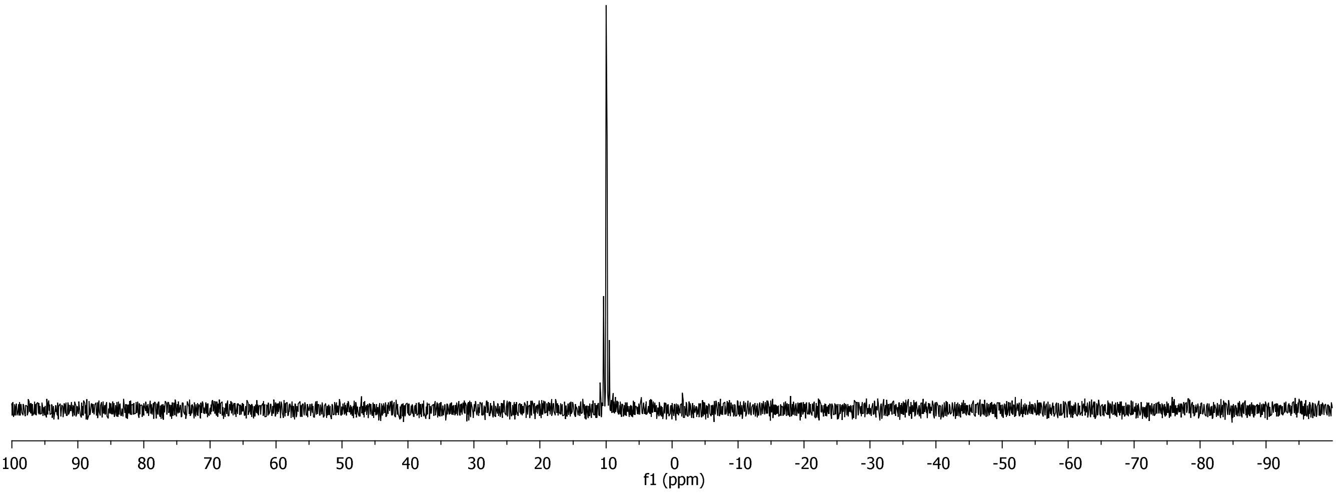
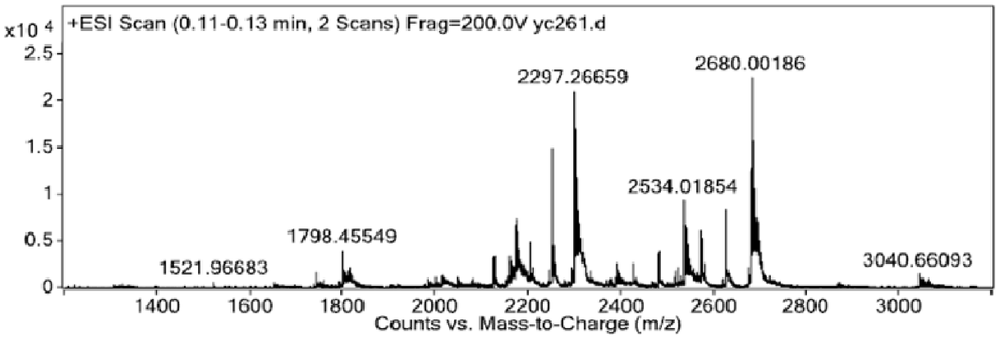
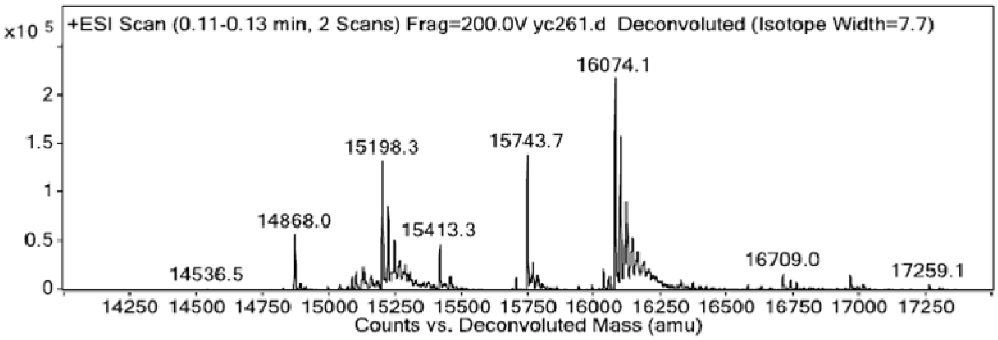


Figure S103. ^{31}P NMR spectrum of compound **25** ($CDCl_3$, 122MHz)





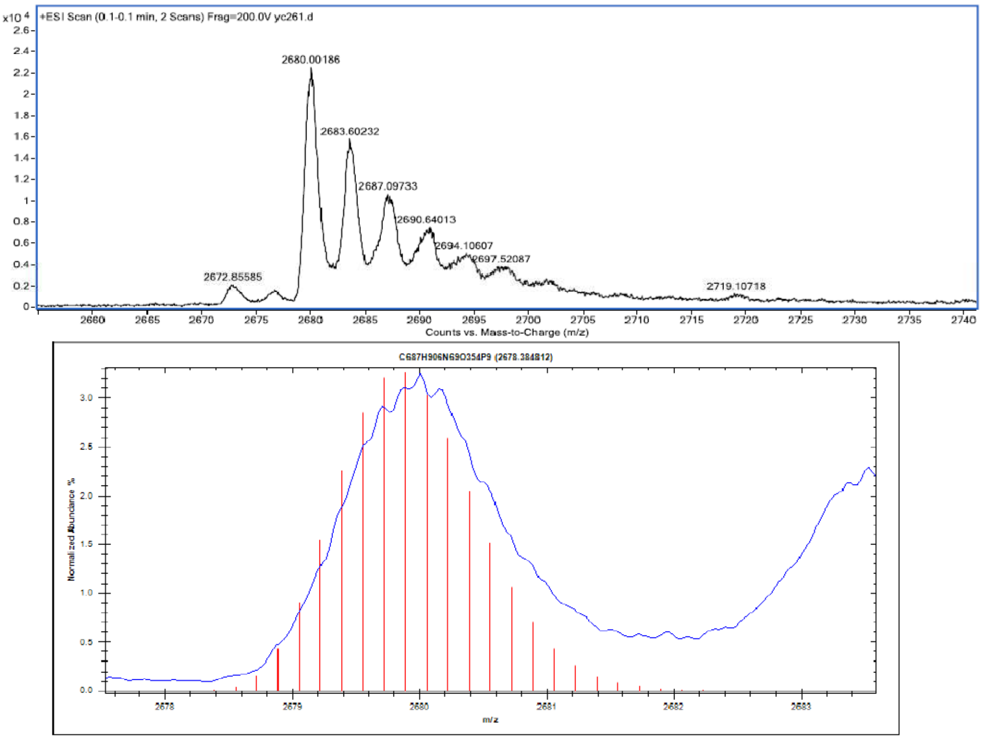
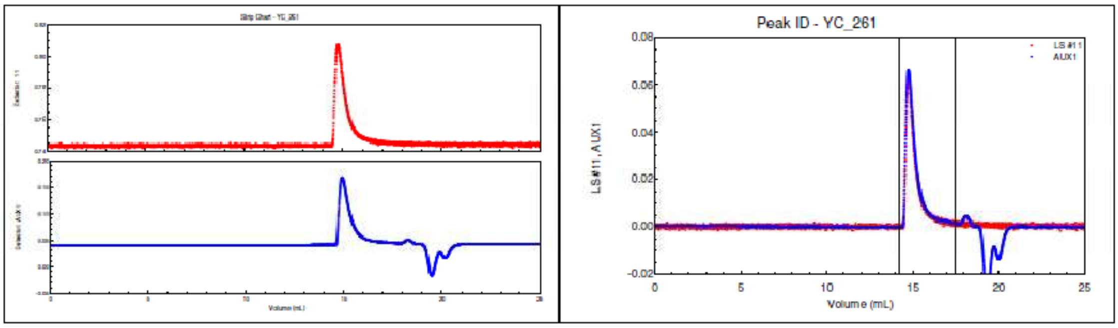
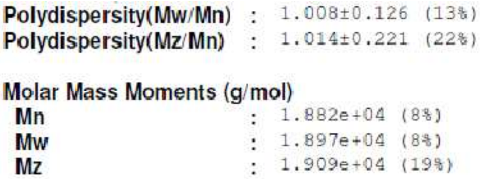


Figure S104. ESI^{+}-MS spectra (deconvolution) of compound **25**

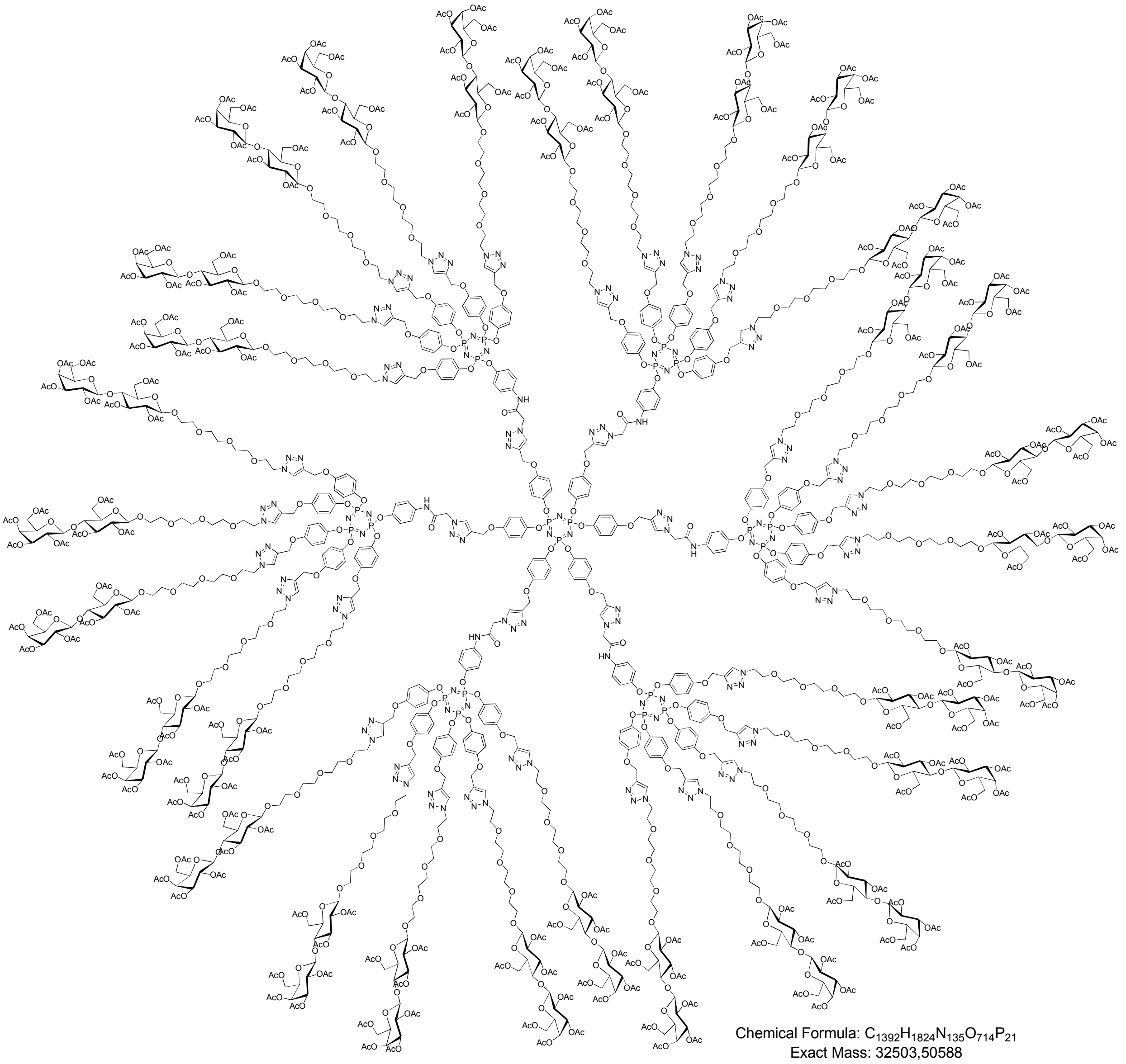



Polydispersity(Mw/Mn) : 1.008±0.126 (13%)
Polydispersity(Mz/Mn) : 1.014±0.221 (22%)

Molar Mass Moments (g/mol)
Mn : 1.882e+04 (8%)
Mw : 1.897e+04 (8%)
Mz : 1.909e+04 (19%)

Figure S105. GPC trace (in THF) for compound **25**

Protected tricontavalent glycodendrimer 26



Chemical Formula: $C_{1392}H_{1824}N_{135}O_{714}P_{21}$
Exact Mass: 32503,50588
Molecular Weight: 32522,30206

To a solution of hexapropargylated cyclotriphosphazene derivative **1** (2.40 mg, 2.36 µmol, 1.0 eq.) in a 1:1 mixture of H_2O/THF_{anh} (5 mL), were added azido derivative **15** (100 mg, 19.0 µmol, 8.1 eq.), $CuSO_4\cdot5H_2O$ (4.71 mg, 18.8 µmol, 8.0 eq.) and sodium ascorbate (3.74 mg, 18.8 µmol, 8.0 eq.). While stirring, the mixture was first heated at 50℃ for 3 hours in a 20 mL vial and at room temperature for additional 18 hours. Ethyl acetate (15 mL) was added and the solution was poured into a separatory funnel containing ethyl acetate (10 mL), washed with saturated aqueous NH_4Cl (2×10 mL), water (10 mL) and brine (5 mL). Organics were collected, dried over Na_2SO_4 and concentrated to dryness *in vacuo* with rotary evaporator. Purification by flash chromatography (SiO_2, DCM/MeOH 100:0 to 85:15) afforded desired multivalent compound **26** (59 mg, 1.81 µmol, **77%**) as a white foam.

R$_f$ = 0.42, DCM/MeOH 92:8.

^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 10.1 (br s, 6H, NH), 7.98 (s, 6H, H_{triazole}), 7.86-7.80 (m, 30H, H_{triazole}), 7.36-7.30 (m, 12H, C$H_{b'}$), 6.97-6.54 (m, 156H, CH_b, CH_c, C$H_{c'}$), 5.40 (br s, 12H, $N_{\text{triazole}}CH_2CONH$), 5.32 ($d_{\text{app}}$, 30H, $H_{4\text{gal}}$), 5.17-5.04 (m, 132H, $H_{3\text{glc}}$, C_qCH_2O, $H_{2\text{gal}}$), 4.93 (dd, $^3J_{2,3}$ = 3.3 Hz, $^3J_{3,4}$ = 7.1 Hz, 30H, $H_{3\text{gal}}$), 4.87-4.82 (m, 30H, $H_{2\text{glc}}$), 4.54-4.42 (m, 150H, CH_2N, $H_{1\text{glc}}$, $H_{6\text{aglc}}$, $H_{1\text{gal}}$), 4.12-4.04 (m, 90H, $H_{6\text{bglc}}$, $H_{6\text{agal}}$, $H_{6\text{bgal}}$), 3.90-3.45 (510H, $H_{5\text{gal}}$, $H_{5\text{glc}}$, $H_{4\text{glc}}$, OCH_2), 2.11-1.92 (m, 630H, COCH_3).

^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 170.2, 170.2, 170.0, 169.9, 169.9, 169.7, 169.5 (7×s, COCH$_3$), 163.9 (C=O), 155.2 (C_{a}), 146.5 ($C_{\text{d'}}$), 144.4 (C_{d}), 144.1 (C_{d}), 143.4 ($C_{triazole}$=CH), 143.2 ($C_{triazole}$=CH), 134.8 ($C_{\text{a'}}$), 125.2 (C_{triazole}=CH), 124.6 (C_{triazole}=CH), 124.1 (C_{triazole}=CH), 121.9 ($C_{\text{c'}}$), 121.7 ($C_{\text{b'}}$), 120.9 (C_{c}), 120.7 (C_{c}), 115.9 (C_{b}), 115.2 (C_{b}), 115.1 (C_{b}), 101.0 ($C_{1\text{gal}}$), 100.5 ($C_{1\text{glc}}$), 76.2 ($C_{4\text{glc}}$), 72.7 ($C_{3\text{glc}}$), 72.5 ($C_{5\text{glc}}$), 71.5 ($C_{2\text{glc}}$), 70.9 ($C_{3\text{gal}}$), 70.5 ($C_{5\text{gal}}$), 70.5, 70.4, 70.4, 70.3, 70.2, 70.1, 70.1, 69.3, 69.1, 69.0 (OCH$_2$), 68.9 ($C_{2\text{gal}}$), 68.9 (OCH$_2$), 66.5 ($C_{4\text{gal}}$), 62.1 (OCH$_2$C=C), 61.9 ($C_{6\text{glc}}$), 61.6 (OCH$_2$), 60.7 ($C_{6\text{gal}}$), 52.7 ($N_{\text{triazole}}CH_2CONH$), 50.2 (N$CH_2$), 50.1 (N$CH_2$), 29.6, 20.8, 20.7, 20.6, 20.5, 20.5, 20.4 (7×s, COCH$_3$).

^{31}P NMR (122 MHz, $CDCl_3$, δ ppm): 10.2-9.7 (m, 21P).

m/z (ESI$^+$-MS) for $C_{1392}H_{1824}N_{135}O_{714}P_{21}$= 32523.3 [$M$+H]$^+$; found 32523.7 (After deconvolution) *with signals corresponding to losses of monomers (~876) and dendron(s) (~5290)).*

MALDI-TOF (DHB matrix) : 32550.1, *with signals corresponding to losses of monomers (~876) and dendron(s) (~5290))*.

NMR diffusion studies ($CDCl_3$): $D = 1.08\times10^{-10}$ m^2/s; d_s = 7.5 nm.

GPC measurements (THF): M_w = 33560 ; M_n = 33090 , PDI (M_w/M_n) = 1.014
($CHCl_3/Et_3N$ (1%)): M_w = 35320 ; M_n = 34480 , PDI (M_w/M_n) = 1.025.

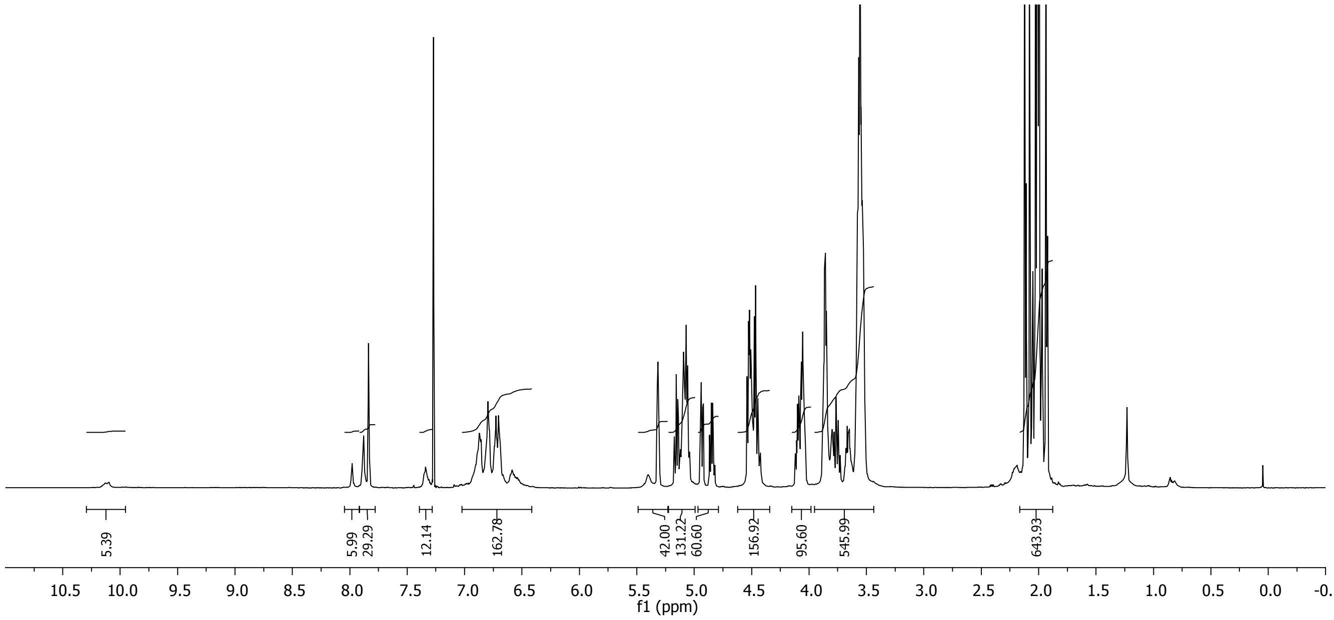


Figure S106. ^{1}H NMR spectrum of compound **26** ($CDCl_3$, 600MHz)

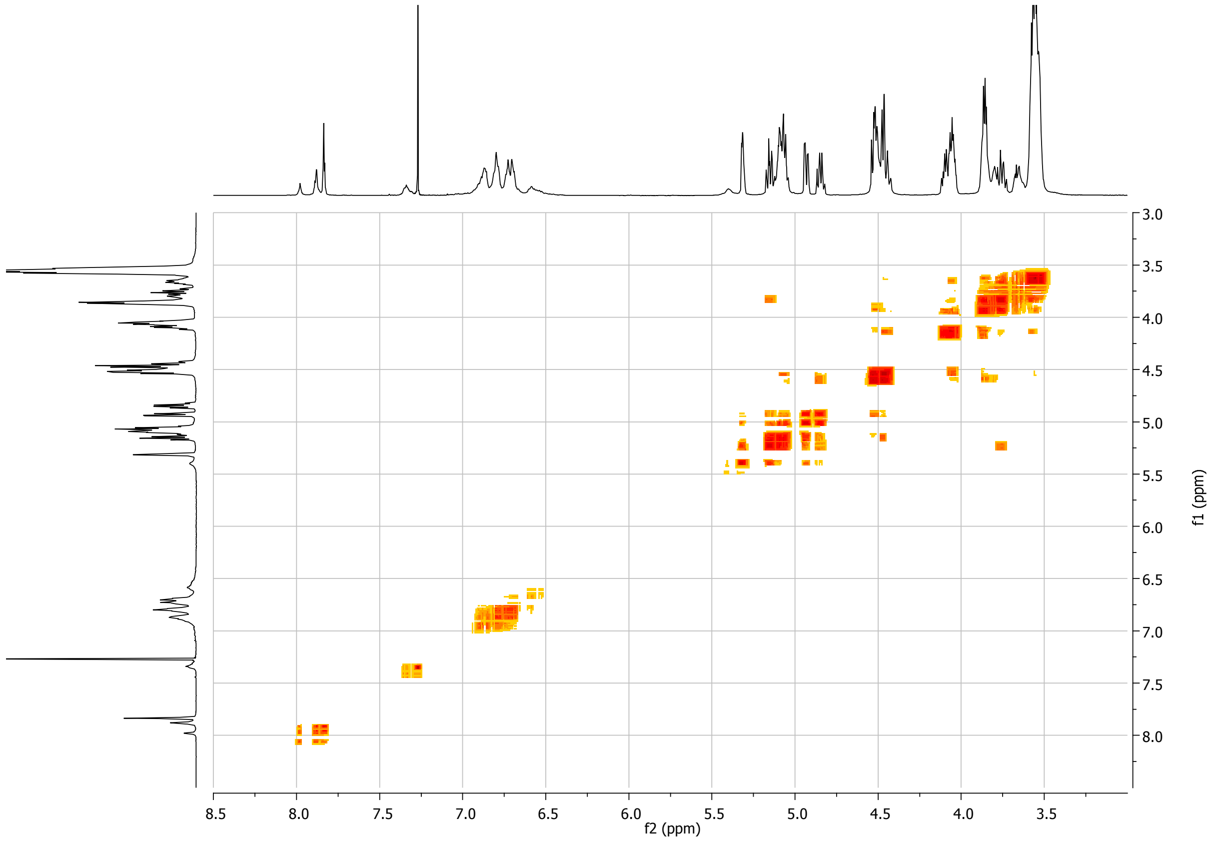


Figure S107. gCOSY spectrum of compound **26**

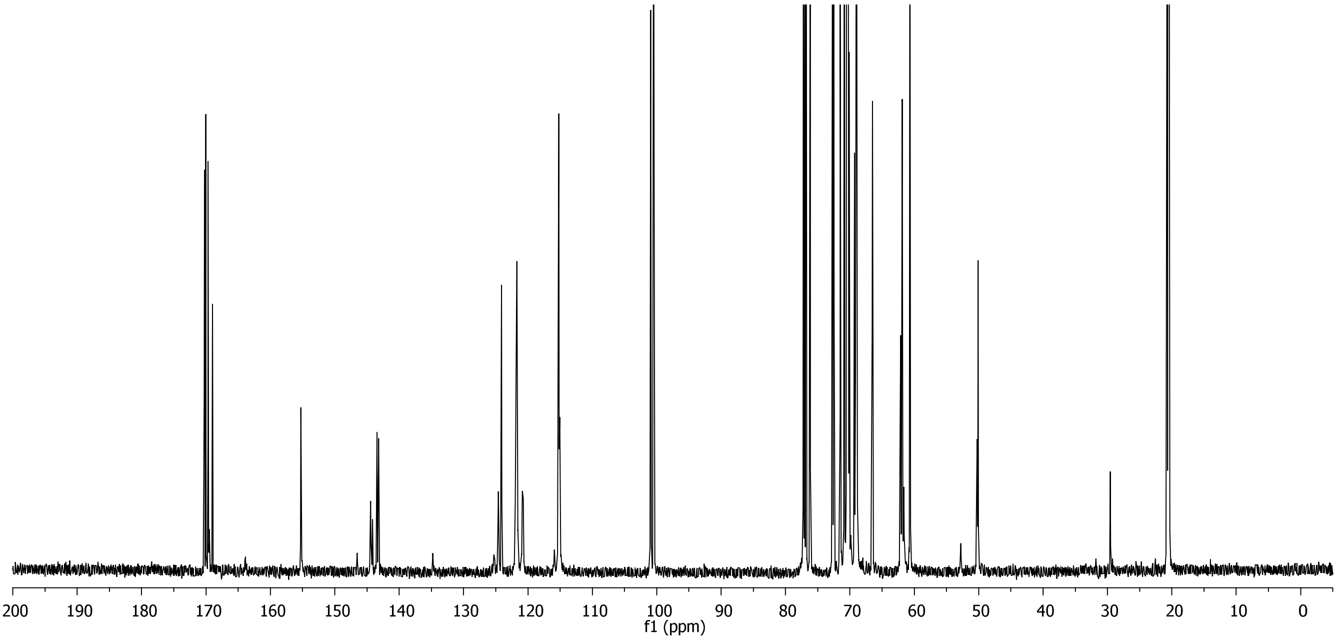


Figure S108. ^{13}C NMR spectrum of compound **26** (CDCl$_3$, 150MHz)

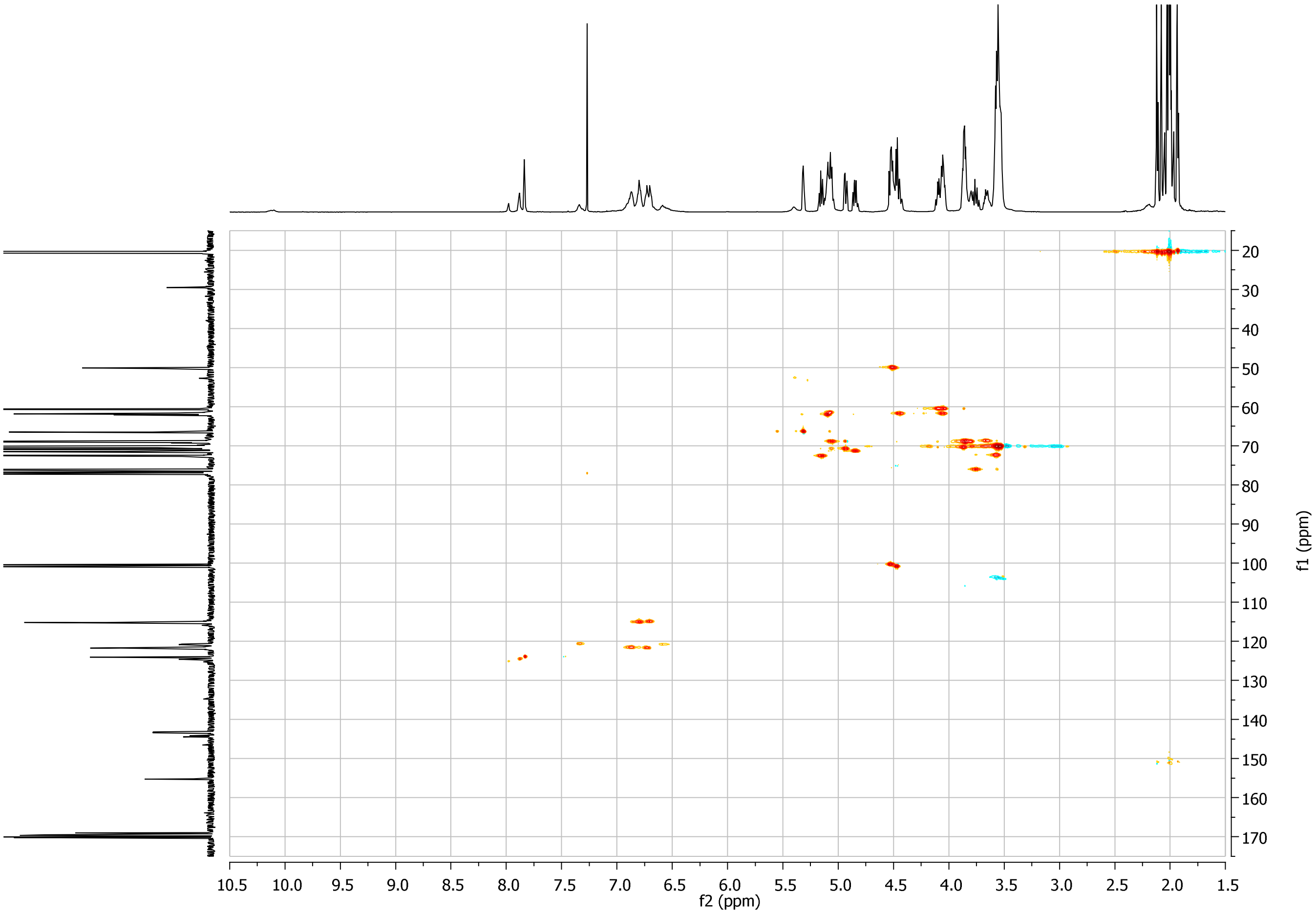


Figure S109. HMQC spectrum of compound **26**

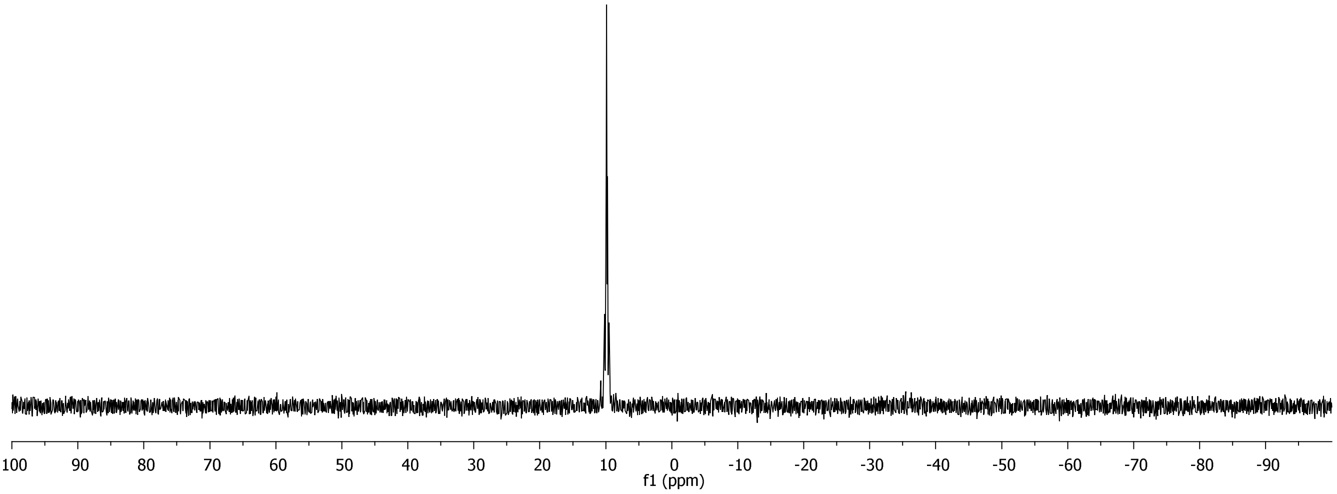


Figure S110. ^{31}P NMR spectrum of compound **26** ($CDCl_3$, 122MHz)

User Spectra

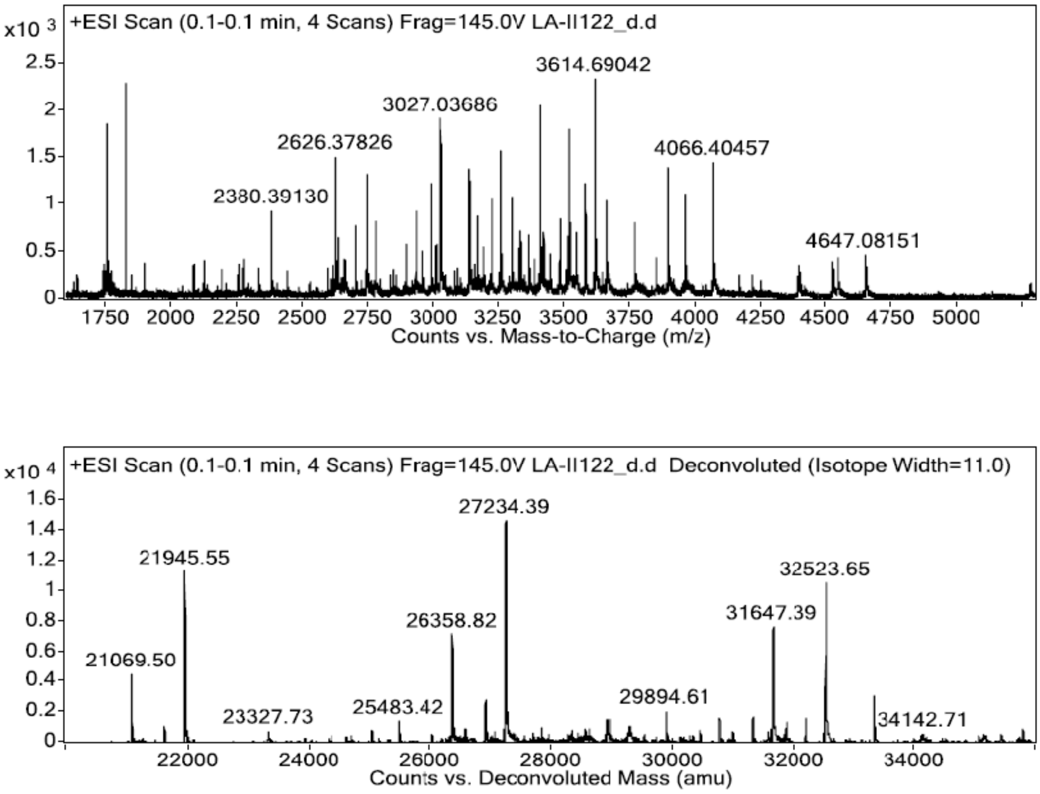


Figure S111. ESI$^+$-MS spectrum (deconvolution) of compound **26**

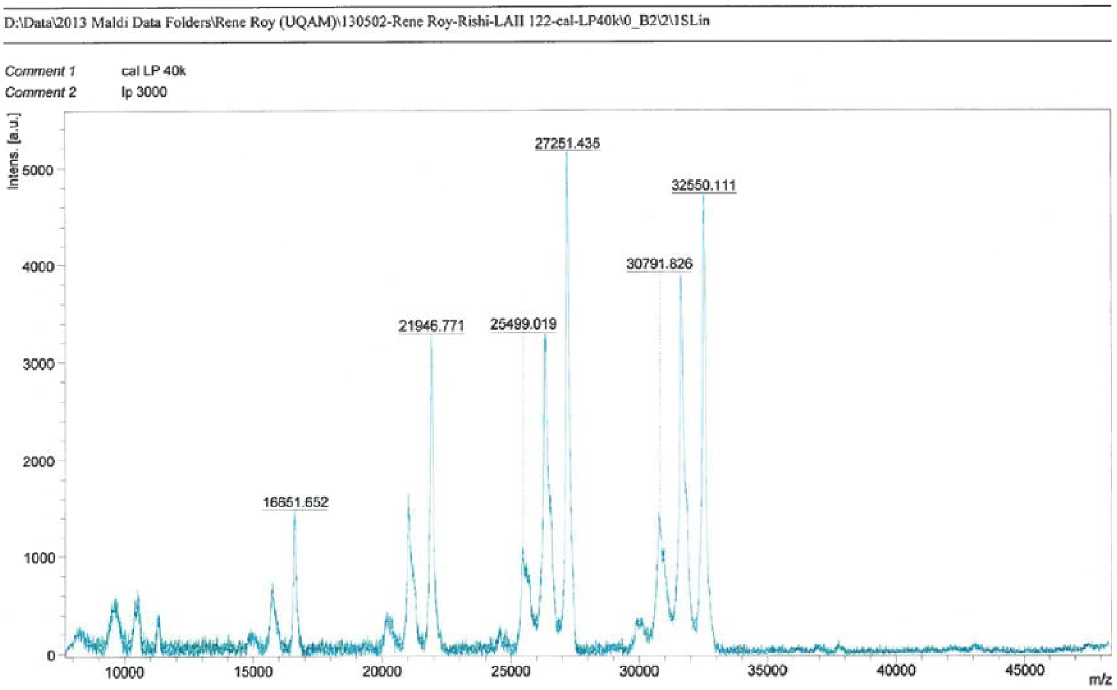
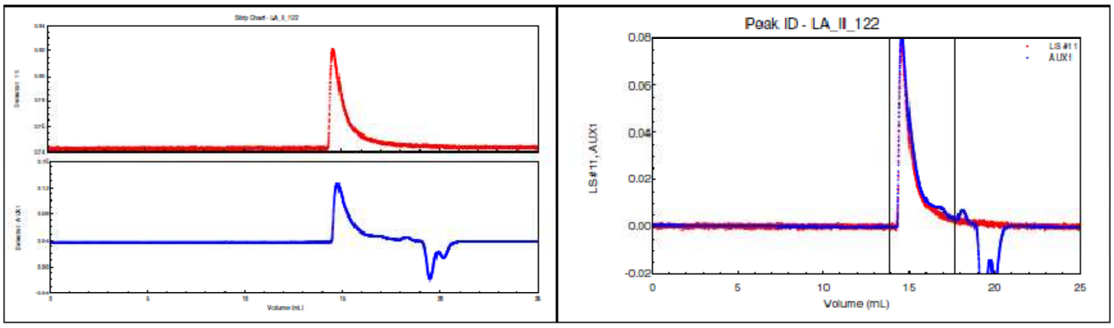


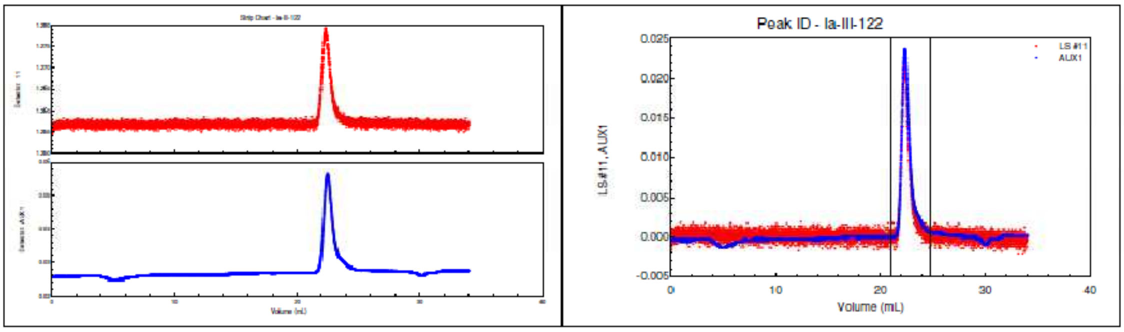
Figure S112. MALDI-TOF (DHB matrix) of compound **26**



```
Polydispersity(Mw/Mn)  :  1.014±0.126  (12%)
Polydispersity(Mz/Mn)  :  1.031±0.231  (22%)

Molar Mass Moments (g/mol)
 Mn                    :  3.309e+04  (8%)
 Mw                    :  3.356e+04  (8%)
 Mz                    :  3.412e+04  (20%)
```

Figure S113. GPC trace (in THF) for compound **26**

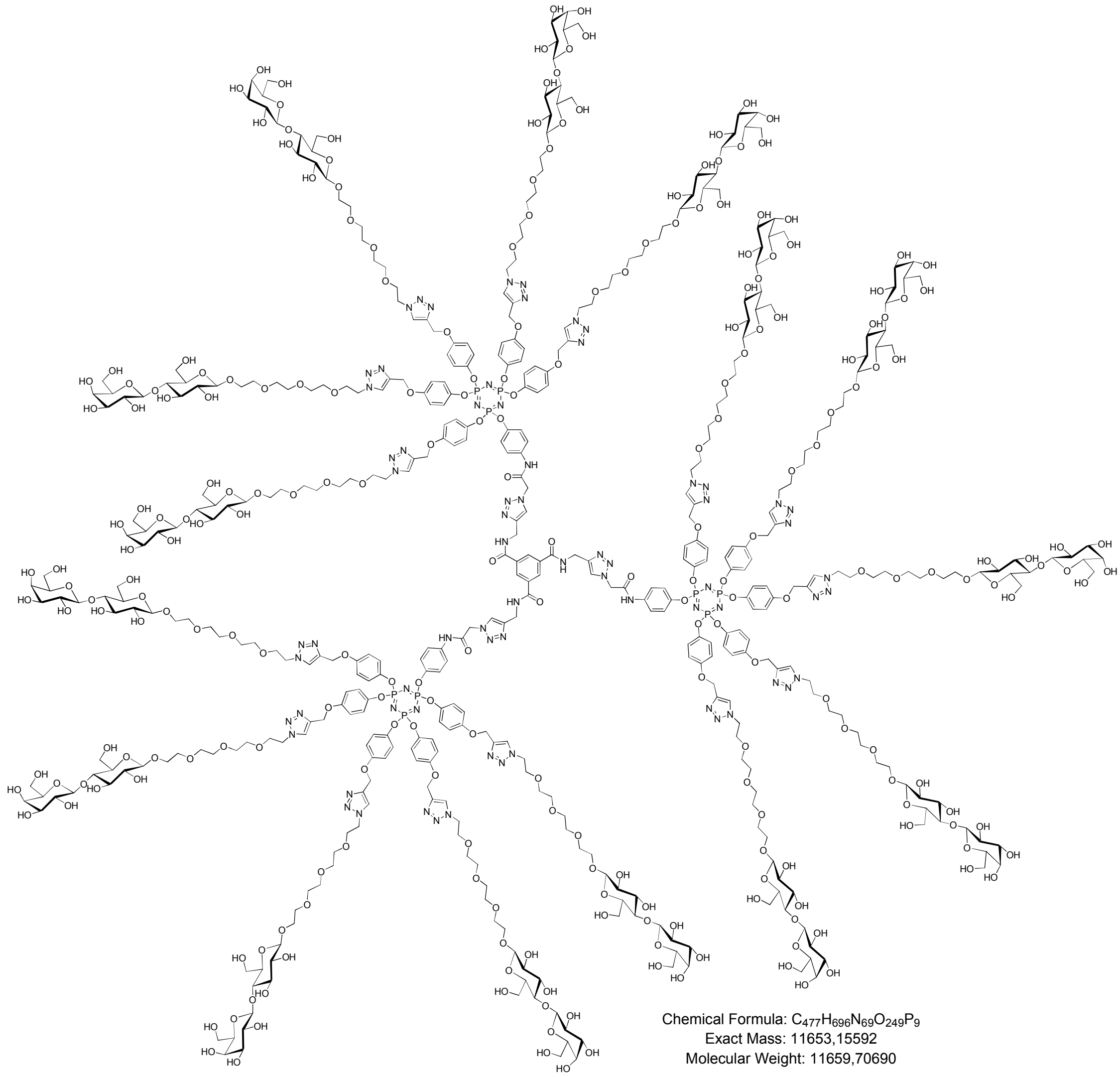


```
Polydispersity(Mw/Mn)  :  1.025±0.176  (17%)
Polydispersity(Mz/Mn)  :  1.049±0.304  (29%)

Molar Mass Moments (g/mol)
 Mn                    :  3.448e+04  (12%)
 Mw                    :  3.532e+04  (11%)
 Mz                    :  3.615e+04  (26%)
```

Figure S114. GPC trace (in $CHCl_3/Et_3N$ (1%)) for compound **26**

Hydroxylated pentadecavalent glycodendrimer 27



Chemical Formula: $C_{477}H_{696}N_{69}O_{249}P_9$
Exact Mass: 11653,15592
Molecular Weight: 11659,70690

Acetylated compound **25** (50.0 mg, 3.11 µmol) was dissolved in a dry mixture of MeOH/DCM (5 mL, 4:1) and a solution of sodium methoxide (1M in MeOH, 5 µL every 20 minutes until precipitation) was added. An additional 100 µL was then injected and the heterogeneous reaction mixture was stirred at room temperature for 18 hours. The solvent was then removed with a Pasteur pipette and another dry mixture of MeOH/DCM (5 mL, 4:1) is added to the residual oil. A vigorous agitation is maintained for an additional 15 min. period. After removal of the solvents with a Pasteur pipette, 2 mL of dry MeOH were added to the viscous residue under agitation. After 15 min., the MeOH was removed and the residue was dissolved in 3 mL of H_2O, and the pH was adjusted to 7 with addition of ion-exchange resin (Amberlite IR 120 H^+). After filtration, the solvent was removed under *vacuum* with rotary evaporator, lyophilized to yield the fully deprotected derivative **27** as an off-white solid (29.0 mg, 2.49 µmol, **80%**).

^{1}**H NMR** (600 MHz, D_2O, δ ppm): 8.27 (s, 3H, CH_{core}), 7.86-7.75 (m, 18H, $H_{triazole}$), 7.10 (br s, 6H, $CH_{b'}$), 6.57-6.47 (m, 66H, CH_b, CH_c, $CH_{c'}$), 5.17 (br s, 6H, $N_{triazole}CH_2CO$), 4.96-4.82 (br s, 36H, $C_{q\text{-}triazole}CH_2O$ + $CONHCH_2C_q$), 4.40-4.30 (m, 60H, $N_{triazole}CH_2CH_2$, H_{1glc}, H_{1gal}), 3.82 (m , 45H, OCH_2CH_2N, LacOCH*H*CH_2), 3.75-3.27 (m, 330H, H_{3glc}, H_{2gal}, H_{3gal}, H_{6bglc}, H_{4gal}, H_{6agal}, H_{6bgal}, H_{6aglc}, H_{5gal}, H_{5glc}, H_{4glc}, LacOCH*H*CH_2, OCH_2), 3.33 (t_{app}, 15H, H_{2glc}).

^{13}**C NMR** (150 MHz, D_2O, δ ppm): 167.1 (*C*=O), 165.2 (*C*=O), 156.6 (C_a), 146.8 ($C_{d'}$), 145.5 (C_d), 144.5 (C_d), 143.6 ($C_{triazole}$=CH), 143.7 ($C_{triazole}$=CH), 133.8 ($C_{q\text{-}core}$), 129.9 (CH_{core}), 125.9 ($C_{triazole}$=*C*H), 125.4 ($C_{a'}$), 122.4 ($C_{triazole}$=*C*H), 121.7 (C_c + $C_{b'}$ + $C_{c'}$), 116.2 (C_b), 103.7 (C_{1gal}), 102.8 (C_{1glc}), 79.1 (C_{4glc}), 76.0 (C_{3glc}), 75.4 (C_{5glc}), 75.0 (C_{5gal}), 73.5 (C_{2glc}), 73.2 (C_{3gal}), 71.6 (C_{2gal}), 70.3, 70.2, 70.0, 69.4, (OCH_2), 69.4 (C_{4gal}), 69.2 (OCH_2), 62.0 (OCH_2C=C), 61.7 (C_{6glc}), 60.7 (C_{6gal}), 53.2 ($N_{triazole}CH_2CO$), 50.7 (NCH_2), 36.8 ($C_{core}CONHCH_2C_q$).

^{31}**P NMR** (122 MHz, D_2O, δ ppm): 10.2 (s, 9P).

m/z (ESI^+-HRMS) for $C_{477}H_{696}N_{69}O_{249}P_9$ = 11660.7 $[M+H]^+$, found 11660.6 (After deconvolution).

NMR diffusion studies (D_2O): $D = 0.70\times10^{-10}$ m^2/s; d_s = 5.7 nm.

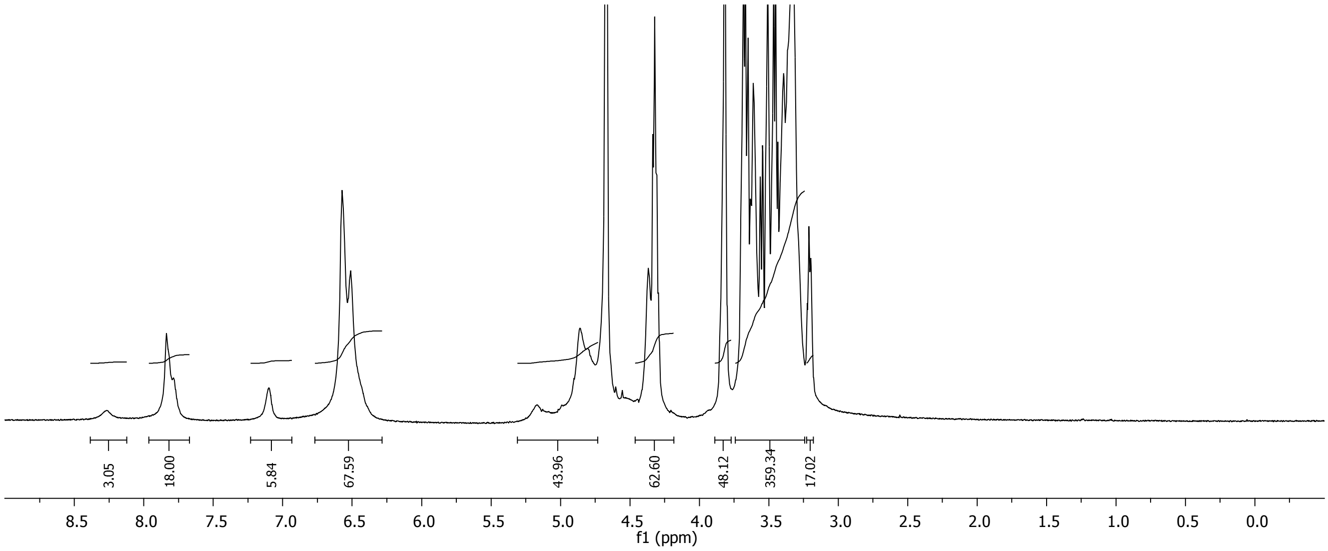


Figure S115. ^{1}H NMR spectrum of compound **27** (D_2O, 600MHz)

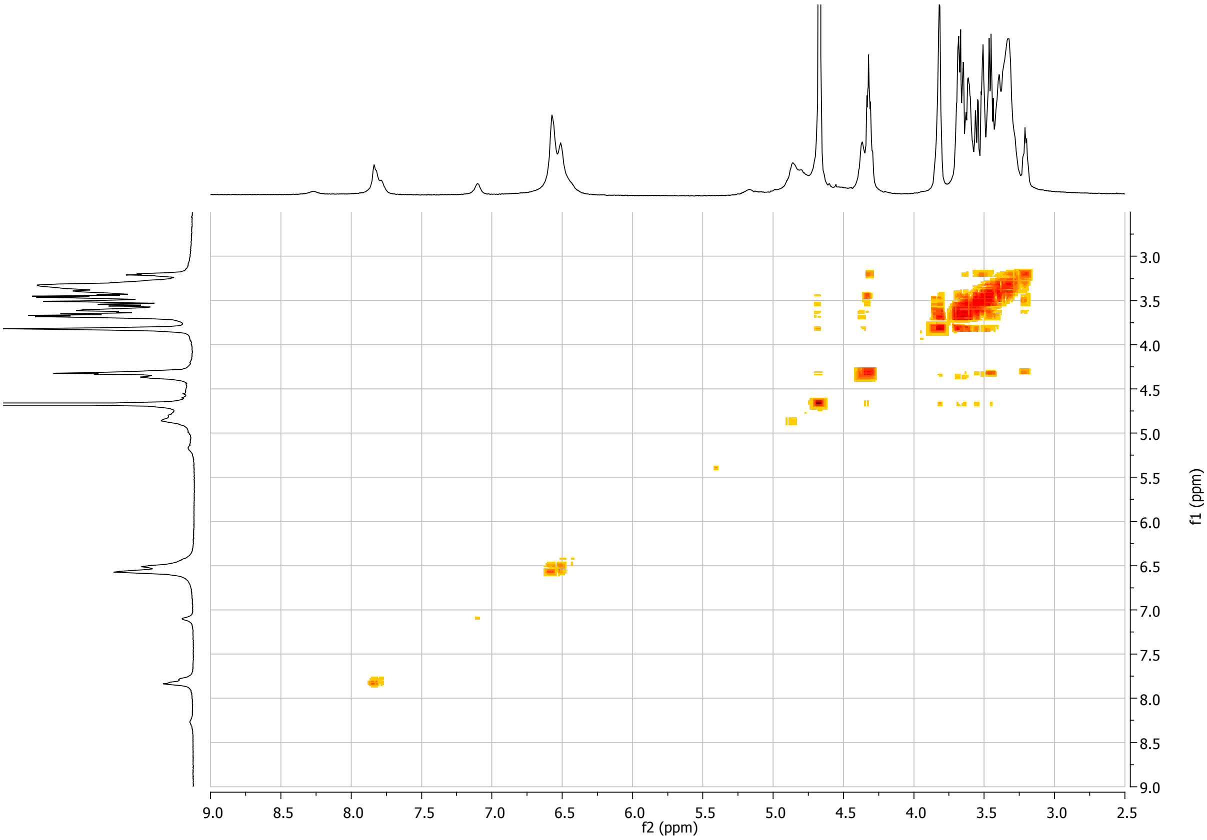


Figure S116. gCOSY spectrum of compound **27**

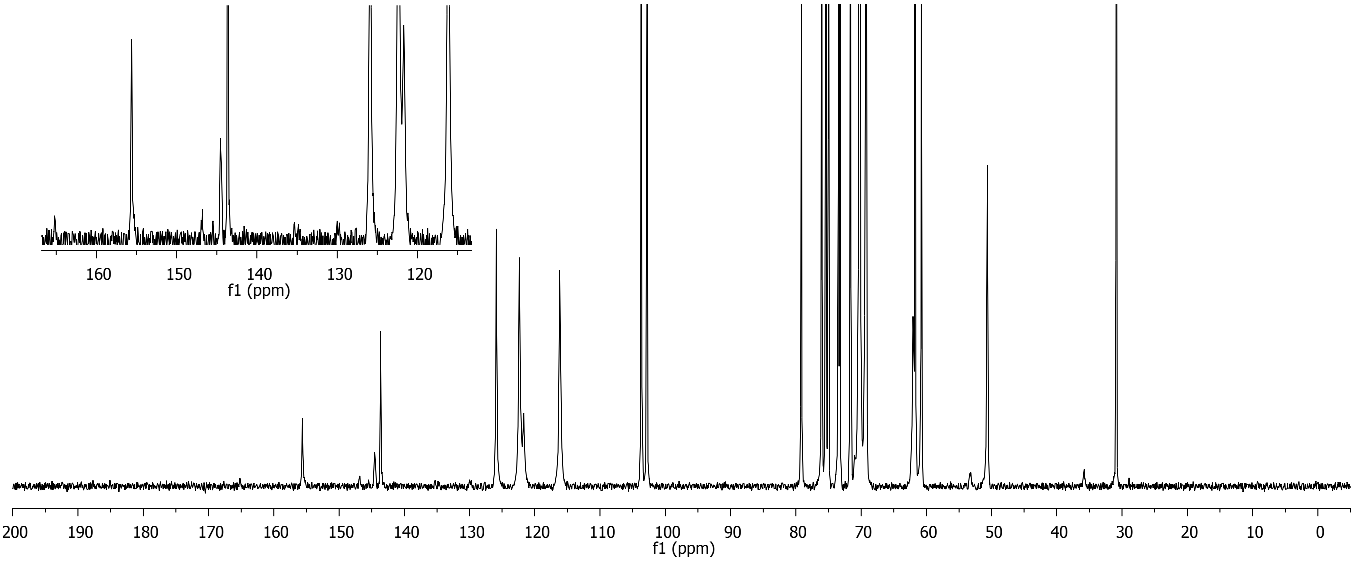


Figure S117. ^{13}C NMR spectrum of compound **27** (D_2O, 150MHz, acetone as reference) (*insert*: Zoom of the aromatic section)

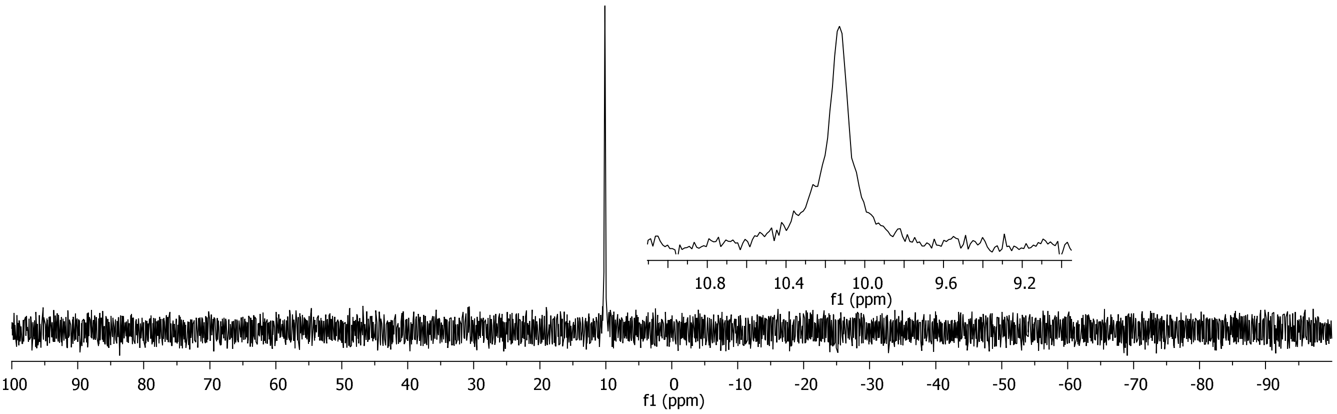


Figure S118. ^{31}P NMR spectrum of compound **27** (D_2O, 122MHz)

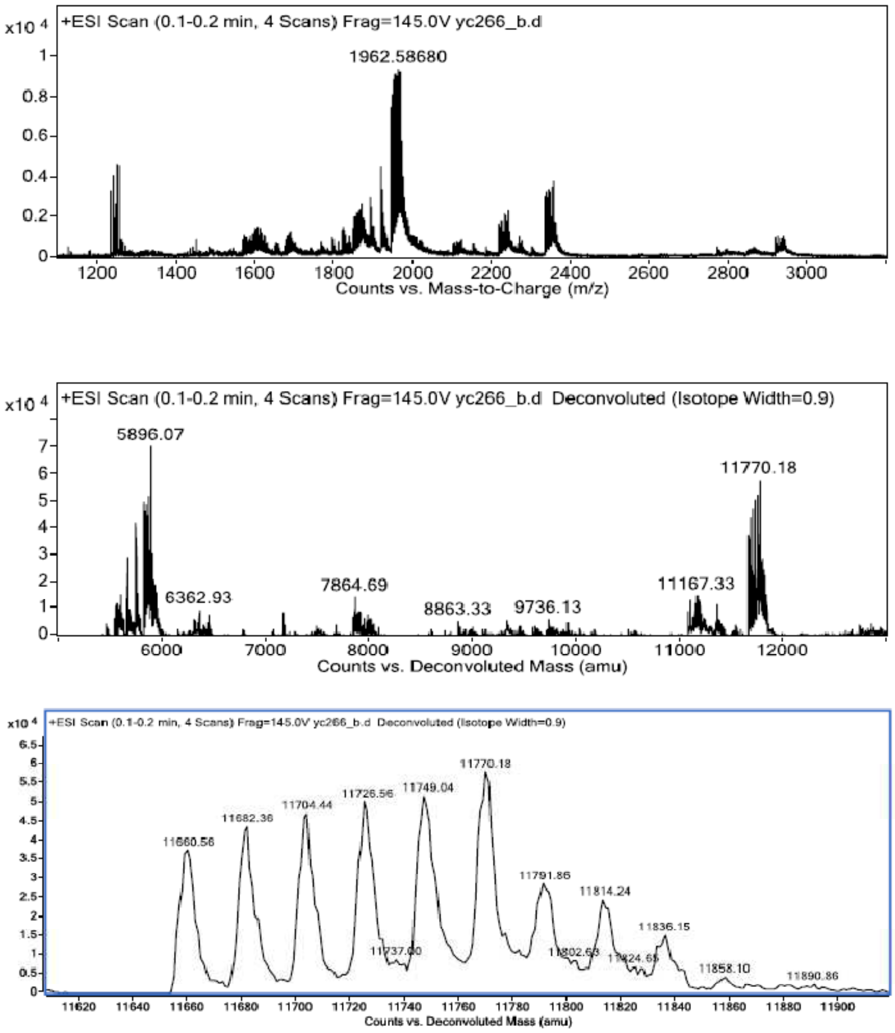
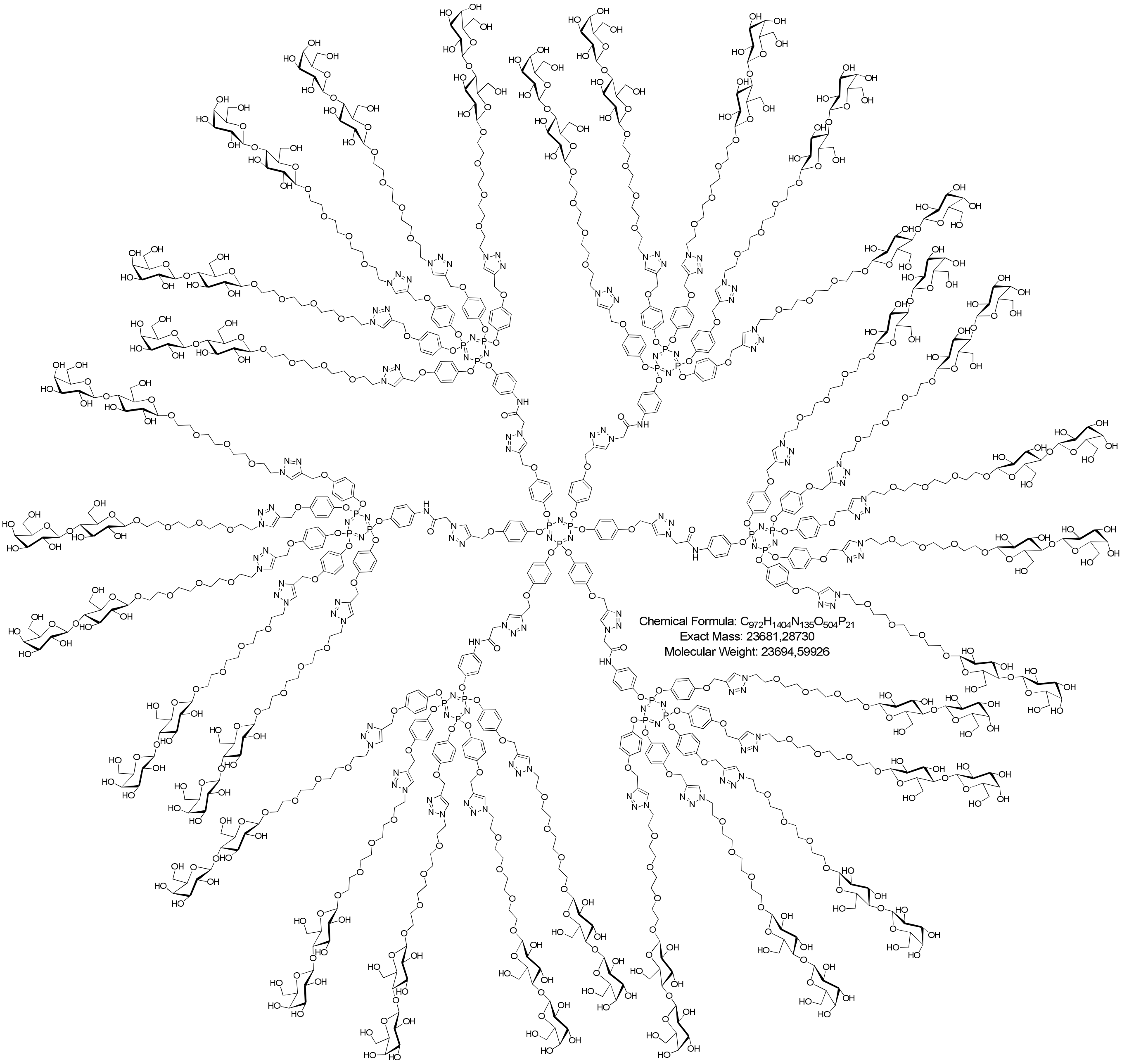


Figure S119. ESI^{+}-MS spectrum of compound **27**

Hydroxylated tricontavalent glycodendrimer 28



Chemical Formula: $C_{972}H_{1404}N_{135}O_{504}P_{21}$
Exact Mass: 23681,28730
Molecular Weight: 23694,59926

Acetylated compound **26** (50.0 mg, 1.54 µmol) was dissolved in a dry mixture of MeOH/DCM (5 mL, 4:1) and a solution of sodium methoxide (1M in MeOH, 5 µL every 20 minutes until precipitation) was added. An additional 100 µL was then injected and the heterogeneous reaction mixture was stirred at room temperature for 18 hours. The solvent was then removed with a Pasteur pipette and another dry mixture of MeOH/DCM (5 mL, 4:1) is added to the residual oil. A vigorous agitation is maintained for an additional 15 min. period. After removal of the solvents with a Pasteur pipette, 2 mL of dry MeOH were added to the viscous residue under agitation. After 15 min., the MeOH was removed and the residue was dissolved in 3 mL of H_2O, and the pH was adjusted to 7 with addition of ion-exchange resin (Amberlite IR 120 H^+). After filtration, the solvent was removed under *vacuum* with rotary evaporator, lyophilized to yield the fully deprotected derivative **28** as an off-white solid (29.0 mg, 1.22 µmol, **93%**).

^{1}H NMR (600 MHz, D_2O, δ ppm): 7.99 (m, 36H, H_{triazole}), 7.28 (br s, 12H, $CH_{b'}$), 6.99 (m, 156H, CH_b, CH_c, $CH_{c'}$, $CH_{\text{ar-core}}$), 5.10-4.90 (br s, 72H, $C_{\text{q-triazole}}CH_2O$), 4.56-4.41 (m, 132H, $N_{\text{triazole}}CH_2CH_2$, $N_{\text{triazole}}CH_2CO$, $H_{1\text{glc}}$, $H_{1\text{gal}}$), 3.93 (m, 90H, OCH_2CH_2N, LacOCH*H*CH_2), 3.81-3.34 (m, 690H, $H_{3\text{glc}}$, $H_{2\text{gal}}$, $H_{3\text{gal}}$, $H_{6\text{bglc}}$, $H_{4\text{gal}}$, $H_{6\text{agal}}$, $H_{6\text{bgal}}$, $H_{6\text{aglc}}$, $H_{5\text{gal}}$, $H_{5\text{glc}}$, $H_{4\text{glc}}$, LacOCH*H*CH_2, OCH_2, $H_{2\text{glc}}$).

^{13}C NMR (150 MHz, D_2O, δ ppm): 167.1 (*C*=O) *not visible*, 165.2 (*C*=O) *not visible*, 156.6 (C_a), 154.3 ($C_{\text{a-core}}$), 146.8 ($C_{d'}$), 145.5 (C_d), 144.6 (C_d), 143.7 ($C_{triazole}$=CH), 143.7 ($C_{triazole}$=CH), 136.5 ($C_{a'}$), 125.9 (C_{triazole}=*C*H), 122.4 (C_{triazole}=*C*H), 121.0, 120.7 (C_c + $C_{b'}$ + $C_{c'}$), 116.2 (C_b, $C_{\text{b-core}}$), 103.7 ($C_{1\text{gal}}$), 102.8 ($C_{1\text{glc}}$), 79.1 ($C_{4\text{glc}}$), 76.0 ($C_{3\text{glc}}$), 75.4 ($C_{5\text{glc}}$), 75.0 ($C_{5\text{gal}}$), 73.5 ($C_{2\text{glc}}$), 73.2 ($C_{3\text{gal}}$), 71.6 ($C_{2\text{gal}}$), 70.3, 70.2, (OCH_2), 69.4 ($C_{4\text{gal}}$), 69.2 (OCH_2), 62.1 (OCH_2C=C), 61.7 ($C_{6\text{glc}}$), 60.8 ($C_{6\text{gal}}$), 53.2 ($N_{\text{triazole}}CH_2CO$), 50.7 ($NCH_2$).

^{31}P NMR (122 MHz, D_2O, δ ppm): 10.2 (s, 21P).

m/z (MALDI-TOF) for $C_{972}H_{1404}N_{135}O_{504}P_{21}$ = 23694.6, found 23755.9 (*with signals corresponding to losses of dendron(s)*).

NMR diffusion studies (D_2O): $D = 0.56\times10^{-10}$ m^2/s; d_s = 7.2 nm.

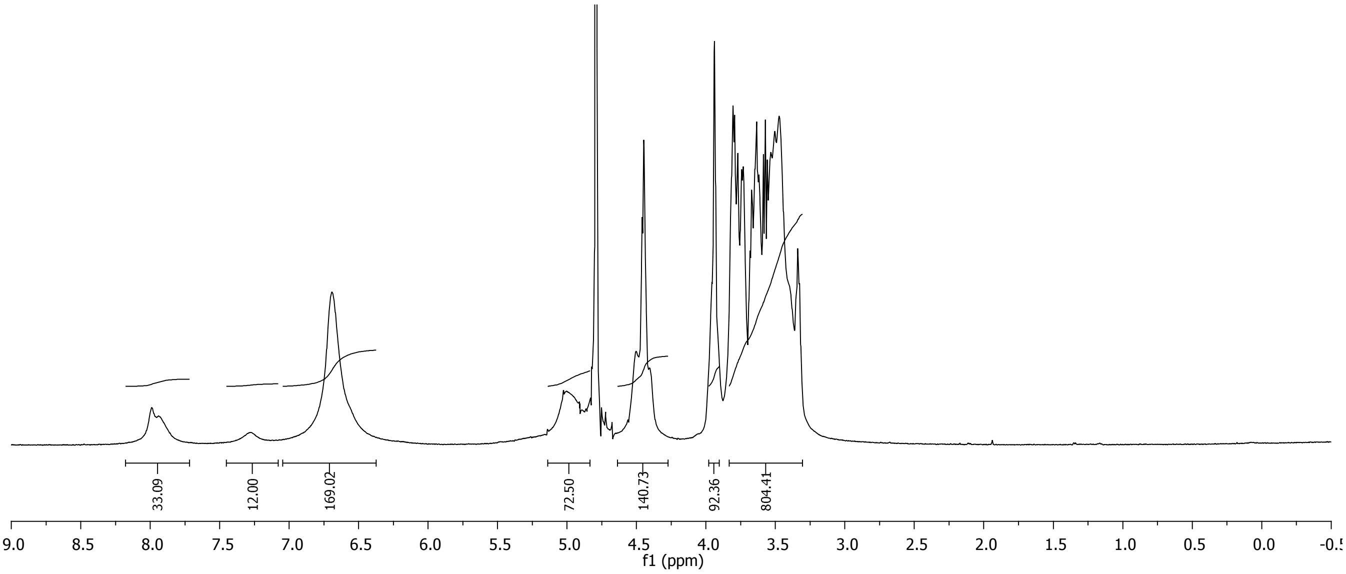


Figure S120. ^{1}H NMR spectrum of compound **28** (D_2O, 600MHz)

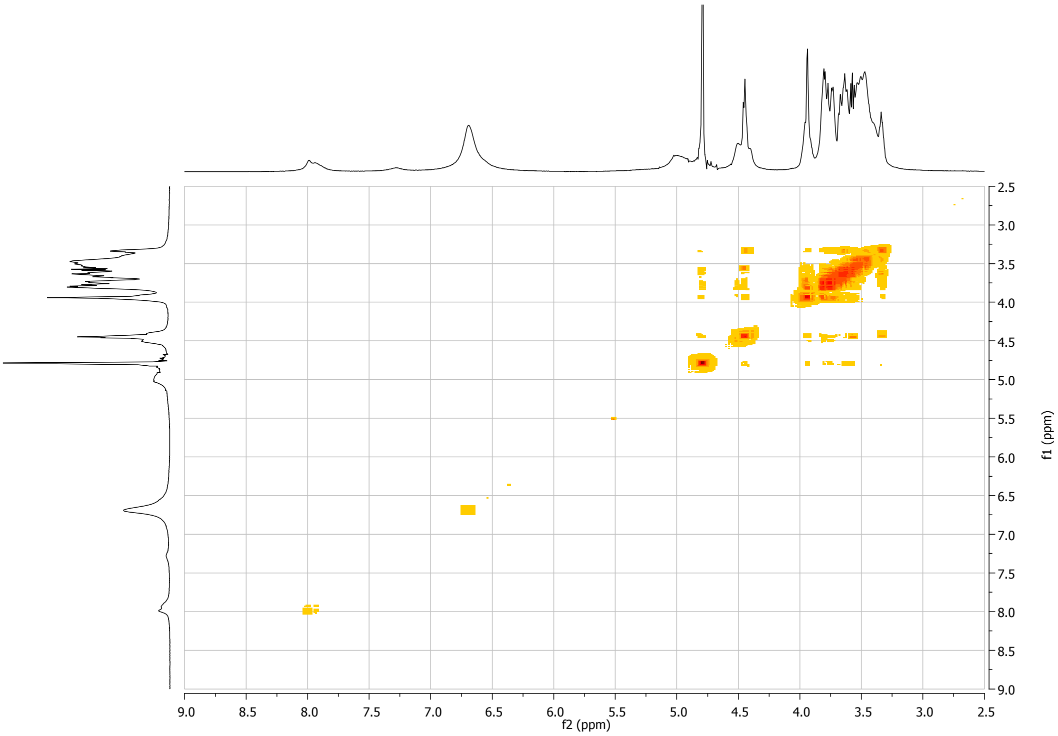


Figure S121. gCOSY spectrum of compound **28**

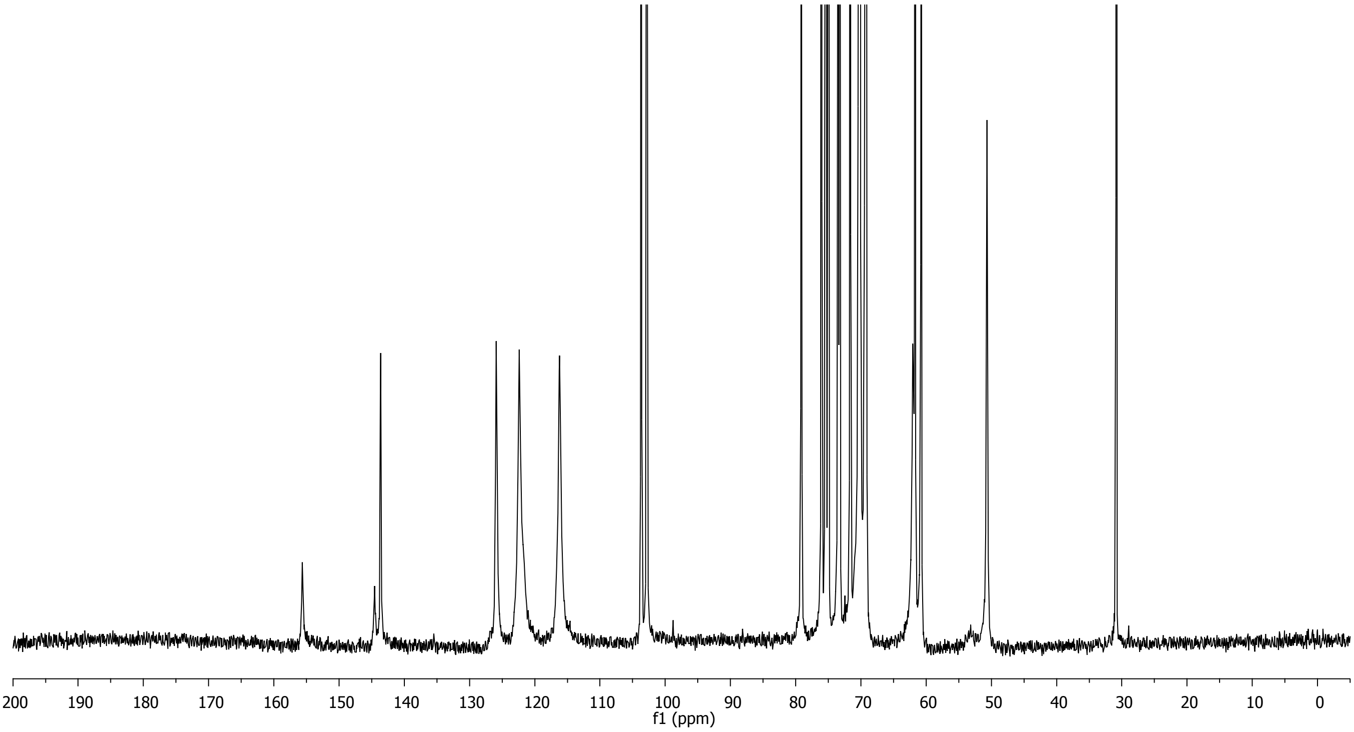


Figure S122. ^{13}C NMR spectrum of compound **28** (D_2O, 150MHz, acetone as reference)

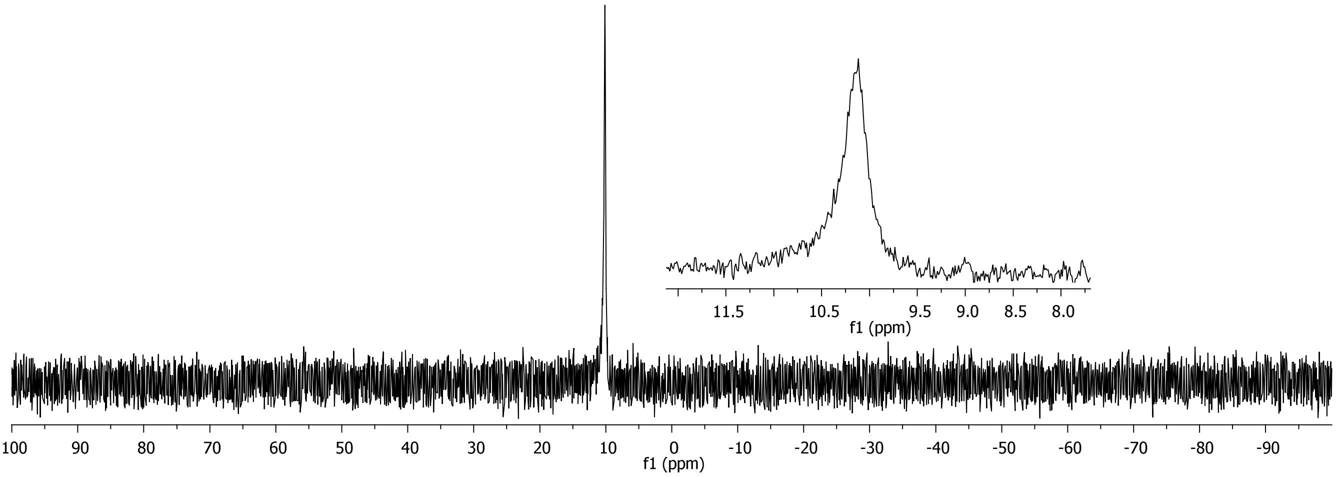


Figure S123. ^{31}P NMR spectrum of compound **28** (D_2O, 122MHz)

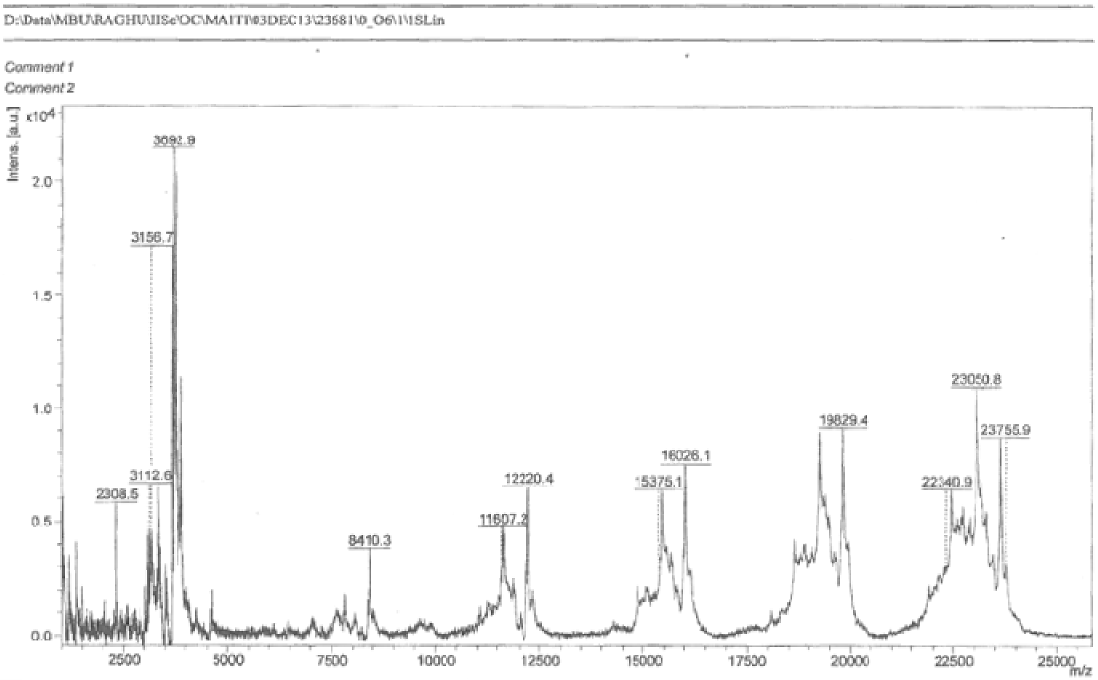


Figure S124. MALDI-TOF (DHB matrix) spectrum for compound **26** (D_2O, 600MHz)

AB_{15} glycodendron with a focal Cl 29

Chemical Formula: $C_{638}H_{897}ClN_{69}O_{347}P_3$
Exact Mass: 15204,35667
Molecular Weight: 15213,57717

To a stirring solution of **6** (9.8 mg, 9.3 µmol, 1.0 eq.) and dendron **14** (174.2 mg, 60.7 µmol, 6.5 eq.) in dry THF (2.5 mL) were added 2.5 mL of H_2O and a mixture of $CuSO_4 \cdot 5H_2O$ (13.2 mg, 52.8 µmol, 5.7 eq.) and sodium ascorbate (10.5 mg, 52.8 µmol, 5.7 eq.). After stirring for 3 hours at 50^oC in a 20 mL vial, the reaction was left stirring at room temperature for 18 hours (additional $CuSO_4 \cdot 5H_2O$ (7.0 mg) and sodium ascorbate (4.0 mg) were incorporated in the mixture after 5 hours of reaction). EtOAc (50 mL) was added and the solution was washed successively with a saturated aqueous solution of NH_4Cl (3×25 mL), water (2×20 mL) and brine (10 mL). The organic phase was then dried over $MgSO_4$ and concentrated under reduced pressure. Column chromatography on silica (DCM/MeOH 100:0 to 93:7) afforded the desired compound **29** (103.0 mg, 6.77 µmol, **73%**) as a colorless oil.

R_f = 0.18, DCM/MeOH 94:6
^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 10.1 (5H, N*H*) *not visible*, 9.48 (br s, 1H, N*H*), 7.93-7.90 (m, 5H, $H_{\text{triazole int}}$), 7.72-7.68 (s, 15H, $H_{\text{triazole ext}}$), 7.35 (m, 2H, $CH_{b'}$), 6.97-6.57 (m, 22H, CH_b, CH_c, $CH_{c'}$), 5.30 (d_{app}, 15H, H_{4gal}), 5.15 (t_{app}, 15H, H_{3glc}), 5.08-5.05 (m, 25H, C_qCH_2O, H_{2gal}), 4.93 (dd, $^3J_{2,3}$ = 3.4 Hz, $^3J_{3,4}$ = 7.0 Hz, 15H, H_{3gal}), 4.84 (t_{app}, 15H, H_{2glc}),

4.53-4.44 (m, 105H, $C_q\mathit{CH_2}O$, $OCH_2\mathit{CH_2}N$, H_{1glc}, H_{6aglc}, H_{1gal}), 4.17 (s, 2H, $C\mathit{H_2}Cl$), 4.11-4.03 (m, 45H, H_{6bglc}, H_{6agal}, H_{6bgal}), 3.88-3.55 (m, 295H, $NHCO\mathit{CH_2}N_{triazole}$, $O\mathit{CH_2}CH_2N$, H_{5gal}, H_{5glc}, H_{4glc}, $OC\mathit{H_2}$, $HNC_qC\mathit{H_2}O$), 2.11-1.92 (m, 315H, $COC\mathit{H_3}$).

^{13}C NMR (150 MHz, $CDCl_3$, δ ppm): 170.3, 170.2, 170.0, 169.9, 169.7, 169.5, 169.0 (7×s, *C*OCH$_3$), 167.1 (*C*ONH), 165.1 (*C*ONH), 155.3 (C_a), 147.3 ($\mathit{C}_{d'}$), 144.6 (C_d), 144.3 (C_d), 144.3, 144.2 ($\mathit{C}_{triazole}$=CH), 143.5 ($\mathit{C}_{triazole}$=CH), 134.6 ($\mathit{C}_{a'}$), 125.4 ($C_{triazole}$=*C*H), 125.1 ($C_{triazole}$=*C*H), 123.7 ($C_{triazole}$=*C*H), 121.8 (C_c), 120.9 ($\mathit{C}_{b'}$), 120.8 ($\mathit{C}_{c'}$), 115.9, 115.1 (C_b), 100.9 (C_{1gal}), 100.5 (C_{1glc}), 76.1 (C_{4glc}), 72.7 (C_{3glc}), 72.5 (C_{5glc}), 71.5 (C_{2glc}), 70.9 (C_{3gal}), 70.5 (C_{5gal}), 70.5, 70.4, 70.3, 70.1, 69.2 ($O\mathit{C}H_2$), 68.9 (C_{2gal}), 68.9 ($O\mathit{C}H_2$), 68.5 ($C_q\mathit{C}H_2O$), 66.5 (C_{4gal}), 64.5 ($O\mathit{C}H_2C=C$), 62.0 (C_q), 61.9 (C_{6glc} + $C_q\mathit{C}H_2O$), 60.7 (C_{6gal}), 60.3 ($O\mathit{C}H_2$), 52.5 ($N_{triazole}\mathit{C}H_2CONH$), 49.9 ($N\mathit{C}H_2$), 43.5 ($CO\mathit{C}H_2Cl$), 20.7, 20.7, 20.6, 20.5, 20.5, 20.4 (7×s, CO*C*H$_3$).

^{31}P NMR (122 MHz, $CDCl_3$, δ ppm): 9.8 (m, 3P).

m/z (ESI$^+$ MS) for $C_{638}H_{897}ClN_{69}O_{347}P_3$ = 15214.6 [*M*+H]$^+$, found 15214.3 (After deconvolution).

NMR diffusion studies ($CDCl_3$): $D = 1.57\times10^{-10}$ m^2/s; d_s = 5.1 nm.

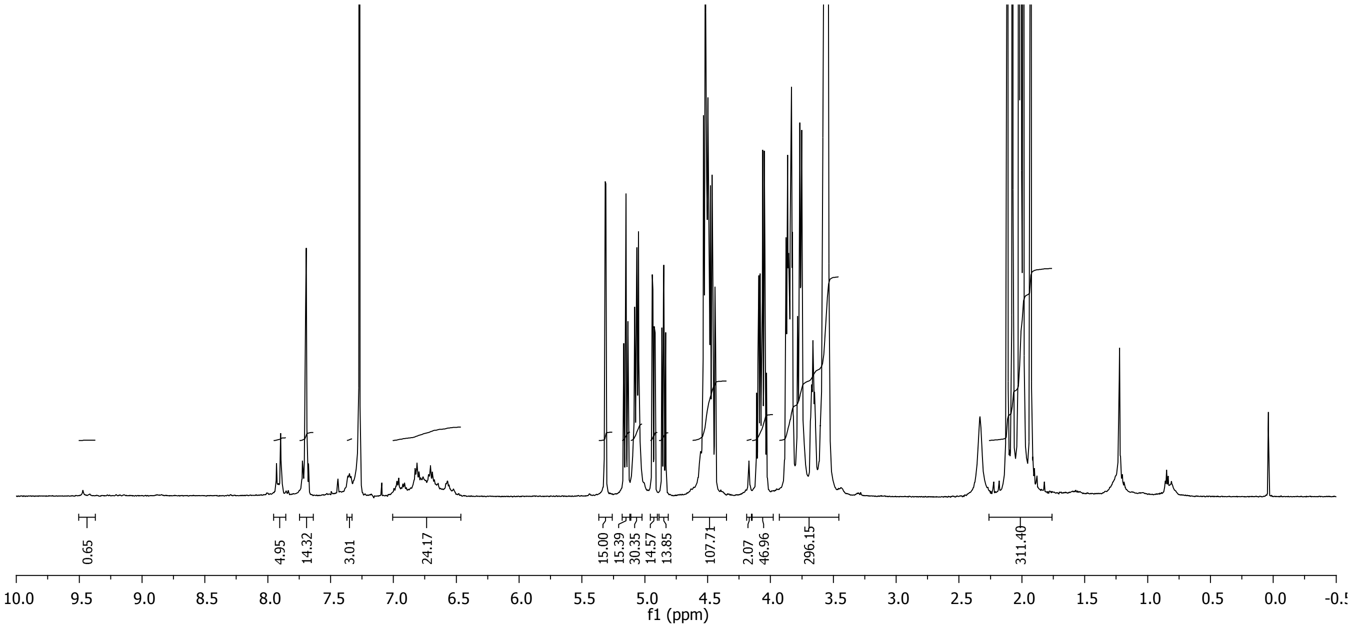


Figure S125. ^{1}H NMR spectrum of compound **29** ($CDCl_3$, 600MHz)

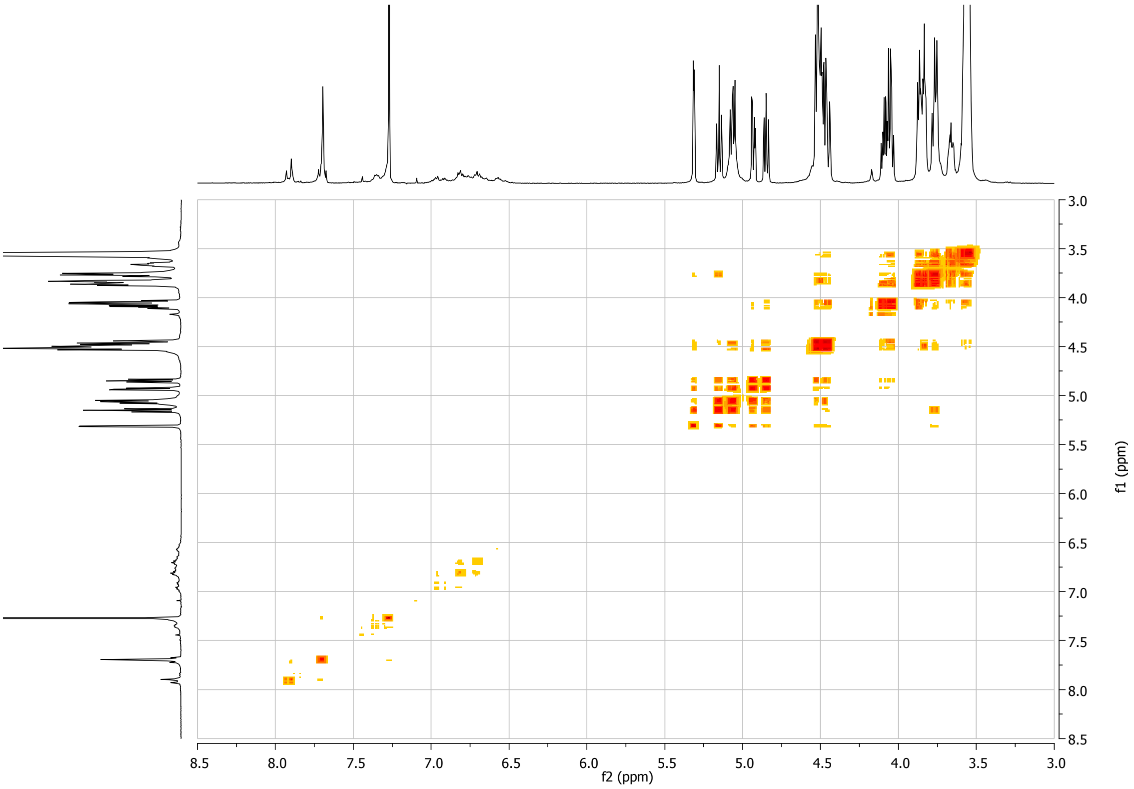


Figure S126. gCOSY spectrum of compound **29**

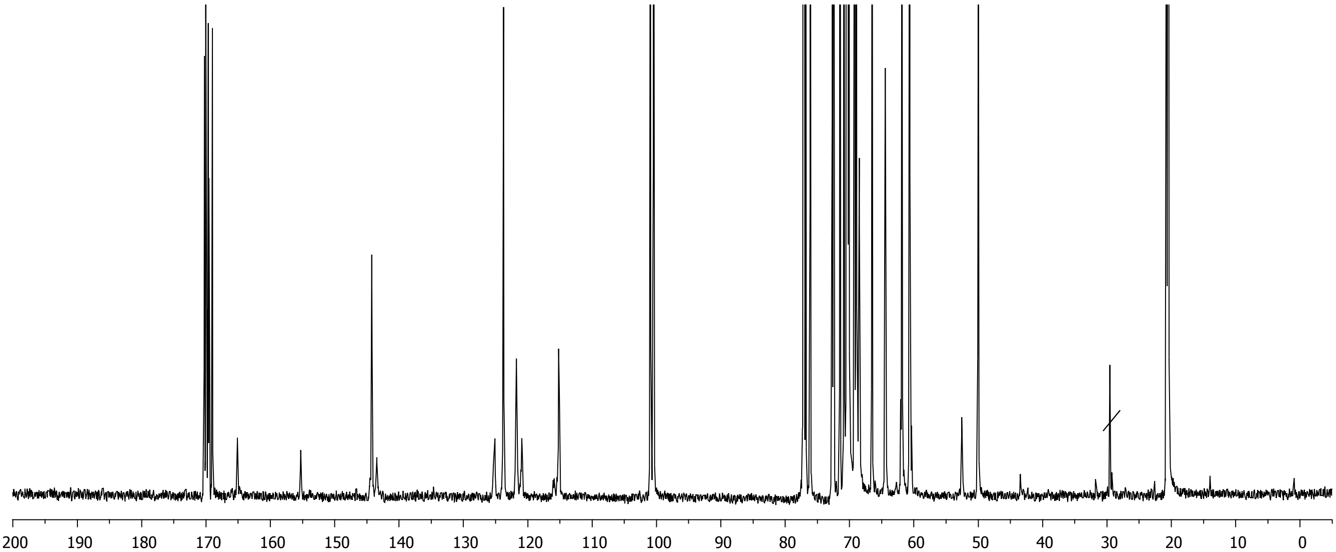


Figure S127. ^{13}C NMR spectrum of compound **29** (CDCl$_3$, 150MHz)

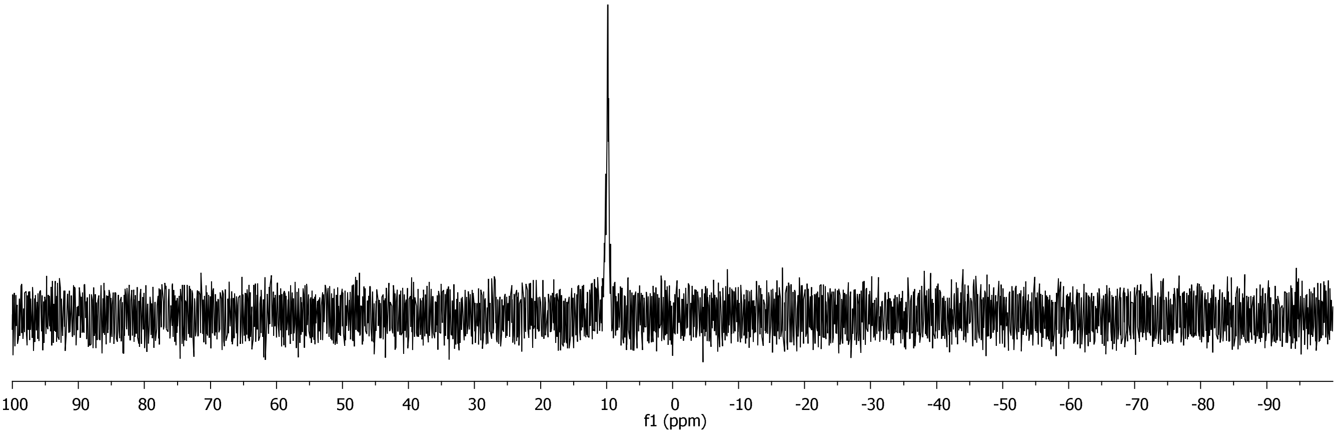


Figure S128. ^{31}P NMR spectrum of compound **29** ($CDCl_3$, 122MHz)

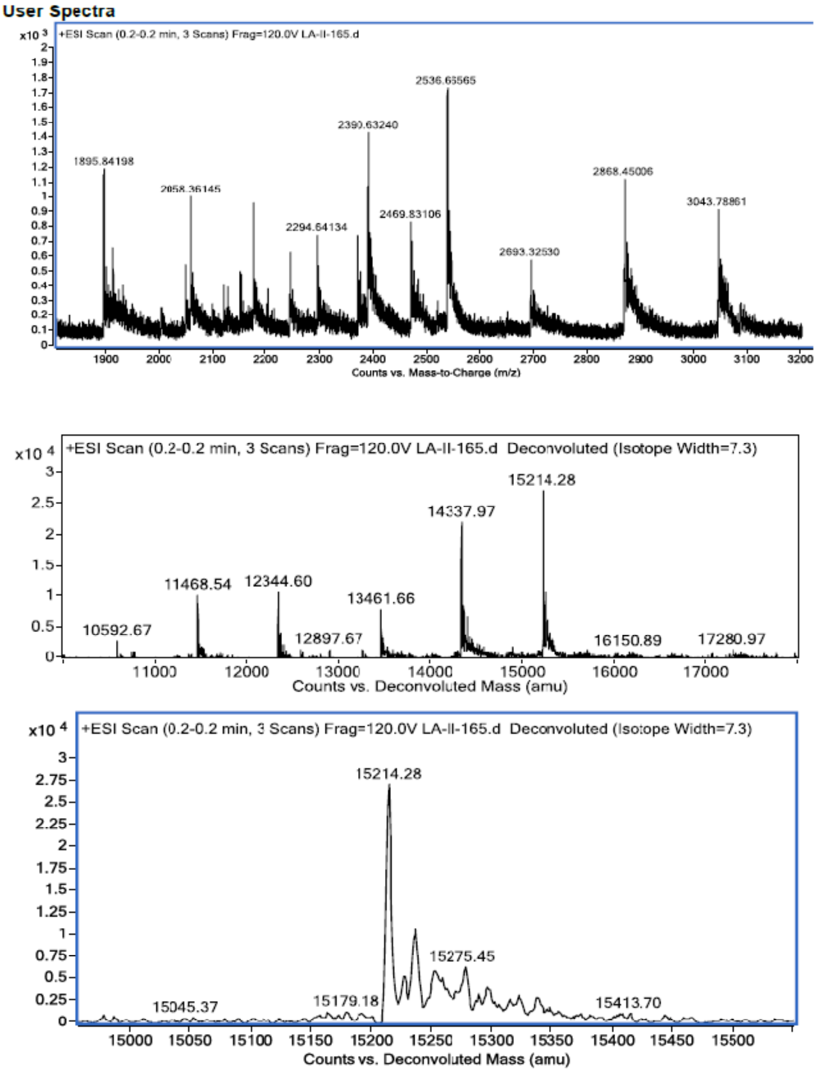


Figure S129. ESI$^+$-MS spectrum (deconvolution) of compound **29**

AB$_{15}$ glycodendron with a focal N$_3$ 30

Chemical Formula: $C_{638}H_{897}N_{72}O_{347}P_3$
Exact Mass: 15211,39704
Molecular Weight: 15220,14427

To a stirring solution of **29** (129 mg, 8.48 µmol, 1.0 eq) in dry DMF (2 mL) under a nitrogen atmosphere were added sodium azide (5.0 mg, 76 µmol, 9.0 eq.) and sodium iodide (1.0 mg, 1.7 µmol, 0.2 eq.). After stirring at 70^{o}C for 5 hours under a nitrogen atmosphere, the mixture was stirred at room temperature for additional 15 hours. The solvent was removed under reduced pressure and EtOAc was added. Then the organic was washed successively with water (4×20 mL) and brine (3×10 mL). The organic phase was then dried over Na_2SO_4 and concentrated under reduced pressure. Column chromatography on silica (DCM/MeOH 100:0 to 90:10) afforded the desired compound **30** (98.0 mg, 6.44 µmol, **76%**) as a colorless oil.

R$_f$ = 0.18, DCM/MeOH 94:6

^{1}H NMR (600 MHz, CDCl$_3$, δ ppm): 10.1 (5H, N*H*) *not visible*, 9.48 (br s, 1H, N*H*), 7.93-7.90 (m, 5H, $H_{\text{triazole int}}$), 7.73-7.67 (s, 15H, $H_{\text{triazole ext}}$), 7.33 (m, 2H, CH_{b}’), 6.99-6.57 (m, 22H, CH_b, CH_c, C$H_{c'}$), 5.30 (d$_{\text{app}}$, 15H, $H_{4\text{gal}}$), 5.16 (t$_{\text{app}}$, 15H, $H_{3\text{glc}}$), 5.09-5.04 (m, 25H, C$_q$CH_2O, $H_{2\text{gal}}$), 4.92 (dd, $^3J_{2,3}$ = 3.4 Hz, $^3J_{3,4}$ = 7.0 Hz, 15H, $H_{3\text{gal}}$), 4.84 (t$_{\text{app}}$, 15H, $H_{2\text{glc}}$), 4.53-4.44 (m, 105H, $C_\mathrm{q}CH_2O$, OCH_2CH_2N, H_1glc, H_6aglc, H_1gal), 4.11-4.03 (m, 47H, H_6bglc, H_6agal, H_6bgal, CH_2N_3), 3.84-3.52 (m, 295H, $NHCOCH_2N_\mathrm{triazole}$, OCH_2CH_2N, H_5gal, H_5glc, H_4glc, OCH_2, $HNC_\mathrm{q}CH_2O$), 2.11-1.92 (m, 315H, $COCH_3$).

^{13}C NMR (150 MHz, $CDCl_3$, δ ppm): 170.2, 170.2, 170.0, 169.9, 169.6, 169.5, 168.9 (7×s, *C*OCH$_3$), 166.0 (*C*ONH), 165.0 (*C*ONH), 155.2 (C_a), 147.3 ($C_\mathrm{d'}$), 144.6 (C_d), 144.5 (C_d), 144.3, 144.2 ($C_{triazole}$=CH), 143.4 ($C_{triazole}$=CH), 134.6 ($C_\mathrm{a'}$), 125.3 ($\mathrm{C_{triazole}}$=*C*H), 125.1 ($\mathrm{C_{triazole}}$=*C*H), 123.7 ($\mathrm{C_{triazole}}$=*C*H), 121.7 (C_c), 120.8 ($C_\mathrm{b'}$), 120.8 ($C_\mathrm{c'}$), 115.8, 115.1 (C_b), 100.9 (C_1gal), 100.4 (C_1glc), 76.1 (C_4glc), 72.6 (C_3glc), 72.4 (C_5glc), 71.4 (C_2glc), 70.8 (C_3gal), 70.4 (C_5gal), 70.4, 70.3, 70.2, 69.2 (O*C*H$_2$), 68.9 (C_2gal), 68.9 (O*C*H$_2$), 68.4 ($\mathrm{C_q}CH_2$O), 66.4 (C_4gal), 64.4 (O*C*H$_2$C=C), 62.0 (C_q), 61.9 (C_6glc + $\mathrm{C_q}CH_2$O), 60.7 (C_6gal), 60.3 (O*C*H$_2$), 52.5 ($\mathrm{N_{triazole}}CH_2$CONH), 52.1 (CO*C*H$_2N_3$), 49.9 (N*C*H$_2$), 20.7, 20.7, 20.6, 20.5, 20.5, 20.4 (7×s, CO*C*H$_3$).

^{31}P NMR (122 MHz, $CDCl_3$, δ ppm): 9.8 (m, 3P).

m/z (ESI$^+$ MS) for $C_{638}H_{897}ClN_{69}O_{347}P_3$ = 15221.1 [*M*+H]$^+$, found 15220.6 (After deconvolution).

GPC measurements (THF): M_w = 16580 ; M_n = 15400 , PDI ($M_\mathrm{w}/M_\mathrm{n}$) = 1.077.

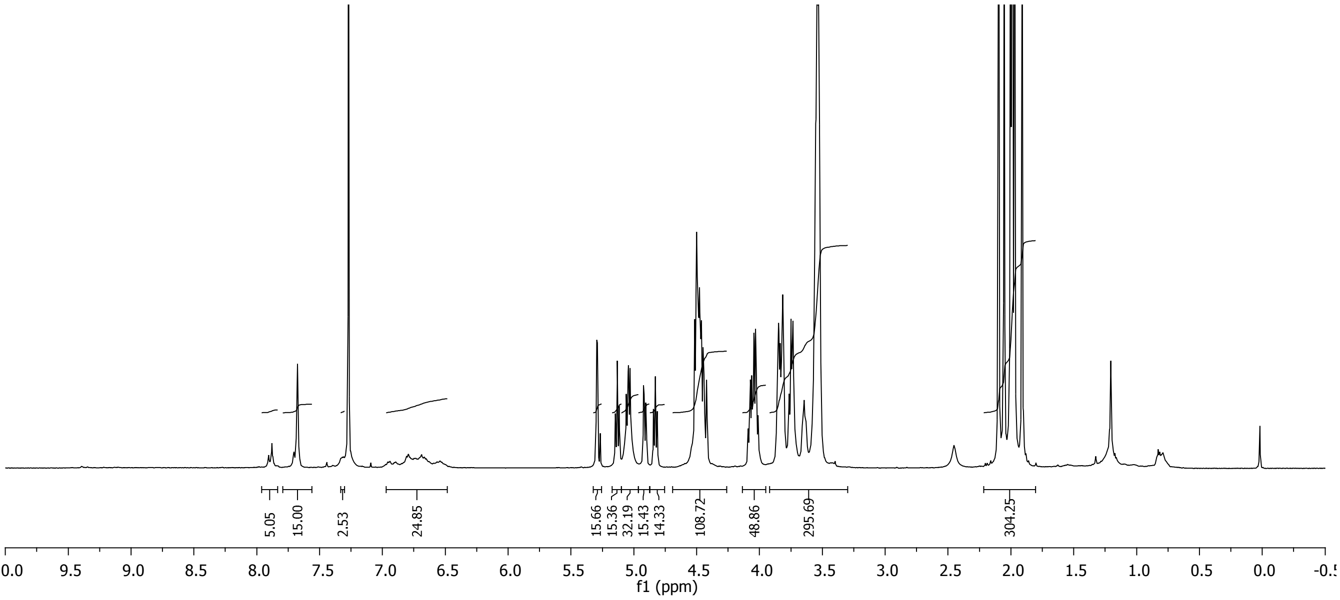


Figure S130. ^{1}H NMR spectrum of compound **30** ($CDCl_3$, 600MHz)

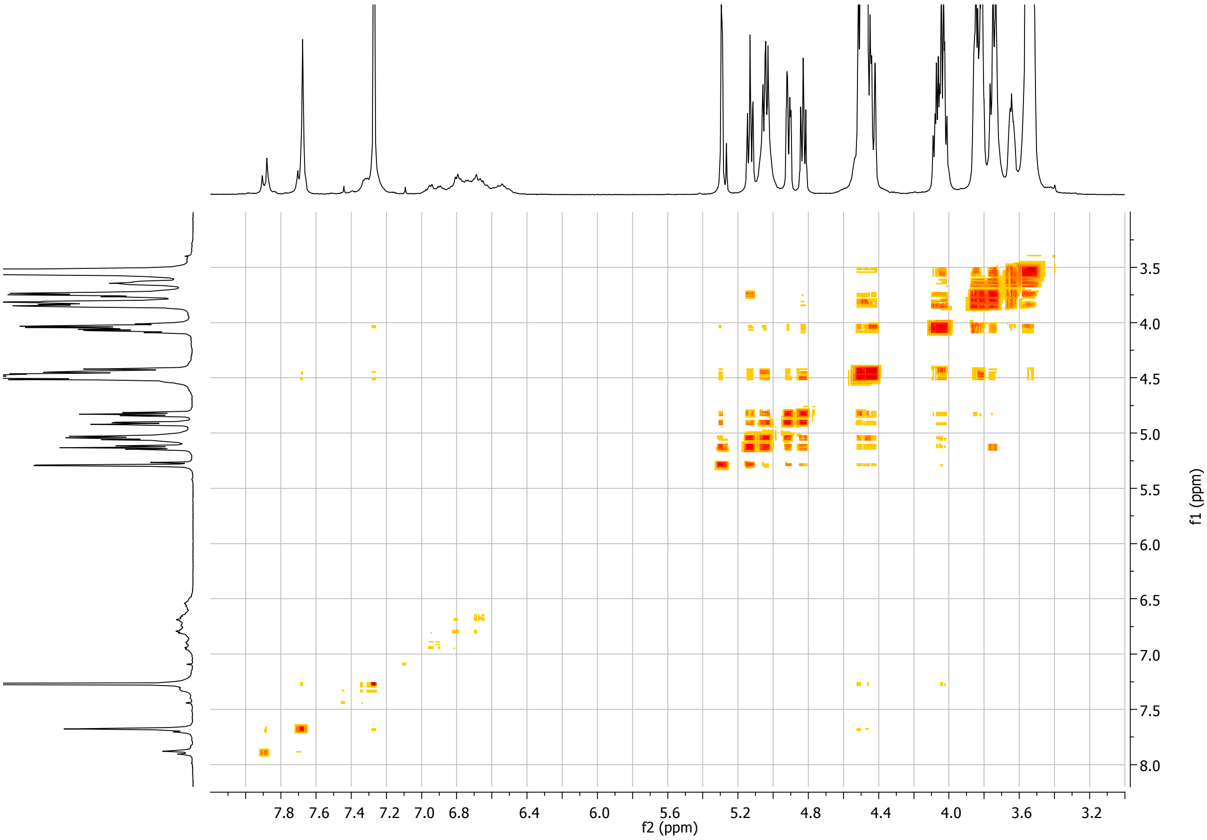


Figure S131. gCOSY spectrum of compound **30**

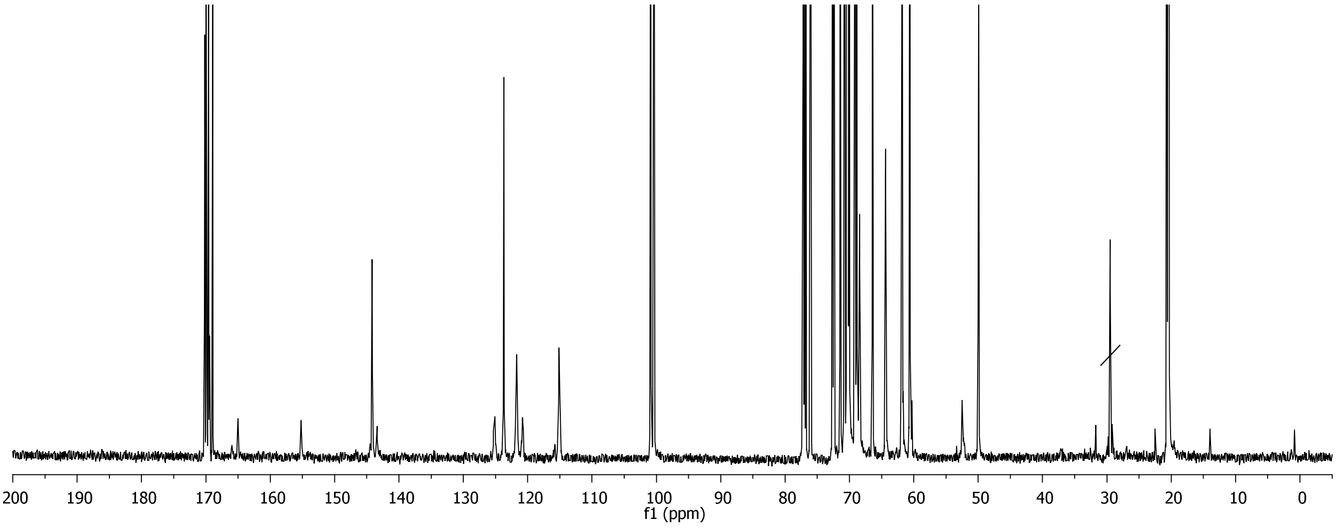


Figure S132. ^{13}C NMR spectrum of compound **30** ($CDCl_3$, 150MHz)

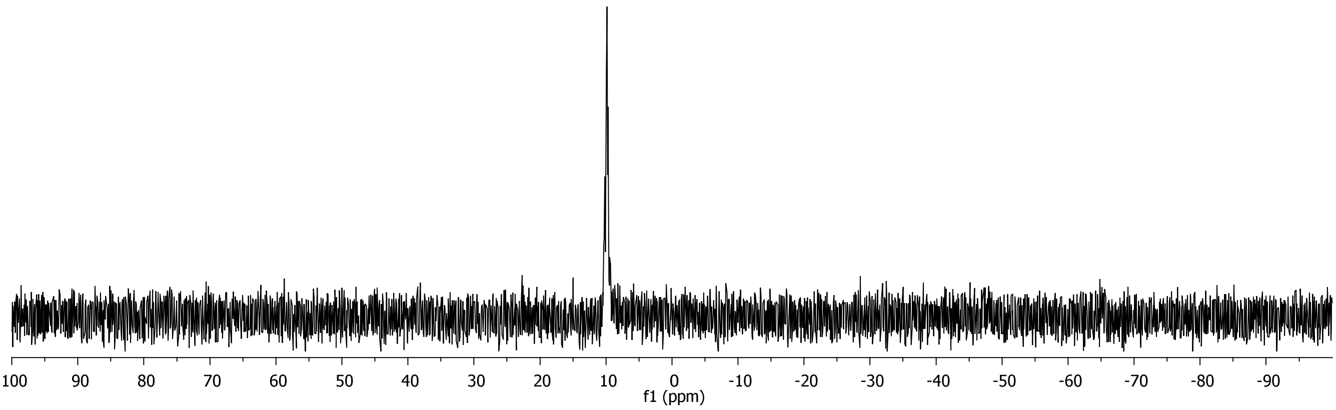


Figure S133. ^{31}P NMR spectrum of compound **30** ($CDCl_3$, 122MHz)

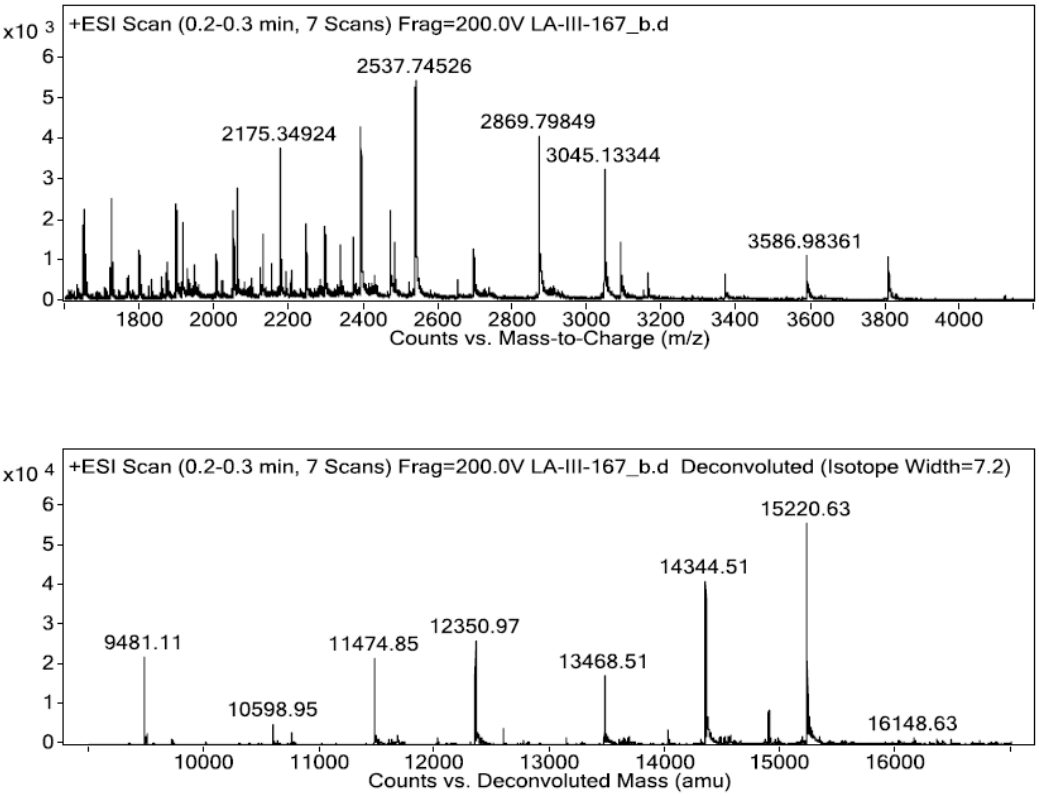
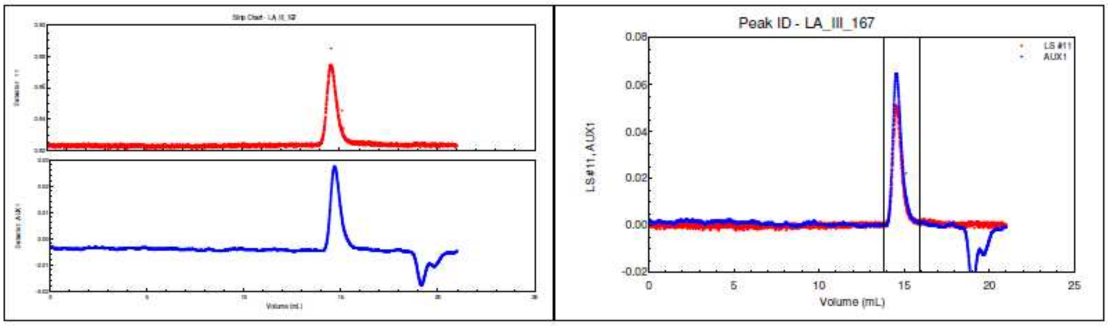
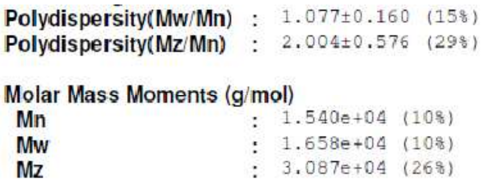


Figure S134. ESI+-MS spectrum (deconvolution) of compound **30**





```
Polydispersity(Mw/Mn)  :  1.077±0.160 (15%)
Polydispersity(Mz/Mn)  :  2.004±0.576 (29%)

Molar Mass Moments (g/mol)
  Mn                   :  1.540e+04 (10%)
  Mw                   :  1.658e+04 (10%)
  Mz                   :  3.087e+04 (26%)
```

Figure S135. GPC trace (in THF) for compound **30**

AB_{25} glycodendron with a focal N_3 31

Chemical Formula: $C_{1168}H_{1527}ClN_{114}O_{597}P_{18}$
Exact Mass: 27292,75985
Molecular Weight: 27309,00830

To a solution of cyclotriphosphazene core **6** (1.86 mg, 1.76 µmol, 1.0 eq.) in a 1:1 mixture of H_2O/THF_{anh} (5 mL), were added azido derivative **15** (60 mg, 11.4 µmol, 6.5 eq.), $CuSO_4 \cdot 5H_2O$ (2.86 mg, 11.4 µmol, 6.5 eq.) and sodium ascorbate (2.23 mg, 11.4 µmol, 6.5 eq.). While stirring, the mixture was first heated at 50℃ for 3 hours in a 20 mL vial and at room temperature for additional 18 hours. Ethyl acetate (15 mL) was added and the solution was poured into a separatory funnel containing ethyl acetate (10 mL), washed with saturated aqueous NH_4Cl (2×10 mL), water (10 mL) and brine (5 mL). Organics were collected, dried over Na_2SO_4 and concentrated to dryness *in vacuo* with rotary evaporator. Purification by flash chromatography (SiO_2, DCM/MeOH 100:0 to 85:15) afforded desired multivalent compound **31** (40.0 mg, 1.46 µmol, **83%**) as a yellowish foam.

R_f = 0.32, DCM/MeOH 92:8.

^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 10.15 (br s, 5H, N*H*), 9.45 (br s, 1H, N*H*COCH$_2$Cl), 8.03 + 7.98 (2×s, 5H, $H_{int.triazole}$), 7.89-7.83 (m, 25H, $H_{ext.triazole}$), 7.35-7.30 (m, 12H, C$H_{b'}$), 6.97-6.54 (m, 132H, CH_b, CH_c, C$H_{c'}$), 5.40 (br s, 10H, $N_{triazole}CH_2CONH$), 5.32 (d_{app}, 25H, H_{4gal}), 5.17-5.04 (m, 110H, H_{3glc}, C_qCH_2O, H_{2gal}), 4.93 (dd, $^3J_{2,3}$ = 3.3 Hz, $^3J_{3,4}$ = 7.1 Hz, 25H, H_{3gal}), 4.87-4.82 (m, 25H, H_{2glc}), 4.54-4.42 (m, 125H, CH_2N, H_{1glc}, H_{6aglc}, H_{1gal}), 4.22 (br s, 2H, $NHCOCH_2Cl$), 4.11-4.02 (m, 75H, H_{6bglc}, H_{6agal}, H_{6bgal}), 3.92-3.44 (m, 425H, H_{5gal}, H_{5glc}, H_{4glc}, OCH_2), 2.11-1.92 (m, 525H, $COCH_3$).

^{13}C NMR (150 MHz, $CDCl_3$, δ ppm): 170.3, 170.2, 170.0, 169.9, 169.7, 169.5, 169.0 (7×s, $COCH_3$), 164.4 (C=O), 163.9 (C=O), 155.2 (C_a), 146.6 ($C_{d'}$), 144.5 (C_d), 144.2 (C_d), 143.5 ($C_{triazole}$=CH), 143.3 ($C_{triazole}$=CH), 134.8 ($C_{a'}$), 125.3 ($C_{triazole}$=CH), 124.6 ($C_{triazole}$=CH), 124.1 ($C_{triazole}$=CH), 121.9 ($C_{c'}$), 121.8 ($C_{b'}$), 120.9 (C_c), 120.8 (C_c), 116.0 (C_b), 115.3 (C_b), 115.1 (C_b), 101.0 (C_{1gal}), 100.5 (C_{1glc}), 76.2 (C_{4glc}), 72.7 (C_{3glc}), 72.5 (C_{5glc}), 71.5 (C_{2glc}), 70.9 (C_{3gal}), 70.5 (C_{5gal}), 70.5, 70.4, 70.4, 70.3, 70.2, 70.1, 70.1, 69.3, 69.1, 69.0 (OCH_2), 68.9 (C_{2gal}), 68.9 (OCH_2), 66.5 (C_{4gal}), 62.1 (OCH_2C=C), 61.9 (C_{6glc}), 61.6 (OCH_2), 60.7 (C_{6gal}), 52.7 ($N_{triazole}CH_2CONH$), 50.3 (NCH_2), 50.1 (NCH_2), 43.5 ($NHCOCH_2Cl$), 20.8, 20.7, 20.6, 20.5, 20.5, 20.4 (7×s, $COCH_3$).

^{31}P NMR (122 MHz, $CDCl_3$, δ ppm): 10.2-9.7 (m, 18P).

m/z MALDI-TOF (DHB matrix) for $C_{1168}H_{1527}ClN_{114}O_{597}P_{18}$= 27309.0 ; found 27241.4.

NMR diffusion studies ($CDCl_3$): $D = 1.19\times10^{-10}$ m^2/s; d_s = 6.8 nm.

GPC measurements ($CHCl_3/Et_3N$ (1%)): M_w = 26040 ; M_n = 25230 , PDI (M_w/M_n) = 1.032.

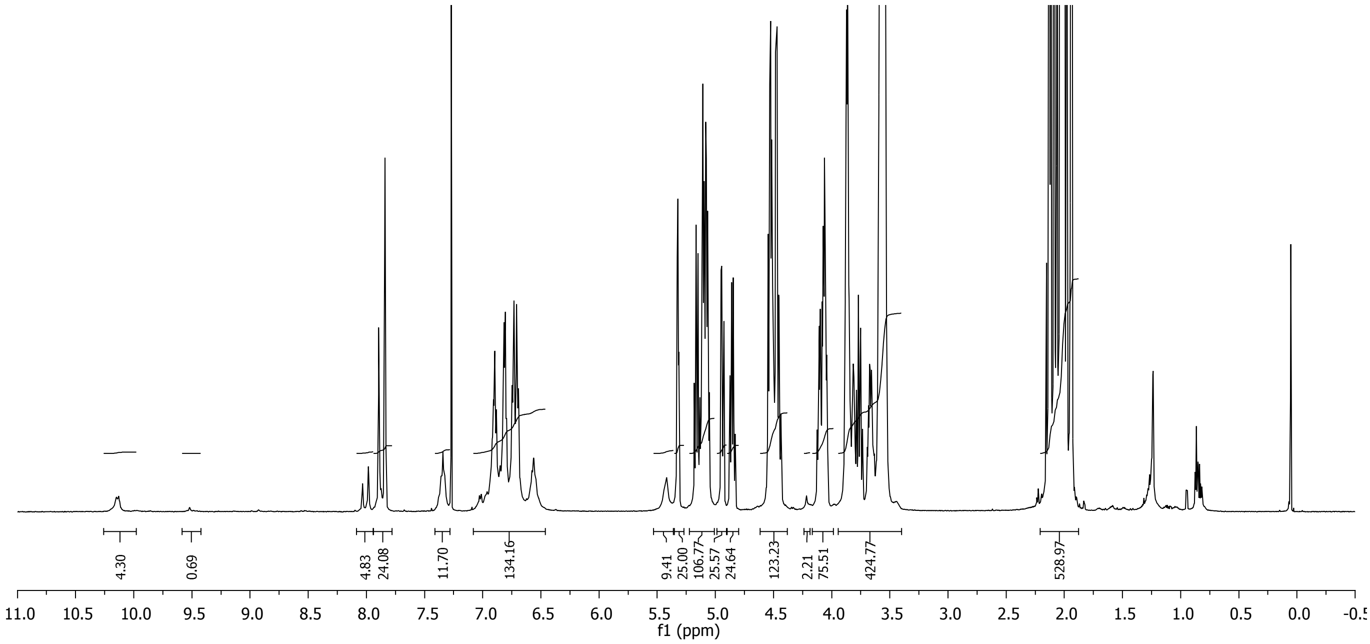


Figure S136. ^{1}H NMR spectrum of compound **31** ($CDCl_3$, 600MHz)

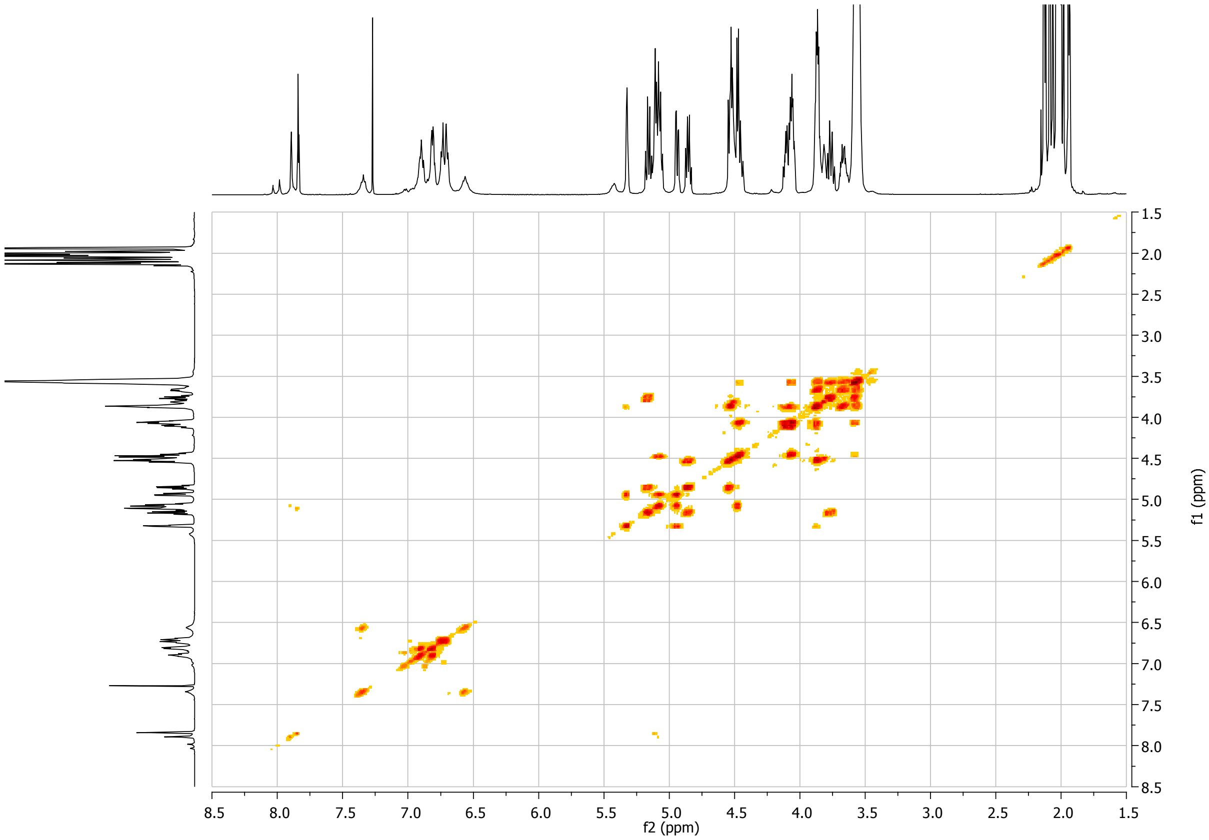


Figure S137. gCOSY spectrum of compound **31**

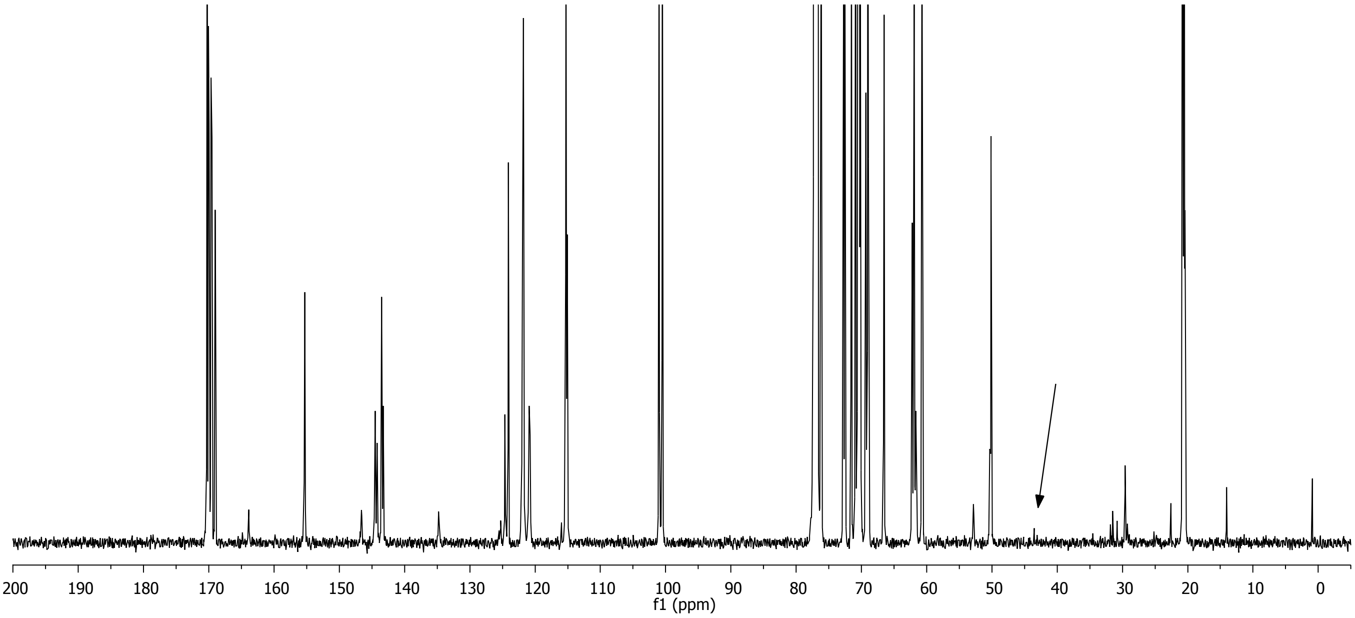


Figure S138. ^{13}C NMR spectrum of compound **31** ($CDCl_3$, 150MHz)

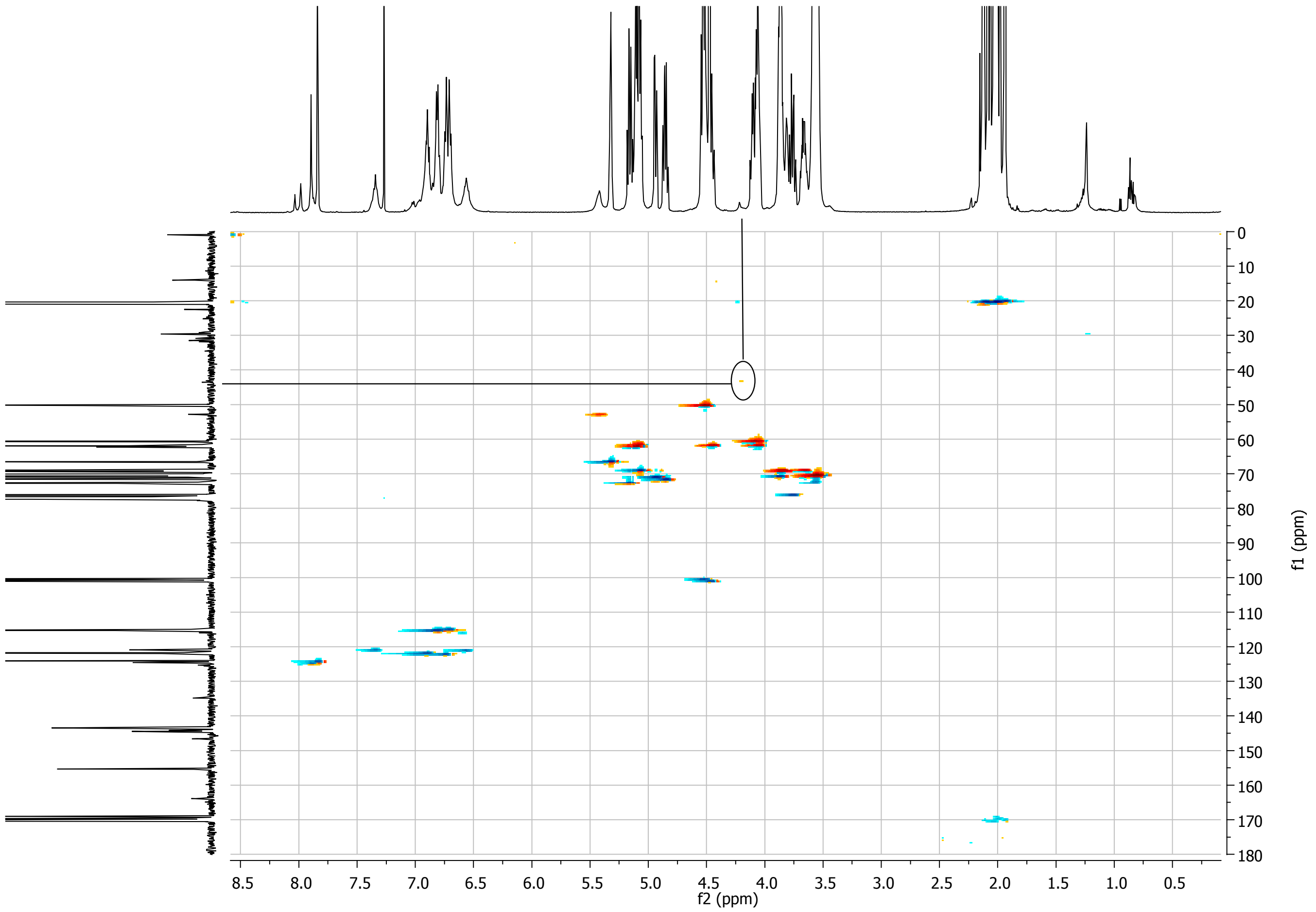


Figure S139. HETCOR spectrum of compound **31**

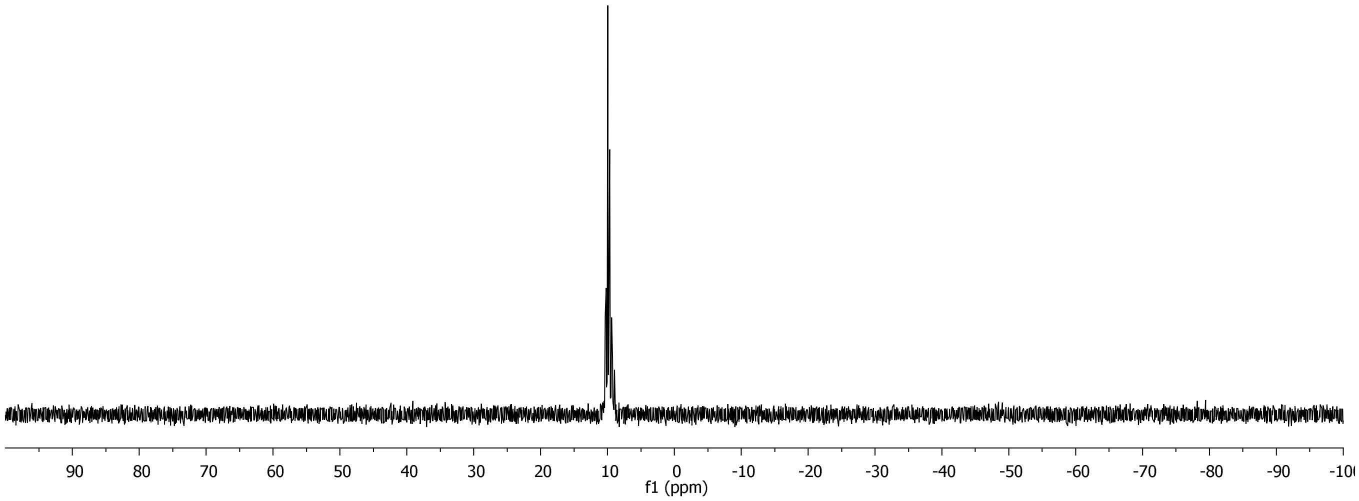


Figure S140. ^{31}P NMR spectrum of compound **31** ($CDCl_3$, 122MHz)

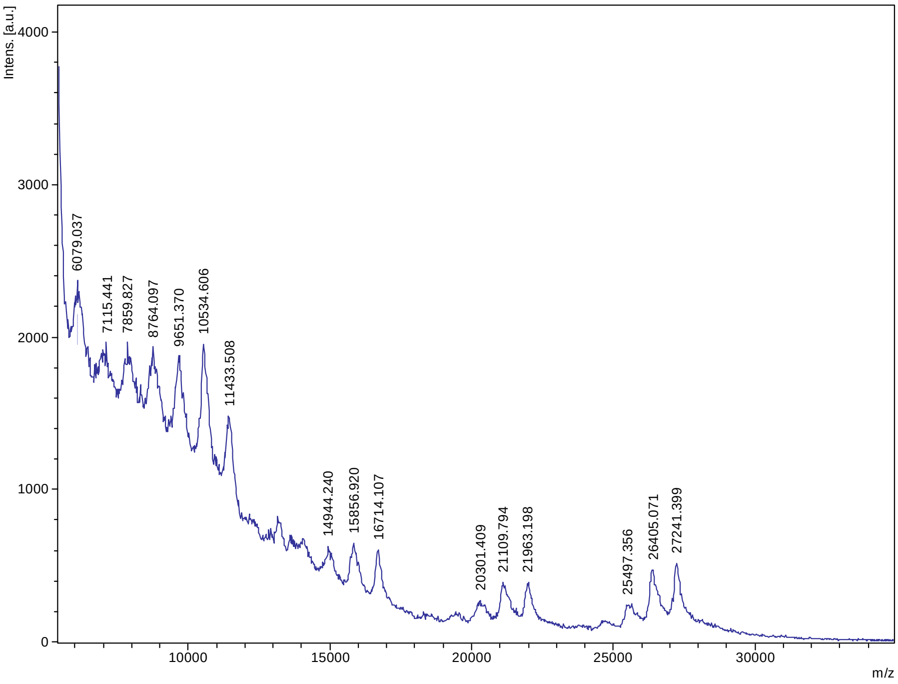
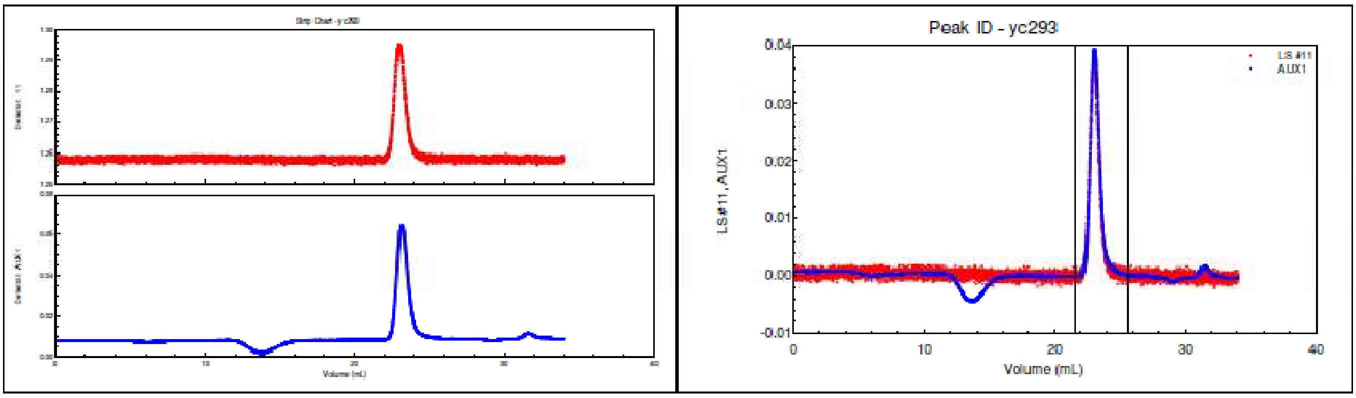
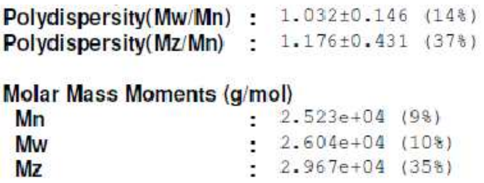


Figure S141. MALDI-TOF spectrum (DHB matrix) of compound **31**

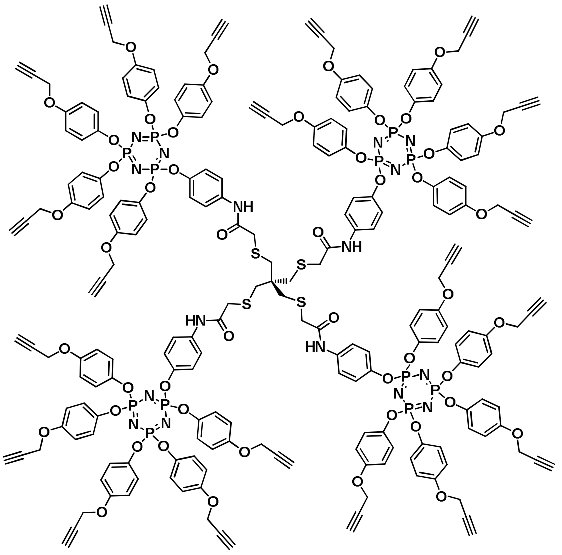



Polydispersity(Mw/Mn) : 1.032±0.146 (14%)
Polydispersity(Mz/Mn) : 1.176±0.431 (37%)

Molar Mass Moments (g/mol)
Mn : 2.523e+04 (9%)
Mw : 2.604e+04 (10%)
Mz : 2.967e+04 (35%)

Figure S142. GPC trace ($CHCl_3$/Et_3N (1%)) for compound **31**

Hypercore with 20 peripheral propargylic functions 34



To a solution of tetrathioacetylated pentaerythritol core **32** (3.42 mg, 9.28 µmol, 1.0 eq.) and chloroacetamide dendron **6** (51.0 mg, 48.3 µmol, 5.2 eq.) in dry EtOH (1.5 mL) were added at room temperature finely ground NaOH (2.97 mg, 74.3 µmol, 8.0 eq.) and $NaBH_4$ (3.00 mg, 74.4 µmol, 8.0 eq.) under a nitrogen atmosphere. The white solution was warmed up to 35℃ for 3 h.. Insoluble brown oil quickly formed corresponding to the desired compound. The solvent was then removed *via* syringe and the residual oil was rinsed once with cold EtOH while stirring (2×2.5 mL). Finally, the oil was solubilized in CH_2Cl_2 and purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 100:0 to 99:1) to afford desired icosapropargylated core **34** (31.0 mg, 7.71 µmol, **83%**) as an off-white foam.

R_f = 0.29, CH_2Cl_2/MeOH 98:2

^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 8.53 (br s, 4H, N*H*), 7.39 (d, 8H, *J* = 9.0 Hz, C*H*$_{b'}$), 6.88-6.76 (m, 88H, C*H*$_b$, C*H*$_c$, C*H*$_{c'}$), 4.63 (m, 40H, OC*H*$_2$C≡CH), 3.39 (br s, 8H, SC*H*$_2$CONH), 2.84 (br s, 8H, C$_q$C*H*$_2$S), 2.54 (m, 20H, C≡C*H*).

^{13}C NMR (150 MHz, $CDCl_3$, δ ppm): 166.4 (*C*=O), 154.5 (*C*$_a$), 147.1 (*C*$_{d'}$), 144.7 (*C*$_d$ (×2)), 134.3 (*C*$_{a'}$), 121.8 (*C*$_c$ (×2)), 121.4 (*C*$_{b'}$), 121.0 (*C*$_{c'}$), 115.4 (*C*$_b$ (×2)), 78.6 (*C*≡CH), 78.4 (*C*≡CH), 76.0 (C≡*C*H), 75.8 (C≡*C*H (×2)), 56.2 (O*C*H$_2$ (×3)), 44.0 (*C*$_q$), 38.5 (S*C*H$_2$CONH), 37.4 (C$_q$*C*H$_2$S).

^{31}P NMR (122 MHz, $CDCl_3$, δ ppm): 9.71 (t_{app}, 12P).

m/z (ESI$^+$-MS) for $C_{217}H_{176}N_{16}O_{48}P_{12}S_4$ = 2137.3851 $[M+2H]^{2+}$; found 2137.3857; 1425.2592 $[M+3H]^{3+}$; found 1425.2595.

GPC measurements ($CHCl_3$): M_w = 4625 ; M_n = 4540 , PDI (M_w/M_n) = 1.019.

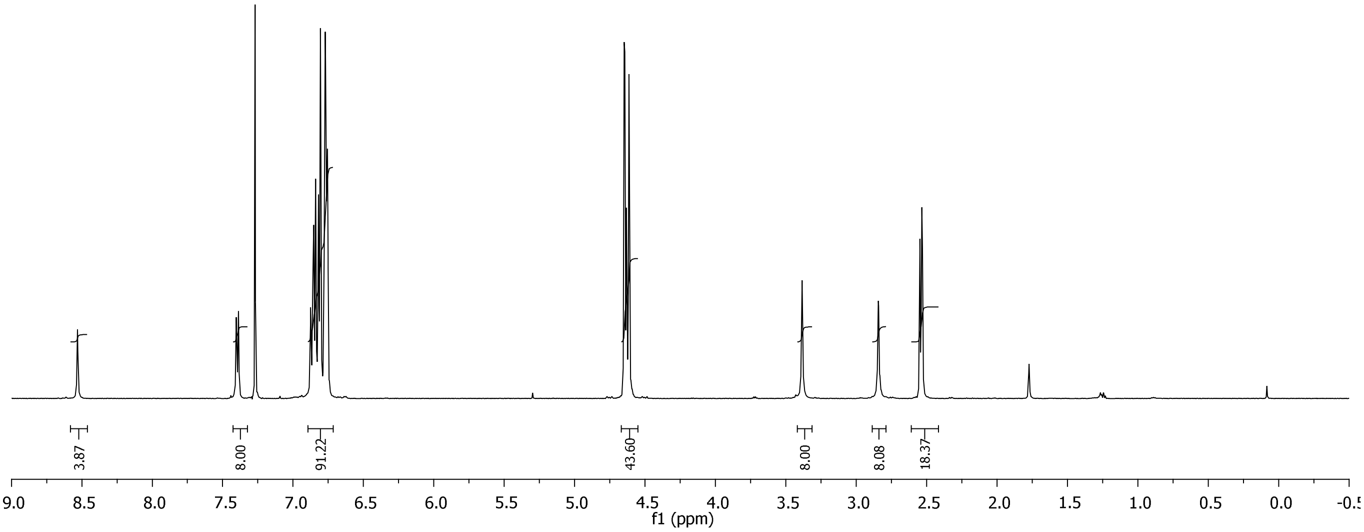


Figure S143. ^{1}H NMR spectrum of compound **34** ($CDCl_3$, 600MHz)

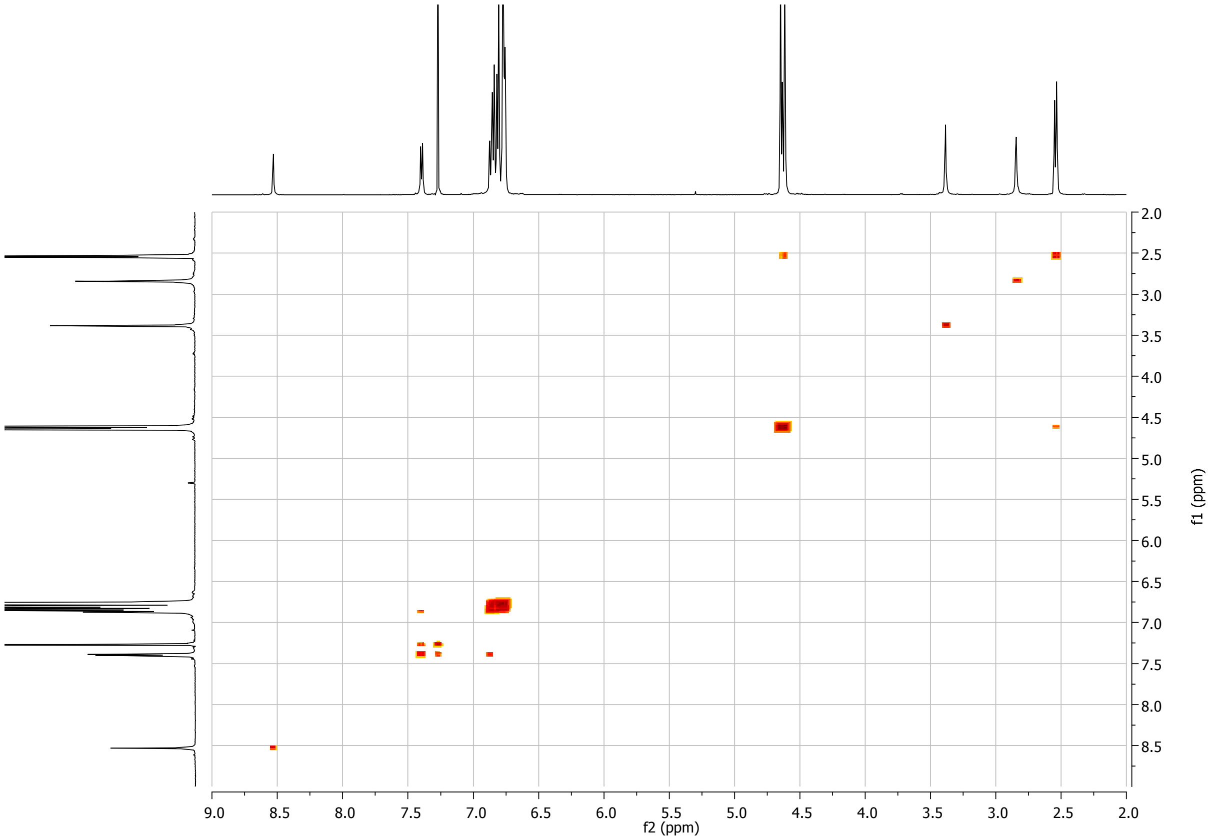


Figure S144. gCOSY spectrum of compound **34**

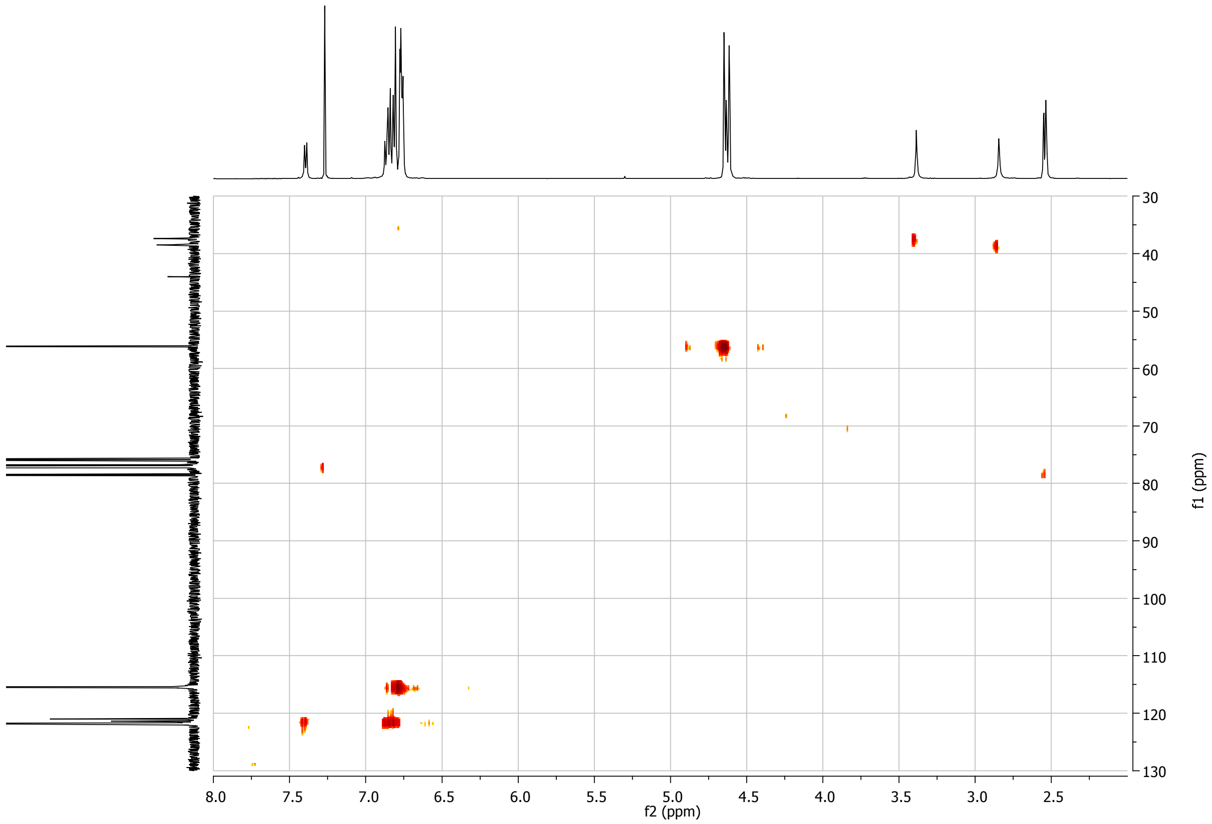


Figure S145. HETCOR spectrum of compound **34**

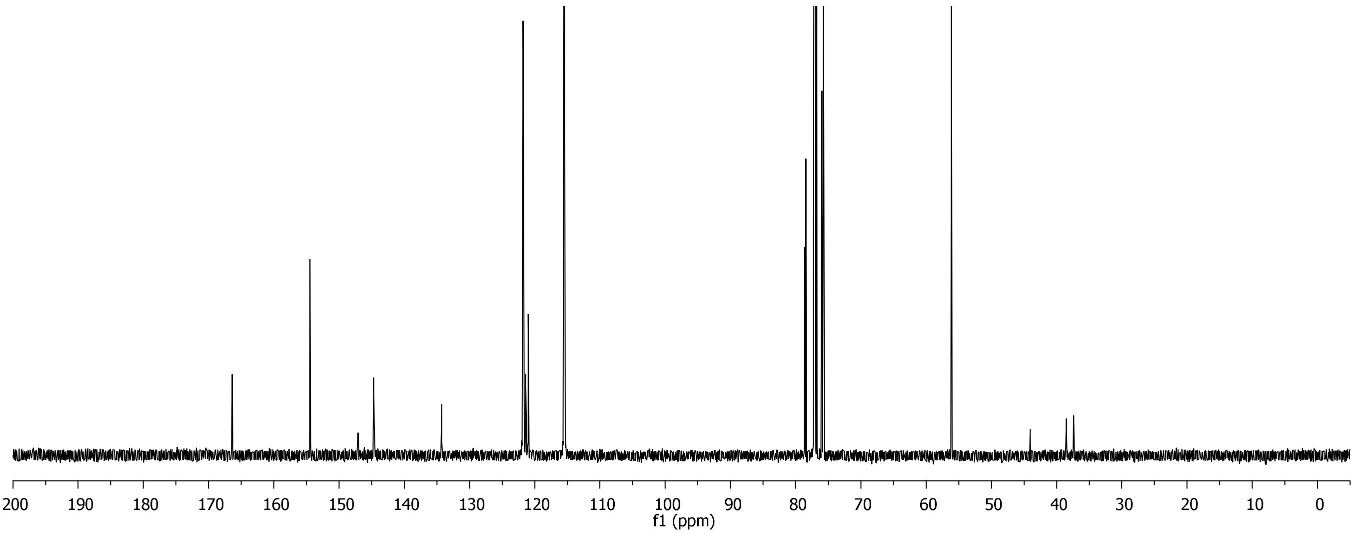


Figure S146. ^{13}C NMR spectrum of compound **34** ($CDCl_3$, 150MHz)

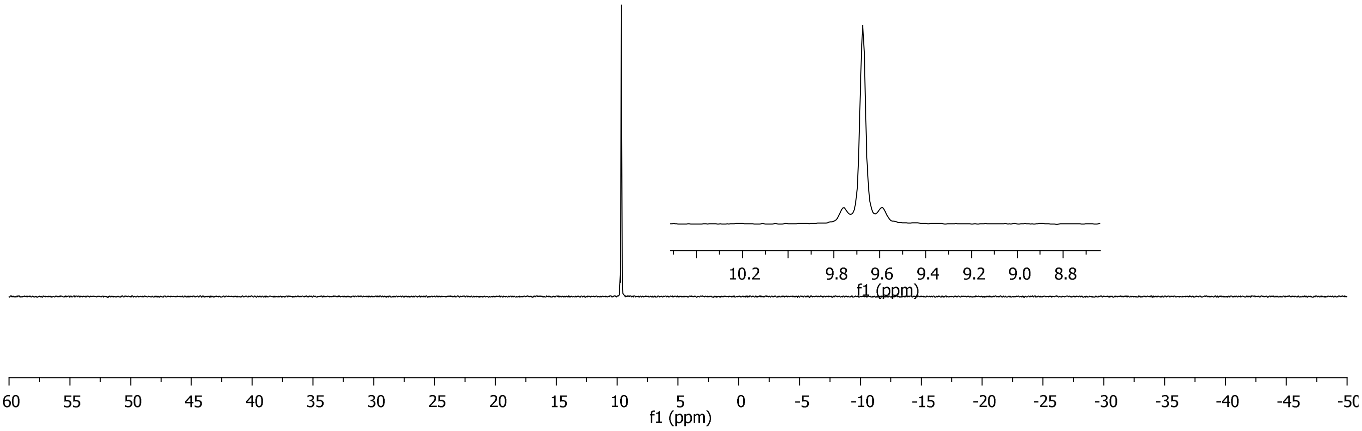
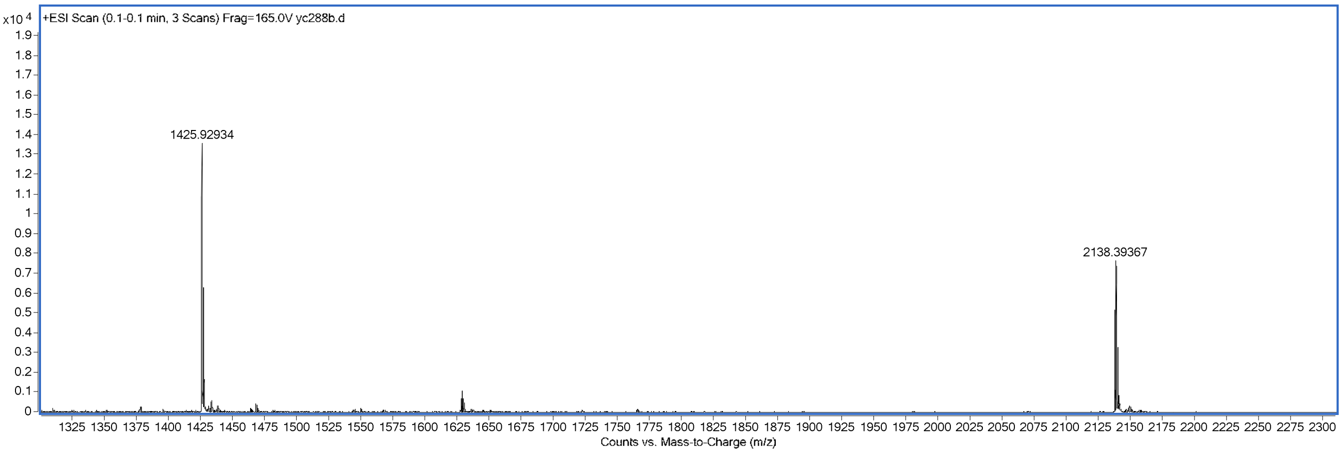
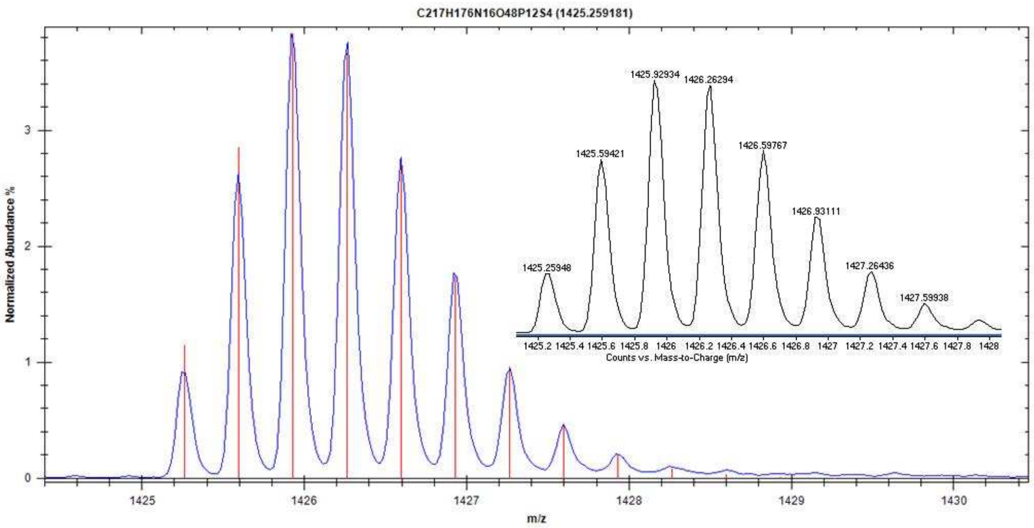
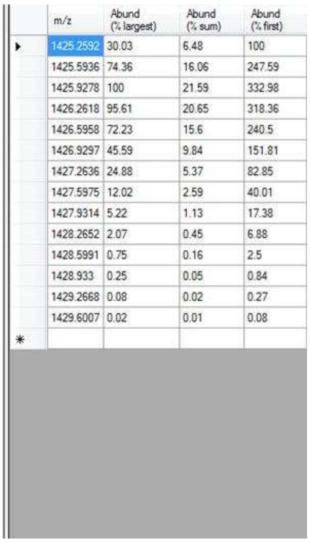


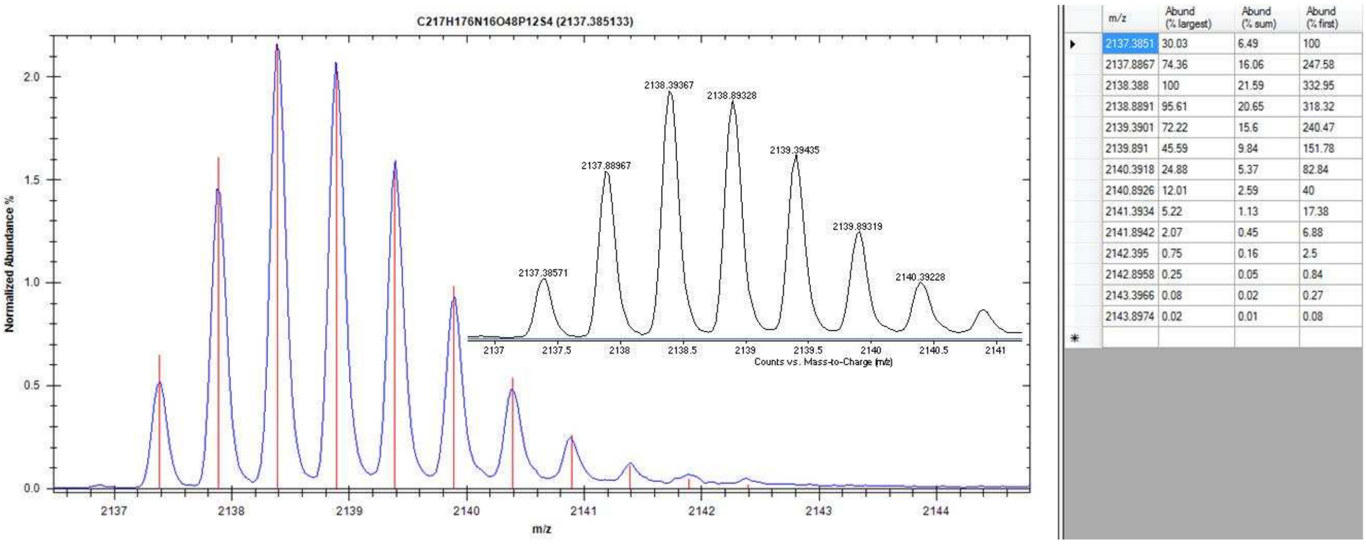
Figure S147. ^{31}P NMR spectrum of compound **34** ($CDCl_3$, 122MHz)





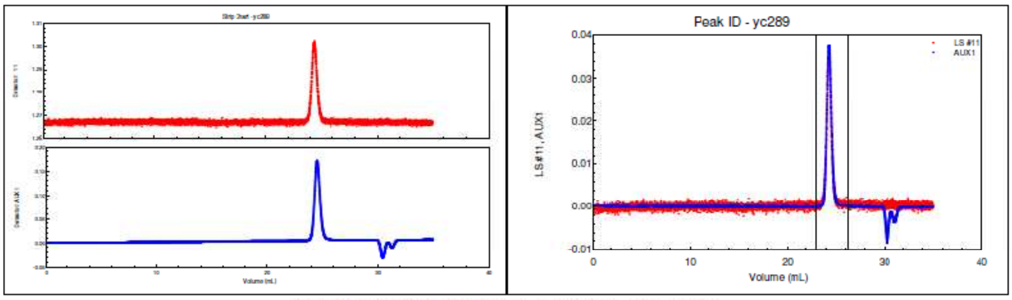


m/z	Abund (% largest)	Abund (% sum)	Abund (% first)
1425.2592	30.03	6.48	100
1425.5936	74.36	16.06	247.59
1425.9278	100	21.59	332.98
1426.2618	95.61	20.65	318.36
1426.5958	72.23	15.6	240.5
1426.9297	45.59	9.84	151.81
1427.2636	24.88	5.37	82.85
1427.5975	12.02	2.59	40.01
1427.9314	5.22	1.13	17.38
1428.2652	2.07	0.45	6.88
1428.5991	0.75	0.16	2.5
1428.933	0.25	0.05	0.84
1429.2668	0.08	0.02	0.27
1429.6007	0.02	0.01	0.08



	m/z	Abund (% largest)	Abund (% sum)	Abund (% first)
▸	2137.3851	30.03	6.49	100
	2137.8867	74.36	16.06	247.58
	2138.388	100	21.59	332.95
	2138.8891	95.61	20.65	318.32
	2139.3901	72.22	15.6	240.47
	2139.891	45.59	9.84	151.78
	2140.3918	24.88	5.37	82.84
	2140.8926	12.01	2.59	40
	2141.3934	5.22	1.13	17.38
	2141.8942	2.07	0.45	6.88
	2142.395	0.75	0.16	2.5
	2142.8958	0.25	0.05	0.84
	2143.3966	0.08	0.02	0.27
	2143.8974	0.02	0.01	0.08
*				

Figure S148. ESI^+-HRMS spectrum of compound **34**

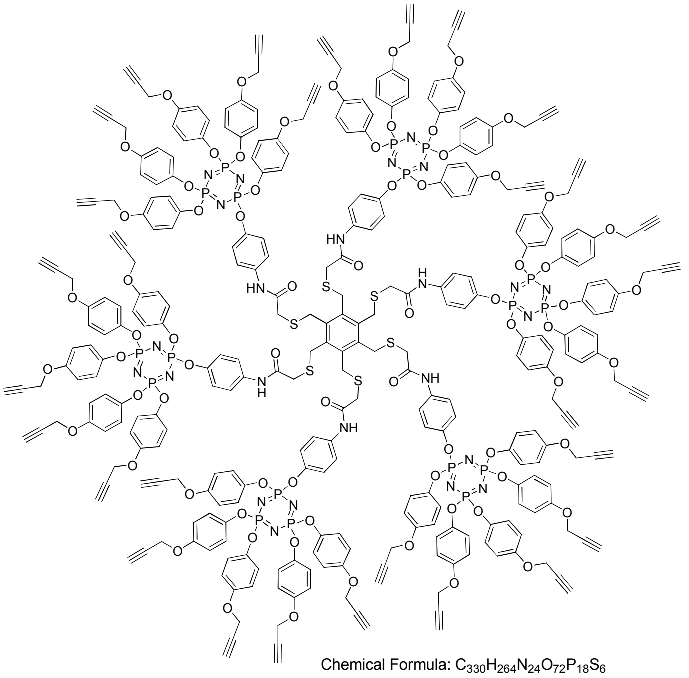


```
Polydispersity(Mw/Mn)  :  1.019±0.158 (15%)
Polydispersity(Mz/Mn)  :  1.052±0.305 (29%)

Molar Mass Moments (g/mol)
 Mn                    :  4.540e+03 (10%)
 Mw                    :  4.625e+03 (11%)
 Mz                    :  4.776e+03 (26%)
```

Figure S149. GPC trace (in $CHCl_3$) of compound **34**

Hypercore with 30 peripheral propargylic functions 35



Chemical Formula: $C_{330}H_{264}N_{24}O_{72}P_{18}S_6$
Exact Mass: 6463,13357
Molecular Weight: 6467,66248

To a solution of hexakis(thioacetyl)benzene core **33**[4] (3.67 mg, 6.02 µmol, 1.0 eq.) and chloroacetamide dendron **6** (50.0 mg, 47.4 µmol, 7.9 eq.) in dry EtOH (2.0 mL) were added at room temperature finely ground NaOH (3.50 mg, 87.5 µmol, 14.5 eq.) and $NaBH_4$ (3.50 mg, 92.5 µmol, 15.3 eq.) under a nitrogen atmosphere. The white solution was warmed up to 35℃ for 3 h. and an insoluble oil quickly formed. The solvent was removed *via* syringe and the residual oil was rinced with EtOAc while stirring (3×10 mL). Finally, the oil was solubilized in CH_2Cl_2 and purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 100:0 to 99.5:0.5) to afford desired tricontapropargylated core **35** (29 mg, 4.48 µmol, **74%**) as an off-white foam. *Degradation occurs after 3 days at -20^{o}C.*

R_f = 0.11, CH_2Cl_2/MeOH 98:2
^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 8.58 (br s, 6H, N*H*), 7.42 (d, 12H, *J* = 9.0 Hz, $CH_{b'}$), 6.90-6.73 (m, 132H, CH_b, CH_c, $CH_{c'}$), 4.60 (m, 60H, $OCH_2C{\equiv}CH$), 4.12 (br s, 12H, $C_{core}CH_2S$), 3.28 (br s, 12H, SCH_2CONH), 2.53 (m, 30H, $C{\equiv}CH$).
^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 167.7 (*C*=O), 154.6 (C_a), 147.2 ($C_{d'}$), 144.7 (C_d), 136.2 ($C_{q\ core}$), 134.6 ($C_{a'}$), 121.7 (C_c), 121.5 ($C_{b'}$), 121.2 ($C_{c'}$), 115.4 (C_b), 78.7 ($C{\equiv}CH$), 78.6 ($C{\equiv}CH$), 75.9 ($C{\equiv}CH$), 75.9 ($C{\equiv}CH$), 56.3 (OCH_2), 56.2 (OCH_2), 37.8 (SCH_2CONH), 31.2 ($C_{core}CH_2S$).
^{31}P NMR (122 MHz, $CDCl_3$, δ ppm): 9.69 (s_{app}, 18P).
m/z (MALDI-TOF/DHB matrix) for $C_{330}H_{264}N_{24}O_{72}P_{18}S_6$ = 6467.6; found 6468.9.
GPC measurements (THF): M_w = 7152 ; M_n = 6399 , PDI (M_w/M_n) = 1.12.

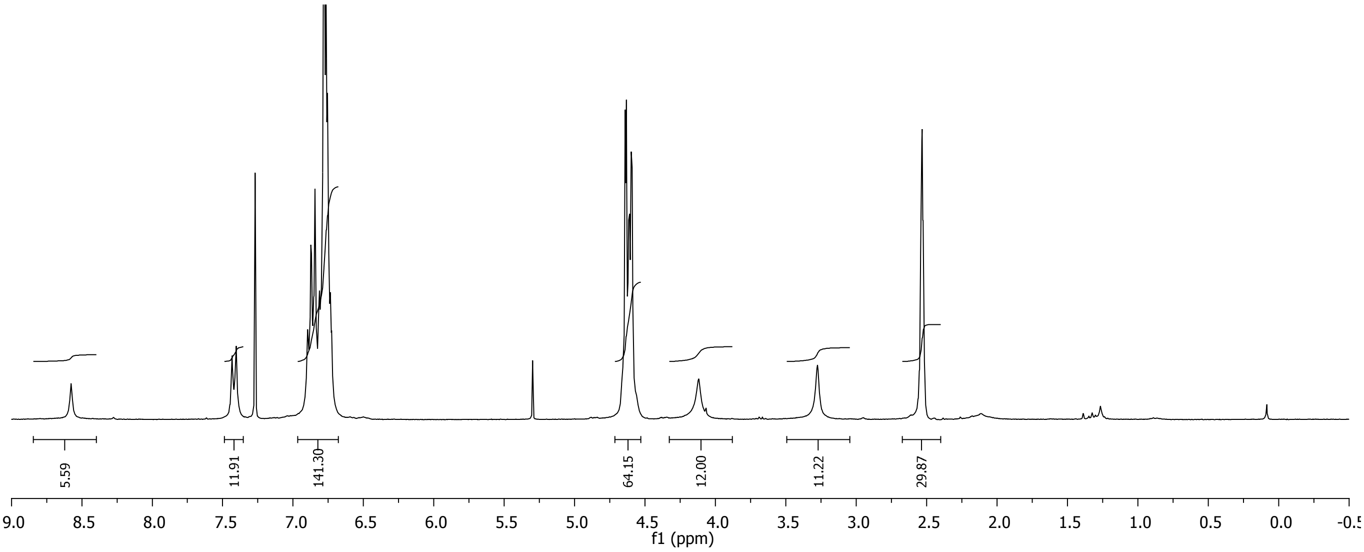


Figure S150. ^{1}H NMR spectrum of compound **35** ($CDCl_3$, 300MHz)

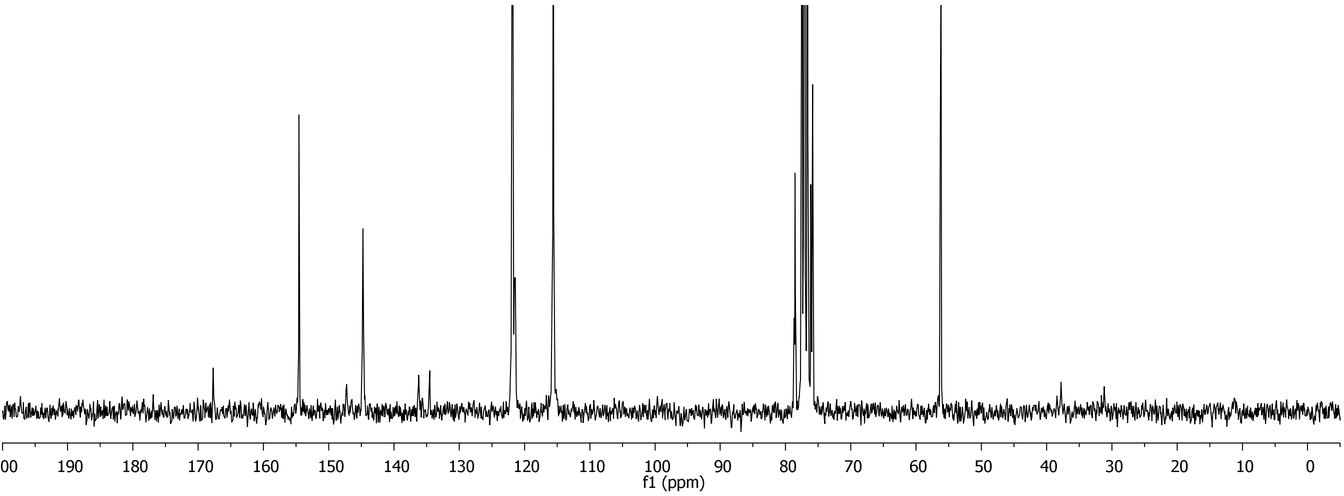


Figure S151. ^{13}C NMR spectrum of compound **35** ($CDCl_3$, 75MHz)

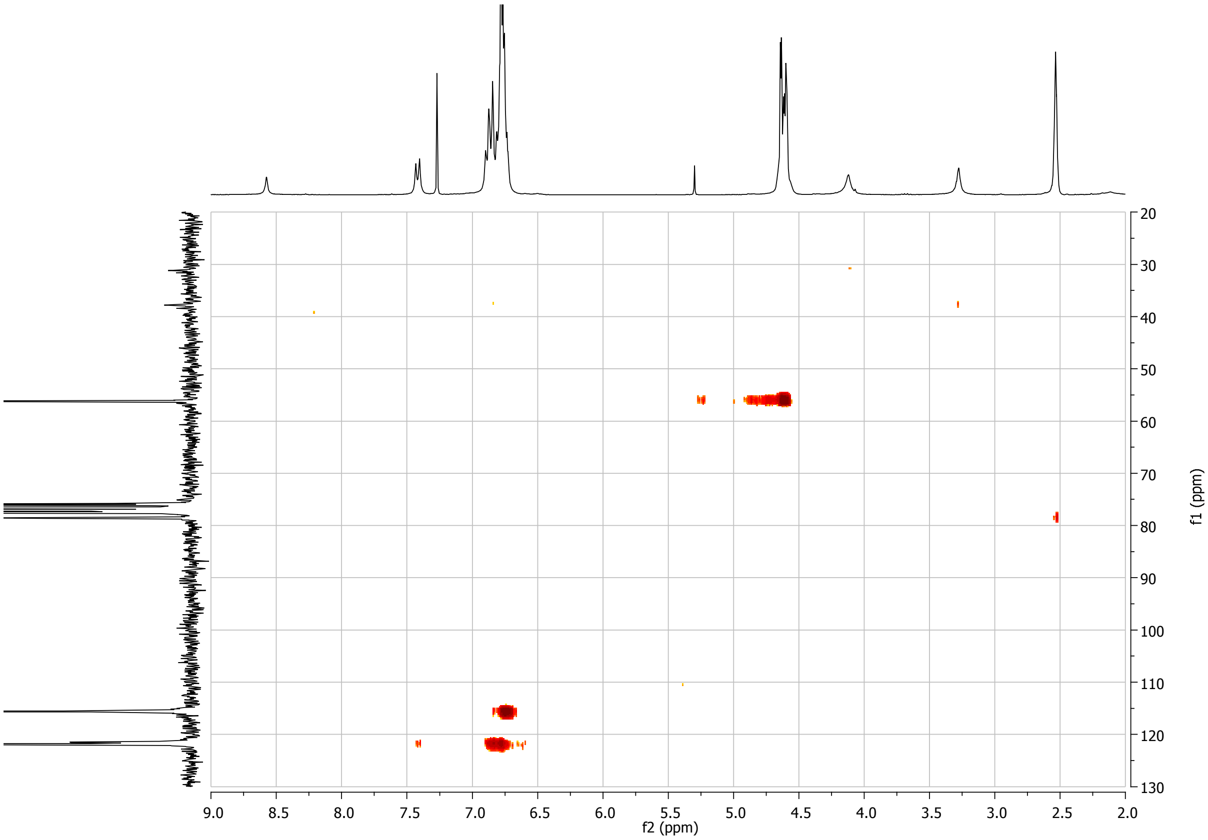


Figure S152. HETCOR spectrum of compound **35**

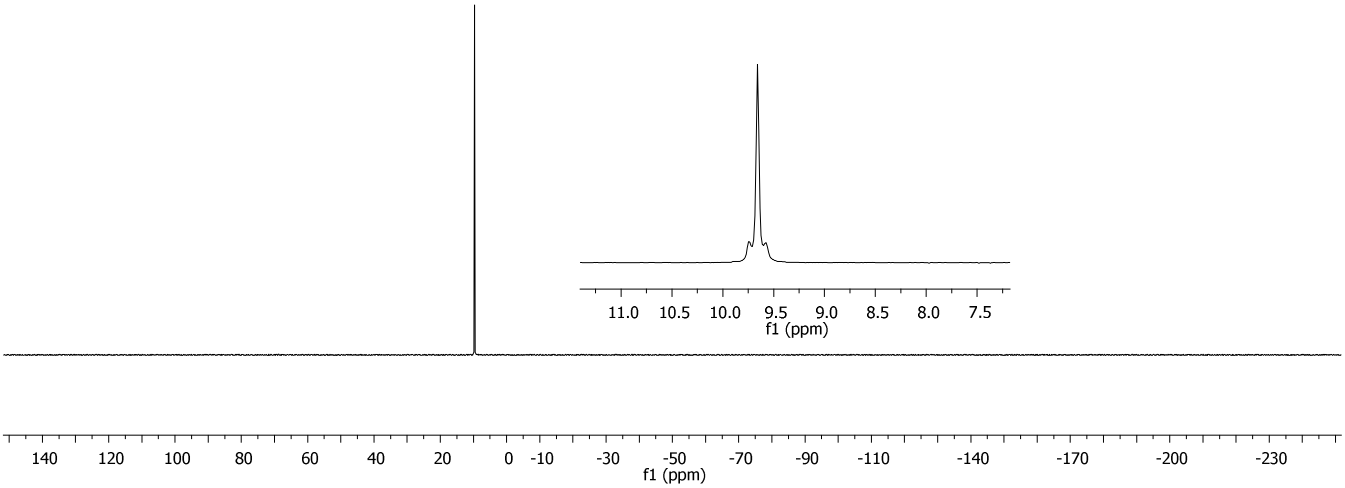


Figure S153. ^{31}P NMR spectrum of compound **35** ($CDCl_3$, 122MHz)

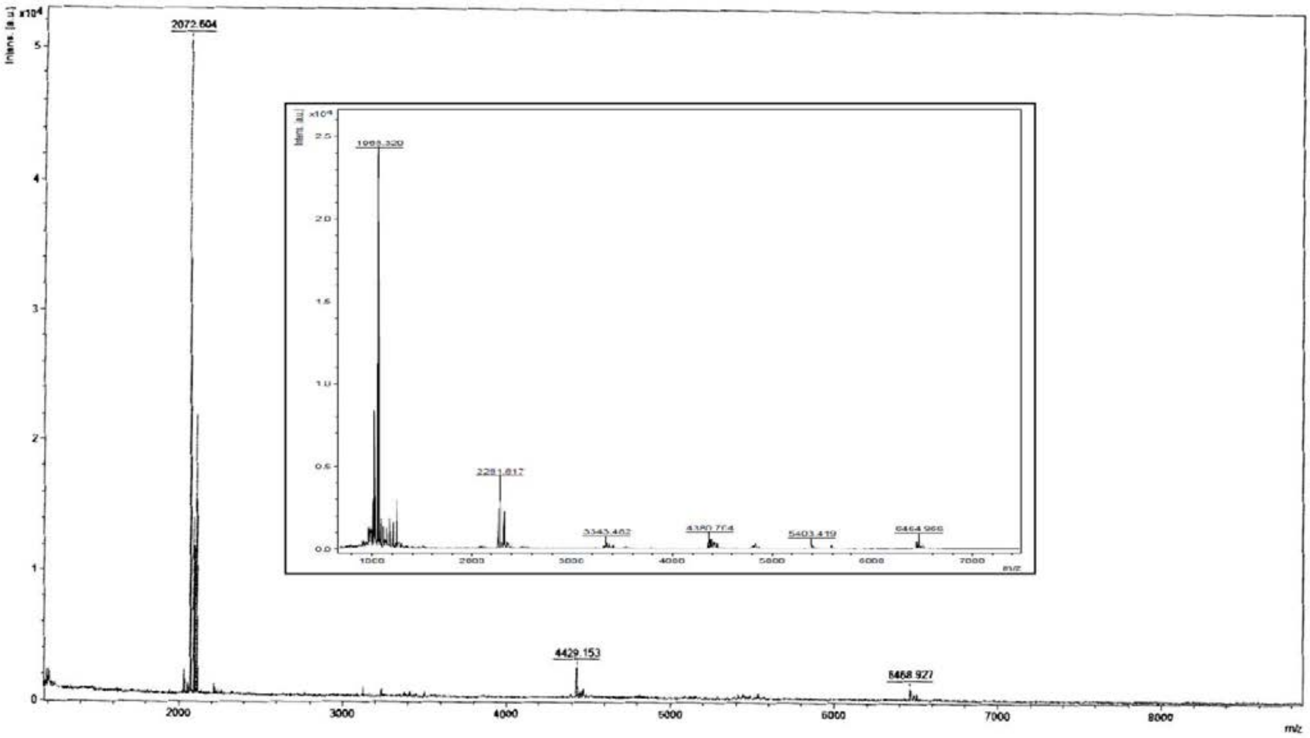
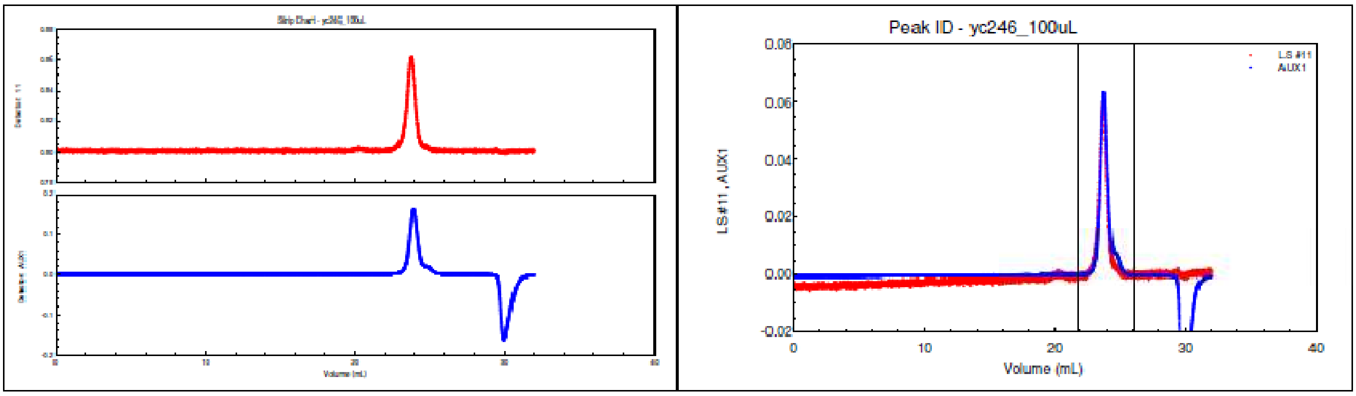


Figure S154. MALDI-TOF (DHB matrix) spectrum of compound **35** (*insert*: MALDI-TOF of **35**, 3 days after synthesis)

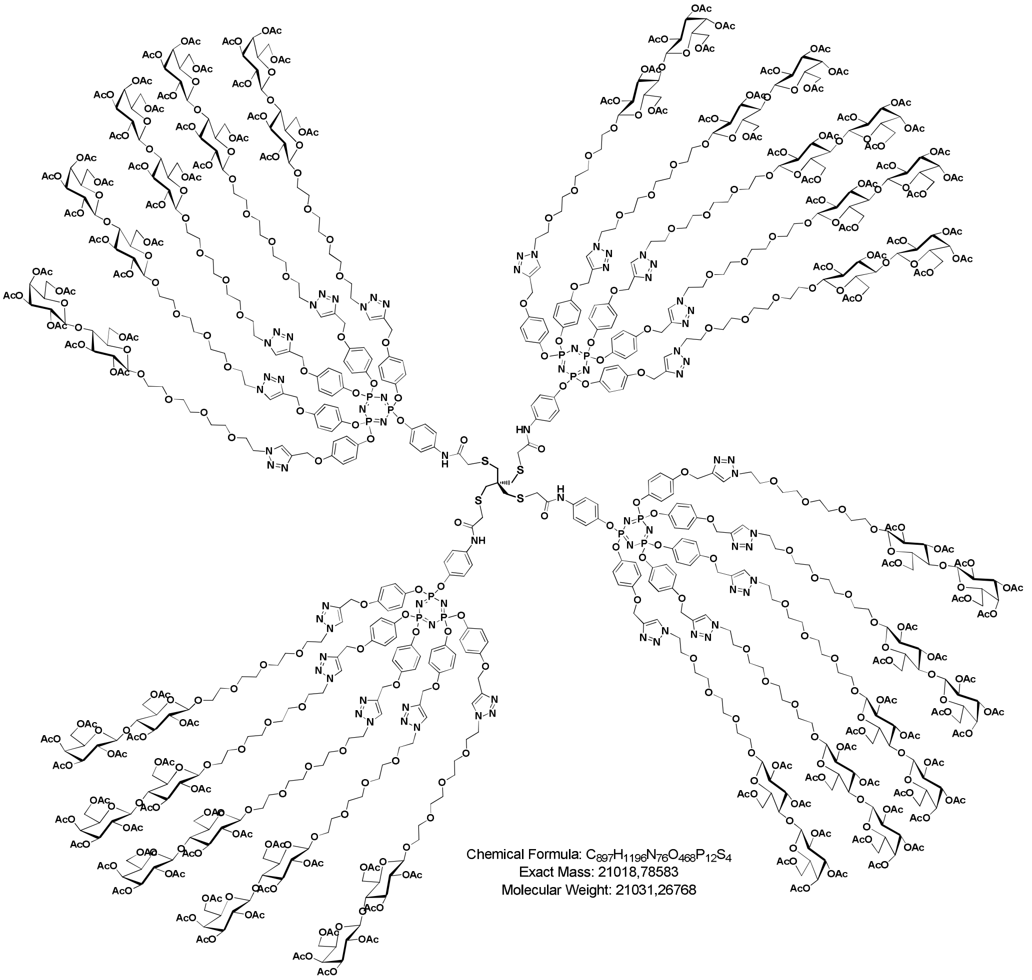


Polydispersity(Mw/Mn) : 1.118±0.150 (13%)
Polydispersity(Mz/Mn) : 1.248±0.326 (26%)

Molar Mass Moments (g/mol)
Mn : 6.399e+03 (9%)
Mw : 7.152e+03 (9%)
Mz : 7.985e+03 (24%)

Figure S155. GPC trace (in THF) for compound **35**

Icosavalent glycodendrimer 36



To a solution of icosapropargylated core **34** (11.0 mg, 2.58 µmol, 1.0 eq.) in a 1:1 mixture of H_2O/THF (4.0 mL) were added azido derivative **10** (72.0 mg, 0.086 mmol, 33.3 eq.), $CuSO_4 \cdot 5H_2O$ (17.4 mg, 0.069 mmol, 27.0 eq.) and sodium ascorbate (13.7 mg, 0.069 mmol, 27.0 eq.). While stirring, the mixture was first heated at 50℃ for 3 hours in a 20 mL vial and at room temperature for additional 18 hours. Noteworthy is the fact that 5 mg of $CuSO_4 \cdot 5H_2O$ and 4 mg of sodium ascorbate were added to the solution after the 3 hours of heating. Ethyl acetate (15 mL) was added and the solution was poured into a separatory funnel containing ethyl acetate (10 mL), washed with saturated aqueous NH_4Cl (2×10 mL), water (10 mL) and brine (5 mL). Organics were collected, dried over Na_2SO_4 and concentrated to dryness *in vacuo* with rotary evaporator. Purification by flash chromatography (SiO_2, DCM/MeOH 100:0 to 85:15) afforded desired multivalent compound **36** (43.0 mg, 2.00 µmol, **74%**) as a yellowish foam.

R_f = 0.40, DCM/MeOH 92:8

^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 9.70 (br s, 4H, NH), 7.85-7.84 (2×s, 20H, $H_{triazole}$), 7.44-7.40 (m, 8H, C$H_{b'}$), 6.90-6.56 (m, 88H, CH_b, CH_c, C$H_{c'}$), 5.32 (d_{app}, 20H, H_{4gal}), 5.18-5.06 (m, 80H, H_{3glc}, C_qCH_2O, H_{2gal}), 4.95 (dd, $^3J_{2,3}$ = 3.3 Hz, $^3J_{3,4}$ = 7.1 Hz, 20H, H_{3gal}), 4.88-4.83 (m, 20H, H_{2glc}), 4.54-4.42 (m, 100H, CH_2N, H_{1glc}, H_{6aglc}, H_{1gal}), 4.13-4.05 (m, 60H,

H_{6bglc}, H_{6agal}, H_{6bgal}), 3.88-3.45 (m, 348H, H_{5gal}, H_{5glc}, H_{4glc}, OCH_2, SCH_2CONH), 2.81 (br s, 8H, C_qCH_2S), 2.11-1.92 (m, 420H, COCH_3).

^{13}C NMR (150 MHz, $CDCl_3$, δ ppm): 170.3, 170.2, 170.1, 170.0, 169.7, 169.5, 169.0 (7×s, COCH$_3$), 167.7 (NHC=O), 155.2 (C_a), 146.5 ($C_{d'}$), 144.4 (C_d), 144.3 (C_d), 143.4 ($C_{triazole}$=CH), 143.3 ($C_{triazole}$=CH), 135.4 ($C_{a'}$), 124.5 (C$_{triazole}$=CH), 124.1 (C$_{triazole}$=CH), 121.8 (C_c), 121.7 (C_c), 121.0 ($C_{c'}$), 120.9 ($C_{b'}$), 115.2 (C_b), 101.0 (C_{1gal}), 100.5 (C_{1glc}), 76.2 (C_{4glc}), 72.7 (C_{3glc}), 72.5 (C_{5glc}), 71.5 (C_{2glc}), 70.9 (C_{3gal}), 70.5 (C_{5gal}), 70.5, 70.4, 70.4, 70.3, 70.2, 70.1, 70.1, 69.3, 69.1, 69.0 (OCH$_2$), 68.9 (C_{2gal}), 68.9 (OCH$_2$), 66.5 (C_{4gal}), 62.2 (OCH$_2$C=C), 61.9 (C_{6glc}), 61.8 (OCH$_2$), 60.8 (C_{6gal}), 50.2 (NCH$_2$), 50.1 (NCH$_2$), 44.0 (C_q, not *visible*), 38.4 (SCH$_2$CONH), 37.6 (C$_q$$CH_2$S), 29.6, 20.8, 20.7, 20.6, 20.5, 20.5, 20.4 (7×s, COCH$_3$).

^{31}P NMR (122 MHz, $CDCl_3$, δ ppm): 9.8 (t_{app}, 12P).

m/z (MALDI-TOF-MS/DHB matrix) for $C_{897}H_{1196}N_{76}O_{468}P_{12}S_4$= 21031.3; found 21098.1 (*with successive losses of monomers and dendrons*).

NMR diffusion studies ($CDCl_3$): $D = 1.17\times10^{-10}$ m^2/s; d_s = 7.0 nm.

GPC measurements ($CHCl_3$/Et_3N (1%)): M_w = 25870 ; M_n = 24610 , PDI (M_w/M_n) = 1.051.

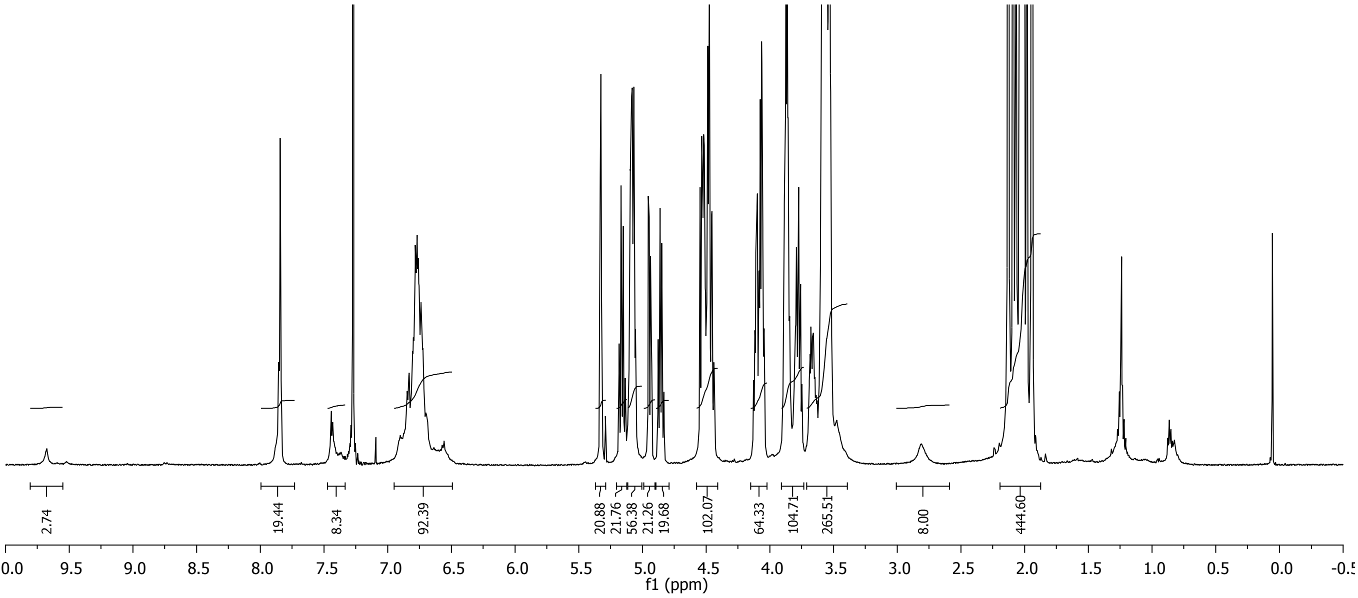


Figure S156. ^{1}H NMR spectrum of compound **36** ($CDCl_3$, 600MHz)

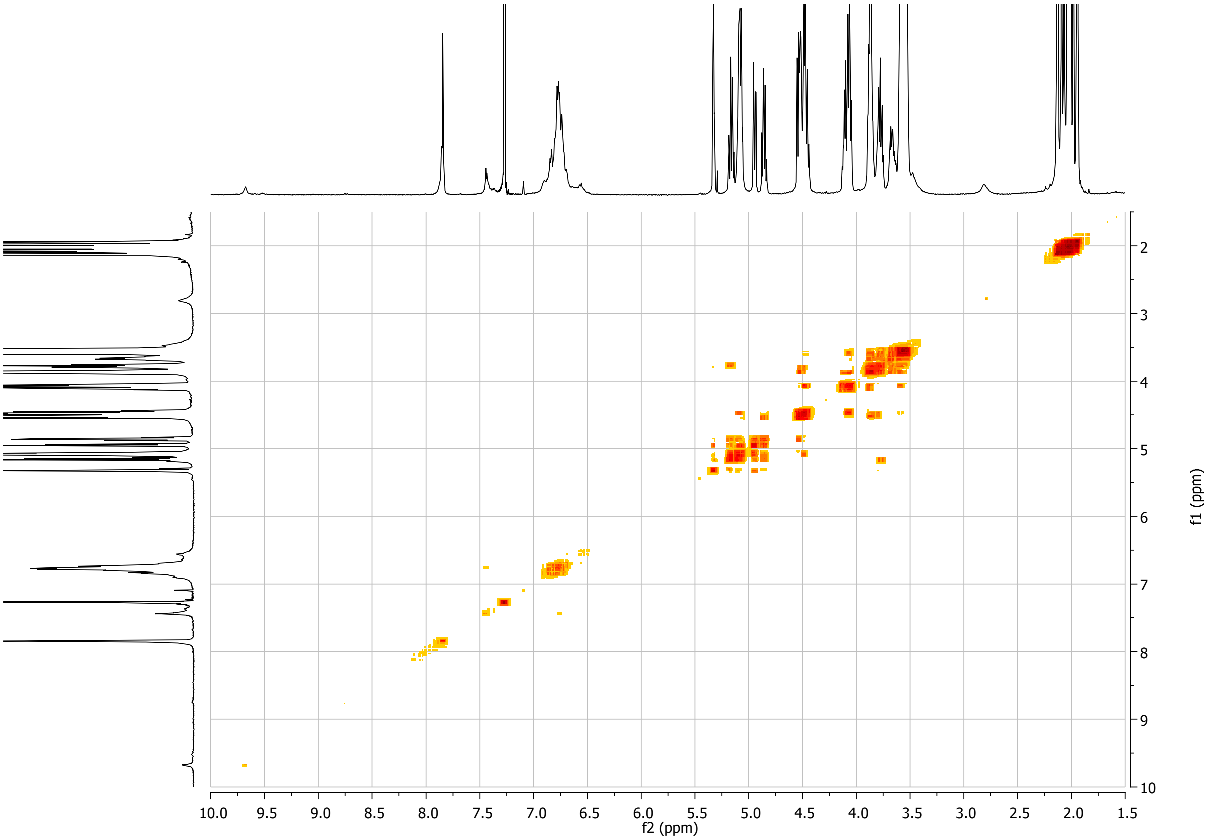


Figure S157. gCOSY spectrum of compound **36**

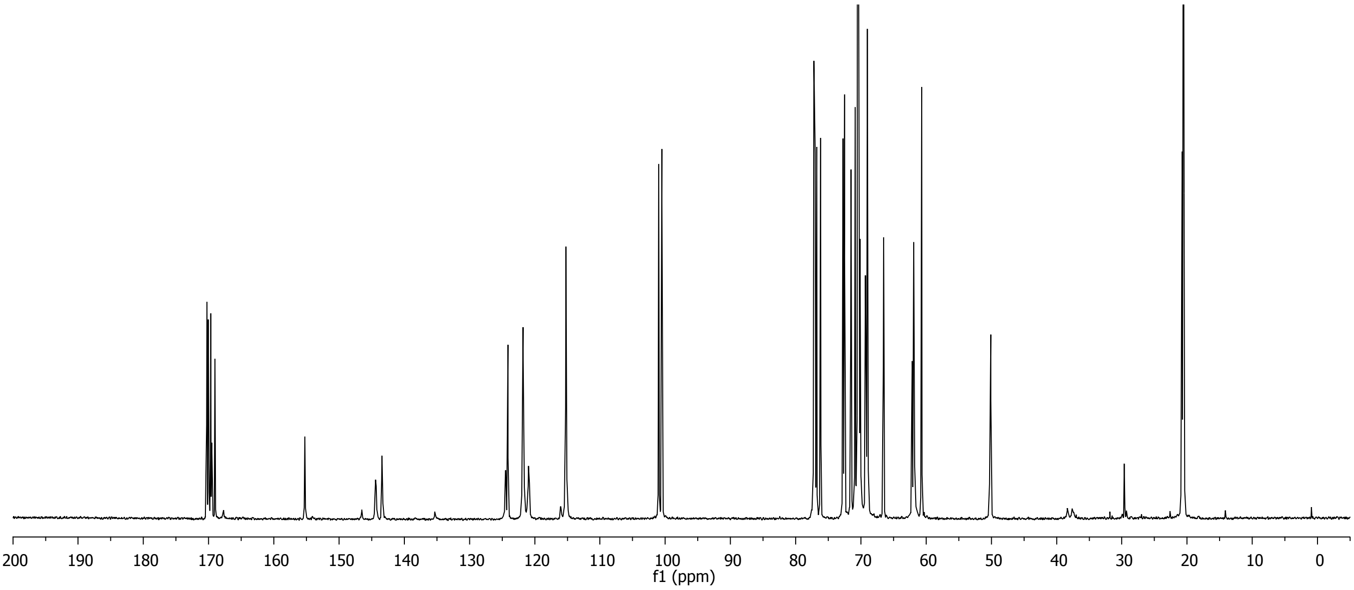


Figure S158. ^{13}C NMR spectrum of compound **36** ($CDCl_3$, 150MHz)

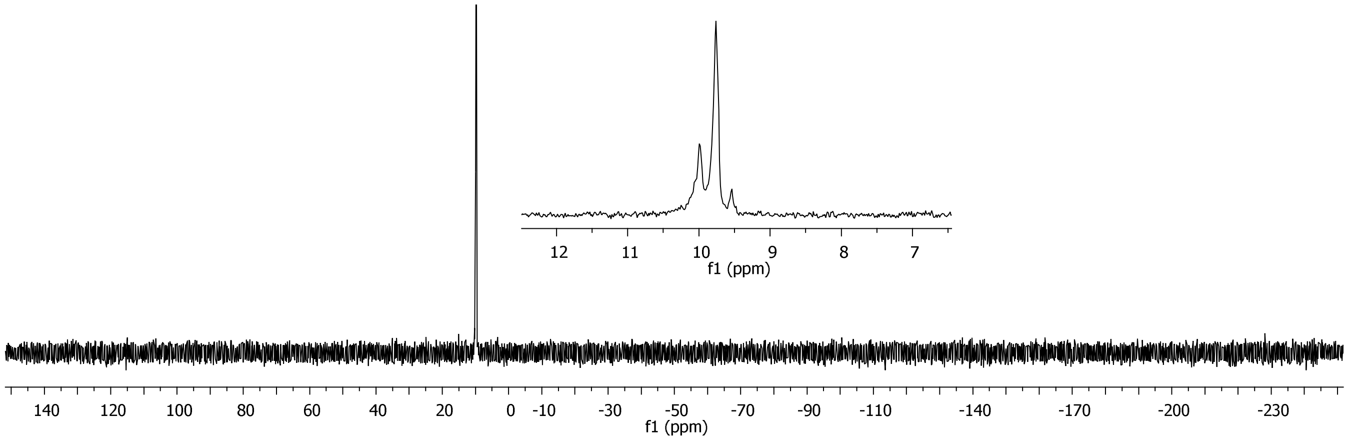


Figure S159. ^{31}P NMR spectrum of compound **35** (CDCl$_3$, 122MHz)

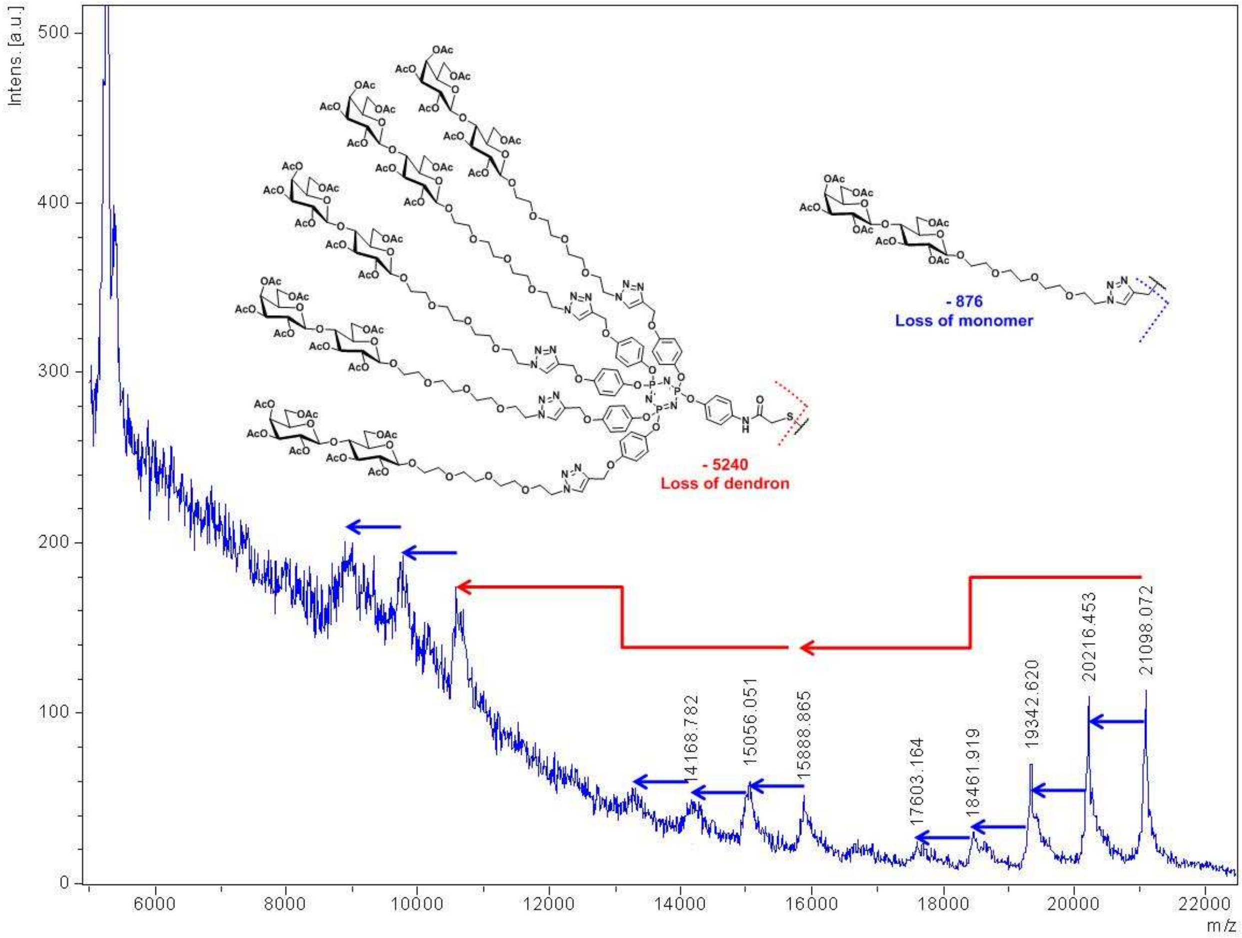
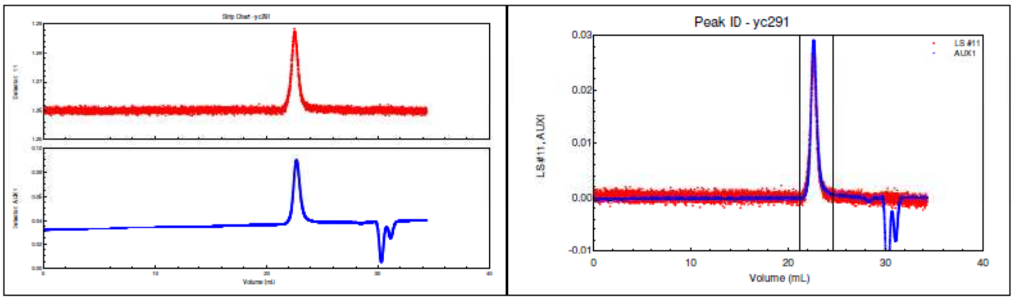


Figure S160. MALDI-TOF spectrum of compound **36** with successive fragmentations.

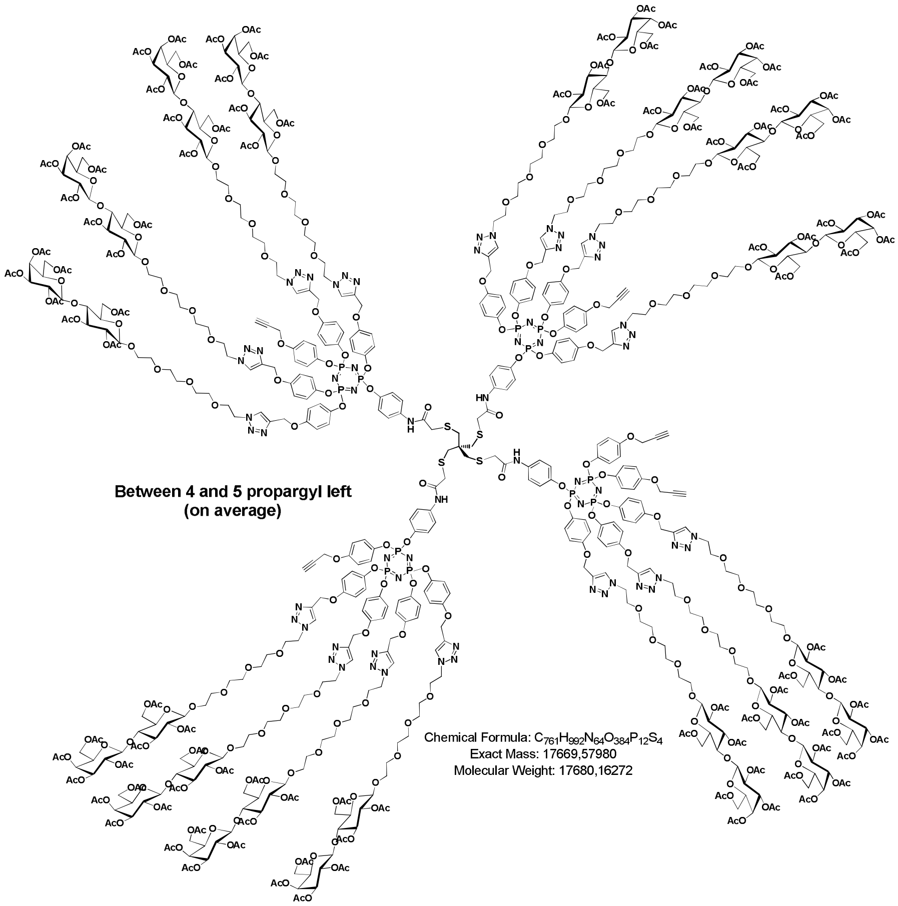


```
Polydispersity(Mw/Mn)  :  1.051±0.159 (15%)
Polydispersity(Mz/Mn)  :  1.176±0.383 (33%)

Molar Mass Moments (g/mol)
 Mn                    :  2.461e+04 (10%)
 Mw                    :  2.587e+04 (11%)
 Mz                    :  2.895e+04 (30%)
```

Figure S161. GPC trace ($CHCl_3$/Et_3N (1%)) for compound **36**

Defectuous glycodendrimer 36a (*location of propargylic functions is arbitrary*)



Between 4 and 5 propargyl left (on average)

Chemical Formula: $C_{761}H_{992}N_{64}O_{384}P_{12}S_4$
Exact Mass: 17669,57980
Molecular Weight: 17680,16272

To a solution of icosapropargylated core **34** (10.2 mg, 2.39 µmol, 1.0 eq.) in a 1:1 mixture of H_2O/THF_{anh} (4.0 mL) were added azido derivative **10** (32.0 mg, 0.038 mmol, 16.0 eq.), $CuSO_4{\cdot}5H_2O$ (12.0 mg, 0.048 mmol, 20.0 eq.) and sodium ascorbate (9.5 mg, 0.048 mmol, 20.0 eq.). While stirring, the mixture was first heated at 50°C for 3 hours in a 20 mL vial and at room temperature for additional 18 hours. Ethyl acetate (15 mL) was added and the solution was poured into a separatory funnel containing ethyl acetate (10 mL), washed with saturated aqueous NH_4Cl (2×10 mL), water (10 mL) and brine (5 mL). Organics were collected, dried over Na_2SO_4 and concentrated to dryness *in vacuo* with rotary evaporator. Purification by flash chromatography (SiO_2, DCM/MeOH 100:0 to 85:15) afforded desired mixture of defectuous multivalent compounds containing 4-5 propargylic functions on average **36a** (36.0 mg, 2.04 µmol, **85%**) as an off-white foam.

R_f = 0.40, DCM/MeOH 92:8.

^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 9.70 (br s, 4H, N*H*), 7.85-7.84 (2×s, 16H, $H_{triazole}$), 7.44-7.40 (m, 8H, $CH_{b'}$), 6.90-6.56 (m, 88H, CH_b, CH_c, $CH_{c'}$), 5.32 (d_{app}, 16H, H_{4gal}), 5.18-5.06 (m, 64H, H_{3glc}, C_qCH_2O, H_{2gal}), 4.95 (dd, $^3J_{2,3}$ = 3.3 Hz, $^3J_{3,4}$ = 7.1 Hz, 16H, H_{3gal}), 4.88-4.83 (m, 16H, H_{2glc}), **4.65 (m, ~8H, CH_2OC≡CH)**, 4.54-4.42 (m, 80H, CH_2N, H_{1glc}, H_{6aglc}, H_{1gal}), 4.13-4.05 (m, 48H, H_{6bglc}, H_{6agal}, H_{6bgal}), 3.88-3.45 (m, 280H, H_{5gal}, H_{5glc}, H_{4glc}, OCH_2, SCH_2CONH), 2.81 (br s, 8H, C_qCH_2S), **2.53 (br s, ~4H, CH_2OC≡C*H*)**, 2.11-1.92 (m, 336H, $COCH_3$).

^{13}C NMR (150 MHz, CDCl$_3$, δ ppm): 170.3, 170.2, 170.1, 170.0, 169.7, 169.5, 169.0 (7×s, COCH$_3$), 167.7 (NHC=O), 155.3 (C_a), 154.4 (C_a), 146.5 ($C_{d'}$), 144.5 (C_d), 144.3 (C_d), 143.4 (C_{triazole}=CH), 143.3 (C_{triazole}=CH), 135.4 ($C_{a'}$), 124.5 (C$_{\mathrm{triazole}}$=CH), 124.5 (C$_{\mathrm{triazole}}$=CH), 124.1 (C$_{\mathrm{triazole}}$=CH), 121.8 (C_c), 121.7 (C_c), 121.0 ($C_{c'}$), 120.9 ($C_{b'}$), 115.5 (C_b), 115.2 (C_b), 101.0 ($C_{1\mathrm{gal}}$), 100.5 ($C_{1\mathrm{glc}}$), **78.7 (*C*≡CH)**, **78.5 (*C*≡CH)**, 76.2 ($C_{4\mathrm{glc}}$), **76.0 (C≡*C*H)**, **75.8 (C≡*C*H)**, 72.8 ($C_{3\mathrm{glc}}$), 72.5 ($C_{5\mathrm{glc}}$), 71.6 ($C_{2\mathrm{glc}}$), 70.9 ($C_{3\mathrm{gal}}$), 70.5 ($C_{5\mathrm{gal}}$), 70.5, 70.4, 70.4, 70.3, 70.2, 70.1, 70.1, 69.3, 69.1, 69.0 (OCH$_2$), 68.9 ($C_{2\mathrm{gal}}$), 68.9 (OCH$_2$), 66.5 ($C_{4\mathrm{gal}}$), 62.2 (OCH$_2$C=C), 61.9 ($C_{6\mathrm{glc}}$), 61.8 (OCH$_2$), 60.7 ($C_{6\mathrm{gal}}$), **56.1 (O*C*H$_2$C≡CH)**, 50.1 (NCH$_2$), 50.1 (NCH$_2$), 44.2 (C_q), 38.4 (SCH$_2$CONH), 37.4 (C$_q$$CH_2$S), 29.6, 20.8, 20.7, 20.6, 20.5, 20.5, 20.4 (7×s, COCH$_3$).

^{31}P NMR (122 MHz, CDCl$_3$, δ ppm): 9.8 (t$_{\mathrm{app}}$, 12P).

m/z (MALDI-TOF-MS/DHB matrix) : From 21005.2 (click completion) to 7574 with signals corresponding to successive losses of monomers (~876 MW).

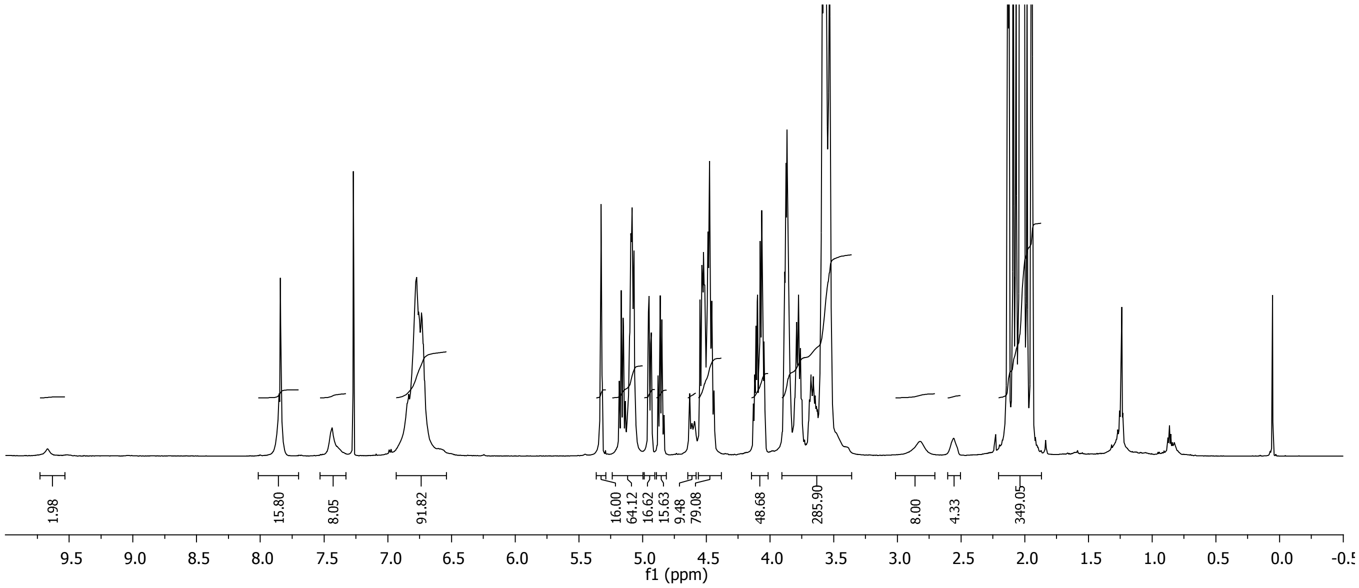


Figure S162. ^{1}H NMR spectrum of compound **36a** (CDCl$_3$, 600MHz)

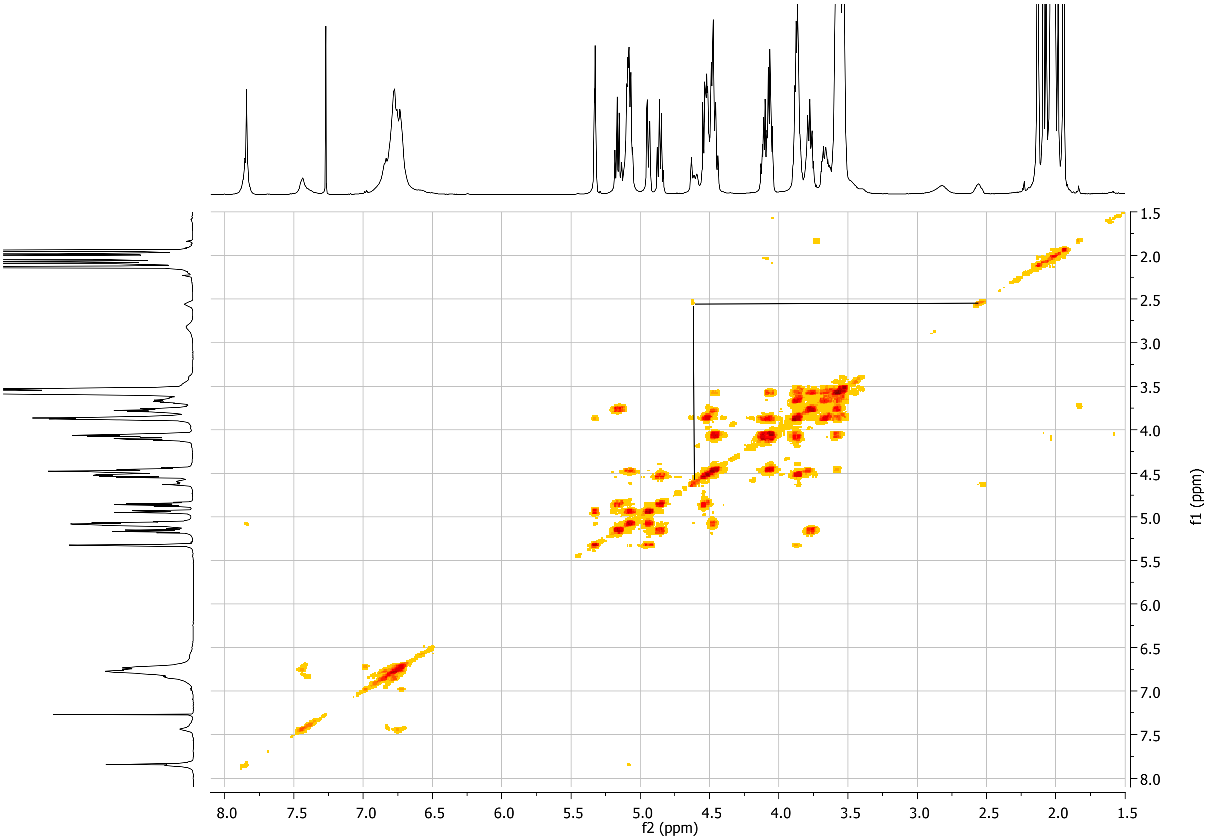


Figure S163. gCOSY spectrum of compound **36a**

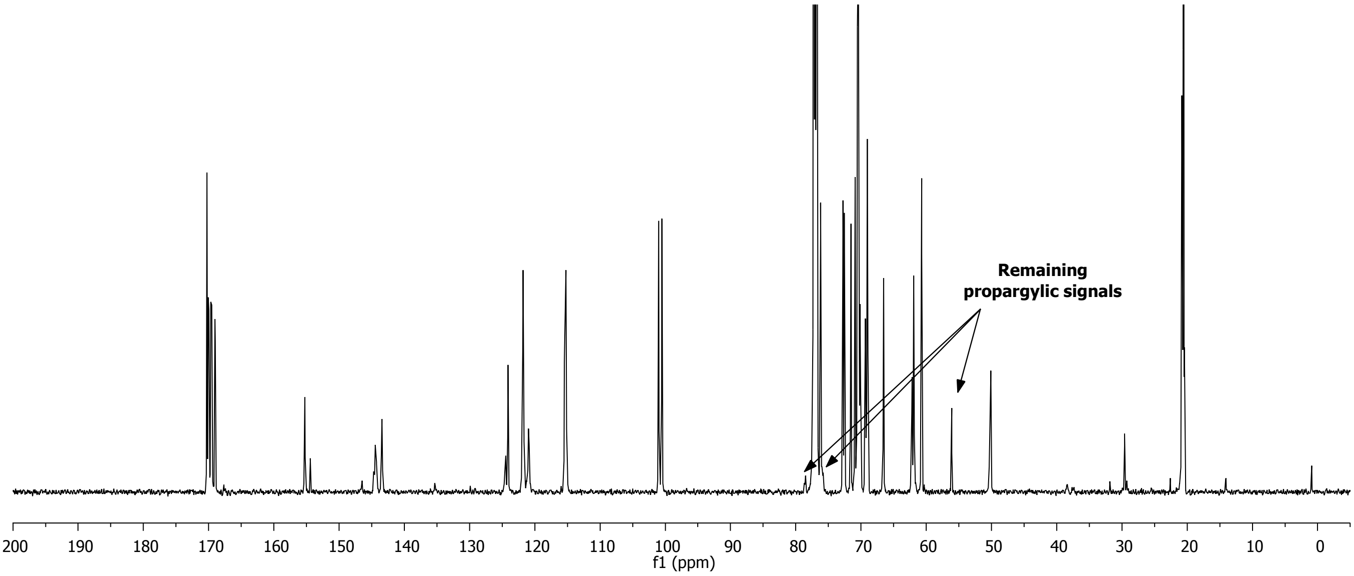


Figure S164. ^{13}C NMR spectrum of compound **36a** ($CDCl_3$, 150MHz)

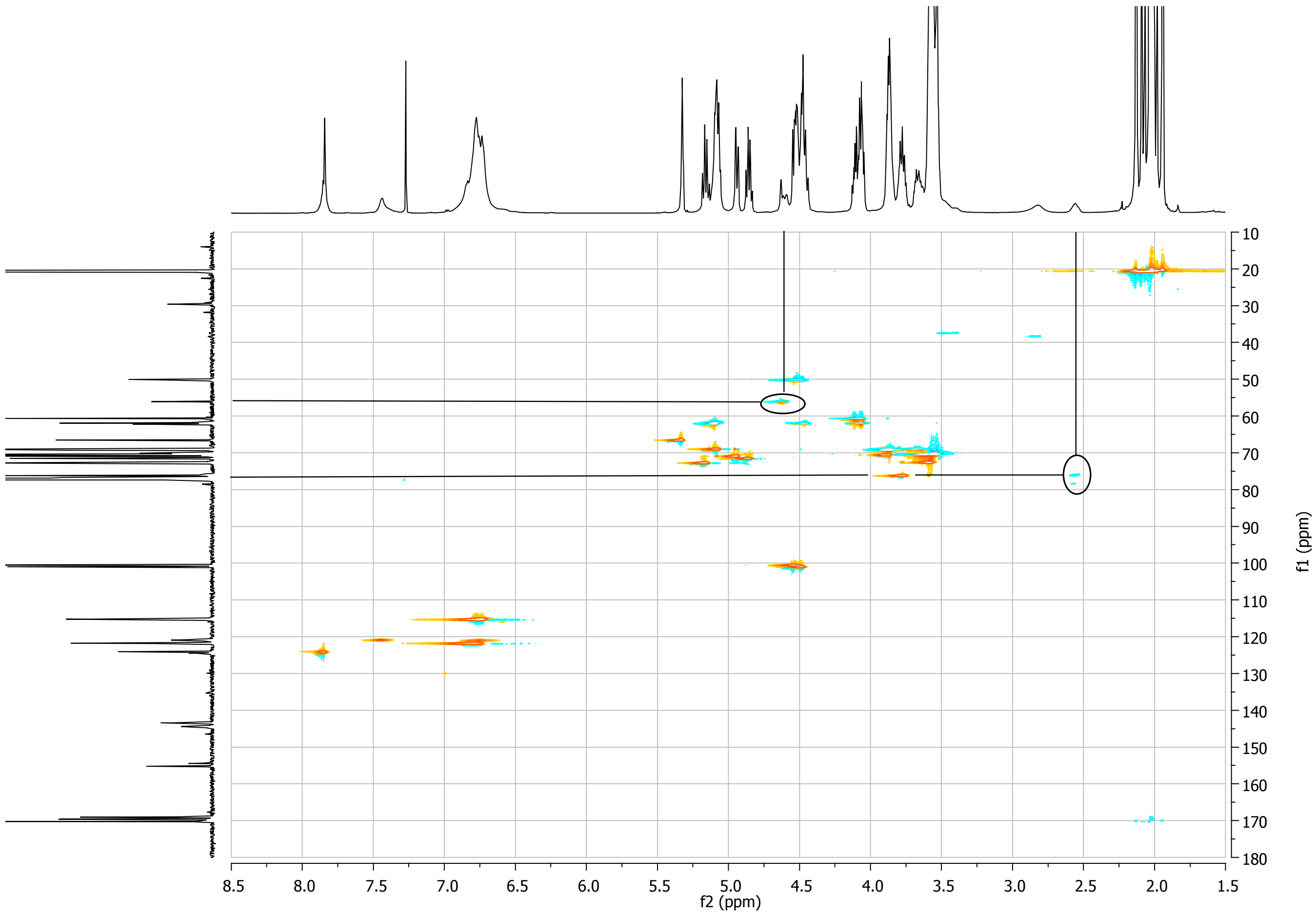


Figure S165. HSQC spectrum of compound **36a**

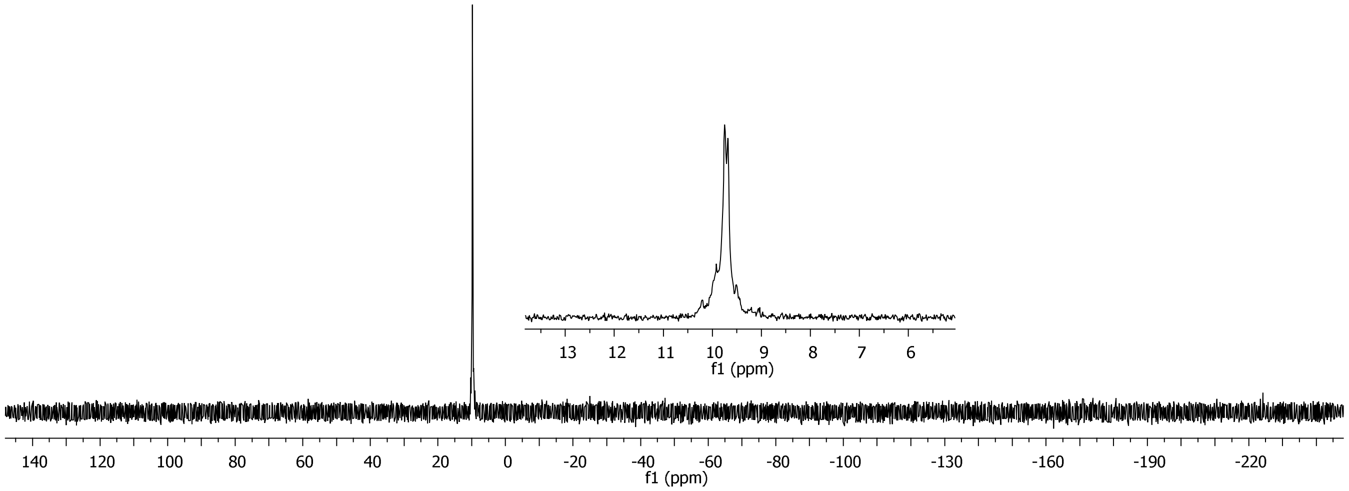


Figure S166. ^{31}P NMR spectrum of compound **36a** (CDCl$_3$, 122MHz)

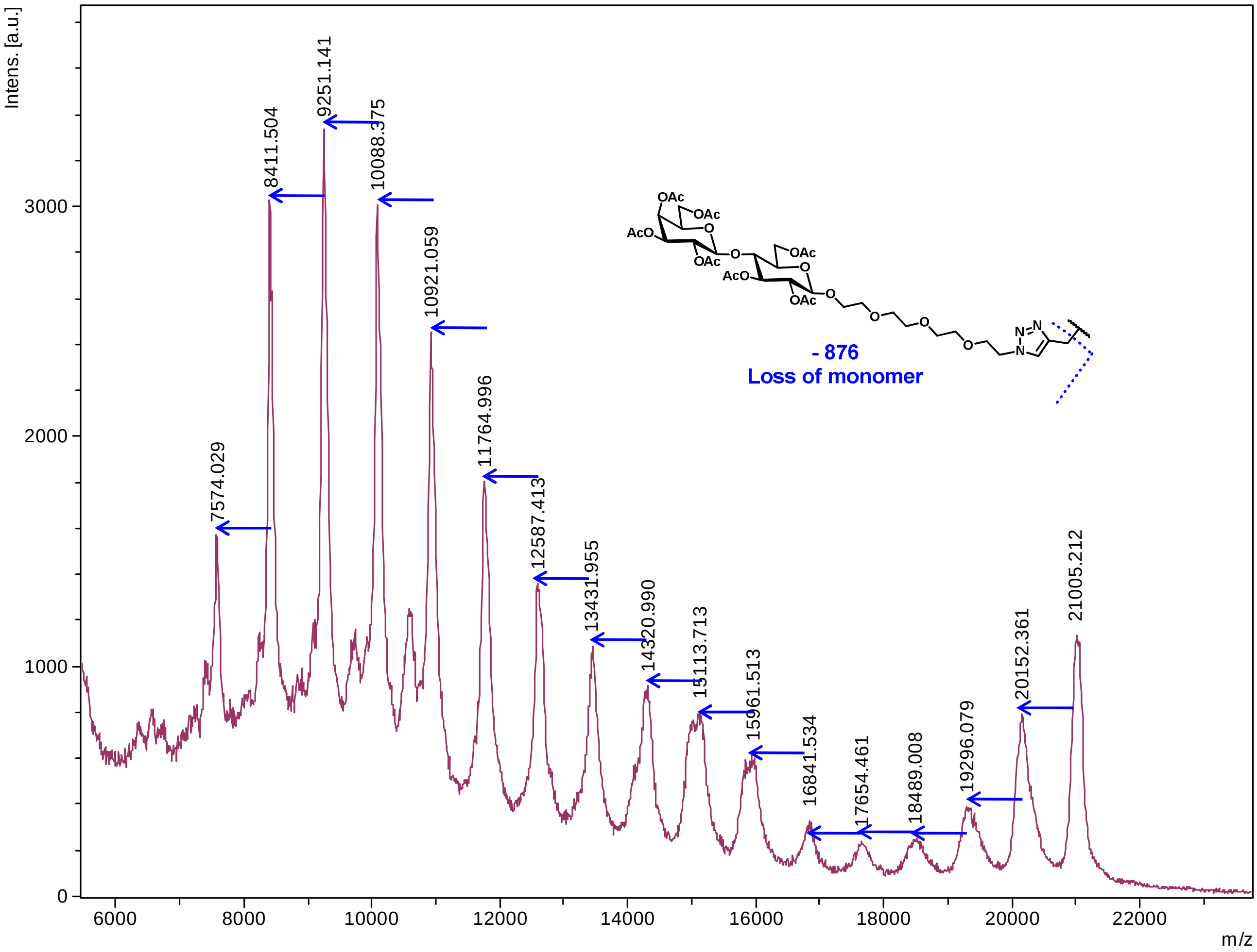
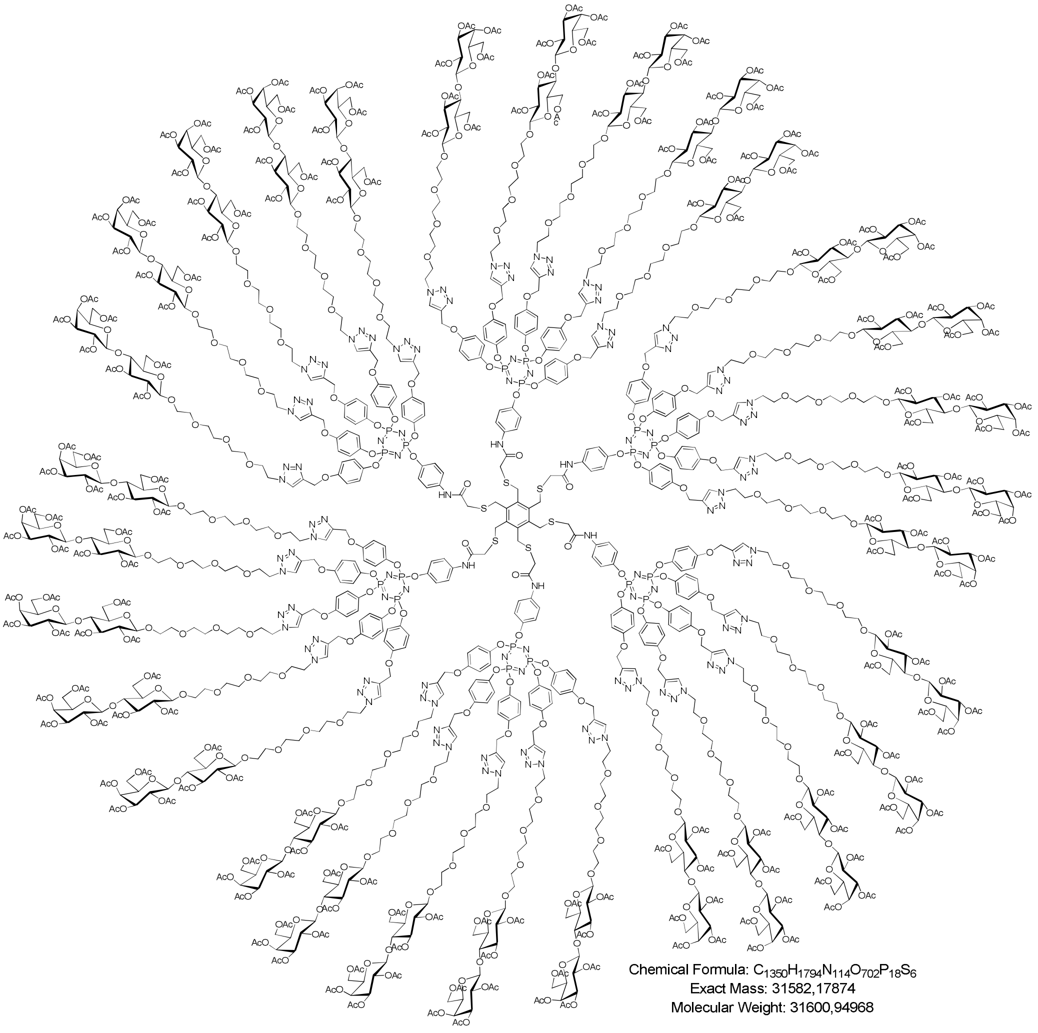


Figure S167. MALDI-TOF (DHB matrix) spectrum of compound **36a** with successive losses of monomers.

Protected tricontavalent glycodendrimer 37



Chemical Formula: $C_{1350}H_{1794}N_{114}O_{702}P_{18}S_6$
Exact Mass: 31582,17874
Molecular Weight: 31600,94968

To a solution of tricontapropargylated core **35** (11.0 mg, 1.70 µmol, 1.0 eq.) in a 1:1 mixture of H_2O/THF_{anh} (4.0 mL) were added azido derivative **10** (71.2 mg, 0.085 mmol, 50.0 eq.), $CuSO_4\cdot 5H_2O$ (17.0 mg, 0.068 mmol, 40.0 eq.) and sodium ascorbate (13.5 mg, 0.068 mmol, 40.0 eq.). While stirring, the mixture was first heated at 50℃ for 3 hours in a 20 mL vial and at room temperature for additional 18 hours. Noteworthy is the fact that 6mg of $CuSO_4\cdot 5H_2O$ and 4mg of sodium ascorbate were added to the solution after the 3 hours of heating. Ethyl acetate (15 mL) was added and the solution was poured into a separatory funnel containing ethyl acetate (10 mL), washed with saturated aqueous NH_4Cl (2×10 mL), water (10 mL) and brine (5 mL). Organics were collected, dried over Na_2SO_4 and concentrated to dryness *in vacuo* with rotary evaporator. Purification by flash chromatography (SiO_2, DCM/MeOH 100:0 to 85:15) afforded desired multivalent compound **37** (40.0 mg, 1.27 µmol, **74%**) as a yellowish foam.

R_f = 0.27, DCM/MeOH 94:6

^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 9.82 (br s, 6H, N*H*), 7.85-7.84 (br s, 30H, $H_{triazole}$), 7.46-7.40 (m, 12H, C$H_{b'}$), 6.95-6.50 (m, 132H, CH_b, CH_c, C$H_{c'}$), 5.33 (d_{app}, 30H, H_{4gal}), 5.19-5.07 (m, 120H, H_{3glc}, C_qCH_2O, H_{2gal}), 4.94 (dd, $^3J_{2,3}$ = 3.3

Hz, ${}^3J_{3,4}$ = 7.1 Hz, 30H, H_{3gal}), 4.88-4.83 (m, 30H, H_{2glc}), 4.55-4.46 (m, 150H, CH_2N, H_{1glc}, H_{6aglc}, H_{1gal}), 4.20 (br s, 12H, $C_{core}CH_2S$), 4.13-4.05 (m, 90H, H_{6bglc}, H_{6agal}, H_{6bgal}), 3.89-3.40 (m, 522H, H_{5gal}, H_{5glc}, H_{4glc}, OCH_2, SCH_2CONH), 2.11-1.92 (m, 630H, COCH_3).

^{13}C NMR (150 MHz, $CDCl_3$, δ ppm): 170.3, 170.2, 170.1, 170.0, 169.7, 169.5, 169.0 (7×s, *C*OCH$_3$), 169.3 (NH*C*=O), 155.2 (C_a), 154.5 (C_a), 146.5 ($C_{d'}$) (*not visible*), 144.4 (C_d), 144.3 (C_d), 143.4 ($C_{triazole}$=CH), 143.3 ($C_{triazole}$=CH), 136.2 ($C_{q\ core}$), 135.4 ($C_{a'}$), 124.5 ($C_{triazole}$=*C*H), 124.1 ($C_{triazole}$=*C*H), 121.8 (C_c), 121.7 (C_c), 121.0 ($C_{c'}$), 120.9 ($C_{b'}$), 115.2 (C_b), 101.0 (C_{1gal}), 100.5 (C_{1glc}), 76.2 (C_{4glc}), 72.7 (C_{3glc}), 72.5 (C_{5glc}), 71.5 (C_{2glc}), 70.9 (C_{3gal}), 70.5 (C_{5gal}), 70.5, 70.4, 70.4, 70.3, 70.2, 70.1, 70.1, 69.3, 69.1, 69.0 (O*C*H$_2$), 68.9 (C_{2gal}), 68.9 (O*C*H$_2$), 66.5 (C_{4gal}), 62.1 (O*C*H$_2$C=C), 61.9 (C_{6glc}), 61.8 (O*C*H$_2$), 60.7 (C_{6gal}), 50.2 (N*C*H$_2$), 50.1 (N*C*H$_2$), 37.8 (S*C*H$_2$CONH), 31.2 ($C_{core}CH_2S$) (*not visible*), 29.6, 20.8, 20.7, 20.6, 20.5, 20.5, 20.4 (7×s, CO*C*H$_3$).

^{31}P NMR (122 MHz, $CDCl_3$, δ ppm): 9.8 (m, 18P).

m/z (MALDI-TOF-MS/DHB matrix) for $C_{1350}H_{1794}N_{114}O_{702}P_{18}S_6$ = 31600; found 31478 (*with signals corresponding to successive losses of monomer(s)*.

NMR diffusion studies ($CDCl_3$): $D = 1.34\times10^{-10}$ m^2/s; d_s = 6.2 nm.

GPC measurements ($CHCl_3/Et_3N$ (1%)): M_w = 42710 ; M_n = 39580 , PDI (M_w/M_n) = 1.079.

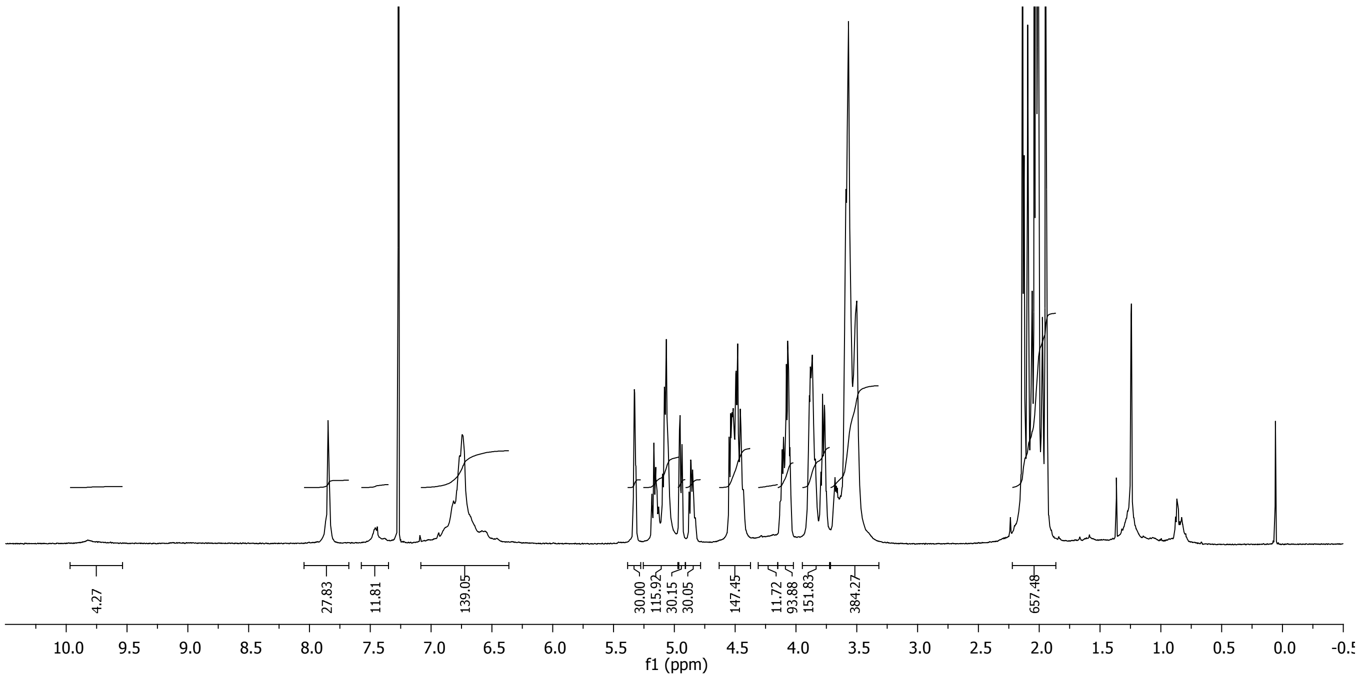


Figure S168. ^{1}H NMR spectrum of compound **37** ($CDCl_3$, 600MHz)

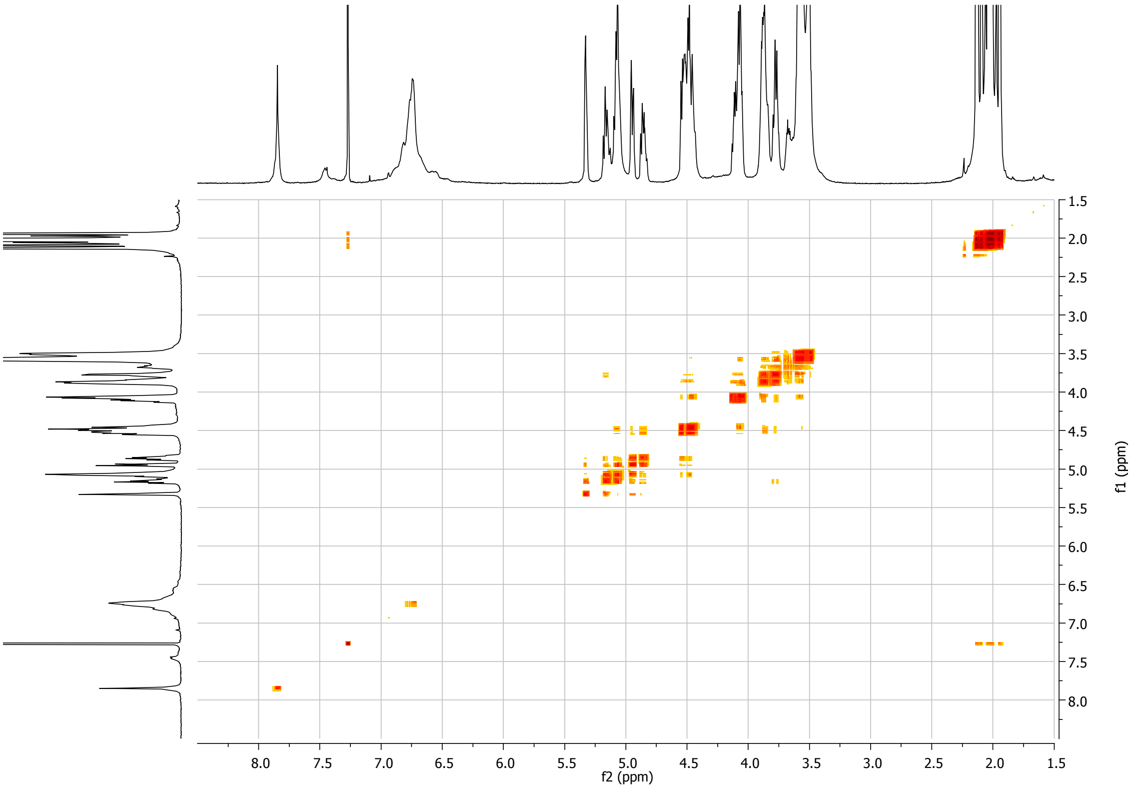


Figure S169. gCOSY spectrum of compound **37**

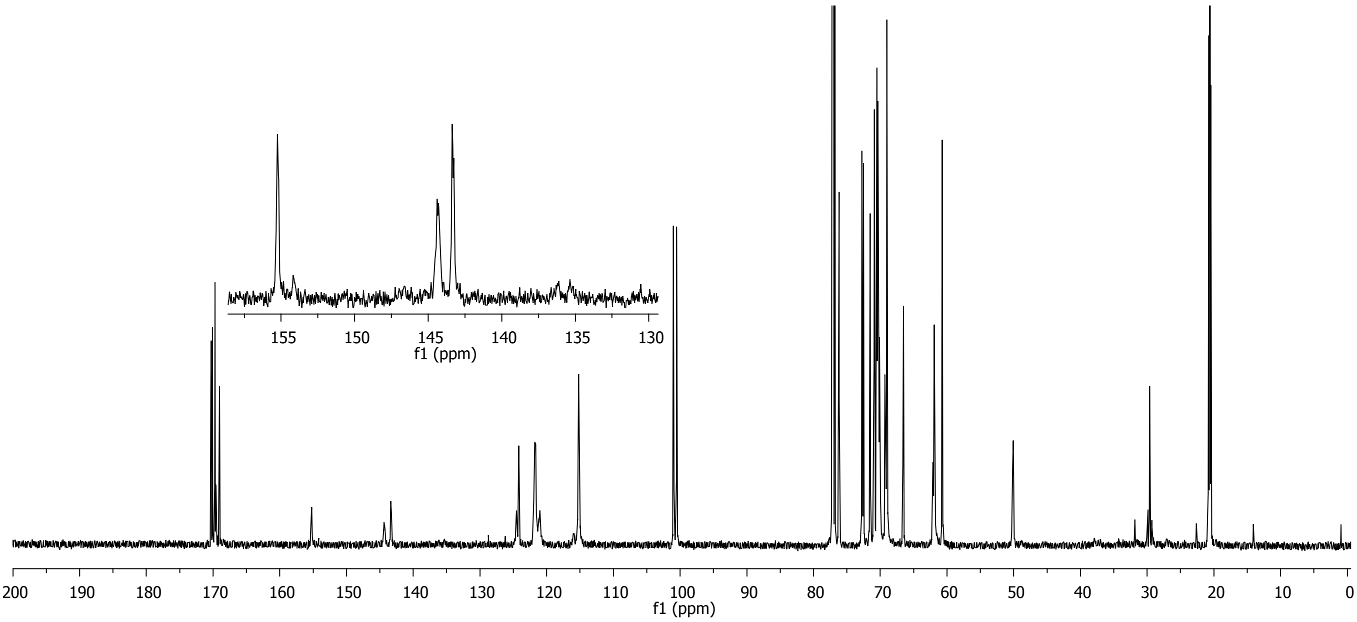


Figure S170. ^{13}C NMR spectrum of compound **37** ($CDCl_3$, 150MHz) (*insert*: zoom on aromatic section)

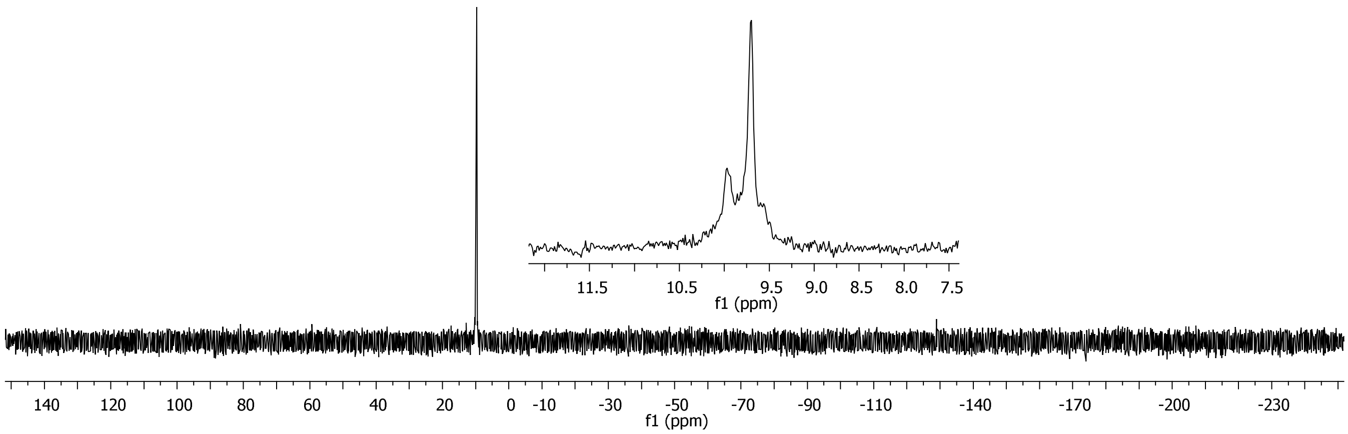
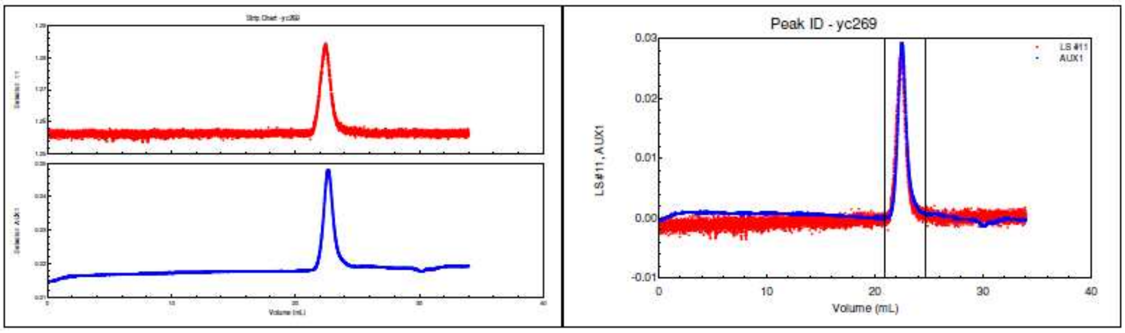


Figure S171. ^{31}P NMR spectrum of compound **37** ($CDCl_3$, 122MHz)



```
Polydispersity(Mw/Mn)  :  1.079±0.170 (16%)
Polydispersity(Mz/Mn)  :  1.193±0.320 (27%)

Molar Mass Moments (g/mol)
  Mn                   :  3.958e+04 (11%)
  Mw                   :  4.271e+04 (10%)
  Mz                   :  4.720e+04 (24%)
```

Figure S172. GPC trace ($CHCl_3$/Et_3N (1%)) for compound **37**

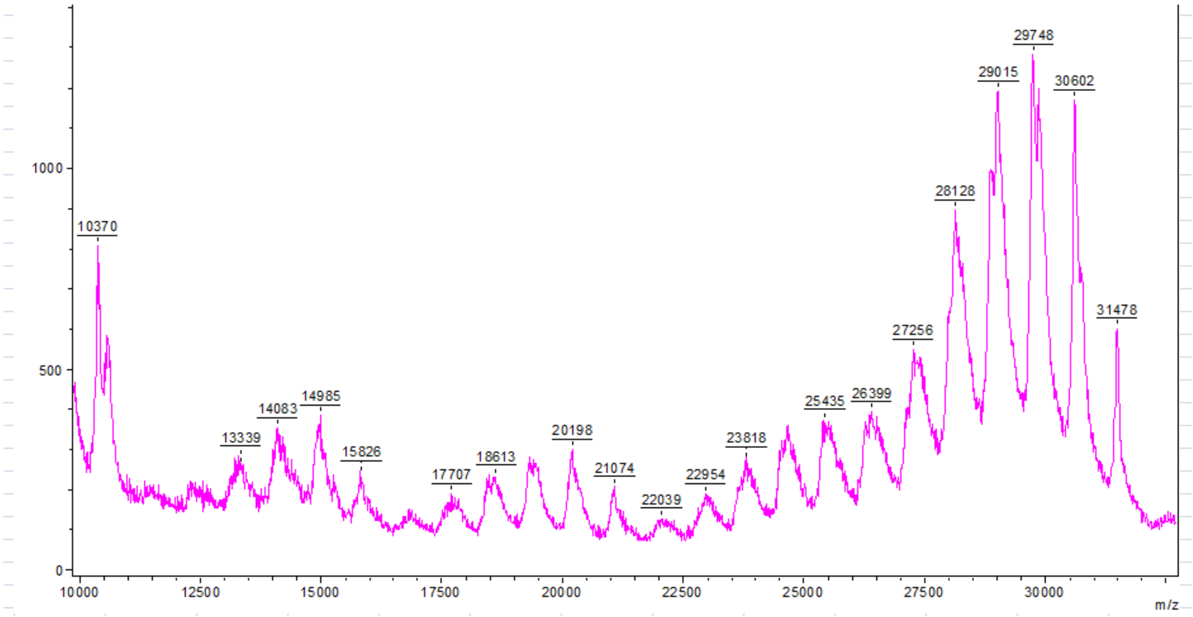
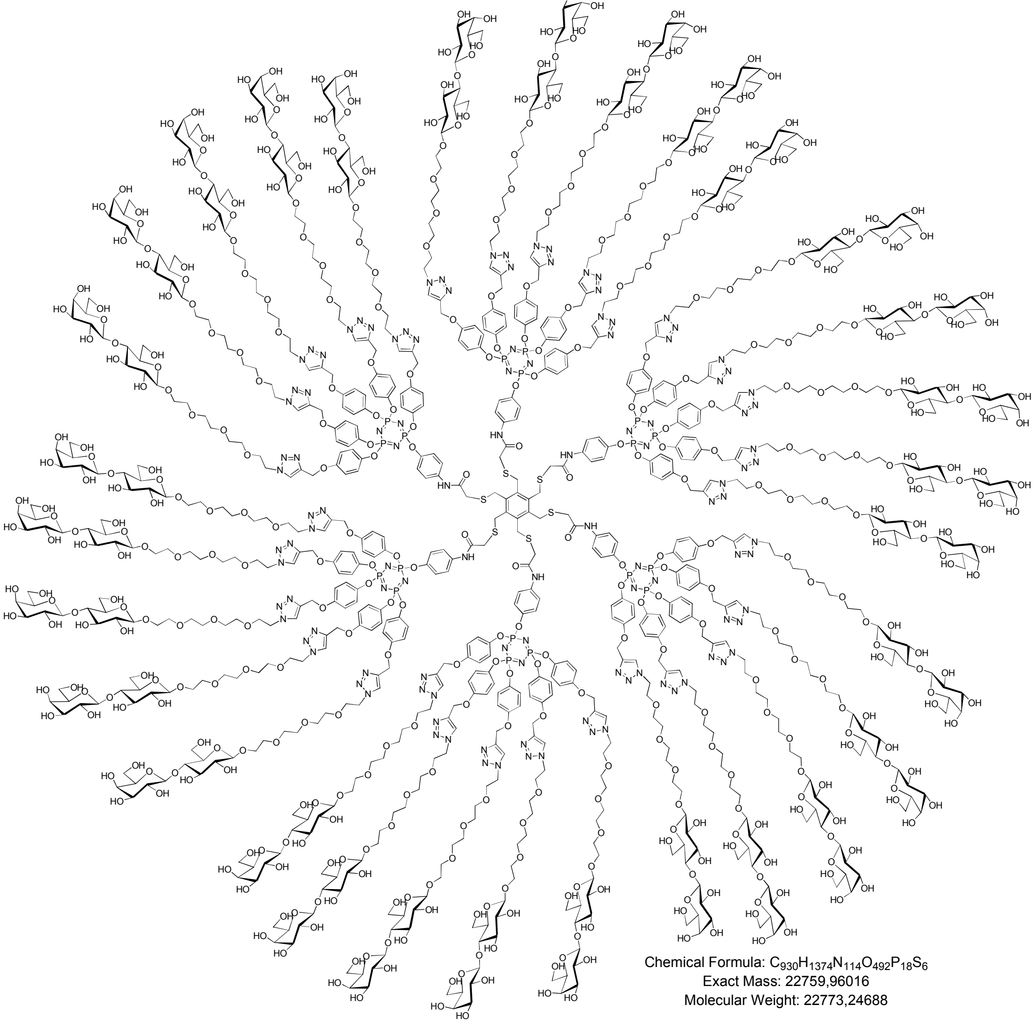


Figure S173. MALDI-TOF (DHB matrix) spectrum of compound **37** with successive losses of monomers

Hydroxylated tricontavalent glycodendrimer 38



Chemical Formula: $C_{930}H_{1374}N_{114}O_{492}P_{18}S_6$
Exact Mass: 22759,96016
Molecular Weight: 22773,24688

Acetylated compound **37** (34.0 mg, 1.08 µmol) was dissolved in a dry mixture of MeOH/DCM (5 mL, 4:1) and a solution of sodium methoxide (1M in MeOH, 5 µL every 20 minutes until precipitation) was added. An additional 100 µL was then injected and the heterogeneous reaction mixture was stirred at room temperature for 18 hours. The solvent was then removed with a Pasteur pipette and another dry mixture of MeOH/DCM (4 mL, 3:1) is added to the residual oil. A vigorous agitation is maintained for an additional 15 min. period. After removal of the solvents with a Pasteur pipette, 2 mL of dry MeOH were added to the viscous residue under agitation. After 15 min., the MeOH was removed and the residue was dissolved in 3 mL of H_2O, and the pH was adjusted to 7 with addition of ion-exchange resin (Amberlite IR 120 H^+). After filtration, the solvent was removed under *vacuum* with rotary evaporator, lyophilized to yield the fully deprotected tricontavalent derivative **38** as an off-white solid (20.0 mg, 0.88 µmol, **83%**).

^{1}H NMR (600 MHz, D_2O, δ ppm): 7.99 (m, 30H, H_{triazole}), 7.28 (br s, 12H, C$H_{b'}$), 6.99 (br s, 132H, CH_b, CH_c, C$H_{c'}$), 5.10-4.90 (br s, 60H, $C_{\mathrm{q\text{-}triazole}}CH_2O$), 4.58-4.32 (m, 132H, $N_{\mathrm{triazole}}CH_2CH_2$, $C_{\mathrm{core}}CH_2S$, $H_{1\mathrm{glc}}$, $H_{1\mathrm{gal}}$), 3.97-3.25 (m, 792H,

OCH_2CH_2N, LacOCH*H*CH_2, H_{3glc}, H_{2gal}, H_{3gal}, H_{6bglc}, H_{4gal}, H_{6agal}, H_{6bgal}, H_{6aglc}, H_{5gal}, H_{5glc}, H_{4glc}, LacOCH*H*CH_2, OCH_2, H_{2glc}, SCH_2CONH).

^{13}C NMR (150 MHz, D_2O, δ ppm): ~165.0 (*C*=O) *(not visible)*, 155.6 (C_a), 145.0 ($C_{d'}$) *(not visible)*, 144.6 (C_d), 143.7 ($C_{triazole}$=CH), 136.2 ($C_{q\ core}$) (*not visible*), 130.7 ($C_{a'}$) (*not visible*), 126.0 ($C_{triazole}$=CH), 122.4 (C_c + $C_{b'}$ + $C_{c'}$), 116.2 (C_b), 103.7 (C_{1gal}), 102.8 (C_{1glc}), 79.1 (C_{4glc}), 76.0 (C_{3glc}), 75.4 (C_{5glc}), 75.0 (C_{5gal}), 73.5 (C_{2glc}), 73.2 (C_{3gal}), 71.6 (C_{2gal}), 70.3, 70.2, (OCH_2), 69.4 (C_{4gal}), 69.2 (OCH_2), 62.1 (OCH_2C=C), 61.7 (C_{6glc}), 60.8 (C_{6gal}), 50.7 (NCH_2), 37.8 (SCH_2CONH) (*not visible*), 31.2 ($C_{core}CH_2S$) (*not visible*).

^{31}P NMR (122 MHz, D_2O, δ ppm): 10.1 (br s, 18P).

m/z (MALDI-TOF/ DHB matrix) for $C_{930}H_{1374}N_{114}O_{492}P_{18}S_6$ = 22773.2, found 22862.0.

NMR diffusion studies (D_2O): $D = 0.65\times10^{-10}$ m^2/s; d_s = 6.2 nm.

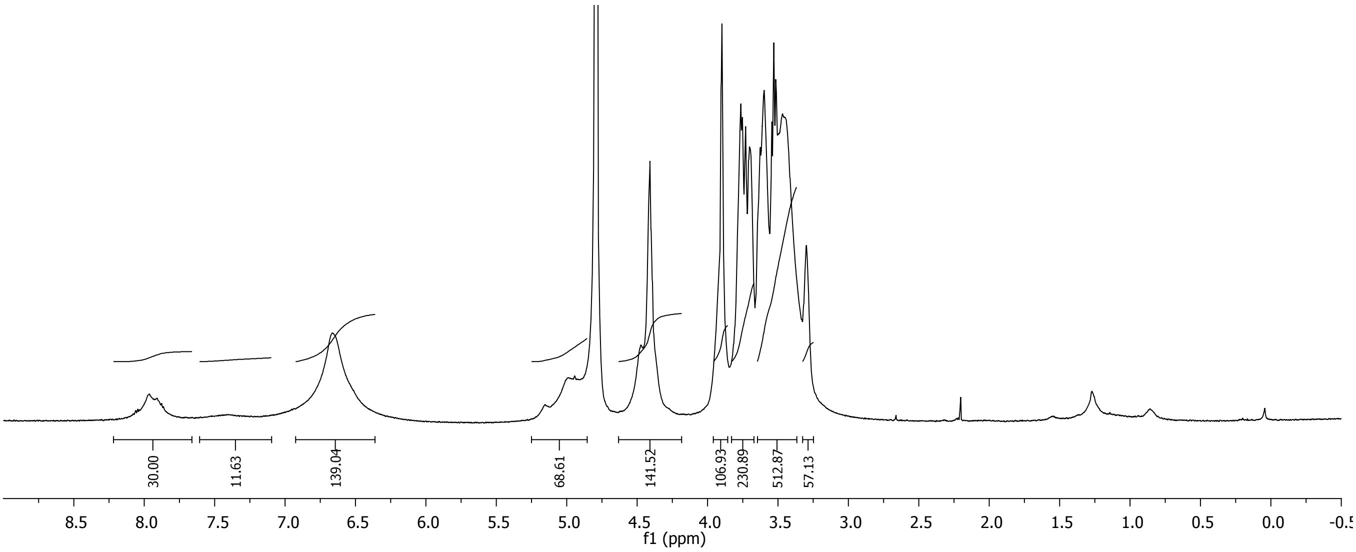


Figure S174. ^{1}H NMR spectrum of compound **38** (D_2O, 600MHz)

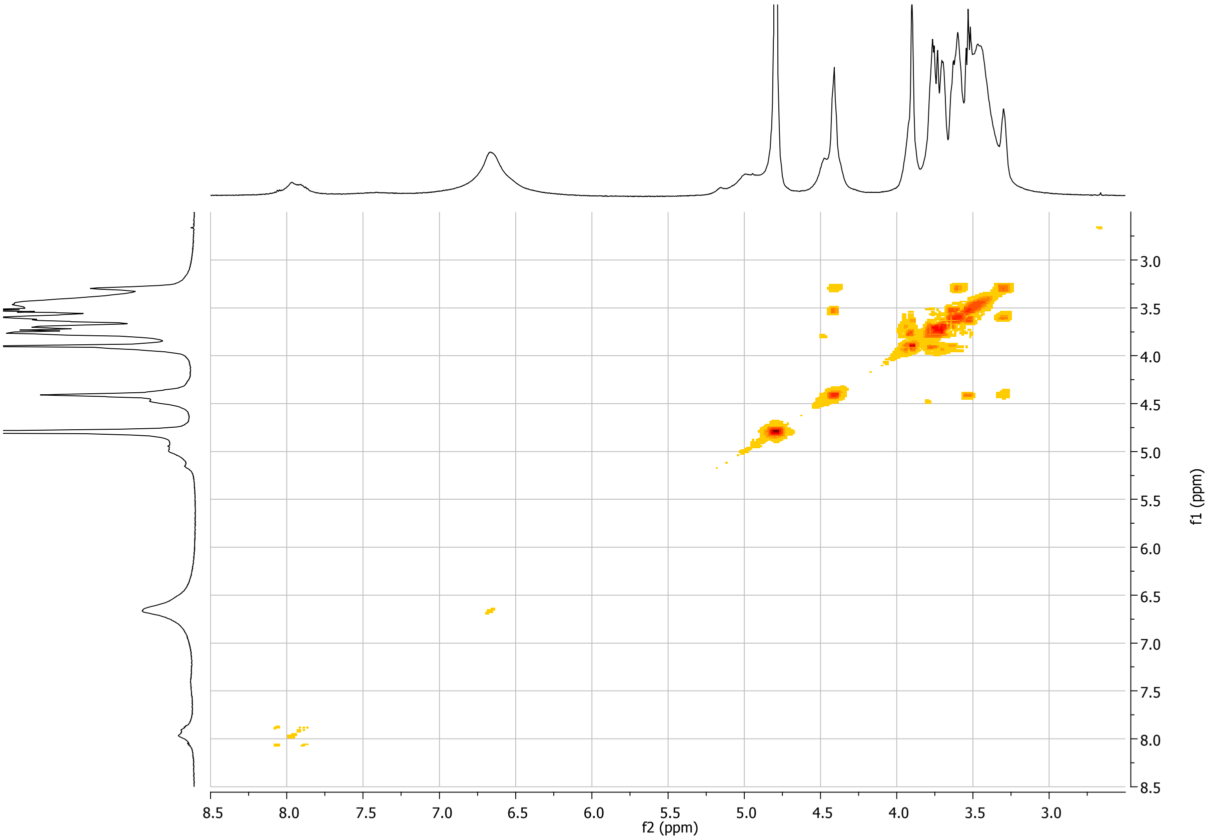


Figure S175. gCOSY spectrum of compound **38**

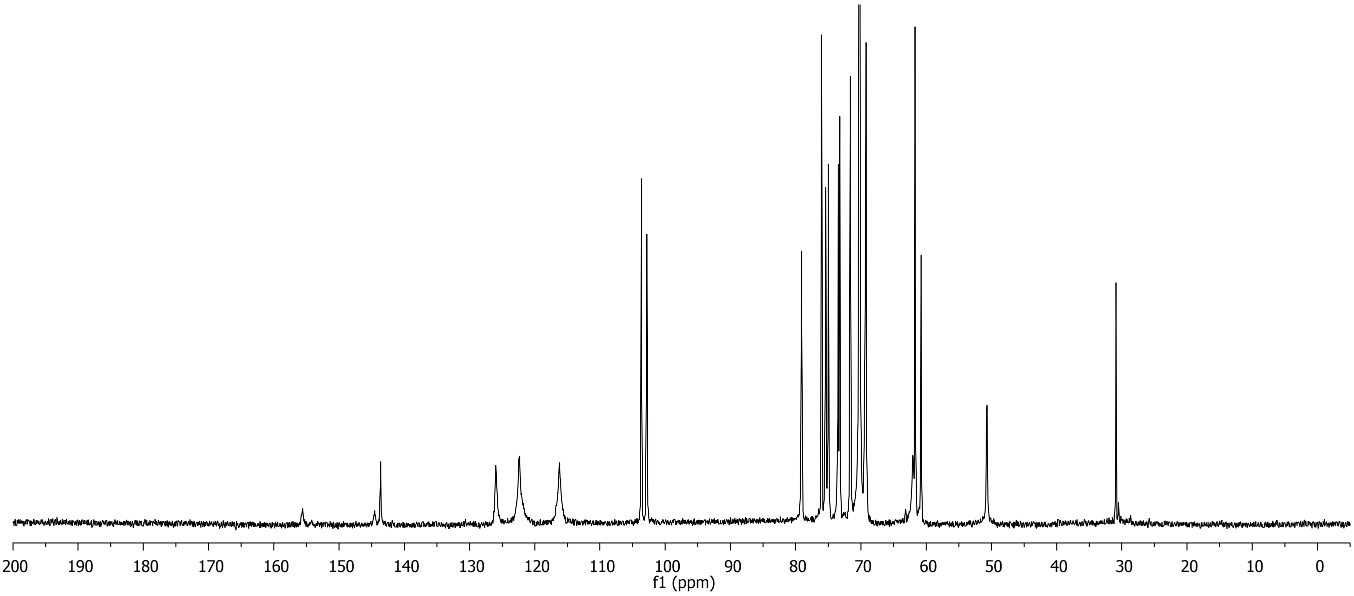


Figure S176. ^{13}C NMR spectrum of compound **38** (D_2O, 150MHz, acetone as reference)

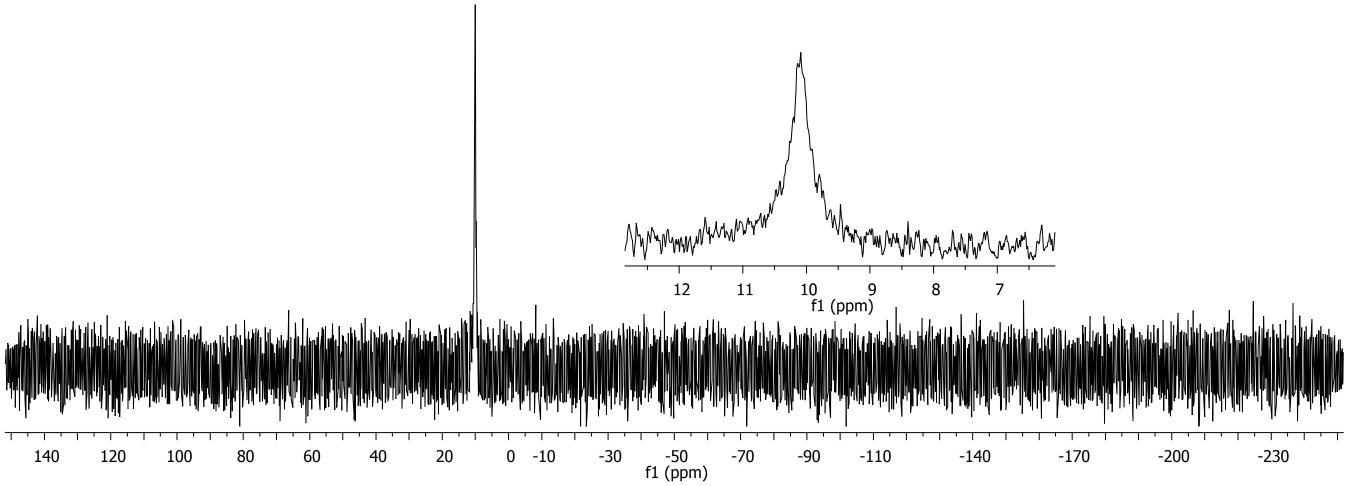


Figure S177. ^{31}P NMR spectrum of compound **38** (D_2O, 122MHz)

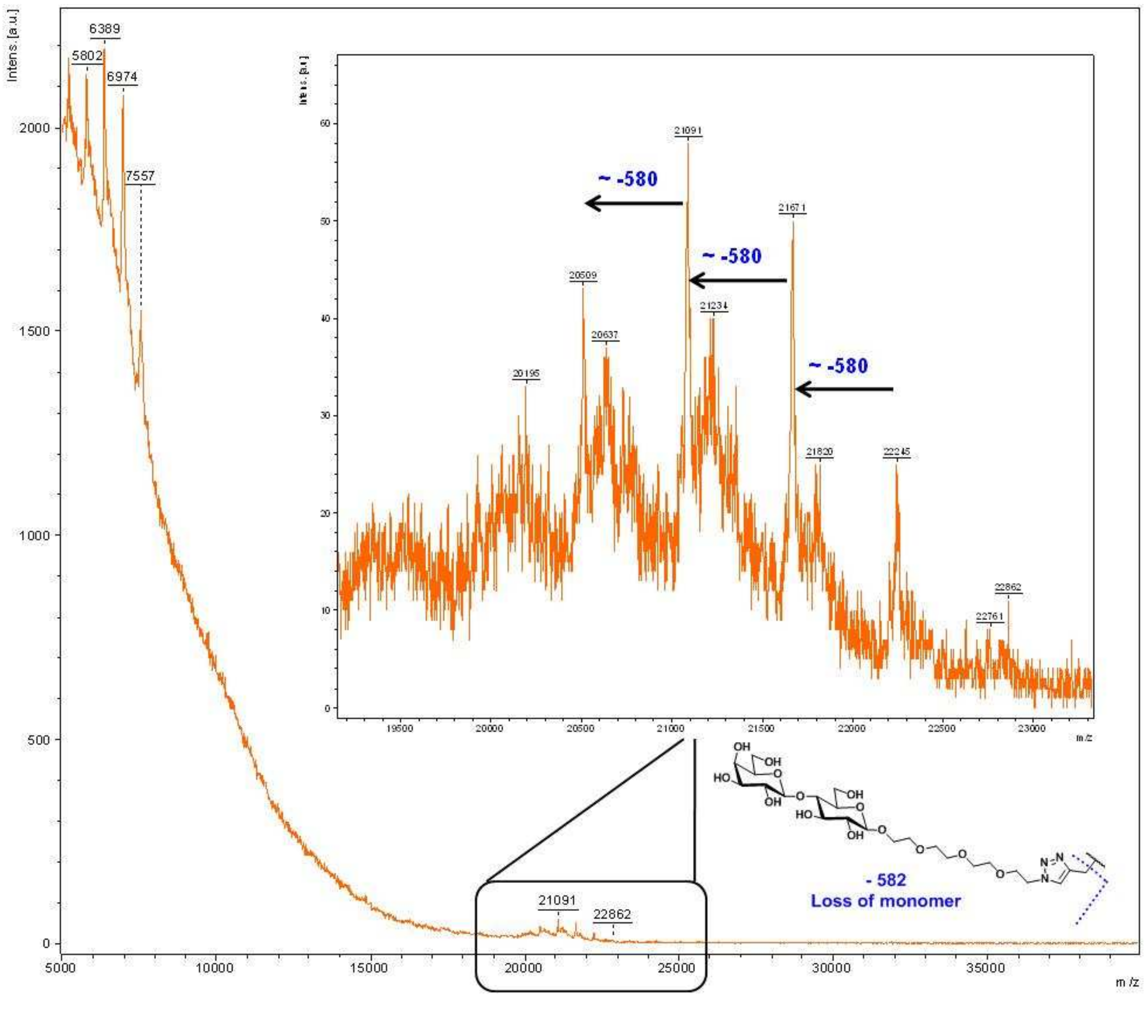
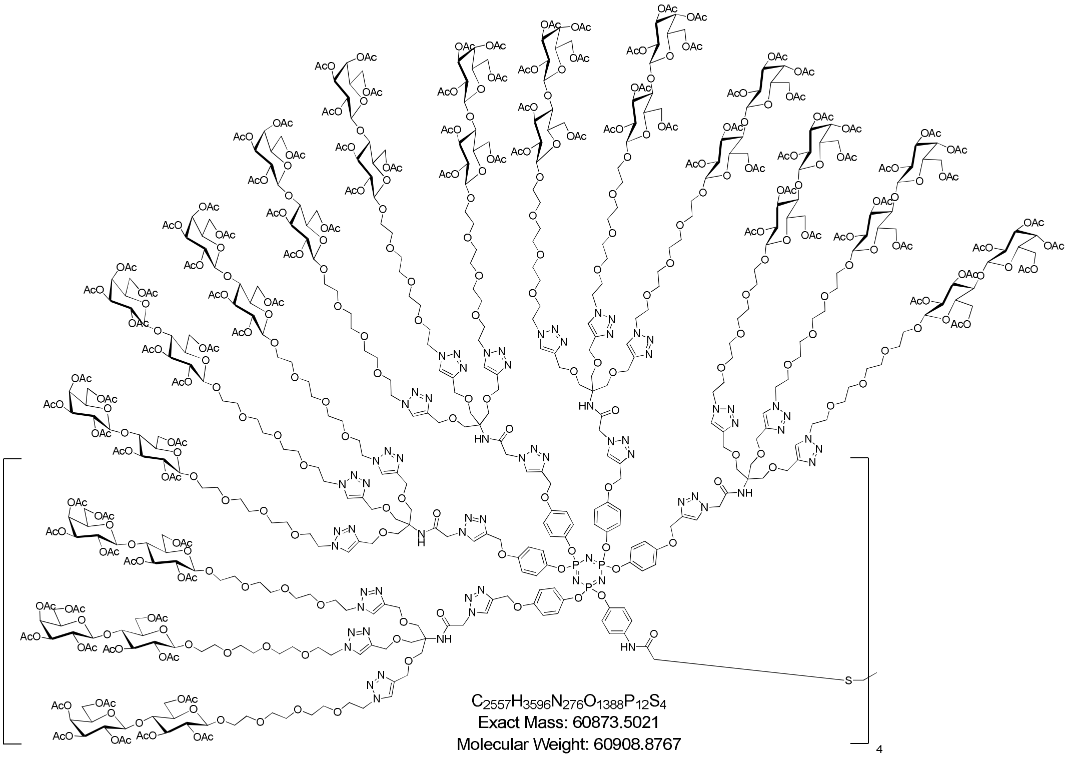


Figure S178. MALDI-TOF (DHB matrix) spectrum of compound **38** with successive losses of monomers

Hexacontavalent glycodendrimer 39


$C_{2557}H_{3596}N_{276}O_{1388}P_{12}S_4$
Exact Mass: 60873.5021
Molecular Weight: 60908.8767

To a solution of icosapropargylated cyclotriphosphazene derivative **34** (2.35 mg, 0.55 µmol, 1.0 eq.) in a 1:1 mixture of H_2O/THF_{anh} (3 mL), were added azido derivative **14** (51.8 mg, 18.3 µmol, 33.3 eq.), $CuSO_4{\cdot}5H_2O$ (4.7 mg, 18.6 µmol, 34.0 eq.) and sodium ascorbate (3.7 mg, 18.6 µmol, 34.0 eq.). While stirring, the mixture was first heated at 50℃ for 3 hours in a 20 mL vial and at room temperature for additional 18 hours. Noteworthy is the fact that 2.5 mg of $CuSO_4{\cdot}5H_2O$ and 2mg of sodium ascorbate were added to the solution after the 3 hours of heating. Ethyl acetate (30 mL) was added and the solution was poured into a separatory funnel containing ethyl acetate (20 mL), washed with saturated aqueous NH_4Cl (2×20 mL), water (20 mL) and brine (10 mL). Organics were collected, dried over Na_2SO_4 and concentrated to dryness *in vacuo* with rotary evaporator. Purification by flash chromatography (SiO_2, DCM/MeOH 100:0 to 90:10) afforded desired multivalent compound **39** (26.0 mg, 0.43 µmol, **74%**) as a yellowish oil.

$\mathbf{R_f}$ = 0.15, DCM/MeOH 94:6.

$^{\mathbf{1}}$**H NMR** (600 MHz, $CDCl_3$, δ ppm): 7.93 (s, 20H, $H_{\text{int-triazole}}$), 7.73 (s, 60H, $H_{\text{ext-triazole}}$), 7.28 (br s, 12H, $CH_{b'}$ + NH_{int}), 6.99-6.60 (br s, 108H, CH_b, CH_c, $CH_{c'}$ + NH_{ext}), 5.33 (br s, 60H, $H_{4\text{gal}}$), 5.19 (t_{app}, 60H, $H_{3\text{glc}}$), 5.10-5.02 (m, 100H, $C_{\text{q-triazole}}CH_2O$, $H_{2\text{gal}}$), 4.95 (dd, $^3J_{2,3}$ = 3.4 Hz, $^3J_{3,4}$ = 7.0 Hz, 60H, $H_{3\text{gal}}$), 4.83 (t_{app}, 60H, $H_{2\text{glc}}$), 4.54-4.47 (m, 420H, $C_{\text{q-triazole}}CH_2OCH_2$, OCH_2CH_2N, $H_{1\text{glc}}$, $H_{6\text{aglc}}$, $H_{1\text{gal}}$), 4.10-4.02 (m, 180H, $H_{6\text{bglc}}$, $H_{6\text{agal}}$, $H_{6\text{bgal}}$), 3.86-3.53 (m, 1188H, $C_{\text{q-triazole}}CH_2OCH_2C_{\text{triazole}}$, $NHCOCH_2N_{\text{triazole}}$, OCH_2CH_2N, $H_{5\text{gal}}$, $H_{5\text{glc}}$, $H_{4\text{glc}}$, OCH_2, $HNCOCH_2S$), 2.82 (br s, 8H, C_qCH_2S), 2.11-1.92 (m, 1260H, $COCH_3$).

^{13}**C NMR** (150 MHz, $CDCl_3$, δ ppm (***<u>145000 scans</u>***)): 170.2, 170.2, 170.0, 169.9, 169.6, 169.5, 168.9 (7×s, *C*OCH_3), 166.3 (*C*ONH$_{\text{int}}$), 165.2 (*C*ONH$_{\text{ext}}$), 155.3 (C_{a}), 154.0 (C_{a}), 149.9 ($C_{\text{d'}}$), 144.3 (C_{d}), 144.2 ($C_{triazole}$=CH), 143.3 ($C_{triazole}$=CH), 135.2 ($C_{\text{a'}}$), 125.4 (C_{triazole}=*C*H), 123.9 (C_{triazole}=*C*H), 121.8 (C_{c}), 121.4 ($C_{\text{b'}}$), 116.1 (C_{b}), 115.2 (C_{b}), 101.0 ($C_{1\text{gal}}$), 100.4 ($C_{1\text{glc}}$), 76.2 ($C_{4\text{glc}}$), 72.8 ($C_{3\text{glc}}$), 72.6 ($C_{5\text{glc}}$), 71.6 ($C_{2\text{glc}}$), 70.9 ($C_{3\text{gal}}$), 70.5 ($C_{5\text{gal}}$), 70.4, 70.3, 70.2, 70.2, 70.0, 69.3 (O*C*H_2), 69.0 ($C_{2\text{gal}}$), 68.9 (O*C*H_2), 68.6 (C_q*C*H_2O), 66.6 ($C_{4\text{gal}}$), 64.5 (O*C*H_2C=C), 62.0 ($C_{6\text{glc}}$), 61.9 (C_q), 60.6 ($C_{6\text{gal}}$), 60.3 (N*C*H_2), 52.5 (HNCO*C*H_2N_{triazole}), 49.9 (O*C*H_2), 45.9 (C_q), 37.4 (S*C*H_2CONH), 37.0 (C_q*C*H_2S), 20.9, 20.8, 20.6, 20.5, 20.5, 20.4 (7×s, CO*C*H_3).

^{31}**P NMR** (122 MHz, $CDCl_3$, δ ppm): 10.0-9.6 (m, 12P).

m/z (MALDI-TOF/DHB matrix) for $C_{2557}H_{3596}N_{276}O_{1388}P_{12}S_4$= 60908.9; found: 59682-centered Gaussian.

NMR diffusion studies ($CDCl_3$): $D = 1.07\times10^{-10}$ m^2/s; $d_s = 7.6$ nm.

GPC measurements ($CHCl_3/Et_3N$ (1%)): $M_w = 76570$; $M_n = 75530$, PDI (M_w/M_n) = 1.014.

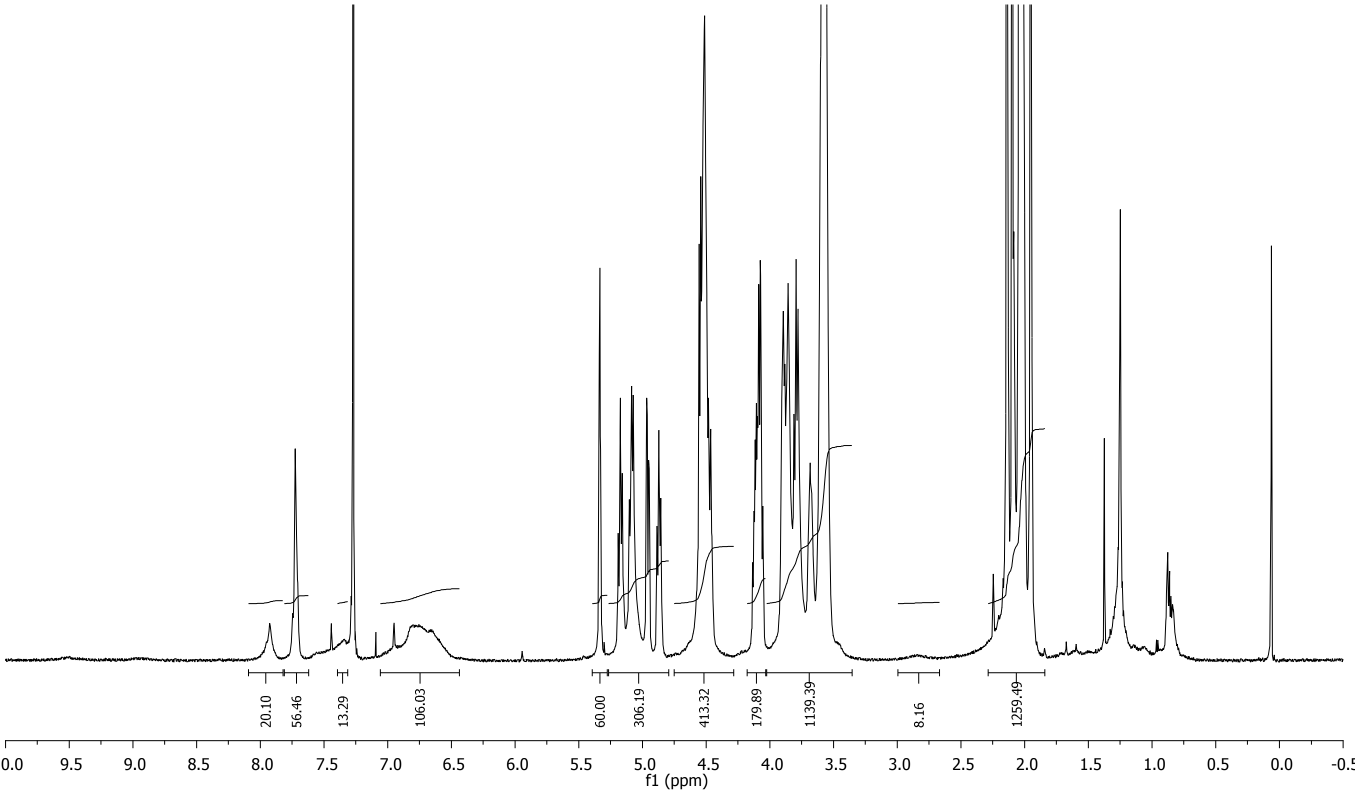


Figure S179. ^{1}H NMR spectrum of compound **39** ($CDCl_3$, 600MHz)

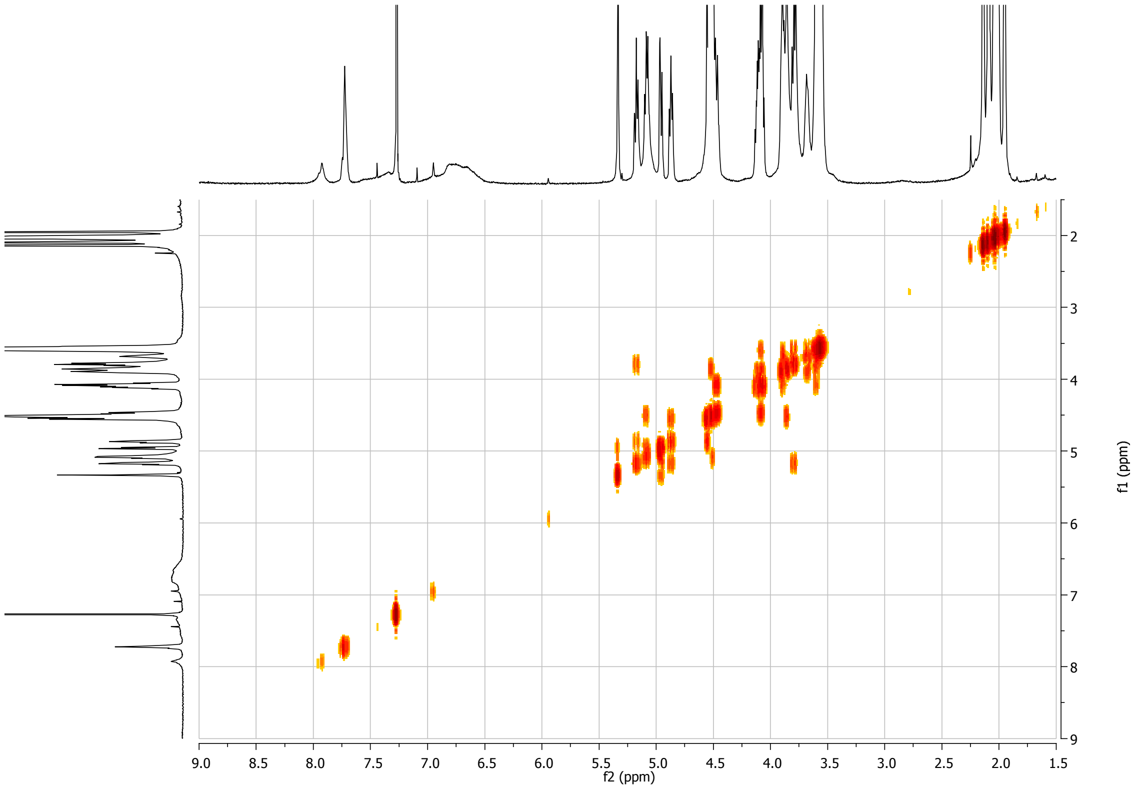


Figure S180. gCOSY spectrum of compound **39**

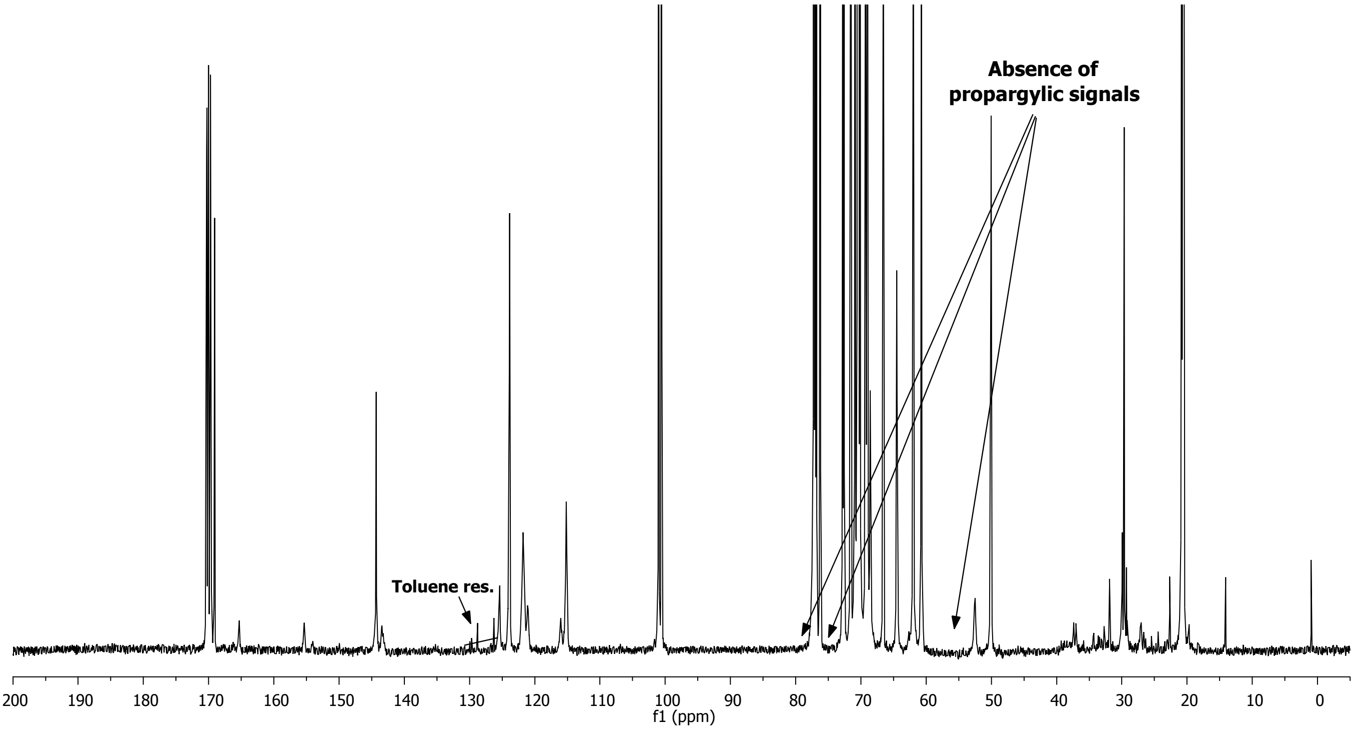


Figure S181. ^{13}C NMR spectrum of compound **39** ($CDCl_3$, 150MHz, 145000 scans)

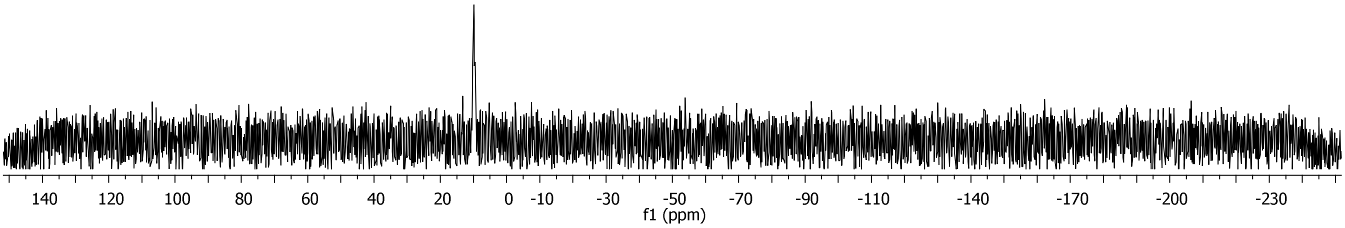


Figure S182. ^{31}P NMR spectrum of compound **39** ($CDCl_3$, 122MHz)

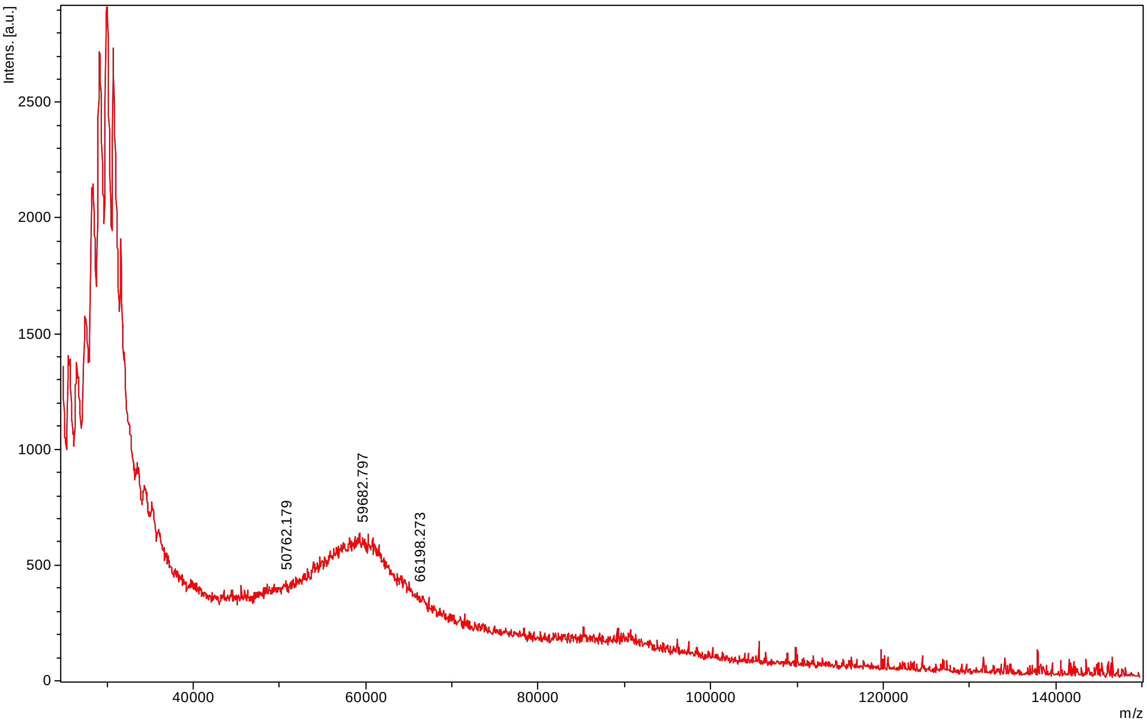
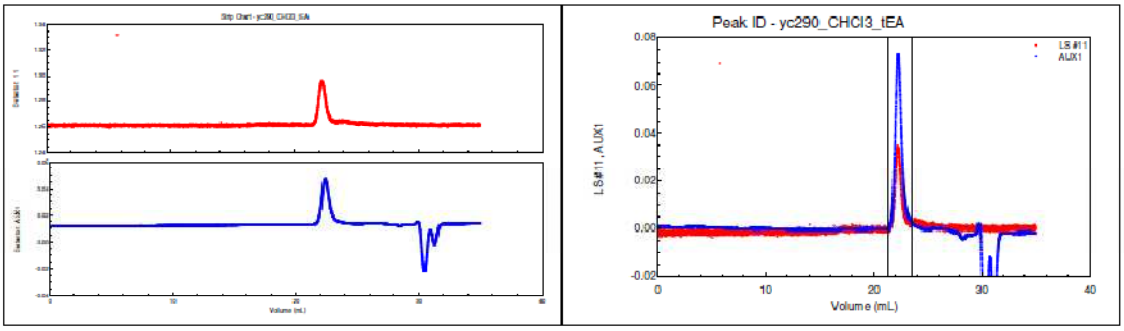


Figure S183. MALDI-TOF (DHB matrix) of compound **39**

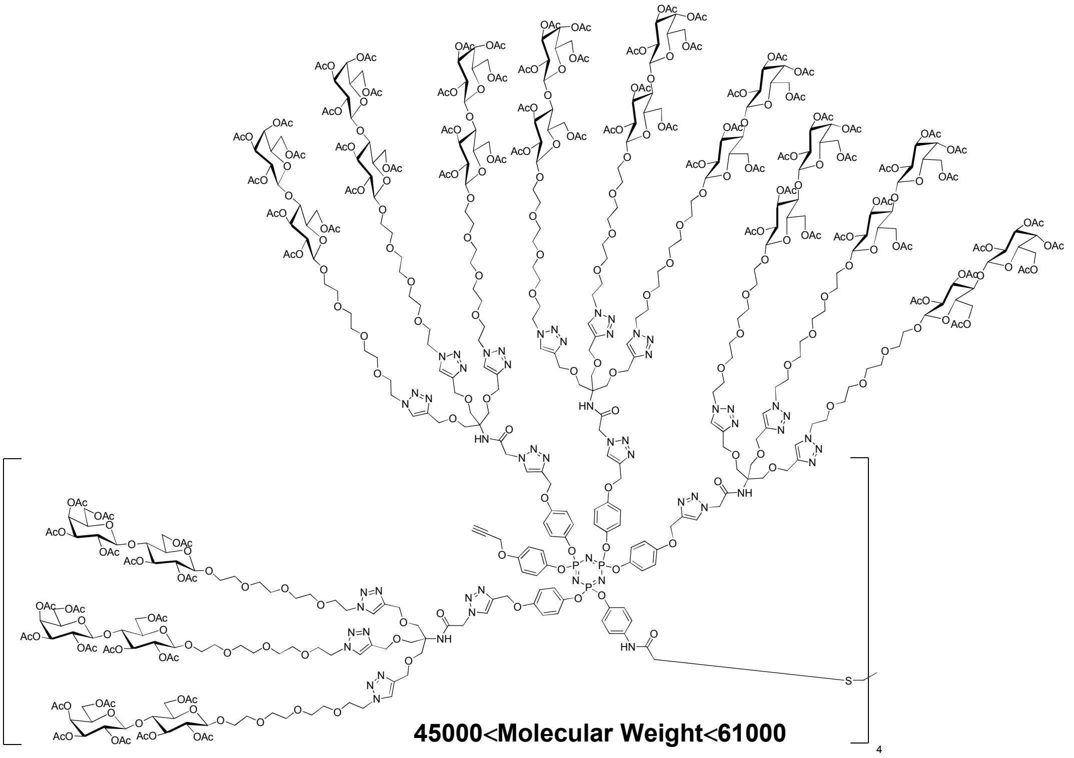


```
Polydispersity(Mw/Mn)  :  1.014±0.132 (13%)
Polydispersity(Mz/Mn)  :  1.038±0.248 (24%)

Molar Mass Moments (g/mol)
 Mn                    :  7.553e+04 (9%)
 Mw                    :  7.657e+04 (9%)
 Mz                    :  7.840e+04 (22%)
```

Figure S184. GPC trace ($CHCl_3$/Et_3N (1%)) for compound **39**

Defectuous glycodendrimer 39a (*location of propargylic functions is arbitrary*)



To a solution of icosapropargylated cyclotriphosphazene derivative **34** (2.66 mg, 0.62 µmol, 1.0 eq.) in a 1:1 mixture of H_2O/THF_{anh} (3 mL), were added azido derivative **14** (30.0 mg, 10.6 µmol, 17.0 eq.), $CuSO_4 \cdot 5H_2O$ (5.3 mg, 21.1 µmol, 34.0 eq.) and sodium ascorbate (4.2 mg, 21.1 µmol, 34.0 eq.). While stirring, the mixture was first heated at 50°C for 3 hours in a 20 mL vial and at room temperature for additional 18 hours. Ethyl acetate (30 mL) was added and the solution was poured into a separatory funnel containing ethyl acetate (20 mL), washed with saturated aqueous NH_4Cl (2×20 mL), water (20 mL) and brine (10 mL). Organics were collected, dried over Na_2SO_4 and concentrated to dryness *in vacuo* with rotary evaporator. Purification by flash chromatography (SiO_2, DCM/MeOH 100:0 to 90:10) afforded desired mixture of compounds presenting an average of 3 remaining propargylic functionalities **39a** (24.0 mg, 0.47 µmol, **75%**) (*based on a MW = 52414 for 17 grafted dendrons*) as a colorless oil.

$\mathbf{R_f}$ = 0.15, DCM/MeOH 94:6.

^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 7.93 (s, 17H, $H_{\text{int-triazole}}$), 7.73 (s, 48H, $H_{\text{ext-triazole}}$), 7.28 (br s, 12H, $CH_{b'}$ + NH_{int}), 6.99-6.60 (br s, 105H, CH_b, CH_c, $CH_{c'}$ + NH_{ext}), 5.33 (br s, 51H, $H_{4\text{gal}}$), 5.19 (t_{app}, 51H, $H_{3\text{glc}}$), 5.10-5.02 (m, 85H, $C_{\text{q-triazole}}CH_2O$, $H_{2\text{gal}}$), 4.95 (dd, $^3J_{2,3}$ = 3.4 Hz, $^3J_{3,4}$ = 7.0 Hz, 51H, $H_{3\text{gal}}$), 4.83 (t_{app}, 51H, $H_{2\text{glc}}$), **4.70-4.60 (br s, 6H, $OCH_2C{\equiv}CH$ res.)**, 4.54-4.47 (m, 357H, $C_{\text{q-triazole}}CH_2OCH_2$, OCH_2CH_2N, $H_{1\text{glc}}$, $H_{6\text{aglc}}$, $H_{1\text{gal}}$), 4.10-4.02 (m, 153H, $H_{6\text{bglc}}$, $H_{6\text{agal}}$, $H_{6\text{bgal}}$), 3.86-3.53 (m, 1011H, $C_{\text{q-triazole}}CH_2OCH_2C_{\text{triazole}}$, $NHCOCH_2N_{\text{triazole}}$, OCH_2CH_2N, $H_{5\text{gal}}$, $H_{5\text{glc}}$, $H_{4\text{glc}}$, OCH_2, $HNCOCH_2S$), 2.82 (br s, 8H, C_qCH_2S), **2.65 (2×br s, 3H, $OCH_2C{\equiv}CH$ res.)**, 2.11-1.92 (m, 1071H, $COCH_3$).

^{13}C NMR (150 MHz, $CDCl_3$, δ ppm): 170.2, 170.2, 170.0, 169.9, 169.6, 169.5, 168.9 (7×s, $COCH_3$), 166.3 ($CONH_{\text{int}}$), 165.2 ($CONH_{\text{ext}}$), 155.3 (C_a), 154.0 (C_a), 149.9 ($C_{d'}$), 144.3 (C_d), 144.2 ($C_{triazole}$=CH), 143.3 ($C_{triazole}$=CH), 135.2 ($C_{a'}$), 125.4 ($C_{triazole}$=CH), 123.9 ($C_{triazole}$=CH), 121.8 (C_c), 121.4 ($C_{b'}$), 116.1 (C_b), 115.2 (C_b), 101.0 (C_{1gal}), 100.4 (C_{1glc}), 76.2 (C_{4glc}), 72.8 (C_{3glc}), 72.6 (C_{5glc}), 71.6 (C_{2glc}), 70.9 (C_{3gal}), 70.5 (C_{5gal}), 70.4, 70.3, 70.2, 70.2, 70.0, 69.3 (OCH_2), 69.0 (C_{2gal}), 68.9 (OCH_2), 68.6 (C_qCH_2O), 66.6 (C_{4gal}), 64.5 (OCH_2C=C), 62.0 (C_{6glc}), 61.9 (C_q), 60.6 (C_{6gal}), 60.3 (NCH_2), **56.1 (OCH_2C≡CH res.)**, 52.5 (HNCO$CH_2N_{triazole}$), 49.9 (OCH_2), 45.9 (C_q), 37.4 (SCH_2CONH), 37.0 (C_qCH_2S), 20.9, 20.8, 20.6, 20.5, 20.5, 20.4 (7×s, COCH_3).

m/z (MALDI-TOF/DHB matrix), found: 50696-centered Gaussian.

GPC measurements ($CHCl_3/Et_3N$ (1%)): M_w = 73780 ; M_n = 72270 , PDI (M_w/M_n) = 1.021

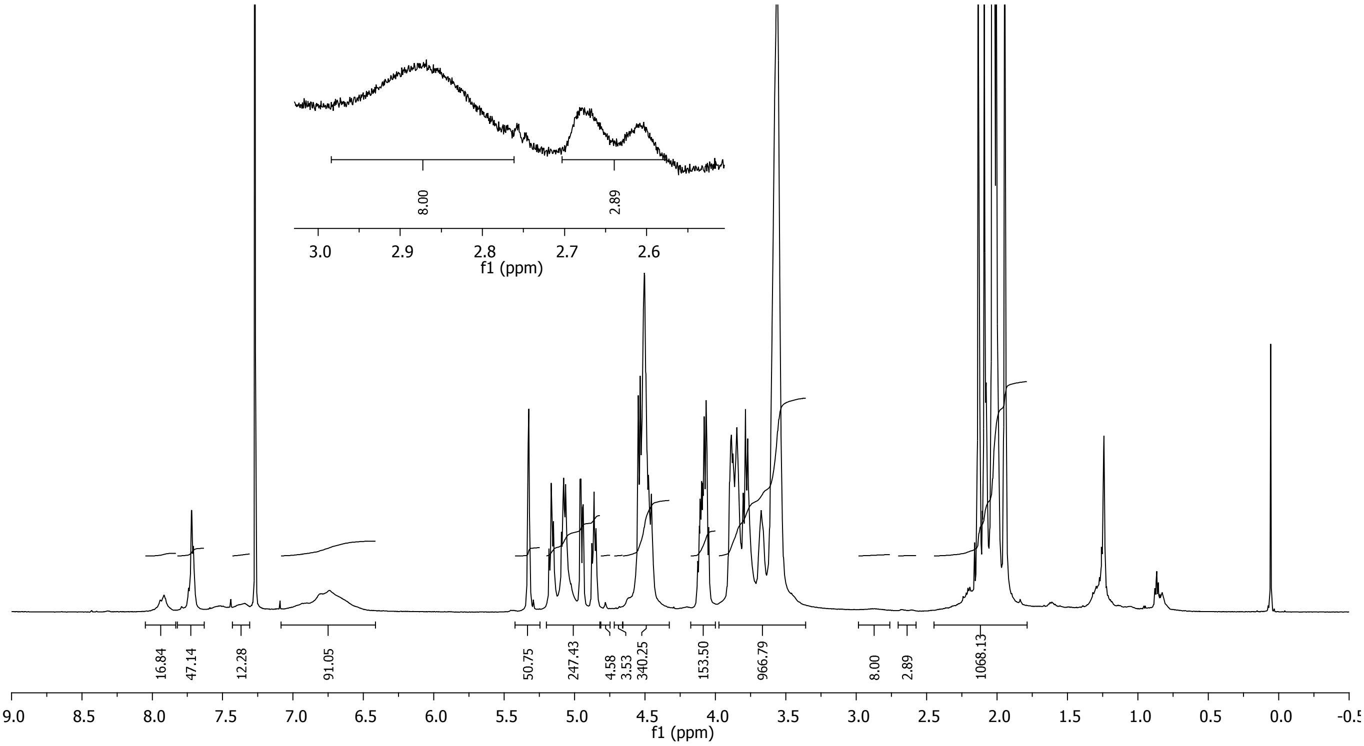


Figure S185. ^{1}H NMR spectrum of compound **39a** ($CDCl_3$, 600MHz)

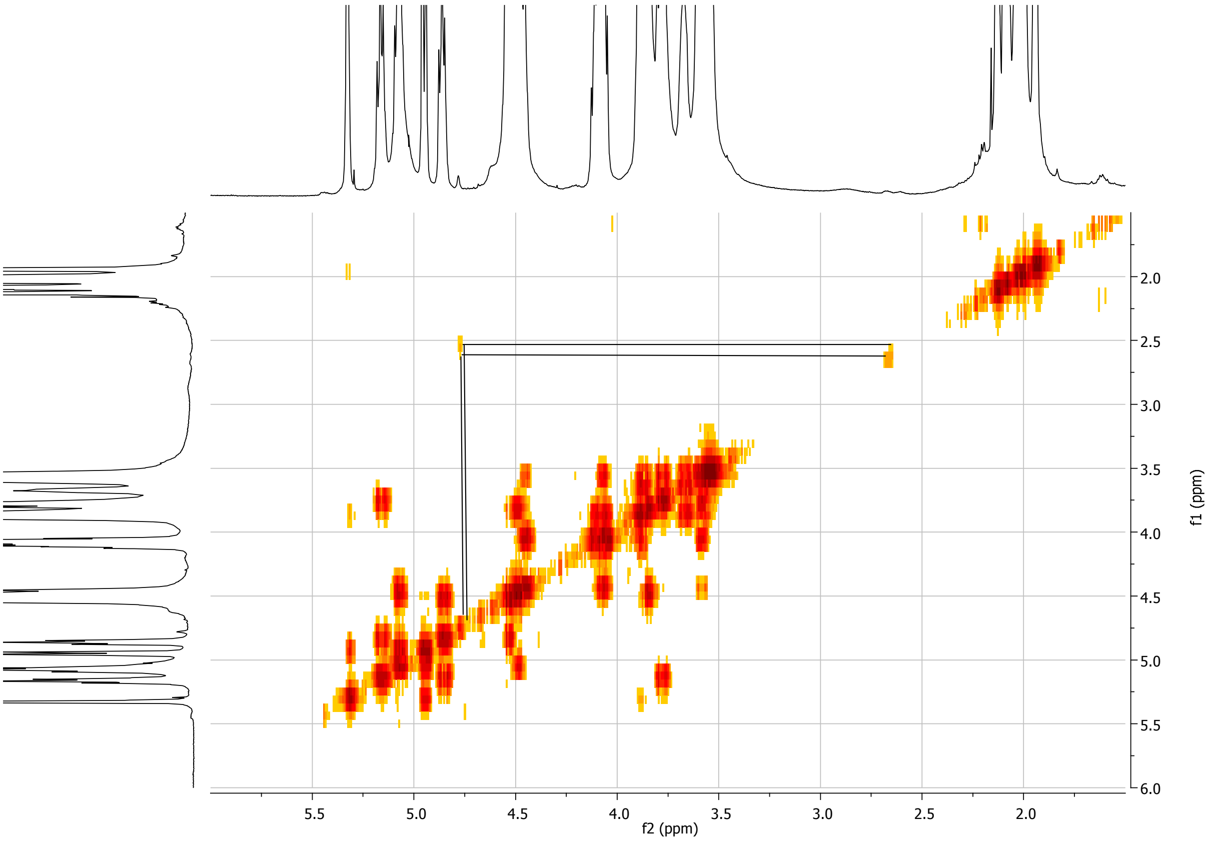


Figure S186. gCOSY spectrum of compound **39a**

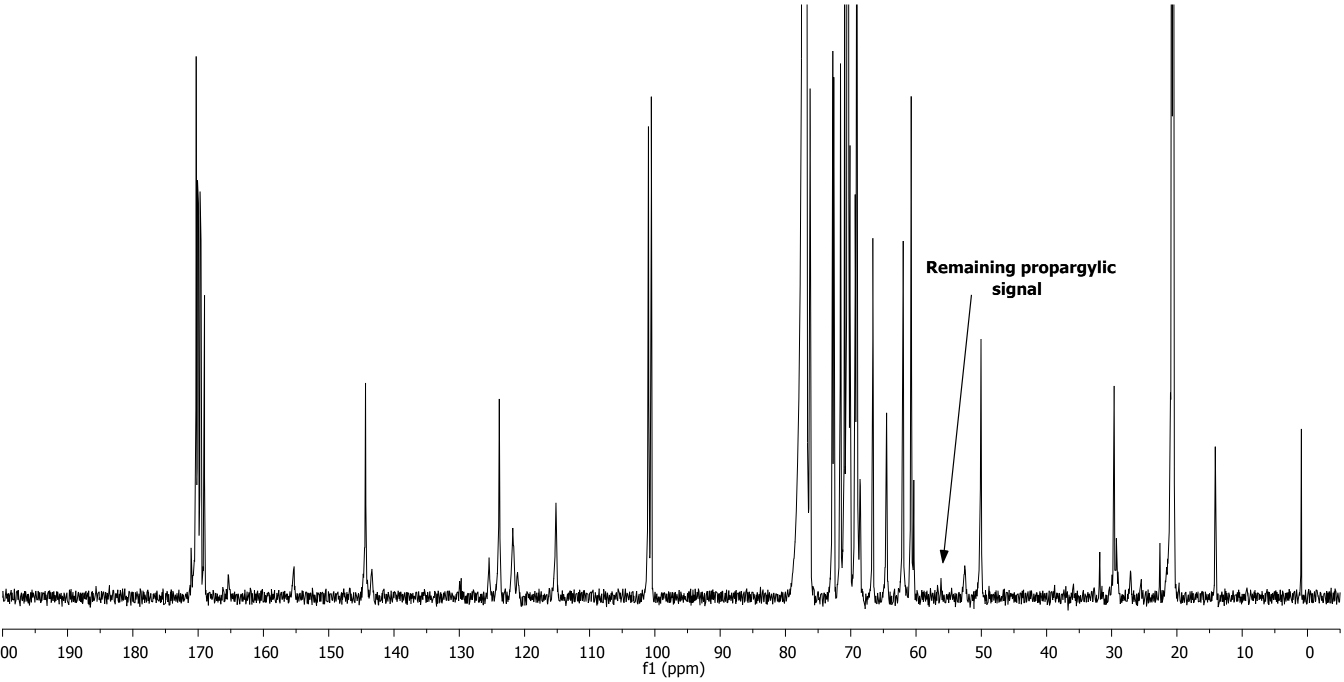


Figure S187. ^{13}C NMR spectrum of compound **39a** (CDCl$_3$, 150MHz, 58000 scans)

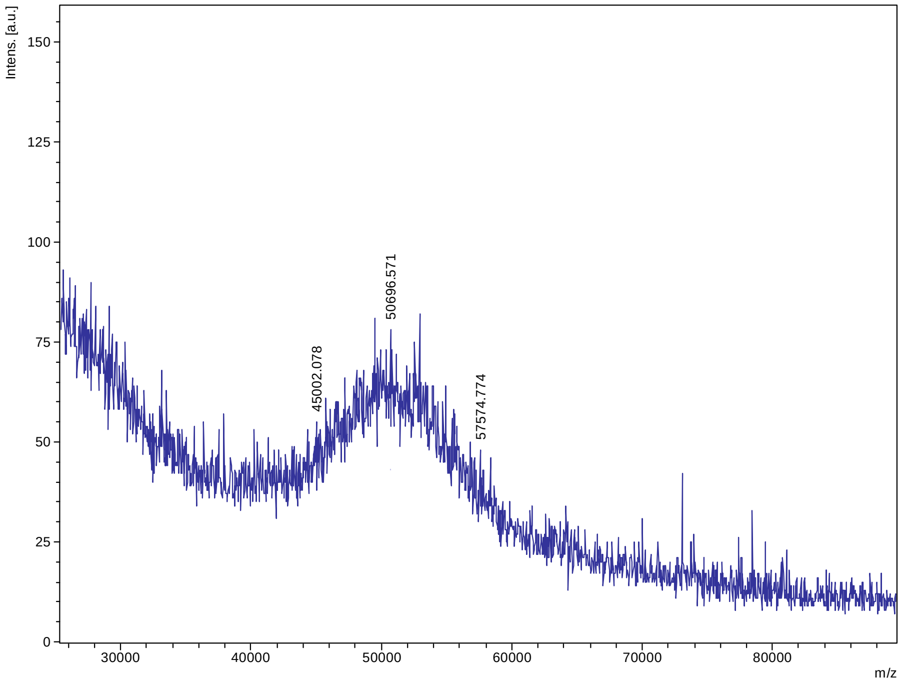
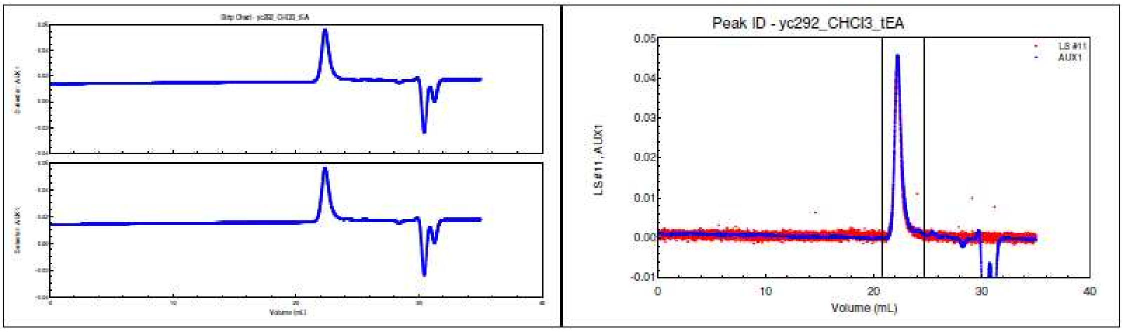


Figure S188. MALDI-TOF (DHB matrix) spectrum of compound **39a**

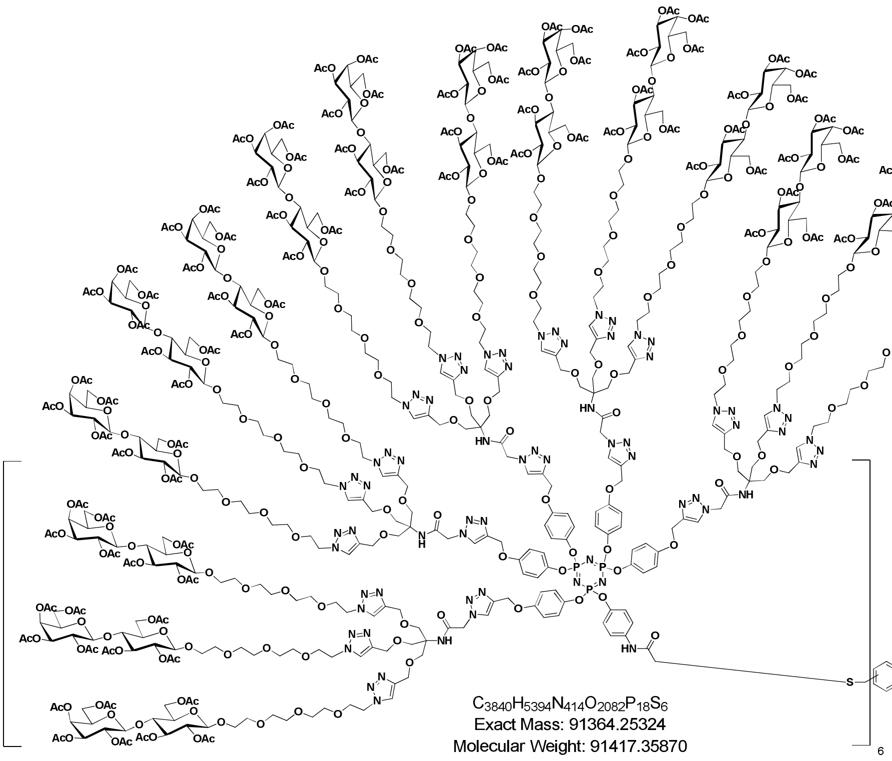


```
Polydispersity(Mw/Mn)  :  1.021±0.145 (14%)
Polydispersity(Mz/Mn)  :  1.063±0.283 (27%)

Molar Mass Moments (g/mol)
  Mn                   :  7.227e+04 (9%)
  Mw                   :  7.378e+04 (10%)
  Mz                   :  7.683e+04 (24%)
```

Figure S189. GPC trace ($CHCl_3/Et_3N$ (1%)) for compound **39a**

Protected nonacontavalent glycodendrimer 40



$C_{3840}H_{5394}N_{414}O_{2082}P_{18}S_6$
Exact Mass: 91364.25324
Molecular Weight: 91417.35870

To a solution of tricontapropargylated cyclotriphosphazene derivative **35** (3.80 mg, 0.59 µmol, 1.0 eq.) in a 1:1 mixture of H_2O/THF_{anh} (4 mL), were added azido dendron **14** (83.2 mg, 29.4 µmol, 50.0 eq.), $CuSO_4\cdot 5H_2O$ (6.10 mg, 23.5 µmol, 40.0 eq.) and sodium ascorbate (4.80 mg, 23.5 µmol, 40.0 eq.). While stirring, the mixture was first heated at 50℃ for 3 hours in a 20 mL vial and at room temperature for additional 18 hours. Noteworthy is the fact that 3.0 mg of $CuSO_4\cdot 5H_2O$ and 2.0 mg of sodium ascorbate were added to the solution after the 3 hours of heating. Ethyl acetate (5 mL) was added and the solution was poured into a separatory funnel containing ethyl acetate (20 mL), washed with saturated aqueous NH_4Cl (2×20 mL), water (20 mL) and brine (10 mL). Organics were collected, dried over Na_2SO_4 and concentrated to dryness *in vacuo* with rotary evaporator. Purification by flash chromatography (SiO_2, DCM/MeOH 100:0 to 90:10) afforded desired multivalent compound **40** (38.0 mg, 0.42 µmol, **72%**) as a pale oil.

$\mathbf{R_f}$ = 0.13, DCM/MeOH 94:6.

^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 7.93 (s, 30H, $H_{\text{int-triazole}}$), 7.73 (s, 90H, $H_{\text{ext-triazole}}$), 7.28 (br s, 42H, $CH_{b'}$ + NH_{ext}), 6.99-6.60 (br s, 138H, CH_b, CH_c, $CH_{c'}$ + NH_{int}), 5.32 (br s, 90H, H_{4gal}), 5.16 (t_{app}, 90H, H_{3glc}), 5.10-5.02 (m, 150H, $C_{\text{q-triazole}}CH_2O$, H_{2gal}), 4.95 (dd, $^3J_{2,3}$ = 3.4 Hz, $^3J_{3,4}$ = 7.0 Hz, 90H, H_{3gal}), 4.86 (t_{app}, 90H, H_{2glc}), 4.54-4.47 (m, 630H, $C_{\text{q-triazole}}CH_2OCH_2$, OCH_2CH_2N, H_{1glc}, H_{6aglc}, H_{1gal}), 4.14-4.02 (m, 282H, $C_{\text{core}}CH_2S$, H_{6bglc}, H_{6agal}, H_{6bgal}), 3.95-3.25 (m, 1782H, $C_{\text{q-triazole}}CH_2OCH_2C_{\text{triazole}}$, $NHCOCH_2N_{\text{triazole}}$, OCH_2CH_2N, H_{5gal}, H_{5glc}, H_{4glc}, OCH_2, $HNCOCH_2S$), 2.11-1.92 (m, 1890H, $COCH_3$).

^{13}C NMR (150 MHz, $CDCl_3$, δ ppm): 170.2, 170.2, 170.0, 169.9, 169.6, 169.5, 168.9 (7×s, $COCH_3$), 165.9 ($CONH_{\text{int}}$), 165.6 ($CONH_{\text{ext}}$), 155.3 (C_a), 149.9 ($C_{d'}$) *(not visible)*, 144.3 (C_d), 144.2 ($C_{triazole}$=CH), 143.3 ($C_{triazole}$=CH), 136.2 ($C_{\text{q core}}$)

(not visible), 135.2 ($C_{a'}$) *(not visible)*, 125.5 ($C_{triazole}$=*C*H), 123.9 ($C_{triazole}$=*C*H), 121.8 (C_c), 121.4 ($C_{b'}$), 116.1 (C_b), 115.1 (C_b), 101.0 (C_{1gal}), 100.5 (C_{1glc}), 76.2 (C_{4glc}), 72.8 (C_{3glc}), 72.6 (C_{5glc}), 71.6 (C_{2glc}), 70.9 (C_{3gal}), 70.5 (C_{5gal}), 70.4, 70.3, 70.2, 70.2, 70.0, 69.3 (O*C*H_2), 69.0 (C_{2gal}), 68.9 (O*C*H_2), 68.6 (C_q*C*H_2O), 66.6 (C_{4gal}), 64.5 (O*C*H_2C=C), 62.0 (C_{6glc}), 61.9 (C_q), 60.6 (C_{6gal}), 60.3 (N*C*H_2), 52.5 (HNCO*C*$H_2N_{triazole}$), 49.9 (O*C*H_2), 37.3 (S*C*H_2CONH), 31.2 (C_{core}*C*H_2S), 20.9, 20.8, 20.6, 20.5, 20.5, 20.4 (7×s, CO*C*H_3).

^{31}P NMR (122 MHz, $CDCl_3$, δ ppm): 10.0-9.2 (m, 18P).

m/z (MALDI-TOF/DHB matrix) for $C_{3840}H_{5394}N_{414}O_{2082}P_{18}S_6$= 91417.4; found: 79824-centered Gaussian.

NMR diffusion studies ($CDCl_3$): $D = 0.81\times10^{-10}$ m^2/s; d_s = 10.1 nm.

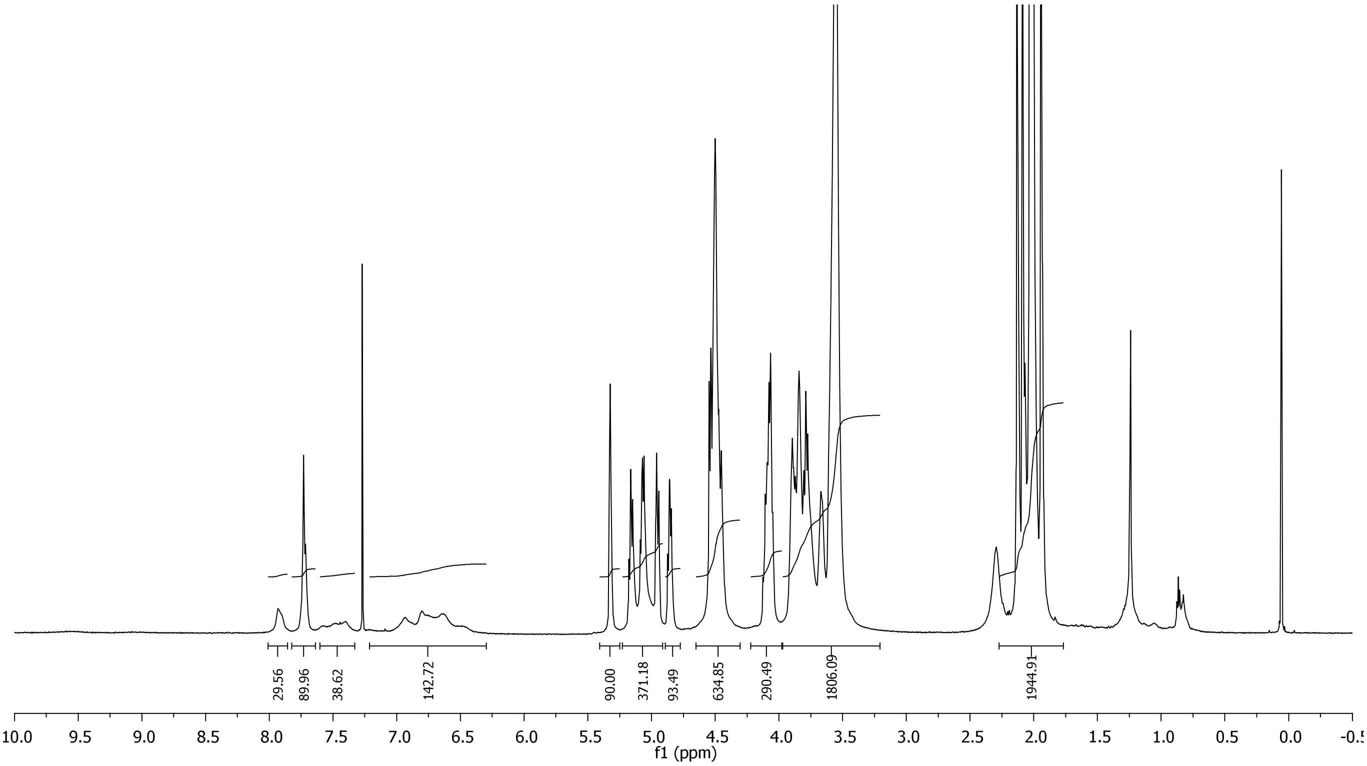


Figure S190. ^{1}H NMR spectrum of compound **40** ($CDCl_3$, 600MHz)

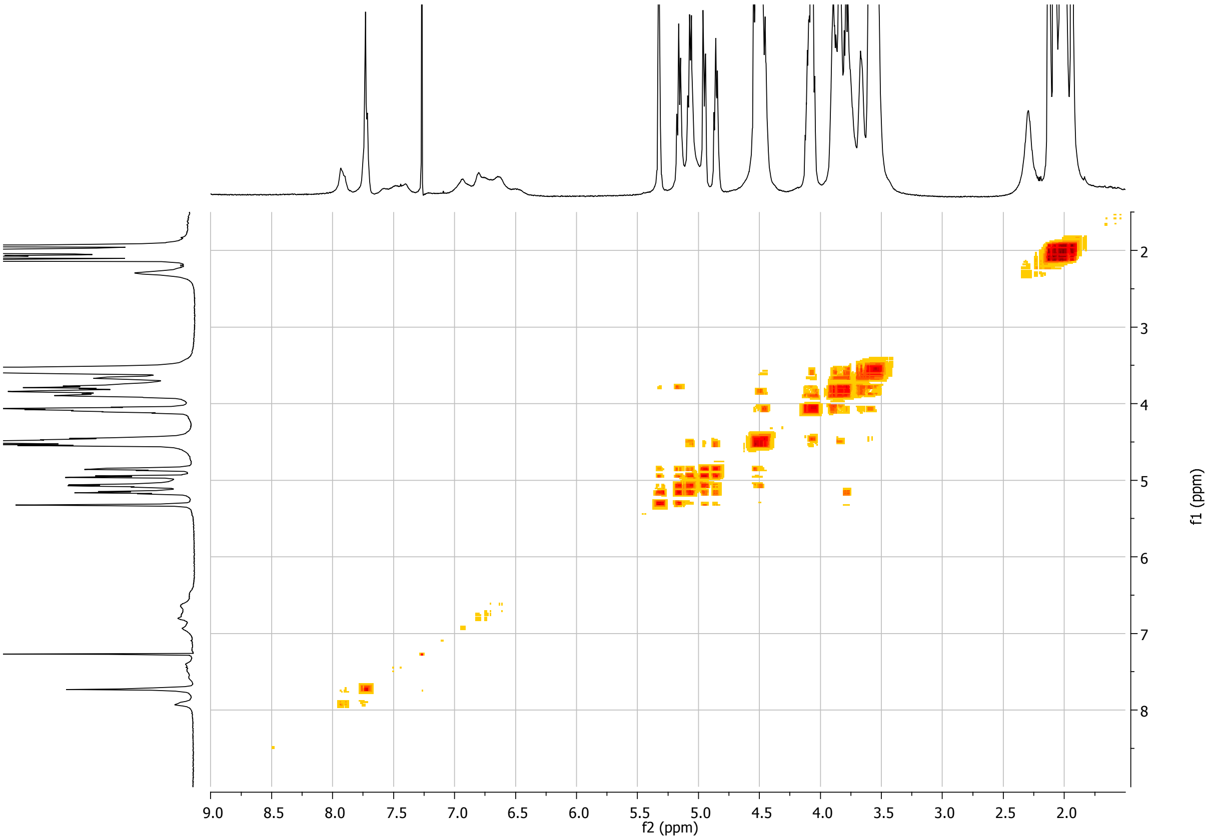


Figure S191. gCOSY spectrum of compound **40**

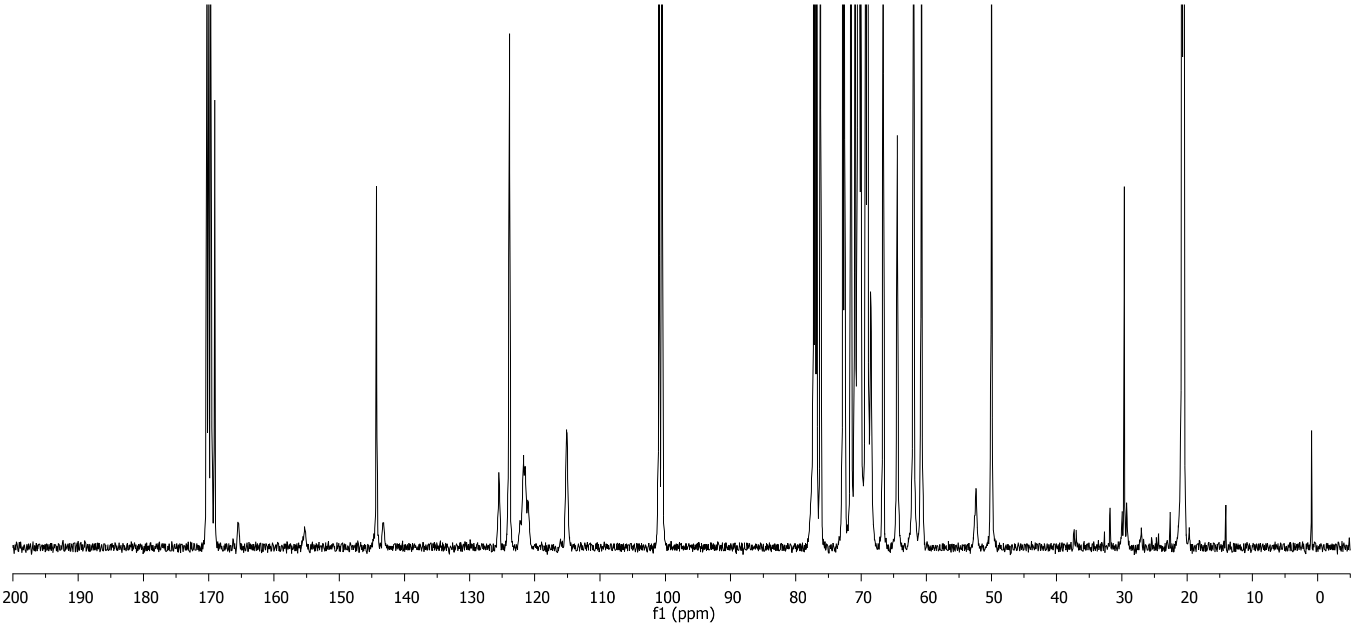


Figure S192. ^{13}C NMR spectrum of compound **40** (CDCl$_3$, 150MHz, 60000 scans)

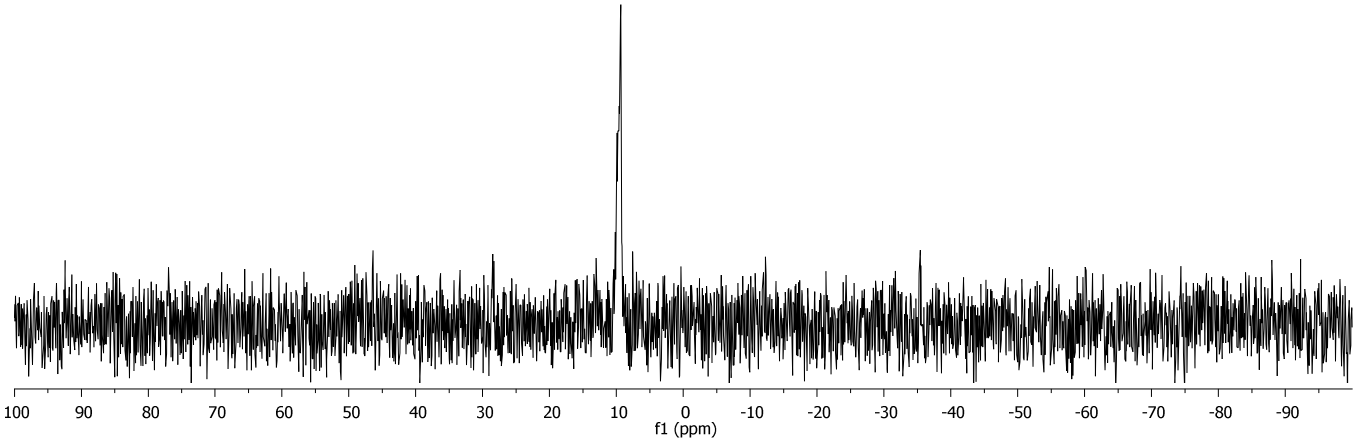


Figure S193. ^{31}P NMR spectrum of compound **40** ($CDCl_3$, 122MHz)

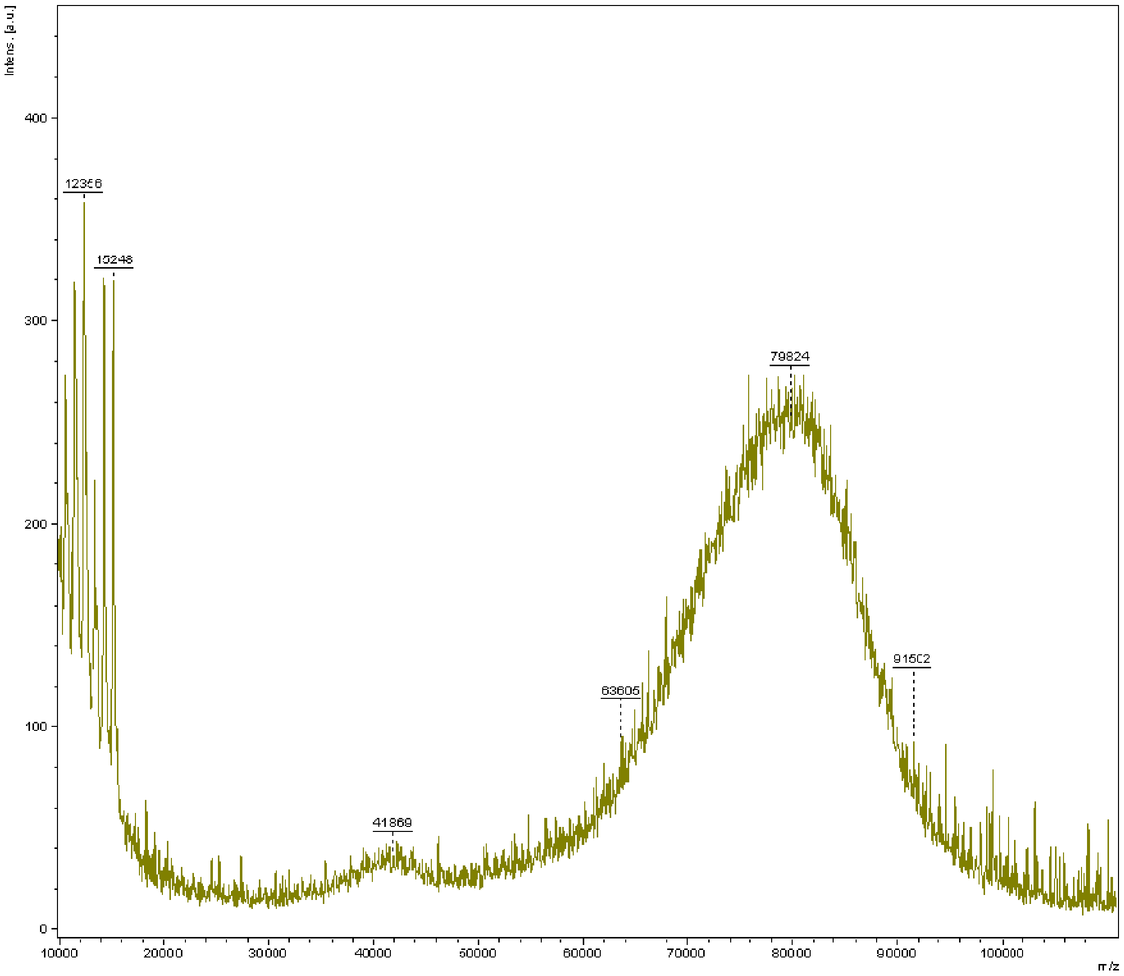
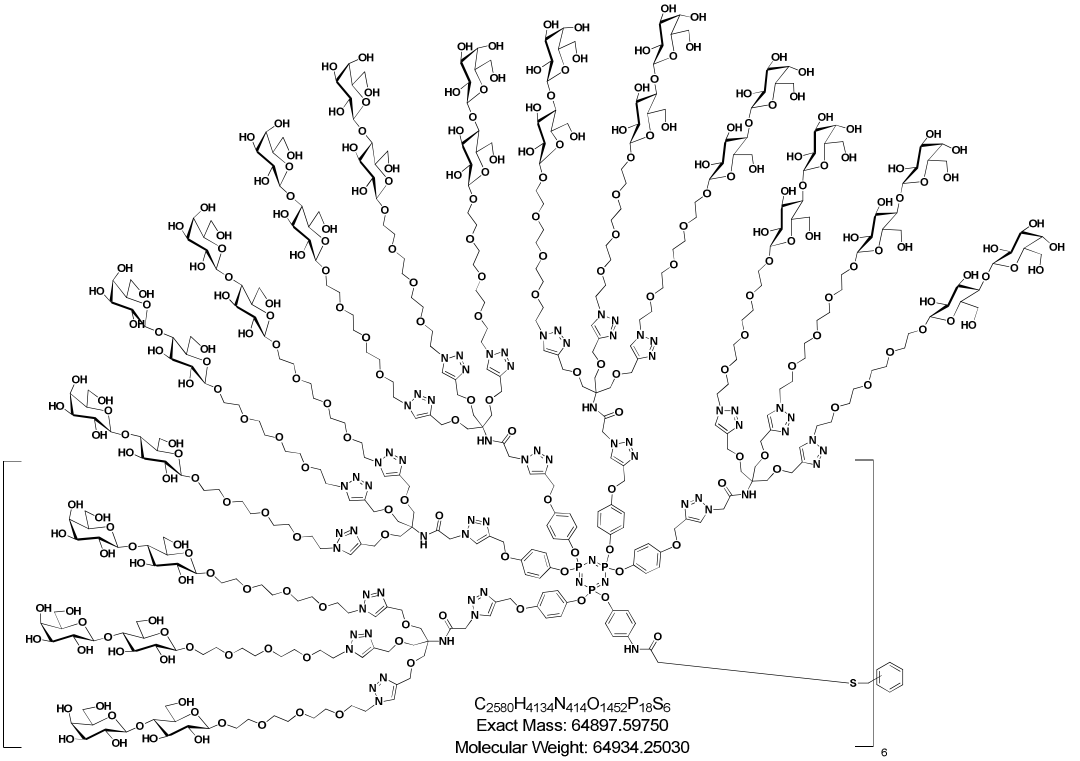


Figure S194. MALDI-TOF (DHB matrix) spectrum of compound **40**

Hydroxylated nonacontavalent glycodendrimer 41



$C_{2580}H_{4134}N_{414}O_{1452}P_{18}S_6$
Exact Mass: 64897.59750
Molecular Weight: 64934.25030

Acetylated compound **40** (22.0 mg, 0.24 µmol) was dissolved in dry MeOH/DCM (3+0.5 mL) and a solution of sodium methoxide (1M in MeOH, 5 µL every 20 minutes until precipitation) was added. An additional 100 µL was then injected and the heterogeneous reaction mixture was stirred at room temperature for 18 hours. The solvent was then removed with a Pasteur pipette and another dry mixture of MeOH/DCM (5 mL, 4:1) is added to the residual oil. A vigorous agitation is maintained for an additional 15 min. period. After removal of the solvents with a Pasteur pipette, 2 mL of dry MeOH were added to the viscous residue under agitation. After 15 min., the MeOH was removed and the residue was dissolved in 3 mL of H_2O, and the pH was adjusted to 7 with addition of ion-exchange resin (Amberlite IR 120 H^+). After filtration, the solvent was removed under *vacuum* with rotary evaporator, lyophilized to yield the fully deprotected compound **41** as a white solid (14.0 mg, 0.22 µmol) in an 85% yield.

^{1}H NMR (600 MHz, D_2O, δ ppm): 8.15-7.89 (m, 120H, $H_{triazole}$), 7.55-7.28 (br s, 12H, $CH_{b'}$), 6.84-6.77 (m, 132H, CH_{ar}), 5.20-5.14 (m, 120H, $NHCOCH_2N$, C_qCH_2O), 4.62-4.44 (m, 540H, CH_2N, $C_{q\text{-}triazole}CH_2O$, 36H, H_{1glc}, H_{1gal}), 4.02-3.55 (m, 2430, OCH_2CH_2N, H_{3glc}, H_{2gal}, H_{3gal}, H_{6bglc}, H_{6agal}, H_{6bgal}, H_{6aglc}, H_{5gal}, H_{5glc}, H_{4glc}, H_{4gal}, $LacOCH_2CH_2$, OCH_2, NHC_qCH_2O), 3.22 (t_{app}, 90H, H_{2glc}).
^{13}C NMR (150 MHz, $CDCl_3$, δ ppm): 167.1 ($C_{ext}ONH$), 165.0 ($C_{int}ONH$) (*not visible*), 155.8-155.7 (2×C_a), 144.6 (C_d), 143.7 ($C_{triazole}$=CH), 136.2 ($C_{ar\text{-}core}$) (*not visible*), 127.0 ($C_{triazole}$=CH), 125.9 ($C_{triazole}$=CH), 122.4 (C_c), 116.3 (C_b), 103.6 (C_{1gal}), 102.8 (C_{1glc}), 79.1 (C_{4glc}), 76.0 (C_{3glc}), 75.4 (C_{5glc}), 75.0 (C_{5gal}), 73.5 (C_{2glc}), 73.2 (C_{3gal}), 71.6 (C_{2gal}), 70.3, 70.2, 70.2, 70.2, 70.1 (OCH_2), 69.3 (C_{4gal}), 69.2 (OCH_2), 68.1 (C_qCH_2O), 64.2 (OCH_2C=C), 62.0 (C_q) (*not visible*), 61.7

(*C*$_{6glc}$), 60.9 (*C*$_{6gal}$), 60.8 (O*C*H$_2$), 53.0 (N$_{triazole}$*C*H$_2$CO), 50.6 (*C*H$_2$N), 37.8 (S*C*H$_2$CONH) (*not visible*), 31.2 (C$_{ar}$*C*H$_2$S) (*not visible*).

^{31}P NMR (122 MHz, D$_2$O, δ ppm): 10.7-9.5 (m, 18P).

m/z (MALDI-TOF/DHB matrix) for $C_{2580}H_{4134}N_{414}O_{1452}P_{18}S_6$ = 64934.3, found 56530-centered Gaussian.

NMR diffusion studies (D$_2$O): *D* = 0.60×10^{-10} m^2/s; *d*$_s$ = 6.6 nm

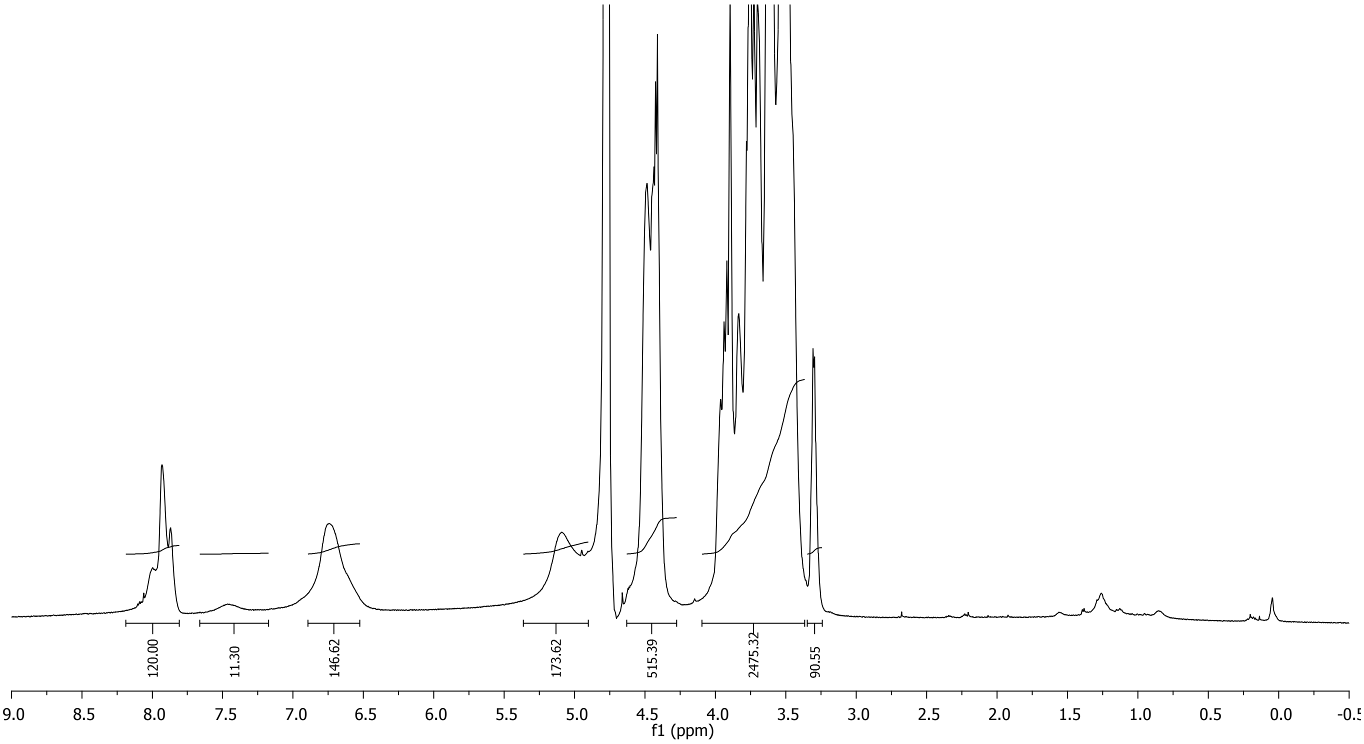


Figure S195. ^{1}H NMR spectrum of compound **41** (D$_2$O, 600MHz)

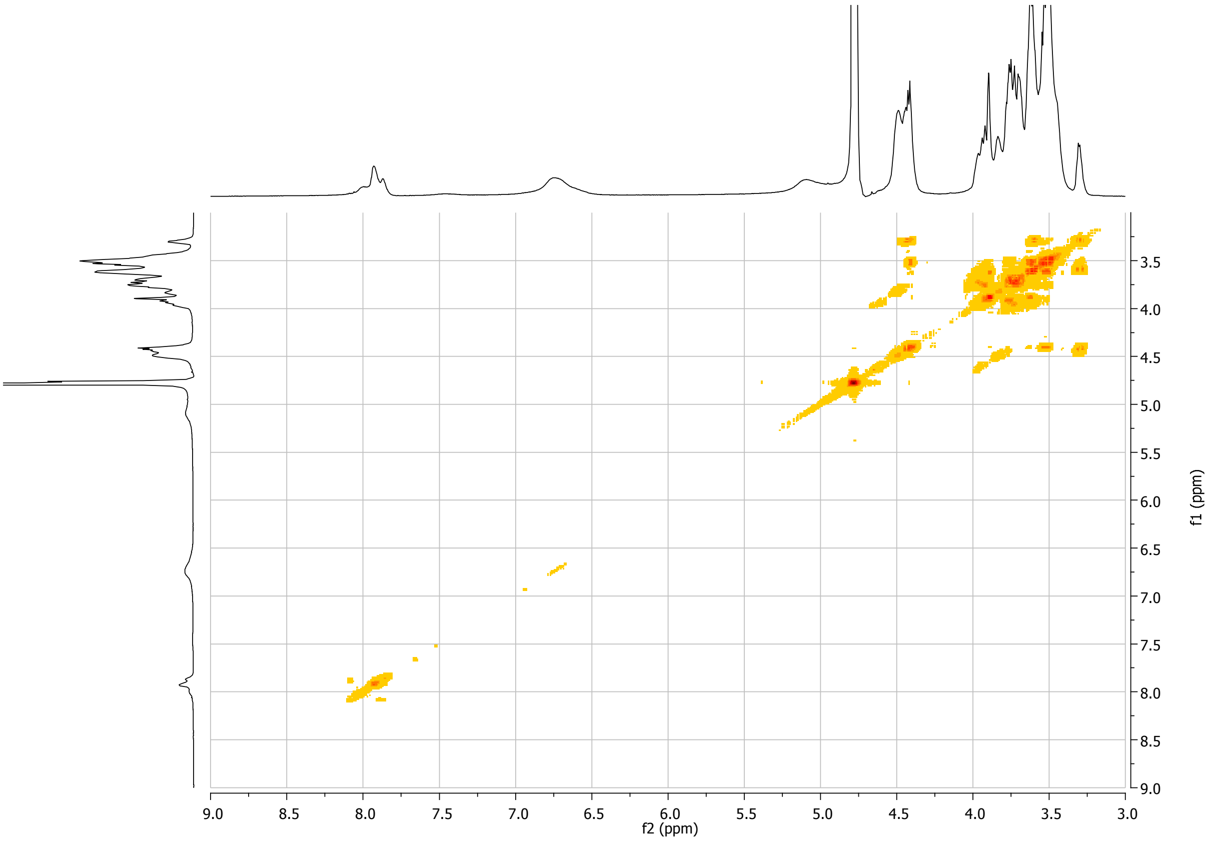


Figure S196. gCOSY spectrum of compound **41**

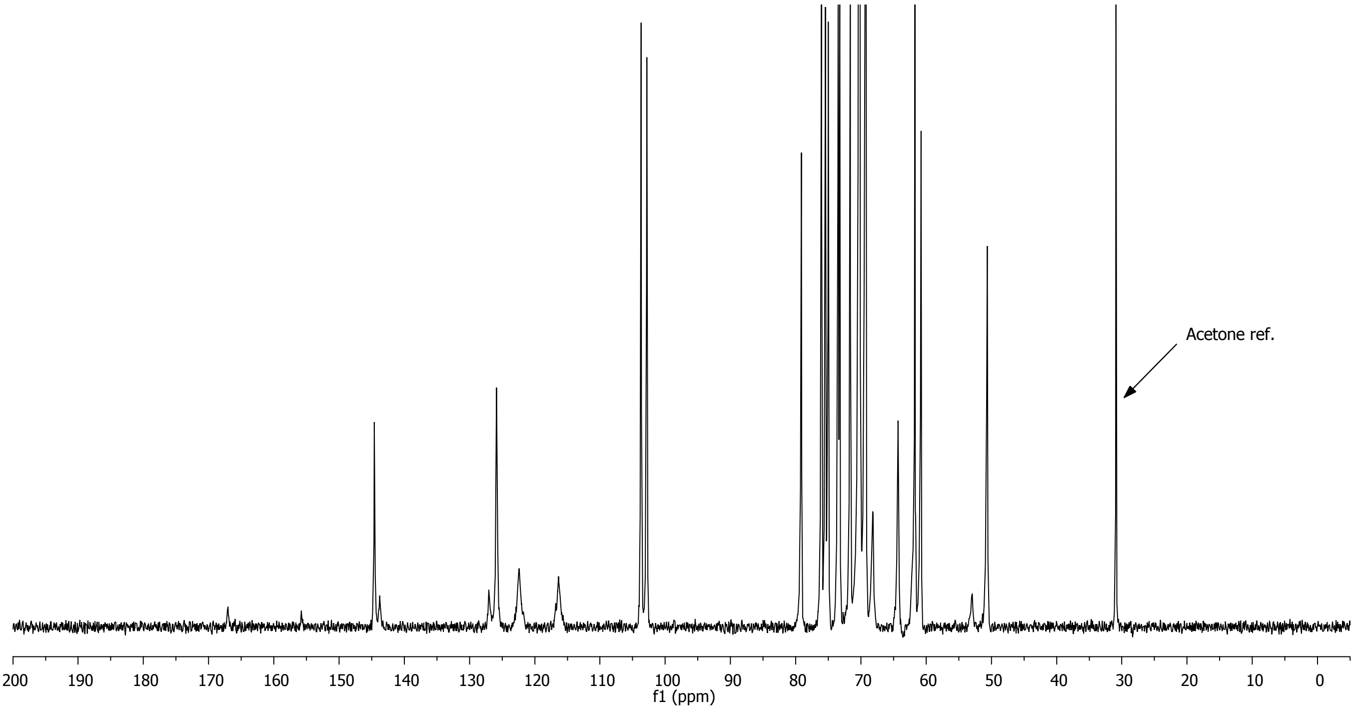


Figure S197. ^{13}C NMR spectrum of compound **41** (D_2O, 150MHz, acetone as reference, 81000 scans)

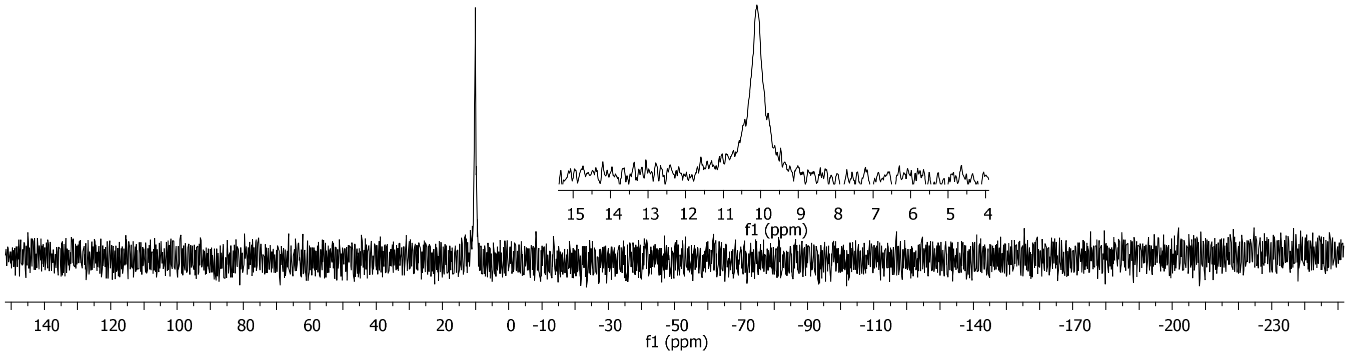


Figure S198. ^{31}P NMR spectrum of compound **41** (D_2O, 122MHz)

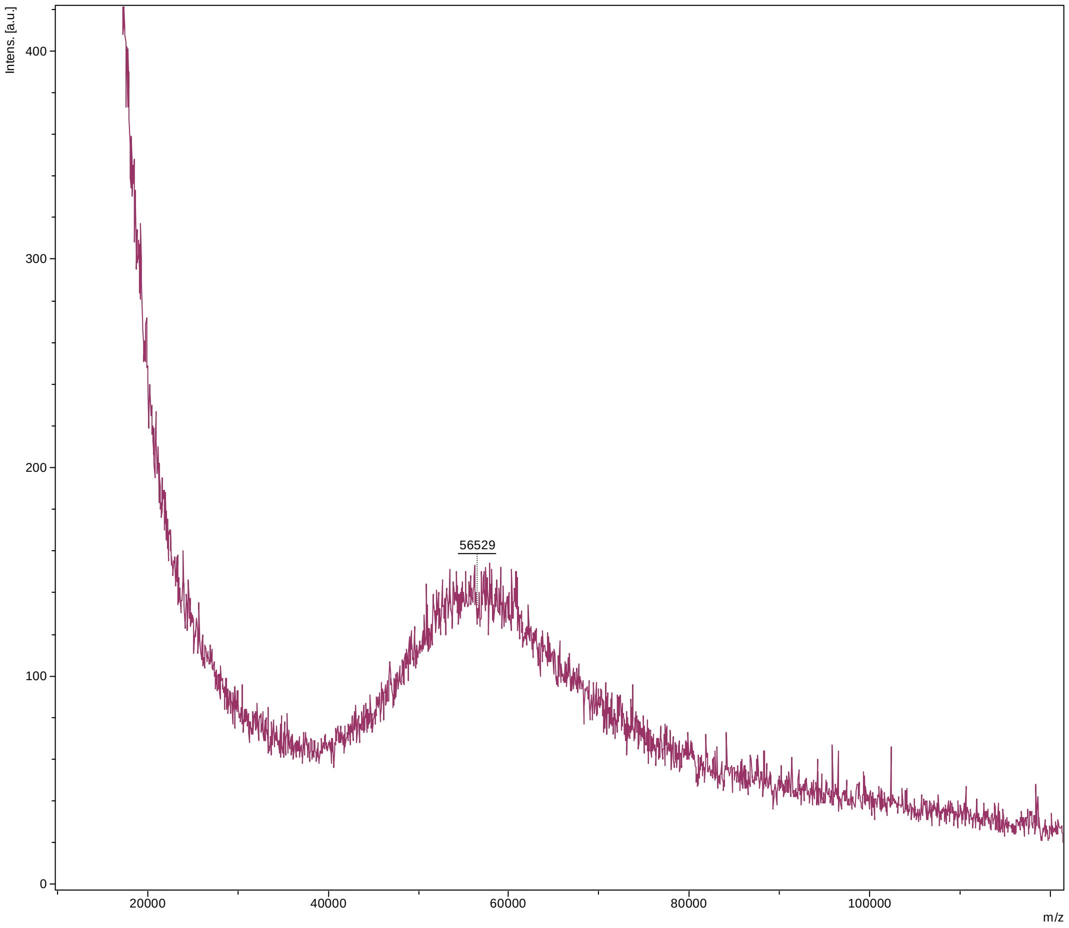
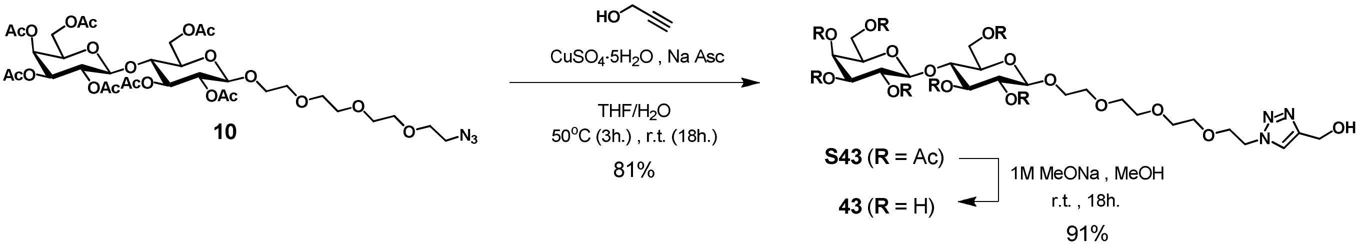


Figure S199. MALDI-TOF (DHB matrix) spectrum of compound **41**

Synthesis of monomeric reference 43



To a solution of 2-(2-{2-[2-(2-azido-ethoxy)-ethoxy]-ethoxy}-ethyl) 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside **10**[1] (100.0 mg, 119.3 μmol, 1.0 eq.) in a 1:1 mixture of H_2O/THF_{anh} (5 mL), were added propargyl alcohol (28.1 mg, 29.1 μL, 501.3 μmol, 4.2 eq.), $CuSO_4 \cdot 5H_2O$ (14.9 mg, 59.7 μmol, 0.5 eq.) and sodium ascorbate (11.8 mg, 59.7 μmol, 0.5 eq.). While stirring, the mixture was first heated at 50℃ for 3 hours in a 20 mL vial and at room temperature for additional 18 hours. Ethyl acetate (15 mL) was added and the solution was poured into a separatory funnel containing ethyl acetate (10 mL), washed with saturated aqueous NH_4Cl (2×10 mL), water (10 mL) and brine (5 mL). Organics were collected, dried over Na_2SO_4 and concentrated to dryness *in vacuo* with rotary evaporator. Purification by flash chromatography (SiO_2, DCM/MeOH 100:0 to 92:8) afforded desired compound **S43** (86.0 mg, 96.6 μmol, **81%**) as a white foam.

R_f = 0.30, DCM/MeOH 94:6
^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 7.75 (s, 1H, H_{triazole}), 5.29 (d_{app}, 1H, $H_{4\text{gal}}$), 5.14 (dd, $^3J_{4,3}$ = 9.4 Hz, $^3J_{3,2}$ = 9.1 Hz, 1H, $H_{3\text{glc}}$), 5.05 (dd, $^3J_{2,1}$ = 10.5 Hz, $^3J_{3,2}$ = 8.0 Hz, 1H, $H_{2\text{gal}}$), 4.93 (dd, $^3J_{2,3}$ = 10.5 Hz, $^3J_{3,4}$ = 3.4 Hz, 1H, $H_{3\text{gal}}$), 4.83 (dd, $^3J_{2,1}$ = 9.4 Hz, $^3J_{3,2}$ = 8.0 Hz, 1H, $H_{2\text{glc}}$), 4.73 (br s, 2H, CH_2OH), 4.53 (d, $^3J_{1,2}$ = 9.4 Hz, 1H, $H_{1\text{glc}}$), 4.50 (t_{app}, 2H, CH_2N), 4.48 (dd, $^2J_{6\text{a.6b}}$ = 12.0 Hz, $^3J_{5.6\text{a}}$ = 2.1 Hz, 1H, $H_{6\text{aglc}}$), 4.47 (d, $^3J_{1,2}$ = 7.9 Hz, 1H, $H_{1\text{gal}}$), 4.12-4.00 (m, 3H, $H_{6\text{bglc}}$, $H_{6\text{agal}}$, $H_{6\text{bgal}}$), 3.90-3.52 (m, 17H, OCH_2, $H_{4\text{glc}}$, $H_{5\text{gal}}$, $H_{5\text{glc}}$,), 3.30 (br s, 1H, OH), 2.15 (s, 3H, $COCH_3$), 2.12 (s, 3H, $COCH_3$), 2.06 (s, 3H, $COCH_3$), 2.04 (3s, 9H, 3×$COCH_3$), 1.96 (s, 3H, $COCH_3$).
^{13}C NMR (150 MHz, $CDCl_3$, δ ppm): 170.3, 170.2, 170.0, 169.9, 169.7, 169.6, 169.0 (7×s, $COCH_3$), 147.7 ($C_{\text{q triazole}}$), 122.9 (CH_{triazole}), 100.9 ($C_{1\text{gal}}$), 100.4 ($C_{1\text{glc}}$), 76.6 ($C_{4\text{glc}}$), 72.6 ($C_{3\text{glc}}$), 72.5 ($C_{5\text{glc}}$), 71.5 ($C_{2\text{glc}}$), 70.8 ($C_{3\text{gal}}$), 70.5 ($C_{5\text{gal}}$), 70.3, 70.3, 70.2, 70.2 (OCH_2), 69.3 ($C_{2\text{gal}}$), 69.0, 68.9 (OCH_2), 66.5 ($C_{4\text{gal}}$), 61.8 ($C_{6\text{glc}}$), 60.7 ($C_{6\text{gal}}$), 56.3 (CH_2OH), 50.0 (CH_2N), 20.8, 20.8, 20.7, 20.6, 20.6, 20.6, 20.5 (7×s, $COCH_3$).
m/z (ESI^+-HRMS) for $C_{37}H_{55}N_3O_{22}$ = 894.3350 $[M+H]^+$; found 894.3361 ; 916.3169 $[M+Na]^+$; found 916.3181.

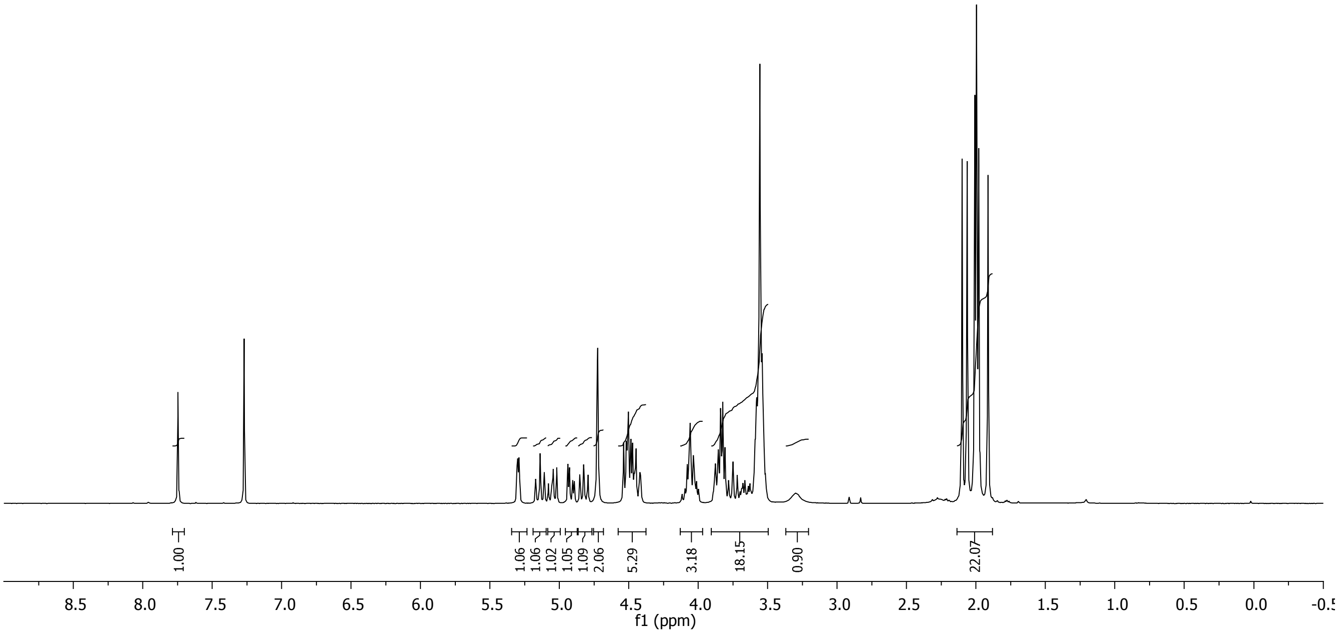


Figure S200. ^{1}H NMR spectrum of compound **S43** ($CDCl_3$, 600MHz)

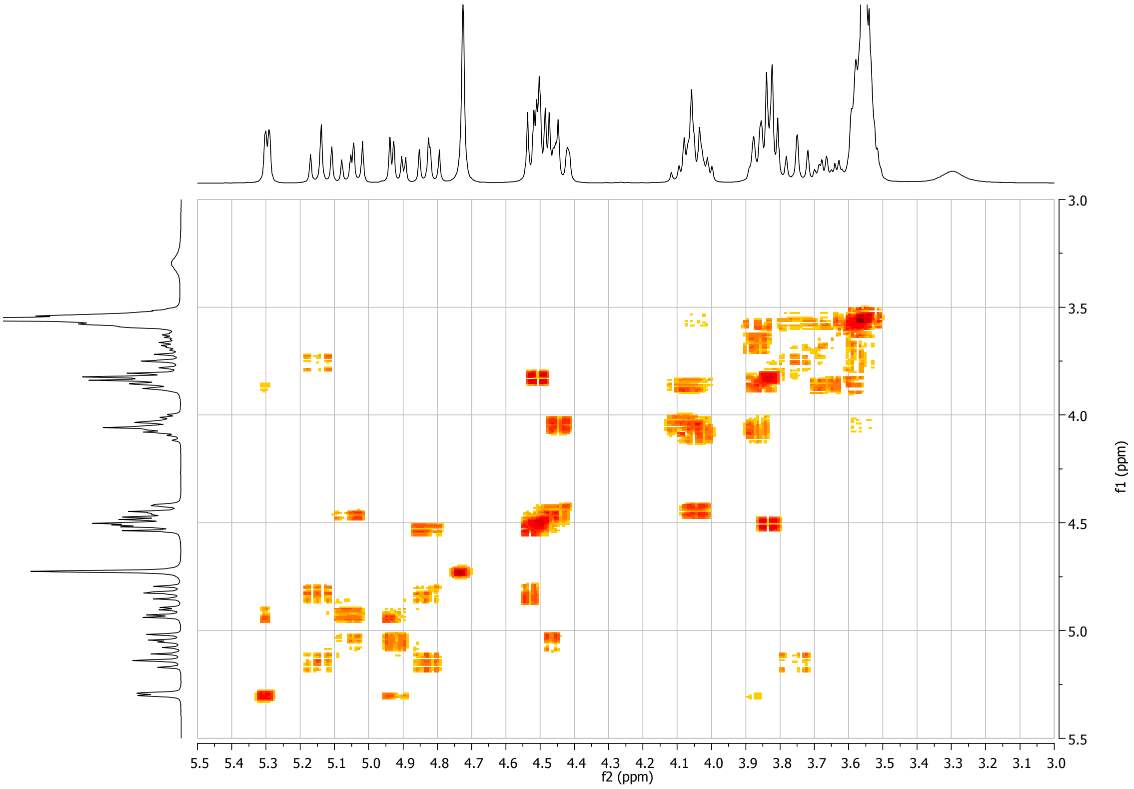


Figure S201. gCOSY spectrum of compound **S43**

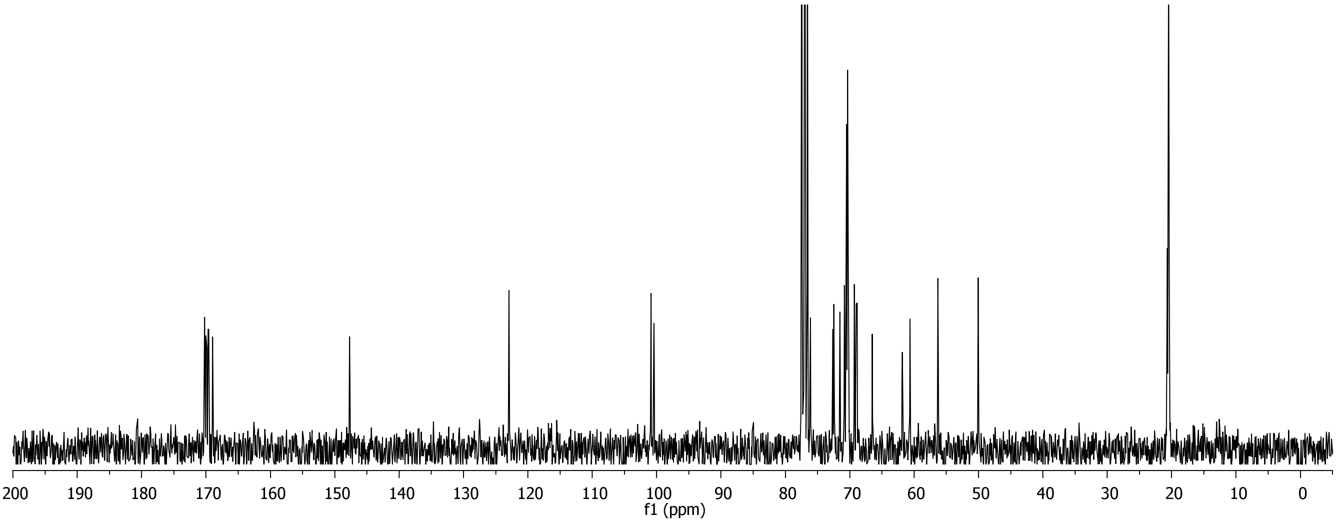
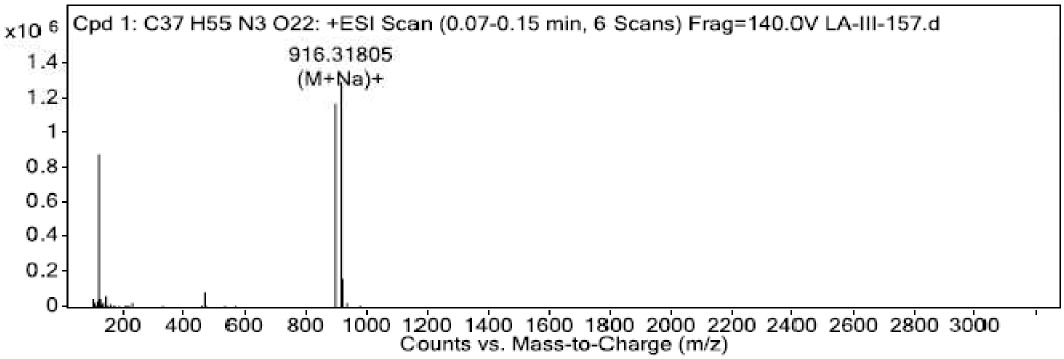
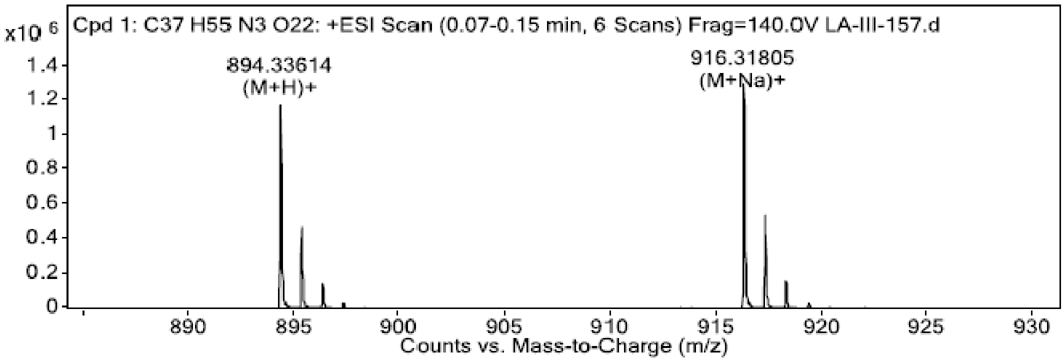


Figure S202. ^{13}C NMR spectrum of compound **S43** ($CDCl_3$, 150MHz)

MS Spectrum



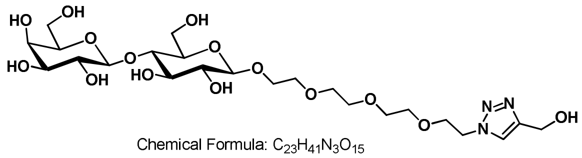
MS Zoomed Spectrum



MS Spectrum Peak List

Ion	Formula	Abund	Observed m/z	Calc m/z	Diff (ppm)
(M+H)+	C37H56N3O22	1193152.62	894.33614	894.335	1.27
(M+Na)+	C37H55N3NaO22	1308225.57	916.31805	916.31694	1.21

Figure S203. ESI^{+}-HRMS spectrum of compound **S43**



Chemical Formula: $C_{23}H_{41}N_3O_{15}$
Exact Mass: 599,25377
Molecular Weight: 599,58274

Acetylated compound **S43** (86.0 mg, 96.2 µmol) was dissolved in dry MeOH (4 mL) and a solution of sodium methoxide (1M in MeOH, 150 µL) was added. The reaction mixture was stirred at room temperature for 24 hours. The pH was adjusted to 7 with addition of ion-exchange resin (Amberlite IR 120 H^+). After filtration, the solvent was removed under *vacuum* with rotary evaporator, lyophilized to yield the fully deprotected reference **43** as a white solid (52.5 mg, 87.6 µmol, **91%**).

^{1}**H NMR** (300 MHz, D_2O, δ ppm): 8.03 (s, 1H, H_{triazole}), 4.73 (s, 2H, OCH_2C_{triazole}), 4.64 (t, J = 5.0 Hz, 2H, CH_2N), 4.52 (d, J = 7.9 Hz, 1H, H_{1glc}), 4.46 (d, J = 7.7 Hz, 1H, H_{1gal}), 4.08-3.53 (m, 25H, OCH_2CH_2N, OCH_2, H_{3glc}, H_{2gal}, H_{3gal}, H_{6bglc}, H_{4gal}, H_{6agal}, H_{6bgal}, H_{6aglc}, H_{5gal}, H_{5glc}, H_{4glc}), 3.36 (m, 6H, H_{2glc}).
^{13}**C NMR** (75 MHz, D_2O, δ ppm): 147.5 ($C_{triazole}$=CH), 125.1 (C_{triazole}=CH), 103.6 (C_{1gal}), 102.7 (C_{1glc}), 79.0 (C_{4glc}), 76.0 (C_{3glc}), 75.4 (C_{5glc}), 75.0 (C_{5gal}), 73.5 (C_{2glc}), 73.2 (C_{3gal}), 71.6 (C_{2gal}), 70.3, 70.2, 70.1, 70.1, 69.4, (OCH_2), 69.2 (C_{4gal}), 61.7 (C_{6glc}), 60.7 (C_{6gal}), 55.3 (OCH_2C_{triazole}), 50.7 (NCH_2).
m/z (ESI^+-HRMS) for $C_{23}H_{41}N_3O_{15}$ = 600.2610 $[M+H]^+$; found 600.2618 ; 622.2430 $[M+Na]^+$; found 622.2438.

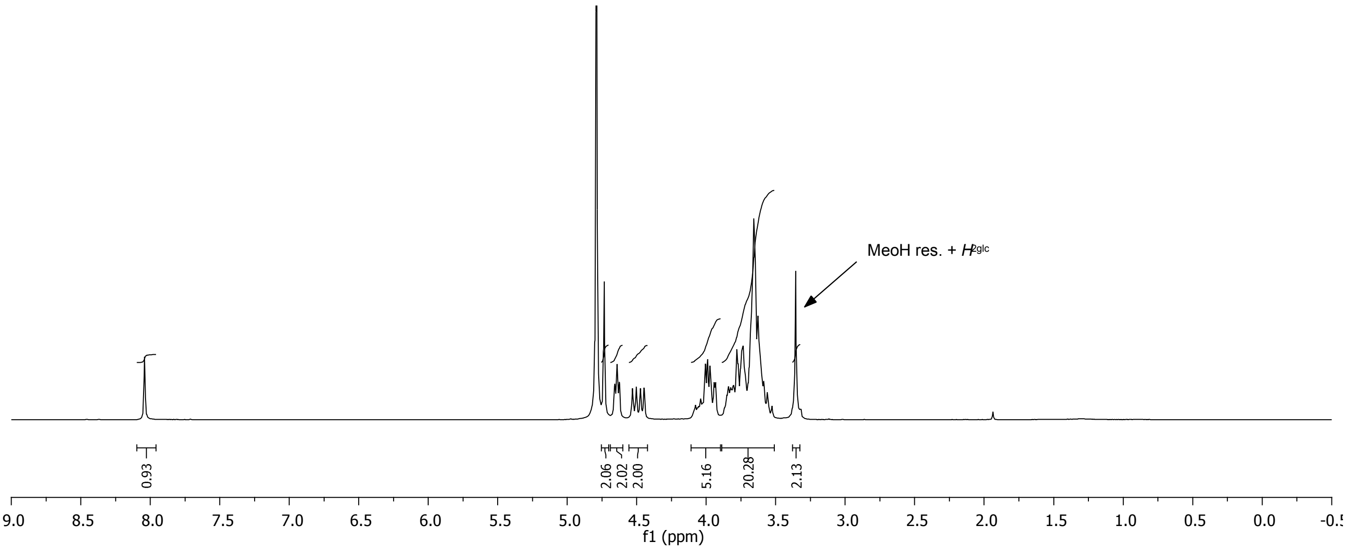


Figure S204. ^{1}H NMR spectrum of compound **43** (D_2O, 300MHz)

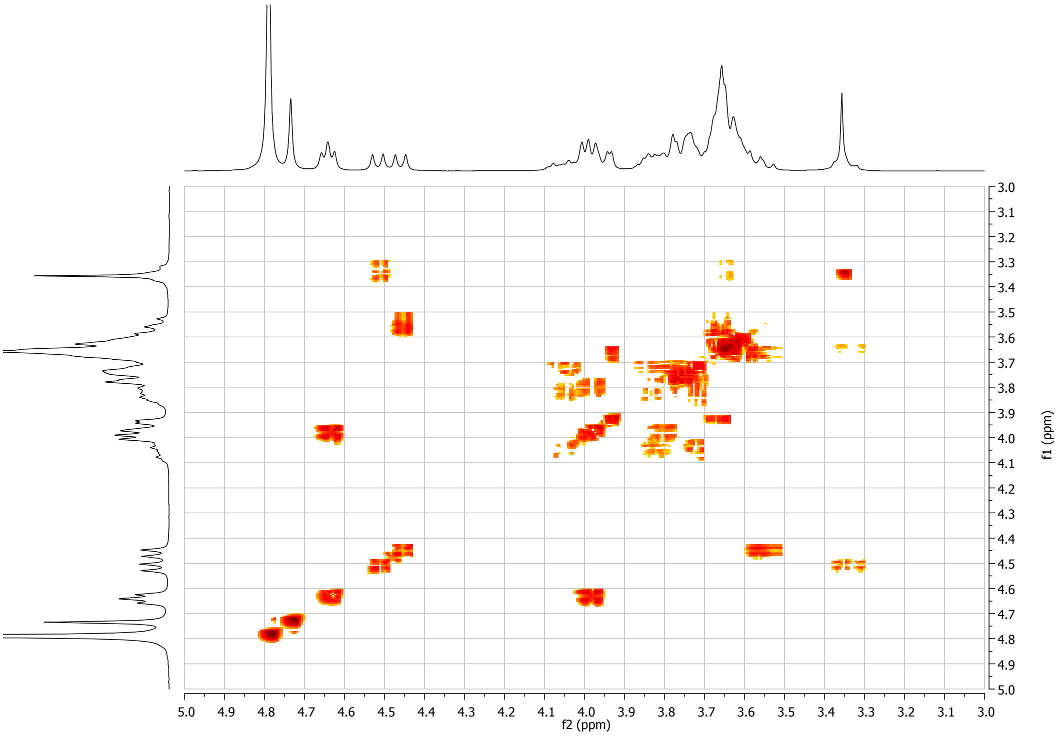


Figure S205. gCOSY spectrum of compound **43**

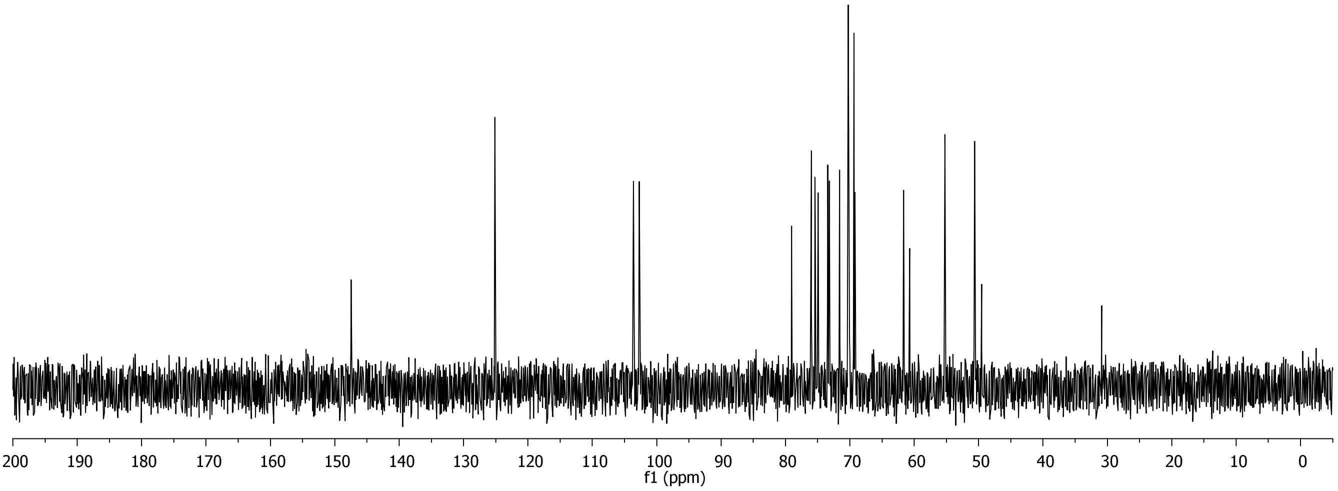
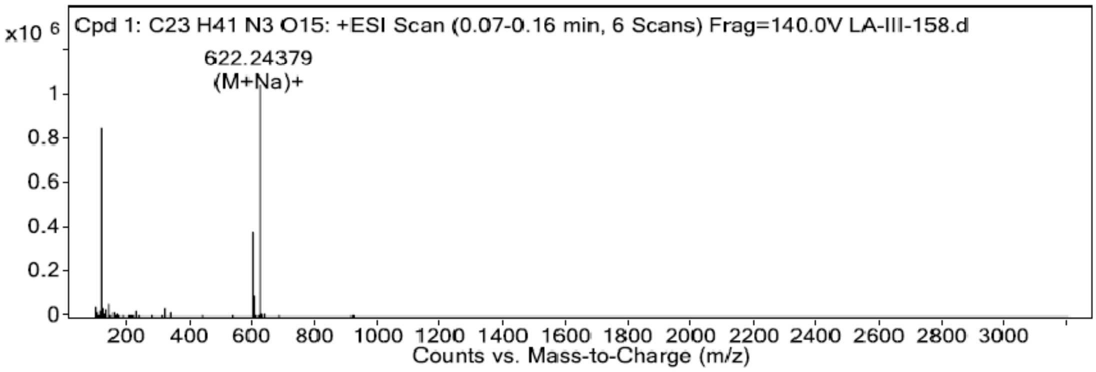
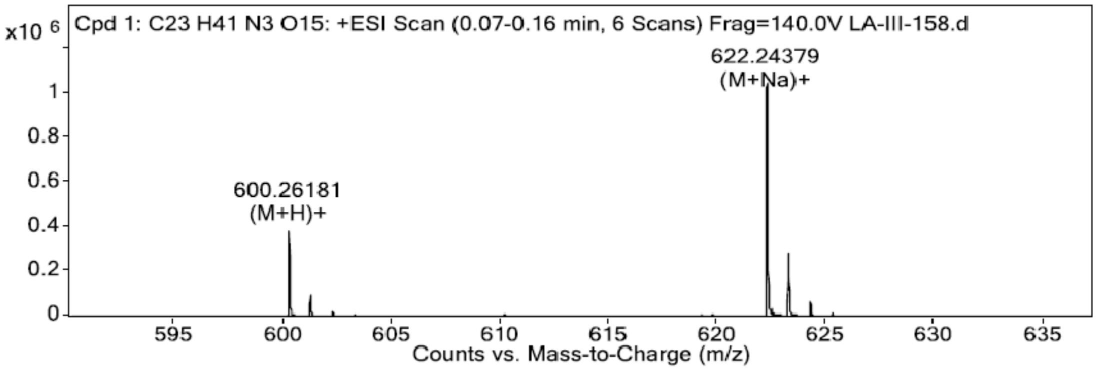


Figure S206. ^{13}C NMR spectrum of compound **43** (D_2O, 75MHz)

MS Spectrum



MS Zoomed Spectrum

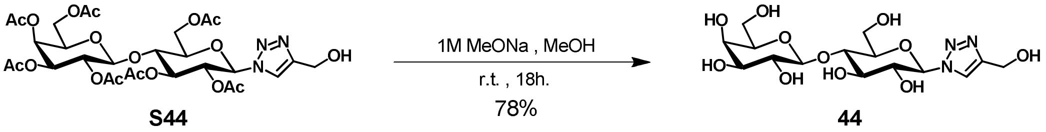


MS Spectrum Peak List

Ion	Formula	Abund	Observed m/z	Calc m/z	Diff (ppm)
(M+H)+	C23H42N3O15	393220.81	600.26181	600.26104	1.28
(M+Na)+	C23H41N3NaO15	1074960.28	622.24379	622.24299	1.28

Figure S207. ESI^{+}-HRMS spectrum of compound **43**

Synthesis of monomeric reference lacking PEG chain 44



Acetylated compound **S44**[7] (100.0 mg, 139.0 µmol) was dissolved in dry MeOH (4 mL) and a solution of sodium methoxide (1M in MeOH, 150 µL) was added. The reaction mixture was stirred at room temperature for 24 hours. The pH was adjusted to 7 with addition of ion-exchange resin (Amberlite IR 120 H^+). After filtration, the solvent was removed under *vacuum* with rotary evaporator, lyophilized to yield the fully deprotected reference **44** as a white solid (45.6 mg, 108.0 µmol, **78%**).

^{1}H NMR (300 MHz, D_2O, δ ppm): 8.19 (s, 1H, H_{triazole}), 5.76 (d, J = 9.2 Hz, 1H, $H_{1\text{glc}}$), 4.72 (s, 2H, CH_2OH), 4.48 (d, J = 7.8 Hz,1H, $H_{1\text{gal}}$), 4.04 (t_{app}, 1H, $H_{2\text{glc}}$), 3.95–3.64 (m,10H, $H_{3\text{glc}}$, $H_{3\text{gal}}$, $H_{4\text{glc}}$, $H_{4\text{gal}}$, $H_{5\text{glc}}$, $H_{5\text{gal}}$, $H_{6\text{glc}}$, $H_{6\text{gal}}$), 3.54 (dd, J = 7.7 Hz, J = 7.8 Hz, 2H, $H_{2\text{gal}}$).

^{13}C NMR (75 MHz, D_2O, δ ppm): 148.2 (C_{triazole}), 120.2 (CH_{triazole}), 101.1 ($C_{1\text{gal}}$), 85.5 ($C_{1\text{glc}}$), 75.9 ($C_{4\text{glc}}$), 75.5 ($C_{3\text{glc}}$), 72.5 ($C_{5\text{glc}}$), 70.9 ($C_{2\text{glc}}$), 70.8 ($C_{3\text{gal}}$), 70.5 ($C_{5\text{gal}}$), 69.0 ($C_{2\text{gal}}$), 66.5 ($C_{4\text{gal}}$), 61.7 ($C_{6\text{gal}}$), 60.8 ($C_{6\text{glc}}$), 56.3 (CH_2OH).

m/z (ESI^+ HRMS) for $C_{15}H_{25}N_3O_{11}$ = 424.1562 $[M+H]^+$, found: 424.1556; 446.1381 $[M+Na]^+$, found: 446.1372.

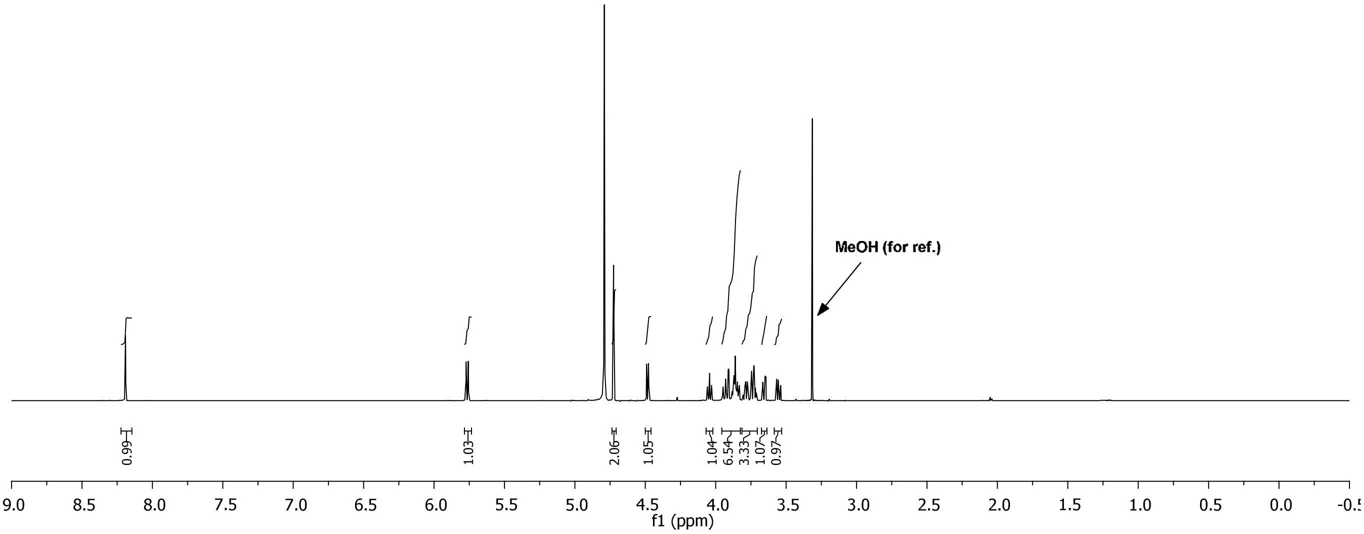


Figure S208. ^{1}H NMR spectrum of compound **44** (D_2O, 600MHz)

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[7] R. Kumar, P. R. Maulik and A. K. Misra, *Glycoconj. J.* 2008, **25**, 595–602.

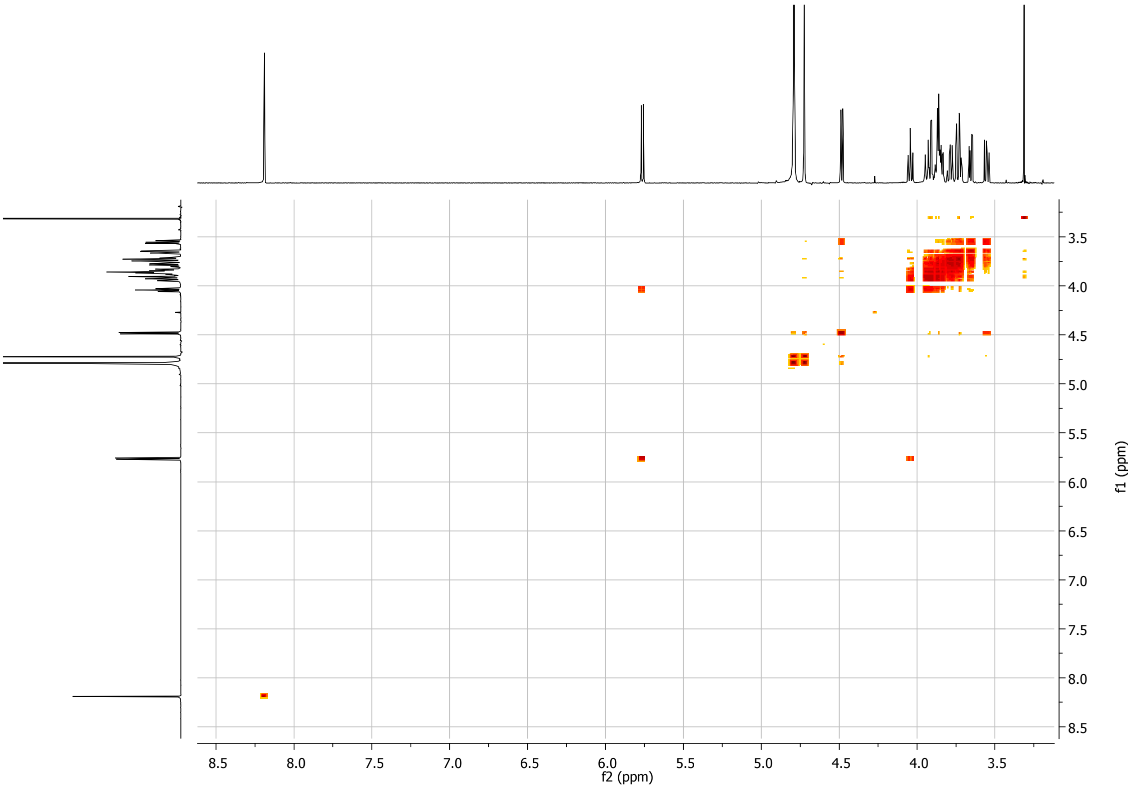


Figure S209. gCOSY spectrum of compound **44**

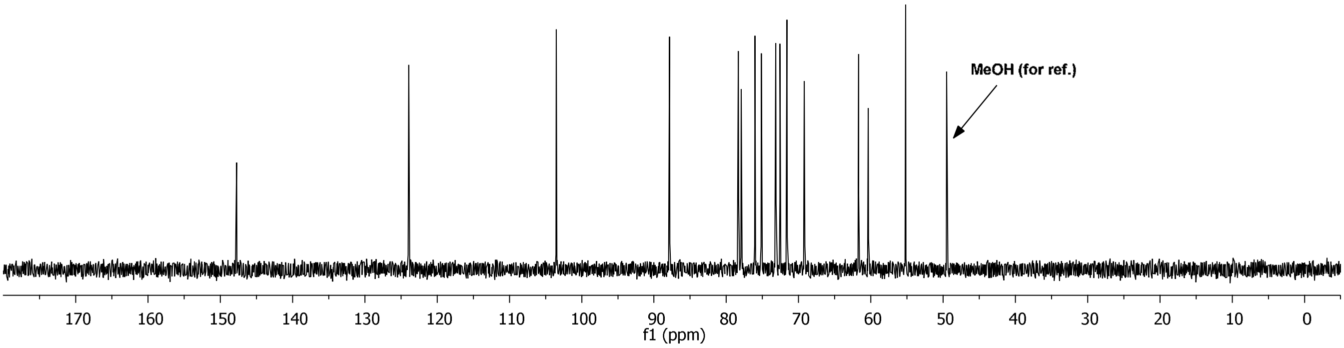
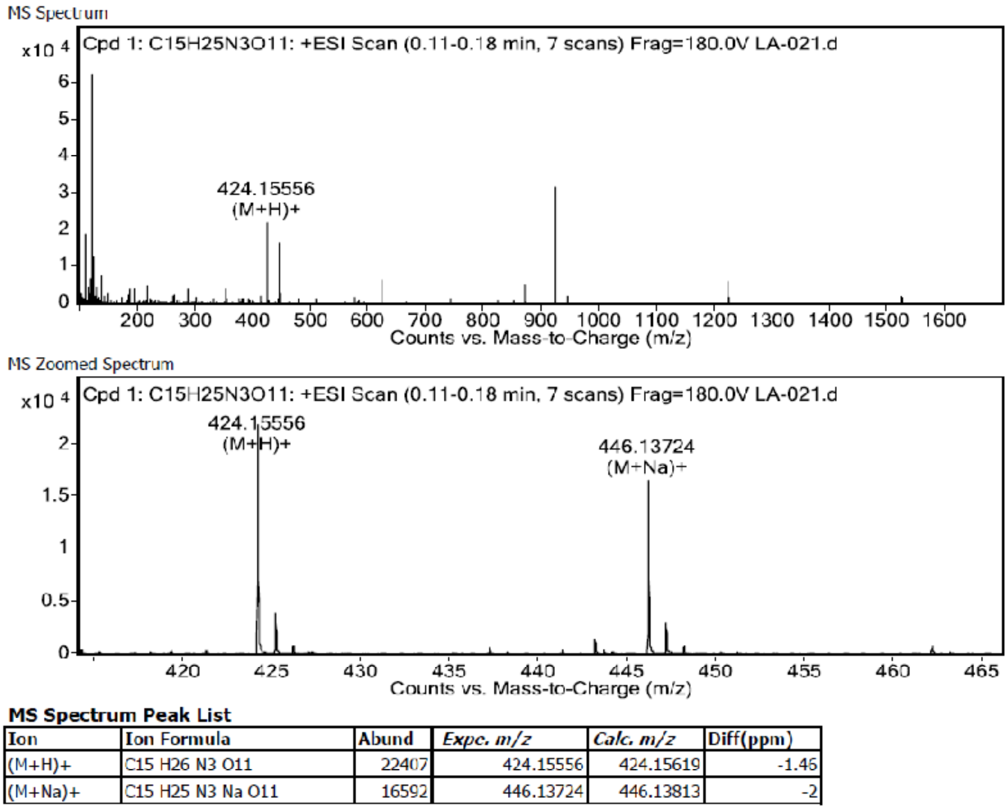


Figure S210. ^{13}C NMR spectrum of compound **44** (D_2O, 150MHz)



MS Spectrum

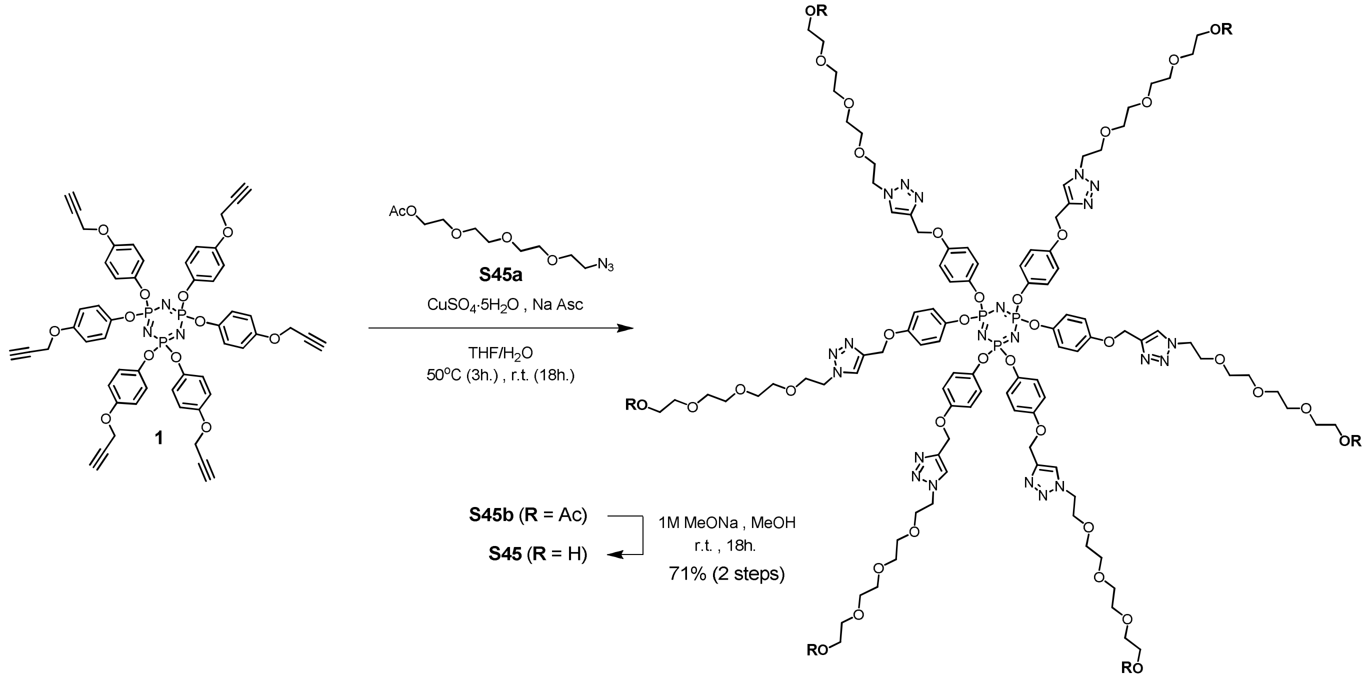
MS Zoomed Spectrum

MS Spectrum Peak List

Ion	Ion Formula	Abund	*Expc. m/z*	*Calc. m/z*	Diff(ppm)
(M+H)+	C15 H26 N3 O11	22407	424.15556	424.15619	-1.46
(M+Na)+	C15 H25 N3 Na O11	16592	446.13724	446.13813	-2

Figure S211. ESI$^+$-HRMS spectrum of compound **44**

Negative control 45



To a solution of propargylated derivative **1** (30.0 mg, 29.4 µmol, 1.0 eq.) in a 1:1 mixture of H_2O/THF_{anh} (5 mL), were added acetylated tetra(ethylene)glycol azide **S45a** (92.4 mg, 354 µmol, 12.0 eq., *previously obtained from acetylation of hydroxylated derivative in classical conditions* (*Ac_2O/Pyridine/$DMAP_{cat.}$ at 25°C, o.n., R_f=0.6 (3%MeOH in DCM))*), $CuSO_4 \cdot 5H_2O$ (80.0 mg, 320 µmol, 10.8 eq.) and sodium ascorbate (70.0 mg, 320 µmol, 10.8 eq.). While stirring, the mixture was first heated at 50℃ for 3 hours in a 20 mL vial and at room temperature for additional 18 hours. Ethyl acetate (15 mL) was added and the solution was poured into a separatory funnel containing ethyl acetate (10 mL), washed with saturated aqueous NH_4Cl (2×10 mL), water (10 mL) and brine (5 mL). Organics were collected, dried over Na_2SO_4 and concentrated to dryness *in vacuo* with rotary evaporator. Purification by flash chromatography (SiO_2, DCM/MeOH 99:1 to 96:4) afforded desired acetylated multivalent compound **S45b** which was directly dissolved in dry MeOH (4 mL). A solution of sodium methoxide (1M in MeOH, 150 µL)) was added. The reaction mixture was stirred at room temperature for 18 hours. The pH was adjusted to 7 with addition of ion-exchange resin (Amberlite IR 120 H^+). After filtration, the solvent was removed under *vacuum* with rotary evaporator and purification by flash chromatography (SiO_2, DCM/MeOH 85:15) to afford pure reference **S45** as viscous oil (48.8 mg, 20.9 µmol, **71%** (2 steps)).

R_f = 0.12, DCM/MeOH 85:15.
^{1}H NMR (300 MHz, CD_3OD, δ ppm): 8.1 (s, 6H, $H_{triazole}$), 6.87-6.77 (m, 24H, CH_{ar}), 5.14 (br s, 12H, $OCH_2C_{triazole}$), 4.55 (t, J = 5.0 Hz, 12H, $CH_2N_{triazole}$), 3.85 (t, J = 5.0 Hz, 12H, $CH_2CH_2N_{triazole}$), 3.63-3.48 (m, 72H, OCH_2).
^{13}C NMR (75 MHz, CD_3OD, δ ppm): 156.9 (C_a), 145.8 ($C_{triazole}$=CH), 144.7 (C_d), 126.3 ($C_{triazole}$=CH), 123.0 (C_c), 116.8 (C_b), 73.7 ($C_{triazole}CH_2O$), 71.5, 71.5, 71.4, 70.3, 62.9, 62.2 (OCH_2), 51.4 (NCH_2).
^{31}P NMR (122 MHz, CD_3OD, δ ppm): 10.1 (m, 3P).

m/z (ESI$^+$-HRMS) for $C_{102}H_{144}N_{210}O_{36}P_3$= 1166.9721 [*M*+2H]$^+$; found 1166.9663; 1188.9540 [*M*+2Na]$^{2+}$; found 1188.9547.

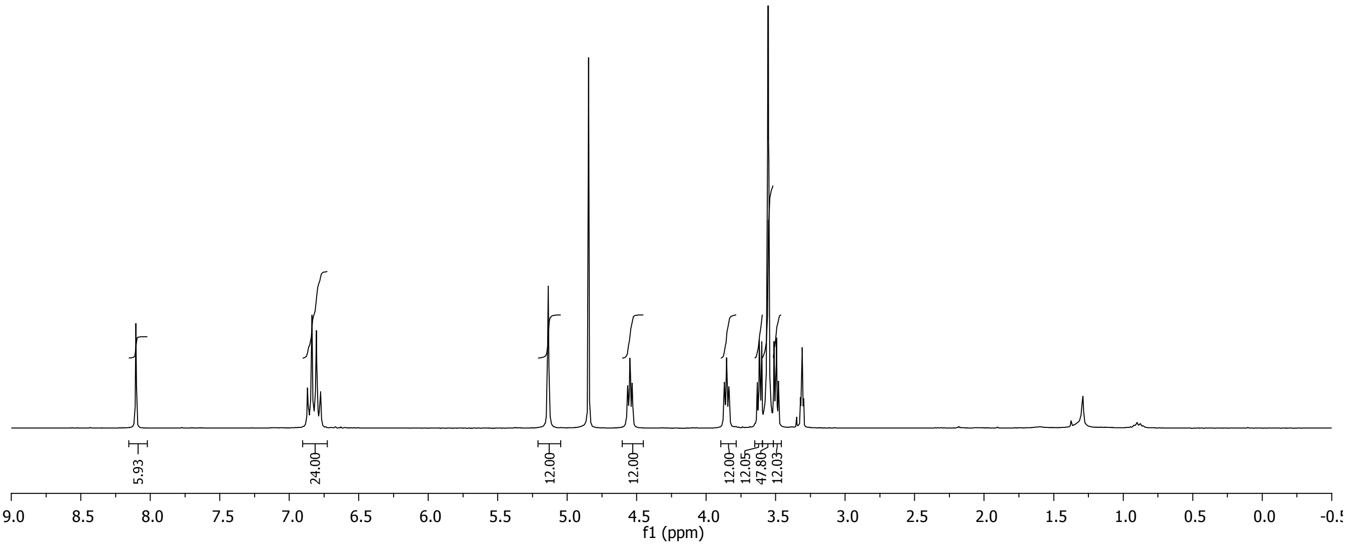


Figure S212. ^{1}H NMR spectrum of compound **45** (CD_3OD, 300MHz)

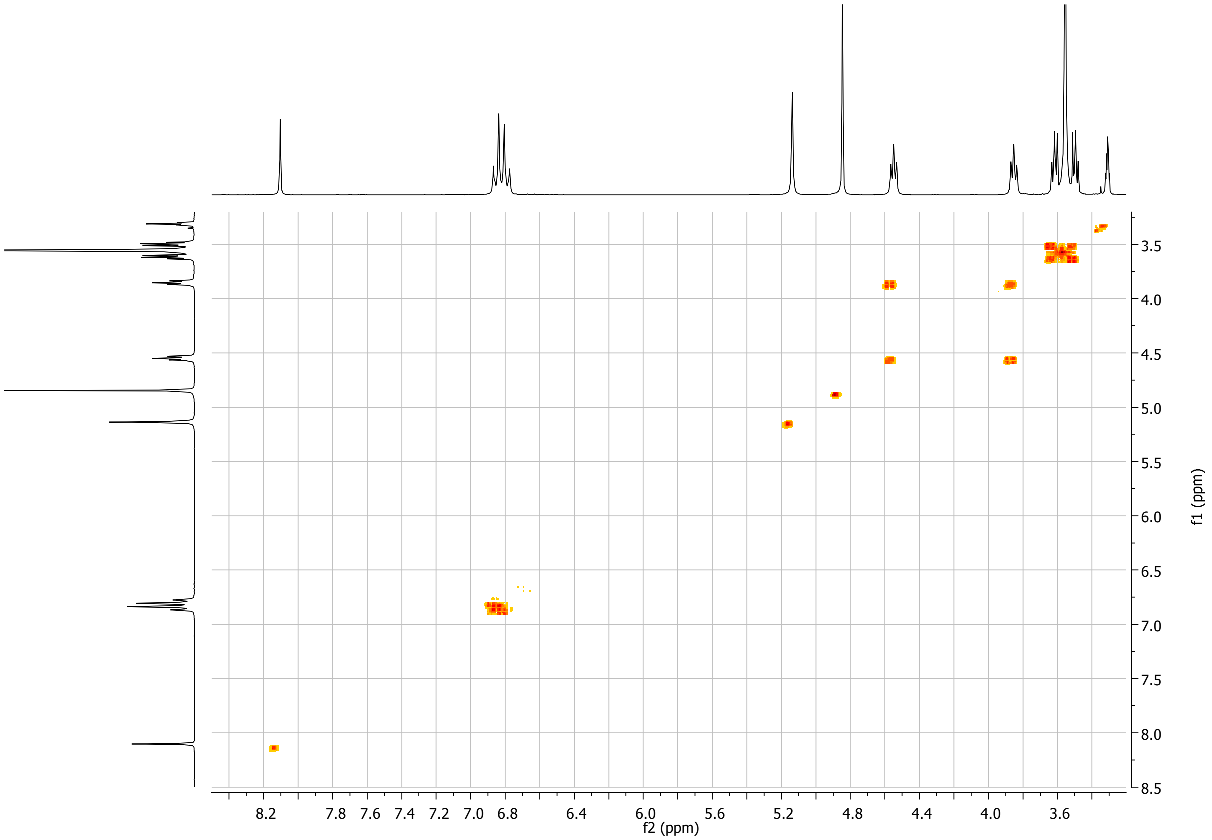


Figure S213. gCOSY spectrum of compound **45**

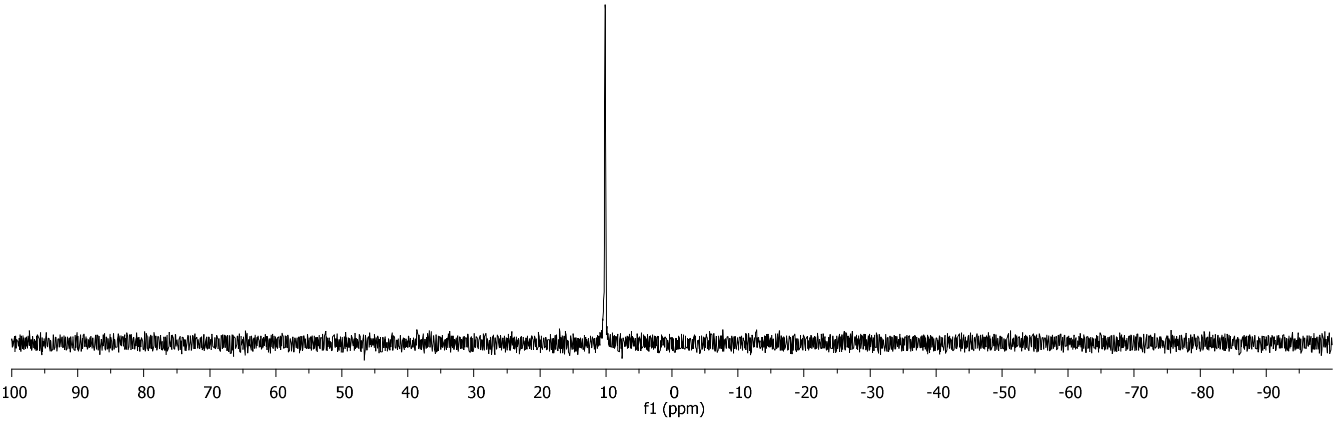


Figure S214. ^{13}P NMR spectrum of compound **45** (CD_3OD, 122MHz)

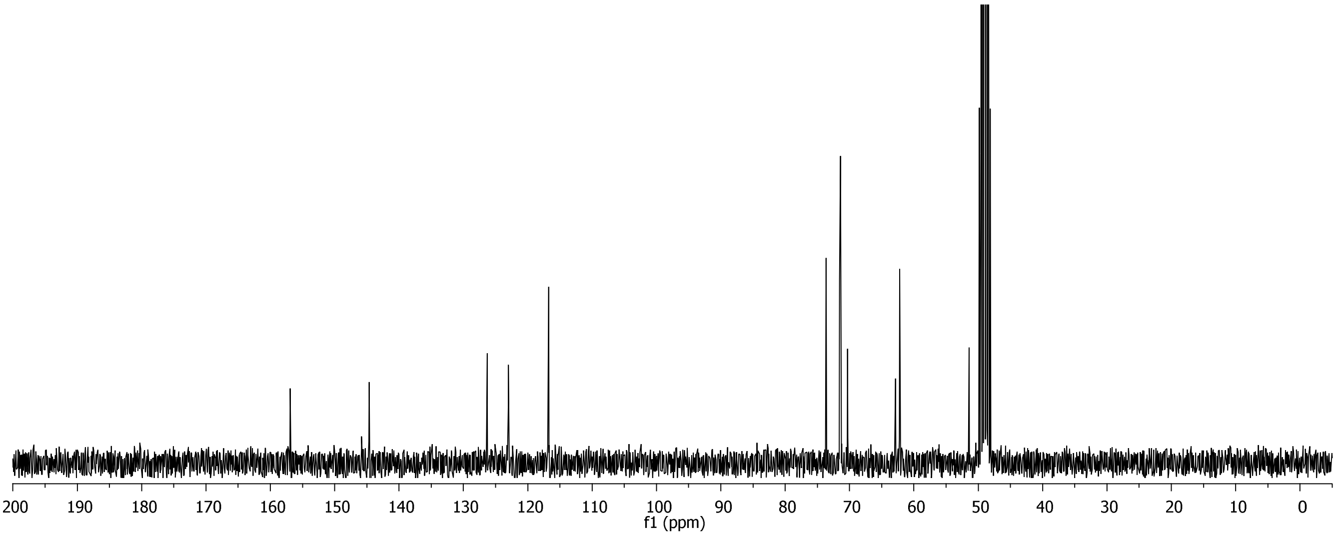
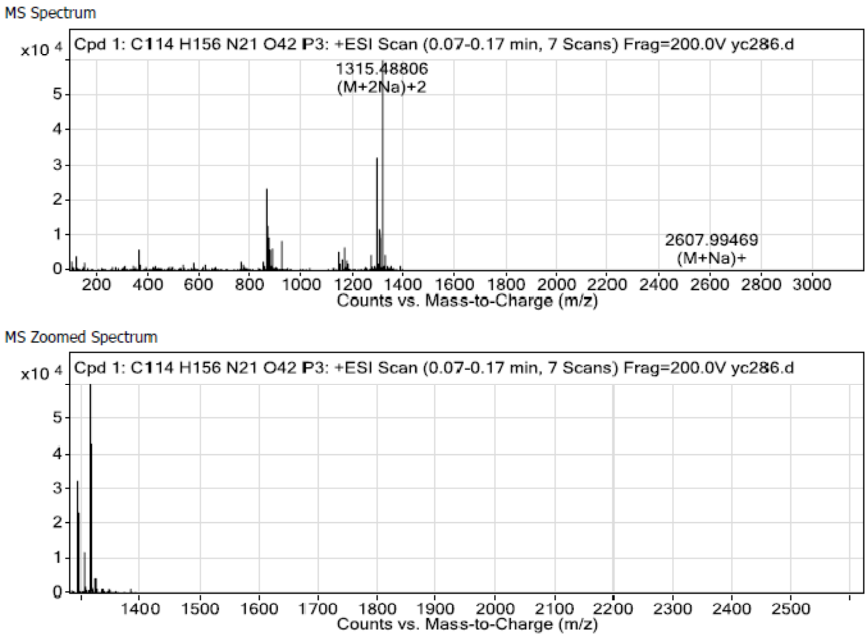


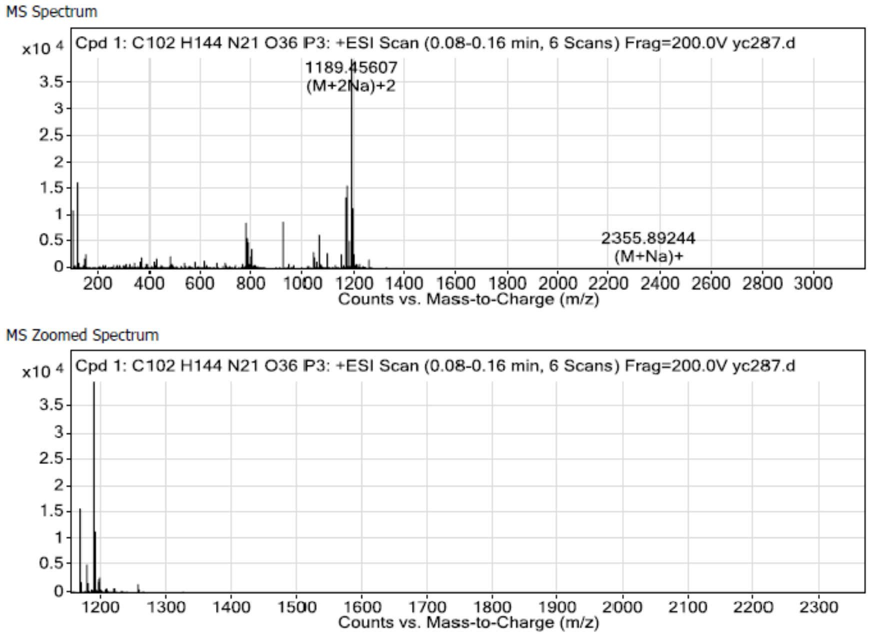
Figure S215. ^{13}C NMR spectrum of compound **45** (CD_3OD, 75MHz)



MS Spectrum Peak List

Ion	Formula	Abund	Observed m/z	Calc m/z	Diff (ppm)
(M+2H)+2	C114H156N21O42P3	23800.17	1292.99974	1293.00376	3.11
(M+2Na)+2	C114H156N21O42P3	44595.1	1314.98672	1314.9857	-0.77

Figure S216. ESI^{+}-HRMS spectrum of compound **S45b**

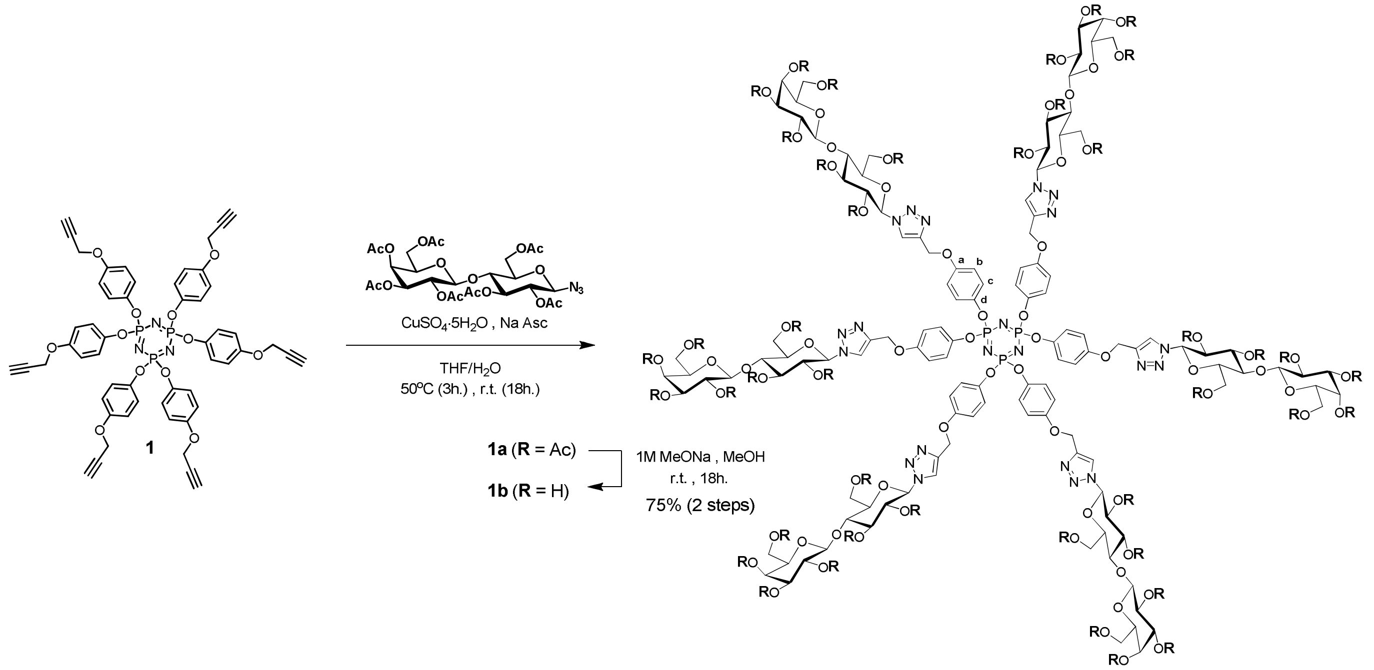


MS Spectrum Peak List

Ion	Formula	Abund	Observed m/z	Calc m/z	Diff (ppm)
(M+2H)+2	C102H144N21O36P3	13457.15	1166.96627	1166.97206	4.96
(M+2Na)+2	C102H144N21O36P3	31620.56	1188.9547	1188.95401	-0.58

Figure S217. ESI^{+}-HRMS spectrum of compound **45**

Synthesis of hexavalent analog of 1 lacking PEG chains



To a solution of propargylated derivative **1** (13.5 mg, 13.1 µmol, 1.0 eq.) dissolved in a vial in a 1:1 mixture of H_2O/THF_{anh} (5 mL), were added lactosyl azide[8] (72.6 mg, 110.0 µmol, 8.4 eq.), $CuSO_4 \cdot 5H_2O$ (23.5 mg, 94.1 µmol, 7.2 eq.) and sodium ascorbate (18.6 mg, 94.1 µmol, 7.2 eq.). While stirring, the mixture was first heated at 50°C for 3 hours in a 20 mL vial and at room temperature for additional 18 hours. Ethyl acetate (15 mL) was added and the solution was poured into a separatory funnel containing ethyl acetate (10 mL), washed with saturated aqueous NH_4Cl (2×10 mL), water (10 mL) and brine (5 mL). Organics were collected, dried over Na_2SO_4 and concentrated to dryness *in vacuo* with rotary evaporator. Purification by flash chromatography (SiO_2, DCM/MeOH 99:1 to 96:4) afforded desired acetylated multivalent compound **1a** (57.2 mg, 9.99 µmol, 76%) which was directly dissolved in dry MeOH (4 mL). A solution of sodium methoxide (1M in MeOH, 150 µL)) was added. The reaction mixture was stirred at room temperature for 18 hours. The solvent was then removed with a Pasteur pipette and dry MeOH (3 mL) is added to the residual solid. A vigorous agitation is maintained for an additional 15 min. period. After removal of the solvent with a Pasteur pipette, 3 mL of H_2O were added to the solid residue. The pH was adjusted to 7 with addition of ion-exchange resin (Amberlite IR 120 H^+). After filtration, the solvent was removed under *vacuum* with rotary evaporator to afford pure reference **1b** as viscous colorless oil (30.5 mg, 9.30 µmol, **75%** (2 steps)).

^{1}H NMR (300 MHz, D_2O, δ ppm): 7.94 (s, 6H, H_{Triazole}), 6.49 (br s, 24H, CH_{arom}), 5.49 (d, J = 9.2 Hz, 6H, H_{1glc}), 4.48 (br s,6H, H_{1gal}), 3.85-3.43 (m, 90H, H_{2glc}, H_{3glc}, H_{3gal}, H_{4glc}, H_{4gal}, H_{5glc}, H_{5gal}, H_{6glc}, H_{6gal}, $OCH_2C_{\text{q-triazole}}$, H_{2gal}).
^{13}C NMR (75 MHz, D_2O, δ ppm): 154.5 (C_a), 143.5 (C_{Triazole}), 142.8 (C_d), 123.9 (CH_{Triazole}), 121.3 (C_c), 116.5 (C_b), 102.6 (C_{1gal}), 86.9 (C_{1glc}), 77.2 (C_{4glc}), 77.2 (C_{3glc}), 74.9 (C_{5glc}), 74.2 (C_{2glc}), 72.1 (C_{3gal}), 71.6 (C_{5gal}), 70.5 (C_{2gal}), 68.1 (C_{4gal}), 60.7 (C_{6gal}), 60.6 (OCH_2), 59.3 (C_{6glc}).

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[8] F. D. Tropper, F. O. Andersson, S. Braun and R. Roy, *Synthesis* 1992, 618–620.

^{31}P NMR (122 MHz, $CDCl_3$, δ ppm): 10.3 (s, 3P).

m/z (ESI$^+$-HRMS) for $C_{126}H_{168}N_{21}O_{72}P_3$ = 1632.9564 [*M*+2Na]$^{2+}$; found 1632.9574.

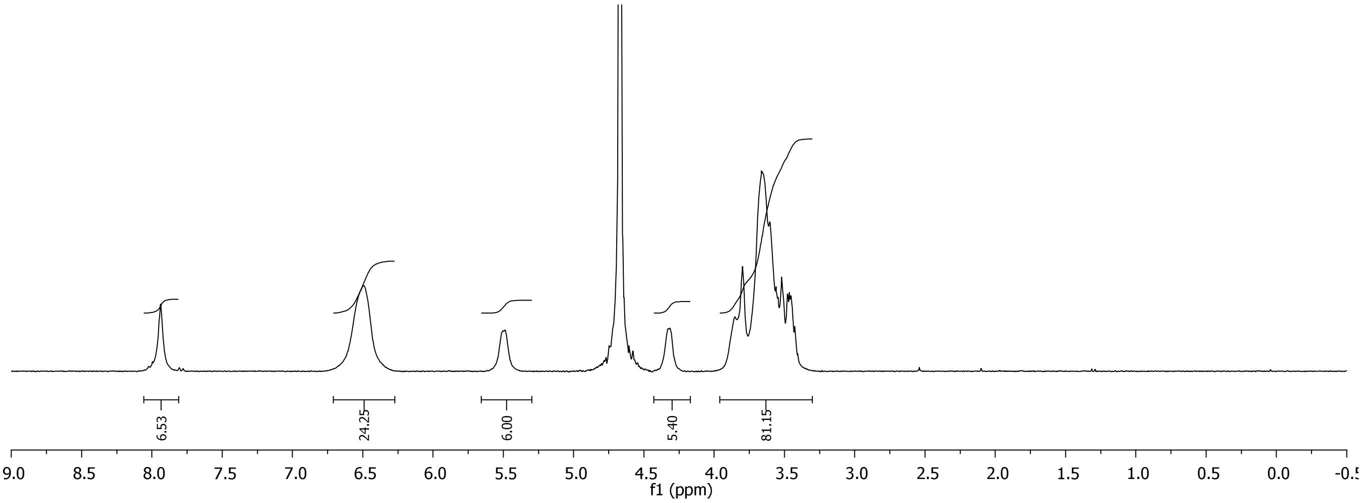


Figure S218. ^{1}H NMR spectrum of compound **1b** (D_2O, 300MHz)

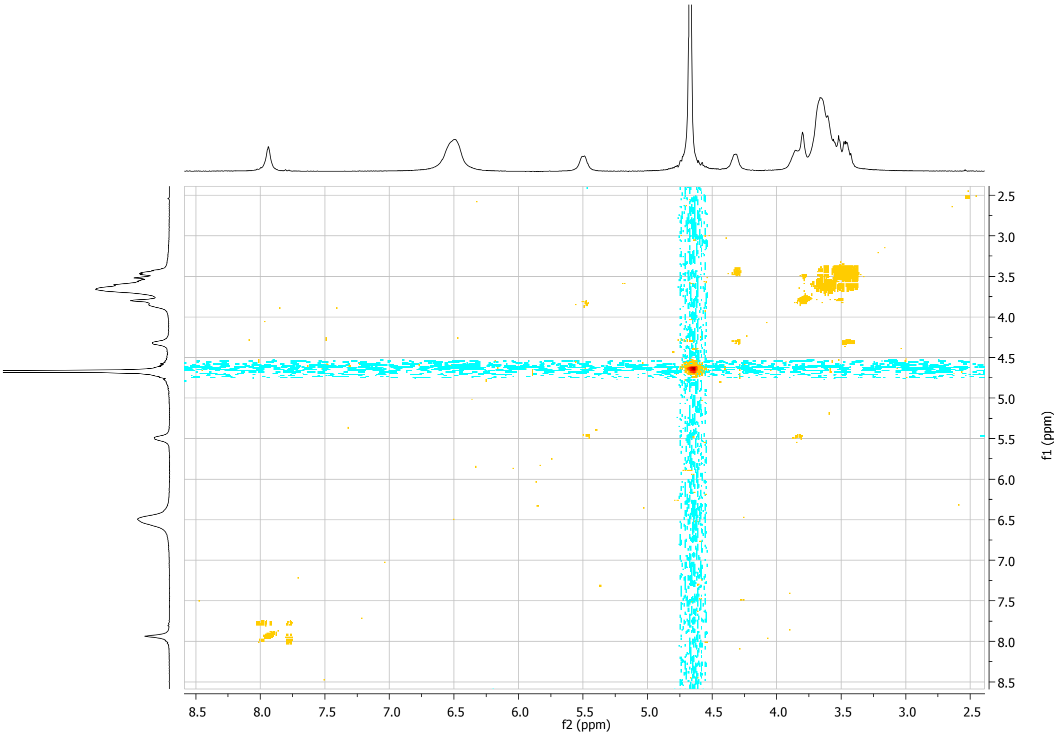


Figure S219. gCOSY spectrum of compound **1b**

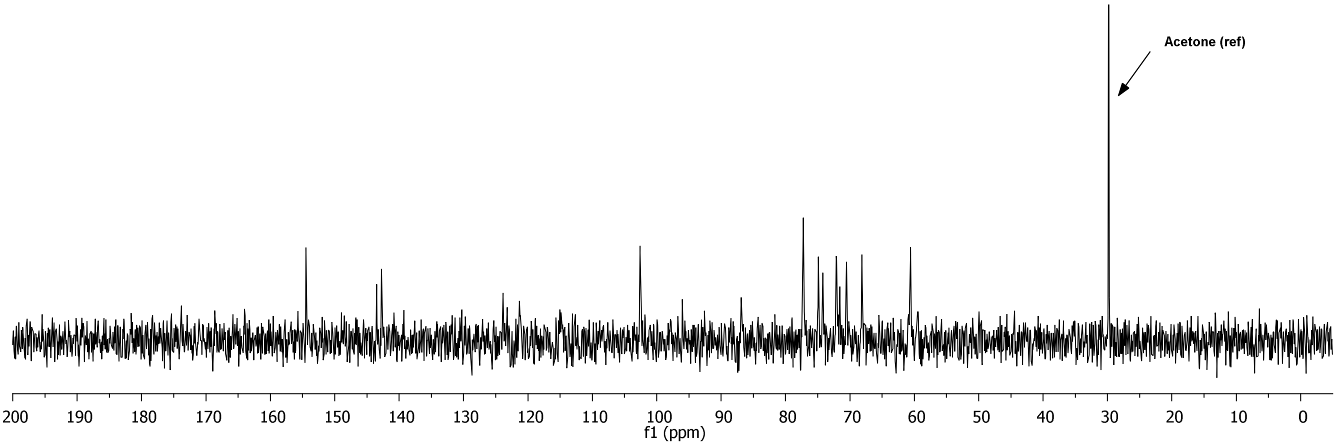


Figure S220. ^{13}C NMR spectrum of compound **1b** (D_2O, 75MHz)

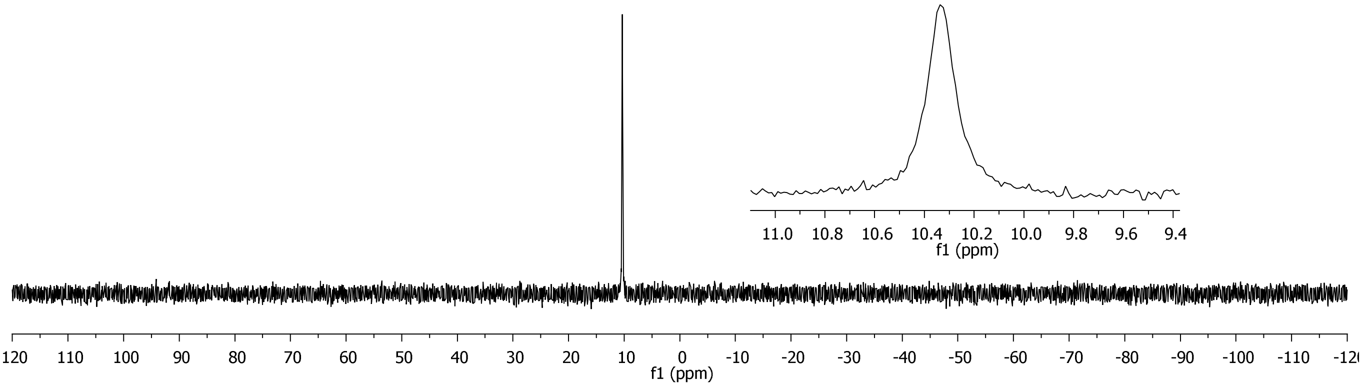
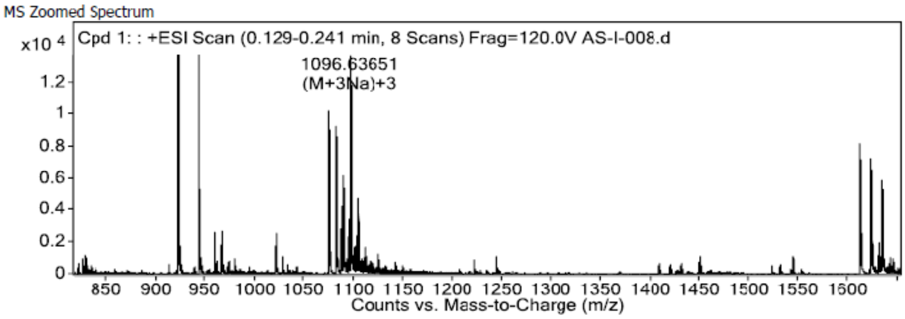


Figure S221. ^{13}P NMR spectrum of compound **1b** (D_2O, 122 MHz)

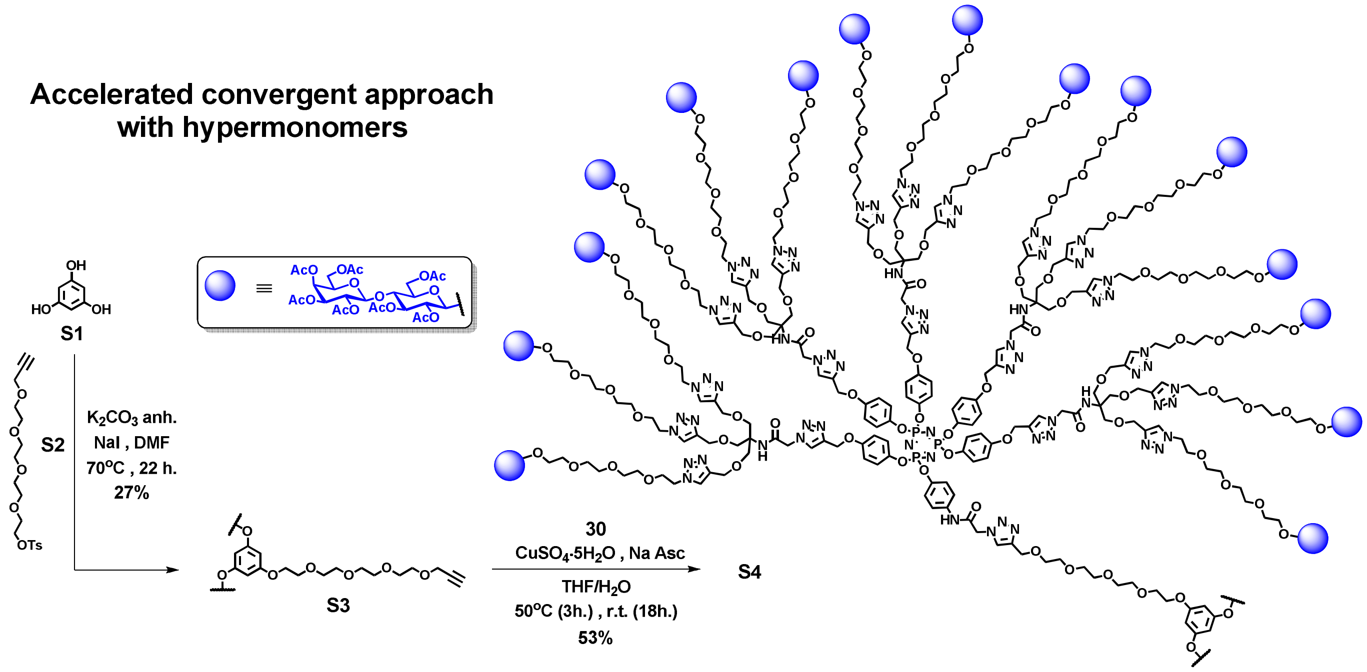


MS Spectrum Peak List

Ion	Ion Formula	Abund	*Expe. m/z*	*Calc. m/z*	Diff(ppm)
(M+4Na)+4	C126H168N21Na4O72P3	948.2	827.97384	827.9728	1.27
(M+3H)+3	C126H171N21O72P3	7035.6	1074.32156	1074.31871	2.66
(M+3Na)+3	C126H168N21Na3O72P3	9349.4	1096.30229	1096.30065	1.49
(M+2H)+2	C126H170N21O72P3	5351.3	1610.97588	1610.97442	0.91
(M+2Na)+2	C126H168N21Na2O72P3	4041	1632.95736	1632.95637	0.61

Figure S222. ESI^{+}-HRMS spectrum of compound **1b**

Synthetic sequence for the construction of "onion peel" glycodendrimer with 45 peripheral protected lactosides



A highly accelerated convergent approach based on the three-fold coupling of AB_{15} hypermonomer around an extended core was investigated (Scheme 10). To this end, three tetra(ethylene)glycol chains containing one terminal propargylic function (**S2**)[9] were introduced onto commercial phloroglucinol **S1**. NMR spectra of **S3** clearly indicated desired *O*-alkylations with characteristic signal of CH_{ar} in ^{1}H NMR at $\delta 6.03$ ppm integrating for three protons, together with two distinctive signals in ^{13}C NMR at $\delta 160.6$ and 94.4 ppm for $C_{ar}O$ and CH_{ar}, respectively. Relative integrations corresponding to terminal propargylic signals are in addition in full agreement with those from the aromatic section, thus confirming the three-fold substitution. Application of Cu-catalyzed click reaction in the presence of dendron **30** and core **S3** furnished the desired "onion peel" glycodendrimer **S4** containing 45 peripheral lactoside units, in a satisfactory yield of 53%. Once again, NMR analyses clearly indicated the absence of characteristic signals from precursor **30**, notably the triplet at $\delta 2.43$ ppm in ^{1}H NMR for $-CH_2C{\equiv}CH$ and the distinctive signal at $\delta 58.4$ ppm in ^{13}C NMR for $-CH_2C{\equiv}CH$. On the other hand, expected central aromatic's signals mentioned earlier clearly pointed out, confirming the integrity of the macromolecule **S4** (*See SI*). Unfortunately, in deep contrast with other structures presented herein (*See the following section*), analytical efforts towards the complete characterization of compound **S4** were unsuccessful, especially for MALDI-TOF MS and GPC techniques. Protocoles' optimization concerning Mass Spectrometry analyses (matrix) for **S4** is currently under investigation.

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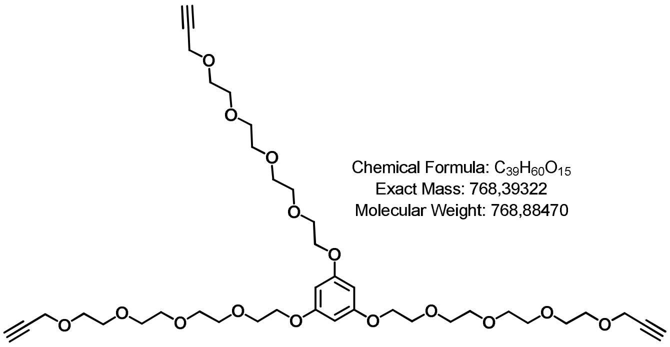
[9] X.-L. Sun, C. L. Stabler, C. S. Cazalis and E. L. Chaikof, *Bioconjugate Chem.*, 2006, **17**, 52–57.

PEGylated core S3


Chemical Formula: $C_{39}H_{60}O_{15}$
Exact Mass: 768,39322
Molecular Weight: 768,88470

To a solution of phloroglucinol **S1** (12.4 mg, 98.3 µmol, 1.0 eq.) in $DMF_{anh.}$ (2 mL), were added K_2CO_3 (dried at 200°C under vacuum) (81.5 mg, 590 µmol, 6.0 eq.) and NaI (1.47 mg, 9.83 µmol, 0.1 eq.) under a N_2 atmosphere. A solution of di-functional PEG **S2**[9] in 0.5 mL of $DMF_{anh.}$ was then slowly added and the resulting mixture was heated at 70°C for 22 hours. Ethyl acetate (25 mL) was added and the solution was poured into a separatory funnel containing ethyl acetate (10 mL), washed with saturated aqueous NH_4Cl (3×30 mL), water (20 mL) and brine (15 mL). Organics were collected, dried over Na_2SO_4 and concentrated to dryness *in vacuo* with rotary evaporator. Purification by flash chromatography (SiO_2, DCM/MeOH 100:0 to 99:1) afforded desired core **S3** (20.4 mg, 26.5 µmol, **27%**) as a yellowish foam.

$\mathbf{R_f}$ = 0.20, DCM/MeOH 97:3

^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 6.11 (s, 3H, CH_{ar}), 4.20 (d, J = 1.9 Hz, 6H, $CH_2C{\equiv}CH$), 4.07 (t, J = 4.9 Hz, 6H, $C_{ar}OCH_2CH_2$), 3.83 (t, J = 4.9 Hz, 6H, $C_{ar}OCH_2CH_2$), 3.70-3.67 (m, 36H, OCH_2CH_2O), 2.44 (d, J = 1.9 Hz, 3H, $CH_2C{\equiv}CH$).

^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 160.5 ($C_{ar}O$), 94.4 (CH_{ar}), 79.7 ($C{\equiv}CH$), 74.5 ($C{\equiv}CH$), 70.8, 70.6, 70.4, 69.6, 69.1, 67.4 (OCH_2CH_2O), 58.4 ($CH_2C{\equiv}CH$).

m/z (ESI^+-HRMS) for $C_{39}H_{60}O_{15}$ = 769.4005 $[M+H]^+$; found 769.3993 ; 791.3824 $[M+Na]^+$; found 791.3813.

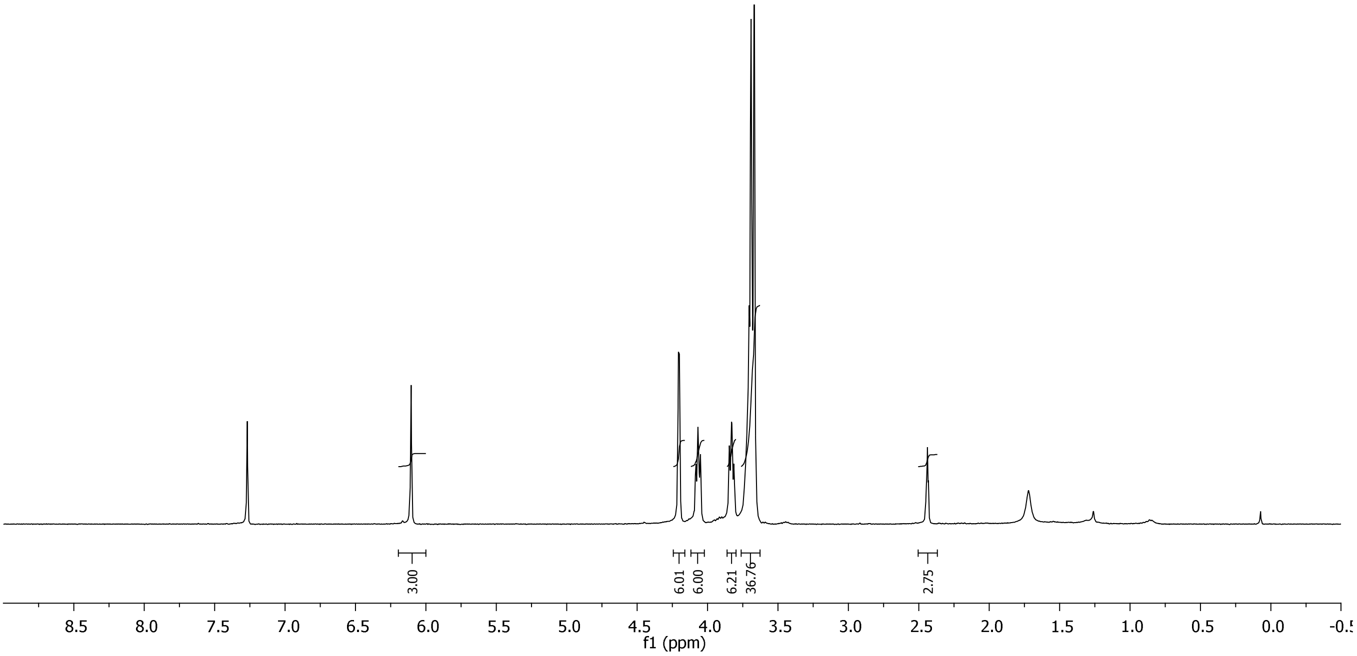


Figure S223. ^{1}H NMR spectrum of compound **S3** ($CDCl_3$, 300MHz)

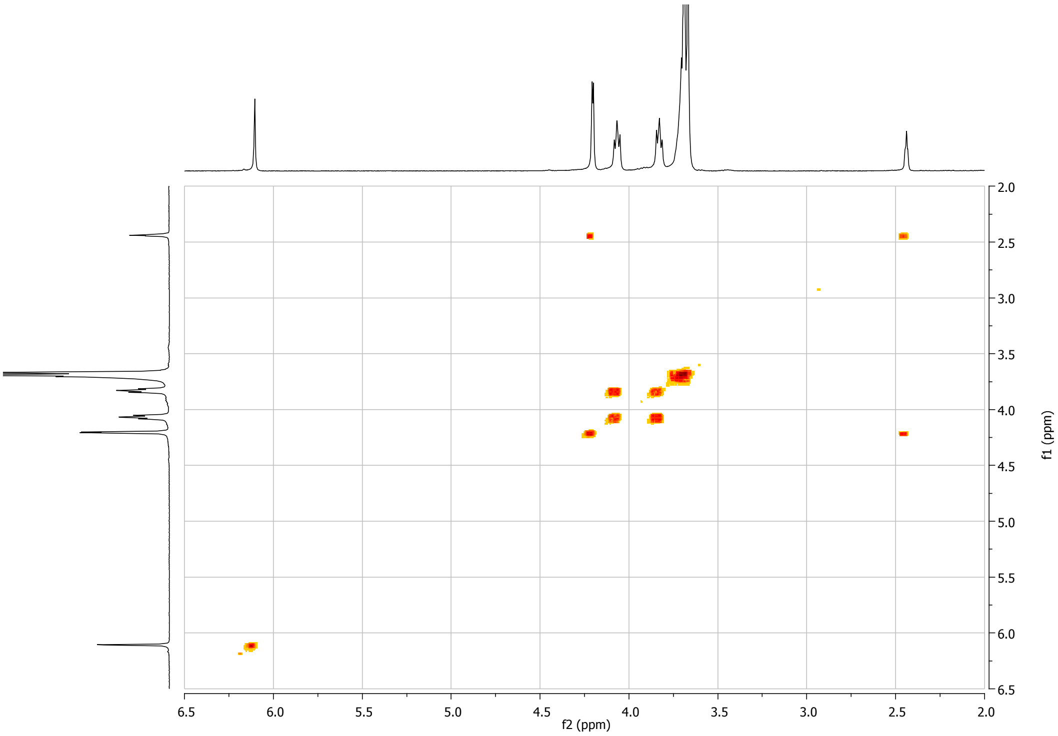


Figure S224. gCOSY spectrum of compound **S3**

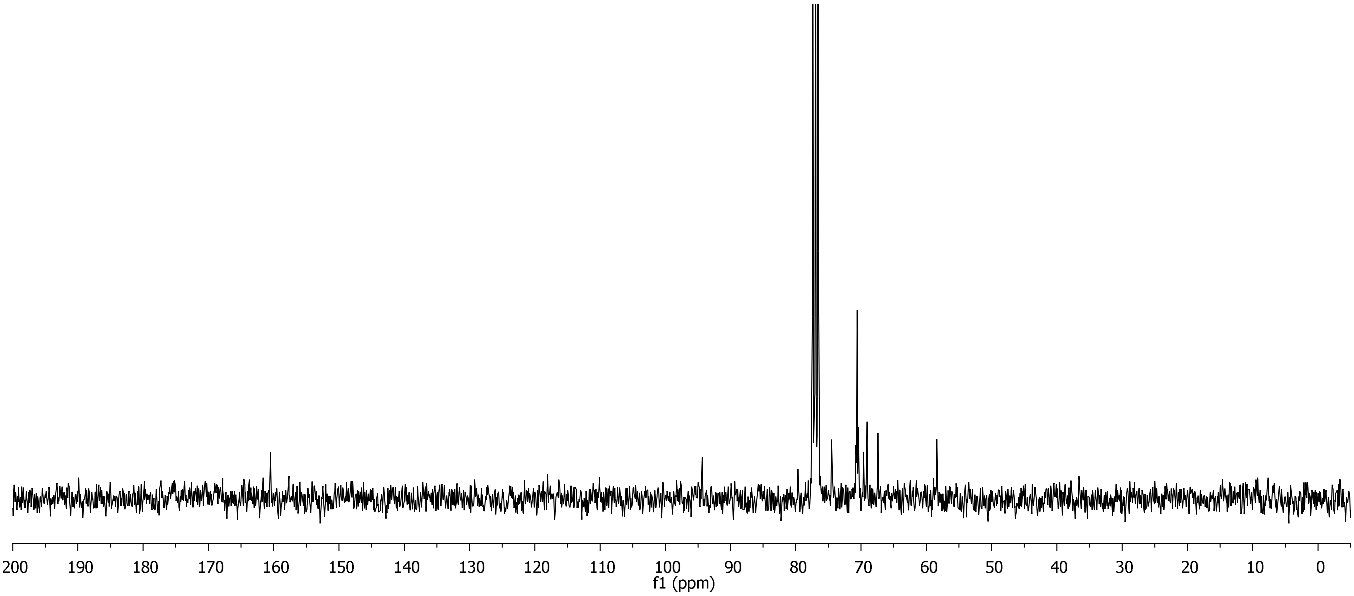
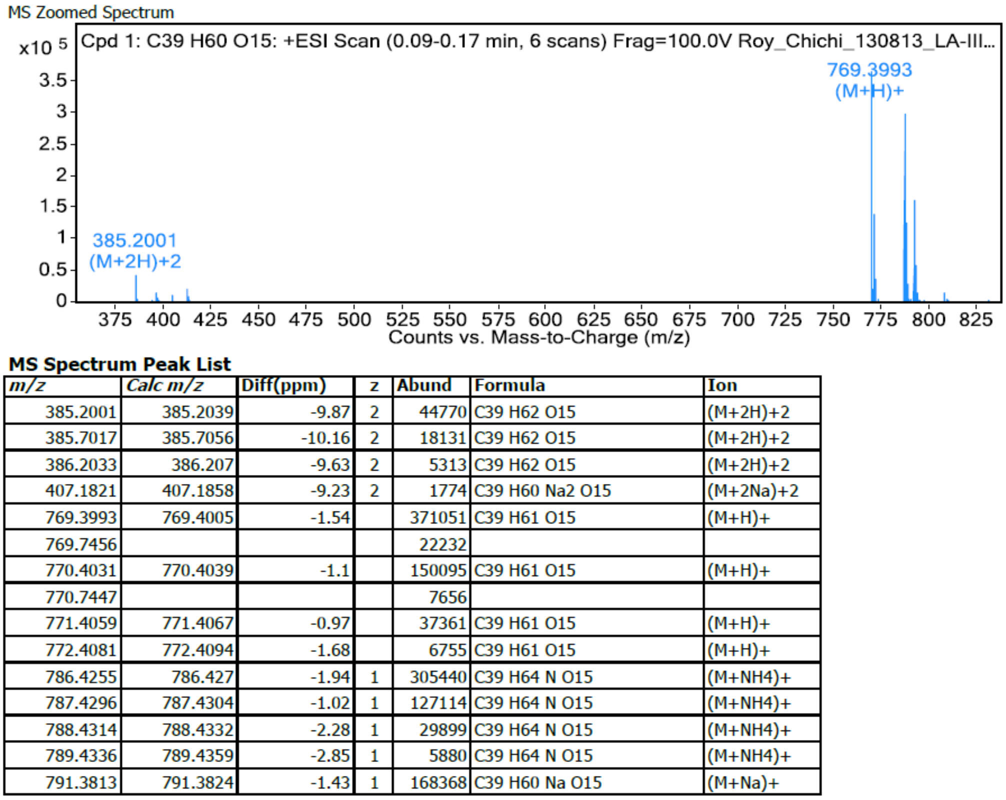


Figure S225. ^{13}C NMR spectrum of compound **S3** ($CDCl_3$, 75MHz)

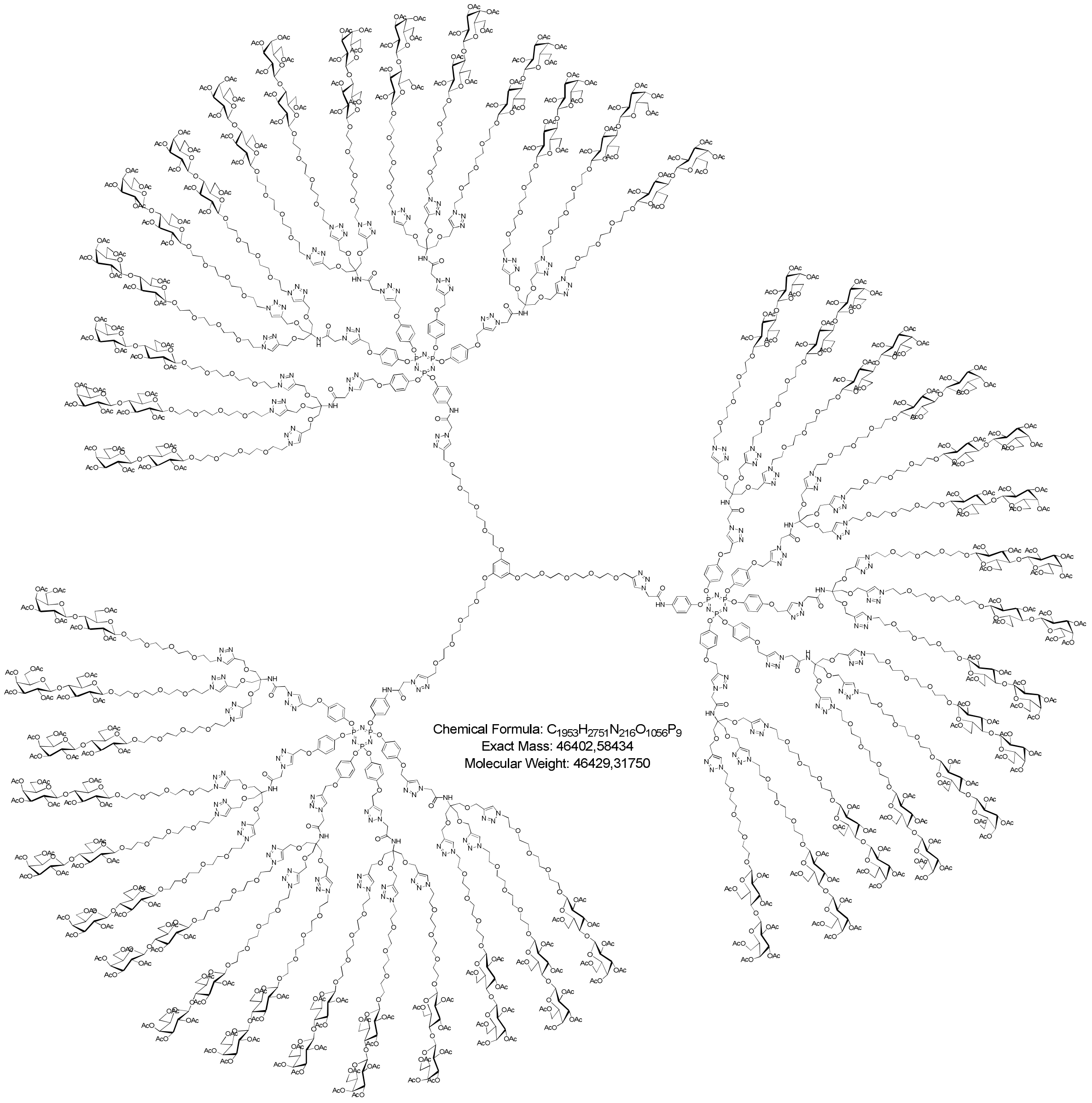


MS Spectrum Peak List

m/z	*Calc m/z*	Diff(ppm)	z	Abund	Formula	Ion
385.2001	385.2039	-9.87	2	44770	C39 H62 O15	(M+2H)+2
385.7017	385.7056	-10.16	2	18131	C39 H62 O15	(M+2H)+2
386.2033	386.207	-9.63	2	5313	C39 H62 O15	(M+2H)+2
407.1821	407.1858	-9.23	2	1774	C39 H60 Na2 O15	(M+2Na)+2
769.3993	769.4005	-1.54		371051	C39 H61 O15	(M+H)+
769.7456				22232		
770.4031	770.4039	-1.1		150095	C39 H61 O15	(M+H)+
770.7447				7656		
771.4059	771.4067	-0.97		37361	C39 H61 O15	(M+H)+
772.4081	772.4094	-1.68		6755	C39 H61 O15	(M+H)+
786.4255	786.427	-1.94	1	305440	C39 H64 N O15	(M+NH4)+
787.4296	787.4304	-1.02	1	127114	C39 H64 N O15	(M+NH4)+
788.4314	788.4332	-2.28	1	29899	C39 H64 N O15	(M+NH4)+
789.4336	789.4359	-2.85	1	5880	C39 H64 N O15	(M+NH4)+
791.3813	791.3824	-1.43	1	168368	C39 H60 Na O15	(M+Na)+

Figure S226. ESI+HRMS spectrum of compound **S3**

Protected glycodendrimer with 45 peripheral lactosides S4



Chemical Formula: $C_{1953}H_{2751}N_{216}O_{1056}P_9$
Exact Mass: 46402,58434
Molecular Weight: 46429,31750

To a stirring solution of core **S3** (0.96 mg, 1.25 μmol, 1.0 eq.) and hypermonomer **30** (80.2 mg, 5.27 μmol, 4.2 eq.) in dry THF (2.5 mL) were added 2.5 mL of H_2O and a mixture of $CuSO_4{\cdot}5H_2O$ (2.84 mg, 11.3 μmol, 9.0 eq.) and sodium ascorbate (2.23 mg, 1.13 μmol, 9.0 eq.). After stirring for 3 hours at 50^oC in a 20 mL vial, the reaction was left stirring at room temperature for 18 hours (additional $CuSO_4{\cdot}5H_2O$ (1.00 mg) and sodium ascorbate (0.80 mg) were incorporated in the mixture after 5 hours of reaction). EtOAc (25 mL) was added and the solution was washed successively with a saturated aqueous solution of NH_4Cl (3×15 mL), water (2×10 mL) and brine (10 mL). The organic phase was then dried over $MgSO_4$ and concentrated under reduced pressure. Column chromatography on silica (DCM/MeOH 100:0 to 93:7) afforded the desired compound **S4** (30.7 mg, 0.66 μmol, **53%**) as a colorless oil.

R$_f$ = 0.15, DCM/MeOH 94:6

^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): ~8.00 (3H, N*H*) (*not visible*), 7.92-7.90 (m, 18H, $H_{\text{triazole int}}$), 7.74-7.69 (s, 45H, $H_{\text{triazole ext}}$), 7.40-7.28 (br s, 21H, N*H* + $CH_{b'}$), 7.03-6.50 (m, 66H, CH_b, CH_c, $CH_{c'}$), 6.07 (s, 3H, CH_{ar}), 5.34 (d_{app}, 45H, H_{4gal} + br s (6H, $N_{triazole}CH_2CONH$)), 5.17 (t_{app}, 45H, H_{3glc}), 5.10-5.07 (m, 75H, C_qCH_2O, H_{2gal}), 4.93 (dd, $^3J_{2,3}$ = 3.4 Hz, $^3J_{3,4}$ = 7.0 Hz, 45H, H_{3gal}), 4.84 (t_{app}, 45H, H_{2glc}), 4.55-4.46 (m, 315H, C_qCH_2O, OCH_2CH_2N, H_{1glc}, H_{6aglc}, H_{1gal}), 4.13-4.05 (m, 135H, H_{6bglc}, H_{6agal}, H_{6bgal}), 3.89-3.55 (m, 933H, $NHCOCH_2N_{triazole}$, OCH_2CH_2N, H_{5gal}, H_{5glc}, H_{4glc}, OCH_2, HNC_qCH_2O), 2.11-1.92 (m, 945H, $COCH_3$).

^{13}C NMR (150 MHz, $CDCl_3$, δ ppm): 170.3, 170.3, 170.1, 170.0, 169.7, 169.6, 169.0 (7×s, $COCH_3$), 166.1 (*C*ONH), 165.1 (*C*ONH), **160.4 ($C_{ar}O$)**, 155.4 (C_a), 147.3 ($C_{d'}$), 144.3 (C_d), 144.3, 144.2 ($C_{triazole}$=CH), 143.5 ($C_{triazole}$=CH), 134.7 ($C_{a'}$), 125.2 ($C_{triazole}$=*C*H), 125.2 ($C_{triazole}$=*C*H), 123.8 ($C_{triazole}$=*C*H), 121.8 (C_c), 121.1 ($C_{b'}$), 120.9 ($C_{c'}$), 115.9, 115.3 (C_b), 100.9 (C_{1gal}), 100.5 (C_{1glc}), **94.2 (CH_{ar})**, 76.2 (C_{4glc}), 72.6 (C_{3glc}), 72.5 (C_{5glc}), 71.5 (C_{2glc}), 70.9 (C_{3gal}), 70.5 (C_{5gal}), 70.5, 70.4, 70.3, 70.1, 69.2 (OCH_2), 68.9 (C_{2gal}), 68.9 (OCH_2), 68.5 (C_qCH_2O), 67.3 (CH_2O), 66.5 (C_{4gal}), 64.5 (OCH_2C=C), 62.0 (C_q), 61.9 (C_{6glc} + C_qCH_2O), 60.7 (C_{6gal}), 60.3 (OCH_2), 52.5 ($N_{triazole}CH_2CONH$), 50.1 (NCH_2), 20.7, 20.7, 20.6, 20.5, 20.5, 20.4 (7×s, $COCH_3$).

^{31}P NMR (122 MHz, $CDCl_3$, δ ppm): 10.2- 9.8 (m, 9P).

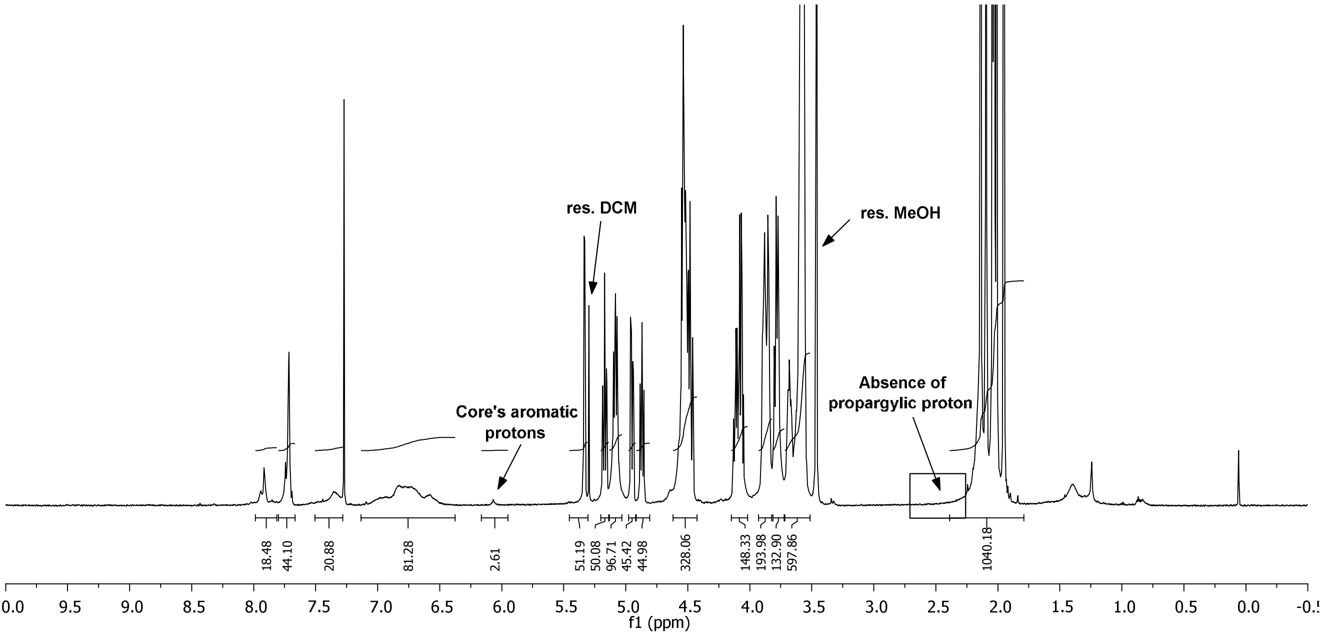


Figure S227. ^{1}H NMR spectrum of compound **S4** ($CDCl_3$, 600MHz)

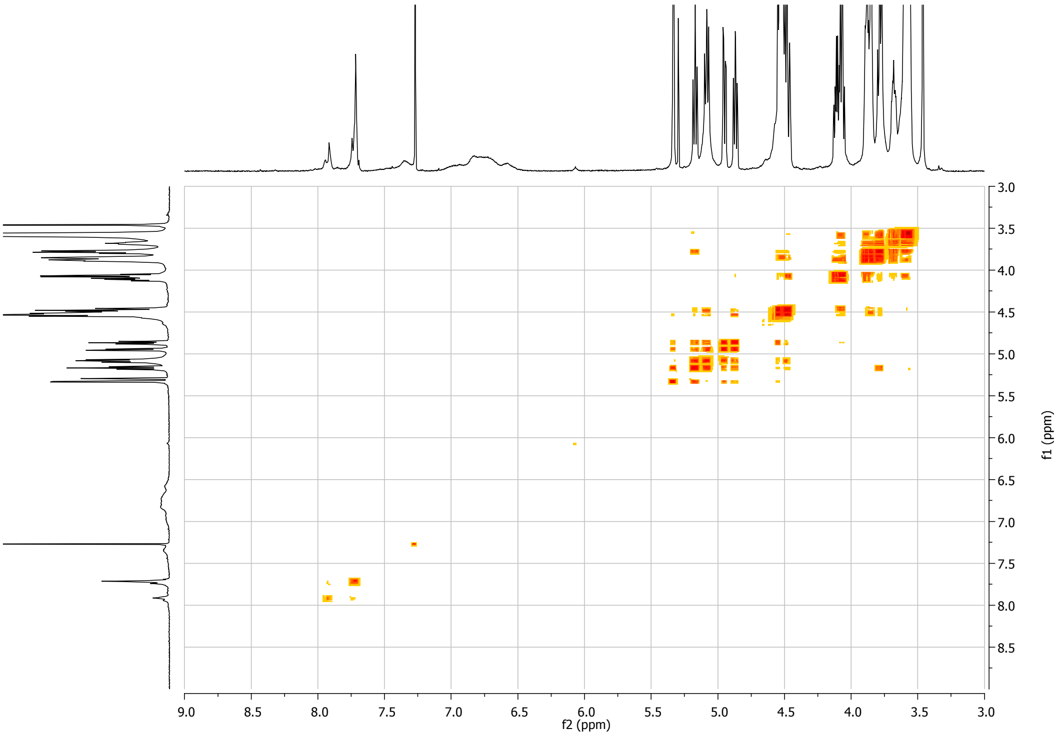


Figure S228. gCOSY spectrum of compound **S4**

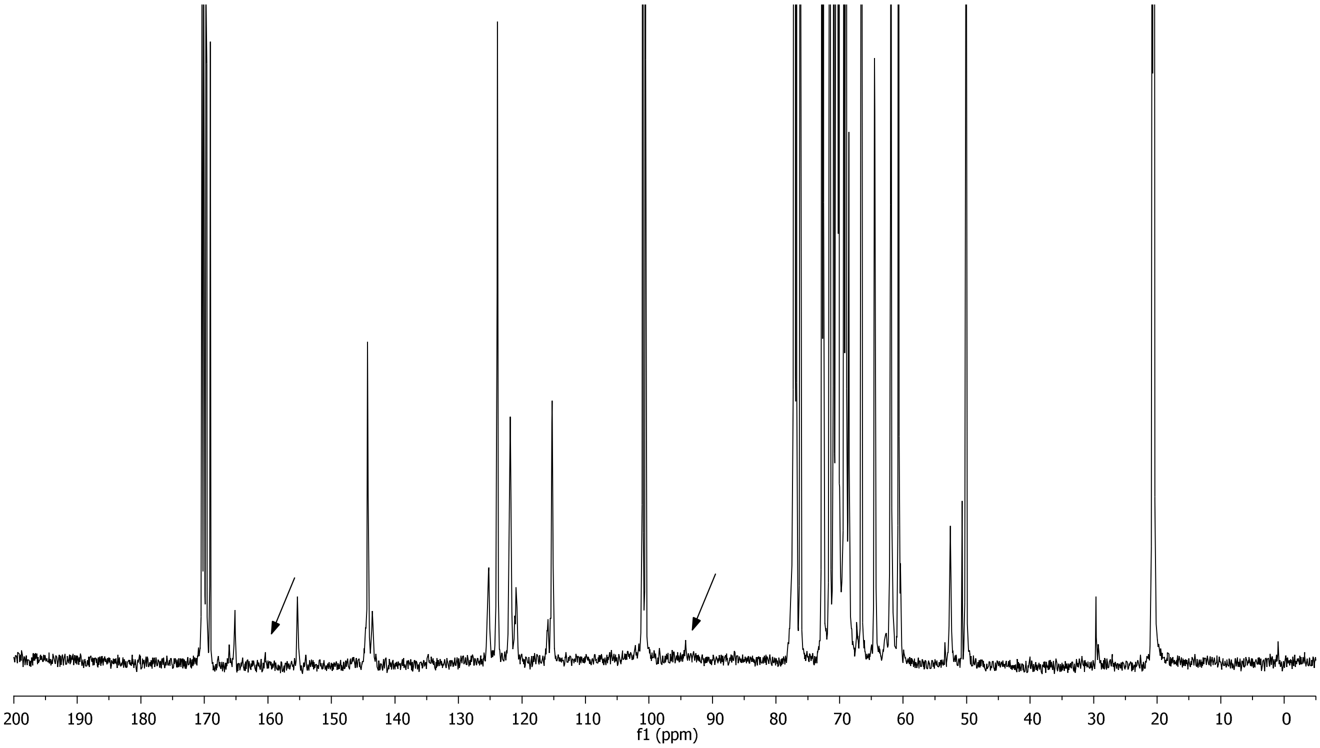


Figure S229. ^{13}C NMR spectrum of compound **S4** ($CDCl_3$, 150MHz). Arrows indicated central C_{ar}-O *and* C_{ar}H.

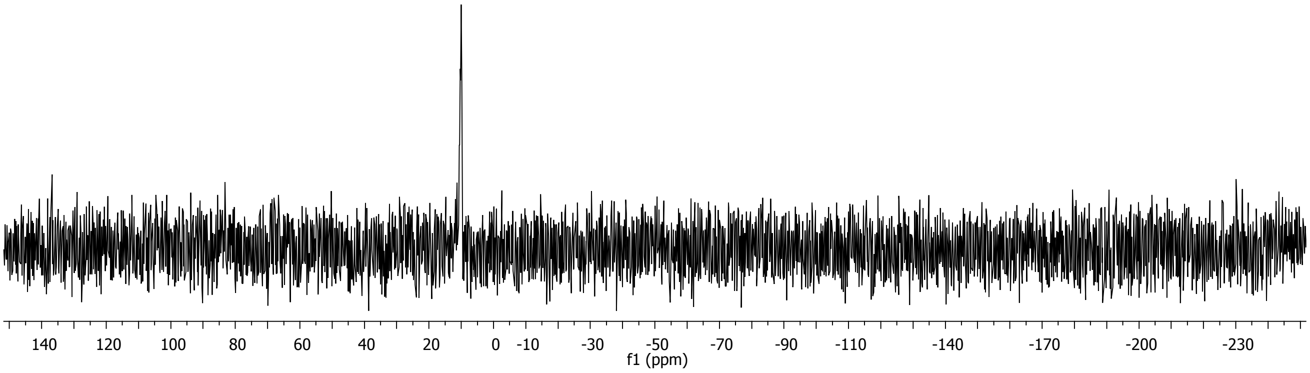


Figure S230. ^{31}P NMR spectrum of compound **S4** ($CDCl_3$, 122MHz)

3. Diffusion NMR experiments

NMR diffusion experiments: NMR diffusion measurements were performed at 25°C on a Varian Inova Unity 600 spectrometer (Agilent, Santa Clara, CA, USA) operating at a frequency of 599.95 MHz for ^{1}H using a 5mm broadband z-gradient temperature-regulated probe. The temperature was calibrated with 1,2-ethanediol according to a standard procedure.[10] The diffusion experiment employed a bipolar pulse-field gradient stimulated echo sequence as proposed by Wu et al.[11] Gradient pulse durations δ were set between 3 and 5 ms while diffusion times (Δ) were 30 to 150 ms to ensure that the echo intensities were attenuated by at least 80%. A complete attenuation curve was obtained by measuring 30 gradient strengths, which were linearly incremented between 1.8 and 54.2 G/cm. Hard 90° 1H pulses of 15µs were used and 36 k data points were recorded with 16 scans acquired for each gradient strength. A recycle delay of 3.0 s was used. The gradient strength was calibrated by back calculation of the coil constant from diffusion experiments on a 20% H_2O/80% D_2O standard ($D = 1.97\text{x}10^{-9}$ m^2 s^{-1}).[12]

Diffusion rates were extracted from the slope of the straight lines obtained by plotting ln(I) against the gradient-pulse power squared according to the following equation: $\ln(I)=-D\gamma^2G^2\delta^2(\Delta-\delta/3-\tau/2)+\ln(I_0)$where I is the relative intensity of a chosen resonance ($I = I_0\exp-[D\gamma^2G^2\delta^2(\Delta-\delta/3-\tau/2)]$), G=gradient strength, γ=proton gyromagnetic ratio, D=diffusion rate, δ=gradient duration, Δ=diffusion delay, and τ=pulse length for bipolar pulses. All diffusion spectra were processed in MatNMR.[13]

The diffusion rates (D) were calculated from the decay of the signal intensity with increasing field gradient strength of the H_{4gal} proton (δ = 5.30 ppm) for the samples in $CDCl_3$ (acetylated conjugates) or the $H_{triazole}$ proton (δ=7.90 ppm) for the samples in D_2O (hydroxylated derivatives). In all cases, mono-exponential behavior was observed, resulting in a linear decay of the logarithm of the signal intensity as a function of the gradient strength squared. The linearity of the data was consistent with a monomolecular behavior in each case, confirming the absence of aggregation phenomena in aqueous solution.

The measurement of the diffusion rate (D) allows calculating the solvodynamic diameter of a molecule.[14] The dendrimers are considered as spherical molecular objects, and characterized by an apparent diffusion coefficient D. The application of the Stokes-Einstein equation gives an estimate of the diameter of the molecule.

Stokes-Einstein equation:

$$D = K_BT / 6\pi\eta r_s$$

D: Diffusion rate (m^2.s^{-1}); K_B: Boltzmann's constant ($K_B = 1.38 \times 10^{-23}$ m^2.kg.s^{-2}.K^{-1}); T: Temperature (K) (T = 298.15 K); η: solvent viscosity en Pa s; r_s: Solvodynamic radius of the species.

---

[10] S. Berger and S. Braun, *200 and More NMR Experiments−A Practical Course;* Wiley-VCH: Weinheim, 2004; pp 145–148.
[11] D. H. Wu, A. D. Chen, C. S. and Johnson Jr., *J. Magn. Reson., Ser. A* 1995, **115**, 260–264.
[12] M. Holz and H. Weingärtner, *J. Magn. Reson.* 1991, **92***,* 115–125.
[13] J. D. van Beek, *J. Magn. Reson.* 2007**, 187***,* 19–26.
[14] M. D. Diaz and Berger, S. *Carbohydr. Res.* 2000, **329**, 1−5.

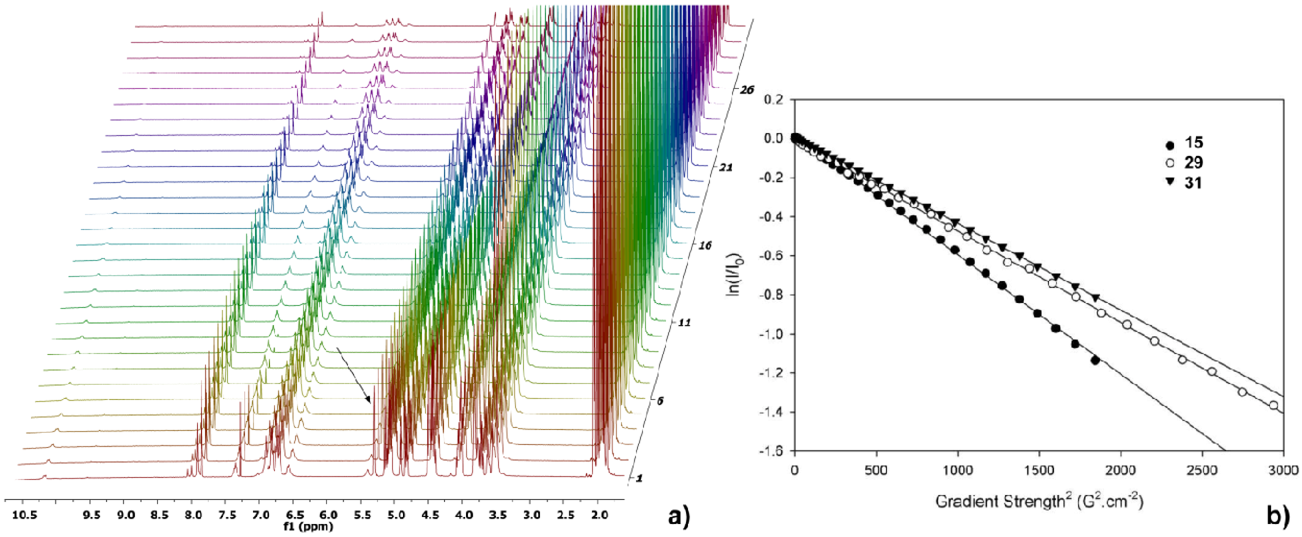


Figure S231. a) Decay of normalized ^{1}H signal for the pentadecavalent dendron **31** in $CDCl_3$ during the PFGSTE experiment. The gradient strength is increased linearly between 1.8 and 54.2 G.cm^{-1}; b) Characteristic echo decays of the H_{4gal} resonances (δ = 5.30 ppm) as a function of squared gradient strength located in dendrons **15**, **29** and **31**. Such linear behavior was also obtained for the decay of the signal intensities of other protons located either in internal regions of the conjugates, including the dendritic core and connecting branches, or in the peripheral saccharidic belt (results not shown). Linear fits, which are plotted as solid lines and used to calculate self-diffusion coefficients, are characteristic of a single molecule and therefore rule out aggregation.

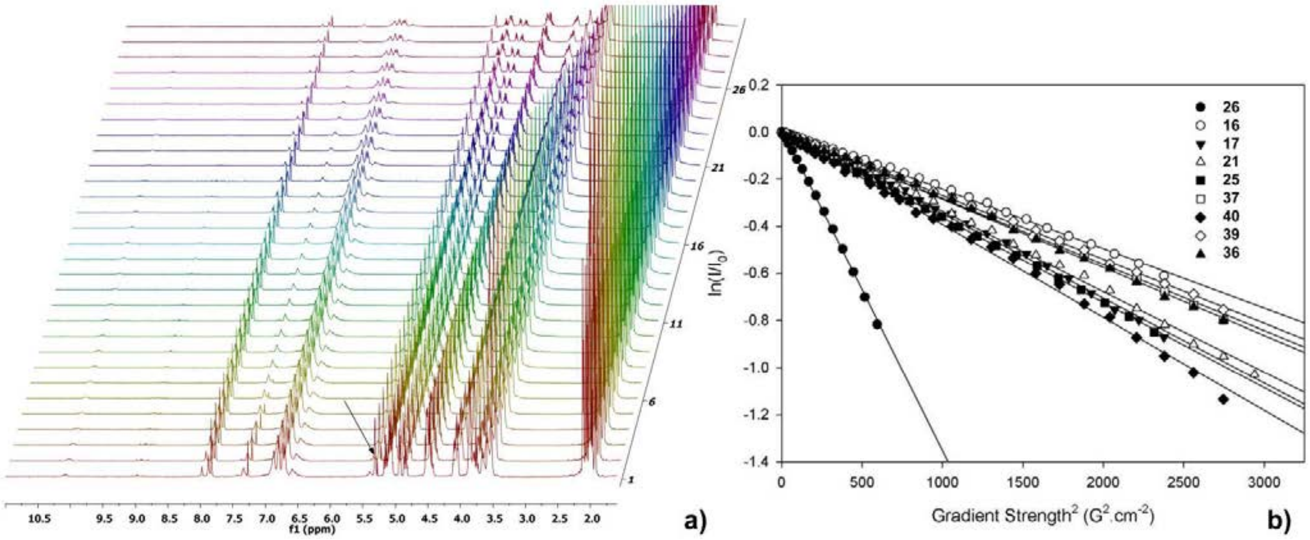


Figure S232. a) Decay of normalized ^{1}H signal for the tricontavalent glycodendrimer **26** in $CDCl_3$ during the PFGSTE experiment. The gradient strength is increased linearly between 1.8 and 54.2 G.cm^{-1}; b) Characteristic echo decays of the H_{4gal} resonances (δ = 5.30 ppm) as a function of squared gradient strength located in lactosylated derivatives **26**, **16**, **17**, **21**, **25**, **37**, **40**, **39**, and **36**. Such linear behavior was also obtained for the decay of the signal intensities of other protons located either in internal regions of the conjugates, including the dendritic core and connecting branches, or in the peripheral saccharidic belt (results not shown). Linear fits, which are plotted as solid lines and used to calculate self-diffusion coefficients, are characteristic of a single molecule and therefore rule out aggregation.

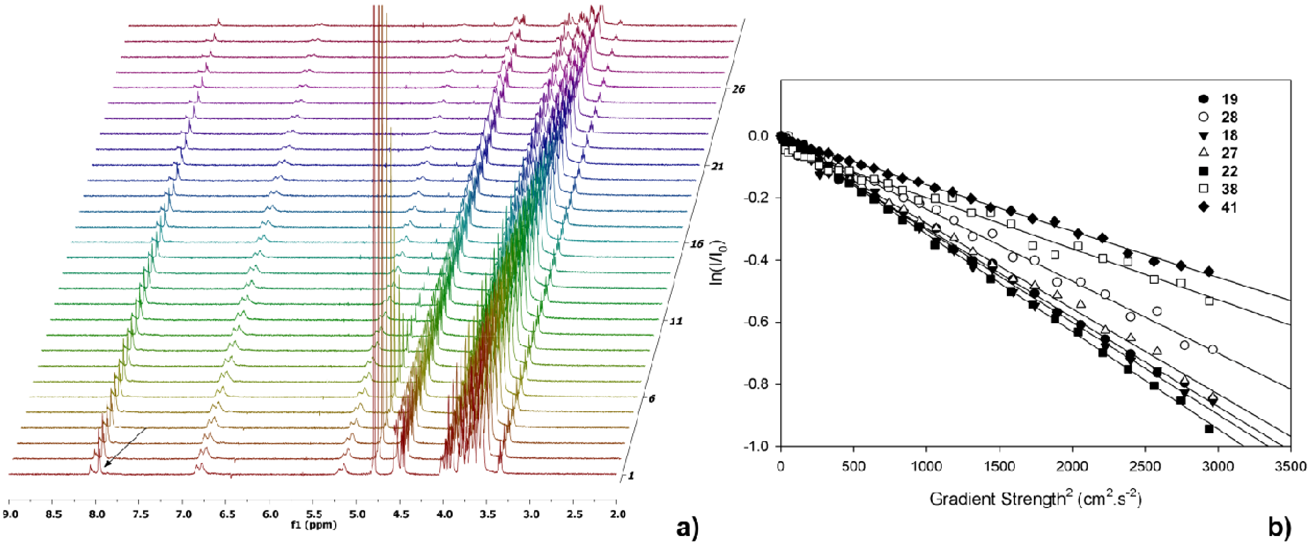


Figure S233. a) Decay of normalized ^{1}H signal for the octadecavalent hydroxylated glycodendrimer **19** in D$_2$O during the PFGSTE experiment. The gradient strength is increased linearly between 1.8 and 54.2 G.cm^{-1}; b) Characteristic echo decays of the H_{triazole} resonances (δ = 7.90 ppm) as a function of squared gradient strength located in lactosylated derivatives **19**, **28**, **18**, **27**, **22**, **38**, and **41**. Such linear behavior was also obtained for the decay of the signal intensities of other protons located either in internal regions of the conjugates, including the dendritic core and connecting branches, or in the peripheral saccharidic belt (results not shown). Linear fits, which are plotted as solid lines and used to calculate self-diffusion coefficients, are characteristic of a single molecule and therefore rule out aggregation.

4. Competitive Surface Plasmon Resonance Studies and Sensorgrams

For LecA: The studies were conducted using a Biacore T200 SPR instrument with a CM5 sensor chip. A continuous flow of HEPES buffer (10 mm HEPES and 150 mm NaCl, 2 mM $CaCl_2$, pH 7.4) was maintained over the sensor surface at a flow rate of 10 µl/min. The CM5 sensor chip was activated with an injection of a solution containing *N*-ethyl-*N´*-(3-diethylaminopropyl) carbodiimide (EDC) (0.2 M) and *N*-hydroxysuccinimide (NHS) (0.05 M) for 7 minutes. Lactoside **42** (200 µg/mL) and Et_3N (1 mM) in NaOAc buffer (pH 4.5) was injected over the activated flow cell at flow rate of 10 µl/min for 2 minute to achieve a ~230 RU immobilization. The immobilization procedure was completed by an injection of ethanolamine hydrochloride (1 M) (70 µL), followed by a flow of the buffer (100 µL/min.), in order to eliminate physically adsorbed compounds. Ethanol amine alone was used in one of the flow-cell as a reference. The solutions of pre incubated (1 h) mixtures of glycodendrimers or monomers (with the various concentrations) and a LecA lectin (1.5 µM) in running HEPES buffer are passed over flow cells of the lactoside and ethanol amine (Association: 3 min and dissociation: 3 min). The sensor chip was regenerated with the serial injections of D-lactose (0.25 M, 3 min), buffer (3 min), D-lactose (0.25 M, 3 min) and buffer (3 min). For each inhibition assay, LecA lectin (1.5 µM) without inhibitor was injected to observe the full adhesion of the lectin onto the sugar-coated surface (0% inhibition). Response units from the surface of lactoside were subtracted from the surface of ethanol amine to eliminate non-specific interactions, as well as, bulk change in RU due to variation in refractive index of the medium. The primary subtracted sensorgrams were analyzed by 1:1 Langmuir model fitting, using the BIAevaluation software. For IC_{50} evaluation, the response units at the equilibrium was considered as the amount of lectin bound to the sugar surface in the presence of a defined concentration of inhibitor. Inhibition curves were obtained by plotting the percentage of inhibition against the inhibitor concentration (on a logarithmic scale) by using Origin 7.0 software (OriginLab Corp.) and IC_{50} values were extracted from a sigmoidal fit of the inhibition curve. The error values are obtained from the fitting of exponential curve.

For truncated hGal-3: The studies were conducted using a Biacore T200 SPR instrument with a CM5 sensor chip. A continuous flow of standard PBS buffer (HyClone®, Phosphate Buffered Saline (10X) 0.067M (PO_4), pH 7.4) was maintained over the sensor surface at a flow rate of 10 µl/min. The CM5 sensor chip was activated with an injection of a solution containing *N*-ethyl-*N´*-(3-diethylaminopropyl) carbodiimide (EDC) (0.2 M) and *N*-hydroxysuccinimide (NHS) (0.05 M) for 7 minutes. Lactoside **42** (200 µg/mL) and Et_3N (1 mM) in NaOAc buffer (pH 4.5) was injected over the activated flow cell at flow rate of 10 µl/min for 2 minute to achieve a ~230 RU immobilization. The immobilization procedure was completed by an injection of ethanolamine hydrochloride (1 M) (70 µL), followed by a flow of the buffer (100 µL/min.), in order to eliminate physically adsorbed compounds. Ethanol amine alone was used in one of the flow-cell as a reference. The solutions of pre incubated (15 min) mixtures of glycodendrimer or monomers (with the various concentrations) and a truncated galectin-3 (7.5 µM) in running PBS buffer are passed over flow cells of the lactoside and ethanol amine (Association: 3 min and dissociation: 3 min). The sensor chip was regenerated with the serial injections of D-lactose (0.25 M, 3 min), buffer (3 min), D-lactose (0.25 M, 3 min) and buffer (3 min). For each inhibition assay, truncated hGal-3 (7.5 µM) without inhibitor was injected to observe the full adhesion of the lectin onto the sugar-coated surface (0% inhibition). Response units from the surface of lactoside were subtracted from the surface of ethanol amine to eliminate non-specific interactions, as well as, bulk change in RU due to variation in refractive index of the medium. The primary subtracted sensorgrams were analyzed by 1:1 Langmuir model fitting, using the BIAevaluation software. For IC_{50} evaluation, the response units at the equilibrium was considered as the amount of lectin bound to the sugar surface in the presence of a defined concentration of inhibitor. Inhibition curves were obtained by plotting the percentage of inhibition against the inhibitor concentration (on a logarithmic scale) by using Origin 7.0 software (OriginLab Corp.) and IC_{50} values were extracted from a sigmoidal fit of the inhibition curve. The error values are obtained from the fitting of exponential curve.

Sensorgrams and inhibitory curves with LecA

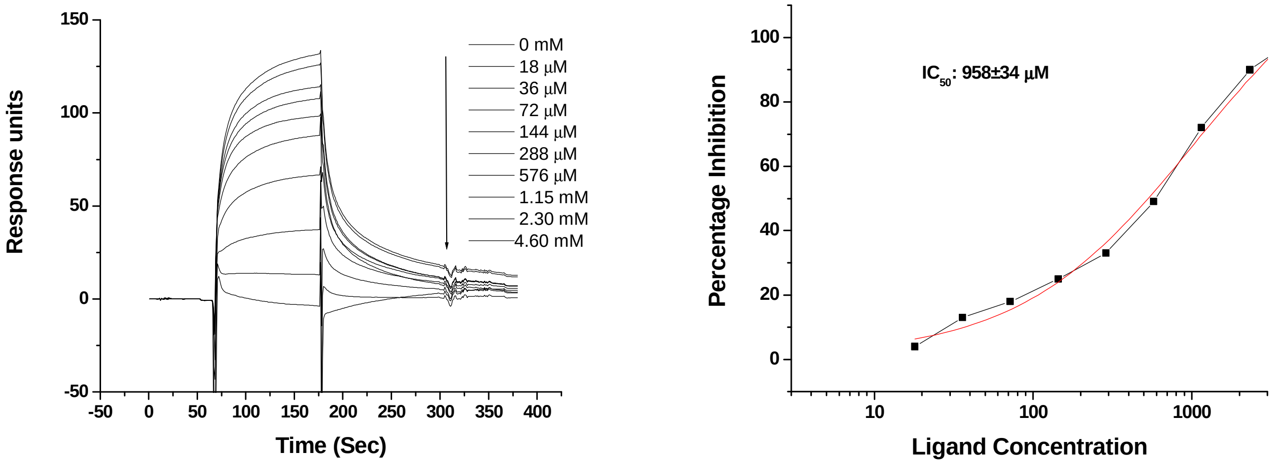


Figure S234. (*left*) Sensorgrams obtained by injection of LecA (1.5 μM) lectin incubated with different concentrations of monomeric **43** varying from 18 μM (top curve) to 4.60 mM (bottom curve) on the surface of immobilized lactoside **42**. (*right*) The inhibitory curve for the compound **43**.

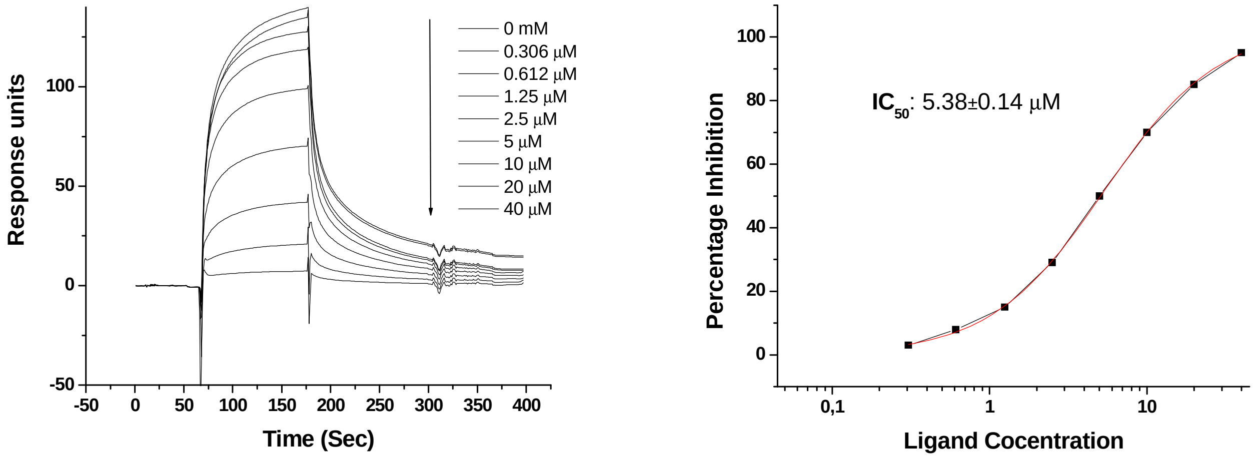


Figure S235. (*left*) Sensorgrams obtained by injection of LecA (1.5 μM) lectin incubated with different concentrations of hexavalent **18** varying from 0.306 μM (top curve) to 40 μM (bottom curve) on the surface of immobilized lactoside **42**. (*right*) The inhibitory curve for the compound **18**.

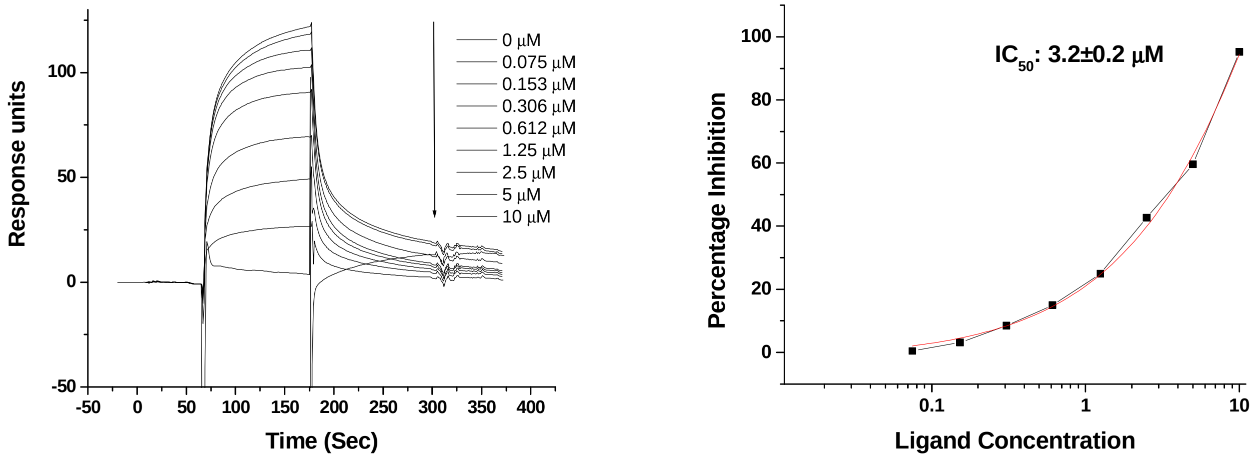


Figure S236. (*left*) Sensorgrams obtained by injection of LecA (1.5 µM) lectin incubated with different concentrations of decavalent **22** varying from 0.075 µM (top curve) to 10 µM (bottom curve) on the surface of immobilized lactoside **42**. (*right*) The inhibitory curve for the compound **22**.

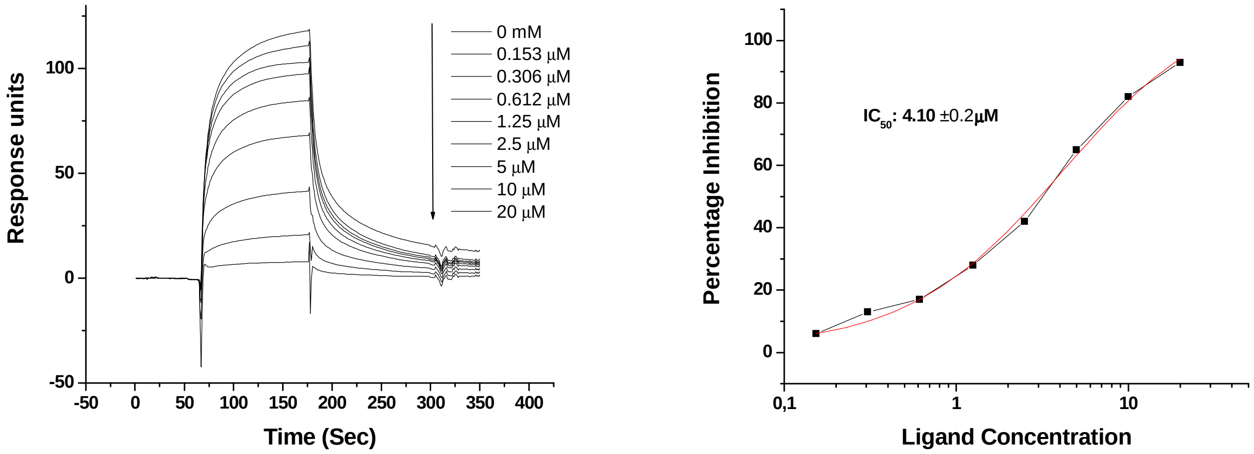


Figure S237. (*left*) Sensorgrams obtained by injection of LecA (1.5 µM) lectin incubated with different concentrations of pentadecavalent **27** varying from 0.153 µM (top curve) to 20 µM (bottom curve) on the surface of immobilized lactoside **42**. (*right*) The inhibitory curve for the compound **27**.

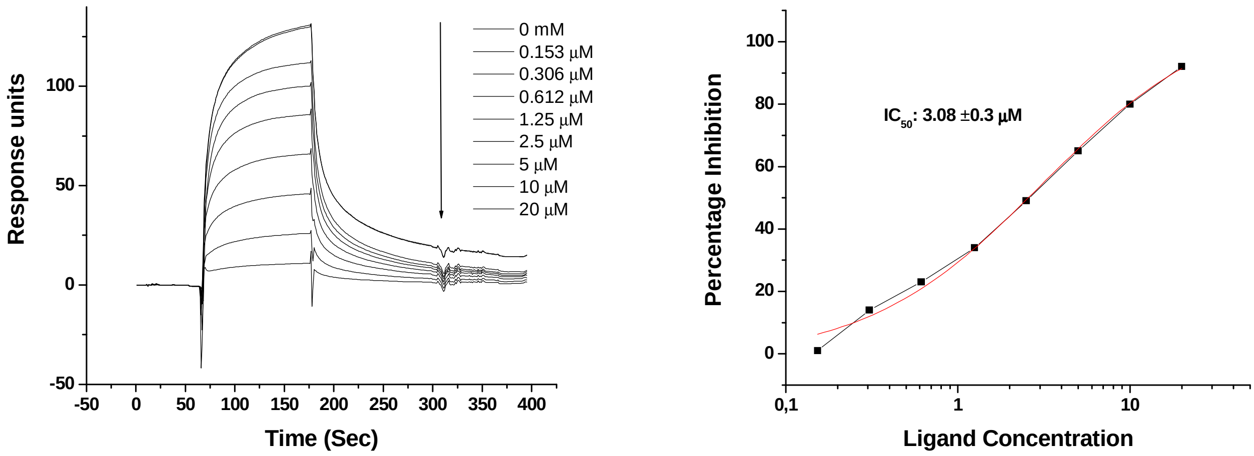


Figure S238. (*left*) Sensorgrams obtained by injection of LecA (1.5 µM) lectin incubated with different concentrations of octadecavalent **19** varying from 0.153 µM (top curve) to 20 µM (bottom curve) on the surface of immobilized lactoside **42**. (*right*) The inhibitory curve for the compound **19**.

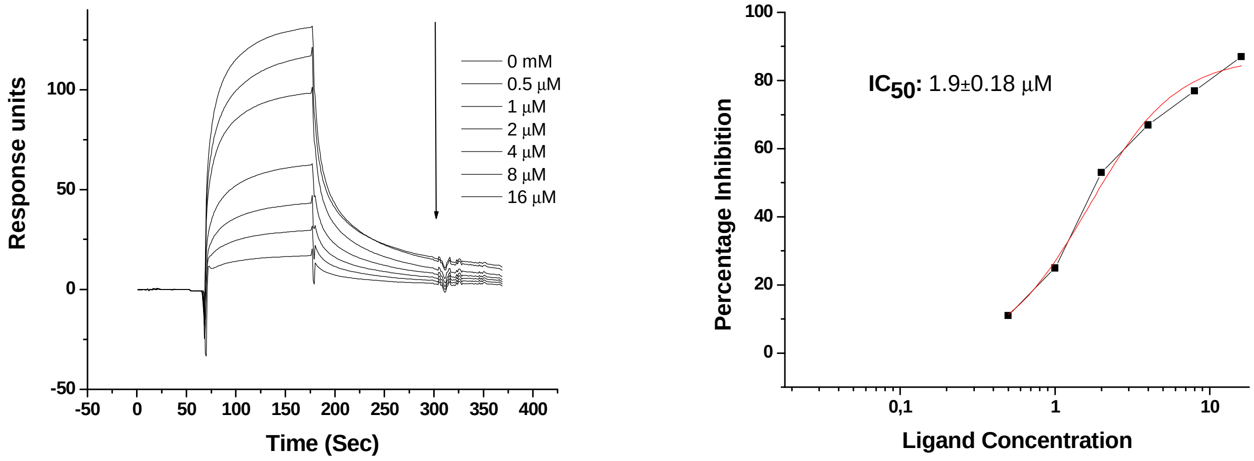


Figure S239. (*left*) Sensorgrams obtained by injection of LecA (1.5 µM) lectin incubated with different concentrations of tricontavalent **28** varying from 0.5 µM (top curve) to 16 µM (bottom curve) on the surface of immobilized lactoside **42**. (*right*) The inhibitory curve for the compound **28**.

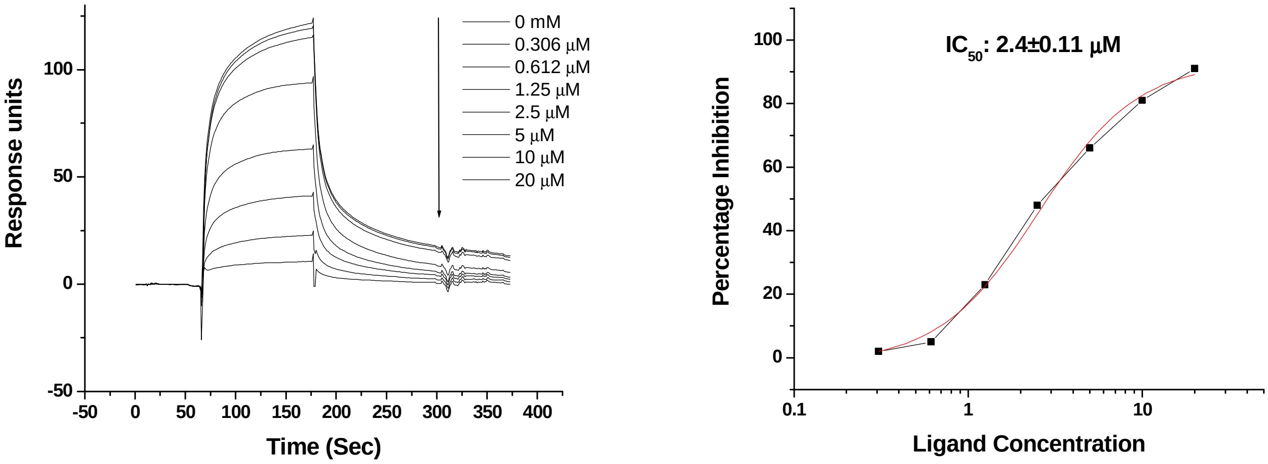


Figure S240. (*left*) Sensorgrams obtained by injection of LecA (1.5 µM) lectin incubated with different concentrations of tricontavalent **38** varying from 0.306 µM (top curve) to 20 µM (bottom curve) on the surface of immobilized lactoside **42**. (*right*) The inhibitory curve for the compound **38**.

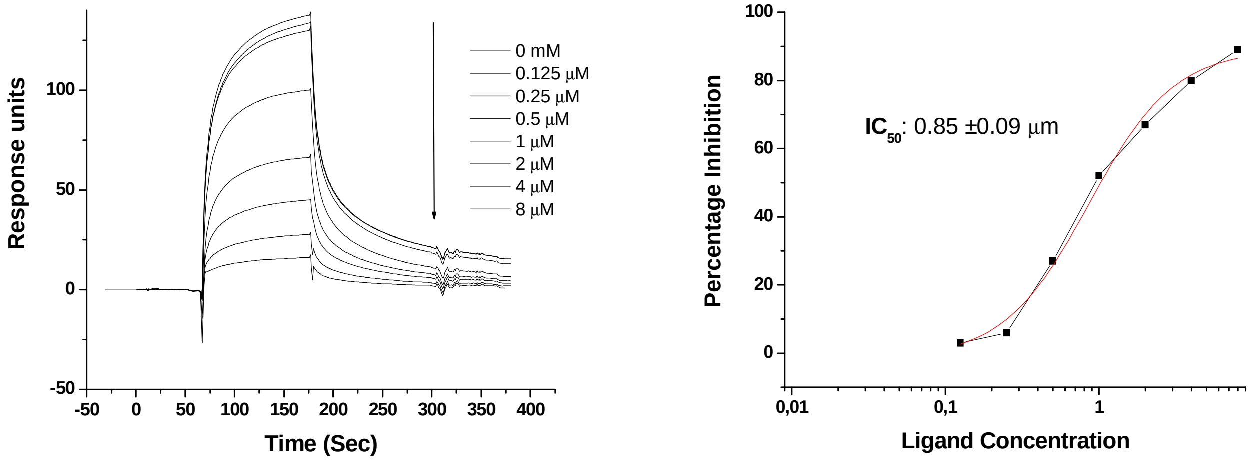


Figure S241. (*left*) Sensorgrams obtained by injection of LecA (1.5 µM) lectin incubated with different concentrations of nonacontavalent **41** varying from 0.125 µM (top curve) to 8 µM (bottom curve) on the surface of immobilized lactoside **42**. (*right*) The inhibitory curve for the compound **41**.

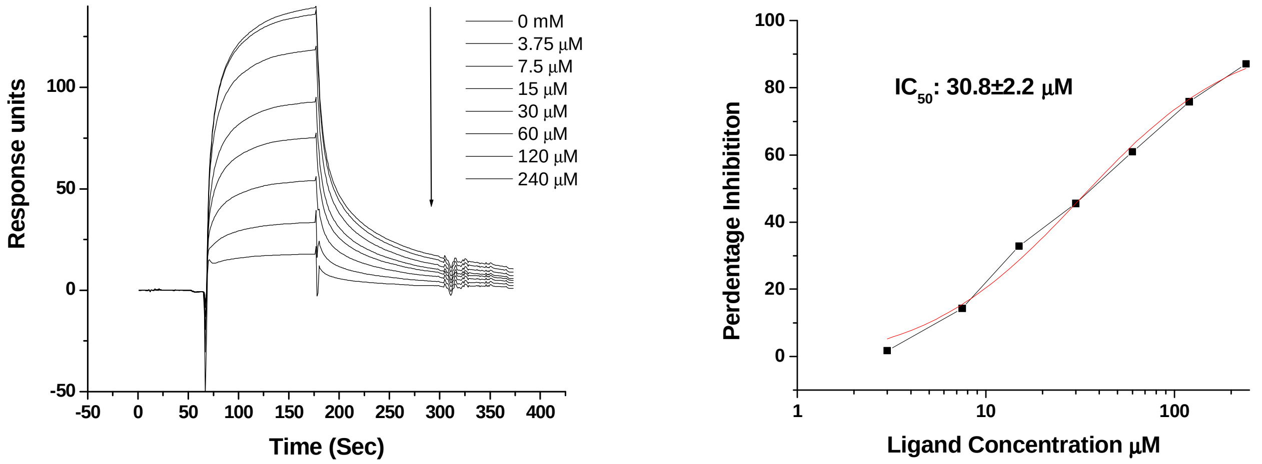


Figure S242. (*left*) Sensorgrams obtained by injection of LecA (1.5 µM) lectin incubated with different concentrations of "short" hexavalent reference (containing 6 Lactoside but without PEG chains) varying from 3.75 µM (top curve) to 240 µM (bottom curve) on the surface of immobilized lactoside **42**. (*right*) The inhibitory curve for this compound.

<u>Sensorgrams and inhibitory curves with truncated hGal-3</u>

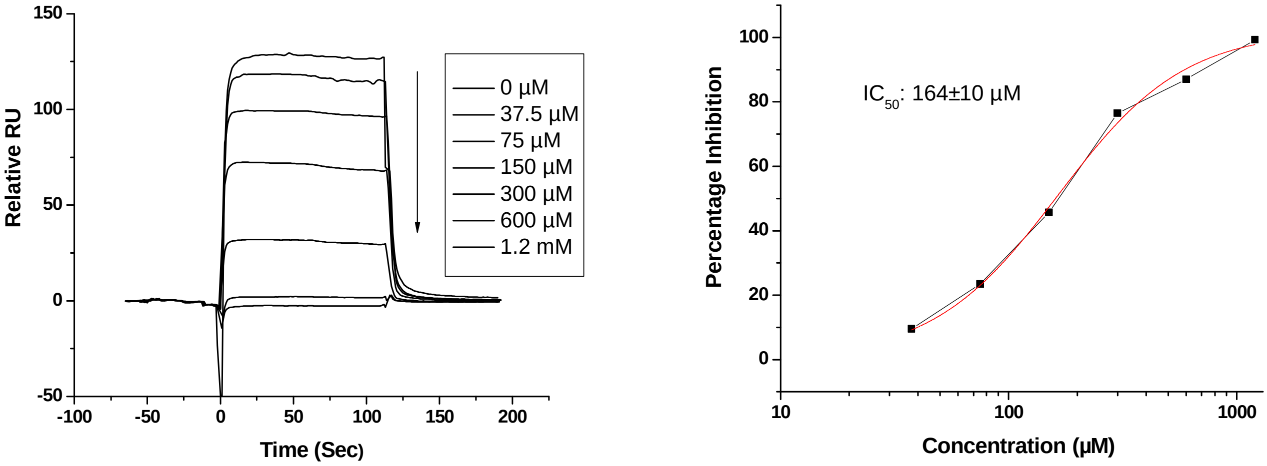


Figure S243. (*left*) Sensorgrams obtained by injection of truncated hGal-3 (7.5 µM) lectin incubated with different concentrations of monomeric **43** varying from 37.5 µM (top curve) to 1.2 mM (bottom curve) on the surface of immobilized lactoside **42**. (*right*) The inhibitory curve for the compound **43**.

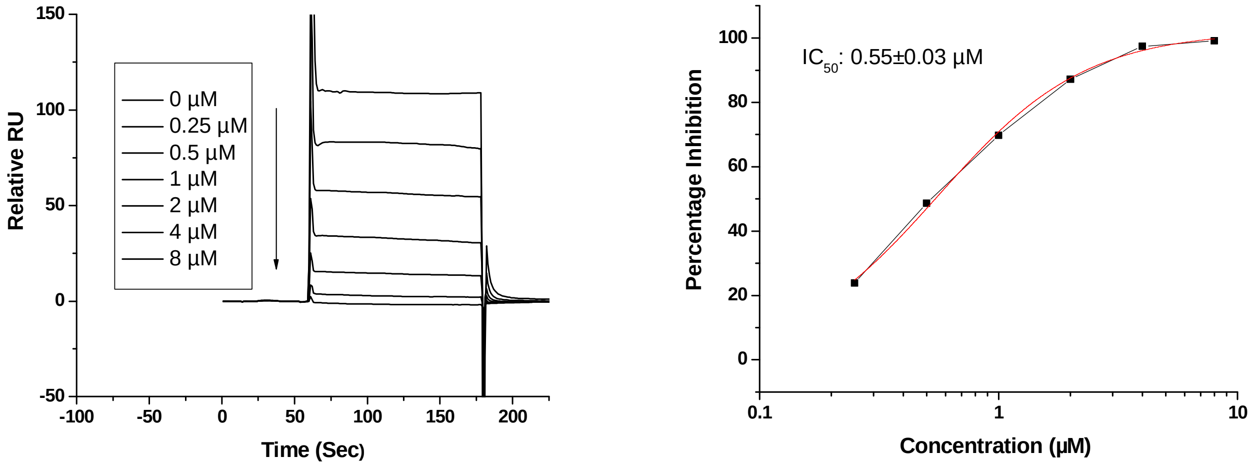


Figure S244. (*left*) Sensorgrams obtained by injection of truncated hGal-3 (7.5 µM) lectin incubated with different concentrations of hexavalent **18** varying from 0.25 µM (top curve) to 8 µM (bottom curve) on the surface of immobilized lactoside **42**. (*right*) The inhibitory curve for the compound **18**.

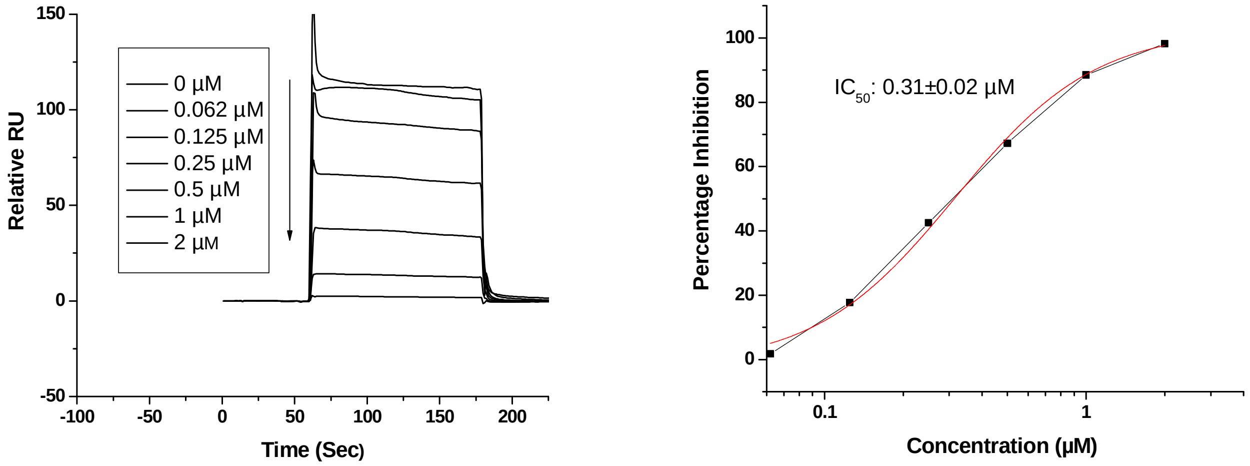


Figure S245. (*left*) Sensorgrams obtained by injection of truncated hGal-3 (7.5 µM) lectin incubated with different concentrations of decavalent **22** varying from 0.062 µM (top curve) to 2 µM (bottom curve) on the surface of immobilized lactoside **42**. (*right*) The inhibitory curve for the compound **22**.

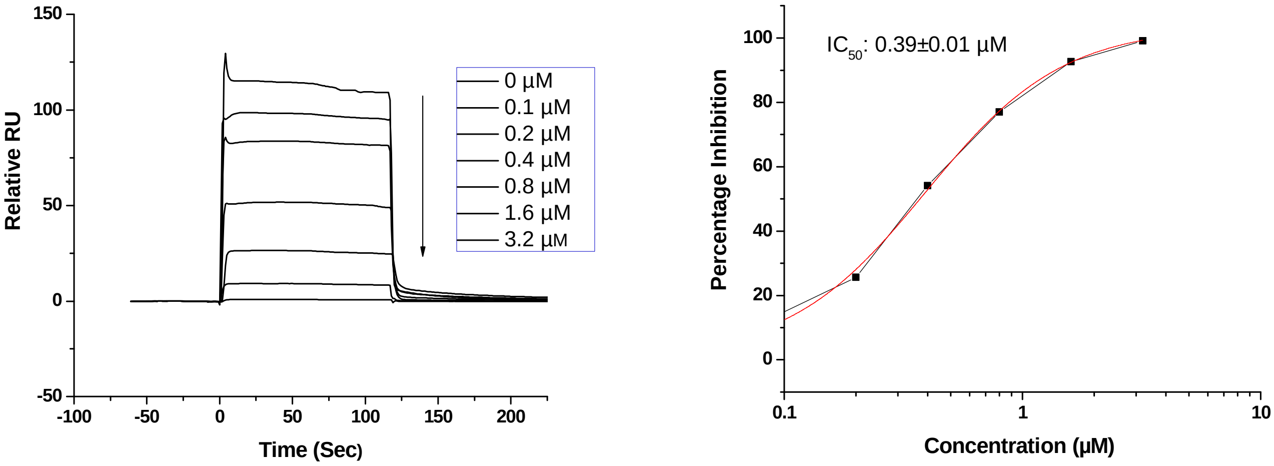


Figure S246. (*left*) Sensorgrams obtained by injection of truncated hGal-3 (7.5 μM) lectin incubated with different concentrations of pentadecavalent **27** varying from 0.1 μM (top curve) to 3.2 μM (bottom curve) on the surface of immobilized lactoside **42**. (*right*) The inhibitory curve for the compound **27**.

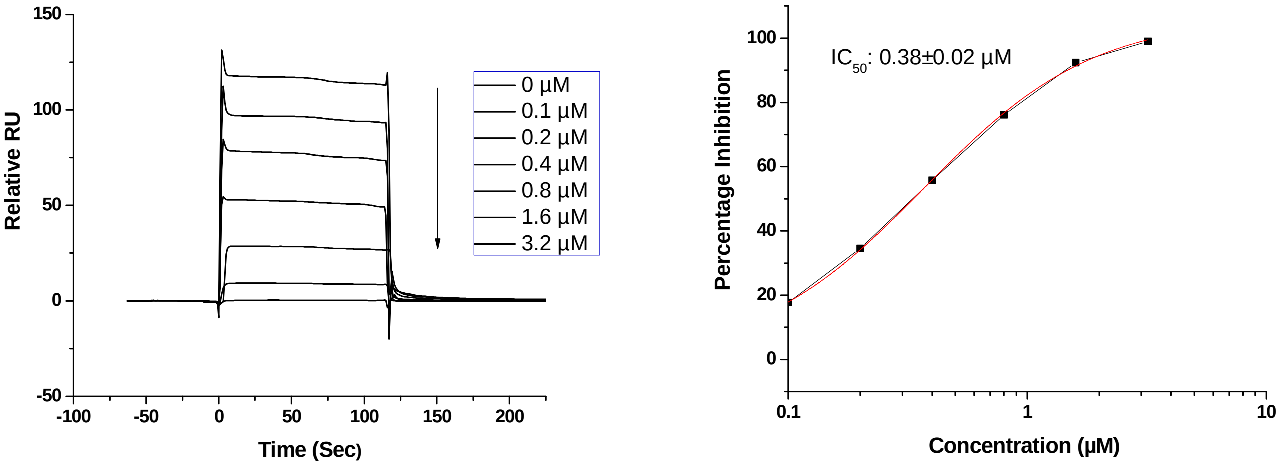


Figure S247. (*left*) Sensorgrams obtained by injection of truncated hGal-3 (7.5 μM) lectin incubated with different concentrations of octadecavalent **19** varying from 0.1 μM (top curve) to 3.2 μM (bottom curve) on the surface of immobilized lactoside **42**. (*right*) The inhibitory curve for the compound **19**.

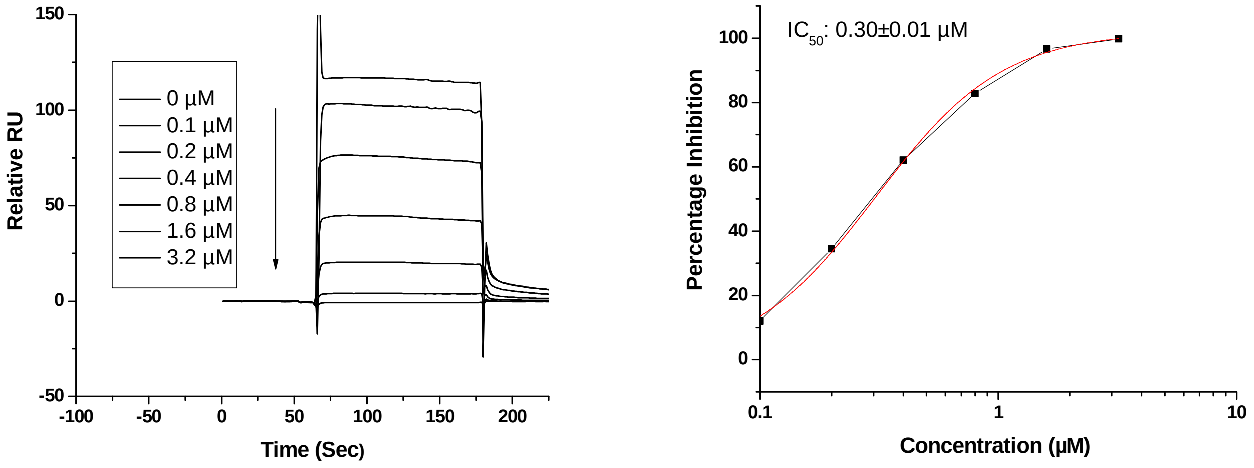


Figure S248. (*left*) Sensorgrams obtained by injection of truncated hGal-3 (7.5 µM) lectin incubated with different concentrations of tricontavalent **28** varying from 0.1 µM (top curve) to 3.2 µM (bottom curve) on the surface of immobilized lactoside **42**. (*right*) The inhibitory curve for the compound **28**.

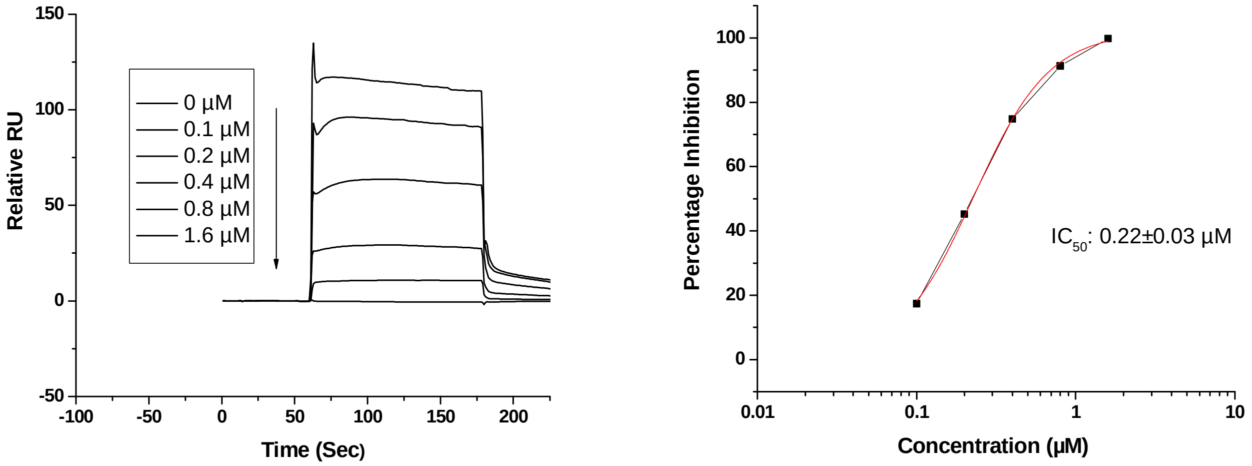


Figure S249. (*left*) Sensorgrams obtained by injection of truncated hGal-3 (7.5 µM) lectin incubated with different concentrations of tricontavalent **38** varying from 0.1 µM (top curve) to 1.6 µM (bottom curve) on the surface of immobilized lactoside **42**. (*right*) The inhibitory curve for the compound **38**.

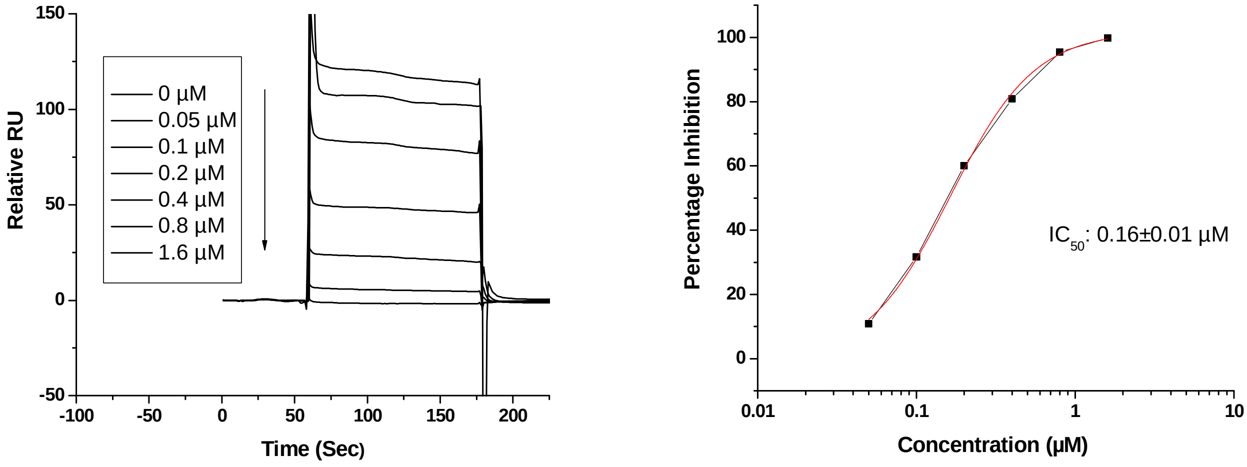


Figure S250. (*left*) Sensorgrams obtained by injection of truncated hGal-3 (7.5 µM) lectin incubated with different concentrations of nonacontavalent **41** varying from 0.05 µM (top curve) to 1.6 µM (bottom curve) on the surface of immobilized lactoside **42**. (*right*) The inhibitory curve for the compound **41**.

5. X-Ray crystallographic analysis

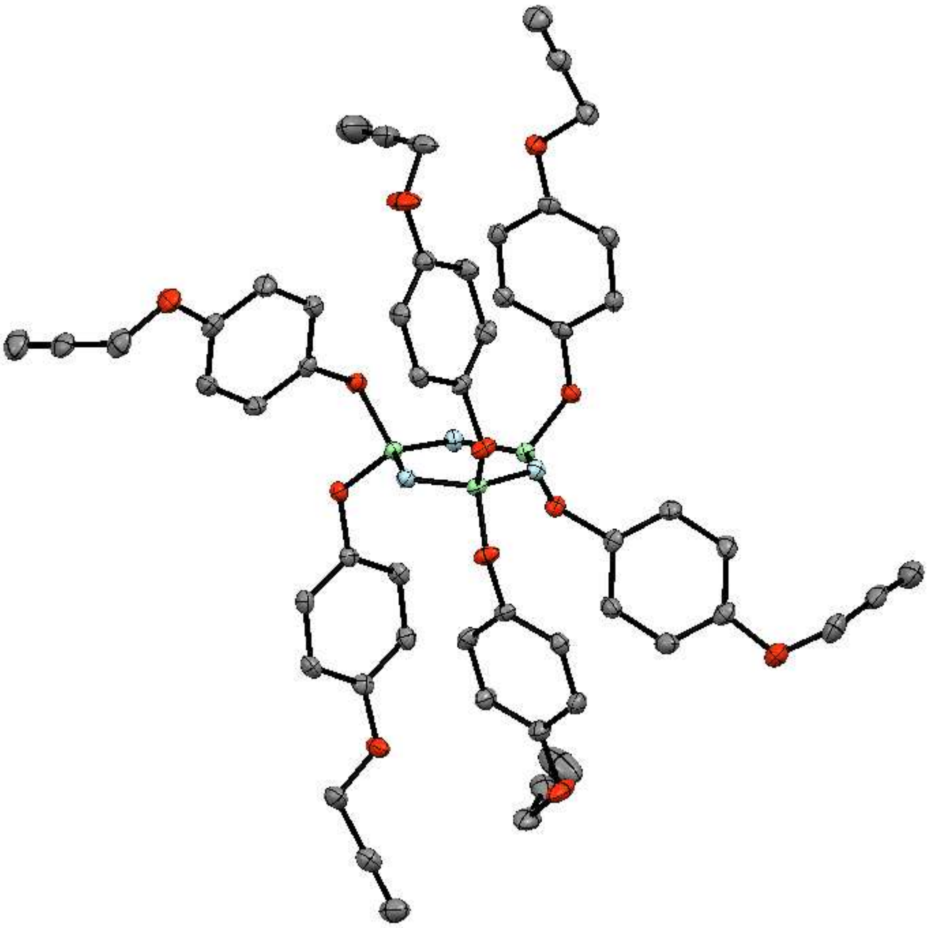
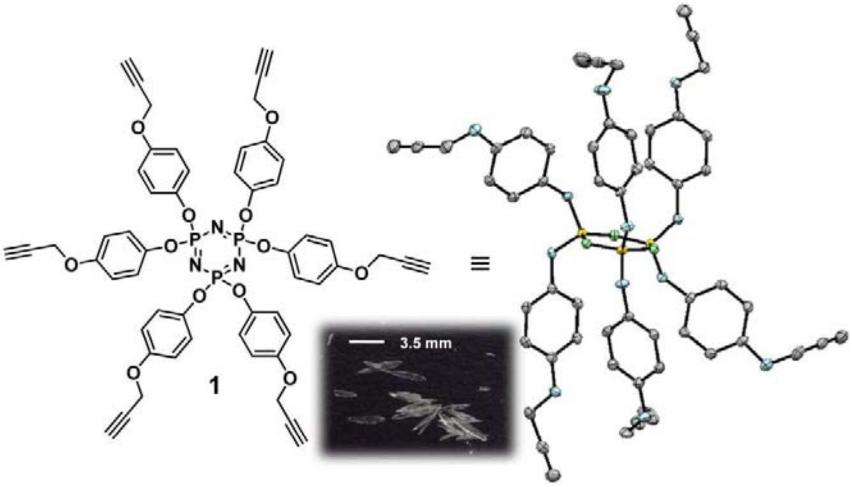


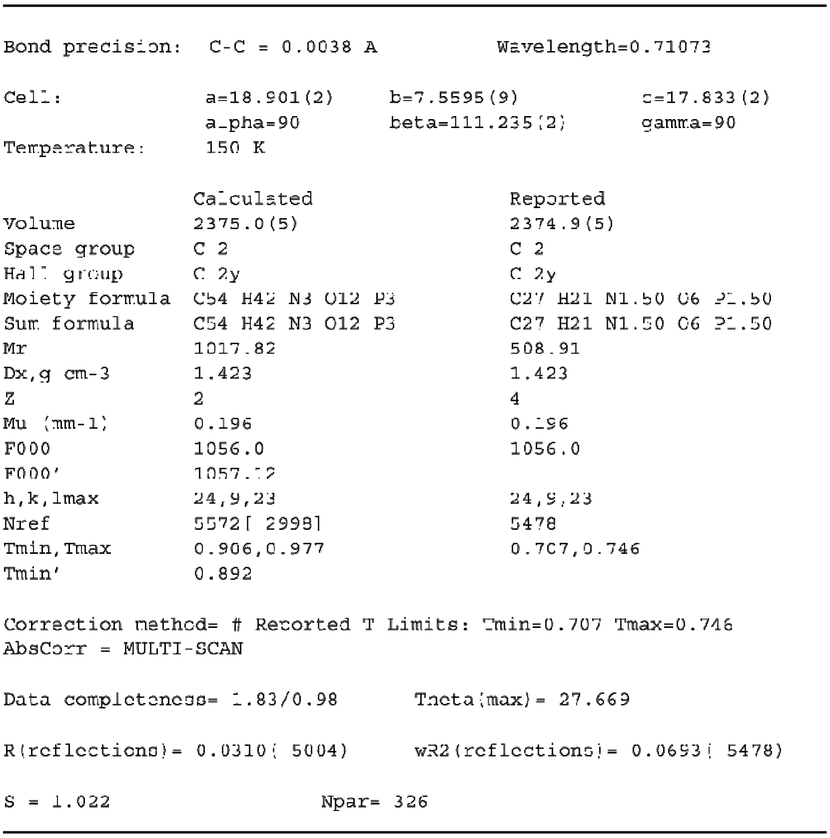
Figure S251. ORTEP at 50% thermal ellipsoid probability of the elementary unit cell of **1**. Hydrogen atoms are omitted for clarity.

Crystal Structure Report for 1

A colorless plate-like specimen of $C_{27}H_{21}N_{1.50}O_6P_{1.50}$, approximate dimensions 0.120 mm × 0.418 mm × 0.583 mm, was used for X-ray crystallographic analysis on a Bruker APEX DUOusing Molybdenum radiation (0.71073Å wavelength) at 150K. A total of 1464 frames were collected. The total exposure time was 4.07 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 14096 reflections to a maximum θ angle of 27.67° (0.77 Å resolution), of which 5478 were independent (average redundancy 2.573, completeness = 99.3%, R_{int} = 2.64%) and 5004 (91.35%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 18.901(2) Å, $\underline{b}$ = 7.5595(9) Å, $\underline{c}$ = 17.833(2) Å, β = 111.235(2)°, volume = 2375.0(5) $Å^3$, are based upon the refinement of the XYZ-centroids of 5832 reflections above 20 σ(I) with 4.624° < 2 θ < 55.03°. Data were corrected for absorption effec ts using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.948. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7066 and 0.7456. The structure was solved and refined using the Bruker

SHELXTL Software Package, using the space group C 1 2 1 (*C*2, #5), with Z = 4 for the formula unit, $C_{27}H_{21}N_{1.50}O_6P_{1.50}$. The final anisotropic full-matrix least-squares refinement on F^2 with 326 variables converged at R1 = 3.10%, for the observed data and wR2 = 6.93% for all data. The goodness-of-fit was 1.022. The largest peak in the final difference electron density synthesis was 0.213 $e^-/Å^3$ and the largest hole was -0.296 $e^-/Å^3$ with an RMS deviation of 0.041 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.423 g/cm^3 and F(000), 1056 e^-.





```
Bond precision:  C-C = 0.0038 A          Wavelength=0.71073

Cell:            a=18.901(2)     b=7.5595(9)         c=17.833(2)
                 alpha=90        beta=111.235(2)     gamma=90
Temperature:     150 K

                Calculated                  Reported
Volume          2375.0(5)                   2374.9(5)
Space group     C 2                         C 2
Hall group      C 2y                        C 2y
Moiety formula  C54 H42 N3 O12 P3           C27 H21 N1.50 O6 P1.50
Sum formula     C54 H42 N3 O12 P3           C27 H21 N1.50 O6 P1.50
Mr              1017.82                     508.91
Dx,g cm-3       1.423                       1.423
Z               2                           4
Mu (mm-1)       0.196                       0.196
F000            1056.0                      1056.0
F000'           1057.12
h,k,lmax        24,9,23                     24,9,23
Nref            5572[ 2998]                 5478
Tmin,Tmax       0.906,0.977                 0.707,0.746
Tmin'           0.892

Correction method= # Reported T Limits: Tmin=0.707 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.83/0.98       Theta(max)= 27.669

R(reflections)= 0.0310( 5004)      wR2(reflections)= 0.0693( 5478)

S = 1.022                   Npar= 326
```

Table S1. Information on sample, data collection and structure refinement for **1**.

Chemical formula	$C_{27}H_{21}N_{1.50}O_6P_{1.50}$	
Formula weight	508.91 g/mol	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal size	0.120 x 0.418 x 0.583 mm	
Crystal habit	colorless plate	
Crystal system	monoclinic	
Space group	C 1 2 1	
Unit cell dimensions	a = 18.901(2) Å	α = 90°
	b = 7.5595(9) Å	β = 111.235(2)°
	c = 17.833(2) Å	γ = 90°
Volume	2375.0(5) $Å^3$	
Z	4	
Density (calculated)	1.423 g/cm^3	
Absorption coefficient	0.196 mm^{-1}	
F(000)	1056	
Theta range for data collection	1.23 to 27.67°	
Index ranges	-24<=h<=24, -9<=k<=9, -23<=l<=23	
Reflections collected	14096	
Independent reflections	5478 [R(int) = 0.0264]	
Coverage of independent reflections	99.3%	
Absorption correction	multi-scan	
Max. and min. transmission	0.7456 and 0.7066	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5478 / 1 / 326	
Goodness-of-fit on F^2	1.022	
Δ/σ_{max}	0.001	
Final R indices	5004 data; $I>2\sigma(I)$	R1 = 0.0310, wR2 = 0.0667
	all data	R1 = 0.0366, wR2 = 0.0693
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0329P)^2+0.6412P]$	
Absolute structure parameter	0.1(0)	
Largest diff. peak and hole	0.213 and -0.296 $eÅ^{-3}$	
R.M.S. deviation from mean	0.041 $eÅ^{-3}$	

Table S2. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
P1	0.5	0.44796(10)	0.5	0.01529(18)
P2	0.56920(3)	0.12904(8)	0.56291(3)	0.01511(13)
O1	0.43407(11)	0.5366(3)	0.84159(11)	0.0392(5)
O2	0.47457(9)	0.5908(2)	0.55014(9)	0.0208(4)
O3	0.57376(9)	0.0657(2)	0.64912(9)	0.0189(4)
O4	0.73128(10)	0.3698(3)	0.94575(10)	0.0307(4)
O5	0.64702(9)	0.0459(2)	0.56383(9)	0.0185(3)
O6	0.73530(9)	0.0805(2)	0.30021(10)	0.0250(4)
N1	0.57058(11)	0.3380(2)	0.55677(12)	0.0173(4)
N2	0.5	0.0275(4)	0.5	0.0176(6)
C1	0.4482(2)	0.0901(7)	0.8859(2)	0.0698(13)
C2	0.41918(16)	0.2305(5)	0.87093(18)	0.0413(7)
C3	0.38492(17)	0.4062(4)	0.85576(17)	0.0353(7)
C4	0.44249(14)	0.5345(4)	0.76777(15)	0.0241(5)
C5	0.49528(13)	0.6538(3)	0.75968(14)	0.0230(5)
C6	0.50670(13)	0.6666(3)	0.68761(14)	0.0196(5)
C7	0.46537(13)	0.5594(3)	0.62387(13)	0.0173(5)
C8	0.61731(12)	0.1472(3)	0.72243(13)	0.0185(5)
C9	0.58092(13)	0.1761(3)	0.77627(14)	0.0232(5)
C10	0.62149(14)	0.2494(4)	0.85069(15)	0.0275(6)
C11	0.69723(15)	0.2937(3)	0.87079(14)	0.0228(5)
C12	0.80545(16)	0.4430(4)	0.96475(16)	0.0323(6)
C13	0.86563(16)	0.3102(4)	0.99559(15)	0.0304(6)
C14	0.91374(17)	0.2044(5)	0.02319(16)	0.0406(7)
C15	0.66949(13)	0.0541(3)	0.49653(14)	0.0173(5)
C16	0.62500(13)	0.9803(3)	0.42358(14)	0.0195(5)
C17	0.65023(13)	0.9886(3)	0.35964(15)	0.0209(5)
C18	0.71914(13)	0.0683(3)	0.36929(14)	0.0199(5)
C19	0.80514(14)	0.1635(4)	0.30645(15)	0.0263(6)
C20	0.80208(14)	0.2071(3)	0.22548(15)	0.0258(6)
C21	0.80047(16)	0.2484(4)	0.16158(17)	0.0362(7)
C22	0.76514(12)	0.1327(4)	0.44404(13)	0.0218(5)
C23	0.73919(12)	0.1275(4)	0.50782(14)	0.0204(5)
C24	0.73338(14)	0.2623(3)	0.81697(14)	0.0241(5)
C25	0.69281(14)	0.1885(3)	0.74190(14)	0.0231(5)
C26	0.40214(14)	0.4266(3)	0.70432(14)	0.0237(5)
C27	0.41313(14)	0.4403(3)	0.63109(14)	0.0225(5)

Table S3. Bond lengths (Å) for **1**.

P1-O2	1.5839(16)	P1-O2	1.5839(16)
P1-N1	1.587(2)	P1-N1	1.587(2)
P2-N2	1.5799(14)	P2-O3	1.5825(16)
P2-N1	1.584(2)	P2-O5	1.5943(16)
O1-C4	1.382(3)	O1-C3	1.438(3)
O2-C7	1.407(3)	O3-C8	1.410(3)
O4-C11	1.382(3)	O4-C12	1.429(3)
O5-C15	1.412(3)	O6-C18	1.375(3)
O6-C19	1.429(3)	N2-P2	1.5798(14)
C1-C2	1.180(5)	C1-H1	0.95
C2-C3	1.459(5)	C3-H19	0.99
C3-H18	0.99	C4-C26	1.379(3)
C4-C5	1.391(3)	C5-C6	1.382(3)
C5-H3	0.95	C6-C7	1.384(3)
C6-H4	0.95	C7-C27	1.376(3)
C8-C25	1.377(3)	C8-C9	1.386(3)
C9-C10	1.385(3)	C9-H12	0.95
C10-C11	1.385(4)	C10-H17	0.95
C11-C24	1.385(3)	C12-C13	1.466(4)
C12-H15	0.99	C12-H16	0.99
C13-C14	1.177(4)	C14-H2	0.95
C15-C23	1.375(3)	C15-C16	1.385(3)
C16-C17	1.387(3)	C16-H5	0.95
C17-C18	1.388(3)	C17-H6	0.95
C18-C22	1.389(3)	C19-C20	1.462(3)
C19-H9	0.99	C19-H8	0.99
C20-C21	1.171(4)	C21-H7	0.95
C22-C23	1.393(3)	C22-H11	0.95
C23-H10	0.95	C24-C25	1.396(3)
C24-H13	0.95	C25-H14	0.95
C26-C27	1.398(3)	C26-H20	0.95
C27-H21	0.95		

Table S4. Bond angles (°) for **1**.

O2-P1-O2	94.00(12)	O2-P1-N1	111.14(9)
O2-P1-N1	110.74(9)	O2-P1-N1	110.74(9)
O2-P1-N1	111.14(9)	N1-P1-N1	116.79(15)
N2-P2-O3	106.41(8)	N2-P2-N1	117.75(12)
O3-P2-N1	111.87(10)	N2-P2-O5	109.82(9)
O3-P2-O5	98.35(9)	N1-P2-O5	110.84(10)
C4-O1-C3	117.7(2)	C7-O2-P1	125.28(14)
C8-O3-P2	125.21(14)	C11-O4-C12	117.6(2)
C15-O5-P2	122.29(14)	C18-O6-C19	117.27(18)
P2-N1-P1	122.38(13)	P2-N2-P2	121.84(18)
C2-C1-H1	180.0	C1-C2-C3	177.7(4)
O1-C3-C2	112.6(2)	O1-C3-H19	109.1
C2-C3-H19	109.1	O1-C3-H18	109.1
C2-C3-H18	109.1	H19-C3-H18	107.8
C26-C4-O1	124.6(2)	C26-C4-C5	120.2(2)
O1-C4-C5	115.2(2)	C6-C5-C4	120.1(2)
C6-C5-H3	120.0	C4-C5-H3	120.0
C5-C6-C7	119.4(2)	C5-C6-H4	120.3
C7-C6-H4	120.3	C27-C7-C6	121.1(2)
C27-C7-O2	122.2(2)	C6-C7-O2	116.4(2)
C25-C8-C9	121.2(2)	C25-C8-O3	122.5(2)
C9-C8-O3	116.2(2)	C10-C9-C8	119.0(2)
C10-C9-H12	120.5	C8-C9-H12	120.5
C11-C10-C9	120.4(2)	C11-C10-H17	119.8
C9-C10-H17	119.8	O4-C11-C10	115.3(2)
O4-C11-C24	124.6(2)	C10-C11-C24	120.1(2)
O4-C12-C13	112.7(2)	O4-C12-H15	109.1
C13-C12-H15	109.1	O4-C12-H16	109.1
C13-C12-H16	109.1	H15-C12-H16	107.8
C14-C13-C12	177.4(3)	C13-C14-H2	180.0
C23-C15-C16	121.6(2)	C23-C15-O5	117.4(2)
C16-C15-O5	120.9(2)	C15-C16-C17	118.8(2)
C15-C16-H5	120.6	C17-C16-H5	120.6
C16-C17-C18	120.3(2)	C16-C17-H6	119.9
C18-C17-H6	119.9	O6-C18-C17	114.9(2)
O6-C18-C22	124.8(2)	C17-C18-C22	120.3(2)
O6-C19-C20	108.5(2)	O6-C19-H9	110.0
C20-C19-H9	110.0	O6-C19-H8	110.0
C20-C19-H8	110.0	H9-C19-H8	108.4
C21-C20-C19	177.5(3)	C20-C21-H7	180.0
C18-C22-C23	119.4(2)	C18-C22-H11	120.3
C23-C22-H11	120.3	C15-C23-C22	119.6(2)
C15-C23-H10	120.2	C22-C23-H10	120.2
C11-C24-C25	119.7(2)	C11-C24-H13	120.1
C25-C24-H13	120.1	C8-C25-C24	119.5(2)
C8-C25-H14	120.3	C24-C25-H14	120.3
C4-C26-C27	119.8(2)	C4-C26-H20	120.1
C27-C26-H20	120.1	C7-C27-C26	119.3(2)

C7-C27-H21	120.3	C26-C27-H21	120.3

Table S5. Torsion angles (°) for **1**.

O2-P1-O2-C7	-160.5(2)	N1-P1-O2-C7	-46.1(2)
N1-P1-O2-C7	85.43(19)	N2-P2-O3-C8	-166.90(17)
N1-P2-O3-C8	-37.0(2)	O5-P2-O3-C8	79.50(18)
N2-P2-O5-C15	64.96(18)	O3-P2-O5-C15	175.84(17)
N1-P2-O5-C15	-66.86(19)	N2-P2-N1-P1	9.92(18)
O3-P2-N1-P1	-113.81(14)	O5-P2-N1-P1	137.52(13)
O2-P1-N1-P2	-133.46(13)	O2-P1-N1-P2	123.45(14)
N1-P1-N1-P2	-5.10(9)	O3-P2-N2-P2	121.66(7)
N1-P2-N2-P2	-4.76(9)	O5-P2-N2-P2	-132.85(7)
C4-O1-C3-C2	75.2(3)	C3-O1-C4-C26	5.9(4)
C3-O1-C4-C5	-175.0(2)	C26-C4-C5-C6	1.0(4)
O1-C4-C5-C6	-178.2(2)	C4-C5-C6-C7	-0.2(4)
C5-C6-C7-C27	0.0(3)	C5-C6-C7-O2	174.2(2)
P1-O2-C7-C27	-61.8(3)	P1-O2-C7-C6	124.1(2)
P2-O3-C8-C25	-49.7(3)	P2-O3-C8-C9	133.50(19)
C25-C8-C9-C10	0.6(4)	O3-C8-C9-C10	177.5(2)
C8-C9-C10-C11	0.2(4)	C12-O4-C11-C10	-170.6(2)
C12-O4-C11-C24	8.9(4)	C9-C10-C11-O4	178.5(2)
C9-C10-C11-C24	-1.1(4)	C11-O4-C12-C13	-84.8(3)
P2-O5-C15-C23	124.8(2)	P2-O5-C15-C16	-59.4(3)
C23-C15-C16-C17	-3.1(3)	O5-C15-C16-C17	-178.7(2)
C15-C16-C17-C18	0.5(3)	C19-O6-C18-C17	179.2(2)
C19-O6-C18-C22	0.9(3)	C16-C17-C18-O6	-175.2(2)
C16-C17-C18-C22	3.2(4)	C18-O6-C19-C20	-164.5(2)
O6-C18-C22-C23	173.9(2)	C17-C18-C22-C23	-4.3(4)
C16-C15-C23-C22	1.9(4)	O5-C15-C23-C22	177.6(2)
C18-C22-C23-C15	1.9(4)	O4-C11-C24-C25	-178.4(2)
C10-C11-C24-C25	1.1(4)	C9-C8-C25-C24	-0.6(4)
O3-C8-C25-C24	-177.3(2)	C11-C24-C25-C8	-0.3(4)
O1-C4-C26-C27	177.5(2)	C5-C4-C26-C27	-1.5(4)
C6-C7-C27-C26	-0.5(4)	O2-C7-C27-C26	-174.4(2)
C4-C26-C27-C7	1.2(4)		

Table S6. Anisotropic atomic displacement parameters (Å^2) for **1**.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + \ldots + 2hka^{*}b^{*}U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P1	0.0195(4)	0.0119(4)	0.0153(4)	0	0.0074(3)	0
P2	0.0151(3)	0.0138(3)	0.0161(3)	0.0011(2)	0.0052(2)	0.0002(2)
O1	0.0473(12)	0.0541(14)	0.0242(10)	-0.0145(9)	0.0224(9)	-0.0265(11)
O2	0.0321(9)	0.0151(9)	0.0181(8)	0.0014(6)	0.0125(7)	0.0047(7)
O3	0.0202(8)	0.0186(8)	0.0176(8)	0.0012(7)	0.0064(7)	-0.0032(7)
O4	0.0303(10)	0.0401(11)	0.0205(9)	-0.0051(9)	0.0076(8)	-0.0025(9)
O5	0.0157(8)	0.0205(9)	0.0195(8)	0.0015(7)	0.0065(6)	0.0026(7)
O6	0.0216(8)	0.0328(11)	0.0236(9)	-0.0052(7)	0.0118(7)	-0.0064(7)
N1	0.0175(10)	0.0168(10)	0.0173(10)	0.0003(8)	0.0059(8)	-0.0019(8)
N2	0.0163(14)	0.0144(14)	0.0203(15)	0	0.0043(11)	0
C1	0.056(2)	0.090(3)	0.077(3)	0.046(3)	0.040(2)	0.025(2)
C2	0.0310(15)	0.063(2)	0.0332(15)	0.0135(17)	0.0159(12)	-0.0039(17)
C3	0.0364(15)	0.0485(19)	0.0286(15)	-0.0052(13)	0.0210(13)	-0.0161(14)
C4	0.0236(13)	0.0301(14)	0.0202(12)	-0.0033(11)	0.0098(10)	-0.0053(11)
C5	0.0219(12)	0.0262(14)	0.0191(11)	-0.0057(10)	0.0053(9)	-0.0062(10)
C6	0.0176(11)	0.0174(12)	0.0232(12)	0.0000(9)	0.0066(9)	-0.0010(9)
C7	0.0225(12)	0.0157(11)	0.0141(11)	0.0019(9)	0.0072(9)	0.0059(10)
C8	0.0210(11)	0.0160(12)	0.0163(11)	0.0031(9)	0.0041(9)	0.0010(10)
C9	0.0176(11)	0.0300(14)	0.0219(12)	0.0042(10)	0.0071(9)	0.0040(10)
C10	0.0264(13)	0.0362(15)	0.0220(12)	0.0007(12)	0.0112(10)	0.0064(12)
C11	0.0276(13)	0.0225(13)	0.0161(12)	0.0016(9)	0.0052(10)	0.0015(10)
C12	0.0362(15)	0.0326(15)	0.0221(13)	-0.0056(12)	0.0033(11)	-0.0064(13)
C13	0.0323(15)	0.0400(16)	0.0168(13)	-0.0047(12)	0.0063(12)	-0.0070(13)
C14	0.0386(16)	0.054(2)	0.0251(14)	-0.0030(14)	0.0068(12)	0.0074(16)
C15	0.0175(11)	0.0155(11)	0.0204(12)	0.0026(9)	0.0086(9)	0.0050(9)
C16	0.0182(12)	0.0161(12)	0.0245(13)	-0.0015(10)	0.0081(10)	-0.0006(9)
C17	0.0187(12)	0.0200(12)	0.0221(12)	-0.0039(10)	0.0052(10)	-0.0004(9)
C18	0.0212(12)	0.0174(12)	0.0230(12)	-0.0006(9)	0.0104(10)	0.0031(9)
C19	0.0218(12)	0.0298(15)	0.0277(13)	0.0001(11)	0.0096(10)	-0.0054(10)
C20	0.0236(13)	0.0239(14)	0.0323(14)	-0.0018(11)	0.0131(11)	-0.0016(11)
C21	0.0400(16)	0.0404(17)	0.0323(15)	0.0003(14)	0.0180(13)	-0.0071(14)
C22	0.0160(11)	0.0218(12)	0.0276(12)	-0.0013(11)	0.0080(9)	-0.0015(11)
C23	0.0175(11)	0.0210(12)	0.0197(11)	-0.0017(11)	0.0033(9)	-0.0001(11)
C24	0.0207(12)	0.0295(14)	0.0219(12)	0.0010(11)	0.0075(10)	-0.0059(11)
C25	0.0242(12)	0.0295(14)	0.0179(11)	0.0004(10)	0.0105(10)	-0.0016(10)
C26	0.0244(12)	0.0242(13)	0.0244(13)	-0.0050(10)	0.0111(10)	-0.0092(11)
C27	0.0261(13)	0.0197(12)	0.0200(12)	-0.0045(10)	0.0063(10)	-0.0011(11)

Table S7. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for **1**.

	x/a	**y/b**	**z/c**	**U(eq)**
H1	0.4715	-0.0230	0.8979	0.084
H19	0.3371	0.4007	0.8083	0.042
H18	0.3721	0.4430	0.9026	0.042
H3	0.5235	0.7266	0.8038	0.028
H4	0.5426	0.7482	0.6819	0.024
H12	0.5289	0.1460	0.7624	0.028
H17	0.5972	0.2694	0.8882	0.033
H15	0.8134	0.5372	1.0055	0.039
H16	0.8090	0.4978	0.9158	0.039
H2	0.9526	0.1190	1.0455	0.049
H5	0.5781	-0.0750	0.4174	0.023
H6	0.6202	-0.0605	0.3091	0.025
H9	0.8482	0.0825	0.3329	0.032
H8	0.8127	0.2724	0.3392	0.032
H7	0.7992	0.2820	0.1098	0.043
H11	0.8138	0.1799	0.4516	0.026
H10	0.7695	0.1743	0.5588	0.024
H13	0.7856	0.2908	0.8311	0.029
H14	0.7171	0.1669	0.7045	0.028
H20	0.3670	0.3433	0.7103	0.028
H21	0.3848	0.3681	0.5868	0.027