Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Perylenediimide-based glycoclusters as high affinity ligands of bacterial lectins: Synthesis, binding studies and anti-adhesive properties

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General procedures

All reagents for synthesis commercially available (highest purity available for reagent grade compounds) were used without further purification. Solvents were distilled over CaH_2 (CH_2Cl_2), Mg/I_2 (MeOH), Na/benzophenone (THF) or purchased dry. Reactions under microwave activation were performed on a Biotage Initiator system. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F_{254} (Merck). TLC plates were inspected by UV light (λ = 254 nm, 365 nm) and developed by treatment with a mixture of 10% H_2SO_4 in $EtOH/H_2O$ (95:5 v/v) followed by heating. Silica gel column chromatography was performed with silica gel Si 60 (40–63 μm). Optical rotation was measured using a Perkin Elmer polarimeter. NMR spectra were recorded at 293 K, unless stated otherwise. Chemical shifts are referenced relative to deuterated solvent residual peaks. The following abbreviations are used to explain the observed multiplicities: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; p, pseudo and b, broad. Complete signal assignments were based on 1D and 2D NMR correlations COSY and HSQC. High resolution (HR-ESI-QToF) mass spectra were recorded using a Bruker MicroToF-Q II XL spectrometer. The glycoclusters tested in bioassays were purified using automated purification systems with medium pressure chromatography on reverse C_{18} silica gel. Their purity was verified by ^1H and ^{13}C NMR techniques, indicating ca. 95% purity.

General procedure for 1,3-dipolar cycloadditions (Method A)

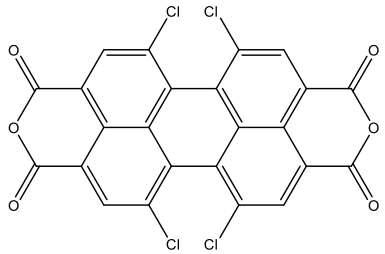
The alkyne-functionalized perylenediimide **5** or **6** (1 eq.), CuI (0.5 eq,), DIPEA (1.5 eq. per alkyne function) and azido-derivative **7** (1.5 eq. per alkyne function) in DMF were introduced into a Biotage Initiator 2-5 mL vial. The vial was sealed with a septum cap and heated at 110°C for 15 min under microwave irradiation (solvent absorption level : High). The crude mixture was concentrated and co-evaporated with toluene 6 times then purified by flash silica gel column chromatography to afford the desired cycloadducts.

General procedure for the Zemplén deacetylation (Method B)

To a suspension of acetylated glycocluster (1 eq.) in distilled MeOH was added MeONa (0.2 eq.). The mixture was stirred at r.t. for 16 hours, neutralized with Amberlite IR-120 resin (H^+ form), filtrated and concentrated *in vacuo* to afford the corresponding hydroxylated glycoclusters.

General procedure for removal of t-butyl protecting groups (Method C)

The *t*-butyl ester derivative (100 mg) was dissolved in CH_2Cl_2/TFA (15 mL, 2/1, v/v) and the solution was stirred at r.t. for 1 h. The progress of the reaction was followed by TLC. Once the removal was observed for all *t*-butyl groups, the solvents were removed under reduced pressure followed by drying under high vacuum. The removal of *t*-butyl groups was monitored by ^1H NMR and low resolution mass spectrometry. The crude material was then deacetylated according to ***Method B*** followed by purification with medium pressure chromatography on reverse C_{18} silica gel to provide the desired hydroxylated glycoclusters.



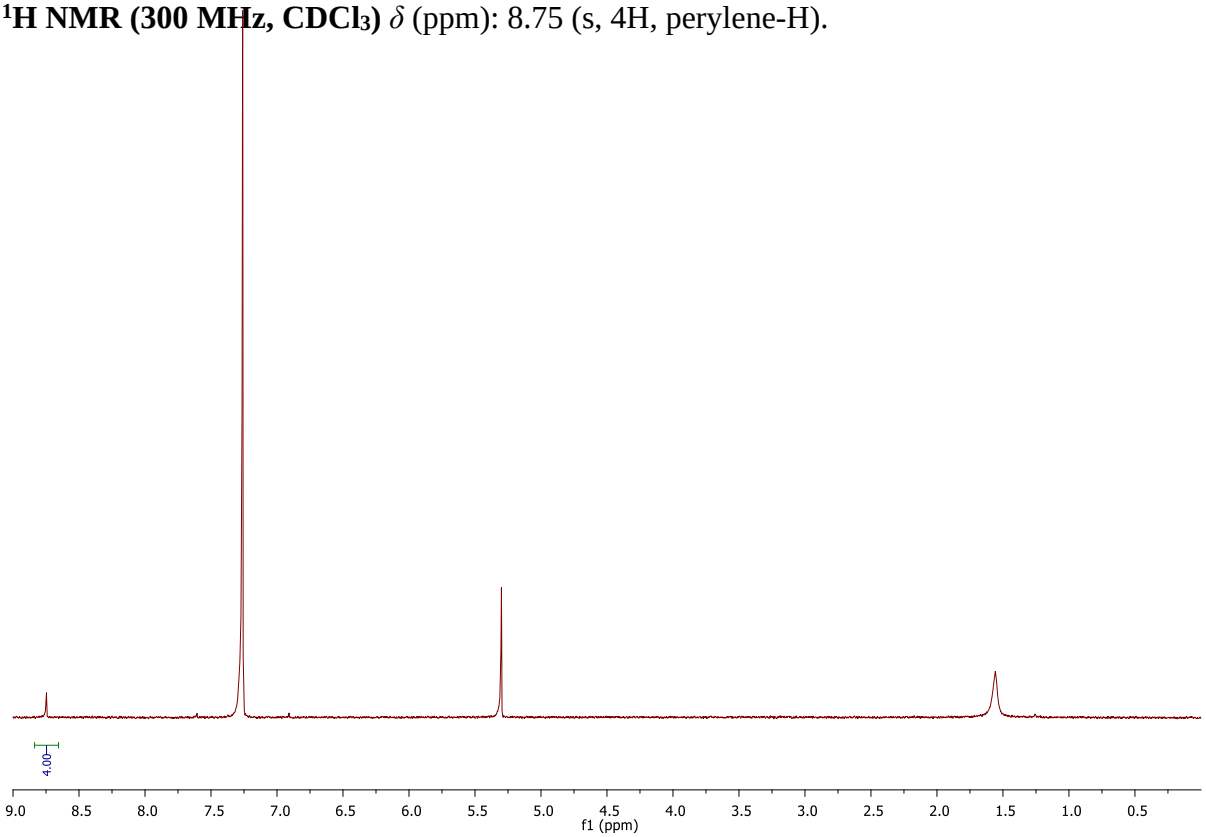
Nia, A. S. *et al. Tetrahedron* **2012**, *68*, 722-729.

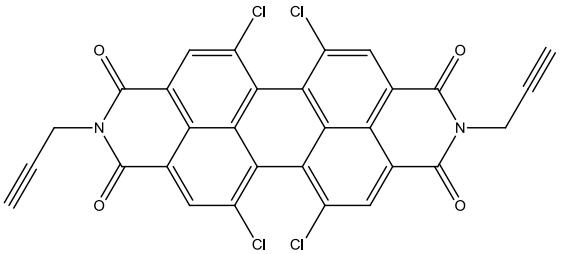
1,6,7,12-Tetrachloroperylene-3,4,9,10-tetracarboxylic dianhydride (2)

Iodine (1.62 g, 6.4 mmol, 0.25 eq.) was added to a solution of 3,4,9,10-perylene tetracarboxylic dianhydride (10 g, 25.5 mmol, 1 eq.) in chlorosulfonic acid (100 mL) at room temperature. The reacting mixture was heated to 70°C for 5 h. Afterwards, the mixture was poured slowly into an ice-water mixture (1 L). The insoluble product was collected by filtration and washed with water until pH reached 7. The crude product was dried at 100°C in oven for 24 h and purified by soxhlet extraction using dichloromethane as solvent during 9 days. The solvent was evaporated off to afford **2** as a red solid.

Yield = 85% (11.52 g).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.75 (s, 4H, perylene-H).



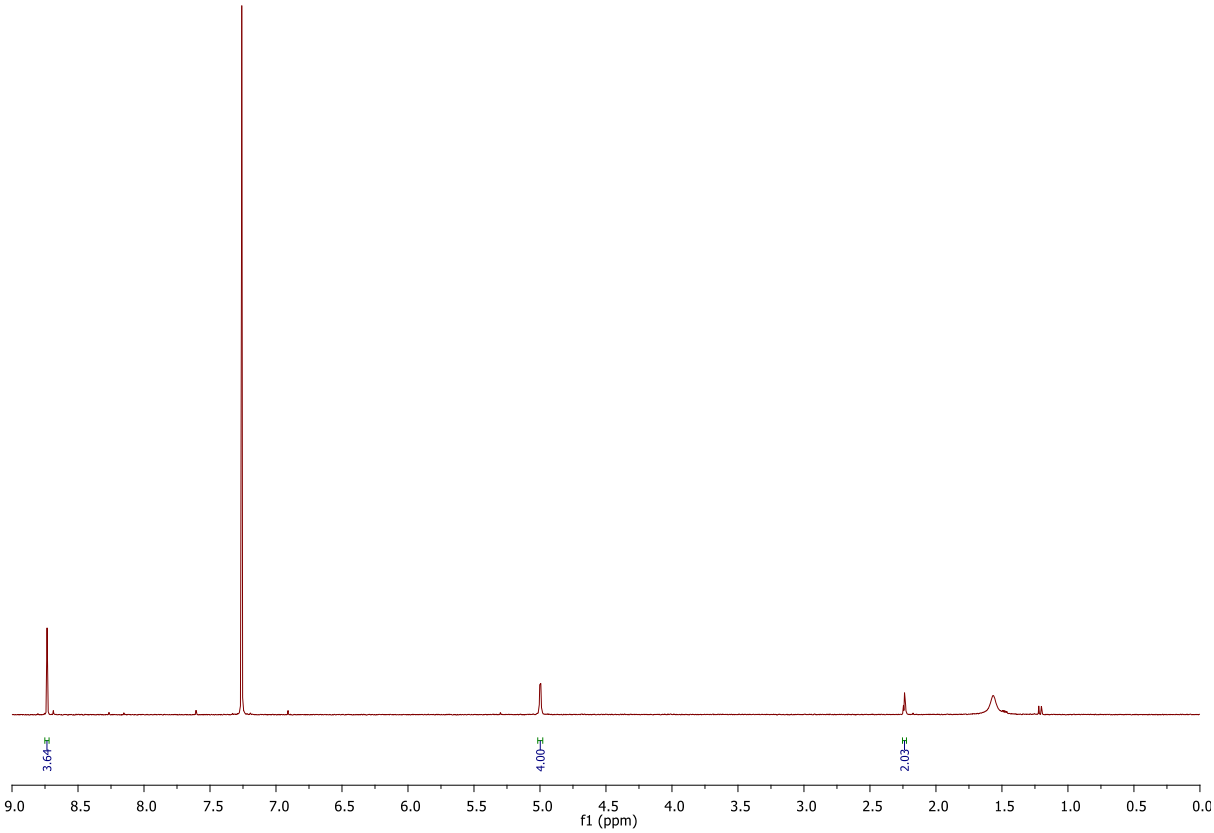


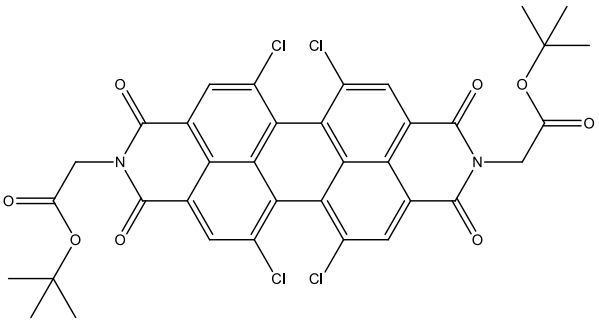
Wang, K.-R. *et al. Org. Biomol. Chem.* **2013**, *11*, 1007-1012.

***N*,*N*'-Bis-propargyl-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic diimide (3)**: Propargylamine (543 µL, 8.49 mmol, 3 eq.) was added to a suspension of **2** (1.50 g, 2.83 mmol, 1 eq.) in isopropanol (180 mL) and the mixture was heated at 90°C for 20 h. The mixture was then poured into water (500 mL) and the suspension was filtered to collect the red solid which was washed with water (2×50 mL) until neutral pH then methanol (2×50 mL). The residue was collected with CH_2Cl_2 (50 mL) and the solvent was evaporated off to afford **3** as a red solid.

Yield = quantitative (1.68 g); $\mathbf{R_f}$ = 0.35 (CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.73 (s, 4H, perylene-H), 5.00 (d, J = 2.4 Hz, 4H, NCH_2), 2.24 (t, J = 2.4 Hz, 2H, C≡CH).





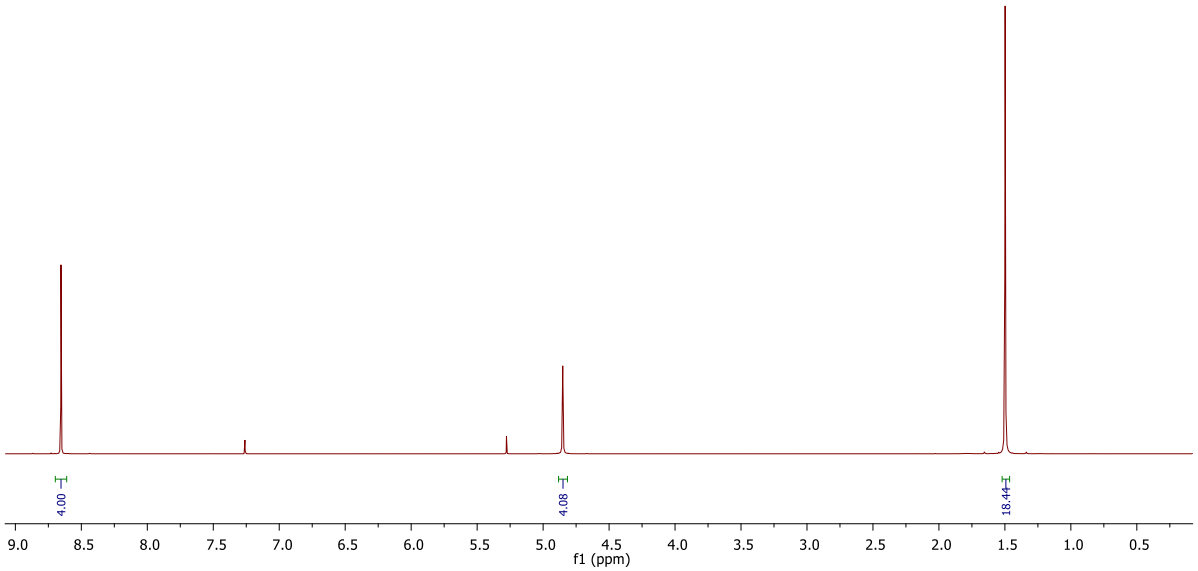
***N*,*N*'-Bis-(*t*-butoxycarbonylmethyl)-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic diimide (4)**: Triethylamine (188 µL, 1.36 mmol, 3.6 eq.) was added to a suspension of **2** (200 mg, 0.377 mmol, 1 eq.) and glycine *t*-butyl ester hydrochloride (190 mg, 1.13 mmol, 3 eq.) in isopropanol (10 mL). The mixture was stirred at 90°C for 22 h. The mixture was then poured into water (100 mL) and the red solid was filtered off then washed with water (2×10mL) until neutral pH. The red residue was collected with CH_2Cl_2 (50 mL) and the solvent was evaporated off. The crude solid was purified by silica gel flash chromatography (CH_2Cl_2/EtOAc 97/3) to afford **4** as a red solid.

Yield = 87% (247 mg); $\mathbf{R_f}$ = 0.30 (CH_2Cl_2/EtOAc 95/5).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.65 (s, 4H, perylene-H), 4.85 (s, 4H, NCH_2), 1.50 (s, 18H, CMe_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.6 (COO), 162.0 (NCO), 135.5 (CCl), 133.3 (CH-ar), 131.5 (C^{IV}-ar), 128.9 (C^{IV}-ar), 123.5 (C^{IV}-ar), 122.9 (C^{IV}-ar), 82.8 (*C*Me_3), 42.4 (NCH_2), 28.1 (C*Me*$_3$).

HR-ESI-QTof (positive mode) *m*/*z*: calcd for $C_{36}H_{26}Cl_4N_2NaO_8$ $[M+Na]^+$ 777.0335, found 777.0320.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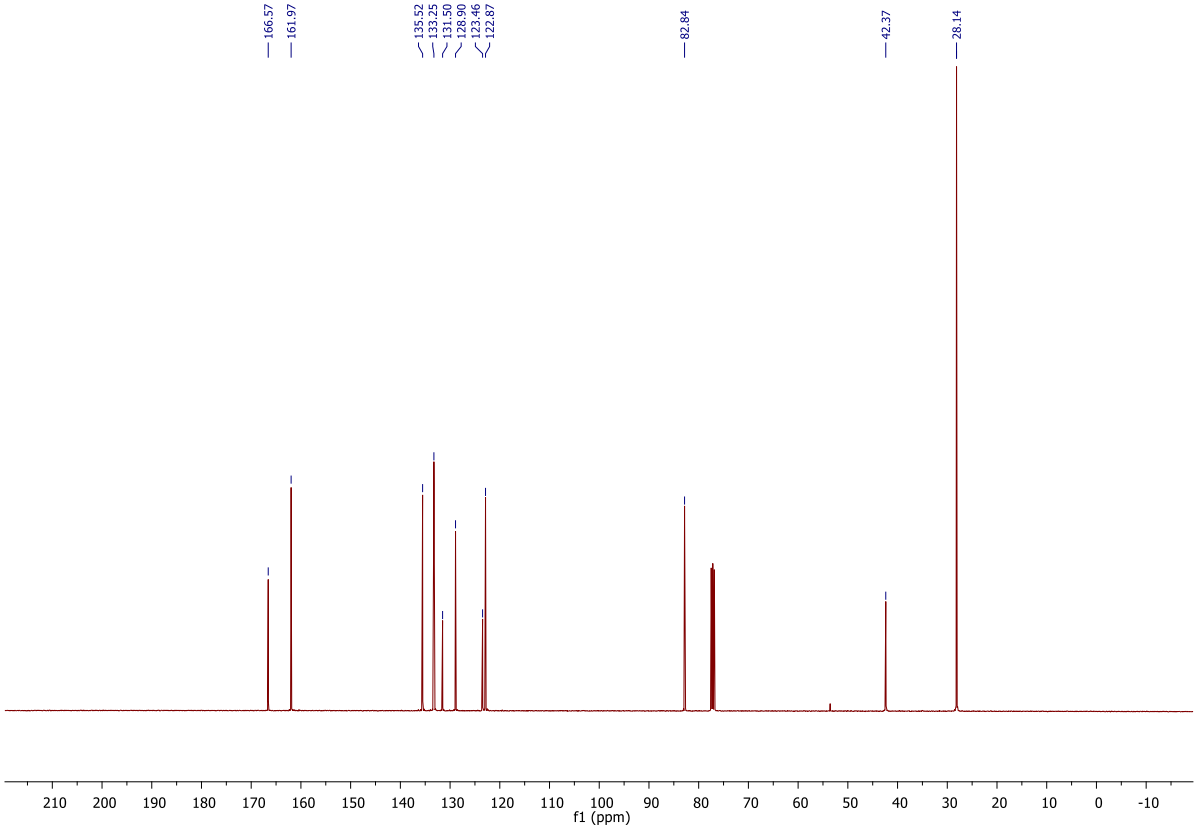
f1 (ppm)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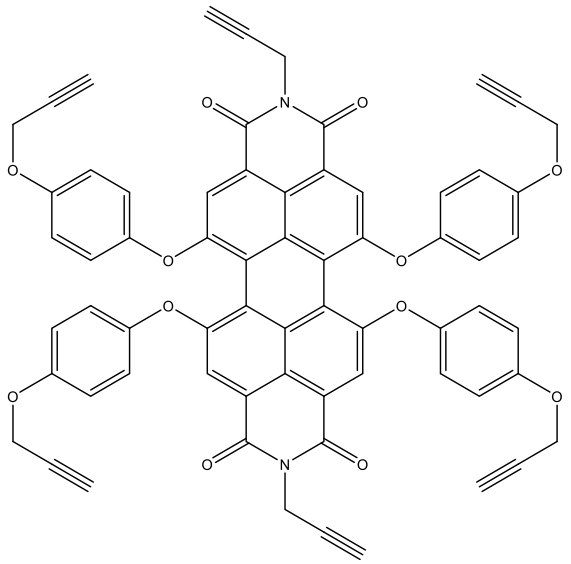
f1 (ppm)

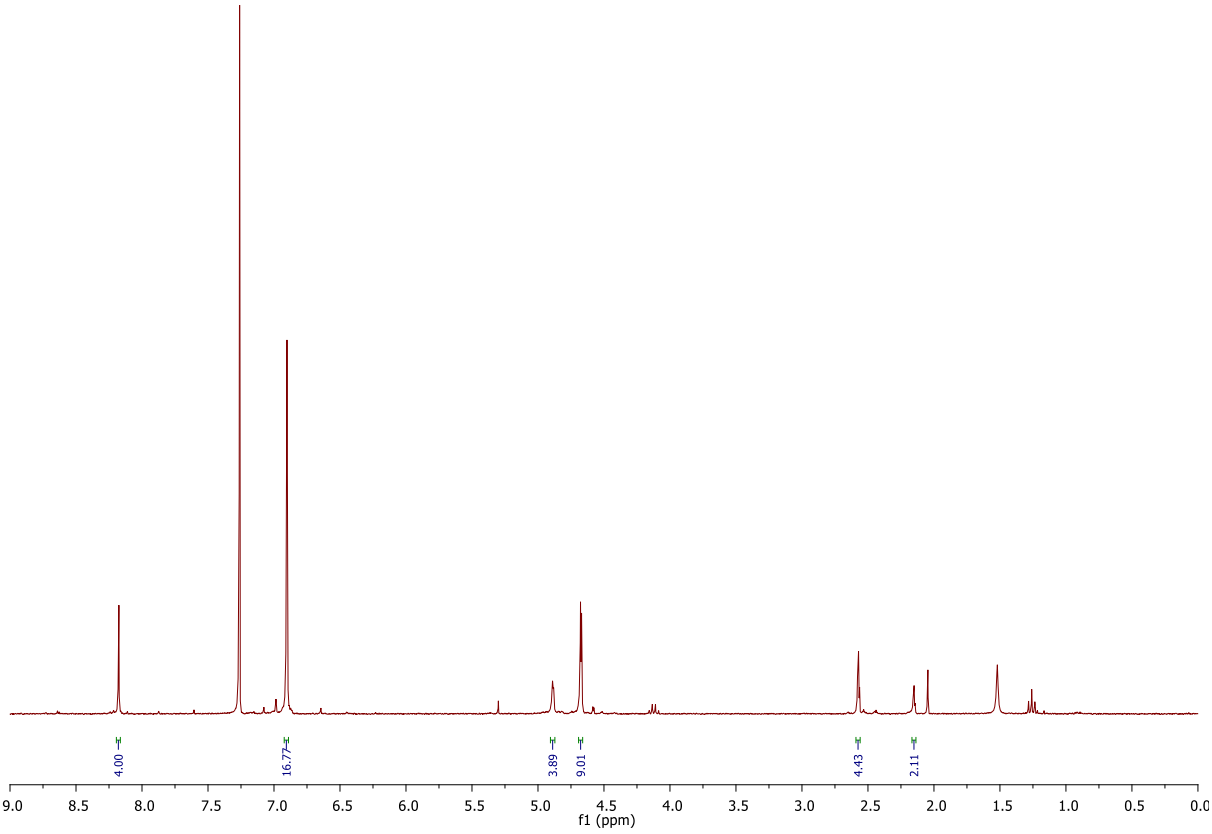


Wang, K.-R. *et al. Org. Biomol. Chem.* **2013**, *11*, 1007-1012.
Srinivasan *et al. J. Org. Chem.* **2001**, *66*, 4299 – 4303 (Propargyloxyphenol)

***N*,*N*'-Bis-propargyl-1,6,7,12-tetra-(4-propargyloxyphenoxy)perylene-3,4,9,10-tetracarboxylic diimide (5) :** Compound **3** (122 mg, 0.20 mmol, 1 eq.) and 4-propargyloxyphenol (179 mg, 1.20 mmol, 6 eq) were mixed in NMP (10 mL). K_2CO_3 (224 mg, 1.62 mmol, 8 eq.) was added at room temperature and the resulting mixture was then heated at 90°C for 15 h. After cooling at room temperature, the reaction mixture was poured into a hydrochloric acid solution (10%, 120 mL) and the solid compound was filtered and washed with water (2×20 mL). The crude product was purified by silica gel flash chromatography (CH_2Cl_2/EtOAc, 99/1) to afford **5** as a red solid.

Yield = 33% (71 mg); $\mathbf{R_f}$ = 0.54 (CH_2Cl_2/AcOEt, 99/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.17 (s, 4H, perylene-H), 6.90 (s, 16H, CH-ar), 4.87 (d, J = 2.1 Hz, 4H, NCH_2), 4.67 (d, J = 2.4 Hz, 8H, OCH_2), 2.57 (t, J = 2.4 Hz, 4H, $CH_2OC{\equiv}C\mathit{H}$), 2.15 (t, J = 2.3 Hz, 2H, $CH_2NC{\equiv}C\mathit{H}$).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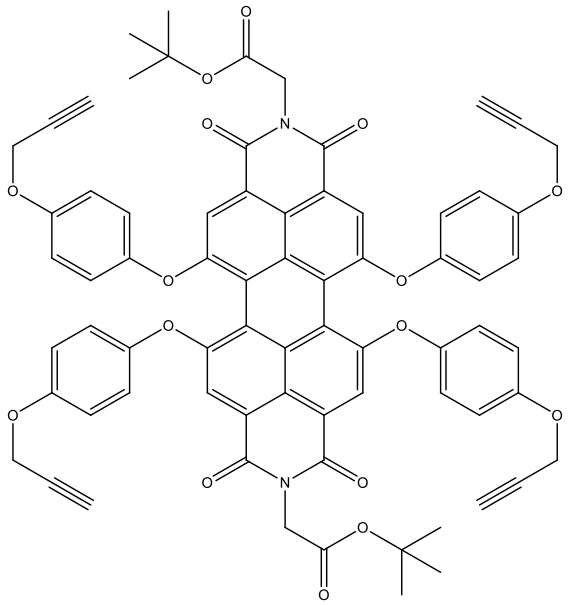


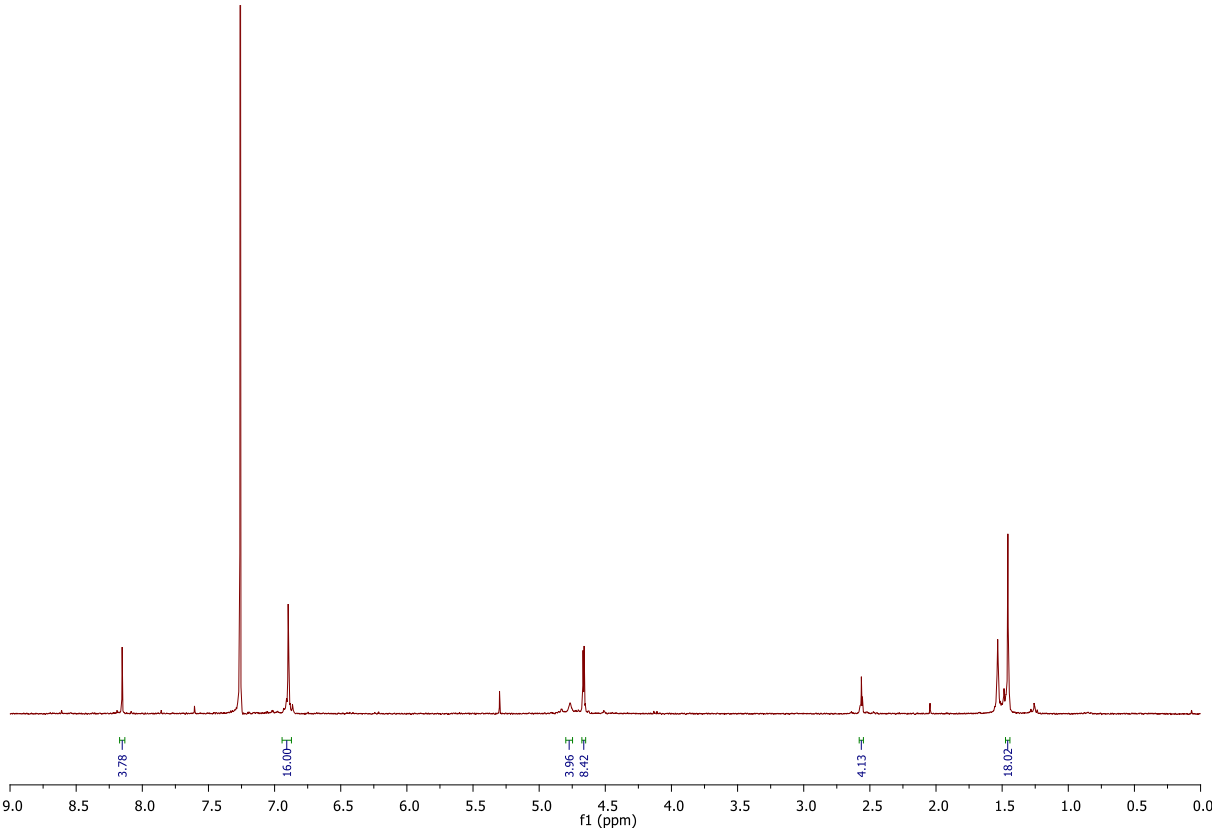
***N*,*N*'-Bis-(*t*-butoxycarbonylmethyl)-1,6,7,12-tetra-(4-propargyloxyphenoxy)perylene-3,4,9,10-tetracarboxylic diimide (6)**: Potassium carbonate (239 mg, 1.73 mmol, 8 eq.) was added to a suspension of **4** (163 mg, 0.216 mmol, 1 eq.) and *p*-propargyloxyphenol (192 mg, 1.30 mmol, 6 eq.) in *N*-methyl-2-pyrrolidone (15 mL). The reaction was stirred at r.t. and turned immediately from dark red to black. After 30 min, the reaction mixture was stirred at 90°C for 15 h. The mixture was then poured into 1N HCl (150 mL) and the deep purple solid was filtered off then washed with water (2×20mL) until neutral pH. The deep purple residue was collected with CH_2Cl_2 (50 mL) then evaporated and purified by silica gel flash chromatography (CH_2Cl_2/EtOAc 97/3) to afford **6** as a deep purple solid.

Yield = 23% (61 mg); $\mathbf{R_f}$ = 0.70 (CH_2Cl_2/EtOAc 99/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.13 (s, 4H, perylene-H), 6.88 (s, 16H, CH-ar), 4.75 (bs, 4H, NCH_2), 4.66 (d, J = 2.4 Hz, 8H, OCH_2), 2.57 (t, J = 2.4 Hz, 4H, C≡CH), 1.46 (s, 18H, CMe_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.1 (COO), 163.1 (NCO), 156.4, 154.6, 149.4 (3×C^{IV}-ar-O), 133.0, 122.1 (2×C^{IV}-ar), 121.3 (CH-ar), 120.4, 119.6 (2×C^{IV}-ar), 119.5 (CH-perylene), 116.5 (CH-ar), 82.5 (*C*Me_3), 78.5 (*C*≡CH), 75.9 (C≡*C*H), 56.5 (OCH_2), 42.2 (NCH_2), 28.2 (C*Me*$_3$).

HR-ESI-QTof (positive mode) *m*/*z*: calcd for $C_{72}H_{54}N_2NaO_{16}$ $[M+Na]^+$ 1225.3366, found 1225.3354.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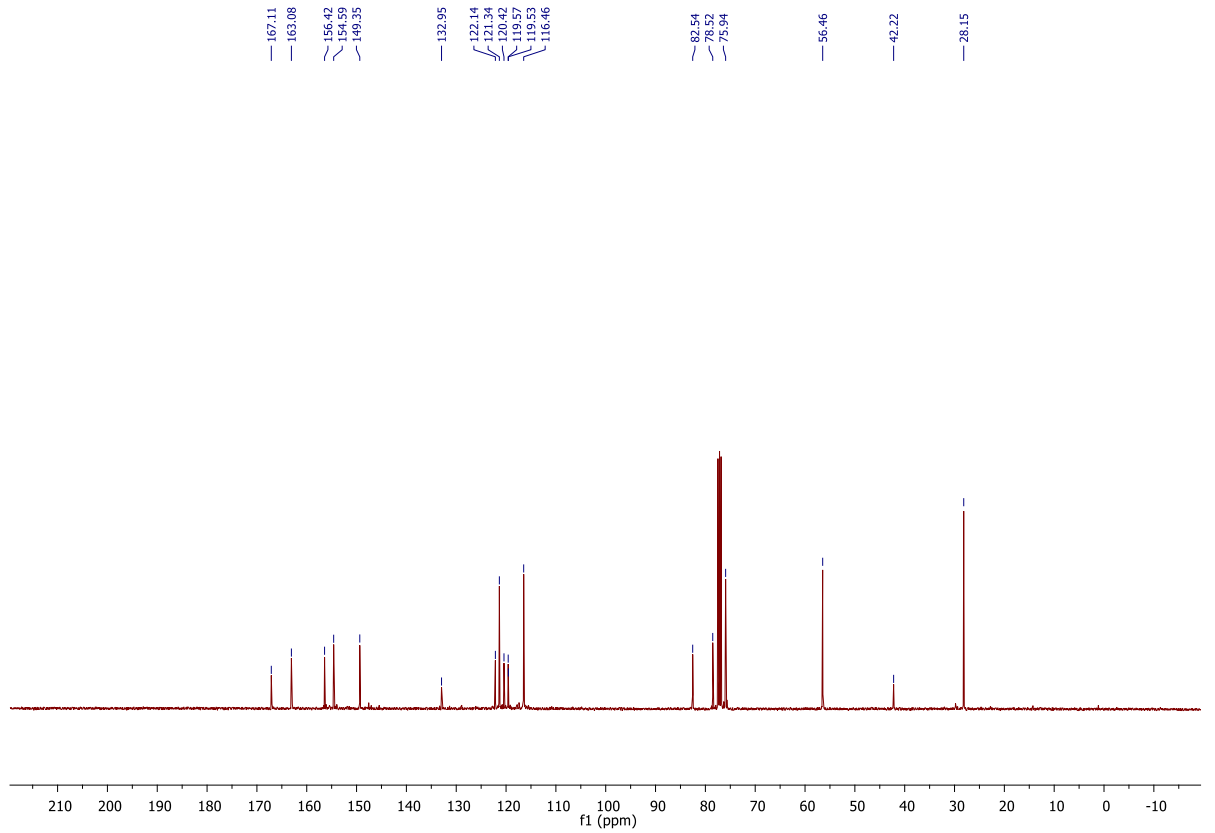
f1 (ppm)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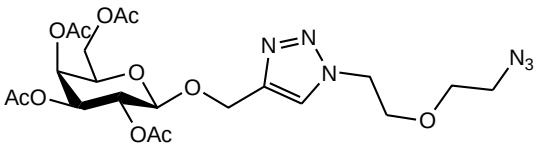
f1 (ppm)



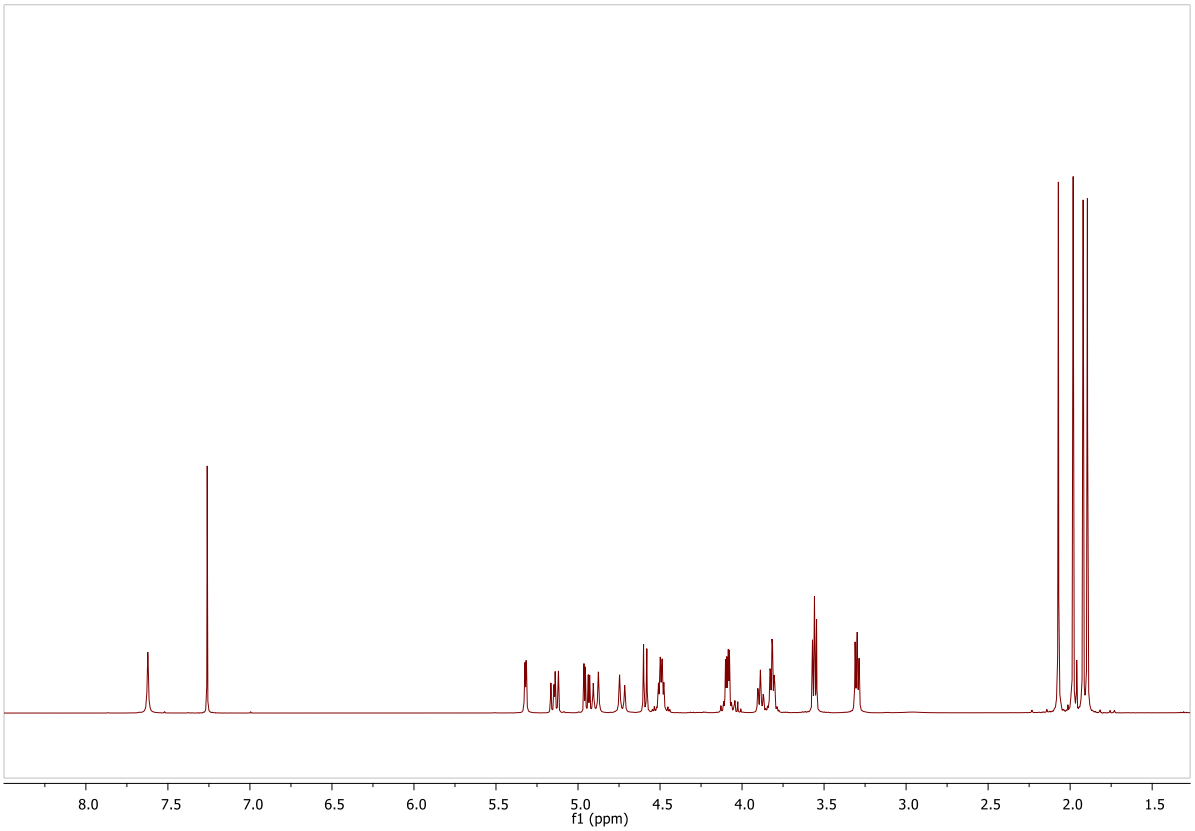
1-(5-Azido-3-oxapentyl)-1,2,3-triazol-4-ylmethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (7e): To a solution of 1,5-diazido-3-oxapentane (2.93 g, 18.8 mmol, 25 eq.) (J. Org. Chem., 1985, 50, 3453-3457; J. Am. Chem. Soc., 2005, 127, 12434-12435) in 24 mL of toluene was added CuI (6 mg, 0.031 mmol, 0.04 eq.) and DIPEA (155 µL, 0.93 mmol, 1.25 eq.). The resulting mixture was stirred at 90°C and propargyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (300 mg, 0.75 mmol, 1 eq.) (J. Am. Chem. Soc. 2007, 129, 11918-11919, Carb. Res. 1998, 307, 351) in 15 mL of toluene was added over a period of 16 h using a motor-driven syringe pump. The mixture was then diluted with ethyl acetate (50 mL) and washed with water (50 mL). The aqueous layer was extracted with ethyl acetate (2×50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography (PE/EtOAc 20/80 to 0/100) to afford **7e** as a colorless oil.

Yield = 90% (378 mg); $\mathbf{R_f}$ = 0.33 (EtOAc), $[\alpha]_D^{25}$ = -30.5 (c 0.19, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.62 (s, 1H, H-triaz), 5.32 (d, *J* = 3.4 Hz, 1H, H-4); 5.14 (dd, *J* = 10.4 Hz, *J* = 7.9 Hz, 1H, H-2), 4.95 (dd, *J* = 10.4 Hz, *J* = 3.4 Hz, 1H, H-3), 4.90 (d, *J* = 12.4 Hz, 1H, GalOC*H*$_2$), 4.74 (d, *J* = 12.4 Hz, 1H, GalOC*H*$_2$), 4.59 (d, *J* = 8.0 Hz, 1H, H-1), 4.52-4.47 (m, 2H, NC*H*$_2$CH$_2$), 4.08 (dd, *J* = 6.6 Hz, *J* = 3.0 Hz, 2H, H-6), 3.92-3.86 (m, 1H, H-5), 3.85-3.79 (m, 2H, NCH$_2$C*H*$_2$), 3.58-3.54 (m, 2H, OC*H*$_2$CH$_2$), 3.32-3.28 (m, 2H, CH$_2$C*H*$_2$), 2.07, 1.98, 1.96, 1.92, 1.89 (s, 12H, 4×COC*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.3, 170.2, 170.0, 169.4 (4×*C*OCH$_3$), 144.0 (C^{IV}-triaz), 124.1 (CH-triaz), 100.2 (C-1), 70.8 (C-3), 70.7 (C-5), 70.1 (O*C*H$_2$CH$_2$), 69.4 (NCH$_2$*C*H$_2$), 68.7 (C-2), 67.0 (C-4), 62.7 (GalO*C*H$_2$), 61.2 (C-6), 50.5 (*C*H$_2$N$_3$), 50.3 (N*C*H$_2$CH$_2$), 20.65, 20.62, 20.58, 20.49 (CO*C*H$_3$).

HR-ESI-QTof (positive mode) *m/z*: calcd $C_{21}H_{31}N_6O_{11}$ $[M+H]^+$ 543.2045, found 543.2036.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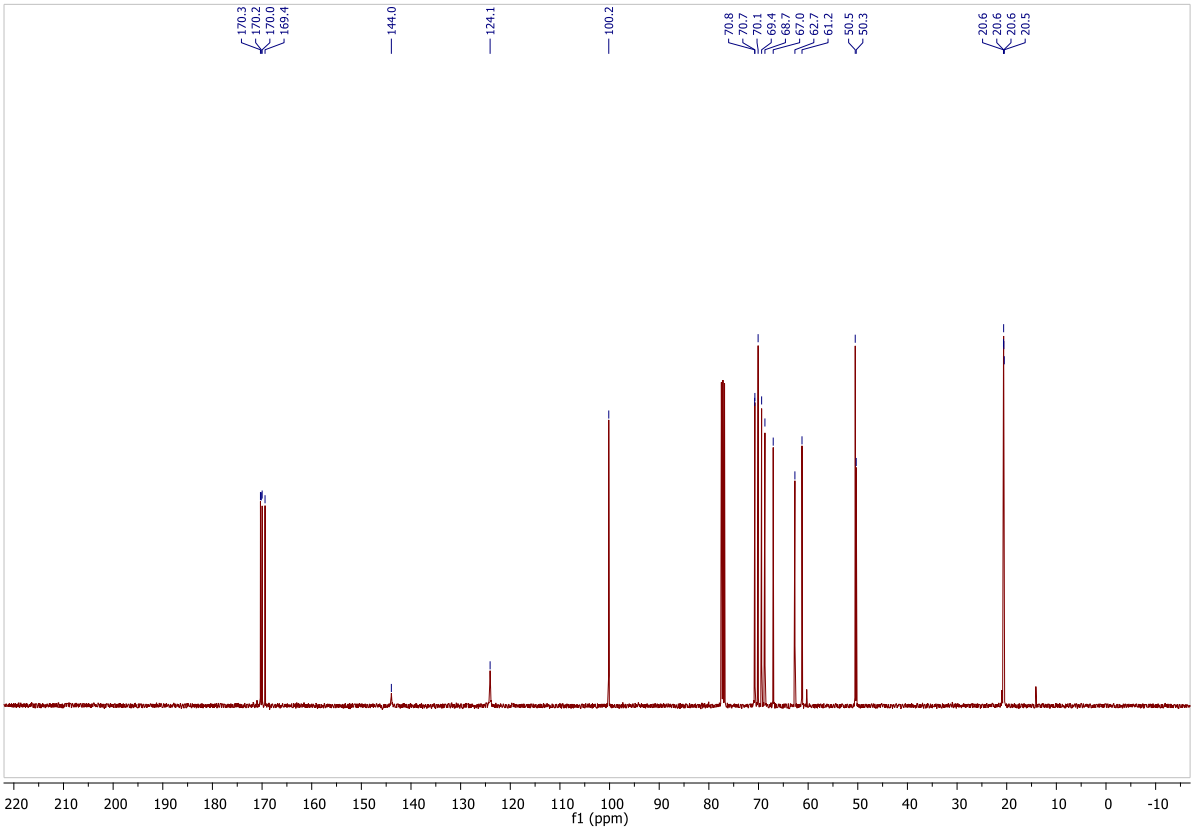
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62.7
61.2
50.5
50.3
20.6
20.6
20.6
20.5
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200
190
180
170
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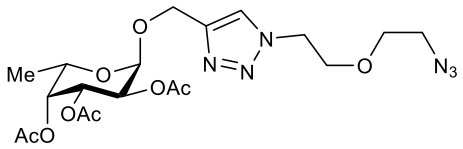
f1 (ppm)



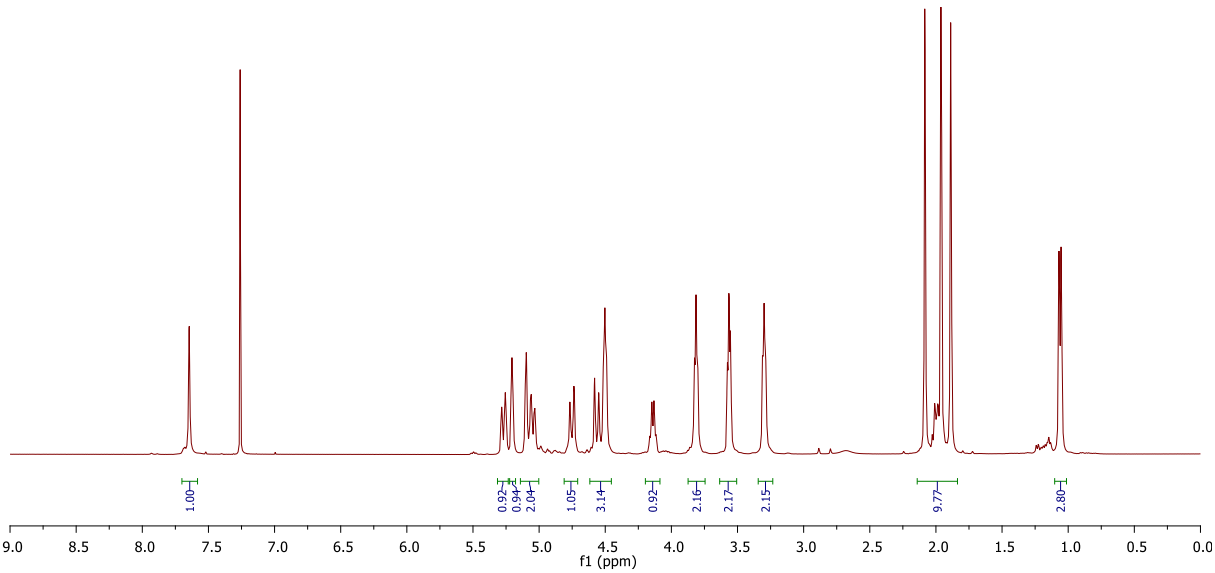
1-(5-Azido-3-oxapentyl)-1,2,3-triazol-4-ylmethyl 2,3,4-tri-*O*-acetyl-α-L-fucopyranoside (7f): To a solution of 1,5-diazido-3-oxapentane (8.09 g, 51.8 mmol, 25 eq.) (J. Org. Chem., 1985, 50, 3453-3457; J. Am. Chem. Soc., 2005, 127, 12434-12435) in 90 mL of toluene was added CuI (16 mg, 0.0.83 mmol, 0.04 eq.) and DIPEA (427 µL, 2.59 mmol, 1.25 eq.). The resulting mixture was stirred at 90°C and propargyl 2,3,4-tri-*O*-acetyl-α-D-fucopyranoside (680 mg, 2.07 mmol, 1 eq.) (J. Am. Chem. Soc. 2007, 129, 11918-11919, Carb. Res. 1998, 307, 351) in 20 mL of toluene was added over a period of 16 h using a motor-driven syringe pump. The mixture was then diluted with ethyl acetate (100 mL) and washed with water (100 mL). The aqueous layer was extracted with ethyl acetate (2×50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography (PE/EtOAc 50/50 to 0/100) to afford **7f** as a colorless oil.

Yield = quantitative (1.107) g; $\mathbf{R_f}$ = 0.28 (PE/EtOAc 1/4), $[\alpha]_D^{25}$ = -92.7 (c 0.35, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.65 (s, 1H, H-triaz), 5.30-5.23 (m, 1H, H-3), 5.22-5.18 (m, 1H, H-4), 5.12-5.08 (m, 1H, H-1), 5.07-5.01 (m, 1H, H-2), 4.75 (d, *J* = 12.1 Hz, 1H, OCH_2), 4.57 (d, *J* = 12.2 Hz, 1H, FucOCH_2), 4.53-4.46 (m, 2H, NCH_2CH_2), 4.18-4.10 (m, 1H, H-5), 3.81 (t, *J* = 4.6 Hz, 2H, NCH_2CH_2), 3.57 (t, *J* = 2.7 Hz, 2H, OCH_2CH_2), 3.30 (t, *J* = 2.6 Hz, 2H, OCH_2CH_2), 2.08, 1.96,1.89 (s, 9H, 3×$COCH_3$), 1.06 (d, *J* = 6.4 Hz, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.5, 170.3, 169.9 (3×$COCH_3$), 143.8 (C^{IV}-triaz), 127.1 (CH-triaz), 95.5 (C-1), 71.1 (C-4), 70.1 (OCH_2CH_2), 69.4 (NCH_2CH_2), 67.90 (C-2), 67.86 (C-3), 64.6 (C-5), 61.1 (FucOCH_2), 50.6 (OCH_2CH_2), 50.3 (NCH_2CH_2), 20.7, 20.62, 20.59 ($COCH_3$), 15.8 (CH_3).

HR-ESI-QTof (positive mode) *m*/*z*: calcd $C_{19}H_{28}N_6NaO_9$ $[M+Na]^+$ 507.1810, found 507.1801.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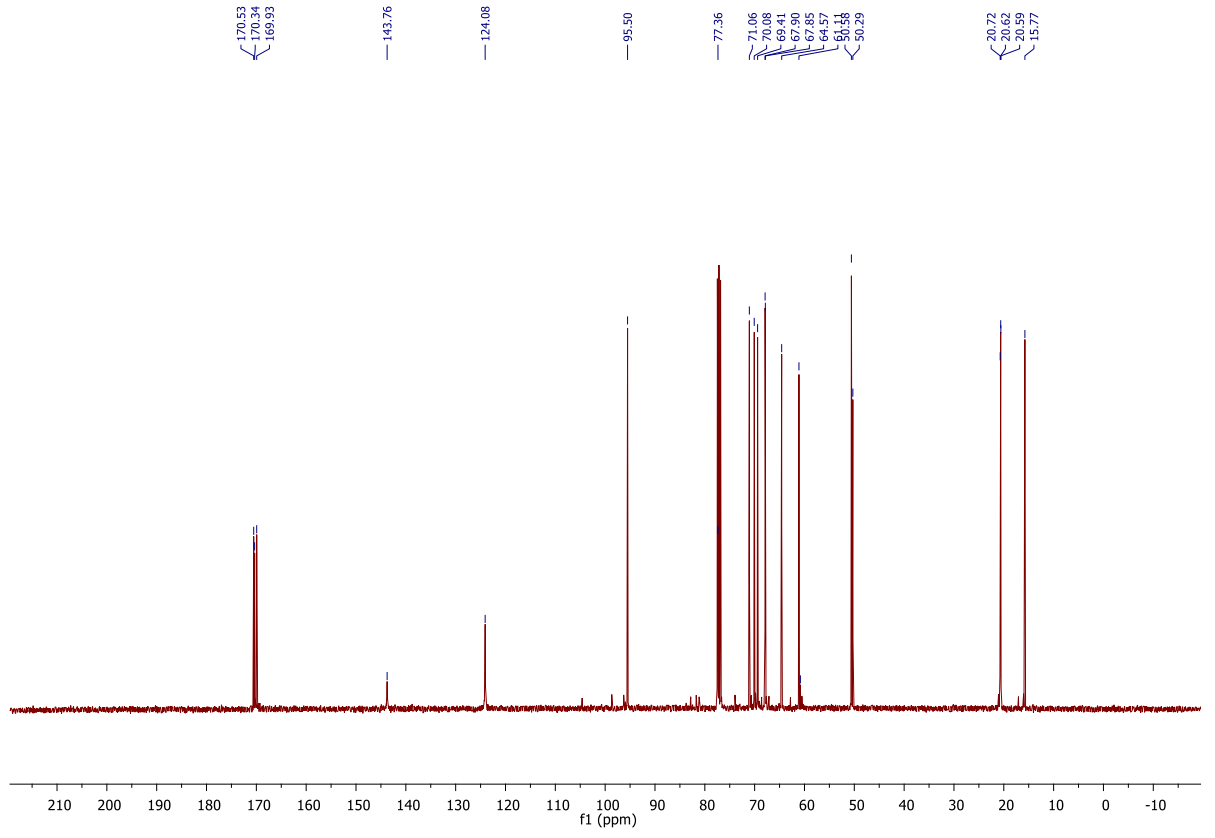
9.77
2.80
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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169.93
143.76
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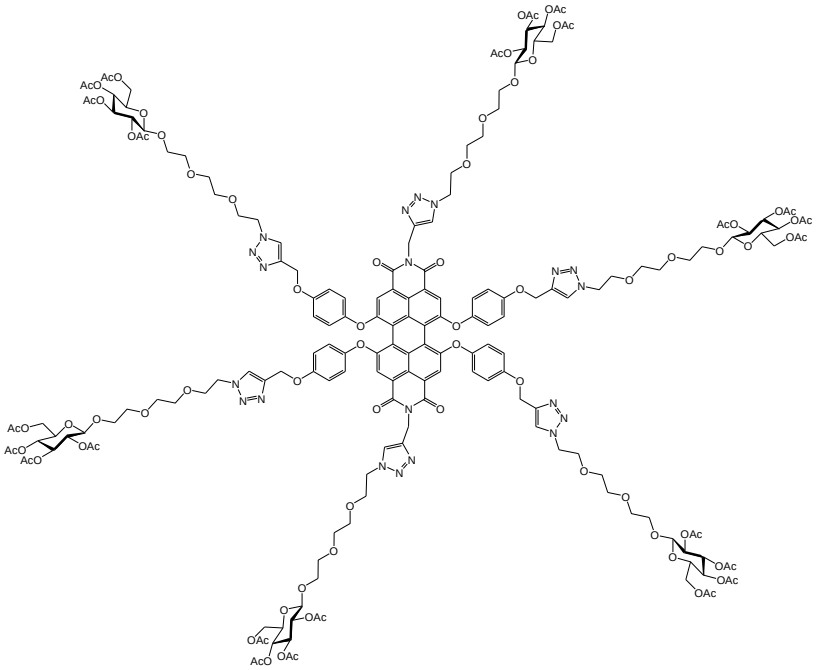
95.50
77.36
71.06
70.08
69.41
67.90
67.85
64.57
61.41
61.38
50.29
20.72
20.62
20.59
15.77
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



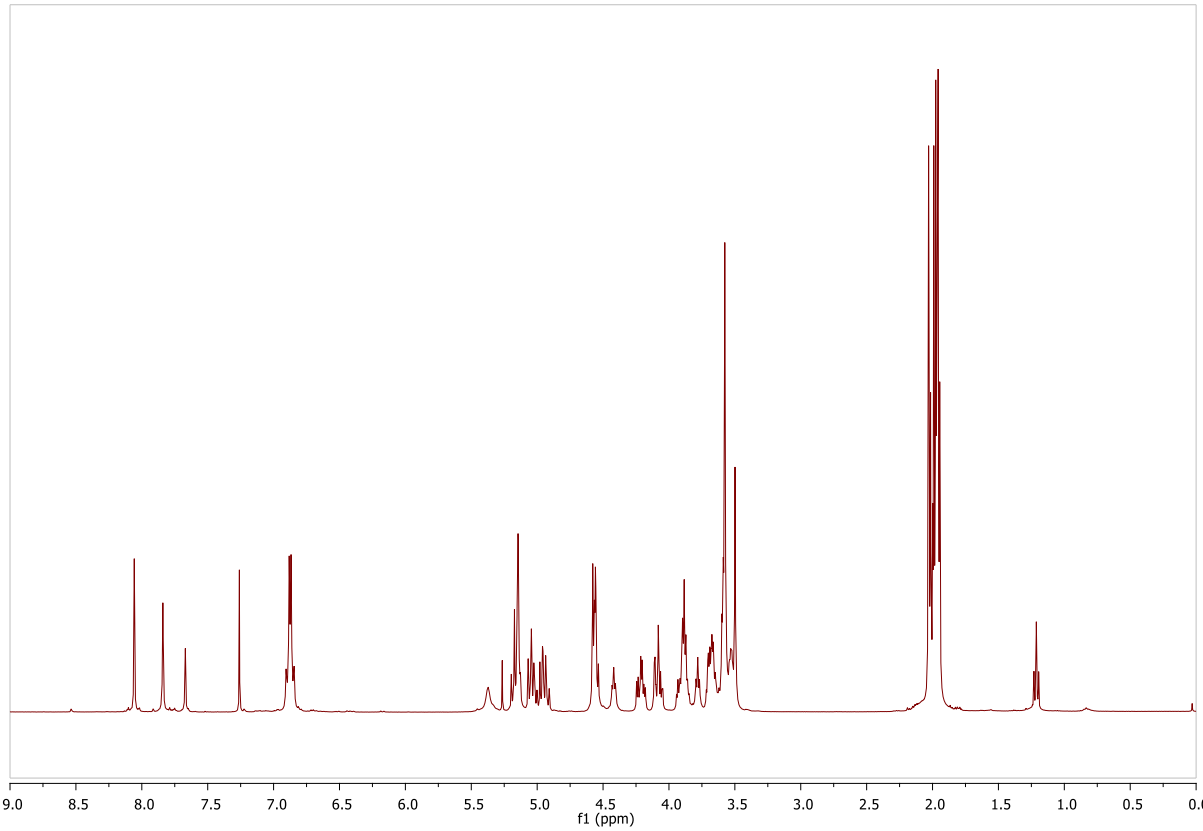
N*,*N*'-Bis-{1-[1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyl}-1,6,7,12-tetra-(4-{1-[1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyloxy}phenoxy)perylene-3,4,9,10-tetracarboxylic diimide (8a):** Obtained as a purple foam following ***Method A: **5** (50 mg, 0.048 mmol, 1 eq.), compound **7a** (216 mg, 0.428 mmol, 9 eq.), CuI (4.5 mg, 0.024 mmol, 0.5 eq.) and DIPEA (74 µL, 0.428 mmol, 9 eq.). Purified by silica gel flash chromatography (CH_2Cl_2/MeOH 99/1 to 95/5).

Yield = 53% (103 mg), $\mathbf{R_f}$ = 0.45 (CH_2Cl_2/MeOH 95/5).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.06 (s, 4H, perylene-H), 7.84 (s, 4H, H-triaz), 7.67 (s, 2H, H-triaz), 6.87 (d, J = 5.7 Hz, 16H, H-ar), 5.37 (bs, 4H, NCH_2-triaz), 5.20-5.11 (m, 14H, OCH_2-triaz, H-3, H-3'), 5.09-5.01 (m, 6H, H-4, H-4'), 5.01-4.88 (m, 6H, H-2, H-2'), 4.60-4.53 (m, 14H, H-1, H-1', NCH_2CH$_2$), 4.42 (t, J = 5.1 Hz, 4H, NCH_2CH$_2$), 4.26-4.17, 4.13-4.04 (2m, 12H, H-6, H-6'), 3.96-3.84 (m, 14H, OCH$_2$), 3.78 (t, J = 5.2 Hz, 4H, OCH$_2$), 3.73-3.63 (m, 12H, H-5, H-5', OCH$_2$), 3.63-3.47 (m, 36H, OCH$_2$), 2.05-1.92 (m, 72H, 4×COCH$_3$).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.7, 170.3, 169.5, 169.4 (4×*C*OCH$_3$), 163.0 (Ar*C*ON), 156.51, 155.45, 148.9 (3×C^{IV}-ar-O), 143.7, 143.2 (2×C^{IV}-triaz), 132.8 (C^{IV}-ar), 124.2 (6C, CH-triaz), 122.3 (C^{IV}-ar), 121.5 (8C, CH-ar), 120.1 (C^{IV}-ar), 119.2 (CH-perylene), 116.2 (8C, CH-ar), 100.86, 100.82 (C-1, C-1'), 72.8 (C-3, C-3'), 71.79, 71.76 (C-5, C-5'), 71.3 (C-2, C-2'), 70.7, 70.6, 70.5, 70.3, 69.5, 69.4, 69.23, 69.17 (5×OCH$_2$), 68.4 (C-4, C-4'), 62.5 (O*C*H$_2$-triaz), 61.9 (C-6, C-6'), 50.4, 50.1 (N*C*H$_2$CH$_2$), 35.3 (N*C*H$_2$-triaz), 20.8-20.6 (4×CO*C*H$_3$).

HR-ESI-QTof (positive mode) *m*/*z*: calcd for $C_{186}H_{226}N_{20}O_{84}$ $[M+2H]^{2+}$ 2041.7008, found 2041.6915.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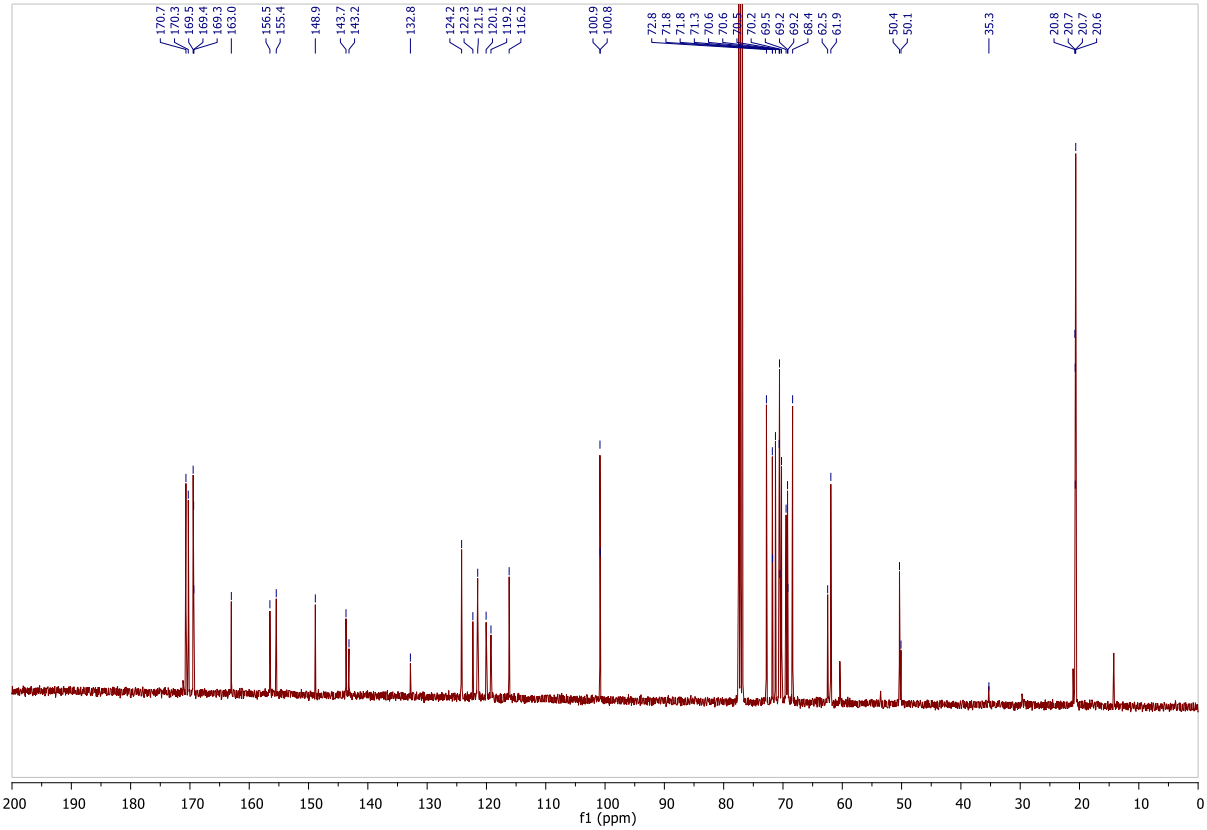
f1 (ppm)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170.3
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169.4
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155.4
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121.5
120.1
119.2
116.2
100.9
100.8
72.8
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71.3
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70.2
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62.5
61.9
50.4
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35.3
20.8
20.7
20.7
20.6
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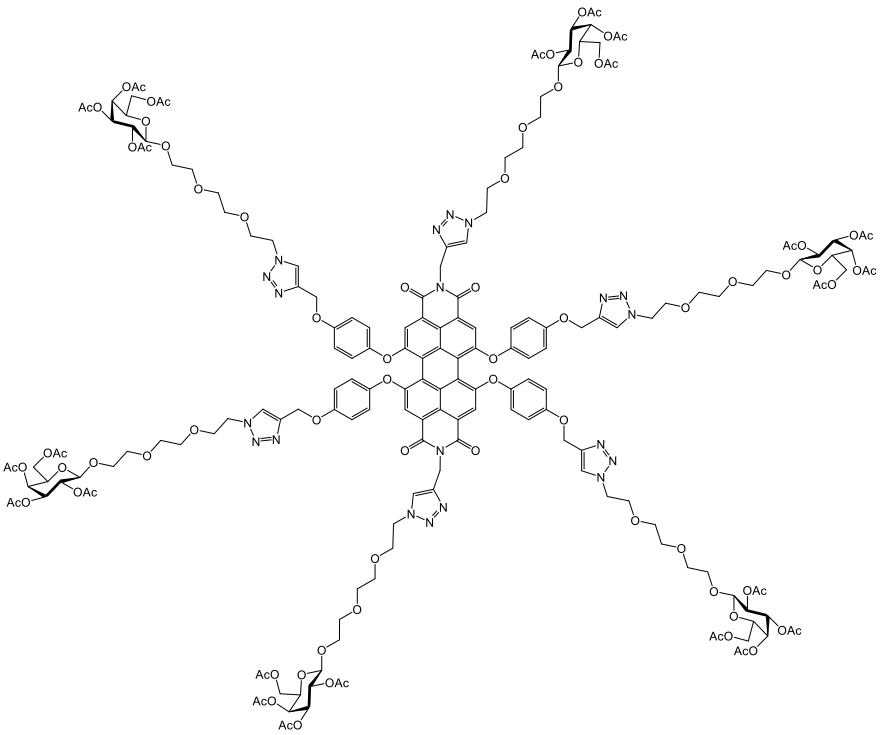
f1 (ppm)



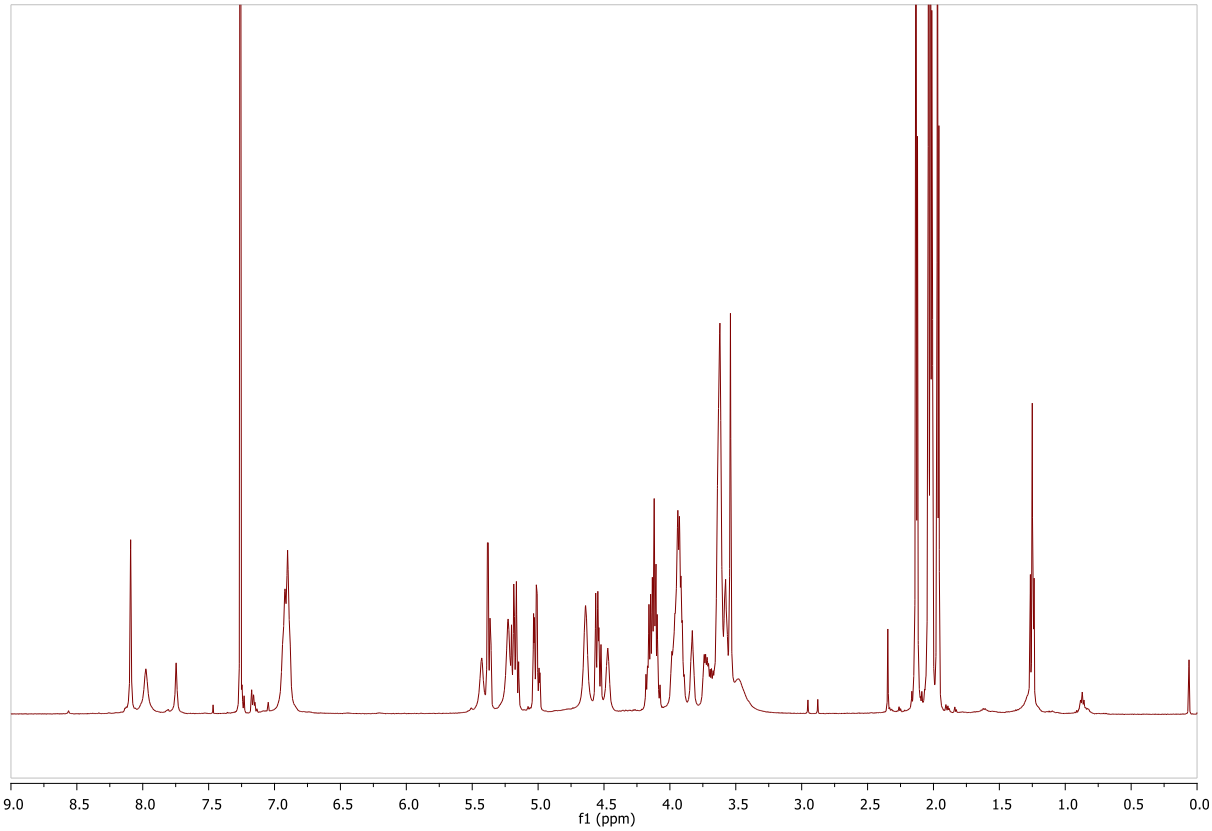
N*,*N*'-Bis-{1-[1-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyl}-1,6,7,12-tetra-(4-{1-[1-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyloxy}phenoxy)perylene-3,4,9,10-tetracarboxylic diimide (8b):** Obtained as a purple foam following ***Method A: **5** (10 mg, 0.010 mmol, 1 eq.), compound **7b** (45 mg, 0.089 mmol, 9.4 eq.), CuI (1 mg, 0.005 mmol, 0.5 eq.) and DIPEA (12 µL, 0.066 mmol, 7 eq.). Purified by silica gel flash chromatography (CH_2Cl_2/MeOH 99/1 to 95/5).

Yield = 77% (30 mg), $\mathbf{R_f}$ = 0.45 (CH_2Cl_2/MeOH 95/5).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.09 (s, 4H, perylene-H), 7.98 (s, 4H, H-triaz), 7.75 (s, 2H, H-triaz), 6.91 (d, J = 9.9 Hz, 16H, H-ar), 5.43 (bs, 4H, NCH_2-triaz), 5.38 (d, J = 3.1 Hz, 4H, H-4), 5.36 (d, J = 3.1 Hz, 2H, H-4'), 5.23 (bs, 8H, OCH_2-triaz), 5.21-5.13 (M, 6H, H-2, H-2'), 5.02 (dd, J = 10.4, 3.2 Hz, 4H, H-3), 5.00 (dd, J = 10.4, 3.3 Hz, 2H, H-3'), 4.64 (s, 8H, NCH_2CH_2), 4.55 (d, J = 8.0 Hz, 4H, H-1), 4.53 (d, J = 8.1 Hz, 2H, H-1'), 4.47 (bs, 4H, NCH_2CH_2), 4.21-4.06 (m, 12H, H-6, H-6'), 4.02-3.87, 3.87-3.79 (2m, 18H, OCH_2, H-5, H-5'), 3.79-3.39 (m, 48H, 4×OCH_2), 2.13, 2.12, 2.04, 2.02, 2.01, 2.01, 1.97, 1.96 (8s, 72H, 24×$COCH_3$).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 170.5, 170.4, 170.3, 169.58, 169.55 (4×$COCH_3$), 163.1 (ArCON), 156.63, 155.58, 149.0 (3×C^{IV}-ar-O), 143.8, 143.3 (2×C^{IV}-triaz), 133.0 (C^{IV}-ar), 124.3 (6C, CH-triaz), 122.4 (C^{IV}-ar), 121.6 (8C, CH-ar), 120.2, 119.4 (2×C^{IV}-ar), 119.3 (CH-perylene), 116.3 (8C, CH-ar), 101.51 (C-1), 101.47 (C-1'), 71.0 (C-3, C-3'), 70.82 (C-5), 70.80, 70.78, 70.74, 70.72, 70.66, 70.38, 70.34, 69.61, 69.56 (C-5', 4×OCH_2), 69.32, 69.29 (GalOCH_2), 69.96 (C-2), 68.95 (C-2'), 67.2 (C-4, C-4'), 62.7 (OCH_2-triaz), 61.4 (C-6), 60.5 (C-6'), 50.5, 50.2 (NCH_2CH_2), 35.4 (NCH_2-triaz), 20.93, 20.91, 20.82, 20.81, 20.7 (4×$COCH_3$).

HR-ESI-QTof (positive mode) m/z: calcd for $C_{186}H_{227}N_{20}O_{84}$ $[M+3H]^{3+}$ 1361.4696, found 1361.4659.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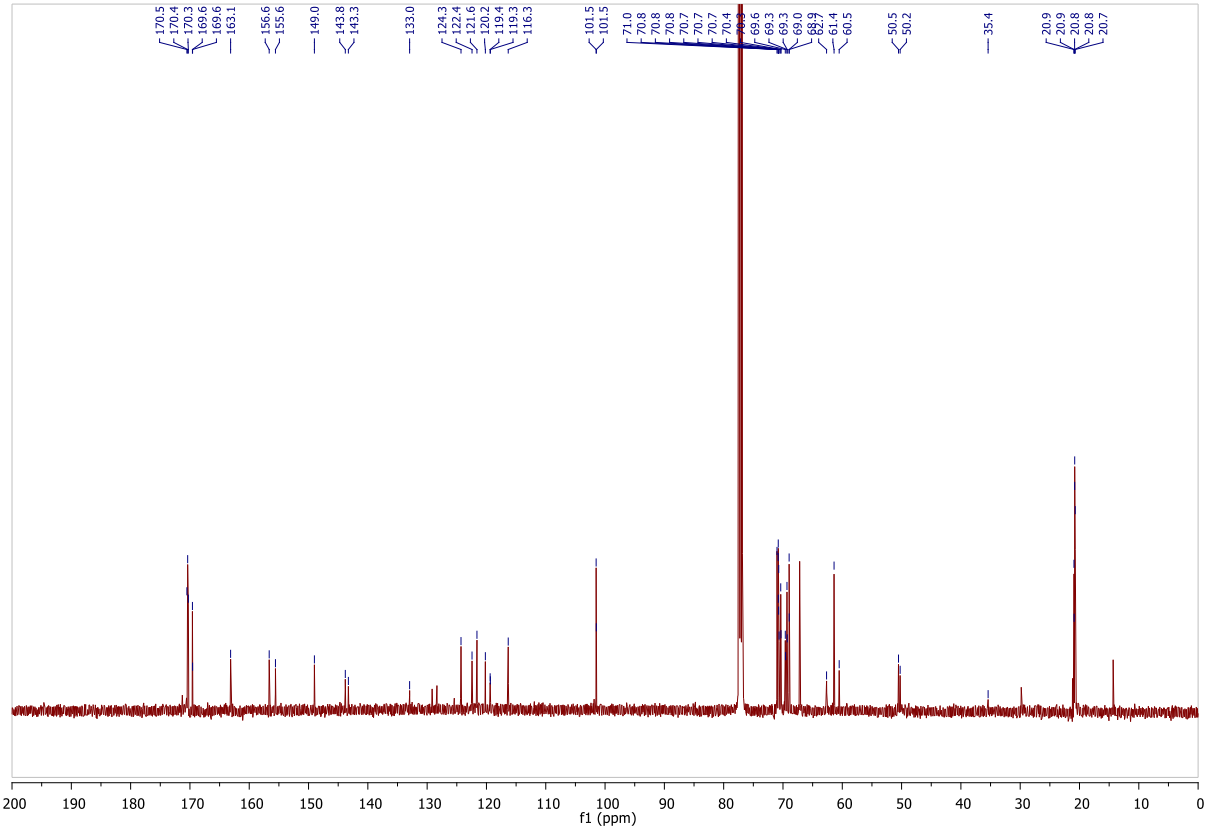
f1 (ppm)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122.4
121.6
120.2
119.4
119.3
116.3
101.5
101.5
71.0
70.8
70.8
70.8
70.7
70.7
70.7
70.4
69.6
69.3
69.3
69.0
61.4
60.5
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50.2
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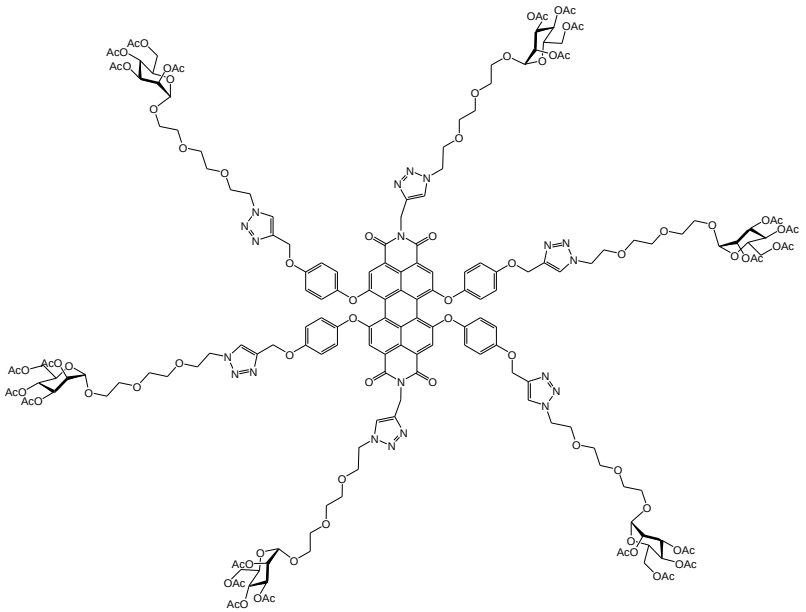
f1 (ppm)



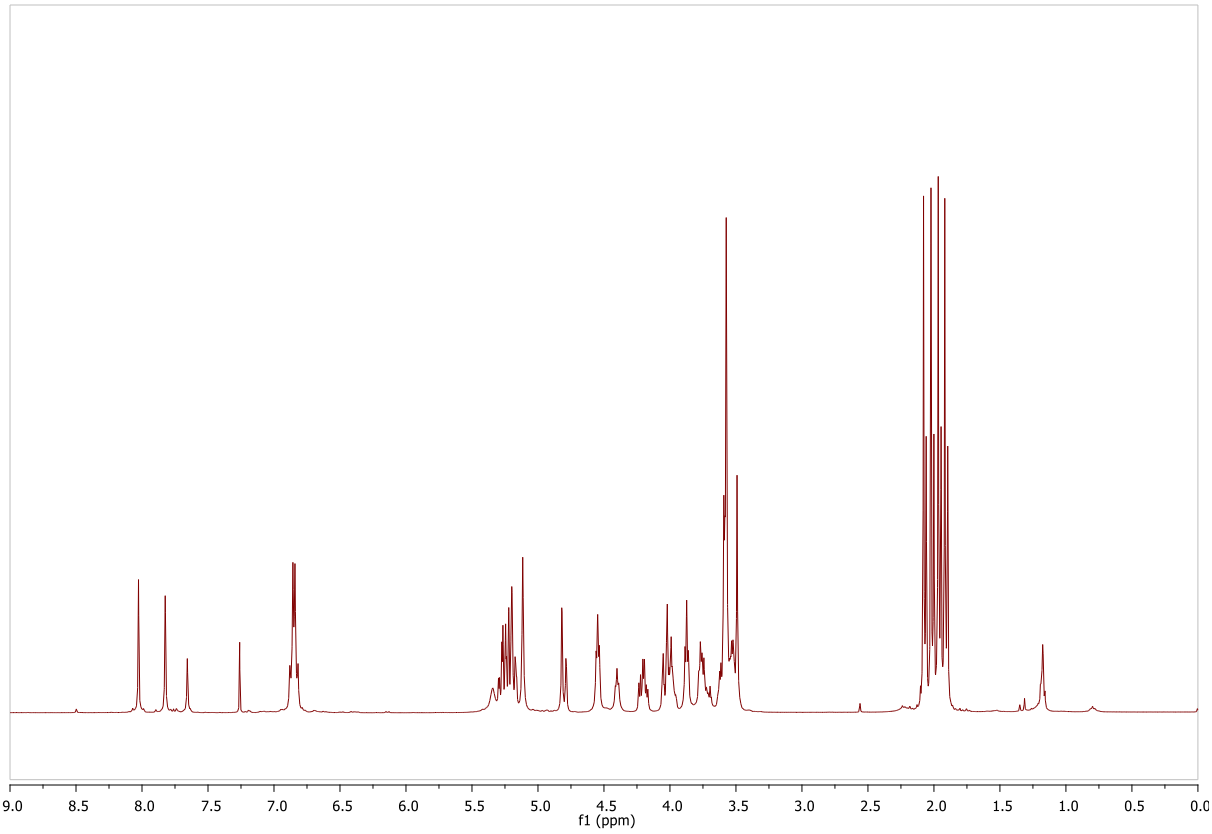
N*,*N*'-Bis-{1-[1-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyl}-1,6,7,12-tetra-(4-{1-[1-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyloxy}phenoxy)perylene-3,4,9,10-tetracarboxylic diimide (8c):** Obtained as a purple foam following ***Method A: **5** (50 mg, 0.048 mmol, 1 eq.), compound **7c** (216 mg, 0.428 mmol, 9 eq.), CuI (4.5 mg, 0.024 mmol, 0.5 eq.) and DIPEA (74 µL, 0.428 mmol, 9 eq.). Purified by silica gel flash chromatography (CH_2Cl_2/MeOH 99/1 to 95/5).

Yield = 67% (130 mg), $\mathbf{R_f}$ = 0.45 (CH_2Cl_2/MeOH 95/5).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.03 (s, 4H, perylene-H), 7.82 (s, 4H, H-triaz), 7.66 (s, 2H, H-triaz), 6.85 (d, J = 6.3 Hz, 16H, H-ar), 5.34 (bs, 4H, NCH_2-triaz), 5.31-5.15 (m, 18H, H-2, H-2', H-3, H-3', H-4, H-4'), 5.12 (bs, 8H, OCH_2-triaz), 4.82 (d, J = 1.0 Hz, 4H, H-1), 4.79 (2d, J = 1.1 Hz, 2H, H-1'), 4.55 (t, J = 4.9 Hz, 8H, NCH_2CH_2), 4.40 (t, J = 4.9 Hz, 4H, NCH_2CH_2), 4.25-4.15 (m, 6H, H-6a, H-6a'), 4.08-3.95 (m, 12H, H-5, H-5', H-6b, H-6b'), 3.87 (t, J = 5.0 Hz, 8H, OCH_2), 3.80-3.47 (m, 52H, OCH_2), 2.08, 2.06, 2.02, 2.00, 1.97, 1.95, 1.92, 1.90 (8s, 72H, 24×$COCH_3$).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.56, 170.54, 170.0, 169.92, 169.86, 169.81, 169.6 (7s, $COCH_3$), 162.9 (ArCON), 156.4, 155.4, 148.8 (3×C^{IV}-ar-O), 143.6, 143.1 (2×C^{IV}-triaz), 132.7 (C^{IV}-ar), 124.1 (6C, CH-triaz), 122.2 (C^{IV}-ar), 121.4 (8C, CH-ar), 119.9 (C^{IV}-ar), 119.1 (CH-perylene, C^{IV}-ar), 116.1 (8C, CH-ar), 97.59, 97.55 (2s, C-1, C-1'), 70.60, 70.54, 70.45, 70.40, 69.9 (3×OCH_2), 69.45, 69.42, 69.37 (OCH_2, C-2, C-2'), 69.0 (C-3, C-3'), 68.4, 68.3 (C-5, C-5'), 67.3, 67.2 (OCH_2), 66.0 (C-4, C-4'), 62.4 (OCH_2-triaz), 62.32, 62.29 (C-6, C-6'), 50.3, 50.0 (NCH_2CH_2), 35.2 (NCH_2-triaz), 20.9-20.8, 20.7-20.6 (2m, 4×$COCH_3$).

HR-ESI-QTof (positive mode) m/z: calcd for $C_{186}H_{224}N_{20}Na_2O_{84}$ $[M+2Na]^{2+}$ 2063.6828, found 2063.6744.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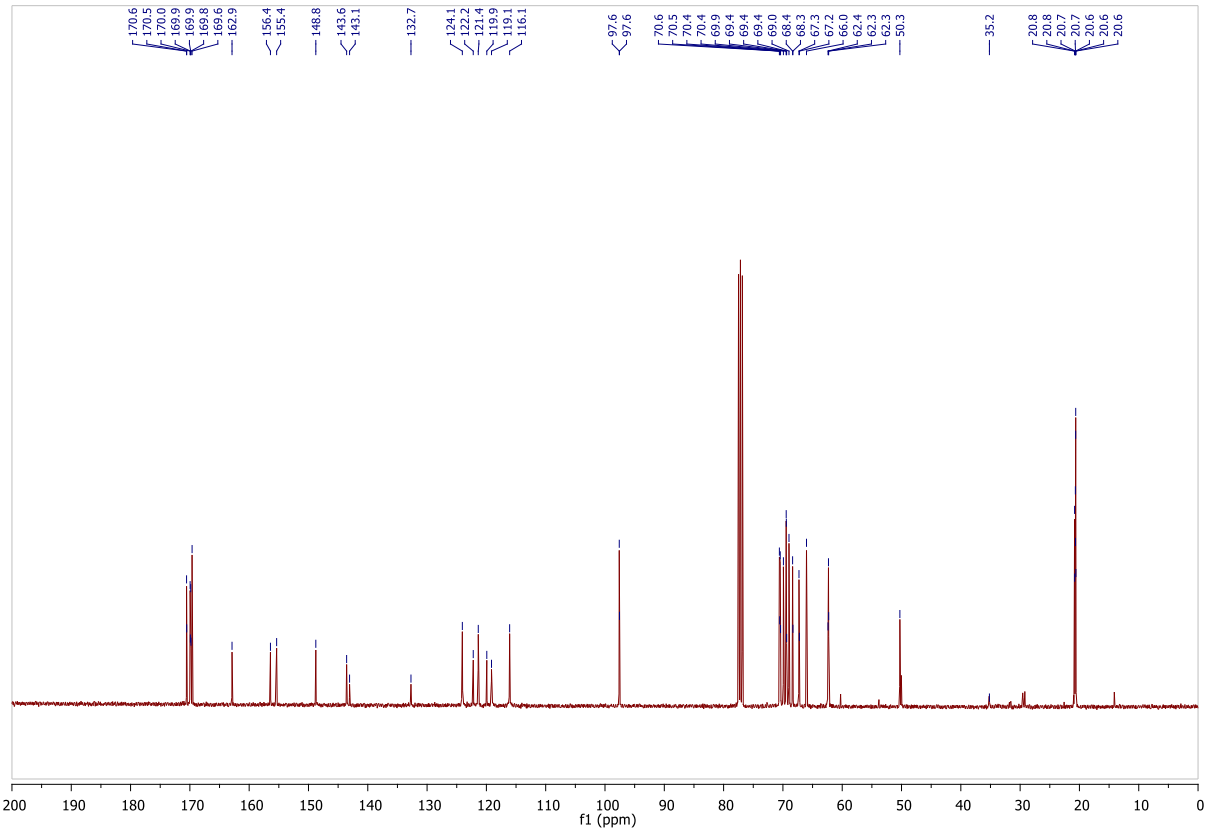
f1 (ppm)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119.9
119.1
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97.6
70.6
70.5
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68.3
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67.2
66.0
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50.3
35.2
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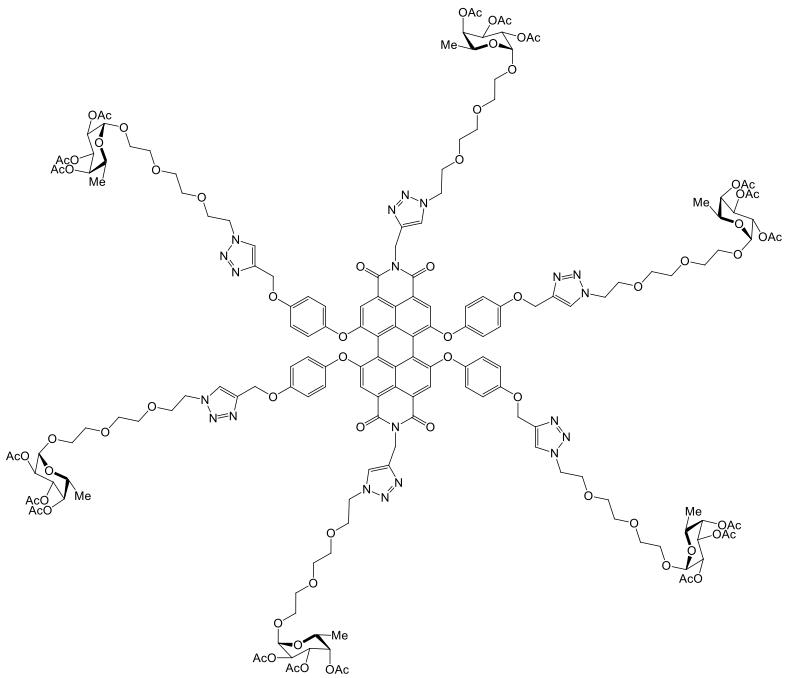
f1 (ppm)



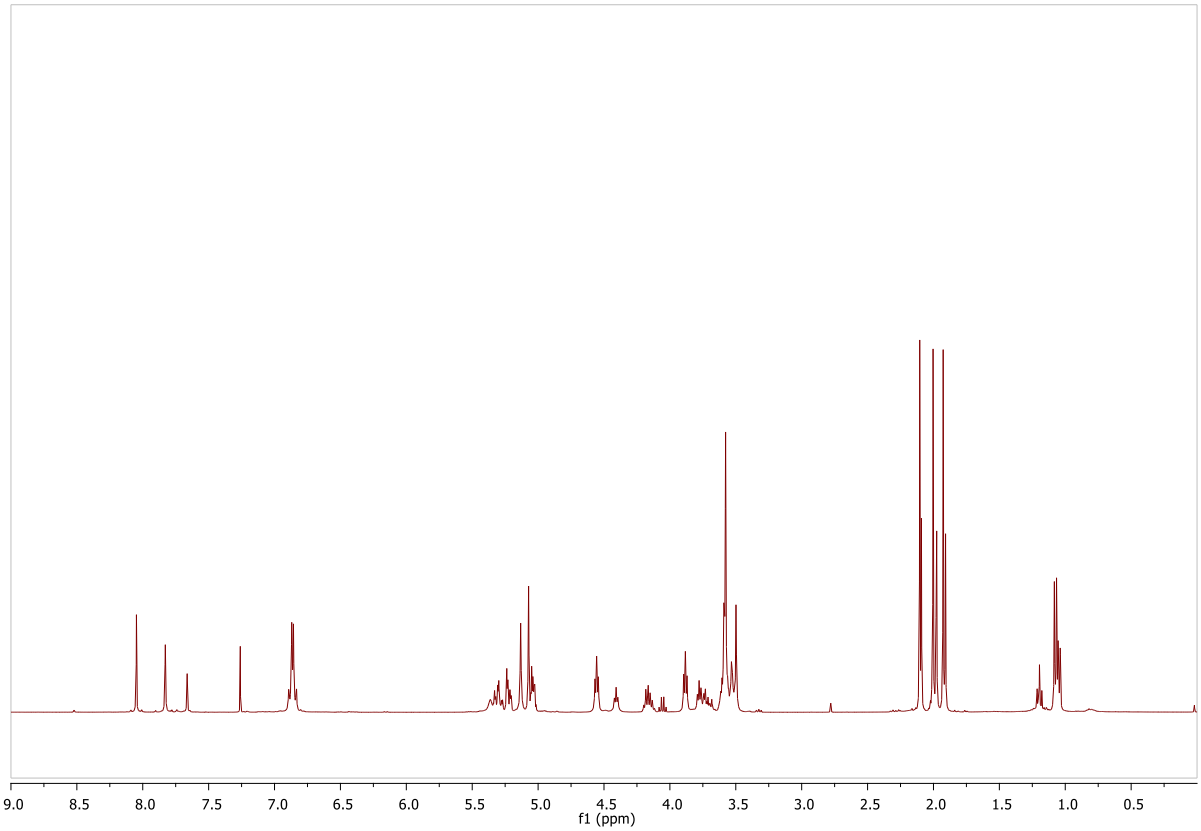
N*,*N*'-Bis-{1-[1-(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyl}-1,6,7,12-tetra-(4-{1-[1-(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyloxy}phenoxy)perylene-3,4,9,10-tetracarboxylic diimide (8d) :** Obtained as a purple foam following ***Method A: **5** (60 mg, 0.057 mmol, 1 eq.), compound **7d** (230 mg, 0.514 mmol, 9 eq.), CuI (5 mg, 0.029 mmol, 0.5 eq.) and DIPEA (89 µL, 0.514 mmol, 10 eq.). Purified by silica gel flash chromatography (CH_2Cl_2/MeOH 99/1 to 95/5).

Yield = 67% (142 mg), $\mathbf{R_f}$ = 0.50 (CH_2Cl_2/MeOH 95/5).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.05 (s, 4H, perylene-H), 7.83 (s, 4H, H-triaz), 7.66 (s, 2H, H-triaz), 6.86 (d, *J* = 5.2 Hz, 16H, H-ar), 5.36 (bs, 4H, NC*H*$_2$-triaz), 5.35-5.26 (m, 6H, H-3, H-3'), 5.24, 5.21 (2dd, *J* = 3.3, 1.0 Hz, 6H, H-4, H-4'), 5.13 (s, 8H, OC*H*$_2$-triaz), 5.07 (s, 6H, H-1, H-1'), 5.06-5.01 (m, 6H, H-2, H-2'), 4.56, 4.41 (2t, *J* = 5.1 Hz, 12H, N*C*H$_2$CH$_2$), 4.21-4.11 (m, 6H, H-5, H-5'), 3.88, 3.78 (2t, *J* = 5.1 Hz, 12H, OCH$_2$), 3.76-3.67 (m, 6H, OCH$_2$), 3.63-3.48 (m, 42H, OCH$_2$), 2.10, 2.09, 2.00, 1.98, 1.92, 1 .91 (6s, 54H, 18×COCH$_3$), 1.07, 1.05 (2d, *J* = 6.6 Hz, 18H, H-6, H-6').

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.59, 170.58, 170.37, 170.35, 170.1, 170.0 (*C*O CH$_3$), 163.0 (Ar*C*ON), 156.5, 155.4, 148.8 (3×C^{IV}-ar-O), 143.7, 143.1 (2×C^{IV}-triaz), 132. 8 (C^{IV}-ar), 124.12, 124.08 (2×CH-triaz), 122.3 (C^{IV}-ar), 121.4 (8C, CH-ar), 120.0 (C^{IV}-ar), 119.2 (CH-perylene, C^{IV}-ar), 116.1 (8C, CH-ar), 96.2 (C-1), 96.1 (C-1'), 71.1 (C-4, C-4'), 70.58, 70.57, 70.5, 70.21, 70.16, 69.5, 69.4 (4×OCH$_2$), 68.15 (C-2), 68.11 (C-2'), 68.0 (C-3, C-3'), 67.31, 67.28 (OCH$_2$), 64.30 (C-5), 64.27 (C-5'), 62.5 (OCH$_2$-triaz), 50.3, 50.1 (N*C*H$_2$CH$_2$), 35.3 (N*C*H$_2$-triaz), 20.81, 20.79, 20.70, 20.68, 20.6 (4×CO*C*H$_3$), 15.9 (C-6), 15.8 (C-6').

HR-ESI-QTof (positive mode) *m*/*z*: calcd for $C_{174}H_{214}N_{20}O_{72}$ $[M+2H]^{2+}$ 1867.6844, found 1867.6779.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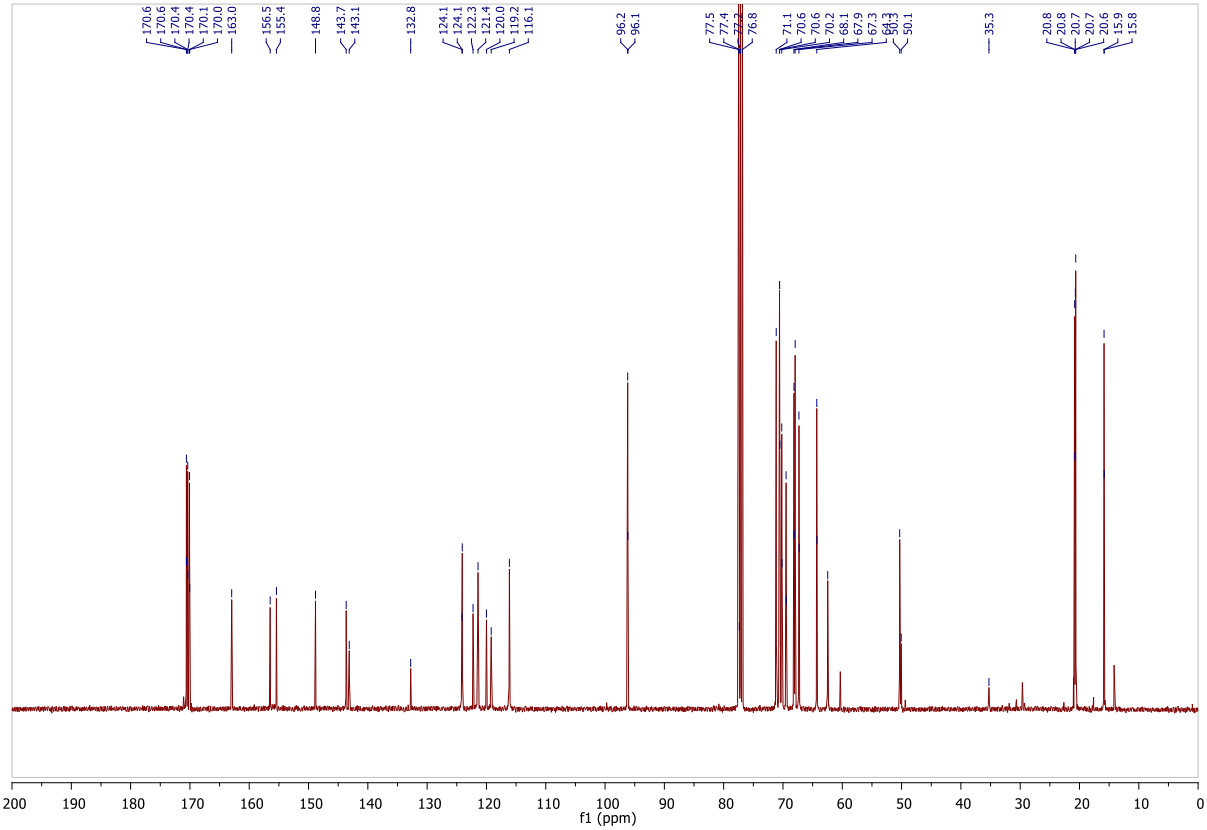
1.5
1.0
0.5
f1 (ppm)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200
190
180
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50
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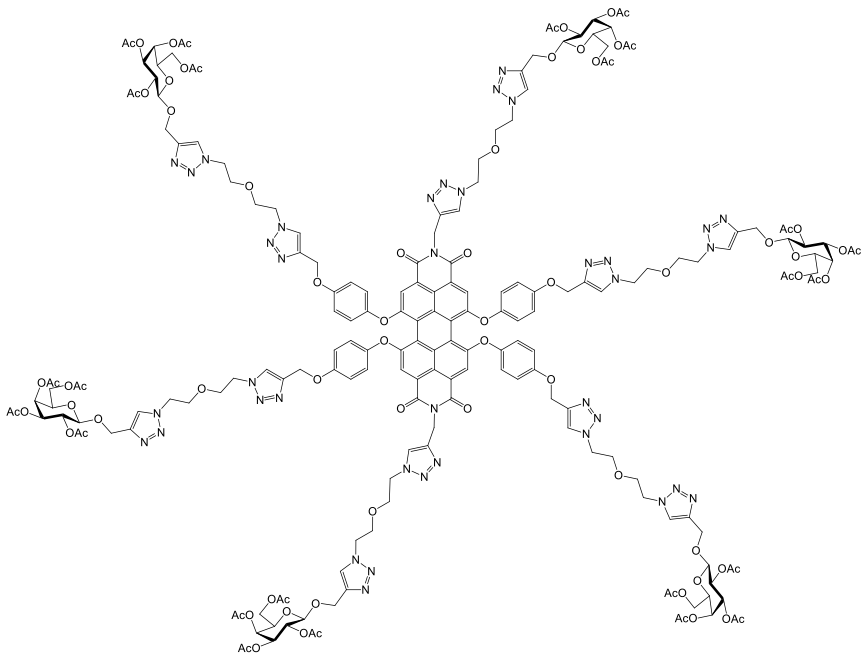
f1 (ppm)



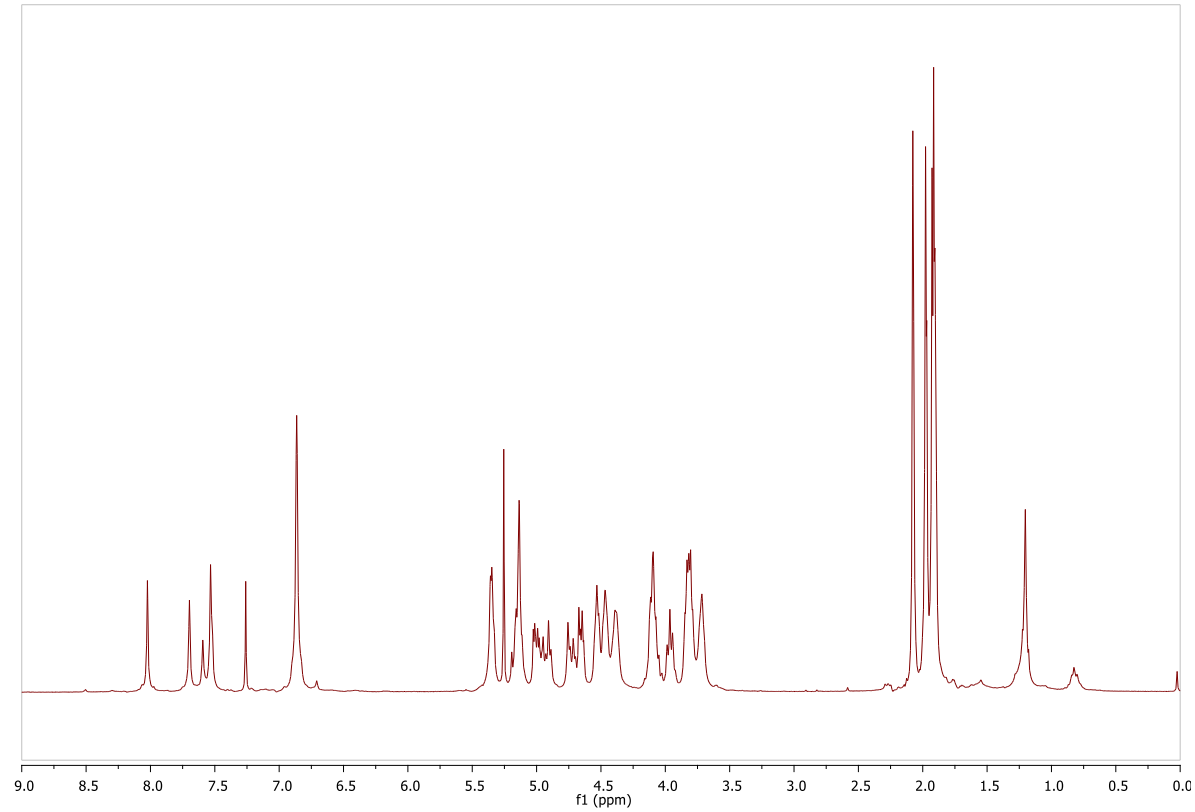
N*,*N*'-Bis-(4-{3-oxa-5-[4-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyloxymethyl)-triazol-1-yl]-pent-1-yl}-triazol-1-ylmethyl)-1,6,7,12-tetra-[4-(4-{3-oxa-5-[4-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyloxymethyl)-triazol-1-yl]-pent-1-yl}-triazol-1-ylmethyl)phenoxy]perylene-3,4,9,10-tetracarboxylic diimide (8e):** Obtained as a purple foam following ***Method A: **5** (50 mg, 0.048 mmol, 1 eq.), **7e** (231 mg, 0.428 mmol, 9 eq.), CuI (4.5 mg, 0.024 mmol, 0.5 eq.) and DIPEA (74 µL, 0.428 mmol, 9 eq.). Purified by silica gel flash chromatography (CH_2Cl_2/MeOH 99/1 to 93/7).

Yield = 65% (133 mg), $\mathbf{R_f}$ = 0.15 (CH_2Cl_2/MeOH 95/5).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.02 (s, 4H, perylene-H), 7.70 (s, 4H, H-triaz), 7.59 (s, 2H, H-triaz), 7.53 (s, 6H, H-triaz), 6.86 (bs, 16H, H-ar), 5.38-5.32 (d, *J* = 3.1 Hz, 6H, H-4, H-4'), 5.21-5.08 (m, 18H, H-3, O*C*H_2-triaz, N*C*H_2-triaz), 5.04-4.87 (m, 12H, H-2, GalO*C*H_2), 4.79-4.61 (m, 12H, H-1, GalO*C*H_2), 4.57-4.33 (m, 24H, N*C*$H_2$$CH_2$), 4.17-4.03 (m, 12H, H-6), 4.01-3.92 (m, 6H, H-5), 3.88-3.67 (m, 24H, OCH_2), 2.08 (bs, 18H, $COCH_3$), 2.00-1.95 (m, 18H, $COCH_3$), 1.94-1.88 (m, 36H, 2×$COCH_3$).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.4, 170.2, 170.0, 169.6, 169.5 (*C*OCH_3), 163.0 (Ar*C*ON), 156.5, 155.3, 148.8 (3×C^{IV}-ar-O), 144.2, 143.8, 143.2 (3×C^{IV}-triaz), 132.8 (C^{IV}-ar), 124.3, 124.1, 123.8 (3×CH-triaz), 122.2 (C^{IV}-ar), 121.5 (8C, CH-ar), 120.0, 119.2 (2×C^{IV}-ar), 119.1 (CH-perylene), 116.2 (8C, CH-ar), 100.5, 100.4 (2s, C-1, C-1'), 70.8 (C-3, C-3', C-5, C-5'), 69.3 (2×OCH_2), 68.8 (C-2, C-2'), 67.1 (C-4, C-4'), 63.0, 62.9 (2s, 2×GalO*C*H_2), 62.3 (O*C*H_2-triaz), 61.2 (C-6, C-6'), 50.10, 50.07, 50.0, 49.8 (4s, N*C*$H_2$$CH_2$), 35.2 (N*C*$H_2$-triaz), 20.8, 20.74, 20.68, 20.65, 20.57 (4×CO*C*H_3).

HR-ESI-QTof (positive mode) *m*/*z*: calcd for $C_{192}H_{221}N_{38}O_{78}$ $[M+3H]^{3+}$ 1435.1826, found 1435.1802.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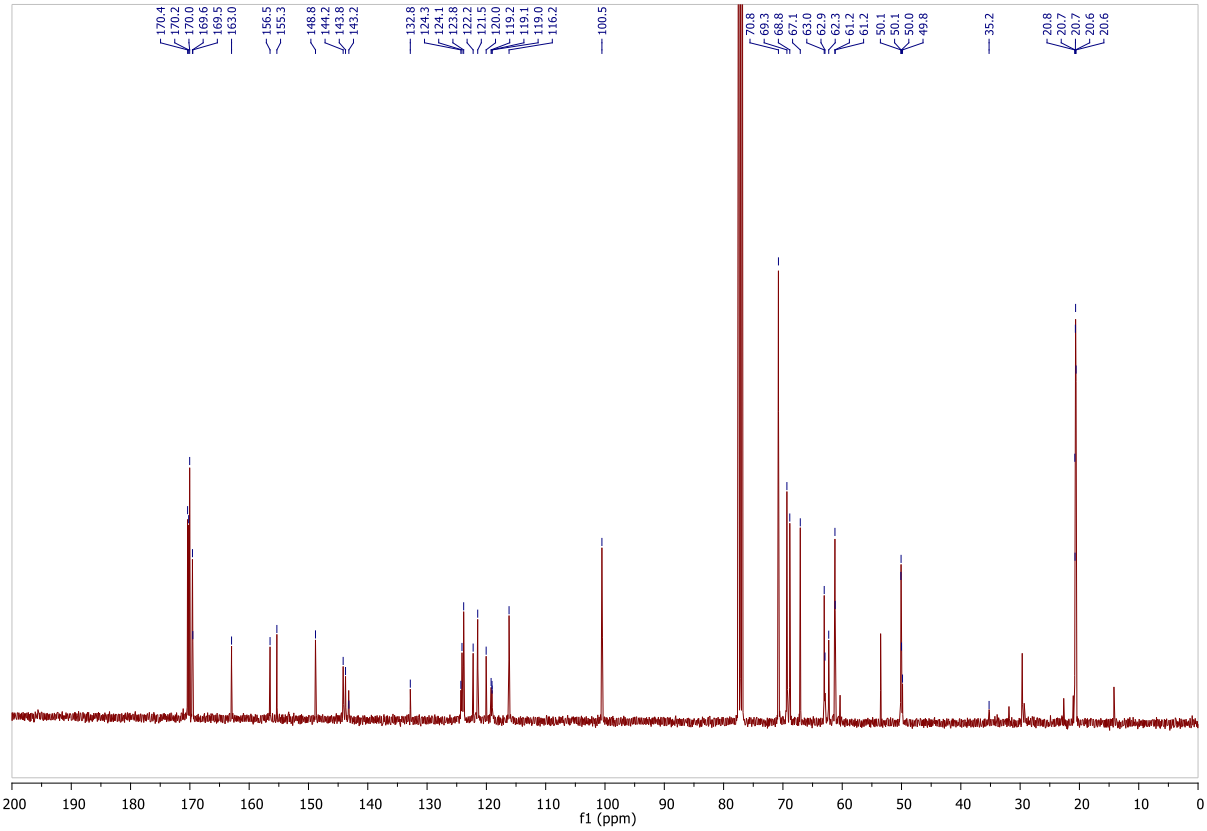
f1 (ppm)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124.3
124.1
123.8
122.2
121.5
120.0
119.2
119.1
119.0
116.2
100.5
70.8
69.3
68.8
67.1
63.0
62.9
62.3
61.2
61.2
50.1
50.1
50.0
49.8
35.2
20.8
20.7
20.7
20.6
20.6
200
190
180
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130
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110
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90
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50
40
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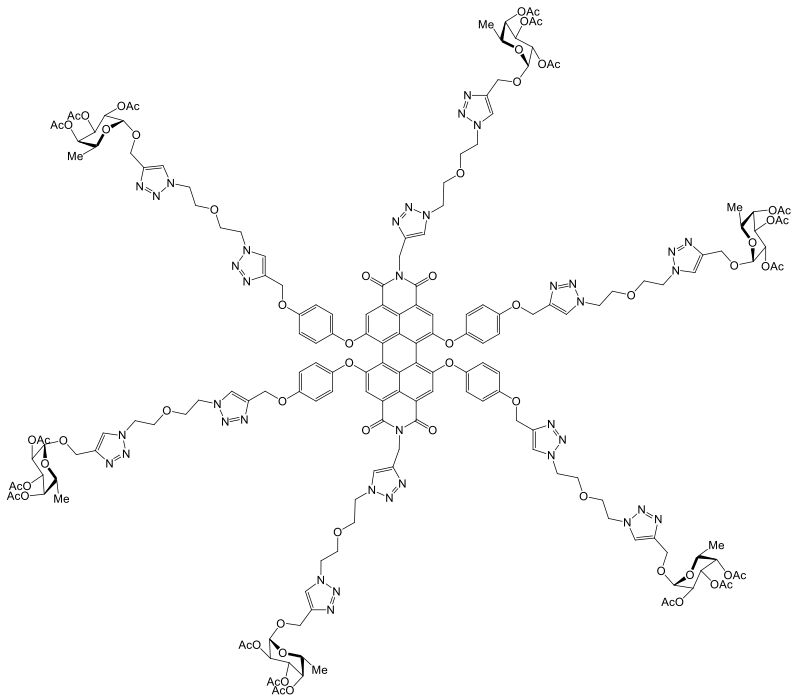
20
10
0
f1 (ppm)



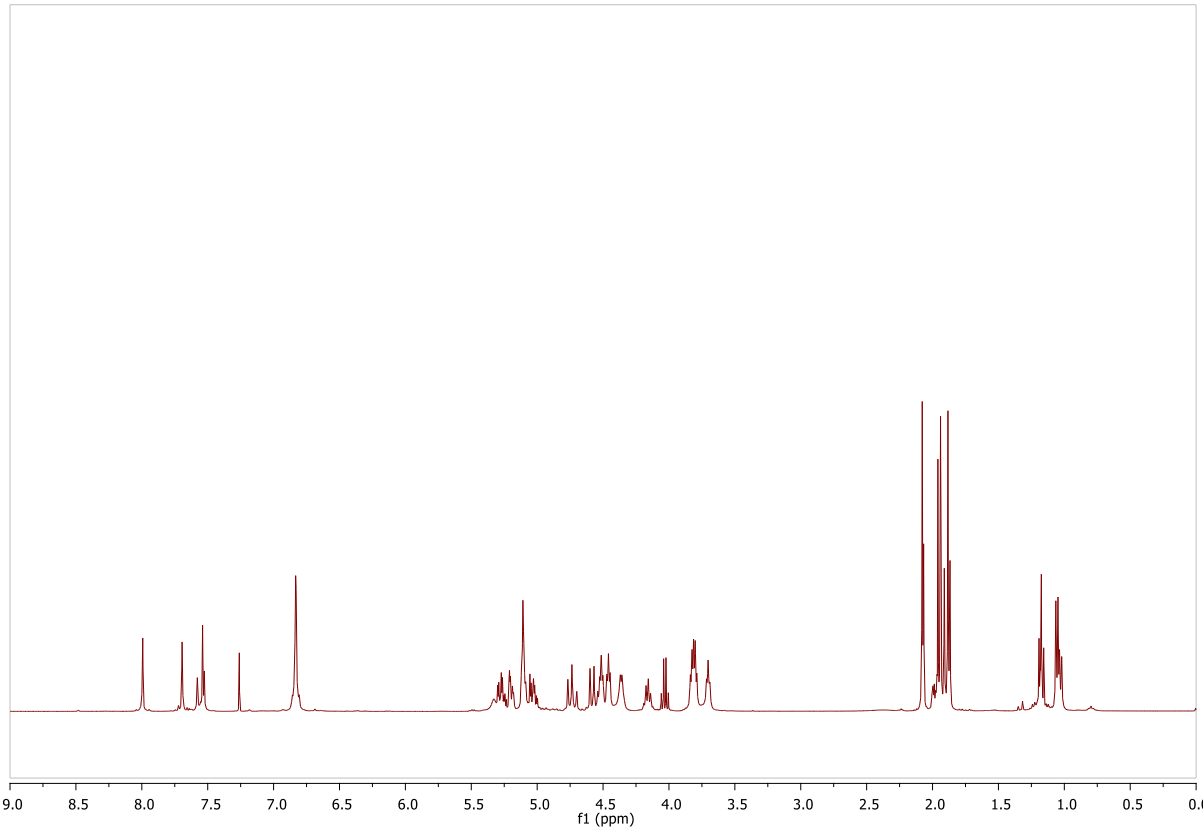
N*,*N*'-Bis-(4-{3-oxa-5-[4-(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyloxymethyl)-triazol-1-yl]-pent-1-yl}-triazol-1-ylmethyl)-1,6,7,12-tetra-[4-(4-{3-oxa-5-[4-(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyloxymethyl)-triazol-1-yl]-pent-1-yl}-triazol-1-ylmethyl)phenoxy]perylene-3,4,9,10-tetracarboxylic diimide (8f):** Obtained as a purple foam following ***Method A: **5** (50 mg, 0.048 mmol, 1 eq.), **7f** (207 mg, 0.428 mmol, 9 eq.), CuI (4.5 mg, 0.024 mmol, 0.5 eq.) and DIPEA (74 µL, 0.428 mmol, 9 eq.). Purified by silica gel flash chromatography (CH_2Cl_2/MeOH 99/1 to 93/7).

Yield = 56% (120 mg), $\mathbf{R_f}$ = 0.15 (CH_2Cl_2/MeOH 95/5).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.99 (s, 4H, perylene-H), 7.69 (s, 4H, H-triaz), 7.58 (s, 2H, H-triaz), 7.54 (s, 4H, H-triaz), 7.53 (s, 2H, H-triaz), 6.83 (bs, 16H, H-ar), 5.28, 5.26 (2dd, *J* = 10.9, 3.3 Hz, 6H, H-3, H-3'), 5.23 (bs, 4H, NC*H*$_2$-triaz), 5.20 (dd, *J* = 8.8, 2.8 Hz, 6H, H-4, H-4'), 5.13-5.08 (m, 14H, H-1, H-1', OC*H*$_2$-triaz), 5.07-4.99 (m, 6H, H-2, H-2'), 4.73 (t, *J* = 13.5 Hz, 6H, FucOC*H*$_2$), 4.62-4.54 (m, 6H, FucOC*H*$_2$), 4.51 (t, *J* = 4.9 Hz, 8H, NC*H*$_2$CH$_2$), 4.46 (t, *J* = 4.9 Hz, 8H, NC*H*$_2$CH$_2$), 4.36 (d, *J* = 4.7 Hz, 8H, NC*H*$_2$CH$_2$), 4.17 (m, 6H, H-5, H-5'), 3.81 (m, 16H, OCH$_2$), 3.70 (t, *J* = 4.9 Hz, 8H, OCH$_2$), 2.08, 2.07, 1.94, 1.91, 1.88, 1.87 (6s, 54H, COCH$_3$), 1.06 (d, *J* = 6.5 Hz, 12H, H-6), 1.03 (d, *J* = 6.5 Hz, 6H, H-6').

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.5, 170.31, 170.29, 169.95, 169.93 (*C*OCH$_3$), 162.9 (Ar*C*ON), 156.4, 155.2, 148.7 (3×C^{IV}-ar-O), 143.72, 143.66, 143.1 (3×C^{IV}-triaz), 132.7 (C^{IV}-ar), 124.3, 123.89, 123.83 (3s, 3×CH-triaz), 122.1 (C^{IV}-ar), 121.4 (8C, CH-ar), 120.0, 119.1 (2×C^{IV}-ar), 119.0 (CH-perylene), 116.1 (8C, CH-ar), 95.4, 95.3 (C-1, C-1'), 71.0 (C-4, C-4'), 69.3 (2×OCH$_2$), 67.9 (C-3, C-3'), 67.8 (C-2, C-2'), 64.61, 64.57 (C-5, C-5'), 62.2 (O*C*H$_2$-triaz), 60.9, 60.8 (2s, 2×FucO*C*H$_2$), 50.04, 49.99, 49.9, 49.8 (N*C*H$_2$CH$_2$), 35.1 (N*C*H$_2$-triaz), 20.73, 20.71, 20.62, 20.60, 20.58 (3×CO*C*H$_3$), 15.78, 15.76 (C-6, C-6').

HR-ESI-QTof (positive mode) *m*/*z*: calcd for $C_{180}H_{209}N_{38}O_{66}$ $[M+3H]^{3+}$ 1319.4717, found 1319.4766.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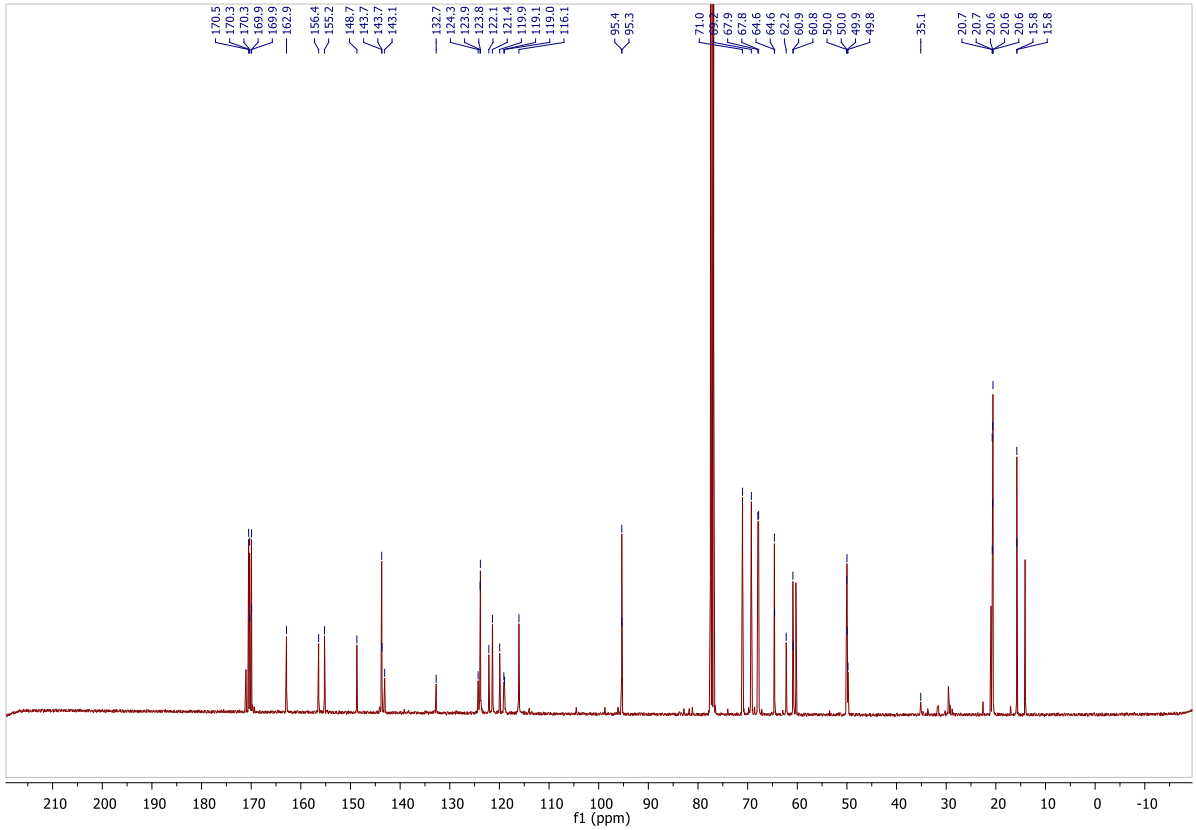
f1 (ppm)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170.3
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67.9
67.8
64.6
64.6
62.2
60.9
60.8
50.0
50.0
49.9
49.8
35.1
20.7
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15.8
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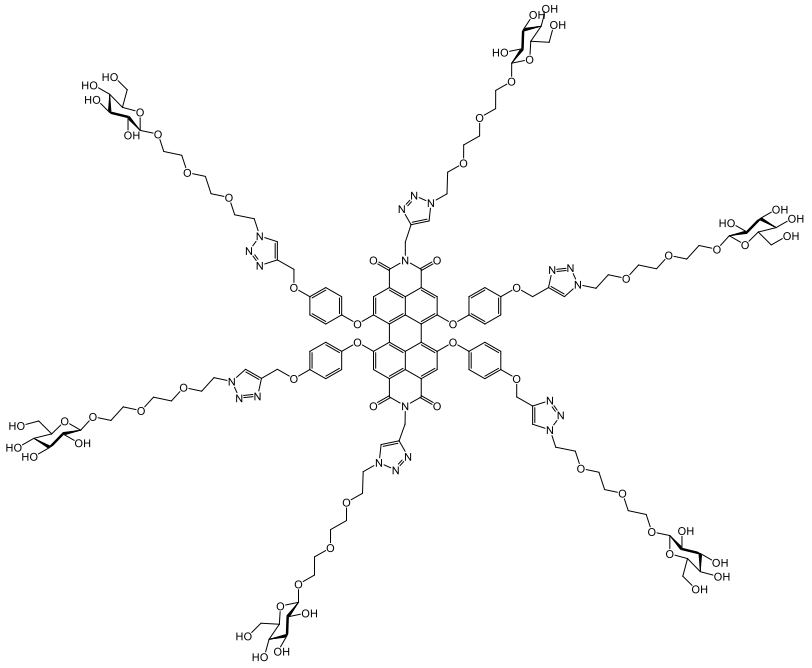
f1 (ppm)



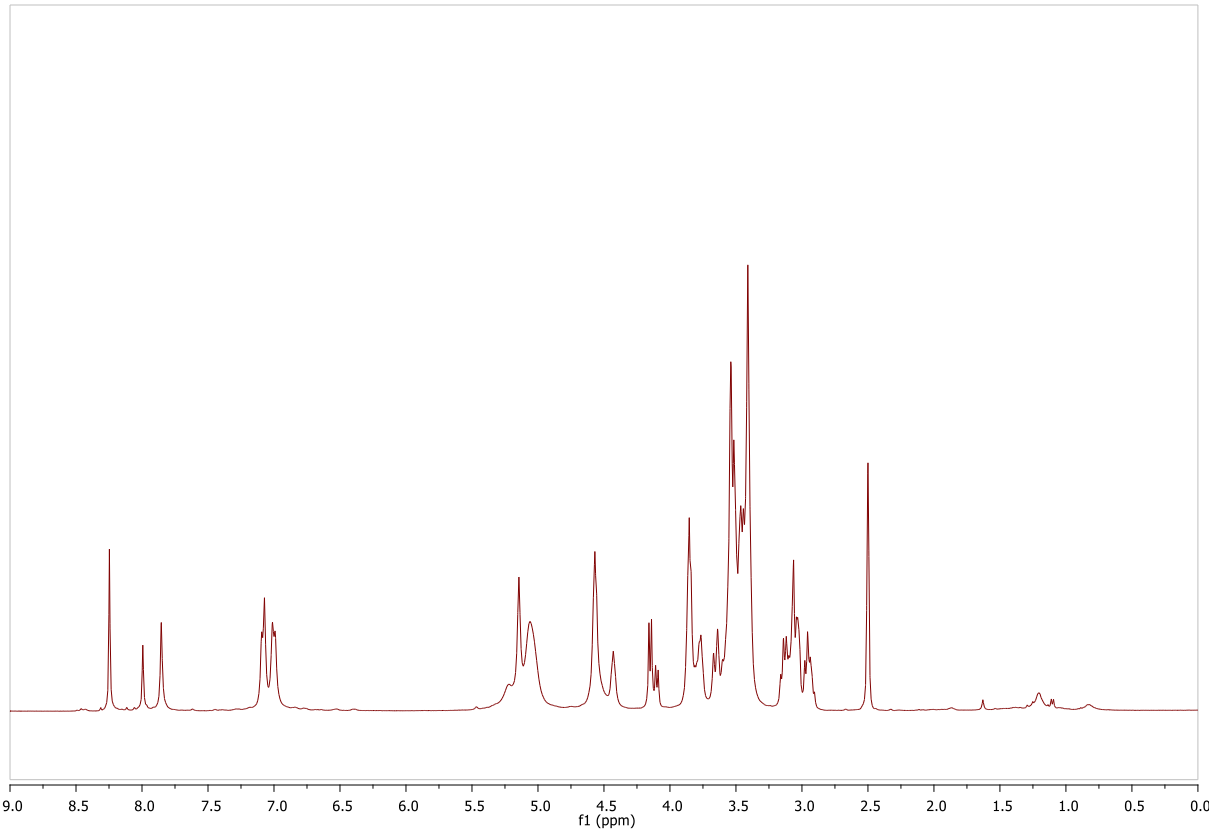
N,N*'-Bis-{1-[1-(β-D-glucopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyl}-1,6,7,12-tetra-(4-{1-[1-(β-D-glucopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyloxy}phenoxy)perylene-3,4,9,10-tetracarboxylic diimide (9a):** Obtained from **8a** (95 mg, 0.023 mmol) as a deep purple foam following ***Method B.

Yield = 98% (70 mg).

^{1}H NMR (400 MHz, DMSO-d$_6$ + εD$_2$O) δ (ppm): 8.25 (s, 4H, H-triaz), 7.99 (s, 2H, H-triaz), 7.85 (s, 4H, perylene-H), 7.04 (dd, *J* = 32.4, 7.9 Hz, 16H, CH-ar), 5.27-4.98 (m, 12H, OC*H*$_2$-triaz, NC*H*$_2$-triaz), 4.57, 4.43 (2bs, 12H, NC*H*$_2$CH$_2$), 4.15, 4.10 (2d, *J* = 7.7 Hz, 6H, H-1, H-1'), 3.93-3.73, 3.73-3.34 (2m, 72H, 5×OCH$_2$, H-6, H-6'), 3.20-2.90 (m, 24H, H-2, H-3, H-4, H-5).

^{13}C NMR (100 MHz, DMSO-d$_6$ + εD$_2$O) δ (ppm): 162.3 (Ar*C*ON), 156.1, 155.3, 148.2 (3×C^{IV}-ar-O), 142.6, 142.5 (2×C^{IV}-triaz), 132.4 (C^{IV}-ar), 125.2, 123.8 (2s, 2×CH-triaz), 122.2 (C^{IV}-ar), 121.5 (CH-ar), 119.0, 118.6 (2×C^{IV}-ar), 117.8 (CH-perylene), 116.2 (CH-ar), 103.0 (C-1, C-1'), 76.9 (C-3, C-3'), 76.7 (C-4, C-4'), 73.4 (C-2, C-2'), 70.1 (C-5, C-5'), 69.75, 69.72, 69.70, 69.6, 69.5, 68.8, 68.7, 67.9 (5×OCH$_2$), 61.6(O*C*H$_2$-triaz), 61.1 (C-6, C-6'), 49.6, 49.4 (N*C*H$_2$CH$_2$), 35.5 (N*C*H$_2$-triaz).

HR-ESI-QTof (positive mode) *m*/*z*: calcd for $C_{138}H_{178}N_{20}O_{60}$ $[M+2H]^{2+}$ 1537.5741, found 1537.5680.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7.5
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3.0
2.5
2.0
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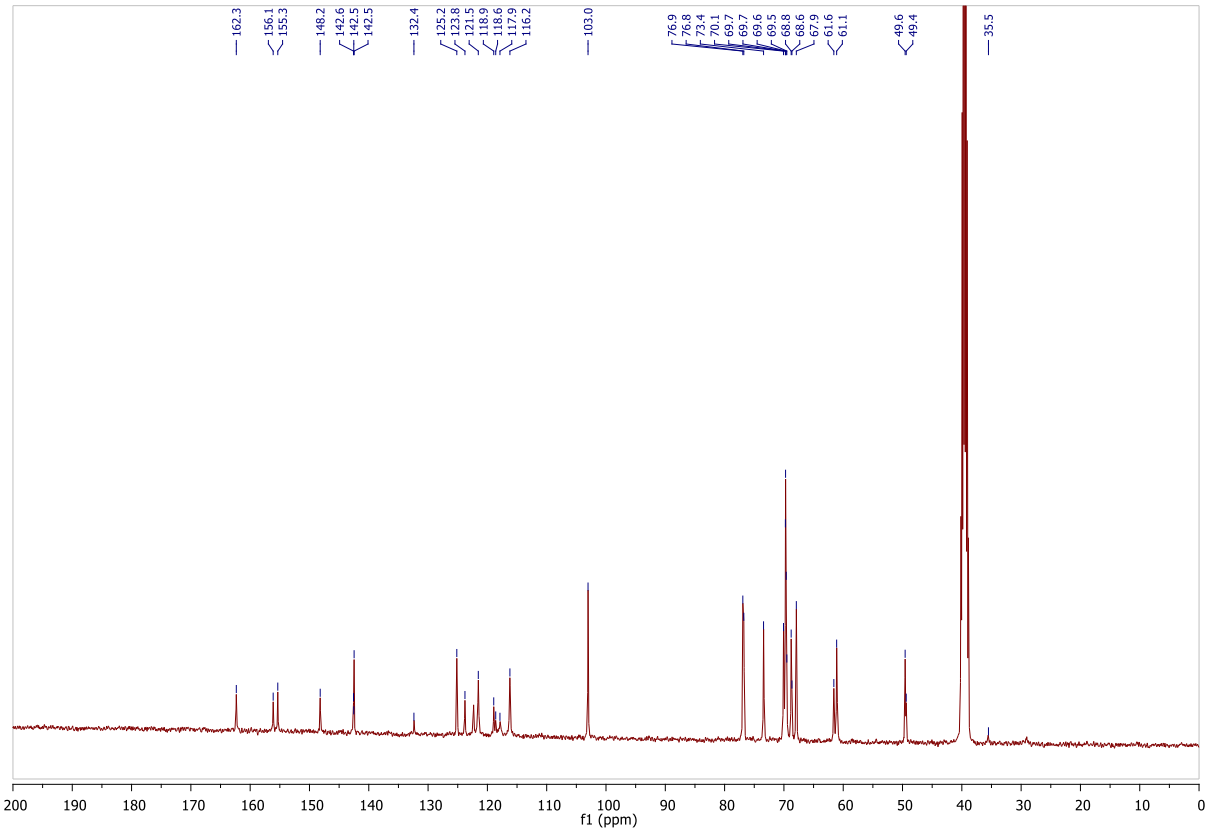
1.0
0.5
0.0
f1 (ppm)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69.6
69.5
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68.6
67.9
61.6
61.1
49.6
49.4
35.5
200
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180
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90
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50
40
30
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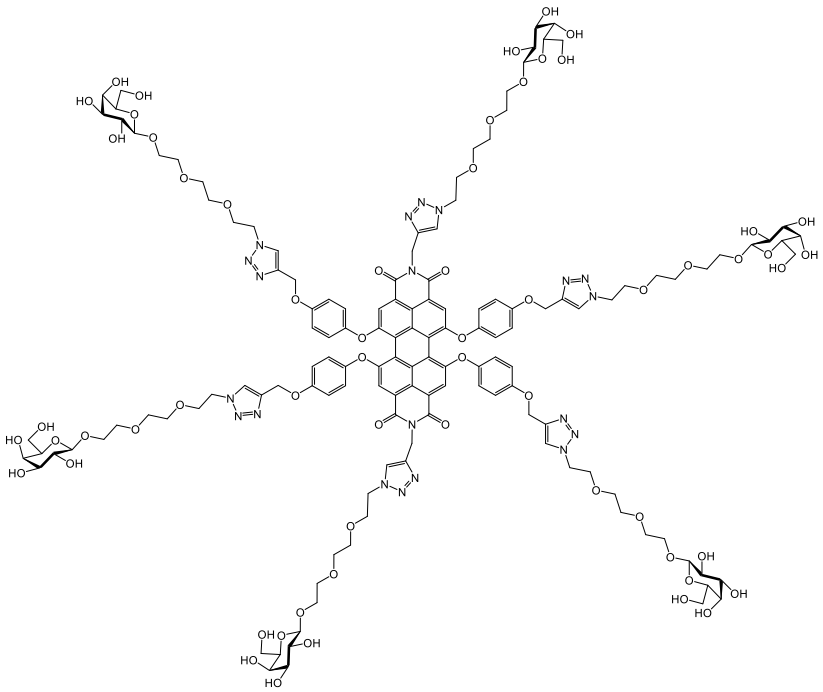
10
0
f1 (ppm)



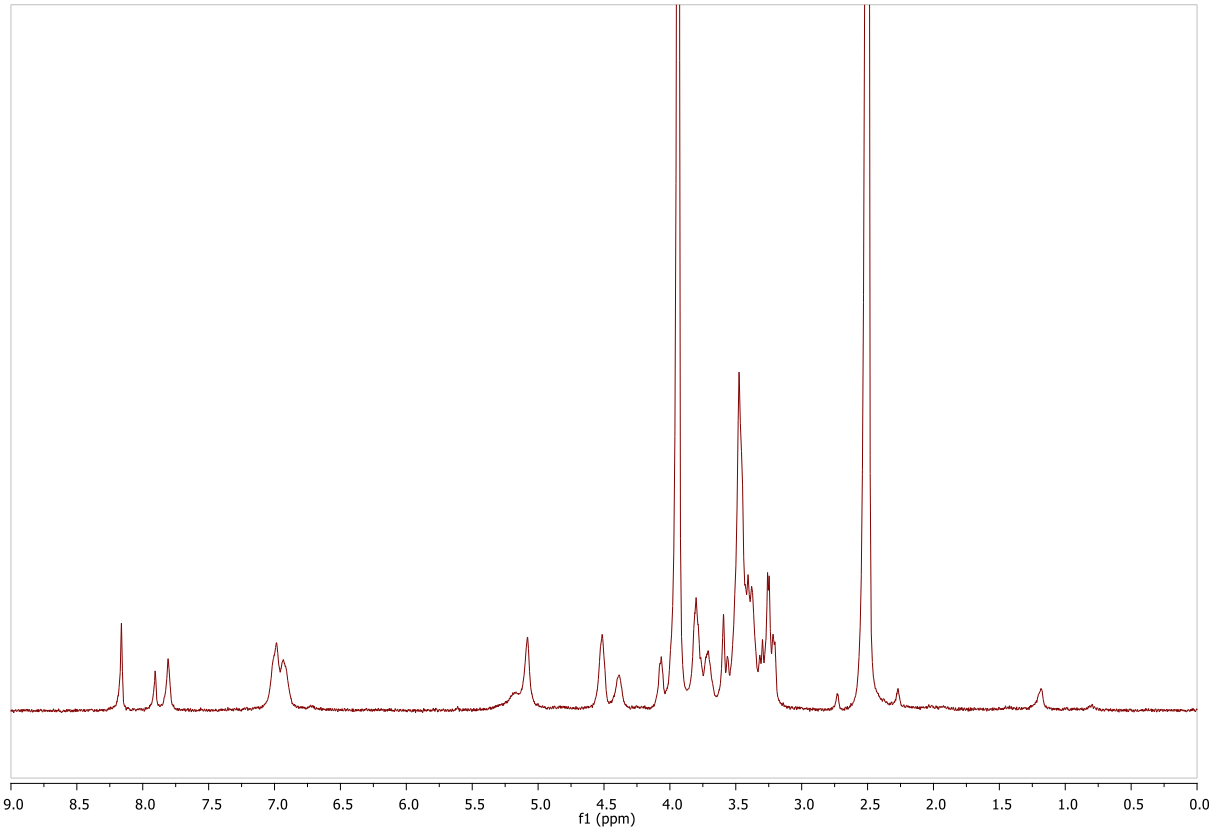
N*,*N*'-Bis-{1-[1-(β-D-galactopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyl}-1,6,7,12-tetra-(4-{1-[1-(β-D-galactopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyloxy}phenoxy)perylene-3,4,9,10-tetracarboxylic diimide (9b):** Obtained from **8b** (112 mg, 0.027 mmol) as a deep purple foam following ***Method B.

Yield = 88% (75 mg).

^{1}H NMR (300 MHz, DMSO-d$_6$ + εD$_2$O) δ (ppm): 8.16 (s, 4H, H-triaz), 7.91 (s, 2H, H-triaz), 7.81 (s, 4H, perylene-H), 6.96 (d, *J* = 15.9 Hz, 16H, CH-ar), 5.08 (s, 12H, OC*H*$_2$-triaz, NC*H*$_2$-triaz), 4.51, 4.38 (2s, 12H, NC*H*$_2$CH$_2$), 4.11-4.04 (m, 6H, H-1), 3.88-3.17 (m, 96H, H-2, H-3, H-4, H-5, H-6, 5×OCH$_2$).

^{13}C NMR (100 MHz, DMSO-d$_6$ + εD$_2$O) δ (ppm): 162.5 (Ar*C*ON), 156.2, 155.5, 148.4 (3×C^{IV}-ar-O), 142.8, 142.7 (2×C^{IV}-triaz), 132.5 (C^{IV}-ar), 125.4, 124.0 (2×CH-triaz), 122.4 (C^{IV}-ar), 121.6 (CH-ar), 119.2, 118.8 (2×C^{IV}-ar), 118.1 (CH-perylene), 116.4 (CH-ar), 103.7 (C-1), 75.4 (C-3), 75.3 (C-2), 73.5 (C-5), 70.7, 70.0, 69.9, 69.8, 69.7, 69.0, 68.8 (OCH$_2$), 68.5-68.2 (m, C-4, OCH$_2$), 68.1 (OCH$_2$), 61.7 (OCH$_2$-triaz), 60.6 (C-6), 49.8, 49.7 (N*C*H$_2$CH$_2$), 35.7 (NCH$_2$-triaz).

HR-ESI-QTof (positive mode) *m*/*z*: calcd for $C_{138}H_{176}N_{20}Na_2O_{60}$ $[M+2Na]^{2+}$ 1559.5580, found 1559.5608.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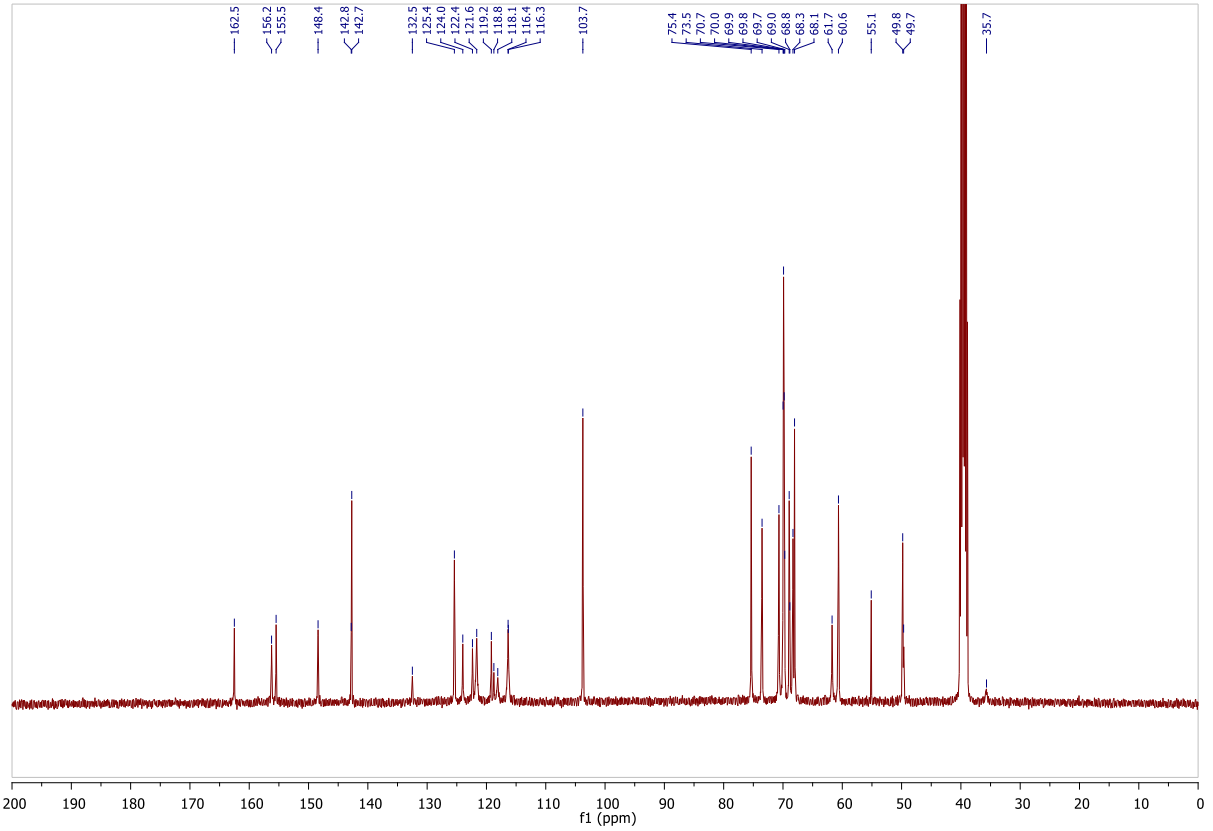
f1 (ppm)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116.4
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69.7
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49.7
35.7
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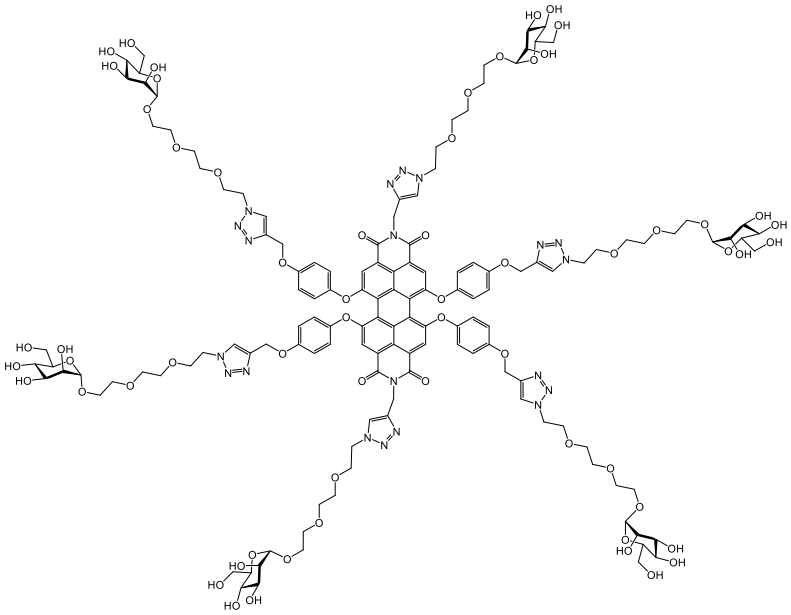
f1 (ppm)



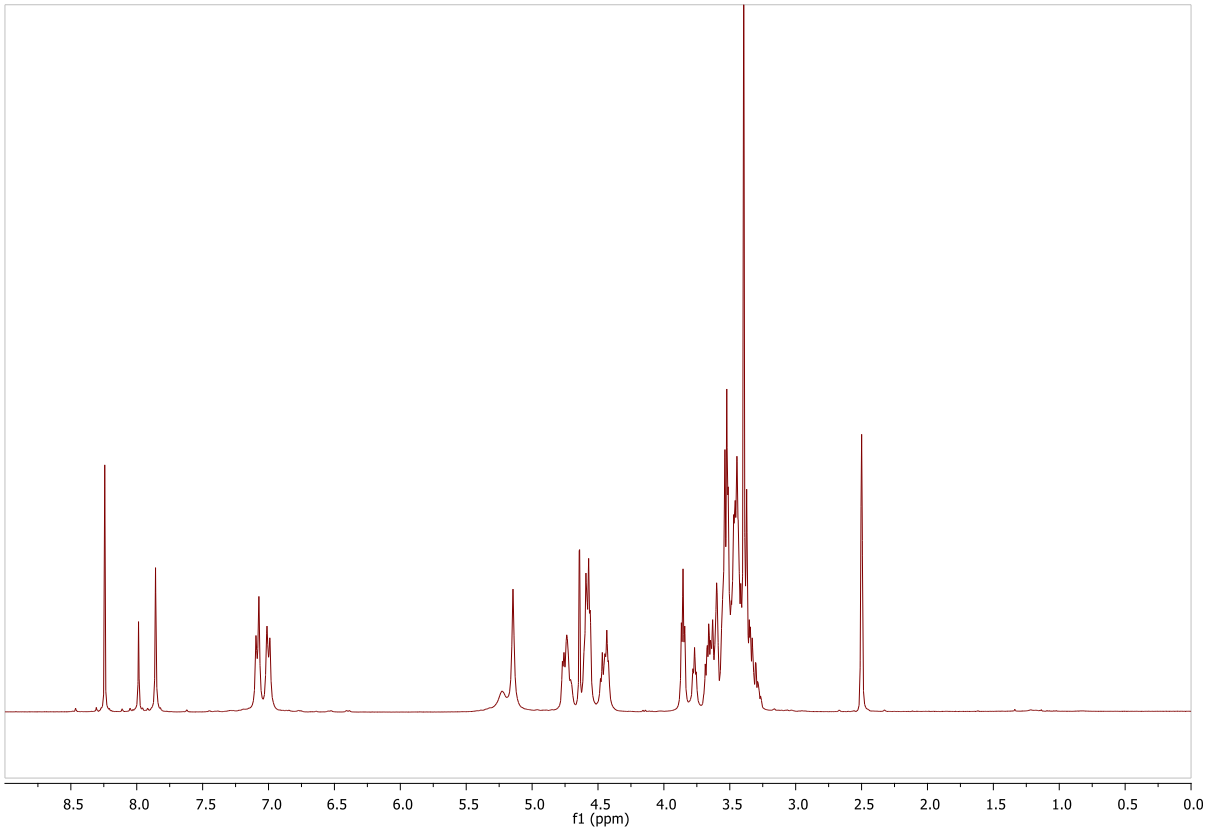
N,N*'-Bis-{1-[1-(α-D-mannopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyl}-1,6,7,12-tetra-(4-{1-[1-(α-D-mannopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyloxy}phenoxy)perylene-3,4,9,10-tetracarboxylic diimide (9c):** Obtained from **8c** (119 mg, 0.029 mmol) as a deep purple foam following ***Method B.

Yield = 87% (78 mg).

^{1}H NMR (400 MHz, DMSO-d$_6$ + εD$_2$O) δ (ppm): 8.24 (s, 4H, H-triaz), 7.99 (s, 2H, H-triaz), 7.86 (s, 4H, perylene-H), 7.04 (dd, J = 33.3, 8.7 Hz, 16H, CH-ar), 5.14 (bs, 12H, OCH_2-triaz, NCH_2-triaz), 4.64 (d, J = 1.2 Hz, 4H, H-1), 4.62-4.54 (m, 10H, H-1', NCH_2CH$_2$), 4.50-4.39 (m, 4H, NCH_2CH$_2$), 3.85 (t, J = 5.1 Hz, 8H, OCH$_2$), 3.77 (t, J = 5.1 Hz, 4H, OCH$_2$), 3.71-3.26 (m, 84H, H-2, H-2', H-3, H-3', H-4, H-4', H-5, H-5', H-6, H-6', 4×OCH$_2$).

^{13}C NMR (100 MHz, DMSO-d$_6$ + εD$_2$O) δ (ppm): 162.3 (Ar*C*ON), 156.1, 155.4, 148.2 (3×C^{IV}-ar-O), 142.6, 142.5 (2×C^{IV}-triaz), 132.3 (C^{IV}-ar), 125.1, 123.8 (2s, 2×CH-triaz), 122.3 (C^{IV}-ar), 121.5 (CH-ar), 118.9, 118.6 (2s, 2×C^{IV}-ar), 117.9 (CH-perylene), 116.2 (CH-ar), 100.0 (C-1, C-1'), 74.0 (C-4, C-4'), 71.0 (C-3, C-3'), 70.3 (C-2, C-2'), 69.74, 69.72, 69.60, 69.56, 69.50, 68.8, 68.7 (4×OCH$_2$), 67.0 (C-5, C-5'), 65.74, 65.70 (OCH$_2$), 61.6 (O*C*H$_2$-triaz), 61.3 (C-6, C-6'), 49.6, 49.4 (2s, N*C*H$_2$CH$_2$) 35.5 (N*C*H$_2$-triaz).

HR-ESI-QTof (positive mode) *m*/*z*: calcd for $C_{138}H_{178}N_{20}O_{60}$ $[M+2H]^{2+}$ 1537.5741, found 1537.5681.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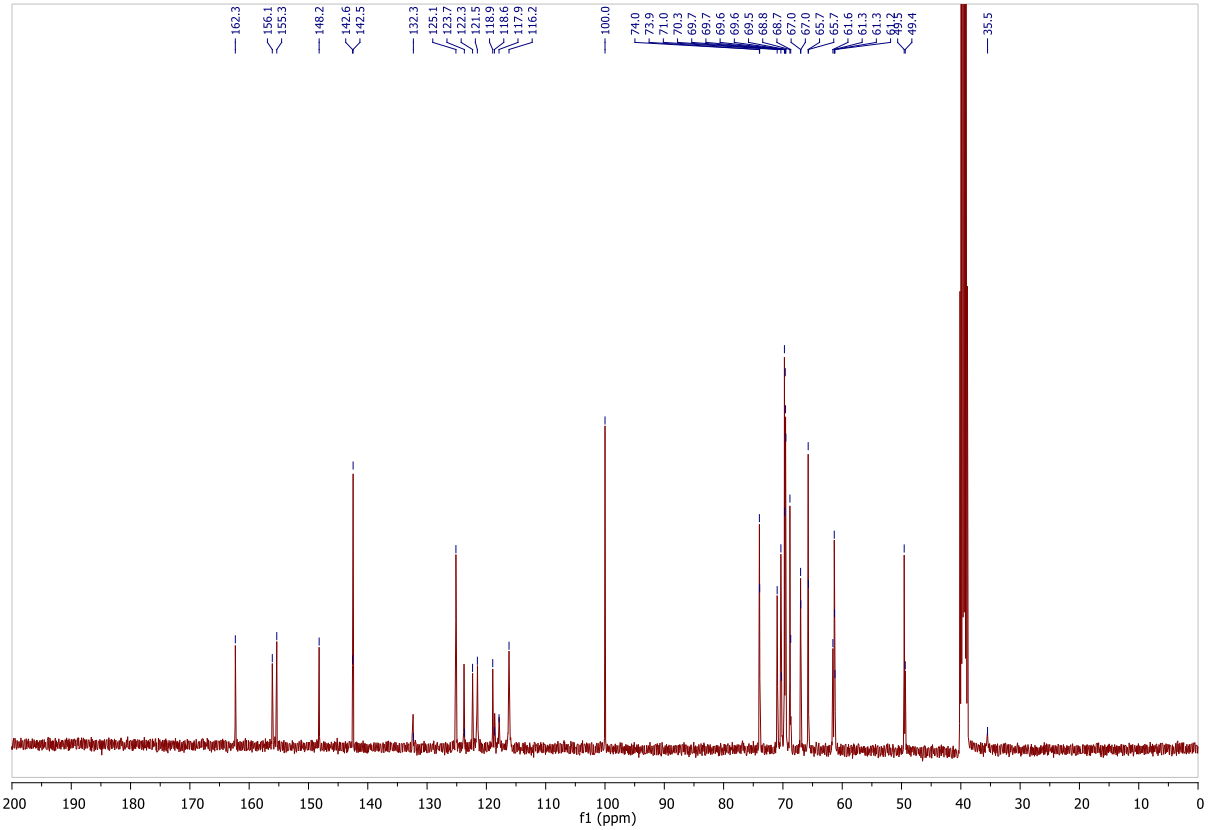
1.0
0.5
0.0
f1 (ppm)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155.3
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125.1
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116.2
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73.9
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70.3
69.7
69.7
69.6
69.6
69.5
68.8
68.7
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67.0
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65.7
61.6
61.3
61.3
49.2
49.4
35.5
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190
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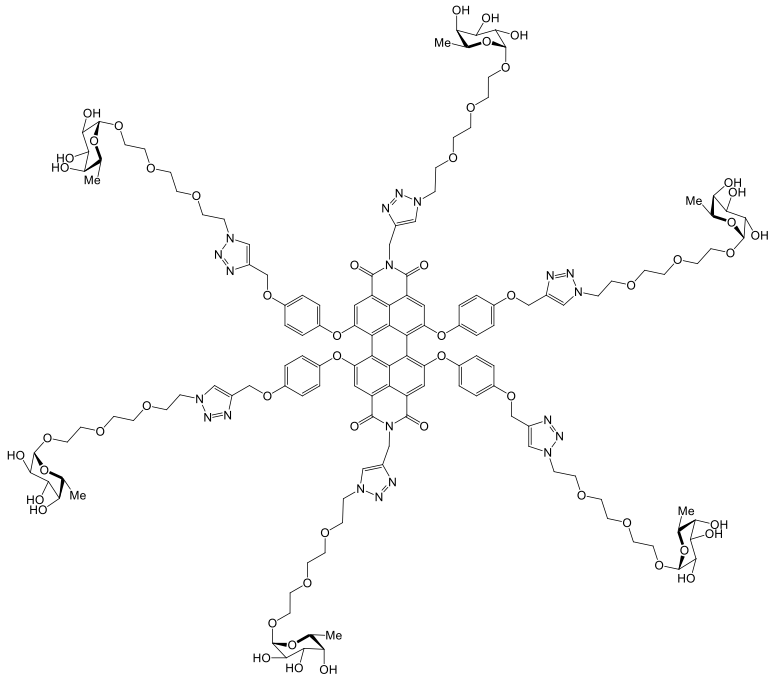
f1 (ppm)



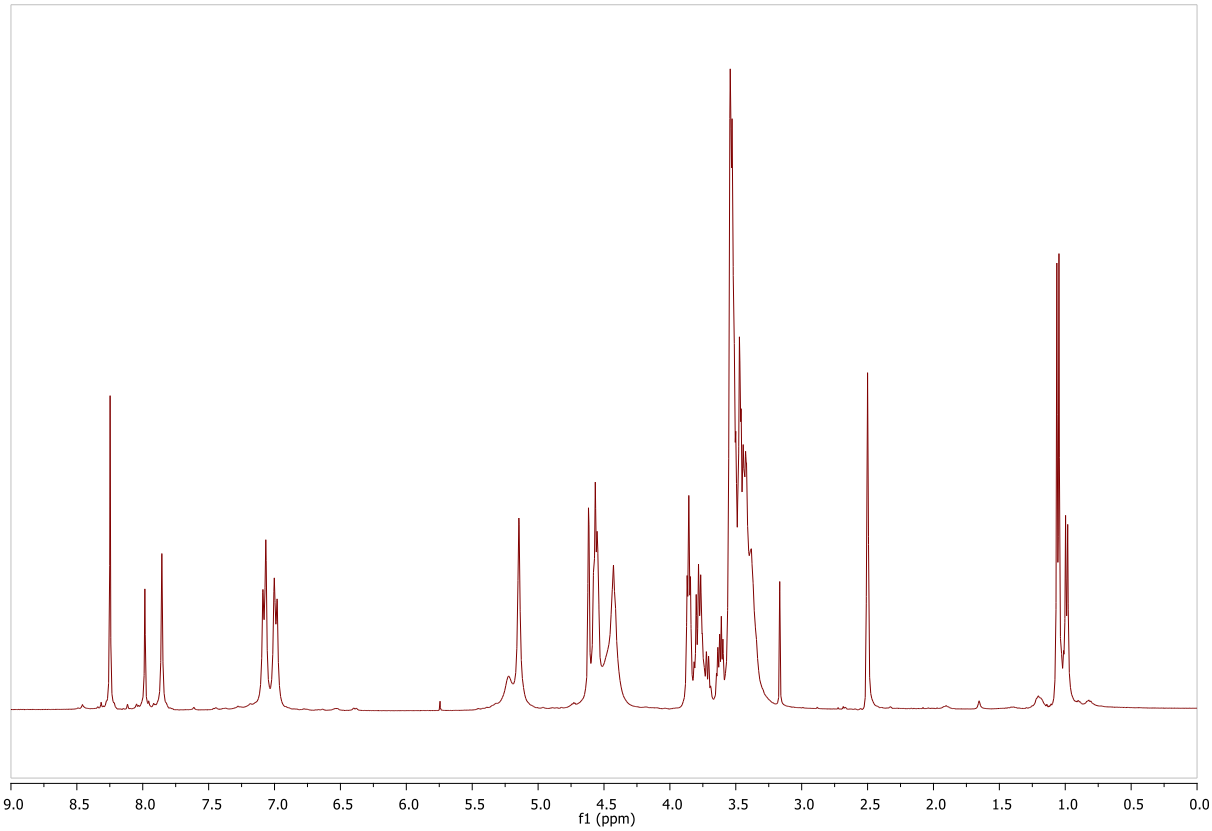
N,N*'-Bis-{1-[1-(α-L-fucopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyl}-1,6,7,12-tetra-(4-{1-[1-(α-L-fucopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyloxy}phenoxy)perylene-3,4,9,10-tetracarboxylic diimide (9d) :** Obtained from **8d** (103 mg, 0.035 mmol) as a deep purple foam following ***Method B.

Yield = 80% (66 mg).

^{1}H NMR (300 MHz, DMSO-d$_6$ + εD$_2$O) δ (ppm): 8.25 (s, 4H, H-triaz), 7.98 (s, 2H, H-triaz), 7.85 (s, 4H, perylene-H), 7.08, 6.99 (2d, J = 8.6 Hz, 16H, CH-ar), 5.22 (bs, 4H, NCH_2-triaz), 5.15 (s, 8H, OCH_2-triaz), 4.70-4.35 (m, 18H, H-1, H-1', NCH_2CH$_2$), 3.95-3.26 (m, 84H, H-2, H-2', H-3, H-3', H-4, H-4', H-5, H-5', 5×OCH$_2$), 1.06, 0.99 (2d, J = 6.5 Hz, 18H, H-6, H-6').

^{13}C NMR (100 MHz, DMSO-d$_6$ + εD$_2$O) δ (ppm): 162.3 (Ar*C*ON), 156.1, 155.3, 148.2 (3×C^{IV}-ar-O), 142.6, 142.5 (2×C^{IV}-triaz), 132.3 (C^{IV}-ar), 125.1, 123.8 (2×CH-triaz), 122.3 (C^{IV}-ar), 121.5 (CH-ar), 118.9, 118.6 (2×C^{IV}-ar), 117.8 (CH-perylene), 116.2 (CH-ar), 99.35, 99.29 (C-1, C-1'), 71.6 (C-4, C-4'), 69.8 (C-3, C-3'), 69.63, 69.56, 69.5, 68.8, 68.7 (4×OCH$_2$), 68.1 (C-2, C-2'), 66.7, 66.6 (FucO*C*H$_2$), 65.94, 65.89 (C-5, C-5'), 61.6 (O*C*H$_2$-triaz), 49.6, 49.4 (N*C*H$_2$CH$_2$), 35.5 (N*C*H$_2$-triaz), 16.5, 16.4 (C-6, C-6').

HR-ESI-QTof (positive mode) *m*/*z*: calcd for $C_{138}H_{178}N_{20}O_{54}$ $[M+2H]^{2+}$ 1489.5893, found 1489.5869.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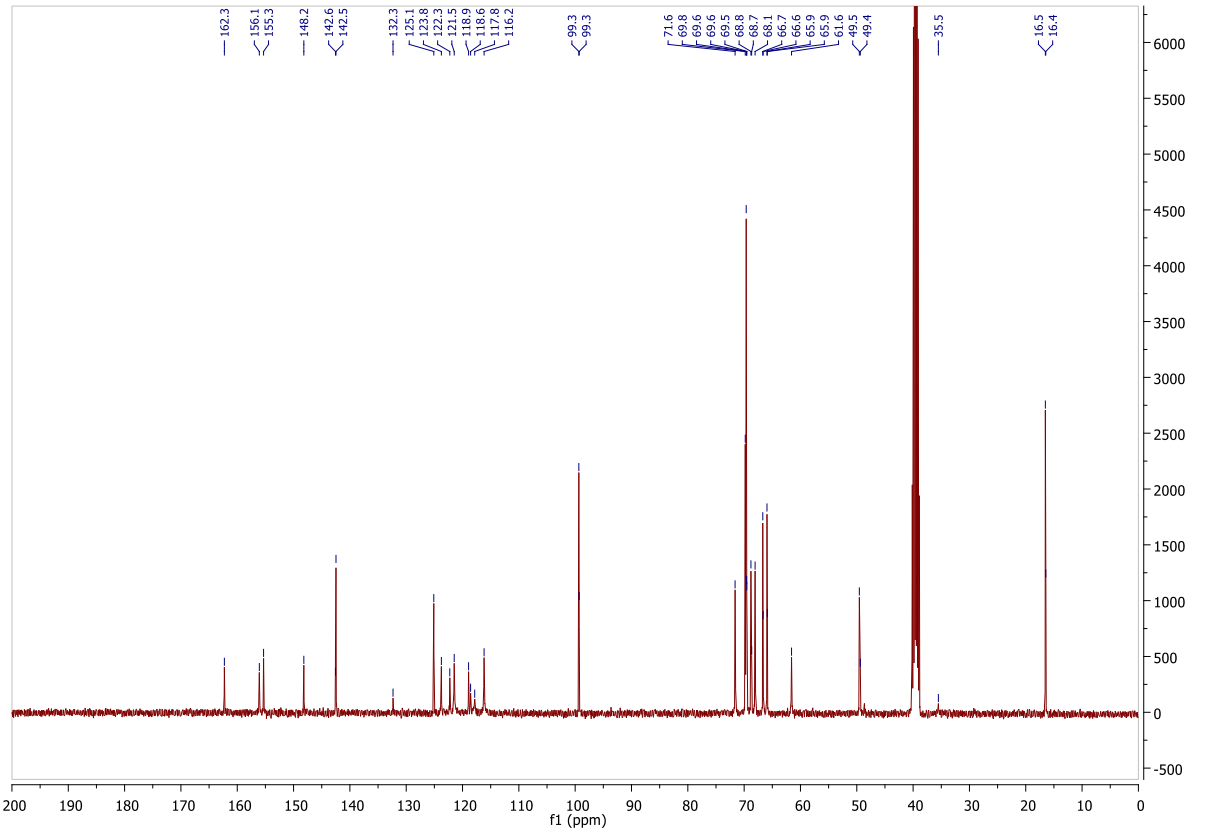
f1 (ppm)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65.9
61.6
49.5
49.4
35.5
16.5
16.4
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
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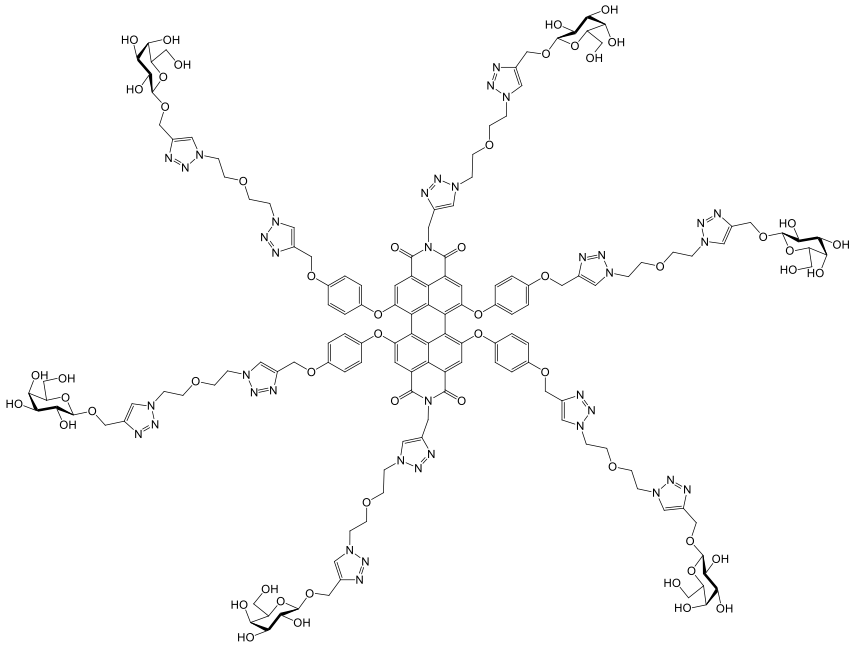


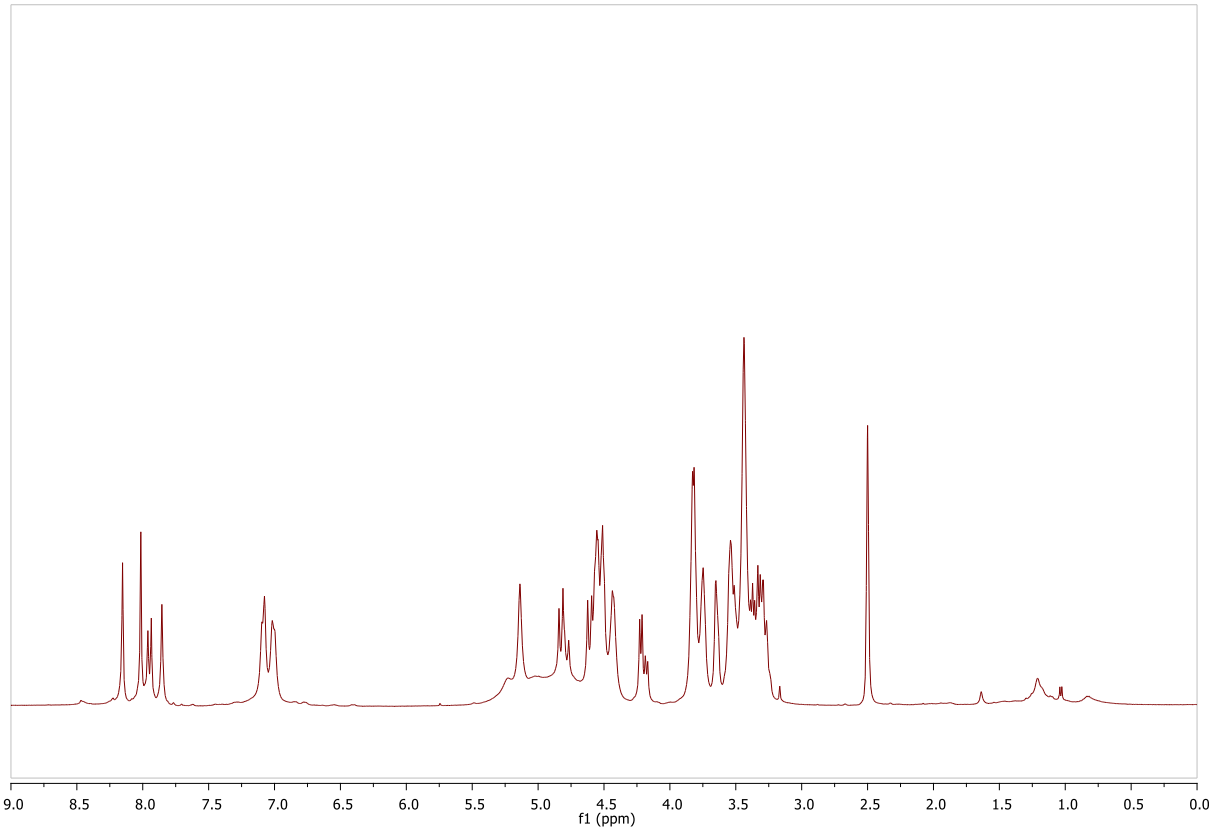
N*,*N*'-Bis-(4-{3-oxa-5-[4-(β-D-galactopyranosyloxymethyl)-triazol-1-yl]-pent-1-yl}-triazol-1-ylmethyl)-1,6,7,12-tetra-[4-(4-{3-oxa-5-[4-(β-D-galactopyranosyloxymethyl)-triazol-1-yl]-pent-1-yl}-triazol-1-ylmethyl)phenoxy]perylene-3,4,9,10-tetracarboxylic diimide (9e):** Obtained from **8e** (111 mg, 0.026 mmol) as a deep purple foam following ***Method B.

Yield = 98% (83 mg).

^{1}H NMR (400 MHz, DMSO-d$_6$ + εD$_2$O) δ (ppm): 8.15 (s, 4H, H-triaz), 8.01 (s, 4H, H-triaz), 7.96 (s, 2H, H-triaz), 7.94 (s, 2H, H-triaz), 7.85 (s, 4H, perylene-H), 7.05 (dd, *J* = 30.8, 7.0 Hz, 16H, CH-ar), 5.18-5.09, 4.86-4.74, 4.65-4.37 (3m, 48H, OC*H*$_2$-triaz, NC*H*$_2$-triaz, GalOC*H*$_2$, NC*H*$_2$CH$_2$), 4.22 (d, *J* = 7.2 Hz, 4H, H-1), 4.18 (d, *J* = 7.2 Hz, 2H, H-1'), 3.87-3.71 (m, 24H, 2×OCH$_2$), 3.67-3.62 (m, 6H, H-4, H-4'), 3.58-3.49 (m, 12H, H-6, H-6'), 3.40-3.23 (m, 18H, H-2, H-2', H-3, H-3', H-5, H-5').

^{13}C NMR (100 MHz, DMSO-d$_6$ + εD$_2$O) δ (ppm): 162.4 (Ar*C*ON), 156.1, 155.4, 148.2 (3×C^{IV}-ar-O), 143.92, 143.85, 142.7, 142.5 (4×C^{IV}-triaz), 132.4 (C^{IV}-ar), 125.2, 124.6, 124.5, 123.9 (4×CH-triaz), 122.4 (C^{IV}-ar), 121.6 (CH-ar), 118.9, 118.6 (2×C^{IV}-ar), 117.9 (CH-perylene), 116.2 (CH-ar), 102.8 (C-1, C-1'), 75.39, 75.35 (C-3, C-3'), 73.5 (C-2, C-2'), 70.6 (C-5, C-5'), 68.6, 68.5 (2×OCH$_2$), 68.2 (C-4, C-4'), 61.53, 61.46, 61.4 (O*C*H$_2$-triaz, GalO*C*H$_2$), 60.6 (C-6, C-6'), 49.4, 49.3, 49.2 (N*C*H$_2$CH$_2$), 35.6 (N*C*H$_2$-triaz).

HR-ESI-QTof (positive mode) *m*/*z*: calcd for $C_{144}H_{173}N_{38}O_{54}$ $[M+3H]^{3+}$ 1099.3981, found 1099.3950.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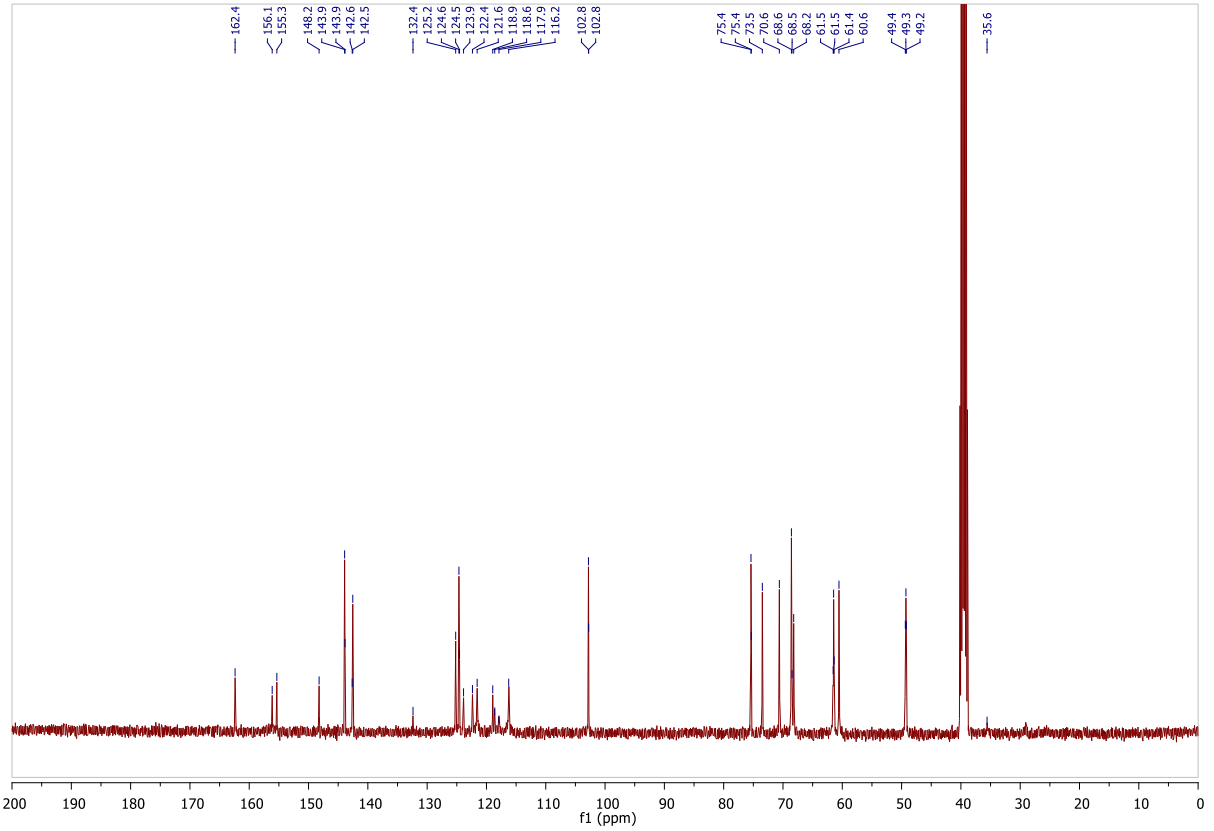
f1 (ppm)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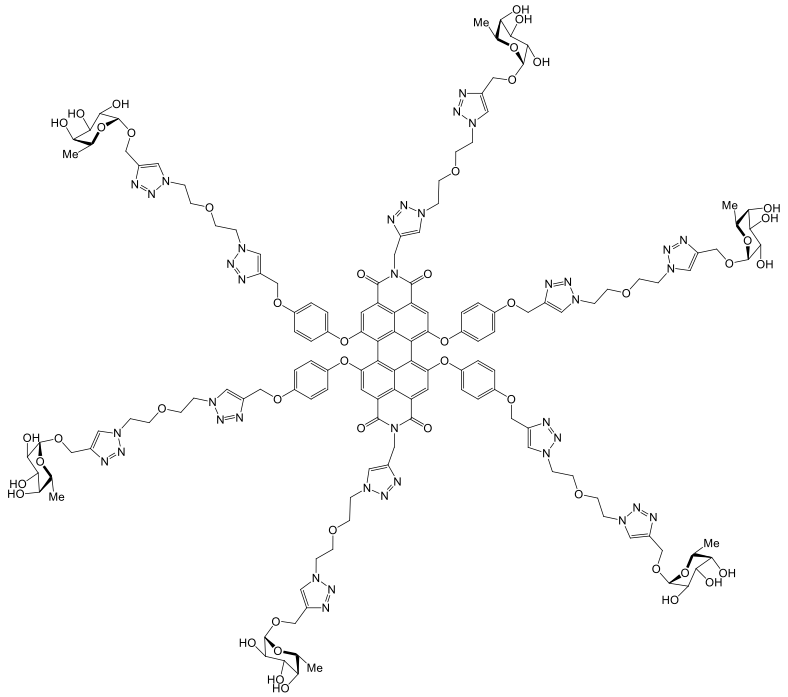
f1 (ppm)



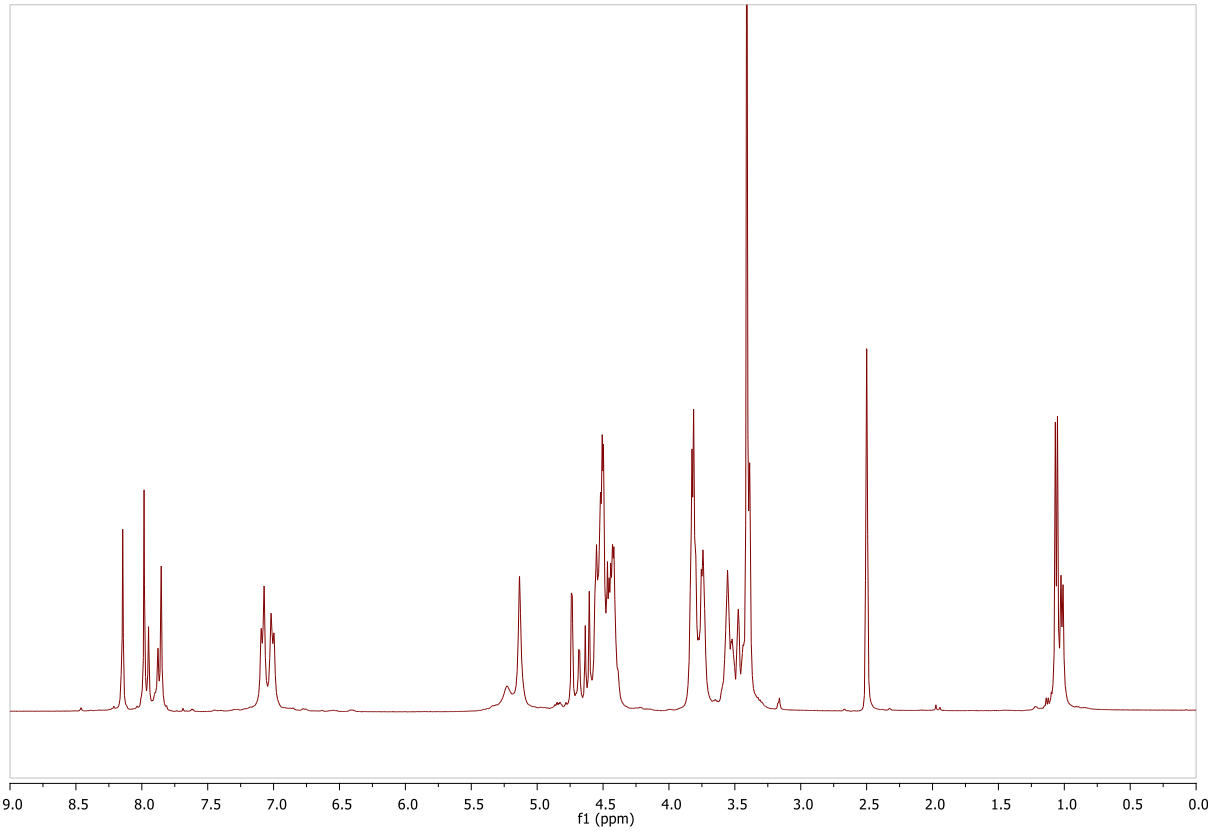
N*,*N*'-Bis-(4-{3-oxa-5-[4-(α-L-fucopyranosyloxymethyl)-triazol-1-yl]-pent-1-yl}-triazol-1-ylmethyl)-1,6,7,12-tetra-[4-(4-{3-oxa-5-[4-(α-L-fucopyranosyloxymethyl)-triazol-1-yl]-pent-1-yl}-triazol-1-ylmethyl)phenoxy]perylene-3,4,9,10-tetracarboxylic diimide (9f):** Obtained from **8f** (93 mg, 0.023 mmol) as a deep purple foam following ***Method B.

Yield = 92% (69 mg).

^{1}H NMR (400 MHz, DMSO-d$_6$ + εD$_2$O) δ (ppm): 8.14 (s, 4H, H-triaz), 7.98 (s, 4H, H-triaz), 7.95 (s, 2H, H-triaz), 7.87 (s, 2H, H-triaz), 7.85 (s, 4H, perylene-H), 7.03 (d, *J* = 8.5 Hz, 8H, CH-ar), 6.98 (d, *J* = 8.5 Hz, 8H, CH-ar), 5.35-5.19 (m, 4H, NC*H*$_2$-triaz), 5.19-3.05 (m, 8H, OC*H*$_2$-triaz), 4.74, 4.68 (2d, *J* = 3.1 Hz, 6H, H-1, H-1'), 4.65-4.38 (m, 36H, 2×NC*H*$_2$CH$_2$, FucOC*H*$_2$), 3.85-3.71 (m, 30H, 2×OCH$_2$, H-5, H-5'), 3.60-3.36 (m, 18H, H-2, H-2', H-3, H-3', H-4, H-4'), 1.06, 1.02 (2d, *J* = 6.4 Hz, 18H, H-6, H-6').

^{13}C NMR (100 MHz, DMSO-d$_6$ + εD$_2$O) δ (ppm): 162.4 (Ar*C*ON), 156.1, 155.3, 148.2 (3×C^{IV}-ar-O), 144.0, 143.9, 142.6, 142.5 (4×C^{IV}-triaz), 132.4 (C^{IV}-ar), 125.2, 124.4, 124.3, 123.9 (4×CH-triaz), 122.3 (C^{IV}-ar), 121.6 (CH-ar), 118.9, 118.6 (2×C^{IV}-ar), 117.8 (CH-perylene), 116.2 (CH-ar), 98.64, 98.58 (C-1, C-1'), 71.7, 71.5 (C-4, C-4'), 69.7 (C-3, C-3'), 68.6, 68.4 (2×OCH$_2$), 68.1, 68.0 (C-2, C-2'), 66.2, 66.1 (C-5, C-5'), 61.5, 60.1, 60.0 (O*C*H$_2$-triaz, FucO*C*H$_2$), 49.4, 49.24, 49.18 (N*C*H$_2$CH$_2$), 35.5 (N*C*H$_2$-triaz), 16.50, 16.45 (C-6, C-6').

HR-ESI-QTof (positive mode) *m*/*z*: calcd for $C_{144}H_{170}N_{38}O_{48}$ $[M+2H]^{2+}$ 1599.6009, found 1599.5999.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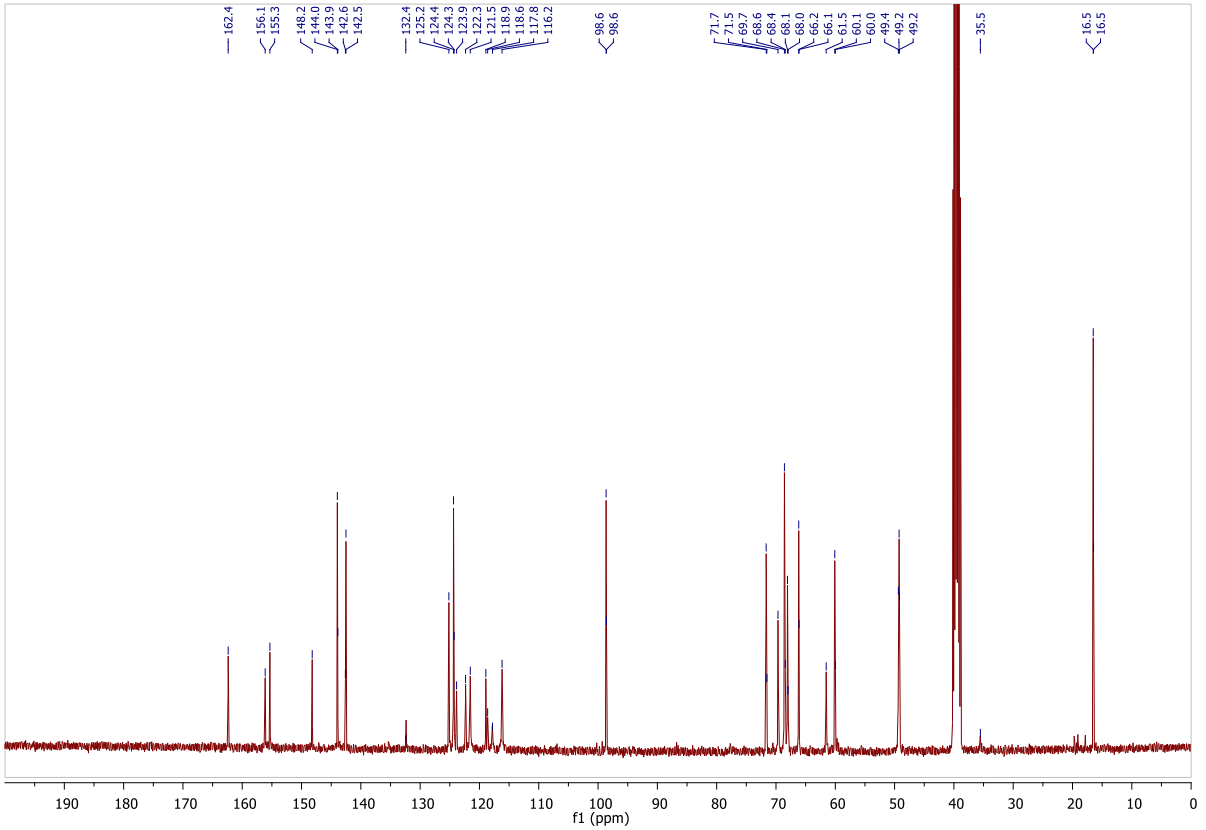
f1 (ppm)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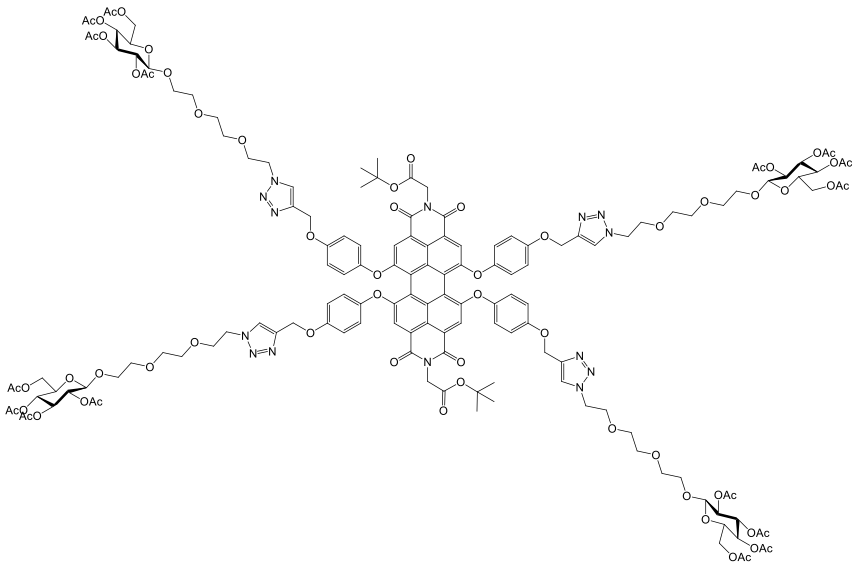
f1 (ppm)



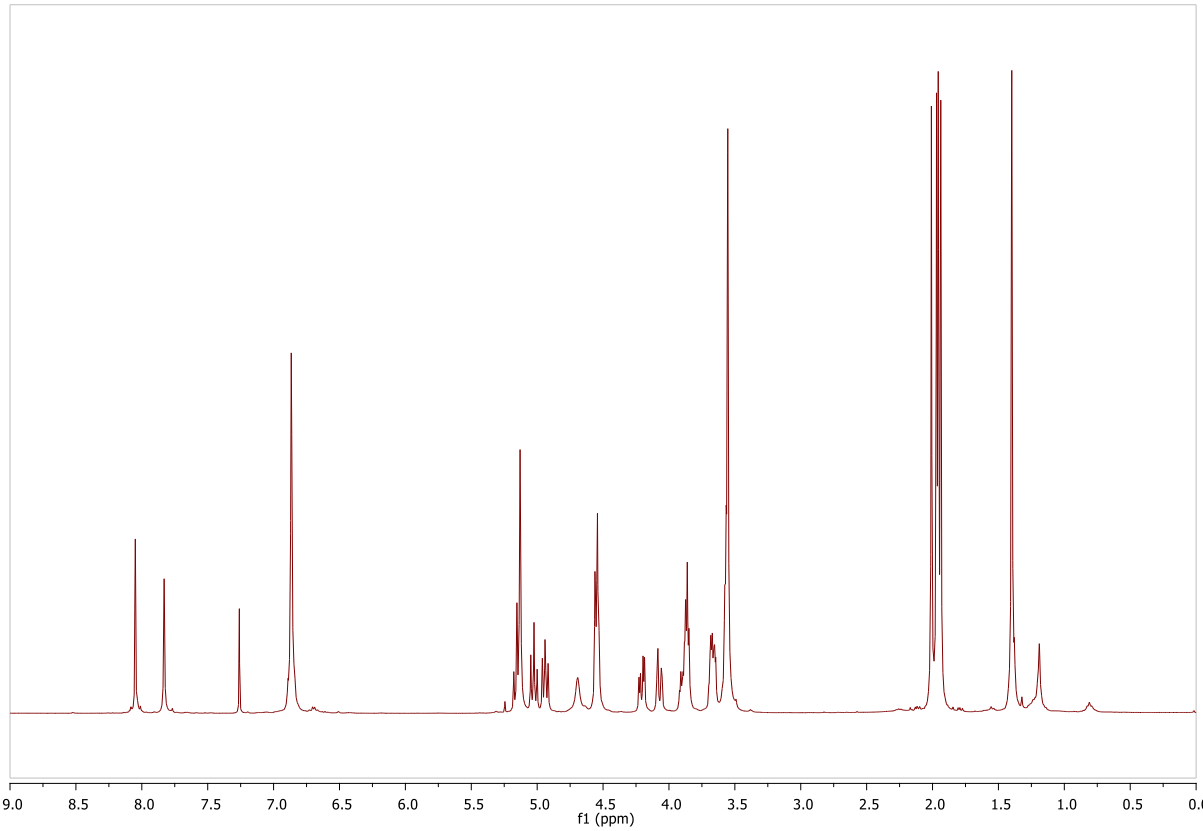
***N*,*N*'-Bis-(*t*-butoxycarbonylmethyl)-1,6,7,12-tetra-(4-{1-[1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyloxy}phenoxy)perylene-3,4,9,10-tetracarboxylic diimide (10a) :** Obtained as a purple foam following **Method A**: **6** (70 mg, 0.058 mmol, 1 eq.), **7a** (176 mg, 0.349 mmol, 6 eq.), CuI (5.5 mg, 0.029 mmol, 0.5 eq.) and DIPEA (58 µL, 0.349 mmol, 6 eq.). Purified by silica gel flash chromatography (CH_2Cl_2/MeOH 99/1 to 96/4).

Yield = 62% (116 mg), $\mathbf{R_f}$ = 0.45 (CH_2Cl_2/MeOH 95/5).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.05 (s, 4H, H-triaz), 7.83 (s, 4H, perylene-H), 6.87 (s, 16H, CH-ar), 5.19-5.10 (m, 12H, H-3, OC*H*$_2$-triaz), 5.02 (dd, *J* = 9.7 Hz, 4H, H-4), 4.97-4.90 (m, 4H, H-2), 4.69 (bs, 4H, NCH_2CO), 4.59-4.51 (m, 12H, NC*H*$_2$CH$_2$, H-1), 4.21 (dd, *J* = 12.3, 4.6 Hz, 4H, H-6a), 4.07 (dd, *J* = 12.3, 1.9 Hz, 4H, H-6b), 3.93-3.83 (m, 12H, OCH_2), 3.71-3.63 (m, 8H, H-5, OCH_2), 3.60-3.51 (m, 24H, OCH_2), 2.01, 1.97, 1.96, 1.94 (4s, 48H, $COCH_3$), 1.40 (s, 18H, CMe_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.6, 170.2, 169.4, 169.3 (4×*C*OCH_3), 166.9 (COO), 162.9 (Ar*C*ON), 156.4, 155.4, 148.8 (3×C^{IV}-ar-O), 143.6 (C^{IV}-triaz), 132.8 (C^{IV}-ar), 124.1 (C^{IV}-triaz), 122.0 (C^{IV}-ar), 121.4 (CH-ar), 120.2, 119.3 (2×C^{IV}-ar), 119.2 (CH-perylene), 116.1 (CH-ar), 100.8 (C-1), 82.3 (*C*Me$_3$), 72.7 (C-3), 71.7 (C-5), 71.2 (C-2), 70.6, 70.5, 70.2, 69.4, 69.2 (5×OCH_2), 68.3 (C-4), 62.4 (O*C*H$_2$-triaz), 61.9 (C-6), 50.3 (N*C*H$_2$CH$_2$), 42.1 (N*C*H$_2$CO), 28.0 (C*Me*$_3$), 20.70, 20.65, 20.57, 20.56 (4×CO*C*H$_3$).

ESI-QTof (positive mode) *m*/*z*: calcd for $C_{152}H_{180}N_{14}O_{64}$ $[M+2H]^{2+}$ 1613.1, found 1613.1.*
* HRMS could not be obtained due to traces of Cu(I) salts.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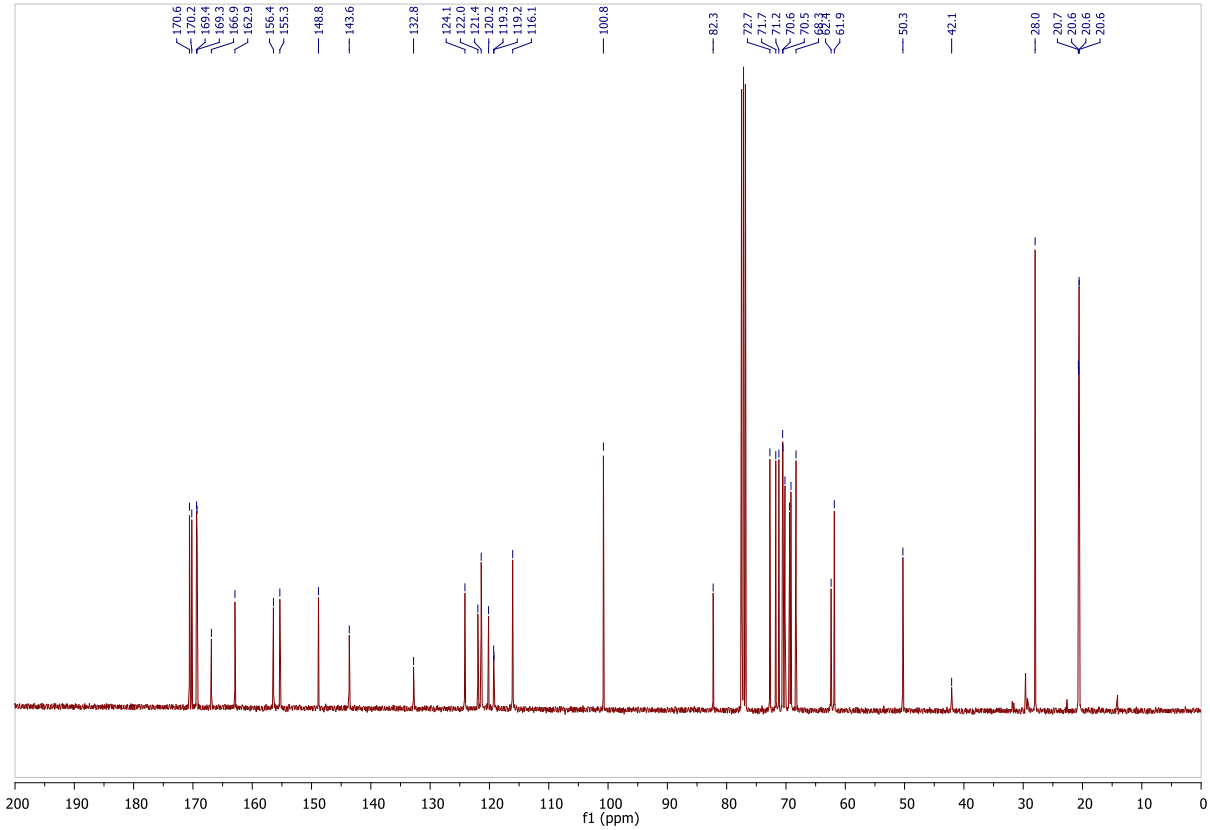
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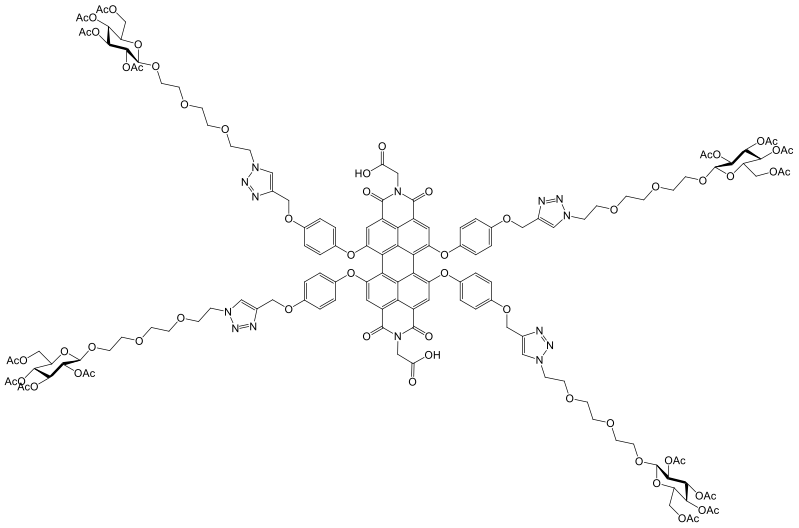
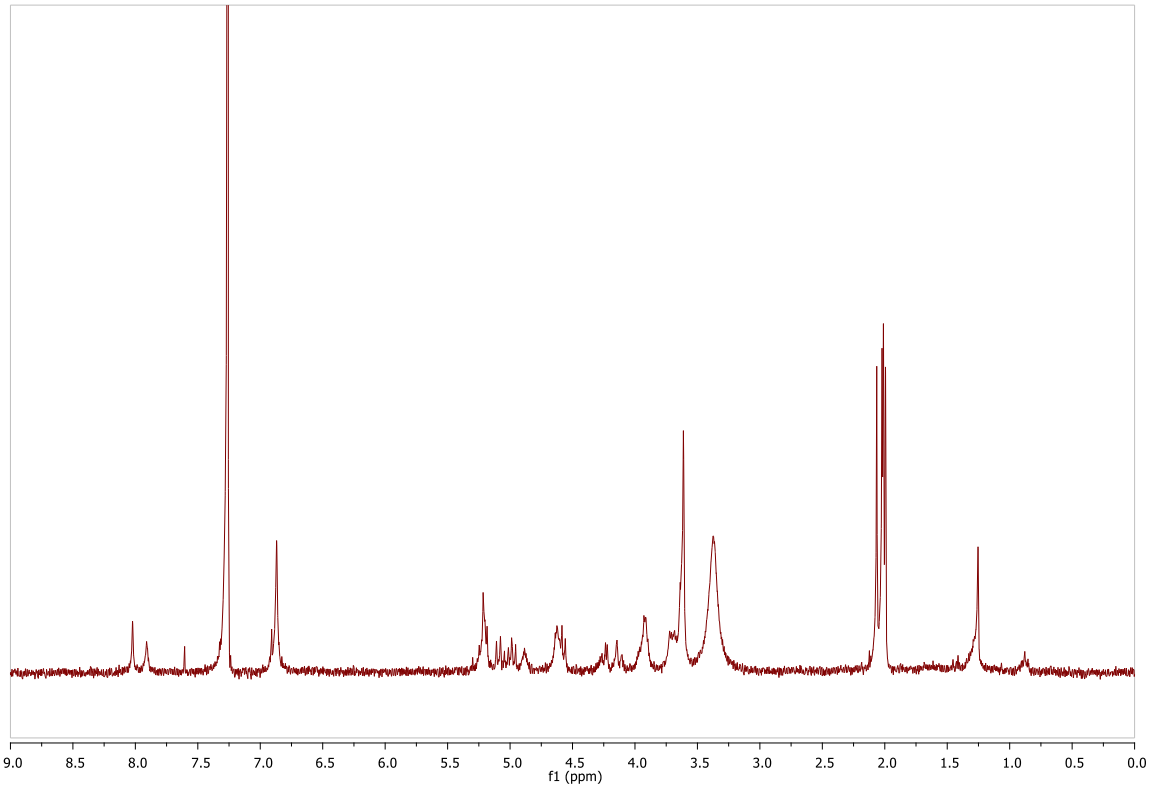
f1 (ppm)

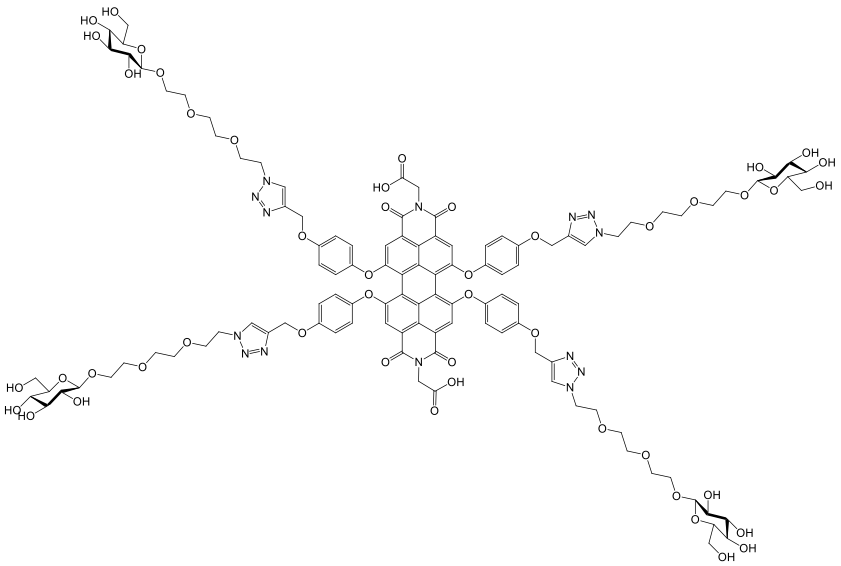


N,N'*-Bis-(carboxymethyl)-1,6,7,12-tetra-(4-{1-[1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyloxy}phenoxy)perylene-3,4,9,10-tetracarboxylic diimide (10a-bis):** Obtained from **10a** (47 mg, 0.039 mmol, 1 eq.) as a purple foam following ***Method C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.02 (s, 4H, H-triaz), 7.91 (s, 4H, perylene-H), 6.87 (s, 16H, CH-ar), 5.26-5.17 (m, 12H, H-3, OC*H*$_2$-triaz), 5.14-5.03 (dd, J = 9.7 Hz, 4H, H-4), 4.98 (m, 4H, H-2), 4.88 (bs, 4H, NCH_2CO), 4.67-4.55 (m, 12H, NCH_2CH_2, H-1), 4.25 (dd, J = 12.1, 5.0 Hz, 4H, H-6a), 4.13 (dd, J = 12.1, 1.7 Hz, 4H, H-6a), 3.99-3.88 (m, 12H, OCH_2), 3.76-3.66 (m, 8H, H-5, OCH_2), 3.66-3.58 (m, 24H, OCH_2), 2.06, 2.02, 2.01, 1.99 (4s, 48H, 4×$COCH_3$).

ESI-QTof (positive mode) *m*/*z*: calcd for $C_{144}H_{162}N_{14}O_{64}$ $[M+2H]^{2+}$ 1557.0, found 1557.0





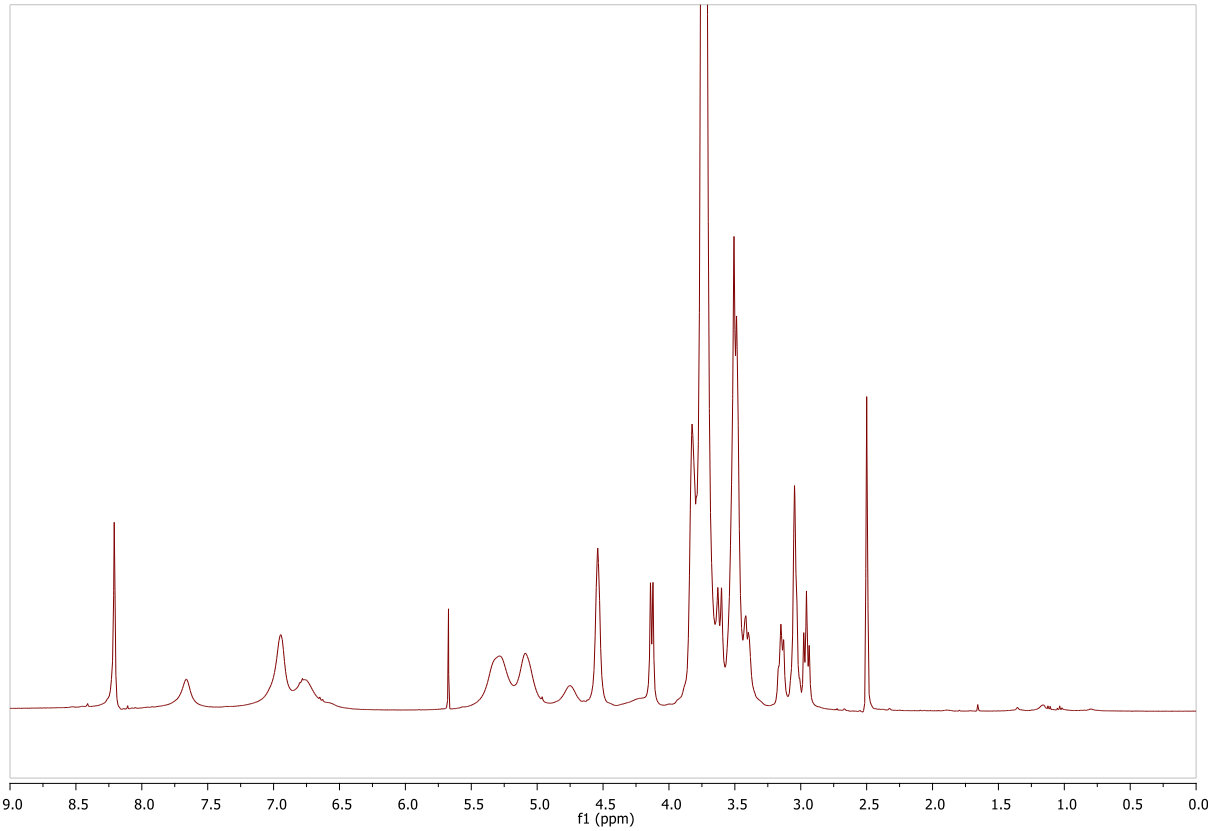
N,N*'-Bis-(carboxymethyl)-1,6,7,12-tetra-(4-{1-[1-(β-D-glucopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyloxy}phenoxy)perylene-3,4,9,10-tetracarboxylic diimide (11a) :** Obtained from **10a-bis** as a deep purple foam following ***Method B.

Yield = 85% (81 mg). After 2 steps

^{1}H NMR (400 MHz, DMSO-d$_6$ + εD$_2$O) δ (ppm): 8.21 (s, 4H, H-triaz), 7.66 (s, 4H, perylene-H), 6.95 (bs, 8H, CH-ar), 6.78 (bs, 8H, CH-ar), 5.18-4.94 (m, 8H, OC*H*$_2$-triaz), 4.54 (m, 8H, NC*H*$_2$CH$_2$), 4.75 (bs, 4H, NC*H*$_2$CO), 4.13 (d, *J* = 7.6 Hz, 4H, H-1), 3.88-3.57 (m, 16H, H-6a, OCH$_2$), 3.57-3.36 (m, 32H, H-6b, OCH$_2$), 3.18-3.11 (m, 4H, H-4), 3.08-3.00 (m, 8H, H-3, H-5), 2.96 (t, *J* = 8.3 Hz, 4H, H-2).

^{13}C NMR (100 MHz, DMSO-d$_6$ + εD$_2$O) δ (ppm): 170.8 (COO), 162.5 (Ar*C*ON), 159.4, 156.1, 155.2, 148.7 (3×C^{IV}-ar-O), 142.9 (C^{IV}-triaz), 132.4 (C^{IV}-ar), 125.5 (CH-triaz), 122.5 (C^{IV}-ar), 121.5 (CH-ar), 119.2, 118.7 (2×C^{IV}-ar), 118.5 (CH-perylene), 116.3 (CH-ar), 103.2 (C-1), 77.1 (C-3), 76.9 (C-4), 73.7 (C-2), 70.3 (C-5), 70.01, 69.95, 69.90, 69.0, 68.2 (5×OCH$_2$), 61.8 (O*C*H$_2$-triaz), 61.4 (C-6), 49.9 (N*C*H$_2$CH$_2$), 44.2 (N*C*H$_2$CO).

HR-ESI-QTof (positive mode) *m*/*z*: calcd for $C_{112}H_{132}N_{14}O_{48}$ $[M+2H]^{2+}$ 1220.4154, found 1220.4135.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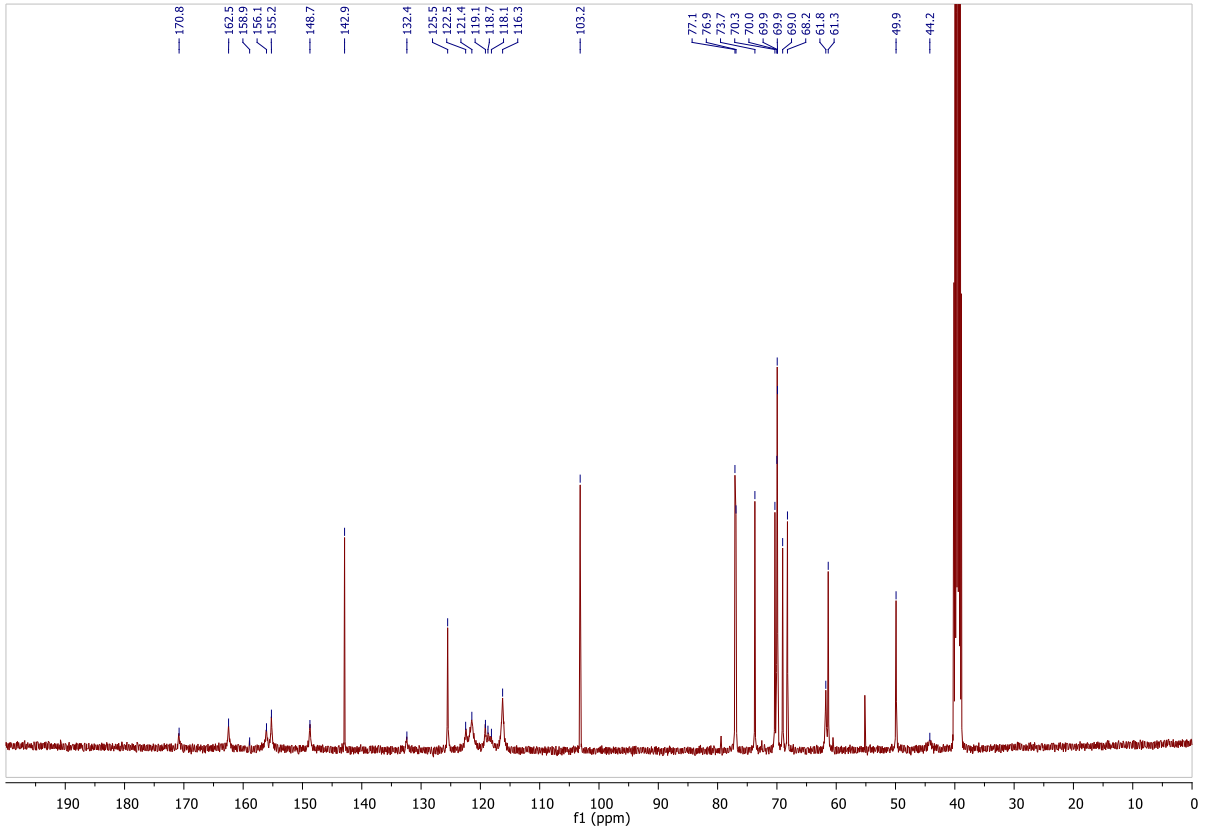
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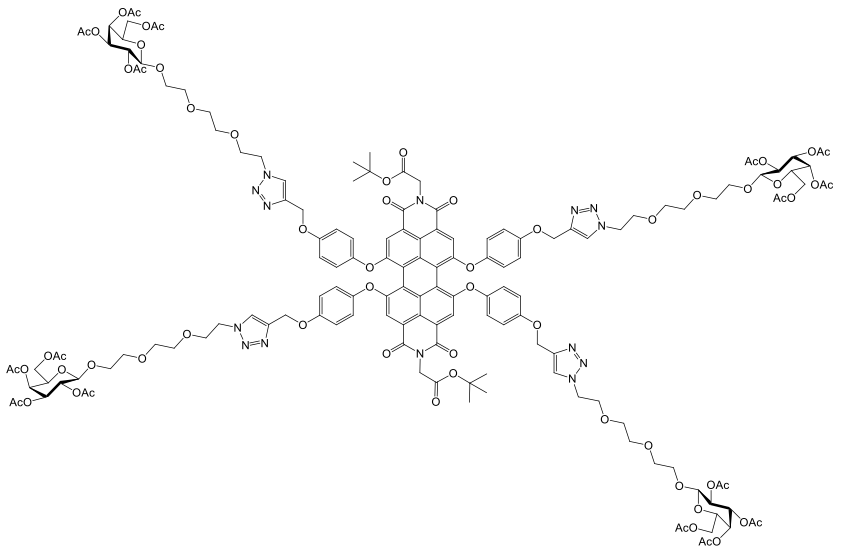


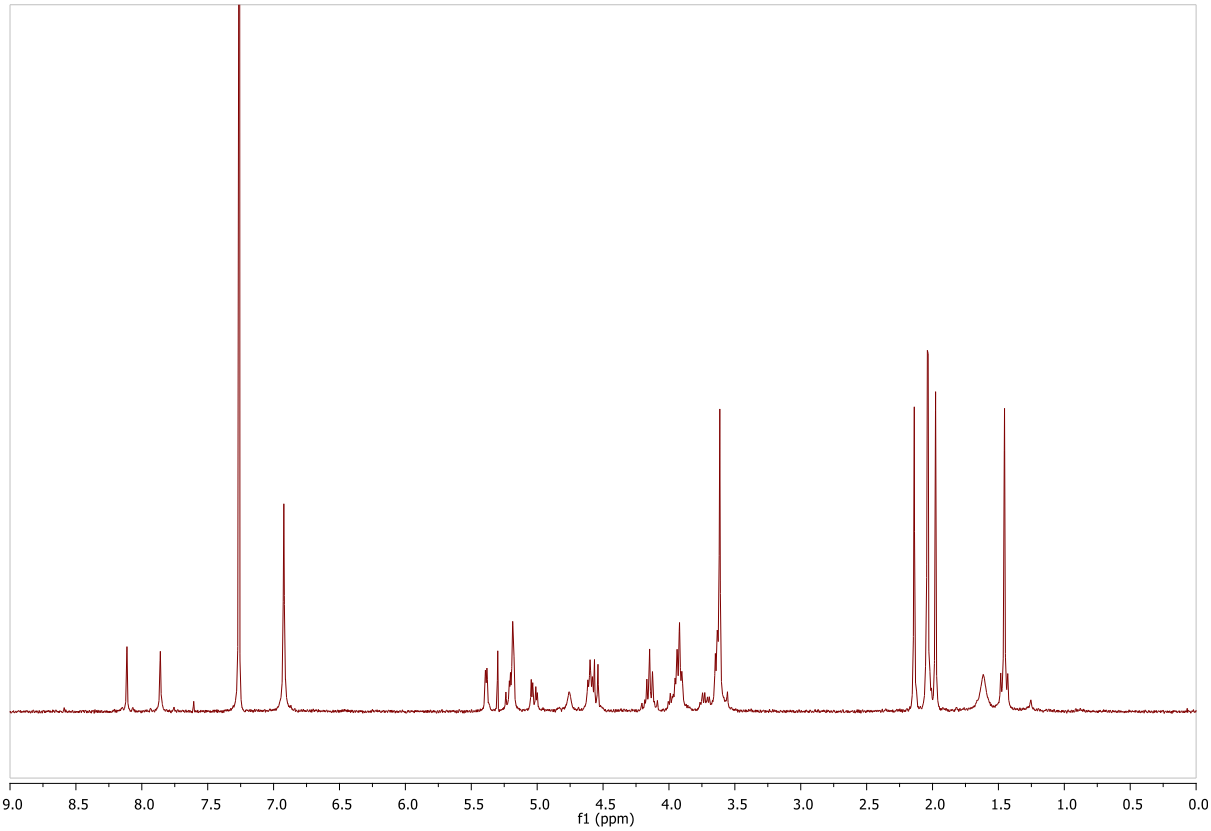
***N*,*N*'-Bis-(*t*-butoxycarbonylmethyl)-1,6,7,12-tetra-(4-{1-[1-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyloxy}phenoxy)perylene-3,4,9,10-tetracarboxylic diimide (10b) :** Obtained as a purple foam following Method A: **6** (47 mg, 0.039 mmol, 1 eq.), **7b** (99 mg, 0.196 mmol, 5 eq.), CuI (4 mg, 0.020 mmol, 0.5 eq.) and DIPEA (34 µL, 0.196 mmol, 5 eq.). Purified by silica gel flash chromatography (CH_2Cl_2/MeOH 99/1 to 96/4).

Yield = 52% (66 mg), $\mathbf{R_f}$ = 0.45 (CH_2Cl_2/MeOH 95/5).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.11 (s, 4H, H-triaz), 7.86 (s, 4H, perylene-H), 6.92 (s, 16H, CH-ar), 5.39 (d, J = 3.4 Hz, 4H, H-4), 5.25-5.15 (m, 12H, H-2, OCH_2-triaz), 5.02 (dd, J = 10.4, 3.4 Hz, 4H, H-3), 4.76 (bs, 4H, NCH_2CO), 4.60 (t, J = 5.2 Hz, 8H, NCH_2CH_2), 4.55 (d, J = 7.9 Hz, 4H, H-1), 4.13 (m, 8H, H-6), 4.02-3.88 (m, 12H, H-5, OCH_2), 3.78-3.54 (m, 32H, 4×OCH_2), 2.14, 2.04, 2.03, 1.98 (4s, 48H, $COCH_3$), 1.46 (s, 18H, CMe_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.5, 170.3, 170.2, 169.5 (4×*C*OCH_3), 167.0 (COO), 163.1 (Ar*C*ON), 156.5, 155.5, 149.0 (3×C^{IV}-ar-O), 132.9 (C^{IV}-ar), 124.2 (C^{IV}-triaz), 122.1 (C^{IV}-ar), 121.5 (CH-ar), 120.3, 119.4 (2×C^{IV}-ar), 119.3 (CH-perylene), 116.2 (CH-ar), 101.4 (C-1), 82.4 (*C*Me_3), 70.9 (C-3), 70.7 (C-5, OCH_2), 70.6, 70.3, 69.5, 69.2 (4×OCH_2), 68.9 (C-2), 67.1 (C-4), 62.5 (O*C*H_2-triaz), 61.3 (C-6), 50.4 (N*C*H_2CH_2), 42.2 (N*C*H_2CO), 28.1 (C*Me*$_3$), 20.9, 20.8, 20.7 (4×CO*C*H_3).

HR-ESI-QTof (positive mode) *m*/*z*: calcd for $C_{152}H_{180}N_{14}O_{64}$ $[M+2H]^{2+}$ 1612.5625, found 1612.5634.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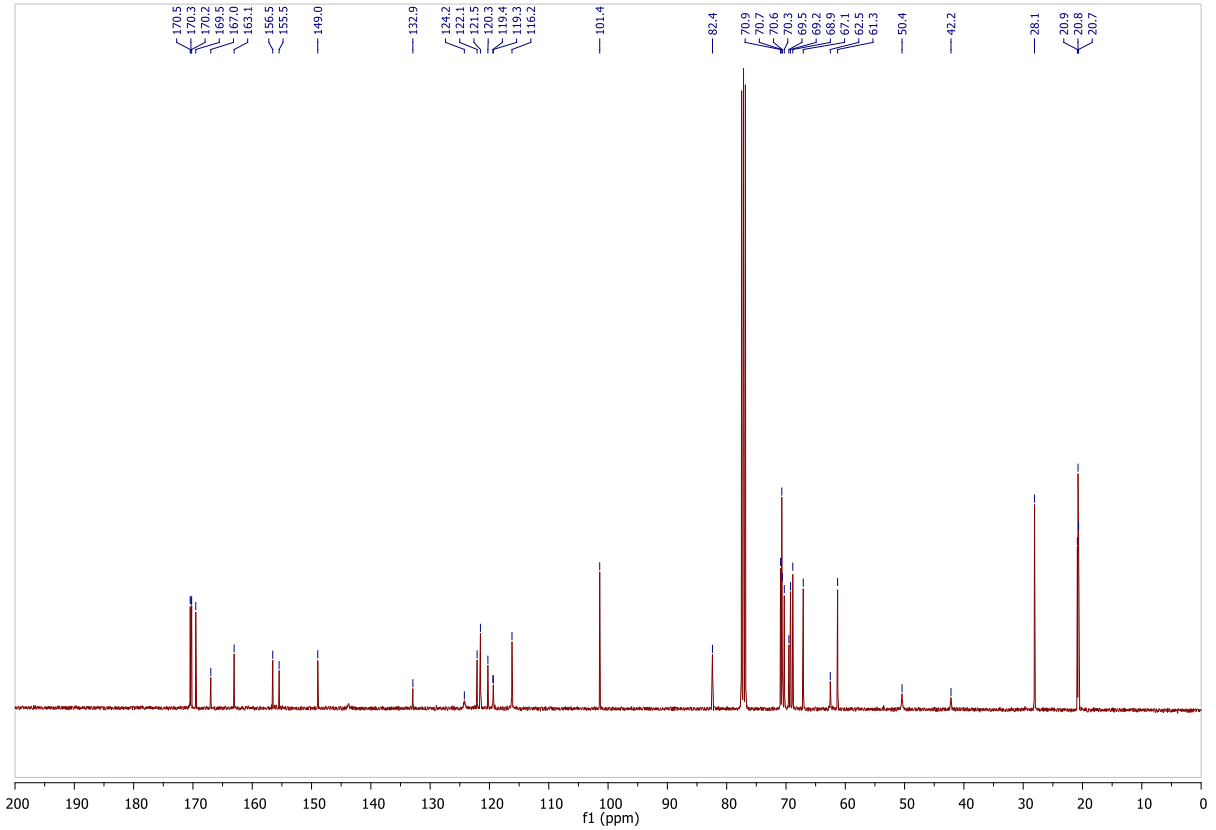
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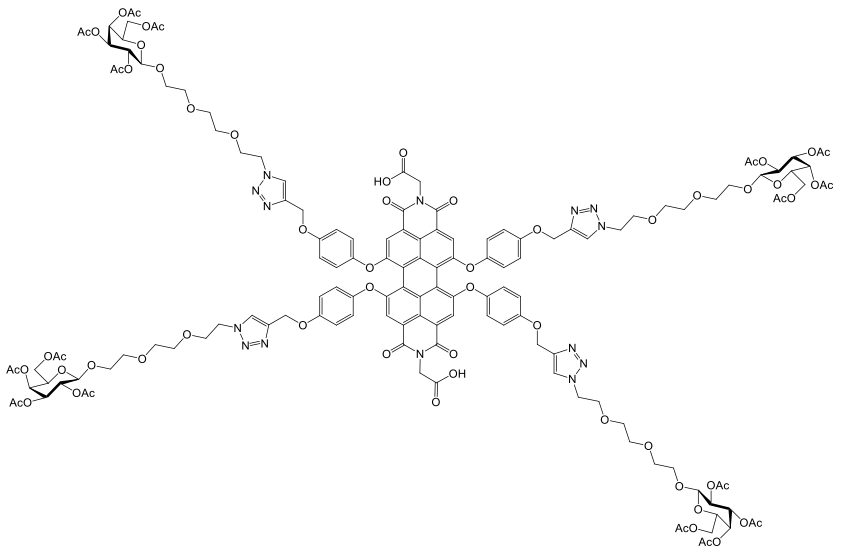
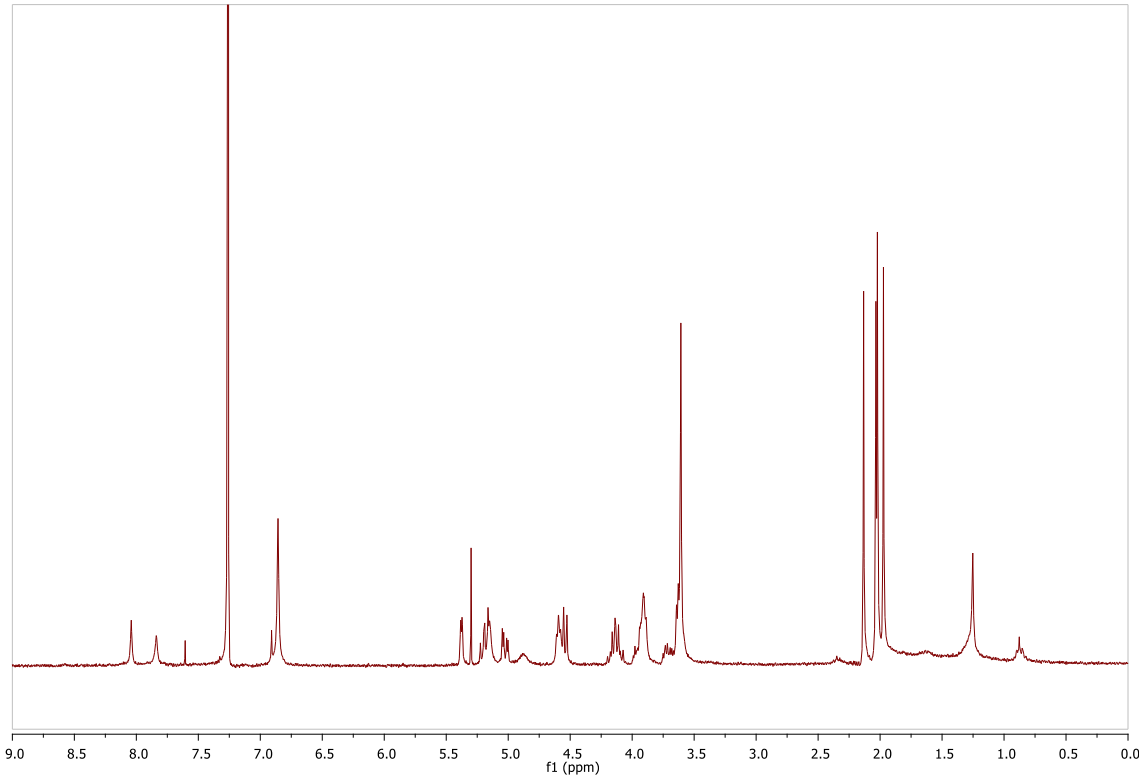


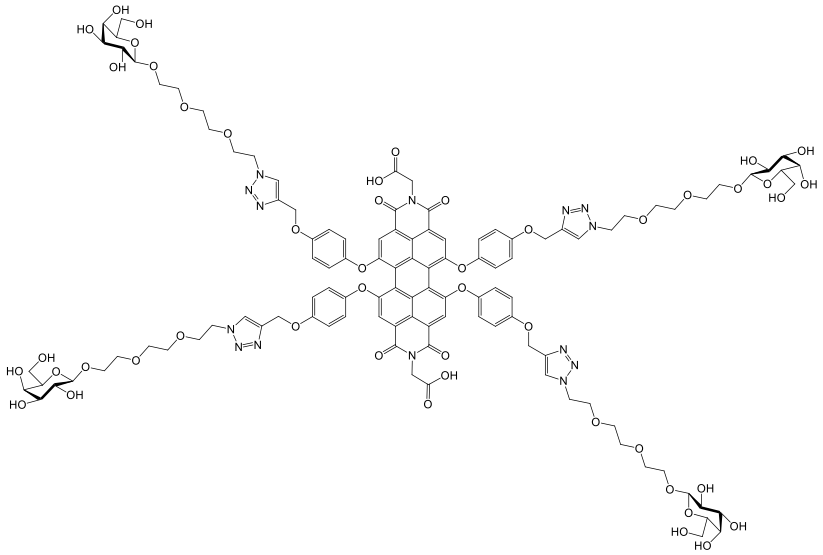
N*,*N*'-Bis-(carboxymethyl)-1,6,7,12-tetra-(4-{1-[1-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyloxy}phenoxy)perylene-3,4,9,10-tetracarboxylic diimide (10b-bis):** Obtained from **10b** (47 mg, 0.039 mmol, 1 eq.) as a purple foam following ***Method C.

R_f = 0.30 (CH_2Cl_2/MeOH 95/5).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.04 (s, 4H, H-triaz), 7.84 (s, 4H, perylene-H), 6.86 (s, 16H, CH-ar), 5.38 (d, *J* = 3.2 Hz, 4H, H-4), 5.19 (dd, *J* = 10.5, 7.9 Hz, 4H, H-2), 5.15 (bs, 8H, OC*H*$_2$-triaz), 5.02 (dd, *J* = 10.4, 3.2 Hz, 4H, H-3), 4.93-4.83 (bs, 4H, NCH_2CO), 4.63-4.57 (m, 8H, NC*H*$_2$CH$_2$), 4.54 (d, *J* = 7.9 Hz, 4H, H-1), 4.14 (m, 8H, H-6), 4.00-3.84 (m, 12H, H-5, OCH_2), 3.77-3.54 (m, 32H, 4×OCH_2), 2.13, 2.03, 2.02, 1.97 (4s, 48H, $COCH_3$).

HR-ESI-QTof (positive mode) *m*/*z*: calcd for $C_{144}H_{164}N_{14}O_{64}$ $[M+2H]^{2+}$ 1556.4999, found 1556.4916.





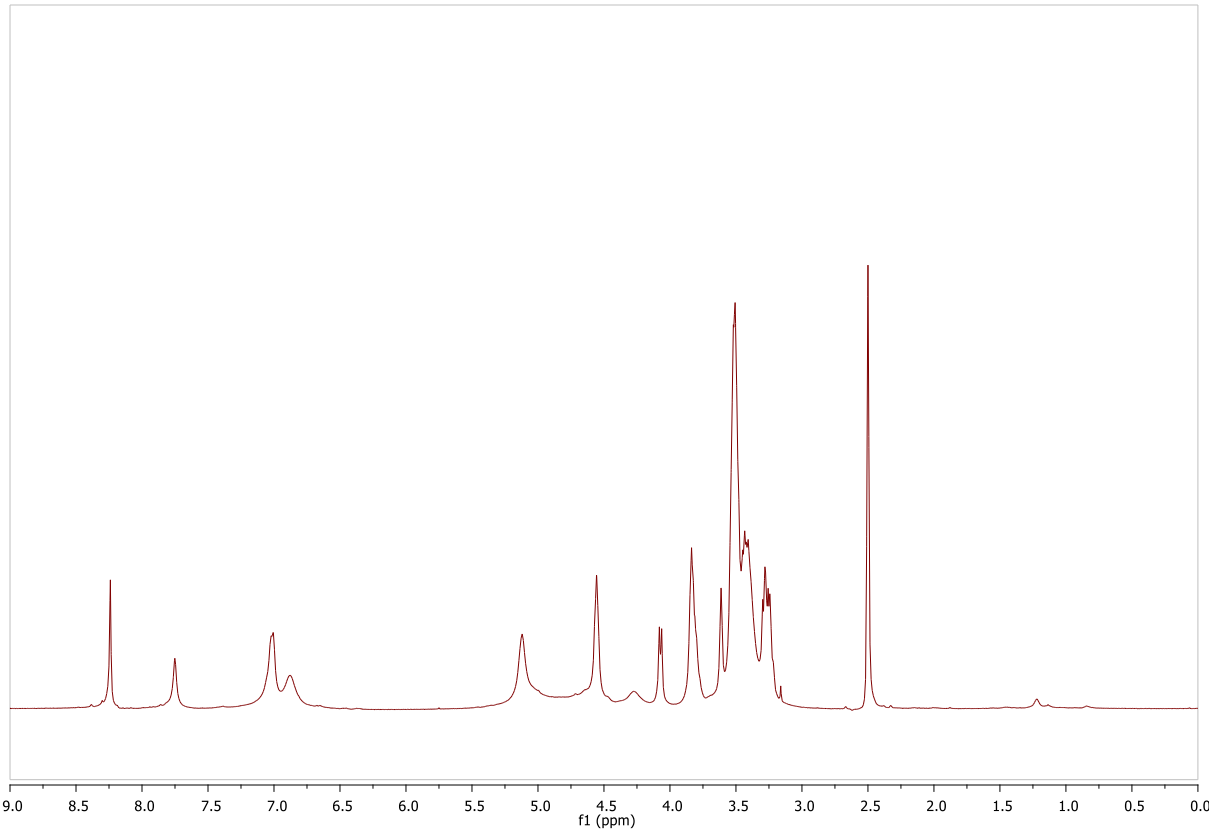
N,N*'-Bis-(carboxymethyl)-1,6,7,12-tetra-(4-{1-[1-(β-D-galactopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyloxy}phenoxy)perylene-3,4,9,10-tetracarboxylic diimide (11b) :** Obtained from **10b-bis** (121 mg, 0.038 mmol) as a deep purple foam following ***Method B.

Yield = 90% (82 mg). After two steps

^{1}H NMR (400 MHz, DMSO-d$_6$ + εD$_2$O) δ (ppm): 8.24 (s, 4H, H-triaz), 7.75 (s, 4H, perylene-H), 7.01 (bs, 8H, CH-ar), 6.88 (bs, 8H, CH-ar), 5.12 (s, 12H, OC*H*$_2$-triaz, NC*H*$_2$-triaz), 4.56 (s, 12H, NC*H*$_2$CH$_2$), 4.07 (d, *J* = 7.0 Hz, 4H, H-1), 3.84 (bs, 12H, OCH$_2$), 3.61(s, 4H, H-4), 3.70-3.34 (m, 52H, OCH$_2$), 3.34-3.20 (m, 12H, H-2, H-3, H-5).

^{13}C NMR (100 MHz, DMSO-d$_6$ + εD$_2$O) δ (ppm): 170.0 (COO), 162.2 (Ar*C*ON), 155.9, 155.0, 148.5 (3×C^{IV}-ar-O), 142.5 (C^{IV}-triaz), 132.2 (C^{IV}-ar), 125.16 (CH-triaz), 122.29 (C^{IV}-ar), 121.3 (CH-ar), 118.9, 118.4 (2×C^{IV}-ar), 117.9 (CH-perylene), 116.1 (CH-ar), 103.6 (C-1), 75.2 (C-3), 73.49 (C-2), 70.53 (C-5), 69.8, 69.7, 69.6, 68.7 (4×OCH$_2$), 68.0 (C-4), 67.74 (OCH$_2$), 61.5 (O*C*H$_2$-triaz), 60.3 (C-6), 49.5 (N*C*H$_2$CH$_2$), 43.9 (N*C*H$_2$CO).

HR-ESI-QTof (positive mode) *m*/*z*: calcd for $C_{112}H_{132}N_{14}O_{48}$ $[M+2H]^{2+}$ 1220.4154, found 1220.4117.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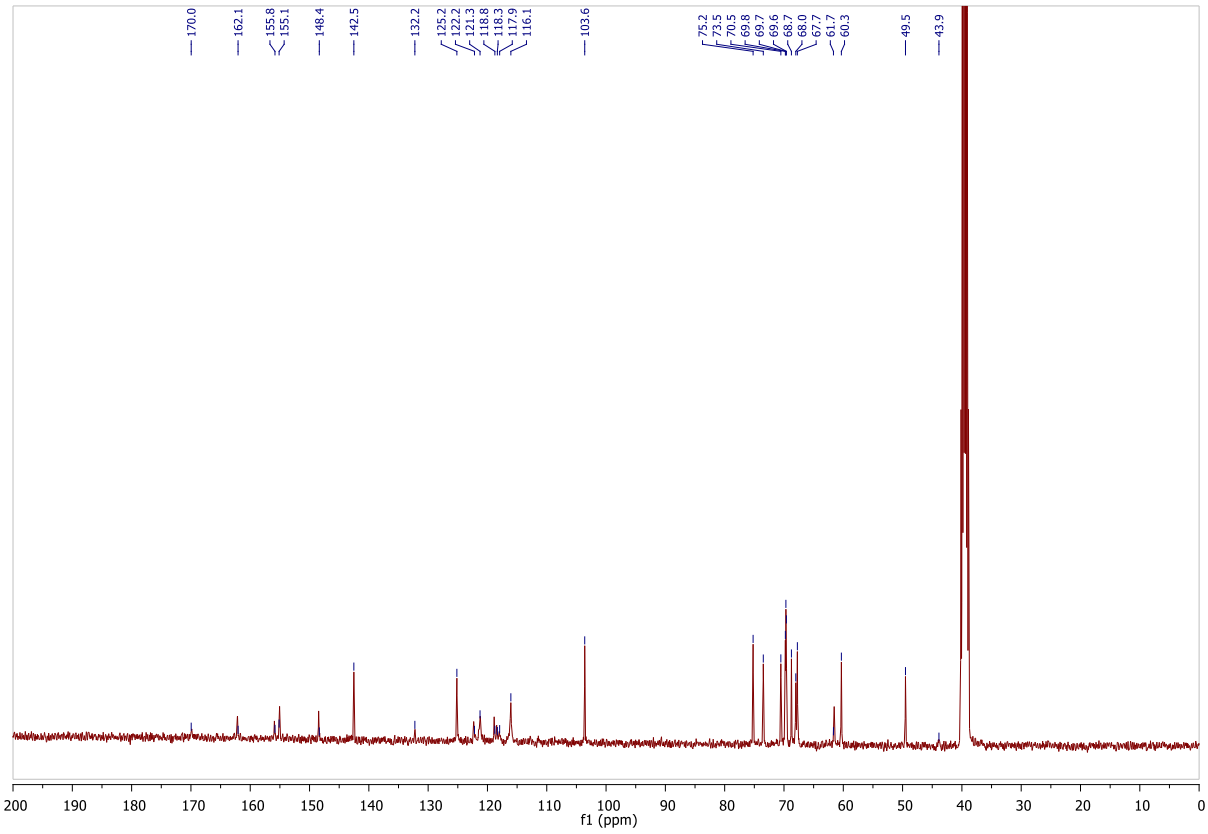
f1 (ppm)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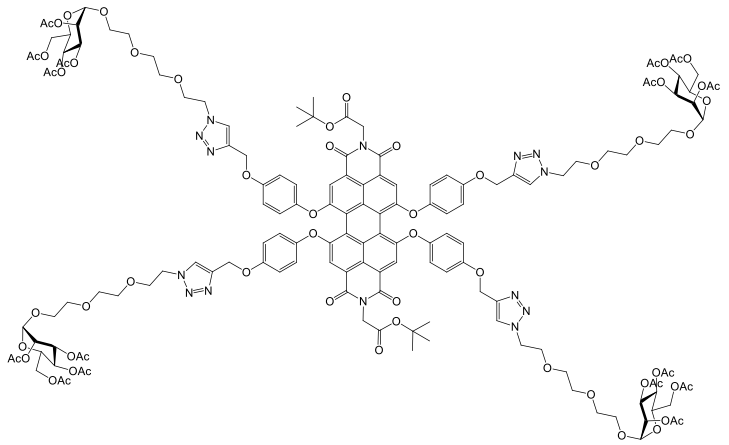


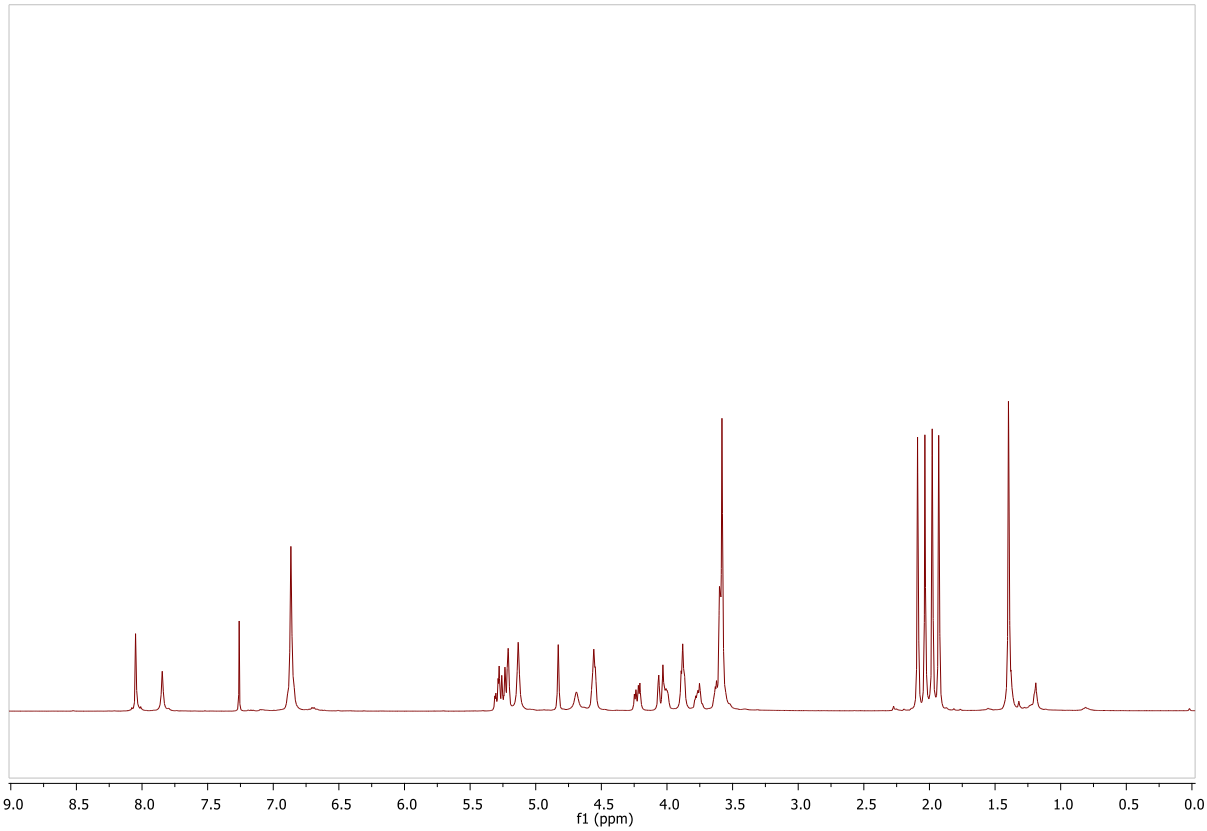
N,N'*-Bis-(*t*-butoxycarbonylmethyl)-1,6,7,12-tetra-(4-{1-[1-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyloxy}phenoxy)perylene-3,4,9,10-tetracarboxylic diimide (10c) :** Obtained as a purple foam following ***Method A: **6** (54 mg, 0.045 mmol, 1 eq.), **7c** (136 mg, 0.270 mmol, 6 eq.), CuI (4 mg, 0.021 mmol, 0.5 eq.) and DIPEA (45 µL, 0.270 mmol, 6 eq.). Purified by silica gel flash chromatography (CH_2Cl_2/MeOH 99/1 to 96/4).

Yield = 73% (105 mg), $\mathbf{R_f}$ = 0.45 (CH_2Cl_2/MeOH 95/5).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.05 (s, 4H, H-triaz), 7.85 (s, 4H, perylene-H), 6.87 (s, 16H, CH-ar), 5.30 (dd, *J* = 10.0, 3.3 Hz, 4H, H-3), 5.25 (d, *J* = 9.6 Hz, 4H, H-4), 5.22-5.19 (m, 4H, H-2), 5.13 (s, 8H, OC*H*$_2$-triaz), 4.83 (s, 4H, H-1), 4.69 (bs, 4H, NCH_2CO), 4.56 (t, *J* = 4.4 Hz, 8H, NC*H*$_2$CH$_2$), 4.23 (dd, *J* = 12.1, 4.7 Hz, 4H, H-6a), 4.08-3.98 (m, 8H, H-6b, H-5), 3.88 (t, *J* = 4.6 Hz, 8H, OCH_2), 3.80-3.72 (m, 4H, ManOC*H*$_2$), 3.65-3.54 (m, 26H, ManOC*H*$_2$, OCH_2), 2.09, 2.03, 1.98, 1.93 (4s, 48H, $COCH_3$), 1.40 (s, 18H, CMe_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.6, 170.0, 169.9, 169.7 (4×*C*OCH_3), 166.9 (COO), 162.9 (Ar*C*ON), 156.5, 155.4, 148.9 (3×C^{IV}-ar-O), 143.6 (C^{IV}-triaz), 132.8 (C^{IV}-ar), 124.2 (C^{IV}-triaz), 122.0 (C^{IV}-ar), 121.4 (CH-ar), 120.2, 119.3 (2×C^{IV}-ar), 119.2 (CH-perylene), 116.1 (CH-ar), 97.7 (C-1), 82.3 (*C*Me$_3$), 70.6, 70.5, 69.9 (3×OCH_2), 69.5, 69.4 (C-2, OCH_2), 69.0 (C-3), 68.4 (C-5), 67.3 (ManO*C*H$_2$), 66.0 (C-4), 62.4, 62.3 (O*C*H$_2$-triaz, C-6), 50.3 (N*C*H$_2$CH$_2$), 42.1 (N*C*H$_2$CO), 28.0 (C*Me*$_3$), 20.9, 20.72, 20.68, 20.66 (4×CO*C*H$_3$).

HR-ESI-QTof (positive mode) *m/z*: calcd for $C_{152}H_{178}N_{14}O_{64}$ $[M+2H]^{2+}$ 1612.5625, found 1612.5598.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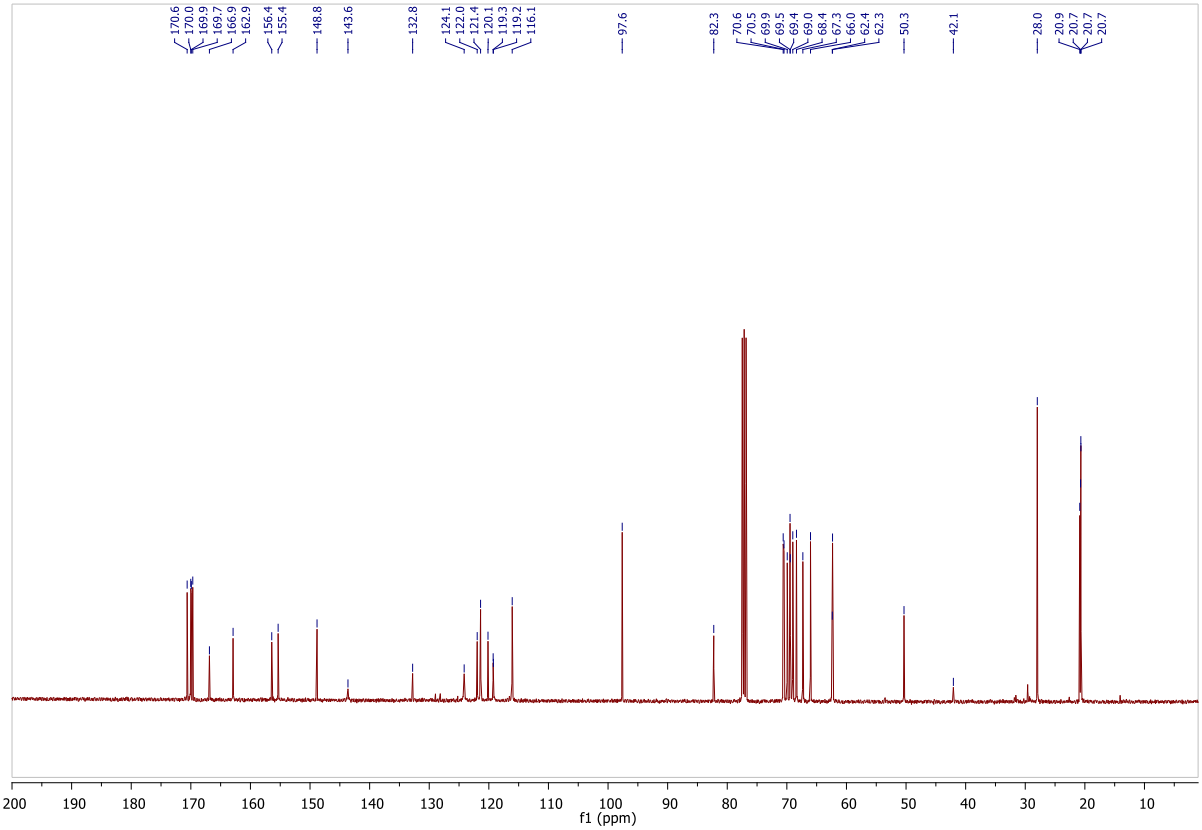
f1 (ppm)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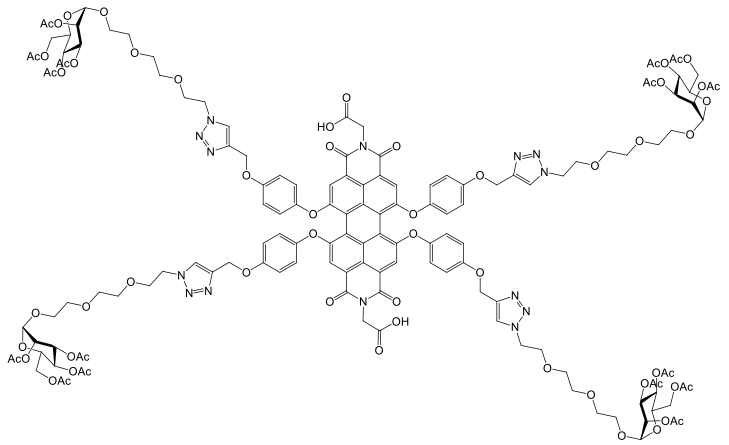
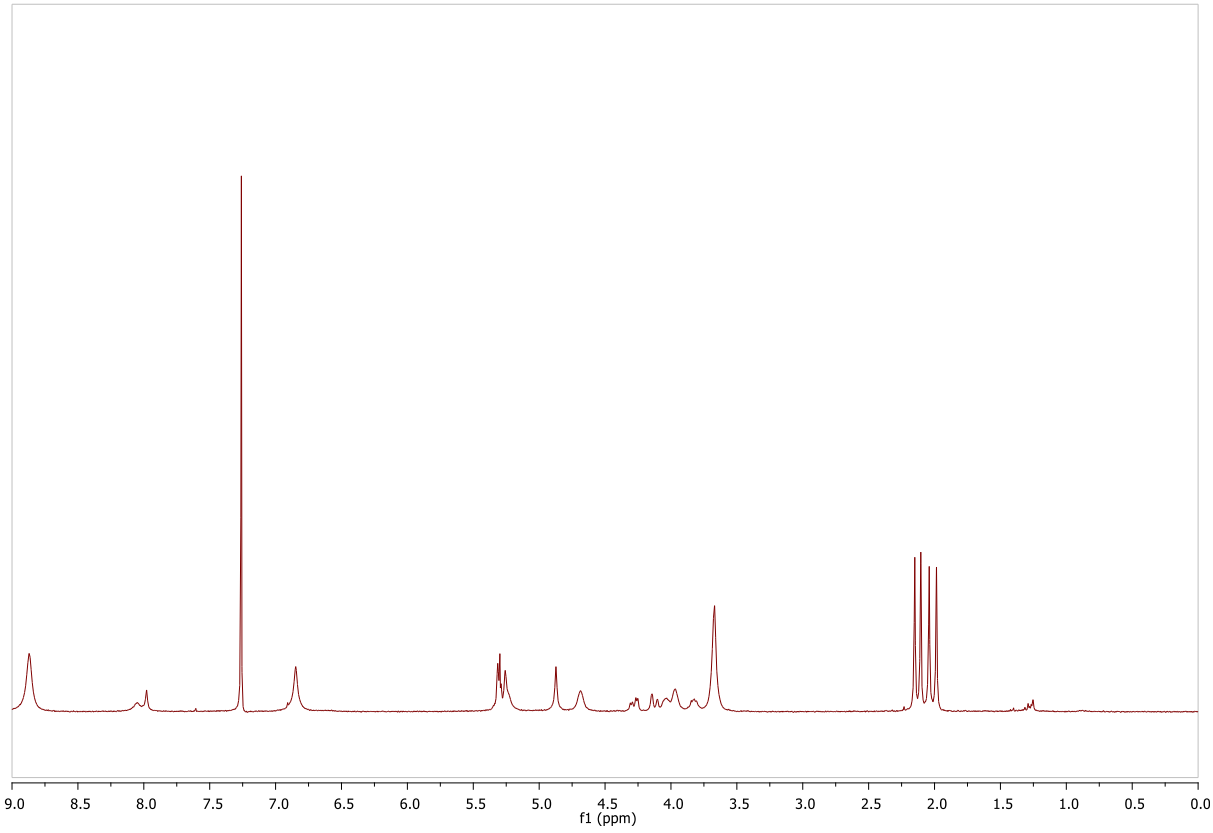
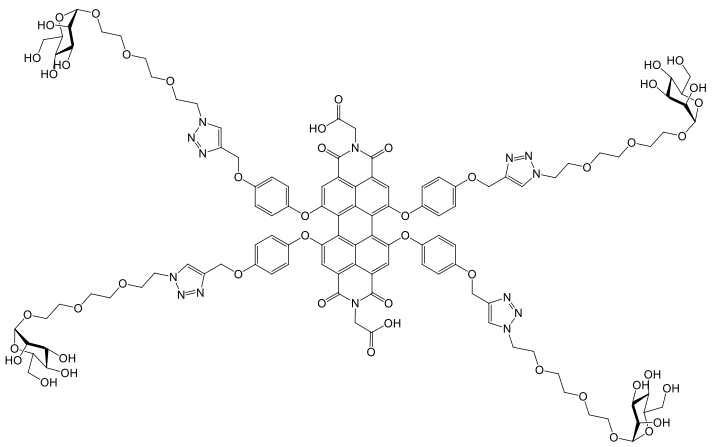


N,N'*-Bis-(carboxylmethyl)-1,6,7,12-tetra-(4-{1-[1-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyloxy}phenoxy)perylene-3,4,9,10-tetracarboxylic diimide (10c-bis) :** Obtained from **10c** (99 mg, 0.307 mmol, 1 eq.) as a purple foam following ***Method C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.05 (bs, 4H, H-triaz), 7.98 (s, 4H, perylene-H), 6.85 (s, 16H, CH-ar), 5.38-5.17 (m, 20H, H-2, H-3, H-4, OC*H*$_2$-triaz), 4.87 (s, 8H, H-1, NCH_2CO), 4.69 (bs, 8H, NC*H*$_2$$CH_2$), 4.28 (dd, *J* = 12.3, 4.5, 4H, H-6a), 4.12 (d, *J* = 12.3, 4H, H-6b), 4.07-4.00 (m, 4H, H-5) , 4.00-3.93 (m, 8H, CH_2), 3.88-3.78 (m, 4H, ManOC*H*$_2$), 3.72-3.61 (m, 26H, ManOCH_2, OCH_2), 2.15, 2.10, 2.04, 1.99 (4s, 48H, $COCH_3$).

ESI-QTof (positive mode) *m/z*: calcd for $C_{144}H_{162}N_{14}O_{64}$ $[M+2H]^{2+}$ 1557.0, found 1557.0





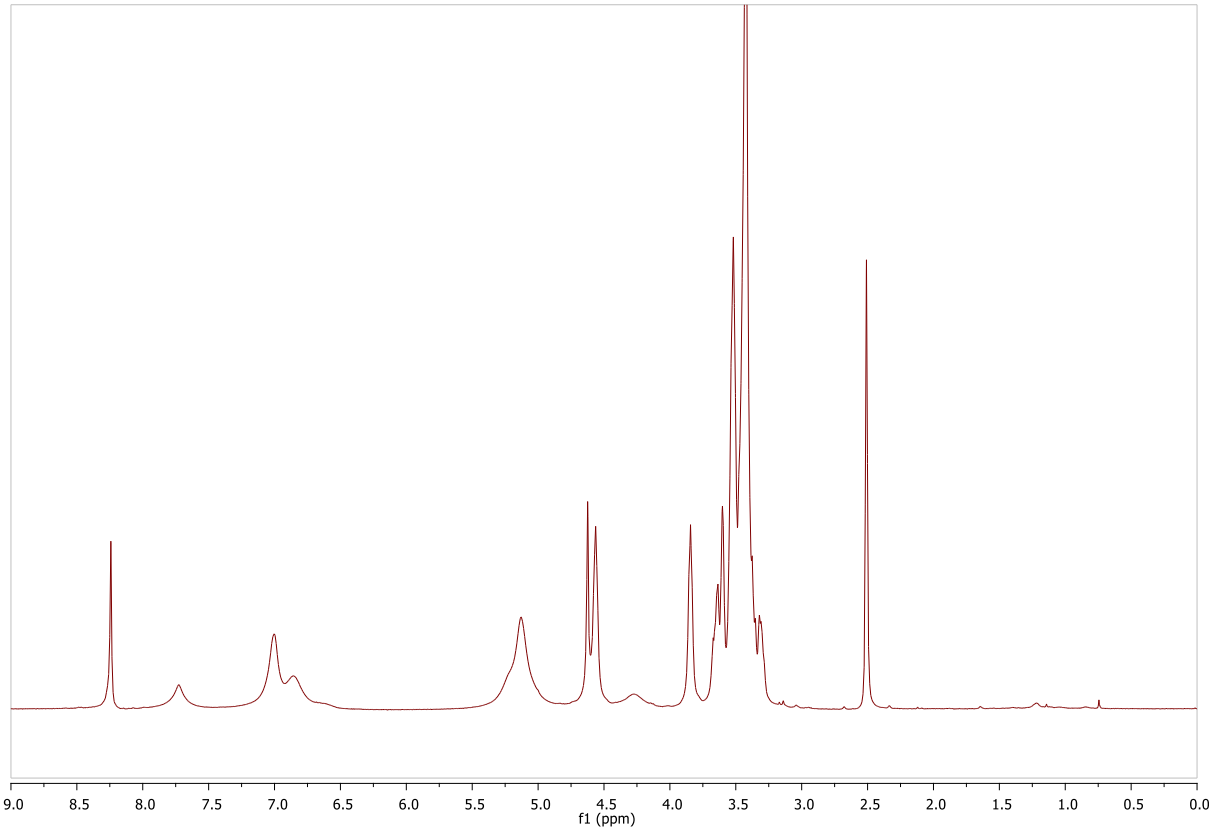
N,N*'-Bis-(carboxylmethyl)-1,6,7,12-tetra-(4-{1-[1-(α-D-mannopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyloxy}phenoxy)perylene-3,4,9,10-tetracarboxylic diimide (11c) :** Obtained from **10c-bis** as a deep purple foam following ***Method B.

Yield = 93% (69 mg). After 2 steps

^{1}H NMR (400 MHz, DMSO-d$_6$ + εD$_2$O) δ (ppm): 8.24 (s, 4H, H-triaz), 7.73 (s, 4H, perylene-H), 7.00 (bs, 8H, CH-ar), 6.86 (bs, 8H, CH-ar), 5.29-4.96 (m, 8H, OC*H*$_2$-triaz), 4.62 (s, 4H, H-1), 4.59-4.53 (m, 8H, NC*H*$_2$CH$_2$), 4.28 (bs, 4H, NC*H*$_2$CO), 3.84 (s, 8H, NC*H*$_2$CH$_2$), 3.74-3.58 (m, 12H, H-2, ManOC*H*$_2$, H-6a), 3.58-3.25 (m, 44H, ManOC*H*$_2$, H-3, H-4, H-5, H-6b, 3×OCH$_2$).

^{13}C NMR (100 MHz, DMSO-d$_6$ + εD$_2$O) δ (ppm): 170.2 (COO), 162.2 (Ar*C*ON), 156.0, 155.1, 148.6 (3×C^{IV}-ar-O), 142.6 (C^{IV}-triaz), 132.3 (C^{IV}-ar), 125.2 (CH-triaz), 122.3 (C^{IV}-ar), 121.3 (CH-ar), 118.9, 118.5 (2×C^{IV}-ar), 118.0 (CH-perylene), 116.1 (CH-ar), 100.0 (C-1), 74.0 (C-4), 70.8 (C-3), 70.2 (C-2), 69.7, 69.6, 69.6, 68.8 (4×OCH$_2$), 67.0 (C-5), 65.8 (ManO*C*H$_2$), 61.5 (O*C*H$_2$-triaz), 61.3 (C-6), 49.5 (N*C*H$_2$CH$_2$), 43.9 (N*C*H$_2$CO).

HR-ESI-QTof (positive mode) *m*/*z*: calcd for $C_{112}H_{132}N_{14}O_{48}$ $[M+2H]^{2+}$ 1220.4154, found 1220.4102.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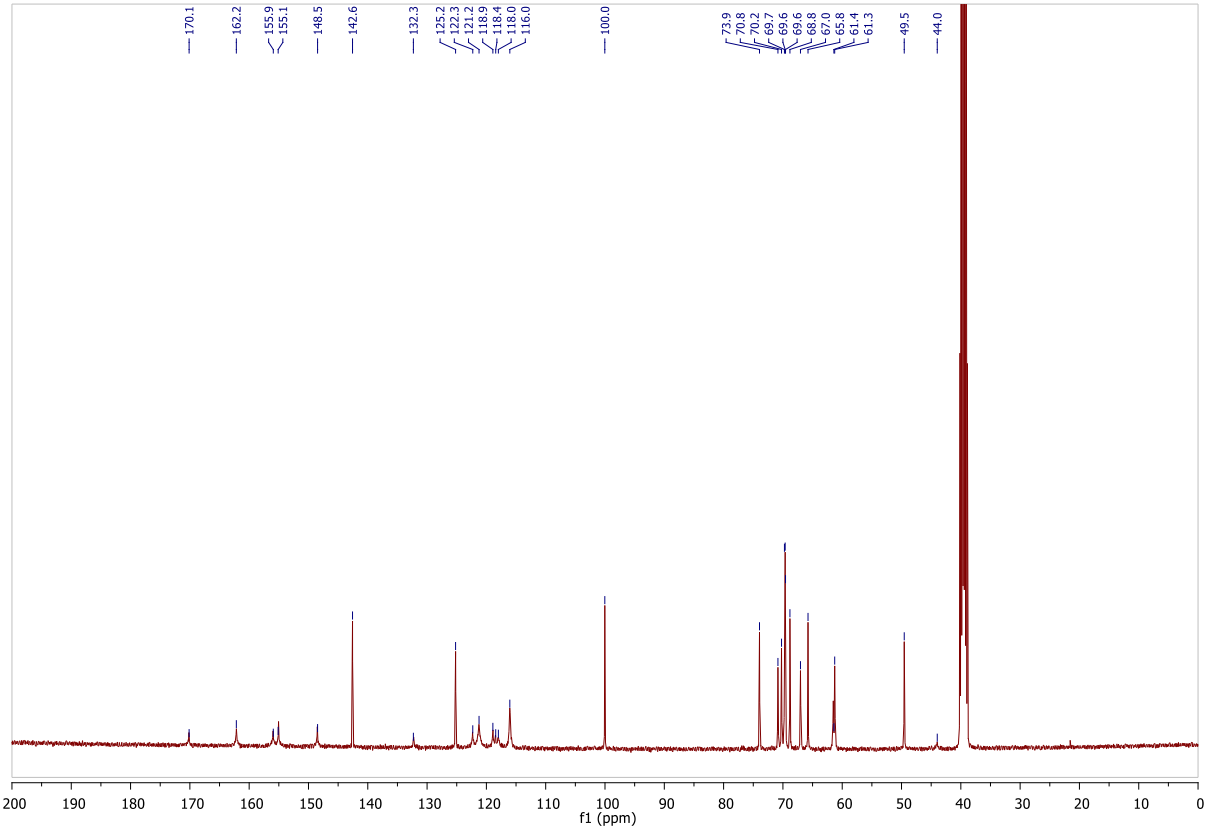
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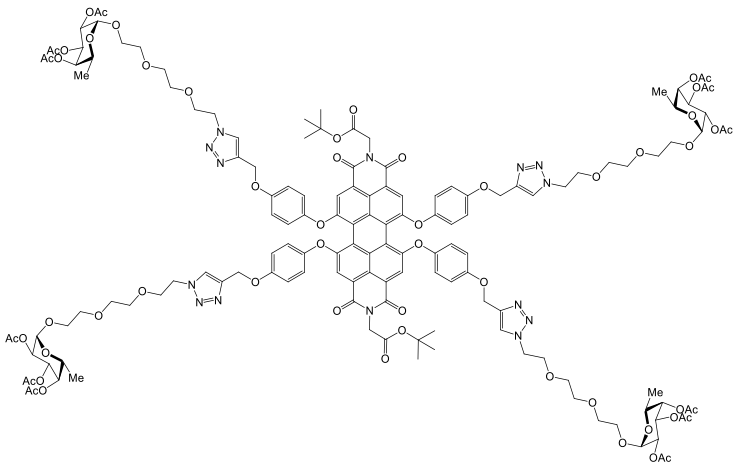


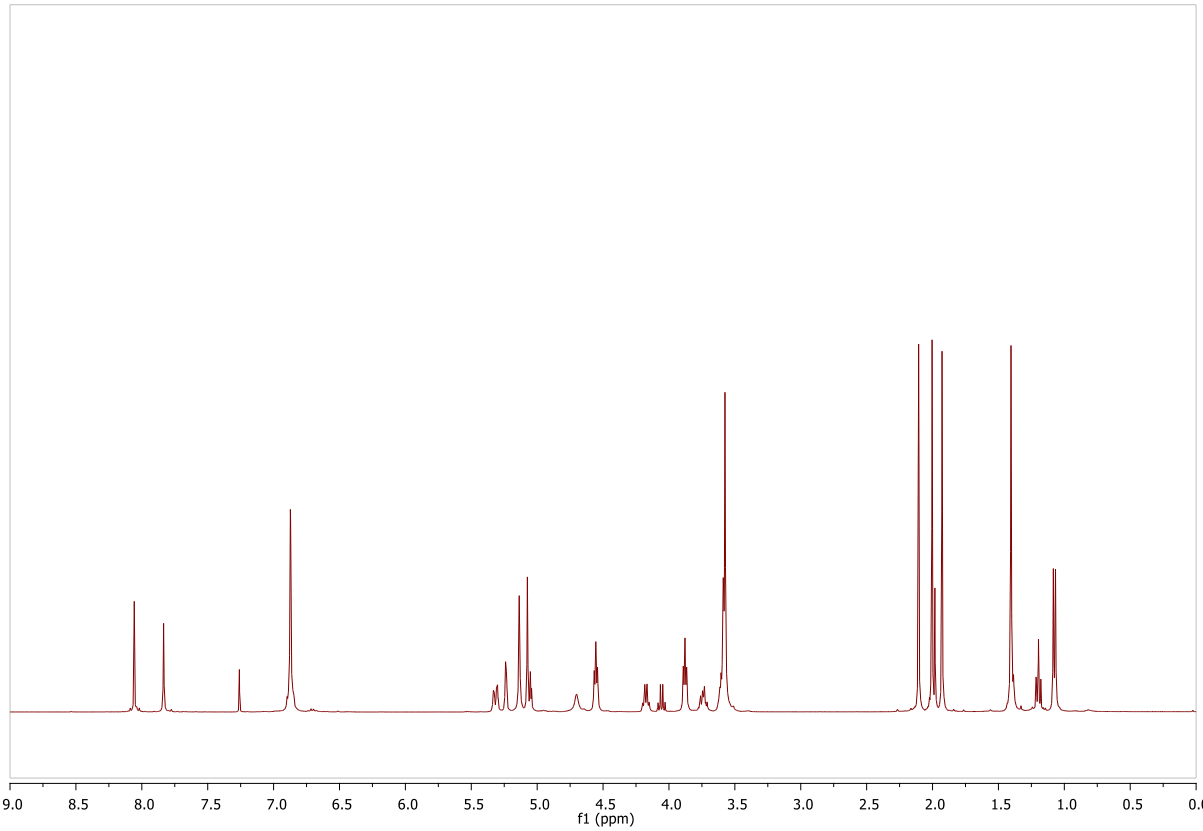
N,N'*-Bis-(*t*-butoxycarbonylmethyl)-1,6,7,12-tetra-(4-{1-[1-(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyloxy}phenoxy)perylene-3,4,9,10-tetracarboxylic diimide (10d) :** Obtained as a purple foam following ***Method A: **6** (70 mg, 0.058 mmol, 1 eq.), **7d** (156 mg, 0.349 mmol, 6 eq.), CuI (5.5 mg, 0.029 mmol, 0.5 eq.) and DIPEA (58 µL, 0.349 mmol, 6 eq.). Purified by silica gel flash chromatography (CH_2Cl_2/MeOH 98/2 to 96/4).

Yield = 69% (120 mg), $\mathbf{R_f}$ = 0.45 (CH_2Cl_2/MeOH 95/5).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.06 (s, 4H, H-triaz), 7.83 (s, 4H, perylene-H), 6.87 (s, 16H, CH-ar), 5.32 (dt, J = 12.4, 2.7 Hz, 4H, H-2), 5.25-5.22 (m, 4H, H-4), 5.14 (bs, 8H, OCH_2-triaz), 5.08-5.04 (m, 8H, H-1, H-3), 4.70 (bs, 4H, NCH_2CO), 4.55 (t, J = 5.0 Hz, 8H, NCH_2CH_2), 4.17 (q, J = 6.3 Hz, 4H, H-5), 3.88 (t, J = 5.1 Hz, 8H, OCH_2), 3.78-3.70 (m, 4H, FucOCH_2), 3.64-3.52 (m, 28H, OCH_2, FucOCH_2), 2.11, 2.00, 1.93 (3s, 36H, $COCH_3$), 1.40 (s, 18H, CMe_3), 1.08 (d, J = 6.5 Hz, 12H, H-6).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.6, 170.4, 170.1 (3s, 3×*C*OCH_3), 166.9 (COO), 162.9 (Ar*C*ON), 156.5, 155.4, 148.9 (3×C^{IV}-ar-O), 143.7, 132.8 (2×C^{IV}-ar), 124.1 (C^{IV}-triaz), 122.0 (C^{IV}-ar), 121.4 (CH-ar), 120.2 (C^{IV}-ar), 119.32, 119.27 (2s, CH-perylene), 116.1 (CH-ar), 96.2 (C-1), 82.3 (*C*Me_3), 71.1 (C-4), 70.6 (2×OCH_2), 70.2 (OCH_2), 69.5 (OCH_2), 68.2 (C-3), 68.0 (C-2), 67.3 (FucO*C*H_2), 64.3 (C-5), 62.5 (O*C*H_2-triaz), 50.3 (N*C*H_2CH_2), 42.1 (N*C*H_2CO), 28.0 (C*Me*$_3$), 20.8, 20.7, 20.6 (3×CO*C*H_3), 15.9 (C-6).

HR-ESI-QTof (positive mode) *m*/*z*: calcd for $C_{144}H_{172}N_{14}O_{56}$ $[M+2H]^{2+}$ 1496.5515, found 1496.5467.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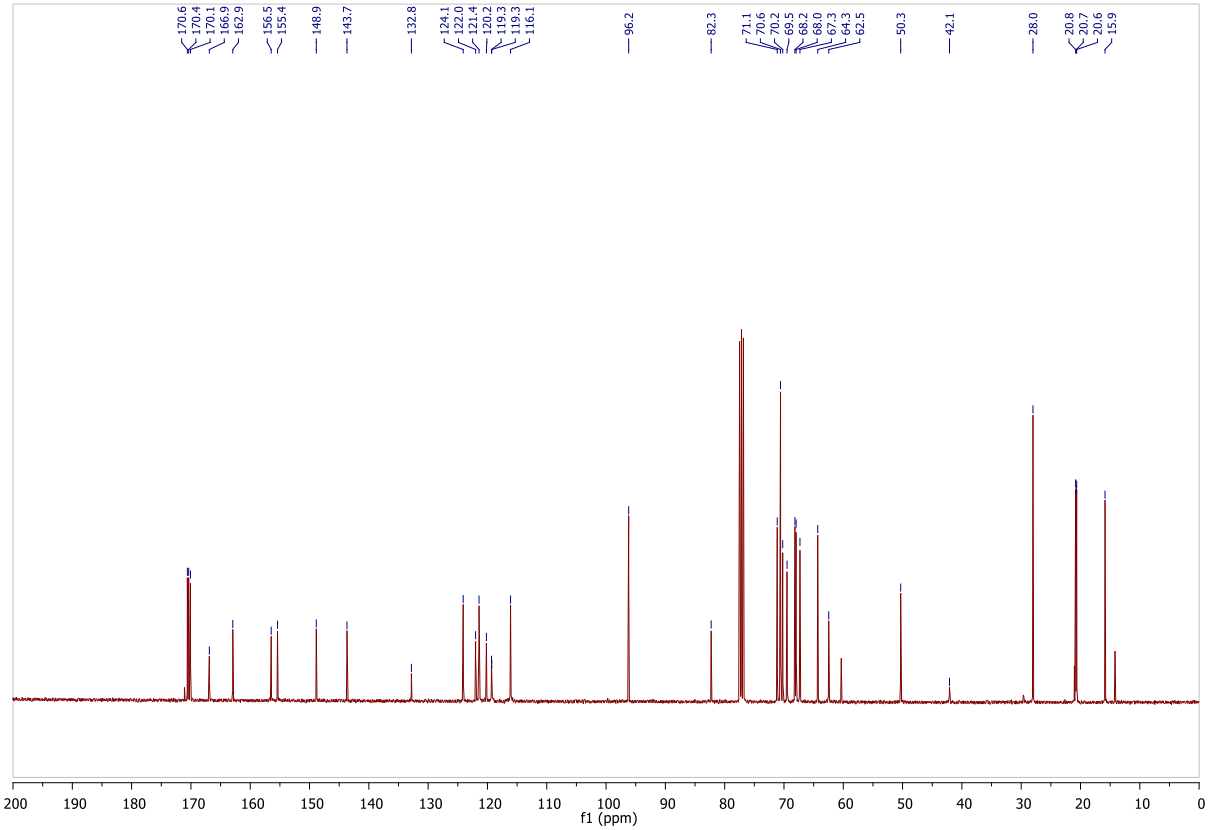
f1 (ppm)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20.7
20.6
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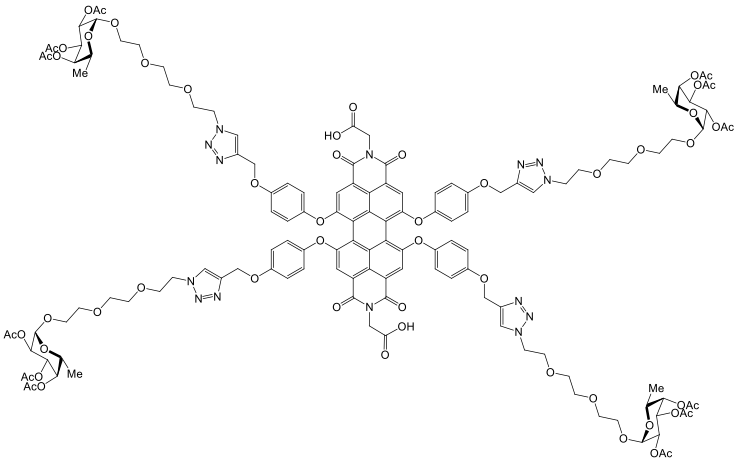
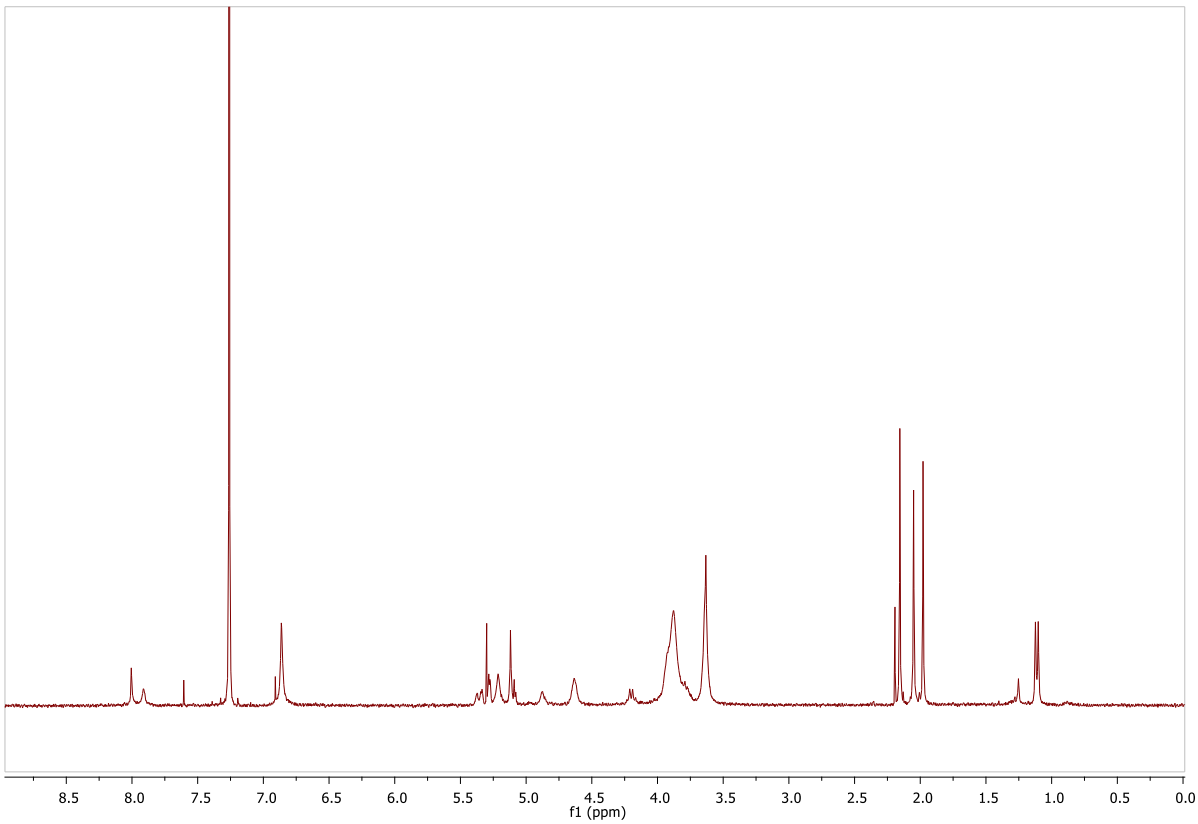


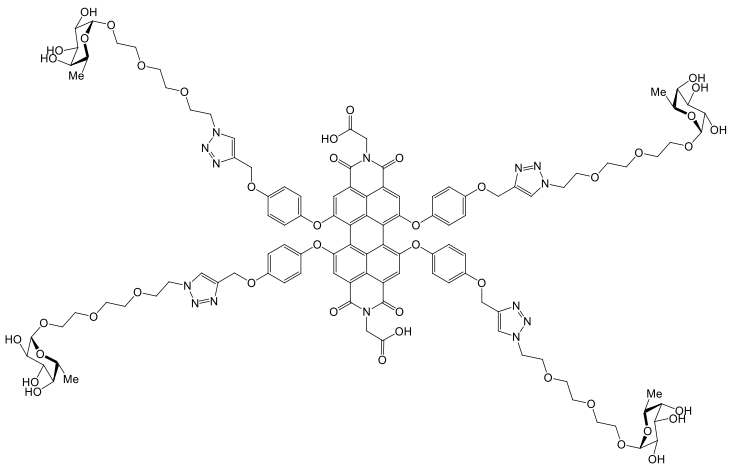
N,N'*-Bis-(carboxymethyl)-1,6,7,12-tetra-(4-{1-[1-(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyloxy}phenoxy)perylene-3,4,9,10-tetracarboxylic diimide (10d-bis):** Obtained from **10d** (112 mg, 0.039 mmol, 1 eq.) as a purple foam following ***Method C.

R_f = 0.30 (CH_2Cl_2/MeOH 95/5).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.01 (s, 4H, H-triaz), 7.91 (s, 4H, perylene-H), 6.86 (s, 16H, CH-ar), 5.41-5.32 (m, 4H, H-2), 5.28 (d, *J* = 2.3 Hz, 4H, H-4), 5.21 (bs, 8H, OCH_2-triaz), 5.14-5.07 (m, 8H, H-1, H-3), 4.87 (bs, 4H, NCH_2CO), 4.67-4.58 (m, 8H, NCH_2CH_2), 4.20 (dd, *J* = 12.9, 6.3 Hz, 4H, H-5), 4.00-3.71, 3.71-3.56 (2m, 40H, OCH_2), 2.16, 2.05, 1.98 (3s, 36H, $COCH_3$), 1.11 (d, *J* = 6.4 Hz, 12H, H-6).

ESI-QTof (positive mode) *m/z*: calcd for $C_{136}H_{154}N_{14}O_{56}$ $[M+2H]^{2+}$ 1441.0, found 1441.5.





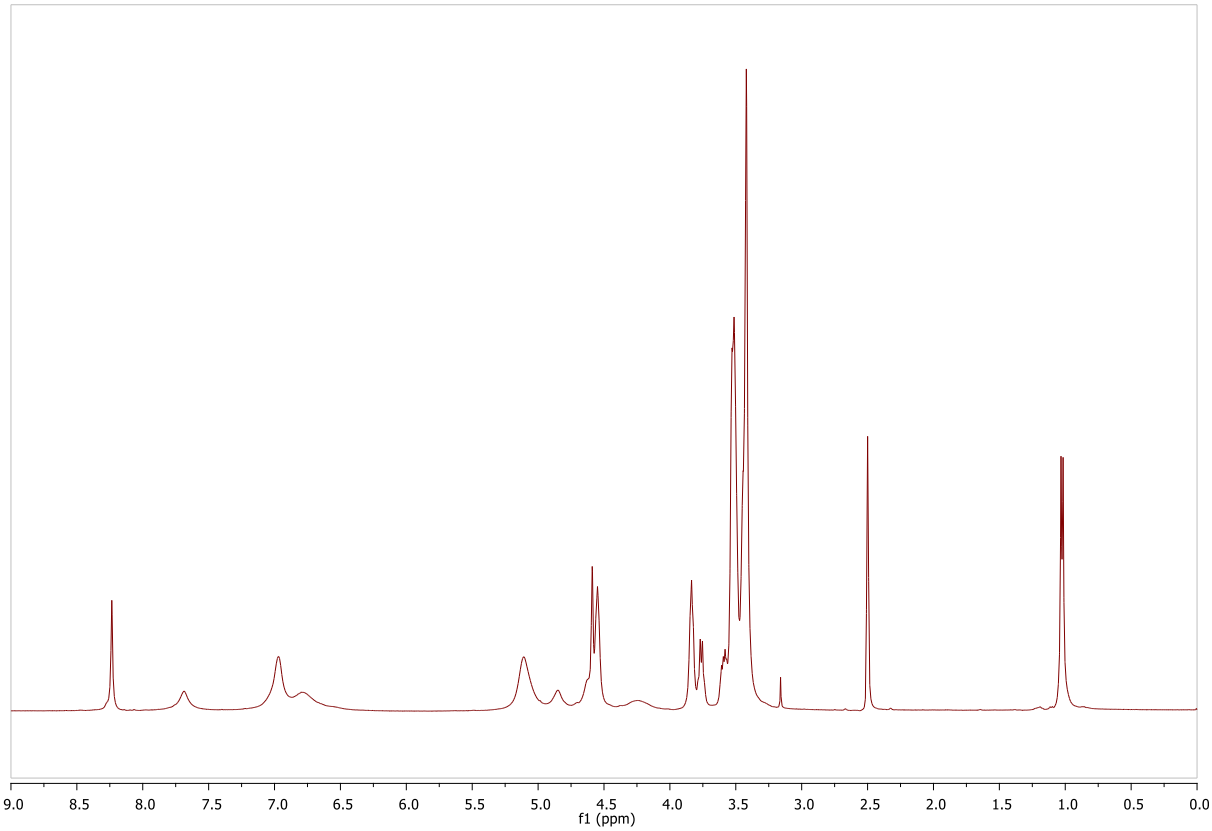
N*,*N*'-Bis-(carboxymethyl)-1,6,7,12-tetra-(4-{1-[1-(α-L-fucopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethyloxy}phenoxy)perylene-3,4,9,10-tetracarboxylic diimide (11d) :** Obtained from **10d-bis** as a deep purple foam following ***Method B.

Yield = 98% (87 mg). After 2 steps

^{1}H NMR (400 MHz, DMSO-d$_6$ + εD$_2$O) δ (ppm): 8.23 (s, 4H, H-triaz), 7.69 (s, 4H, perylene-H), 6.97 (bs, 8H, CH-ar), 6.80 (bs, 8H, CH-ar), 5.19-5.00 (m, 8H, OC*H*$_2$-triaz), 4.66-4.50 (m, 12H, NC*H*$_2$CH$_2$, H-1), 4.25 (bs, 4H, NCH$_2$CO), 3.89-3.71 (m, 12H, H-5, OCH$_2$), 3.65-3.32 (m, 44H, 4×OCH$_2$, H-2, H-3, H-4), 1.02 (d, J = 6.4 Hz, 12H, H-6).

^{13}C NMR (100 MHz, DMSO-d$_6$ + εD$_2$O) δ (ppm): 170.2 (COO), 162.1 (Ar*C*ON), 156.0, 155.1, 148.6 (3×C^{IV}-ar-O), 142.6 (C^{IV}-triaz), 132.2 (C^{IV}-ar), 125.2 (CH-triaz), 122.3 (C^{IV}-ar), 121.2 (CH-ar), 118.9, 118.4 (2×C^{IV}-ar), 117.8 (CH-perylene), 115.8 (CH-ar), 99.3 (C-1), 71.6 (C-4), 69.8, 69.6, 68.8 (4×OCH$_2$), 68.1 (C-2), 66.6 (FucO*C*H$_2$), 66.0 (C-5), 61.6 (O*C*H$_2$-triaz), 49.6 (N*C*H$_2$CH$_2$), 44.1 (NCH$_2$CO), 16.6 (C-6).

HR-ESI-QTof (positive mode) *m*/*z*: calcd for C$_{112}$H$_{132}$N$_{14}$O$_{44}$ [M+2H]$^{2+}$ 1188.4255, found 1188.4224.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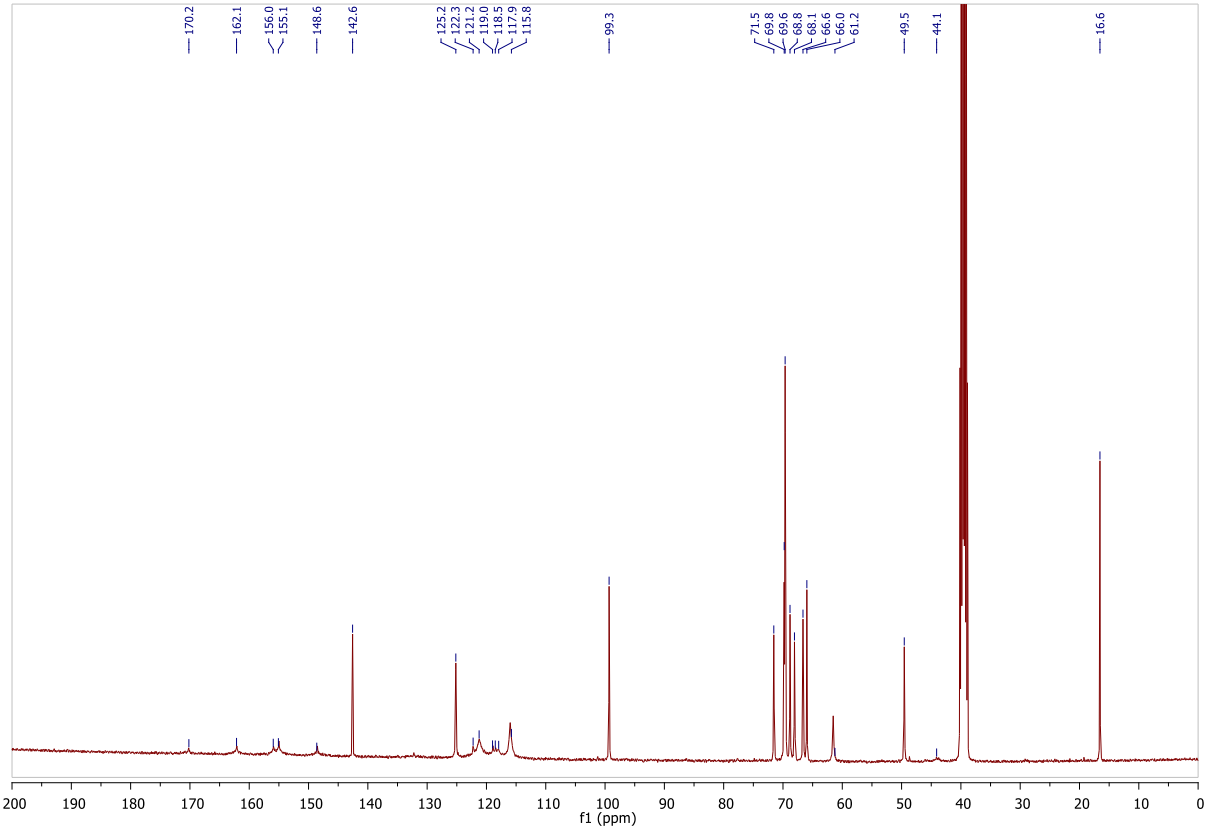
f1 (ppm)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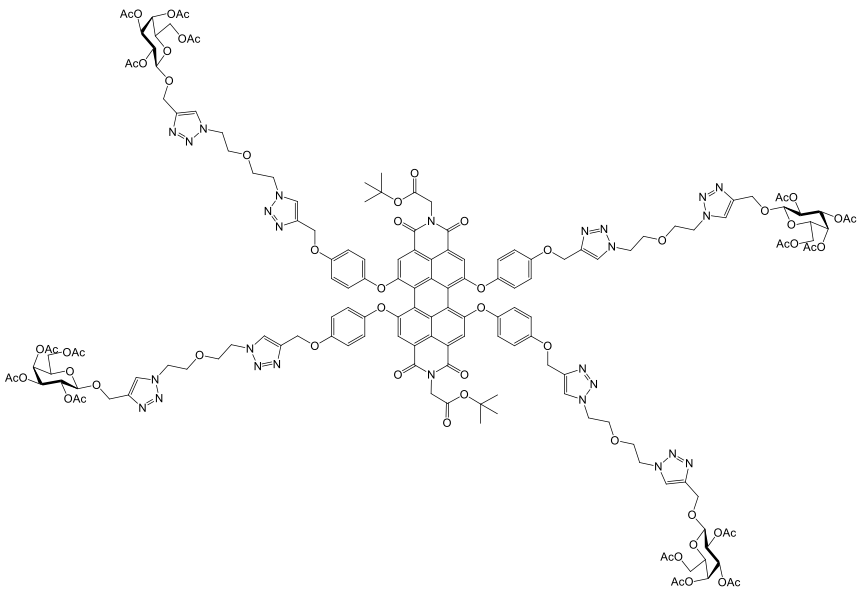
f1 (ppm)



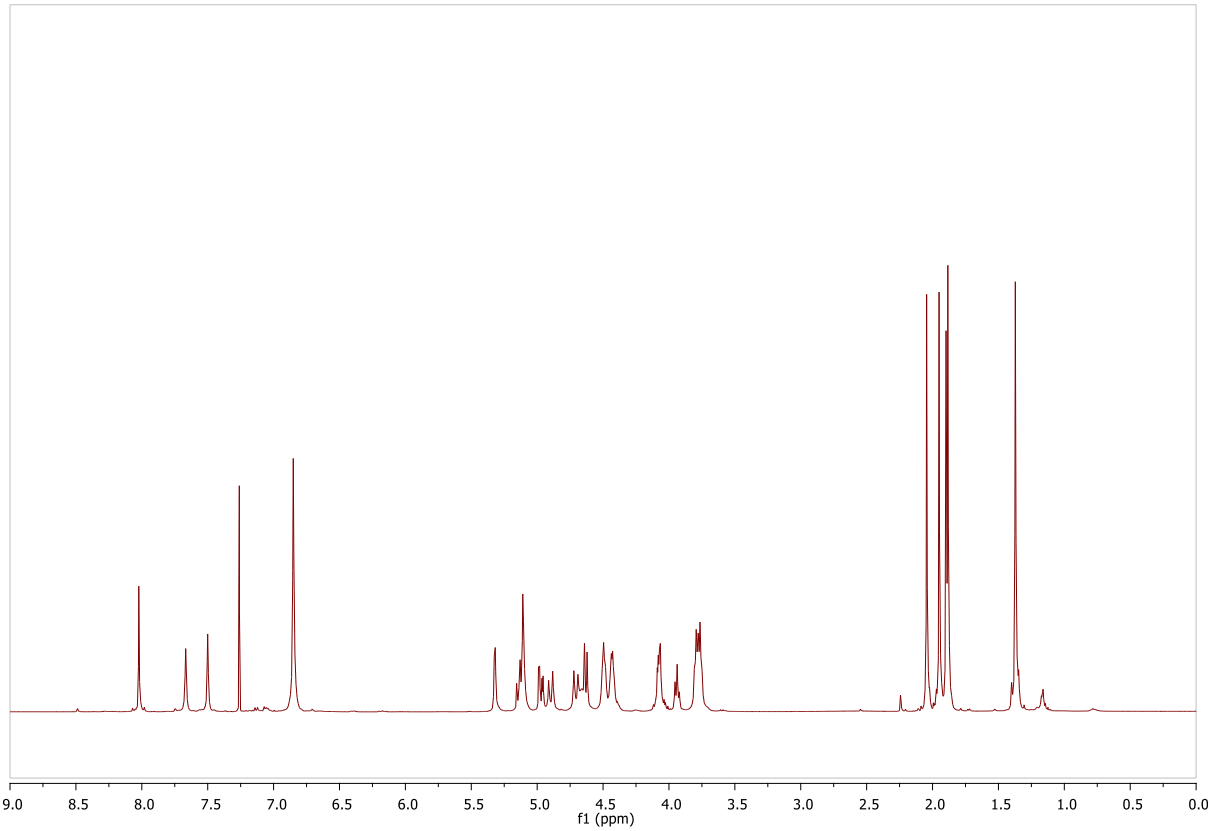
N,N'*-Bis-(*t*-butoxycarbonylmethyl)-1,6,7,12-tetra-[4-(4-{3-oxa-5-[4-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyloxymethyl)-triazol-1-yl]-pent-1-yl}-triazol-1-ylmethyl)phenoxy]perylene-3,4,9,10-tetracarboxylic diimide (10e) :** Obtained as a purple foam following ***Method A: **6** (80 mg, 0.067 mmol, 1 eq.), **7e** (216 mg, 0.399 mmol, 6 eq.), CuI (6 mg, 0.032 mmol, 0.5 eq.) and DIPEA (66 µL, 0.399 mmol, 6 eq.). Purified by silica gel flash chromatography (CH_2Cl_2/MeOH 99/1 to 95/5).

Yield = 76% (171 mg), $\mathbf{R_f}$ = 0.30 (CH_2Cl_2/MeOH 95/5).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.02 (s, 4H, perylene-H), 7.67 (s, 4H, H-triaz), 7.50 (s, 4H, H-triaz), 6.85 (s, 16H, H-ar), 5.32 (d, J = 3.1 Hz, 4H, H-4), 5.17-5.07 (m, 12H, H-2, OCH_2-triaz), 4.97 (dd, J = 10.5, 3.4 Hz, 4H, H-2), 4.90 (d, J = 12.4 Hz, 4H, GalOCH_2), 4.71 (d, J = 12.4 Hz, 4H, GalOCH_2), 4.66 (bs, 4H, NCH_2CO), 4.63 (d, J = 7.9 Hz, 4H, H-1), 4.53-4.46, 4.46-4.38 (2m, 16H, NCH_2CH_2), 4.12-4.02 (m, 8H, H-6), 3.94 (t, J = 6.6 Hz, 4H, H-5), 3.83-3.72 (m, 16H, 2×OCH_2), 2.04, 1.95, 1.90, 1.88 (4s, 48H, 4×$COCH_3$), 1.37 (s, 18H, CMe_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.3, 170.1, 169.9, 169.4 (4×*C*OCH_3), 166.8 (COO), 162.8 (Ar*C*ON), 156.3, 155.2, 148.8 (3×C^{IV}-ar-O), 144.0, 143.6 (2×C^{IV}-triaz), 132.7 (C^{IV}-ar), 124.0, 123.8 (2s, 2×*C*H-triaz), 121.9 (C^{IV}-ar), 121.3 (8C, CH-ar), 120.1, 119.2 (2×C^{IV}-ar), 119.1 (CH-perylene), 116.0 (8C, CH-ar), 100.4 (C-1), 82.2 (*C*Me_3), 70.6 (s, 2C, C-3, C-5), 69.20, 69.18 (2×OCH_2), 68.7 (C-2), 66.9 (C-4), 62.9 (GalO*C*H_2), 62.2 (O*C*H_2-triaz), 61.1 (C-6), 50.0 (NCH_2CH_2), 42,0 (NCH_2CO), 27.9 (C*Me*$_3$), 20.7, 20.6, 20.53, 20.46 (4×CO*C*H_3).

HR-ESI-QTof (positive mode) *m*/*z*: calcd for $C_{156}H_{176}N_{26}O_{60}$ $[M+2H]^{2+}$ 1686.5755, found 1686.5743.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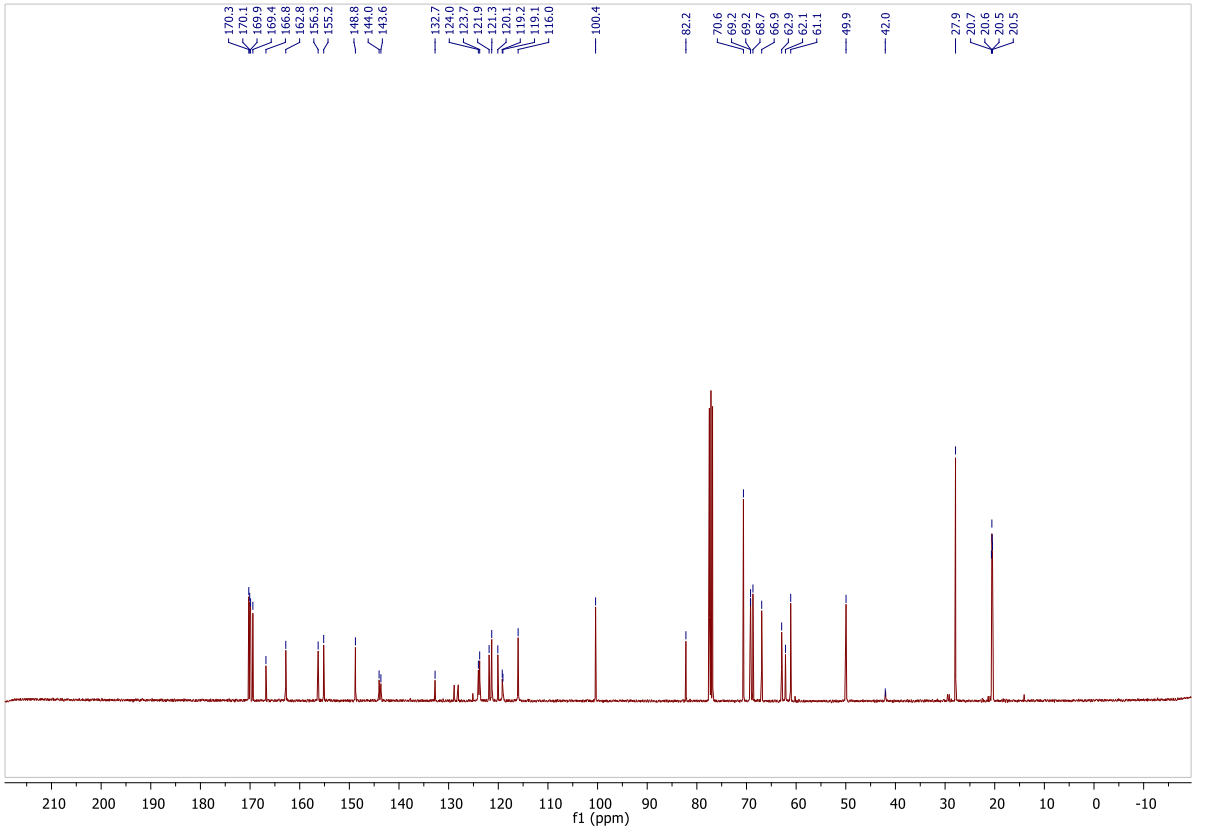
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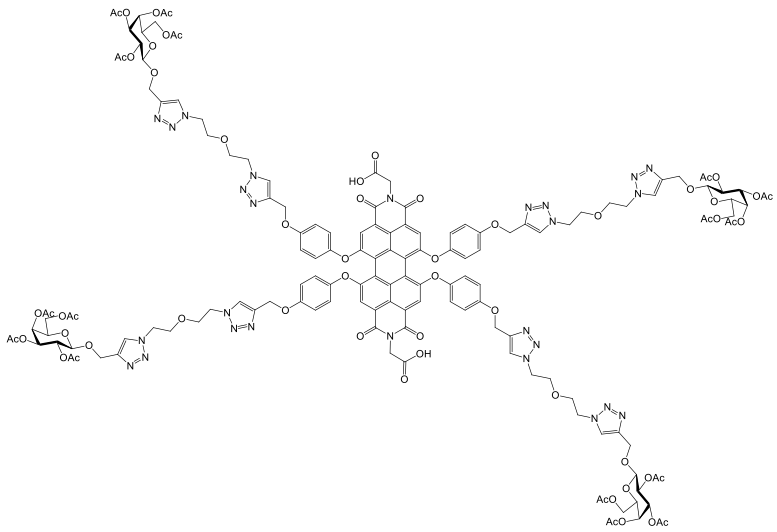
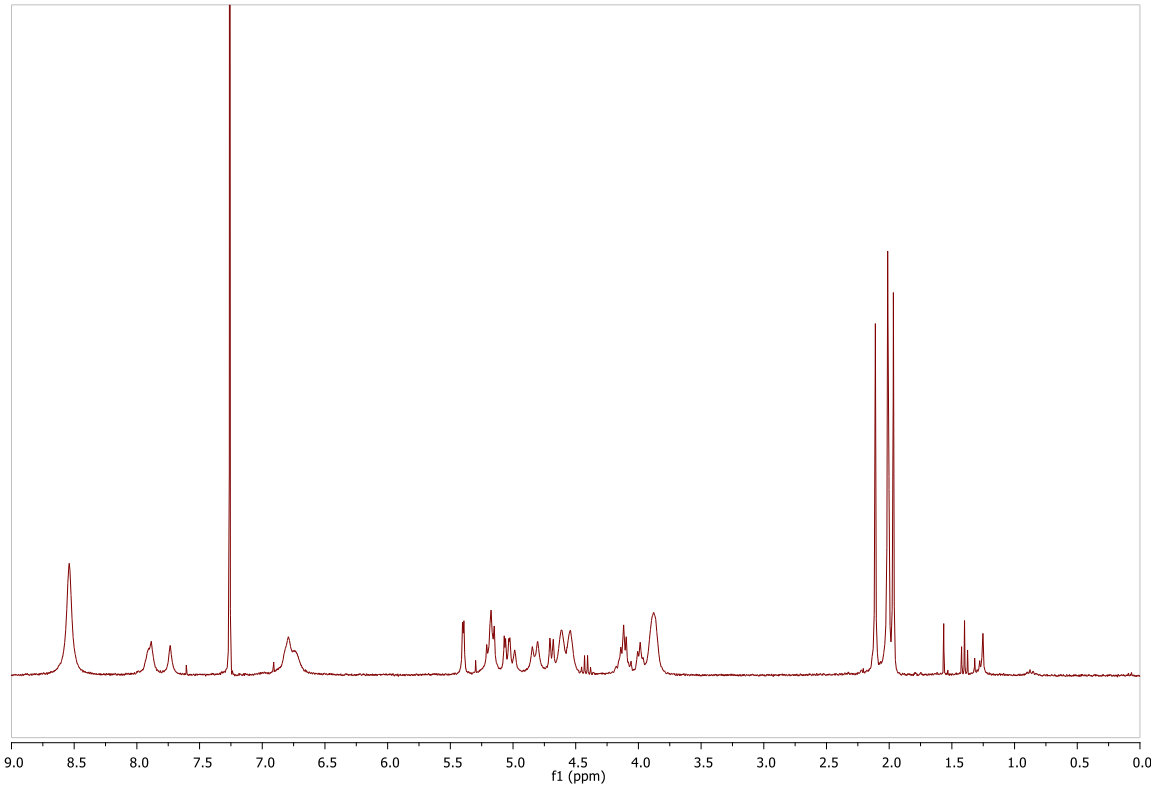
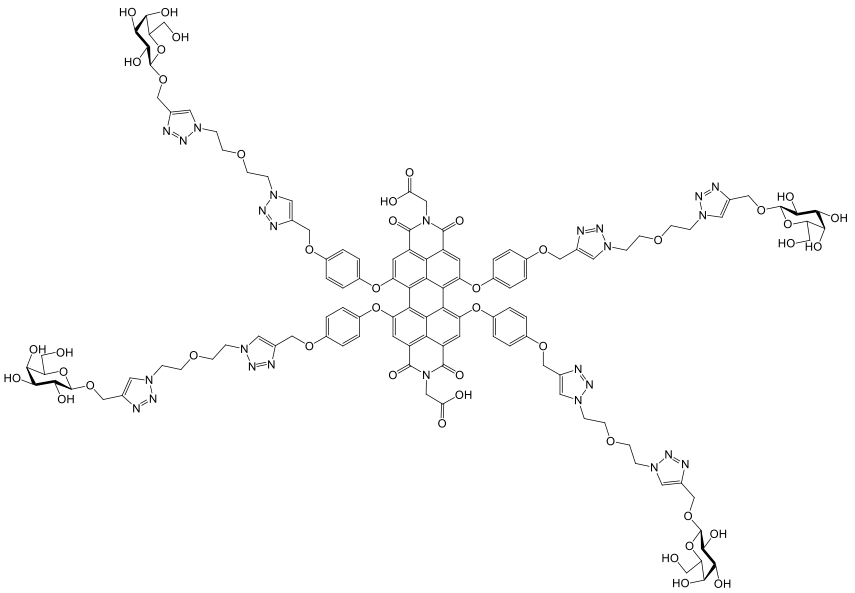


N,N'*-Bis-(carboxymethyl)-1,6,7,12-tetra-[4-(4-{3-oxa-5-[4-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyloxymethyl)-triazol-1-yl]-pent-1-yl}-triazol-1-ylmethyl)phenoxy]perylene-3,4,9,10-tetracarboxylic diimide (10e-bis) :** Obtained from **10e** (155 mg, 0.060 mmol, 1 eq.) as a purple foam following ***Method C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.93-7.83 (m, 8H, perylene-H, H-triaz), 7.73 (s, 4H, H-triaz), 6.77 (d, J = 13.4 Hz, 16H, H-ar), 5.40 (d, J = 3.2 Hz, 4H, H-4), 5.23-5.11 (m, 12H, H-2, OCH_2-triaz), 5.09-4.96 (m, 8H, GalOCH_2, H-2), 4.83 (d, J = 12.3 Hz, 4H, GalOCH_2, NCH_2CO), 4.69 (d, J = 8.1 Hz, 4H, H-1), 4.66-4.58, 4.59-4.50 (2m, 16H, NCH_2CH_2), 4.12 (m, 8H, H-6), 3.98 (t, J = 6.6 Hz, 4H, H-5), 3.93-3.82 (m, 16H, 2×OCH_2), 2.11, 2.01, 2.01, 1.97 (4s, 48H, 4×$COCH_3$).

ESI-QTof (positive mode) *m/z*: calcd for $C_{148}H_{160}N_{26}O_{60}$ $[M+2H]^{2+}$ 1631.0, found 1631.0





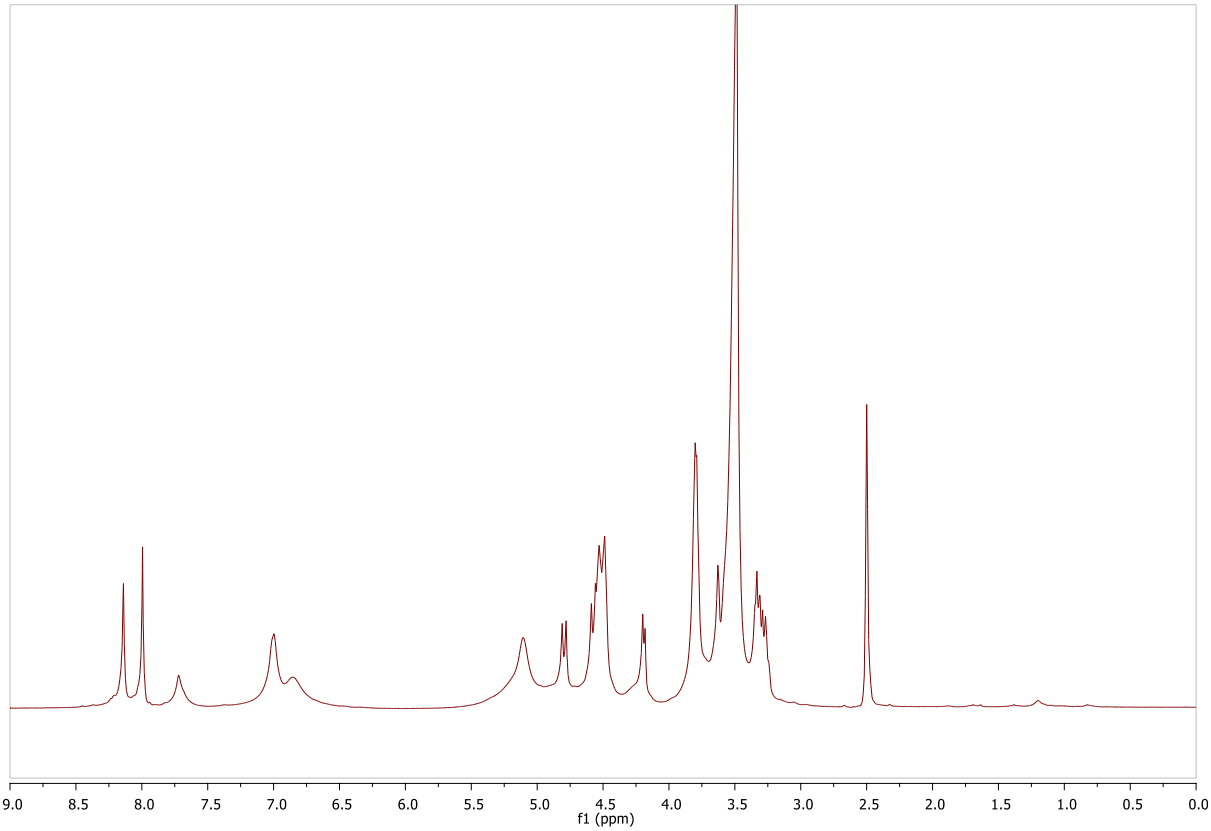
N*,*N*'-Bis-(carboxymethyl)-1,6,7,12-tetra-[4-(4-{3-oxa-5-[4-(β-D-galactopyranosyloxymethyl)-triazol-1-yl]-pent-1-yl}-triazol-1-ylmethyl)phenoxy]perylene-3,4,9,10-tetracarboxylic diimide (11e) :** Obtained from **10e-bis** (155 mg, 0.046 mmol) as a deep purple foam following ***Method B.

Yield = 91% (108 mg). After two steps

^{1}H NMR (400 MHz, DMSO-d$_6$ + εD$_2$O) δ (ppm): 8.14 (s, 4H, H-triaz), 7.99 (s, 4H, H-triaz), 7.72 (bs, 4H, perylene-H), 7.00, 6.86 (2bs, 16H, CH-ar), 5.11 (bs, 8H, OC*H*$_2$-triaz), 4.80 (d, *J* = 12.0 Hz, 4H, GalOC*H*$_2$), 4.68-4.39 (m, 24H, NC*H*$_2$CH$_2$, NCH$_2$CO, GalOC*H*$_2$), 4.19 (d, *J* = 7.2 Hz, 4H, H-1), 3.96-3.71 (m, 16H, 2×OCH$_2$), 3.71-3.61 (m, 4H, H-4), 3.61-3.39 (m, 8H, H-6), 3.39-3.18 (m, 12H, H-2, H-3, H-5).

^{13}C NMR (100 MHz, DMSO-d$_6$ + εD$_2$O) δ (ppm): 170.2 (COO), 162.2 (Ar*C*ON), 156.1, 155.0, 148.5 (3×C^{IV}-ar-O), 144.0, 142.7 (2×C^{IV}-triaz), 132.3 (C^{IV}-ar), 125.3, 124.8 (2×CH-triaz), 122.3 (C^{IV}-ar), 121.3 (CH-ar), 119.0, 118.5 (2×C^{IV}-ar), 118.0 (CH-perylene), 116.0 (CH-ar), 102.9 (C-1), 75.4 (C-3), 73.5 (C-2), 70.6 (C-5), 68.7 (4C, OCH$_2$), 68.1 (C-4), 61.5 (O*C*H$_2$-triaz, GalO*C*H$_2$), 60.5 (C-6), 49.4, 49.4 (NC*H*$_2$CH$_2$), 44.2 (N*C*H$_2$CO).

HR-ESI-QTof (positive mode) *m*/*z*: calcd for $C_{116}H_{128}N_{26}O_{44}$ $[M+2H]^{2+}$ 1294.4283, found 1294.4232.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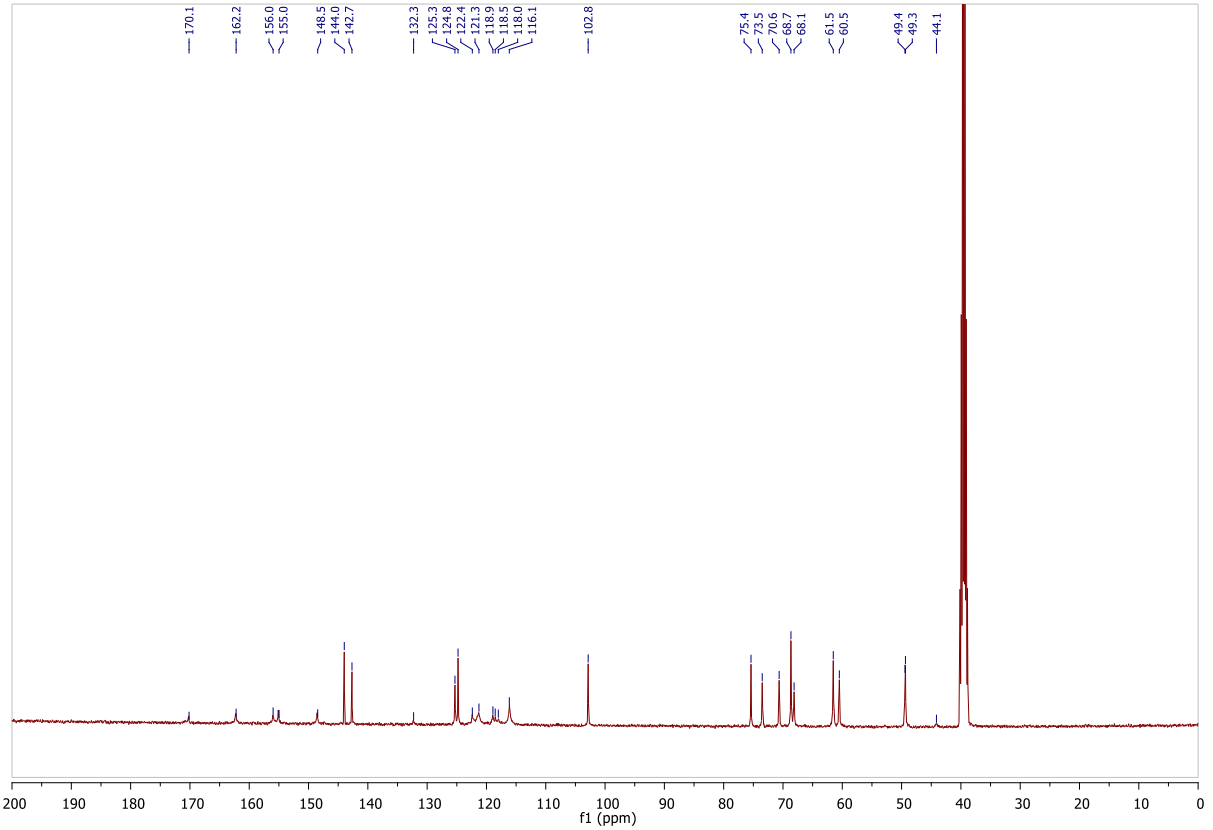
f1 (ppm)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68.1
61.5
60.5
49.4
49.3
44.1
200
190
180
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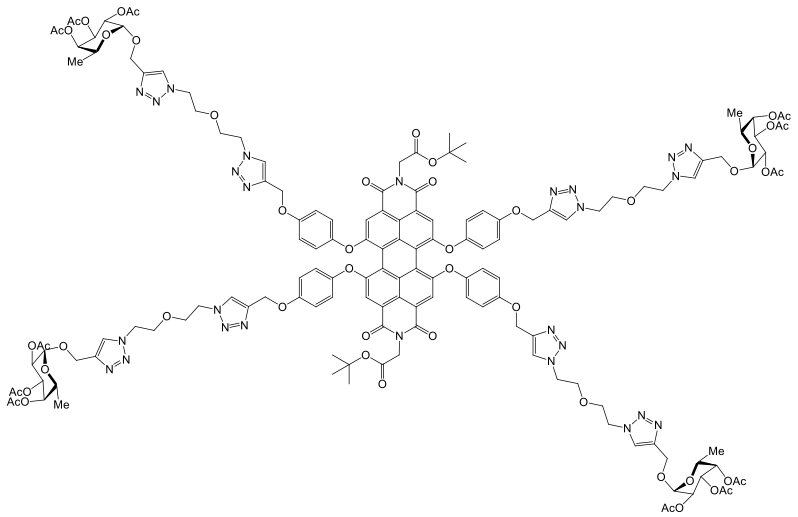


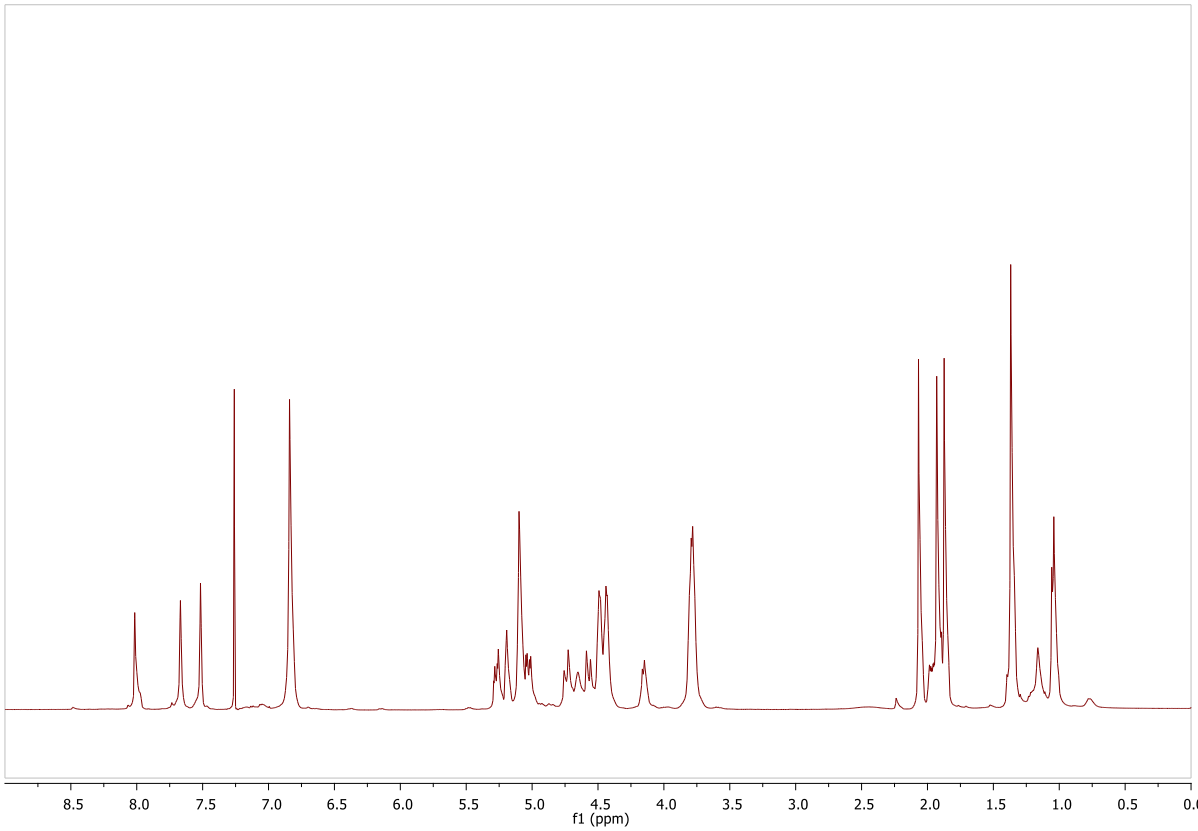
N*,*N*'-Bis-(*t*-butoxycarbonylmethyl)-1,6,7,12-tetra-[4-(4-{3-oxa-5-[4-(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyloxymethyl)-triazol-1-yl]-pent-1-yl}-triazol-1-ylmethyl)phenoxy]perylene-3,4,9,10-tetracarboxylic diimide (10f):** Obtained as a purple foam following ***Method A: **6** (75 mg, 0.062 mmol, 1 eq.), **7f** (181 mg, 0.374 mmol, 6 eq.), CuI (6 mg, 0.031 mmol, 0.5 eq.) and DIPEA (62 µL, 0.374 mmol, 6 eq.). Purified by silica gel flash chromatography (CH_2Cl_2/MeOH 99/1 to 95/5).

Yield = 76% (149 mg), $\mathbf{R_f}$ = 0.30 (CH_2Cl_2/MeOH 95/5).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.02 (s, 4H, perylene-H), 7.67 (s, 4H, H-triaz), 7.52 (s, 4H, H-triaz), 6.84 (s, 16H, H-ar), 5.27 (dd, *J* = 10.8, 3.2 Hz, 4H, H-3), 5.20 (d, *J* = 3.2 Hz, 4H, H-4), 5.14-5.06 (m, 12H, H-1, OC*H*$_2$-triaz), 5.03 (dd, *J* = 10.8, 3.6 Hz, 4H, H-2), 4.74 (d, *J* = 12.3 Hz, 4H, FucOC*H*$_2$), 4.65 (bs, 4H, NCH_2CO), 4.57 (d, *J* = 12.3 Hz, 4H, FucOC*H*$_2$), 4.52-4.47, 4.47-4.38 (2m, 16H, NC*H*$_2$CH$_2$), 4.18-4.11 (m, 4H, H-5), 3.85-3.70 (m, 16H, 2×OCH_2), 2.07, 1.93, 1.87 (3s, 36H, 3×$COCH_3$), 1.37 (s, 18H, CMe_3), 1.05 (d, *J* = 6.3 Hz, 12H, H-6).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.6, 170.4, 170.0 (3×*C*OCH_3), 166.9 (COO), 162.9 (Ar*C*ON), 156.4, 155.2, 148.9 (3×C^{IV}-ar-O), 143.8 (2×C^{IV}-triaz), 132.8 (C^{IV}-ar), 123.9 (s, 2×CH-triaz), 121.9 (C^{IV}-ar), 121.4 (8C, CH-ar), 120.2, 119.3 (2×C^{IV}-ar), 119.2 (CH-perylene), 116.1 (8C, CH-ar), 95.4 (C-1), 82.3 (*C*Me_3), 71.1 (C-4), 69.3 (2×OCH_2), 68.0 (C-2), 67.8 (C-3), 64.7 (C-5), 62.3 (O*C*H$_2$-triaz), 60.9 (FucO*C*H$_2$), 50.1, 50.0 (2s, 2×N*C*H$_2$CH$_2$), 42.0 (N*C*H$_2$CO), 28.0 (C*Me*$_3$), 20.8, 20.7, 20.6 (3s, 3×CO*C*H$_3$), 15.8 (C-6).

HR-ESI-QTof (positive mode) *m*/*z*: calcd for $C_{148}H_{169}N_{26}O_{52}$ $[M+3H]^{3+}$ 1047.3788, found 1047.3779.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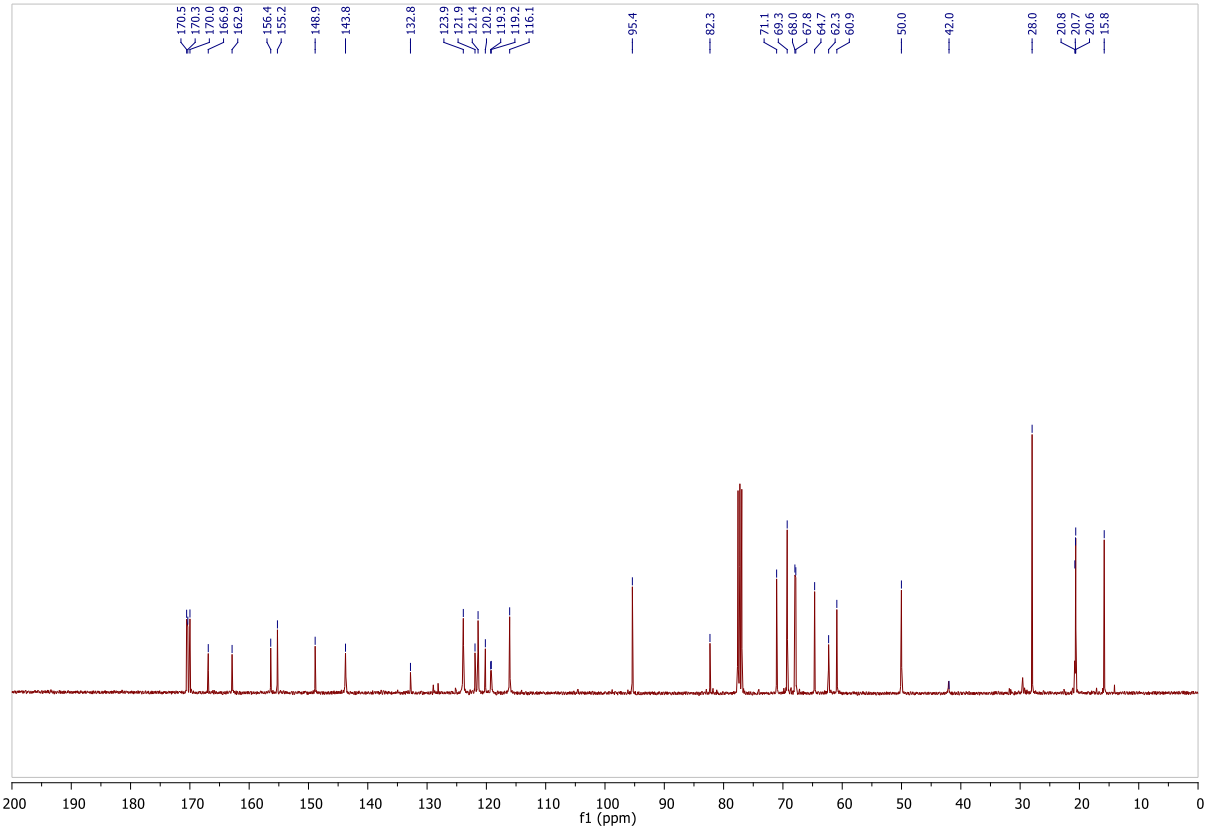
0.0
f1 (ppm)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62.3
60.9
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42.0
28.0
20.8
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15.8
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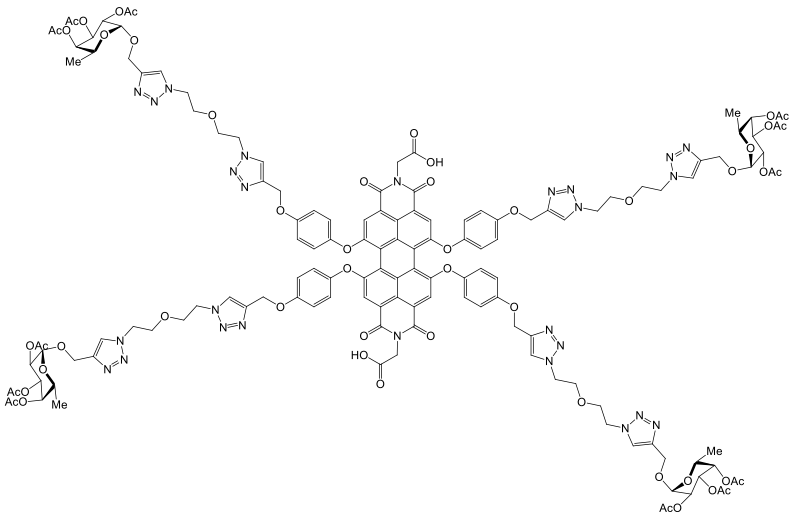
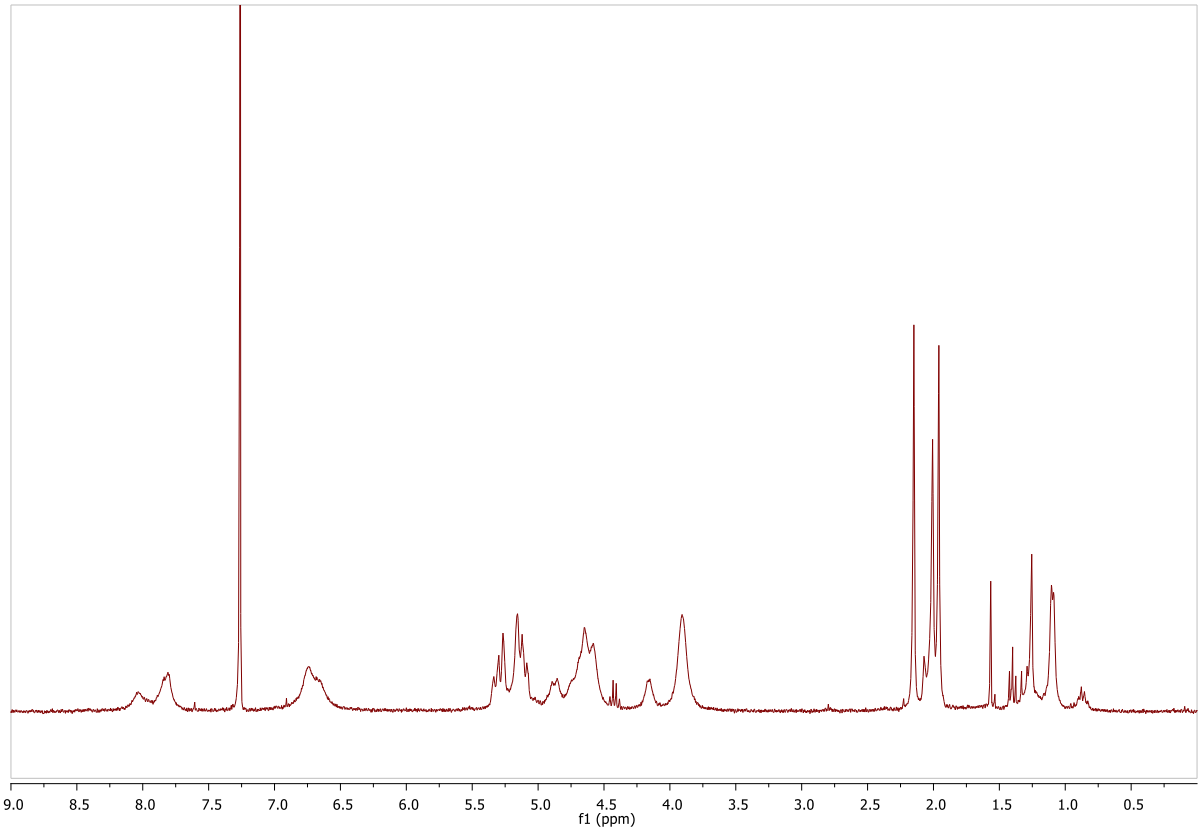
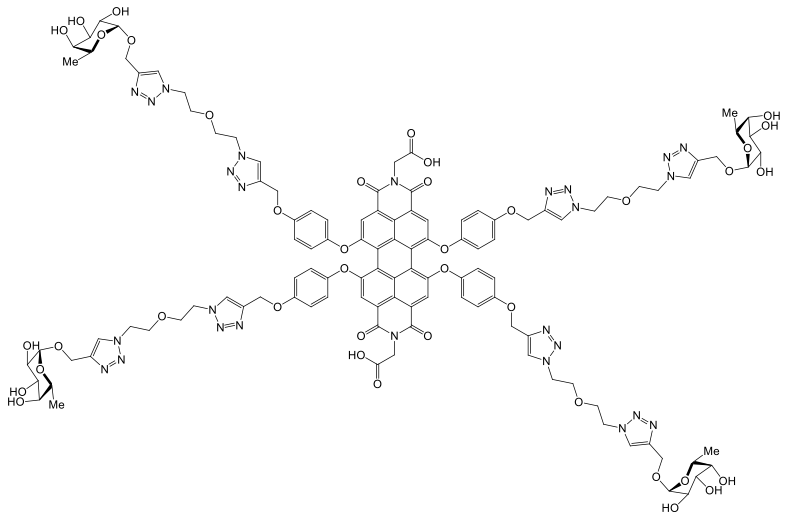
f1 (ppm)



N,N'*-Bis-(carboxymethyl)-1,6,7,12-tetra-[4-(4-{3-oxa-5-[4-(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyloxymethyl)-triazol-1-yl]-pent-1-yl}-triazol-1-ylmethyl)phenoxy]perylene-3,4,9,10-tetracarboxylic diimide (10f-bis) :** Obtained from **10f** (136 mg, 0.054 mmol, 1 eq.) as a purple foam following ***Method C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.14-7.93 (s, 4H, perylene-H), 7.93-7.71 (m, 8H, H-triaz), 6.74 (s, 16H, H-ar), 5.32 (d, J = 11.3 Hz, 4H, H-3), 5.28-5.23 (m, 4H, H-4), 5.20-5.05 (m, 16H, H-1, H-2, OCH_2-triaz), 4.94-4.81 (m, 4H, FucOCH_2), 4.81-4.50 (m, 24H, NCH_2CO, FucOCH_2, NCH_2CH_2), 4.22-4.09 (m, 4H, H-5), 3.99-3.89 (m, 16H, 2×OCH_2), 2.15, 2.01, 1.96 (3s, 36H, 3×$COCH_3$), 1.10 (d, J = 4.8 Hz, 12H, H-6).
ESI-QTof (positive mode) m/z: calcd for $C_{140}H_{152}N_{26}O_{52}$ $[M+2H]^{2+}$ 1515.0, found 1515.0.





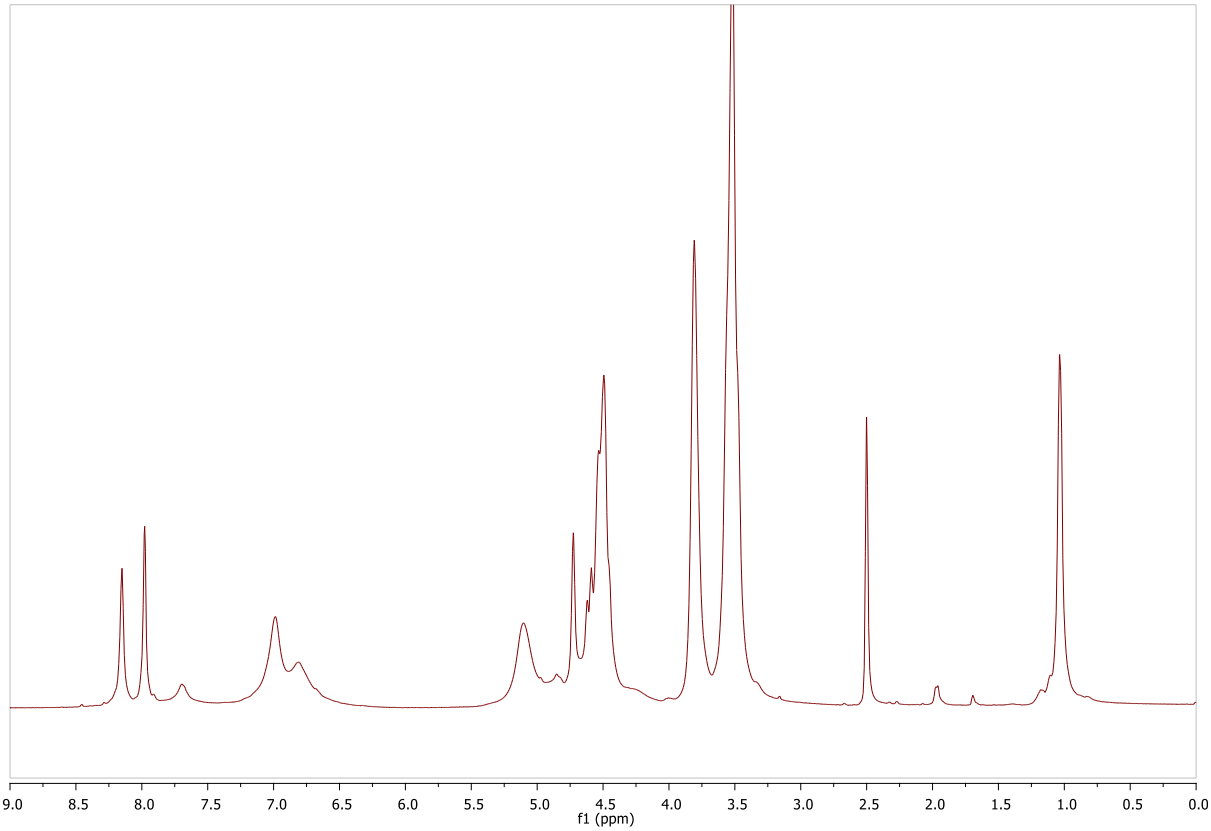
N,N*'-Bis-(carboxymethyl)-1,6,7,12-tetra-[4-(4-{3-oxa-5-[4-(α-L-fucopyranosyloxymethyl)-triazol-1-yl]-pent-1-yl}-triazol-1-ylmethyl)phenoxy]perylene-3,4,9,10-tetracarboxylic diimide (11f) :** Obtained from **10f-bis** (136 mg, 0.043 mmol) as a deep purple foam following ***Method B.

Yield = 93% (102 mg). After two steps

^{1}H NMR (400 MHz, DMSO-d$_6$ + εD$_2$O) δ (ppm): 8.15 (s, 4H, H-triaz), 7.98 (s, 4H, H-triaz), 7.70 (bs, 4H, perylene-H), 6.99, 6.81 (2bs, 16H, CH-ar), 5.10 (bs, 8H, OC*H*$_2$-triaz), 4.73 (s, 4H, H-1), 4.67-4.33 (m, 28H, 2×NC*H*$_2$CH$_2$, FucOC*H*$_2$, NCH$_2$CO), 3.94-3.69 (m, 20H, 2×OCH$_2$, H-5), 3.69-3.32 (m, 12H, H-2, H-3, H-4), 1.04 (m, 12H, H-6).

^{13}C NMR (100 MHz, DMSO-d$_6$ + εD$_2$O) δ (ppm): 170.4 (COO), 162.3 (Ar*C*ON), 155.8, 155.2, 148.7 (3×C^{IV}-ar-O), 144.1, 142.7 (2×C^{IV}-triaz), 132.4 (C^{IV}-ar), 125.3, 124.5 (2×CH-triaz), 122.4 (C^{IV}-ar), 121.3 (CH-ar), 118.9, 118.4 (2×C^{IV}-ar), 118.1 (CH-perylene), 116.1 (CH-ar), 98.7 (C-1), 71.6 (C-4), 69.6 (C-3), 68.7 (2×OCH$_2$), 68.1 (C-2), 66.2 (C-5), 61.6 (O*C*H$_2$-triaz), 60.1 (FucO*C*H$_2$), 49.4, 49.3 (N*C*H$_2$CH$_2$), 44.2 (N*C*H$_2$CO), 16.5 (C-6).

HR-ESI-QTof (positive mode) *m*/*z*: calcd for $C_{116}H_{128}N_{26}O_{40}$ $[M+2H]^{2+}$ 1262.4385, found 1262.4361.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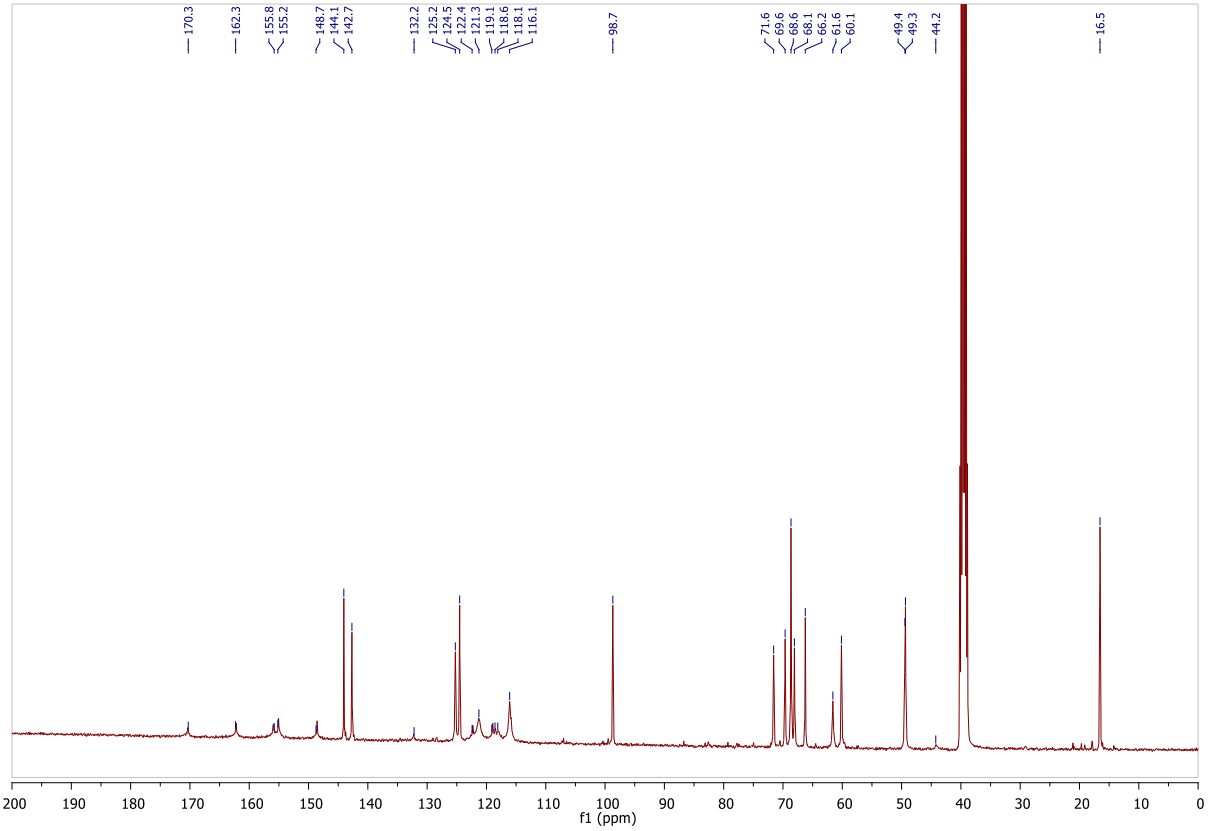
f1 (ppm)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f1 (ppm)

Isothermal titration microcalorimetry (ITC)

Recombinant lyophilized LecA was dissolved in buffer (20 mM TRIS-HCl, 100 μM $CaCl_2$, 100 mM NaCl, pH 7.5) and degassed. Protein concentration (100 μM) was checked by measurement of optical density by using a theoretical molar extinction coefficient of 28000. Glycoclusters were dissolved directly into the same buffer, degassed, and placed in the injection syringe (concentrations: 240 and 360 μM). ITC was performed using a VP-ITC MicroCalorimeter from MicroCal Incorporated. LecA was placed into the 1.4478 mL sample cell, at 25°C. Titration was performed with 10 μL injections of carbohydrate ligands every 300 s. Data were fitted using the "one-site model" using MicroCal Origin 7 software according to standard procedures. Fitted data yielded the stoichiometry (n), the association constant (K_a), and the enthalpy of binding (ΔH). Other thermodynamic parameters (i.e., changes in free energy ΔG and entropy ΔS) were calculated from the equation $\Delta G = \Delta H - T\Delta S = -RT\ln K_a$ in which T is the absolute temperature and R = 8.314 $J.mol^{-1}.K^{-1}$. Two or three independent titrations were performed for each ligand tested.

Recombinant lyophilized LecB was dissolved in buffer (20 mM TRIS-HCl, 100 μM $CaCl_2$, 100 mM NaCl, pH 7.5) and degassed. Protein concentration (50 μM) was checked by measurement of optical density by using a theoretical molar extinction coefficient of 28000. Glycoclusters were dissolved directly into the same buffer, degassed, and placed in the injection syringe (concentration: 120 μM). ITC was performed using a VP-ITC MicroCalorimeter from MicroCal Incorporated. LecB was placed into the 1.4478 mL sample cell, at 25°C. Titration was performed with 10 μL injections of carbohydrate ligands every 300 s. Data were fitted using the "one-site model" using MicroCal Origin 7 software according to standard procedures. Fitted data yielded the stoichiometry (n), the association constant (K_a), and the enthalpy of binding (ΔH). Other thermodynamic parameters (i.e., changes in free energy ΔG and entropy ΔS) were calculated from the equation $\Delta G = \Delta H - T\Delta S = -RT\ln K_a$ in which T is the absolute temperature and R = 8.314 $J.mol^{-1}.K^{-1}$. Two or three independent titrations were performed for each ligand tested.

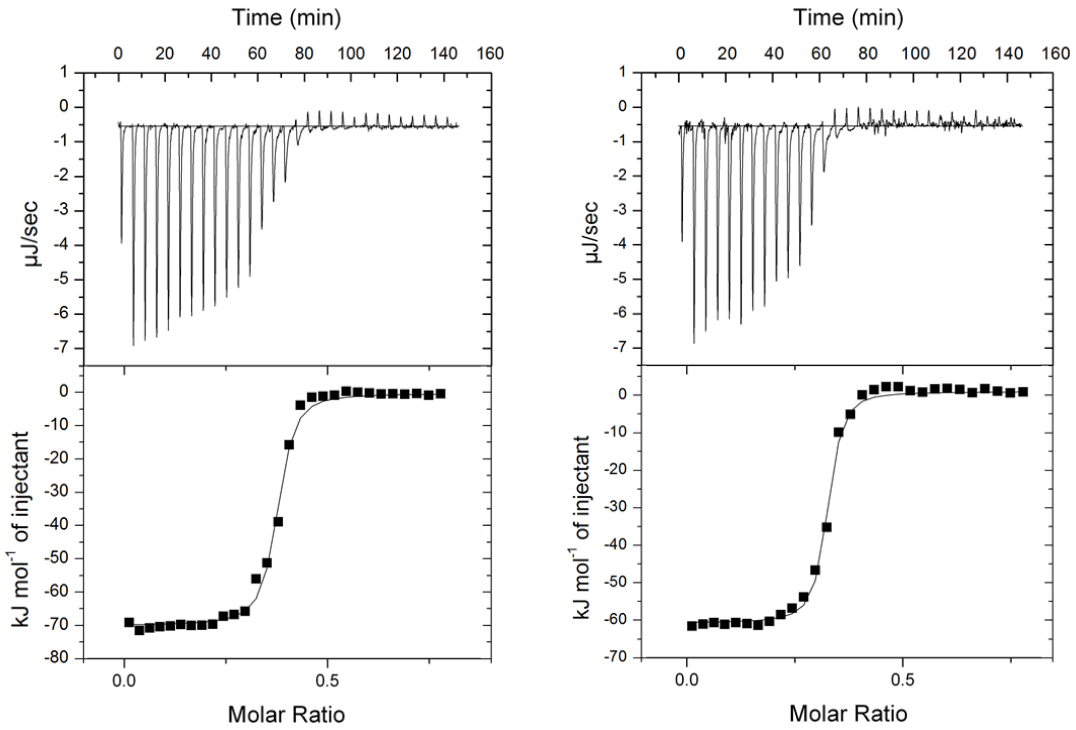

Figure S1. Raw ITC data (top) obtained by injections of glycocluster **11b**: PDI-$(EG_3\text{-}Gal)_4$ (0.36 mM) to a solution of LecA (0.1 mM) and the corresponding integrated titration curve (bottom)

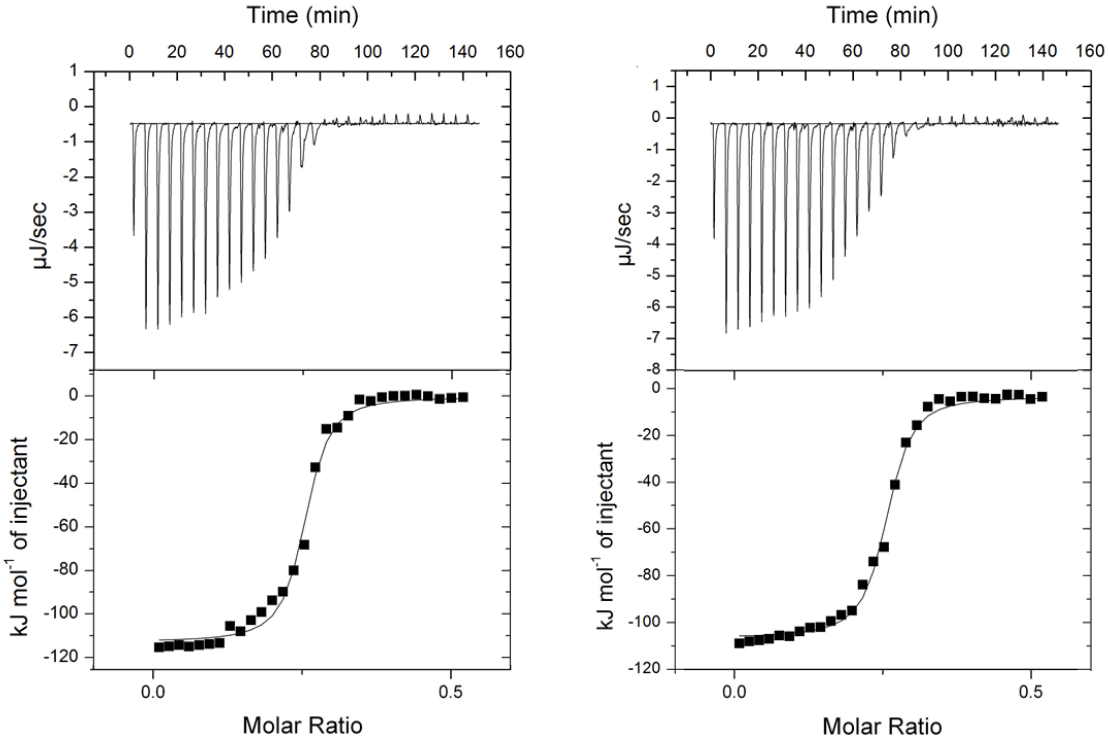

Figure S2. Raw ITC data (top) obtained by injections of glycocluster **9b**: PDI-$(EG_3\text{-}Gal)_6$ (0.24 mM) to a solution of LecA (0.1 mM) and the corresponding integrated titration curve (bottom)

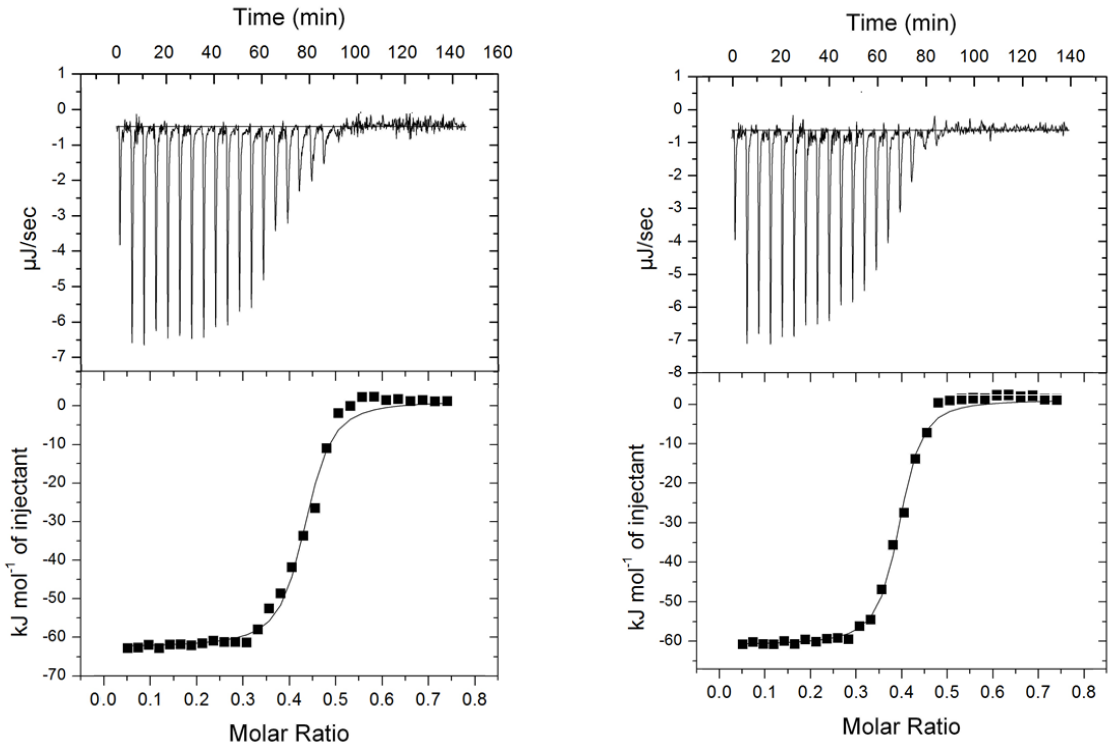

Figure S3. Raw ITC data (top) obtained by injections of glycocluster **11e**: PDI-(TzEgTz-Gal)$_4$ (0.36 mM) to a solution of LecA (0.1 mM) and the corresponding integrated titration curve (bottom)

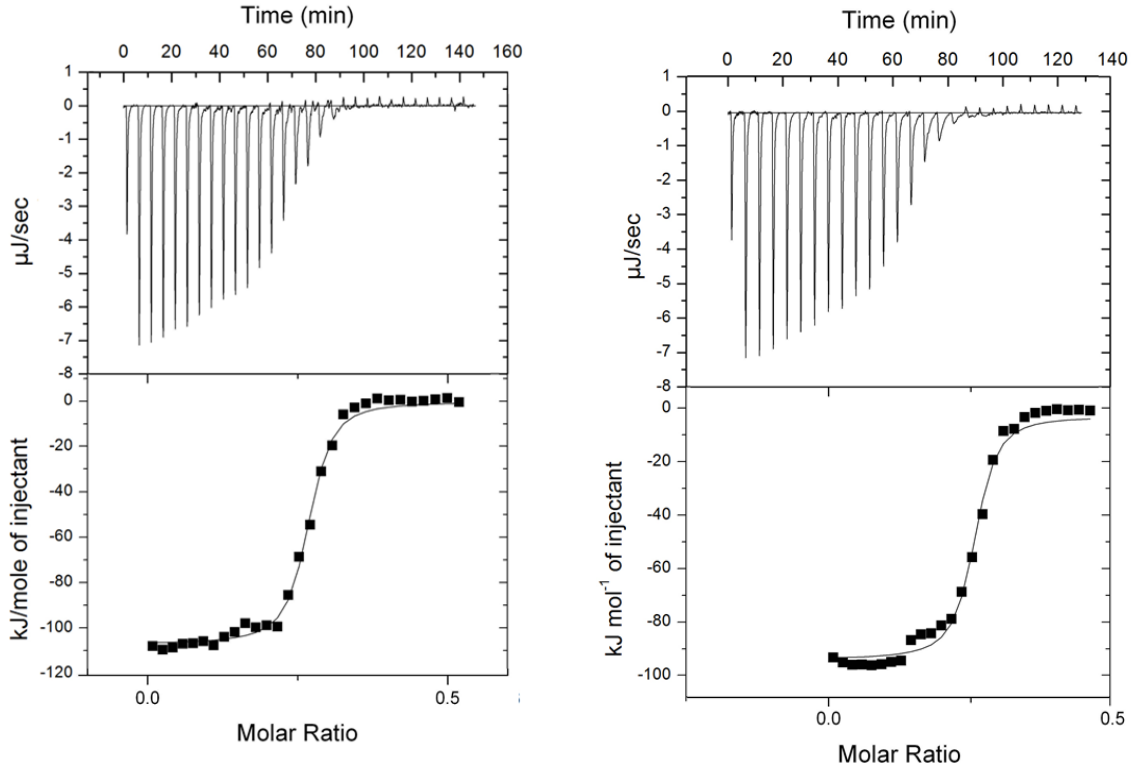

Figure S4. Raw ITC data (top) obtained by injections of glycocluster **9e**: PDI-(TzEgTz-Gal)$_6$ (0.24 mM) to a solution of LecA (0.1 mM) and the corresponding integrated titration curve (bottom)

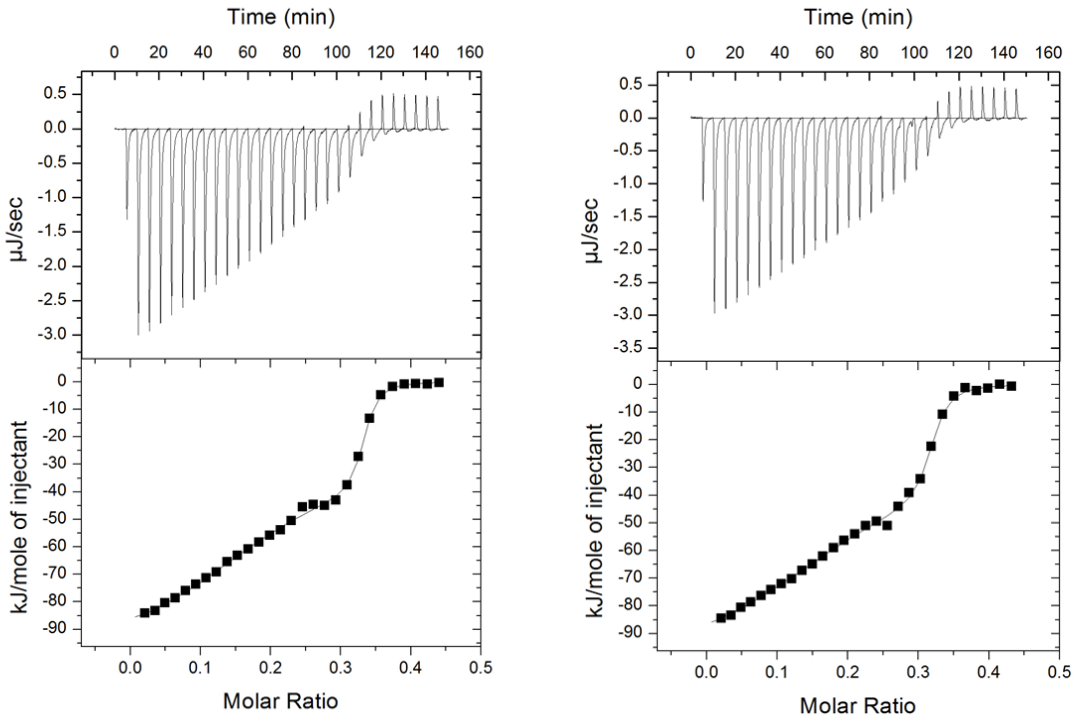

Figure S5. Raw ITC data (top) obtained by injections of glycocluster **11d:** PDI-$(EG_3\text{-}Fuc)_4$ (0.2 mM) to a solution of LecB (0.1 mM) and the corresponding integrated titration curve (bottom)

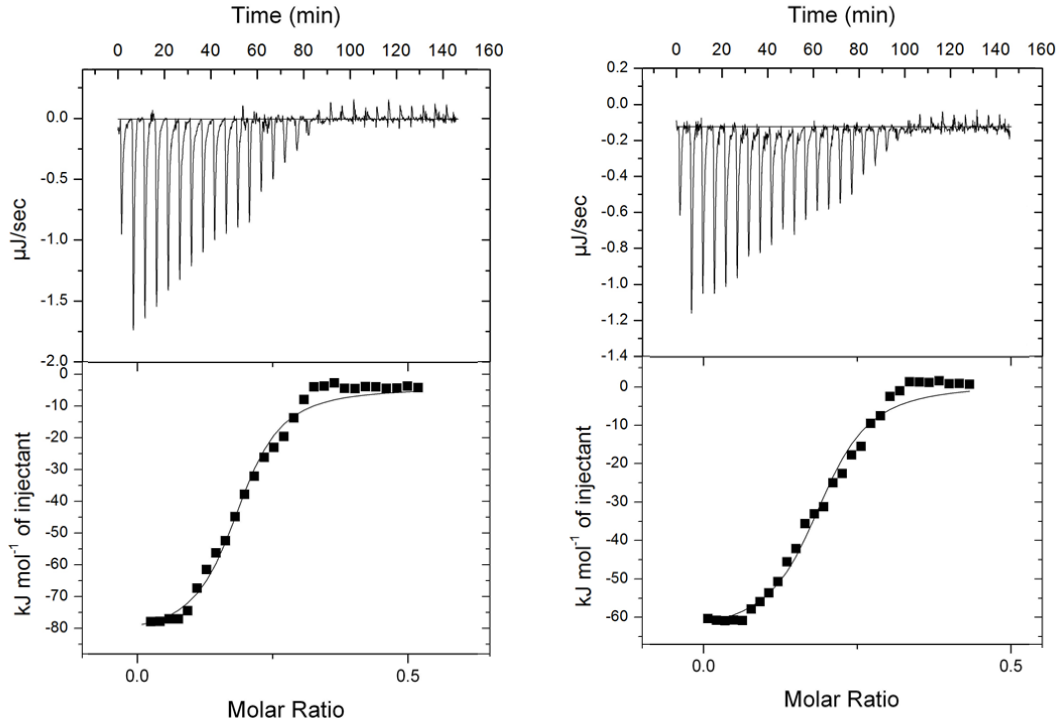

Figure S6. Raw ITC data (top) obtained by injections of glycocluster **9d**: PDI-$(EG_3\text{-}Fuc)_6$ (0.12 mM for the left panel and 0.1 mM for the right panel) to a solution of LecB (0.05 mM) and the corresponding integrated titration curve (bottom)

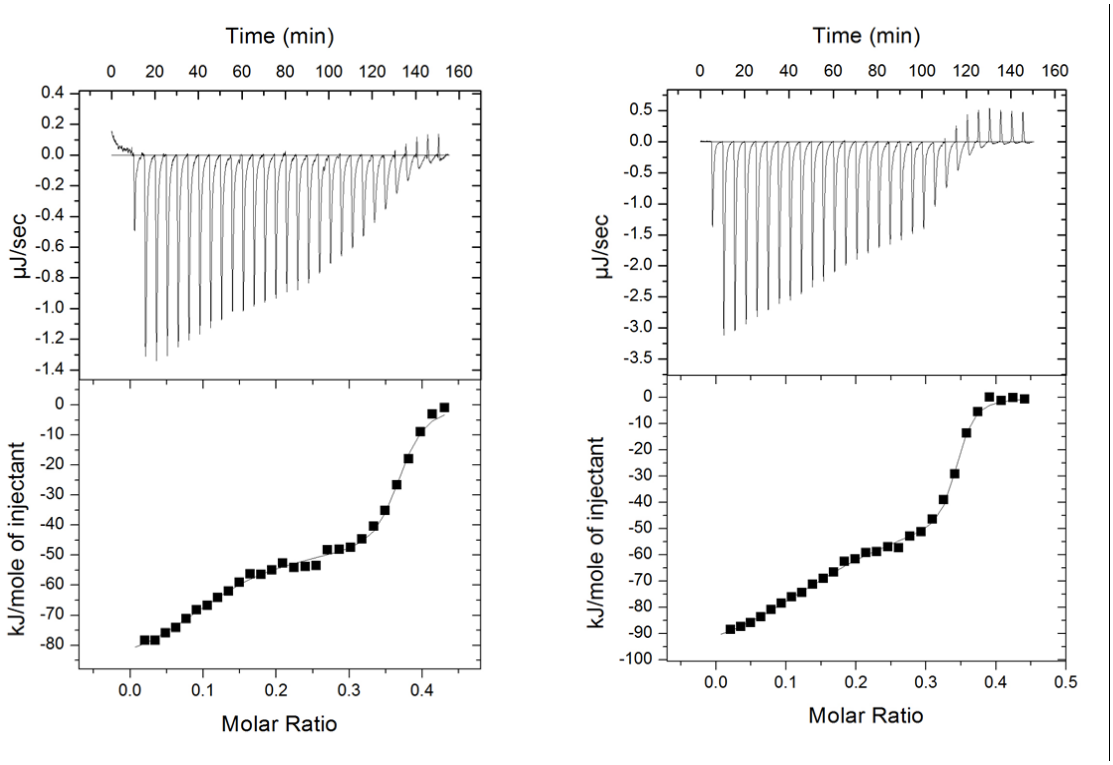

Figure S7. Raw ITC data (top) obtained by injections of glycocluster **11f:** PDI-(TzEgTz-Fuc)$_4$ (0.2 mM) to a solution of LecB (0.1 mM) and the corresponding integrated titration curve (bottom)

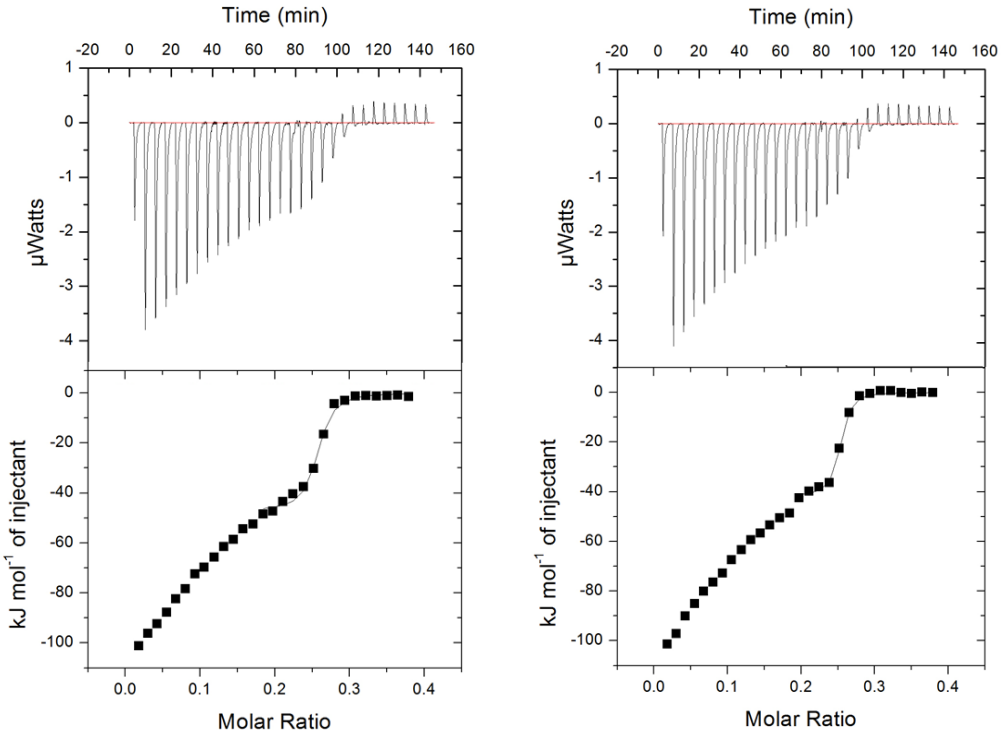

Figure S8. Raw ITC data (top) obtained by injections of glycocluster **9f:** PDI-(TzEgTz-Fuc)$_6$ (0.2 mM) to a solution of LecB (0.114 mM) and the corresponding integrated titration curve (bottom)

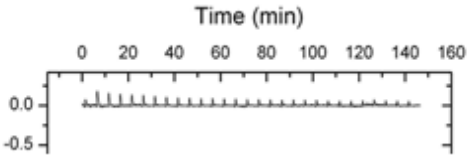

Figure S9. Raw ITC data obtained by injections of glycocluster **11a**: PDI-$(EG_3\text{-}Glc)_4$ (0.1 mM) to a solution of LecA (0.05 mM)

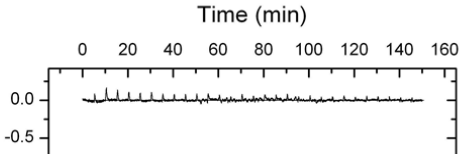

Figure S10. Raw ITC data obtained by injections of glycocluster **11a**: PDI-$(EG_3\text{-}Glc)_4$ (0.1 mM) to a solution of LecB (0.05 mM)

Fluorescence spectroscopy measurements

Preparation of stock solution. PDIs were suspended in ultrapure water at an initial concentration of 20 mM.

UV-vis for PDIs. In a typical UV-vis assay, a **PDI** (with a final concentration of 50 μM) was dissolved in different solvents (DMF, DMSO, EtOH, MeOH or H_2O), followed by an incubation for 30 s. Then, the UV-vis spectrum was measured on a Varian Cary 500 spectrophotometer.

Fluorescence spectroscopy for PDIs. In a typical fluorescence assay, a **PDI** (with a final concentration of 12.5 μM) was dissolved in different solvents (DMF, DMSO, EtOH, MeOH or H_2O), followed by an incubation for 30 s. Then, the fluorescence spectrum was measured on a Varian Cary Eclipse fluorescence spectrophotometer with an excitation wavelength of 410 nm.

Epithelial cell adhesion assay

Adherent A549 cells were cultured in cell culture flasks containing Iscove' s modified Dulbecco' s medium supplemented with 10% (v/v) fetal calf serum (Dustcher, Vilmorin, France) and 1% penicillin/streptomycin. Cells were incubated at 37 °C with a 5% (v/v) CO_2 until they formed a confluent monolayer. Cells were seeded in 96-well cell culture plates containing IMDM (10^5 cells/well) and incubated at 37 °C. *Pseudomonas aeruginosa* PAO1 strain was used as reference strain. A single colony was inoculated into Lysogeny Broth Lennox media (LB) and grown overnight at 37 °C with orbital shaking. Thirty minutes before the infection, cells were washed twice with PBS and IMDM with or without PDI-based glycoclusters (0 or 10 mM) was added to the wells. Bacteria calibrated at a density of 10^8 CFU/mL were incubated with the cells at a multiplicity of infection of 10 bacteria for a cell (MOI 10) for 1 h at 37°C with a 5% (v/v) CO_2. Nonadherent bacteria were removed by washing five times with PBS. Cells were lysed by incubation during 30 min at 37 °C with PBS 1% triton-X100 (v/v). Live CFU were enumerated after a 24 h incubation at 37 °C, after serial dilution and plating on BCP agar plates.

Fluorescent Probes and Confocal Laser Scanning Microscopy (CLSM)

A549 alveolar epithelial cells were cultured in IMDM medium over 48 h at 37 °C with penicillin/streptomycin 1X. An amount of 50 000 cells were deposited per well in 8 well culture slide (Falcon). Macrophages were then infected with *P. aeruginosa* expressing green fluorescent protein (GFP) at a multiplicity of infection of 20 for a cell (MOI 20) during 3 h. Simultaneously, PDI-based glycoclusters were added to the medium (20 mM). After incubation at 37 °C, wells were washed five times with PBS. Then macrophage nuclei were stained with 4′,6′-diamidino-2-phenylindole (DAPI) (1000×). Cells were fixated with 4% formaldehyde. Culture slides were read with an LSM 710 confocal microscope at 120× magnification (Carl Zeiss, Switzerland).