SUPPORTING INFORMATION

Photoresponsive Capture and Release of Lectins in Multilamellar Complexes

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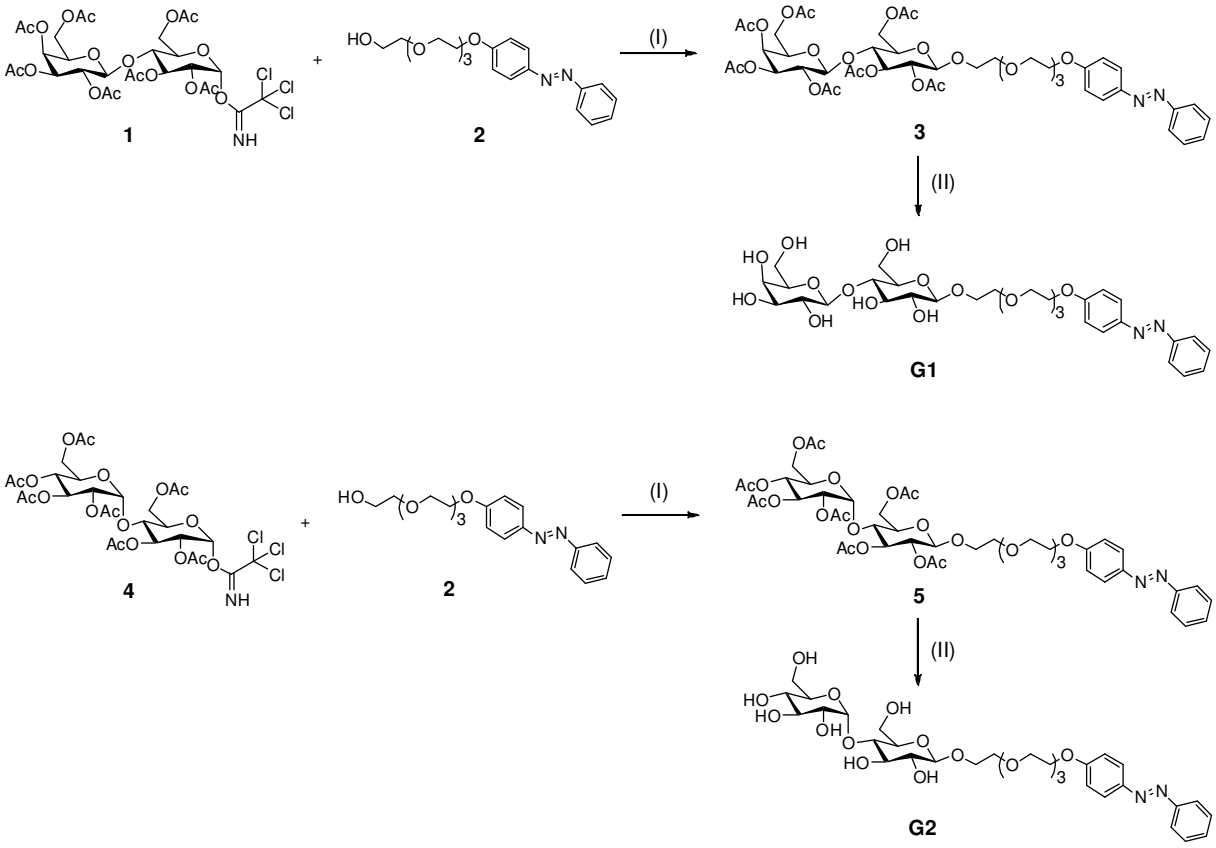
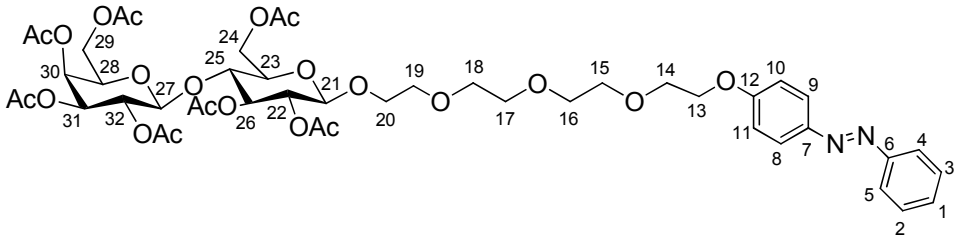
Synthesis

The synthesis of compounds **1** (ref S1), **2** (ref S2) and **4** (ref S1) have been reported elsewhere. The synthesis of conjugates **G1** and **G2** involves a Lewis acid catalyzed coupling of the peracetylated trichloroacetimidates of lactose and maltose. Deprotection with NaOMe in methanol provides the desired products **G1** and **G2**.



Scheme S1. Synthesis of conjugates **G1** and **G2**: (I) TMSOTf, MS 4 Å, CH_2Cl_2, (II) NaOMe, and MeOH.

2‘,3‘,4‘,6‘-tetra-O-acetyl-β-D-galactopyranosyl-(1→4)-2-[2-(2-phenyldiazenyl)phenoxy ethoxy)-ethoxy]ethanol-2,3,4-tri-O-acetyl-β-D-glucopyranoside (3)



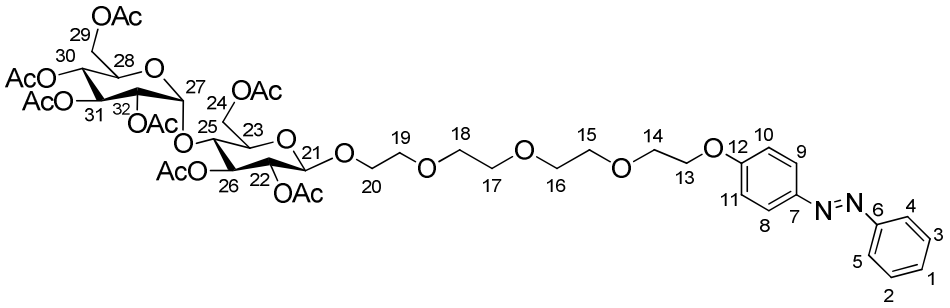
Compound **1** (0.5 g, 0.64 mmol) and **2** (0.24 g, 0.64 mmol) were dissolved in 50 mL of CH_2Cl_2. After that 40 mg molecular sieves with a pore size of 4 Å were added and the resulting solution was cooled down to -25°C. After stirring for 10 min TMSOTf (0.06 mL, 0.074 g, 0.33 mmol) was added and continued stirring for additional 2h. Subsequently the solution was filtered, extracted twice with saturated $NaHCO_3$ and once with brine solution. The organic layer was dried over $MgSO_4$and after evaporating of the solvent an orange viscous oil was obtained which was purified via column chromatography eluting with EtOAc/pentane 2:1 (R_f = 0.29). Yield: 252 mg (40 %, 0.25 mmol).

ESI-HRMS (m/z): Calculated for $[C_{46}H_{60}N_2O_{22}Na]^+$: 1015.3541; Found: 1015.3534.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.90 – 7.83 (m, 4H, 4,5,8,9-H), 7.50 – 7.38 (m, 3H, 1, 2, 3-H), 7.02-6.99 (m, 2H, 10, 11-H), 5.31 (d, *J* = 2.8 Hz, 1H, 21-H), 5.20 – 5.05 (m, 2H, 25, 30-H), 4.95-4.85 (ddd, *J* = 17.6, 10.0, 5.7 Hz, 2H, 26, 31-H), 4.55-4.44 (dd, *J* = 25.9, 8.0 Hz, 3H), 3.92 – 3.82 (m, 4H), 3.92 – 3.82 (m, 3H), 3.79-3.55 (d, *J* = 70.3 Hz, 15H, 13, 14, 15, 16, 17, 18, 19, 20-H), 2.12 (s, 3H, OAc-H), 2.09 (s, 3H, OAc-H), 2.04-2.01 (m, 2.6 Hz, 12H, OAc-H), 1.94 (s, 3H, OAC-H).

^{13}C NMR (75 MHz, $CDCl_3$, 298K): δ = 170.44, 170.40, 170.21, 170.11, 169.83, 169.73, 169.14, 161.34, 152.77, 147.10, 130.46, 129.10, 124.77, 122.61, 114.90, 101.14, 100.67, 76.36, 72.89, 72.65, 71.70, 71.04, 70.93, 70.73, 70.69, 70.34, 69.67, 69.14, 67.79, 66.65, 62.08, 60.84, 20.93, 20.88, 20.77, 20.69, 20.57.

2‘,3‘,4‘,6‘-tetra-O-acetyl-α-D-glucopyranosyl-(1→4)-2-[2-(2-phenyldiazenyl)phenoxy ethoxy)-ethoxy]ethanol-2,3,4-tri-O-acetyl-β-D-glucopyranoside (5)



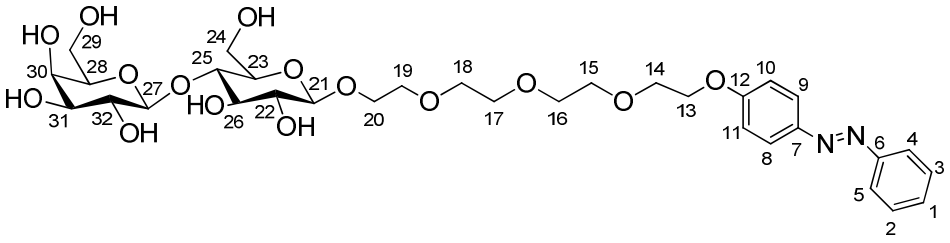
Compound **4** (0.5 g, 0.64 mmol) and **2** (0.24 g, 0.64 mmol) were dissolved in 50 mL of CH_2Cl_2. After that 40 mg molecular sieves with a pore size of 4 Å were added and the resulting solution was cooled down to -25°C. After stirring for 10 min TMSOTf (0.07 mL, 0.086 g, 0.39 mmol) was added and stirred for additional 2h. Subsequently the solution was filtered, extracted twice with saturated $NaHCO_3$and once with water. The organic layer was dried over $MgSO_4$ and after evaporating of the solvent an orange viscous oil was obtained which was purified via column chromatography eluting with EtOAc/pentane 2:1 (Rf = 0.29). Yield: 271 mg (42 %, 0.27 mmol).

ESI-HRMS (m/z): Calculated for $[C_{46}H_{60}N_2O_{22}Na]^+$: 1015.3541; Found: 1015.3549.

^{1}H NMR (300 MHz, $CDCl_3$, 298K): δ = 7.94 – 7.84 (m, 4H, 4,5,8,9-H), 7.54 – 7.37 (m, 3H, 1, 2, 3-H), 7.08 – 6.97 (m, 2H, 10, 11-H), 5.43 (d, J = 3.84 Hz, 1H, 27-H), 5.24 (t, *J* = 9.1 Hz, 1H, 32-H), 5.04 (t, *J* = 9.8 Hz, 1H, 22-H), 4.83 (ddd, *J* = 11.7, 9.2, 6.0 Hz, 2H, 26-H), 4.60 (d, *J* = 7.9 Hz, 1H, 25-H), 4.47 (dd, *J* = 12.1, 2.6 Hz, 1H, 30-H), 4.29 – 4.15 (m, 4H), 4.00 – 3.82 (m, 4H), 3.78 – 3.53 (m, 15H, 13, 14, 15, 16, 17, 18, 19, 20-H), 2.13 (s, 3H, OAc-H), 2.09 (s, 3H,OAc-H), 2.03 (s, 3H), 2.00 (m, 12H, OAc-H).

^{13}C NMR (75 MHz, $CDCl_3$, 298K): δ = 170.68, 170.62, 170.36, 170.09, 169.82, 169.56, 161.39, 152.83, 152.61, 147.17, 130.52, 129.10, 124.84, 122.67, 114.94, 100.45, 95.64, 75.53, 72.78, 72.19, 71.00, 70.77, 70.36, 70.09, 69.73, 69.44, 69.25, 68.58, 68.09, 67.84, 62.92, 61.59, 21.05, 20.99, 20.82, 20.79, 20.72

α-D-galactopyranosyl-(1→4)-2-[2-(2-phenyldiazenyl)phenoxyethoxy)-ethoxy]ethanol-β-D-glucopyranoside (G1)



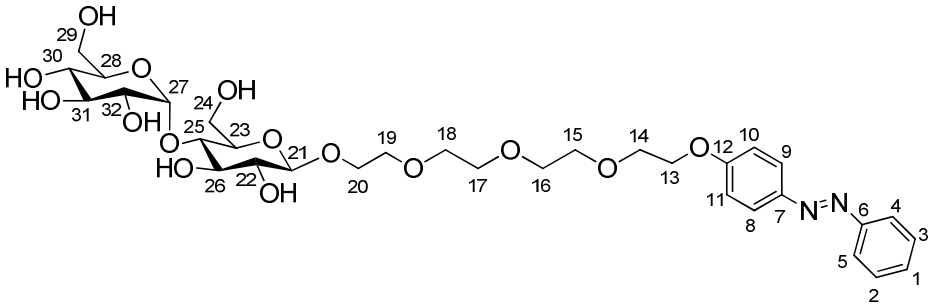
Compound **5** (252 mg 0.25 mmol) was dissolved in 10 mL of dry methanol and cooled to 0°C after 10 min a catalytical amount (10 mg) of NaOMe was added and the resulting solution was stirred over night. Afterwards the solution was neutralized with dilute acetic acid and the solvent was evaporated. The crude product was purified via column chromatography eluting with CH_2Cl_2/ MeOH 7:3 (Rf = 0.4). The product was obtained as an orange solid and dried under high vacuum. Yield: 112 mg (65 %, 0.16 mmol).

ESI-HRMS (m/z): Calculated for $[C_{32}H_{46}N_2O_{15}Na]^+$: 721.2796; Found: 721.2787.

^{1}H NMR (600 MHz, MeOD, 298K): δ = 7.93 – 7.88 (m, 2H, 4, 5-H), 7.87 – 7.84 (m, 2H, 8, 9-H), 7.49 (m, 3H, 1, 2, 3-H), 7.14 – 7.08 (m, 2H, 10, 11-H), 4.34 (dd, *J* = 11.0, 7.8 Hz, 2H, 21, 27-H), 4.24 (dd, *J* = 5.4, 3.9 Hz, 2H), 4.03 – 3.97 (m, 1H), 3.94 – 3.87 (m, 3H), 3.85 (d, *J* = 4.2 Hz, 1H), 3.82 (dd, *J* = 6.9, 3.8 Hz, 1H), 3.79 – 3.76 (m, 1H), 3.75 – 3.62 (m, 13H, 13, 14, 15, 16, 17, 18, 19-H), 3.61 – 3.52 (m, 4H, 24, 29-H), 3.48 (dd, *J* = 9.7, 3.3 Hz, 1H, 23-H), 3.43 – 3.38 (m, 1H, 28-H).

^{13}C NMR (151 MHz, MeOD): δ = 162.94, 154.06, 148.31, 131.62, 130.18, 125.74, 123.49, 116.06, 105.12, 103.99, 80.73, 77.04, 76.48, 76.23, 74.79, 74.69, 72.51, 71.65, 71.40, 71.34, 71.25, 70.67, 70.27, 69.57, 69.00, 62.48, 61.87.

α-D-glucopyranosyl-(1→4)-2-[2-(2-phenyldiazenyl)phenoxyethoxy)-ethoxy]ethanol-β-D-glucopyranoside (G2)



Compound **3** (271 mg, 0.27 mmol) was dissolved in 10 mL of dry methanol and cooled to 0°C after 10 min a catalytical amount (10 mg) of NaOMe was added and the resulting solution was stirred over night. Afterwards the solution was neutralized with dilute acetic acid and the solvent was evaporated. The crude product was purified via column chromatography eluting with CH_2Cl_2/ MeOH 7:3 (Rf = 0.3). The product was obtained as an orange solid and dried under high vacuum.Yield:129 mg (68 %, , 0.18 mmol).

ESI-HRMS (m/z): Calculated for $[C_{32}H_{46}N_2O_{15}Na]^+$: 721.2796; Found: 721.2784.

^{1}H NMR (600 MHz, MeOD, 298K): δ = 7.95 – 7.91 (m, 2H, 4, 5-H), 7.89 – 7.84 (m, 2H,8,9-H), 7.58 – 7.43 (m, 3H, 1, 2, 3-H), 7.16 – 7.06 (m, 2H, 10,11-H), 5.16 (d, *J* = 3.9 Hz, 1H, 21-H), 4.32 (d, *J* = 7.8 Hz, 1H, 27-H), 4.28 – 4.24 (m, 2H, 22, 32-H), 4.05 – 3.97 (m, 1H), 3.94 – 3.88 (m, 2H), 3.85 – 3.79 (m, 2H), 3.77 – 3.59 (m, 16H, 13, 14, 15 ,16 , 17, 18, 19, 20-H), 3.54 (t, *J* = 9.3 Hz, 1H), 3.46 (dd, *J* = 9.7, 3.8 Hz, 1H), 3.37 (ddd, *J* = 9.9, 4.7, 2.2 Hz, 1H, 28-H), 3.30-3.24 (m, 2H, 23, 25-H).

^{13}C NMR (151 MHz, MeOD, 298K): δ = 162.98, 154.08, 148.32, 131.62, 130.18, 125.74, 123.49, 116.05, 104.21, 102.96, 81.35, 77.65, 76.61, 75.06, 74.77, 74.62, 74.14, 71.70, 71.50, 71.47, 71.40, 71.33, 70.70, 69.62, 69.02, 62.73, 62.12.

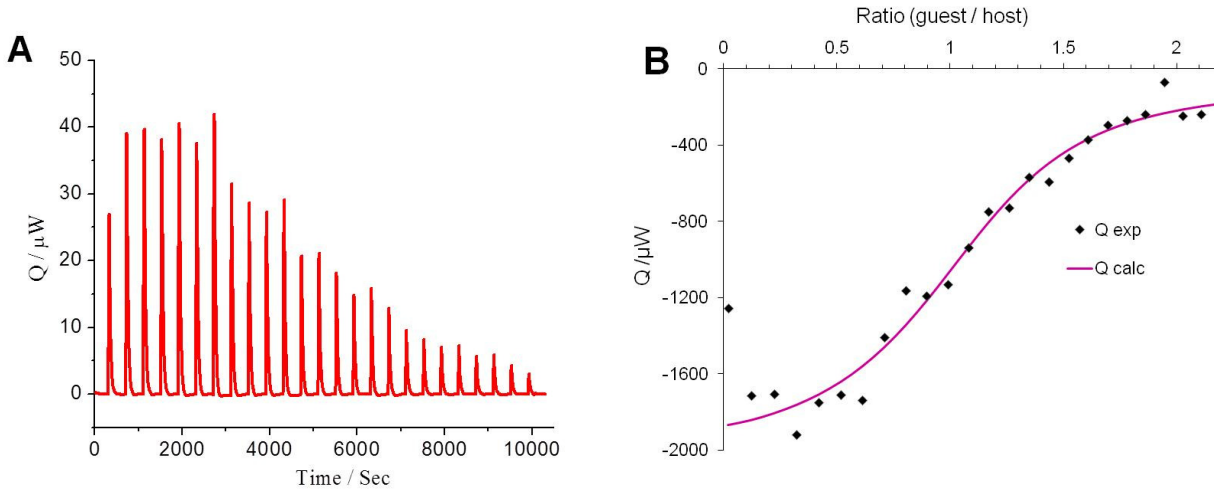


Figure S1. ITC data corresponding to the host guest interaction of α-CD with *trans*-**G1**. A solution of α-CD (10 mM in 20 mM HEPES buffer) was titrated into a solution of *trans*-**G1** (1 mM in 20 mM HEPES buffer). A) Injection peaks (raw data vs. time). B) Integration of the injection peaks (heat vs. guest/host ratio.)

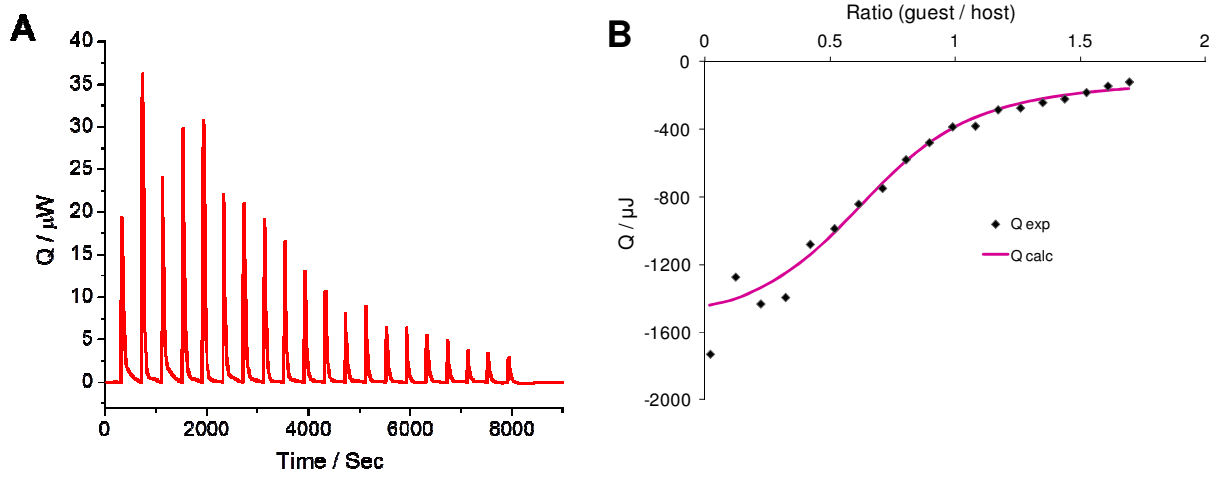


Figure S2. ITC data corresponding to the host guest interaction of α-CD with *trans*-**G2**. A solution of α-CD (10 mM in 20 mM HEPES buffer) was titrated into a solution of *trans*-**G2** (1 mM in 20 mM HEPES buffer). A) Injection peaks (raw data vs. time) and B) integration of the injection peaks (heat vs. guest/host ratio.)

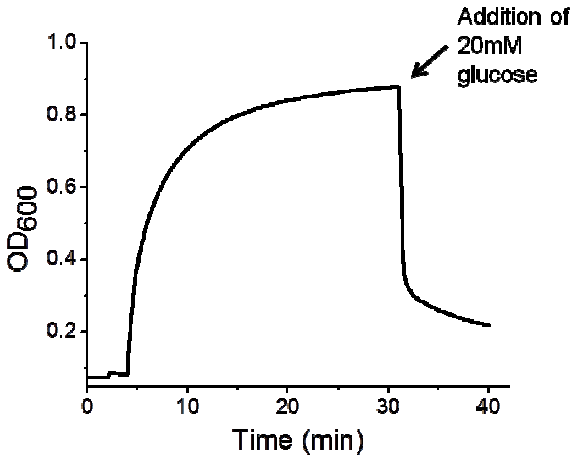


Figure S3. Formation and disruption of a ternary complex of vesicles of α-CD, conjugate *trans*-**G2** and Con A. Time dependent optical density measurement at λ = 600 nm.

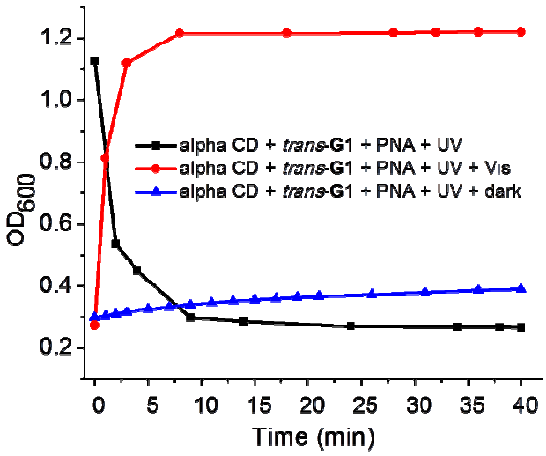


Figure S4. Time-dependent increase and decrease of OD600 under irradiation with UV light (350 nm), visible light (455 nm) and in the dark (following UV light irradiation).

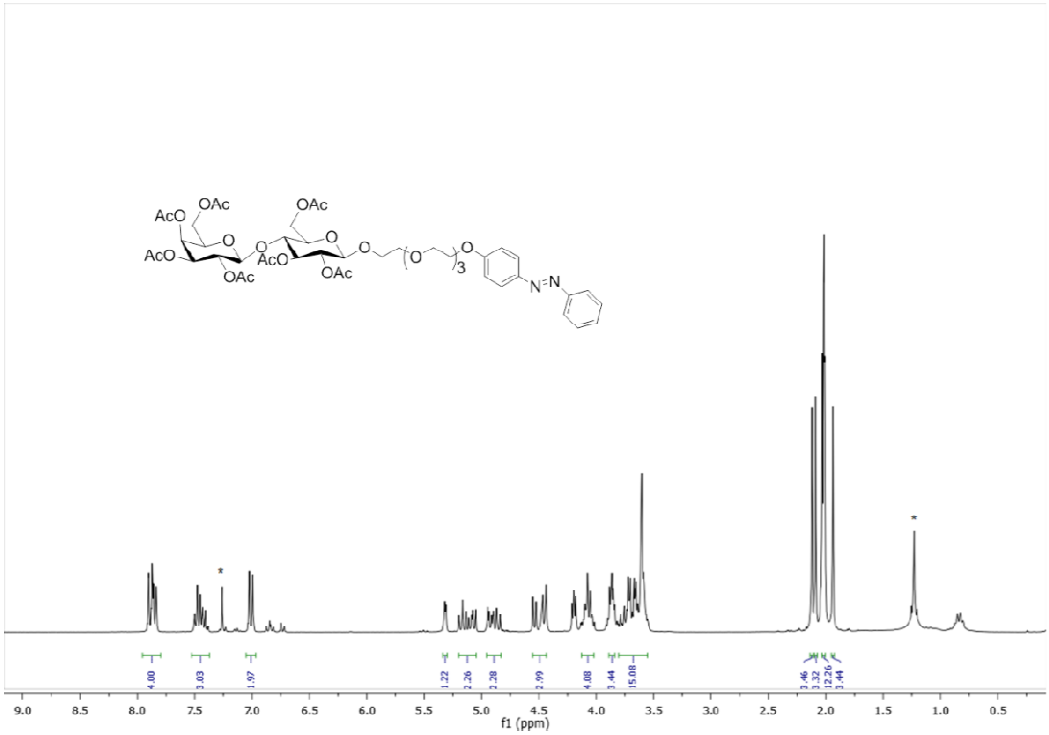


Figure S4. ^{1}H-NMR of compound **3** in $CDCl_3$ at 298 K.

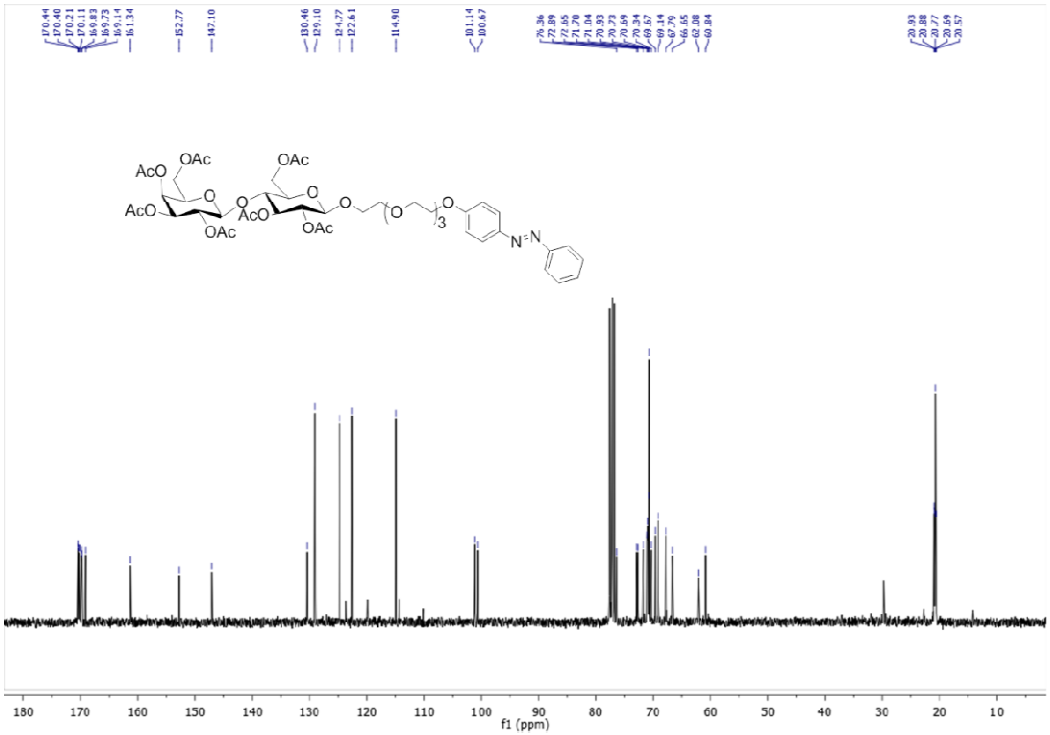


Figure S5. ^{13}C-NMR of compound **3** in $CDCl_3$ at 298 K.

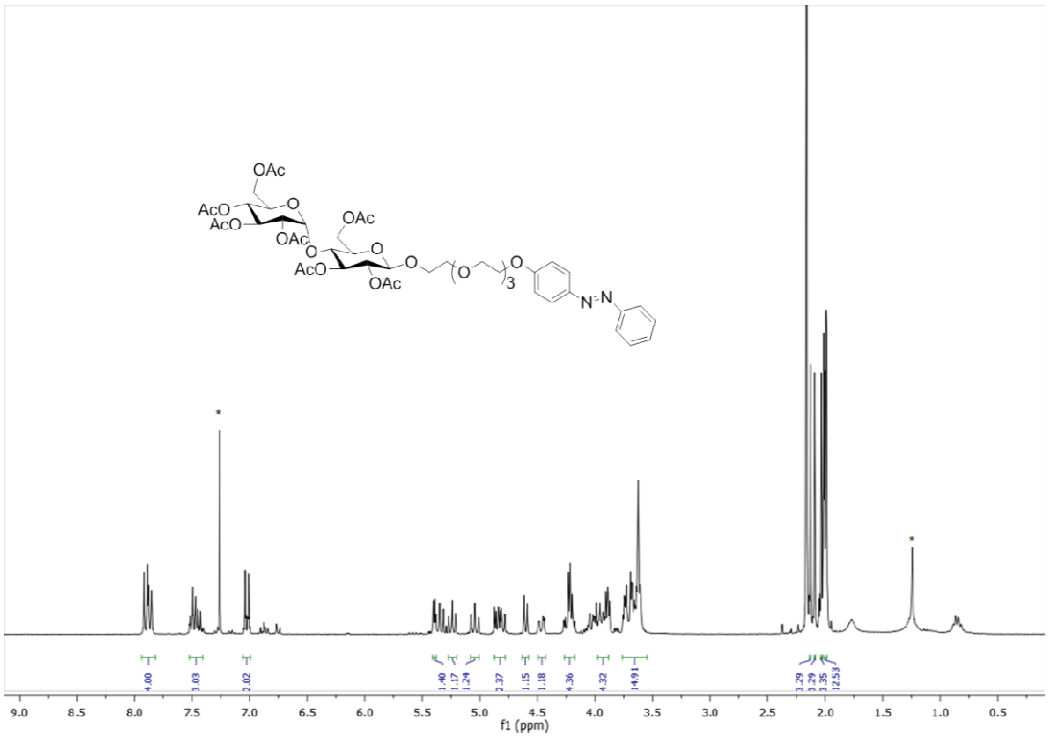


Figure S6. ^{1}H-NMR of compound **5** in $CDCl_3$ at 298 K.

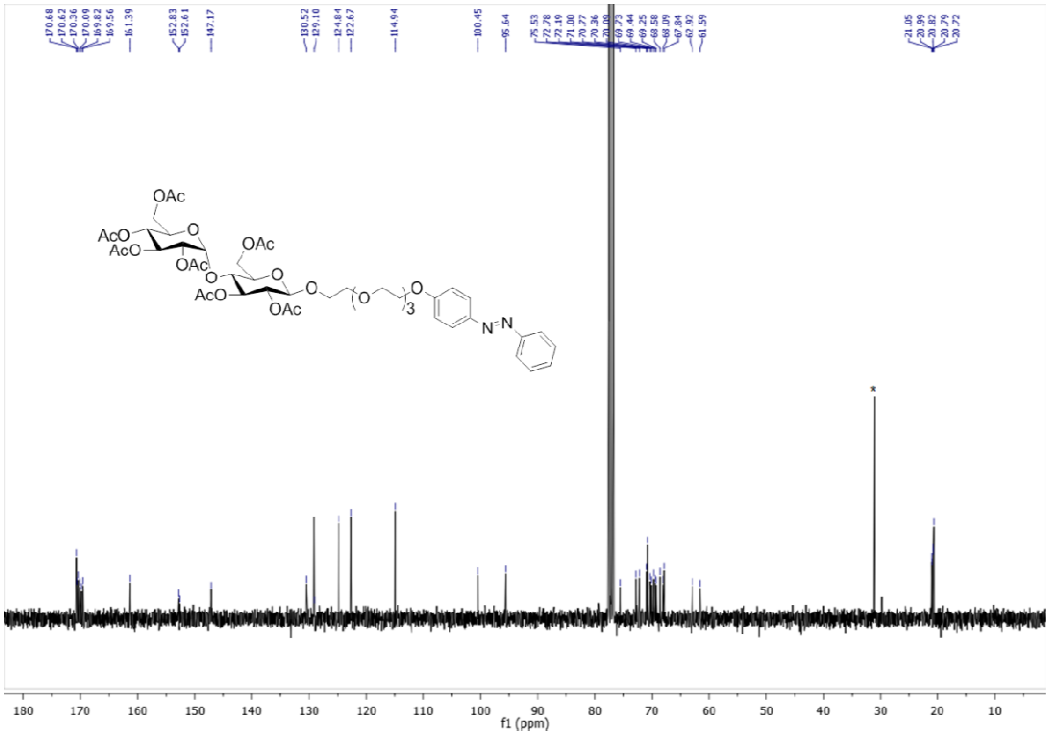


Figure S7. ^{13}C-NMR of compound **5** in $CDCl_3$ at 298 K

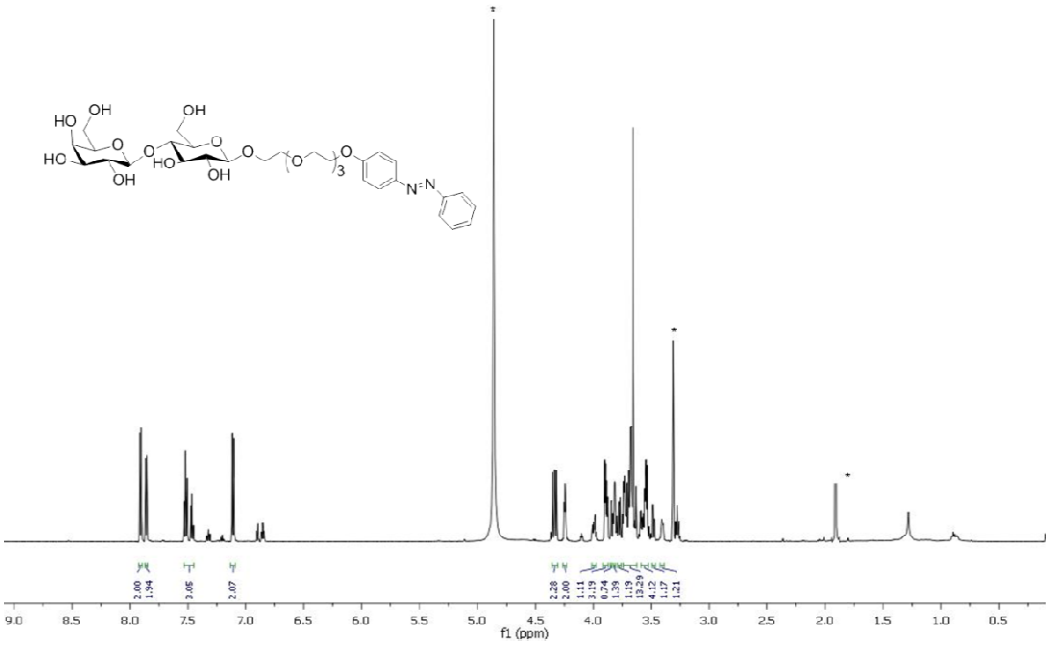


Figure S8. [1]H-NMR of compound **G1** in MeOD at 298 K.

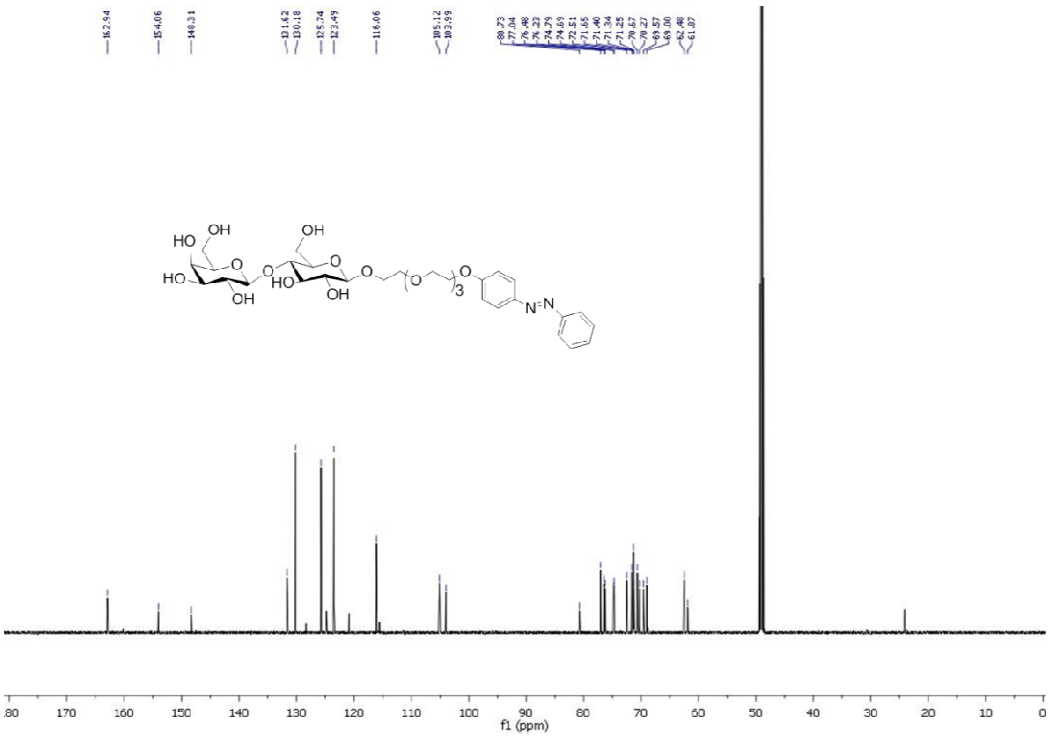


Figure S9. [13]C-NMR of compound **G1** in MeOD at 298 K.

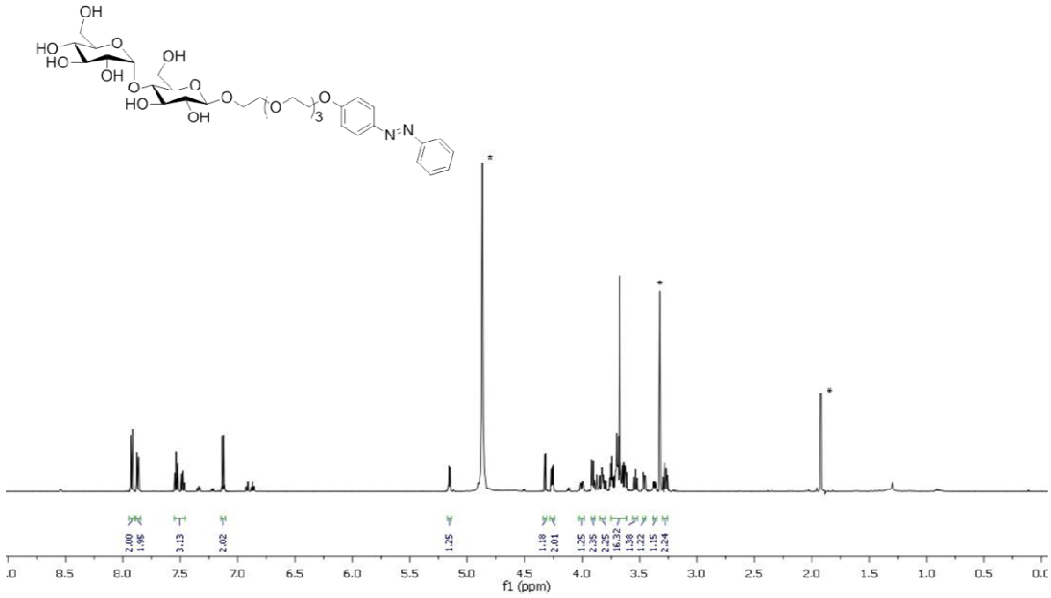


Figure S10. [1]H-NMR of compound **G2** in MeOD at 298 K.

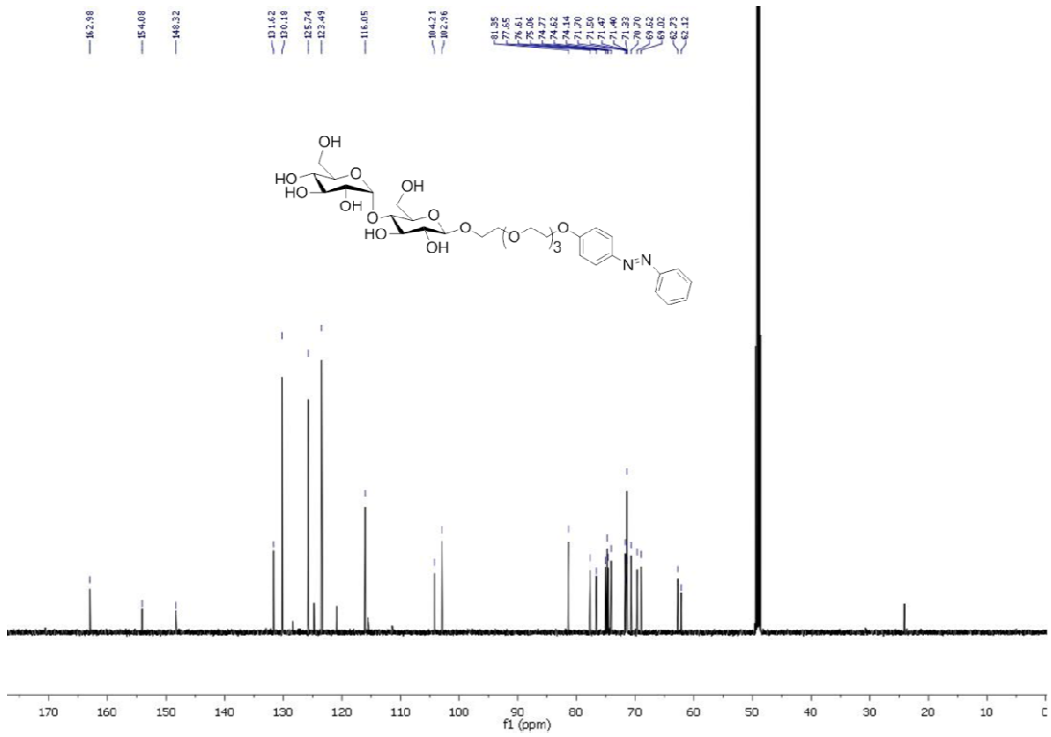


Figure S11. [13]C-NMR of compound **G2** in MeOD at 298 K.

References:

[S1] Cheng, H.; Cao, X.; Xian, M.; Fang, L.; Cai, T. B.; Ji, J.J.; Tunac, J.B.; Sun, D.; Wang, P.G. *J. Med. Chem*. **2005**, *48*, 645-652.

[S2] Nalluri, S. K. M.; Voskuhl, J.; Bultema, J. L.; Boekema, E. J.; Ravoo, B. J. *Angew. Chem. Int. Ed.* **2011,** 50, 9747-9751.