Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supporting Information

Switching first contact: Photocontrol of *E. coli* adhesion to human cells

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1. Materials and Methods

General methods

Analytical thin layer chromatography (TLC) was performed on silica gel plates (GF 254, Merck). Visualization was achieved by UV light and/or with 10% sulfuric acid in ethanol followed by heat treatment at ~180 °C. Flash chromatography was performed on silica gel 60 (Merck, 230-400 mesh, particle size 0.040-0.063 mm) by using distilled solvents. Melting points (mp) were determined on a Büchi M-56 apparatus. Optical rotations were measured with a Perkin-Elmer 241 polarimeter (sodium D-line: 589 nm, length of cell: 1 dm) in the solvents indicated. Proton (^{1}H) nuclear magnetic resonance spectra and carbon (^{13}C) nuclear magnetic resonance spectra were recorded on a Bruker DRX-500 and AV-600 spectrometer. Chemical shifts are referenced to the residual proton of the NMR solvent. Data are presented as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, and br=broad signal), coupling constant in hertz (Hz) and, integration. Full assignment of the peaks was achieved with the aid of 2D NMR techniques (^{1}H/^{1}H COSY and ^{1}H/^{13}C HSQC. All NMR spectra of the *E*-isomers of the azobenzene derivatives were recorded after they were kept for 16 h in the dark at 40 °C. Infrared (IR) spectra were measured with a Perkin Elmer FT-IR Paragon 1000 (ATR) spectrometer and were reported in cm^{-1}. ESI mass spectra were recorded on a LCQ Classic from Thermo Finnigan and HRMS ESI spectra on an Agilent 6224 ESI-TOF. UV-vis absorption spectra were performed on Perkin-Elmer Lambda-241 at a temperature of 20 °C ± 1 °C.

Bacterial Culture

E. coli (strain pPKL1162) were inoculated in LB medium (10 mL) (Sigma-Aldrich, St. Louis, MO) in presence of chloramphenicol (50 mg/L) and ampicillin (100 mg/L) (both Sigma-Aldrich) and grown at 37°C overnight under constant agitation. Then, the bacteria were centrifuged and washed two times with DPBS +Ca^{2+}/Mg^{2+} (Life Technologies, Carlsbad, St. Louis, MO) and once with cell medium. Then, the bacteria were resuspended in cell medium (10 mL) and the optical density at 600 nm was determined. For the experiments under static conditions, a 1:10 or 1:20 dilution of a suspension with OD_{600}=0.1 was used. Under flow conditions, the dilution was 1:50.

Cell Culture

HMEC-1 (CDC, Atlanta, GA) were seeded in collagen coated 8-well LabTekII-slides (Nunc, Rochester, NY) or in collagen coated Luer $I^{0.8}$ channels (IBIDI, Martinsried, Germany) and grown to confluency. The cells were cultured in MDCB-131 medium with 1% glutamax, 10% FBS, hEGF (10 ng/mL) (all Life Technologies), and hydocortisone (1 µg/mL) (Sigma-Aldrich) at 37°C in 5% CO_2-atmosphere.

Fluorescence Microscopy

Confocal fluorescence images were obtained with a commercially available spinning-disk inverted microscope (Zeiss).

Software

Images were analysed using ImageJ. For data visualization and analysis, OriginPro 8G was used. Figures were prepared with Corel Draw 12.

2. Synthesis of glycoconjugates

(*E*)-*p*-[*p'*-(Hydroxy)]phenylazophenyl α-D-mannopyranoside (3)[1] was obtained by employing a new procedure: To a solution of *p*-aminophenyl α-D-mannopyranoside[2] (**1**, 1.07 g, 3.94 mmol) in water (11 mL) 37% hydrochloric acid (310 µL, 3.94 mmol) was added and the reaction mixture was cooled to 0 °C. Then an ice-cold solution of sodium nitrite (272 mg, 3.94 mmol) in water (11 mL) was added dropwise at 0 °C. The reaction mixture was stirred for 2 h at 0 °C and then added dropwise to an ice cold solution of phenol (371 mg, 3.94 mmol), sodium hydroxide (158 mg, 3.94 mmol) and sodium carbonate (438 mg, 4.14 mmol) in water (11 mL). It was stirred for 2 h at 0 °C and afterwards the reaction mixture was acidified by adding hydrochloric acid. The precipitated solid was filtered off and washed with water. The crude product was recrystallised from water and methanol (4:1). The azobenzene mannoside **3** was obtained as an orange solid (737 mg, 1.98 mmol, 50%). R_f=0.09 (dichloromethane/methanol, 9:1); m.p. 259 °C; $[\alpha]_D^{23}$=+148.0 (*c*=0.6 in methanol); ^{1}H NMR (500 MHz, DMSO-d_6, 300 K): δ = 7.81-7.74 (m, 4H, Ar-H$_{ortho}$, Ar-H$_{ortho'}$), 7.25-7.22 (m, 2H, Ar-H$_{meta'}$), 6.94-6.91 (m, 2H, Ar-H$_{meta}$), 5.49 (d, $^3J_{1,2}$=1.8 Hz, 1H, H-1), 5.06 (d~br s, 1H, OH$_{C-2}$), 4.83 (d~br s, 1H, OH$_{C-4}$), 4.76 (d~br s, 1H, OH$_{C-3}$), 4.44 (t~br s, 1H, OH$_{C-6}$), 3.86 (m$_c$, 1H, H-2), 3.71-3.69 (m, 1H, H-3), 3.62-3.59 (m, 1H, H-6), 3.54-3.48 (m, 2H, H-4, H-6'), 3.41-3.37 (m, 1H, H-5) ppm; ^{13}C NMR (126 MHz, DMSO-d_6, 300 K): δ = 160.5 (C-Ar$_{para'}$), 158.1 (C-Ar$_{para}$), 147.0 (C-Ar$_{ipso}$), 145.2 (C-Ar$_{ipso'}$), 124.5 (C-Ar$_{ortho}$), 123.7 (C-Ar$_{ortho'}$), 117.1 (C-Ar$_{meta'}$), 115.9 (C-Ar$_{meta}$), 98.7 (C-1), 75.2 (C-5), 70.6 (C-3), 69.9 (C-2), 66.7 (C-4), 61.0 (C-6) ppm; IR (ATR): $\tilde{\nu}$ =3602, 3184, 2934, 1584, 1492, 1223, 1050, 953, 847 cm^{-1}; ESI-MS: *m/z* calcd for $C_{18}H_{20}N_2O_7$: 399.1 [M+Na]$^+$; found 399.2.

(*E*)-*p*-[*p'*-(Hydroxy)]phenylazophenyl β-D-glucopyranoside (4)[1] was obtained by employing a new procedure: To a solution of *p*-aminophenyl β-D-glucopyranoside[3] (**2**, 206 mg, 759 µmol) in water (5 mL) 37% hydrochloric acid (60.0 µL, 759 µmol) was added and the reaction mixture was cooled to 0 °C. Then an ice-cold solution of sodium nitrite (52.0 mg, 759 µmol) in water (5 mL) was added dropwise at 0 °C. The reaction mixture was stirred for 2 h at 0 °C and then added dropwise to an ice cold solution of phenol (71.0 mg, 759 µmol), sodium hydroxide (30.0 mg, 759 µmol) and sodium carbonate (84.0 mg, 797 µmol) in water (5 mL). It was stirred for 2 h at 0 °C and afterwards the reaction mixture was acidified by adding hydrochloric acid. The precipitated solid was filtered off and washed with water. The crude product was recrystallised from water. The azobenzene mannoside **4** was obtained as an orange solid (245 mg, 651 µmol, 86%). R_f=0.20 (dichloromethane/methanol, 9:1); m.p. 225 °C; $[\alpha]_D^{23}$=-56.0 (*c*=0.8 in methanol); ^{1}H NMR (600 MHz, MeOH-d_4, 300 K): δ = 7.83-7.77 (m, 4H, Ar-H$_{ortho}$, Ar-H$_{ortho'}$), 7.23-7.21 (m, 2H, Ar-H$_{meta'}$), 6.91-6.89 (m, 2H, Ar-H$_{meta}$), 5.03-4.99 (m, 1H, H-1), 3.92 (dd, $^2J_{6,6'}$=12.1 Hz, $^3J_{5,6}$=2.1 Hz, 1H, H-6), 3.73 (dd, $^2J_{6,6'}$=12.1 Hz, $^3J_{5,6'}$=5.7 Hz, 1H, H-6'), 3.52-3.48 (m, 3H, H-2, H-3, H-5), 3.44-3.40 (m, 1H, H-4) ppm; ^{13}C NMR (150 MHz, MeOH-d_4, 300 K): δ = 161.7 (C-Ar$_{para'}$), 160.8 (C-Ar$_{para}$), 149.4 (C-Ar$_{ipso}$), 147.5 (C-Ar$_{ipso'}$), 125.6 (C-Ar$_{ortho}$), 124.9 (C-Ar$_{ortho'}$), 117.9 (C-Ar$_{meta'}$), 116.7 (C-Ar$_{meta}$), 102.0 (C-1), 78.3 (C-3), 78.0 (C-5), 74.9 (C-2), 71.3 (C-4), 62.5 (C-6) ppm; IR (ATR): $\tilde{\nu}$ =3625, 3258, 2900, 1583, 1494, 1215, 1071, 1007, 843 cm^{-1}; ESI-MS: *m/z* calcd for $C_{18}H_{20}N_2O_7$: 399.1 [M+Na]$^+$; found 399.2.

(*E*)-*p*-[*p'*-(Propargyloxy)]phenylazophenyl α-D-mannopyranoside (5): To a suspension of azobenzene mannoside **3** (24.0 mg, 63.8 µmol) in a 1:1-mixture of acetonitrile and acetone (4 mL) potassium carbonate (35.0 mg, 255 µmol), potassium iodide (1.10 mg, 6.38 µmol) and propargyl bromide (80% in toluene, 6.00 µL, 63.8 µmol) were added. The reaction mixture was stirred for 6 h at 60 °C and for 16 h at room temperature. Then the solvent was evaporated. Purification of the crude product by

column chromatography (dichloromethane/methanol, 10:1→9:1→5:1) gave **5** as an orange solid (20.0 mg, 48.3 µmol, 76%). R_f=0.30 (ethyl acetate/methanol, 8:1); m.p. 227 °C; $[\alpha]_D^{23}$=+25.7 (*c*=0.5 in methanol); ^{1}H NMR (600 MHz, DMSO-*d*$_6$, 298 K): δ=7.87-7.82 (m, 4H, Ar-H$_{ortho}$, Ar-H$_{ortho'}$), 7.27-7.25 (m, 2H, Ar-H$_{meta'}$), 7.19-7.16 (m, 2H, Ar-H$_{meta}$), 5.51 (d, $^3J_{1,2}$=1.5 Hz, 1H, H-1), 5.09 (d, $^3J_{2,OH}$=4.4 Hz, 1H, OH$_{C-2}$), 4.92 (d, $^4J_{OCH2,C≡CH}$=2.3 Hz, 2H, OCH$_2$), 4.86 (d, $^3J_{3,OH}$=5.9 Hz, 1H, OH$_{C-3}$), 4.80 (d, $^3J_{4,OH}$=6.0 Hz, 1H, OH$_{C-4}$), 4.47 (t~dd, $^3J_{6,OH}$=6.0 Hz, $^3J_{6',OH}$=6.0 Hz, 1H, OH$_{C-6}$), 3.87-3.86 (m, 1H, H-2), 3.71 (ddd, $^3J_{3,4}$=9.3 Hz, $^3J_{3,OH}$=5.9 Hz, $^3J_{2,3}$=3.4 Hz, 1H, H-3), 3.64 (t, $^4J_{OCH2,C≡CH}$=2.3 Hz, 1H, C≡CH), 3.60 (ddd, $^2J_{6,6'}$=11.8 Hz, $^3J_{6,OH}$=6.0 Hz, $^3J_{5,6}$=2.0 Hz, 1H, H-6), 3.54-3.46 (m, 2H, H-4, H-6'), 3.40-3.37 (m, 1H, H-5) ppm; ^{13}C NMR (150 MHz, DMSO-*d*$_6$, 298 K): δ=159.4 (C-Ar$_{para'}$), 158.5 (C-Ar$_{para}$), 146.9 (C-Ar$_{ipso}$), 146.6 (C-Ar$_{ipso'}$), 124.1 (C-Ar$_{ortho}$), 124.0 (C-Ar$_{ortho'}$), 117.1 (C-Ar$_{meta'}$), 115.5 (C-Ar$_{meta}$), 98.7 (C-1), 78.9 (*C*≡CH), 78.7 (C≡*C*H), 75.2 (C-5), 70.6 (C-3), 69.9 (C-2), 66.6 (C-4), 61.0 (C-6), 55.8 (OCH$_2$) ppm; IR (ATR): $\tilde{\nu}$ =3400, 3291, 2939, 1580, 1493, 1227, 1123, 1008, 985, 840 cm^{-1}; UV-Vis (DMSO): λ^{max} (*ε*)=359 nm (21738 L mol^{-1} cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{21}H_{22}N_2O_7$: 415.1505 $[M+H]^+$; found 415.1514.

(*E*)-*p*-[*p'*-(Propargyloxy)]phenylazophenyl β-D-glucopyranoside (6): To a suspension of azobenzene glucoside **4** (83.0 mg, 221 µmol) in acetone (5 mL) potassium carbonate (122 mg, 884 µmol), potassium iodide (4.00 mg, 22.1 µmol) and propargyl bromide (80% in toluene, 20.0 µL, 221 µmol) were added. The reaction mixture was stirred for 4 h at 60 °C and then the solvent was evaporated. Purification of the crude product by column chromatography (dichloromethane/methanol, 9:1) gave **6** as an orange solid (89.0 mg, 215 µmol, 97%). R_f=0.38 (dichloromethane/methanol, 9:1); m.p. 203 °C; $[\alpha]_D^{23}$=-46.7 (*c*=0.7 in methanol); ^{1}H NMR (600 MHz, DMSO-*d*$_6$, 300 K): δ=7.87-7.83 (m, 4H, Ar-H$_{ortho}$, Ar-H$_{ortho'}$), 7.21-7.19 (m, 2H, Ar-H$_{meta'}$), 7.18-7.16 (m, 2H, Ar-H$_{meta}$), 5.39 (d, $^3J_{2,OH}$=4.7 Hz, 1H, OH$_{C-2}$), 5.12 (d, $^3J_{3,OH}$=4.5 Hz, 1H, OH$_{C-3}$), 5.06 (d, $^3J_{4,OH}$=5.3 Hz, 1H, OH$_{C-4}$), 5.01 (d, $^3J_{1,2}$=7.3 Hz, 1H, H-1), 4.92 (d, $^4J_{OCH2,C≡CH}$=2.3 Hz, 2H, OCH$_2$), 4.60 (t~dd, $^3J_{6,OH}$=5.8 Hz, $^3J_{6',OH}$=5.8 Hz, 1H, OH$_{C-6}$), 3.73-3.70 (m, 1H, H-6), 6.63 (t, $^4J_{OCH2,C≡CH}$=2.3 Hz, 1H, C≡CH), 3.51-3.47 (m, 1H, H-6'), 3.41-3.38 (m, 1H, H-5), 3.32-3.26 (m, 2H, H-2, H-3), 3.22-3.18 (m, 1H, H-4) ppm; ^{13}C NMR (150 MHz, DMSO-*d*$_6$, 300 K): δ=159.6 (C-Ar$_{para'}$), 159.4 (C-Ar$_{para}$), 146.9 (C-Ar$_{ipso}$), 146.6 (C-Ar$_{ipso'}$), 124.1 (C-Ar$_{ortho}$), 124.0 (C-Ar$_{ortho'}$), 116.7 (C-Ar$_{meta'}$), 115.5 (C-Ar$_{meta}$), 100.1 (C-1), 78.9 (*C*≡CH), 78.7 (C≡*C*H), 77.2 (C-5), 76.6 (C-3), 73.2 (C-2), 69.7 (C-4), 61.0 (C-6), 55.8 (OCH$_2$) ppm; IR (ATR): $\tilde{\nu}$ =3250, 2920, 1583, 1495, 1232, 1012, 835 cm^{-1}; UV-Vis (DMSO): λ^{max} (*ε*)=359 nm (17123 L mol^{-1} cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{21}H_{22}N_2O_7$: 415.1505 $[M+H]^+$; found 415.1517.

3. ^{1}H and ^{13}C NMR spectra of synthetic compounds

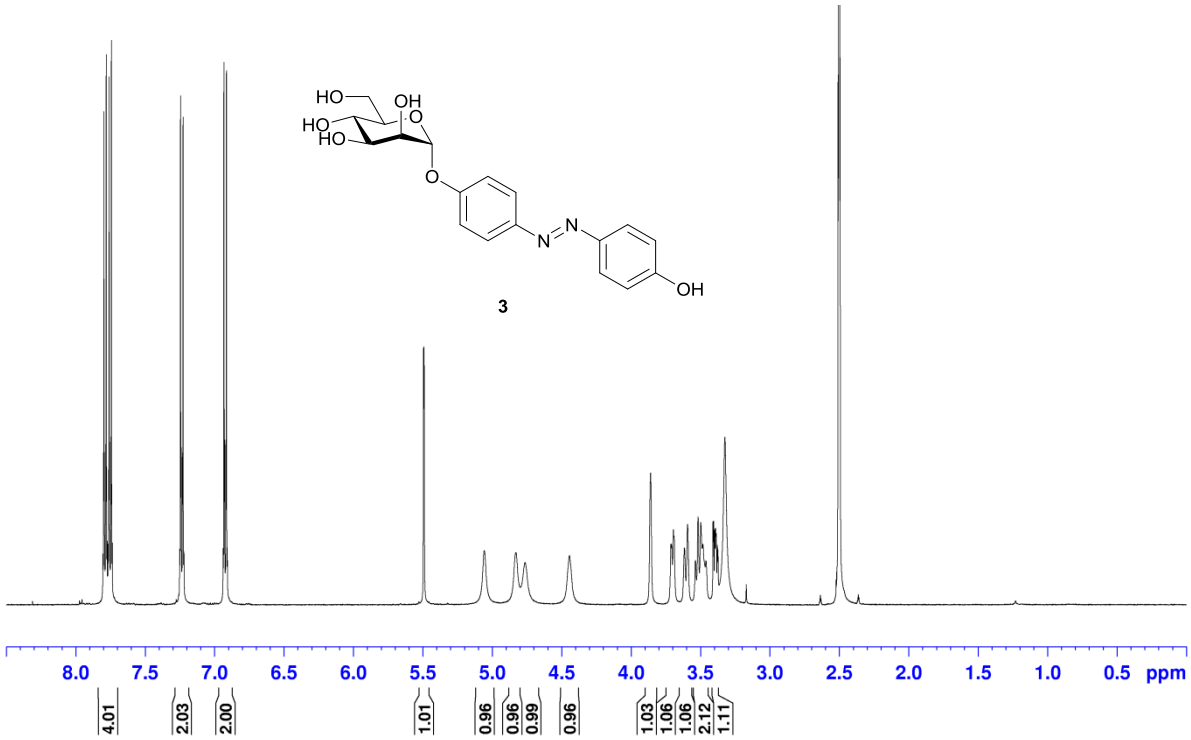

Figure S1. ^{1}H NMR spectrum of **3** (500 MHz, DMSO-d_6, 300 K).

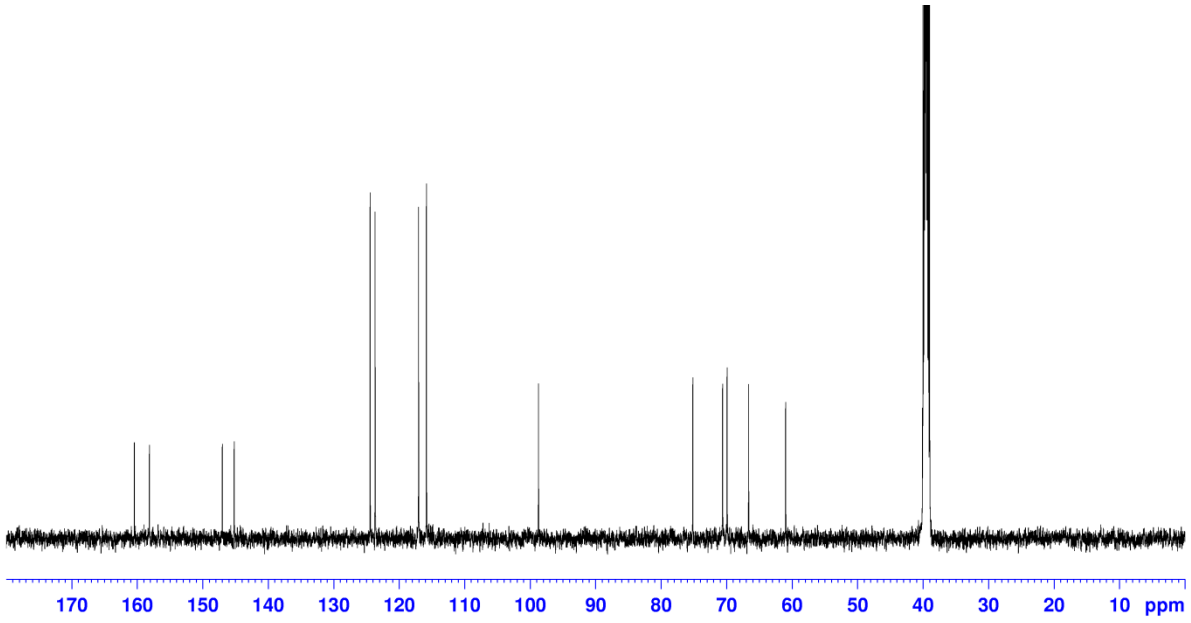

Figure S2. ^{13}C NMR spectrum of **3** (126 MHz, DMSO-d_6, 300 K).

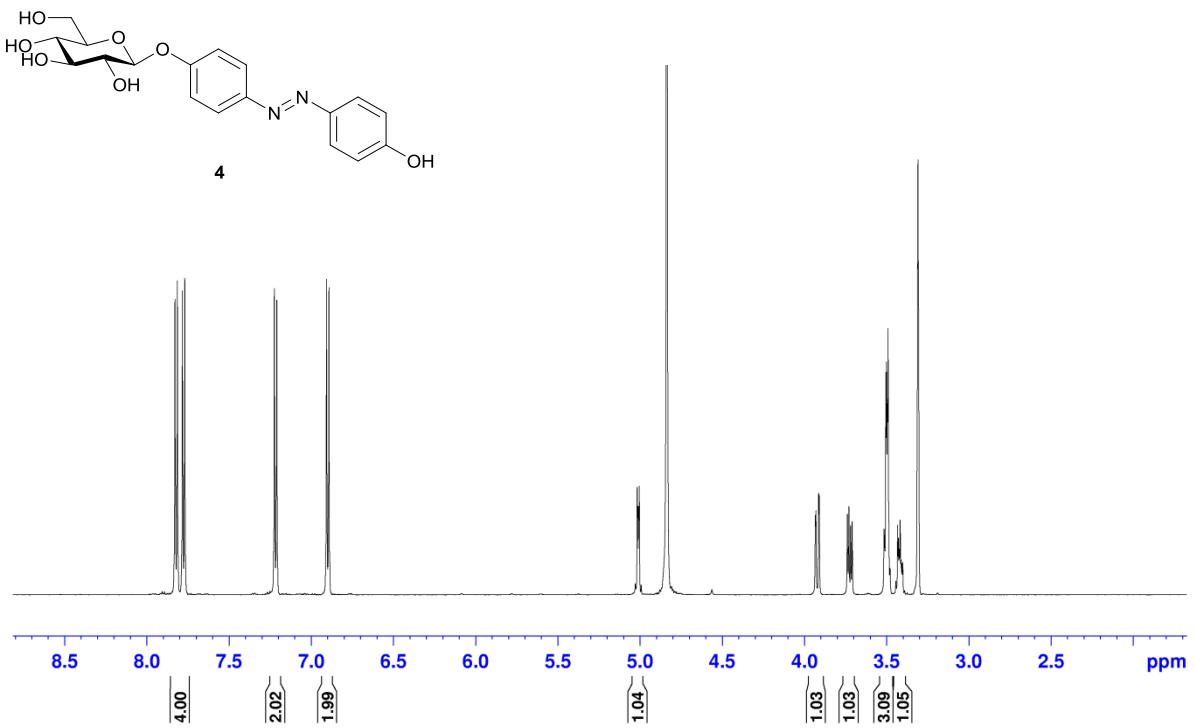

Figure S3. ^{1}H NMR spectrum of **4** (600 MHz, MeOH-d_4, 300 K).

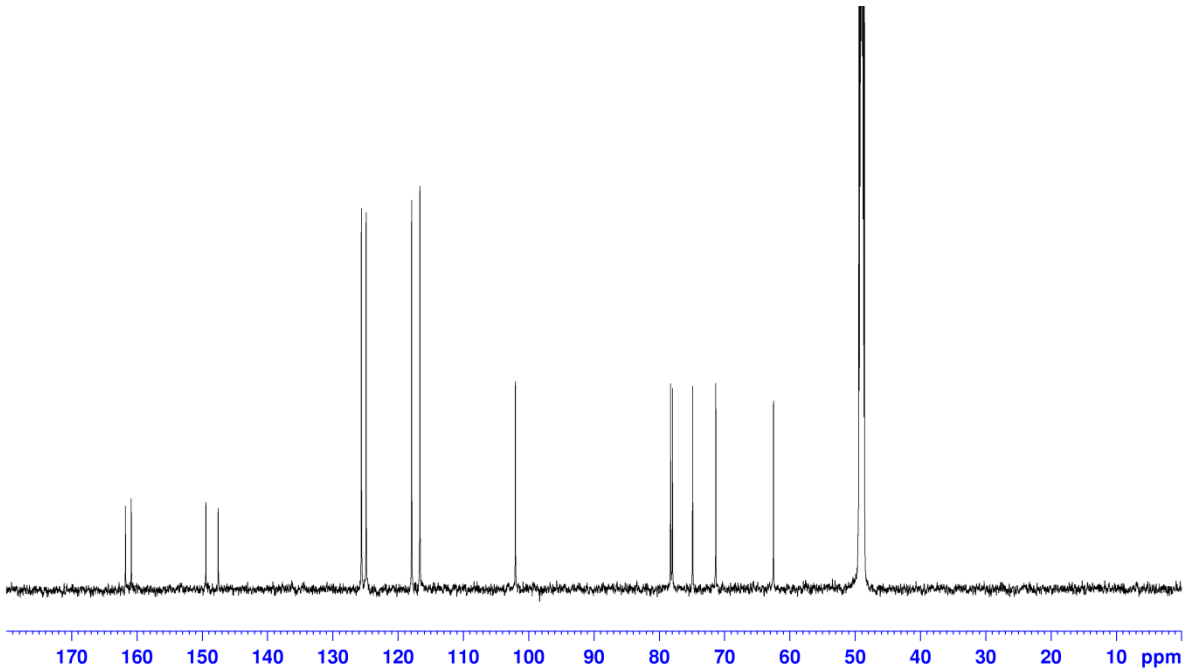

Figure S4. ^{13}C NMR spectrum of **4** (150 MHz, MeOH-d_4, 300 K).

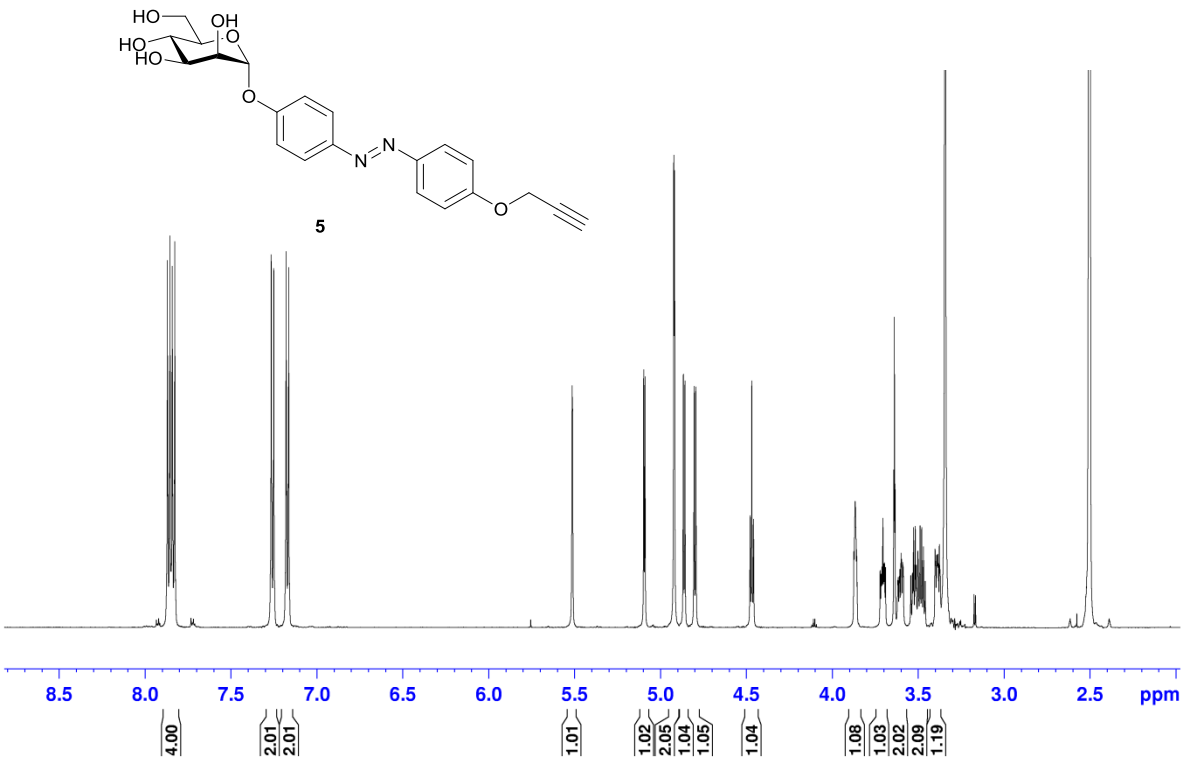

Figure S5. ^{1}H NMR spectrum of **5** (600 MHz, DMSO-d_6, 298 K).

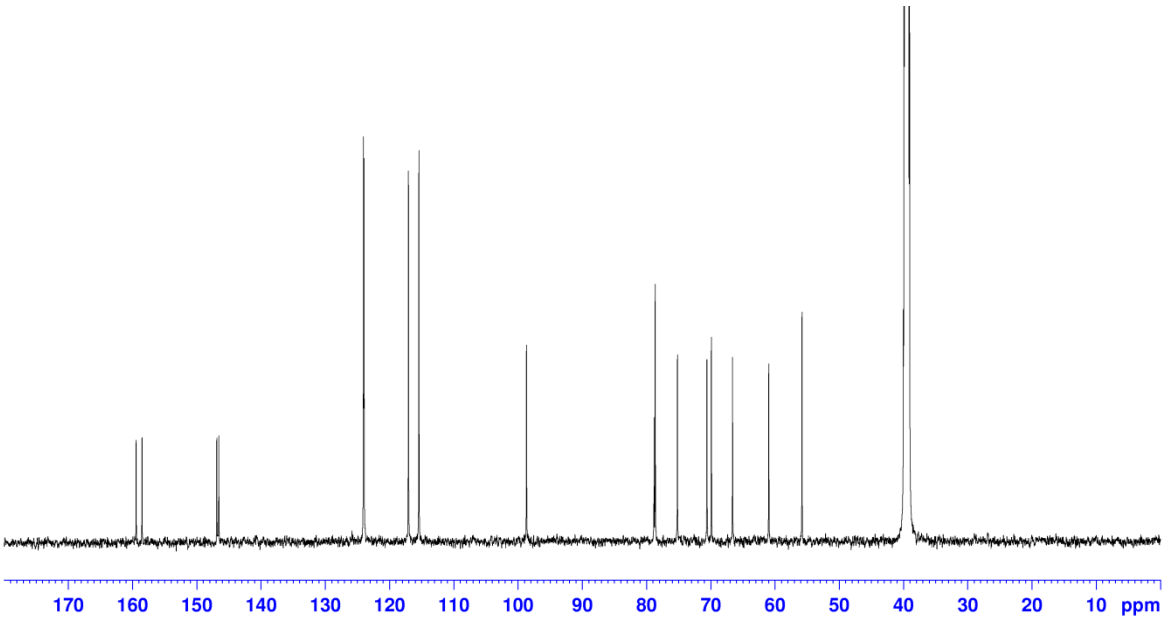

Figure S6. ^{13}C NMR spectrum of **5** (150 MHz, DMSO-d_6, 298 K).

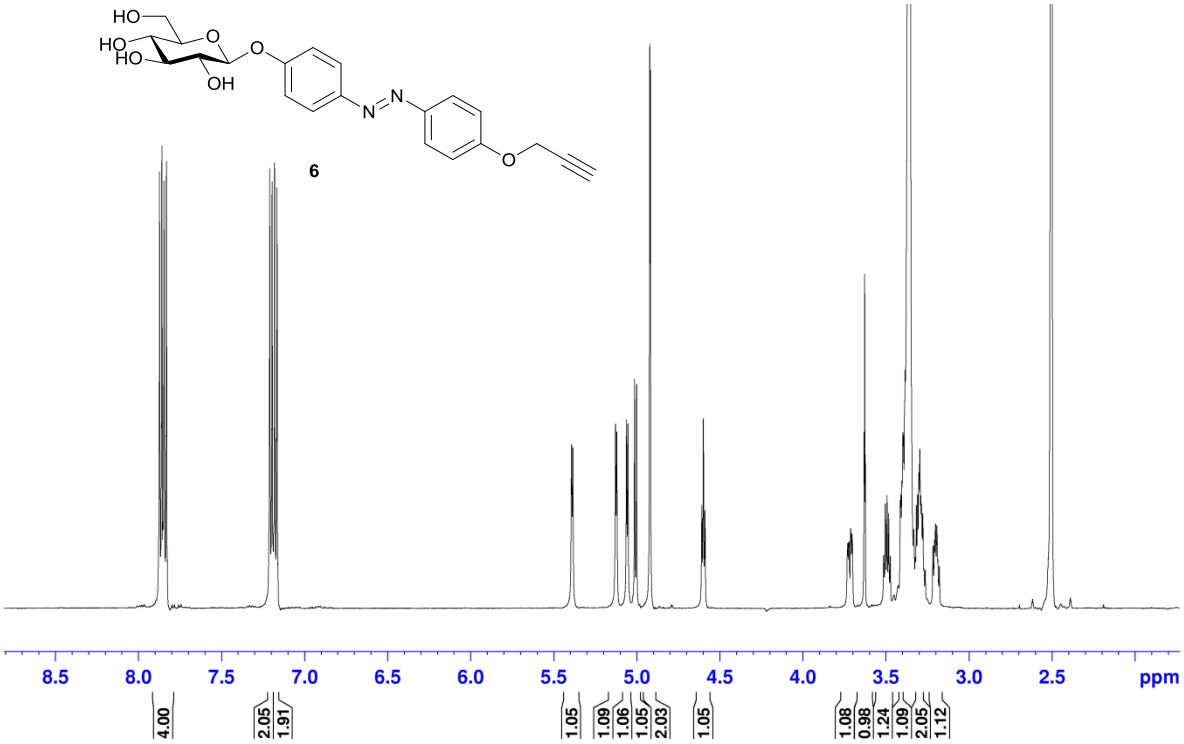

Figure S7. ^{1}H NMR spectrum of **6** (600 MHz, DMSO-d_6, 300 K).

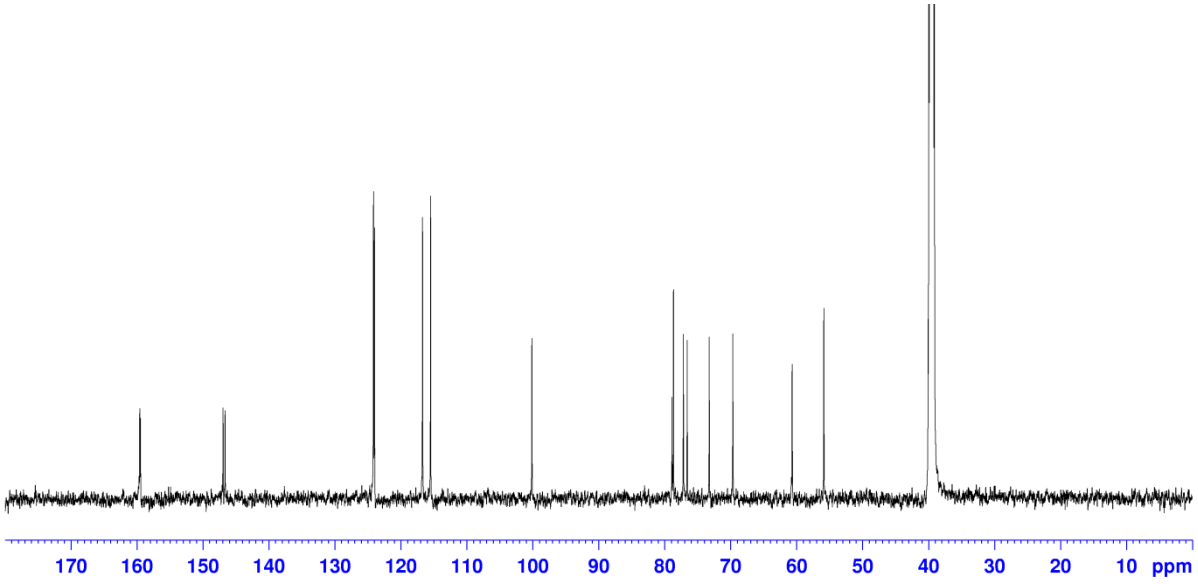

Figure S8. ^{13}C NMR spectrum of **6** (150 MHz, DMSO-d_6, 300 K).

4. Irradiation experiments

Irradiation was performed using a LED (emitting 365 nm light) from the Nichia Corporation (NC4U133A) with a FWHW of 9 nm and optical power output (P_O) ~1 W. *E*/*Z* ratios were determined by irradiating the sample in the NMR tube followed by ^{1}H NMR spectroscopy. The respective *E*-configured azobenzene (5-10 mg) was dissolved in DMSO-d_6 (500 µL) in a NMR tube and irradiated for 15 min at 365 nm. The distance between the LED and the sample in the NMR tube was about ~5 cm. Photostationary states (PSS) were reached after approx. 15 min. Then, the sample was kept in the dark, and ^{1}H NMR spectroscopy was performed immediately afterwards. The photostationary states (PSS) were determined by integration of the anomeric H-1 protons of the prepared compounds.

In analogy, for UV-vis spectroscopy, the *E*-configured azobenzene derivatives were dissolved in DMSO in a UV cuvette, irradiated for 15 min at 365 nm with a distance between LED and cuvette of ~5 cm. UV-vis spectra were recorded immediately afterwards. The absorption spectra showed an increase of the absorbance in the n-π* transition and simultaneous decrease in the π-π* transition, indicating the formation of the respective *Z* isomer. Extinction coefficients (ε) were deduced from UV-vis spectra measured at seven different concentrations (5 µM, 10 µM, 20 µM, 40 µM, 70 µM, 60 µM and 80 µM).

The kinetics of thermal $Z \rightarrow E$ relaxation process were determined by NMR spectroscopy in the dark. The half-life $\tau_{1/2}$ was determined as $\tau_{1/2} = \ln 2/k$. After irradiation, the ^{1}H NMR spectra of the samples were recorded in regular intervals (3 h) over a period of 5 to 6 days. For the determination of the half-life the *Z* and *E* signals of the respective azobenzene moiety were integrated. A signal that was not influenced by irradiation was set as reference. The decay of the integral of the *Z*- and the increase of the integral of the *E*-species were plotted and an exponential decay of first order fitted to the data.

NMR spectra of *Z*-configured compounds and UV-vis spectra

(*Z*)-*p*-[*p'*-(Propargyloxy)]phenylazophenyl α-D-mannopyranoside (5):

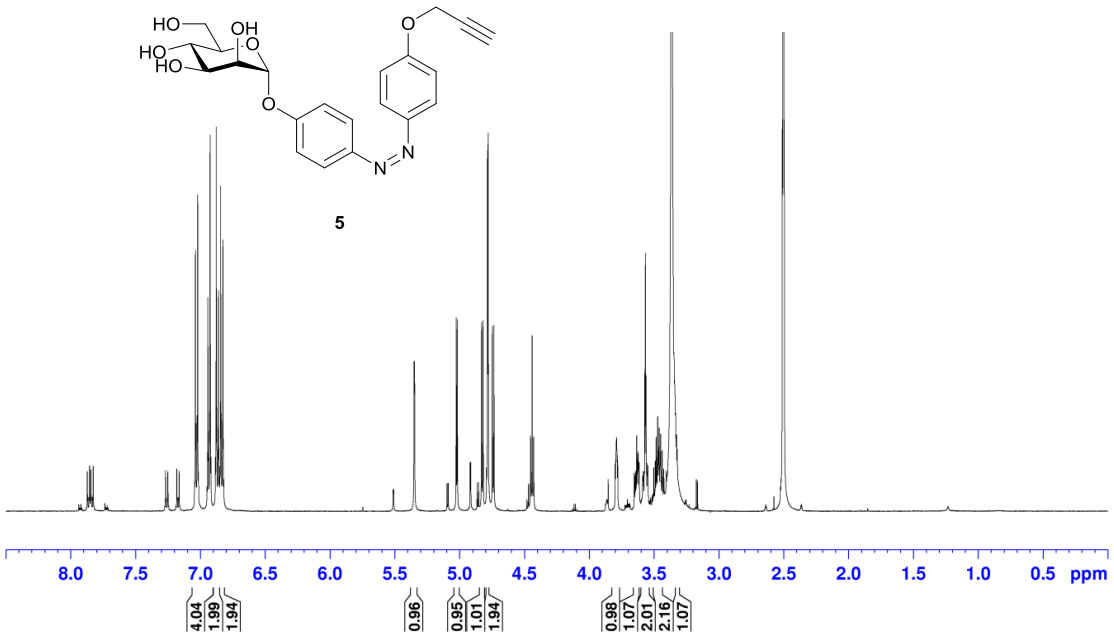

Figure S9. ^{1}H NMR spectrum of **5** (500 MHz, DMSO-d_6, 300 K).

^{1}H NMR (500 MHz, DMSO-d_6, 300 K): δ=7.04-6.91 (m, 4H, Ar-H$_{ortho}$, Ar-H$_{ortho'}$), 6.88-6.85 (m, 2H, Ar-H$_{meta'}$), 6.85-6.82 (m, 2H, Ar-H$_{meta}$), 5.35 (d, $^{3}J_{1,2}$=1.8 Hz, 1H, H-1), 5.02 (d, $^{3}J_{2,OH}$=4.5 Hz, 1H, OH$_{C-2}$), 4.83 (d, $^{3}J_{3,OH}$=5.7 Hz, 1H, OH$_{C-3}$), 4.78 (d, $^{4}J_{OCH2,C\equiv CH}$=2.4 Hz, 2H, OCH$_2$), 4.74 (d, $^{3}J_{4,OH}$=6.1 Hz, 1H, OH$_{C-4}$), 4.44 (t~dd, $^{3}J_{6,OH}$=6.0 Hz, $^{3}J_{6',OH}$=6.0 Hz, 1H, OH$_{C-6}$), 3.80-3.78 (m, 1H, H-2), 3.65-3.61 (m, 1H, H-3), 3.59-3.54 (m, 2H, C≡CH, H-6), 3.51-3.44 (m, 2H, H-4, H-6'), 3.35-3.32 (m, 1H, H-5) ppm.

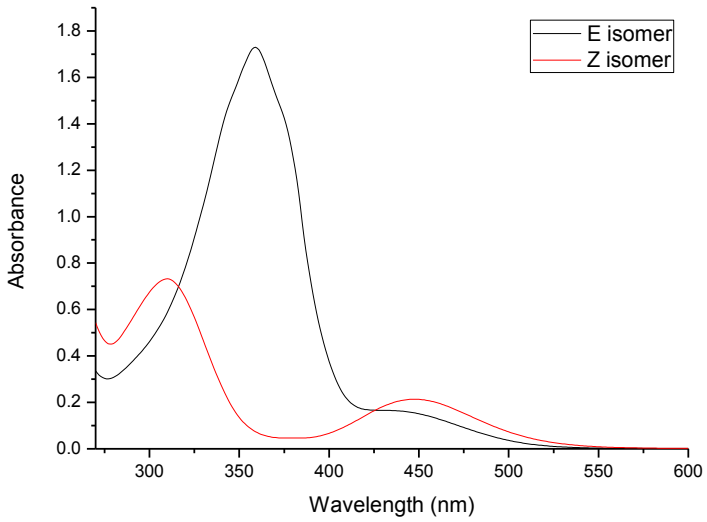

Figure S10. UV-Vis spectra of **5**: *E* isomer in black, *Z* isomer in red; irradiation with 365 nm and 440 nm, respectively, in DMSO at 293 K.

(*Z*)-*p*-[*p'*-(Propargyloxy)]phenylazophenyl β-D-glucopyranoside (6):

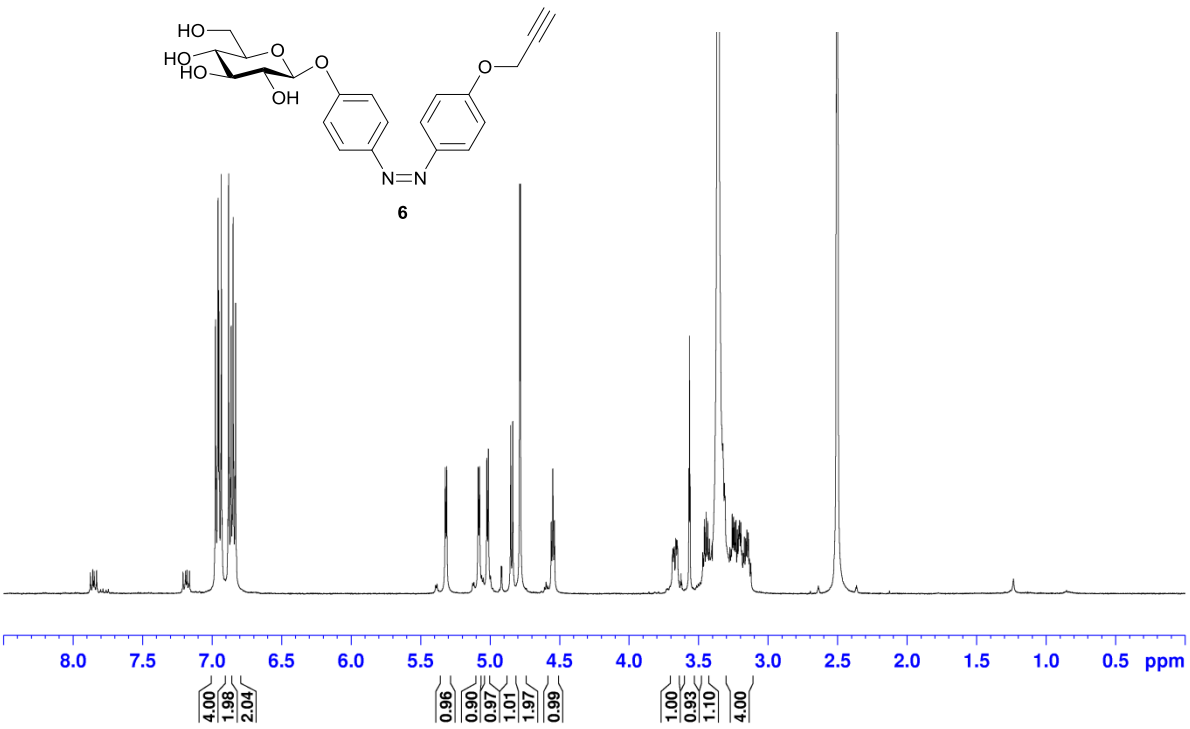

Figure S11. ^{1}H NMR spectrum of **6** (500 MHz, DMSO-d_6, 300 K).

^{1}H NMR (500 MHz, DMSO-d_6, 300 K): δ=6.98-6.93 (m, 4H, Ar-H$_{ortho}$, Ar-H$_{ortho'}$), 6.89-6.86 (m, 2H, Ar-H$_{meta'}$), 6.86-6.83 (m, 2H, Ar-H$_{meta}$), 5.32 (d, $^{3}J_{2,OH}$=5.0 Hz, 1H, OH$_{C-2}$), 5.08 (d, $^{3}J_{3,OH}$=4.8 Hz, 1H, OH$_{C-3}$), 5.02 (d, $^{3}J_{4,OH}$=5.3 Hz, 1H, OH$_{C-4}$), 4.85 (d, $^{3}J_{1,2}$=7.6 Hz, 1H, H-1), 4.78 (d, $^{4}J_{OCH2,C≡CH}$=2.4 Hz, 2H, OCH$_2$),4.55 (t~dd, $^{3}J_{6,OH}$=5.7 Hz, $^{3}J_{6',OH}$=5.7 Hz, 1H, OH$_{C-6}$), 3.69-3.65 (m, 1H, H-6), 6.57 (t, $^{4}J_{OCH2,C≡CH}$=2.4 Hz, 1H, C≡CH), 3.47-3.40 (m, 1H, H-6'), 3.30-3.12 (m, 4H, H-2, H-3, H-4, H-5) ppm.

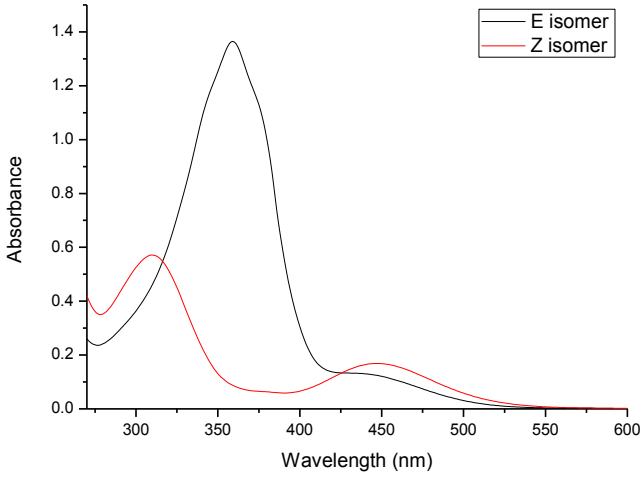

Figure S12. UV-Vis spectra of **6**: *E* isomer in black, *Z* isomer in red; irradiation with 365 nm and 440 nm, respectively, in DMSO at 293 K.

Table S1. Characterization of the *E* and *Z* isomer of the azobenzene derivatives **5** and **6**.

Azobenzene glycoconjugate	H-1 [ppm]	*E*/*Z* (PSS)[a]	λ_{max} [nm]	half-life, $\tau_{1/2}$ [h]
5	5.51 (*E*) 5.35 (*Z*)	1:99	359 (*E*) 310, 448 (*Z*)	30.9
6	5.01 (*E*) 4.85 (*Z*)	9:91	359 (*E*) 310, 447 (*Z*)	44.3

[a] According to the integration ratio of aromatic proton signals in the ^{1}H NMR spectra.

5. Required alkyne concentration for saturation

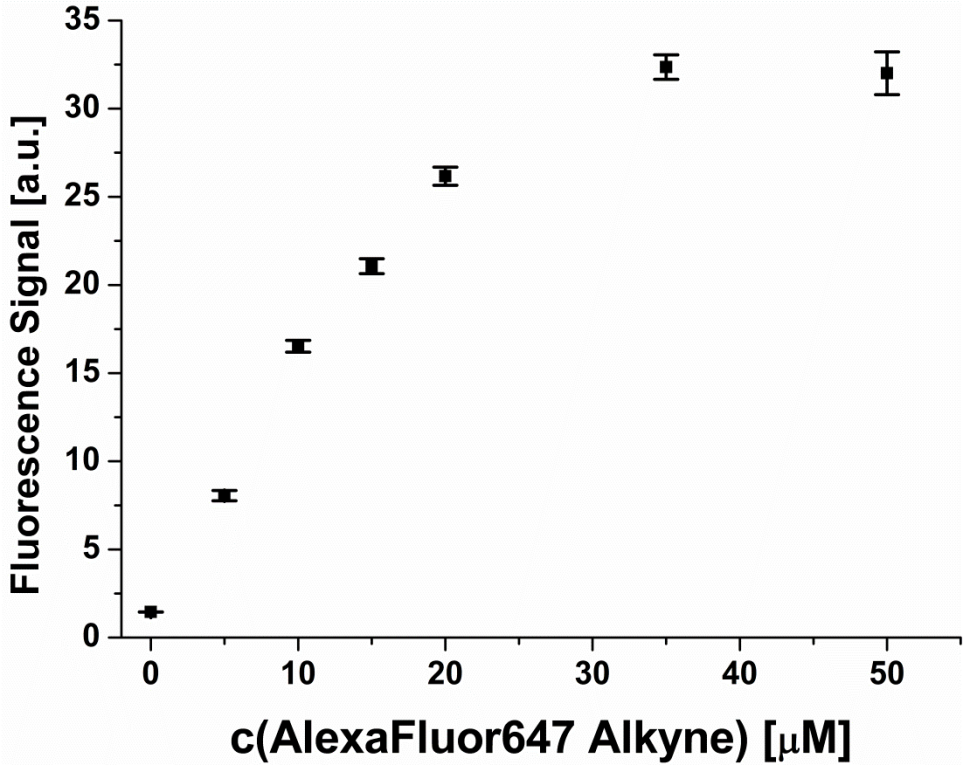

Figure S13. Required alkyne concentration for saturation. HMEC-1 were cultivated in presence of 50 μM Ac_4ManNAz for two days as described. Instead of an azobenzene derivate, a fluorescent alkyne was coupled at various concentrations to the incorporated azido groups under identical conditions. The membrane fluorescence was determined. It can be clearly seen that at 35 μM a plateau is reached. Hence, the concentration of 200 μM azobenzene derivate that we used in our experiment ensures that all available azido groups are tagged.

6. Experimental set up for bacterial adhesion experiments

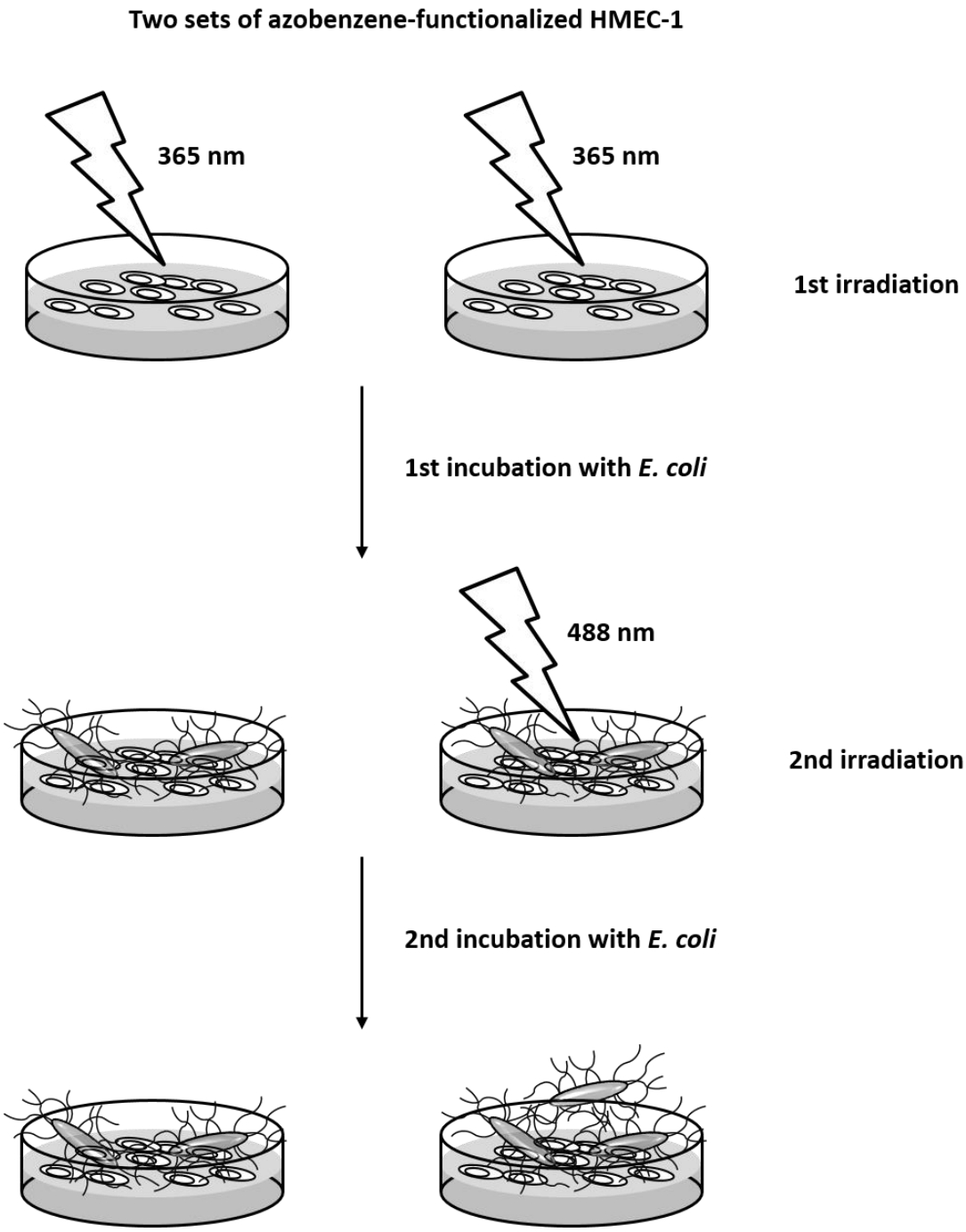

Figure S14. Experimental procedure for bacterial adhesion experiments. Two sets of azobenzene-functionalised HMEC-1 were first irradiated with UV light (365 nm) and then incubated with GFP fluorescent *E. coli* (PKL1162).[2] The number of adhered bacteria was counted employing high-resolution live-cell fluorescence microscopy. In the next step, only one set of cells was irradiated with green light (488 nm), whereas the other set of cells remained untreated. Afterwards, both sets of cells were again incubated with GFP-fluorescent *E. coli* (2nd incubation) and adhesion was again quantified.

6. Microscopic pictures of fluorescent *E. coli* bacteria

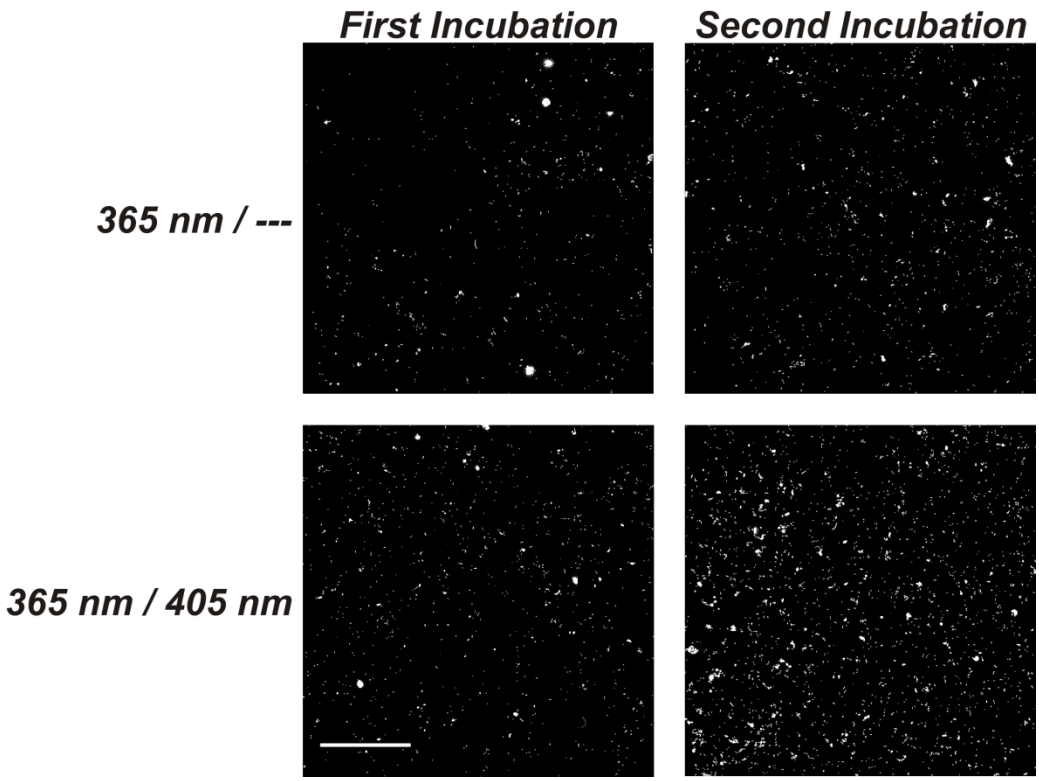

Figure S15. Adhesion of *E. coli* to *Z* and *E*-configured 5. Two sets of HMEC bearing sialic acid cell surface glycoconjugates, modified with *Z*-azobenzene mannoside **5**, were incubated with bacteria (after irradiation with light of 365) (left column). Next, one set of HMEC was irradiated with light of 405 nm to effect *Z*→*E* isomerisation of azobenzene mannoside. Then, both sets of HMEC were incubated again with bacteria. By high-resolution fluorescence microscopy it can be seen that the number of adhered bacteria increases strongly for HMEC in the *E*-state (bottom right), whereas it does not change significantly when HMEC were not irradiated with 405 nm light (leaving **5** in the *Z*-state) (top right). Scale bar = 250 µm.

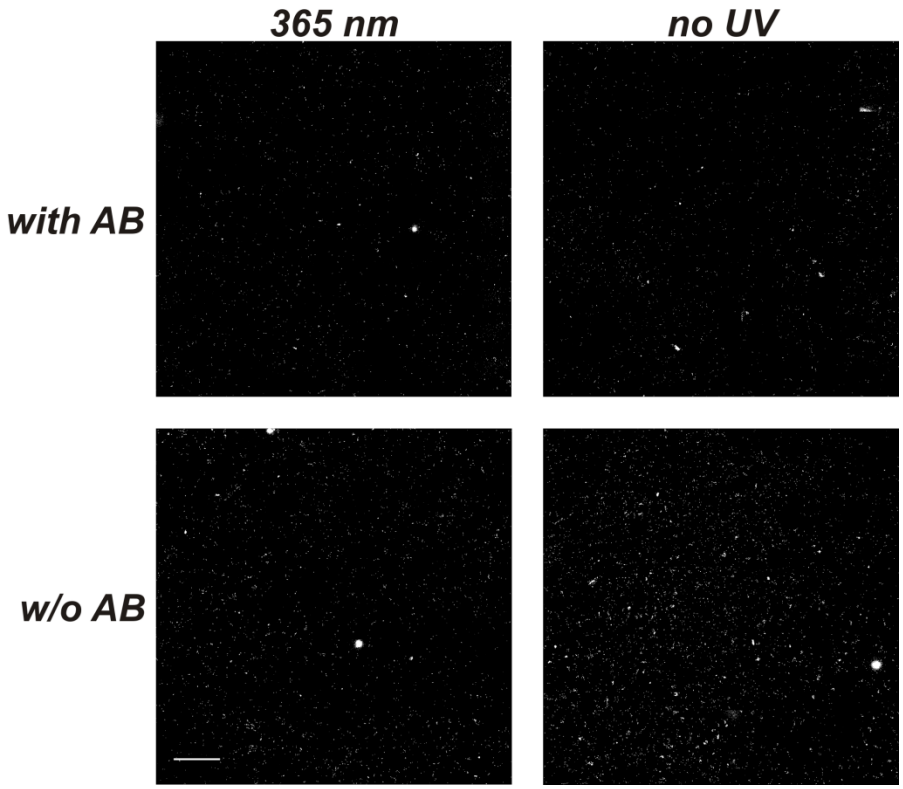

Figure S16. Adhesion of *E. coli* to *Z* and *E*-configured 7. HMEC were modified at their sialic acid cell surface glycoconjugates with either **7**, or remained untreated as control. Next, one set of cells was irradiated with 365 nm light in order to switch the azobenzene residues (AB) to the *Z*-state. The other set was not irradiated. After incubation with bacteria, fluorescence images were obtained. It can be clearly seen that the presence of **7** in both *Z*- and *E*-configuration reduced adhesion of bacteria. Scale bar = 250 µm.

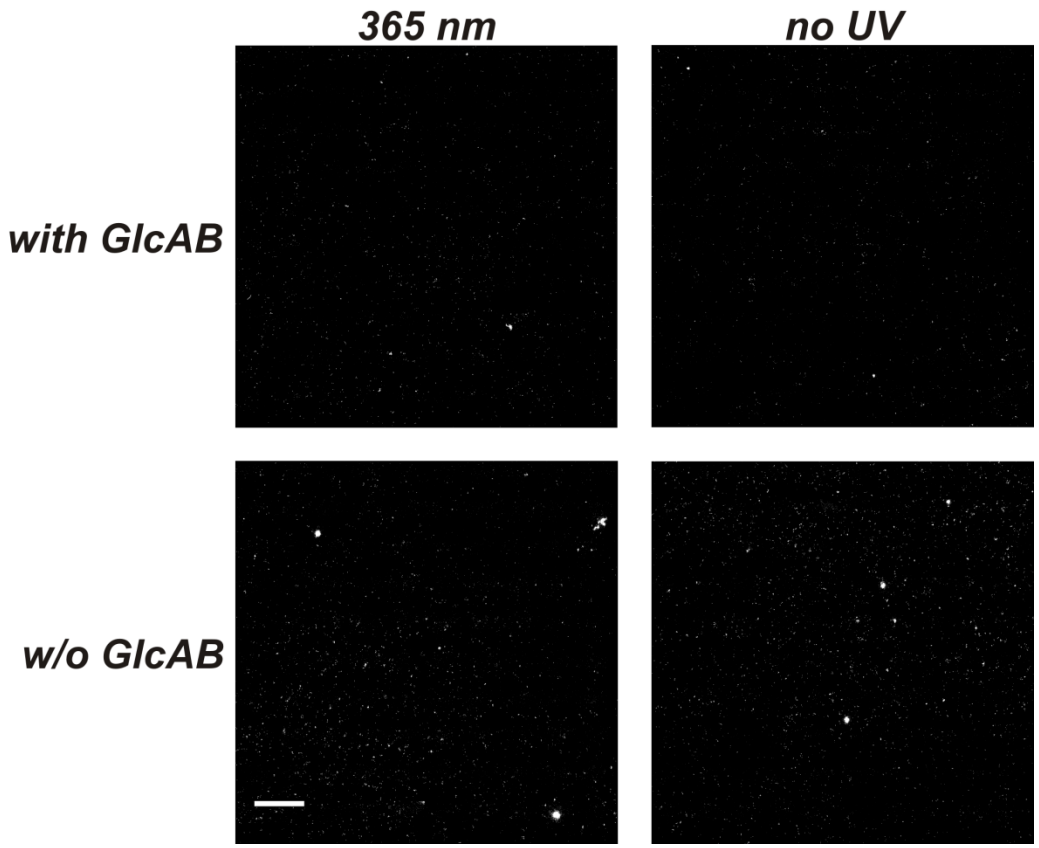

Figure S17. Adhesion of *E. coli* to *Z* and *E*-configured 6. HMEC were modified at sialic acids with **6** or remained untreated as control. Next, one set of cells was irradiated with 365 nm light in order to switch the azobenzene glucosides to the Z-state. The other set was not irradiated. After incubation with bacteria, fluorescence images were obtained. As for **7**, adhesion of bacteria was decreased. Therefore, the glucosyl moiety in **6** cannot serve as specific ligand. Also, unspecific interactions are not increased. Scale bar = 250 µm.

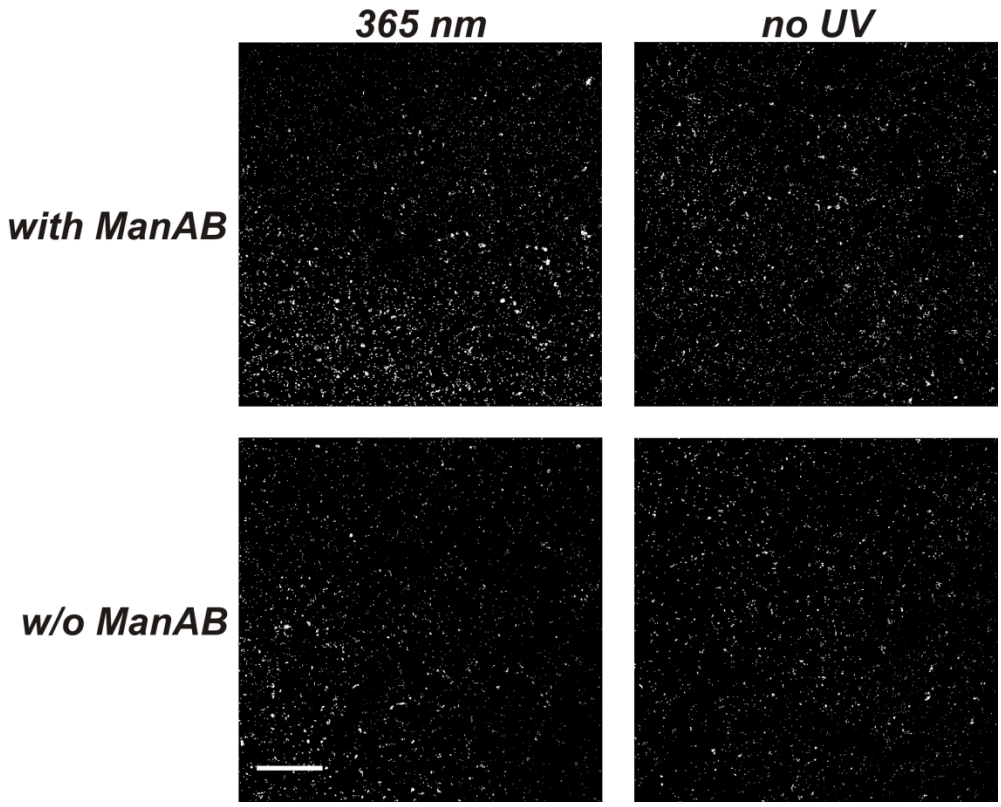

Figure S18. Adhesion of *E. coli* to *Z* and *E*-configured 5 linked to mucin-type proteins. HMEC were modified with **5** at mucin-type cell surface glycoproteins or remained untreated as control. In comparison to labelling of sialic acid glycoconjugates (cf. Fig. S15), this leads to attachment of **5** deeper within the glycan tree. Next, one set of HMEC was irradiated with 365 nm light in order to effect *E*→*Z* isomerisation of azobenzene mannosides. The other set was not irradiated. After incubation with bacteria, fluorescence images were obtained. It can be seen that the additional mannosyl residues increased adhesion in comparison to cells not treated with **5**, however, **E**/*Z* switching had no effect. This is reasonable since in this case, the change in orientation upon switching is small compared to the distance between conjugated azobenzene mannoside units and incoming. Scale bar = 250 µm.

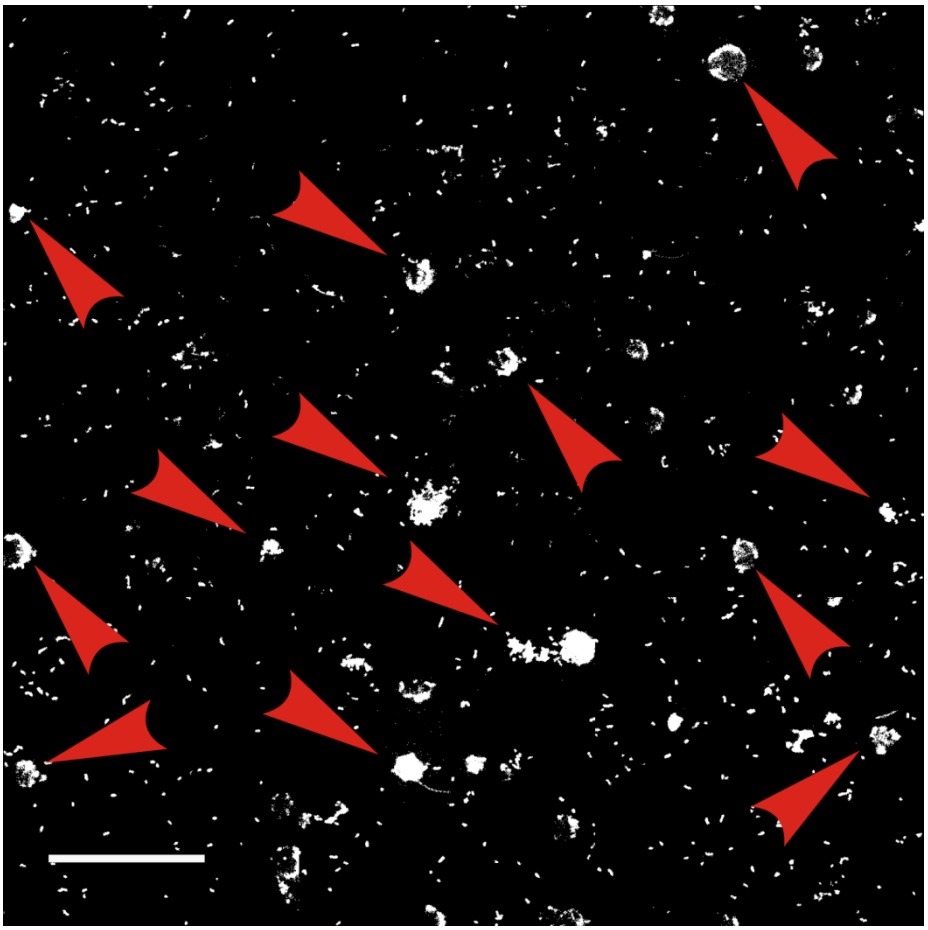

Figure S19. Formation of clumps of *E. coli* under flow conditions. With increasing time of flow, bacteria more and more adhere to already adhered bacteria and not to HMEC-1, forming clumps (some of them indicated by red arrow heads). Scale bar = 100 µm.

8. Literature

[1] V. Chandrasekaran, E. Johannes, H. Kobarg, F. D. Sönnichsen and T. K. Lindhorst, *ChemistryOpen*, 2014, **3**, 99-108.

[2] M. Hartmann, A. K. Horst, P. Klemm and T. K. Lindhorst, *Chem. Commun.*, 2010, **46**, 330-332.

[3] G. R. Gustafson, C. M. Baldino, M.-M. E. O'Donnell, A. Sheldon, R. J. Tarsa, C. J. Verni and D. L. Coffen, *Tetrahedron*, 1998, **54**, 4051-4065.