Supporting Information

Self-Reproducing Micelles Coupled to a Secondary Catalyst

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General Information

Procedures using oxygen- and/or moisture-sensitive materials were performed with anhydrous solvents under an atmosphere of anhydrous argon in flame-dried flasks, using standard Schlenk techniques. Analytical TLC was performed on precoated aluminum-backed plates (Silica Gel 60 F254; Merck), and visualised using aqueous ceric ammonium molybdate (CAM), aqueous basic potassium permanganate, or ninhydrin stains. Flash column chromatography was carried out using Merck Geduran® Si 60 (40-63 μm) silica gel. Compound was loaded on to the columns with Chemtube Hydromatrix from Agilent Technologies. Pressure was applied at the column head via a flow of nitrogen with the solvent system used in parentheses.

Cooling of reaction mixtures to 0 °C was achieved using an ice-water bath. Cooling to –10 °C was achieved using a salt-ice bath. Cooling to –78 °C was achieved using a dry ice-acetone bath.

Chemicals

All chemicals were purchased from Sigma Aldrich or Fluorochem Scientific and used without further purification. Dry $CHCl_3$, THF, CH_2Cl_2, Et_2O, toluene, benzene, hexane, pentane, DMF, and acetonitrile were collected fresh from an mBraun SPS-5 solvent purification system having been passed through anhydrous alumina columns. All other solvents were used as purchased from Sigma-Aldrich, Honeywell, or Fisher Scientific.

Equipment

All NMR spectra were recorded at room temperature. ^{1}H NMR and ^{13}C NMR spectra were recorded using Bruker AVIII HD 400 (400/101 MHz) and AVIII HD 500 (500/126 MHz) spectrometers. Chemical shifts are reported in p.p.m. from the residual solvent peak. Chemical shifts (δ) are given in p.p.m. and coupling constants (J) are quoted in hertz (Hz). Resonances are described as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Assignments were made with the assistance of 2D NMR experiments.

DOSY NMR measurements were performed using a Bruker AVIII HD 500 equipped with a TFI probehead at 298 K using the 2D sequence for diffusion measurement using double stimulated echo for convection compensation and longitudinal eddy current delay, using bipolar gradient pulses for diffusion, and using three spoil gradients (Bruker terminology: dstebpgp35) pulse sequence. The samples were thoroughly mixed using a Vortex Genie 2 mixer (Scientific Industries), and were then clarified using a hand centrifuge (Hettich, model 1011) and then measured. Samples containing saturated alkyne consequently had a small layer of neat alkyne above the D_2O layer; sufficient D_2O was used to ensure that the alkyne layer was not detectible by the NMR probe. Experiments were performed in two stages: initially 1D-edited DOSY experiments were used to optimize the diffusion period to Δ=100 ms. The 2D dstebpgp35 sequence was then used, based on the optimized Δ from the previous procedure and with δ=4 ms, with gradient amplitude ranging from 2 to 85% with 16 points in between. Data were analysed using the T_1T_2 module in TOPSPIN 3.2 and plots were generated using the eddosy module.

High-resolution mass spectra (EI and ESI) were recorded using a Bruker MicroTOF spectrometer by the internal service at the University of Oxford. Low-resolution mass spectra were recorded using a Walters LCT premier XE.

Infrared measurements (thin film) were carried out using a Bruker Tensor 27 FTIR with internal calibration in the range 4000-600 cm^{-1}.

Optical rotations were recorded using a Perkin-Elmer 241 polarimeter at 25 °C in a 10 cm cell in the stated solvent. $[\alpha]_D$ values are given in 10^{-1} deg·cm^2 g^{-1}, with concentration c given as g/100 mL.

Fluorimetry was performed using Edinburgh Instruments Spectrofluorometer FS5 model with Fluoracle software. The slit width for both excitation and emission was set at 1 nm.

DLS measurements were recorded using a Malvern Zetasizer Nano ZS DLS instrument and analysed with Zetasizer software. All samples were prepared in ultrapure Milli-Q water and filtered through 0.2 μm PTFE filters before measuring.

Experimental Procedures and Characterisation of Compounds

General procedure 1: Synthesis of protected surfactant products via CuAAC reaction

Conditions adapted from Shao *et al*.[1] To a stirred suspension of CuI (0.02 eq) in degassed CH_2Cl_2 (160 mM) was added protected maltose azide **1a** (1 eq), DIPEA (0.04 eq), AcOH (0.04 eq) and alkyne (1.4 eq). The resultant solution was stirred for 18 h. The reaction mixture was concentrated *in vacuo*, and the crude was purified with flash column chromatography. The column was eluted with EtOAc:hexane (1:1) to yield the product.

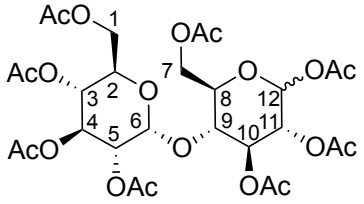
General procedure 2: Acetyl deprotection

Synthesis according to Mahon *et al*.[2] To a stirred suspension of protected sugar (150 mM) in MeOH was added sodium methoxide (0.1 eq). Upon dissolution of the solid and concurrent disappearance of protected sugar (TLC control) the solution was neutralised using Amberlyst 15 resin (H^+ form). The resin was filtered off and washed with MeOH and the filtrate was concentrated *in vacuo*. The residue was dried under high vacuum to give a deprotected sugar as a tacky, hygroscopic white foam.

General procedure 3: Setup of kinetic experiments

Maltose azide **1b** (150 mg, 0.408 mmol, 1 eq, 1.5 mL of 100 mg/mL standard solution in D_2O), $CuSO_4 \cdot 5H_2O$ (6 mg, 0.024 mmol, 0.06 eq, 1 mL of 6 mg/mL standard solution in D_2O) (and deprotected surfactant in the reported concentrations for the seeded reactions) were added to D_2O (2.0 mL) to give a total volume of 4.5 mL in a round bottom flask (25 mL) with a stirrer bar of a similar size for each experiment. The flask was capped with a septum and the solution was degassed by bubbling argon through it for 30 minutes. *O*-phenylenediamine (6.6 mg, 0.061 mmol, 0.15 eq), alkyne (2 eq) and sodium ascorbate (16.2 mg, 0.082 mmol, 0.2 eq) were added. The reaction mixture was stirred at 200 rpm under a continuous flow of argon. Samples for analysis during the kinetic experiments were prepared at regular intervals by diluting 0.1 mL of the reaction mixture in 0.4 mL of D_2O and immediately taking a ^{1}H NMR measurement.

α/β-D-maltose octaacetate



Chemical Formula: $C_{28}H_{38}O_{19}$
Molecular Weight: 678.59

Synthesised according to Harvey *et al*.[3] NaOAc (5.00 g, 61.0 mmol, 1.1 eq) was added to a stirred suspension of D-maltose (10.0 g, 29.2 mmol, 1 eq) in Ac_2O (50 mL) at 140 °C. The reaction was stirred until deemed complete by disappearance of maltose (TLC control, 2:1 petroleum ether/EtOAc) (approx. 1 h). The reaction mixture was diluted with CH_2Cl_2 (50 mL). The organic mixture was washed with saturated aqueous $NaHCO_3$ (3 × 100 mL), dried (Na_2SO_4) and concentrated *in vacuo* to yield the peracetylated D-maltose (23.0 g, quantitative yield, α:β ~ 1:4.55) as an amorphous white solid.

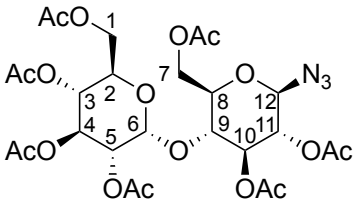
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 (d, *J* = 3.7 Hz, 1H, C<u>H</u>-6), 5.51 (dd, *J* = 10.2, 8.6 Hz, 1H, C<u>H</u>-4), 5.43 (d, *J* = 4.0 Hz, 1H, C<u>H</u>-12), 5.38 (dd, *J* = 10.6, 9.5 Hz, 1H, C<u>H</u>-3), 5.06 (t, *J* = 9.9 Hz, 1H, C<u>H</u>-10), 4.96 (dd, *J* = 10.1, 3.7 Hz, 1H, C<u>H</u>-5), 4.87 (dd, *J* = 10.5, 4.0 Hz, 1H, C<u>H</u>-11), 4.45 (dd, *J* = 12.4, 2.5 Hz, 1H, C<u>H$_a$</u>H$_b$-7), 4.22 (td, *J* = 12.4, 3.5 Hz, 2H, CH$_a$<u>H$_b$</u>-7 and C<u>H$_a$</u>H$_b$-1), 4.10 (dt, *J* = 10.0, 2.9 Hz, 1H, CH$_a$<u>H$_b$</u>-1), 4.04 – 4.02 (m, 1H, C<u>H</u>-9), 4.02 – 3.99 (m, 1H, C<u>H</u>-2), 3.94 (dt, *J* = 10.1, 3.1 Hz, 1H, CH$_a$<u>H$_b$</u>-8), 2.22 (s, 3H, C<u>H$_3$</u>CO), 2.14 (s, 3H, C<u>H$_3$</u>CO), 2.10 (s, 3H, C<u>H$_3$</u>CO), 2.07 (s, 3H, C<u>H$_3$</u>CO), 2.03 (s, 3H, C<u>H$_3$</u>CO), 2.02 (s, 3H, C<u>H$_3$</u>CO), 2.01 (s, 3H, C<u>H$_3$</u>CO), 1.99 (s, 3H, C<u>H$_3$</u>CO).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.69, 170.62, 170.55, 170.09, 170.06, 169.95, 169.51, 169.04, 95.87, 88.93, 72.37, 72.29, 70.20, 70.15, 69.80, 69.34, 68.70, 67.96, 62.48, 61.42, 21.13, 21.04, 20.91, 20.80, 20.73 (2C), 20.71, 20.55.

HRMS (ESI) *m/z* calcd for $C_{28}H_{38}O_{19}Na$ $[M+Na]^+$: 701.1900, found: 701.1896.

Data reported here is for the β-anomer and is consistent with data in the literature.[2]

Hepta-O-acetyl-1-deoxy-1-azido-β-D-maltopyranose (1a)



Chemical Formula: $C_{26}H_{35}N_3O_{17}$
Molecular Weight: 661.57

Synthesised according to Mahon *et al*.[2] The crude maltose octaacetate (40.8 g, 60.1 mmol, 1.0 eq) was dissolved in CH_2Cl_2 (80 mL). HBr (80 mL, 33% solution in AcOH, 7.7 eq) was added slowly at 0 °C and the reaction stirred at rt until complete (TLC control, 3:1 petroleum ether/EtOAc, approx. 3 h). The reaction mixture was diluted with CH_2Cl_2 (100 mL) and H_2O (100 mL). The layers were separated, and the organic layer was washed with saturated aqueous $NaHCO_3$ (3 × 200 mL) and then brine (1 × 200 mL). The organic layer was dried (Na_2SO_4) and concentrated *in vacuo* to give a syrupy yellow oil (43.7 g). The crude bromide was dissolved in $CHCl_3$ (90 mL) and saturated aqueous $NaHCO_3$ (90 mL) was added. Tetrabutylammonium iodide (20 g, 54.1 mmol, 0.9 eq) was added, followed by NaN_3 (slow addition, 5 min, 18.00 g, 213.8 mmol, 4.6 eq) and the reaction was stirred at rt for 18 h. The layers were partitioned and the organic layer washed with H_2O (100 mL), saturated aqueous $NaHCO_3$ (100 mL) and brine (100 mL). The organic layer was dried ($MgSO_4$) and concentrated *in vacuo* to give a brown solid. The crude product was recrystallised from a minimum of hot MeOH to give hepta-O-acetyl-1-deoxy-1-azido-β-D-maltopyranose **2a** (26.0 g, 39.3 mmol, 65% over two steps) as a white crystalline solid.

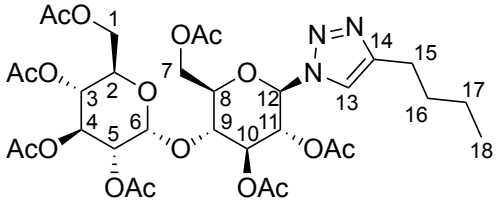
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 (d, *J* = 4.0 Hz, 1H, C<u>H</u>-6), 5.34 (dd, *J* = 10.6, 9.5 Hz, 1H, C<u>H</u>-4), 5.25 (t, *J* = 8.9 Hz, 1H, C<u>H</u>-10), 5.04 (dd, *J* = 10.3, 9.5 Hz, 1H, C<u>H</u>-3), 4.84 (dd, *J* = 10.6, 4.0 Hz, 1H, C<u>H</u>-5), 4.77 (t, = 8.9 Hz, 1H, C<u>H</u>-11), 4.70 (d, *J* = 8.7 Hz, 1H, C<u>H</u>-12), 4.50 (dd, *J* = 12.2, 2.6 Hz, 1H, C<u>H$_a$H$_b$</u>-7), 4.23 (ddd, *J* = 12.3, 4.2, 2.0 Hz, 2H, CH$_a$<u>H$_b$</u>-7 and C<u>H$_a$H$_b$</u>-1), 4.04 (dd, *J* = 12.5, 2.3 Hz, 1H, CH$_a$<u>H$_b$</u>-1), 4.01 (dd, *J* = 9.8, 8.7 Hz, 1H, C<u>H</u>-9), 3.98 – 3.89 (m, 1H, C<u>H</u>-2), 3.77 (ddd, *J* = 9.8, 4.5, 2.6 Hz, 1H, C<u>H</u>-8), 2.15 (s, 3H, C<u>H$_3$</u>CO), 2.09 (s, 3H, C<u>H$_3$</u>CO), 2.04 (s, 3H, C<u>H$_3$</u>CO), 2.03 (s, 3H, C<u>H$_3$</u>CO), 2.02 (s, 3H, C<u>H$_3$</u>CO), 2.00 (s, 3H), 1.99 (s, 3H, C<u>H$_3$</u>CO).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.67, 170.57, 170.24, 170.09, 169.64, 169.56, 95.81, 87.58, 75.20, 74.36, 72.47, 71.61, 70.11, 69.38, 68.75, 68.07, 62.66, 61.59, 50.96, 20.97, 20.90, 20.81, 20.72, 20.69 (3C).

HRMS (ESI) *m/z* calcd for $C_{26}H_{35}O_{17}N_3Na$ $[M+Na]^+$: 684.1859, found: 684.1855.

Consistent with data in the literature.[2]

1-(Hepta-O-acetyl-1-deoxy-β-D-maltopyranosyl)-4-butyl triazole (4a)



Chemical Formula: $C_{32}H_{45}N_3O_{17}$
Molecular Weight: 743.72

Synthesised according to general procedure 1 using maltose azide **1a** (1.00 g, 1.51 mmol), CuI (6 mg, 0.032 mmol), DIPEA (10 µL, 0.06 mmol), AcOH (3.5 µL, 0.06 mmol) and 1-hexyne (173 µL, 1.51 mmol). Flash column chromatography (50% EtOAc in hexane) provided 1-(hepta-O-acetyl-1-deoxy-β-D-maltopyranosyl)-4-butyl triazole **4a** (986 mg, 1.33 mmol, 88%) as a white foam.

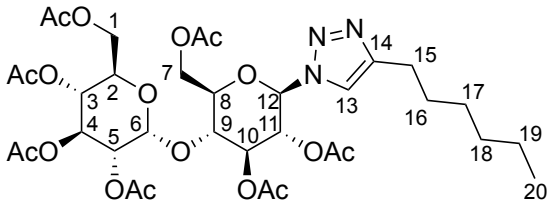
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 0.8 Hz, 1H, C<u>H</u>-13), 5.86 (d, *J* = 9.3 Hz, 1H, C<u>H</u>-12), 5.50 – 5.40 (m, 2H, C<u>H</u>-6 and C<u>H</u>-10), 5.43 – 5.28 (m, 2H, C<u>H</u>-4 and C<u>H</u>-11), 5.08 (t, *J* = 9.9 Hz, 1H, C<u>H</u>-3), 4.88 (dd, *J* = 10.6, 4.0 Hz, 1H, C<u>H</u>-5), 4.48 (dd, *J* = 12.4, 2.4 Hz, 1H, C<u>H$_a$H$_b$</u>-7), 4.27 (dd, *J* = 4.3, 3.0 Hz, 1H, C<u>H$_a$H$_b$</u>-1), 4.24 (t, *J* = 3.7 Hz, 1H, CH$_a$<u>H$_b$</u>-7), 4.17 – 4.11 (m, 1H, C<u>H</u>-9), 4.07 (dd, *J* = 12.6, 2.4 Hz, 1H, CH$_a$<u>H$_b$</u>-1), 4.00 – 3.94 (m, 2H, C<u>H</u>-2 and C<u>H</u>-8), 2.74 – 2.68 (m, 2H, C<u>H$_2$</u>-15), 2.13 (s, 3H, C<u>H$_3$</u>CO), 2.11 (s, 3H, C<u>H$_3$</u>CO), 2.07 (s, 3H, C<u>H$_3$</u>CO), 2.04 (s, 3H, C<u>H$_3$</u>CO), 2.03 (s, 3H, C<u>H$_3$</u>CO), 2.01 (s, 3H, C<u>H$_3$</u>CO), 1.64 (p, *J* = 7.6 Hz, 2H, C<u>H$_2$</u>-16), 1.39 – 1.32 (m, 2H, C<u>H$_2$</u>-17), 0.92 (t, *J* = 7.3 Hz, 3H, C<u>H$_2$</u>-18).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.68, 170.59, 170.44, 170.00 (2C), 169.52, 169.36, 149.18, 118.83, 95.97, 85.21, 75.35 (2C), 72.56, 70.94, 70.09, 69.29, 68.83, 67.99, 62.64, 61.52, 31.28, 25.35, 22.27, 20.92, 20.88, 20.79, 20.70 (3C), 20.25, 13.87.

HRMS (ESI) *m/z* calcd for $C_{32}H_{45}O_{17}N_3Na$ $[M+Na]^+$: 766.2641, found: 766.2632.

IR (ATR) ν (cm^{-1}) thin film, CH_2Cl_2: 2959 (w), 1748 (s), 1434 (w), 1369 (m), 1225 (s), 1036 (s), 899 (w).
$[\alpha]^{25}_D$ = +72.8 (c = 0.63, CH_2Cl_2).

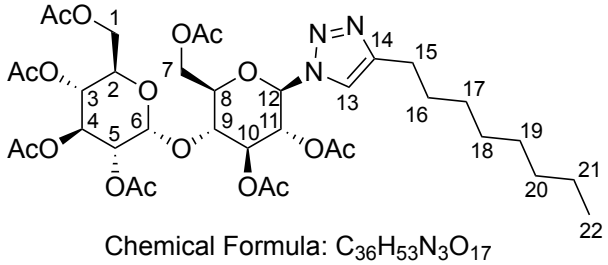
1-(Hepta-O-acetyl-1-deoxy-β-D-maltopyranosyl)-4-hexyl triazole (4b)



Chemical Formula: $C_{34}H_{49}N_3O_{17}$
Molecular Weight: 771.77

Synthesised according to general procedure 1 using maltose azide **1a** (1.00 g, 1.51 mmol), CuI (6 mg, 0.032 mmol), DIPEA (10 µL, 0.06 mmol), AcOH (3.5 µL, 0.06 mmol) and 1-octyne (230 µL, 1.6 mmol). Flash column chromatography (50% EtOAc in hexane) provided 1-(hepta-O-acetyl-1-deoxy-β-D-maltopyranosyl)-4-hexyl triazole **4b** (782 mg, 1.05 mmol, 67%) as a white foam.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H, C<u>H</u>-13), 5.85 (d, *J* = 9.3 Hz, 1H, C<u>H</u>-12), 5.48 – 5.42 (m, 2H, C<u>H</u>-6 and C<u>H</u>-10), 5.42 – 5.30 (m, 2H, C<u>H</u>-4 and C<u>H</u>-11), 5.07 (t, *J* = 9.9 Hz, 1H, C<u>H</u>-3), 4.88 (dd, *J* = 10.6, 4.0 Hz, 1H, C<u>H</u>-5), 4.48 (dd, *J* = 12.4, 2.4 Hz, 1H, C<u>H$_a$H$_b$</u>-7), 4.27 (t, *J* = 4.0 Hz, 1H, C<u>H$_a$H$_b$</u>-1), 4.24 (t, *J* = 4.0 Hz, 1H, CH$_a$<u>H$_b$</u>-7), 4.14 (dd, *J* = 9.8, 8.7 Hz, 1H, C<u>H</u>-9), 4.07 (dd, *J* = 12.4, 2.3 Hz, 1H, CH$_a$<u>H$_b$</u>-1), 4.01 – 3.93 (m, 2H, C<u>H</u>-2 and C<u>H</u>-8), 2.70 (dd, *J* = 8.6, 6.7 Hz, 2H, C<u>H$_2$</u>-15), 2.13 (s, 3H, C<u>H$_3$</u>CO), 2.11 (s, 3H, C<u>H$_3$</u>CO), 2.07 (s, 3H, C<u>H$_3$</u>CO), 2.03 (s, 3H, C<u>H$_3$</u>CO), 2.03 (s, 3H, C<u>H$_3$</u>CO), 2.01 (s, 3H, C<u>H$_3$</u>CO), 1.65 (p, *J* = 7.4 Hz, 2H, C<u>H$_2$</u>-16), 1.29 (m, 6H, (C<u>H$_2$</u>)$_3$-17,18,19), 0.90 – 0.85 (m, 3H, C<u>H$_2$</u>-20).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.67, 170.58, 170.42, 169.99 (2C), 169.51, 169.34, 149.22, 118.82, 96.00, 85.24, 75.39, 75.36, 72.62, 70.97, 70.11, 69.32, 68.86, 68.04, 62.67, 61.56, 31.62, 29.17, 28.86, 25.68, 22.64, 20.92, 20.87, 20.79, 20.70 (2C), 20.25, 14.14.
HRMS (ESI) *m/z* calcd for $C_{34}H_{49}O_{17}N_3Na$ $[M+Na]^+$: 794.2954, found: 794.2945.
Consistent with data in the literature.[4]

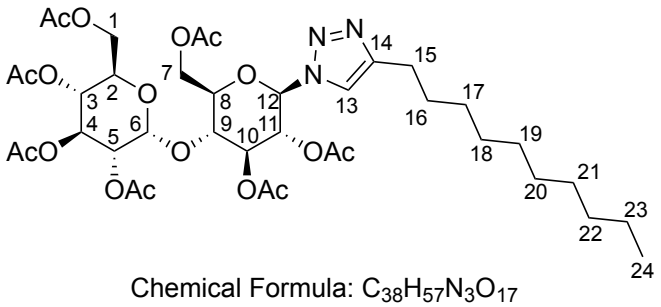
1-(Hepta-O-acetyl-1-deoxy-β-D-maltopyranosyl)-4-octyl triazole (4c)



Chemical Formula: $C_{36}H_{53}N_3O_{17}$
Molecular Weight: 799.82

Synthesised according to general procedure 1 using maltose azide **1a** (1.00 g, 1.51 mmol), CuI (6 mg, 0.032 mmol), DIPEA (10 µL, 0.06 mmol), AcOH (3.5 µL, 0.06 mmol) and 1-decyne (290 µL, 1.6 mmol). Flash column chromatography (50% EtOAc in hexane) provided 1-(hepta-O-acetyl-1-deoxy-β-D-maltopyranosyl)-4-octyl triazole **4c** (1.20 g, 1.50 mmol, quantitative yield) as a white foam.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H, C<u>H</u>-13), 5.86 (d, *J* = 9.3 Hz, 1H, C<u>H</u>-12), 5.48 – 5.42 (m, 2H, C<u>H</u>-6 and C<u>H</u>-10), 5.35 (m, 2H, C<u>H</u>-4 and C<u>H</u>-11), 5.08 (t, *J* = 9.8 Hz, 1H, C<u>H</u>-3), 4.88 (dd, *J* = 10.5, 4.0 Hz, 1H, C<u>H</u>-5), 4.48 (dd, *J* = 12.4, 2.4 Hz, 1H, C<u>H$_a$H$_b$</u>-7), 4.27 (t, *J* = 3.9 Hz, 1H, C<u>H$_a$H$_b$</u>-1), 4.24 (t, *J* = 4.0 Hz, 1H, CH$_a$<u>H$_b$</u>-7), 4.12 (dd, *J* = 9.8, 8.7 Hz, 1H, C<u>H</u>-9), 4.05 (dd, *J* = 12.5, 2.3 Hz, 1H, CH$_a$<u>H$_b$</u>-1), 3.97 (m, 2H, C<u>H</u>-2 and C<u>H</u>-8), 2.74 – 2.67 (m, 2H, C<u>H$_2$</u>-15), 2.13 (s, 3H, C<u>H$_3$</u>CO), 2.11 (s, 3H, C<u>H$_3$</u>CO), 2.07 (s, 3H, C<u>H$_3$</u>CO), 2.03 (s, 3H, C<u>H$_3$</u>CO), 2.03 (s, 3H, C<u>H$_3$</u>CO), 2.01 (s, 3H, C<u>H$_3$</u>CO), 1.84 (s, 3H, C<u>H$_3$</u>CO), 1.65 (m, 2H, C<u>H$_2$</u>-16), 1.36 – 1.21 (m, 10H, (C<u>H$_2$</u>)$_5$-17,18,19,20,21), 0.91 – 0.85 (m, 3H, C<u>H$_2$</u>-22).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.66, 170.58, 170.41, 169.99 (2C), 169.50, 169.32, 149.22, 118.81, 95.99, 85.23, 75.38, 75.35, 72.62, 70.96, 70.11, 69.32, 68.85, 68.04, 62.66, 61.56, 31.93, 29.38, 29.29, 29.22 (2C), 25.69, 22.74, 20.92, 20.86, 20.78, 20.69, 20.25, 14.18.
HRMS (ESI) *m/z* calcd for $C_{36}H_{54}O_{17}N_3$ $[M+H]^+$: 800.3448, found: 800.3441.
Consistent with data in the literature.[4]

1-(Hepta-O-acetyl-1-deoxy-β-D-maltopyranosyl)-4-decyl triazole (4d)



Chemical Formula: $C_{38}H_{57}N_3O_{17}$
Molecular Weight: 827.88

Synthesised according to general procedure 1 using maltose azide **1a** (1.00 g, 1.51 mmol), CuI (6 mg, 0.032 mmol), DIPEA (10 μL, 0.06 mmol), AcOH (3.5 μL, 0.06 mmol) and 1-dodecyne (340 μL, 1.6 mmol). Flash column chromatography (50% EtOAc in hexane) provided 1-(hepta-O-acetyl-1-deoxy-β-D-maltopyranosyl)-4-decyl triazole **4d** (1.01 g, 1.22 mmol, 81%) as a white foam.

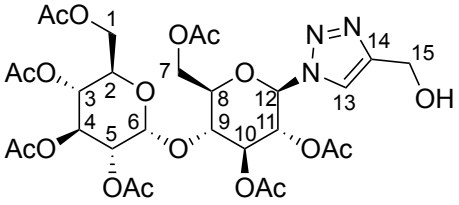
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 1H, C$\underline{H}$-13), 5.83 (d, J = 9.3 Hz, 1H, C$\underline{H}$-12), 5.45 – 5.40 (m, 2H, C$\underline{H}$-6 and C$\underline{H}$-10), 5.39 – 5.26 (m, 2H, C$\underline{H}$-4 and C$\underline{H}$-11), 5.04 (t, J = 9.9 Hz, 1H, C$\underline{H}$-3), 4.85 (dd, J = 10.5, 4.0 Hz, 1H, C$\underline{H}$-5), 4.45 (dd, J = 12.4, 2.4 Hz, 1H, C$\underline{H}_a$H$_b$-7), 4.24 (t, J = 4.1 Hz, 1H, C$\underline{H}_a$H$_b$-1), 4.21 (t, J = 4.1 Hz, 1H, CH$_a\underline{H}_b$-7), 4.11 (dd, J = 9.8, 8.6 Hz, 1H, C$\underline{H}$-9), 4.05 (dd, J = 12.5, 2.4 Hz, 1H, CH$_a\underline{H}_b$-1), 3.95 (ddd, J = 10.0, 4.6, 2.5 Hz, 2H, C$\underline{H}$-2 and C$\underline{H}$-8), 2.66 (dd, J = 8.6, 6.7 Hz, 2H, C$\underline{H}_2$-15), 2.10 (s, 3H, C$\underline{H}_3$CO), 2.08 (s, 3H, C$\underline{H}_3$CO), 2.04 (s, 3H, C$\underline{H}_3$CO), 2.00 (s, 3H, C$\underline{H}_3$CO), 2.00 (s, 3H, C$\underline{H}_3$CO), 1.98 (s, 3H, C$\underline{H}_3$CO), 1.81 (s, 3H, C$\underline{H}_3$CO), 1.62 (p, J = 7.7 Hz, 2H, C$\underline{H}_2$-16), 1.25 (m, 14H, (C$\underline{H}_2$)$_7$-17-23), 0.84 (t, J = 6.7 Hz, 3H, C$\underline{H}_2$-24).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.65, 170.55, 170.40, 169.98, 169.95, 169.48, 169.30, 149.21, 118.80, 95.98, 85.21, 75.37, 72.61, 70.95, 70.10, 69.30, 68.84, 68.03, 62.65, 61.55, 31.97, 29.66, 29.62, 29.42, 29.38, 29.22 (2C), 25.67, 22.75, 20.90, 20.85, 20.76, 20.67 (2C), 20.23, 14.19.

HRMS (ESI) *m/z* calcd for $C_{38}H_{57}O_{17}N_3Na$ $[M+Na]^+$: 850.3580, found: 850.3563.

Consistent with data in the literature.[4]

1-(Hepta-O-acetyl-1-deoxy-β-D-maltopyranosyl)-4-hydroxymethyl triazole (4e)



Chemical Formula: $C_{29}H_{39}N_3O_{18}$
Molecular Weight: 717.6340

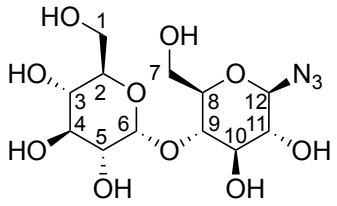
Synthesised according to general procedure 1 using maltose azide **1a** (1.00 g, 1.51 mmol), CuI (6 mg, 0.032 mmol), DIPEA (10 μL, 0.06 mmol), AcOH (3.5 μL, 0.06 mmol) and propargyl alcohol (96 μL, 1.7 mmol). Flash column chromatography (50% EtOAc in hexane) provided 1-(hepta-O-acetyl-1-deoxy-β-D-maltopyranosyl)-4-hydroxymethyl triazole **4e** (755 mg, 1.05 mmol, 70%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H, C$\underline{H}$-13), 5.89 (d, J = 9.3 Hz, 1H, C$\underline{H}$-12), 5.50 – 5.44 (m, 2H, C$\underline{H}$-6 and C$\underline{H}$-10), 5.41 – 5.31 (m, 2H, C$\underline{H}$-4 and C$\underline{H}$-11), 5.07 (t, J = 9.9 Hz, 1H, C$\underline{H}$-3), 4.88 (dd, J = 10.5, 4.0 Hz, 1H, C$\underline{H}$-5), 4.80 (d, J = 5.7 Hz, 2H, C$\underline{H}_2$OH-15), 4.49 (dd, J = 12.5, 2.4 Hz, 1H, C$\underline{H}_a$H$_b$-7), 4.28 – 4.22 (m, 2H, C$\underline{H}_a$H$_b$-1 and CH$_a\underline{H}_b$-7), 4.14 (m, 1H, C$\underline{H}$-9), 4.07 (dd, J = 12.4, 2.3 Hz, 1H, CH$_a\underline{H}_b$-1), 3.98 (m, 2H, C$\underline{H}$-2 and C$\underline{H}$-8), 2.19 (t, J = 6.1 Hz, 1H, CH$_2$O$\underline{H}$-15), 2.13 (s, 3H, C$\underline{H}_3$CO), 2.11 (s, 3H, C$\underline{H}_3$CO), 2.06 (s, 3H, C$\underline{H}_3$CO), 2.03 (s, 6H, C$\underline{H}_3$CO and C$\underline{H}_3$CO), 2.01 (s, 3H, C$\underline{H}_3$CO), 1.86 (s, 3H, C$\underline{H}_3$CO).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.72, 170.64, 170.46, 170.06 (2C), 169.56, 169.43, 120.16, 96.03, 85.41, 75.51, 75.27, 72.48, 71.06, 70.15, 69.35, 68.91, 68.06, 62.59, 61.58, 56.79, 20.97, 20.92, 20.84, 20.74 (3C), 20.37.

HRMS (ESI) *m/z* calcd for $C_{29}H_{39}O_{18}N_3Na$ $[M+Na]^+$: 740.2121, found: 740.2111.

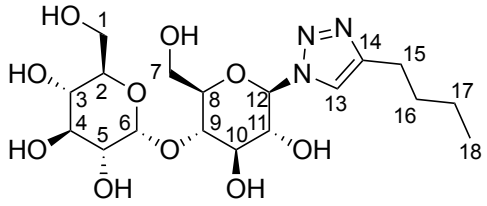
1-Deoxy-1-azido-β-D-maltopyranose (1b)



Chemical Formula: $C_{12}H_{21}N_3O_{10}$
Molecular Weight: 367.31

^{1}H NMR (400 MHz, D_2O) δ 5.37 (d, *J* = 3.9 Hz, 1H, C<u>H</u>-6), 4.71 (d, *J* = 8.8 Hz, 1H, C<u>H</u>-12), 3.92 – 3.87 (m, 1H, C<u>H</u>-11), 3.81 (dd, *J* = 12.1, 2.1 Hz, 1H, C<u>H</u>$_a$H$_b$-7), 3.75 (ddd, *J* = 12.9, 4.3, 2.3 Hz, 2H, C<u>H</u>$_a$H$_b$-1 and CH$_a$<u>H</u>$_b$-7), 3.71 – 3.61 (m, 6H, CH$_a$<u>H</u>$_b$-1 and C<u>H</u>-2 and C<u>H</u>-4 and C<u>H</u>-8 and C<u>H</u>-9 and C<u>H</u>-10), 3.53 (dd, *J* = 9.9, 3.9 Hz, 1H, C<u>H</u>-5), 3.37 (t, *J* = 9.4 Hz, 1H, C<u>H</u>-3), 3.25 (t, *J* = 9.1 Hz, 1H, C<u>H</u>-11).
^{13}C NMR (101 MHz, D_2O) δ 99.47, 89.86, 76.39, 76.12, 76.00, 72.73, 72.62 (2C), 71.56, 69.21, 60.42, 60.37.
HRMS (ESI) *m/z* calcd for $C_{12}H_{20}O_{10}N_3$ $[M-H]^-$: 366.1154, found: 366.1153.
Consistent with data in the literature.[4]

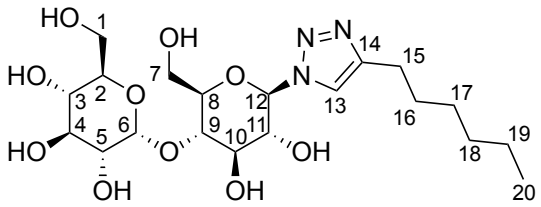
1-(1-Deoxy-β-D-maltopyranosyl)-4-butyl triazole (3a)



Chemical Formula: $C_{18}H_{31}N_3O_{10}$
Molecular Weight: 449.46

Synthesised according to general procedure 2 using protected surfactant **4a** (986 mg, 1.33 mmol) and NaOMe (40 mg, 0.74 mmol). After concentration *in vacuo* surfactant 1-(1-deoxy-β-D-maltopyranosyl)-4-butyl triazole **3a** (422 mg, 0.939 mmol, 71%) was obtained as a hygroscopic, off white foam.
^{1}H NMR (400 MHz, D_2O) δ 7.89 (s, 1H, C<u>H</u>-13), 5.62 – 5.58 (m, 1H, C<u>H</u>-12), 5.36 (d, *J* = 3.9 Hz, 1H, C<u>H</u>-6), 3.90 – 3.85 (m, 2H, C<u>H</u>-11 and C<u>H</u>-4), 3.79 (d, *J* = 11.6 Hz, 1H, C<u>H</u>$_a$H$_b$-7), 3.78 – 3.70 (m, 5H, CH$_a$<u>H</u>$_b$-7 and C<u>H</u>$_a$H$_b$-1 and CH$_a$<u>H</u>$_b$-1 and C<u>H</u>-2 and C<u>H</u>-10), 3.69 – 3.56 (m, 3H, C<u>H</u>4 and C<u>H</u>-8 and C<u>H</u>-9), 3.48 (dd, *J* = 9.9, 3.9 Hz, 1H, C<u>H</u>-5), 3.31 (t, *J* = 9.4 Hz, 1H, C<u>H</u>-3), 2.62 (t, *J* = 7.4 Hz, 2H, C<u>H</u>-15), 1.51 (p, *J* = 7.5 Hz, 2H, C<u>H</u>$_2$-16), 1.25 – 1.13 (m, 2H, C<u>H</u>$_2$-17), 0.77 (t, *J* = 7.4 Hz, 3H, C<u>H</u>$_3$-18).
^{13}C NMR (101 MHz, D_2O) δ 148.93, 122.17, 99.53, 87.12, 77.36, 76.34, 75.62, 72.74, 72.68, 72.04, 71.60, 69.22, 60.37, 60.30, 30.53, 23.98, 21.27, 12.92.
HRMS (ESI) *m/z* calcd for $C_{18}H_{31}O_{10}N_3Na$ $[M+Na]^+$: 472.1902, found: 472.1900.
IR (ATR) ν (cm^{-1}) thin film, MeOH: 3350 (s), 2931 (m), 2360 (w), 1653 (w), 1457 (m), 1041 (s).
$[\alpha]^{25}_D$ = +73.6 (c = 1.00, MeOH).

1-(1-Deoxy-β-D-maltopyranosyl)-4-hexyl triazole (3b)



Chemical Formula: $C_{20}H_{35}N_3O_{10}$
Molecular Weight: 477.51

Synthesised according to general procedure 2 using protected surfactant **4b** (782 mg, 1.01 mmol) and NaOMe (20 mg, 0.37 mmol). After concentration *in vacuo* 1-(1-deoxy-β-D-maltopyranosyl)-4-hexyl triazole **3b** (405 mg, 0.848 mmol, 84%) was obtained as a hygroscopic, off white foam.

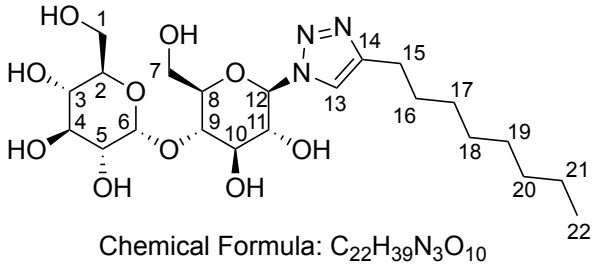
^{1}H NMR (400 MHz, D_2O) δ 7.85 (s, 1H, C<u>H</u>-13), 5.60 – 5.55 (m, 1H, C<u>H</u>-12), 5.34 (d, *J* = 3.9 Hz, 1H, C<u>H</u>-6), 3.92 – 3.54 (m, 10H, C<u>H</u>-11, C<u>H</u>-10, C<u>H$_2$</u>-1, C<u>H$_2$</u>-7, C<u>H$_2$</u>-3, C<u>H</u>-4, C<u>H</u>-8, C<u>H</u>-9), 3.47 (dd, *J* = 9.9, 3.8 Hz, 1H, C<u>H</u>-5), 3.31 (t, *J* = 9.3 Hz, 1H, C<u>H</u>-2), 2.55 (t, *J* = 7.5 Hz, 2H, C<u>H$_2$</u>-15), 1.49 (t, *J* = 7.2 Hz, 2H, C<u>H$_2$</u>-16), 1.46 –1.25 (m, 6H, (C<u>H$_2$</u>)$_3$-17,18,19), 0.71 (d, *J* = 6.5 Hz, 3H, C<u>H$_3$</u>-20).

^{13}C NMR (101 MHz, D_2O) δ 122.14, 99.63, 87.19, 77.37, 76.36, 75.77, 72.78, 72.68, 72.05, 71.64, 69.22, 60.38, 60.31, 30.86, 28.37, 27.98, 24.45, 21.98, 13.40.

HRMS (ESI) *m/z* calcd for $C_{20}H_{36}O_{10}N_3$ $[M+H]^+$: 478.2395, found: 478.2392.

Consistent with data in the literature.[4]

1-(1-Deoxy-β-D-maltopyranosyl)-4-octyl triazole (3c)



Chemical Formula: $C_{22}H_{39}N_3O_{10}$
Molecular Weight: 505.57

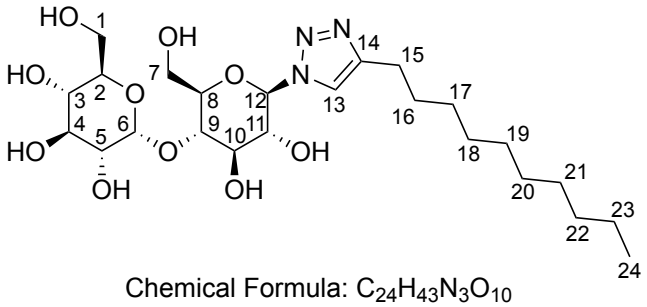
Synthesised according to general procedure 2 using protected surfactant **4c** (2.15 g, 2.79 mmol) and NaOMe (40 mg, 0.74 mmol). After concentration *in vacuo* 1-(1-deoxy-β-D-maltopyranosyl)-4-octyl triazole **3c** (1.30 g, 2.58 mmol, 92%) was obtained as a hygroscopic, off white foam.

^{1}H NMR (400 MHz, D_2O) δ 7.85 (s, 1H, C<u>H</u>-13), 5.50 (d, *J* = 7.7 Hz, 1H, C<u>H</u>-12), 5.33 – 5.27 (m, 1H, C<u>H</u>-6), 3.90 – 3.68 (m, 4H, C<u>H</u>-11 and C<u>H</u>-10 and CH$_a$<u>H$_b$</u>-7 and C<u>H$_a$</u>H$_b$-1), 3.68 – 3.48 (m, 6H, CH$_a$<u>H$_b$</u>-7 and CH$_a$<u>H$_b$</u>-1 and C<u>H</u>-3 and C<u>H</u>-4 and C<u>H</u>-8 and C<u>H</u>-9), 3.47 – 3.38 (m, 1H, C<u>H</u>-5), 3.34 – 3.27 (m, 1H, C<u>H</u>-2,), 2.42 (m, 2H, C<u>H$_2$</u>-15), 1.43 (m, 2H, C<u>H$_2$</u>-16), 1.13 (m, 10H, (C<u>H$_2$</u>)$_5$-17,18,19,20,21), 0.72 (t, *J* = 6.0 Hz, 3H, C<u>H$_3$</u>-22).

^{13}C NMR (101 MHz, D_2O) δ 147.80, 125.66, 99.87, 87.31, 77.38, 76.42 (2C), 72.84 (2C), 72.05, 71.98, 69.14, 62.39, 60.39, 31.77, 29.24 (3C), 28.78, 24.95, 22.51, 13.73. HRMS (ESI) *m/z* calcd for $C_{22}H_{39}O_{10}N_3Na$ $[M+Na]^+$: 528.2528, found: 528.2525.

Consistent with data in the literature.[4]

1-(1-Deoxy-β-D-maltopyranosyl)-4-decyl triazole (3d)



Chemical Formula: $C_{24}H_{43}N_3O_{10}$
Molecular Weight: 533.62

Synthesised according to general procedure 2 using protected surfactant **4d** (1.09 g, 1.32 mmol) and NaOMe (40 mg, 0.74 mmol). After concentration *in vacuo* 1-(1-deoxy-β-D-maltopyranosyl)-4-decyl triazole **3d** (643 mg, 1.20 mmol, 92%) was obtained as a hygroscopic, off white foam.

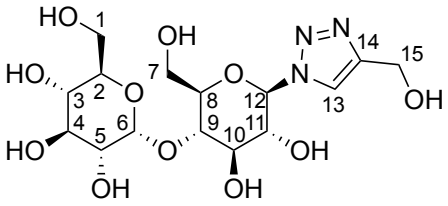
^{1}H NMR (400 MHz, MeOD) δ 7.94 (s, 1H, C<u>H</u>-13), 5.56 (d, *J* = 9.1 Hz, 1H, C<u>H</u>-12), 5.20 (d, *J* = 3.8 Hz, 1H, C<u>H</u>-6), 3.91 (t, *J* = 9.1 Hz, 1H, C<u>H</u>-11), 3.83 – 3.77 (m, 4H, C<u>H$_a$</u>H$_b$-1 and C<u>H$_2$</u>-7 and C<u>H</u>-11), 3.75 – 3.68 (m, 1H, CH$_a$<u>H$_b$</u>-1), 3.68 – 3.62 (m, 3H, C<u>H</u>-3 and C<u>H</u>-4 and C<u>H</u>-8), 3.62 – 3.57 (m, 1H, C<u>H</u>-9), 3.44 (dd, *J* = 9.7, 3.7 Hz, 1H, C<u>H</u>-5), 3.27 (t, *J* = 9.3 Hz, 1H, C<u>H</u>-2), 2.67 (t, *J* = 7.6 Hz, 2H, C<u>H$_2$</u>-15), 1.68 – 1.58 (m, 2H, C<u>H$_2$</u>-16), 1.36 – 1.19 (m, 14,H, (C<u>H$_2$</u>)$_7$-17-23), 0.88 – 0.83 (m, 3H, C<u>H$_3$</u>-24).

^{13}C NMR (101 MHz, MeOD) δ 122.52, 102.90, 89.34, 80.25, 79.54, 78.23, 75.04, 74.85, 74.15, 73.54, 71.45, 62.70, 61.81, 33.05, 30.73, 30.68, 30.49 (2C), 30.45, 30.26, 26.26, 23.72, 14.44.

HRMS (ESI) *m/z* calcd for $C_{24}H_{43}O_{10}N_3Na$ $[M+Na]^+$: 556.2841, found: 556.2841.

Consistent with data in the literature.[4]

1-(1-Deoxy-β-D-maltopyranosyl)-4-hydroxymethyl triazole (3e)



Chemical Formula: $C_{15}H_{25}N_3O_{11}$
Molecular Weight: 423.3750

Synthesised according to general procedure 2 using protected surfactant **4e** (755 mg, 1.05 mmol) and NaOMe (20 mg, 0.37 mmol). After concentration *in vacuo* 1-(1-deoxy-β-D-maltopyranosyl)-4-hydroxymethyl triazole **3e** (338 mg, 0.798 mmol, 76%) was obtained as a hygroscopic, off white foam.

^{1}H NMR (400 MHz, MeOD) δ 8.13 (s, 1H, C<u>H</u>-13), 5.61 (d, *J* = 9.1 Hz, 1H, C<u>H</u>-12), 5.22 (d, *J* = 3.8 Hz, 1H, C<u>H</u>-6), 4.68 (bs, 2H, C<u>H$_2$</u>OH-15), 3.92 (t, *J* = 9.1 Hz, 1H, C<u>H</u>-11), 3.89 – 3.78 (m, 4H, C<u>H$_a$H$_b$</u>-1 and C<u>H$_2$</u>-7 and C<u>H</u>-11), 3.74 (t, *J* = 9.0 Hz, 1H, CH$_a$<u>H$_b$</u>-1), 3.70 – 3.65 (m, 2H, C<u>H</u>-3 and C<u>H</u>-8), 3.65 – 3.57 (m, 2H, C<u>H</u>-4 and C<u>H</u>-9), 3.45 (dd, *J* = 9.7, 3.8 Hz, 1H, C<u>H</u>-5), 3.26 – 3.23 (m, 1H, CH$_2$O<u>H</u>-15).
^{13}C NMR (101 MHz, MeOD) δ 147.58, 122.05, 101.55, 88.10, 78.87, 78.23, 76.81, 73.67, 73.49, 72.78, 72.23, 70.08, 61.33, 60.43, 54.95.
HRMS (ESI) *m/z* calcd for $C_{15}H_{25}O_{11}N_3Na$ $[M+Na]^+$: 446.1381, found: 446.1379.

NMR Spectra of Synthesized Compounds

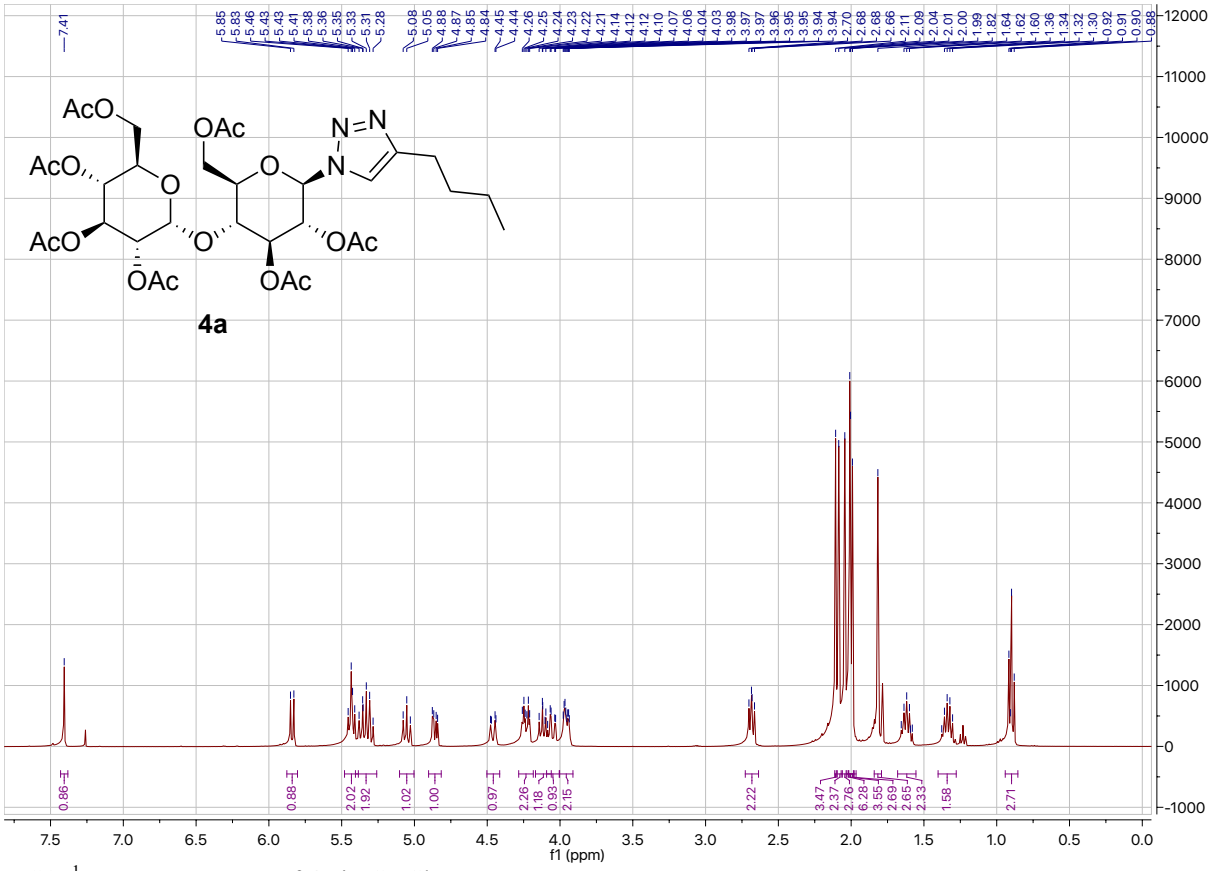


Figure S1: ^{1}H NMR spectrum of **4a** in $CDCl_3$.

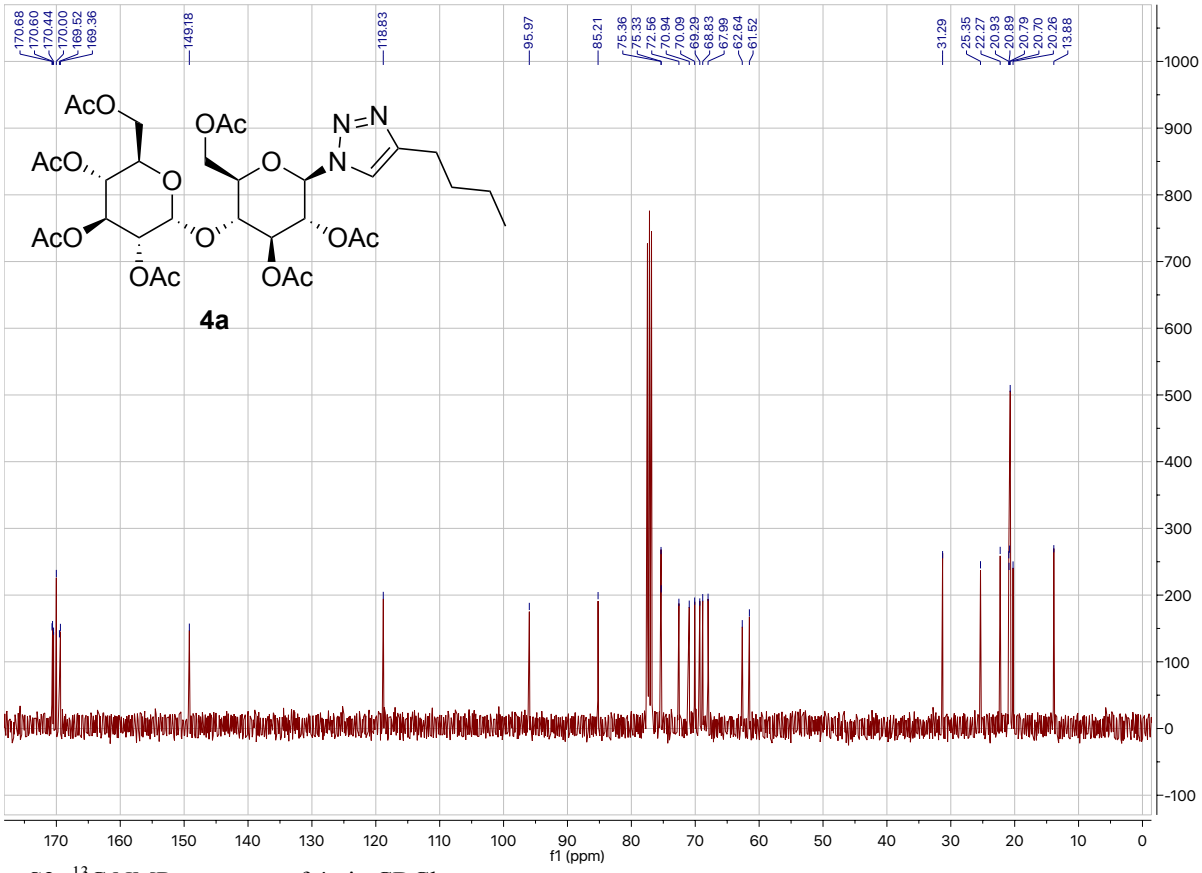


Figure S2: ^{13}C NMR spectrum of **4a** in $CDCl_3$.

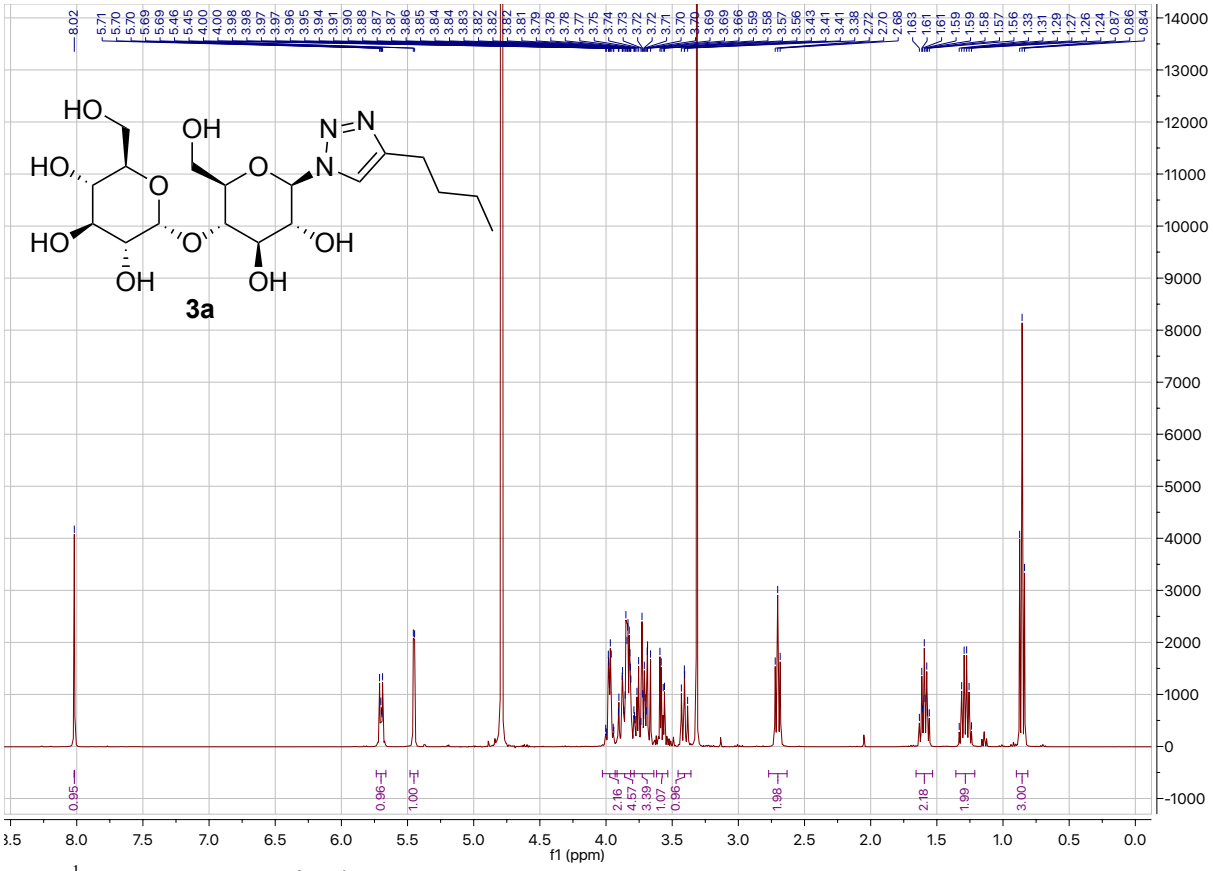


Figure S3: ^{1}H NMR spectrum of **3a** in MeOD.

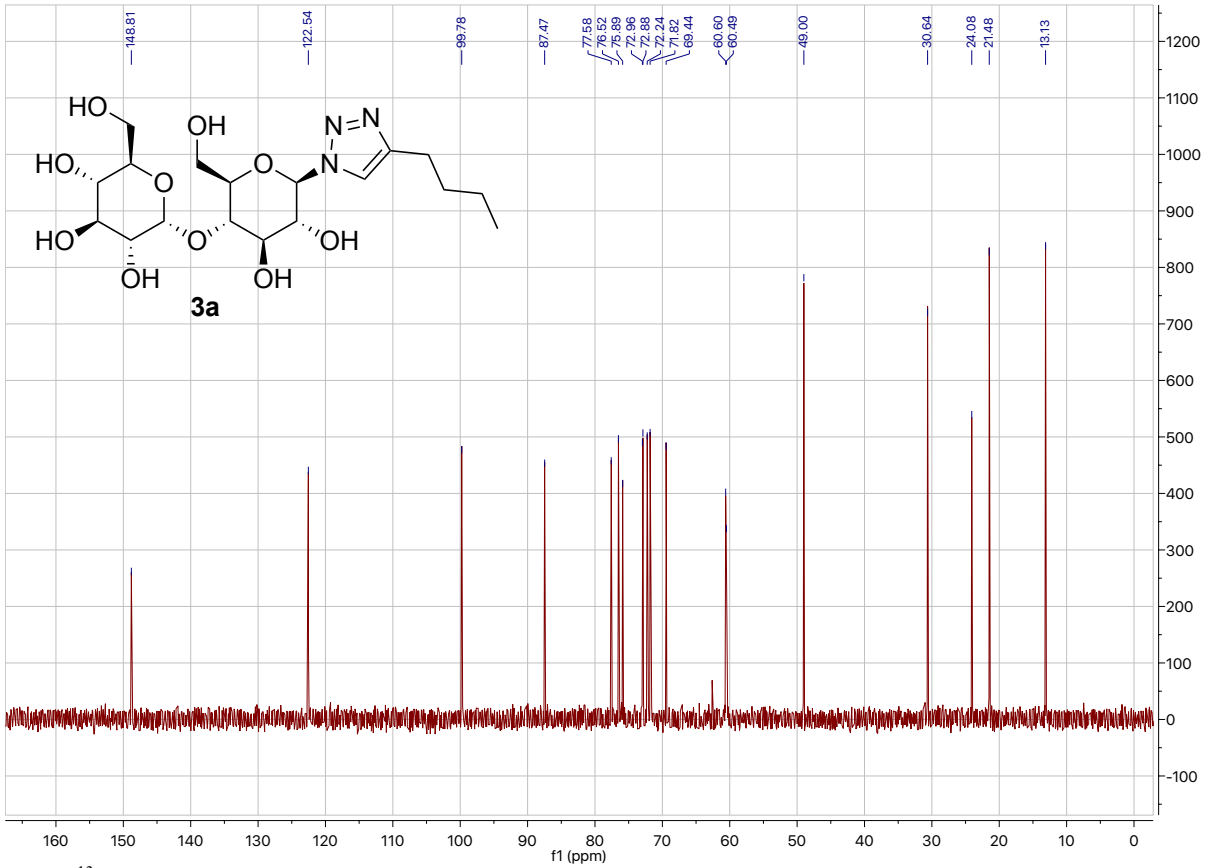


Figure S4: ^{13}C NMR spectrum of **3a** in MeOD.

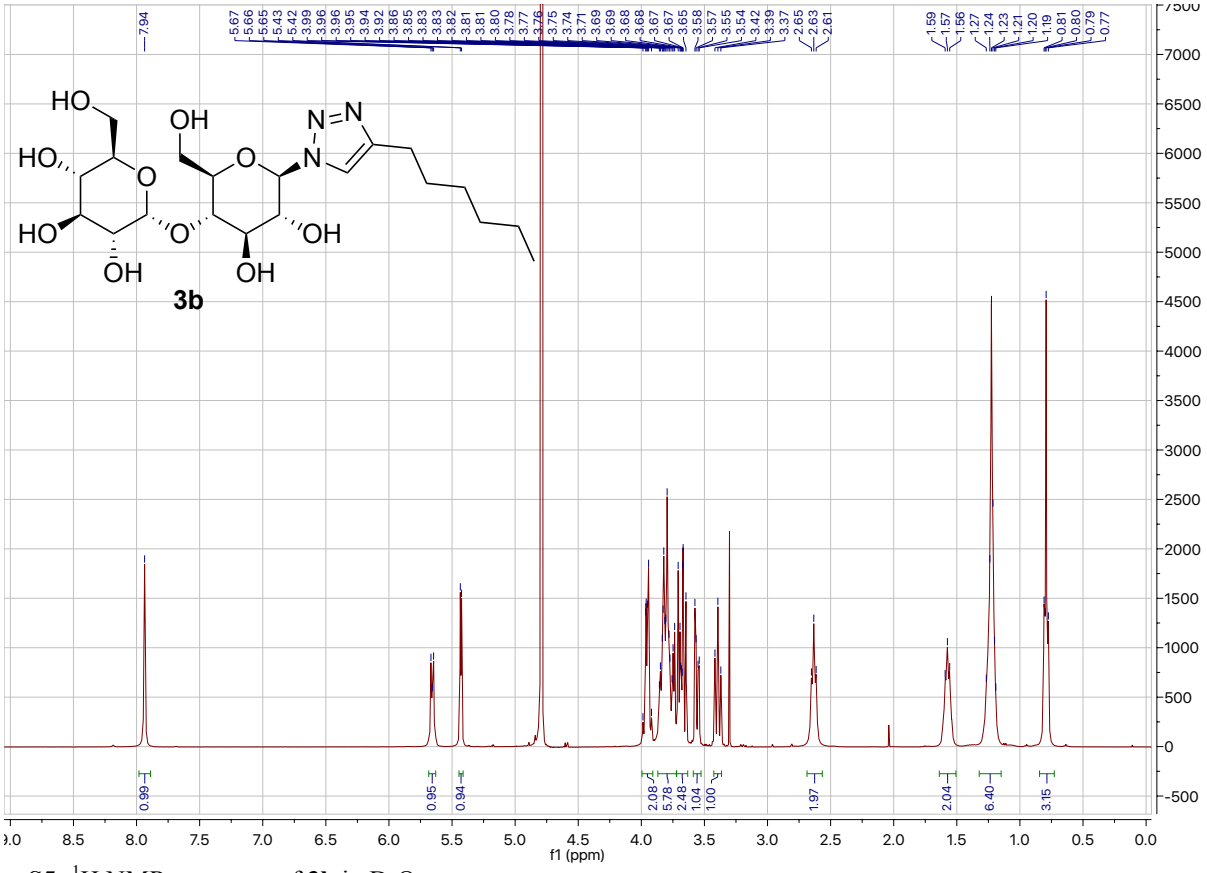


Figure S5: ^{1}H NMR spectrum of **3b** in D_2O.

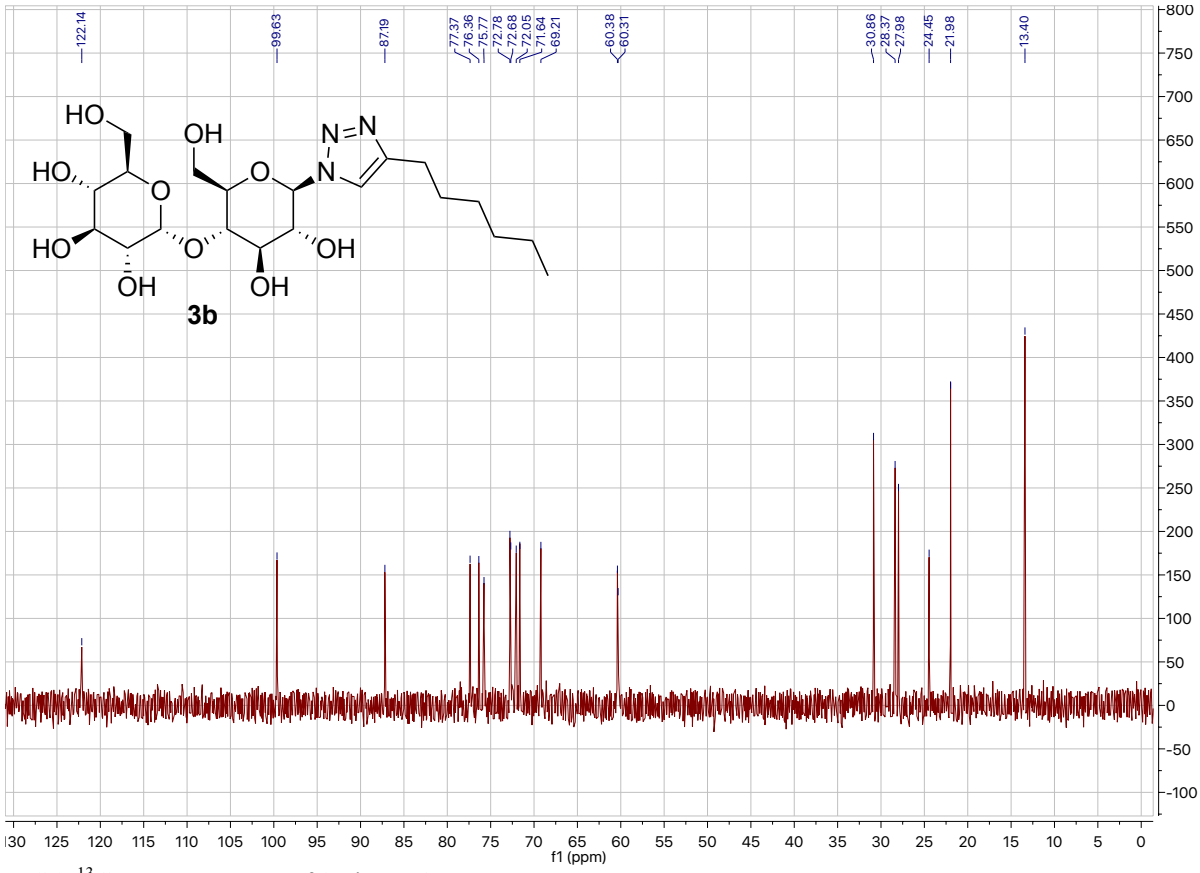


Figure S6: ^{13}C NMR spectrum of **3b** in MeOD.

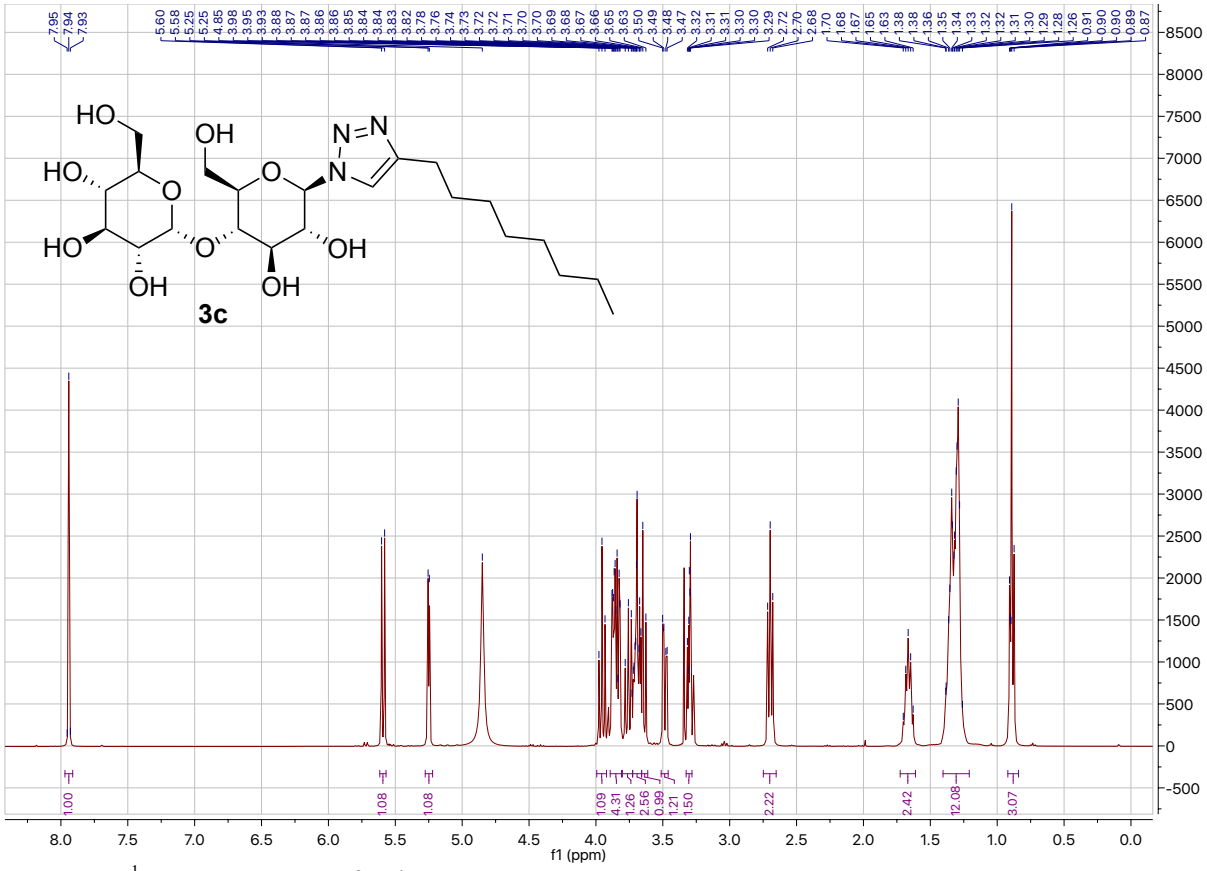


Figure S7: ^{1}H NMR spectrum of **3c** in MeOD.

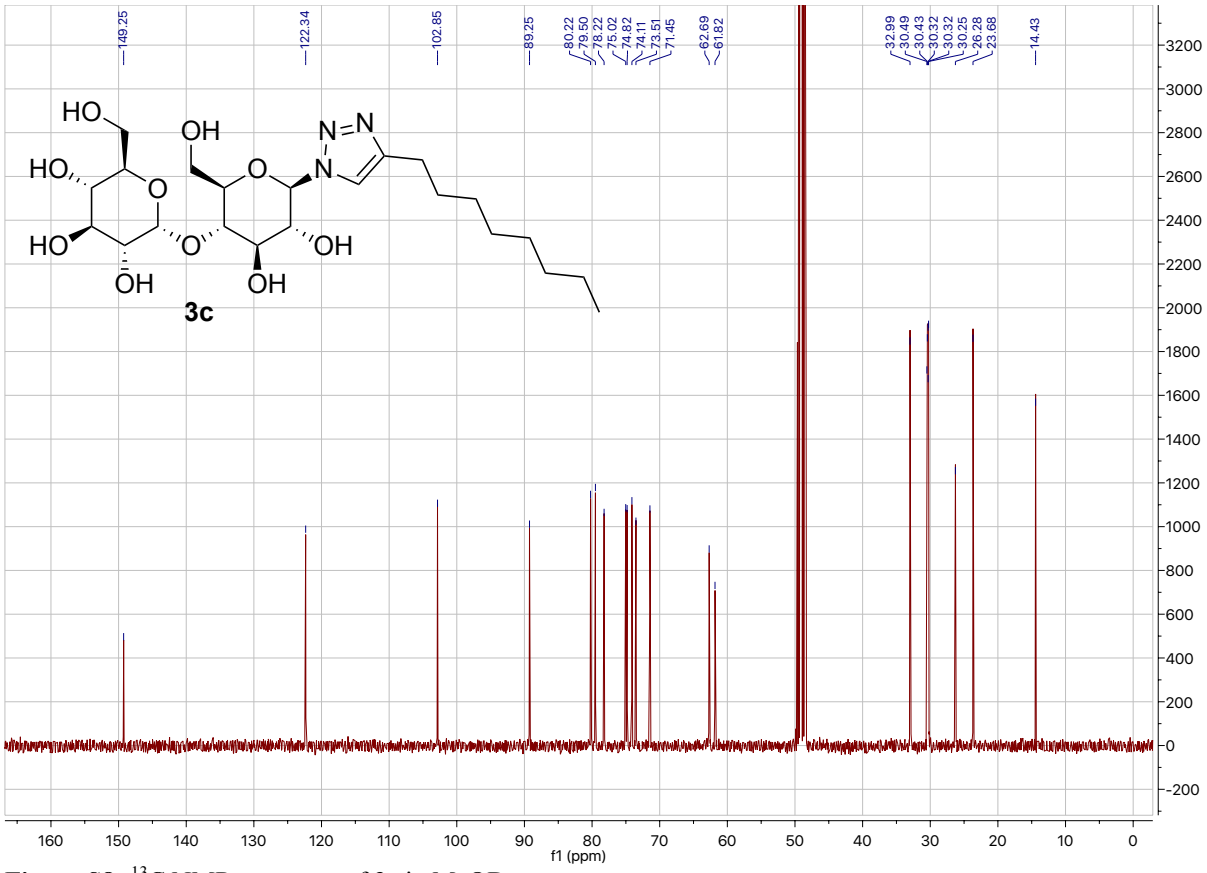


Figure S8: ^{13}C NMR spectrum of **3c** in MeOD.

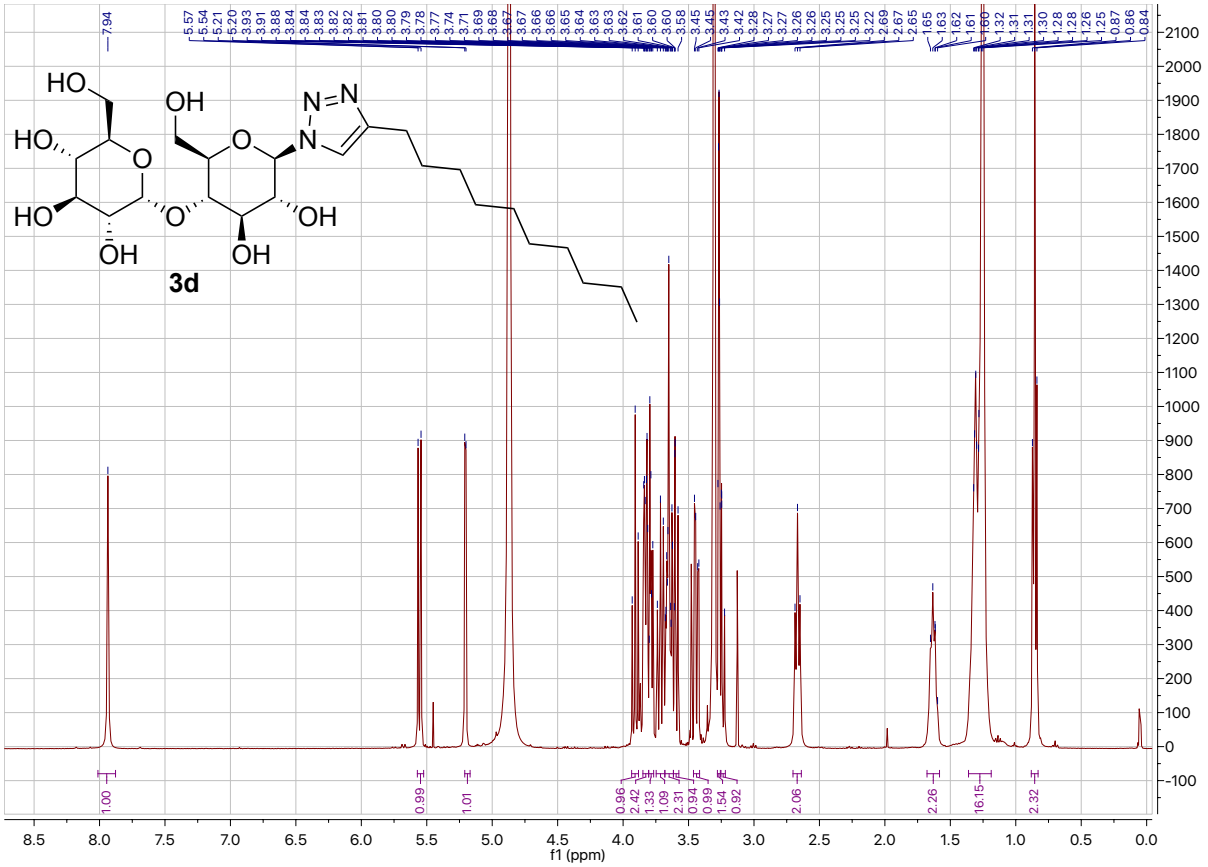


Figure S9: ^{1}H NMR spectrum of **3d** in MeOD.

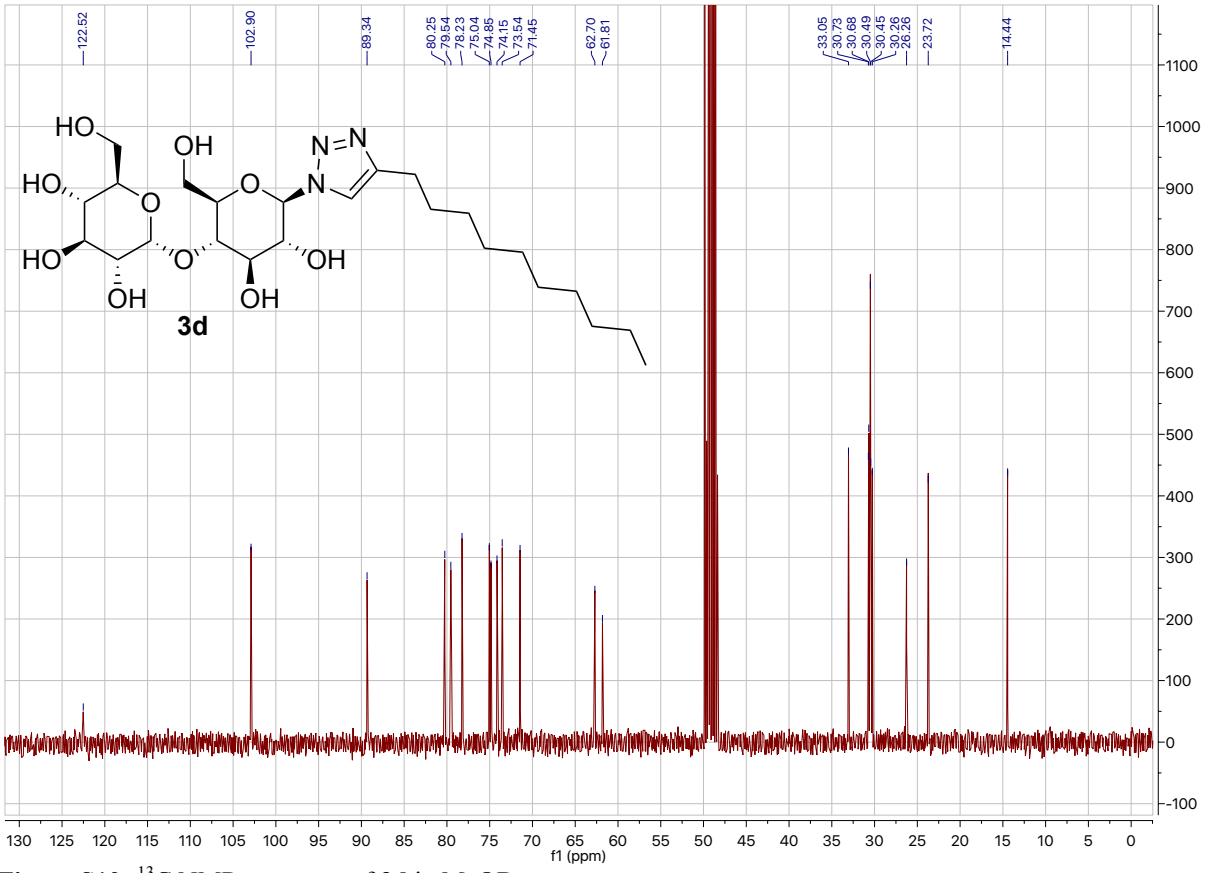


Figure S10: ^{13}C NMR spectrum of **3d** in MeOD.

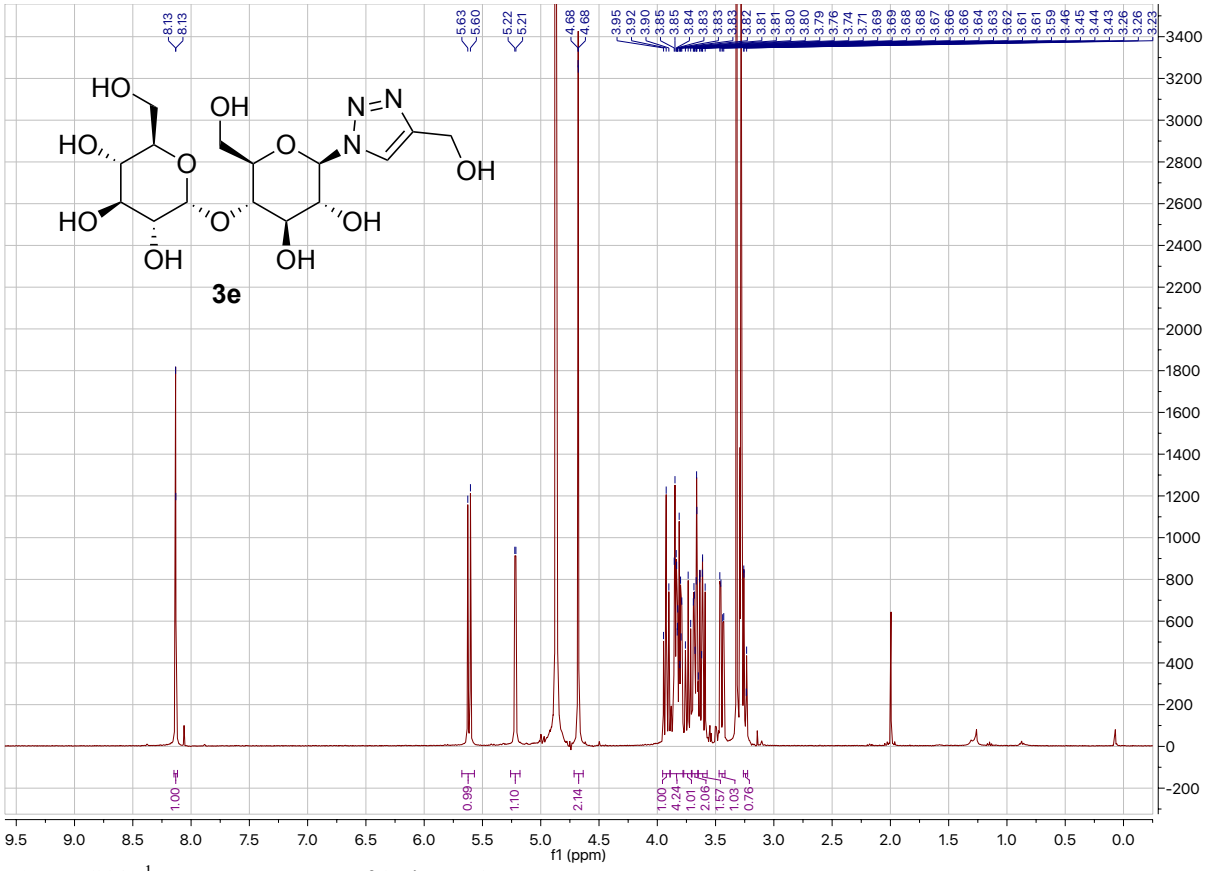


Figure S11: ^{1}H NMR spectrum of **3e** in MeOD.

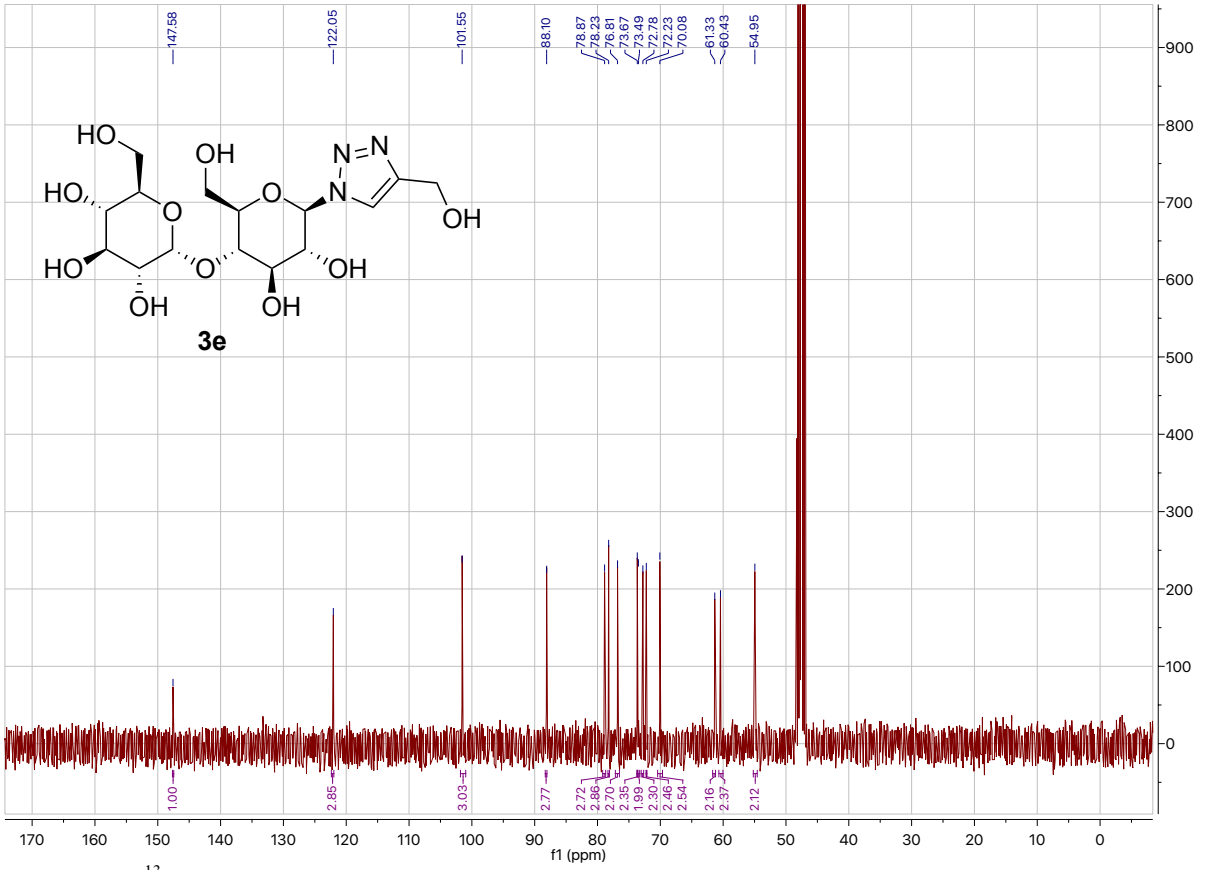


Figure S12: ^{13}C NMR spectrum of **3e** in MeOD.

DOSY Data

Entry	Species present	*D* (surfactant 3c)	*D* (1-decyne)	*D* (ligand)	*D* (azide 2b)	*D* (TMS)
A	Surfactant **3c** (2 mM)	3.6	-	-	-	8.2
B	Surfactant **3c** (24 mM)	1.3	-	-	-	1.2
C	Surfactant **3c** (2 mM) 1-Decyne (saturated)	3.8	ND	-	-	4.1
D	Surfactant **3c** (24 mM) 1-Decyne (saturated)	1.3	0.58	-	-	1.1
E	Lig **A** (saturated)	-	-	9.1	-	7.0
F	$[Cu(Lig\ \mathbf{A})_2]^+$ (6.8 mM)	-	-	5.8	-	13
G	Surfactant **3c** (2 mM) $[Cu(Lig\ \mathbf{A})_2]^+$ (6.8 mM)	3.7	-	5.7	-	8.0
H	Surfactant **3c** (24 mM) $[Cu(Lig\ \mathbf{A})_2]^+$ (6.8 mM)	1.3	-	5.7	-	1.6
I	Azide **2b** (91 mM)	-	-	-	4.3	-
J	Surfactant **3c** (2 mM) Azide **2b** (91 mM)	3.6	-	-	4.4	7.6
K	Surfactant **3c** (24 mM) Azide **2b** (91 mM)	1.2	-	-	4.9	1.2

Table S1: Diffusion coefficients extracted from DOSY experiments. The diffusion coefficients were recorded for all reaction components present in the system during the synthesis of **3c** in water. *D* values reported in 10^{-10} m^2s^{-1}. A decrease in the diffusion coefficient in the presence of surfactant **3c** above the CMC indicates a strong association with the micelle. ND indicates that the diffusion coefficient could not be extracted because of the limited solubility of the compound in water. The Morris' correlation[5] for small molecules predicts a MW of 516 g/mol for entry **A** and a MW of 339.5 g/mol for entry **I**. These predicted values are in close agreement with the actual molecular weights considering the model used for the predictions.

Fluorimetry Data

The critical micelle concentrations of the surfactants was determined with a fluorimetric procedure reported by London *et al*.[6] The fluorescent molecule 1,6-diphenyl-1,3,5-hexatriene (DPH) emits a large increase in fluorescence when present in an apolar environment such as the micellar interior when a surfactant exceeds the critical micelle concentration. This property was used to determine the unknown CMC of various surfactant compounds. Fluorescence measurements were made with an Edinburgh Instruments Spectrofluorometer FS5 model. Instrument control and data processing were performed using Fluoracle software. The excitation wavelength was 358 nm and the emission wavelength was 430 nm. The excitation and emission slits were set at bandwidths of 1 nm. In all experiments, 1 cm path length quartz cuvettes were used. The protocol for CMC determination was as follows: 3 μL of 5 mM DPH dissolved in THF was added to various amounts of surfactant dissolved in a total volume of 3 ml of aqueous solution. The intercept of two trendlines, through the data points before and after the spike in fluorescence, was taken as the CMC.

Note: No increase in fluorescence was observed for surfactant **3a** indicating that a 4-carbon aliphatic tail is likely too short to induce aggregation.

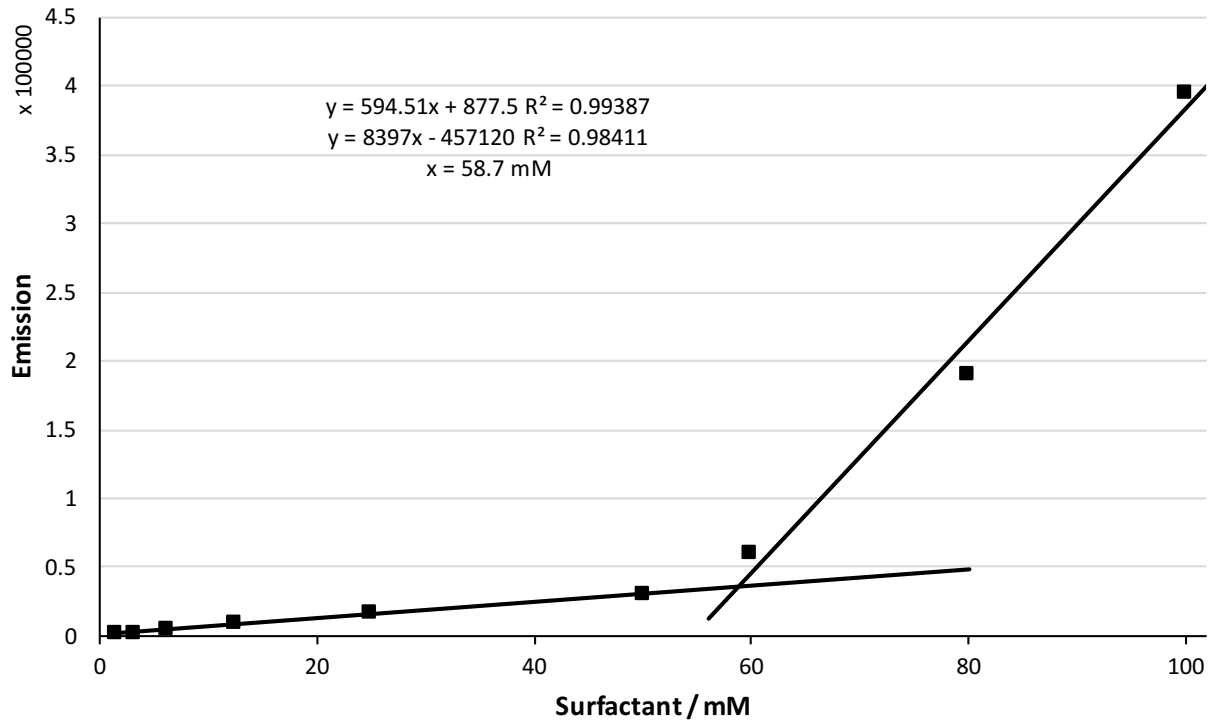


Figure S13: a CMC of 58.7 mM was extracted from a plot of fluorescence measurements at various concentrations for surfactant **3b**.

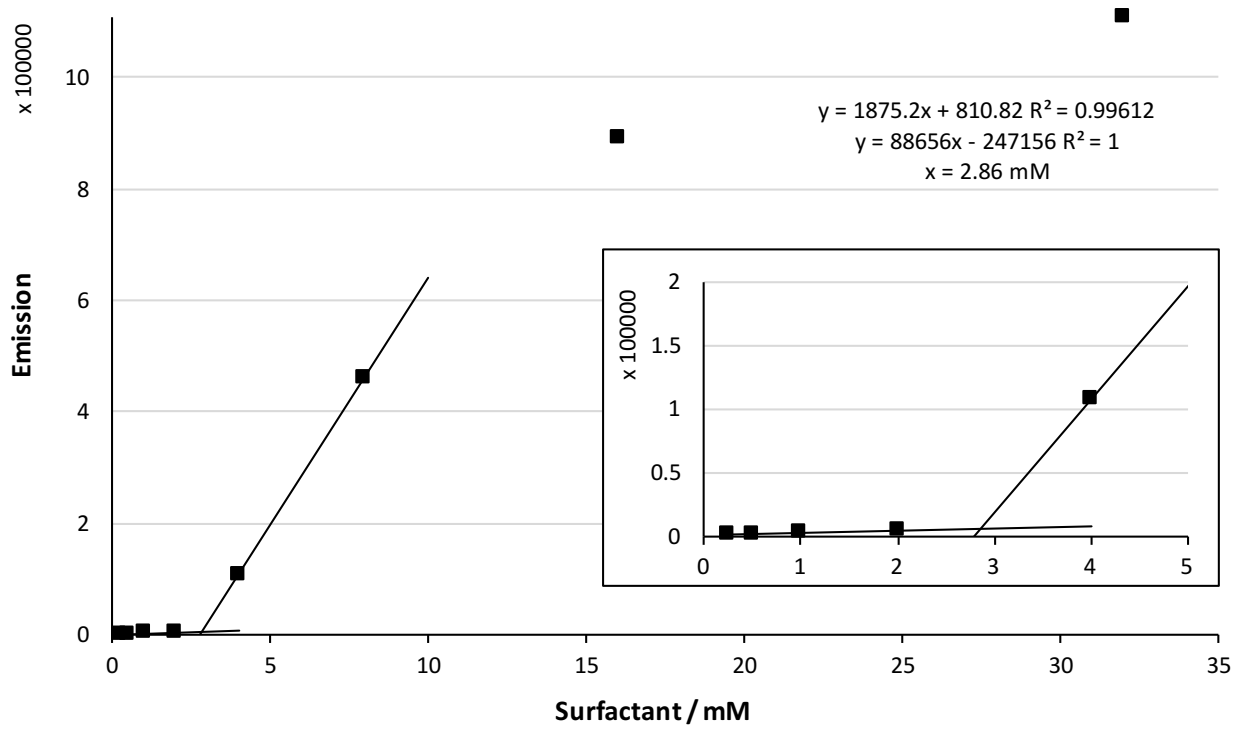


Figure S14: a CMC of 2.86 mM was extracted from a plot of fluorescence measurements at various concentrations for surfactant **3c**.

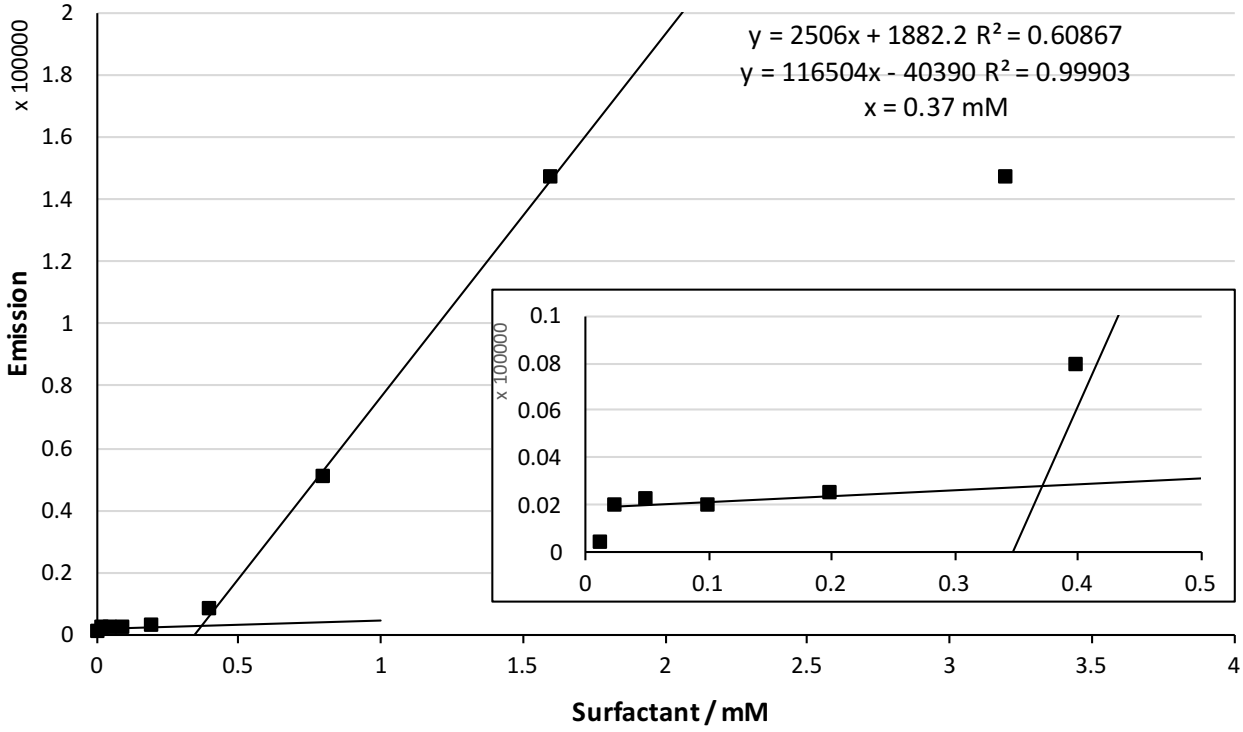


Figure S15: a CMC of 0.37 mM was extracted from a plot of fluorescence measurements at various concentrations for surfactant **3d**.

DLS data

Samples were prepared by dissolving an amount of surfactant in 1 mL of ultrapure Milli-Q water at a concentration above the CMC. This solution was filtered through a 0.2 µm PTFE filter right before performing a DLS measurement.

Note: DLS results for surfactant **3a** showed no aggregation around 10 nm only around 100 nm which can likely be attributed to noise. This is in agreement with the fluorimetry data and indicates that a 4-carbon aliphatic tail is likely too short to induce aggregation.

Sample Name:	EPoctyne52mM 1		
SOP Name:	Standard method.sop		
File Name:	Hexyne+Dodecyne surfactants 08-02-2...	**Dispersant Name:**	Water
Record Number:	11	**Dispersant RI:**	1.330
Material RI:	1.45	**Viscosity (cP):**	0.8872
Material Absorbtion:	0.001	**Measurement Date and Time:**	08 February 2017 10:39 am

Temperature (°C):	25.0	**Duration Used (s):**	70
Count Rate (kcps):	246.6	**Measurement Position (mm):**	3.00
Cell Description:	Disposable micro cuvette (40µl)	**Attenuator:**	9

			Size (d.nm):	**% Intensity:**	**St Dev (d.nm):**
Z-Average (d.nm):	6.744	**Peak 1:**	7.168	93.4	2.824
PdI:	0.238	**Peak 2:**	3533	6.6	1226
Intercept:	0.758	**Peak 3:**	0.000	0.0	0.000
Result quality :	Good				

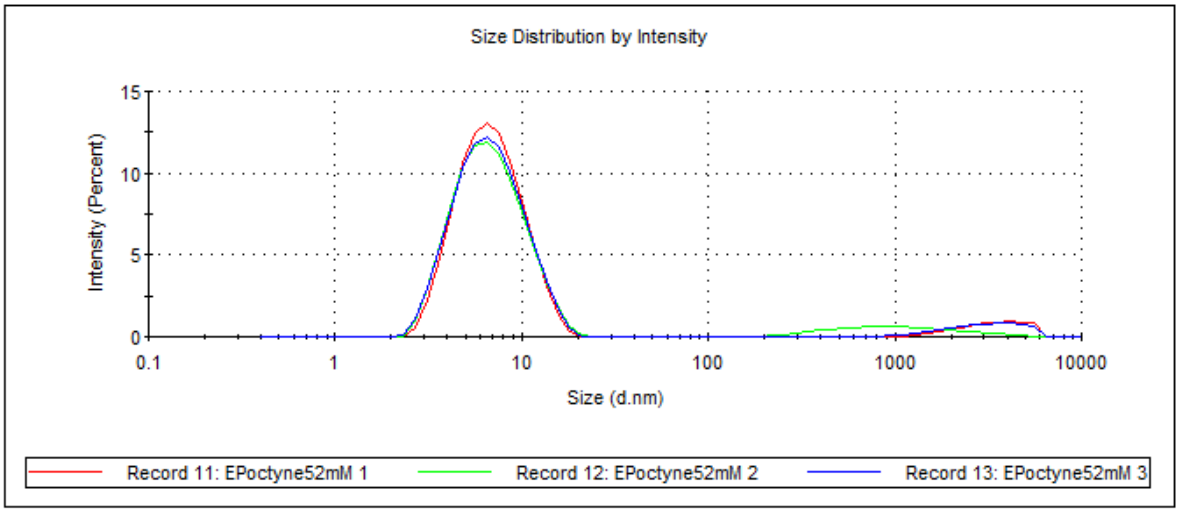


Figure S16: The size distribution by intensity of a DLS measurement of surfactant **3b** at 52 mM indicates micelle aggregates with a size of around 7 nm.

Sample Name:	EP_decyne_24mM 1		
SOP Name:	mansettings.nano		
File Name:	Sarah.dts	**Dispersant Name:**	Water
Record Number:	61	**Dispersant RI:**	1.330
Material RI:	1.59	**Viscosity (cP):**	0.8872
Material Absorbtion:	0.010	**Measurement Date and Time:**	19 December 2016 1:45 pm

Temperature (°C):	25.0	**Duration Used (s):**	60
Count Rate (kcps):	377.7	**Measurement Position (mm):**	3.00
Cell Description:	Disposable micro cuvette (40µl)	**Attenuator:**	11

			Size (d.nm):	**% Intensity:**	**St Dev (d.nm):**
Z-Average (d.nm):	6.983	**Peak 1:**	7.541	90.5	3.117
PdI:	0.260	**Peak 2:**	1543	9.5	960.0
Intercept:	0.730	**Peak 3:**	0.000	0.0	0.000
Result quality :	Good				

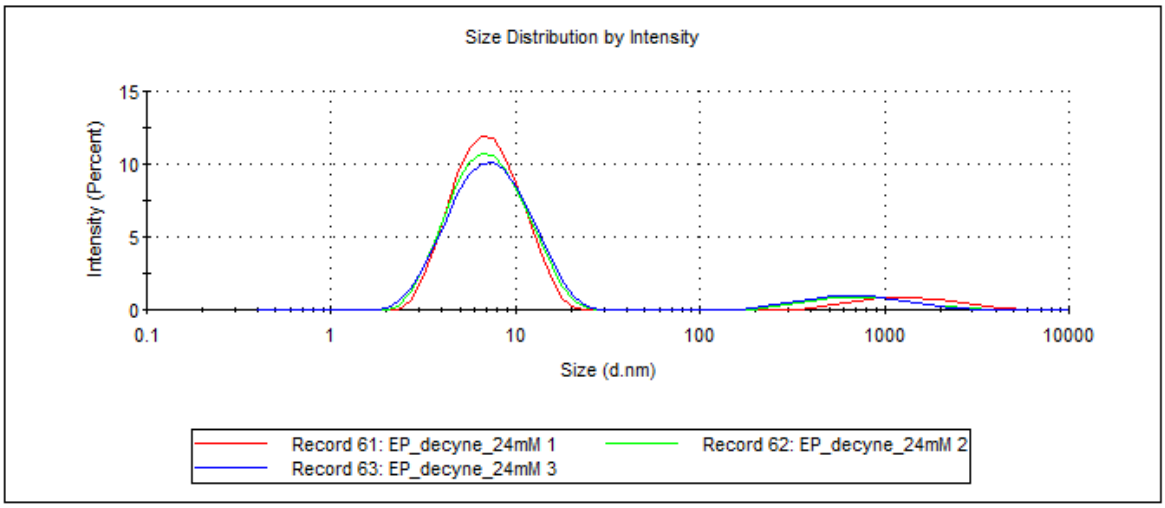


Figure S17: The size distribution by intensity of a DLS measurement of surfactant **3c** at 24 mM indicates micelle aggregates with a size of around 7.5 nm.

Sample Name:	EPdodecyne5mMGeldiluted 1		
SOP Name:	Standard method.sop		
File Name:	Hexyne+Dodecyne surfactants 08-02-2...	**Dispersant Name:**	Water
Record Number:	20	**Dispersant RI:**	1.330
Material RI:	1.45	**Viscosity (cP):**	0.8872
Material Absorbtion:	0.001	**Measurement Date and Time:**	08 February 2017 11:14 am

Temperature (°C):	25.1	**Duration Used (s):**	80
Count Rate (kcps):	114.3	**Measurement Position (mm):**	3.00
Cell Description:	Disposable micro cuvette (40µl)	**Attenuator:**	11

			Size (d.nm):	**% Intensity:**	**St Dev (d.nm):**
Z-Average (d.nm):	11.67	**Peak 1:**	14.59	100.0	7.195
PdI:	0.193	**Peak 2:**	0.000	0.0	0.000
Intercept:	0.731	**Peak 3:**	0.000	0.0	0.000
Result quality :	Good				

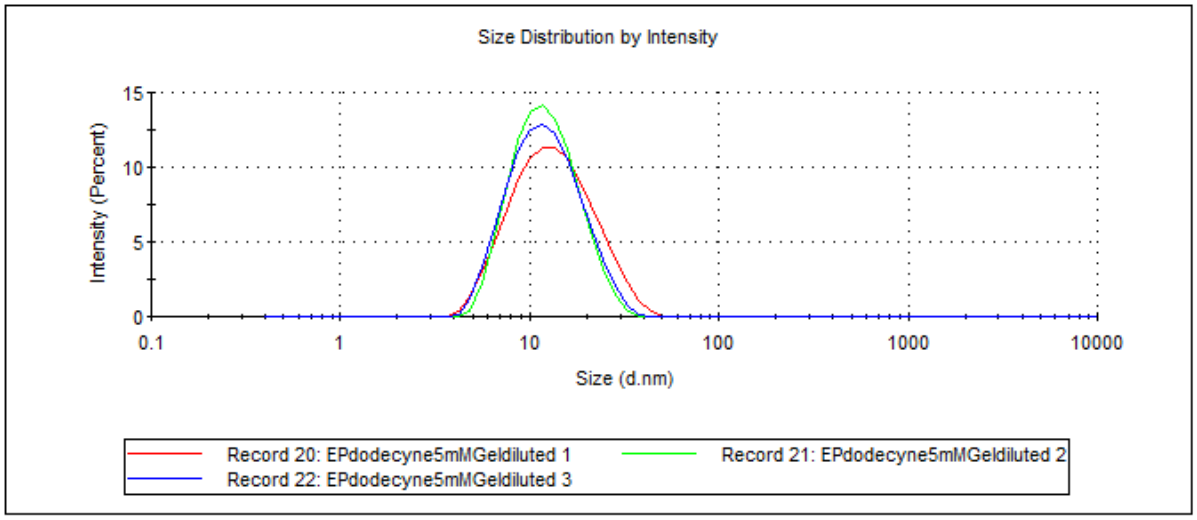


Figure S18: The size distribution by intensity of a DLS measurement of surfactant **3d** at 5 mM indicates micelle aggregates with a size range distributed around 15 nm.

Kinetic Data

^{1}H NMR spectra of key water soluble reaction components in D_2O

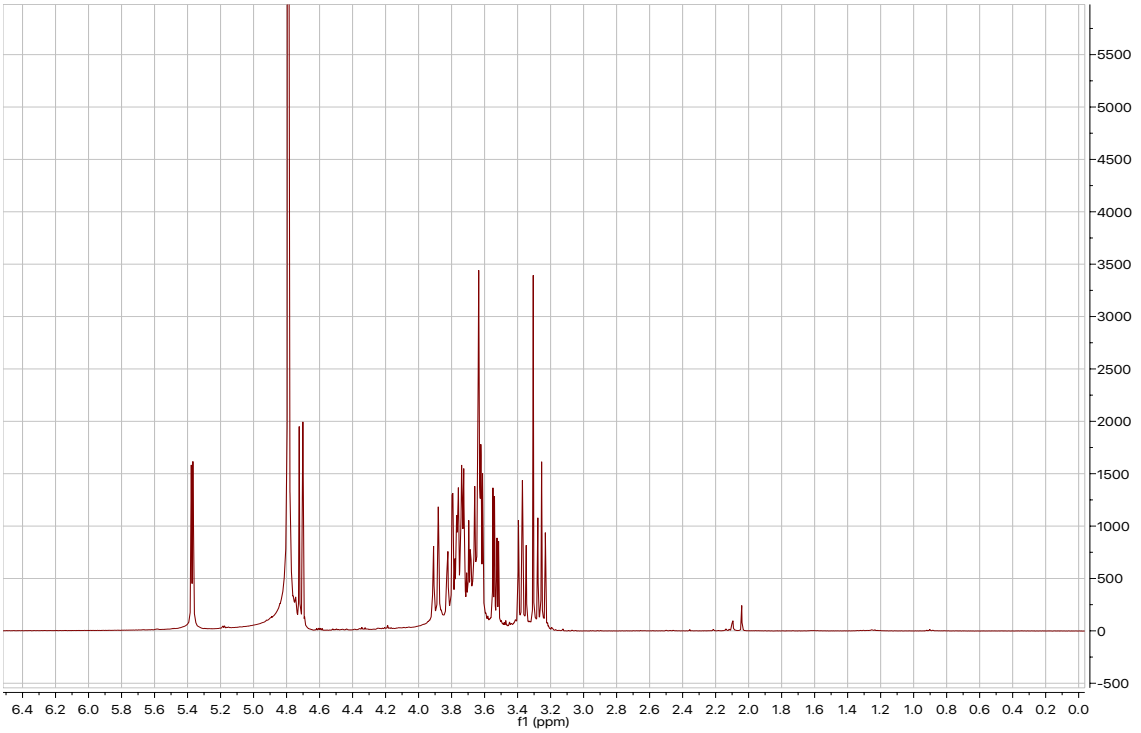


Figure S19: ^{1}H NMR spectrum of 1-deoxy-1-azido-β-D-maltopyranose **1b** in D_2O.

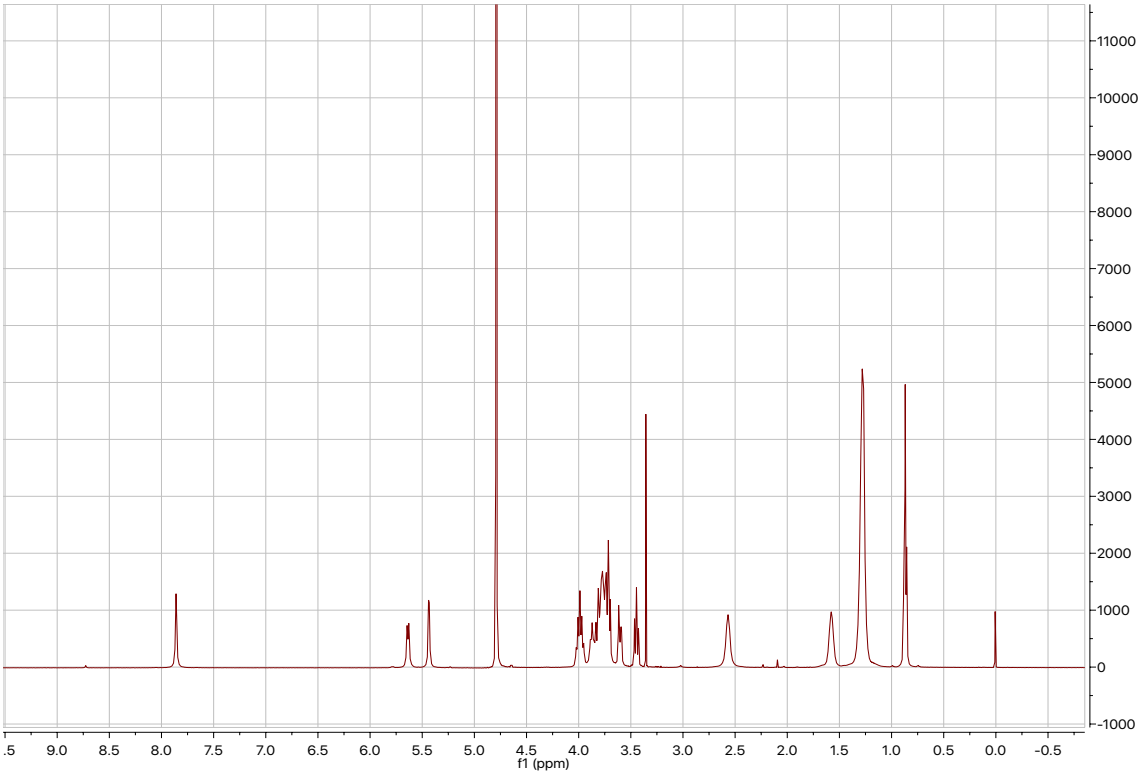


Figure S20: ^{1}H NMR spectrum of 1-(1-deoxy-β-D-maltopyranosyl)-4-octyl triazole **3c** in D_2O.

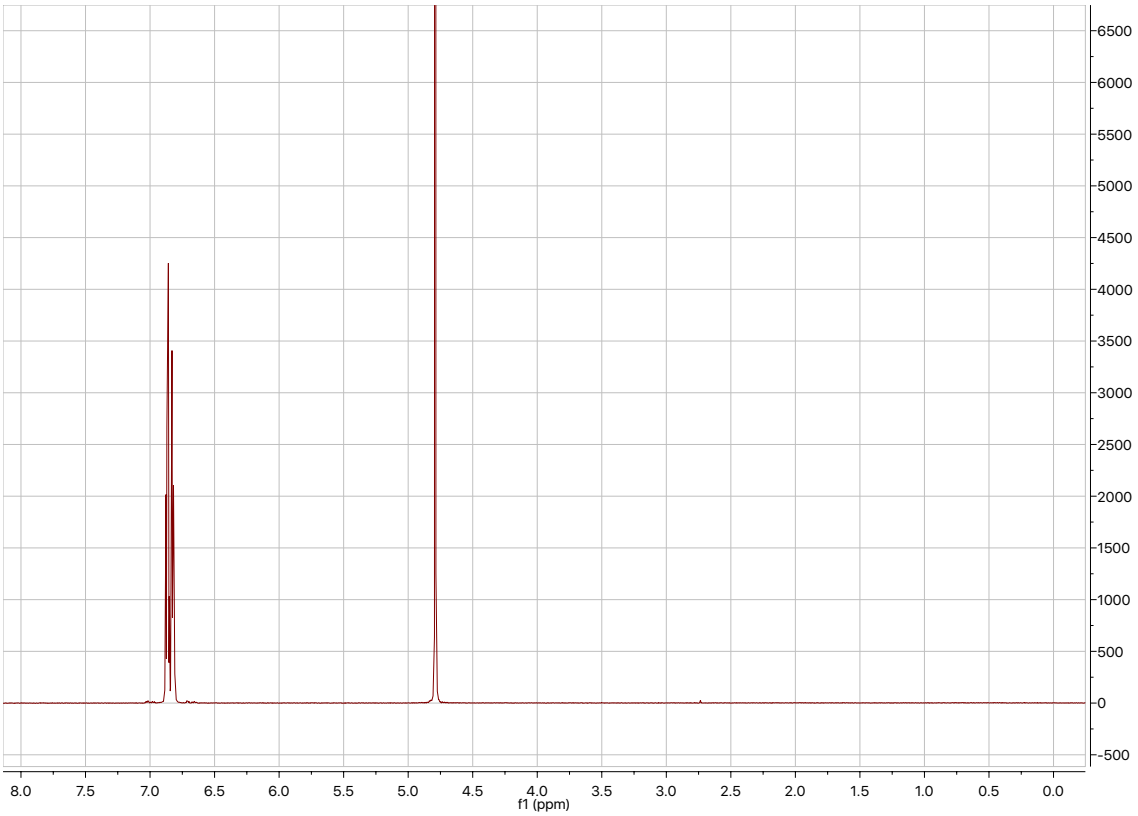


Figure S21: ^{1}H NMR spectrum of *O*-phenylenediamine in D_2O.

Stacked Spectra of Kinetic ^{1}H NMR Experiments

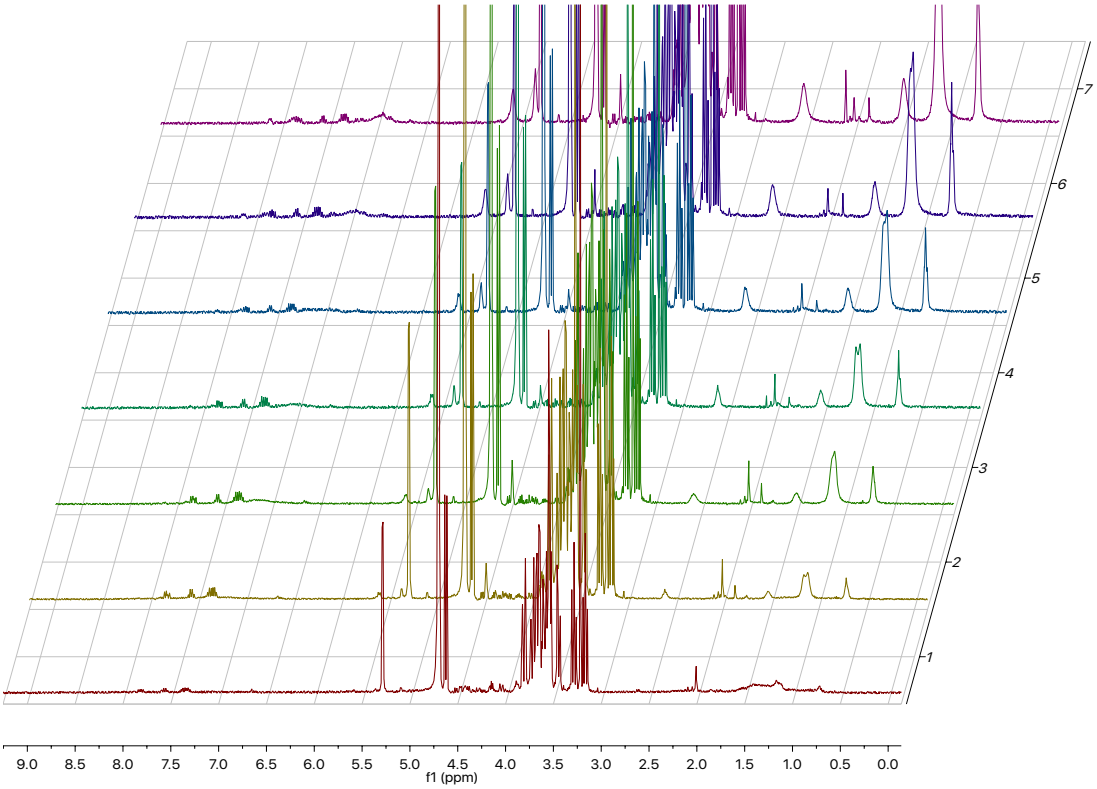


Figure S22: Stacked ^{1}H NMR spectra of the unseeded reaction of **1b** with **2c** and ligand OPD. Data plotted in Figure 3, triangles.

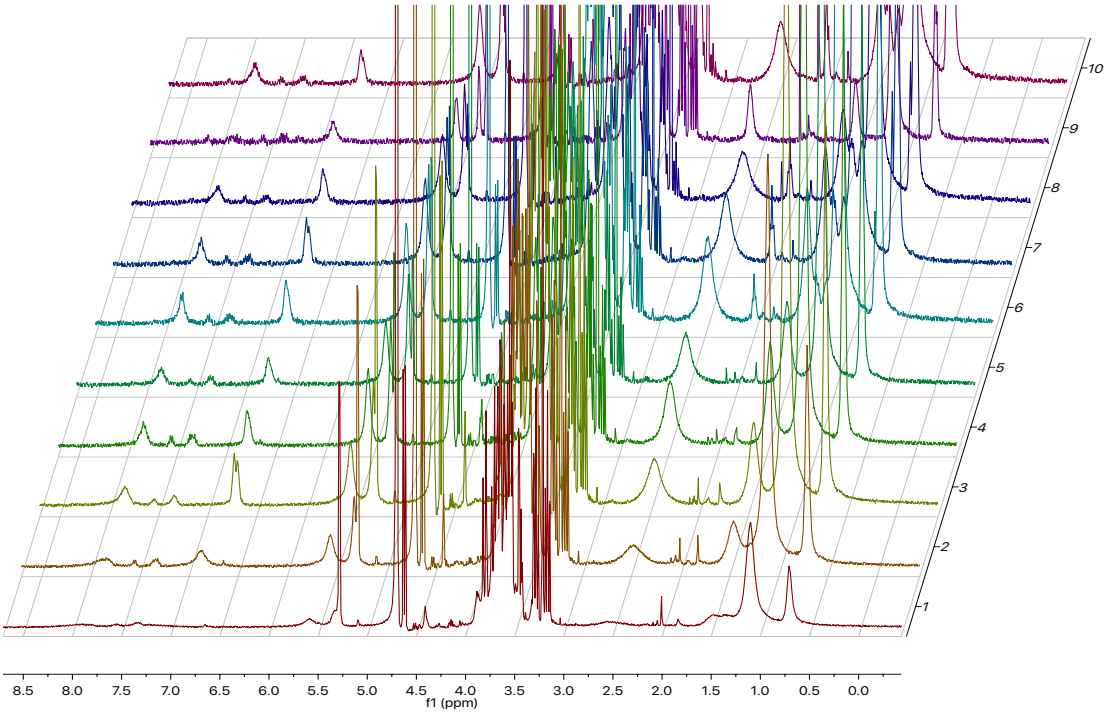


Figure S23: Stacked ^{1}H NMR spectra of the seeded reaction of **1b** with **2c** and ligand OPD seeded with **3c**. Data plotted in Figure 3, squares.

Control experiments

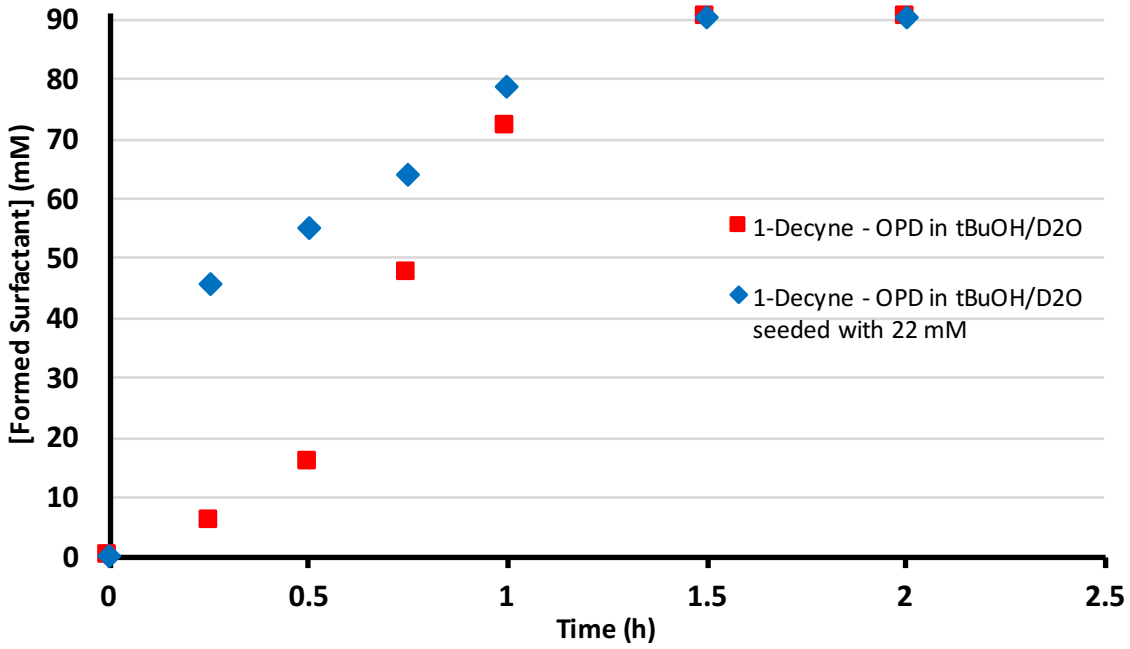


Figure S24: Reaction kinetics for CuAAC of *O*-phenylenediamine (OPD) in *t*BuOH/D_2O (1:1). Complete conversion in 1.5 hours and no lag period is observed. The unseeded reaction still appears to have a sigmoidal rate profile. Seeding the reaction with 22 mM of product removes the sigmoidal shape but the total reaction time remains the same.

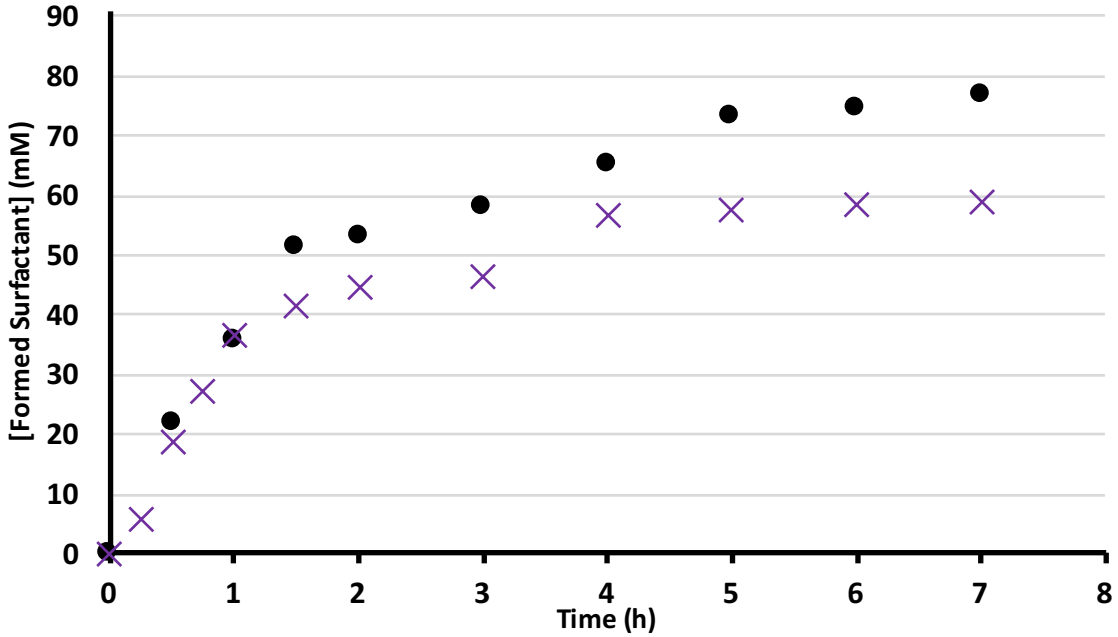


Figure S25: Kinetic profile for seeded reactions using **1** and **2c**. Profile with black circles are under normal conditions when seeding with 22 mM of **3c**. Purple crosses are when seeding with 22 mM of **3c** but the concentration of starting materials is lowered by 22 mM by adding **1b** (113 mg, 0.309 mmol) and **2c** (129 mg, 0.717 mmol) instead of the standard conditions.

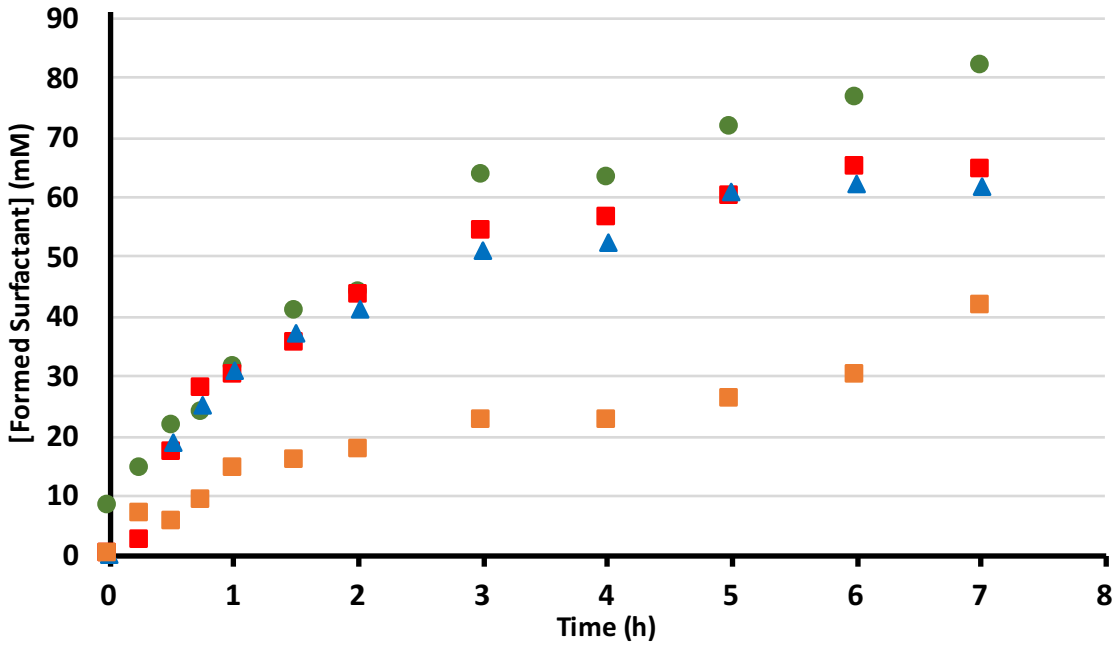


Figure S26: Kinetic profiles for reactions between **1** and **2a** to form **3a** showing inhibition when seeding with higher concentrations. Green circles represent the unseeded reaction. Red squares are when seeded with 50 mM of **3a**. Blue triangles are when seeded with 80 mM of **3e**. Orange squares are when seeded with 80 mM of **3a**. Seeding with a non-surfactant such as **3e** still appears to lead to inhibition indicating that the maltose-triazole moiety might be inhibitively binding to the copper catalyst at higher concentrations.

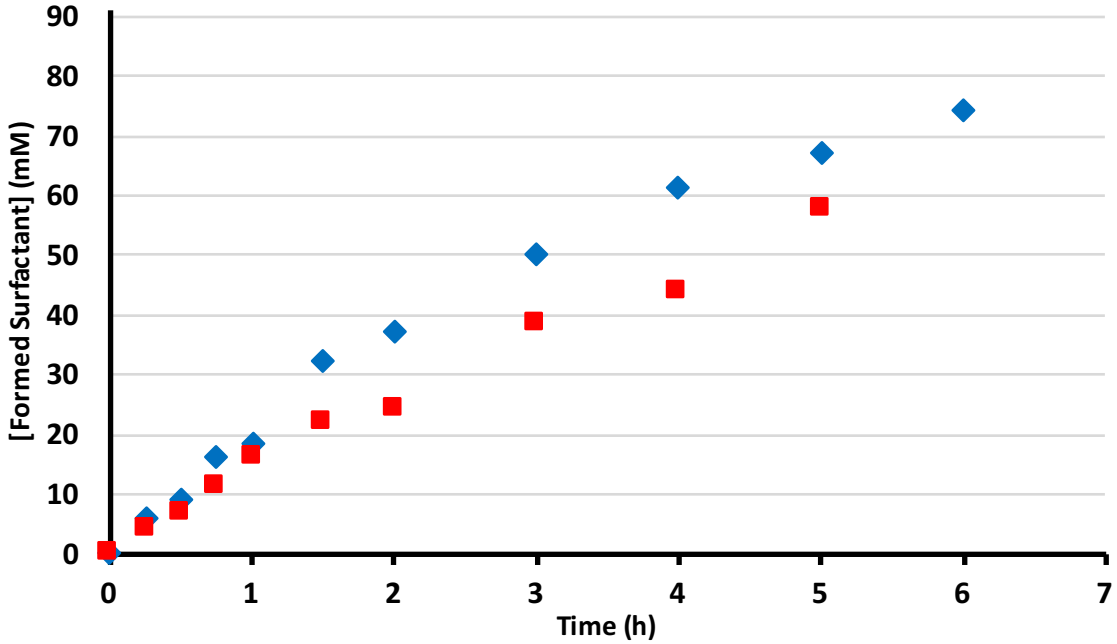


Figure S27: Kinetic profiles for reactions between **1** and **2b** to form **3b** showing a rate acceleration when seeded below the CMC. Red squares are the unseeded conditions while blue diamonds are when seeded with 36 mM of **3b**.

References

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