Supporting Information

Glycosylated Quantum Dots as Fluorometric Nanoprobes for Trehalase

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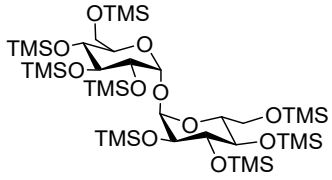
Experimental

General experimental details

All commercial chemicals used were supplied by Sigma Aldrich, Fluorochem, VWR Carbosynth and Tokyo Chemical Industry and used without further purification unless otherwise stated. Deuterated solvents for NMR were purchased from Apollo or VWR. Solvents for synthesis purposes were used at GPR grade. Anhydrous CH_2Cl_2, THF, CH_3CN and Et_2O were obtained using the PureSolv MD-4EN Solvent Purification System. All UV reactions were carried out in a Luzchem photoreactor, LZC-EDU (110 V/ 60 Hz) containing 10 UVA lamps centred at 365 nm. Silica gel 60 (Merck, 230-400 mesh) was used for flash column chromatography. All compounds were subject to purification using silica gel, unless otherwise stated. Analytical thin layer chromatography was carried out with silica gel 60 (fluorescence indicator F254; Merck) and visualised by UV irradiation or molybdenum staining [ammonium molybdate (5.0 g) and concentrated H_2SO_4 (5.3 mL) in 100 mL H_2O]. Melting points are uncorrected and were measured with a Stuart SP-10 melting point apparatus. NMR spectra were recorded using Bruker DPX 400 (400.13 MHz for ^{1}H NMR and 100.61 MHz for ^{13}C NMR), Bruker AV 600 (600.13 MHz for ^{1}H NMR and 150.90 MHz for ^{13}C NMR), Bruker AV 400 (400.13 MHz for ^{1}H NMR and 100.61 MHz for ^{13}C NMR) or Agilent MR400 (400.13 MHz for ^{1}H NMR and 100.61 MHz for ^{13}C NMR) instruments. Chemical shifts, δ, are in ppm units downfield from an internal reference.[1] NMR data was processed using Bruker TopSpin software. The assignment of the signals was confirmed by 2D spectra (COSY, HMBC, HSQC). MALDI-TOF spectra were acquired using a Waters MALDI Q-Tof Premier in positive or negative mode with DCTB (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile) as the MALDI matrix. ESI mass spectra were acquired in positive and negative modes as required, using a Micromass time of flight mass spectrometer (TOF), interfaced to a Waters 2690 HPLC or a Bruker micrOTOF-Q III spectrometer interfaced to a Dionex UltiMate 3000 LC. APCI experiments were carried out on a Bruker micrOTOF-Q III spectrometer interfaced to a Dionex UltiMate 3000 LC or direct insertion probe in positive or negative modes. Specific rotation was recorded in a Rudolph research autopol IV polarimeter with a D-line sodium lamp (589 nm) at 20 °C and are quoted as deg cm^3 g^{-1} dm^{-1}. Infrared spectra (IR) spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer, equipped with a Universal ATR sampling accessory. Carbohydrate positions are named 1 to 6, starting the count at the anomeric position.

2,3,4,6,2',3',4',6'-Octakis-*O*-(trimethylsilyl)-α,α-D-trehalose (2)



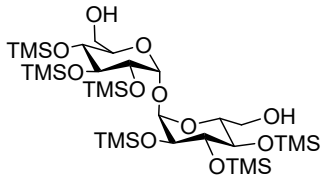
To a stirred suspension of D-trehalose **1** (2.00 g; 5.84 mmol; 1.0 equiv.) and NEt_3 (16.20 mL; 117.00 mmol; 20.0 equiv.) in CH_2Cl_2 (30 mL) at 0 °C, TMSCl (9.60 mL; 76.00 mmol; 13.0 equiv.) was added and the reaction mixture was stirred at rt for 18 h. The mixture was cooled to 0 °C, NEt_3 (8.10 mL; 58.50 mmol; 10.0 equiv.), TMSCl (2.95 mL; 23.4 mmol; 4.0 equiv.) was added and the mixture was stirred for an additional 4 h at rt. The solvents were removed *in vacuo*, the residue taken up with H_2O (100 mL) and extracted with petroleum ether (6 x 50 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated *in vacuo*. Recrystallisation from CH_3OH furnished **2** as a white solid (4.57 g, 85%), which was used without further purification. M.p. 78-79 °C, Lit., 80-82 °C.[2] The isolated compound was in good agreement with the literature.[3]

R_f (PE/EtOAc 95:5 v/v): 0.63

δ_H (400 MHz, $CDCl_3$): 4.93 (2H, d, $J_{1,2} = J_{1',2'} = 3.3$ Hz, H-1, H-1'), 3.91 (2H, app t, H-3, H-3'), 3.83-3.78 (2H, m, H-5, H-5'), 3.75-3.66 (4H, m, H-6ab, H-6ab'), 3.45 (2H, app t, H-4, H-4'), 3.41 (2H, dd, $J_{1,2} = J_{1',2'} = 3.3$ Hz, $J_{2,3} = J_{2',3'} =$ 9.2 Hz, H-2, H-2'), 0.17, 0.16, 0.14, 0.12 (18H, s, 2 x $Si(CH_3)_3$)

HRMS (*m/z* ESI^+): Found: 941.4233 ($[M + H]^+$, $C_{36}H_{86}NaO_{11}Si_8$ Requires: 941.4216)

2,3,4,2',3',4'-Hexakis-*O*-(trimethylsilyl)-α,α-D-trehalose (3)



To a cooled solution of **2** (200 mg; 0.22 mmol; 1.0 equiv.) in CH_3OH/CH_2Cl_2 (20 mL, 3:1 v/v) at 0 °C, K_2CO_3 (30 mg; 0.22 mmol; 2.0 equiv.) was added and the reaction mixture was stirred for 18 h at rt. The reaction was quenched with AcOH (2 mL) and the mixture concentrated *in vacuo*, followed by purification by column chromatography (SiO_2, PE/EtOAc 95:5 v/v - EtOAc) to yield **3** as a white solid

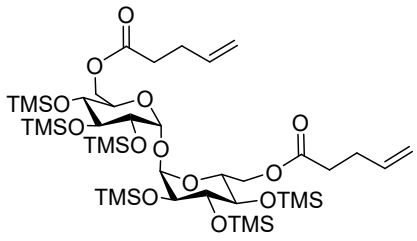
(117 mg, 70%). M.p. 113-114 °C, Lit., 115-118 °C.[2] The isolated compound was in good agreement with the literature.[3]

R_f (PE/EtOAc 8:2 v/v): 0.29

δ_H (400 MHz, $CDCl_3$): 4.92 (2H, d, $J_{1,2} = J_{1',2'} = 2.9$ Hz, H-1, H-1'), 3.91 (2H, app t, H-3, H-3'), 3.88-3.85 (2H, m, H-5, H-5'), 3.76-3.67 (4H, m, H-6ab, H-6ab'), 3.50 (2H, app t, H-4, H-4'), 3.44 (2H, dd, $J_{1,2} = J_{1',2'} = 2.9$ Hz, $J_{2,3} = J_{2',3'} = 8.8$ Hz, H-2, H-2'), 1.87 (2H, bs, 2 x OH), 0.18, 0.17, 0.15 (18H, s, 2 x $Si(CH_3)_3$)

HRMS (*m/z* ESI^+): Found: 797.3434 ($[M + Na]^+$, $C_{30}H_{70}NaO_{11}Si_6$ Requires: 797.3432)

6,6'-Di-*O*-(4-pentenoate)-2,3,4,2',3',4'-hexakis-*O*-(trimethylsilyl)-α,α-D-trehalose (4)



To a stirred solution of **3** (930 mg; 1.20 mmol; 1.0 equiv.), 4-pentenoic acid (0.36 mL; 3.60 mmol; 3.0 equiv.) and DMAP (47 mg; 0.24 mmol; 0.2 equiv.) were added at 0°C. DIC (0.80 mL; 4.80 mmol; 4.0 equiv.) was added and the mixture was stirred at rt for 18 h. The solvents were removed *in vacuo*, followed by purification by column chromatography (SiO_2, Hex/EtOAc 95:5 v/v) to yield **4** as a yellow oil (598 mg, 52%).

R_f (Hex/EtOAc 95:5 v/v): 0.33

$[\alpha]^{20}_D$ (c 0.01, $CHCl_3$): +102

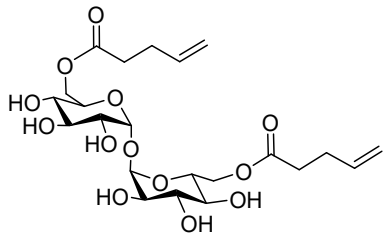
δ_H (400 MHz, $CDCl_3$): 5.91-5.79 (2H, m, 2 x C<u>H</u>=CH_2), 5.12-5.00 (4H, m, 2 x CH=C<u>H</u>$_2$), 4.94 (2H, d, $J_{1,2} = J_{1',2'} = 3.2$ Hz, H-1, H-1'), 4.31 (2H, dd, $J_{5,6a} = J_{5',6a'} = 2.4$ Hz, $J_{6a,6b} = J_{6a',6b'} = 11.9$ Hz, H-6<u>a</u>b, H-6<u>a</u>b'), 4.09 (2H, dd, $J_{5,6b} = J_{5',6b'} = 4.5$ Hz, $J_{6a,6b} = J_{6a',6b'} = 11.9$ Hz, H-6a<u>b</u>, H-6a<u>b</u>'), 4.05-3.99 (2H, m, H-5, H-5'), 3.93 (2H, app t, H-3, H-3'), 3.53-3.44 (4H, m, H-2, H-2', H-4, H-4'), 2.53-2.37 (8H, m, 2 x $COCH_2$, 2 x CH_2), 0.17, 0.16, 0.15 (18H, s, 2 x $Si(CH_3)_3$)

δ_C (100 MHz, $CDCl_3$): 172.4 (2 x C=O), 135.9 (2 x $\underline{C}H=CH_2$), 115.6 (2 x $CH=\underline{C}H_2$), 94.0 (C-1, C-1'), 73.2 (C-3, C-3'), 72.3 (C-2, C-2'), 71.5 (C-4, C-4'), 70.3 (C-5, C-5'), 63.0 (C-6, C-6'), 33.2 (2 x $CO\underline{C}H_2$), 28.4 (2 x CH_2), 0.7, 0.6, 0.2 (2 x $Si(CH_3)_3$)

HRMS (*m/z* ESI^+): Found: 961.4268 ($[M + Na]^+$, $C_{40}H_{82}NaO_{13}Si_6$ Requires: 961.4263)

ν_{max} (film)/cm^{-1}: 2956 (CH stretching), 1743 (C=O stretching), 1251, 1164 (C-O ether stretching), 1077, 877 (Si-C stretching), 622 (CH rocking)

6,6'-Di-*O*-(4-pentenoate)-α,α-D-trehalose (5)



A solution of **4** (350 mg; 0.37 mmol; 1.0 equiv.) in 10% TFA/anhydrous CH_2Cl_2 (0.01 mmol/mL) was stirred at rt for 1 h. The solvents were removed *in vacuo* to yield **5** as a yellow foam (189 mg, >99%), which was used without further purification.

R_f (EtOAc/CH_3OH 8:2 v/v): 0.25

$[\alpha]^{20}_D$ (c 0.01, CH_3OH): +113

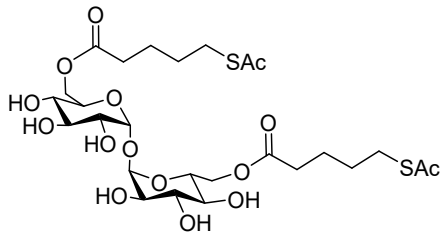
δ_H (400 MHz, CD_3OD): 5.94-5.80 (2H, m, 2 x $C\underline{H}=CH_2$), 5.13-4.98 (6H, m, 2 x $CH=C\underline{H}_2$, H-1, H-1'), 4.38 (2H, dd, $J_{5,6a} = J_{5',6a'} = 1.9$ Hz, $J_{6a,6b} = J_{6a',6b'} = 11.9$ Hz, H-6a<u>b</u>, H-6a<u>b</u>'), 4.23 (2H, dd, $J_{5,6b} = J_{5',6b'} = 5.4$ Hz, $J_{6a,6b} = J_{6a',6b'} = 11.9$ Hz, H-6a<u>b</u>, H-6a<u>b</u>'), 4.07-4.01 (2H, m, H-5, H-5'), 3.80 (2H, app t, H-3, H-3'), 3.49 (2H, dd, $J_{1,2} = J_{1',2'} = 3.7$ Hz, $J_{2,3} = J_{2',3'} = 9.4$ Hz, H-2, H-2'), 3.34-3.32 (2H, m, H-4, H-4'), 2.49-2.43 (4H, m, 2 x $COCH_2$), 2.42-2.35 (4H, m, 2 x CH_2)

δ_C (100 MHz, CD_3OD): 173.7 (2 x C=O), 137.0 (2 x $\underline{C}H=CH_2$), 114.0 (2 x $CH=\underline{C}H_2$), 94.5 (C-1, C-1'), 73.7 (C-3, C-3'), 72.1 (C-2, C-2'), 71.0 (C-4, C-4'), 70.5 (C-5, C-5'), 63.5 (C-6, C-6'), 33.5 (2 x $CO\underline{C}H_2$), 29.3 (2 x CH_2)

HRMS (*m/z* ESI^+): Found: 549.1878 ($[M + Na]^+$, C_{23} $C_{22}H_{34}N_2NaO_{13}$ Requires: 529.1891)

ν_{max} (film)/cm^{-1}: 3382 (OH stretching), 2940 (CH stretching), 1692 (C=O stretching), 1435 (CH bending), 1275 (C-O ester stretching), 991 (C-O ether stretching), 918 (=CH bending), 620 (OH bending)

6,6'-Di-*O*-(acetylthiopentanoate)-α,α-D-trehalose (6)



A solution of **5** (77 mg; 0.15 mmol; 1.0 equiv.), CH_3COSH (0.05 mL; 0.75 mmol; 5.0 equiv.), DPAP (21 mg; 0.08 mmol; 0.5 equiv.) and MAP (12 mg; 0.08 mmol; 0.5 equiv.) was irradiated at 365 nm for 5 h at rt. The reaction mixture was diluted with EtOAc (200 mL) and washed with brine (6 x 100 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent removed *in vacuo*, followed by purification by column chromatography (SiO_2, EtOAc/CH_3OH 85:15 v/v) to yield **6** as a yellow oil (79 mg, 79%).

R_f (EtOAc/CH_3OH 85:15 v/v): 0.20

$[\alpha]^{20}_D$ (c 0.01, CH_3OH): +51

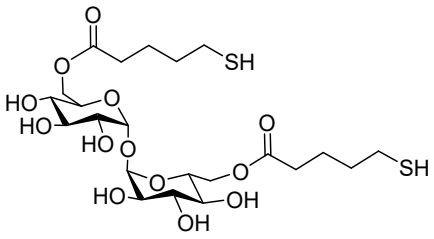
δ_H (400 MHz, CD_3OD): 5.05 (2H, d, $J_{1,2} = J_{1',2'} = 3.8$ Hz, H-1, H-1'), 4.39 (2H, dd, $J_{5,6a} = J_{5',6a'} = 2.2$ Hz, $J_{6a,6b} = J_{6a',6b'} = 11.9$ Hz, H-6ab, H-6ab'), 4.22 (2H, dd, $J_{5,6b} = J_{5',6b'} = 5.5$ Hz, $J_{6a,6b} = J_{6a',6b'} = 11.9$ Hz, H-6ab, H-6ab'), 4.03 (2H, ddd, $J_{5,6a} = J_{5',6a'} = 2.2$ Hz, $J_{5,6b} = J_{5',6b'} = 5.5$ Hz, $J_{4,5} = J_{4',5'} = 9.6$ Hz, H-5, H-5'), 3.80 (2H, app t, H-3, H-3'), 3.51 (2H, dd, $J_{1,2} = J_{1',2'} = 3.8$ Hz, $J_{2,3} = J_{2',3'} = 9.1$ Hz, H-2, H-2'), 3.35 (2H, app t, H-4, H-4'), 2.91 (4H, t, $J = 6.9$ Hz, 2 x CH_2S), 2.40 (4H, t, $J = 6.9$ Hz, 2 x $COCH_2$), 2.33 (3H, s, $SCOCH_3$), 1.74-1.57 (8H, m, 4 x CH_2)

δ_C (100 MHz, CD_3OD): 196.3 (2 x SC=O), 173.8 (2 x C=O), 94.1 (C-1, C-1'), 73.3 (C-3, C-3'), 71.9 (C-2, C-2'), 70.4 (C-4, C-4'), 70.1 (C-5, C-5'), 63.0 (C-6, C-6'), 33.0 (2 x $CO\underline{C}H_2$), 29.3 (2 x $SCO\underline{C}H_3$), 28.8 (2 x CH_2), 28.0 (2 x CH_2S), 23.6 (2 x CH_2)

HRMS (*m/z* APCI$^-$): Found: 657.1871 ([M - H]$^-$, $C_{26}H_{41}O_{15}S_2$ Requires: 657.1892)

ν_{max} (film)/ cm^{-1}: 3371 (OH stretching), 2921, 2855 (CH stretching), 1735, 1689 (C=O stretching), 1355 (CH bending), 1135, 1022 (C-O ester stretching), 650 (OH bending), 555 (S-C stretching)

6,6'-Di-*O*-(mercaptopentanoate)-α,α-D-trehalose (7)



To a stirred solution of **6** (11 mg; 0.02 mmol; 1.0 equiv.) in EtOH (2 mL), N_2H_4 (2 µL; 0.07 mmol; 4.0 equiv.) was added and the reaction was stirred at rt for 1 h. The solvent was removed *in vacuo* to yield **7** as a yellow syrup (10 mg, >99%), which was used without further purification.

R_f (EtOAc/CH_3OH 8:2 v/v): 0.23

$[\alpha]^{20}_D$ (c 0.01, CH_3OH): +111

δ_H (600 MHz, CD_3OD): 5.07 (2H, d, $J_{1,2} = J_{1',2'} = 3.6$ Hz, H-1, H-1'), 4.39 (2H, dd, $J_{5,6a} = J_{5',6a'} = 2.1$ Hz, $J_{6a,6b} = J_{6a',6b'} = 11.9$ Hz, H-6ab, H-6ab'), 4.22 (2H, dd, $J_{5,6b} = J_{5',6b'} = 5.3$ Hz, $J_{6a,6b} = J_{6a',6b'} = 11.9$ Hz, H-6ab, H-6ab'), 4.02 (2H, ddd, $J_{5,6a} = J_{5',6a'} = 2.1$ Hz, $J_{5,6b} = J_{5',6b'} = 5.3$ Hz, $J_{4,5} = J_{4',5'} = 10.2$ Hz, H-5, H-5'), 3.79 (2H, app t, H-3, H-3'), 3.50 (2H, dd, $J_{1,2} = J_{1',2'} = 3.6$ Hz, $J_{2,3} = J_{2',3'} = 9.8$ Hz, H-2, H-2'), 3.38-3.35 (2H, m, H-4, H-4'), 2.57-2.50 (4H, m, 2 x CH_2S), 2.39 (4H, t, $J = 7.2$ Hz, 2 x $COCH_2$), 1.80-1.62 (8H, m, 4 x CH_2)

δ_C (150 MHz, CD_3OD): 173.7 (2 x C=O), 93.8 (C-1, C-1'), 73.3 (C-3, C-3'), 71.7 (C-2, C-2'), 70.5 (C-4, C-4'), 70.2 (C-5, C-5'), 63.1 (C-6, C-6'), 33.1 (2 x $CO\underline{C}H_2$), 33.0 (2 x CH_2), 23.3 (2 x CH_2S), 23.1 (2 x CH_2)

HRMS (*m/z* $APCI^-$): Found: 573.1683 ($[M - H]^-$, $C_{22}H_{37}O_{13}S_2$ Requires: 573.1681)

NMR Spectra

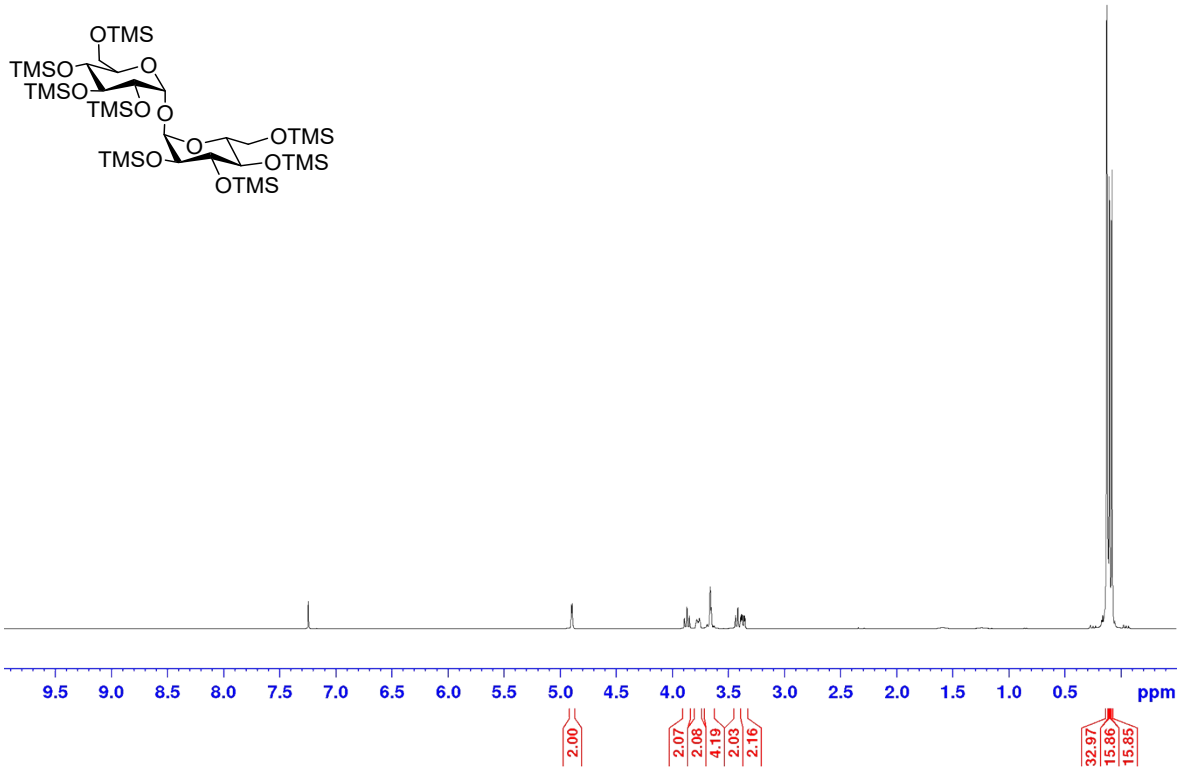


Fig S1. ^{1}H NMR data for 2 (400 MHz, $CDCl_3$)

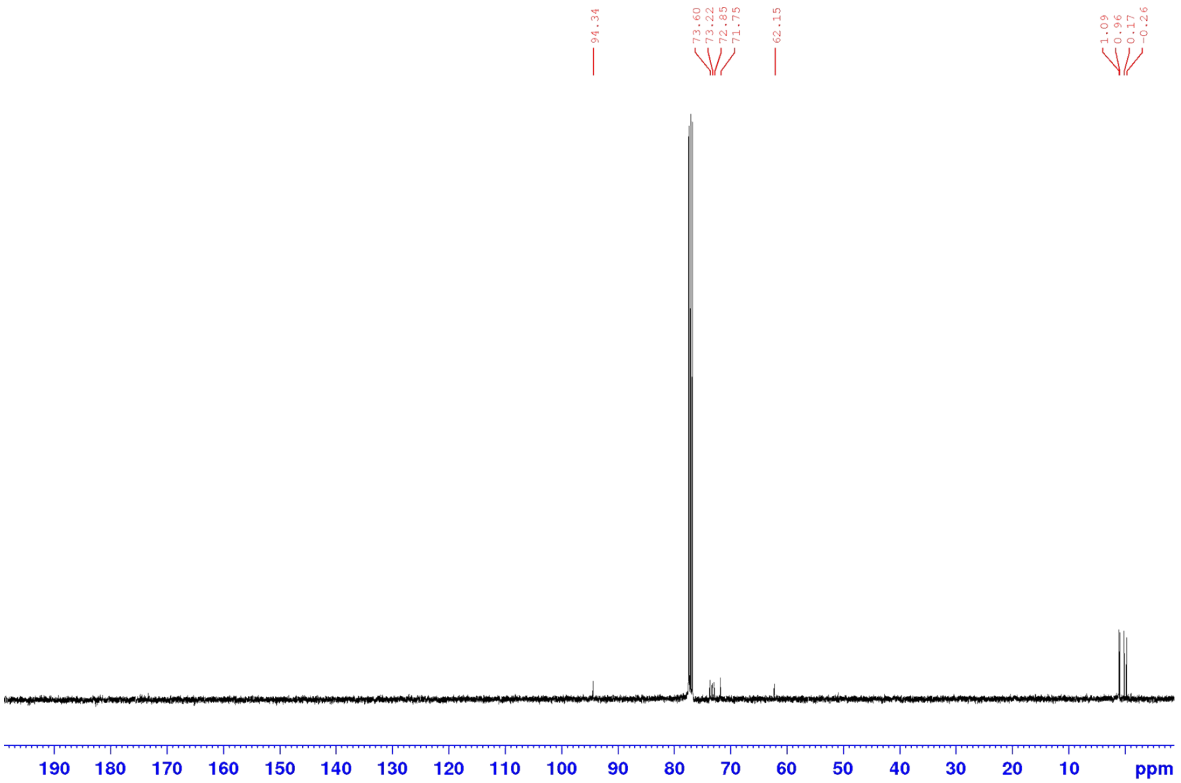


Fig S2. ^{13}C NMR data for 2 (100 MHz, $CDCl_3$)

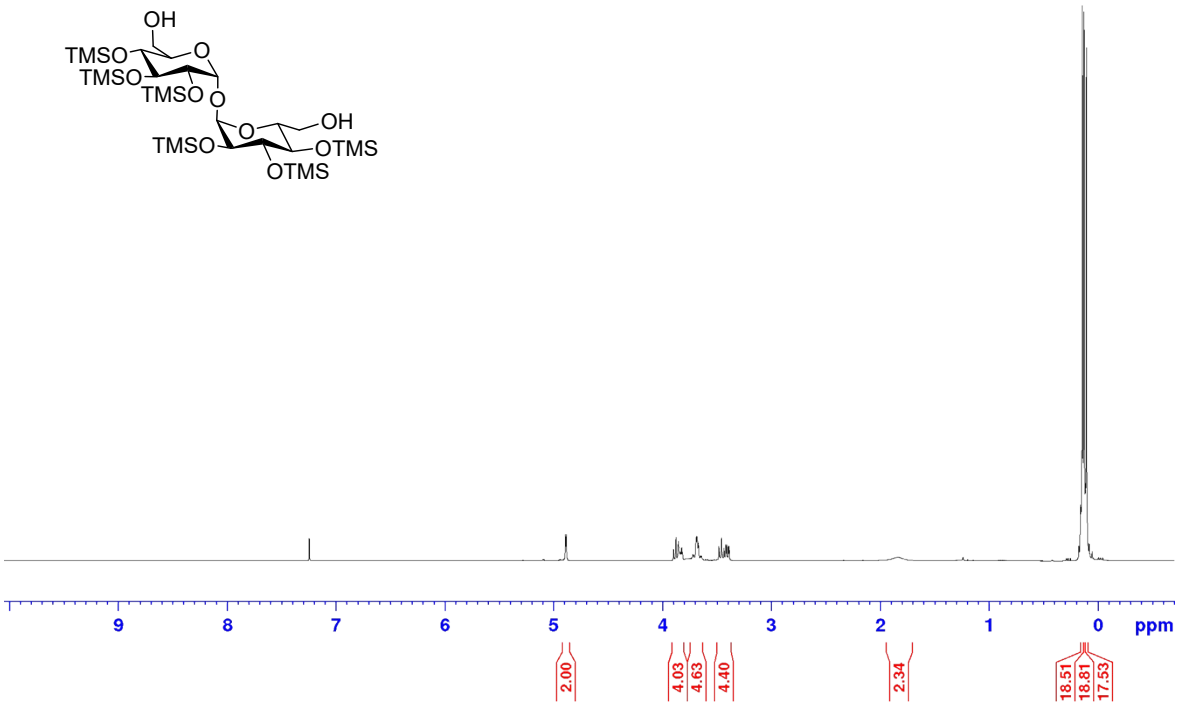


Fig S3. ^{1}H NMR data for 3 (400 MHz, $CDCl_3$)

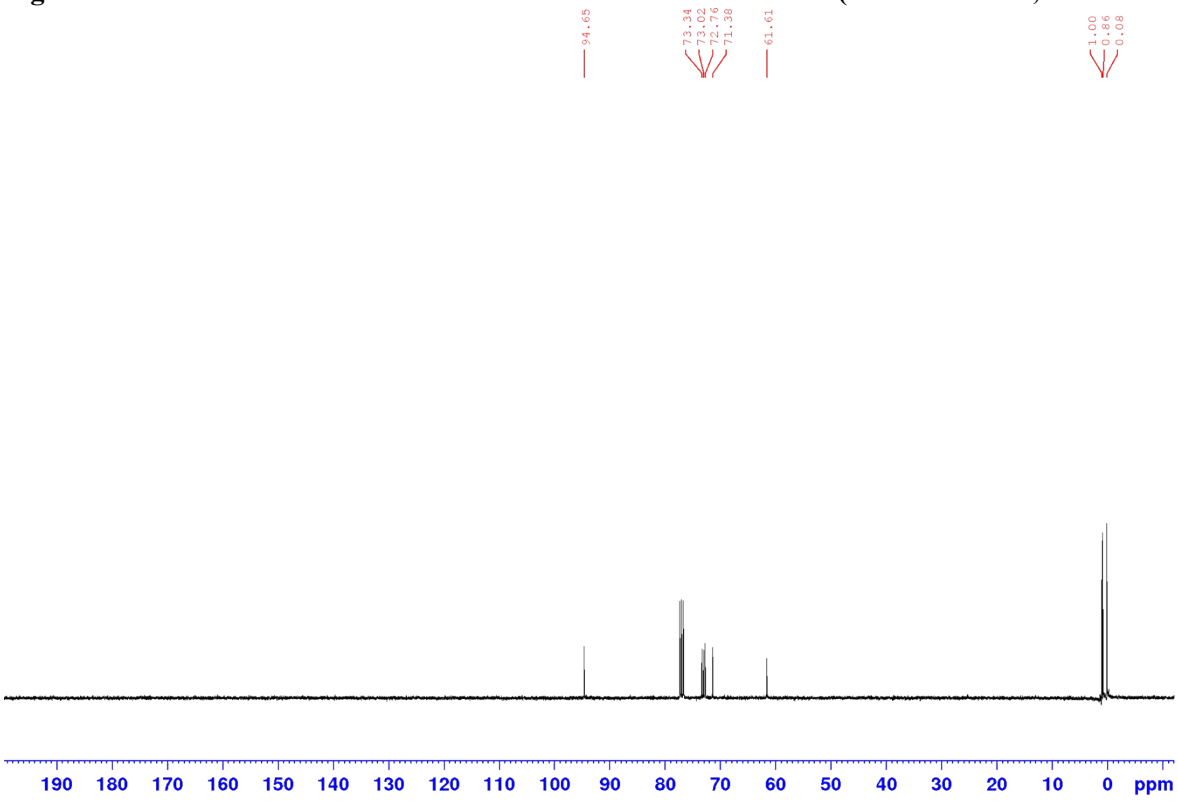


Fig S4. ^{13}C NMR data for 3 (100 MHz, $CDCl_3$)

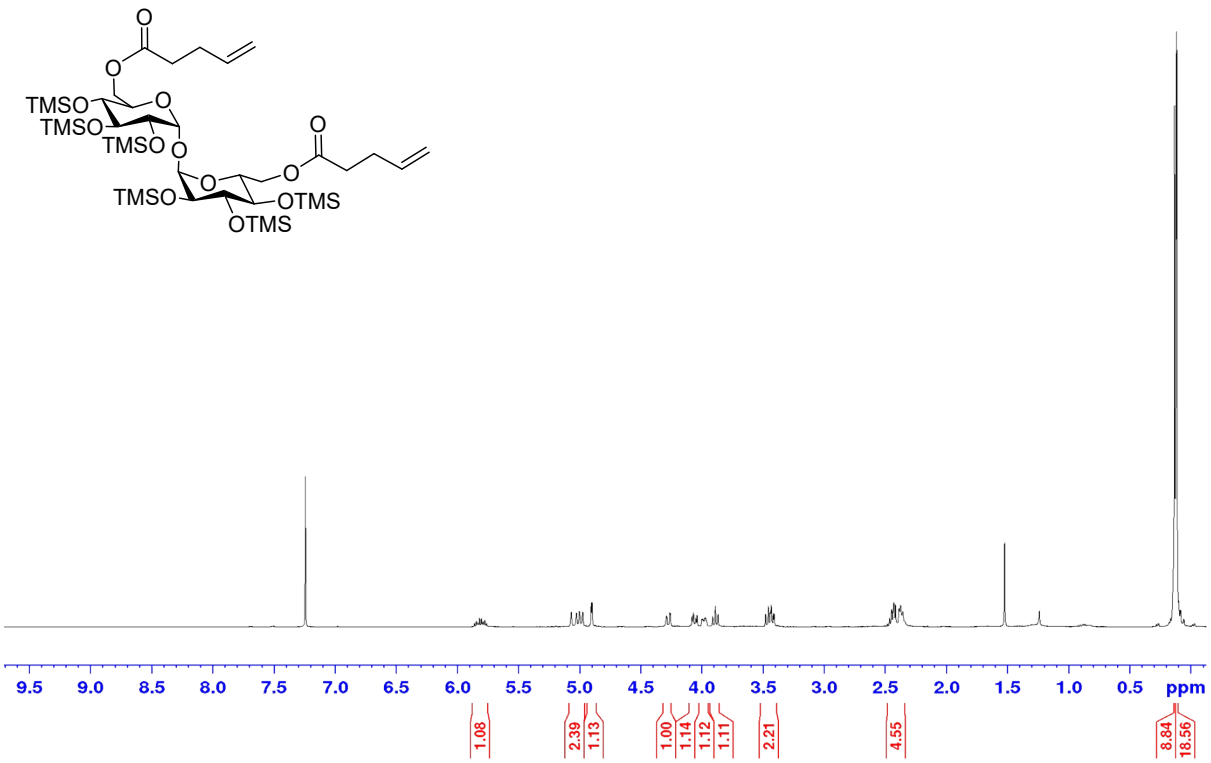


Fig S5. ^{1}H NMR data for 4 (400 MHz, $CDCl_3$)

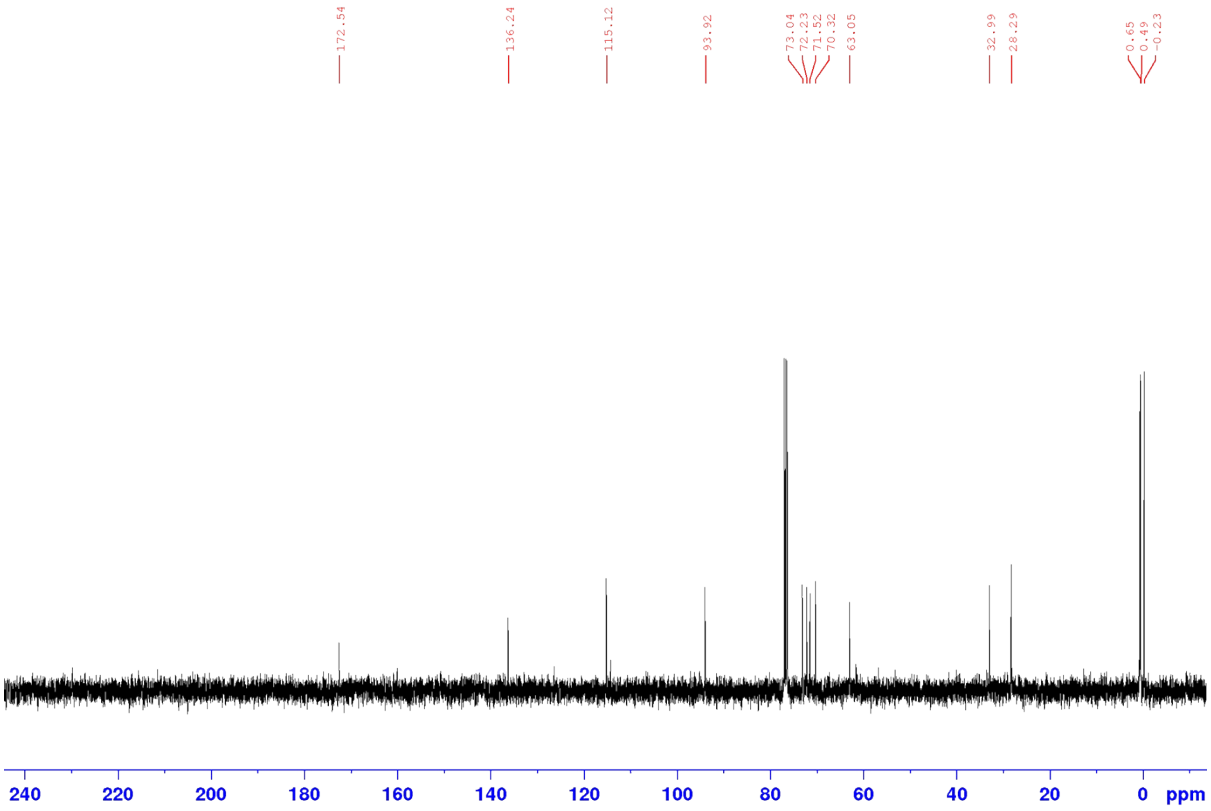


Fig S6. ^{13}C NMR data for 4 (100 MHz, $CDCl_3$)

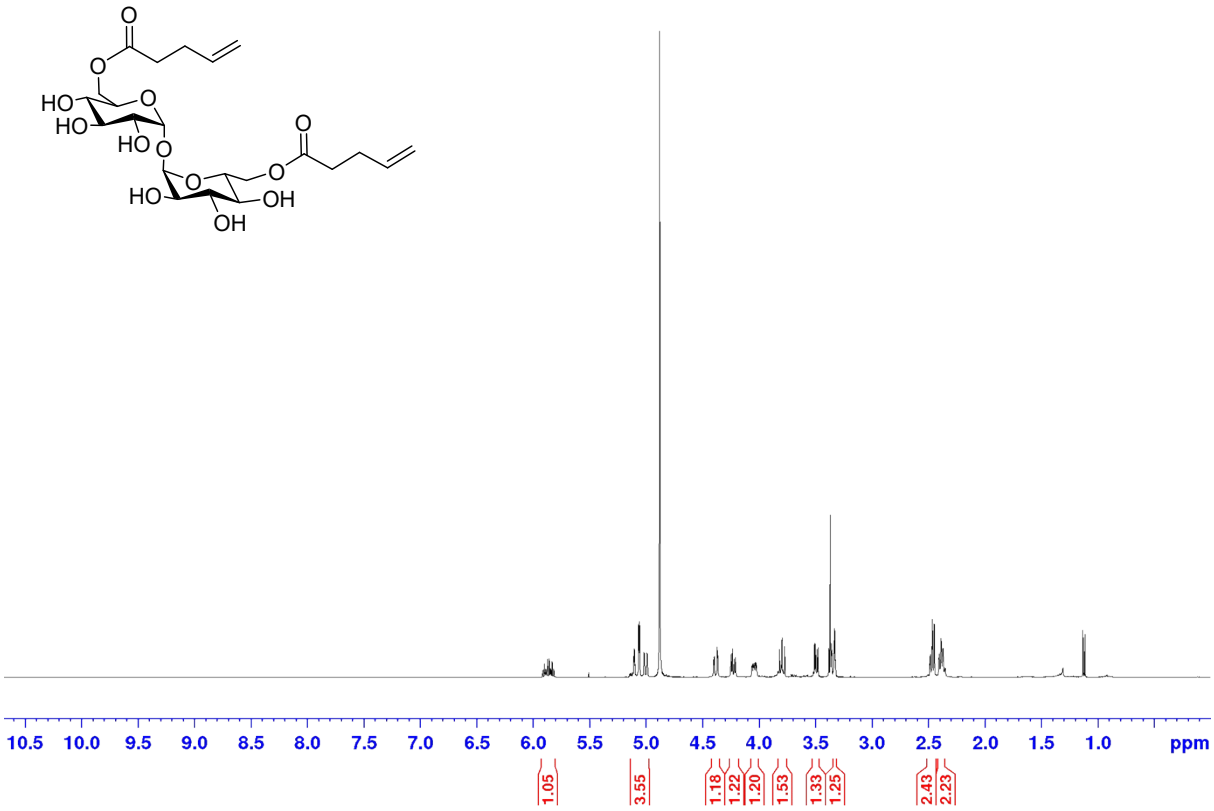


Fig S7. ^{1}H NMR data for 5 (400 MHz, CD_3OD)

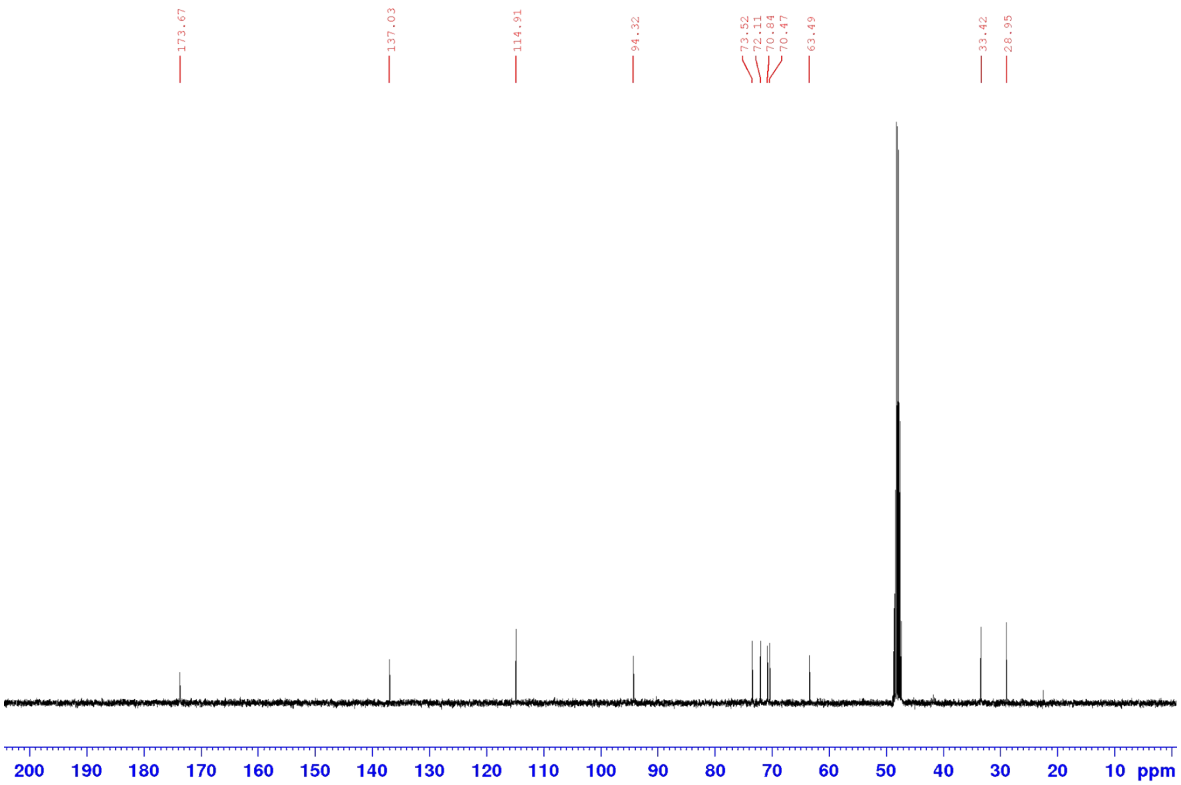
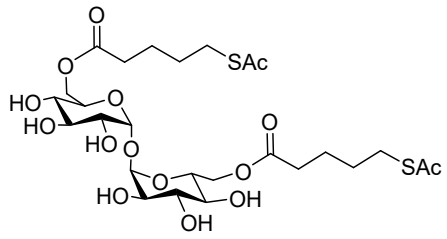


Fig S8. ^{13}C NMR data for 5 (100 MHz, CD_3OD)



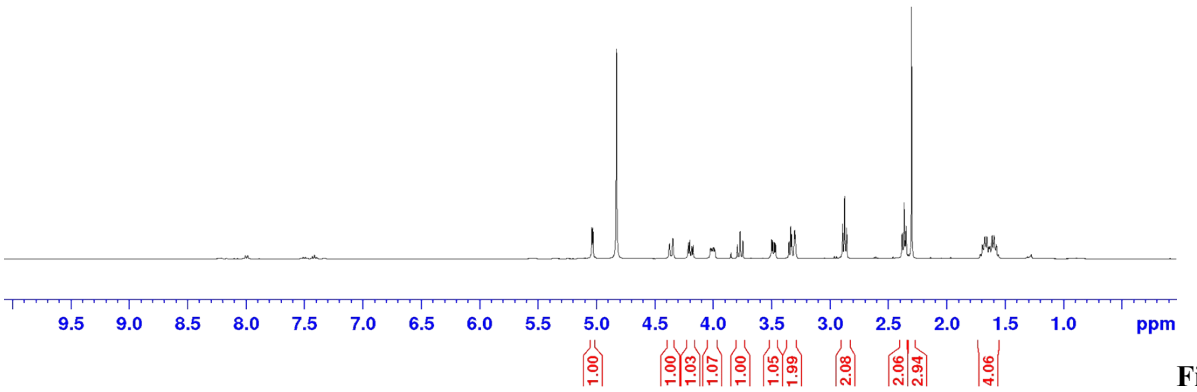


Fig S9. ^{1}H NMR data for 6 (400 MHz, CD_3OD)

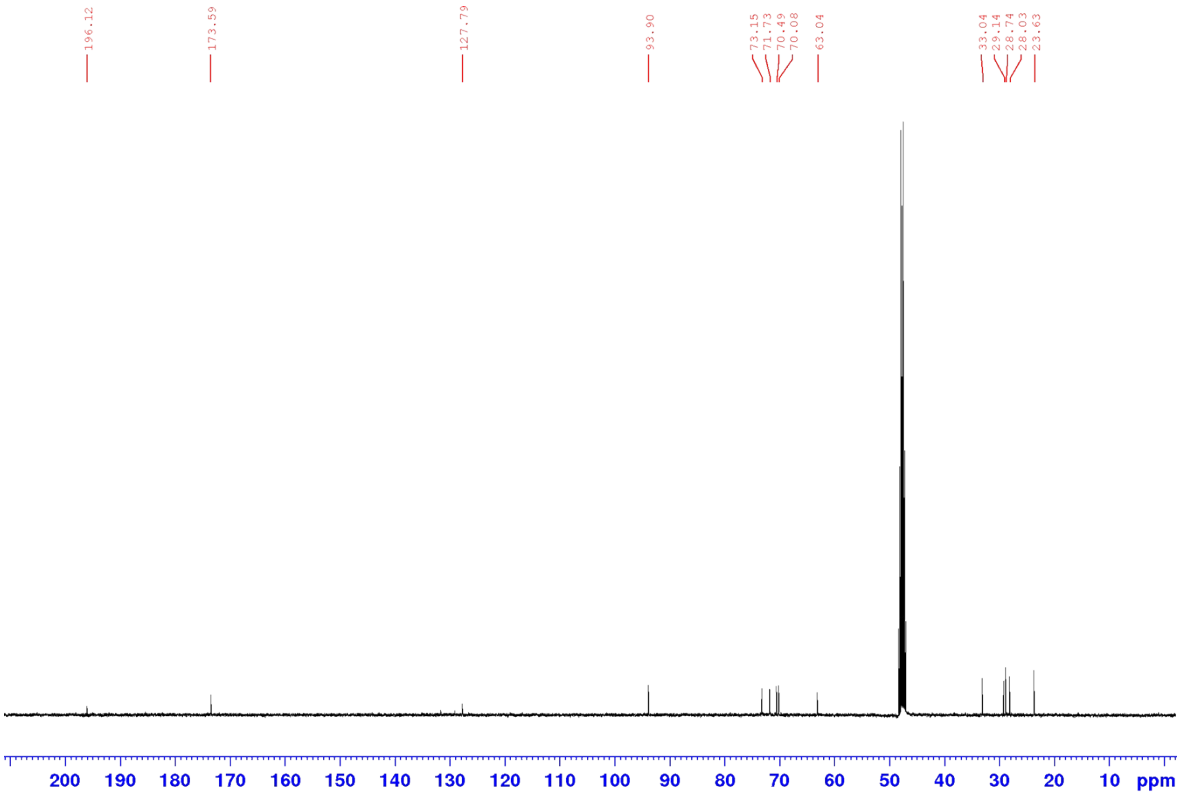


Fig S10. ^{13}C NMR data for 6 (100 MHz, CD_3OD)

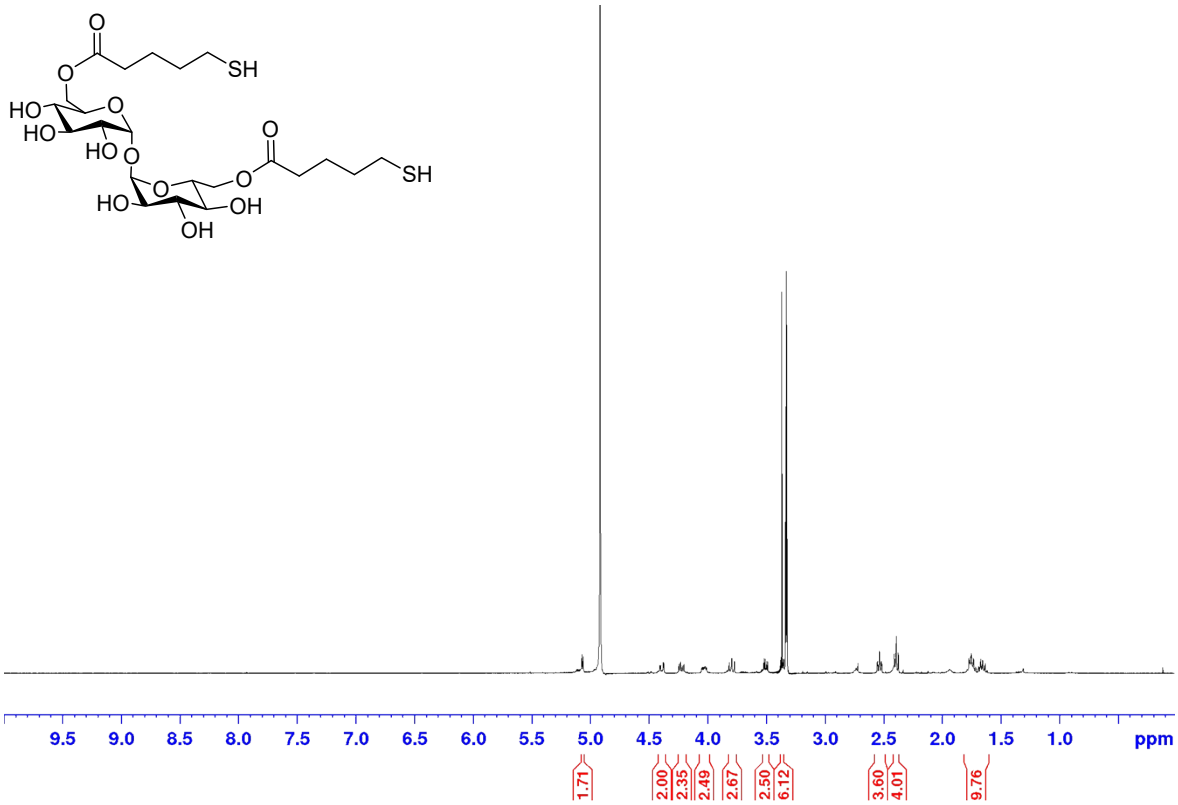


Fig S11. ^{1}H NMR data for 7 (600 MHz, CD_3OD)

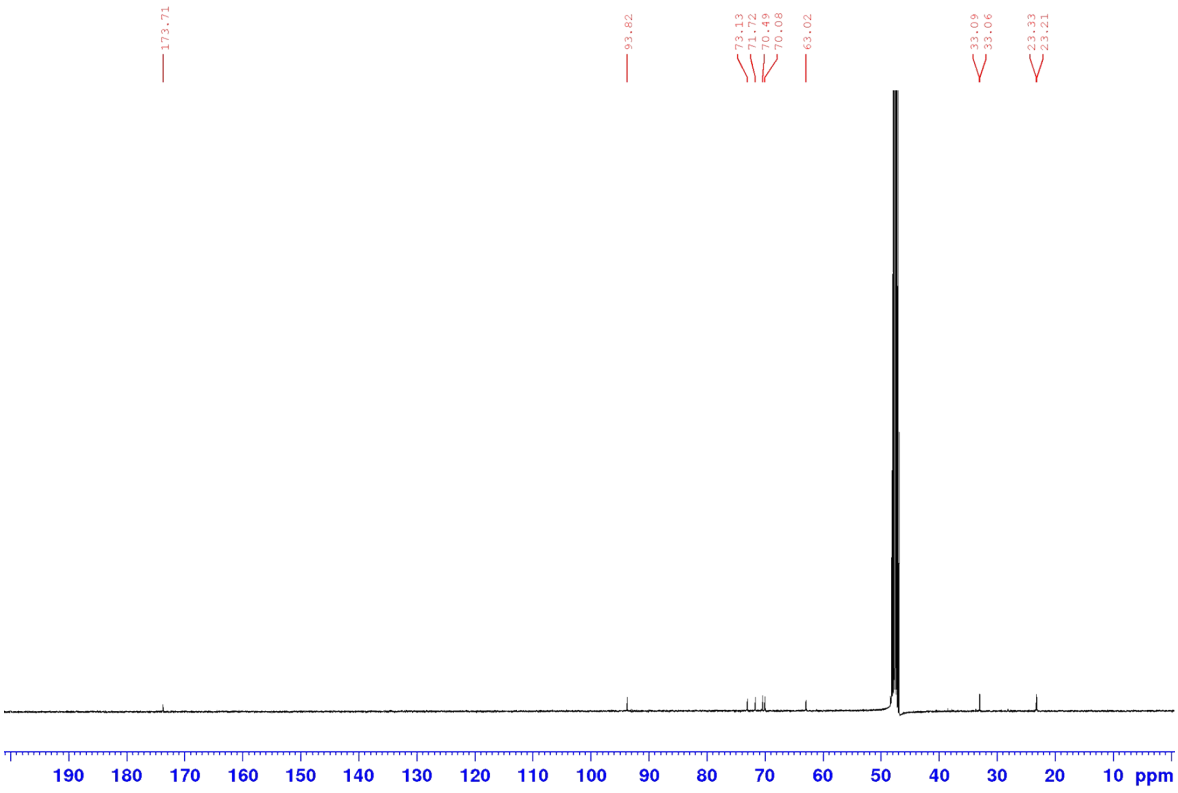


Fig S12. ^{13}C NMR data for 7 (150 MHz, CD_3OD)

Physical Data

Synthesis of QDs

CdSe@ZnS/ZnS alloyed QDs with PL wavelength of 525 nm (green QDs) were synthesised according to a previously reported procedure.[4] CdSe/CdS QDs with PL wavelength of 635 nm (red QDs) were synthesised according to a previously reported procedure.[5]

Equipment

UV-Vis spectroscopy was carried out using a Varian/Cary 50 spectrophotometer. PL spectroscopy was performed using a Cary Eclipse spectrofluorometer. Hydrodynamic radii of nanoparticles were measured on a Malvern Zetasizer Nano Series V5.10. STEM images of the QDs were measured with a Scanning Electron Microscope Merlin (Zeiss, Oberkochen, Germany) operated at 30 kV on copper grids with ultrathin carbon films.

DLS of glucose functionalised QDs

QDs were coated with thiol derivate of glucose and resuspended in aqueous alkaline solution (KOH, pH 11) containing cysteine (0.2 mg/ml). The DLS data of the resulting solution is presented in Fig. S13. The hydrodynamic diameter was in the range of 10 nm, which is correspond to the non-aggregated form of QDs.

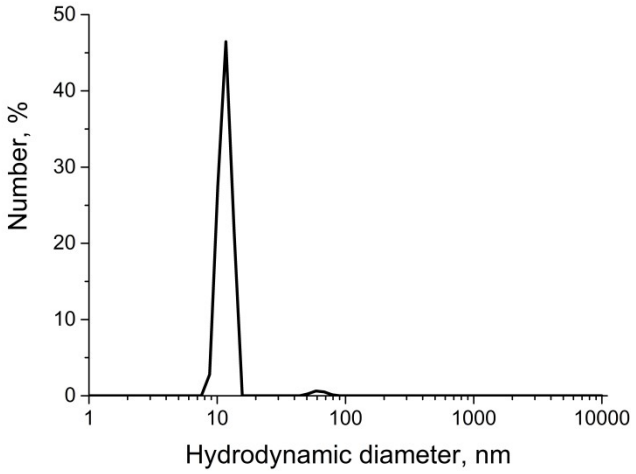


Fig S13. DLS data of QDs coated with thiol derivate of glucose, re-suspended in aqueous alkaline solution containing cysteine

Sensing system based on QDs with different PL wavelengths

To enhance the convenience of a potential naked eye test, QDs with two different PL wavelengths were used (red QDs (CdSe/CdS QDs) with PL at 635 nm and green QDs (CdSe@ZnS/ZnS alloyed QDs) with PL at 525 nm). TEM images of QDs are presented on Fig. S14. The average diameters of the green and red QDs are 12.9 ± 1.7 nm and 5.2 ± 0.8 nm, respectively.

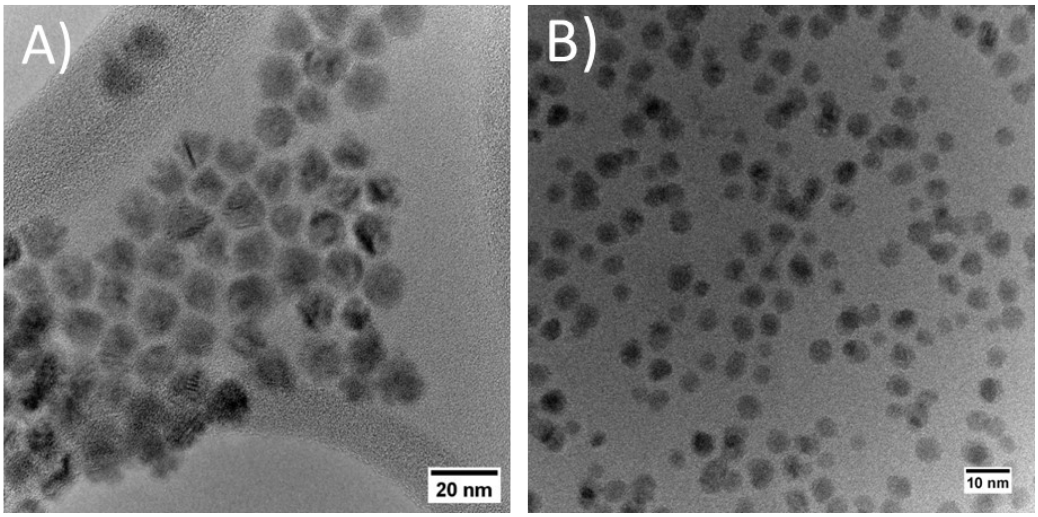


Fig S14. TEM images of (A) green QDs (CdSe@ZnS/ZnS alloyed QDs) and (B) red QDs CdSe/CdS QD.

UV-Vis and PL spectra of the QDs are presented in Figure S15A. Exciton absorption peak maxima of green and red QDs, respectively, were on 520 nm and 592 nm; full width at half maximum of PL peak were 22 nm and 27 nm, respectively. The PL spectrum of green QDs overlaps with the absorption spectrum of red QDs, thus fulfilling the conditions for Förster resonance energy transfer (FRET). When QDs are cross-linked by trehalose and aggregated, the distance between them is short enough, which allows FRET to occur. FRET from green QDs to red QDs lead to partial quenching of the green QD PL, and therefore the mixture possesses a red colour under UV lamp irradiation. After disaggregation free QDs in solution are at a distance much higher than Förster radius, the green QD PL is restored and the mixture becomes green. PL spectra of both the samples can be seen in Fig. S15B.

The PL spectra showed a well-defined emission peak at 525 nm, corresponding to the green QDs, for both samples; however, a significant decrease in the luminescence of the green CdSe/ZnS QDs is observed for control sample of trehalose functionalised QDs. The red QDs can be seen in PL spectra by the well-defined emission peak at 635 nm for both samples, with only a slight increase in their luminescence in control samples. This slight increase in the luminescence of the red QDs in the presence of trehalase, could be due to the passivation of the QD surface by the enzyme molecules or due to aggregation caused quenching. Therefore, it can be stated that quenching of the luminescence of the green QDs is observed in the aggregated QD system, which is depicted by the red line in the PL spectra. The control QD sample, where the QDs were cross-linked together, results in partial quenching of the green QDs and therefore the colour of the sample was red. In contrast, when the QD sample was subjected to treatment with the trehalase enzyme the luminescence of green QDs was restored and the colour of the sample became green.

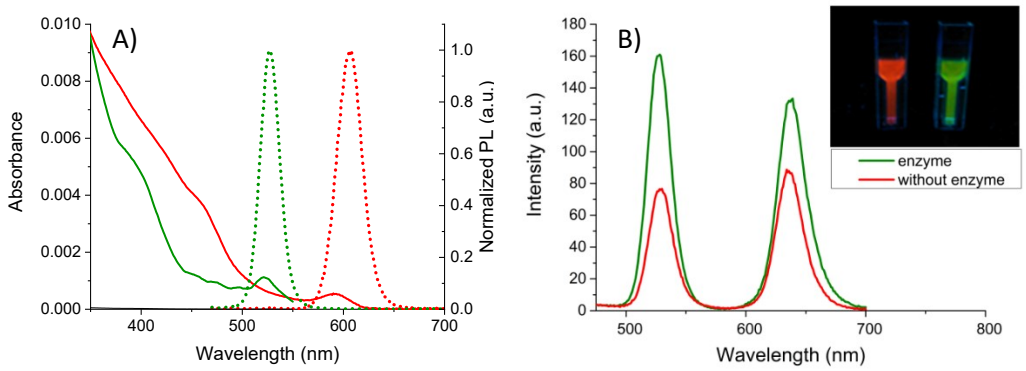


Fig. S15 (A) UV-Vis (solid lines) and PL (dotted lines) spectra of CdSe@ZnS/ZnS QDs (green) and CdSe/CdS QDs (red). (B) PL spectra of the trehalose functionalised QDs, indicating an increase in PL intensity with disaggregation upon treatment with the enzyme (top) and QD samples under UV light (bottom).

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