Supporting Information

MATERIALS AND METHODS

Synthesis

11-bromoundec-1-ene (2)

Phosphorus tribromide (5.3 g, 19.6 mmol, 1.84 ml) was added dropwise to a solution of 10-Undecen-1-ol (10g, 58.7mmol) in diethyl ether (100ml) at -78°C over a period of 10 min and then the mixture was allowed to warm to room temperature and stirred under Ar overnight. The reaction mixture was quenched with water and the layers were separated. The aqueous layer was extracted with ether (5×30 ml) and the combined organic layers were washed with brine and dried over sodium sulfate. After evaporation of the solvent in *vacuo*, the crude product was purified by chromatography column on silica gel (hexane) to give pure product 8.2 g (yield: 60%). ^{1}H NMR ($CDCl_3$) δ 5.85-5.75 (m, 1H), 5.01-4.91 (m, 2H), 3.37- 3.41(t, 2H, *J* = 7.2 Hz), 2.06-1.99(m, 2H), 1.88-1.81(m, 2H), 1.39(br, 2H), 1.29(br, 10H). ^{13}C NMR ($CDCl_3$) δ 139.4, 114.3.3, 34.2, 34.1, 33.0, 31.8, 29.6, 29.3, 29.1, 29.0, 28.4.

Undec-1-en-11-yltetra (ethylene glycol) (3)

A mixture of 1 ml of 50% aqueous sodium hydroxide (0.012 mol) and 23.4 g of tetra (ethylene glycol) (0.12 mol) was stirred for 0.5 h in an oil bath at 100 °C under Ar, and 2.8 g of 11-bromoundec-1-ene (0.012 mol) was then added. At the completion of the reaction as indicated by the TLC analysis, the reaction mixture was cooled and extracted several times with hexane. The combined organic layers were washed with brine and dried over sodium sulfate. After evaporation of the solvent in *vacuo*, the crude product was purified by chromatography column

on silica gel (hexane/ethyl acetate, 1:1) to give pure product 2.5g (yield: 60%). ^{1}H NMR ($CDCl_3$) δ 5.82-5.72 (m, 1H), 4.97-4.87 (m, 2H), 3.68-3.64(t, 2H, *J* = 4.8 Hz), 3.62-3.54 (m, 14H), 3.42-3.39(t, 2H, *J* = 7.2 Hz), 2.01-1.97 (m, 3H), 1.55-1.50(m, 2H), 1.35-1.24 (m, 12H). ^{13}C NMR ($CDCl_3$) δ 139.5, 114.4, 72.8,71.8,70.8,70.7,70.5,70.2, 34.0, 29.8, 29.7, 29.6, 29.3, 29.1, 26.3. MS ES^+ m/z 369.28 (M+Na).

[1-[(Methylcarbonyl)thio]undec-11-yl]-tetra(ethylene glycol) (4)

Solutions of Undec-1-en-11-yltetra (ethylene glycol) (2.66 g, 7.7 mmol) in MeOH (40 ml) containing 3 equivalent of thioacetic acid (1.6 ml) and 5 mg AIBN were purged with Ar for 1 h, then the mixture was irradiated under standard conditions (medium pressure mercury lamp, Pyrex glass filter) until the disappearance of the starting materials as indicated by TLC analysis. At the completion of the reaction, the solvent was removed in *vacuo*, the crude product was purified by chromatography on silica gel (hexane/ethyl acetate 2:1) to give pure product 2.3 g (yield: 70%). ^{1}H NMR ($CDCl_3$) δ 3.62-3.46 (m, 16H), 3.36-3.33(t, 2H, *J* = 6.4 Hz), 2.77-2.73(t, 2H, *J*= 7.2 Hz), 2.21(s, 3H), 2.19(m, 2H), 1.49-1.44(m, 2H), 1.16(br, 14H). ^{13}C NMR ($CDCl_3$) δ 196.1,72.8,71.7, 70.7,70.4.70.1, 61.7, 30.7, 29.7, 29.6, 29.5, 29,2, 28.9,26.2. MS ES^+ m/z 445.34(M+Na).

[1-[(Methylcarbonyl)thio]undec-11-yl]-tetra(ethylene glycol) 2,3,4,6-tetra-O-acetyl-α-D-mannopyranoside (7)

Linker [1-[(Methylcarbonyl)thio]undec-11-yl]-tetra(ethylene glycol) (0.889 g, 2.1 mmol) in 20 ml anhydrous dichloromethane, $HgBr_2$ (0.94 g, 2.4mmol) and $Hg(CN)_2$ (0.65g, 2.4 mmol) were added to a previously flame-dried flask containing 1 g 4 Å molecular sieve. After the mixture was stirred for 1 h under Ar, 2,3,4,6-tetra-O-acetyl-α-D-mannosyl bromide (1.25g, 2.94 mmol)

was added to the mixture. The mixture was stirred in the dark at ambient temperature until the completion of the reaction as indicated by TLC analysis. The resulting mixture was passed through a Celite packed glass funnel, and washed with saturated $NaHCO_3$ and brine. The organic phase was dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The resulting residue was purified by chromatography column on silica gel (hexane/ethyl acetate, 1:1) to give the product 0.96 g (yield: 61%). ^{1}H NMR ($CDCl_3$) δ 5.30-4.80 (m, 3H), 4.68 (br, 1H), 4.11-4.05(m, 1H), 3.93-3.88(m, 2H), 3.68-3.37 (m, 16H), 3.24(t, 2H, *J* = 7.2 Hz), 2.67-2.64(t, 2H, *J* = 6.8 Hz), 2.12(s, 3H), 1.95(s, 3H), 1.90(s, 3H), 1.85(s, 3H), 1.84(br, 2H), 1.78(s, 3H), 1.36(br, 2H), 1.07(br, 14H). ^{13}C NMR ($CDCl_3$) δ 195.7, 170.5, 169.9, 97.7, 71.4, 70.5, 70.0, 69.5, 69.1, 68.4, 67.3, 66.1, 62.7, 62.4, 60.3, 29.6, 29.5, 29.4, 28.7, 20.8. MS ES$^+$ m/z 775.47(M+Na).

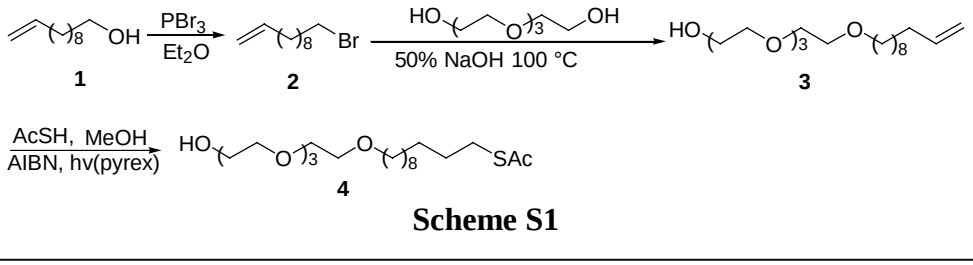
(1-Mercaptoundec-11-yl)tetra (ethylene glycol) D-mannopyranoside conjugate (8)

Anhydrous MeOH was added to [1-(Methylcarbonyl)thio]undec-11-tetra(ethylene glycol) 2,3,4,6-tetra-O-acetyl-α-D-mannopyranoside (0.814g, 1.08 mmol). After the solution was flushed with Ar for 20 min., NaOMe (0.583g, 10.8mmol) was added, the reaction mixture was stirred under Ar at r.t till the completion of the reaction as indicated by the TLC analysis. Dowex cation exchange resin (H form) was added to adjust the pH to 6-7, the resin was filtered off and the filtrate was concentrated in *vacuo*. The resulting residue was purified by chromatography (CH_2Cl_2/MeOH, 5:1) to afford the product (8) 526 mg (yield: 90%). ^{1}H NMR (CD_3OD) δ 4.79 (d, J = 1.8 Hz, 1H), 3.84 (dd, *J* = 4.0 Hz, 1H), 3.80-3.81(m, 2H), 3.72 (m, 1H), 3.71(d, J = 13.2, 2H), δ 3.65-3.64 (m, 16H), 3.36-3.33(t, 2H, *J* = 6.4 Hz), 2.77-2.73(t, 2H, *J* = 7.2 Hz), 2.21(s, 3H), 2.19(m, 2H), 1.49-1.44(m, 2H), 1.16(br, 14H) ^{13}C NMR (CD_3OD) δ 100.5, 73.4, 70.4, 70.2, 69.9, 67.4, 66.6, 61.7, 34.1, 29.5, 29.1, 28.3, 26.0, 23.8. ESI m/z 541.48

RESULTS AND DISCUSSION

Synthesis

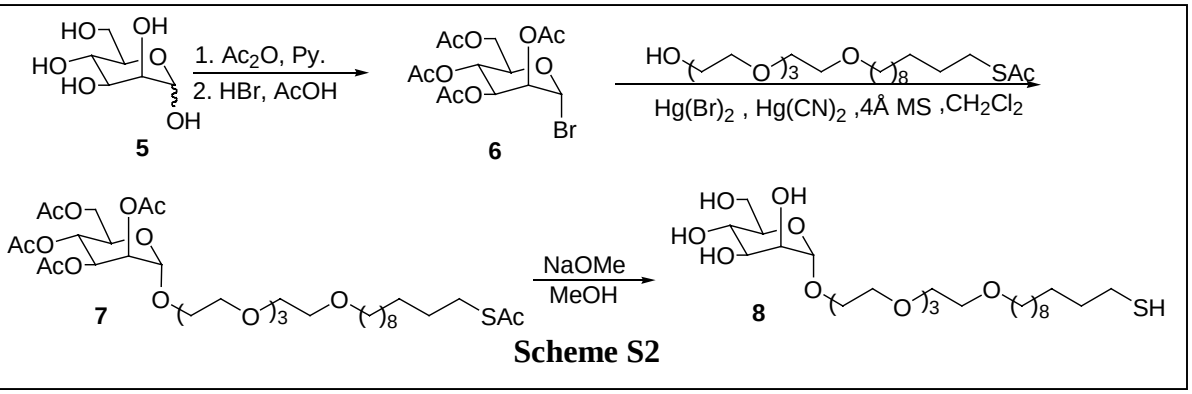
Synthesis of linker [1-[(Methylcarbonyl)thio]undec-11-yl]-tetra(ethylene glycol) is shown in Scheme S1.



Scheme S1

Treatment of the commercially available ω-undecylenyl alcohol with PBr3 and then reaction with tetraethylene glycol gives undec-1-en-11-yl tetra-(ethyleneglycol) (3), which is then treated with thiolacetic acid under photolysis condition initiated by AIBN to provide the desired linker [1-[(methylcarbonyl) thiol] undec-11-tetra(ethylene glycol) (4).

The synthesis of (1-Mercaptoundec-11-yl) tetra (ethylene glycol) D-mannopyranoside conjugate is shown in Scheme S2. Connection of the linker (4) to mannose via a glycosylation reaction promoted by $HgBr_2$ and $Hg(CN)_2$ and then deprotection provides the target compound (8).



Scheme S2

Analysis of Lipopolysaccharides

The whole cell extracts from *E.coli* O86:H2 wild type and *E.coli* W1485 were treated with proteinase K as described by Hitchcock and Brown.[1] After electrophoresis on 12.5% polyacrylamide gel, LPS was detected by silver-staining method according to a previous published protocol.[2]

Figure S1. LPS analysis by SDS–PAGE followed by silver-staining. Lane 1, *E.coli* O86:H2 wild type; lane 2, *E.coli* W1485.

References:

(1) Hitchcock, P. J.; Brown, T. M. *J. Bacteriol.* **1983**, *154*, 269-277.

(2) Wang, L.; Reeves, P. R. *J. Bacteriol.* **1994**, *176*, 4348-4356.