Supporting Information

Magnetic multivalent trehalose glycopolymer nanoparticles for the detection of mycobacteria

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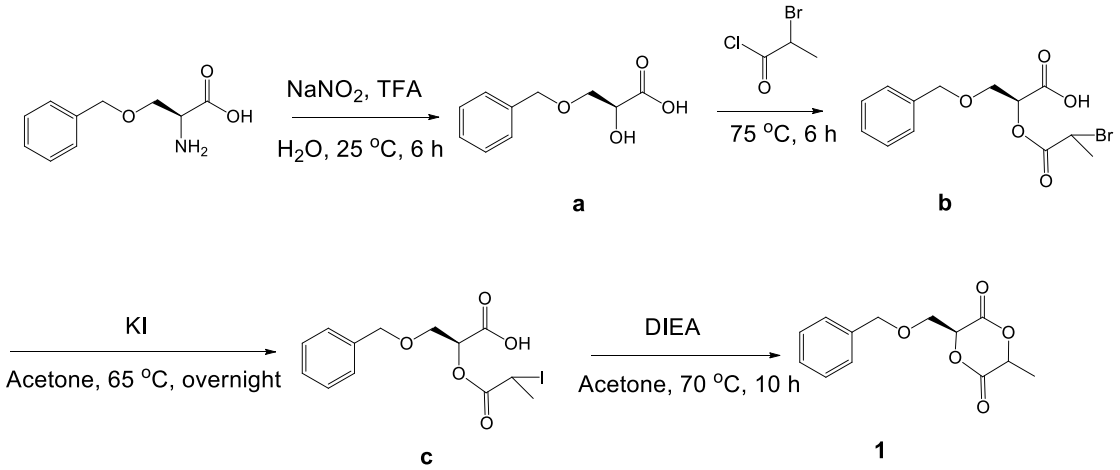
Materials

Benzaldehyde dimethyl acetal, *p*-toluenesulfonic acid, sodium chloride, triethylamine, acetic anhydride, 4-dimethylaminopyridine, hexane, carbon tetrachloride, calcium carbonate, *N*-bromosuccinimide, sodium bicarbonate, sodium azide, sodium methoxide, isopropanol, Amberlite IRC-120 H^+ resin, methanol, trifluoroacetic acid (TFA), sodium nitrite, magnesium sulfate, sodium sulfate, acetic acid, potassium iodide, celite, *N,N*-Diisopropylethylamine (DIEA), tin octoate, $Pd(OH)_2$ on charcoal, *N,N'*-Dicyclohexylcarbodiimide (DCC), pent-4-ynoic acid, copper (I) bromide, phosphorus pentoxide, pentamethyldiethylenetriamine, iron (III) acetylacetonate, 1,2-hexadecanediol, oleic acid, tetrahydrofuran, ethanol, oleylamine, concanavalin A (Con A) and bovine serum albumin (BSA) were purchased from Sigma-

Aldrich and used without further purification. Trehalose anhydrate and 2-bromopropionyl chloride were purchased from TCI-America and used as received. *O*-Benzyl-L-serine was purchased from Chem Impex. Dichloromethane, dimethylformamide, ethyl acetate and dimethyl sulfoxide were purified by distillation over CaH_2. Acetone was distilled from phosphorus pentoxide. Amberlite IRC-120 H^+ resin was activated by washing with NaOH and HCl followed by water. High purity L-lactide was obtained by recrystallization from anhydrous EtOAc. Dialysis membrane (molecule weight cutoff: 3500) was purchased from Spectrum Labs.



Scheme S1. Synthesis of (3-(benzyloxymethyl)-6-methyl-1,4-dioxane-2,5-dione) (**1**).

Synthesis of 3-benzyloxy-2-hydroxypropionic acid (a)[1]

To a 200 mL aqueous solution of 0.7 M trifluoroacetic acid, *O*-benzyl-L-serine (10.0 g, 52 mmol) was added, and the mixture was stirred at room temperature until all the solid was dissolved. An aqueous solution of $NaNO_2$ (50 mL, 1.5 M) was added dropwise with a syringe pump under Ar protection, and the reaction was stirred for another 3 hours. After the consumption of the starting material was confirmed by TLC, NaCl (10.0 g) was added, and the solution was extracted with ethyl acetate for three times followed by washing with brine and drying over $MgSO_4$. After flash column chromatography using CH_2Cl_2/MeOH/AcOH

(v/v/v 100:8:1), the title compound **a** was obtained as a yellow liquid (7.2 g, 72 %). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.41-7.20 (m, 5H, Ar H), 5.33 (s, 1H; -OH), 4.51 (q, J = 12.2 Hz, 2H; ArC*H*$_2$O-), 4.16 (t, J = 4.2 Hz, 1H; -OCH$_2$C*H*(COOH)O-) 3.62 (d, J = 4.4 Hz, 2H; -OC*H*$_2$CH-); IR (ATR): 3324 (m, ν_s(carboxylic and alcoholic O-H)), 3033 (m, ν_s(aromatic C-H)), 2915 (w, ν_{as}(-CH$_2$-)), 2871 (w, ν_s(-CH$_2$- and aliphatic -CH-)), 2645 (w), 2537 (w), 1693 (vs, ν_s(carboxylic C=O)), 1495 (w), 1455 (m, δ_s(-CH$_2$-)), 1412 (m), 1363 (w), 1274 (s), 1225 (m), 1202 (m), 1102 (vs), 1038 (m), 1019 (m), 926 (s), 826 (s), 791 (w), 732 (m, ω(aromatic C-H)), 697 (m, τ(aromatic ring)), 653 (m), 610 (m), 557 (m) cm^{-1}.

Synthesis of 3-(benzyloxy)-2-(2-bromopropanoyloxy)propanoic acid (b)[1]

Compound **a** (10.0 g, 51 mmol) and 2-bromopropionyl chloride (6.3 mL, 61.2 mmol) were mixed in a 50 mL flask filled with Ar. The reaction mixture was heated to 70 ^{o}C and stirred for 6 hours. Upon the completion of the reaction, the crude product was heated at 60 ^{o}C under reduced pressure to remove unreacted 2-bromopropionyl chloride and 2-bromopropionyl acid. After cooling down to room temperature, the residue was washed with water and extracted with ethyl acetate 3 times. The combined organic phase was washed with brine and dried over $MgSO_4$. The product was further purified by flash column chromatography using CH_2Cl_2/MeOH/AcOH (v/v/v 100:2:0.5) to give **b** as a light brown viscous liquid (12.6 g, 75%). ^{1}H NMR (500 MHz, $CDCl_3$): 7.60-7.27 (m, 5H, Ar H), 5.33 (dd, J= 5.2, 2.6 Hz, 1H; -OCH$_2$C*H*(COOH)O-), 4.73-4.33 (m, 3H; ArC*H*$_2$O- and -OCC*H*(Br)CH$_3$), 4.03-3.79 (m, 2H; -OC*H*$_2$CH-), 1.87 (m, 3H; -CH(Br)C*H*$_3$); IR (ATR): 3442 (w, ν_s(carboxylic O-H)), 3032 (w, ν_s(aromatic C-H)), 2928 (w, ν_{as}(-CH$_2$- and –CH$_3$)), 2871 (w, ν_s(-CH$_2$- and aliphatic -CH-)), 2616 (w), 1732 (vs, ν_s(ester C=O)), 1497 (w), 1452 (m, δ_s(-CH$_2$-)), 1211 (m), 1155 (w), 1097 (m), 985 (w), 738 (m, ω(aromatic C-H)), 697 (m, τ(aromatic ring)) cm^{-1}.

Synthesis of 3-(benzyloxy)-2-(2-iodopropanoyloxy)propanoic acid (c)[1]

Compound **b** (8.0 g, 24 mmol) and potassium iodide (40 g, 0.24 mol) were dissolved in dry acetone (100 mL). The reaction was heated at 60 ^{o}C overnight under Ar. Then, the solid salt was removed by passing through celite and the filtrate was concentrated under vacuum. Ethyl acetate was added to the oily residue and the solution was filtered again to remove trace potassium iodide/potassium bromide. The organic phase was washed with 2 M aq. $Na_2S_2O_3$ three times and dried over $MgSO_4$. ($Na_2S_2O_3$ was used to remove I_2.) After evaporation of the solvent, compound **c** was obtained as a brown viscous liquid (7.5 g, 82%). The product was used directly without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52-7.28 (m, 5H, Ar H), 5.31 (m, 1H; -OCH_2CH(COOH)O-), 4.74-4.41 (m, 3H; ArCH_2O- and -OCC*H*(Br)CH_3), 4.00-3.80 (dd, J = 48.3, 10.4 Hz, 2H; -OCH_2CH-), 2.02 (m, 3H; -CH(I)CH_3); IR (ATR): 3440 (w, ν_s(carboxylic O-H)), 3030 (w, ν_s(aromatic C-H)), 2924 (w, ν_{as}(-CH_2- and –CH_3)), 2867 (w, ν_s(-CH_2- and aliphatic -CH-)), 2620 (w), 1728 (vs, ν_s(ester C=O)), 1496 (w), 1452 (m, δ_s(-CH_2-)), 1362 (w), 1197 (w), 1124 (s), 1094 (s), 1043 (s), 977 (w), 909 (w), 737 (m, ω(aromatic C-H)), 697 (m, τ(aromatic ring)) cm^{-1}.

Synthesis of 3-(benzyloxymethyl)-6-methyl-1,4-dioxane-2,5-dione (1)[1]

A solution of compound **c** (10.0 g, 26.8 mmol) in dry CH_2Cl_2 (100 mL) was added dropwise to refluxing dry acetone (1 L) containing DIEA (8.8 mL, 53.6 mmol) under Ar. It took 10 hours to finish the addition and the reaction was refluxed for another hour. The solvents were removed under reduced pressure and ether was added to dissolve the crude product. Insoluble ammonium iodide was filtered and the filtrate was concentrated. After purification by flash column chromatography using hexane/ethyl acetate (v/v 4:1), the title compound **1** was obtained as a yellow oil (2.1 g, 31%). The diastereomers were used directly without further separation. ^{1}H NMR (500 MHz, $CDCl_3$): (SS) δ 7.44-7.27 (m, 5H, Ar H), 5.00-5.12 (m, 2H; -

OCC*H*(CH_2O-)O- and - OCC*H*(CH_3)O-), 4.58 (d, J = 23.5 Hz, 2H; ArC*H*$_2$O-), 3.98 (d, J = 3.7 Hz, 2H; -OC*H*$_2$CH-), 1.63 (m, 3H; -CHC*H*$_3$); (RS) δ 7.44-7.27 (m, 5H, Ar H), 5.24 (q, J = 7.0 Hz, 1H; -OCC*H*(CH_2O-)O-), 5.00-5.12 (m, 1H; -OCC*H*(CH_2O-)O- and - OCC*H*(CH_3)O-), 3.98 (d, J = 23.5 Hz, 2H; ArC*H*$_2$O-), 4.06 (dd, J = 10.2, 2.0 Hz, 1H; -OC*H*$_2$CH-), 3.91 (dd, J = 10.6, 2.6 Hz, 1H; -OC*H*$_2$CH-) 1.63 (m, 3H,; -CHC*H*$_3$); IR (ATR): 2993 (w, ν_s(aromatic C-H)), 2942 (w, ν_{as}(-CH_2- and –CH_3)), 2872 (w, ν_s(-CH_2- and aliphatic -CH-)), 1747 (vs, ν_s(ester C=O)), 1453 (m, δ_s(-CH_2-)), 1365 (w), 1268 (w), 1182 (s), 1084 (vs), 1046 (m), 865 (w), 739 (m, ω(aromatic C-H)), 698 (m, τ(aromatic ring)) cm^{-1}.

Synthesis of copolymer 3[1]

Monomer **1** (1.0 g, 4.0 mmol), L-lactide (**2**) (1.0 g, 6.9 mmol) and a solution of $Sn(oct)_2$ 10 mg in dry toluene (1 mL) were added into a 5-mL round bottom flask. The mixture was heated to 70 °C under vacuum for 1 hour. The flask was filled with Ar and the temperature was increased to 140 °C. The mixture was stirred until the stir-bar stopped moving. After cooling to room temperature, the solid was dissolved in CH_2Cl_2. Hexanes were added and the precipitates were dried to give copolymer **3** as a dark brown powder (1.48 g, 74%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (Ar H), 5.45-5.00 (-OCC*H*(CH_2O-)O- and -OCC*H*(CH_3)O-), 4.59 (ArC*H*$_2$O-), 3.93 (-OC*H*$_2$CH-), 1.57 (-CHC*H*$_3$); IR (ATR): 2994 (w, ν_s(aromatic C-H)), 2944 (w, ν_{as}(-CH_2- and –CH_3)), 2872 (w, ν_s(-CH_2- and aliphatic -CH-)), 1747 (vs, ν_s(ester C=O)), 1453 (m, δ_s(-CH_2-)), 1364 (w), 1267 (w), 1182 (s), 1082 (vs), 1046 (m), 865 (w), 740 (m, ω(aromatic C-H)), 699 (m, τ(aromatic ring)) cm^{-1}.

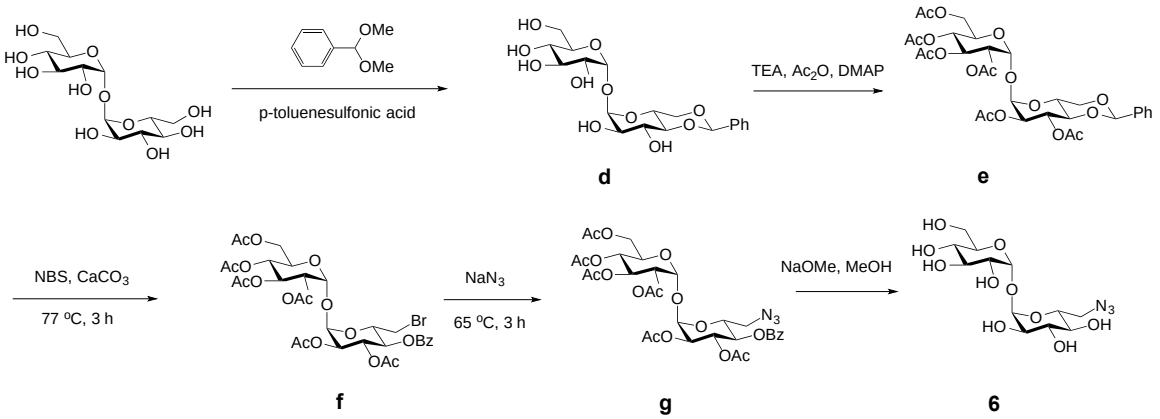
Synthesis of copolymer 4[1]

Copolymer **3** (1.0 g) was dissolved in 50 mL ethyl acetate/methanol (3:1) and $Pd(OH)_2$/C was added. The mixture was purged with Ar for 20 min, and was then filled with H_2 under vigorous stirring. After 12 hours, the solution was filtered through a pile of celite to remove

$Pd(OH)_2/C$, and the filtrate was dried under vacuum to give copolymer **3** as a light brown solid (630 mg, 63%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.0-5.5 (-OCC*H*(CH_2OH)O- and -OCC*H*(CH_3)O-), 4.00 (HOC*H*$_2$CH-), 1.59 (-CHC*H*$_3$); IR (ATR): 3501 (w, ν_s(alcoholic O-H)), 2992 (w), 2945 (w, ν_{as}(-CH_2- and –CH_3)), 2876 (w, ν_s(-CH_2- and aliphatic -CH-)), 1744 (vs, ν_s(ester C=O)), 1452 (m, δ_s(-CH_2-)), 1380 (m), 1182 (s), 1129 (m), 1084 (vs), 864 (w), 743 (w) cm^{-1}.

Synthesis of copolymer 5

Copolymer **4** (100 mg) and pent-4-ynoic acid (40 mg, 0.41 mmol) were added into dry CH_2Cl_2 (10 mL) containing DCC (218 mg, 0.82 mmol) and a catalytic amount of DMAP (5 mg, 0.04 mmol). The solution was stirred for 12 h and the precipitate was filtered. The filtrate was concentrated to 5 mL and was poured into 200 mL hexanes/methanol (v/v 9:1). The precipitate was dried to give the copolymer **5** as yellow solid (67 mg, 59%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.20-5.50 (-OCC*H*(CH_2O-)O- and -OCC*H*(CH_3)O-), 4.59 (-OC*H*$_2$CH-), 2.65 (HC≡CCH_2C*H*$_2$CO-), 2.65-2.50 (HC≡CC*H*$_2$$CH_2$CO-), 2.01 (*H*C≡C$CH_2$$CH_2$CO-), 1.60 (-CHC*H*$_3$); IR (ATR): 3286 (w, ν_{as}(alkyne C-H)), 2992 (w), 2945 (w, ν_{as}(-CH_2- and –CH_3)), 1743(vs, ν_s(ester C=O)), 1451(m, δ_s(-CH_2-)), 1364 (m), 1182 (s), 1131 (w), 1083 (vs), 1044 (w), 865 (w), 753 (w), 651 (m) cm^{-1}.



Scheme S2. Synthesis of 6-azido-6-deoxy-*α,α*-D-trehalose (**6**).

Synthesis of 4,6-benzylidine-*α,α*-D-trehalose (d)[2]

Benzaldehyde dimethyl acetal (1.1 g, 7.0 mmol), trehalose (2.0 g, 5.8 mmol) and *p*-toluenesulfonic acid (0.1 g, 0.58 mmol) were added to DMF (20 mL). The mixture was stirred for 12 hours at room temperature and further heated up to 40 ºC for another 3 hours. The solution was used directly without purification.

Synthesis of 4,6-benzylidine-2,2',3,3',6'-penta-*O*-acetyl-*α,α*-D-trehalose (e)[2]

Triethylamine (14.0 g, 0.14 mol), Ac_2O (7.0 g, 0.70 mol) and DMAP (122 mg, 1.0 mmol) were added into the crude **d**. After stirring overnight, the reaction was transferred to a separatory funnel and brine (7 mL) was added. The crude product was extracted with ethyl acetate for three times. The organic phase was combined, washed with water/brine and concentrated under vacuum. After flash column chromatography using hexane/ethyl acetate (v/v 2:3), compound **e** was obtained as a white solid (1.2 g, 30%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 - 7.38 (m, 2H, Ar H), 7.38 - 7.30 (m, 3H, Ar H), 5.61 (t, *J* = 9.8 Hz, 1H; H-3_a), 5.55 - 5.44 (m, 2H; H-3_b, Ar-C*H*-(OCH_2)(OCH)-), 5.37 (d, *J* = 3.7 Hz, 1H; H-1_b), 5.27 (d, *J* = 3.7 Hz, 1H; H-1_a), 5.09 - 4.93 (m, 3H; H-2_a, H-2_b and H-4_b), 4.25 (dd, *J* = 12.1, 5.5 Hz, 1H; H-6_{b1}), 4.17 (dd, *J* = 10.4, 4.8 Hz, 1H; H-6_{a1}), 4.13 - 4.06 (m, 1H; H-5_b), 4.06 - 3.93 (m, 2H; H-5_a and H-6_{b1}), 3.75 (t, *J* = 10.4 Hz; 1H, H-6_{a2}), 3.69 (t, *J* = 9.6 Hz, 1H; H-4_a), 2.22 - 1.96 (m, 18H; OAc); IR (ATR): 2986 (w, ν_s(aromatic C-H)), 2950 (w, ν_{as}(-CH_2- and –CH_3)), 2870(w, ν_s(-CH_2- and aliphatic -CH-)), 1741 (vs, ν_s(ester C=O)), 1374 (m), 1214 (vs), 1133 (m), 1098 (w), 1021 (s), 980 (m), 956 (m), 906 (m), 803 (w), 767 (w), 702 (m) cm^{-1}.

Synthesis of 4-*O*-benzoyl-6-bromo-2,2',3,3',4',6'-penta-*O*-acetyl-6-deoxy-*α,α*-D-trehalose (f)[2]

Compound **e** (1.0 g, 1.5 mmol) was added into 50 mL of CCl_4 containing NBS (285 mg, 1.6 mmol) and $CaCO_3$ (160 mg, 1.6 mmol). The mixture was refluxed at 77 °C for 3 hours. After cooling to room temperature, the solution was washed with 10% $NaHCO_3$ and water. The organic phase was dried over Na_2SO_4, and the filtrate was concentrated in vacuum. Purification was done by flash column chromatography using hexanes/ethyl acetate (v/v 2:3) to give compound **f** as a white solid (1.0 g, 85%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 - 7.92 (d, *J* = 7.3 Hz, 2H, Ar H), 7.60 (t, *J* = 7.3 Hz, 1H, Ar H), 7.47 (t, *J* = 7.7 Hz, 2H, Ar H), 5.68 (t, *J* = 9.8 Hz, 1H; H-3_a), 5.55 (t, *J* = 9.7 Hz, 1H; H-3_b), 5.36 (m, 2H; H-1_a, H-1_b), 5.21 - 5.18 (m, 2H; H-2_b and H-4_a), 5.17 - 5.00 (m, 2H; H-2_a and H-4_b), 4.25 (m, 2H; H-5_a and H-6_{b1}), 4.16 - 3.97 (m, 2H; H-5_b and H-6_{b2}), 3.49 - 3.25 (m, 2H; H-6_{a1} and H-6_{a2}), 2.28 - 1.76 (m, 18H; OAc); IR (ATR): 2985 (w, ν_s(aromatic C-H)), 2950 (w, ν_{as}(-CH_2- and –CH_3)), 2872 (w, ν_s(-CH_2- and aliphatic -CH-)), 1741 (vs, ν_s(ester C=O)), 1374 (m), 1214 (vs), 1133 (m), 1098 (w), 1037 (s), 980 (m), 958 (m), 907 (m), 803 (w), 767 (m), 702 (m), 652 (m), 604 (m) cm^{-1}.

Synthesis of 4-*O*-benzoyl-6-azido-2,2',3,3',4',6'-penta-*O*-acetyl-6-deoxy-*α*,*α*-D-trehalose (g)[2]

A solution of compound **f** (1.0 g, 1.2 mmol) and NaN_3 (150 mg, 3 mmol) in DMF (10 mL) was heated under Ar at 65 °C for 3 h. After cooling to room temperature, the insoluble material was filtered. 100 mL of CH_2Cl_2 was added into the filtrate, and the mixture was washed with water and brine. The organic layer was dried over Na_2SO_4. The filtered solution was concentrated under reduced pressure to yield compound **g** as a white solid (0.70 g, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 2H, Ar H), 7.60 (t, *J* = 7.3 Hz, 1H, Ar H), 7.47 (t, *J* = 7.6 Hz, 2H, Ar H), 5.68 (t, *J* = 9.8 Hz, 1H; H-3_a), 5.55 (t, *J* = 9.8 Hz, 1H; H-3_b), 5.36 (m, 2H; H-1_a and H-1_b), 5.22 (t, *J* = 9.8 Hz, 1H; H-4_a), 5.17 - 5.00 (m, 3H; H-2_a, H-2_b and H-5_b), 4.25 (dd, *J* = 12.1, 5.6 Hz, 1H; H-6_{b1}), 4.20 - 4.06 (m, 2H; H-5_a and H-5_b), 4.03 (d, *J* = 12.1 Hz, 1H; H-6_{b2}), 3.44 (dd, *J* = 13.4, 7.6 Hz, 1H; H-

6_{a1}), 3.20 (dd, *J* = 13.1, 1.7 Hz, 1H; H-6_{a2}), 2.88 - 1.76 (m, 18H; OAc). IR (ATR): 2960 (w, ν_{as}(-CH_2- and –CH_3)), 2104 (m, ν_{as}(-N_3)), 1746 (vs, ν_s(ester C=O)), 1367 (m), 1211 (vs), 1135 (w), 1065 (w), 1018 (s), 982 (w), 897 (m), 802 (w), 754 (w), 712 (m) cm^{-1}.

Synthesis of 6-azido-6-deoxy-*α,α*-D-trehalose (6)[2]

Compound **g** (1.00 g, 1.3 mmol) and NaOMe (15 mg, 0.27 mmol) were added to methanol (20 mL). After stirring for 1 hour, the mixture was neutralized with Amberlite IRC-120 H^+ resins and filtered. After removing the solvent, the crude was purified by chromatography on silica gel using water/isopropanol/ethyl acetate (v/v/v 1:4:4) to give compound **6** as a white powder (239 mg, 50%). ^{1}H NMR (500 MHz, D_2O): δ 5.24 (m, 2H; H-1_a and H-1_b), 4.06-3.98 (m, 1H; H-5_a), 3.89 (m, 4H; H-5_b, H-3_a, H-3_b and H-6_{b1}), 3.82 (dd, J=11.4, 4.0 Hz, 1H; H-6_{b2}), 3.77-3.66 (m, 3H; H-2_a, H-2_b and H-6_{a1}), 3.61 (dd, J=13.3, 5.5 Hz, 1H; H-6_{a2}), 3.56-3.45 (m, 2H; H-4_a and H-4_b); IR (ATR): 3287 (s, ν_s(alcoholic O-H)), 2928 (m, ν_{as}(-CH_2-)), 2101 (s, ν_{as}(-N_3)), 1651 (w), 1435 (w), 1282 (m), 1146 (w), 1101 (w), 1073 (w), 984 (vs), 941 (w), 840 (w), 803 (w) cm^{-1}.

Synthesis of glycopolymer 7

6-Azido-6-deoxy-*α,α*-D-trehalose **6** (50 mg, 1.3 mmol) and copolymer **5** (50 mg) were dissolved in DMSO (5 mL), and the solution was bubbled with Ar for 1 h. CuBr (3 mg) and pentamethyldiethylenetriamine (10 μL) were added, and the solution was bubbled with Ar for another hour. After the reaction was completed, the mixture was poured into a dialysis membrane (molecule weight cutoff: 3500), and was dialyzed against water for two days. Polymer **7** was obtained as a light yellow powder after lyophilization (57 mg, 76%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.77 (triazole), 5.20 (-OCC*H*(CH_2O-)O- and -OCC*H*(CH_3)O-), 3.00-6.00 (trehalose and -OC*H*$_2$CH-), 2.95-2.60 (HC≡CC*H*$_2$C*H*$_2$CO-), 1.46 (-CHC*H*$_3$); IR (ATR): 3328 (w, ν_s(alcoholic O-H)), 2995 (w), 2945 (w, ν_{as}(-CH_2- and –CH_3)), 2880 (w, ν_s(-CH_2- and

aliphatic -CH-)), 1747 (vs, ν_s(ester C=O)), 1451(m, δ_s(-CH_2-)), 1380 (w), 1361 (w), 1183 (s), 1081 (vs), 864 (m), 751 (m) cm^{-1}.

Calculation of the trehalose content in polymer 7

The trehalose content (percent weight) in polymer **7** was calculated using the following equation:

$$\text{Trehalose}\,(\text{wt}\%) = \frac{\text{Mw(A)}}{\text{Mw(B)} + \text{Mw(C)} \times (\text{n/m})} \times 100\%$$

$$= \frac{325}{537 + 72 \times (7/1)} \times 100\% = 31\%$$

Mw(A): 325, molecular weight of the coupled trehalose, excluding the triazole

Mw(B): 537, molecular weight of the trehalose-coupled repeating unit

Mw(C): 72, molecular weight of the unfunctionalized repeating unit

n/m=7, obtained from the ratio of the integrals at 1.6 ppm (-C*H*$_3$) and 4.6 ppm (PhC*H*$_2$O-) in polymer **3**.

Synthesis of SPIONs (superparamagnetic iron oxide nanoparticles)

SPIONs were synthesized followed a previous procedure.[3] Under Argon protection, iron (III) acetylacetonate (0.35 g, 1.0 mmol) was added into a mixture of 1,2-hexadecanediol (1.8 g, 5.0 mmol), oleic acid (1.2 mL, 3.0 mmol) and oleylamine (1.4 mL). The reaction mixture was heated to 200 ^oC for 2 hours and maintain at 280 ^oC for another hour. Ethanol was added once the reaction was cooled to room temperature. A black solid was collected after centrifugation at 7000 rpm for 10 min, which was further washed with ethanol to remove excess reagents. Finally, the nanoparticles were redispersed in THF and stored at room temperature.

SPIONs encapsulation

The dispersion of the SPIONs in THF (1 mL, 2 mg/mL) was added dropwise into a solution of polymer **7** (5 mL, 1 mg/mL) in water/DMSO (v/v 1:1) under vortex. The mixture was stirred overnight, and was then dialyzed against water. Large aggregates were removed by centrifugation at 3000 rpm for 5 mins and the supernatant containing the magnetic micelles was collected.

Binding of magnetic micelles with lectin

The magnetic micelles (100 μL, 0.25 mg/mL) were added to a solution of Con A (100 μL, 0.1 mg/mL) containing 1.0 mM of $MnCl_2$ and $CaCl_2$ in pH 7.4 PBS buffer, or BSA (0.1 mg/mL) in pH 7.4 PBS buffer, or pH 7.4 PBS only. Aliquots were taken out at different time intervals and were measured by DLS.

Binding of magnetic micelles with bacteria

M. smegmatis mc^2 155, *S. epidermidis* 35984 or *E. coli* ORN 208 were inoculated in enriched Middlebrook 7H9 medium, LB medium or tryptic soy broth, respectively, at 37 ^oC and 250 rpm until OD reached 0.3 (OD_{600} for *M. smegmatis* mc^2 155, OD_{625} for *S. epidermidis* 35984 and *E. coli* ORN 208). Then, the bacteria (3 mL) were collected by centrifuging at 5000 rpm for 3 mins and then redispersed in PBS (3 mL). The bacteria (200 μL, 10^8 CFU/mL) was transferred into a glass vial and magnetic micelles (200 μL, 0.25 mg/mL) was added. The mixture was incubated at 37 ^oC overnight. Aliquots (10 μL) were transferred to chamber slides and the microscopy images were taken.

To prepare TEM samples, the mixture was centrifuged at 5000 rpm for 5 min and the precipitates were redispersed in water. The suspension was dropped onto a 200-mesh Cu grid and dried under vacuum.

Mycobacteria detection

Similar procedures as in bacteria binding study were followed, in which, 200 μL of *M. smegmatis* mc^2 155 (10^3, 10^4, 10^6 and 10^8 CFU/mL) was incubated with magnetic micelles (200 μL, 0.25 mg/mL) at 37 ºC and 250 rpm for 24 hours.

Bacterial viability tests

M. smegmatis mc^2 155, *S. epidermidis* 35984 or *E. coli* ORN 208 (100 μL, 10^6 CFU/mL) in the culture medium was incubated with magnetic micelles (100 μL, 0.25 mg/mL) for 24 hours at 37 ºC and 250 rpm in a 96 well plate. 50 μL of AlamarBlue was added to each well, and the plate was incubated for another hour at 37 ºC. The fluorescence intensity was then measured at 590 nm emission wavelength (560 nm excitation).

Characterization

Proton nuclear magnetic resonance (^{1}H NMR/^{1}H-^{1}H COSY) spectra were recorded on a Bruker 500 MHz spectrometer using deuterated solvent $CDCl_3$, D_2O or DMSO-d_6 (Cambridge Isotope Lab., Inc.). Glycopolymers were characterized on a GPC system (Polymer Labs GPC-50 with Agilent PLgel Guard column 50 x 7.5 mm/Agilent PLgel Mixed-D 300 x 7.5 mm column/Agilent PLgel Mixed-C 300 x 7.5 mm column and Wyatt Technologies Multi Angel Light Scattering (MALLS) running DMF with 0.01 M LiCl at 1 mL/min). Molecular weight was calculated based on PMMA as the standard calibration. FT-IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer. TEM images were taken on Philips EM400T. Hydrodynamic diameters and zeta potential were measured on a DLS system (Delsa™ Nano HC, Beckman). Optical images were taken on a ZEISS Primovert microscope with an Axiocam ERc 5s digital camera.

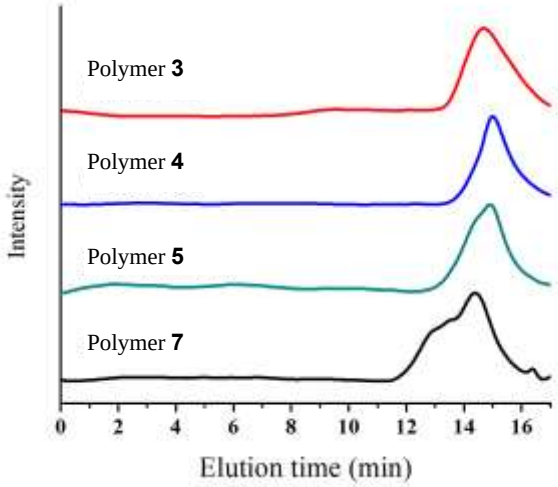


Figure S1. GPC chromatograms of polymers in DMF.

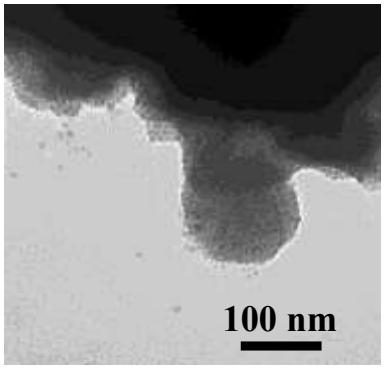


Figure S2. TEM image of oleic acid-coated iron oxide nanoparticles in water.

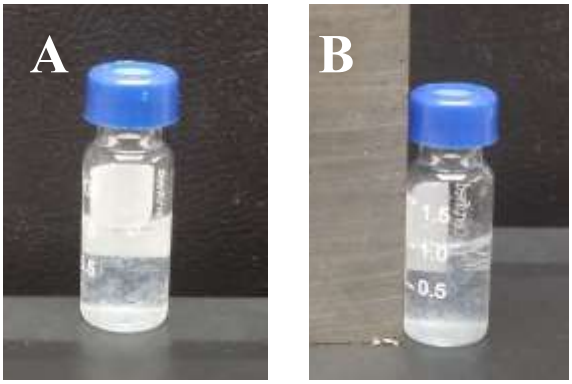


Figure S3. Con A-treated glycopolymer micelle solution in water before (A) and after (B) applying a magnet.

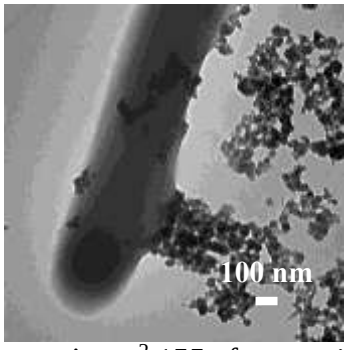


Figure S4. TEM image of *M. smegmatis* mc^2 155 after treating with magnetic glycomicelles. Membrane deformation can be seen.

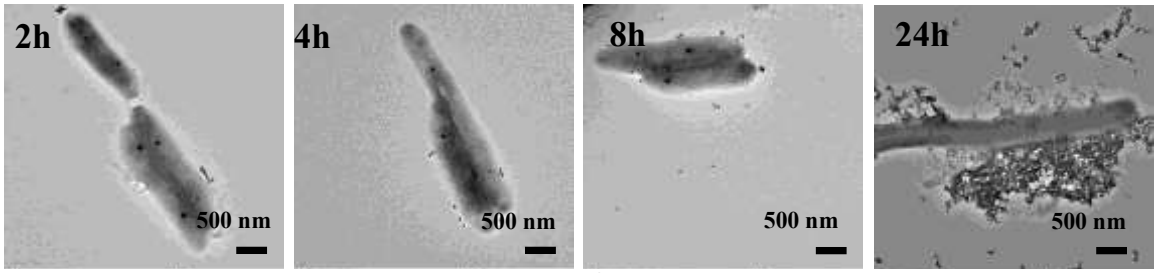


Figure S5. TEM images of *M. smegmatis* mc^2 155 incubated with magnetic micelles for 2 h, 4 h, 8 h and 24 h.

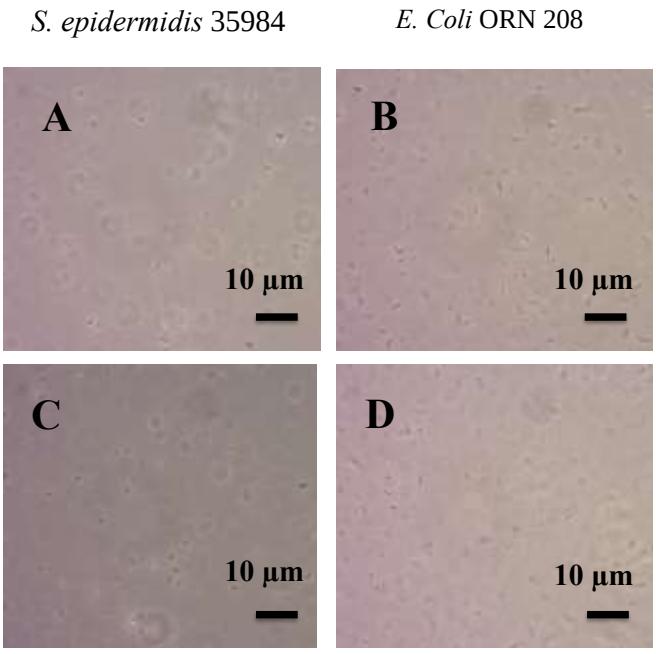


Figure S6. Optical images of magnetic glycomicelles treated with *S. epidermidis* 35984 or *E. Coli* ORN 208 before (A and B) and after (C and D) placing a magnet to the left of the samples.

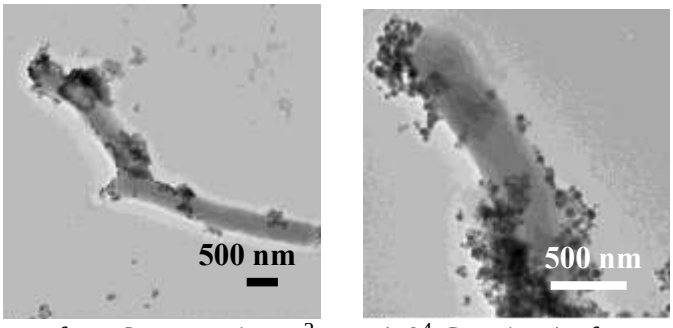


Figure S7. TEM image of *M. Smegmatis* mc^2 155 (10^4 CFU/mL) after treating with magnetic micelles for 24 hours.

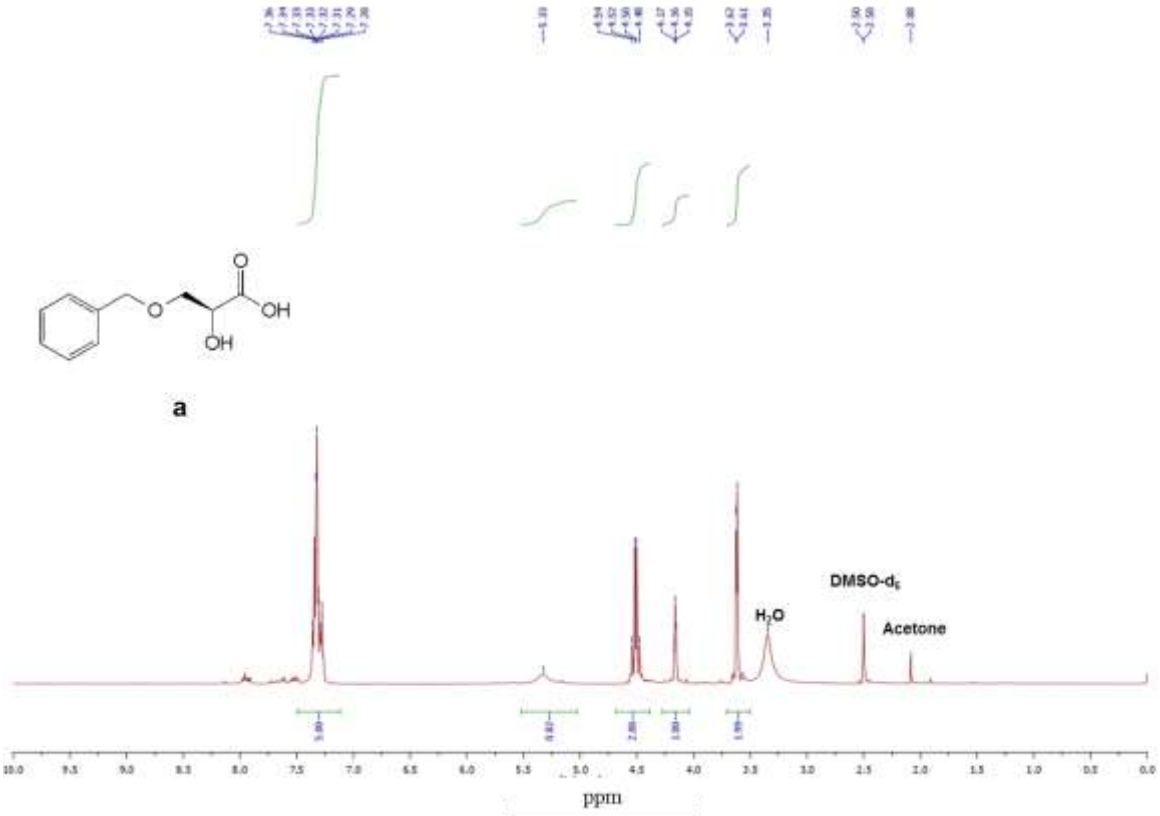


Figure S8. ^{1}H NMR spectrum of compound **a** in DMSO-d_6.

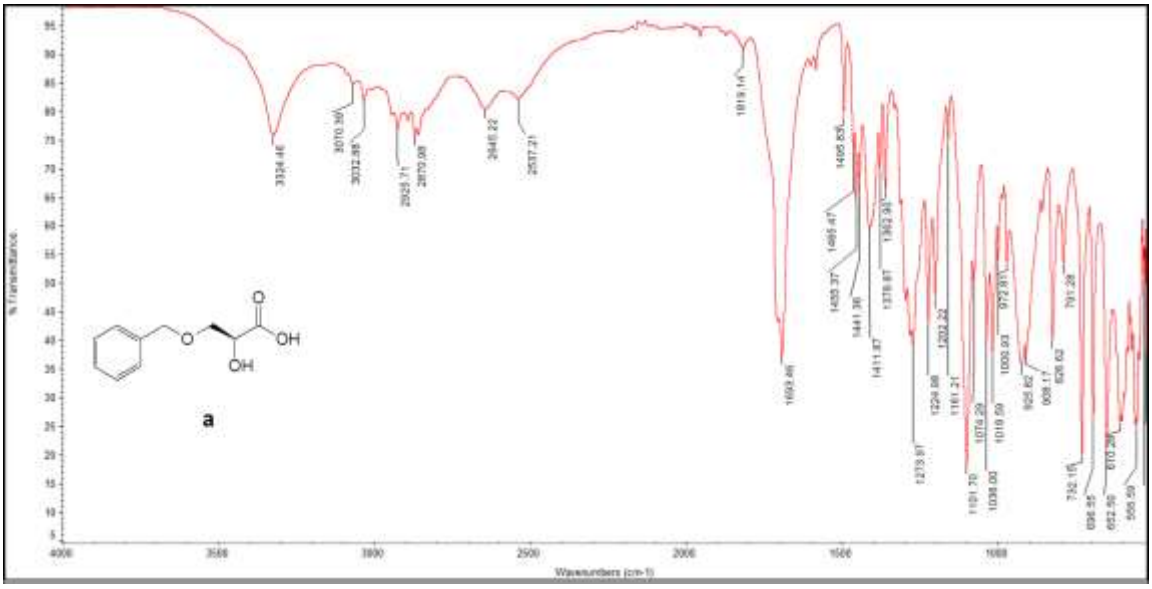


Figure S9. FT-IR spectrum of compound **a**.

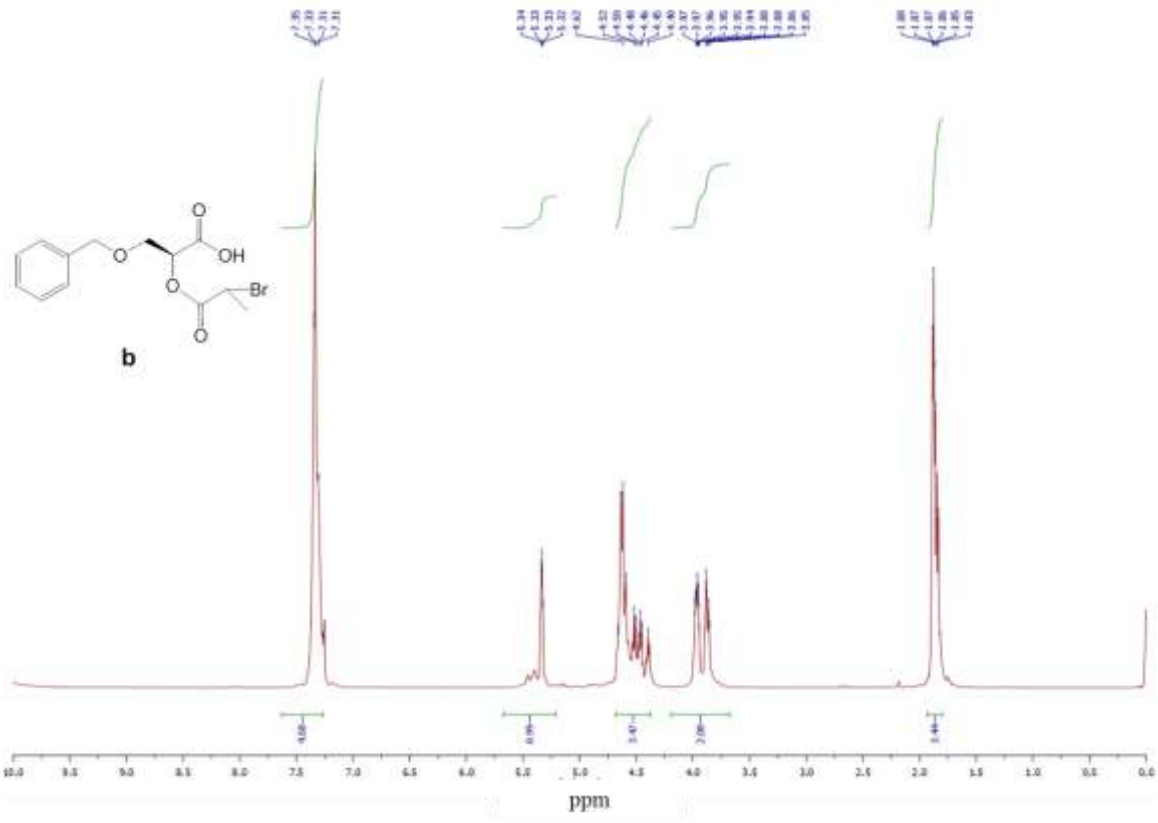


Figure S10. ^{1}H NMR spectrum of compound **b** in $CDCl_3$.

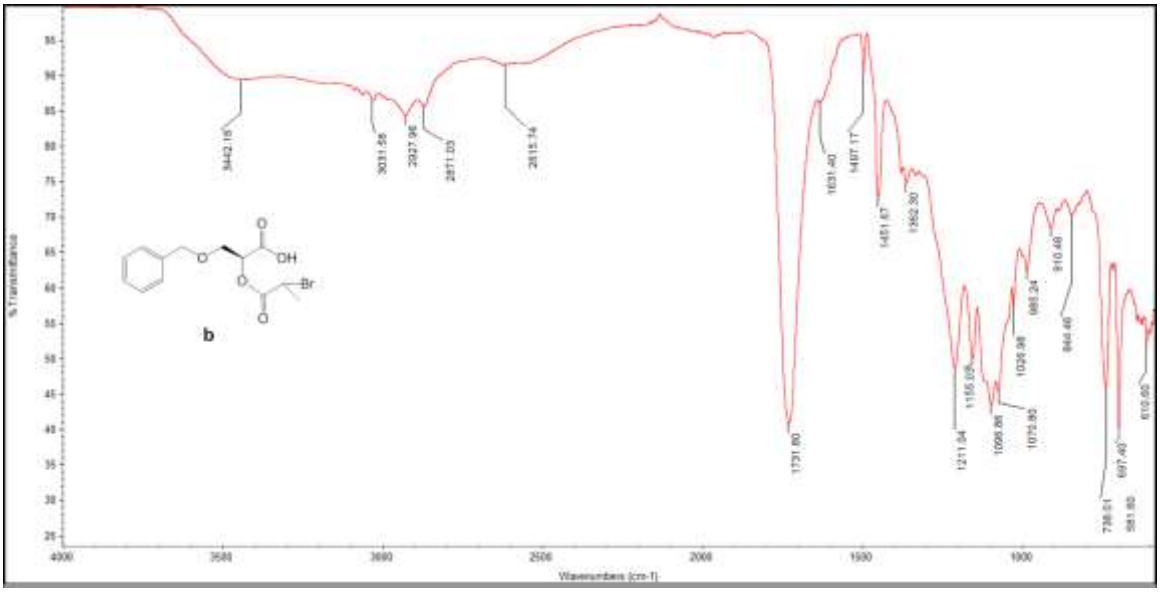


Figure S11. FT-IR spectrum of compound **b**.

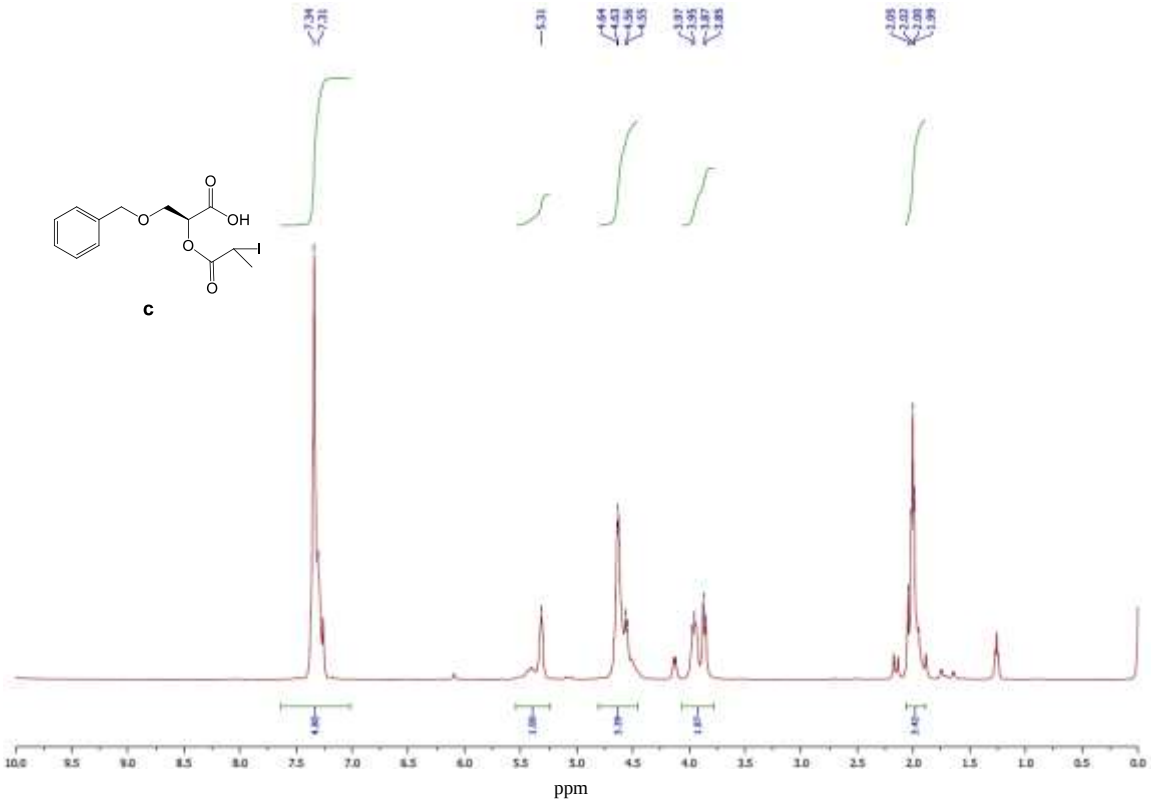


Figure S12. ^{1}H NMR spectrum of compound **c** in $CDCl_3$.

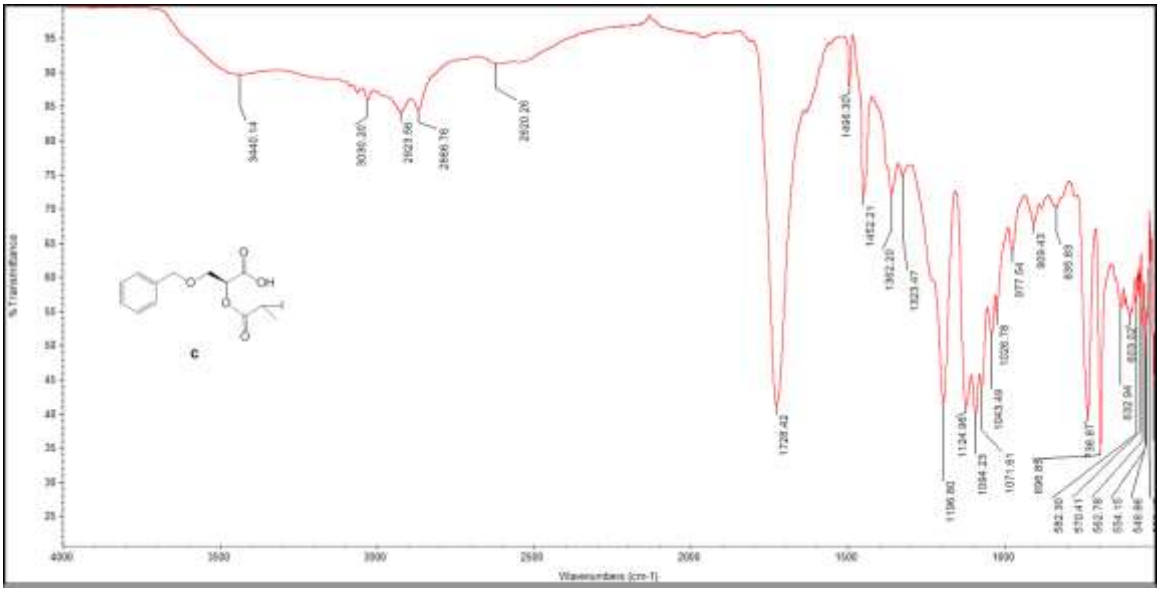


Figure S13. FT-IR spectrum of compound **c**.

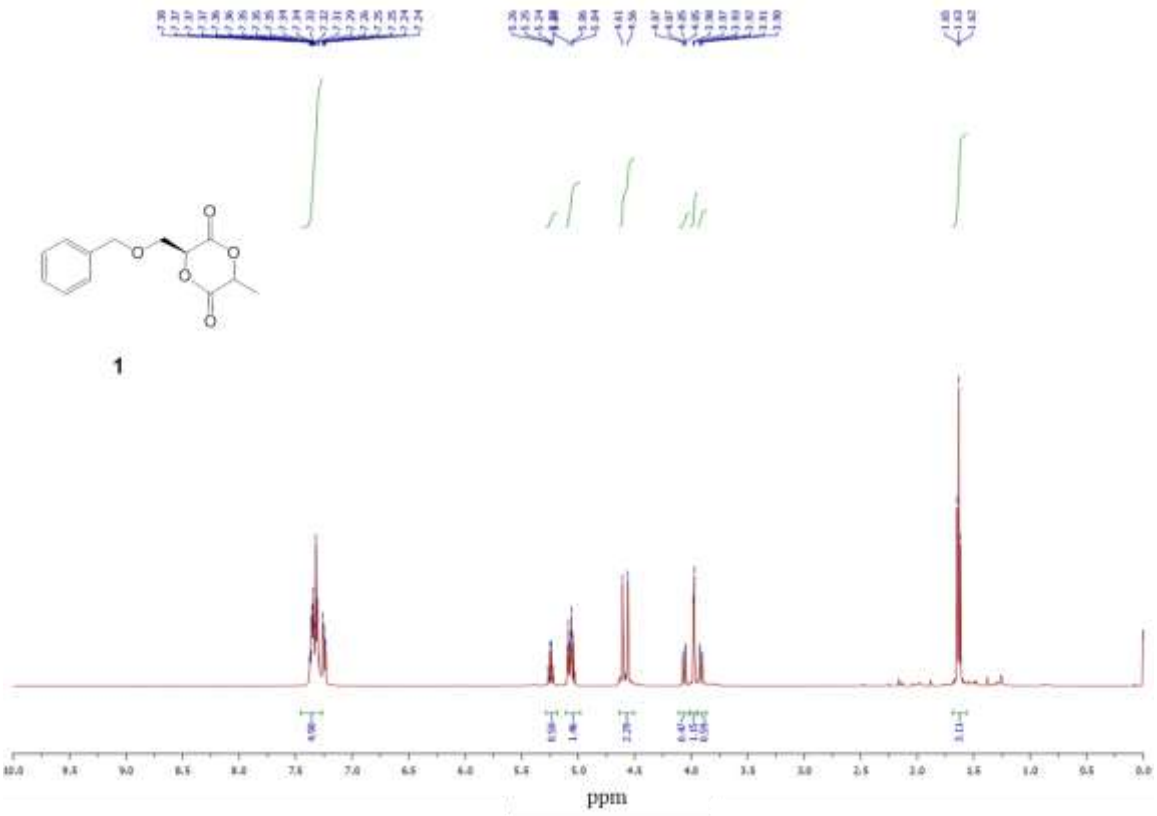


Figure S14. ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

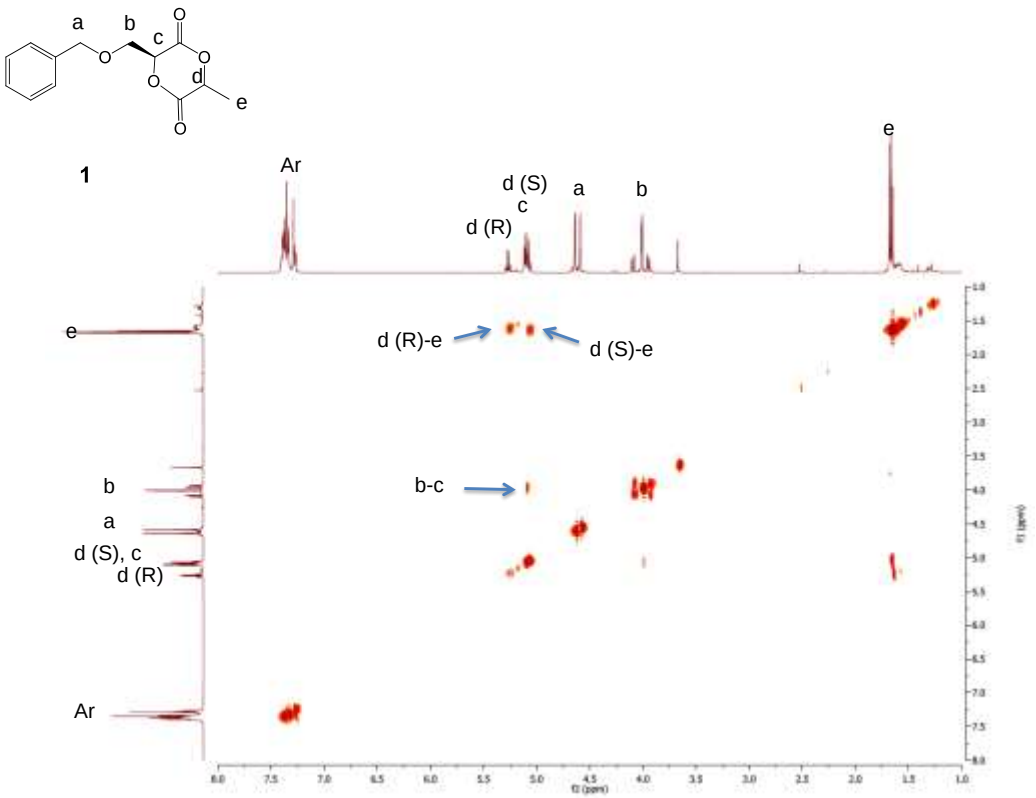


Figure S15. ^{1}H-^{1}H COSY NMR spectrum of compound **1** in $CDCl_3$. The stereochemistry assignment of Hd is based on data reported in the literature.[1]

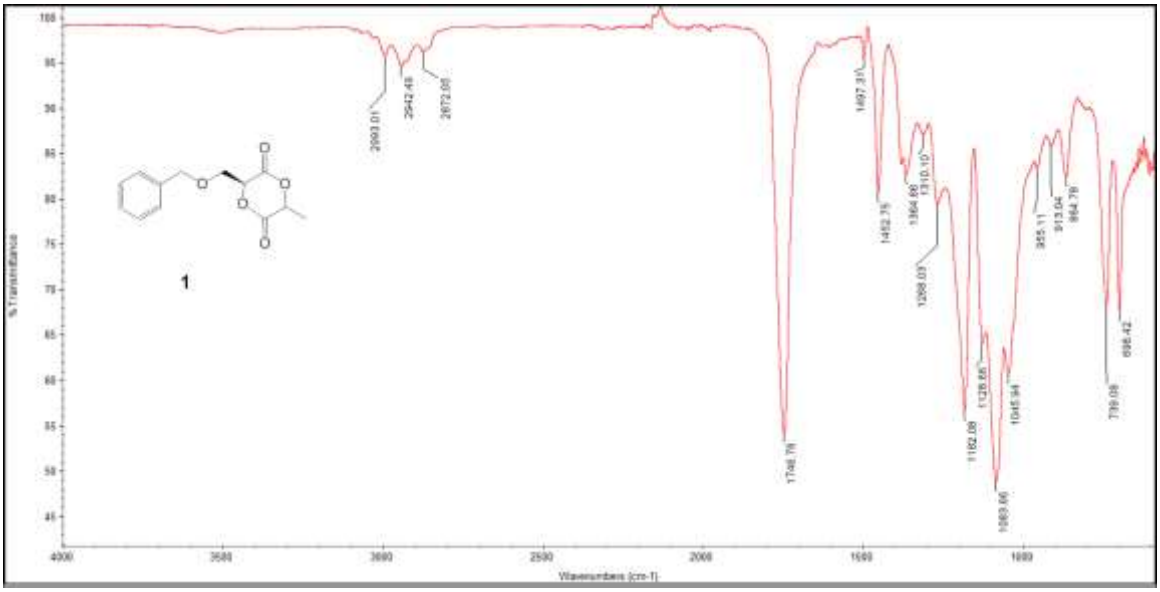


Figure S16. FT-IR spectrum of compound **1**.

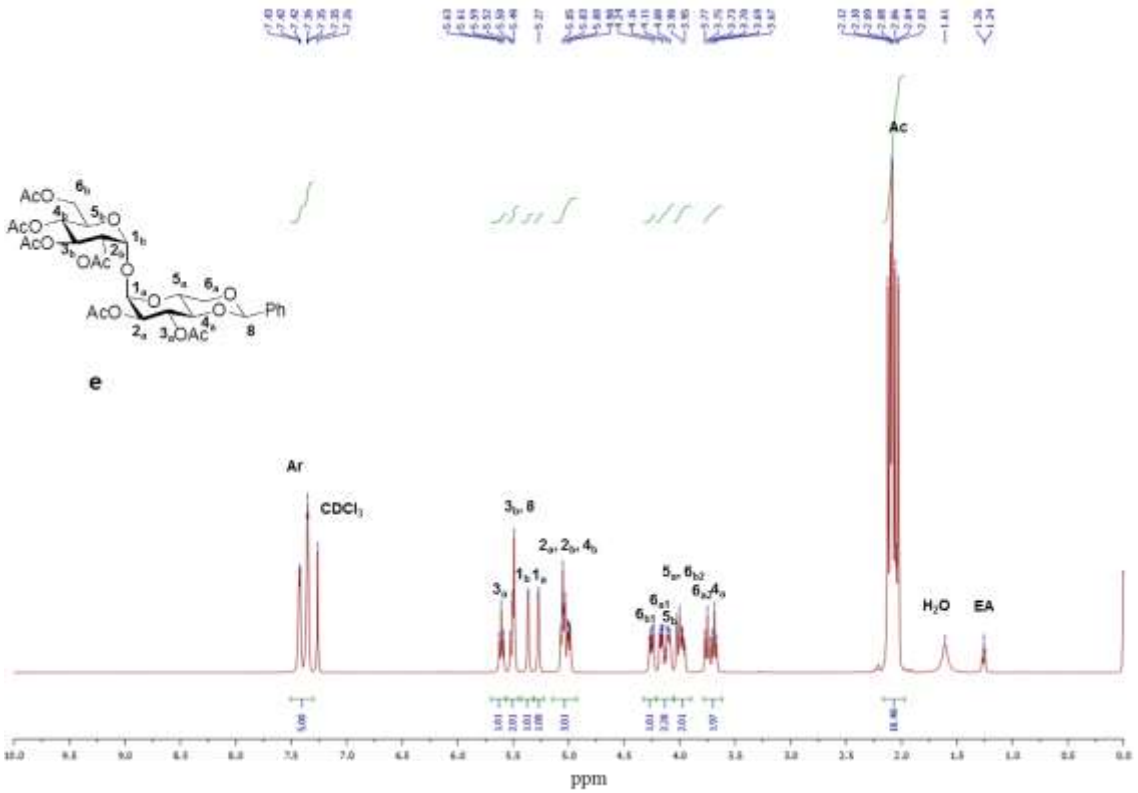


Figure S17. ^{1}H NMR spectrum of compound **e** in $CDCl_3$.

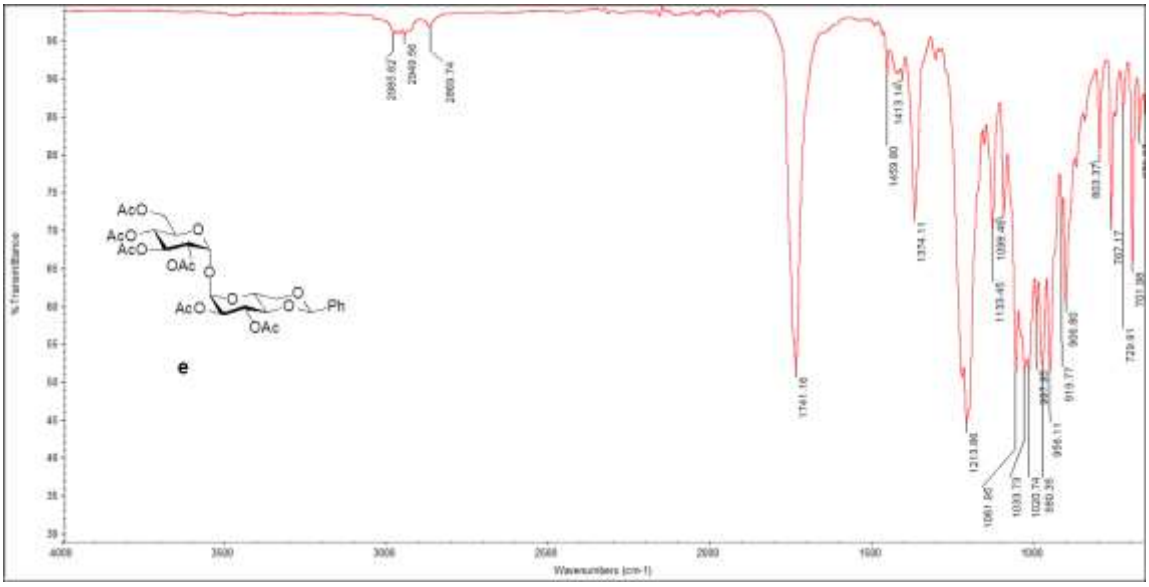


Figure S18. FT-IR spectrum of compound **e**.

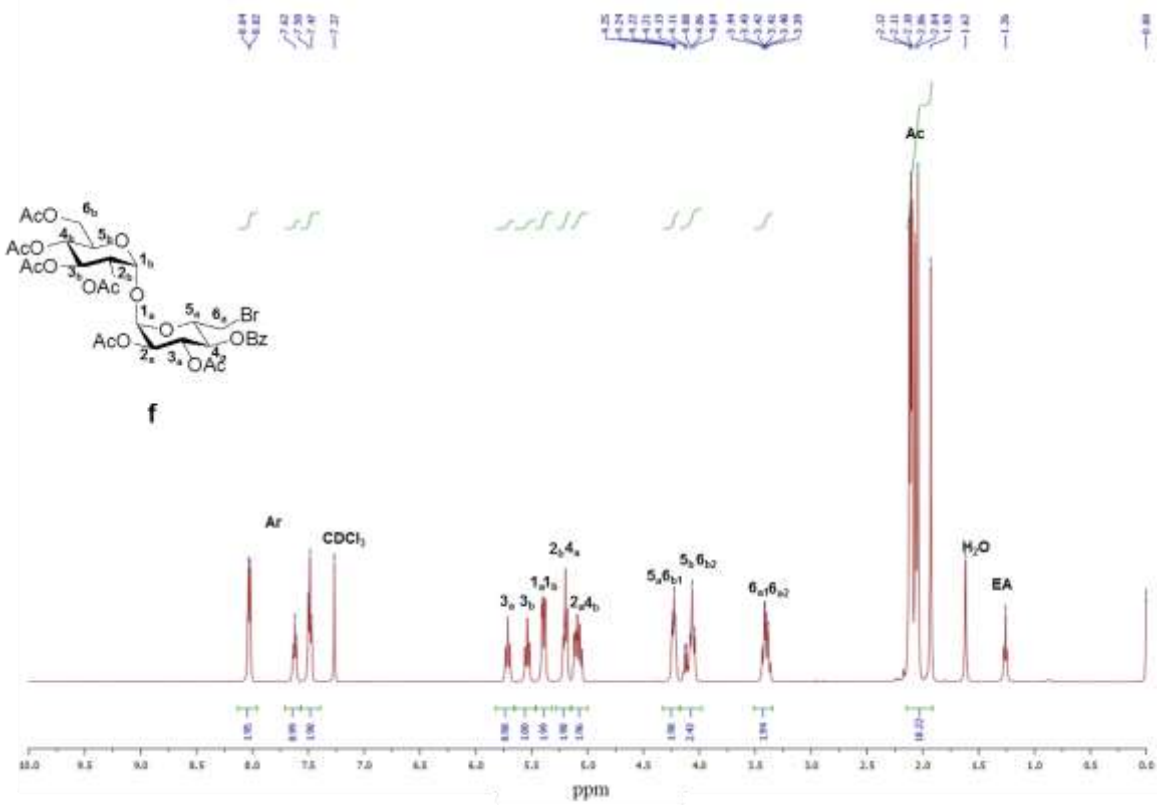


Figure S19. ^{1}H NMR spectrum of compound **f** in $CDCl_3$.

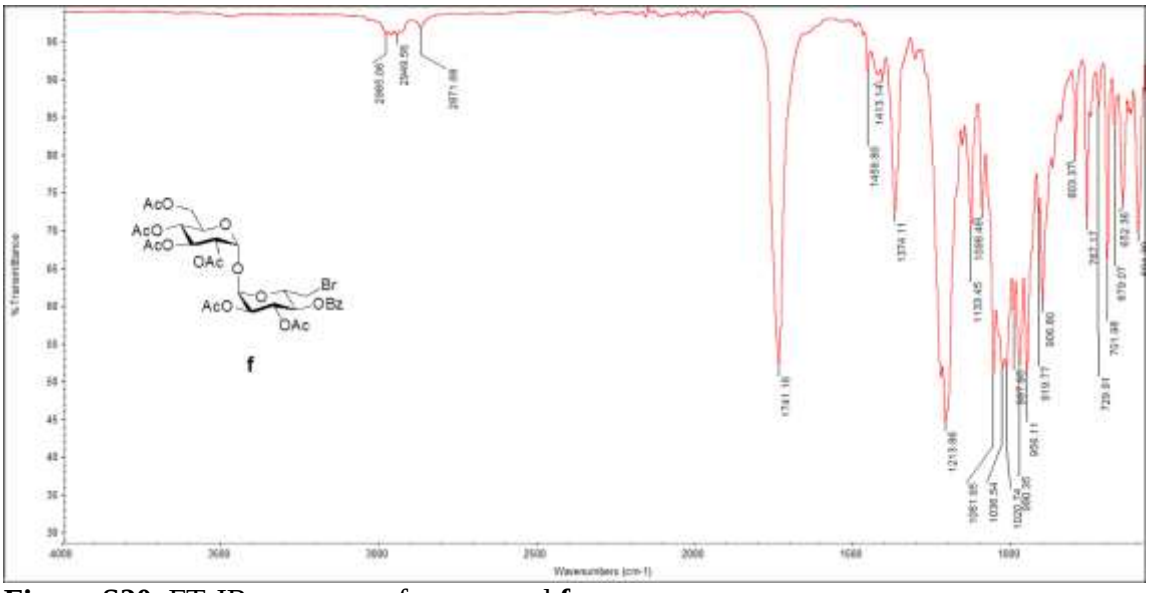


Figure S20. FT-IR spectrum of compound **f**.

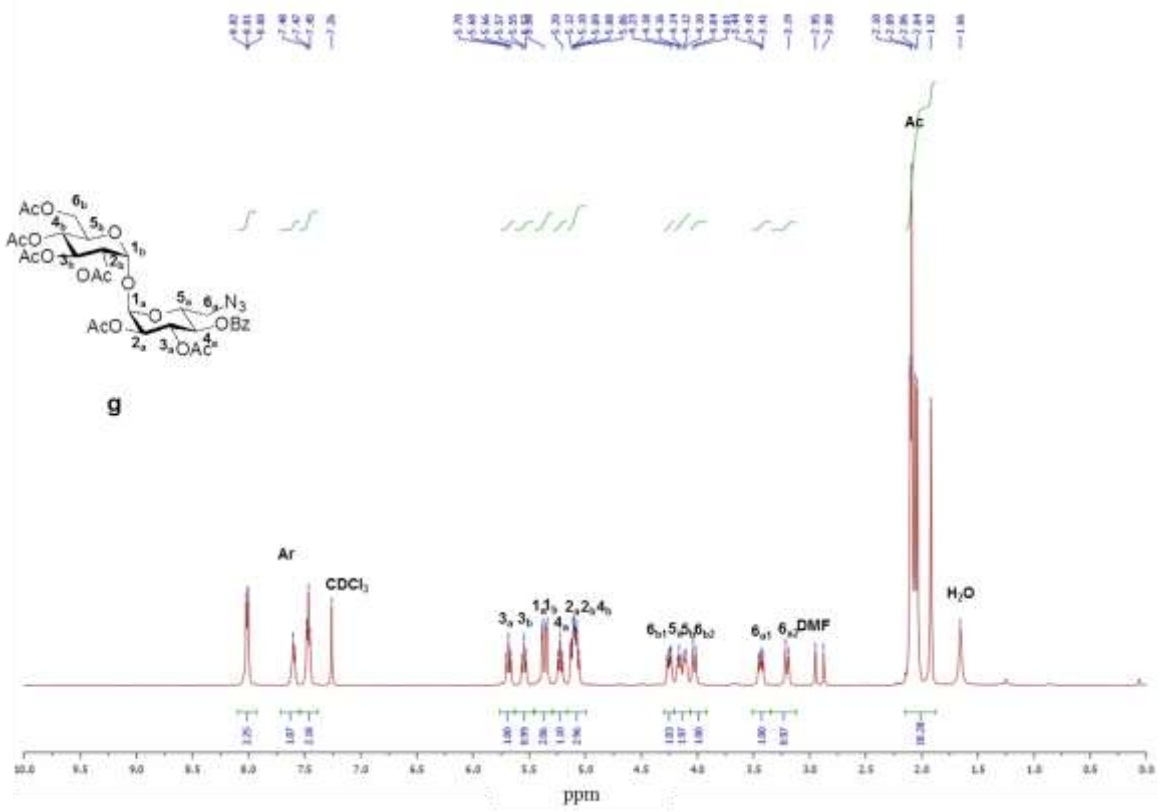


Figure S21. ^{1}H NMR spectrum of compound **g** in $CDCl_3$.

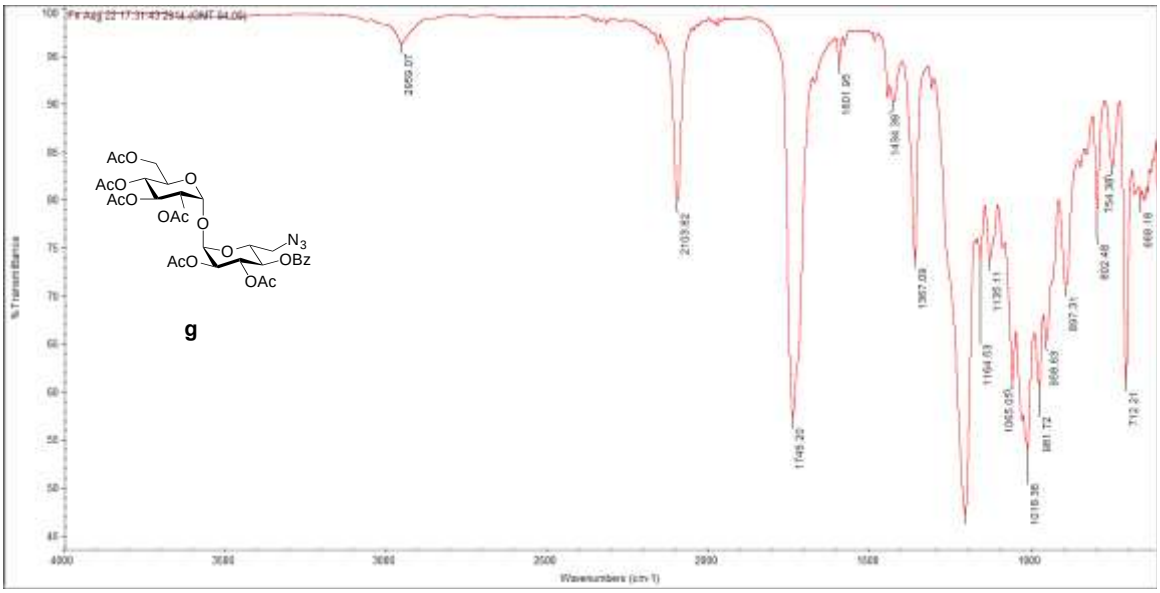


Figure S22. FT-IR spectrum of compound **g**.

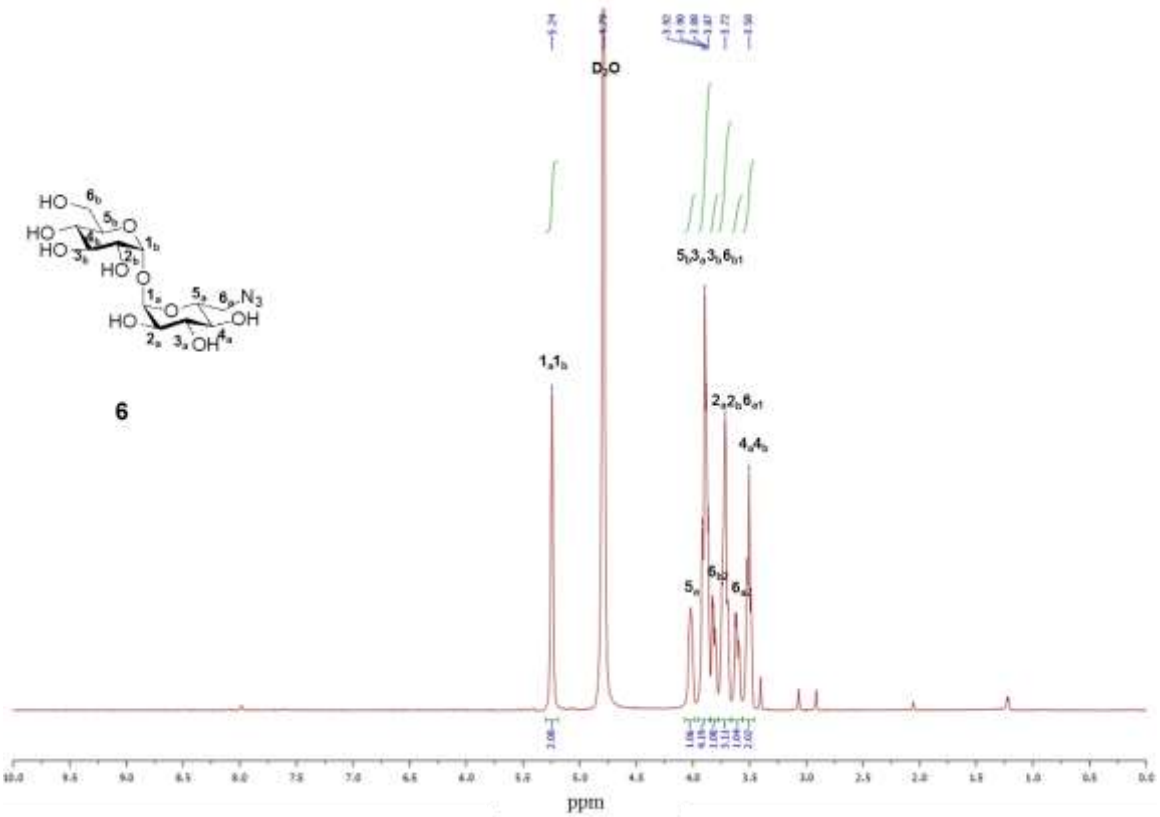


Figure S23. ^{1}H NMR spectrum of compound **6** in D_2O.

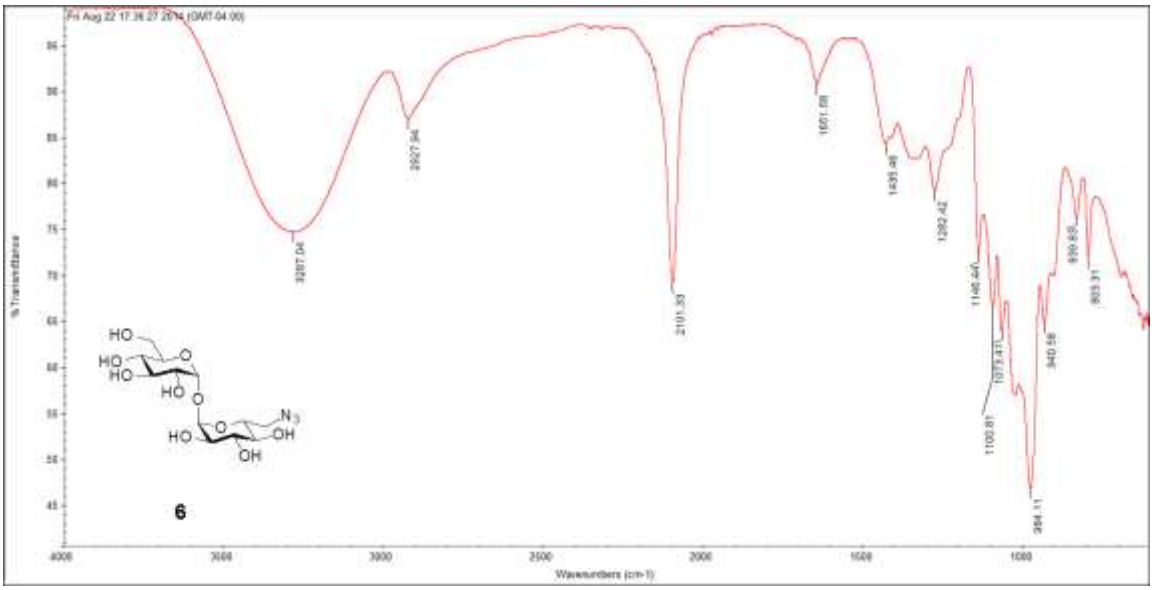


Figure S24. FT-IR spectrum of compound **6**.

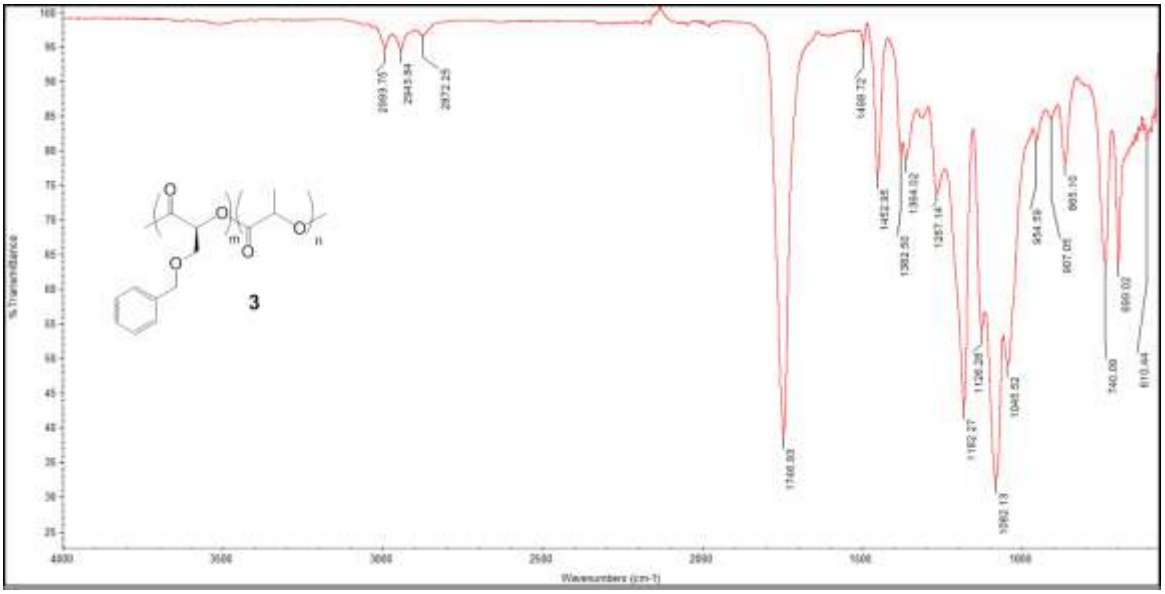


Figure S25. FT-IR spectrum of copolymer **3**.

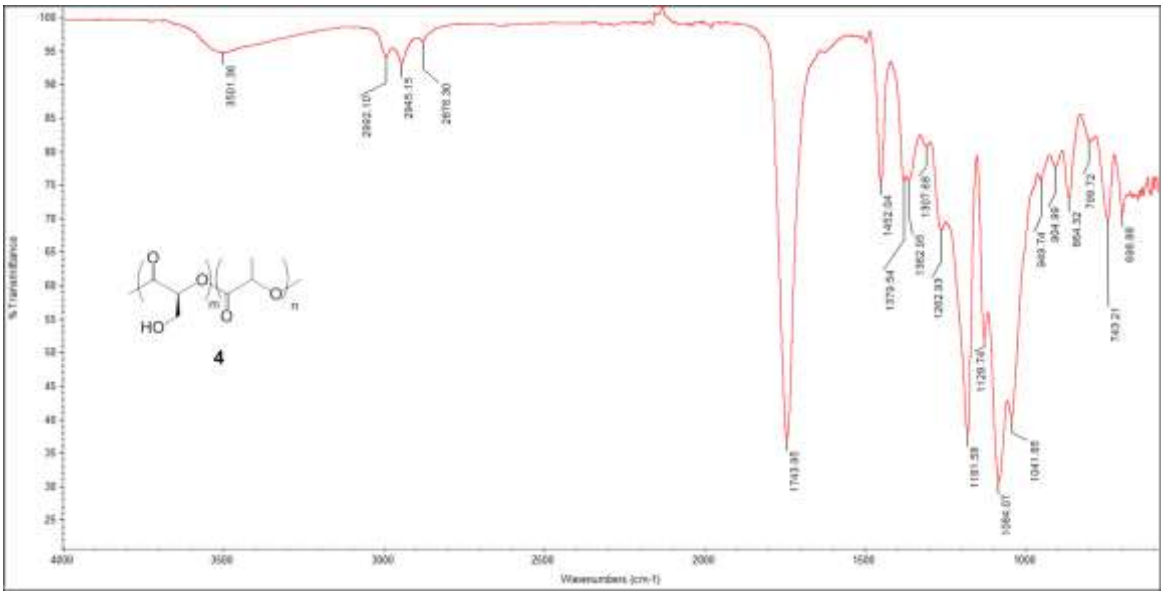


Figure S26. FT-IR spectrum of copolymer **4**.

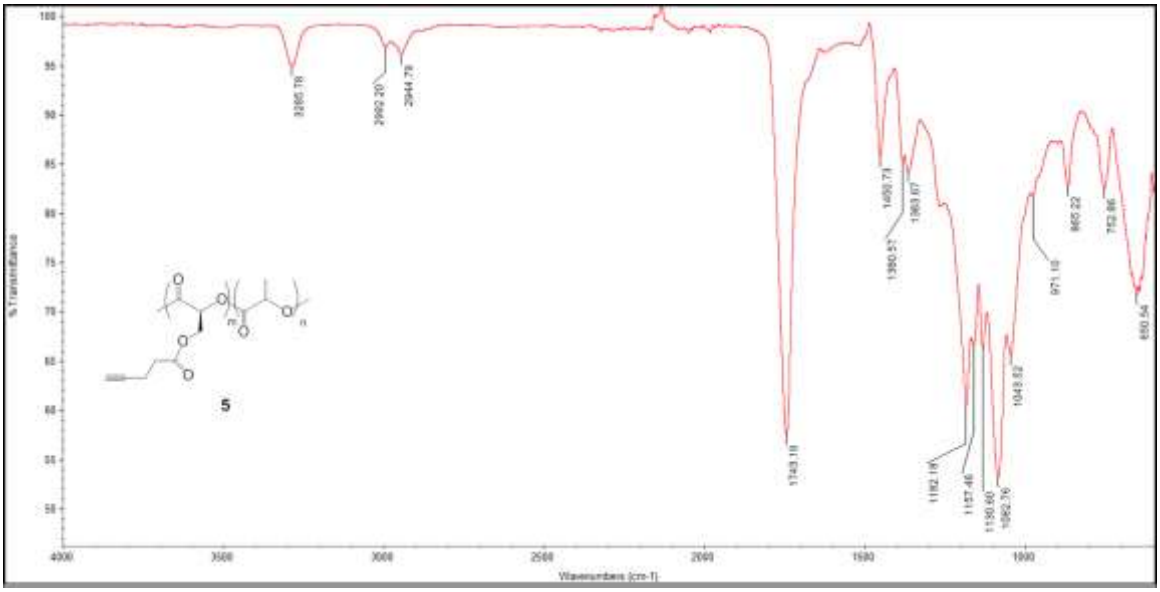


Figure S27. FT-IR spectrum of copolymer **5**.

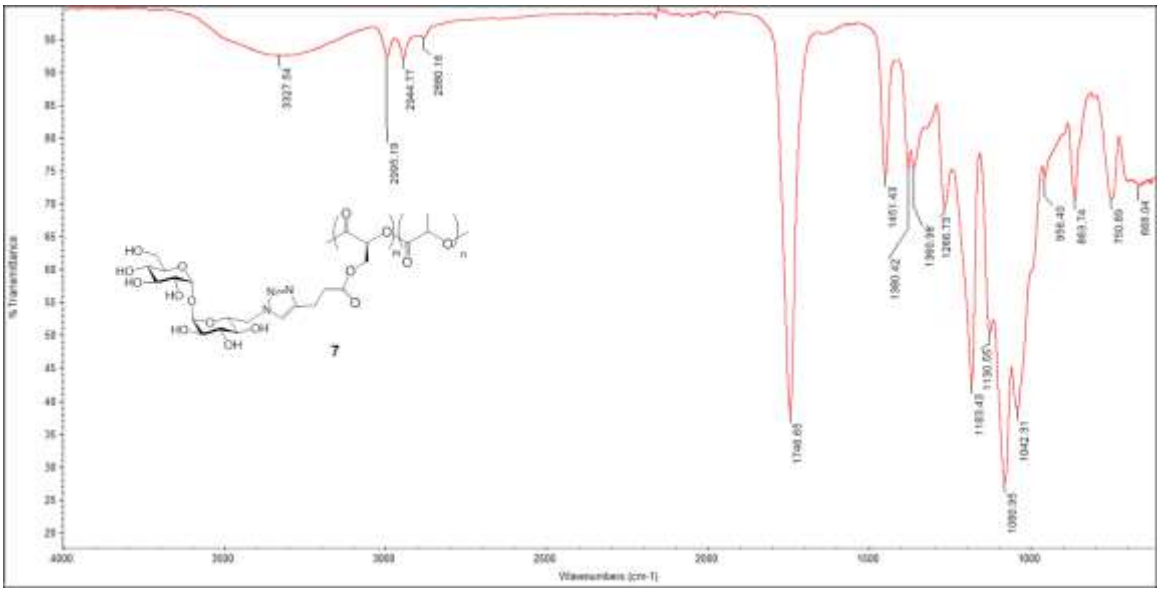


Figure S28. FT-IR spectrum of glycopolymer **7**.

Table S1. Bacterial viability test results. Fluorescent intensity of Alamar Blue-treated bacteria solution with and without incubating with magnetic micelles for 24 hours.

	Fluorescence intensity	Percent viability
M. smegmatis mc^2 155 Control	15943 ± 176	100.0 ± 1.1%
M. smegmatis mc^2 155 with magnetic micelles	14736 ± 527	92.4 ± 3.3%
S. epidermidis 35984 Control	21196 ± 502	100.0 ± 2.4%
S. epidermidis 35984 with magnetic micelles	20105 ± 895	94.9 ± 4.2%
E. coli ORN 208 Control	21695 ± 26	100.0 ± 0.1%
E. coli ORN 208 with magnetic micelles	20715 ± 136	95.0 ± 0.7%

References

[1] W. W. Gerhardt, D. E. Noga, K. I. Hardcastle, A. J. García, D. M. Collard, M. Weck, *Biomacromolecules* 2006, 7, 1735.

[2] a) A. C. Richardson, E. Tarelli, *J. Chem. Soc.* C 1971, 3733; b) K. M. Backus, H. I. Boshoff, C. S. Barry, O. Boutureira, M. K. Patel, F. D'Hooge, S. S. Lee, L. E. Via, K. Tahlan, C. E. Barry, B. G. Davis, *Nat. Chem. Biol.* 2011, 7, 228.

[3] S. Sun, H. Zeng, D. B. Robinson, S. Raoux, P. M. Rice, S. X. Wang, G. Li, *J. Am. Chem. Soc.* 2003, 126, 273.