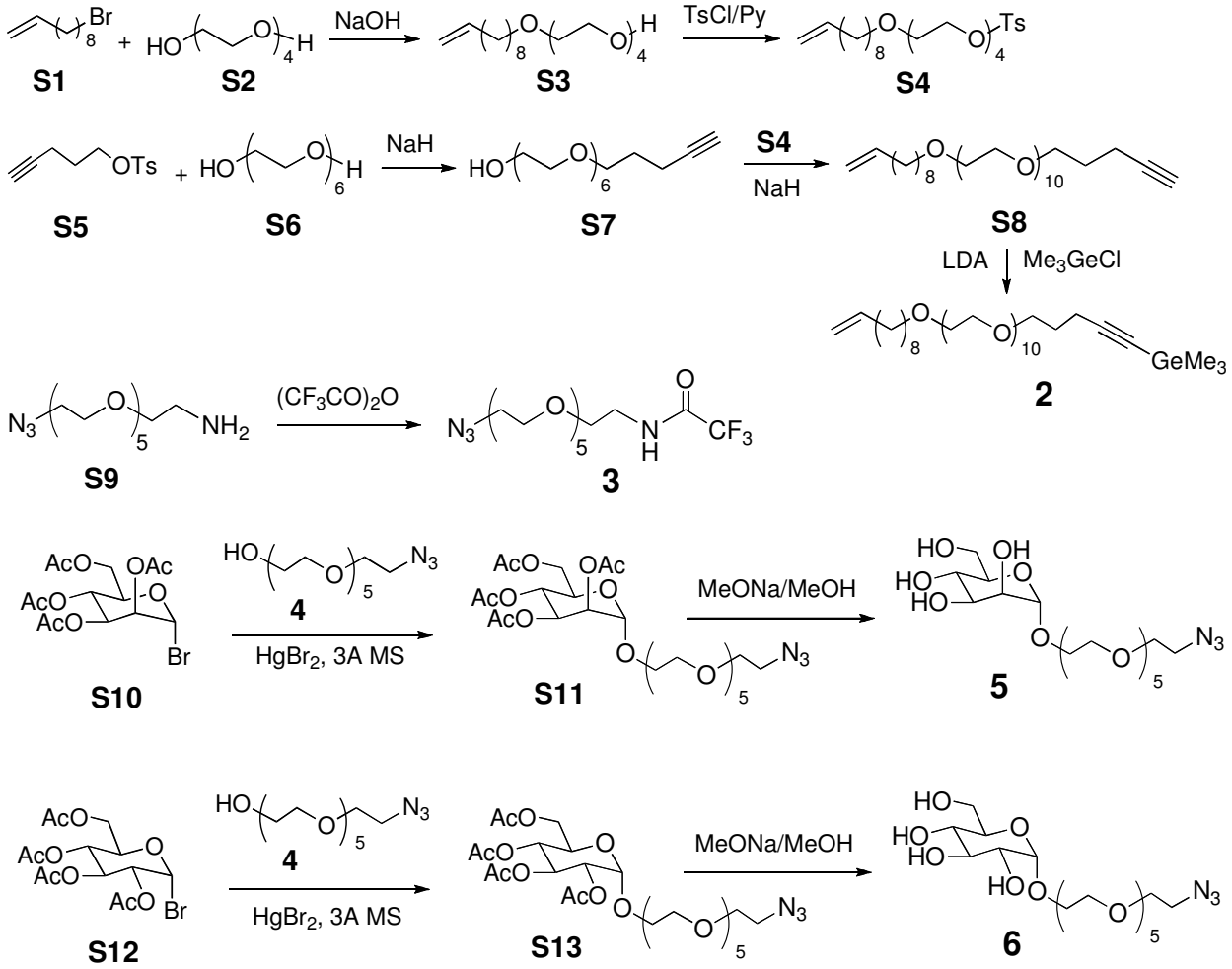
Supporting Information

Biofunctionalization on Alkylated Silicon Substract Surfaces via "Click" Chemistry

Guoting Qin,[†] Catherine Santos,[†] Wen Zhang,[†] Yan Li,[†] Amit Kumar,[†] Uriel J. Erasquin,[†] Kai Liu,[†] Pavel Muradov,[†] Barbara Wells Trautner,[††] Chengzhi Cai*[†]

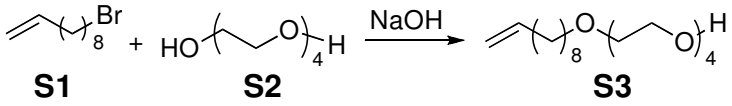
[†] Department of Chemistry, University of Houston, Houston, Texas 77204, and [††] Department of Medicine, Infectious Diseases Section, Baylor College of Medicine, Houston, Texas 77030

Scheme S1.



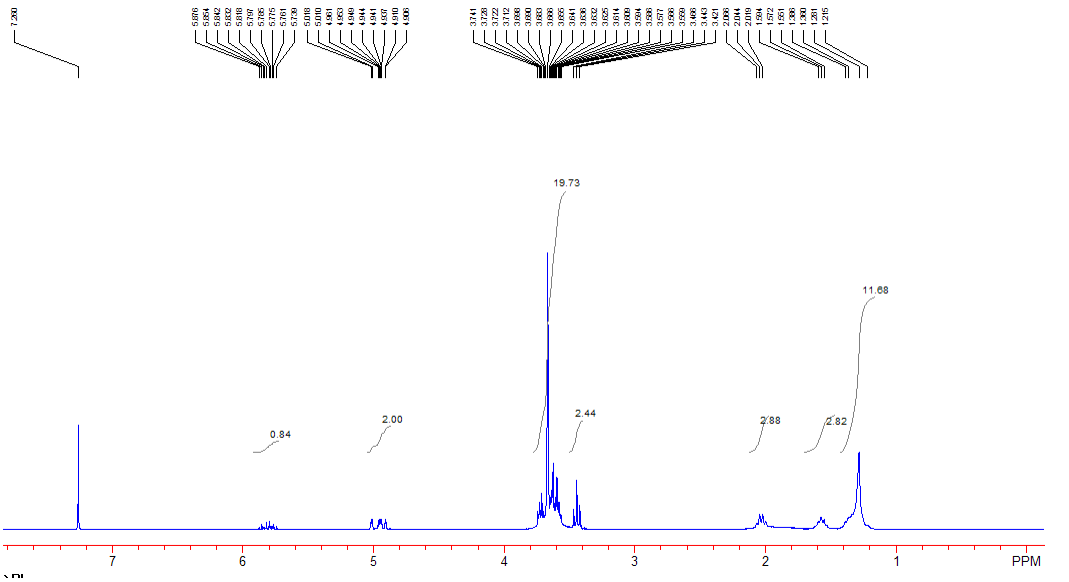
S1 **S2** **S3** **S4** **S5** **S6** **S7** **S8** **2** **S9** **3** **S10** **S11** **5** **S12** **S13** **6**

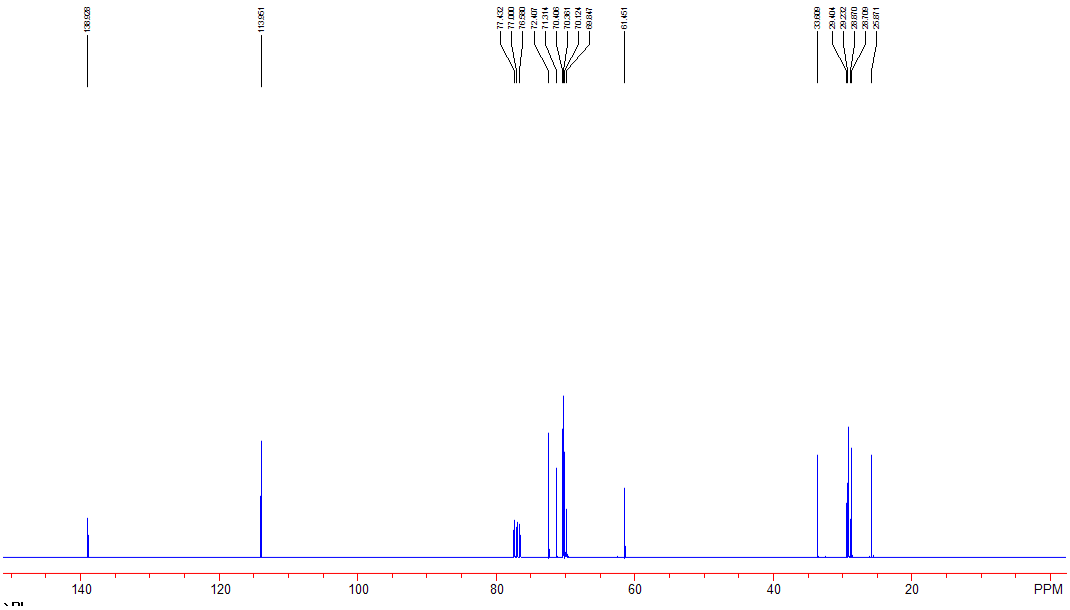
General information: Air sensitive reactions were performed under a nitrogen atmosphere using Schlenk technique. All reagents were purchased from Sigma-Aldrich or Alfa Aesar, and used without purification. Flash chromatography was carried out on silica gel (60Å, Sorbent Technologies). All ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ using residual $CHCl_3$ as internal standard. Electrospray ionization mass spectroscopy (ESI-MS) was carried out on Thermo Finnigan LCQ DECAXP. Usual workup procedure: The reaction was quenched with water, and the mixture was extracted with 3 × CH_2Cl_2. The organic layers were combined, washed with water and brine, dried over Na_2SO_4 or Mg_2SO_4, and filtered.

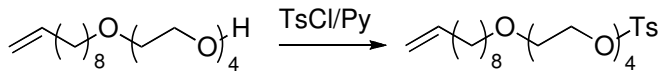


S1 **S2** **S3**

The bromide **S1** (3.0 mL, 15.0 mmol) was slowly (over 5 min) added to a mixture of **S2** (21.2 mL, 123 mmol, 8.2 equiv) and NaOH/H_2O (1:1 w/w, 1 equiv). The reaction mixture was stirred at 70 ^{o}C for 12 h, cooled to room temperature, diluted with hexane and water, and neutralized with 1 N HCl. The aqueous phase was extracted with hexane, and the combined organic extracts were dried over Na_2SO_4, concentrated in vacuum and purified by flash chromatography (ethyl acetate) to give **S3** (3.8 g, 76% yield) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22-1.39 (m, 10H), 1.56-1.60 (m, 2H), 2.02-2.07 (m, 2H), 3.44 (t, *J* = 6.6 Hz, 2H), 3.56-3.74 (m, 16H), 4.91-5.02 (m, 2H), 5.74-5.88 (m, 1H). ^{13}C NMR (30075 MHz, $CDCl_3$) δ 25.9, 28.7, 28.9, 29.2, 29.4, 33.6, 61.5, 69.8, 70.1, 70.36, 70.41, 71.3, 72.4, 114.0, 138.9. MS(ESI): *m*/*z* 355 (M^++Na).



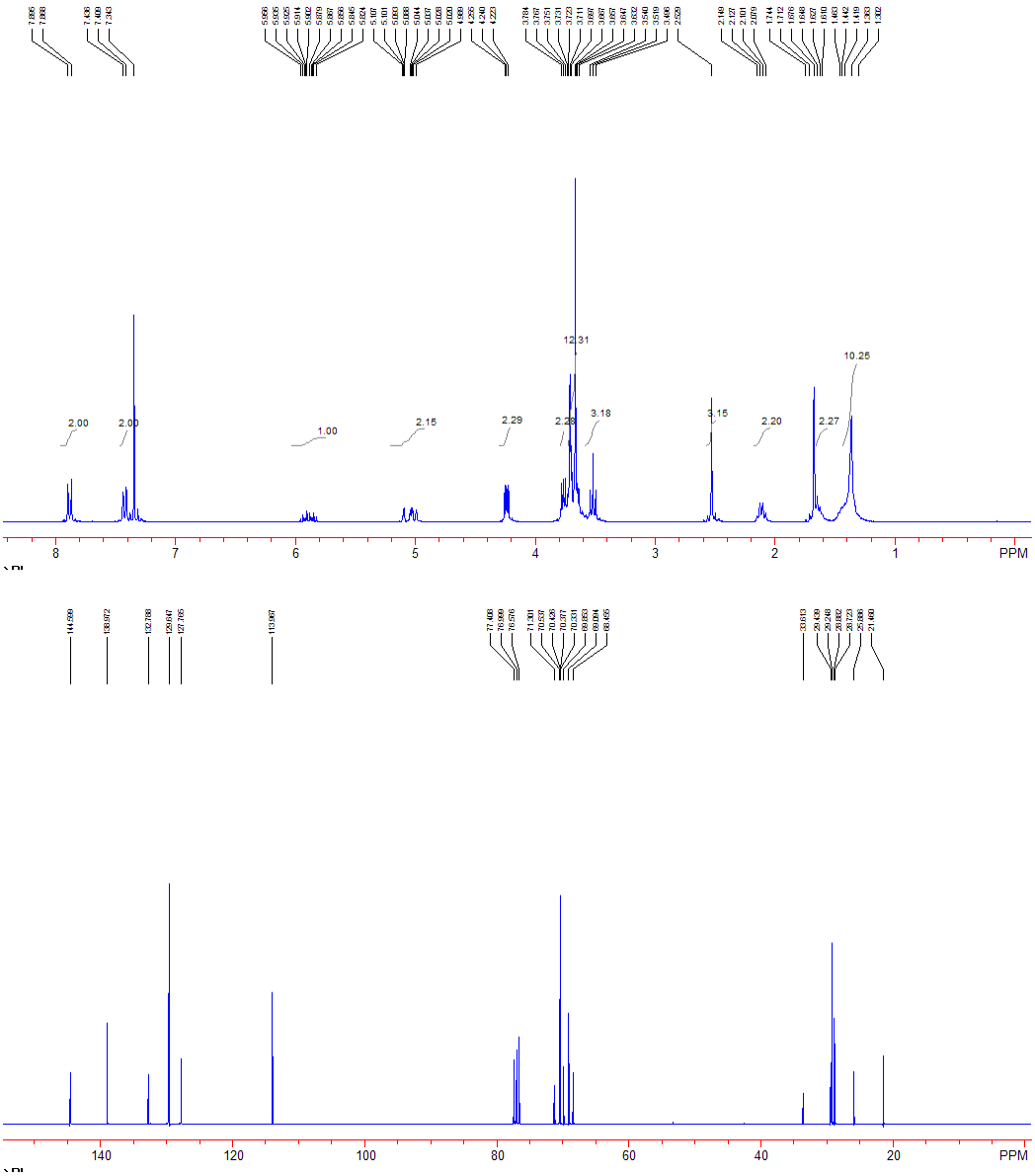


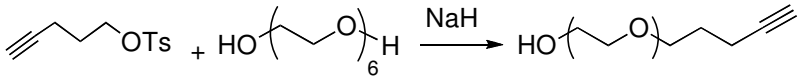


S3 **S4**

To a solution of **S3** (3.8 g, 11.4 mmol) and anhydrous pyridine (1.4 mL, 17.2 mmol) in anhydrous dichloromethane (25 mL) was added *p*-toluenesulfonyl chloride (3.3 g, 17 mmol, 1.5 equiv). The reaction mixture was stirred at room temperature overnight. The mixture was

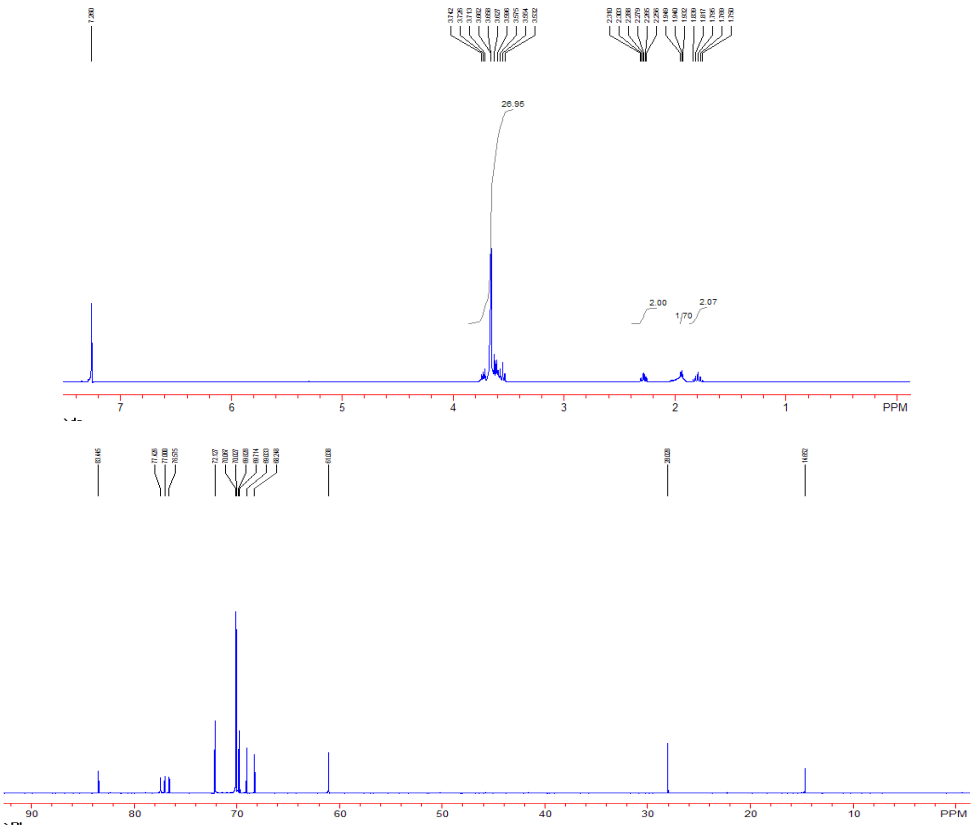
concentrated in vacuum and purified by flash chromatography (ethyl acetate) to give **S4** as a colorless oil (4.0 g, 72% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31-1.46 (m, 10H), 1.61-1.74 (m, 2H), 2.11 (q, *J* = 6.6 Hz, 2H), 2.53 (s, 3H), 3.52 (t, *J* = 6.9 Hz, 2H), 3.63-3.73 (m, 12H), 3.77 (t, *J* = 4.8 Hz, 2H), 4.24 (t, *J* = 5.1 Hz, 2H), 4.99-5.11 (m, 2H), 5.82-5.96 (m, 1H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.88 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 25.9, 28.7, 28.9, 29.2, 29.4, 33.6, 68.5, 69.1, 69.9, 70.33, 70.38, 70.43, 70.54, 71.30, 114.0, 127.8, 129.6, 132.8, 139.0, 144.6. ESI-MS: m/z 509 $[M+Na]^+$.

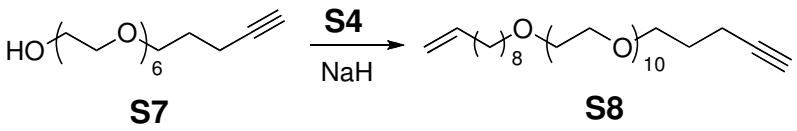




S5 **S6** **S7**

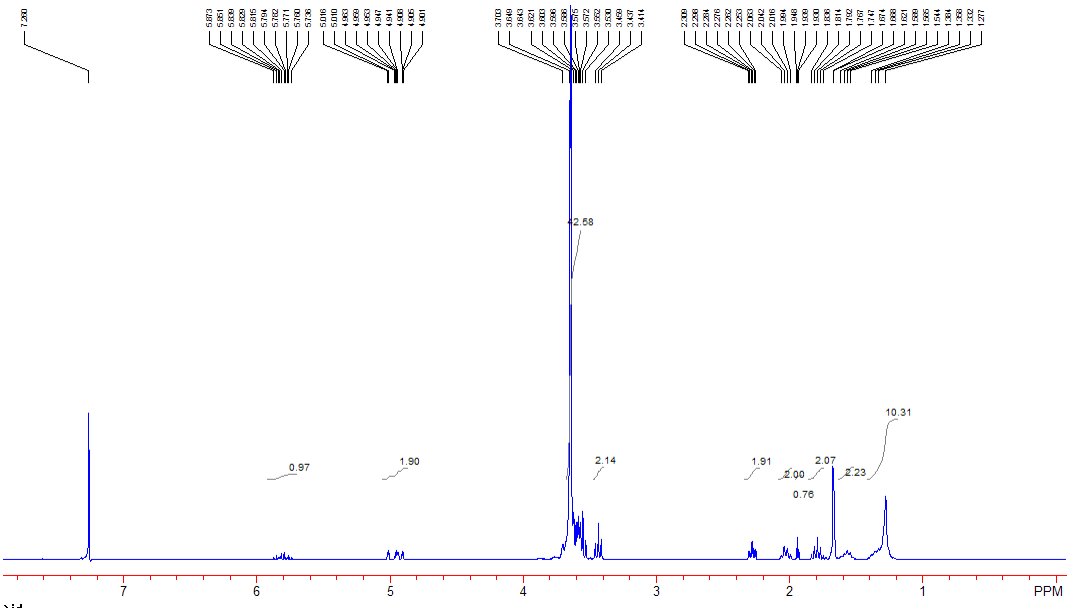
To a soln. of **S6** (1.6 g, 5.5 mmol) in dry THF (20 mL), NaH (232 mg, ~5.5 mmol, 57-63% in oil) was slowly added under nitrogen at 0 ^{o}C. The mixture was stirred for 1 h, treated with a soln. of **S5** in dry THF (10 mL), and stirred at room temperature overnight. The reaction was quenched by water. The mixture was extracted by CH_2Cl_2 (3 × 30 mL). The organic layers were combined, washed with water (30 mL) and brine (30 mL), dried over Na_2SO_4, and filtered. The residue was purified by flash chromatography (ethyl acetate) to give product **S7** (1.5 g, 86% yield) as light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.80 (tt, *J* = 5.7, 6.6 Hz, 2H), 1.94 (t, J = 2.4 Hz, 1H), 2.28 (dt, J = 2.7, 6.9 Hz, 2H), 3.53-3.74 (m, 26H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.7, 28.0, 61.0, 68.2, 69.0, 69.7, 69.8, 70.03, 70.07, 72.1, 83.4. ESI-MS: m/z 371 $[M+Na]^{+}$.

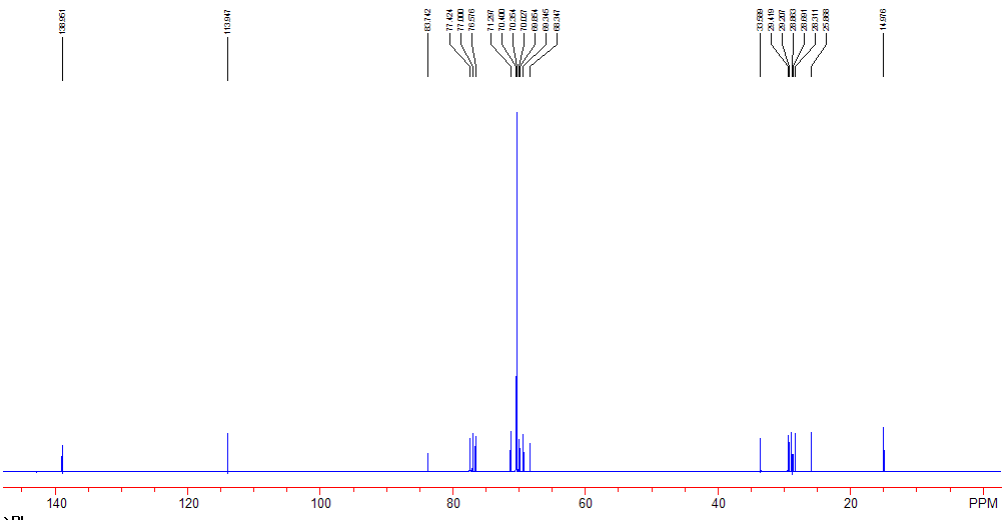


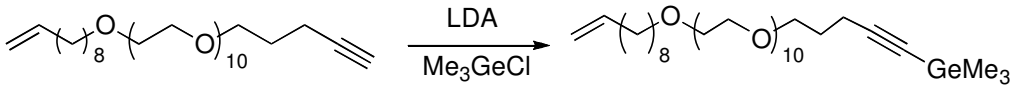


S7 **S8**

To a soln. of **S7** (0.8 g, 2.3 mmol) in dry THF (10 mL) was added NaH (200 mg, 5.0 mmol, 57-63% in oil) under nitrogen at 0 ^{o}C. The mixture was stirred for 1 h, treated with a soln. of **S4** (1.1 g, 2.3 mmol) in dry THF (10 mL), and stirred at room temperature overnight. The reaction was quenched by water. The mixture was extracted with CH_2Cl_2 (3 × 30 mL). The organic layers were combined, washed with water (30 mL) and brine (30 mL), dried over Na_2SO_4, and filtered. The residue was purified by flash chromatography (ethyl acetate/methanol = 20/1) to give **S8** (1.1 g, 72% yield) as light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.28-1.38 (m, 10H), 1.54-1.62 (m, 2H), 1.79 (tt, *J* = 6.0, 6.6 Hz, 2H), 1.94 (t, *J* = 2.7 Hz, 1H), 2.03 (q, *J* = 6.6 Hz, 2H), 2.28 (dt, *J* = 2.7, 6.9 Hz, 2H), 3.44 (t, *J* = 6.9 Hz, 2H), 3.53-3.70 (m, 42H), 4.90-5.02 (m, 2H), 5.74-5.87 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.0, 25.9, 28.3, 28.7, 28.9, 29.2, 29.4, 33.6, 68.3, 69.3, 69.9, 70.0, 70.35, 70.40, 71.3, 83.7, 113.9, 139.0. ESI-MS: m/z 685 $[M+Na]^{+}$.

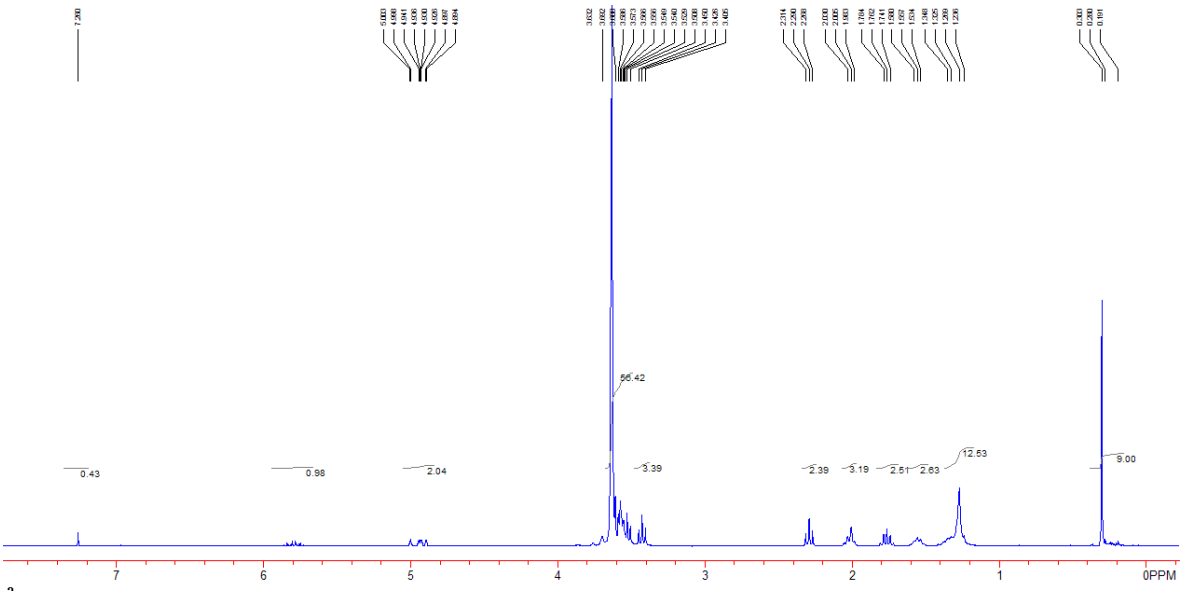


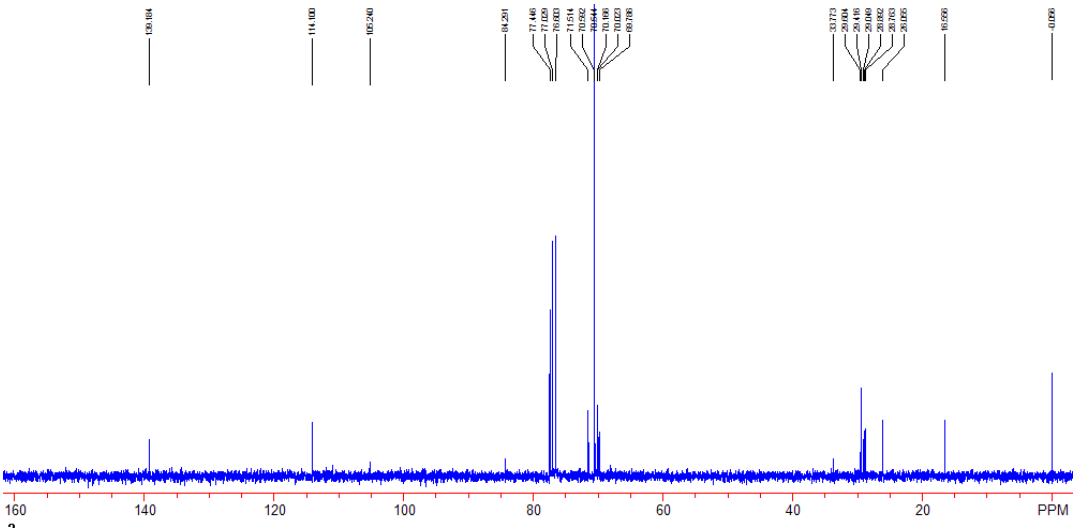


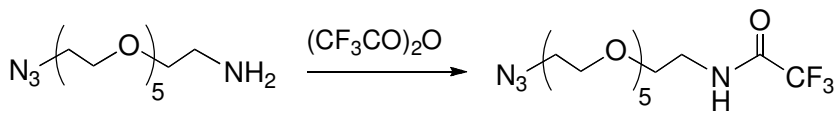


S8 **2**

At –76ºC, to a stirred soln. of **S8** (51 mg, 0.077 mmol) in dry THF (1 mL) under nitrogen was slowly added a soln. of LDA (1.8 M in THF/benzene/haptane, 0.12 ml, 0.22 mmol). After stirring for 2 h at –76 °C, Me_3GeCl (32 μL, 0.26 mmol) was added. The mixture was stirred at –76 °C for 2 h, and then warmed up to room temperature and stirred overnight. Usual workup and flash chromatography (methanol/ethyl acetate = 1/99) afforded **2** (22 mg, 37% yield) as pale yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.30 (s, 9H), 1.24-1.37 (m, 12H), 1.53-1.58 (m, 2H), 1.72-1.80 (m, 2H), 1.98-2.05 (m, 2H), 2.29 (t, *J* = 6.9 Hz, 2H), 3.43 (t, *J* = 6.6 Hz, 2H), 3.50-3.64 (m, 40H), 4.89-5.01 (m, 2H), 5.72-5.86 (m, 1H).) ^{13}C-NMR (300 MHz, $CDCl_3$) δ –0.09, 26.06, 28.76, 28.89, 29.04, 29.42, 29.61, 33.78, 69.79, 70.02, 7.17, 70.54-70.59 (m), 71.51, 84.29, 105.24, 114.10, 139.18. MS(ESI): *m*/*z* 798 $[M+H_2O]^+$



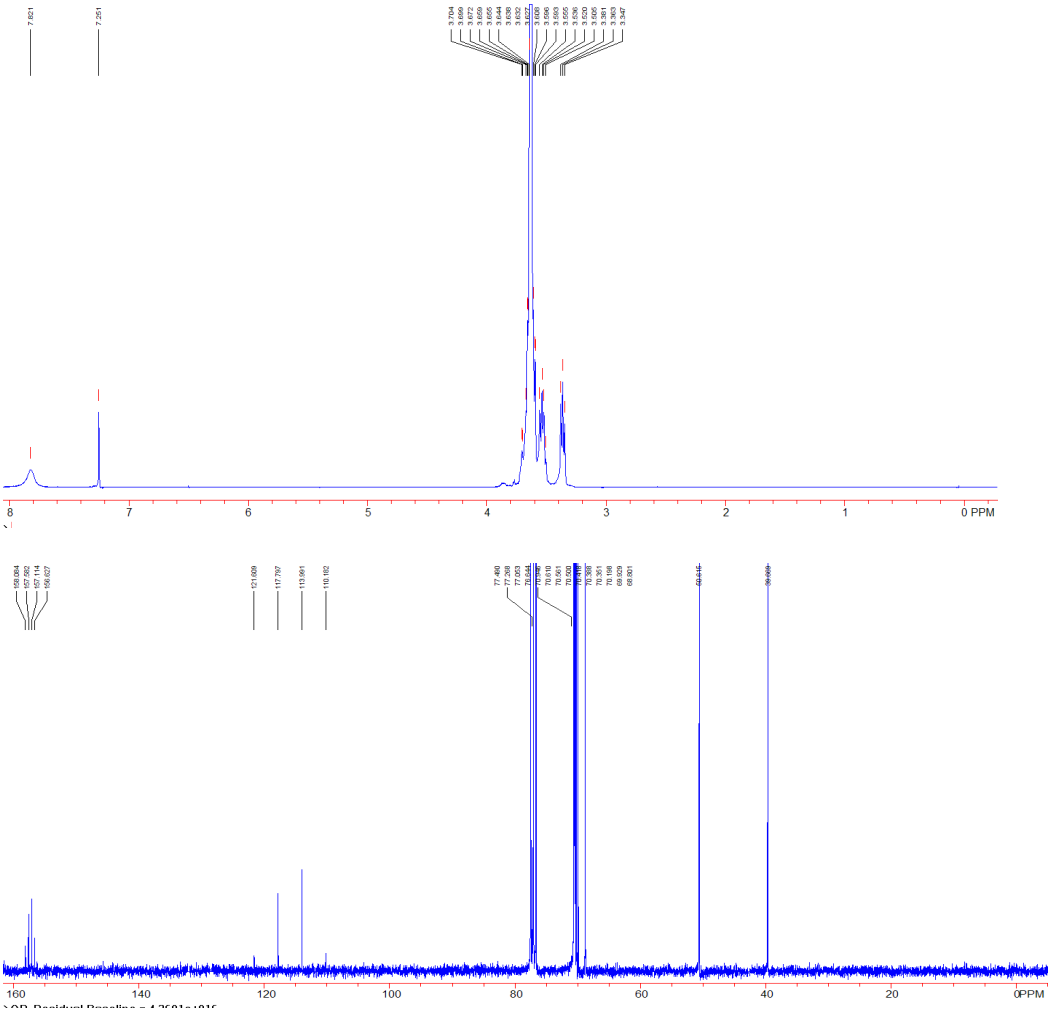


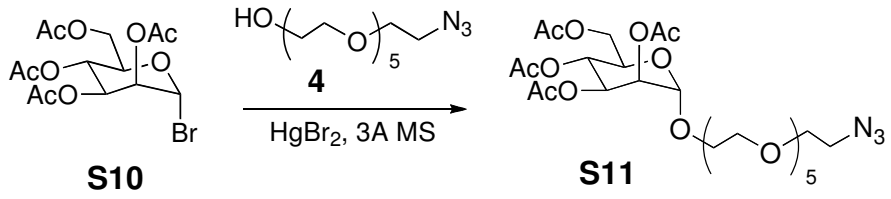


S9 **3**

To a solution of **S9**[1] (100 mg, 0.37 mmol) in dry THF (1.0 mL) at room temperature was added triflouroacetic anhydride (116 mg, 0.56 mmol). The reaction mixture was stirred overnight, and then concentrated in vacuum. The residue was purified by silica gel column chromatography to give **3** (141 mg, 95%) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26-7.40 (m, 1 H),

3.69-3.56 (m, 20 H), 3.53-3.50 (m, 2 H), 3.34 (m, 2 H); ^{13}C NMR (75 MHz, CDCl3) δ 157.3 (q, J = 37.5 Hz), 115.9 (d, J = 287 Hz), 71.2, 70.6, 70.5, 70.5, 70.4, 70.3, 70.2, 69.9, 68.8, 50.6, 39.7. ESI-MS: m/z 425 $[M+Na]^+$.

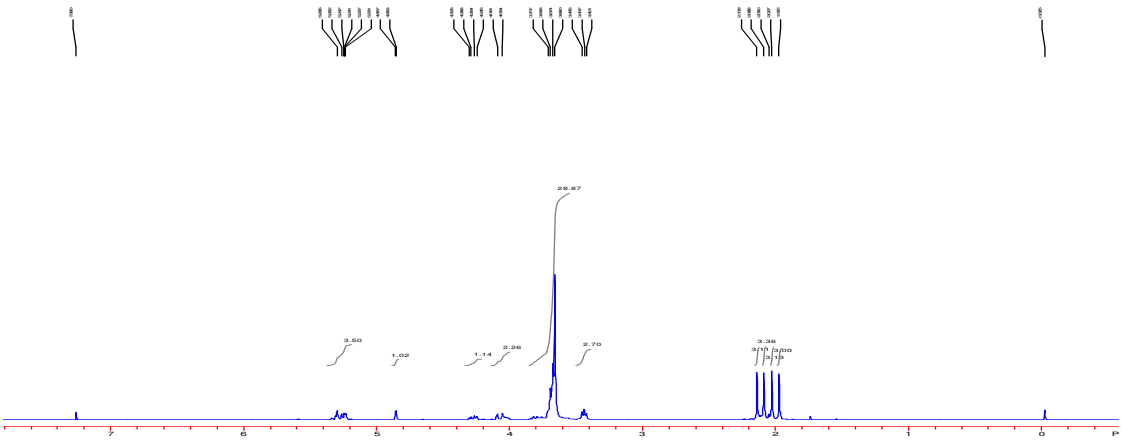


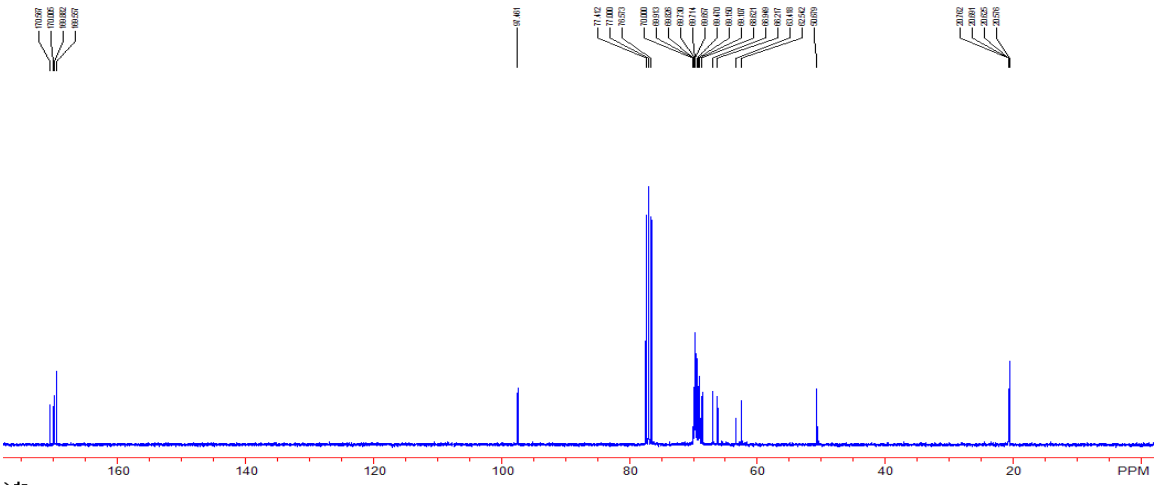


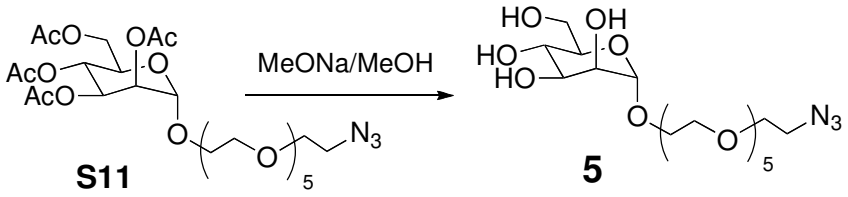
S10 **S11**

Powdered molecular sieves (3A) and **4** (308 mg, 0.875 mmol) were added to a stirred solution of **S10**[2] (240 mg, 0.584 mmol) in dry CH_2Cl_2 (5 mL). After 15 min, $HgBr_2$ (210 mg, 0.584 mmol)

was added. The mixture was stirred overnight, diluted with CH_2Cl_2 (20 mL) and filtered over a pad of celite. The organic phase was washed with 5% KI (3 × 15 mL) and water (3 × 15 mL), dried over Na_2SO_4. Flash chromatography (EtOAc : CH_2Cl_2 = 1 : 1) provided **S11** (150 mg, 40%) as light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.00 (s, 3H), 2.05 (s, 3H), 2.11 (s, 3H), 2.16 (s, 3H), 3.46 (t, *J* = 4.8 Hz, 2H), 3.68-3.73 (m, 26H), 4.06-4.12 (m, 2H), 4.30 (dd, *J* = 6.0, 12.9 Hz, 1H), 4.88 (s, 1H), 5.26-5.33 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.58, 20.63, 20.7, 20.8, 50.6, 62.5, 63.4, 66.2, 67.0, 68.6, 69.1, 69.2, 69.5, 69.66, 69.71, 69.73, 69.8, 69.9, 70.0, 97.5, 169.6, 169.9, 170.0, 170.6. ESI-HRMS: m/z 638 $[M+H]^+$. ESI-HRMS: Calcd. for $C_{26}H_{44}O_{15}N_3$: 638.2774; found: m/z 638.2645.

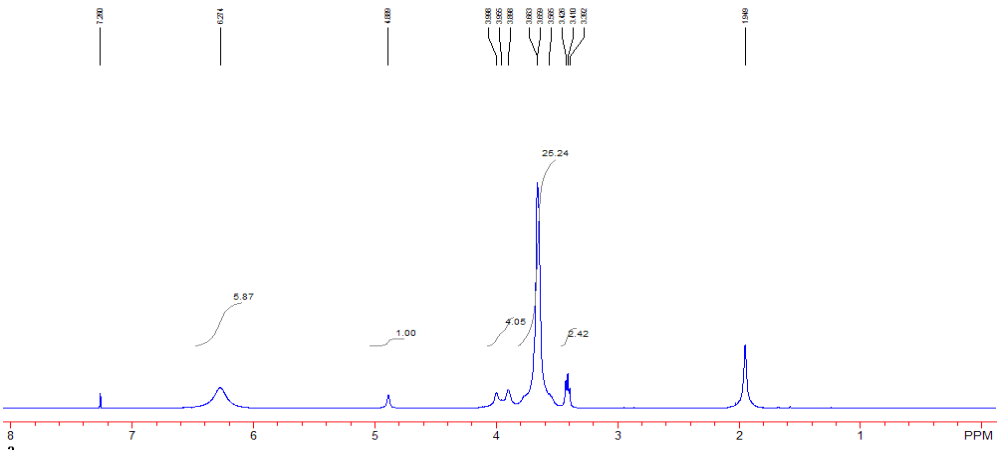


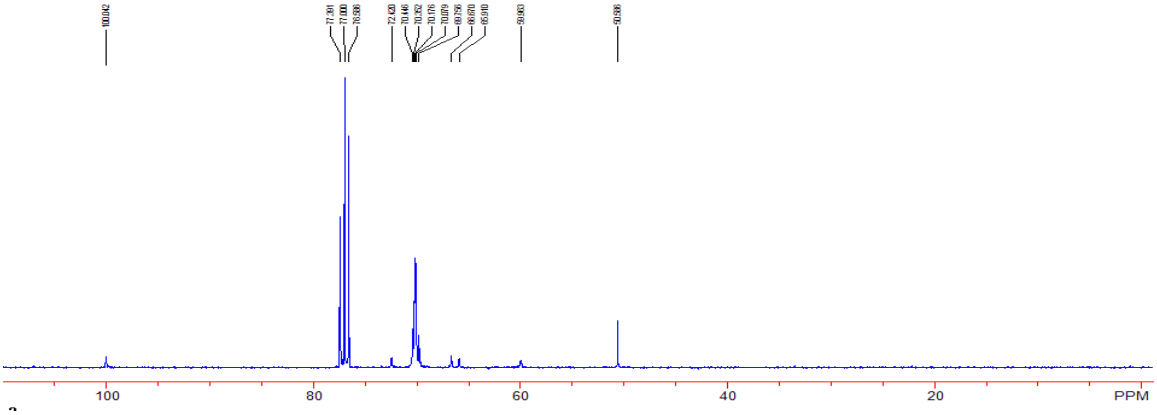


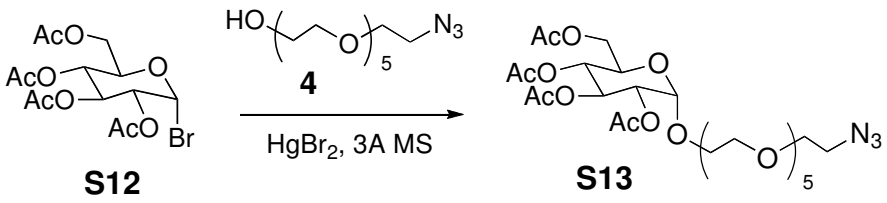


S11 **5**

To a solution of **S11** (110 mg, 0.18 mmol) in MeOH (4 mL) was added MeONa (49 mg, 0.72 mmol) at 0 ^{o}C. The mixture was allowed to warm to room temperature and stirred overnight. The mixture was diluted with ether, and neutralized with HCl. Flash chromatography (EtOAc : MeOH = 20 : 1 to 15 : 1) provided **5** (40 mg, 48% yield) as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.41 (t, *J* = 5.4 Hz, 2H), 3.58-3.71 (m, 24H), 3.89 (s, 2H), 4.00 (s, 2H), 4.89 (s, 1H), 6.27 (s, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 50.6, 60.0, 65.9, 66.7, 69.8, 70.1, 70.2, 70.35, 70.44, 72.4, 100.0. ESI-MS: m/z 492 $[M+Na]^+$.

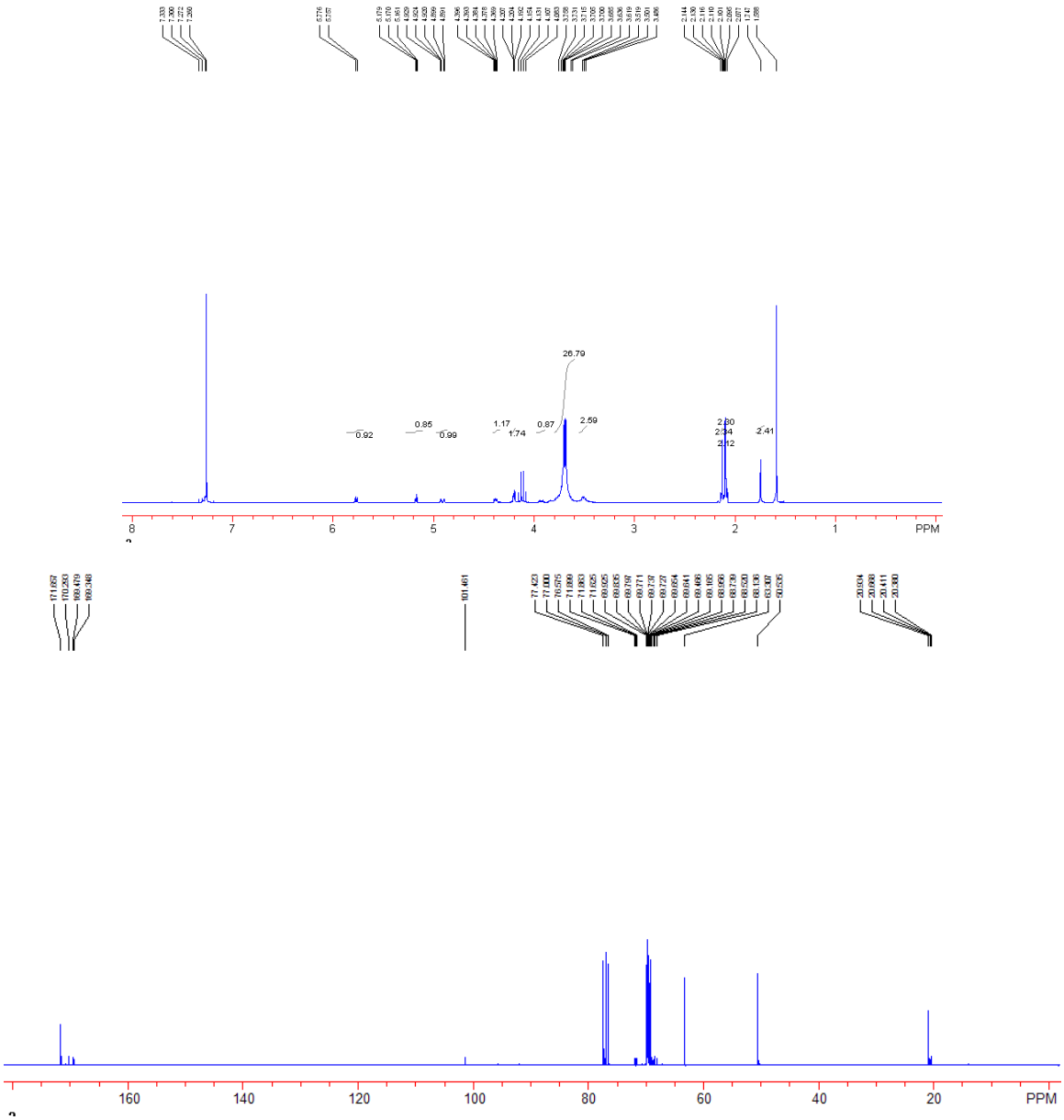


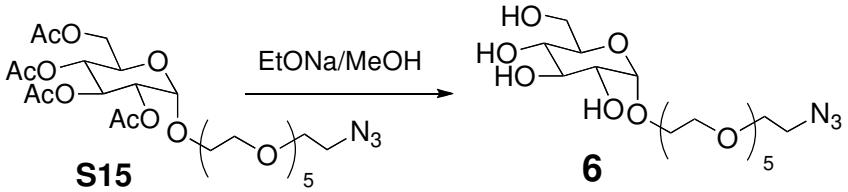




S12 **S13**

Powdered molecular sieves (3A) and **4** (608 mg, 1.73 mmol) were added to **S12** (472 mg, 1.15 mmol) in dry CH_2Cl_2 (5 mL). After stirring for 15 min, $HgBr_2$ (420 mg, 1.17 mmol) was added, and the mixture was stirred overnight. The mixture was diluted with CH_2Cl_2 (20 mL) and filtered over a pad of celite. The organic phase was washed with 5% KI (3 × 15 mL) and water (3 × 15 mL), dried over Na_2SO_4. Flash chromatography (EtOAc : CH_2Cl_2 = 1 : 1) gave **S13** as a light yellow oil (150 mg, 21% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.75 (s, 3H), 2.09 (s, 3H), 2.10 (s, 3H), 2.13 (s, 3H), 3.50 (t, *J* = 5.1 Hz, 2H), 3.64-3.94 (m, 26H), 4.19-4.22 (m, 2H), 4.37-4.40 (m, 2H), 4.91 (dd, *J* = 2.4 Hz, 1H), 5.17 (dd, J = 3.3, 2.7 Hz, 1H), 5.76 (d, J = 5.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) d 20.38, 20.41, 20.7, 20.9, 50.5, 63.3, 68.2, 68.5, 68.7, 69.0, 69.2, 69.5, 69.64, 69.65, 69.73, 69.74, 69.77, 69.80, 69.84, 69.9, 71.6, 71.86, 71.90, 101.5, 169.3, 169.5, 170.3, 171.7. ESI-MS: m/z 660 $[M+Na]^+$.

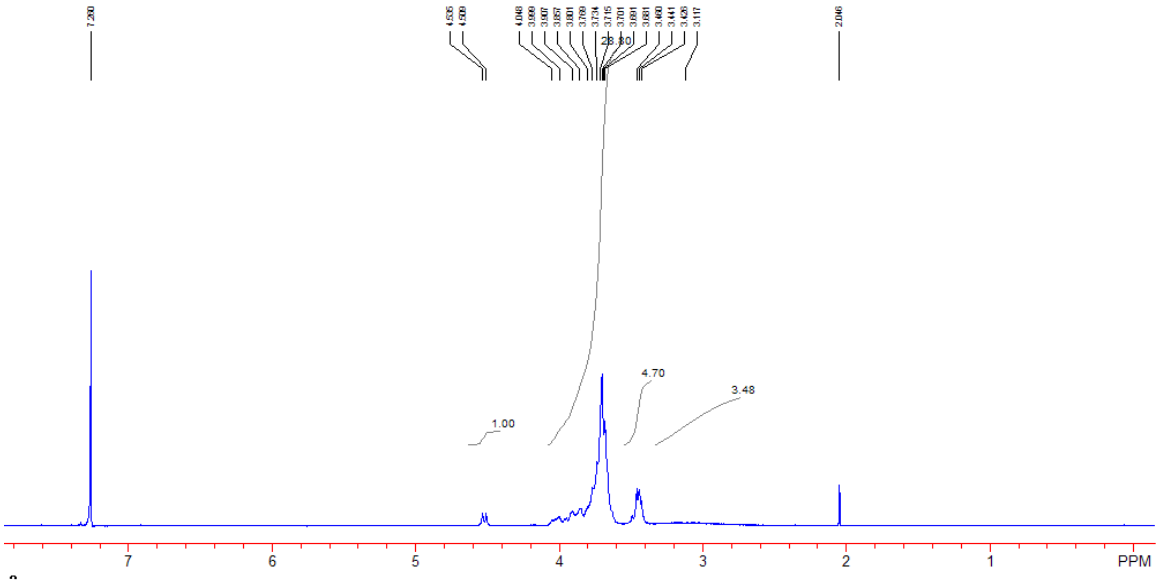


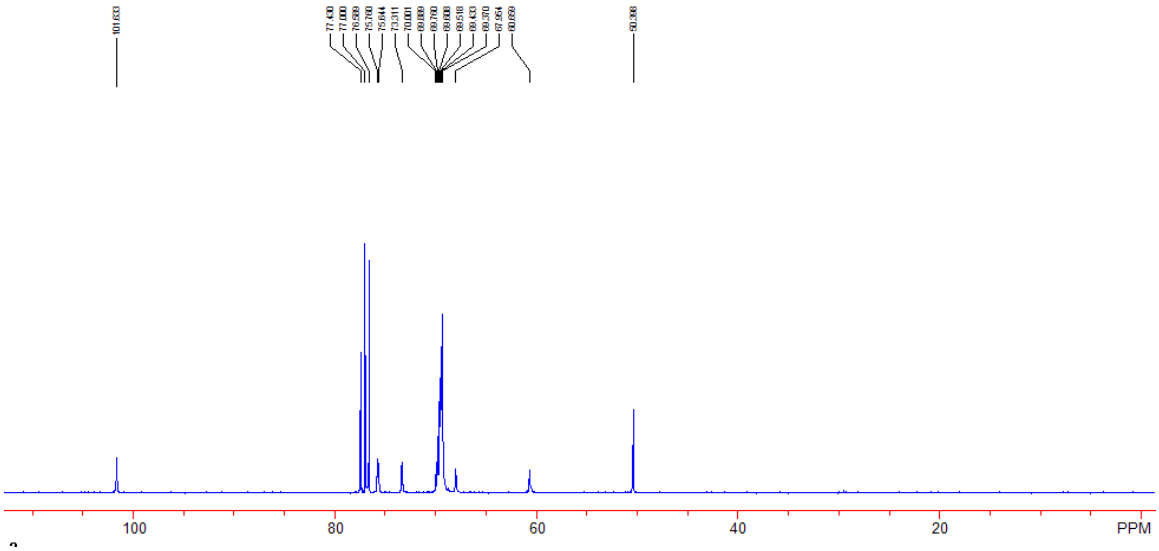


S15 **6**

EtONa (94 mg, 1.385 mmol) was added to a soln. of **S15** (211 mg, 0.346 mmol) in MeOH (5 mL) at 0 ^{o}C under N_2. The mixture was allowed to warm to room temperature and stirred

overnight. The mixture was then neutralized with 35% HCl in ether to pH = 7 and concentrated. Flash chromatography (EtOAc : MeOH = 10 : 1 to 5 : 1) gave **6** as a colorless oil (40 mg, 25% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.14 (br, 3H), 3.41-3.51 (m, 4H), 3.64-4.05 (m, 28H), 4.52 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) d 50.4, 60.7, 68.0, 69.37, 69.43, 69.5, 69.6, 69.8, 69.9, 70.0, 73.3, 75.7, 75.8, 101.6. ESI-MS: m/z 492 $[M+Na]^+$.





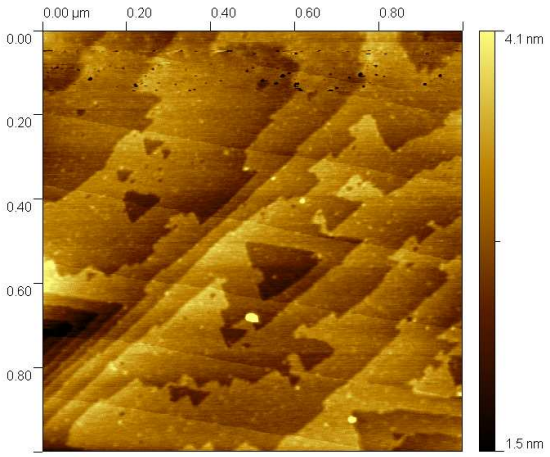


Figure S1. Tapping mode AFM image of a hydrogen-terminated silicon (111) surface.

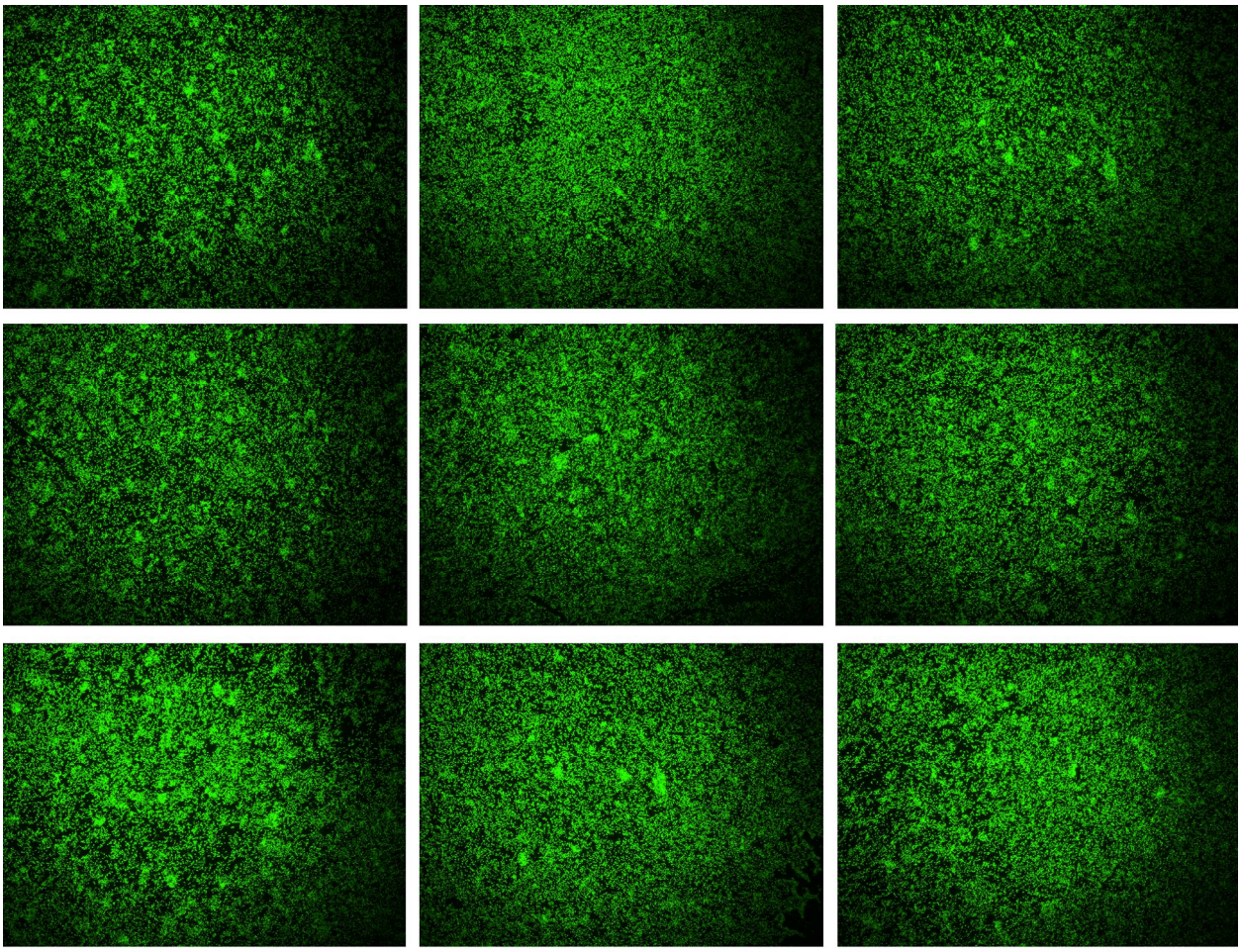


Figure S2. Fluorescence images on 9 randomly chosen locations on a mannose-presenting film (**E**) upon incubation with *fim+ E. coli.*

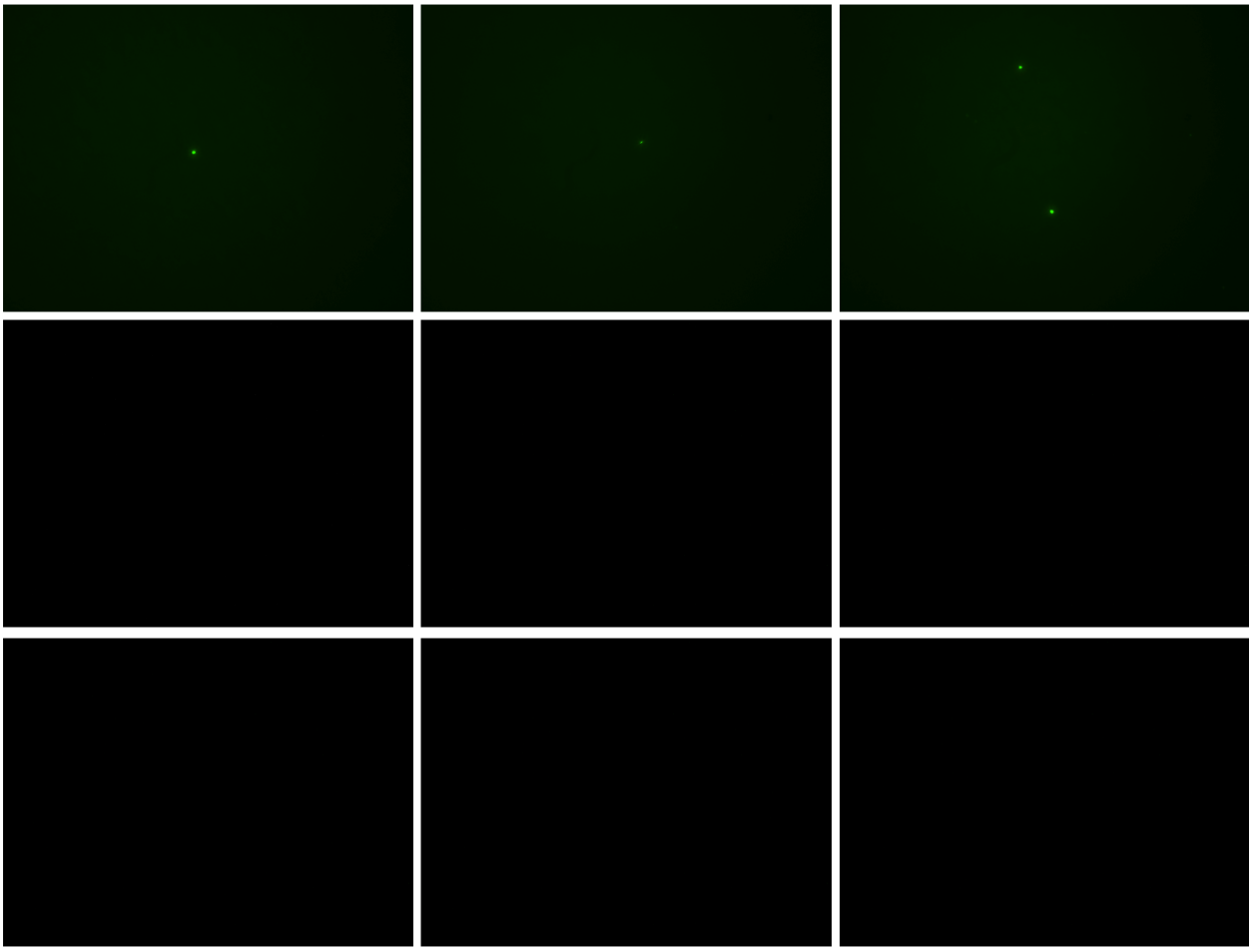


Figure S3. Fluorescence images on 9 randomly chosen locations on a mannose-presenting film (**E**) upon incubation with *fim– E. coli.*

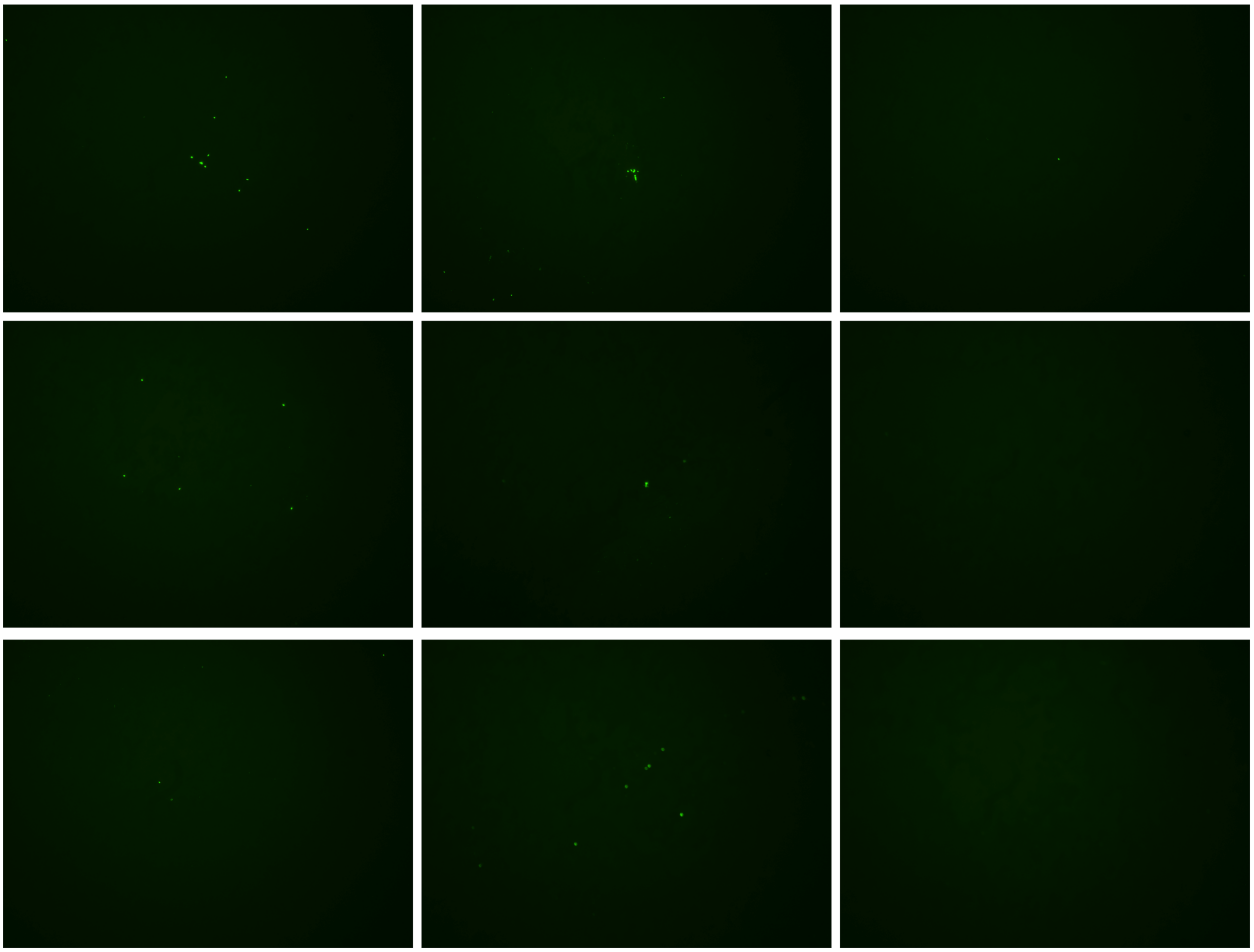


Figure S4. Fluorescence images on 9 randomly chosen locations on a glucose-presenting film (**F**) upon incubation with *fim*+ *E. coli.*

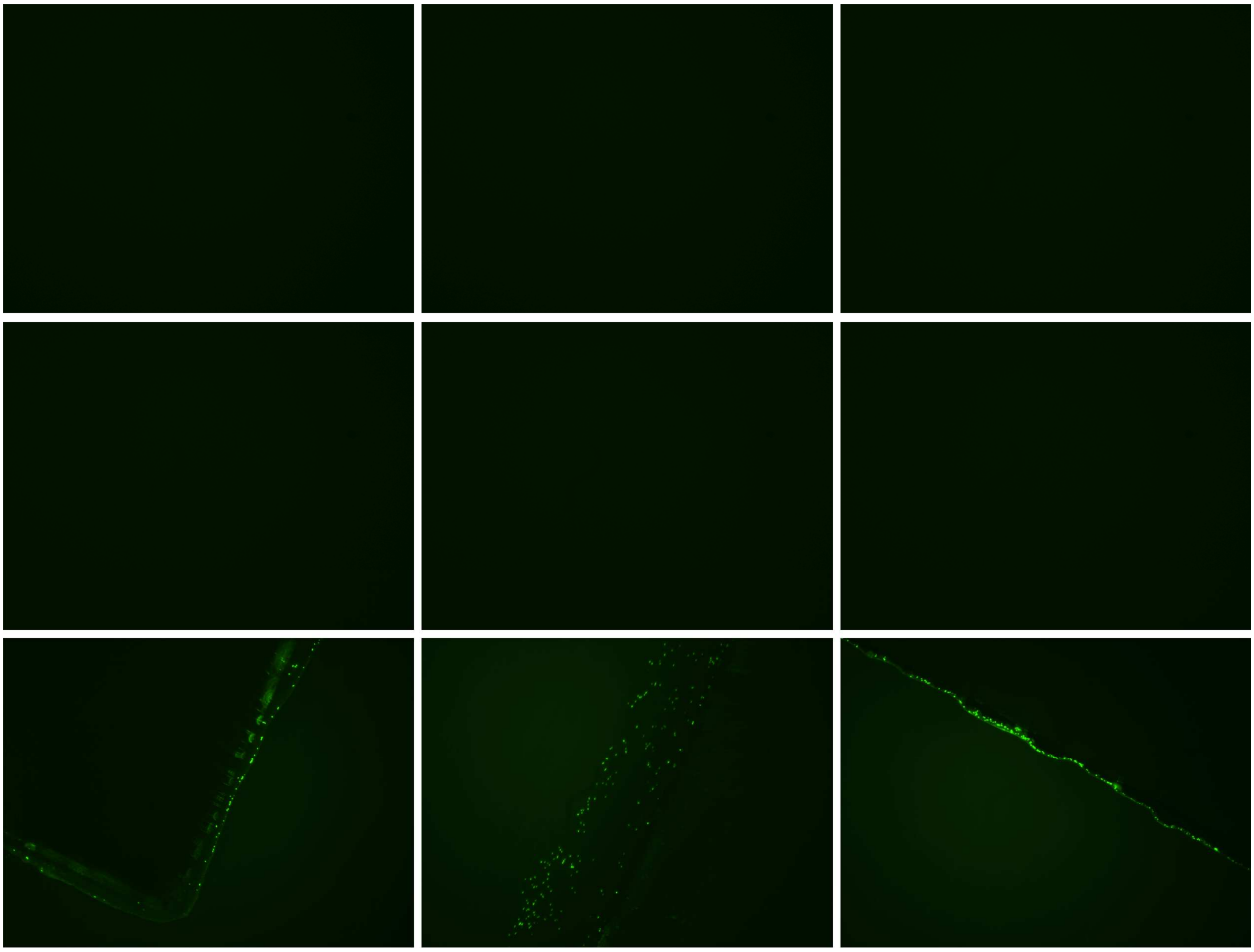


Figure S5. Fluorescence images on 9 randomly chosen locations on an ethynyl-presenting film (**B**) upon incubation with *fim+ E. coli.* The last row shows the presence of bacteria near the edge of the sample.

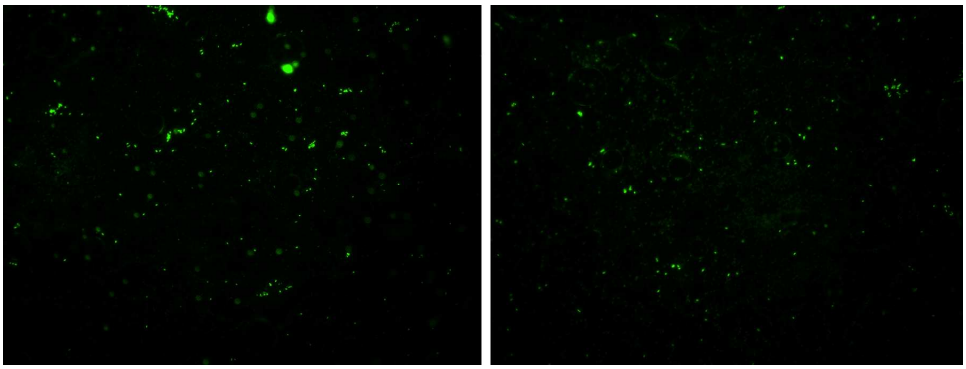


Figure S6. Fluorescence images on 2 randomly chosen locations on a mannose-presenting film (**E**) upon incubation with *fim*+ *E. coli* that were pre-saturated with mannose in the incubation solution.

References:

(1) Larsson, A.; Angbrant, J.; Ekeroth, J.; Mansson, P.; Liedberg, B. *Sensors Actuators B*. **2006**, *113*, 730.
(2) Beignet, J.; Tiernan, J.; Woo, C. H.; Kariuki, B. M.; Cox, L. R. *J. Org. Chem.* **2004**, *69*, 6341.