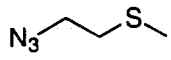
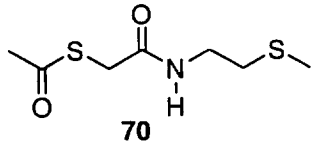
7:7:5 i-PrOH:Ethyl Acetate:Water; ^{1}H NMR (300 MHz, DMSO- d_6) δ 6.24 (s, 2H), 5.78-5.67 (m, 28H), 4.84 (s, 14H), 4.49-4.43 (m, 12H), 3.87-3.30 (m, 80H), 3.05-2.64 (m, 12H).



69

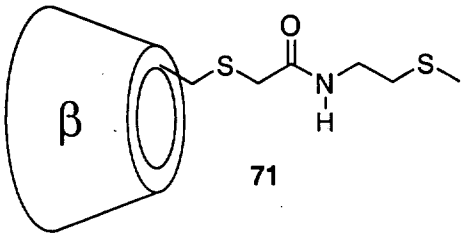
To a solution of NaN_3 (3.51 g; 54.0 mmol; 3.0 eq.) in H_2O (20 mL) was added a solution of 2–chloroethyl methyl sulfide **68** (2.0 g; 18.0 mmol; 1.0 eq.) in CH_2Cl_2 (20 mL) . and a catalytic amount (~10 mol%) of tetrabutylammonium chloride. This mixture was rigorously stirred at 30 °C for 3 h. The organic layer was separated from the aqueous layer and was dried ($MgSO_4$), filtered and concentrated to yield 1-azido-2-methylsulfanyl-ethane **69** (1.70 g, 81%) as a clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.48 (t, J = 7.0, 2H), 2.70 (t, J = 7.0, 2H), 2.17 (s, 3H).



70

To a solution of 1-azido-2-methylsulfanyl-ethane **69** (1.00 g; 8.6 mmol; 1.0 eq.) and triphenylphosphine (2.24 g; 8.6 mmol; 1.0 eq.) in THF (30 mL), was added water (0.15 mL; 8.6 mmol; 1.0 eq.). The reaction mixture was heated to 35 °C for 3 h, after which it was cooled to 25 °C and then to 0 °C. To this mixture was added freshly

distilled triethylamine (1.8 mL; 12.9 mmol; 1.5 eq.). Chloroacetyl chloride (1.46 g; 12.9 mmol; 1.5 eq.) was then added dropwise, and the resulting reaction mixture was allowed to warm to 25 °C. Potassium thioacetate (4.90 g; 43 mmol; 5.0 eq.) was then added to the reaction mixture, which was then heated to 50 °C for 18 h. The solution was then concentrated under reduced pressure, and the residue was purified by column chromatography on silica (gradient: 100% CH_2Cl_2 to 10% MeOH/CH_2Cl_2) to give thioacetic acid *S*-[(methylsulfanyl-ethyl carbamoyl)-methyl]ester **70** (1.20 g, 67%) as an off–white solid. Rf = 0.85 (10% MeOH/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.68 (bs, 1H), 3.56 (s, 2H), 3.44 (m, 2H), 2.62 (t, *J* = 6.5, 2H), 2.41 (s, 3H), 2.10 (s, 3H).



71

To a solution of **70** (0.50 g; 2.41 mmol; 30.0 eq.) in MeOH (50 mL) was added NaOH (0.20 g; 5.0 mmol; 62.2 eq.). The resulting mixture was stirred at 50 °C for 10 minutes. TLC showed the disappearance of the starting thioacetate and an appearance of a new spot at Rf = 0.65 (10% MeOH/CH_2Cl_2). The solution was concentrated under reduced pressure. To this residue was added a mixture of β–CD–6–I (0.10 g; 0.08 mmol; 1.0 eq.) and K_2CO_3 (55 mg; 0.4 mmol; 5.0 e.q.) in DMF (20 mL). The reaction flask was evacuated and backfilled with argon three times. The mixture was heated to 55 °C for

24 h. Water (180 mL) was then added to the reaction mixture. This mixture was filtered and was then purified by reverse phase column chromatography eluted with MeOH/H_2O mixture (linear gradient 80% H_2O - 80% MeOH). The methanol of the fractions that contained the product was removed under reduced pressure, and the residual aqueous solution was lyophilized. This gave monomer **71** (80 mg, 78%) as a white solid. Rf = 0.56 (7:7:7:4 iPrOH: EtOAc: H_2O: NH_4OH); ^1H NMR (300 MHz, D_2O) δ 5.05-4.90 (m, 7H), 4.10-3.17 (m, 44H), 2.85 (m, 2H), 2.59 (t, J = 6.6, 2H), 2.14 (s, 3H)