SUPPORTING INFORMATION

Sequential Phosphine Catalyzed, Nucleophilic Thiol-Ene/Radical-Mediated Thiol-Yne Reactions and the Facile, Orthogonal Synthesis of Polyfunctional Materials

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Experimental

Materials. Propargyl acrylate, hexylamine, captopril, thiocholesterol, 6-mercaptohexanol, butyl 3-mercaptopropionate, thioglycerol**,** 3-(mercaptopropyl)trimethoxysilane, and thiomalic acid were purchased from Aldrich Chemical Co. 3-Mercaptopropyl isobutyl POSS® was purchased from Hybrid Plastics. Pentaerythritol tetramercaptoprionate was donated by Bruno Bock (purity > 83%). All solvents and reagents were used as received.

Synthesis of the 4-functional alkyne (14). Pentaerythritol tetramercaptoprionate (2.44 g, 5 mmol) was mixed with hexylamine (30μL, ~1 mol%). To this mixture was added propargyl acrylate (2.20 g, 20 mmol). The reaction was left for 1 hr to ensure complete reaction. The reaction was monitored by IR and NMR spectroscopies.

Synthesis of 16-functional alcohol. 14 (0.116 g, 0.125 mmol) was mixed with thioglycerol (0.108 g, 1 mmol) and 2 wt% α,α-dimethoxy-α-phenylacetophenone in a 20mL glass scintillation vial. Samples were irradiated using a medium pressure Hg lamp (light intensity 9.25mW/cm^2) until thiol and yne were completely converted as determined by RT FTIR spectroscopy.

Synthesis of 16-functional acid. 14 (0.116 g, 0.125 mmol) in 2g of a 50:50 mixture of dichloromethane/methanol was mixed with thiomalic acid (0.150 g, 1 mmol) and 2 wt% α,α-dimethoxy-α-phenylacetophenone in a 20 mL glass scintillation vial. Samples were irradiated using a medium pressure Hg lamp (light intensity 9.25mW/cm^2) until thiol and yne were completely converted as determined by RT FTIR spectroscopy.

Synthesis of 8-functional alcohol. 14 (0.116 g, 0.125 mmol) was mixed with 6-mercapto-1-hexanol (0.134 g, 1 mmol) and 2 wt% α,α-dimethoxy-α-phenylacetophenone in a 20 mL glass scintillation vial. Samples were irradiated using a medium pressure Hg lamp (light intensity 9.25mW/cm^2) until thiol and yne were completely converted as determined by RT FTIR spectroscopy.

Synthesis of 8-functional acid. 14 (0.116 g, 0.125 mmol) was mixed with 3-mercaptopropionic acid (0.162 g, 1 mmol) and 2 wt% α,α-dimethoxy-α-phenylacetophenone in a 20 mL glass scintillation vial. Samples were irradiated using a medium pressure Hg lamp (light intensity 9.25mW/cm^2) until thiol and yne were completely converted as determined by RT FTIR spectroscopy.

Synthesis of 8-functional captopril. 14 (0.116 g, 0.125 mmol) in 2g of a 50:50 mixture of dichloromethane/methanol was mixed with captopril (0.217 g, 1 mmol) and 2 wt% α,α-dimethoxy-α-phenylacetophenone in a 20 mL glass scintillation vial. Samples were irradiated using a medium pressure Hg lamp (light intensity 9.25mW/cm^2) until thiol and yne were completely converted as determined by RT FTIR spectroscopy.

Synthesis of 8-functional POSS. 14 (0.116 g, 0.125 mmol) in 2g of a benzene was mixed with mercaptopropyl isobutyl POSS® (0.891 g, 1 mmol) and 2 wt% α,α-dimethoxy-α-phenylacetophenone in a 20 mL glass scintillation vial. Samples were irradiated using a medium pressure Hg lamp (light intensity 9.25mW/cm^2) until thiol and yne were completely converted as determined by RT FTIR spectroscopy.

Synthesis of 8-functional adamantane. 14 (0.116 g, 0.125 mmol) in 2g of a benzene was mixed with 1-adamantanethiol (0.163 g, 1 mmol) and 2 wt% α,α-dimethoxy-α-phenylacetophenone in a 20 mL glass scintillation vial. Samples were irradiated using a medium pressure Hg lamp (light intensity 9.25mW/cm^2) until thiol and yne were completely converted as determined by RT FTIR spectroscopy.

Characterization

Instrumentation

MALDI-TOF mass spectrometry (MALDI-TOF MS) was performed on a Bruker Reflex III Instrument equipped with a 337 nm N_2 laser in the reflector mode using both positive and negative modes and 20kV acceleration voltage. α-Cyano-4-hydroxycinnamic acid (CHCA) and trans-indole acrylic acid (IAA) were used as matrices for molecular weight determination.

NMR spectra were recorded on a Bruker 300 (53 mm). ^{13}C NMR characterization and ^{1}H NMR characterization with samples (10%v/v) dissolved in d_6-benzene, DMSO-d_6, or $CDCl_3$ used for deuterium shimming and locking.

FT-IR spectra were recorded using a modified Bruker 88 spectrometer. Samples were sandwiched between two sodium chloride salt plates at a thickness of ~20 micron. Each spectrum was collected over 32 scans. The data were analyzed with the Bruker OPUS/IR Version 4.0 software.

Real-time FTIR (RTIR) was used to monitor kinetics of each reaction. Sample thicknesses were approximately 200 microns. Real-time FTIR was used to monitor the loss of thiol (2570 cm^{-1}), acrylate (812cm^{-1}) and yne (2120 cm^{-1}) functional groups. The light intensity of the high pressure mercury lamp delivered to the sample via a light pipe was ~ 20 mW/cm^2.

Results

*Conversion data for reaction of **14** with 3-mercaptopropylisobutyl POSS*

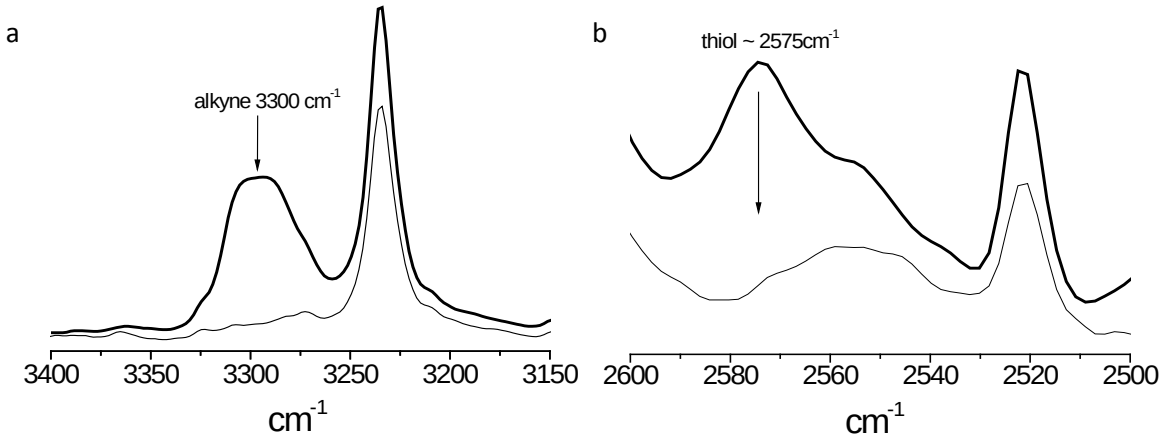


Figure S1. *(a) FTIR spectra demonstrating the consumption of alkyne functional groups for the reaction between **14** and 3-mercaptopropylisobutyl POSS and (b) FTIR spectra for the same reaction demonstrating the consumption of thiol functional groups for the reaction between **14** and with 3-mercaptopropylisobutyl POSS*

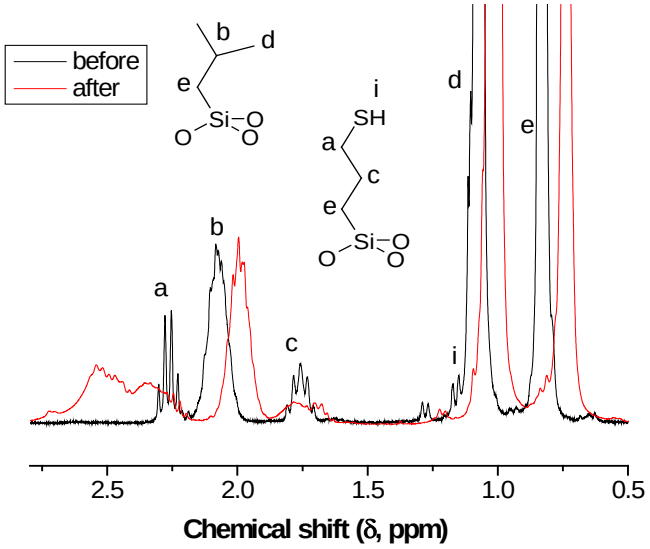


Figure S2. *^{1}H NMR before (black) and after (red) reaction of thiol-POSS and **14**. Note the overall shift and the disappearance of the strong peaks associated with carbons adjacent to thiol*

*Conversion data for reaction of **14** with 1-adamantanethiol*

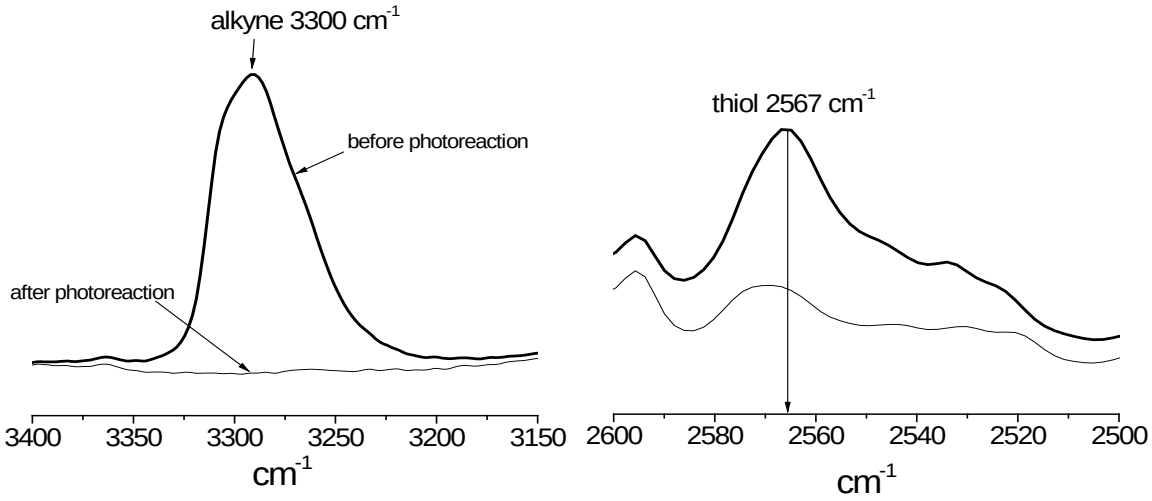


Figure S3. *(a) FTIR spectra demonstrating the consumption of alkyne functional groups for the reaction between **14** and 1-adamantanethiol and (b) FTIR spectra for the same reaction demonstrating the consumption of thiol functional groups for the reaction between **14** and 1-adamantanethiol (2567 cm^{-1} completely disappears and broad signal at 2572 cm^{-1} is not associated with thiol).*

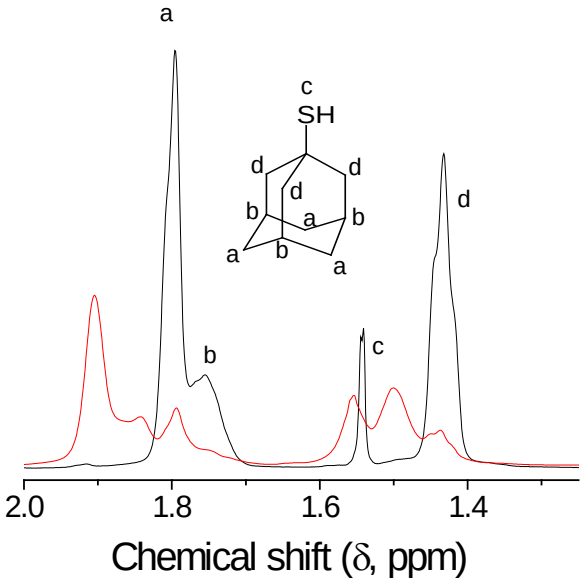
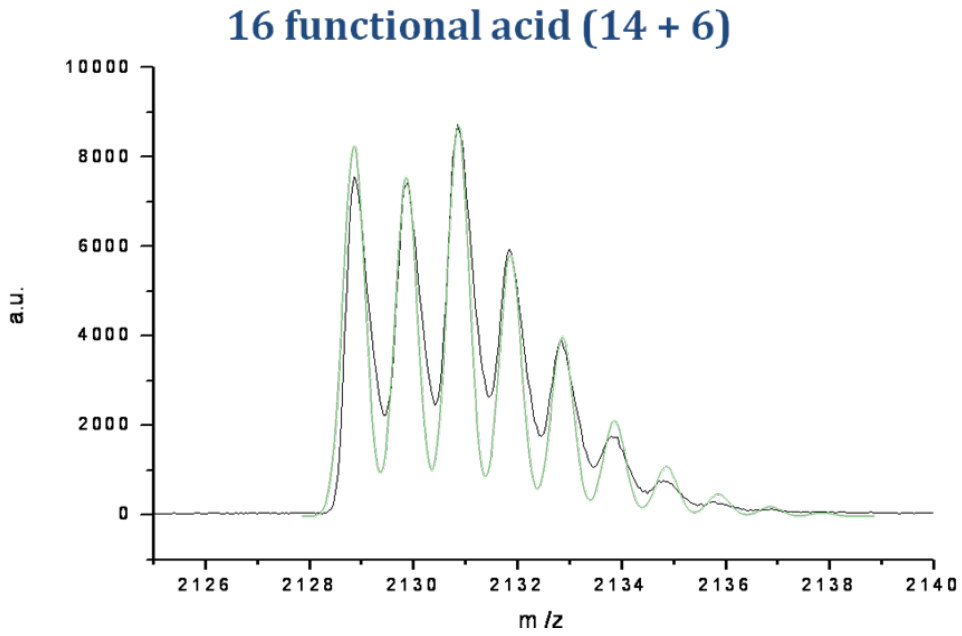
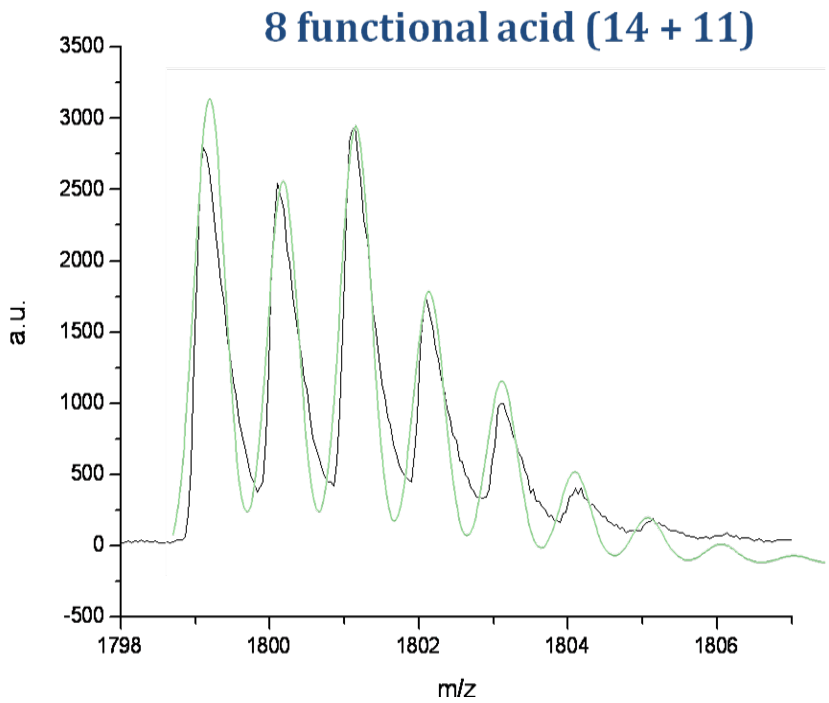


Figure S4. *^{1}H NMR before (black) and after (red) reaction of 1-adamantanethiol and **14**. Note the overall shift and the disappearance of the strong peak associated the thiol proton (1.53 ppm)*

Predicted (green) and measured (black) isotopic distributions for the multifunctional products

As noted in the main text, these measured and predicted isotopic distributions, assuming quantitative reaction verify successful synthesis of the target multifunctional species, Figure S4.





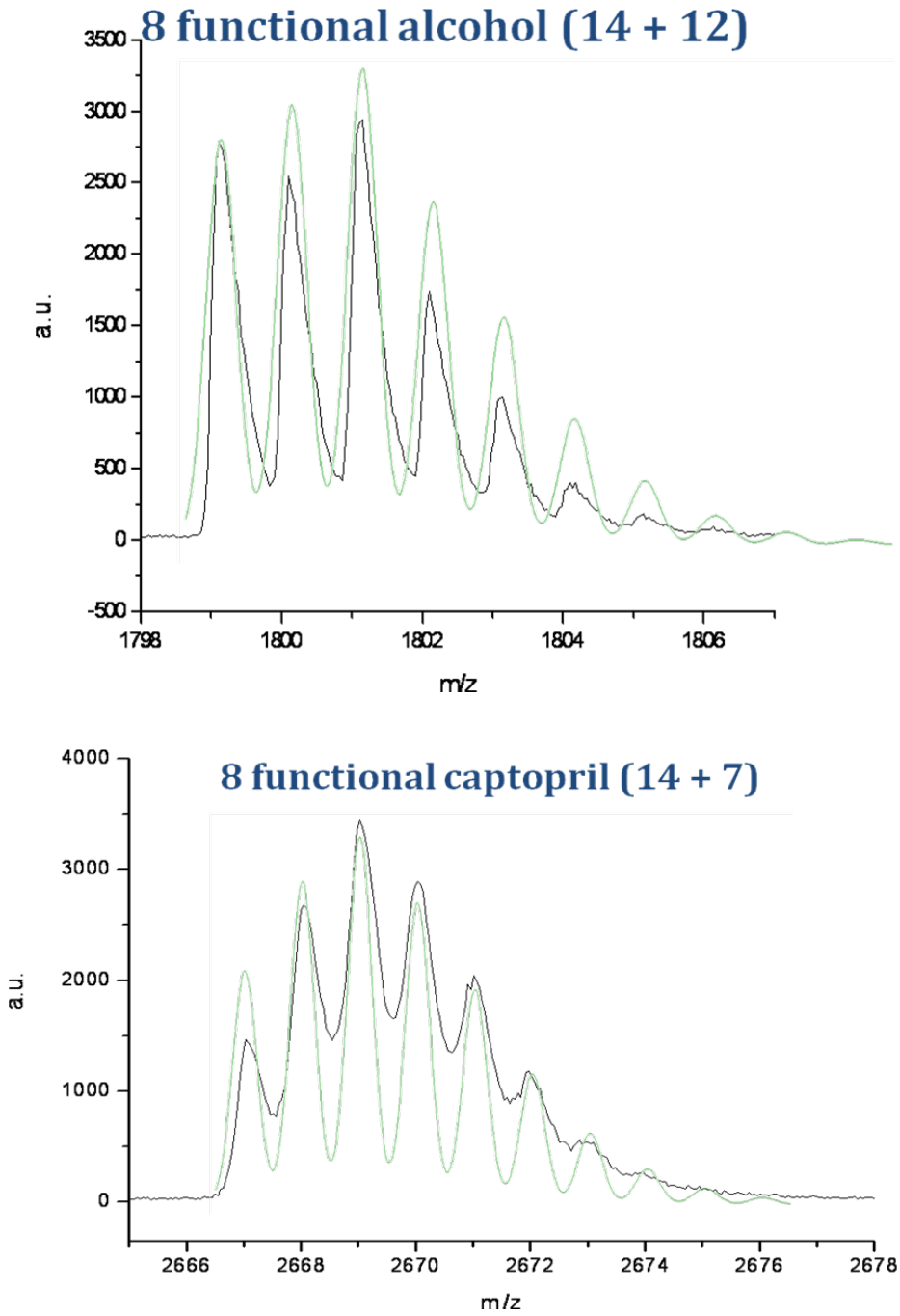
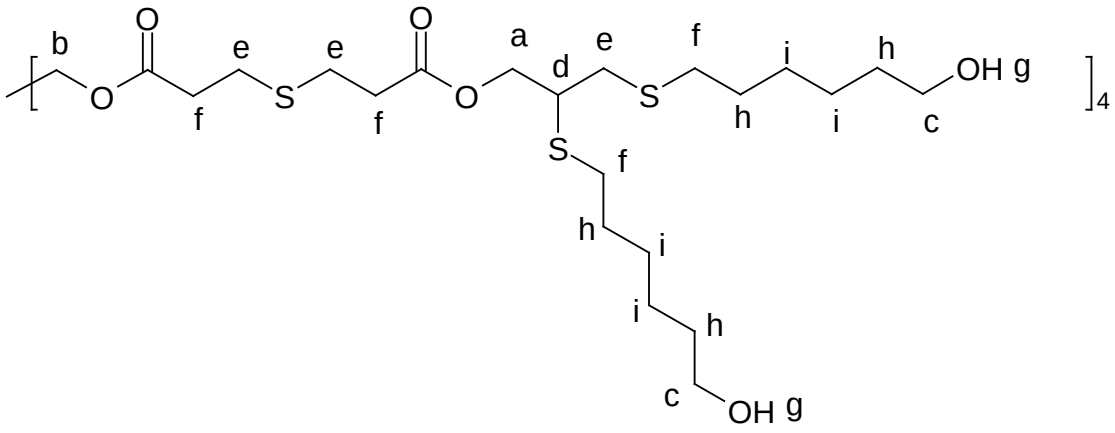
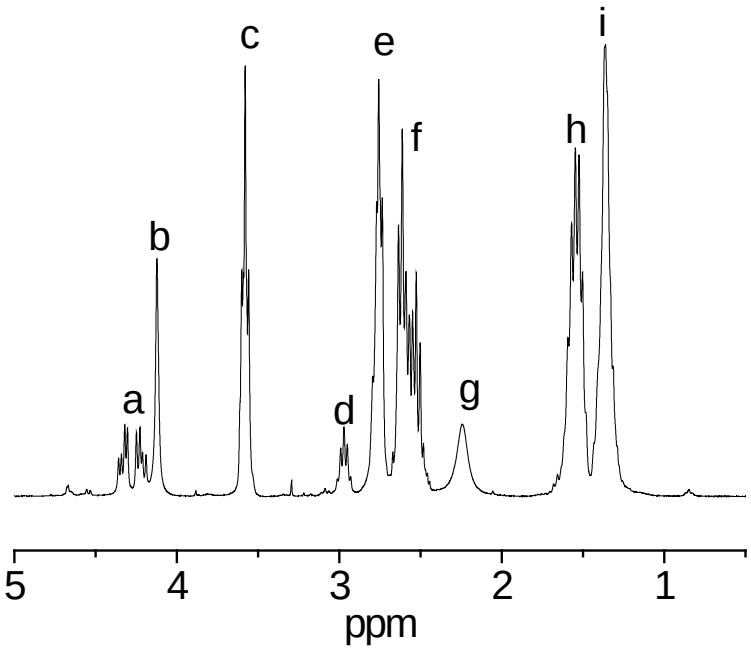


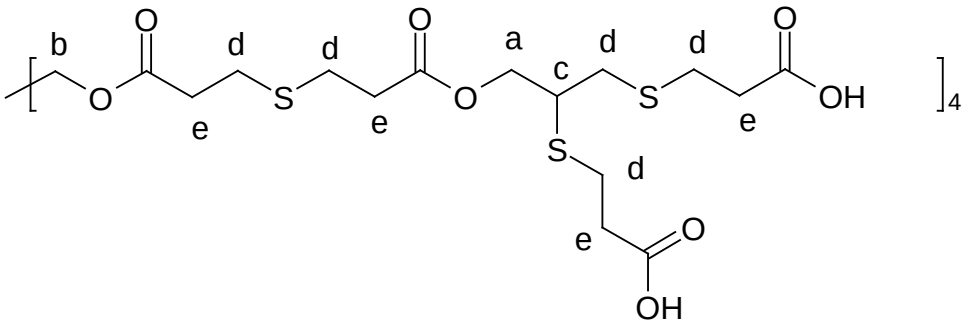
Figure S4. *Measured (black) and predicted (green) isotopic mass distributions for the products from the reaction of* ***14*** *with* ***6***, ***7***, ***11***, *and* ***12***.

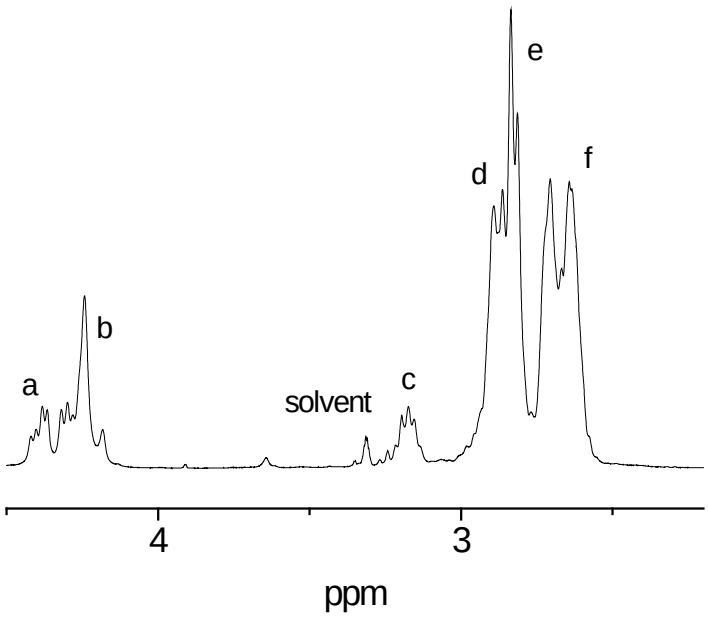




^{1}H NMR ($CDCl_3$), δ (ppm): 4.427-4.159 8H m, 4.165-4.055 8H s, 3.660-3.496 16H m, 3.042-2.896 4H m, 2.870-2.685 24H m, 2.687-2.446 32H m, 2.428-2.052 8H (9H) broad s, 1.620-1.420 32H m, 1.450-1.250 32H (36H) broad s

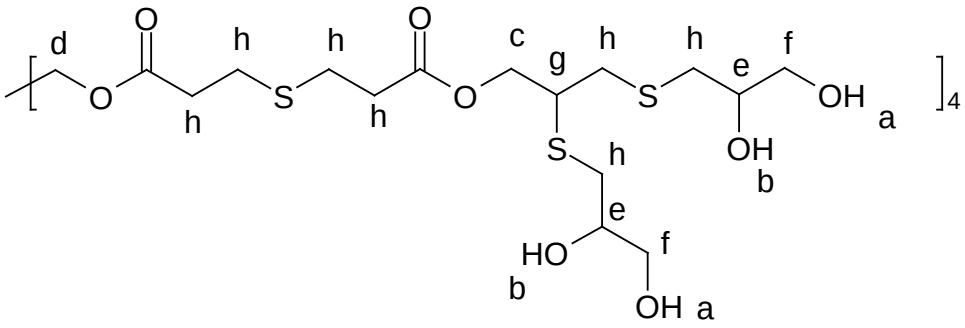
Figure S5. *Chemical structure and ^{1}H NMR spectrum of the 8-functional alcohol*

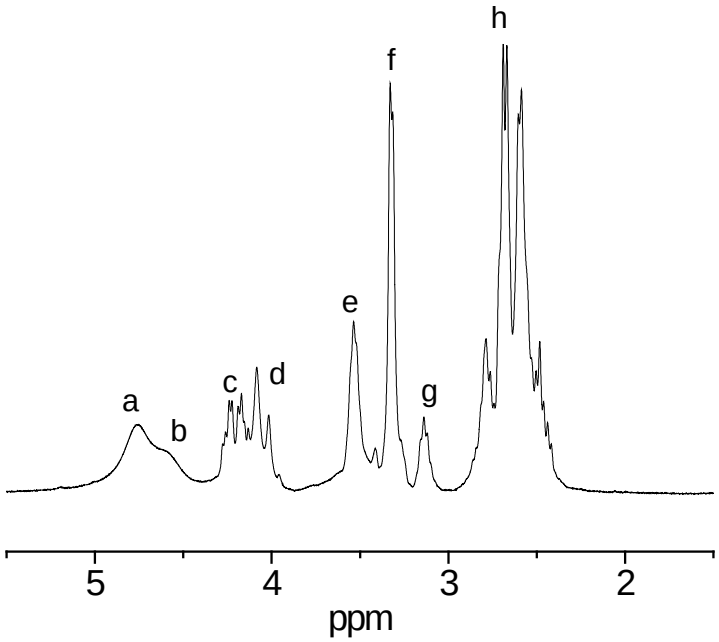




^{1}H NMR (d_4-methanol), δ (ppm): 4.12-4.50 (16H, a+b, m), 3.10-3.22 (4H, c, t), 2.50-3.02 (40H, m), 2.76-2.49 (32H, m)

Figure S6. *Chemical structure and ^{1}H NMR spectrum of the 8-functional acid*





^{1}H NMR (d_6-DMSO), δ (ppm): 2.32-2.92 (56H, broad m), 3.06-3.20 (4H, broad t), 3.20-3.44 (16H, broad d), 3.44-3.60 (8H, broad t), 3.88-4.33 (16H, m), 4.35-5.16 (16H)

Figure S7. *Chemical structure and ^{1}H NMR spectrum of the 16-functional alcohol*

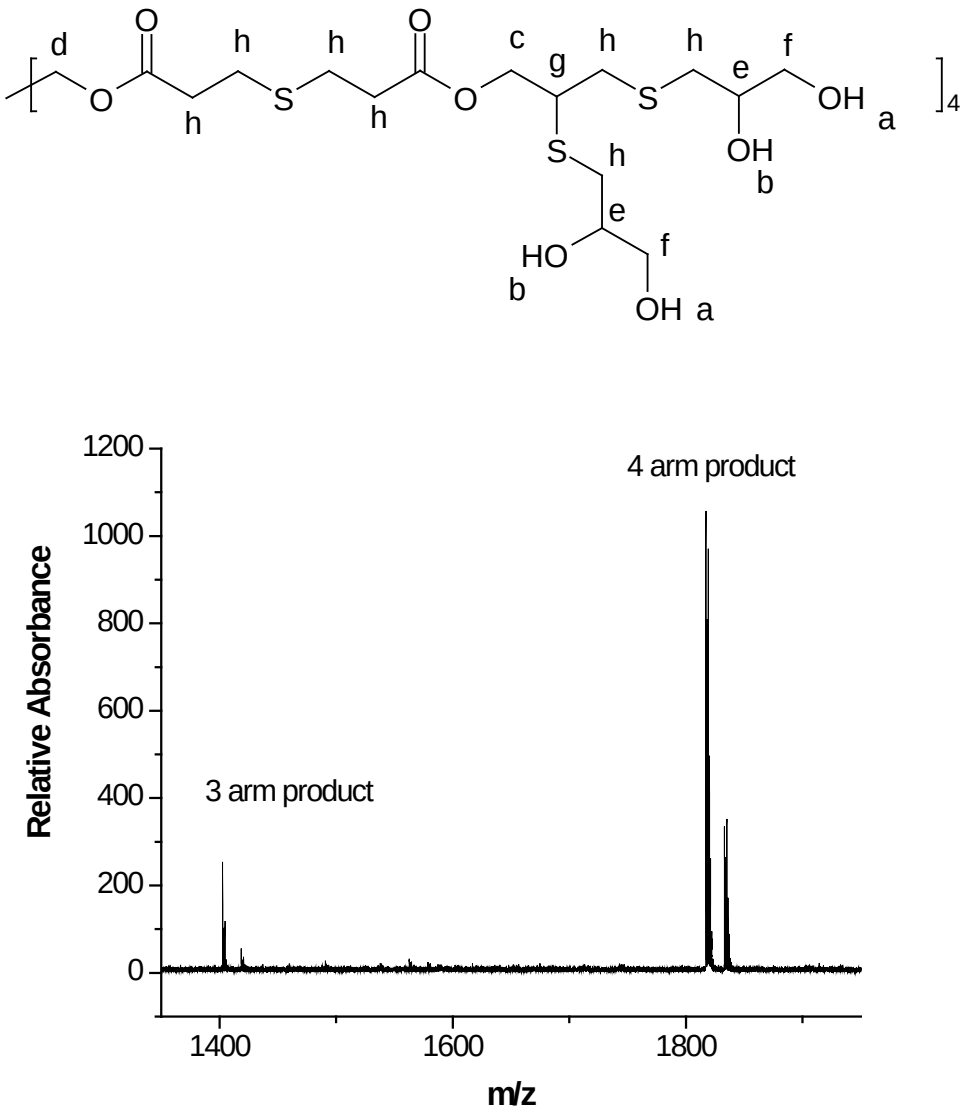


Figure S8. *MALDI-TOF MS spectrum of the 16-functional alcohol highlighting the presence of 3-arm products*