

## Electronic Supplemental Information (ESI)

### **Multiarm star polymers based on thiol-ene photoclick cyclodextrin cores**

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## Experimental

### **Materials**

$\alpha$ -,  $\beta$ -, and  $\gamma$ -Cyclodextrins (CDs, TCI America) were dried under vacuum at 100 °C overnight before use. Allyl bromide (99%, Alfa Aesar),  $\alpha$ -bromoisobutyryl bromide (99%, Alfa Aesar), 2-chloropropionyl chloride (96%, Alfa Aesar), thioethylene glycol (98%, Alfa Aesar), sodium hydride (60 % dispersion in mineral oil, Sigma-Aldrich), 2,2-Dimethoxy-2-phenylacetophenone (DMPA, 99%, Sigma-Aldrich), N,N-dimethylformamide (DMF, 99.8%, anhydrous, EMD Millipore), hexanes (95%, anhydrous, EMD Millipore), pyridine (anhydrous, 99.5+%, Alfa Aesar), ethyl ether (98%, EMD), and methanol (were used as received. Styrene ( $\geq 99\%$ , Sigma-Aldrich), methyl methacrylate (MMA, 99%, Sigma-Aldrich), tert-butyl methacrylate (tBA, 98%, Sigma-Aldrich) were vacuum distilled before use. N-isopropylacrylamide (NIPAM,  $> 98\%$ , TCI America) was recrystallized twice in toluene/n-hexane.

CuBr (99.999%, Sigma-Aldrich), CuCl ( $\geq 99\%$ , Sigma-Aldrich), N,N,N',N'',N''' - pentamethyldiethylene triamine (PMDETA, 99%, Sigma-Aldrich), tris[2-(dimethylamino)ethyl]amine (Me<sub>6</sub>TREN) was prepared according to the literature.

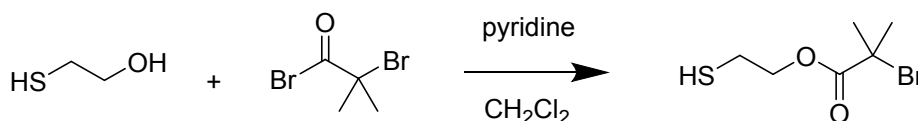
### **Instrumentation and Analysis**

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were acquired with a VXR400 spectrometer in d<sub>6</sub>-DMSO or CDCl<sub>3</sub>. The lamp used in thiol-ene click reactions was a VWR handheld lamp UV-AC, which emits 365 nm light at 6W.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra of CDs and their derivatives was recorded in positive reflectron or linear mode on a Bruker Autoflex III spectrometer. The instrument is equipped with a Nd:YAG laser (355 nm). For CDs and perallylated CDs, sample solutions (in THF or H<sub>2</sub>O) were prepared by mixing the analyte (1 mg/mL),  $\alpha$ -cyano-4-hydroxycinnamic acid (CHCA, Sigma-Aldrich, 10 mg/mL), and sodium iodide (1 mg/mL) in a volume ratio of 4/10/1. A small amount of the mixture solution was deposited on the sample plate and allowed to dry at the ambient environment. For photoclick CD cores and debrominated 21Br-S- $\beta$ -CD, samples were prepared by vortexing the analyte (2 mg) and dithranol (200-300 mg) in the presence of 3 small steel BBs for at least 5 minutes. A small bit of powder was applied onto the sample plate with the back of a wood Q-tip. External calibration was done using mixtures of peptides and proteins with masses from 379 to 8566. The theoretical isotopic distributions of compounds were calculated with a resolution of 0.001 by using ChemCalc.<sup>1</sup>

GPC analysis of polymer molecular weight and polydispersity was performed on a Waters Breeze HPLC system at 35 °C with THF as the eluent at a flow rate of 1 mL/min. The system is equipped with a refractive index detector and a dual UV/Vis detector together with Styragel HR2, HR4 and HR5 columns. Polystyrene standards were used to generate the calibrate curve.

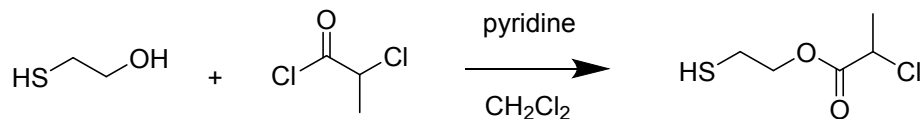
### Synthesis of HS-EBiB (2-mercaptoethyl-2-bromo-2-methylpropanoate)



The synthesis of HS-EBiB is similar to the literature.<sup>2</sup>  $\alpha$ -bromoisobutyryl bromide (10 mL, 80.9 mmol) was slowly dropped into a solution of thioethylene glycol (6.24 mL, 89 mmol) and pyridine (6.5 mL, 80.4 mmol) in anhydrous methylene chloride (150 mL) at 0 °C. The mixture was kept stirring at room temperature overnight. After reaction, the precipitate was filtered off. The methylene chloride solution was washed with DI water and brine successively before drying with anhydrous MgSO<sub>4</sub>. Evaporation of solvent afforded a clear liquid. The product was purified by vacuum distillation as a colorless liquid (9.5 g, yield 52%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.55 (t, 1H, -SH), 1.92 (s, 6H, - $\text{CH}_3$ ), 2.75-2.81 (q, 2H, - $\text{CH}_2\text{SH}$ ), 4.28 (t, 2H, - $\text{CH}_2\text{O}$ -);  $^{13}\text{C}$  NMR (150.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  23.02, 30.70, 55.58, 66.98, 171.34.

### Synthesis of HS-ECP (2-mercaptoethyl-2-chloropropanoate)



The synthesis of HS-ECP is the same as the synthesis of HS-EBiB except that 2-chloropropanoyl chloride (7.9 mL, 80.9 mmol) was used. Vacuum distillation afforded the pure product (7.5 g, yield 55%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.52 (t, 1H, -SH), 1.70 (d, 3H, - $\text{CH}_3$ ), 2.76-2.81 (q, 2H, - $\text{CH}_2\text{SH}$ ), 4.26-4.32 (m, 2H, - $\text{CH}_2\text{O}$ -), 4.39-4.44 (q, 1H, - $\text{CHCl}$ );  $^{13}\text{C}$  NMR (150.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.40, 22.99, 52.28, 66.91, 169.74.

### General procedure for synthesis of perallylated CDs

Into a 500 mL 3-neck flask equipped with a dropping funnel and a magnetic stirrer, NaH (12 g, 0.3 mol, 4 equiv per OH function) (60% in mineral oil) was charged under Ar. It was suspended in 80 mL DMF after being washed with dry hexane (3×30 mL). Then a solution of CD in DMF (4 g in 40 mL) was transferred into the dropping funnel via syringe and slowly dropped into the flask at 0 °C. After addition, the suspension mixture was kept stirring at 0 °C for 1 hr. Subsequently, allyl bromide (26 mL, 0.3 mol, 4 equiv per OH function) was added dropwise through the dropping funnel. The mixture was allowed to warm to room temperature and kept stirring for 3 hr under Ar. Then 5 mL methanol was added to quench unreacted NaH. DMF and unreacted allyl bromide were removed by vacuum. The residue was dissolved in ethyl acetate and washed three times with water and brine. The organic phase was isolated and dried with anhydrous  $\text{MgSO}_4$ . Evaporation of ethyl acetate afforded viscous oil. All products were obtained quantitatively. No further purification is necessary.

**Allyl- $\alpha$ -CD** (hexakis(2,3,6-tri-*O*-allyl)- $\alpha$ -CD): 6.6 g, yield: 95%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.2-4.6 (m, 72H), 4.8-5.4 (m, 42H), 5.8-6.2 (m, 18H);  $^{13}\text{C}$  NMR (150.9 MHz,

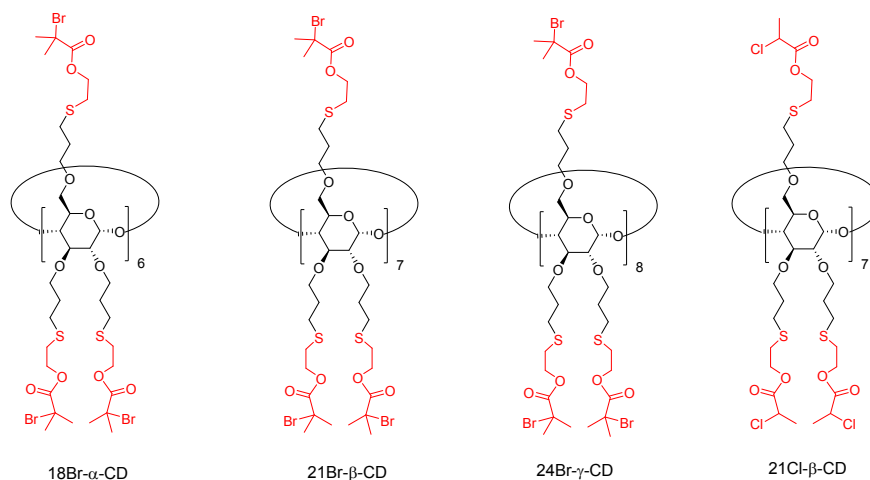
CDCl<sub>3</sub>):  $\delta$  69.04(C6), 71.24 (C5), 71.90, 72.19, 74.62, 78.50 (C4), 79.70 (C2), 81.98 (C3), 100.64 (C1), 115.81, 116.70, 116.80, 135.06, 135.51, 136.79.  
MALDI-TOF (*m/z*): calculated, 1692.88 for C<sub>90</sub>H<sub>132</sub>O<sub>30</sub>; found, 1715.79 for [M+Na]<sup>+</sup>.

**Allyl- $\beta$ -CD** (heptakis(2,3,6-tri-*O*-allyl)- $\beta$ -CD): 6.5 g, yield: 93%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.3-4.6 (84H); 4.9-5.4 (49H); 5.7-6.1 (21H); <sup>13</sup>C NMR (150.9 MHz, CDCl<sub>3</sub>):  $\delta$  69.05(C6), 70.97 (C5), 72.10, 72.15, 74.44, 79.02 (C4), 79.19 (C2), 79.99 (C3), 98.69 (C1), 115.57, 116.68, 116.74, 134.86, 135.36, 136.19.  
MALDI-TOF (*m/z*): calculated, 1975.03 for C<sub>105</sub>H<sub>154</sub>O<sub>35</sub>; found, 1998.12 for [M+Na]<sup>+</sup>.

**Allyl- $\gamma$ -CD** (octakis(2,3,6-tri-*O*-allyl)- $\gamma$ -CD): 6.8 g, yield: 98%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.2-4.6 (m, 96H), 4.9-5.4 (m, 56H), 5.7-6.2 (m, 24H); <sup>13</sup>C NMR (150.9 MHz, CDCl<sub>3</sub>):  $\delta$  68.75(C6), 70.90 (C5), 72.00, 72.32, 74.53, 78.53 (C4), 79.20 (C2), 80.15 (C3), 98.64 (C1), 115.48, 116.75, 116.92, 134.74, 135.29, 136.03.  
MALDI-TOF (*m/z*): calculated, 2257.17 for C<sub>120</sub>H<sub>176</sub>O<sub>40</sub>; found, 2280.16 for [M+Na]<sup>+</sup>.

### General procedure for thiol-ene photoclick reactions

In a small glass vial, perallylated CD (0.2 g, 2.1 mmol allyl) and DMPA (32 mg, 0.125 mmol) were dissolved in HS-EBiB (0.75g, 3.3 mmol). The clear viscous mixture was exposed to 365 nm for 30 min at room temperature without removing air and stirring. After reaction the solution was precipitated into hexanes. The precipitate was isolated and dissolved in a small amount of ethyl ether before precipitating into cold methanol. This was repeated twice. The clear, viscous liquid was dried under vacuum at 60 °C overnight. The product was obtained quantitatively.



**21Br-S- $\beta$ -CD** (heptakis(2,3,6-tri-*O*-(6-(3-thiahexyl)-2-bromo-2-methylpropanoate)- $\beta$ -CD): 0.65 g, yield: 95%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.6-2.2, 2.5-3.0, 3.1-4.1, 4.2-4.4, 5.0-5.2;  $^{13}\text{C}$  NMR (150.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  28.56, 28.89, 29.18, 29.78, 29.93, 30.72, 30.75, 55.62, 55.67, 55.73, 64.85, 64.88, 64.93, 69.83, 71.43 (C6), 72.37 (C5), 80-81 (C2, C3, C4), 98.22 (C1), 171.25, 171.29, 171.32. MALDI-TOF ( $m/z$ (100%)): calculated, 6767.29 for  $\text{C}_{231}\text{H}_{385}\text{O}_{77}\text{Br}_{21}\text{S}_{21}\text{Na}^+$ ; found, 6768.66.

**18Br-S- $\alpha$ -CD** (hexakis(2,3,6-tri-*O*-(6-(3-thiahexyl)-2-bromo-2-methylpropanoate)- $\alpha$ -CD): 0.62 g, yield: 91%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.6-2.2, 2.5-3.0, 3.1-4.1, 4.2-4.4, 5.0-5.2;  $^{13}\text{C}$  NMR (150.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  28.61, 28.85, 29.09, 29.73, 29.83, 29.88, 30.70, 55.58, 55.61, 55.67, 64.82, 64.90, 69.91, 71.43, 72.24, 76.68, 77.00, 77.31, 80.08, 80.50, 97.68, 171.24, 171.30. MALDI-TOF ( $m/z$ (100%)): calculated, 5803.25 for  $\text{C}_{198}\text{H}_{330}\text{O}_{66}\text{Br}_{18}\text{S}_{18}\text{Na}^+$ ; found, 5804.89.

**24Br-S- $\gamma$ -CD** (octakis(2,3,6-tri-*O*-(6-(3-thiahexyl)-2-bromo-2-methylpropanoate)- $\gamma$ -CD): 0.64 g, yield: 94%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.6-2.2, 2.5-3.0, 3.1-4.1, 4.2-4.4, 5.0-5.2;  $^{13}\text{C}$  NMR (150.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  28.48, 28.86, 29.21, 29.76, 29.91, 30.55, 30.72, 55.61, 55.65, 55.72, 64.83, 64.88, 64.92, 69.74, 71.51, 72.30, 76.68, 77.00, 77.31, 80.48, 98.20, 171.20, 171.25, 171.28. MALDI-TOF ( $m/z$ (100%)): calculated, 7729.34 for  $\text{C}_{264}\text{H}_{440}\text{O}_{88}\text{Br}_{24}\text{S}_{24}\text{Na}^+$ ; found, 7735.26.

**21Cl-S- $\beta$ -CD** (heptakis(2,3,6-tri-*O*-(6-(3-thiahexyl)-2-chloropropanoate)- $\beta$ -CD): The synthetic route of 21Cl-S- $\beta$ -CD is listed below. The procedure is the same as 21Br-S- $\beta$ -CD except HS-Cl was used. 0.5 g, yield: 91%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.6-1.7, 1.7-2.0, 2.5-2.8, 3.1-4.1, 4.2-4.3, 4.3-4.5, 5.0-5.2.

### **Reductive debromination of 21Br-S- $\beta$ -CD**

21Br-S- $\beta$ -CD (0.1 g, 0.31 mmol Br) and AIBN (25 mg, 0.15 mmol, 0.5 eqv. of Br) was dissolved in 3 mL toluene. The solution was degassed with Ar for 10 minutes. Then tributyltin hydride (0.27 g, 0.93 mmol, 3 equiv per Br) was injected into the solution. The mixture was heated to 65 °C under Ar. The reaction was kept overnight. After reaction, the mixture was precipitated into n-hexane with a few drops of methanol. The crude product was purified by precipitating into n-hexane for three times before drying in a vacuum oven at 65 °C overnight. 0.06 g product obtained. Yield = 79%. MALDI-TOF ( $m/z$ ): calculated, 5107.19 for C<sub>23</sub>H<sub>40</sub>O<sub>5</sub>S<sub>2</sub>Na<sup>+</sup>; found, 5106.84 for [M+Na]<sup>+</sup>.

### **Example synthesis of PS star by ATRP**

Styrene (8.0 mL, 60.75 mmol), 21Br-S- $\beta$ -CD (30 mg, 0.1 mmol -Br), CuBr (14 mg, 0.1 mmol), and bpy (30.6 mg, 0.2 mmol) were charged into a 25 mL Schlenk flask. The mixture was subjected to three cycles of freeze-pump-thaw before inserting the flask into an oil bath at 90 °C. The polymerization was carried out in bulk under Argon. After polymerization, a drop of the solution was taken out for <sup>1</sup>H NMR analysis to calculate the monomer conversion (11%). The remaining solution was dropped into methanol under vigorous stirring. The precipitate was collected by filtration. The purified product was obtained by dissolving the precipitate in THF, passing it through a short column of neutral alumina, and finally precipitating it in methanol before drying under vacuum at 45 °C overnight. 0.8 g polymer ( $M_n = 71,600$  Da,  $pdi = 1.05$ ) was obtained.

### **Example synthesis of PtBA star by ATRP**

tBA (6.7 mL, 46 mmol), 21Br-S- $\beta$ -CD (30 mg, 0.1 mmol -Br), CuBr (14 mg, 0.1 mmol), and methyl ethyl ketone (4.0 mL) were charged into a 25 mL Schlenk flask. After the mixture was subjected to three cycles of freeze-pump-thaw, under Argon, PMDETA (20  $\mu$ L, 0.1 mmol) was quickly injected into the flask with a microsyringe. The mixture was kept stirring for a couple of minutes at room temperature before inserting the flask into an oil bath at 60 °C. The remaining solution was diluted with MEK, passed through a short column of neutral alumina, and then precipitated into methanol/water (1/1). The precipitate was collected by filtration and dried under vacuum at 45 °C overnight. 1.4 g

polymer ( $M_n = 193,400$  Da,  $pdi = 1.05$ ) was obtained. The monomer conversion was 20%.

### **Example synthesis of PMMA star by ATRP**

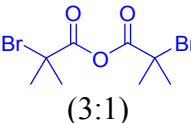
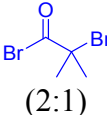
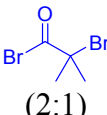
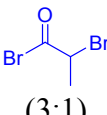
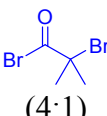
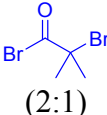
MMA (6.0 mL, 46 mmol), 21Br-S- $\beta$ -CD (15 mg, 0.05 mmol -Br), CuCl (5 mg, 0.05 mmol), bpy (15.3 mg, 0.1 mmol) and diphenyl ether (6.0 mL) were charged into a 25 mL Schlenk flask. The mixture was subjected to three cycles of freeze-pump-thaw before inserting the flask into an oil bath at 60 °C. The remaining solution was precipitated into methanol. The precipitate was collected by filtration. The purified product was obtained by dissolving the precipitate in THF, passing it through a short column of neutral alumina, and precipitating it in methanol twice before drying under vacuum at 45 °C overnight. 0.4 g polymer ( $M_n = 86,600$  Da,  $pdi = 1.08$ ) was obtained. The monomer conversion was 8%.

### **Example synthesis of PNIPAM star by Cu-mediated reversible deactivation radical polymerization (Cu-RDRP)**

NIPAM (1.2 g, 10.5 mmol), 21Cl-S- $\beta$ -CD (39 mg, 0.15 mmol -Cl), CuCl (15 mg, 0.15 mmol), and isopropanol/MEK (0.8/1.2 mL) were charged into a 10 mL Schlenk flask. After the mixture was subjected to three cycles of freeze-pump-thaw, under Argon, Me6TREN (40.2  $\mu$ L, 0.15 mmol) was quickly injected into the flask with a microsyringe. The mixture was kept stirring for a couple of minutes at room temperature before inserting the flask into an oil bath at 40 °C. The remaining solution was diluted with 10 mL THF and precipitated into ethyl ether. The precipitate was collected by filtration. The purified product was obtained by dissolving the precipitate in THF, passing it through a short neutral alumina column, and precipitating it in ethyl ether twice before drying under vacuum at RT overnight. 0.6 g polymer ( $M_n = 44,800$  Da,  $pdi = 1.16$ ) was obtained. The monomer conversion was 50%.

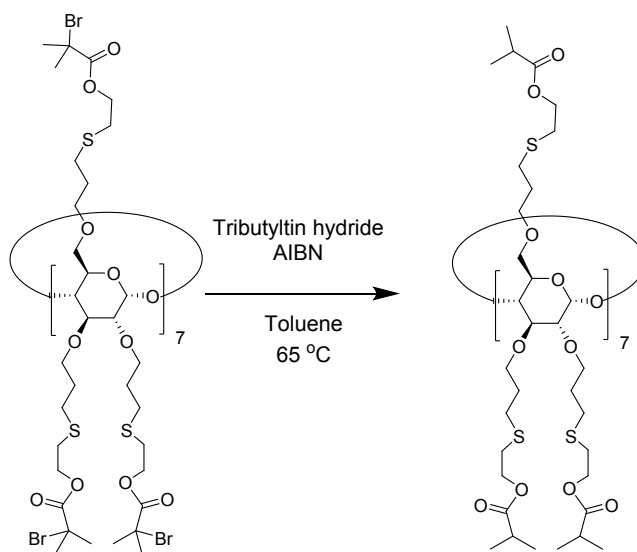
1. L. Patiny and A. Borel, *Journal of Chemical Information and Modeling*, 2013, **53**, 1223-1228.
2. B. Li, B. Yu, W. T. S. Huck, F. Zhou and W. Liu, *Angewandte Chemie International Edition*, 2012, **51**, 5092-5095.

**Table S1.** Summary of previous work in synthesis of fully functionalized  $\beta$ -cyclodextrin cores.

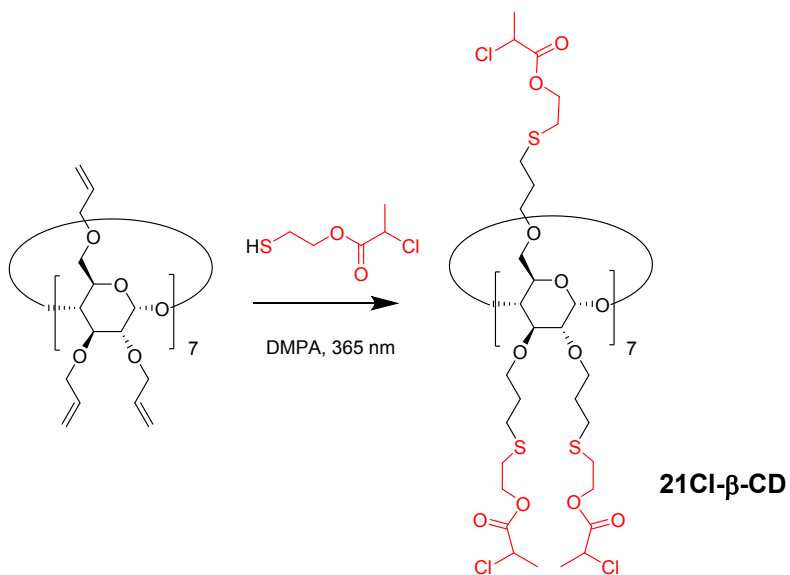
Previous Work	Reagent (molar ratio to -OH)	Solvent	Reaction Conditions	Purification	Reported Yield (%)	Product Degree of Functionalization (Characterization)
Haddleton et al. (Ref. 15)	 (3:1)	Pyridine	96 hr at RT	Silica gel column	17	21 -OHs functionalized (100%) (NMR + FTIR + Elemental analysis)
Muller et al. (Ref. 16)	 (2:1)	Pyridine	1) 24 hr at RT; 2) Reflux for 3 hr	Silica gel column + crystn.	19	21 -OHs functionalized (100%) (NMR + MALDI-TOF MS)
Xiao et al. (Ref. 17)	 (2:1)	NMP	1) 2 hr at 0 °C; 2) 18 hr at RT	Dialysis or crystn.	89 (dialysis), 67 (crystn.)	Degree of functionalization unclear (NMR + FTIR; no data of MALDI-TOF MS)
Liu et al. (Ref. 29)	 (3:1)	NMP	96 hr at RT	Silica gel column	14	21 -OHs functionalized (100%) (NMR + MALDI-TOF MS)
Becer et al. (Ref. 26)	 (4:1)	NMP	1) 2 hr at 0 °C; 2) 56 hr at RT	Repeat precipitation	68.5	16 -OHs functionalized (NMR + MALDI-TOF MS)
Zhong et al. (Ref. 32)	 (2:1)	NMP	1) 2 hr at 0 °C; 2) 22 hr at RT	Silica gel column	75	14 -OHs functionalized (NMR + MALDI-TOF MS)

NMP: N-methyl-2-pyrrolidone

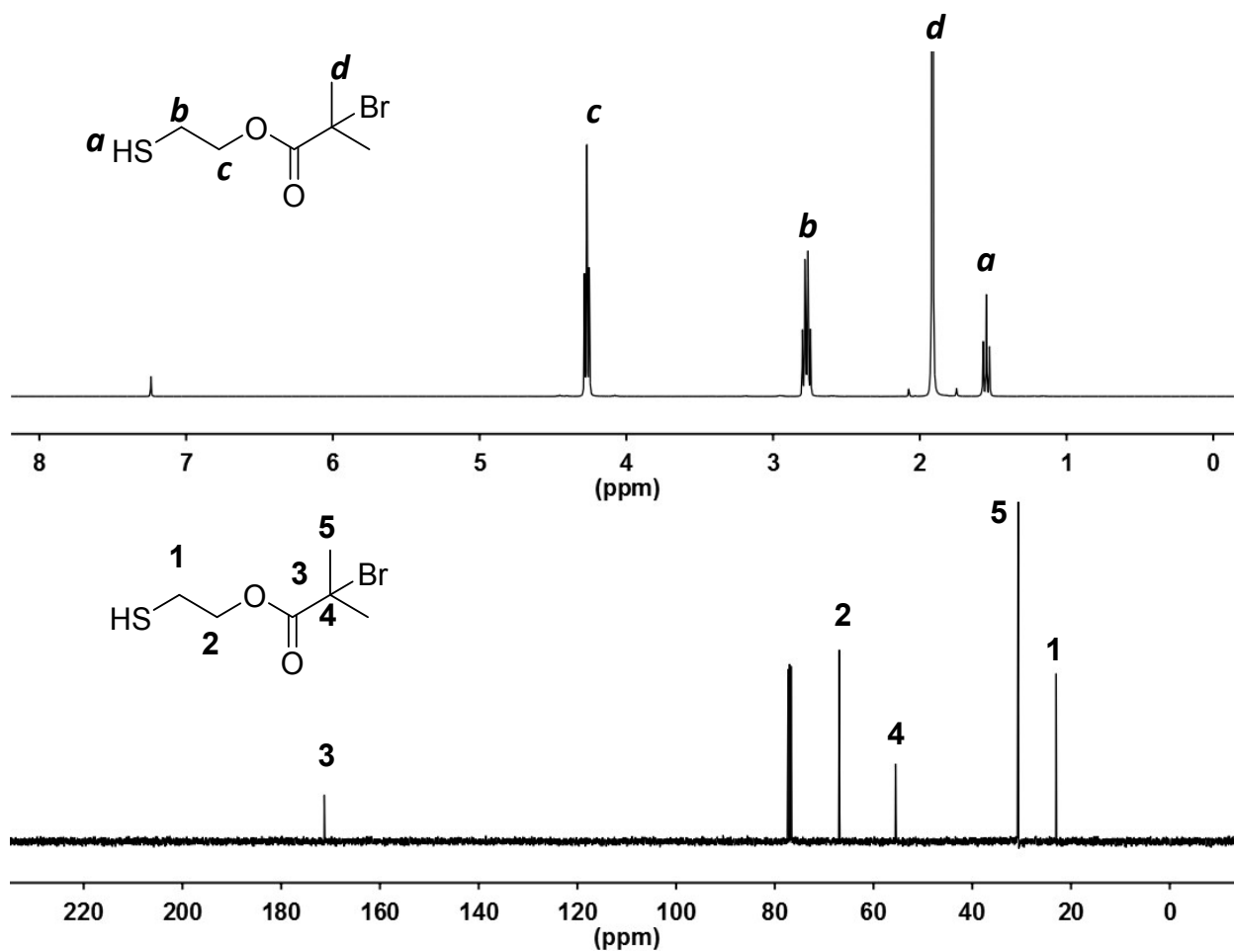




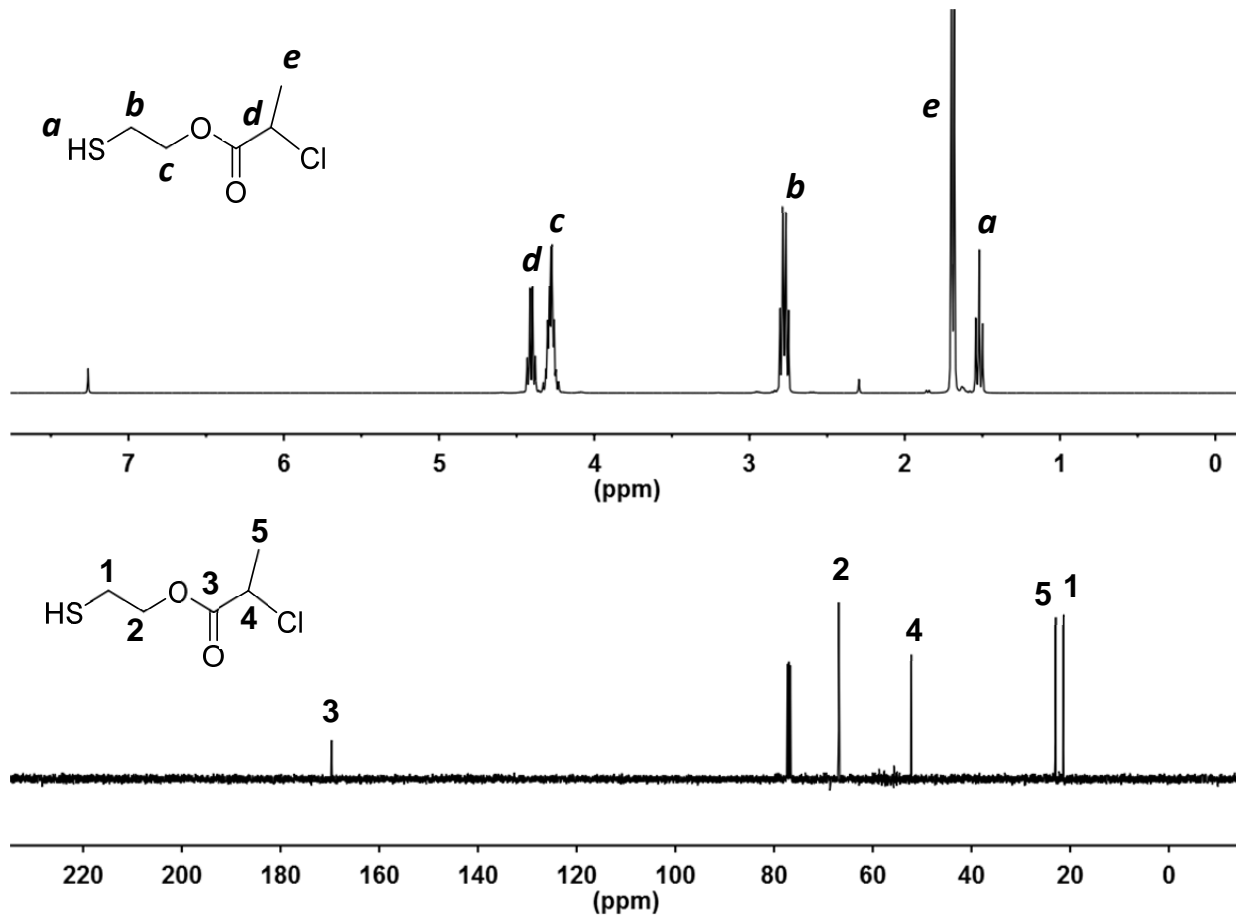
**Scheme S1.** Reductive debromination of 21Br-S-β-CD with tributyltin hydride.



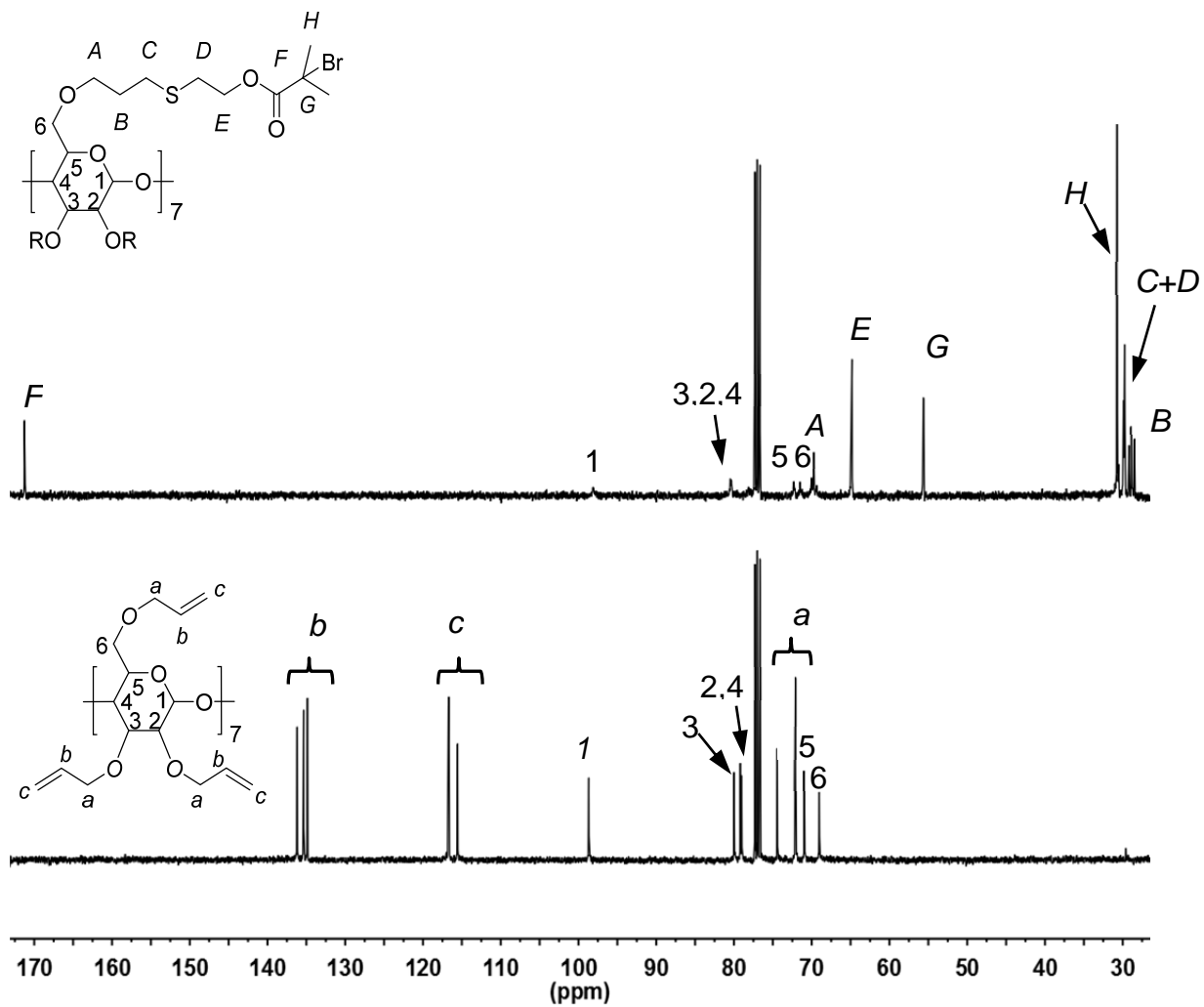
**Scheme S2.** The synthetic route of 21Cl-S-β-CD.



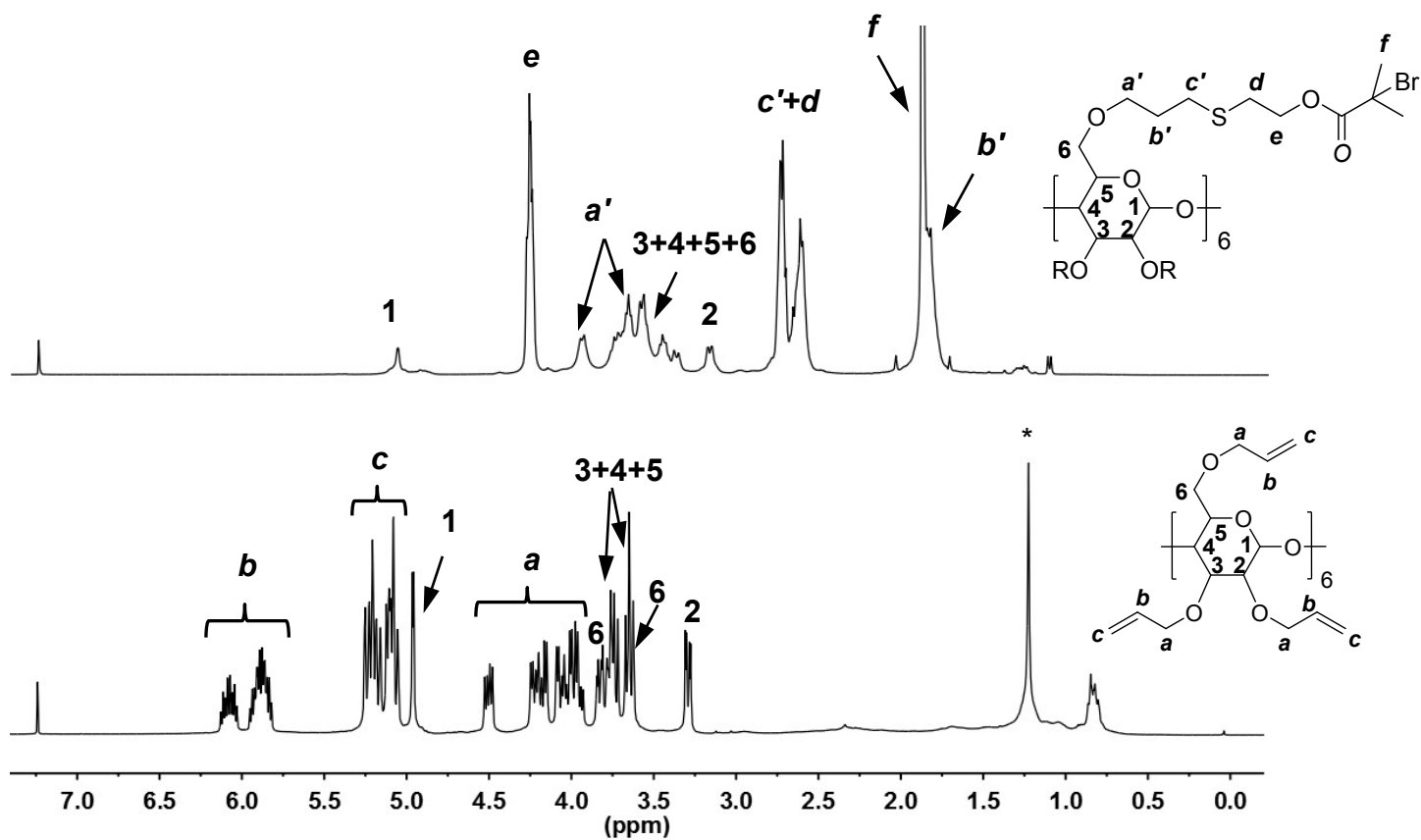
**Figure S1.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of HS-EBiB in CDCl<sub>3</sub>.



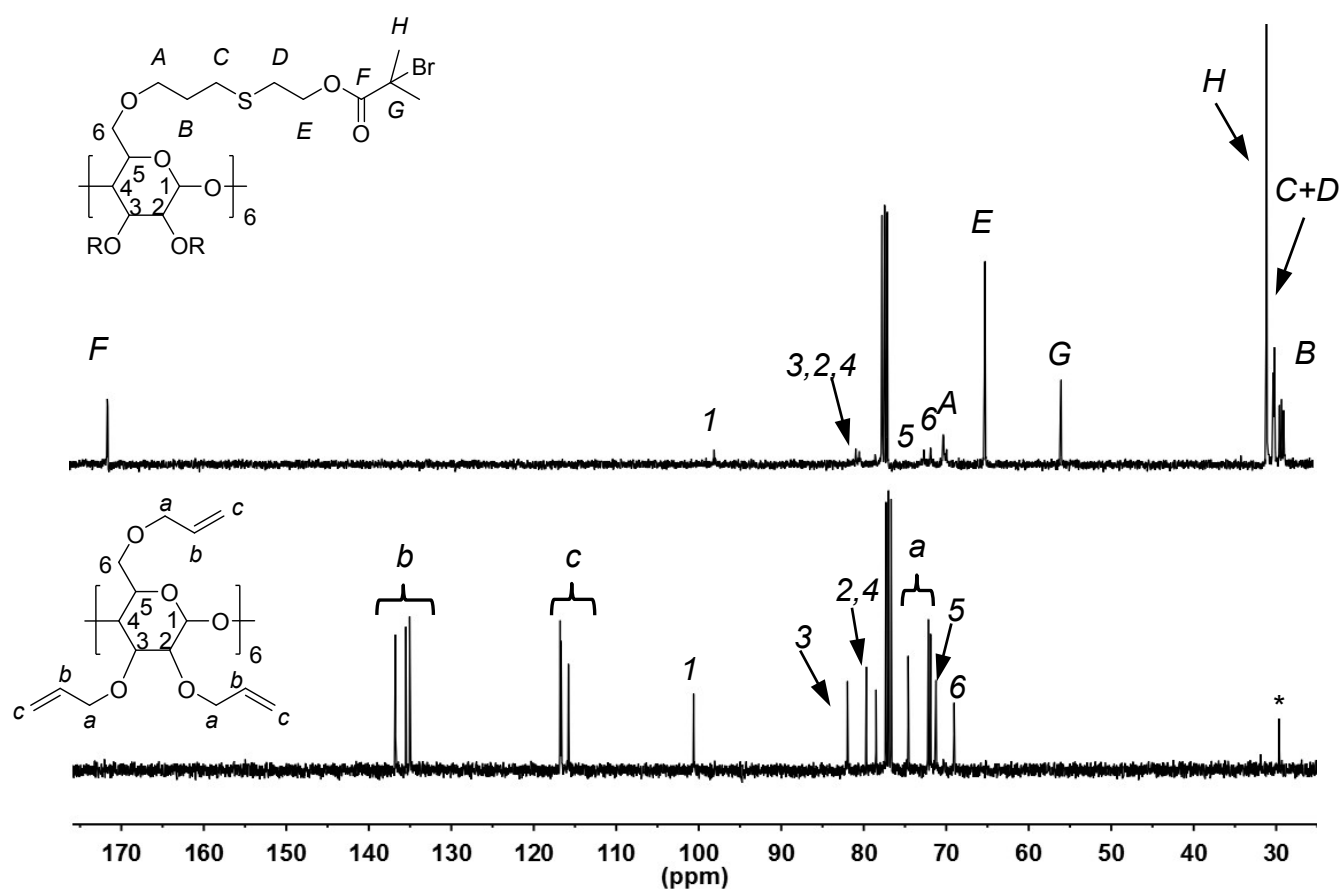
**Figure S2.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of HS-ECP in CDCl<sub>3</sub>.



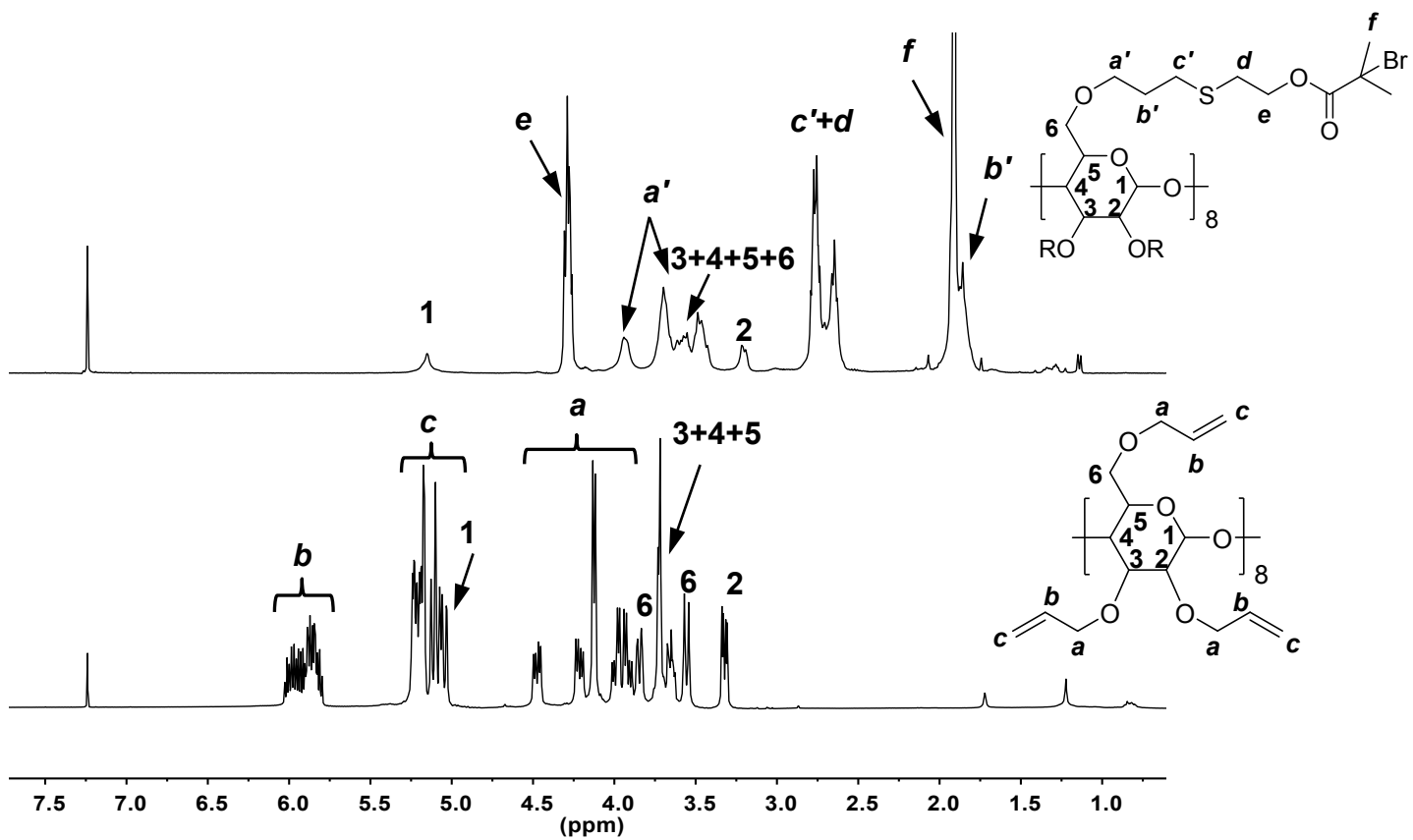
**Figure S3.**  $^{13}\text{C}$  NMR spectra of 21Br-S- $\beta$ -CD and allyl- $\beta$ -CD in  $\text{CDCl}_3$ .



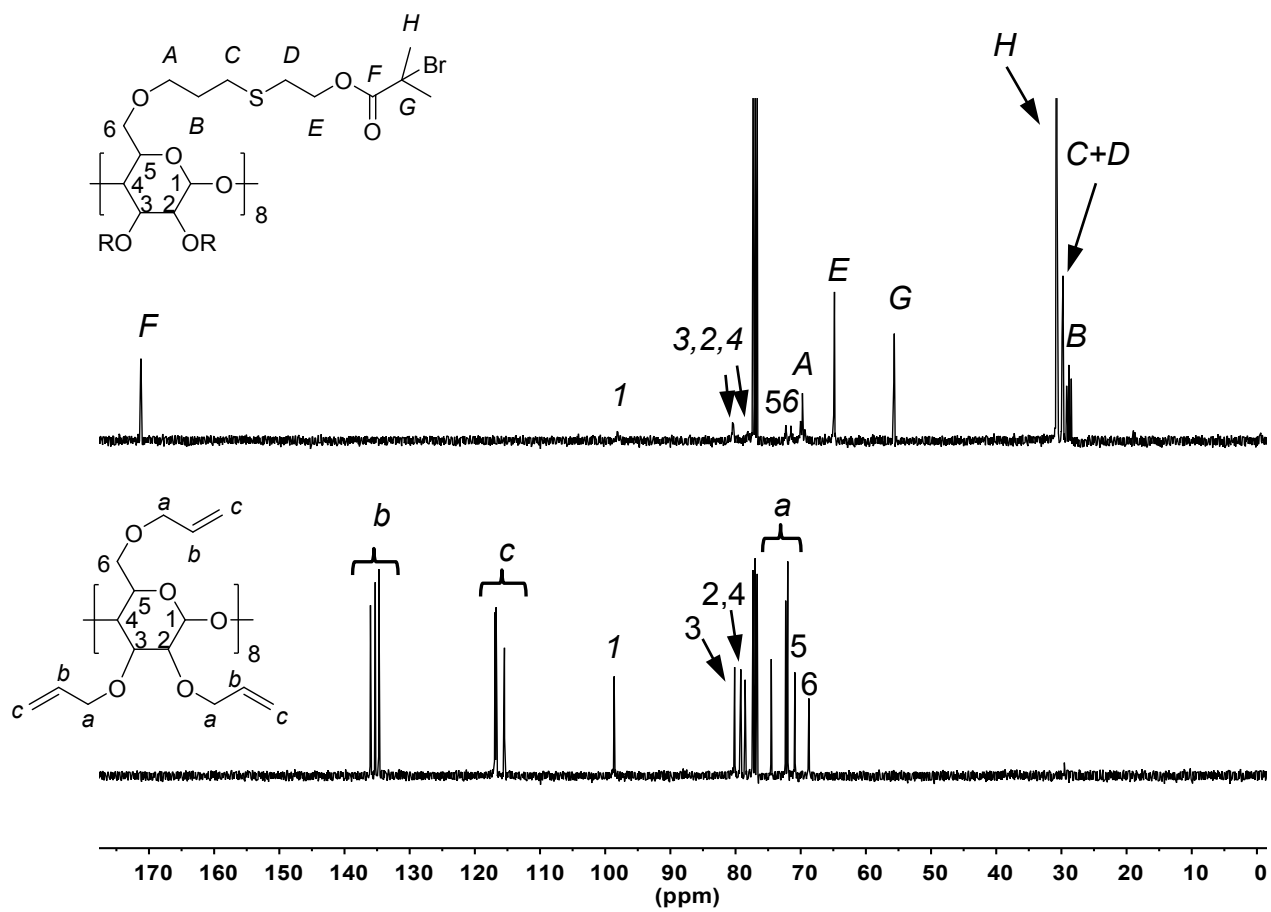
**Figure S4.** <sup>1</sup>H NMR spectra of 18Br-S- $\alpha$ -CD and allyl- $\alpha$ -CD in CDCl<sub>3</sub>.



**Figure S5.**  $^{13}\text{C}$  NMR spectra of 18Br-S- $\alpha$ -CD and allyl- $\alpha$ -CD in  $\text{CDCl}_3$ .

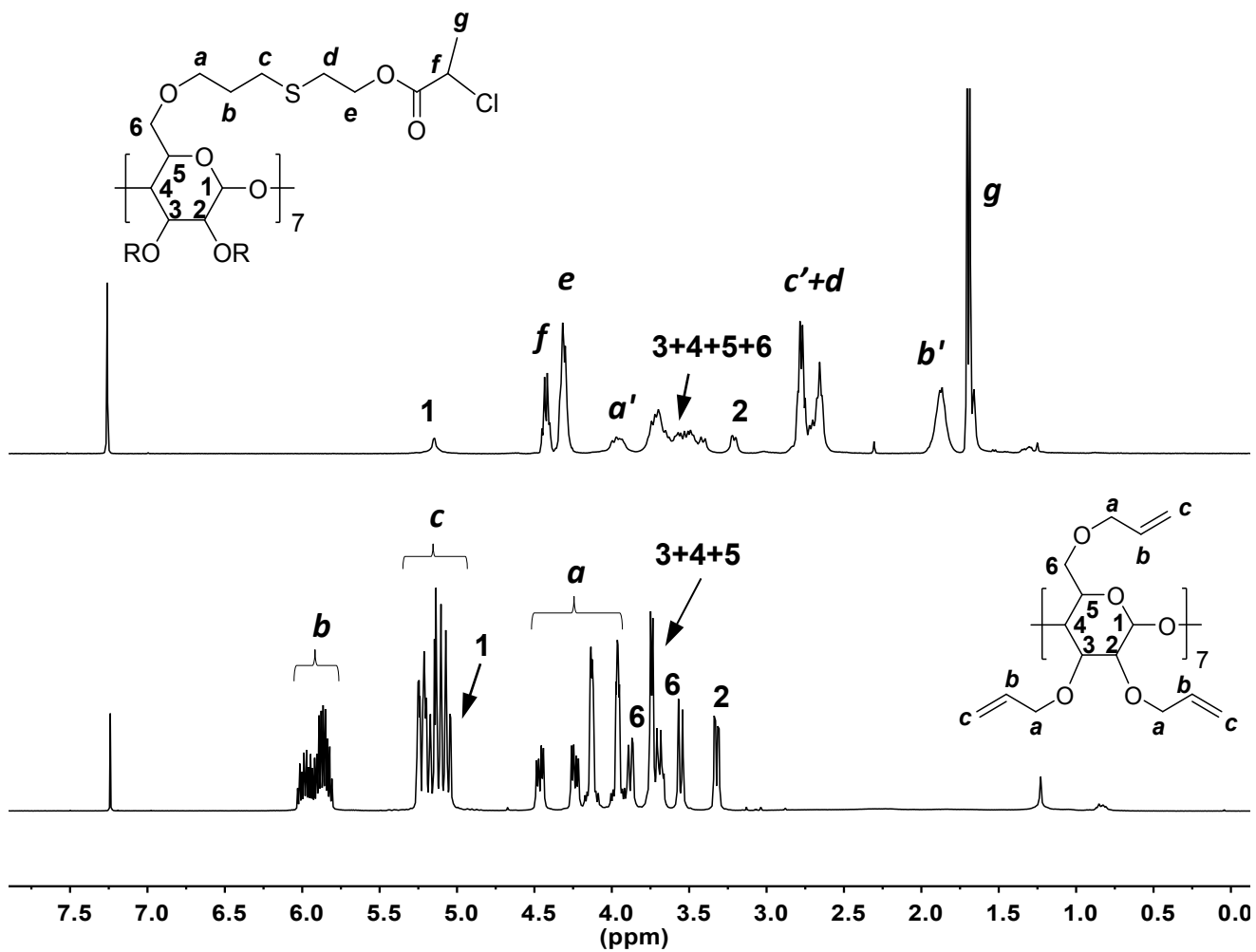


**Figure S6.**  $^1\text{H}$  NMR spectra of 24Br-S- $\gamma$ -CD and allyl- $\gamma$ -CD in  $\text{CDCl}_3$ .

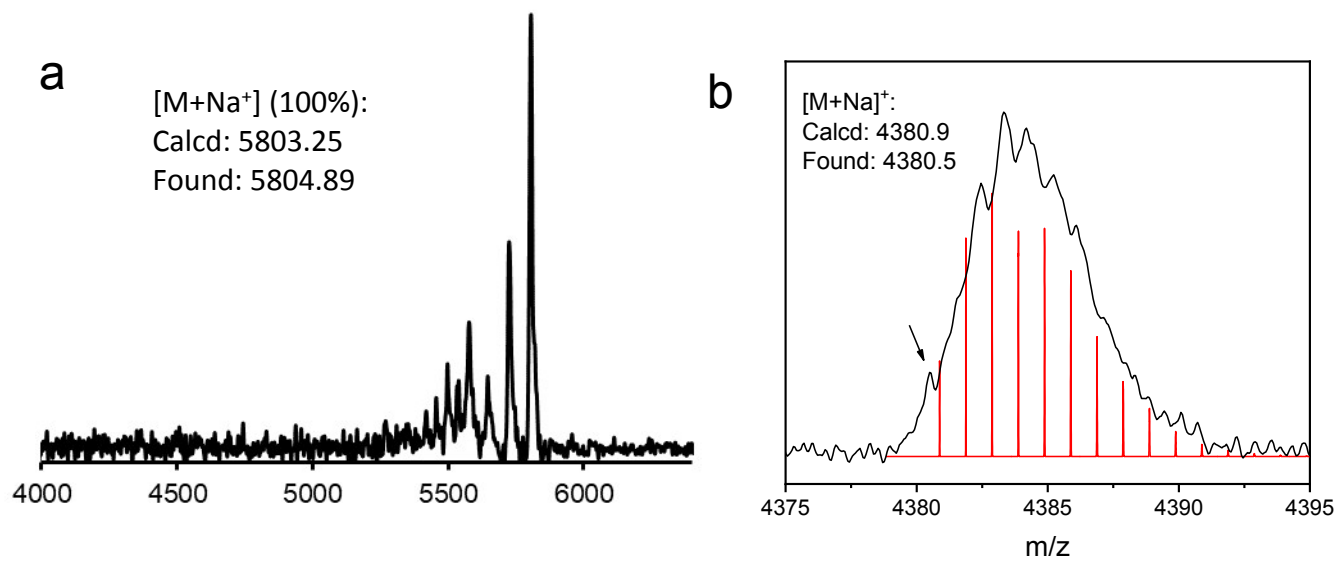


**Figure S7.**  $^{13}\text{C}$  NMR spectra of 24Br-S- $\gamma$ -CD and allyl- $\gamma$ -CD in  $\text{CDCl}_3$ .

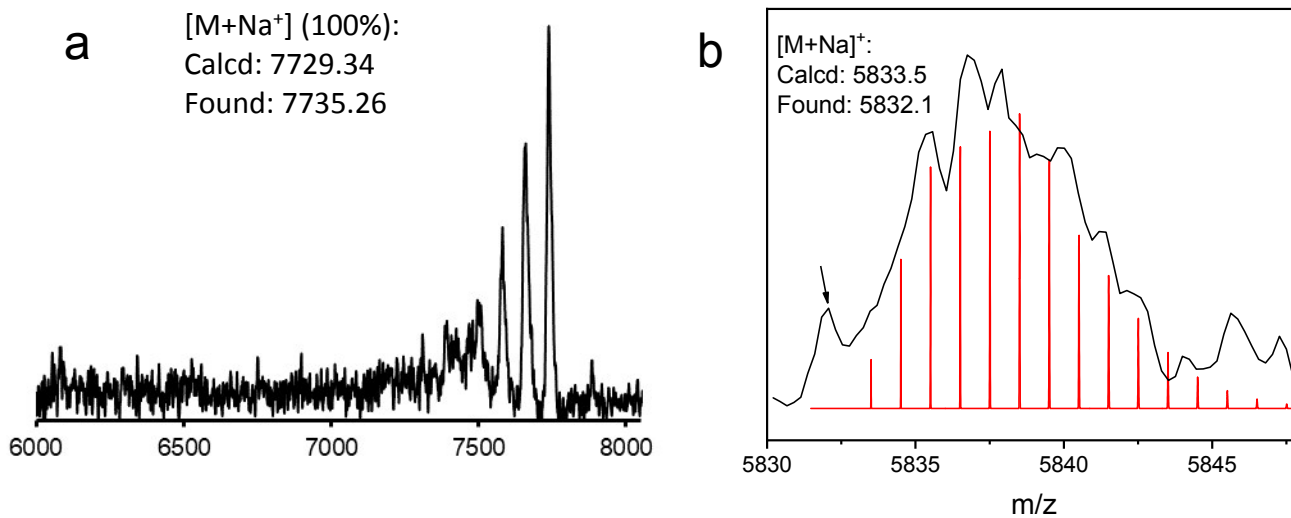




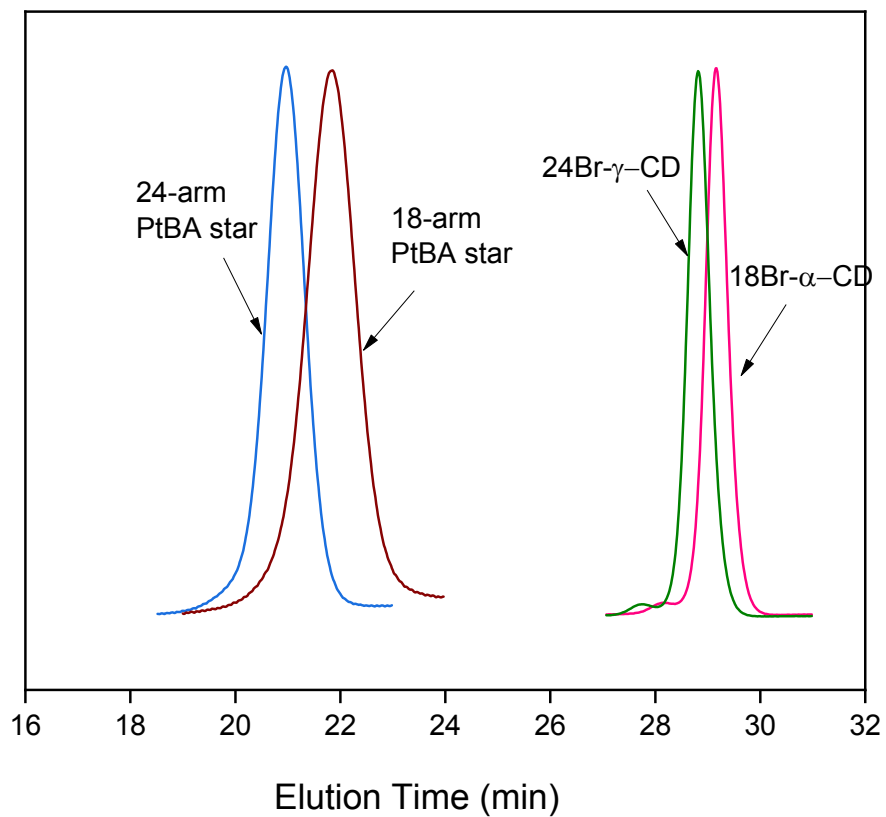
**Figure S8.**  $^1\text{H}$  NMR spectra of 21Cl-S- $\beta$ -CD and allyl- $\beta$ -CD in  $\text{CDCl}_3$ .



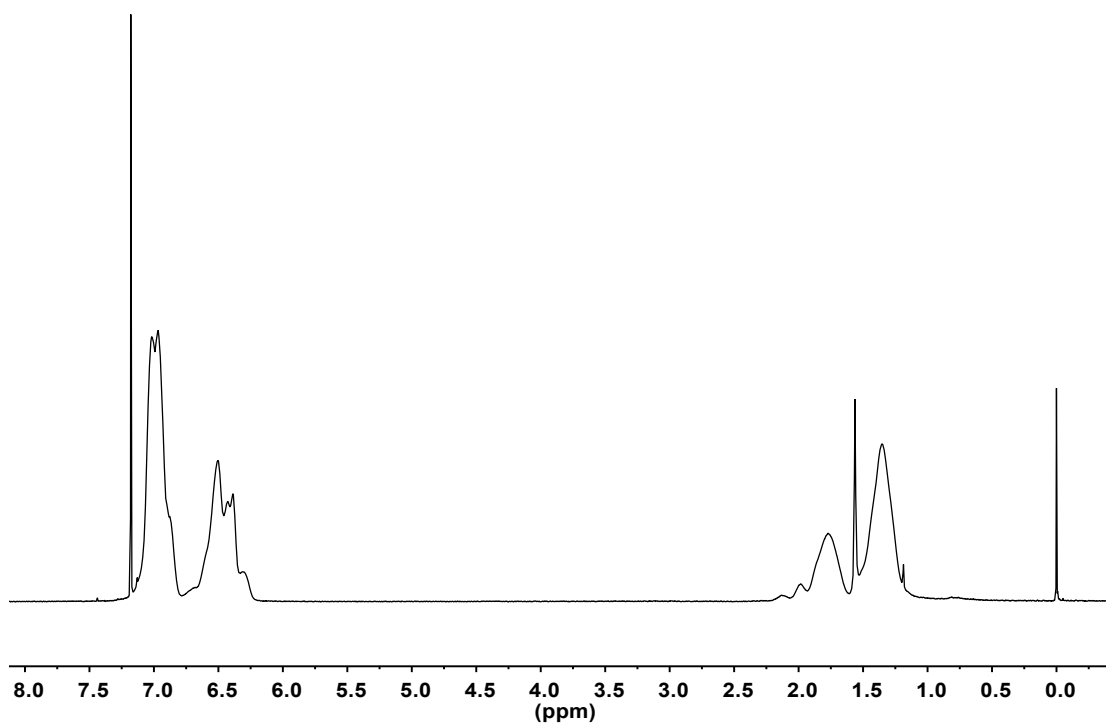
**Figure S9.** (a) MALDI-TOF mass spectrum of 18Br-S- $\alpha$ -CD and (b) the experimental (black) and theoretical (red) isotope distributions of debrominated 18Br-S- $\alpha$ -CD ([M+Na<sup>+</sup>], C<sub>198</sub>H<sub>348</sub>O<sub>66</sub>S<sub>18</sub>Na<sup>+</sup>).



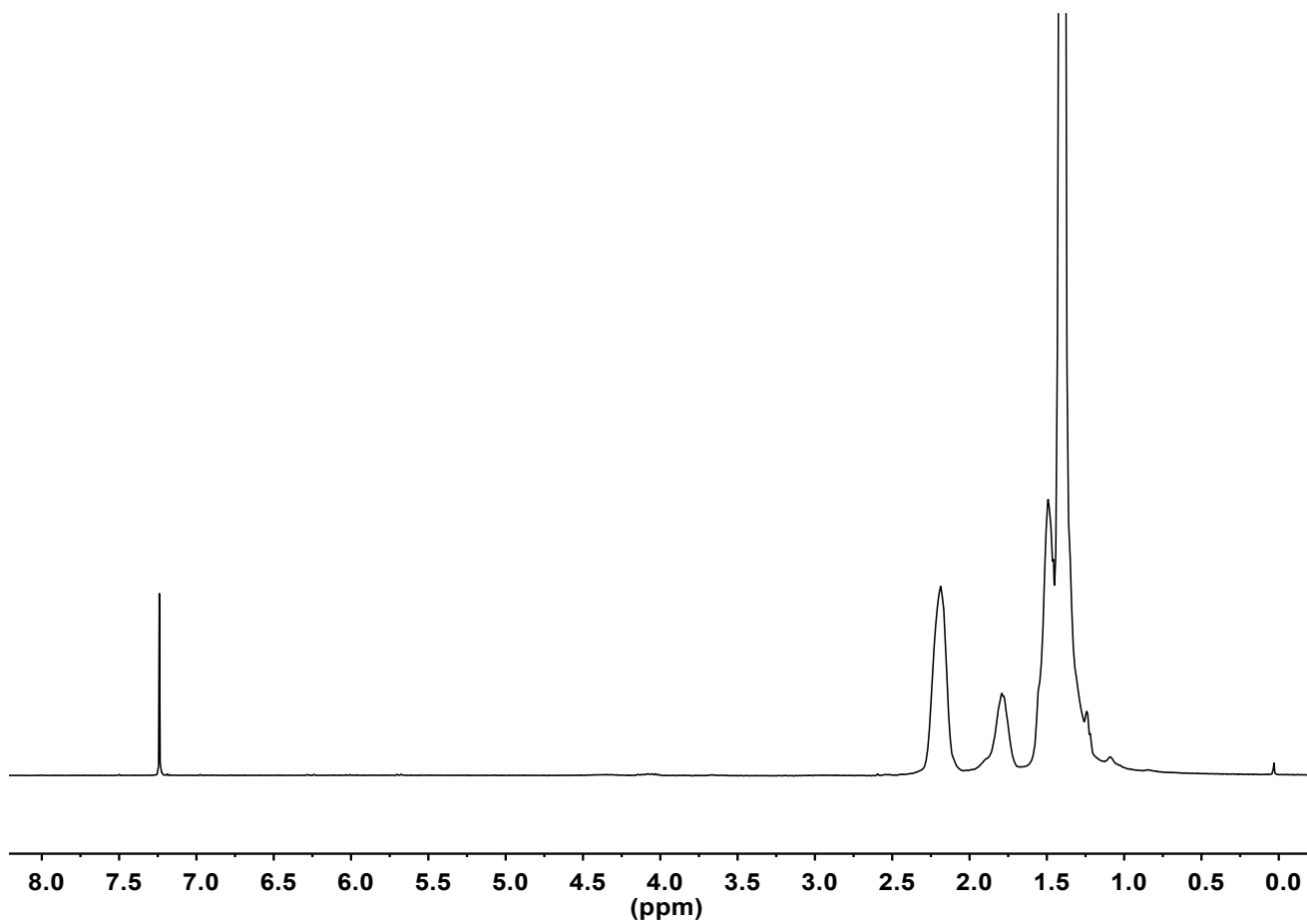
**Figure S10.** (a) MALDI-TOF mass spectrum of 24Br-S- $\gamma$ -CD and (b) the experimental (black) and theoretical (red) isotope distributions of debrominated 24Br-S- $\gamma$ -CD ([M+Na<sup>+</sup>], C<sub>264</sub>H<sub>464</sub>O<sub>88</sub>S<sub>24</sub>Na<sup>+</sup>).



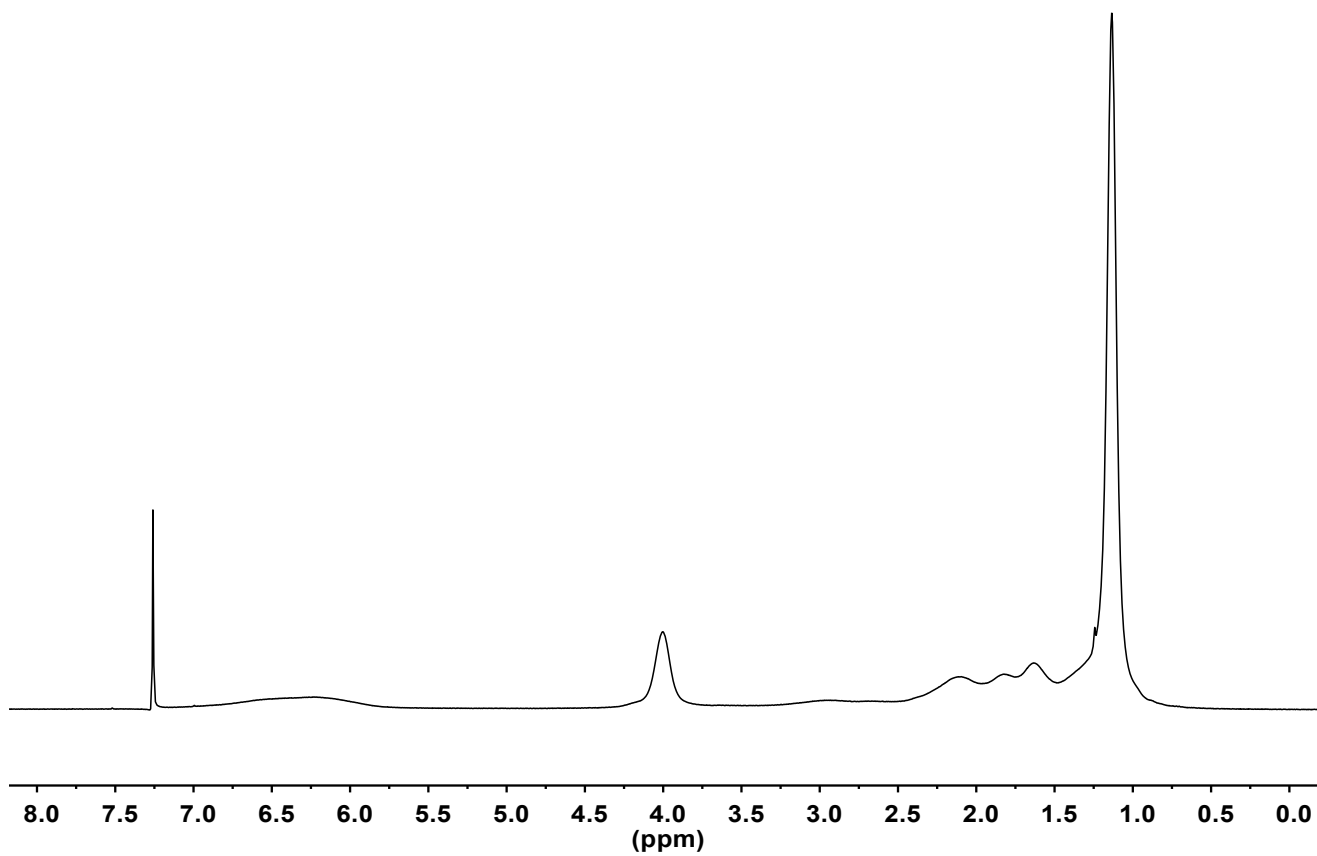
**Figure S11.** GPC traces of 18-arm PtBA ( $M_n=102300$  Da, PDI=1.05) and 24-arm PtBA ( $M_n=157200$  Da, PDI=1.06), together with 18Br-S- $\alpha$ -CD and 24Br-S- $\gamma$ -CD.



**Figure S12.** <sup>1</sup>H NMR spectrum of 21-arm polystyrene star in CDCl<sub>3</sub>.



**Figure S13.** <sup>1</sup>H NMR spectrum of 21-arm poly(tert-butyl acrylate) star in CDCl<sub>3</sub>.



**Figure S14.**  $^1\text{H}$  NMR spectrum of 21-arm poly(N-isopropyl acrylamide) star in  $\text{CDCl}_3$ .