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Supplementary information

Synthesis of cyclodextrin derivatives for enantiodifferentiating photocyclodimerization of 2-anthracenecarboxylate

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SUPPLEMENTARY INFORMATION

Synthesis of Cyclodextrin Derivatives to Control the Stereochemistry of Enantiodifferentiating Photocyclodimerization of 2-Anthracenecarboxylate Taking Place inside Their Cavities

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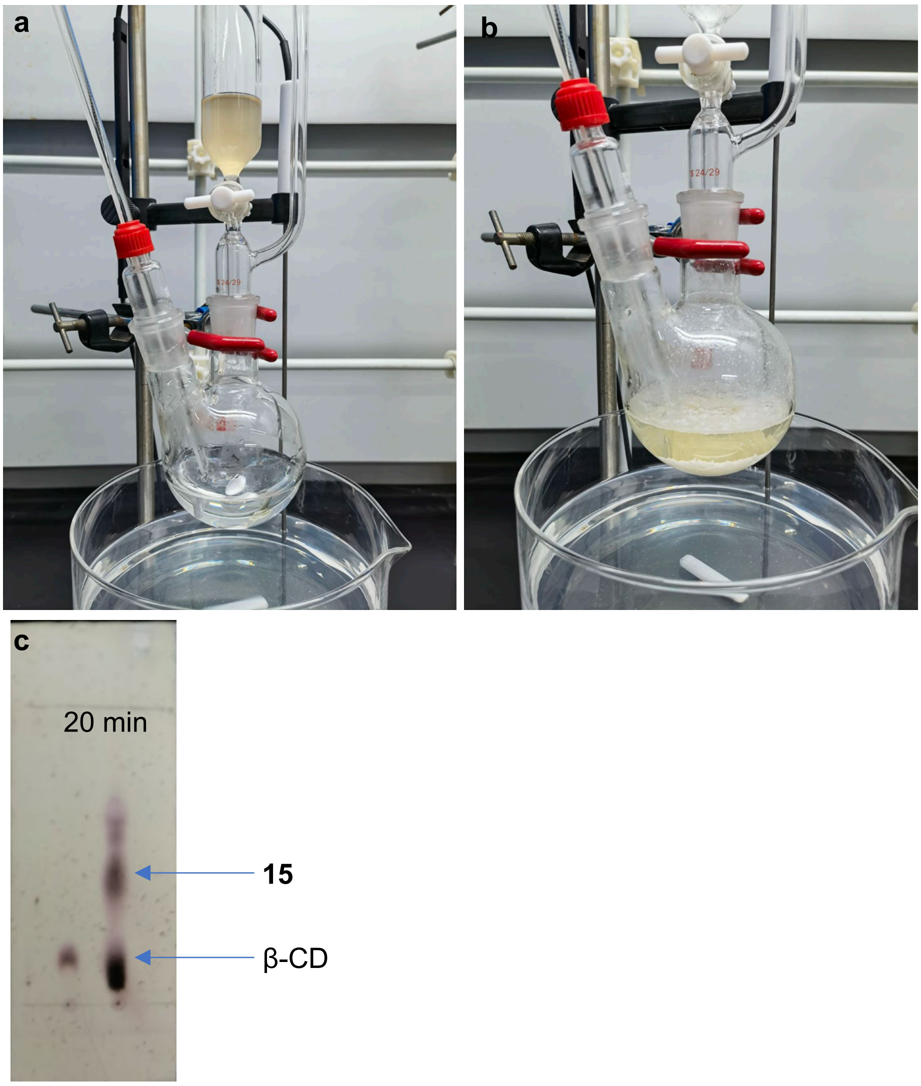
Synthesis of NS-β-CD 15

β-CD (7.0 g, 6.2 mmol) and NaOH (740.0 mg, 18.5 mmol) were mixed in water (70 mL) and the solution was stirred at 40 ºC for 10 min, and then added 20 mL 2-naphthalenesulfonyl chloride (7.0 g, 30.9 mmol) of acetonitrile solution over 5 min and stirred the reaction mixture for additional 15 min. The reaction mixture was cooled down and then filtered, and the filtrate was concentrated with a rotary evaporator under vacuum until yellowish precipitation appeared. The yellowish precipitation was removed by filtration. The filtered solution was applied to a reversed-phase column with a gradient elution from water to 30% aqueous EtOH to give **15** as a yellowish solid.



Supplementary Figure 1. Glassware setup for the synthesis of of NS-*β*-CD **15**. **a**,**b**, Photographs of the initial (**a**) and end (**b**) state of the reaction mixture of *β*-CD and 2-naphthalenesulfonyl chloride. **c**, Sulfonylation progress for *β*-CD as monitored by TLC (7:7:5 EtOAc/isopropanol/H_2O).

NS-*β*-CD 15.

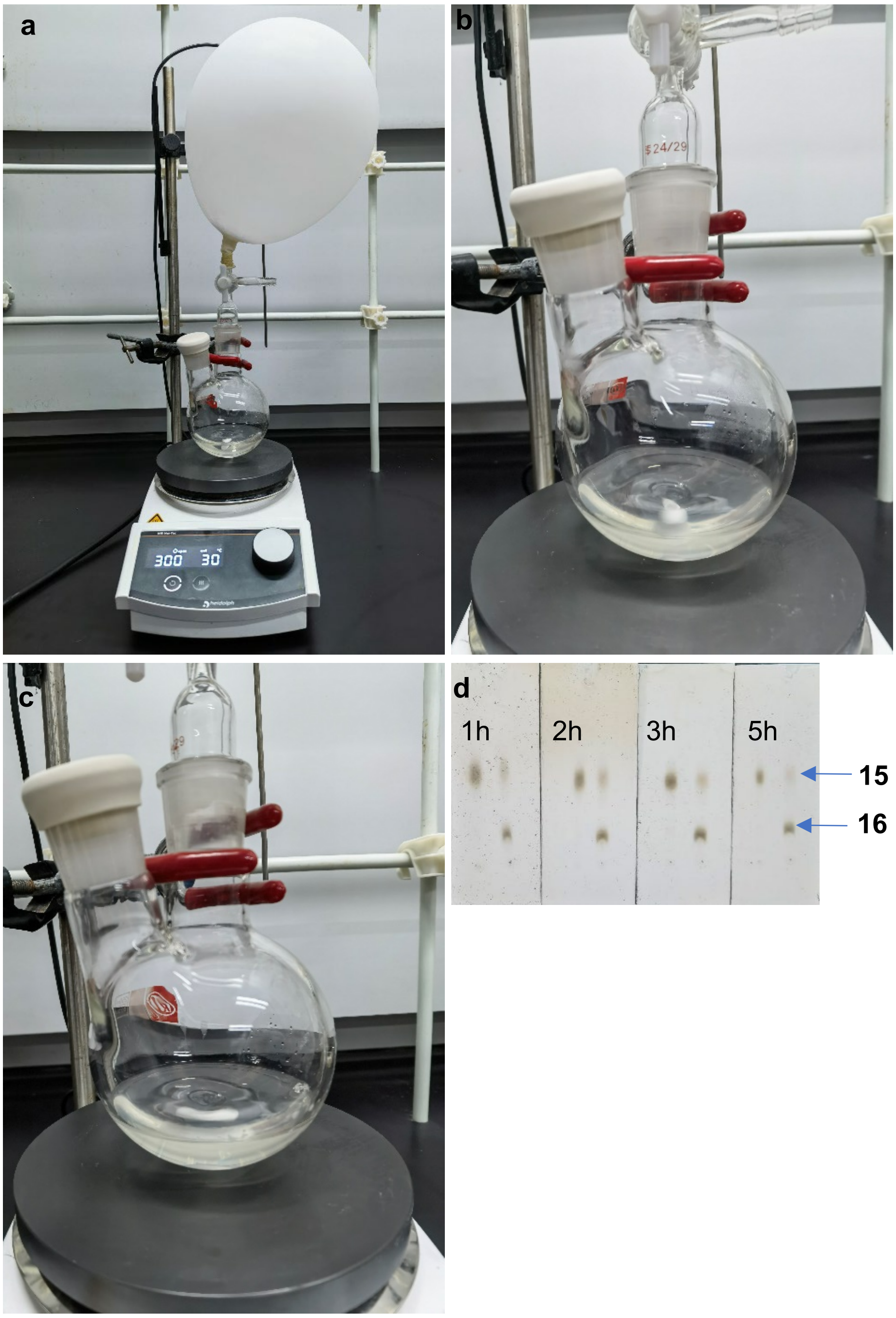
^{1}H NMR (400 MHz, DMSO-d_6:D_2O = 1:1, v/v) δ 8.51 (s, 1H), 8.07 (t, *J* = 8.9 Hz, 2H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.89 – 7.84(m, 1H), 7.74 – 7.61 (m, 2H), 4.92 – 4.80 (m, 7H), 4.00 (d, *J* = 10.6 Hz, 1H), 3.91 – 3.22 (m, 41H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 134.89, 133.87, 131.55, 129.63, 129.57, 129.47, 129.22, 127.93, 127.82, 124.14, 123.03, 102.31, 102.25, 102.00, 101.92, 101.76, 100.57, 84.43, 82.70, 82.65, 82.01, 81.98, 81.54, 81.41, 81.30, 76.63, 73.20, 73.09, 73.04, 72.61, 72.55, 72.46, 72.25, 72.12, 72.00, 70.34, 60.59, 60.53, 60.12, 59.97.

HR-MS (ESI) *m/z* calcd. for $C_{52}H_{76}NaO_{37}S$ $[M+Na]^+$: 1,347.3679, found: 1,347.3768.

Synthesis of NS-β-CD 16

NS-*β*-CD **15** (3.6 g, 2.7 mmol) and K_2CO_3 (0.9 g, 6.5 mmol) were mixed in water (360 mL) and the solution was stirred at 25 °C for 4.5 h. Then the pH of the reaction mixture was adjusted to 7 with dilute HCl and the resulting solution was concentrated to 100 mL with a rotary evaporator. The concentrated solution was filtered and then applied to a reversed-phase column with a gradient elution from water to 5% aqueous EtOH to give **16** as a white solid.



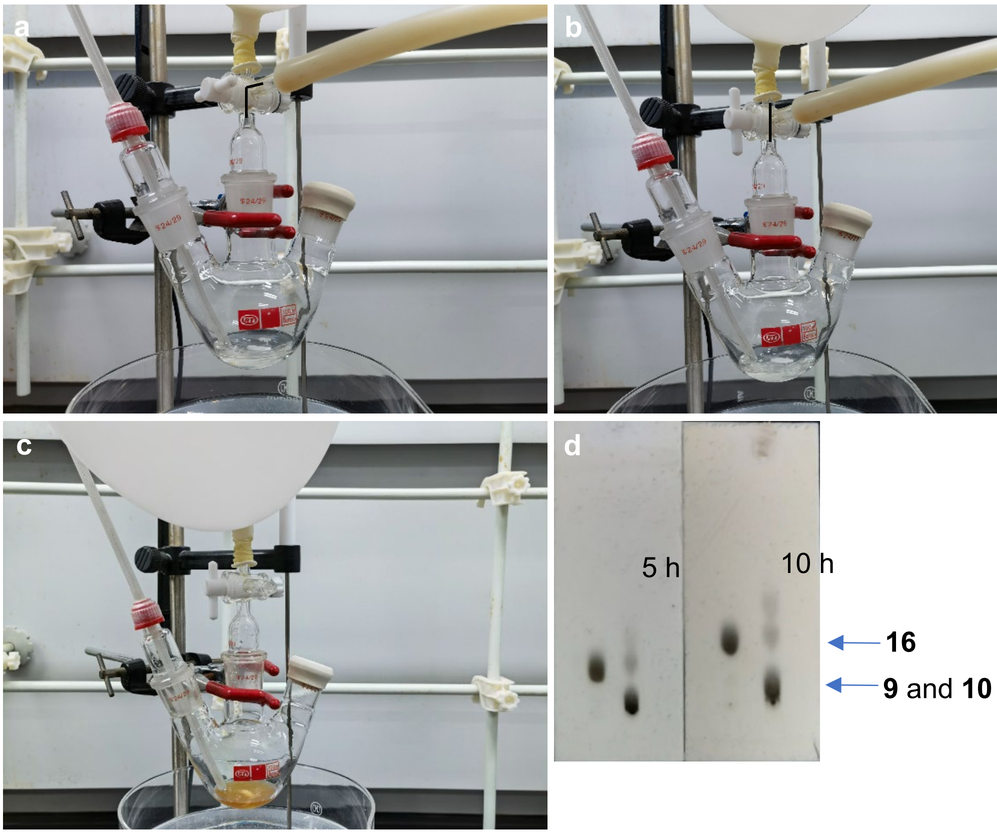
Supplementary Figure 2. Glassware setup for the synthesis of of 2^{A},3^{A}-alloepoxy-*β*-CD **16**. **a-c**, Photographs of the state of NS-*β*-CD **15** stirred in an aqueous K_2CO_3 solution at 0 min (**a**), 10 min (**b**) and 5 h (**c**). **d**, Epoxidation progress for NS-*β*-CD **15** as monitored by TLC (7:7:5 EtOAc/isopropanol/H_2O).

2^A,3^A-Alloepoxy-*β*-CD 16.

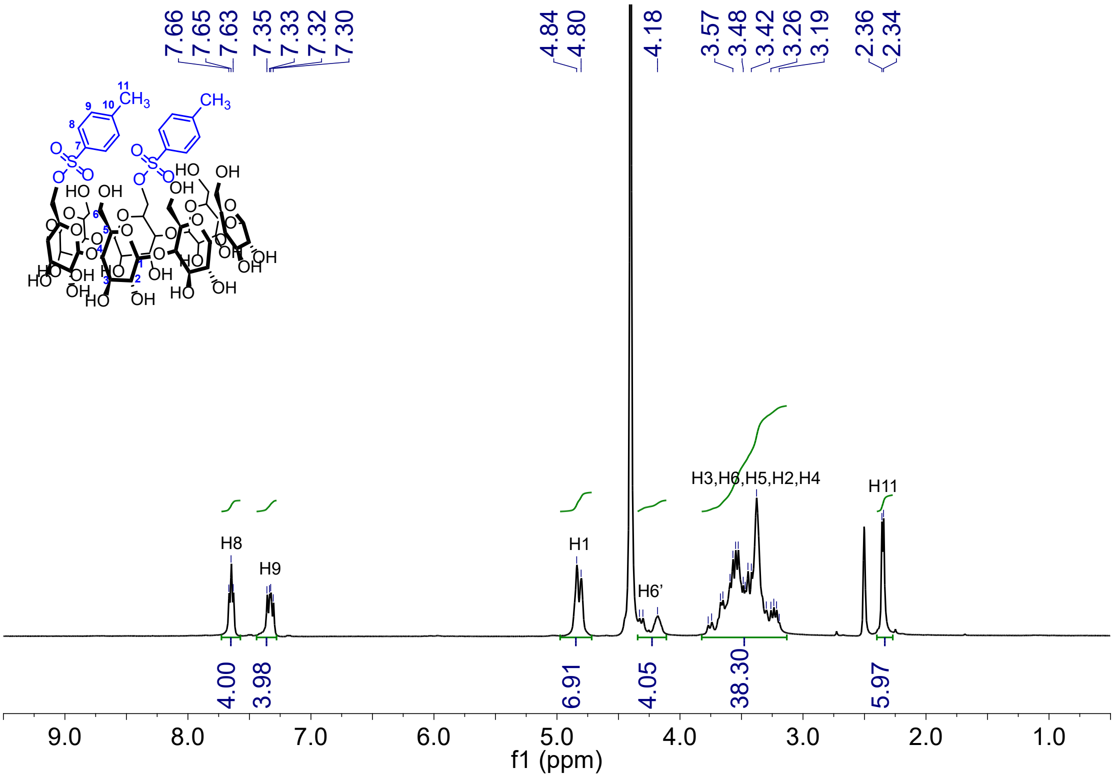
^{1}H NMR (400 MHz, DMSO-d_6:D_2O = 1:1, v/v) δ 5.05 (d, J = 3.3 Hz, 1H), 4.87 – 4.69 (m, 6H), 3.85-3.78 (m, 1H), 3.67 (d, J = 9.4 Hz, 1H), 3.64 – 3.21 (m, 40H).

^{13}C NMR (101 MHz, DMSO-d_6) δ103.44, 103.10, 102.58, 96.70, 82.83, 82.37, 81.89, 80.28, 76.08, 75.12, 74.53, 74.37, 74.00, 73.66, 73.43, 73.34, 73.18, 72.97, 72.18, 70.37, 61.69, 61.41, 57.24, 54.86.

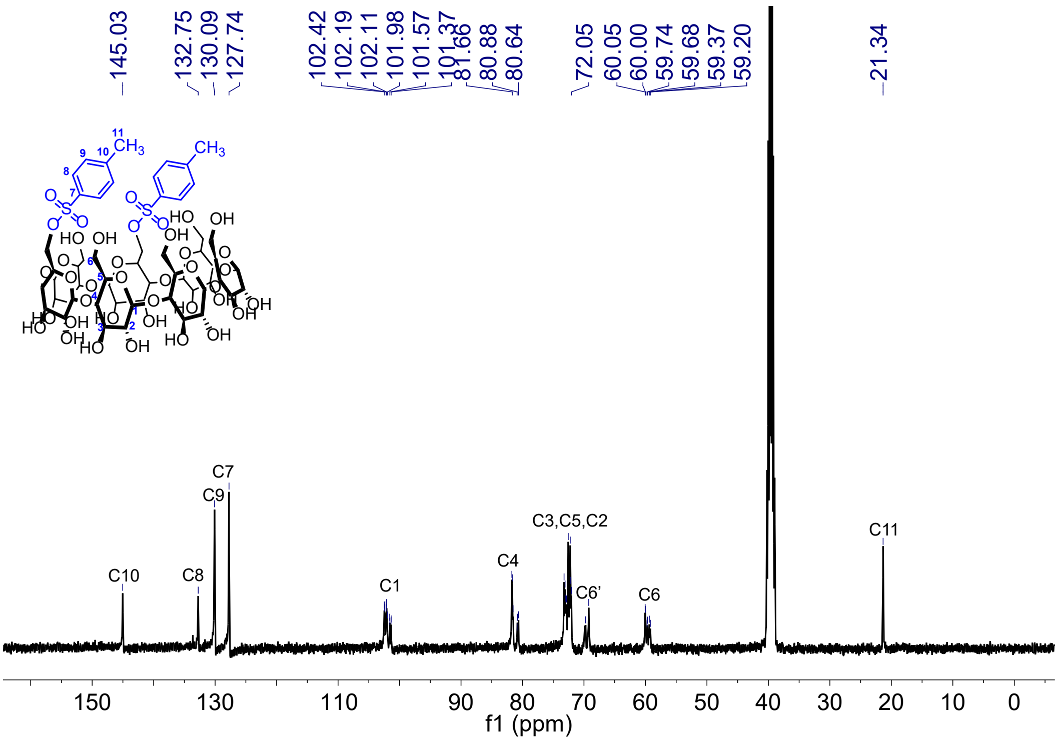
HR-MS (ESI) *m/z* calcd. for $C_{42}H_{68}NaO_{34}$ [M+Na]$^+$: 1,139.3485, found: 1,139.3501.



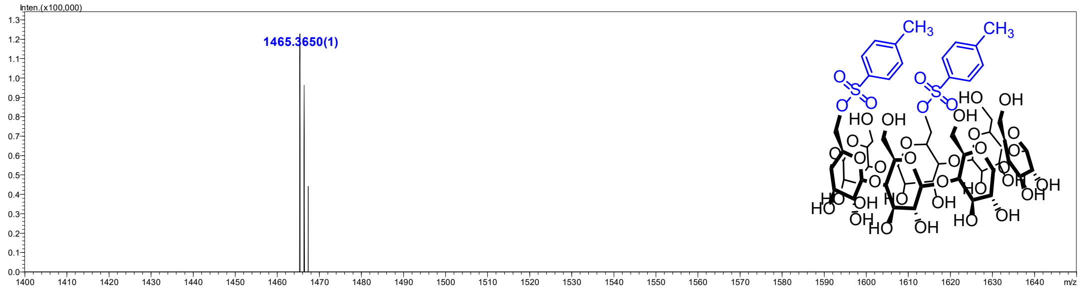
Supplementary Figure 3. Glassware setup for the synthesis of **9** and **10**. **a-c**, Photographs of the initial (**a**,**b**) and end (**c**) state of the reaction mixture of $2^A,3^A$-alloepoxy-*β*-CD and $Na_2S•9H_2O$. **d**, Reaction progress for the synthesis of **9** and **10** as monitored by TLC (7:7:5 EtOAc/isopropanol/H_2O).



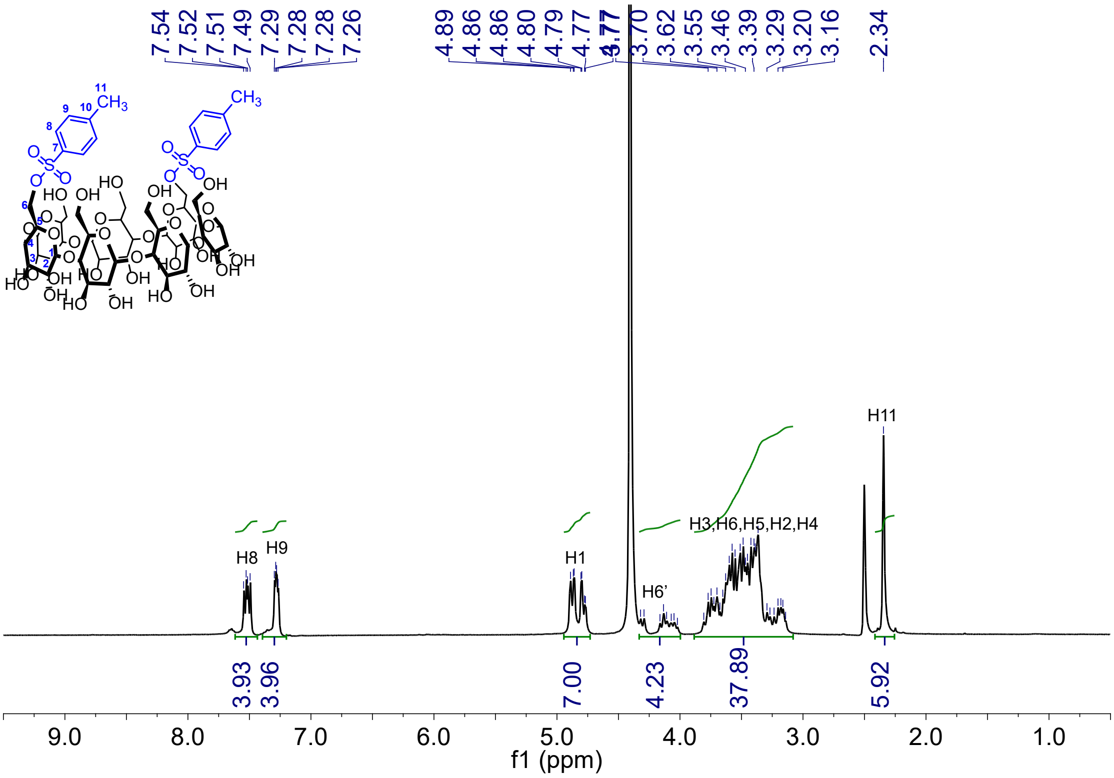
Supplementary Figure 4. ^{1}H NMR spectrum of 6^{A},6^{C}-di-*O*-tosyl-*β*-CD **11** (400 MHz, DMSO-d_6:D_2O = 1:1, v/v, 298 K).



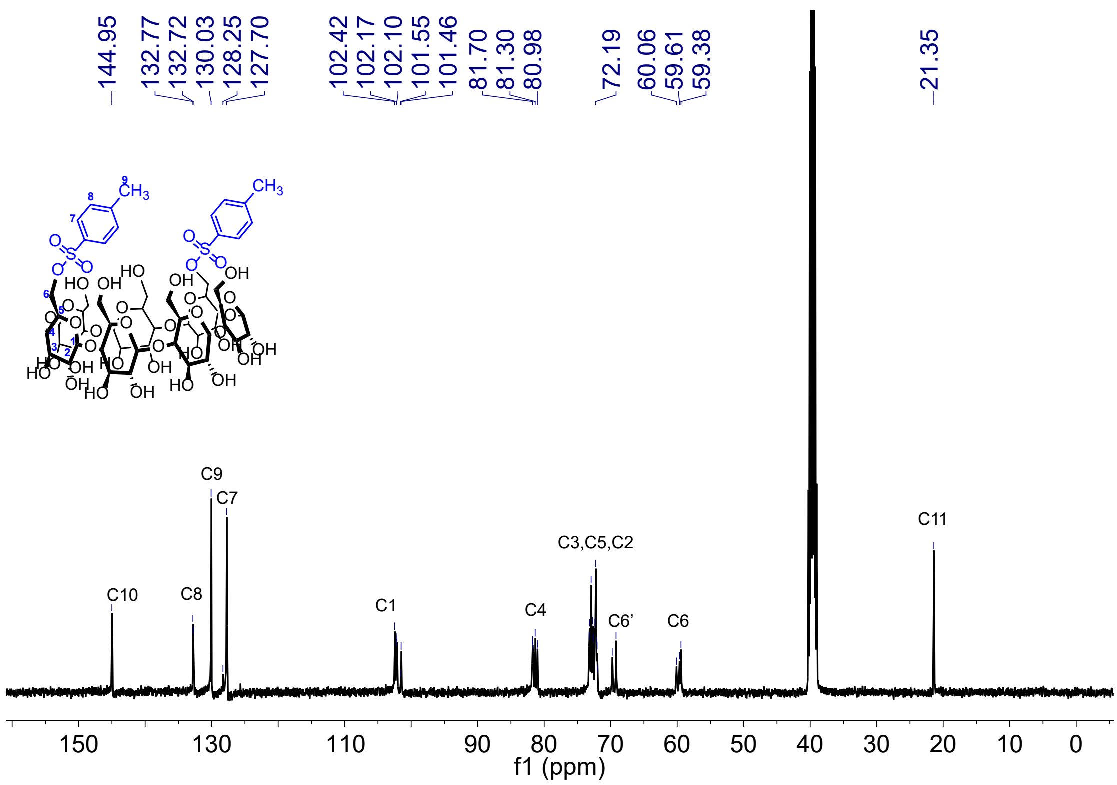
Supplementary Figure 5. ^{13}C NMR spectrum of 6^{A},6^{C}-di-*O*-tosyl-*β*-CD **11** (101 MHz, DMSO-d_6, 298 K).



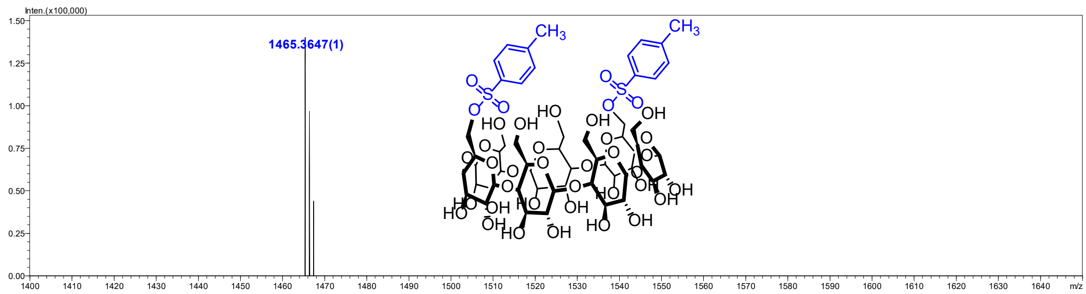
Supplementary Figure 6. HR-MS (ESI) spectrum of $6^{A},6^{C}$-di-*O*-tosyl-*β*-CD **11**.



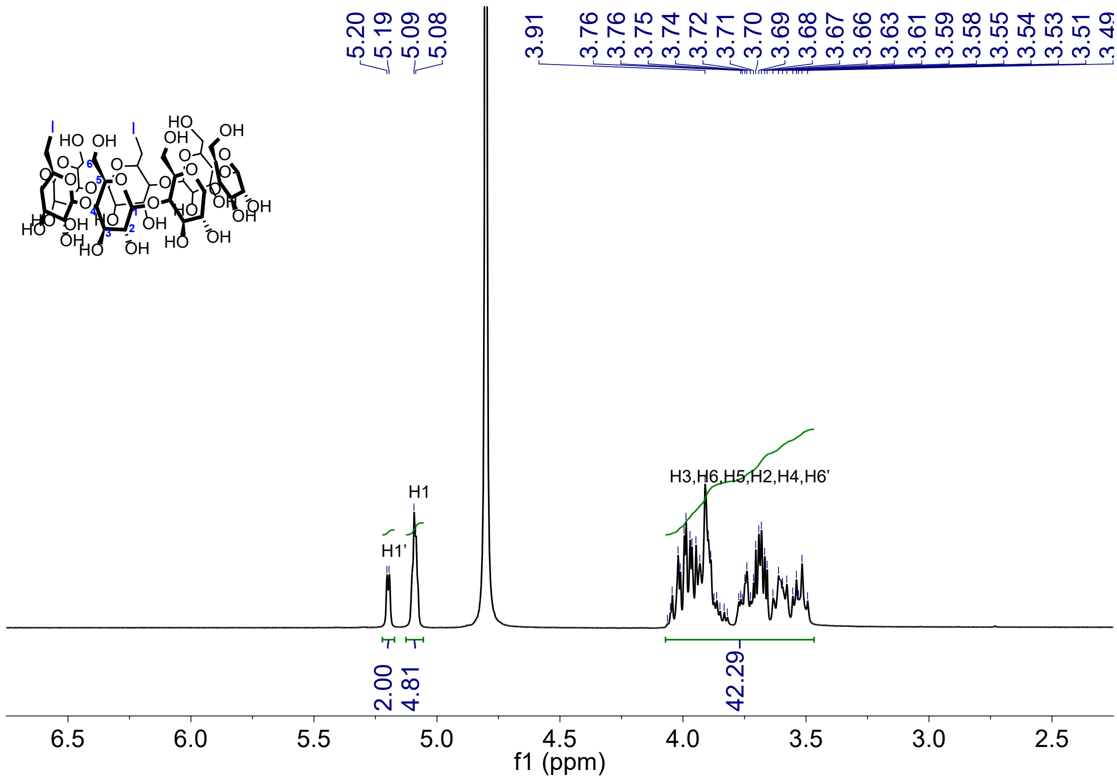
Supplementary Figure 7. ^{1}H NMR spectrum of $6^{A},6^{D}$-di-*O*-tosyl-*β*-CD **12** (400 MHz, DMSO-d_6: D_2O = 1:1, v/v, 298 K).



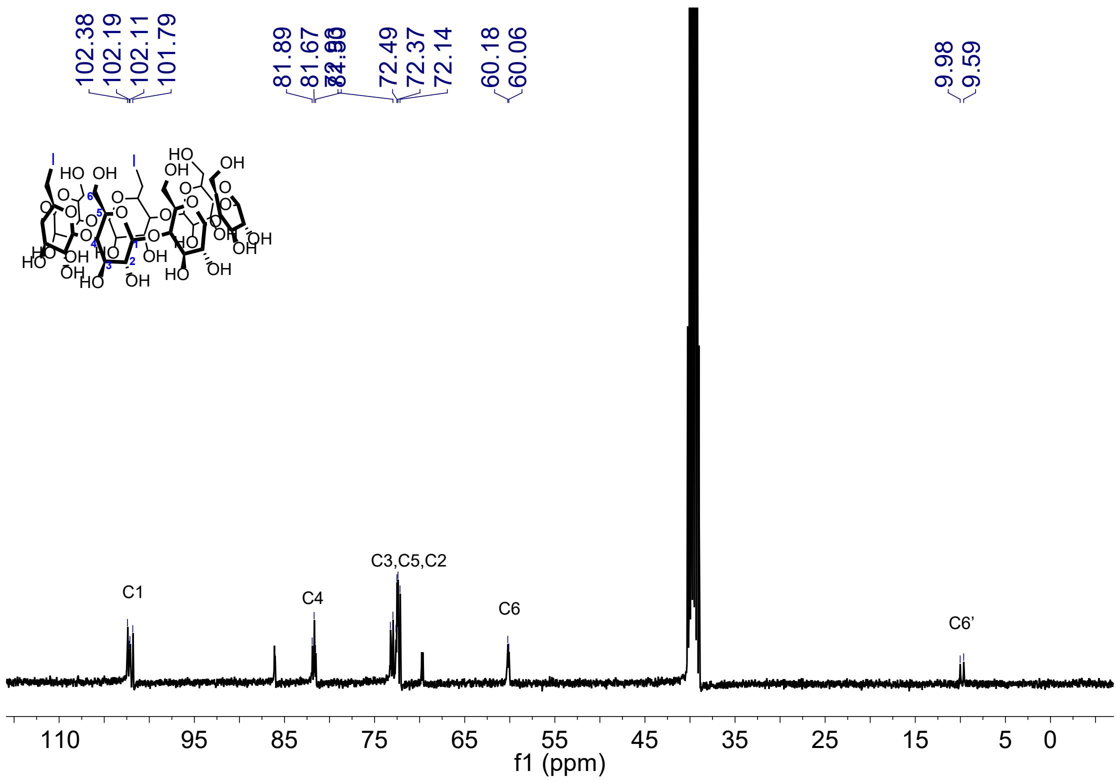
Supplementary Figure 8. ^{13}C NMR spectrum of 6^{A},6^{D}-di-*O*-tosyl-*β*-CD **12** (101 MHz, DMSO-d_6, 298 K).



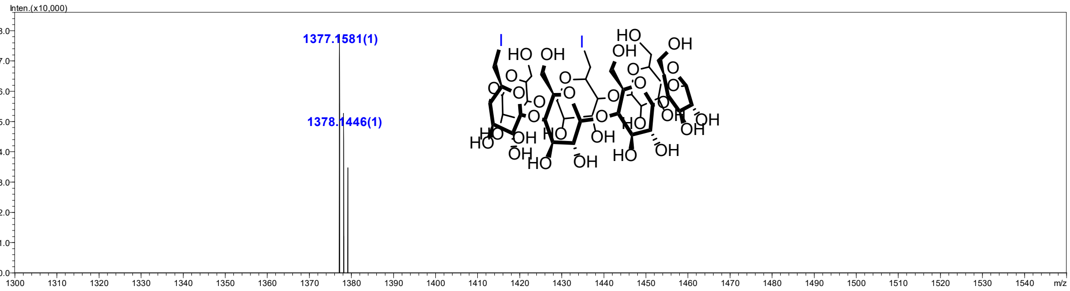
Supplementary Figure 9. HR-MS (ESI) spectrum of 6^{A},6^{D}-di-*O*-tosyl-*β*-CD **12**.



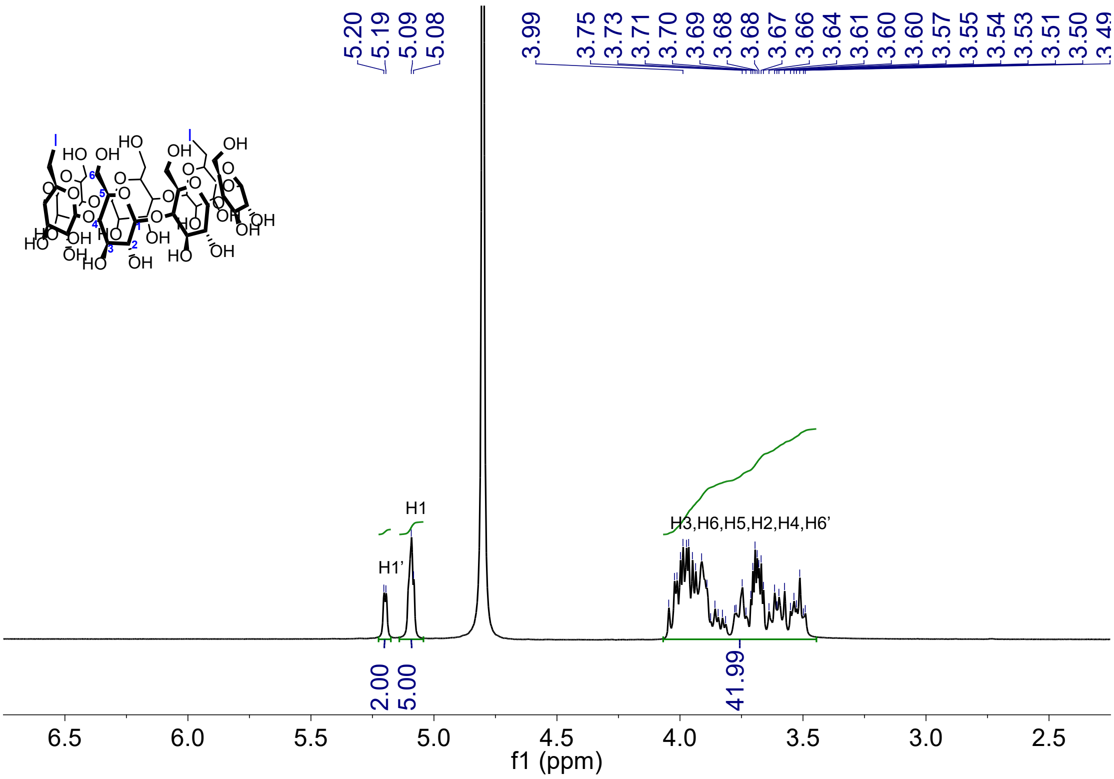
Supplementary Figure 10. ^{1}H NMR spectrum of $6^{A},6^{C}$-diiodo-*β*-CD **13** (400 MHz, D_2O, 298 K).



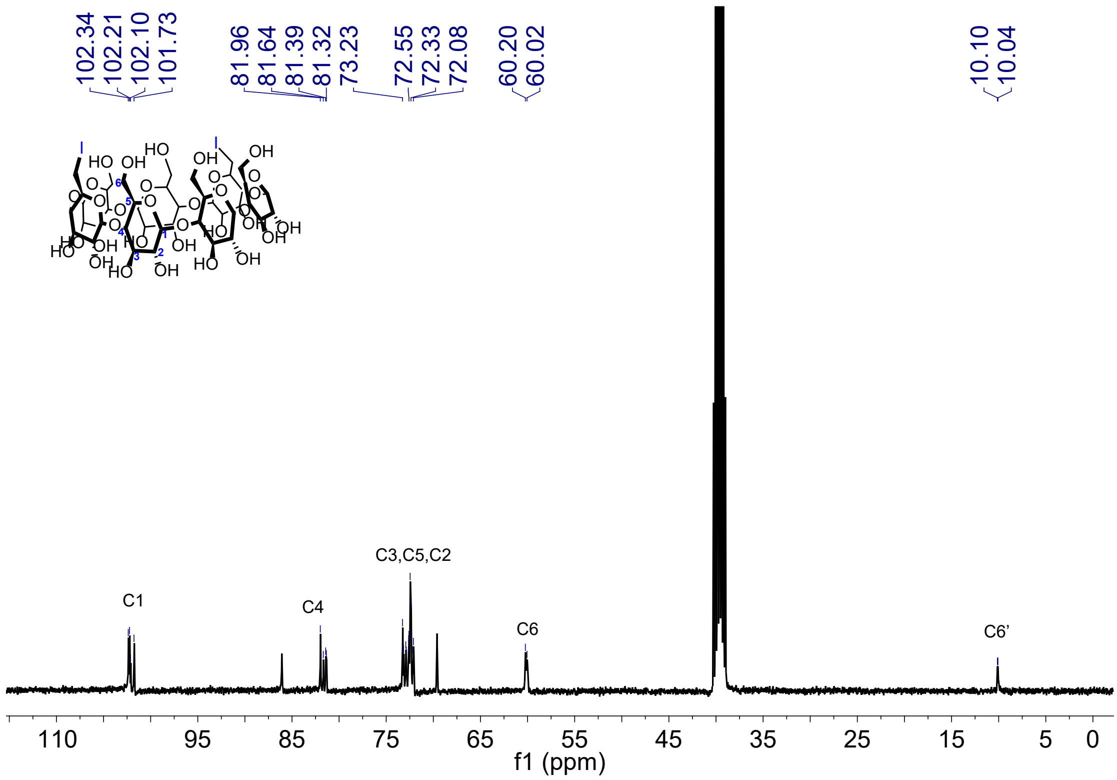
Supplementary Figure 11. ^{13}C NMR spectrum of $6^{A},6^{C}$-diiodo-*β*-CD **13** (101 MHz, DMSO-d_6, 298 K).



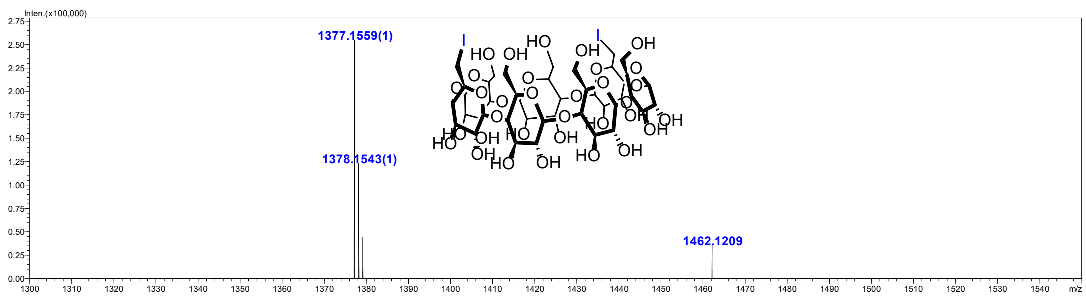
Supplementary Figure 12. HR-MS (ESI) spectrum of 6^{A},6^{C}-diiodo-β-CD **13**.



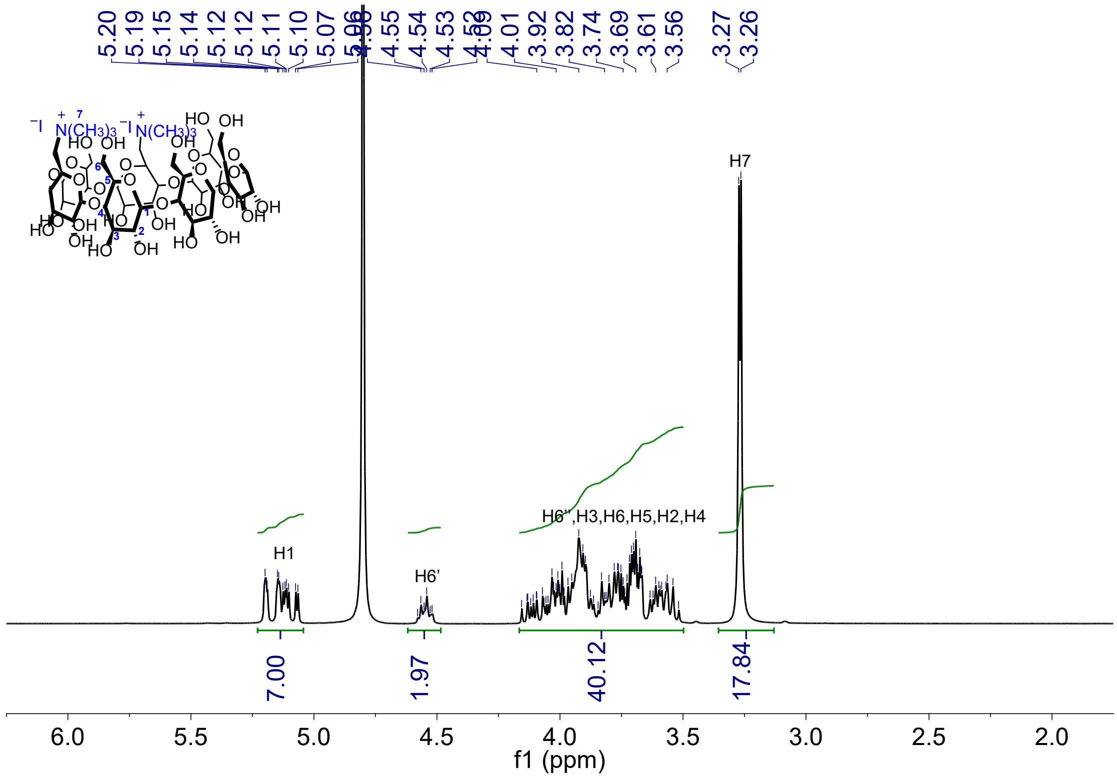
Supplementary Figure 13. ^{1}H NMR spectrum of 6^{A},6^{D}-diiodo-β-CD **14** (400 MHz, D_2O, 298 K).



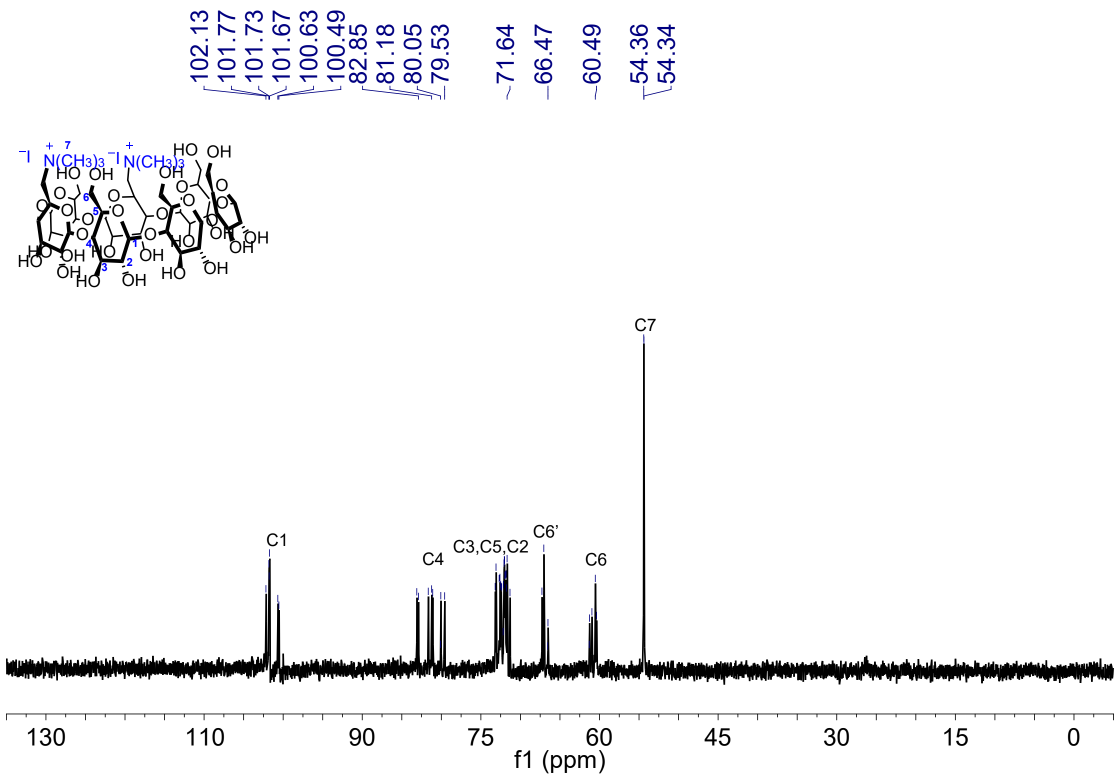
Supplementary Figure 14. ^{13}C NMR spectrum of $6^A,6^D$-diiodo-β-CD **14** (101 MHz, DMSO-d_6, 298 K).



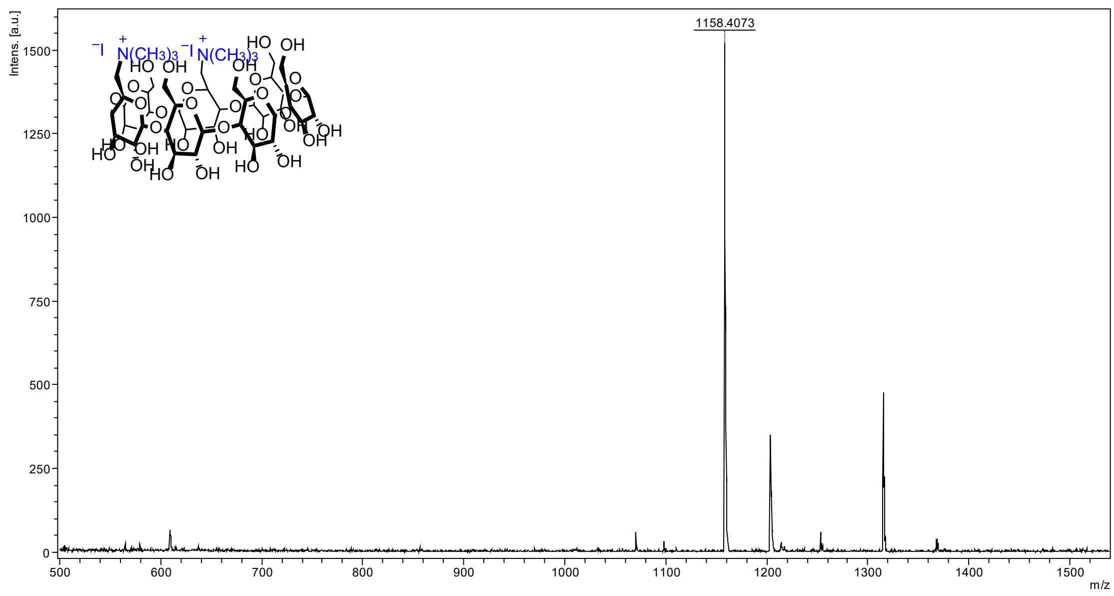
Supplementary Figure 15. HR-MS (ESI) spectrum of $6^A,6^D$-diiodo-β-CD **14**.



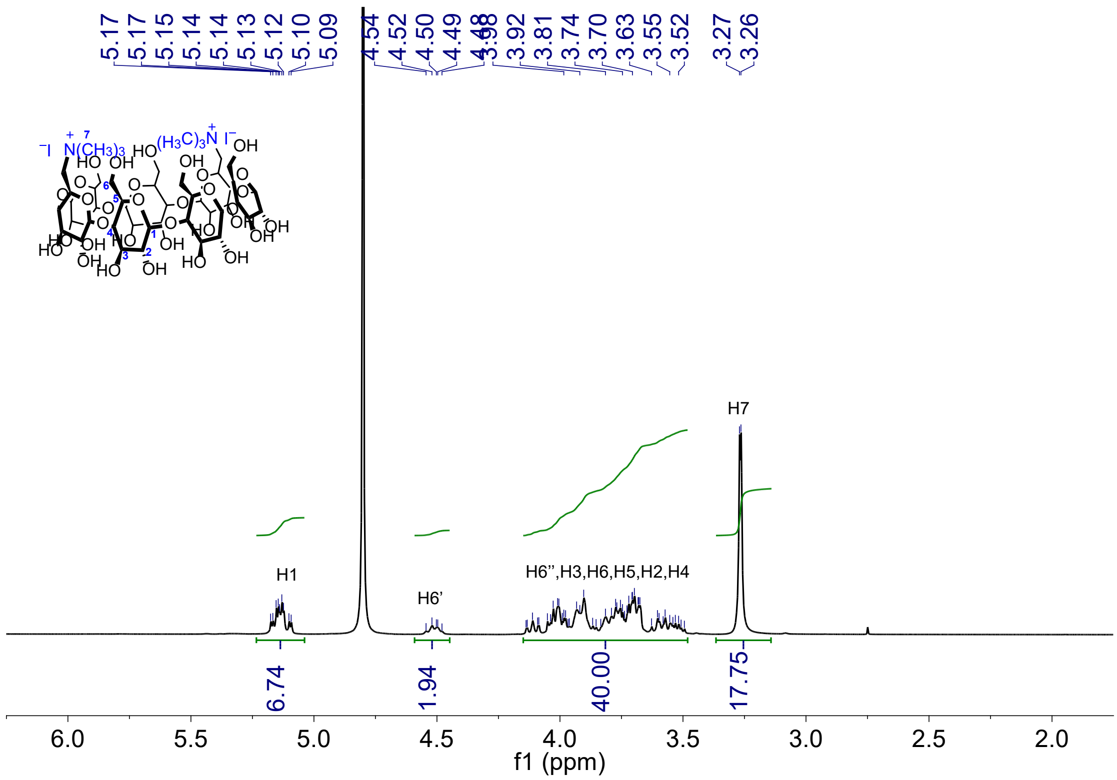
Supplementary Figure 16. ^{1}H NMR spectrum of $6^{A},6^{C}$-TMA$_2$-*β*-CD **7** (400 MHz, D_2O, 298 K).



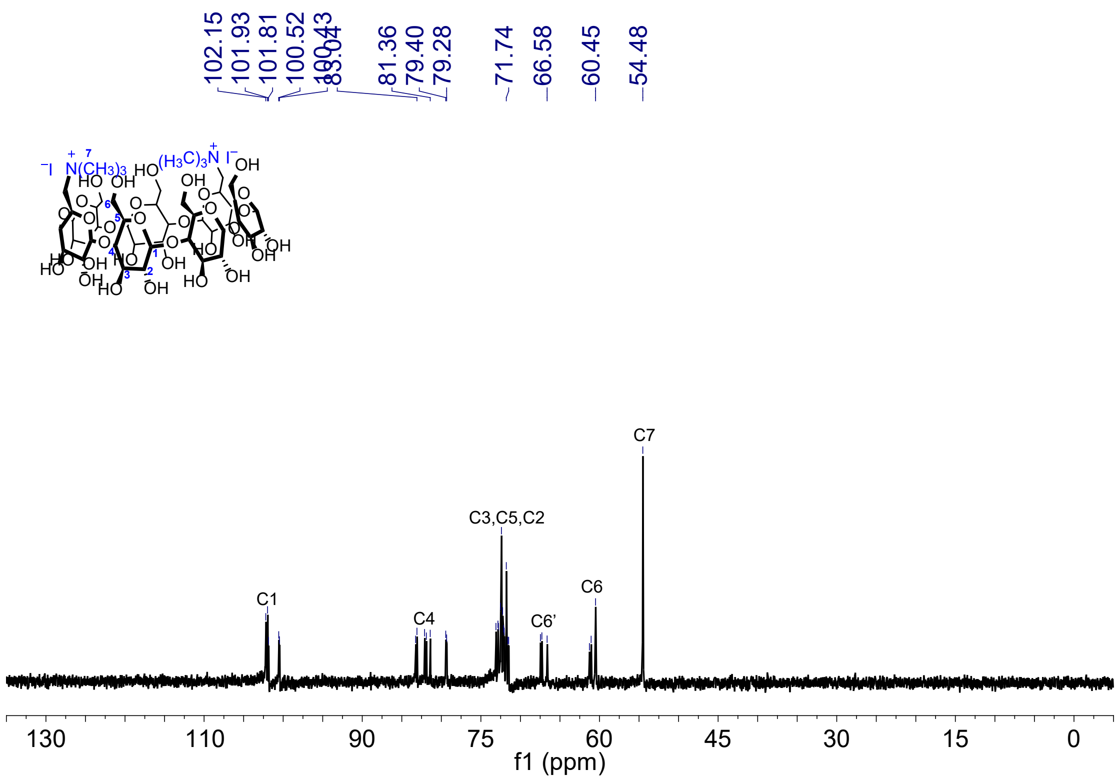
Supplementary Figure 17. ^{13}C NMR spectrum of $6^{A},6^{C}$-TMA$_2$-*β*-CD **7** (101 MHz, D_2O, 298 K).



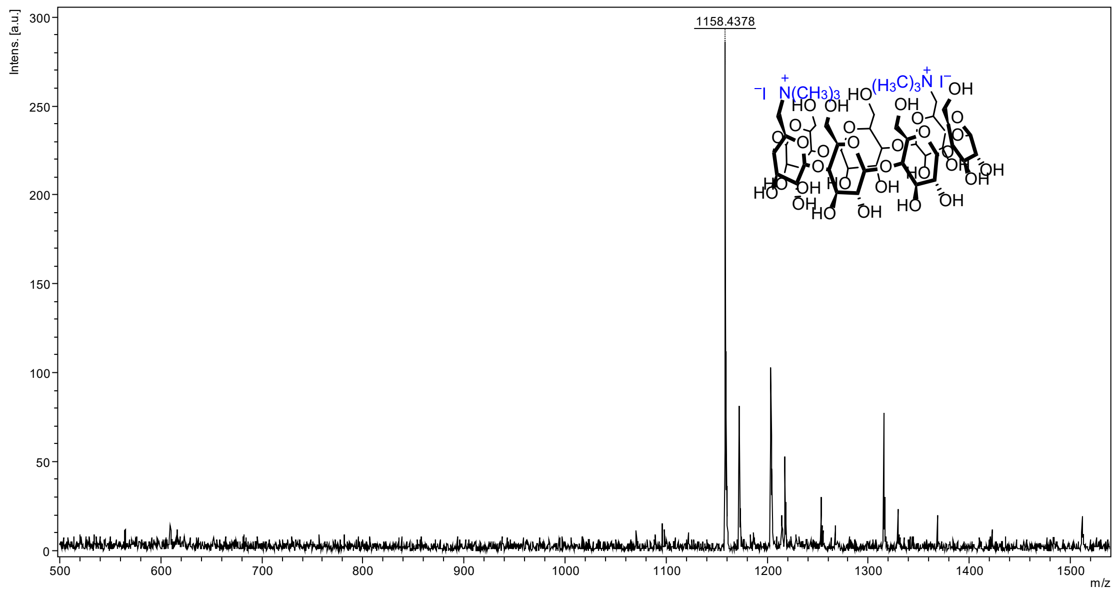
Supplementary Figure 18. MALDI-TOF mass spectrum of $6^{A},6^{C}$-TMA$_2$-β-CD **7**.



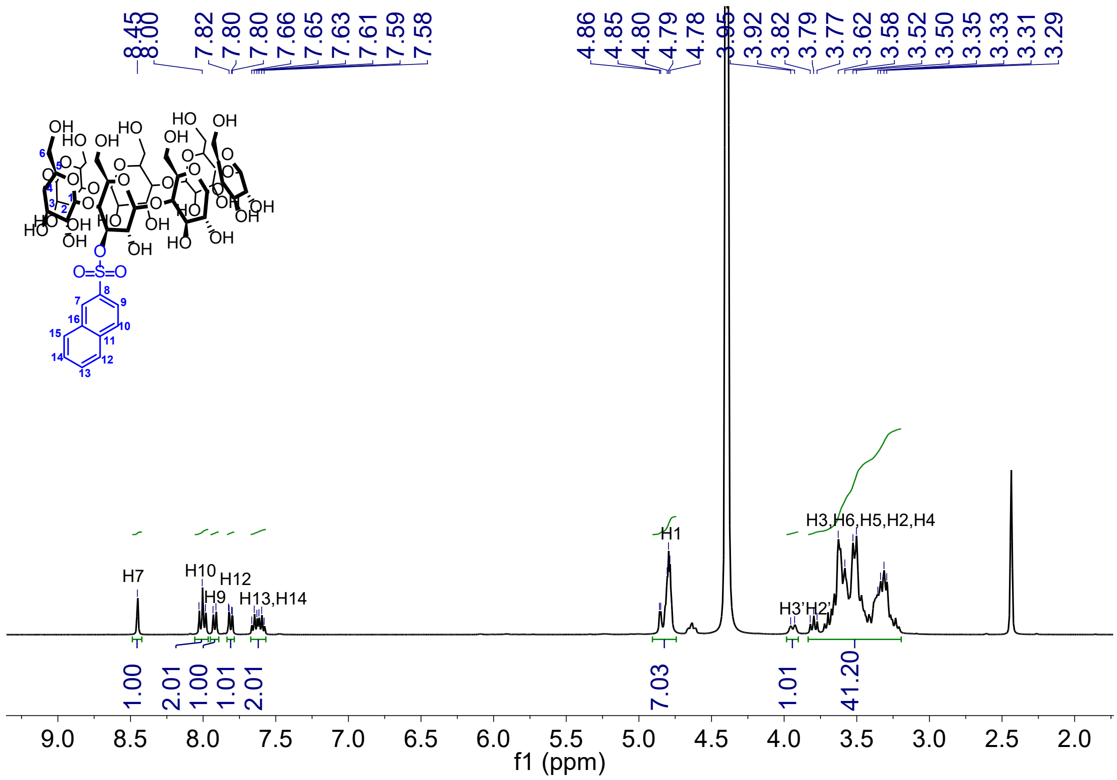
Supplementary Figure 19. ^{1}H NMR spectrum of $6^{A},6^{D}$-TMA$_2$-β-CD **8** (400 MHz, D_2O, 298 K).



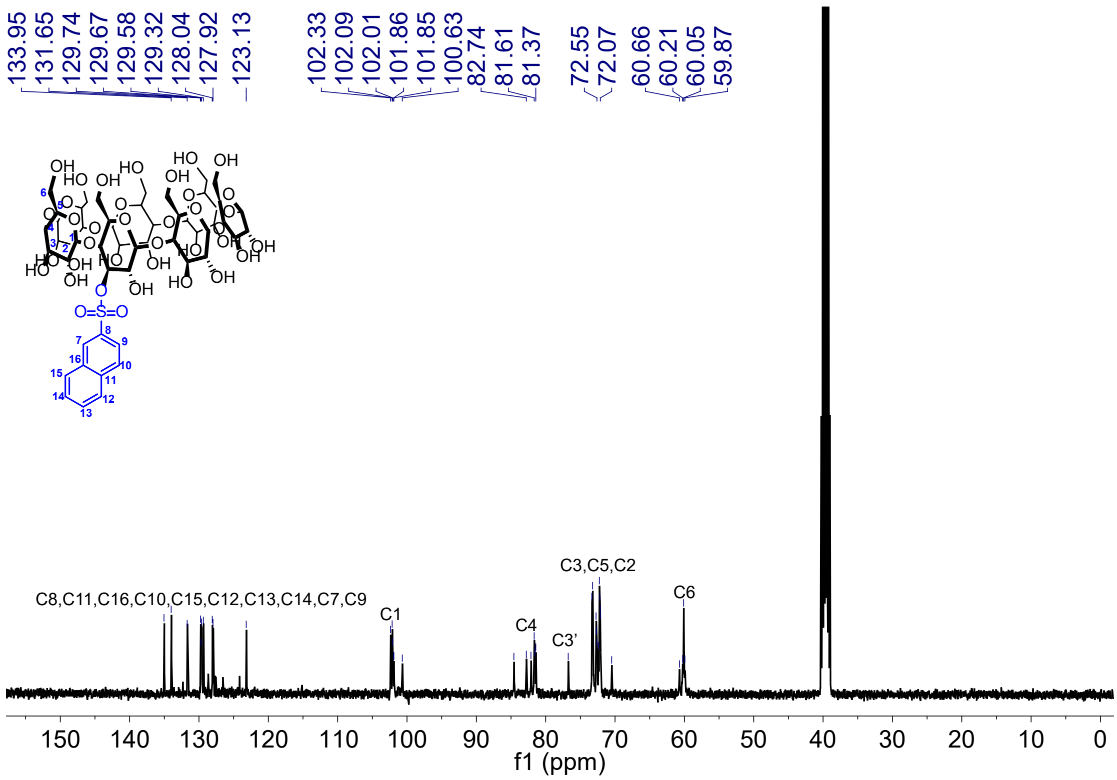
Supplementary Figure 20. ^{13}C NMR spectrum of $6^{A},6^{D}$-TMA$_2$-*β*-CD **8** (101 MHz, D_2O, 298 K).



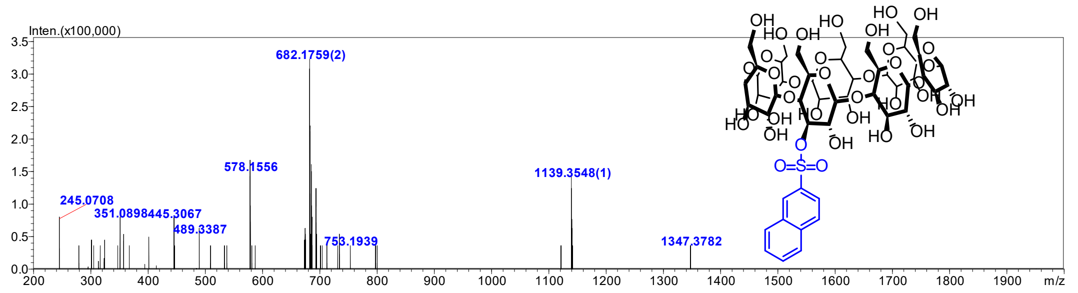
Supplementary Figure 21. MALDI-TOF mass spectrum of $6^{A},6^{D}$-TMA$_2$-*β*-CD **8**.



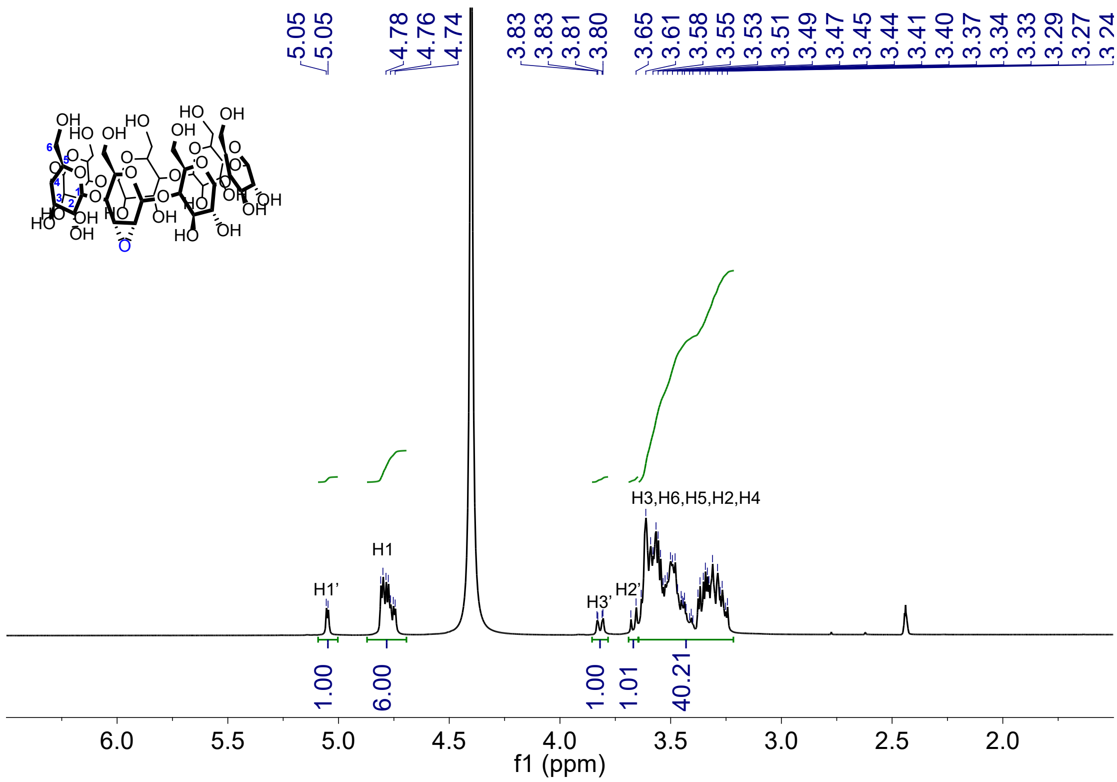
Supplementary Figure 22. ^{1}H NMR spectrum of NS-*β*-CD **15** (400 MHz, DMSO-d_6: D_2O = 1:1, v/v, 298 K).



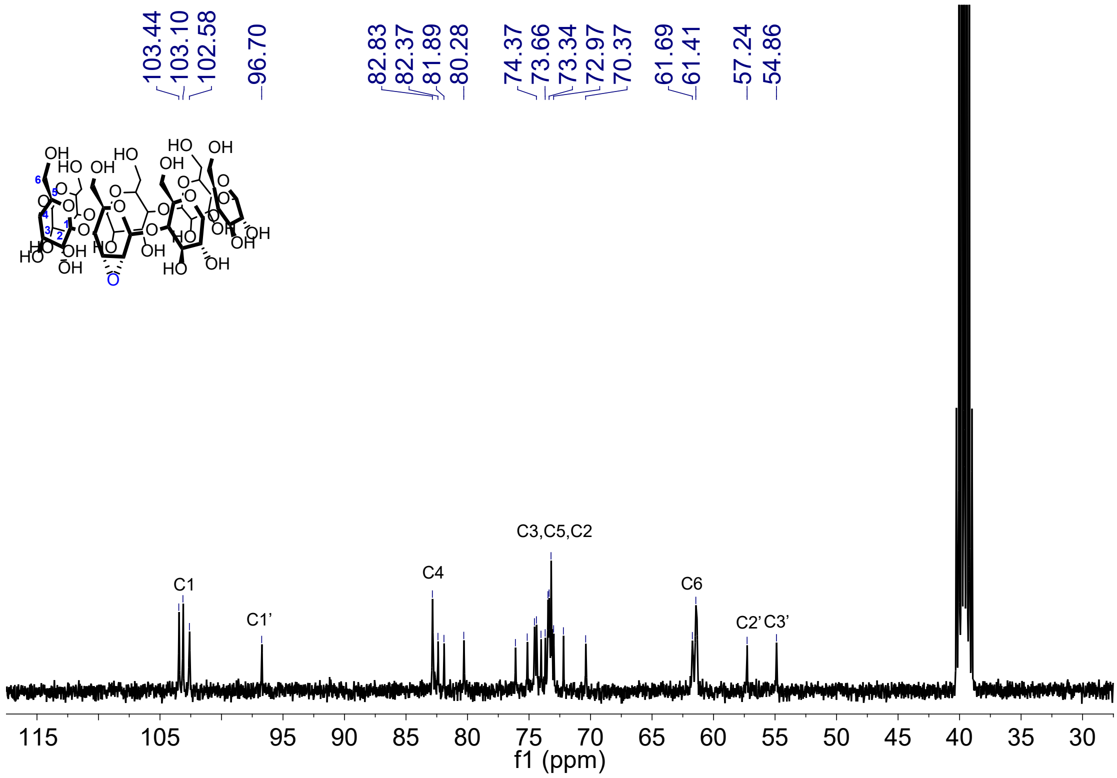
Supplementary Figure 23. ^{13}C NMR spectrum of NS-*β*-CD **15** (101 MHz, DMSO-d_6, 298 K).



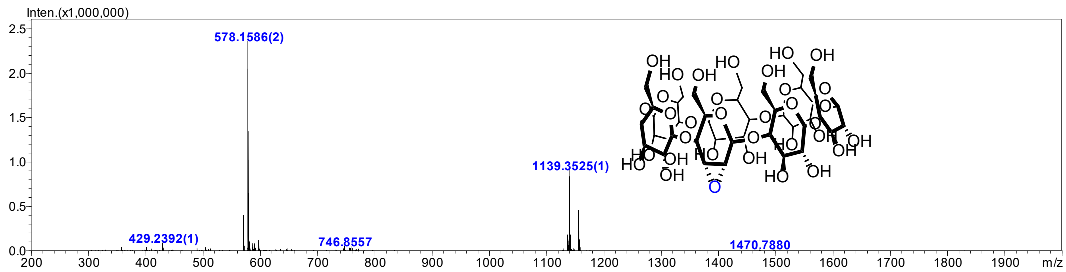
Supplementary Figure 24. HR-MS (ESI) spectrum of NS-*β*-CD **15**.



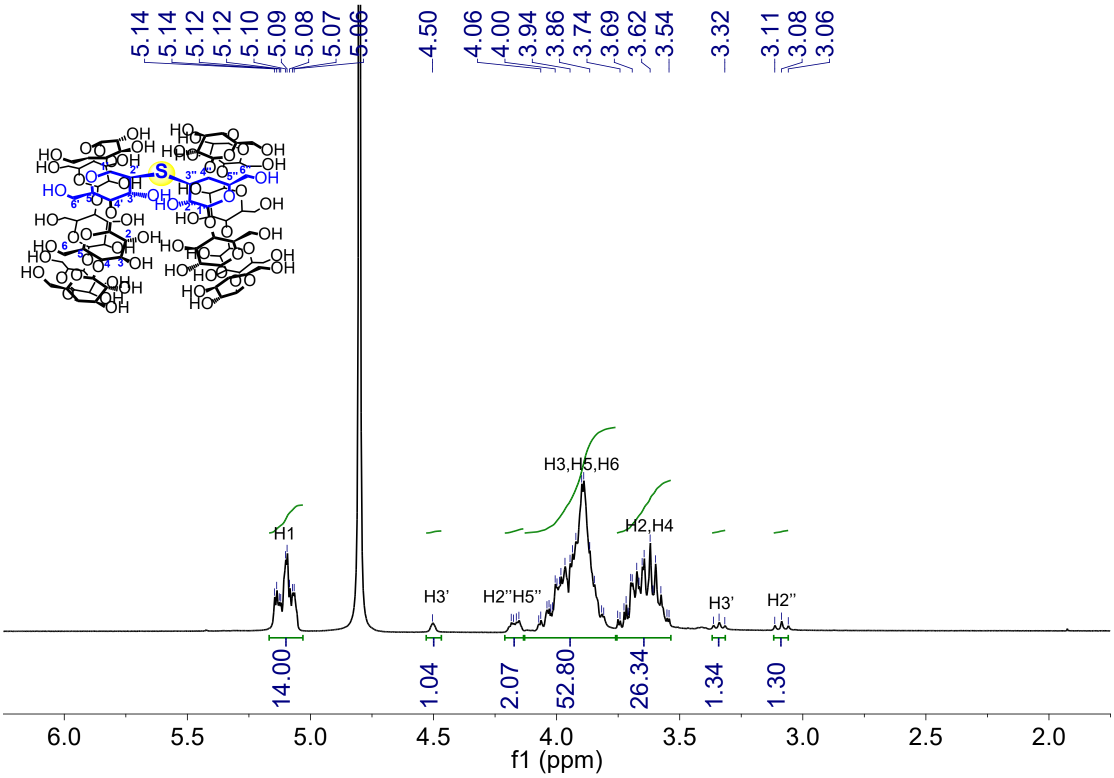
Supplementary Figure 25. ^{1}H NMR spectrum of $2^{A},3^{A}$-alloepoxy-*β*-CD **16** (400 MHz, DMSO-d_6: D_2O = 1:1, v/v, 298 K).



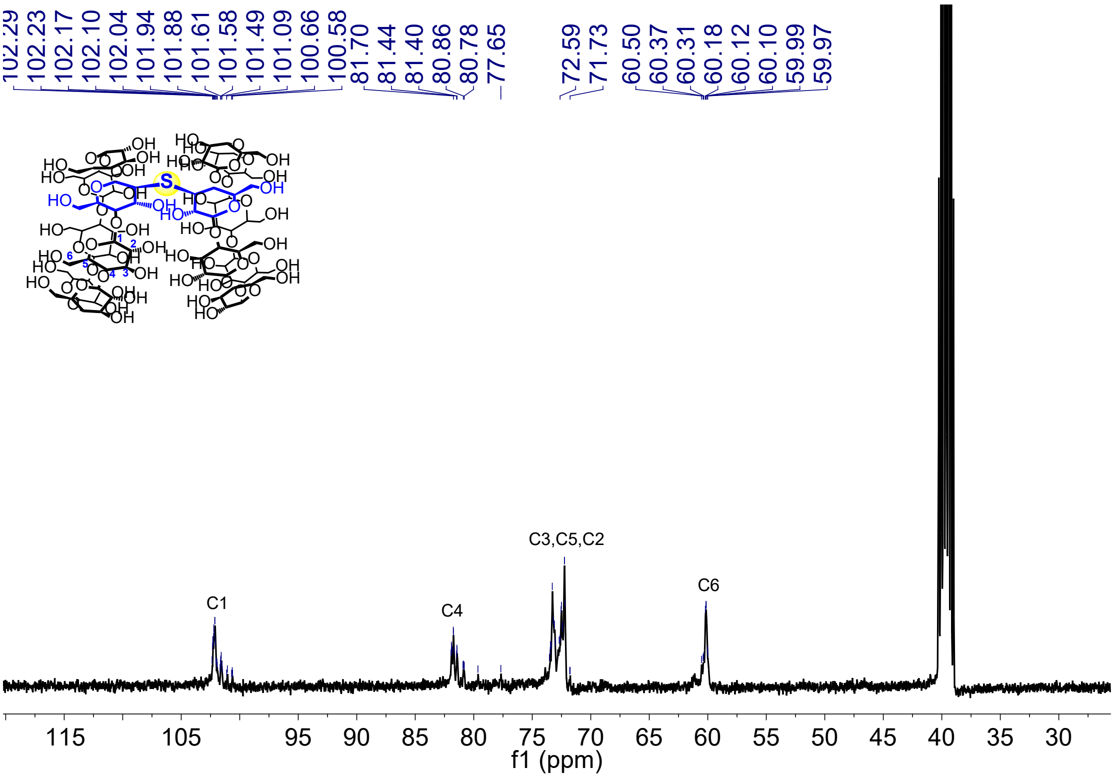
Supplementary Figure 26. ^{13}C NMR spectrum of 2^{A},3^{A}-alloepoxy-*β*-CD **16** (101 MHz, DMSO-d_6, 298 K).



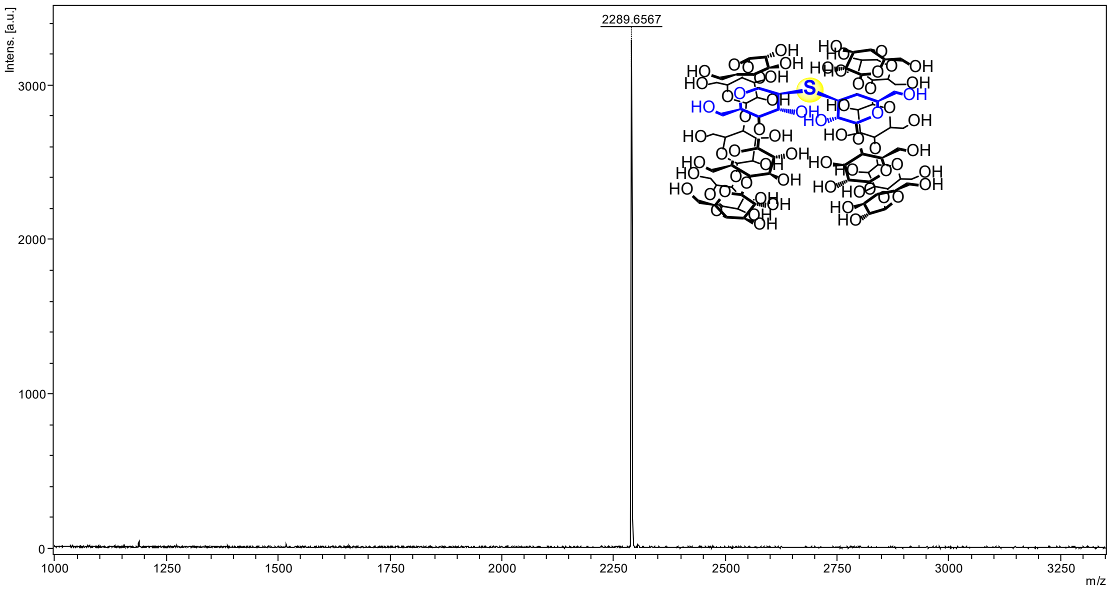
Supplementary Figure 27. HR-MS (ESI) spectrum of 2^{A},3^{A}-alloepoxy-*β*-CD **16**.



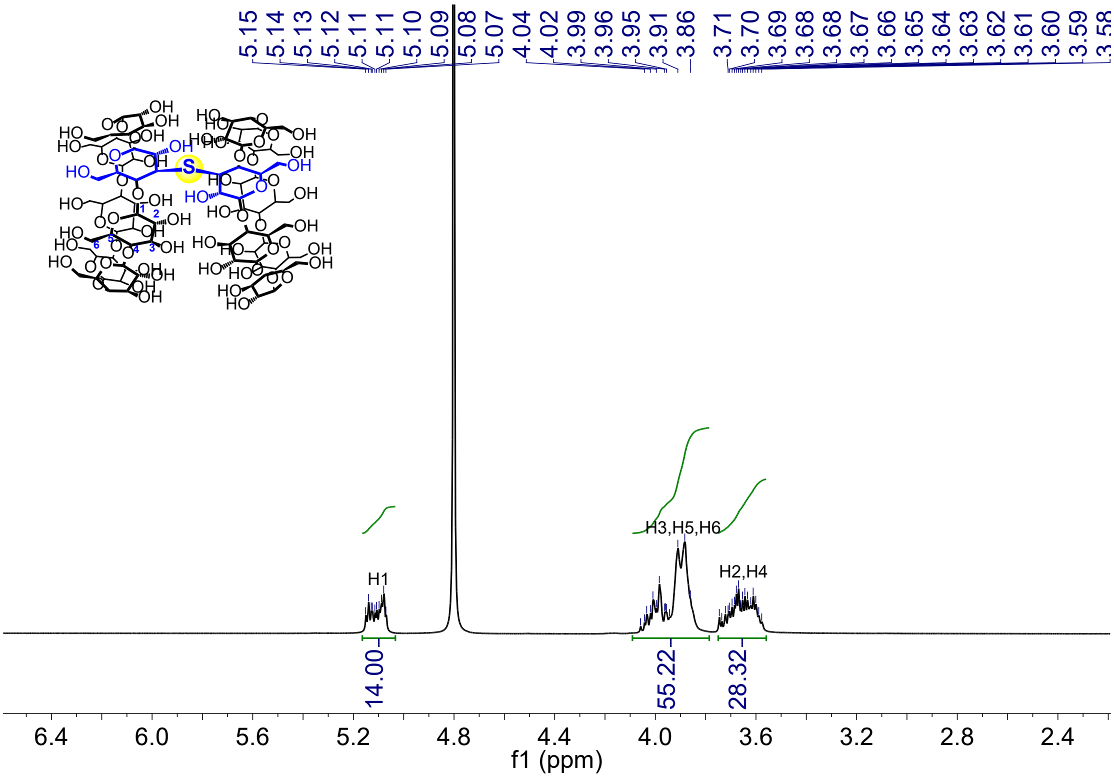
Supplementary Figure 28. ^{1}H NMR spectrum of **9** (400 MHz, D_2O, 298 K).



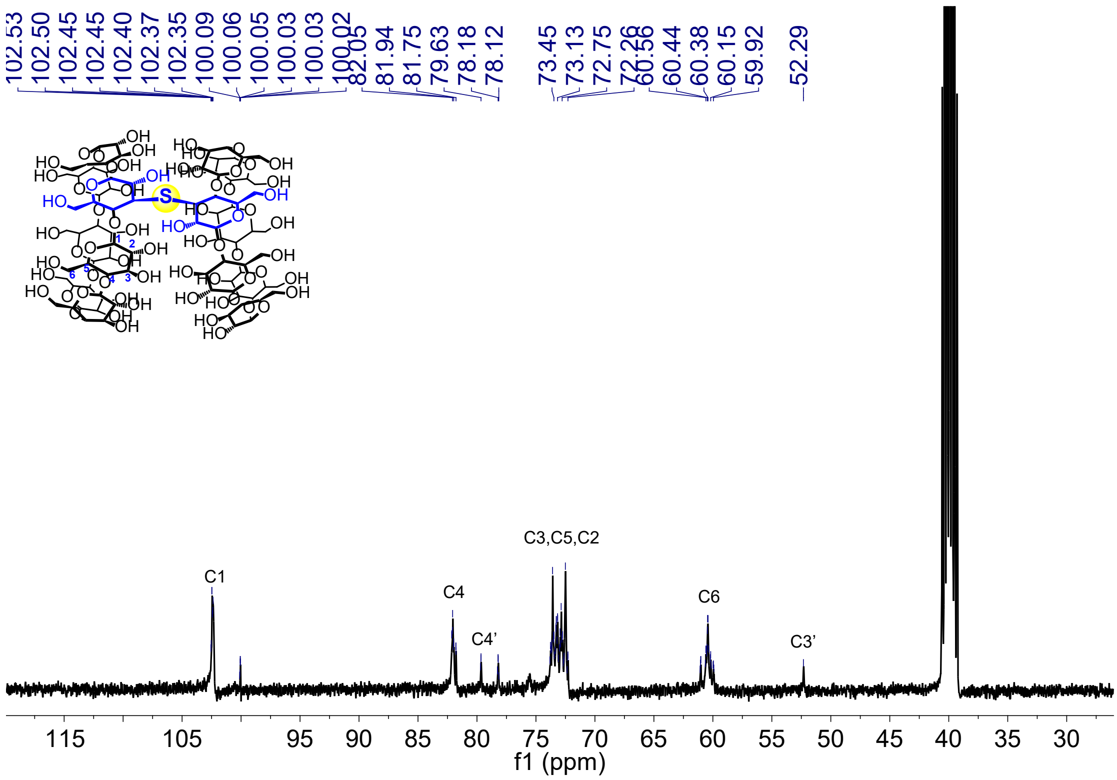
Supplementary Figure 29. ^{13}C NMR spectrum of **9** (101 MHz, DMSO-d_6, 298 K).



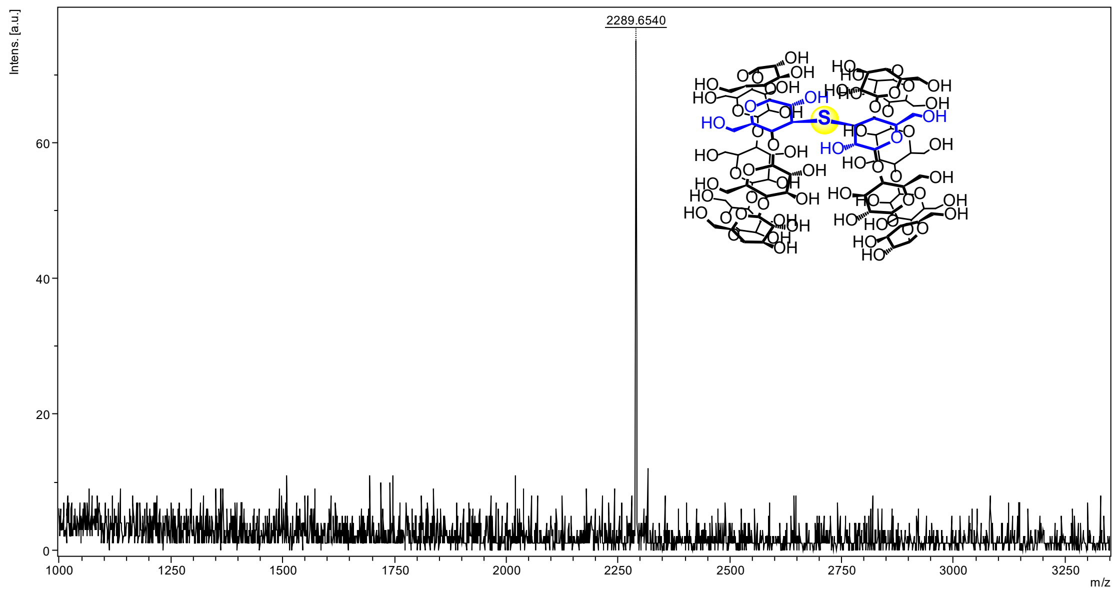
Supplementary Figure 30. MALDI-TOF mass spectrum of **9**.



Supplementary Figure 31. ^{1}H NMR spectrum of **10** (400 MHz, D_2O, 298 K).



Supplementary Figure 32. ^{13}C NMR spectrum of **10** (101 MHz, DMSO-d_6, 298 K).



Supplementary Figure 33. MALDI-TOF mass spectrum of **10**.