Supporting information

Synergetic Effects in the Enantiodifferentiating Photocyclodimerization of 2-Anthracenecarboxylic Acid Mediated by β-Cyclodextrin-Pillar[5]arene-Hybridized Hosts

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TABLE OF CONTENTS

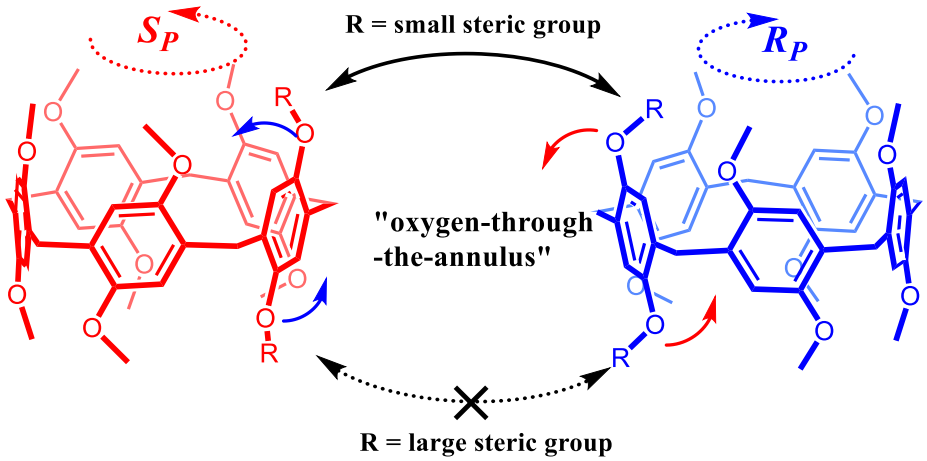
1. General

Materials and Instruments

All reagents were commercially available and used without further purification. Doubly distilled water and HPLC-grade solvents were used for photoreactions and spectral measurements. NMR spectra were recorded on a Bruker AMX-400 at 400 MHz for ^{1}H and 101 MHz for ^{13}C, where the residual proton of solvent, TMS or DMF were used as the internal standard. MALDI-TOF HRMS spectra were obtained with a Waters-Q-TOF Premiers (ESI). UV-vis and circular dichroism spectra were recorded on JASCO V-650 and J-1500 spectrometer, respectively. The diastereoisomers of hosts were resolved by HPLC, using a column of $5C_{18}$-PAQ eluted with a 67:33 (v/v) mixture of water and acetonitrile at 35 °C. Chiral HPLC analyses were performed on a Shimadzu UFLC system equipped with SPD-20A and RF-20A detectors, using a tandem column of Inertsil ODS-2 and Daicel Chiralcel OJ-R eluted with a 64:36:0.1 (v/v) mixture of water, acetonitrile, and trifluoroacetic acid at 35 °C.

Preparation of Sample Solutions

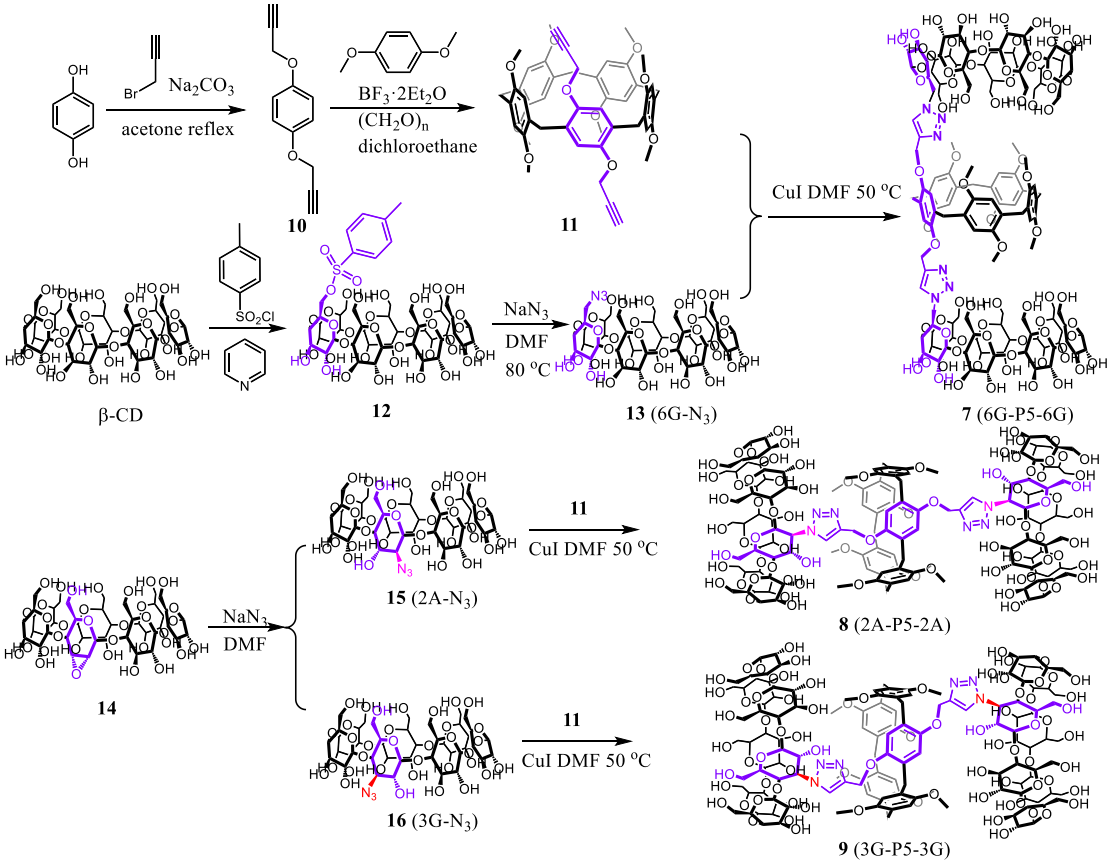
Borate buffer solutions (BBS) at pH = 9.0 were prepared by dissolving appropriate amounts of $Na_2B_4O_7{\cdot}10H_2O$ in distilled water ([buffer] = 25 mM, at 25 °C). Both UV-vis and circular dichroism spectra were measured in 1 cm cell unless stated otherwise. All photoreactions were carried out in a buffer solution under Ar irradiated with a 200-mW LED (365 nm).



Scheme S1. Representation for the S_P and R_P conformational interconversion of the enantiomeric P5 pair.

2. Synthesis and Characterization of Hosts

Compound **10**[1], **14**[2], **15**[3] and **16**[3] were prepared by the reported procedures.



Scheme S2. Synthetic routes for trimers.

Synthesis

10. An acetone solution (60.0 mL) containing hydroquinone (2.2 g, 20.0 mmol) and Na_2CO_3 (6.9 g, 49.9 mmol) was stirred at 25°C for 10 min, propargyl bromide (8.5 g, 71.2 mmol) was then added dropwise within 3 minutes. The reaction mixture was stirred and refluxed under nitrogen for additional 16 hours. the reaction was monitored by TLC (petroleum ether: ethyl acetate = 3:1) to confirm the reaction was completed. Then, the reaction mixture was cooled down and filtered. The crude product was purified by column chromatography (petroleum ether: ethyl acetate = 3:1) to give **10** as faint yellow solid in 78.0% yield (2.9 g). ^{1}H NMR (400 MHz, acetone-d_6) δ: 6.98 (s, 4H), 4.74 (s, 4H), 3.04 (t, J = 2.4 Hz, 2H). ^{13}C NMR (101 MHz, acetone-d_6) δ: 205.50, 152.44, 116.20, 115.88, 115.52, 79.18, 75.93, 55.99.

11. Compound **10** (2.5 g, 13.4 mmol), 1,4-dimethoxybenzene (7.5 g, 54.1 mmol) and polyoxymethylene (4.8 g) was dissolved in 250 mL dichloroethane, the mixture was stirred at 25°C for 10 min, and then BF_3•Et_2O (8.5 g, 71.2 mmol) was added dropwise within 30 seconds. The reaction mixture was stirred at 25°C for additional 16 minutes, then water (10.0 mL) was added to quench the reaction. The solvent was removed under reduced pressure, and then the residue was dissolved in dichloromethane, washed 3 times with water and dried over Na_2SO_4. The solvent was then removed under reduced pressure. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (petroleum ether: ethyl acetate = 10:1) to give **11** as white solid in

9.3% yield (1.0 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 2H), 6.81 (s, 2H), 6.80 (s, 2H), 6.78 (s, 2H), 6.75 (s, 2H), 4.49 (d, *J* = 2.4 Hz, 4H), 3.79 – 3.76 (m, 10H), 3.69 (d, *J* = 5.1 Hz, 12H), 3.65 (s, 12H), 2.08 (t, *J* = 2.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.65, 150.60, 150.54, 149.36, 129.10, 128.43, 128.34, 128.13, 127.89, 115.48, 114.05, 113.83, 113.75, 113.62, 78.99, 74.73, 56.37, 55.79, 55.70, 55.67, 55.58, 29.62, 29.54. MALDI-HRMS: *m/z* calcd. for $[M]^+$: 798.3404, found: 798.3896.

12. A pyridine solution (200.0 mL) containing β-CD (20.0 g, 17.6 mmol) and tosyl chloride (24.0 g, 125.8 mmol) was stirred at 25°C for 6 hours, after the fully consumption of the raw meterials monitored by TLC, 10.0 ml water was added to quench the reaction. The solvent was removed in *vacuo* and the crude product was purified by reverse-phase column chromatography, a gradient elution from water to 40% aqueous EtOH (2.0 L) was used to give pure **12** as white powder in 23.8% yield (5.4 g) after freeze drying. ^{1}H NMR (400 MHz, DMSO-d_6+D_2O (1:1, v/v)) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 4.87 – 4.75 (m, 7H), 4.31 (d, *J* = 4.33 Hz, 1H), 4.22– 4.17 (m, 1H), 3.70– 3.16 (m, 40H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6+D_2O (1:1, v/v)) δ 146.28, 132.44, 130.21, 127.68, 101.98, 101.73, 100.91, 81.41, 81.06, 80.76, 80.61, 73.32, 72.90, 72.22, 71.98, 71.66, 71.53, 70.47, 69.48, 59.84, 21.43. ^{13}C NMR (101 MHz, D_2O). MALDI-HRMS: *m/z* calcd. for $[M+Na]^+$: 1311.3678, found: 1311.3816.

13. Compound **12** (3.0 g, 2.3 mmol) and NaN_3 (2.5 g, 38.4 mmol) was dissolved in a mixed solution of 30 mL DMF and 3.0 mL water, the mixture was stirred at 80°C for 5.5 hours. After the reaction mixture was cooled, the solvent was removed in vacuo, and the crude product was purified by reverse-phase column chromatography, a gradient elution from water to 40% aqueous EtOH (2.0 L) was used to give pure **13** as white powder in 70.0% yield (1.87 g) after freeze-drying. ^{1}H NMR (400 MHz, D_2O) δ 4.99 (d, *J* = 3.1 Hz, 7H), 3.91 – 3.70 (m, 28H), 3.61 – 3.48 (m, 14H). ^{13}C NMR (101 MHz, D_2O) δ 101.89, 101.68, 82.08, 81.13, 73.13, 72.88, 72.01, 71.87, 70.60, 60.21. MALDI-HRMS: *m/z* calcd. for $[M+H]^+$: 1160.3835, found: 1160.3735.

15 and **16**. Compound **14** (1.0 g, 0.7 mmol) and NaN_3 (0.8 g, 12.8 mmol) was dissolved in a mixed solution of 10.0 mL DMF and 1.0 mL water, the mixture was stirred at 80°C for 5.5 hours. After the reaction mixture was cooled, the solvent was removed in vacuo, and the crude product was purified by reverse-phase column chromatography, a gradient elution from water to 15% aqueous EtOH (2.0 L) was used to give pure **15** (2A-N_3) and **16** (3G-N_3) after freeze-drying.

15 (2A-N_3) (white powder, 89.0 mg, yield: 11.4%): ^{1}H NMR (400 MHz, D_2O) δ 5.10 (d, *J* = 4.0 Hz, 2H), 5.01 – 4.94 (m, 4H), 4.81 (d, *J* = 7.3 Hz, 1H), 4.28 – 4.24 (m, 1H), 3.98 – 3.63 (m, 31H), 3.61 – 3.50 (m, 10H). ^{13}C NMR (101 MHz, D_2O) δ 101.93, 101.82, 101.14, 80.92, 80.67, 80.32, 78.78, 78.69, 75.93, 73.32, 73.14, 72.92, 72.59, 72.38, 72.08, 72.04, 71.84, 71.68, 71.63, 71.51, 71.08, 69.01, 63.61, 60.29, 60.04, 59.97, 59.44. MALDI-HRMS: *m/z* calcd. for $[M+H]^+$: 1160.3835, found: 1160.3797.

16 (3G-N_3) (white powder, 303.0 mg, yield: 38.8%): ^{1}H NMR (400 MHz, D_2O) δ 4.99 (d, *J* = 3.6 Hz, 7H), 3.91 – 3.76 (m, 28H), 3.65 – 3.41 (m, 14H). ^{13}C NMR (101 MHz, D_2O) δ 101.78, 101.72, 101.54, 101.41, 100.68, 81.05, 80.77, 80.64, 77.98, 73.02, 72.44, 71.97, 71.78, 71.51, 71.37, 65.70, 60.21. MALDI-HRMS: *m/z* calcd. for $[M+H]^+$: 1160.3835; found , 1160.3921. MALDI-HRMS: *m/z* calcd. for $[M+H]^+$: 1160.3835, found: 1160.3921.

7 (6G-P5-6G). Compound **11** (73.0 mg, 97.7 μmol), **13** (244.0 mg, 210.5 μmol) and CuI (80.0 mg, 420.0 μmol) was dissolved in 5.0 mL DMF, the mixture heated to 50°C and was stirred under nitrogen for 16 hours. After the reaction mixture was cooled, the solvent was removed in *vacuo*, and the crude product was purified by reverse-phase column chromatography, a gradient elution from 50% to 70% aqueous EtOH (2.0 L) was used to give pure **7** (6G-P5-6G) as white powder in 39.4% yield (120.0 mg)

after freeze-drying. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.17 (s, 2H), 7.01 (s, 2H), 6.79 – 6.72 (m, 8H), 5.87 – 5.71 (m, 7H), 5.07 – 4.97 (m, 4H), 4.84 – 4.82 (m, 10H), 4.65 – 4.55 (m, 4H), 4.00 – 3.95 (m, 2H), 3.68 – 3.55 (m, 80H), 3.37 – 3.33 (m, 30H), 3.21 – 3.12 (m, 2H), 2.97 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.91, 150.37, 149.68, 143.51, 143.51, 127.91, 127.83, 126.10, 113.66, 102.41, 81.90, 73.35, 72.70, 72.53, 60.26, 55.96, 55.84, 55.75, 31.25. MALDI-HRMS: *m/z* calcd. for $[M+Na]^+$: 3141.0855, found: 3141.0844.

8 (2A-P5-2A). Compound **11** (25.4 mg, 34.0 μmol), **15** (85.0, 73.3 μmol) and CuI (27.8 mg, 146.0 μmol) was dissolved in 1.5 mL DMF, the mixture heated to 50°C and was stirred under nitrogen for 16 hours. After the reaction mixture was cooled, the solvent was removed in *vacuo*, and the crude product was purified by reverse-phase column chromatography, a gradient elution from 50% to 70% aqueous EtOH (2.0 L) was used to give pure **8** (2A-P5-2A) as white powder in 34.0 % yield (36.0 mg) after freeze-drying. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.8 Hz, 2H), 7.01 (s, 2H), 6.82 – 6.74 (m, 7H), 6.57 (d, *J* = 2.9 Hz, 1H), 5.98 – 5.50 (m, 5H), 5.37 (s, 2H), 5.03 – 4.86 (m, 14H), 4.57 – 4.54 (d, *J* = 5.8 Hz, 4H), 4.18 (d, *J* = 11.6 Hz, 2H), 3.99 (s, 4H), 3.68 – 3.53 (m, 84H), 3.37 – 3.26 (d, *J* = 9.8 Hz, 26H), 3.10 – 3.09 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.10, 132.69, 107.31, 87.00, 78.11, 77.30, 65.10, 60.80. MALDI-HRMS: *m/z* calcd. for $[M+Na]^+$: 3141.0855, found: 3141.0888.

9 (3G-P5-3G). Compound **11** (73 mg, 97.7 μmol), **16** (400.0, 343.0 μmol) and CuI (80.0 mg, 420.0 μmol) was dissolved in 5.0 mL DMF, the mixture heated to 50°C and was stirred under nitrogen for 16 hours. After the reaction mixture was cooled, the solvent was removed in *vacuo*, and the crude product was purified by reverse-phase column chromatography, a gradient elution from 50% to 70% aqueous EtOH (2.0 L) was used to give pure **9** (3G-P5-3G) as white powder in 55.8 % yield (170.0 mg) after freeze-drying. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.5 Hz, 2H), 7.00 (d, *J* = 11.4 Hz, 2H), 6.83 – 6.71 (m, 8H), 6.00 – 5.52 (m, 4H), 5.01 (s, 4H), 4.86 – 4.80 (m, 10H), 4.63 (s, 2H), 4.37 – 4.27 (m, 4H), 3.89 – 3.68 (m, 36H), 3.63 – 3.40 (m, 56H), 3.34 – 3.27 (m, 20H), 2.92 (d, *J* = 9.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.21, 155.09, 154.54, 133.34, 132.83, 132.71, 131.41, 118.50, 107.15, 86.84, 78.06, 77.25, 65.06, 60.79, 60.70. MALDI-HRMS: *m/z* calcd. for $[M+Na]^+$: 3141.0855, found: 3141.0875.

3. NMR and HR-MS Spectra

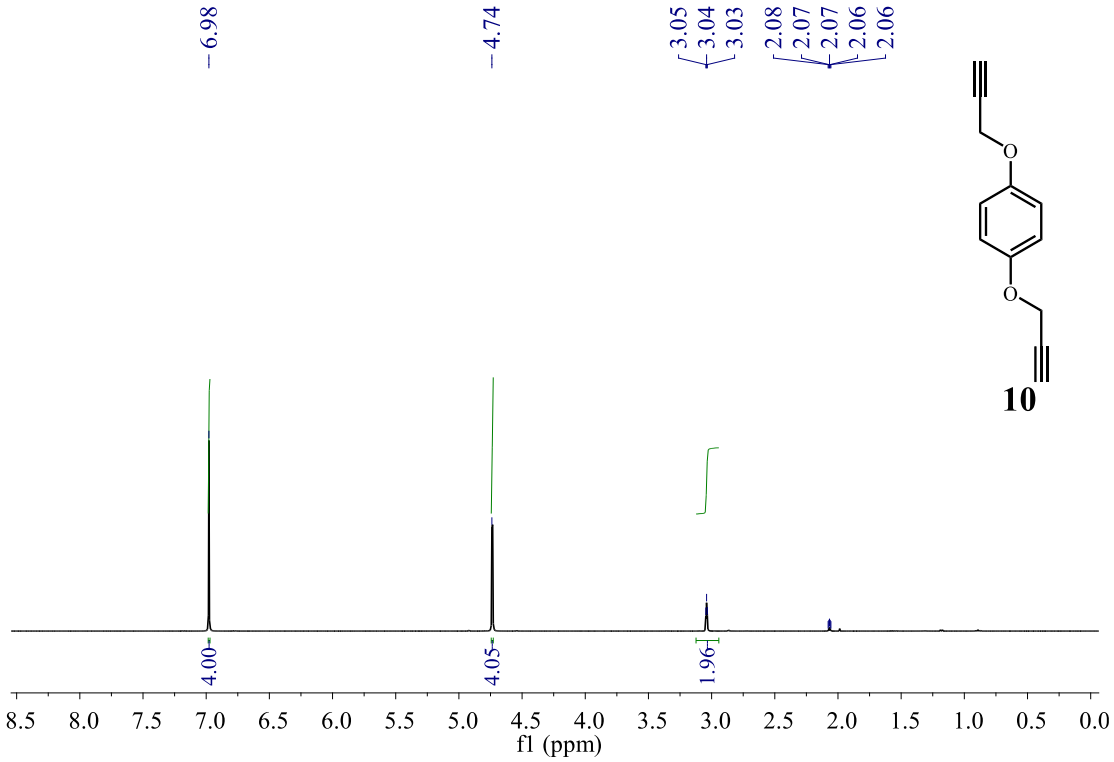


Figure S1. ^{1}H NMR spectrum of **10** (400 MHz, acetone-d_6).

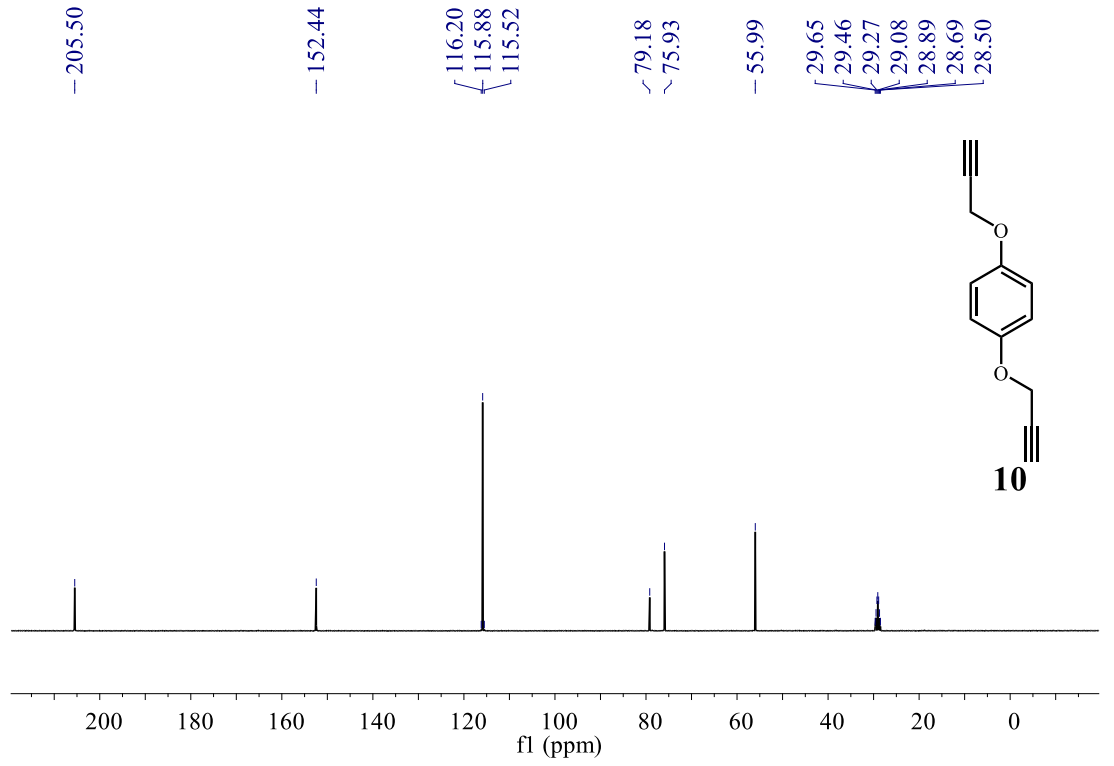


Figure S2. ^{13}C NMR spectrum of **10** (101 MHz, acetone-d_6).

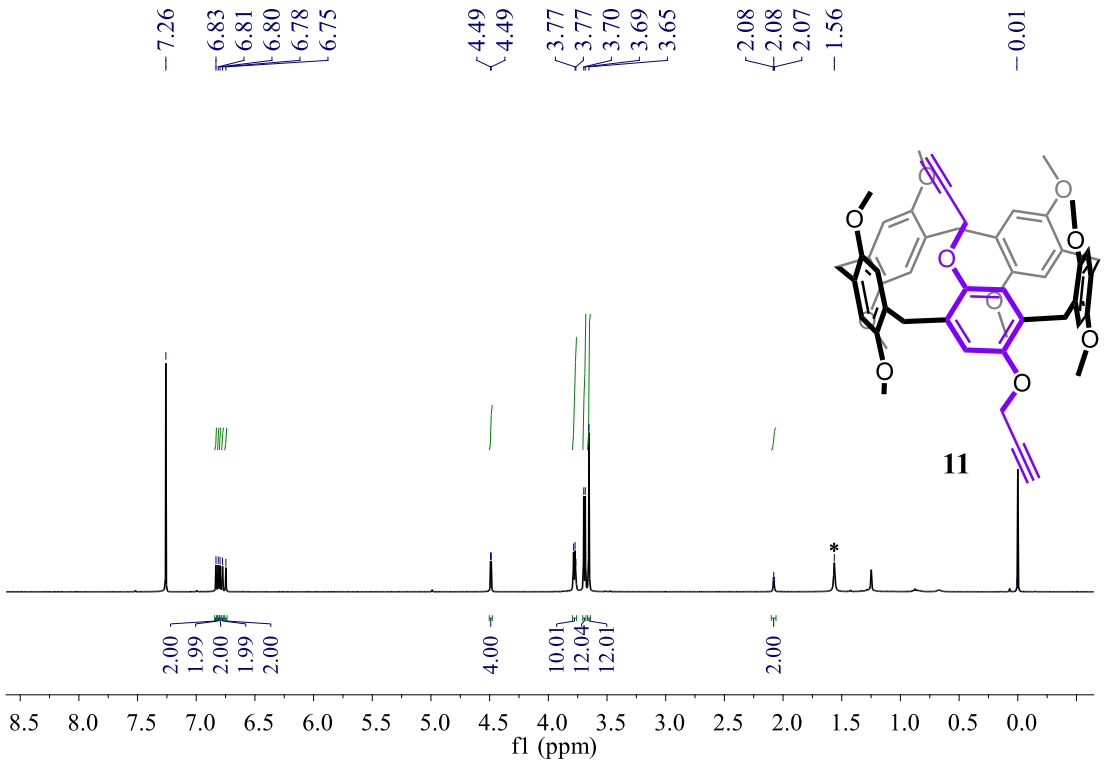


Figure S3. ^{1}H NMR spectrum of **11** (400 MHz, $CDCl_3$). The signal with the symbol * is due to trace amount of water.

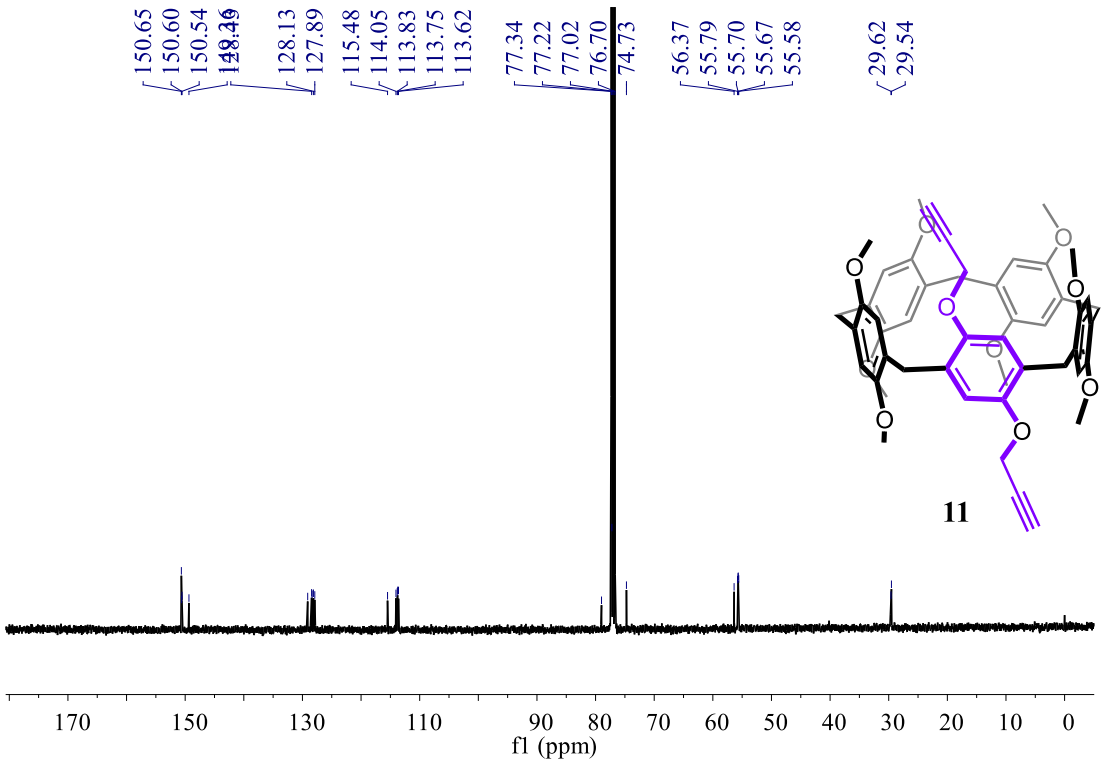


Figure S4. ^{13}C NMR spectrum of **11** (101 MHz, $CDCl_3$).

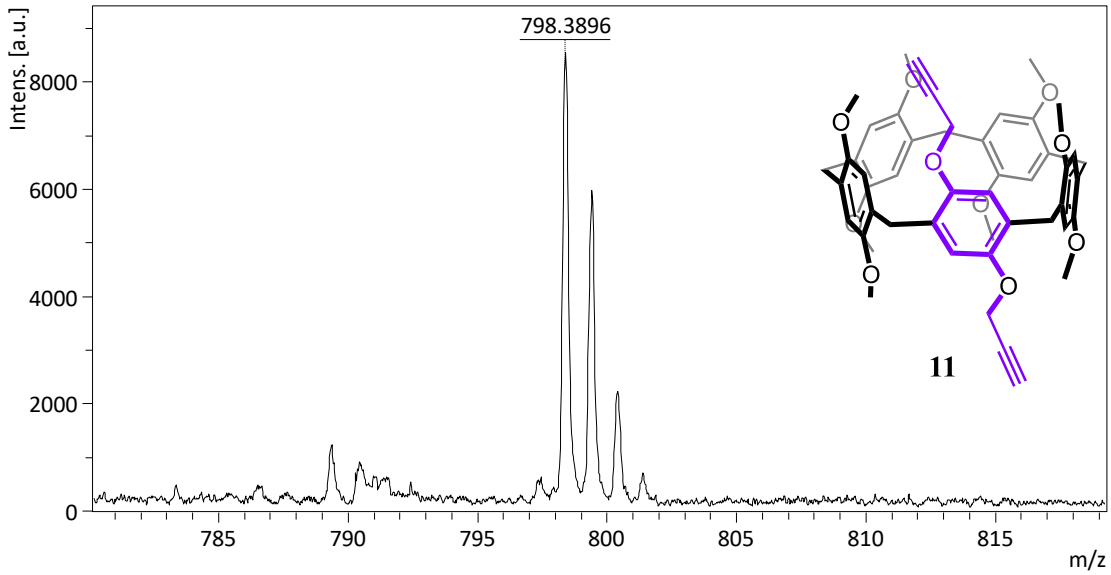


Figure S5. MALDI-HRMS spectrum of **11**.

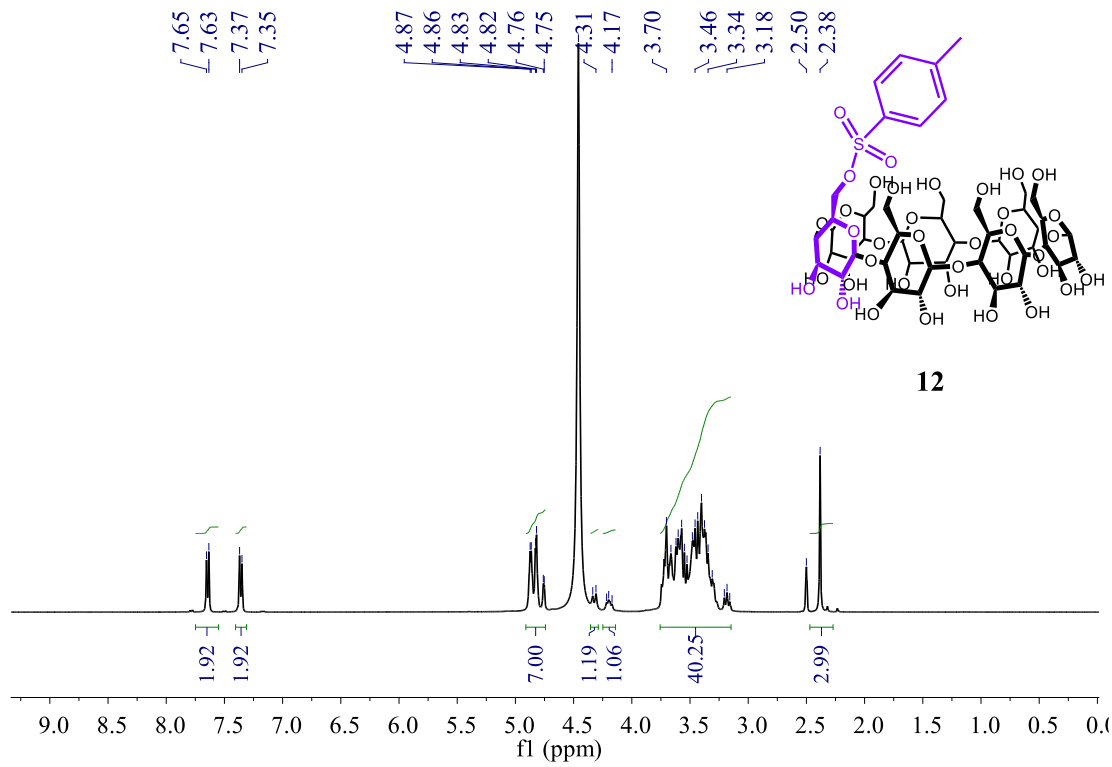


Figure S6. ^{1}H NMR spectrum of **12** (400 MHz, DMSO-d_6: D_2O = 1:1, v/v).

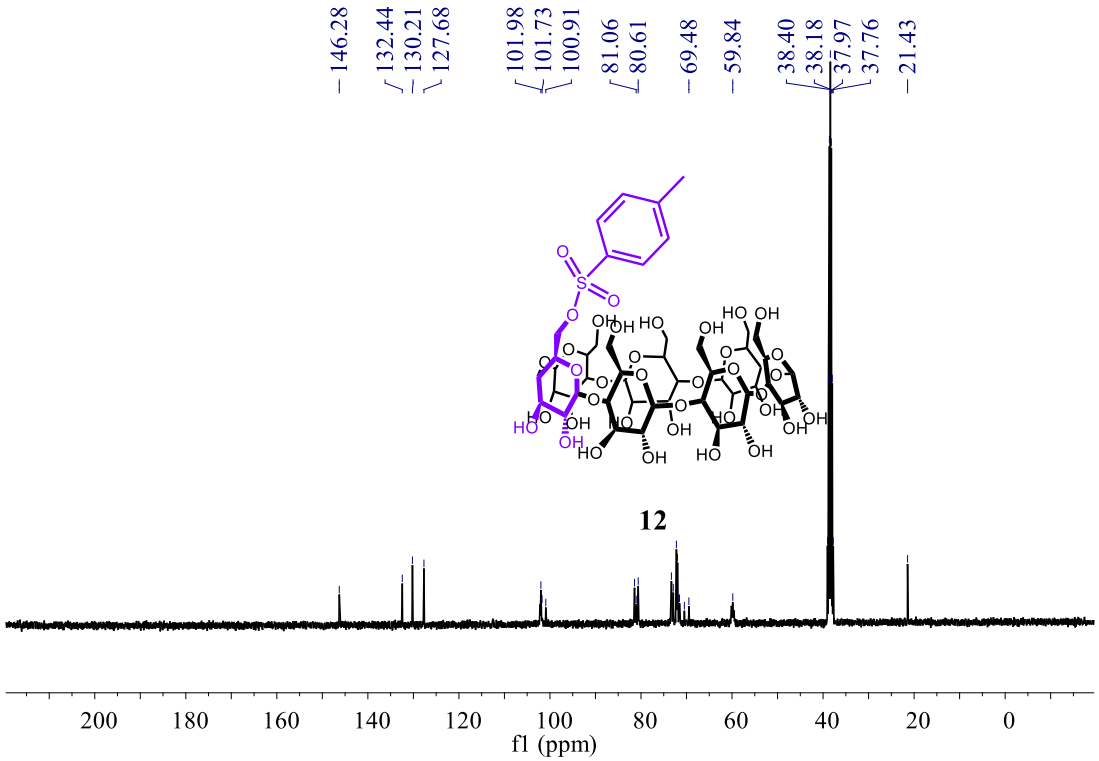


Figure S7. ^{13}C NMR spectrum of **12** (101 MHz, DMSO-d_6: D_2O = 1:1, v/v).

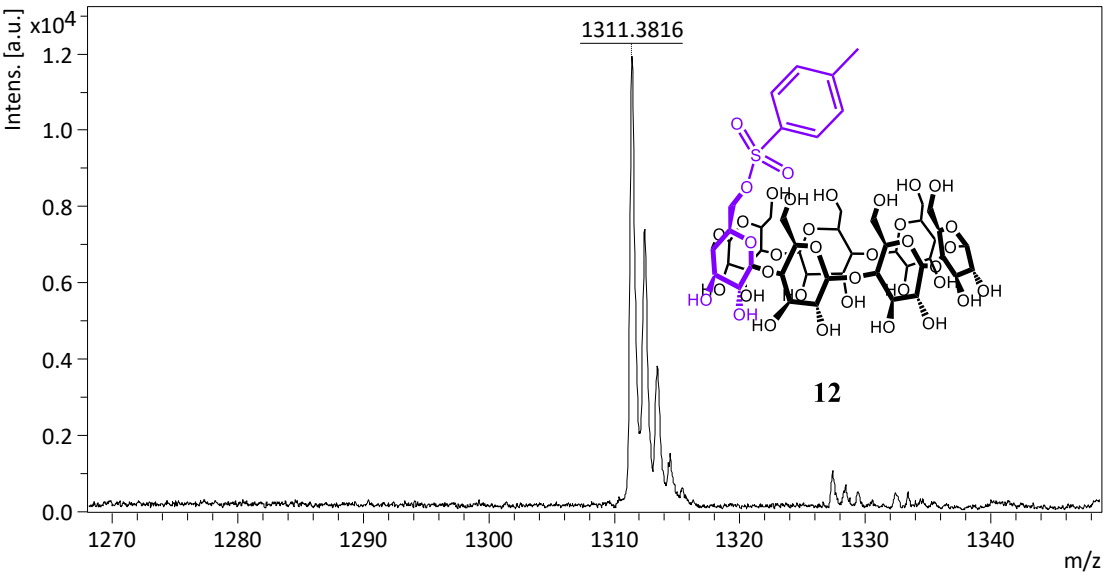


Figure S8. MALDI-HRMS spectrum of **12**.

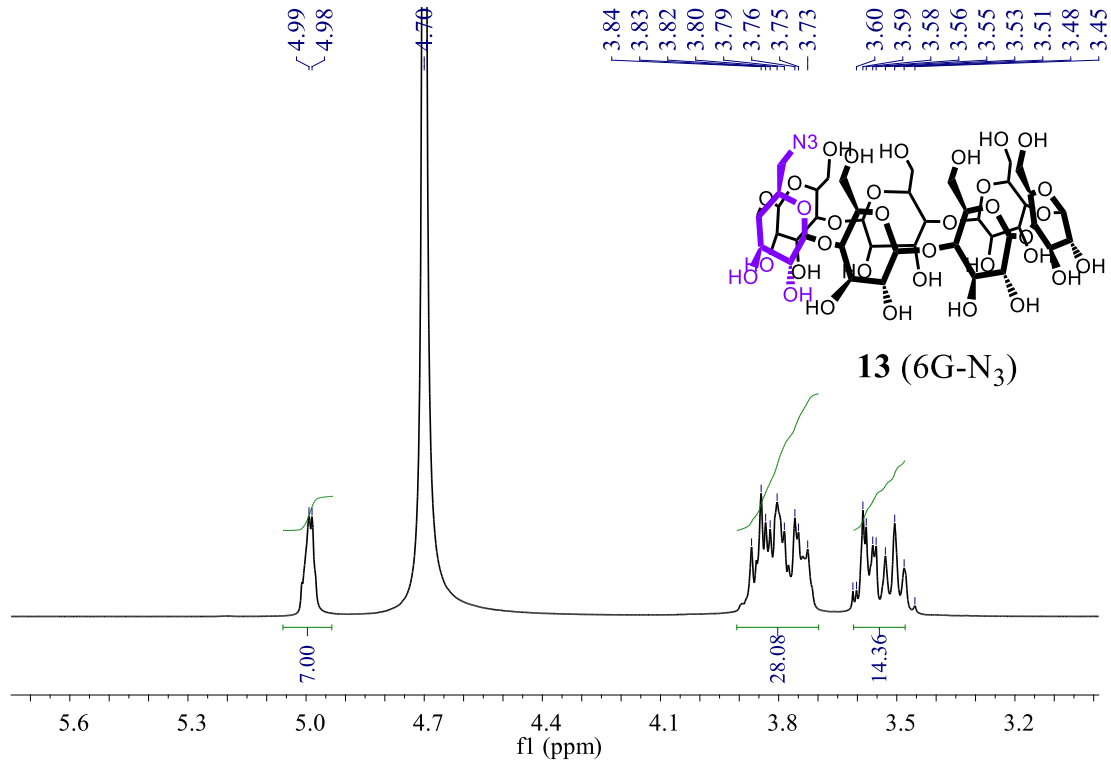


Figure S9. ^{1}H NMR spectrum of **13** (400 MHz, D_2O).

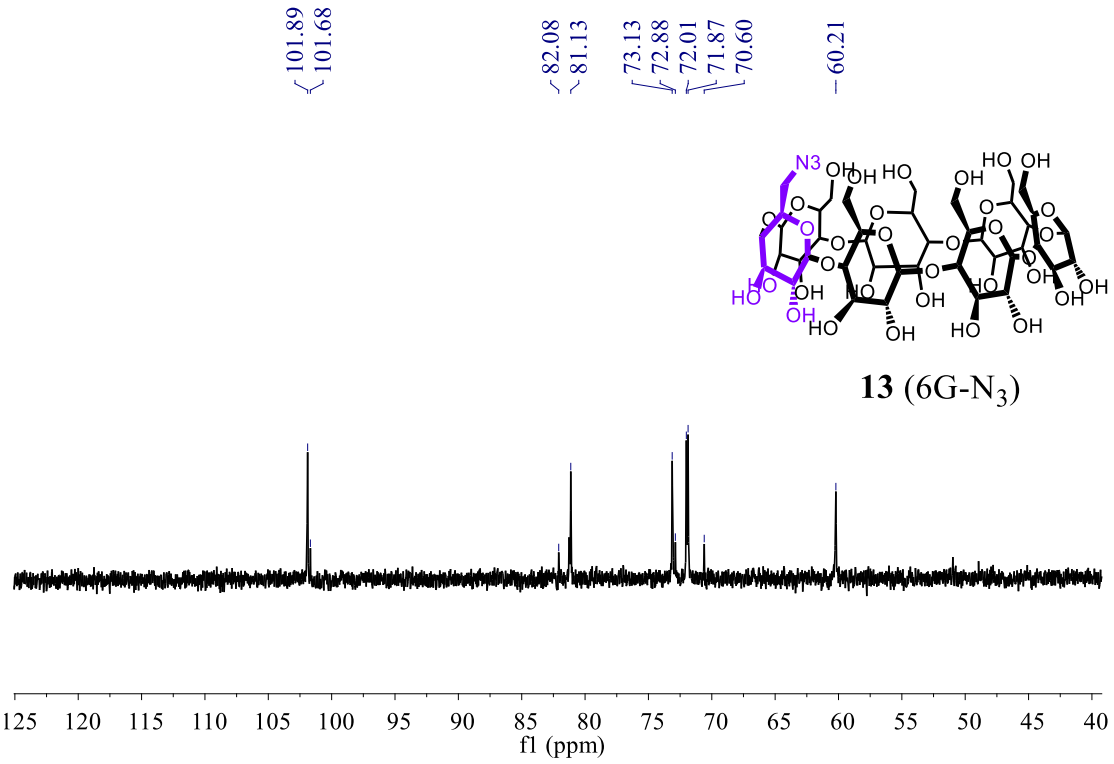


Figure S10. ^{13}C NMR spectrum of **13** (101 MHz, D_2O).

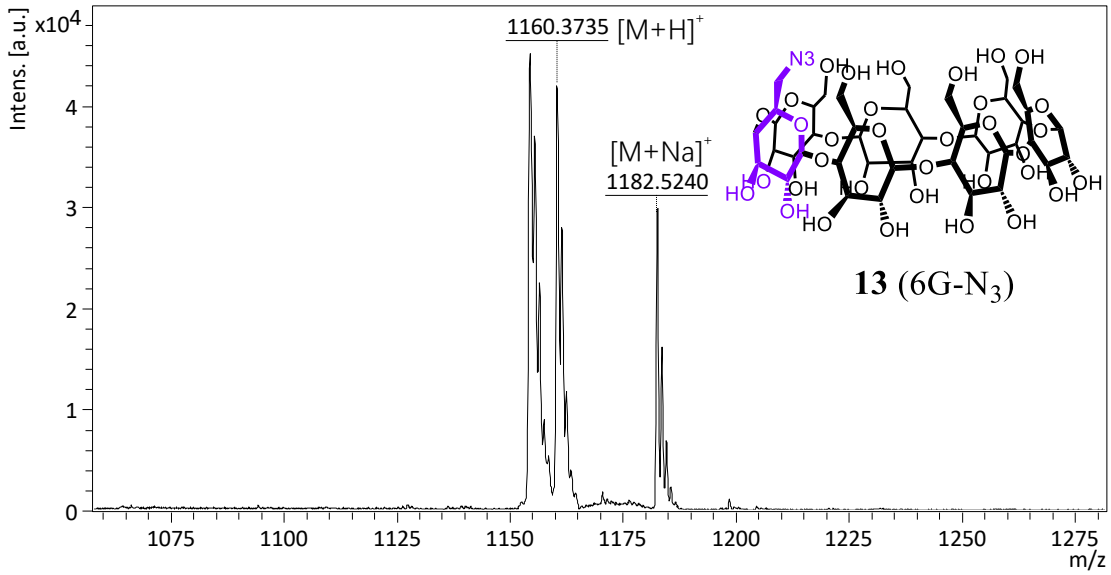


Figure S11. MALDI-HRMS spectrum of **13**.

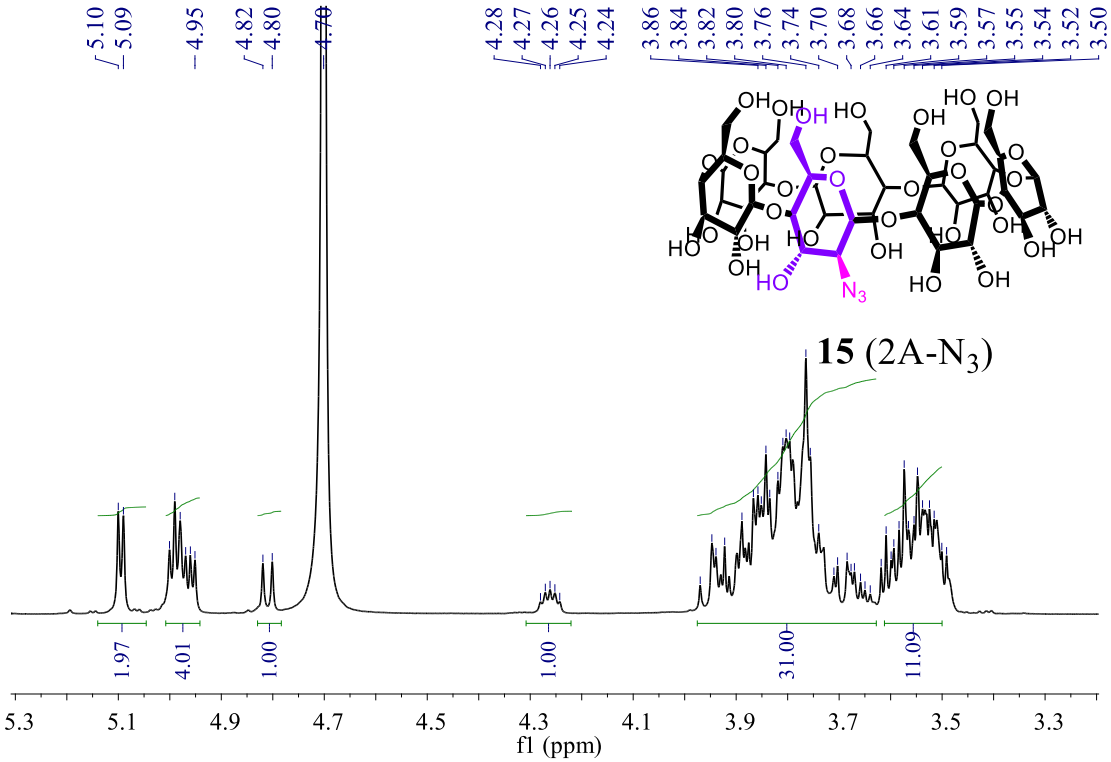


Figure S12. ^{1}H NMR spectrum of **15** (400 MHz, D_2O).

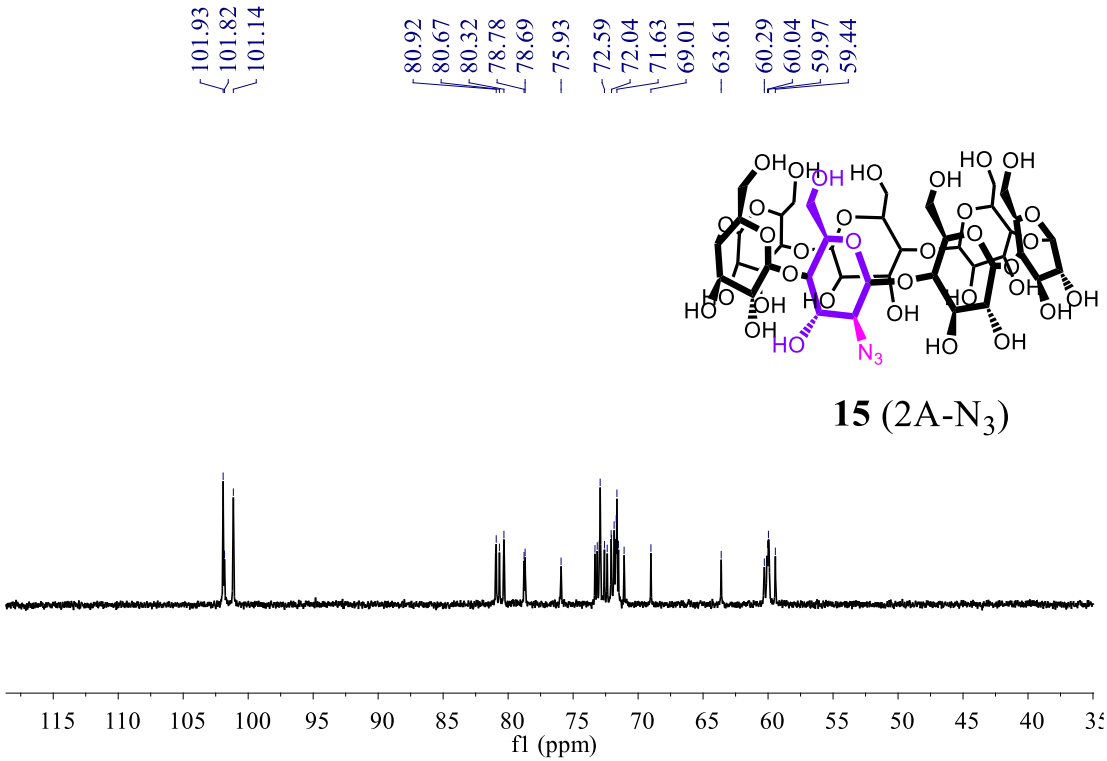


Figure S13. ^{13}C NMR spectrum of **15** (101 MHz, D_2O).

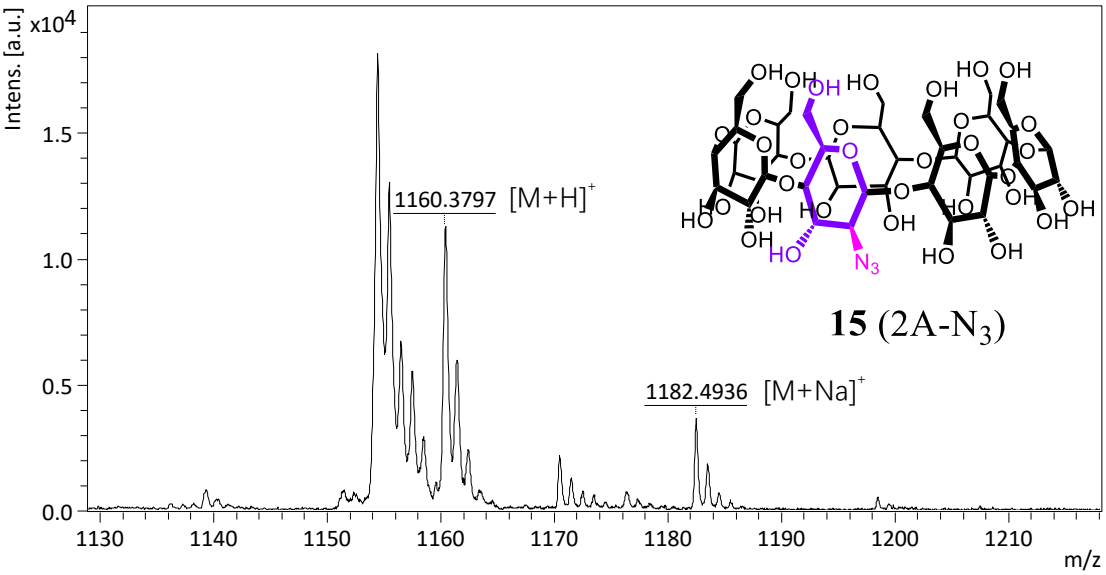


Figure S14. MALDI-HRMS spectrum of **15**.

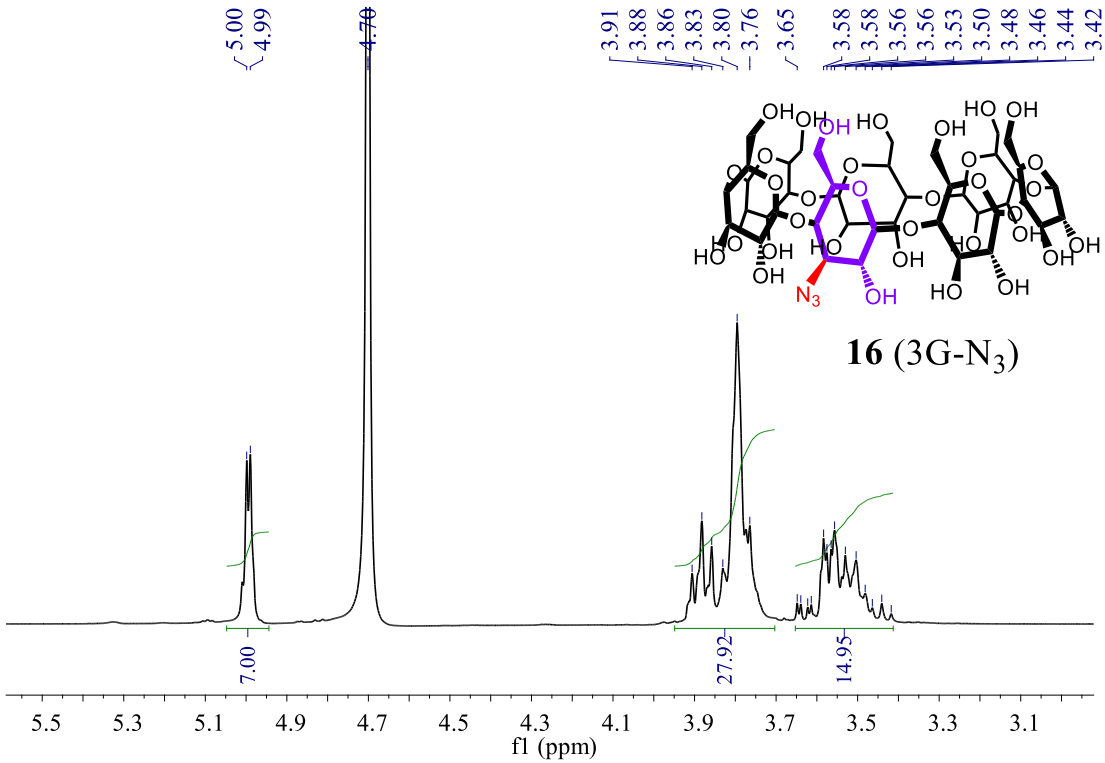


Figure S15. ^{1}H NMR spectrum of **16** (400 MHz, D_2O).

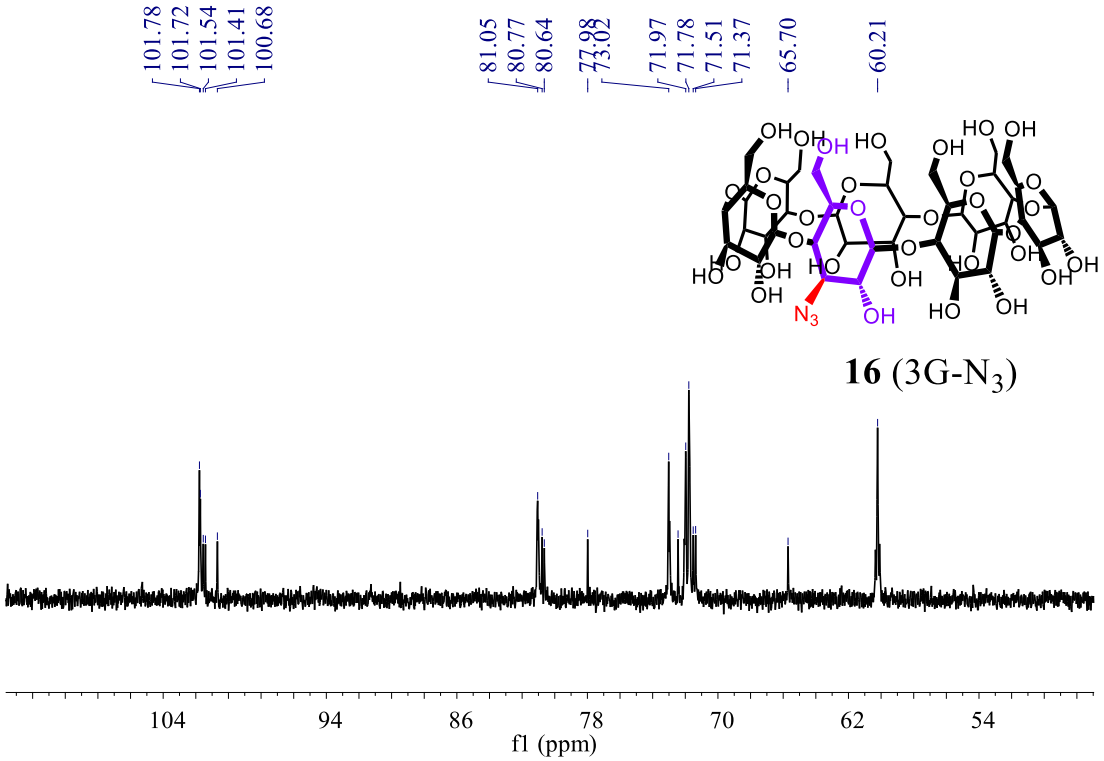


Figure S16. ^{13}C NMR spectrum of **16** (101 MHz, D_2O).

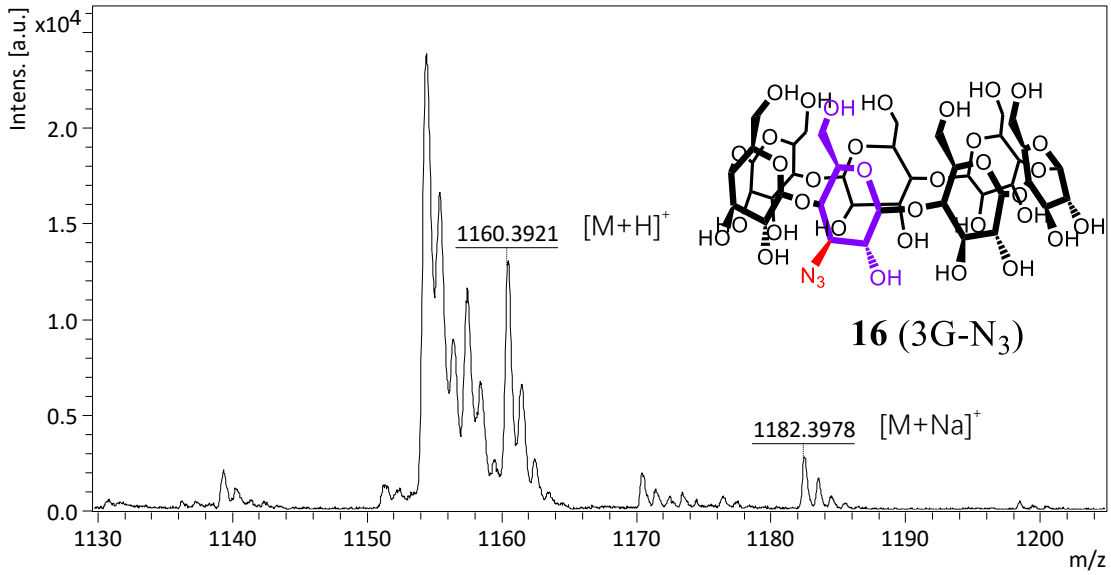


Figure S17. MALDI-HRMS spectrum of **16**.

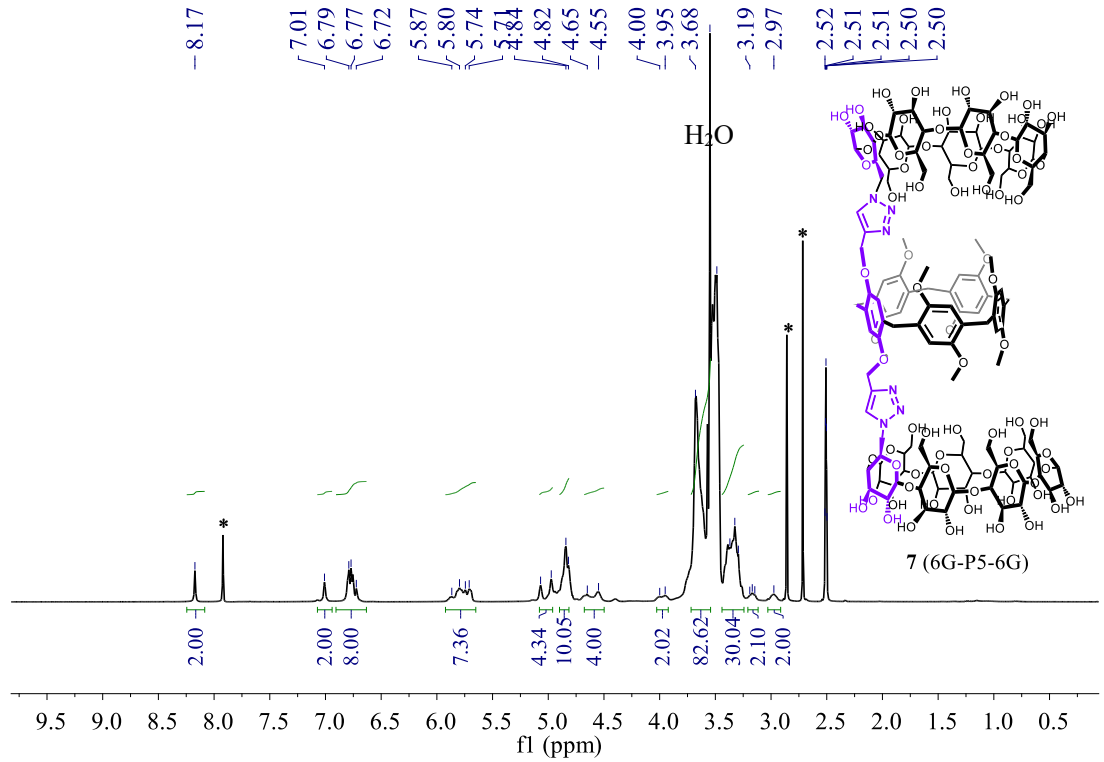


Figure S18 ^{1}H NMR spectrum of **7** (400 MHz, DMSO-d_6). *DMF.

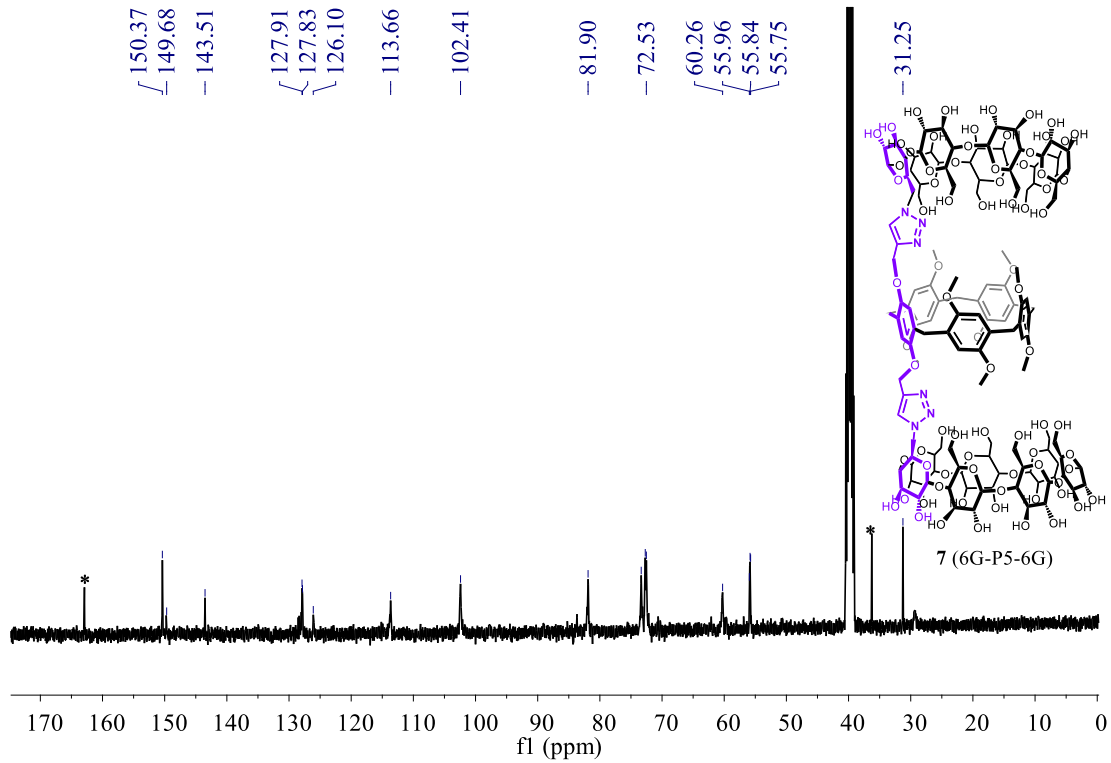


Figure S19. ^{13}C NMR spectrum of **7** (101 MHz, DMSO-d_6). *DMF

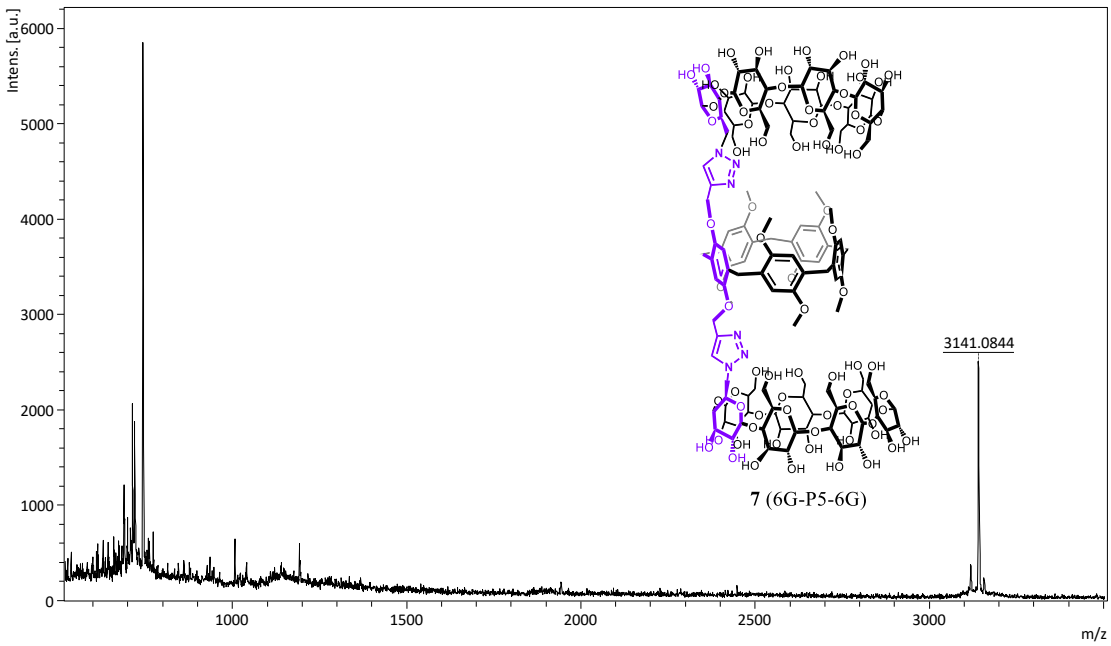


Figure S20. MALDI-HR-MS spectrum of **7**.

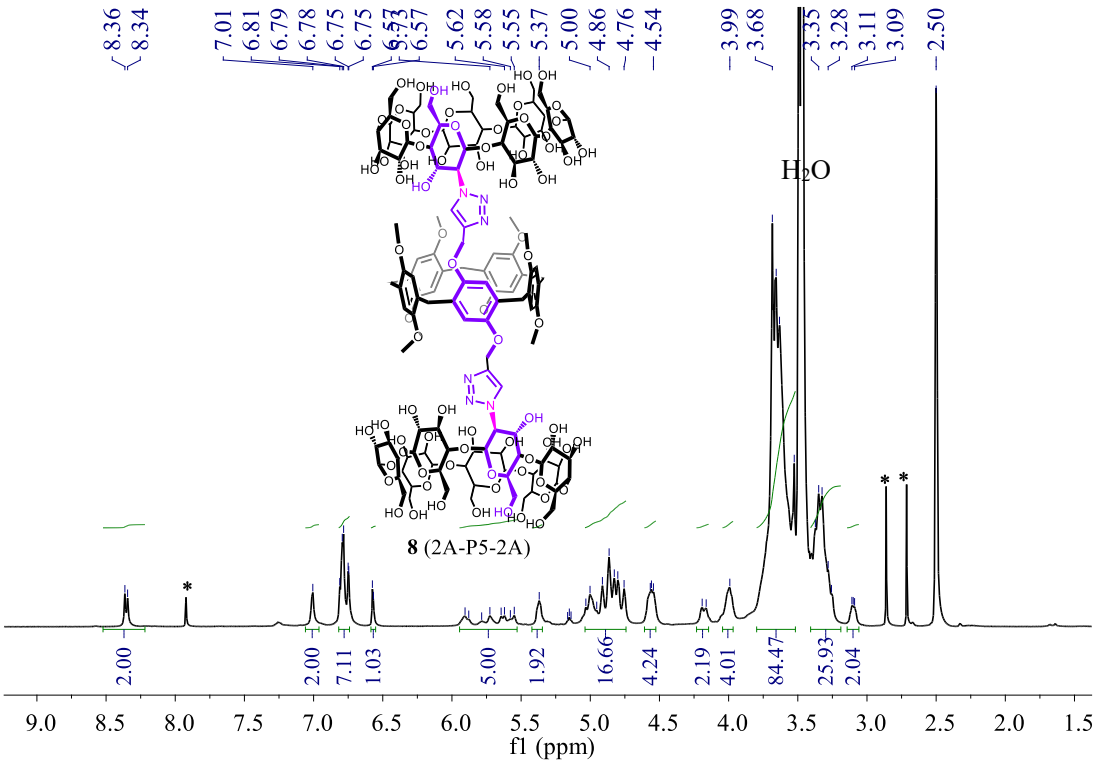


Figure S21 ^{1}H NMR spectrum of **8** (400 MHz, DMSO-d_6). *DMF.

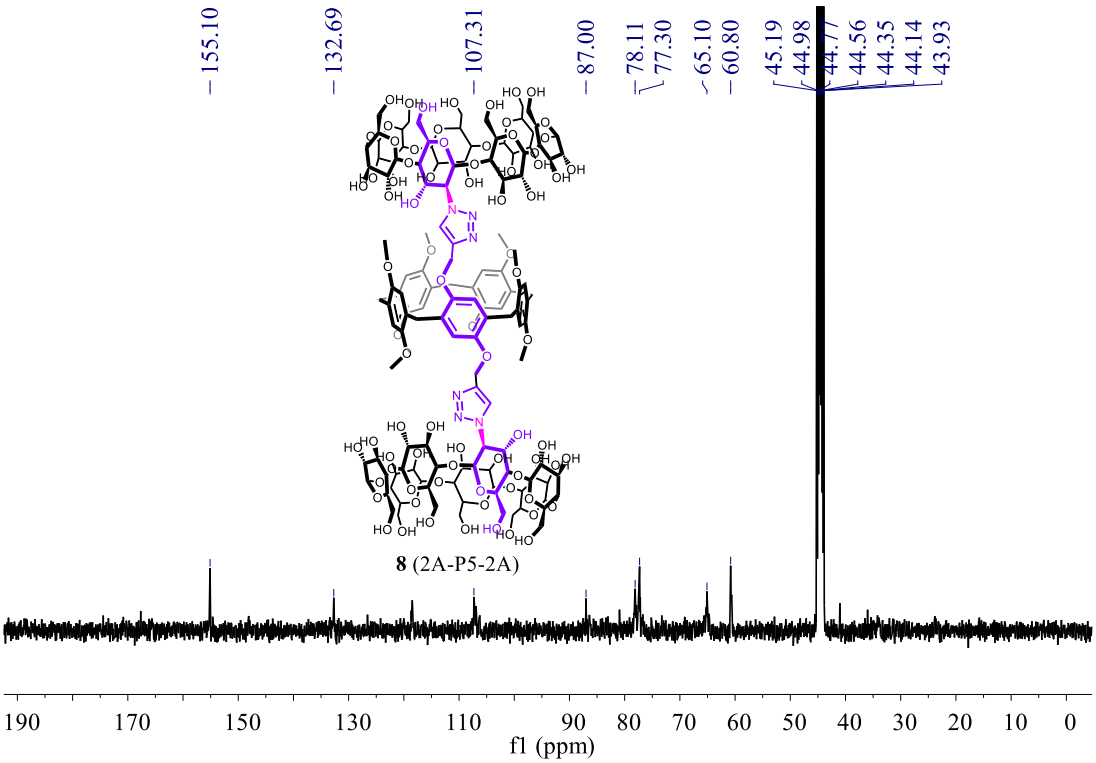


Figure S22. ^{13}C NMR spectrum of **8** (101 MHz, DMSO-d_6).

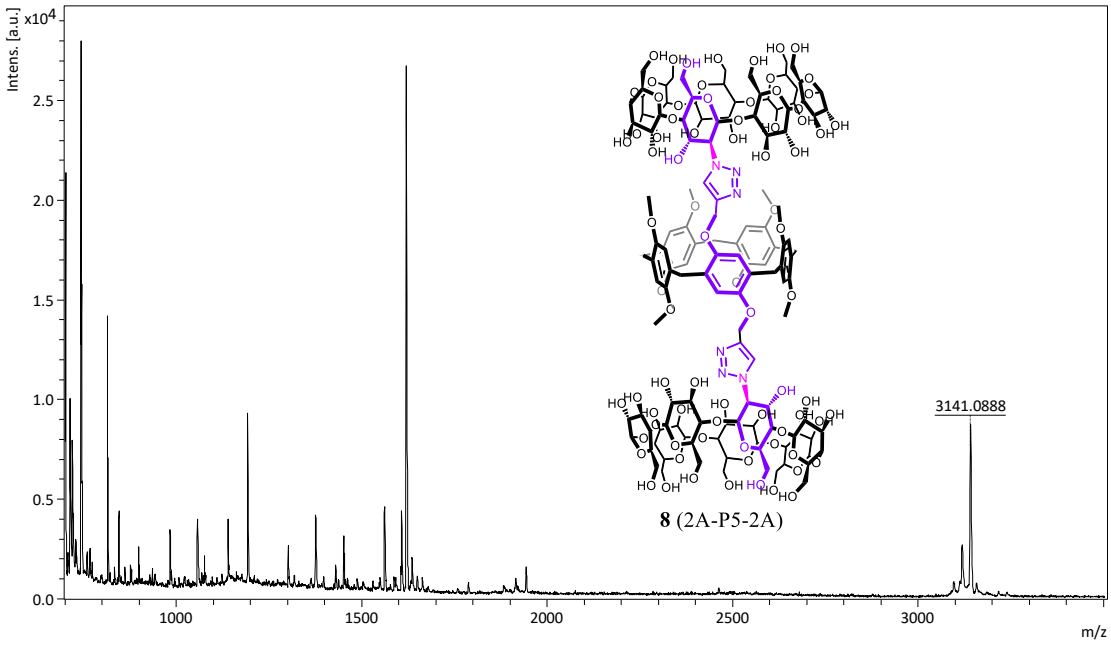


Figure S23. MALDI-HR-MS spectrum of **8**.

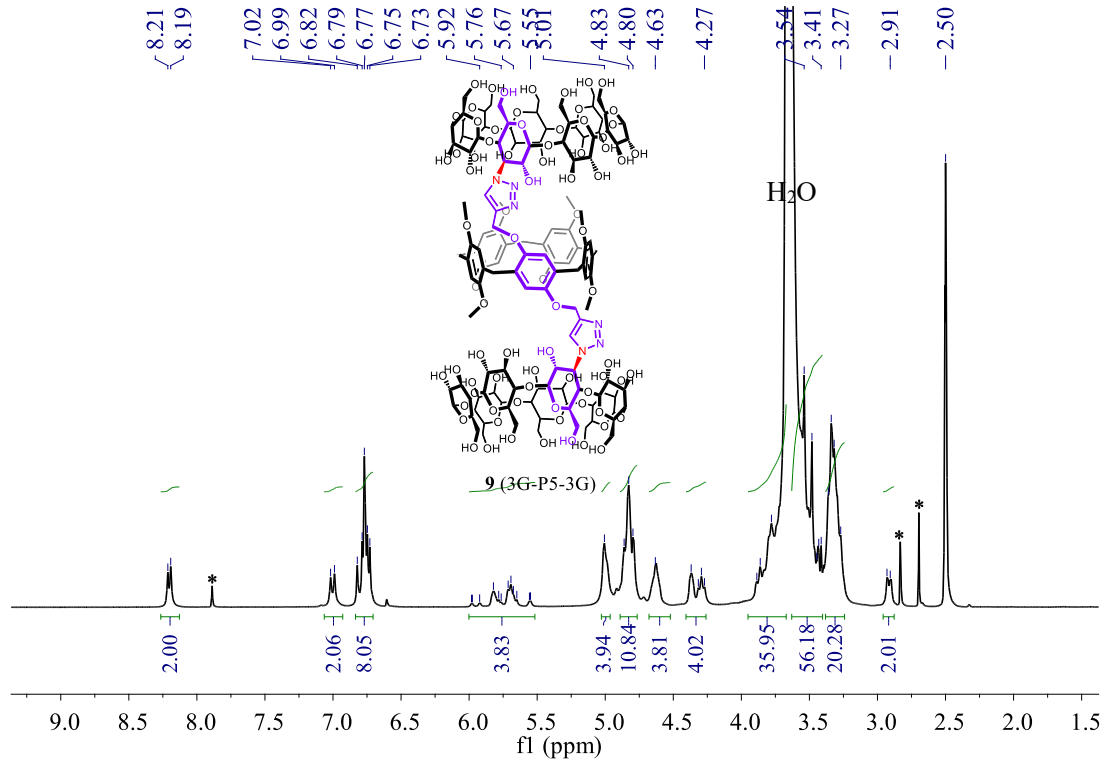


Figure S24 ^{1}H NMR spectrum of **9** (400 MHz, DMSO-d_6). *DMF.

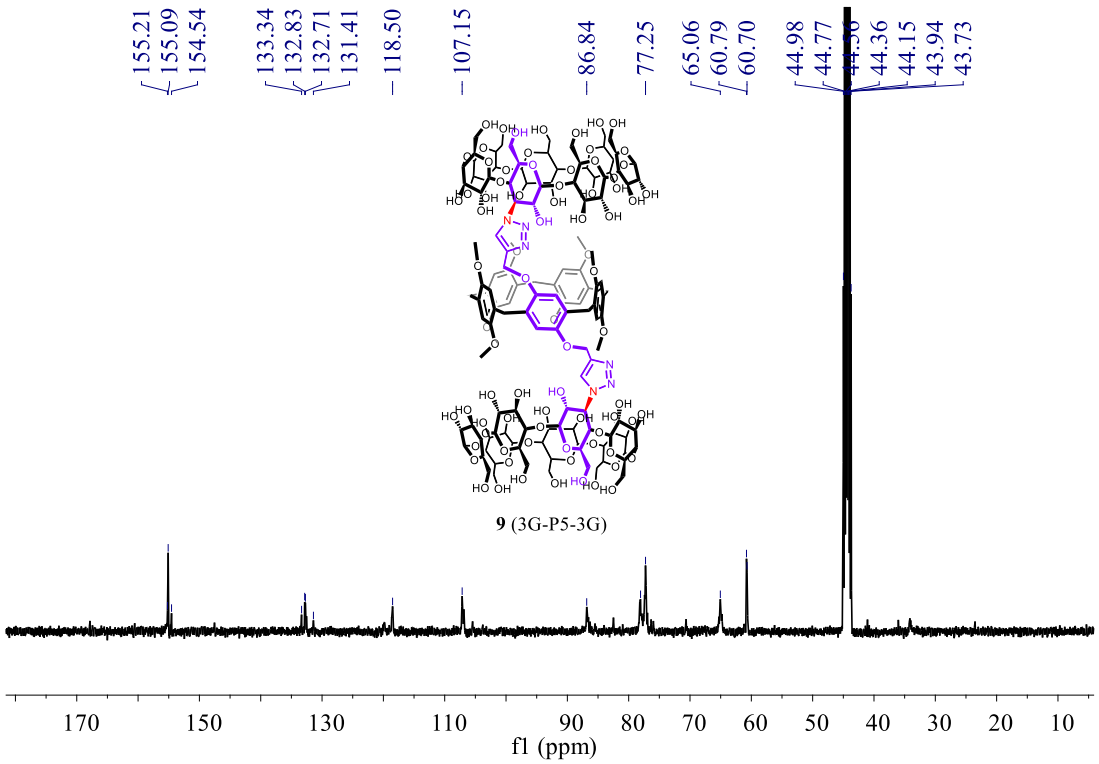


Figure S25. ^{13}C NMR spectrum of **9** (101 MHz, DMSO-d_6).

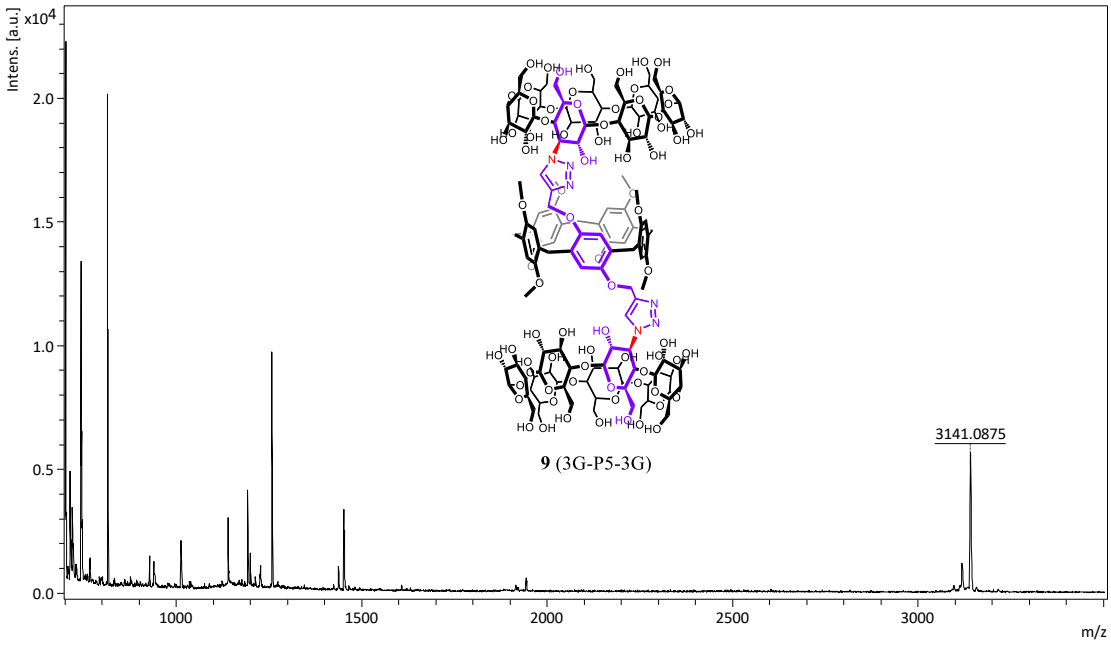


Figure S26. MALDI-HR-MS spectrum of **9**.

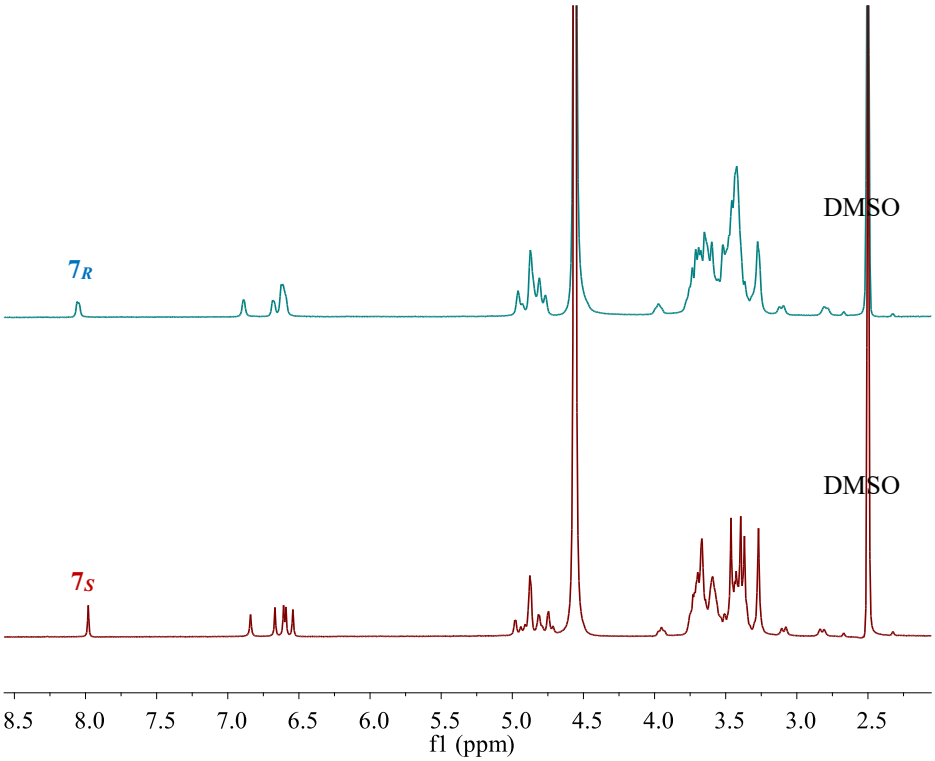


Figure S27. ^{1}H NMR spectra of **7*S*** (dark red) and **7*R*** (dark cyan) (400 MHz, DMSO-d_6: D_2O = 5:2, v/v) at room temperature.

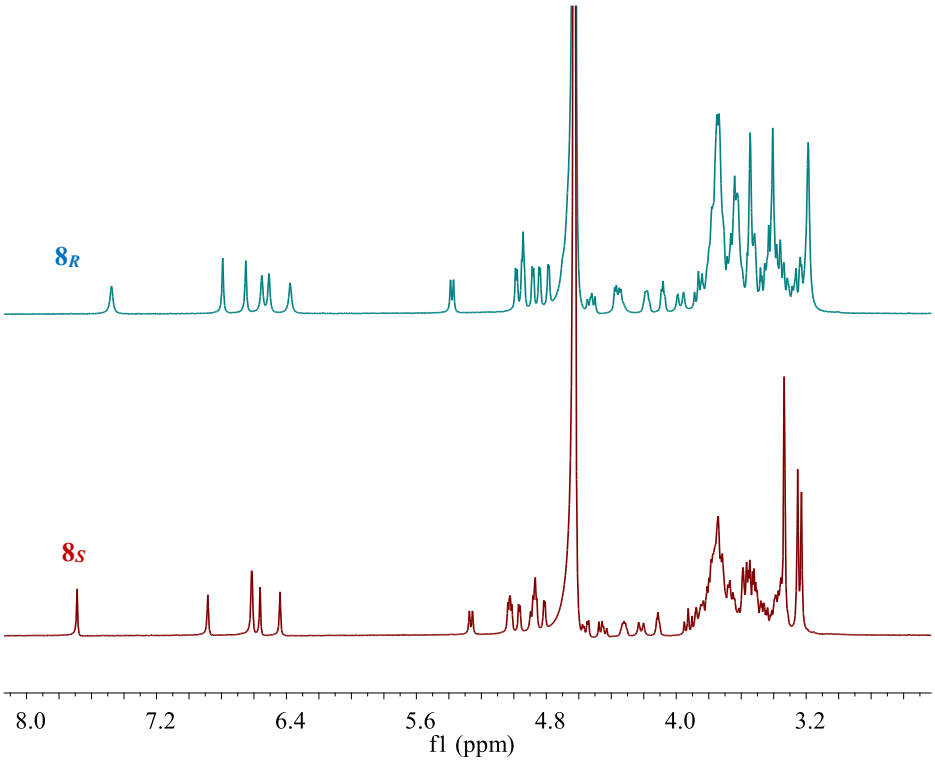


Figure S28. ^{1}H NMR spectra of **8*S*** (dark red) and **8*R*** (dark cyan) (400 MHz, D_2O) at room temperature.

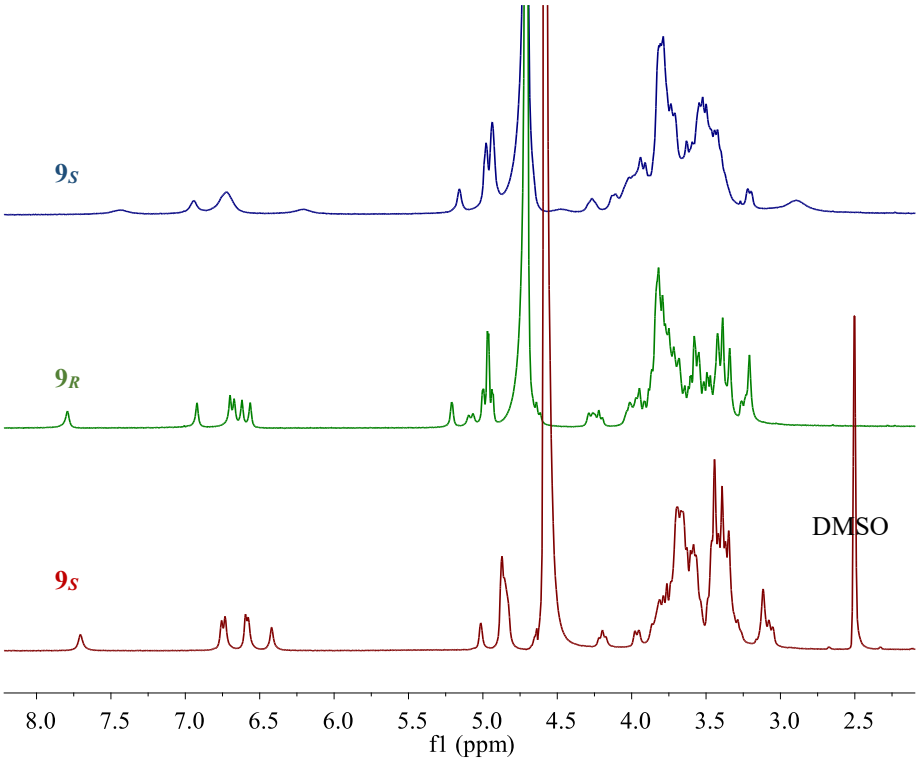


Figure S29. ^{1}H NMR spectra of **9*S*** (dark blue) and **9*R*** (dark cyan) (400 MHz, D_2O), and **9*S*** in a mixed solvent (dark red, 400 MHz, DMSO-d_6: D_2O = 5:1, v/v) at room temperature.

4. Binding Behavior

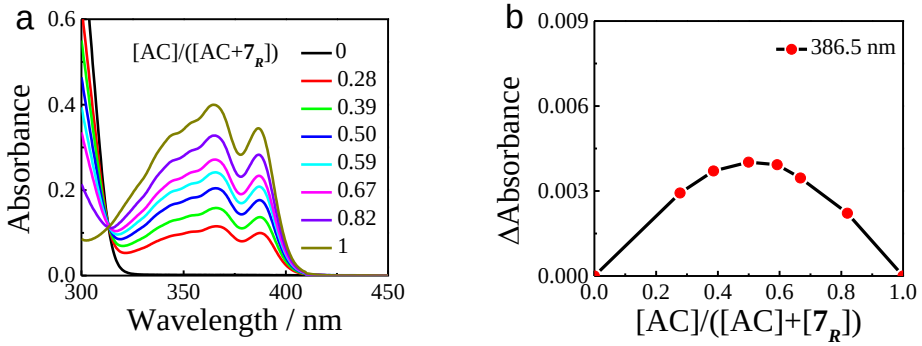


Figure S30. a) UV-vis spectra of AC and **7*R*** in different fractions (pH = 9.0, [buffer] = 25 mM) at 25 °C, where the total concentration ([AC] + [**7*R***] = 0.1 mM) as kept constant at 0.1 mM. b) The Job plots of the absorbance changes at 386.5 nm).

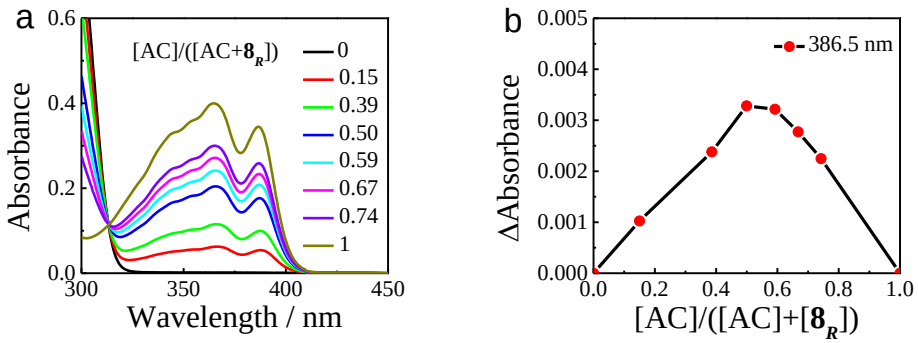


Figure S31. a) UV-vis spectra of AC and $\mathbf{8}_R$ in different fractions (pH = 9.0, [buffer] = 25 mM) at 25 °C, where the total concentration ([AC] + [$\mathbf{8}_R$] = 0.1 mM) as kept constant at 0.1 mM. b) The Job plots of the absorbance changes at 386.5 nm).

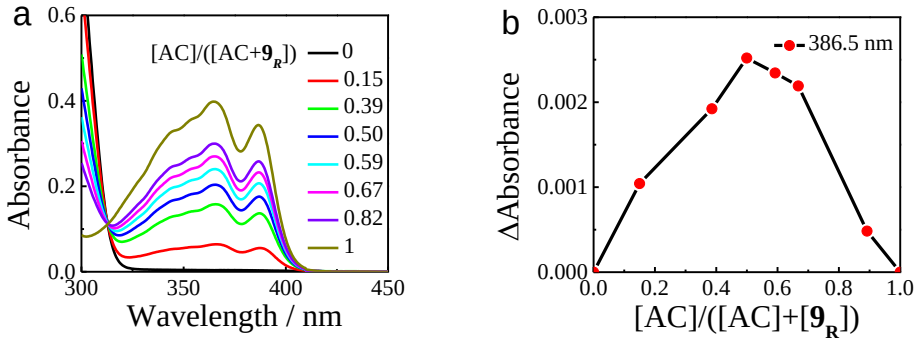


Figure S32. a) UV-vis spectra of AC and $\mathbf{9}_R$ in different fractions (pH = 9.0, [buffer] = 25 mM) at 25 °C, where the total concentration ([AC] + [$\mathbf{9}_R$] = 0.1 mM) as kept constant at 0.1 mM. b) The Job plots of the absorbance changes at 368.5 nm).

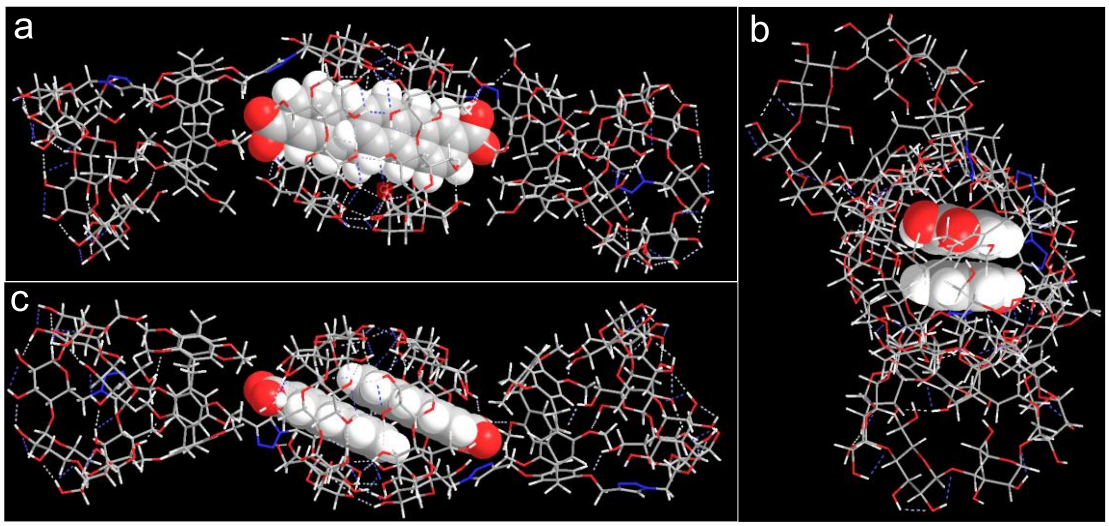


Figure S33. MM2-optimized structures 2:2 complexes of AC with trimer CD host $\mathbf{7}_R$: (a) front view, (b) left view, (c) top view. Color code: white for hydrogen, grey for carbon, red for oxygen, blue for nitrogen, blue and white dotted line for hydrogen bond.

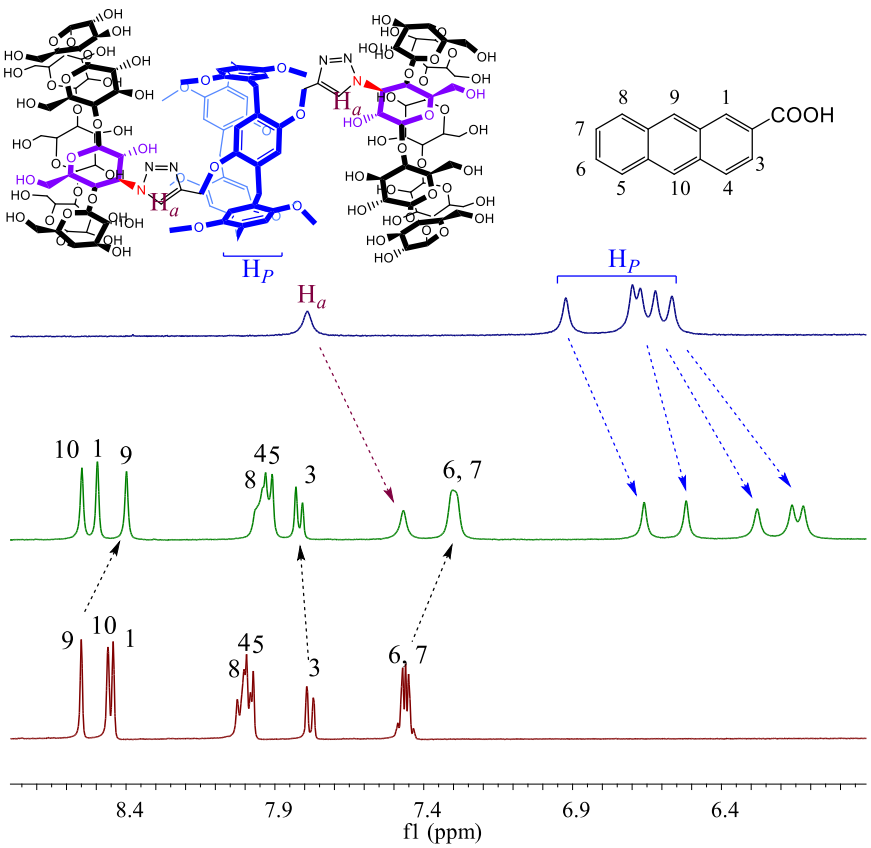


Figure S34. ^{1}H NMR spectra (400 MHz, D_2O) of $\mathbf{9}_R$ (2.0 mM), $\mathbf{9}_R$ +AC ([AC] = 2[$\mathbf{9}_R$] = 4.0 mM), AC (4.0 mM) in D_2O contain 10 mM NaOH.

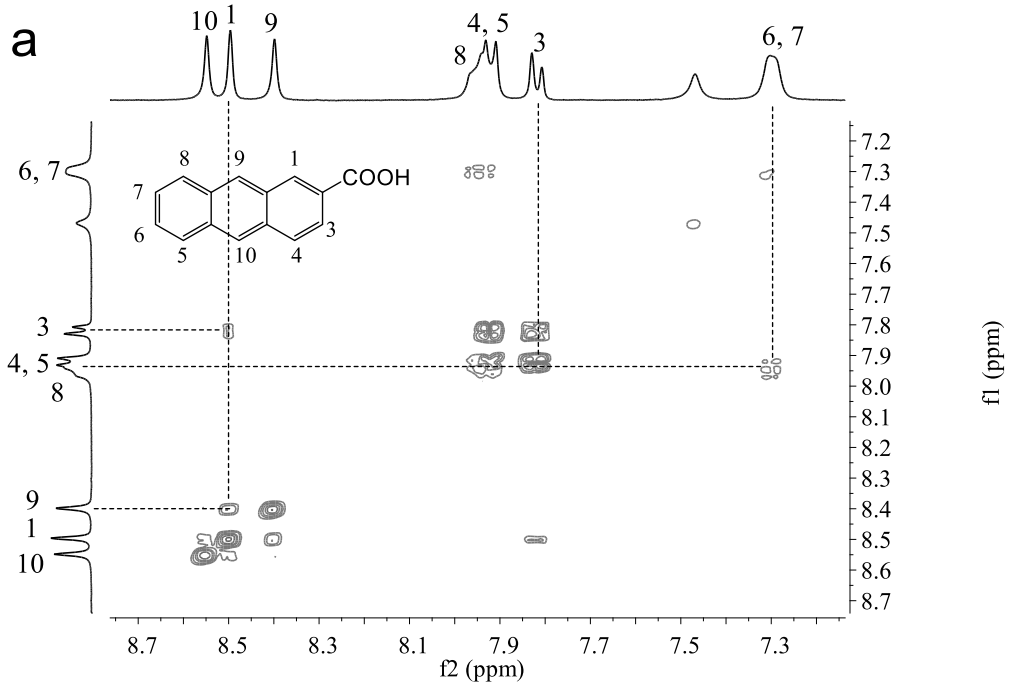


Figure S35. ^{1}H-^{1}H COSY NMR spectra of $\mathbf{9}_R$+AC ([AC] = 2[$\mathbf{9}_R$] = 4.0 mM) in D_2O contain 10 mM NaOH (400 MHz, D_2O).

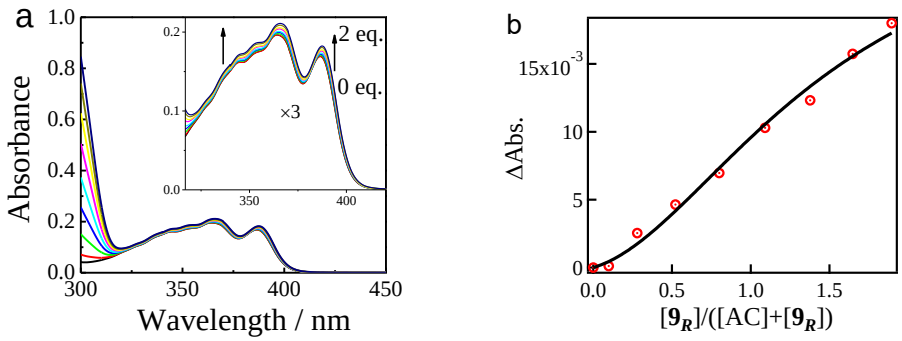


Figure S36. a) UV-vis spectra of AC (0.05 mM) with increasing the concentration of $\mathbf{9}_{R}$ in buffer (pH = 9.0, 25 mM) at 25 °C. b) A least-mean-squares fit of the absorption changes at 389 nm gave the 1:1 association constant (K_1) and the 1:2 association constant (K_2), K_1 = 43200 ± 3000 M^{-1}, K_2 = 520 ± 40 M^{-1}.

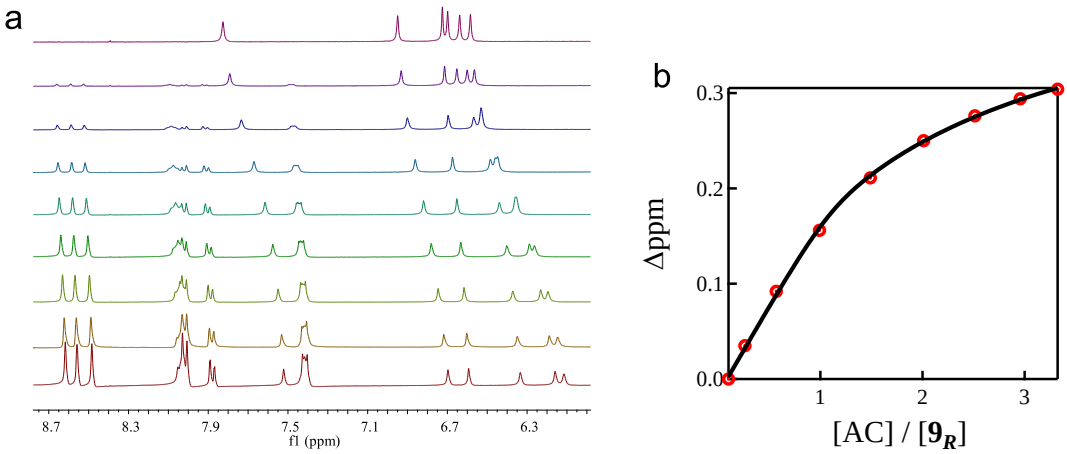


Figure S37. a) NMR spectra of $\mathbf{9}_{R}$ (0.05 mM) with increasing the concentration of **AC** in buffer ([NaOH] = 10 mM) at 25 °C. b) A least-mean-squares fit of the peak changes at 7.83 ppm (Ha) gave the 1:1 association constant (K_1) and the 1:2 association constant (K_2), K_1 = 46000 ± 2800 M^{-1}, K_2 = 480 ± 50 M^{-1}.

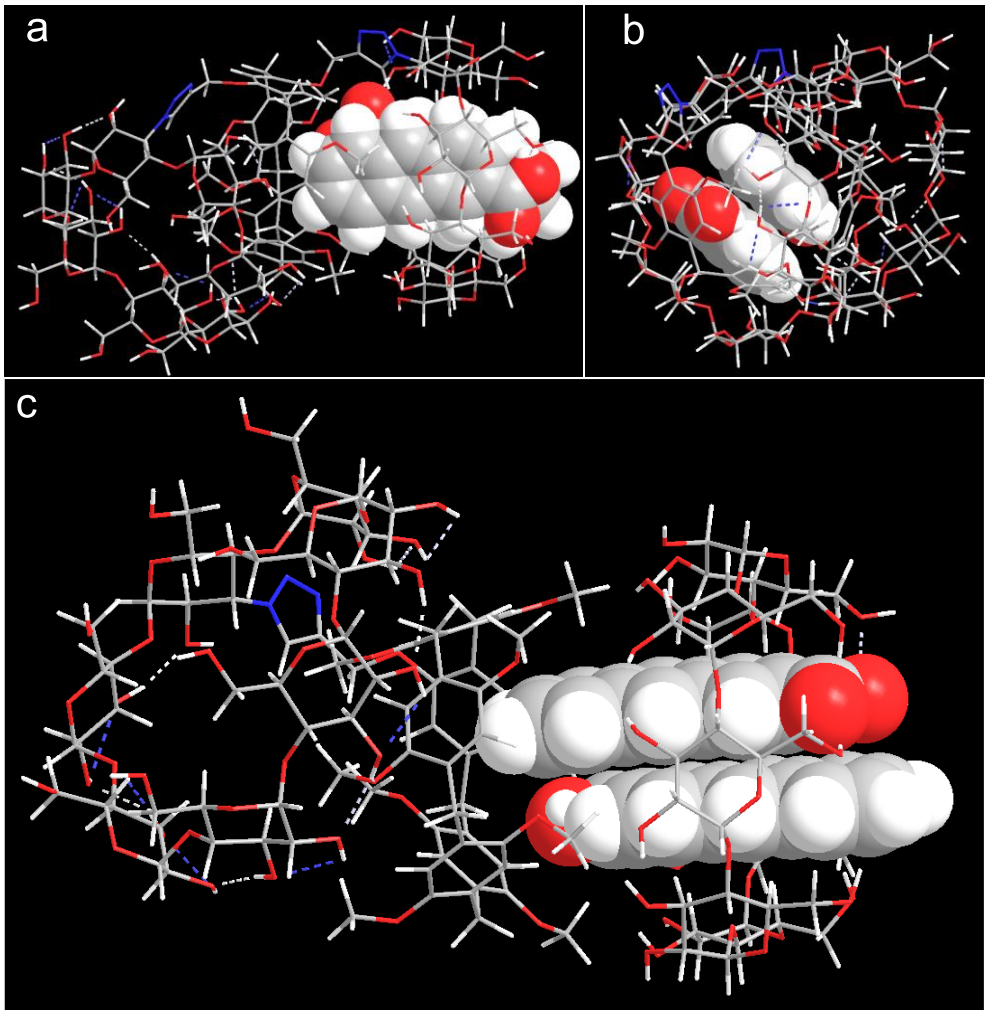


Figure S38. MM2-optimized structures 1:2 complexes of AC with trimer CD host **9*R***: (a) front view, (b) left view, (c) top view. Color code: white for hydrogen, grey for carbon, red for oxygen, blue for nitrogen, blue and white dotted line for hydrogen bond.

5. Photoreaction Studies

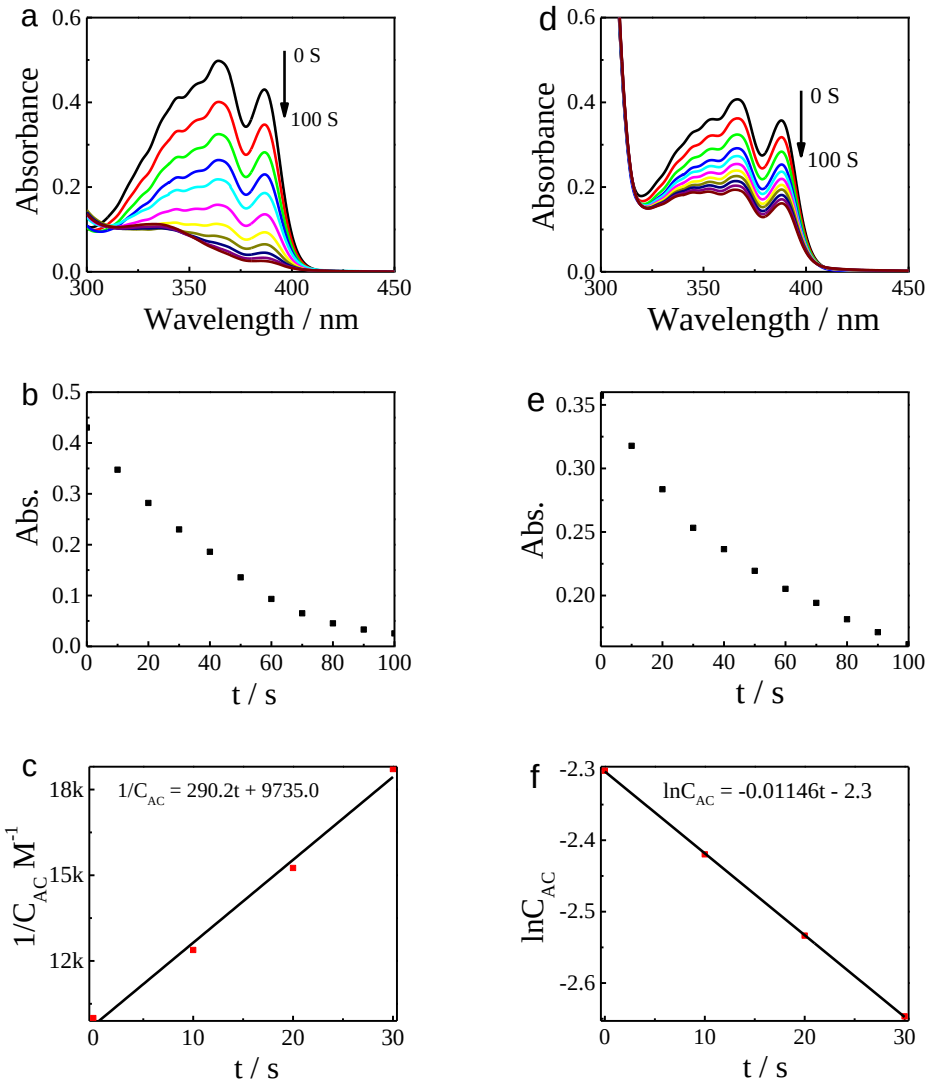


Figure S39. (a) UV-vis spectral changes upon photolysis (irradiation by 200 mW LED at 365 nm) of AC (0.1 mM) in buffer (pH = 9.0) at 25 °C. (b) Absorbance changes at 386.5 nm upon photolysis of AC. (c) Second-order kinetics plot, affording k_2 = 290.2 ± 17.1 M^{-1} s^{-1}. Thus, if [AC] = 0.1 mM, then k_2[AC] = 0.029 s^{-1}. (d) UV-vis spectral change upon photolysis (irradiation by 200 mW LED at 365 nm) of AC (0.1 mM) in the presence of 0.2 mM $\mathbf{9}_R$ in buffer (pH = 9.0) at 25 °C. (e) Absorbance changes at 388 nm upon photolysis of AC in the presence of $\mathbf{9}_R$. (f) First-order kinetics plot, affording k_1 = 0.0115 ± 0.00007 s^{-1}. The real acceleration as 14-fold by $\mathbf{9}_R$ when concentration of AC is 0.1 mM.

Table S1. Supramolecular Photocyclodimerization of 2-Anthracenecarboxylate (AC) Mediated by Native and Chiral Hosts in Borate Buffer (pH 9.0) at Different Temperature [a]

[$\mathbf{9}_R$]/ mM	T/°C	[CsCl] / M	Conv. [b] /%	yield [b] /%						nonclassical [c] /%	ee [b] /%			
				1	**2**	**3**	**4**	**5**	**6**		**2**	**3**	**5**	**6**
0.2	-20	6	20	18	4	11	10	45	12	57	-25	-10	63	34
	-10	6	16	18	4	12	13	42	11	53	-21	-9	62	26
	0.5	6	19	18	4	11	12	43	12	55	-20	-9	62	22
0.2	0.5	0	28	34	28	17	13	6	2	5	-18	-15	87	*d*
0.1	0.5	0	36	35	32	14	10	7	2	7	-5	-6	86	*d*
0.05	0.5	0	53	37	35	14	10	3	2	6	-2	-2	83	*d*

[a] [AC] = 0.1 mM, pH = 9.0; irradiated at 365 nm for 30 min with a 200-mW LED, unless stated otherwise. [b] Determined by HPLC. [c] Nonclassical cyclodimer content: [(**5** + **6**)/(**1** + **2** + **3** + **4** + **5** + **6**)] × 100. [d] Not determined due to the extremely low yield (<0.1%) or affected by high and broad peak of AC.

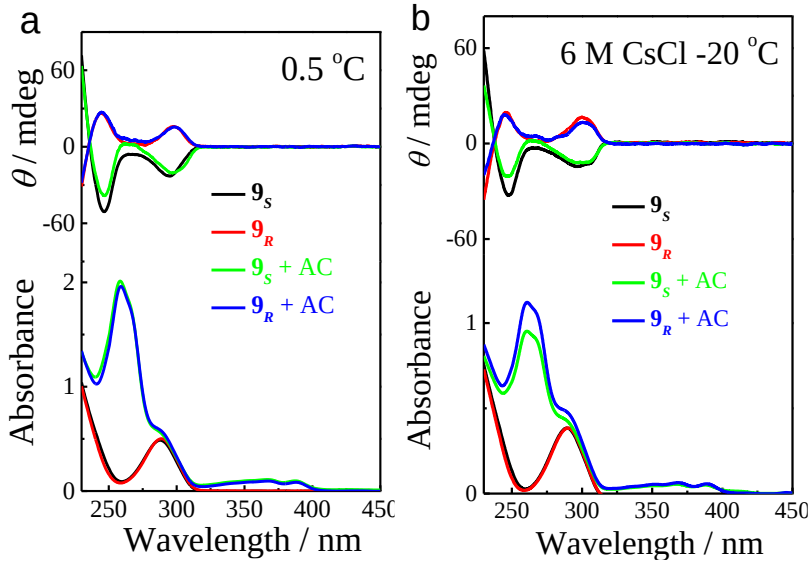


Figure S40. Circular dichroism (top) and UV (bottom) spectra of $\mathbf{9}_S$, $\mathbf{9}_R$ in presence and absence of AC in buffer ([buffer] = 25 mM, [host] = 0.2 mM = 2[AC], pH = 9.0) at different conditions. a) 0.5 °C. b) Containing CsCl (6 M) at 0.5 °C. All measured in 2 mm cell.

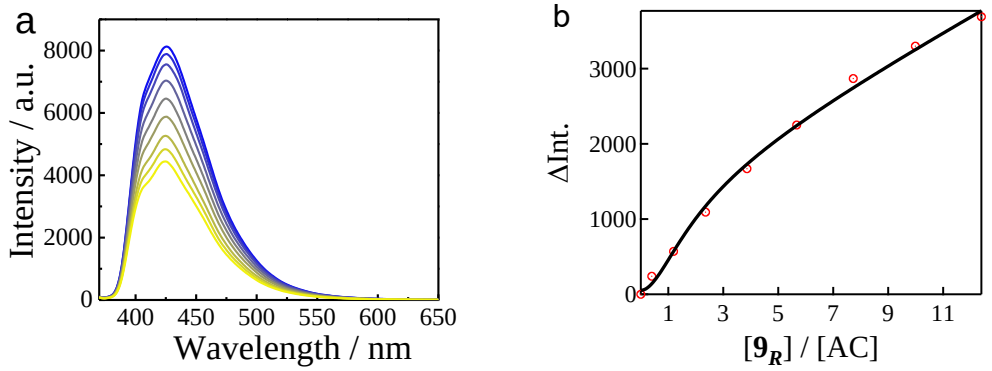


Figure S41. a) Fluorescence spectra of **AC** (0.02 mM) with increasing the concentration of $\mathbf{9}_R$ in buffer ([CsCl] = 500 mM) at 25 °C. b) A least-mean-squares fit of the peak changes at 425.5 nm gave the 1:1 association constant (K_1) and the 1:2 association constant (K_2), K_1 = 75000 ± 14000 M^{-1}, K_2 = 1100 ± 200 M^{-1}.

6. Reference

1 O. A. Zhikol, S. V. Shishkina, V. V. Lipson, A. N. Semenenko, A. V. Mazepa, A. V. Borisov and P. V. Mateychenko, *New J. Chem*., 2019, **43**, 13112-13121.

2 J. Ji, W. Wu, W. Liang, G. Cheng, R. Matsushita, Z. Yan, X. Wei, M. Rao, D.-Q. Yuan and G. Fukuhara, *J. Am. Chem. Soc.*, 2019, **141**, 9225-9238.

3 D.-Q. Yuan, T. Tahara, W.-H. Chen, Y. Okabe, C. Yang, Y. Yagi, Y. Nogami, M. Fukudome and K. Fujita, *J. Org. Chem.*, 2003, **68**, 9456-9466.