Electronic Supporting Information

Cagearenes: synthesis, characterization, and application for programmed vapour release

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1. Experimental Section

1.1 General Methods

All reagents and solvents were purchased from commercial sources and used without further purification. Manipulations were performed under a normal laboratory atmosphere unless otherwise noted. Nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature using Bruker AVANCE III 400/500 and Agilent DD2 600 spectrometers, with working frequencies of 400/500/600 and 100/125/150 MHz for ^{1}H and ^{13}C, respectively. Chemical shifts were reported in ppm relative to the residual internal non-deuterated solvent signals ($CDCl_3$: $\delta = 7.26$ ppm). High resolution mass spectroscopic measurements were performed on Bruker Daltonics Autoflex III (MALDI-TOF). Single crystal X-ray data sets were measured on an Oxford Gemini A Ultra diffractometer (Mo-Kα radiation, $\lambda = 0.71073$ Å, Atlas CCD detector).

1.2 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out on a thermogravimetric analyzer (TGA2, METTLER TOLEDO, Switzerland). The samples were heated at a rate of 10 °C per min.

1.3 Powder X-ray Diffraction

Powder X-ray diffraction (PXRD) data were collected on a Rigaku Smartlab 9 kW X-ray diffractometer operating at 45 kV/200 mA using the Cu Kα line ($\lambda = 1.5418$ Å). PXRD patterns were measured over the 2θ range of 3−30° with 10° per min.

1.4 BET Surface Area Measurement

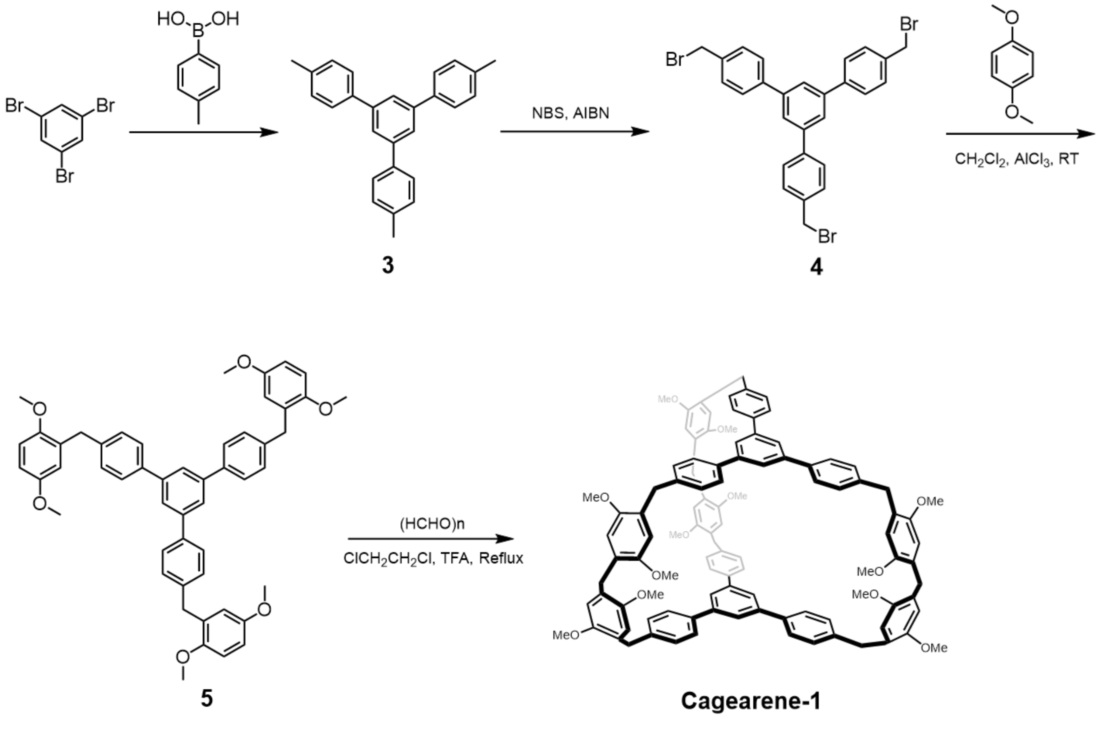
Brunauer-Emmett-Teller (BET) surface area measurement was performed on a Quantachrome AUTOSORB-1-C surface area analyzer. Samples were degassed under dynamic vacuum for 12 h at 200 °C before each measurement. N_2 isotherms were measured using a liquid nitrogen bath (77 K).

1.5 Adsorption Experiments

Pure **cagearene-1** was obtained through column chromatography. Then, desolvated **cagearene-1** were recrystallized from ethyl acetate first and dried under vacuum at 120 °C overnight.

For each solid-vapour sorption experiment, an open 2 mL vial containing 10.0 mg of activated **cagearene-1** adsorbent was placed in a sealed 20 mL vial containing 0.5 mL of solvent or solvent mixture (50:50 *v*/*v*). After absorption, the open 2 mL vial containing 10.0 mg of activated **cagearene-1** adsorbent was put into a drying oven at 40 °C for 5 min to remove the vapours at the solid surface. Relative uptake amount in the **cagearene-1** adsorbent was determined by ^{1}H NMR integrals of the corresponding proton signals after completely dissolving materials in $CDCl_3$. Gas chromatographic characterizations were also performed in order to determine the relative uptake amounts of mixed solvents by the **cagearene-1** solid. Desorption experiments after saturation were carried out by thermogravimetric analysis.

2. Synthesis and Characterization of Compounds



Scheme S1 Synthesis of **cagearene-1**.

Compounds **3** and **4**: They were synthesized according to the literature.[S1,S2]

Compound **5**: 1,3,5-Tris(4*p*-bromomethylphenyl)benzene **4** (585 mg, 1.0 mmol) and 1,4-dimethoxybenzene (1.38 g, 10.0 mmol) were combined in a reaction flask. Anhydrous dichloromethane (DCM, 50 mL) was added. After the mixture was stirred over ten minutes, aluminum chloride ($AlCl_3$) (133 mg, 1.0 mmol) in DCM was added. The resulting mixture was stirred at room temperature for another 2 h until quenched with water. The organic layer was washed with water and brine, and concentrated through reduced pressure distillation. The residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 7:1) to give the product as white powder (347 mg, 46 %).

Melting point: 183–186 °C. The ^{1}H NMR spectrum of compound **5** is shown in Fig. S1. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71(s, 3H), 7.57(d, J = 8 Hz, 6H), 7.30 (d, J = 8 Hz, 6H), 6.80 (m, 3H), 6.70–6.72 (m, 6H), 4.00 (s, 6H), 3.76 (s, 9H), 3.71 (s, 9H). The ^{13}C NMR spectrum of compound **5** is shown in Fig. S2. ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.61, 151.76, 142.17, 140.22, 138.90, 129.44, 127.30, 124.72, 116.94, 114.70, 111.51, 111.38, 56.09, 55.69, 35.78. The MS spectrum of compound **5** is shown in Fig. S3. MS (MALDI-TOF): m/z calcd for $[\mathbf{M}]^+$ $C_{51}H_{48}O_6^+$, 756.3451; found 756.3468 (error: 2.2 ppm).

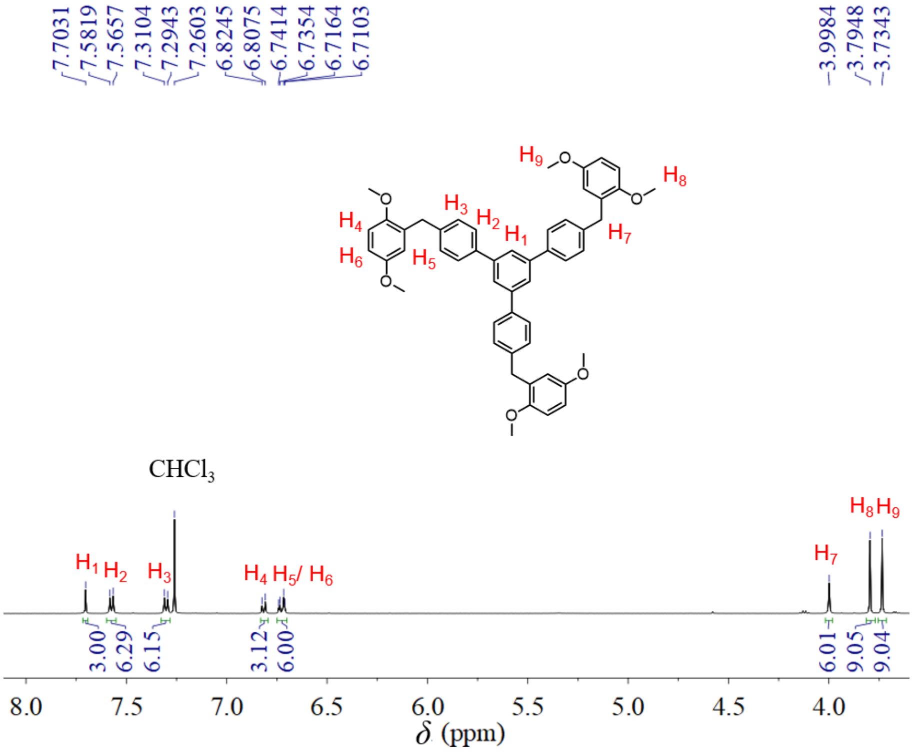


Fig. S1 ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of compound **5**.

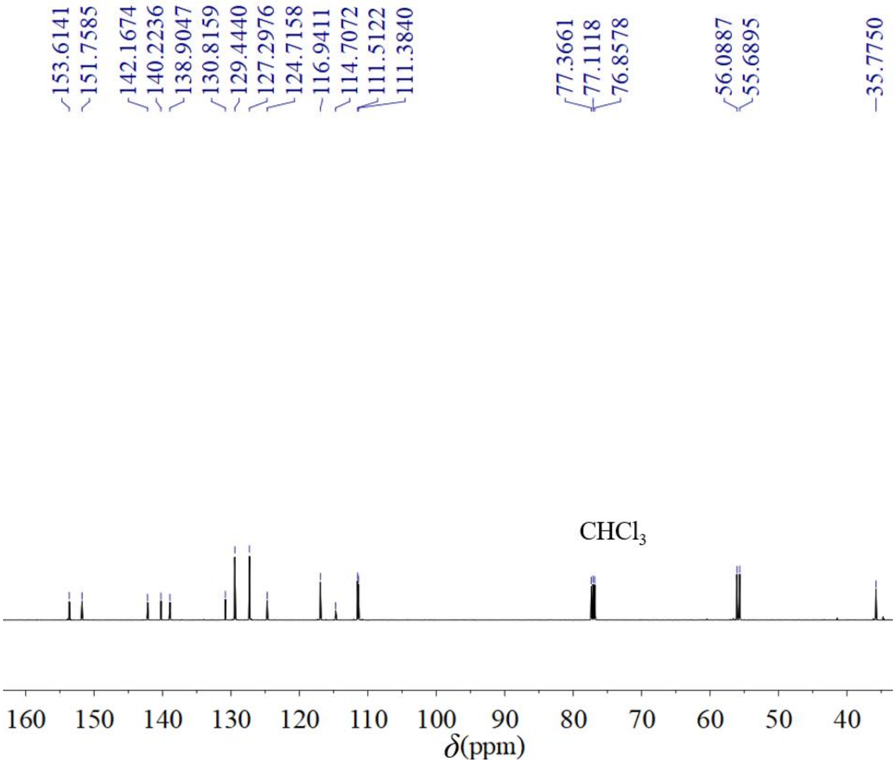


Fig. S2 ^{13}C NMR spectrum (125 MHz, 298 K, $CDCl_3$) of compound **5**.

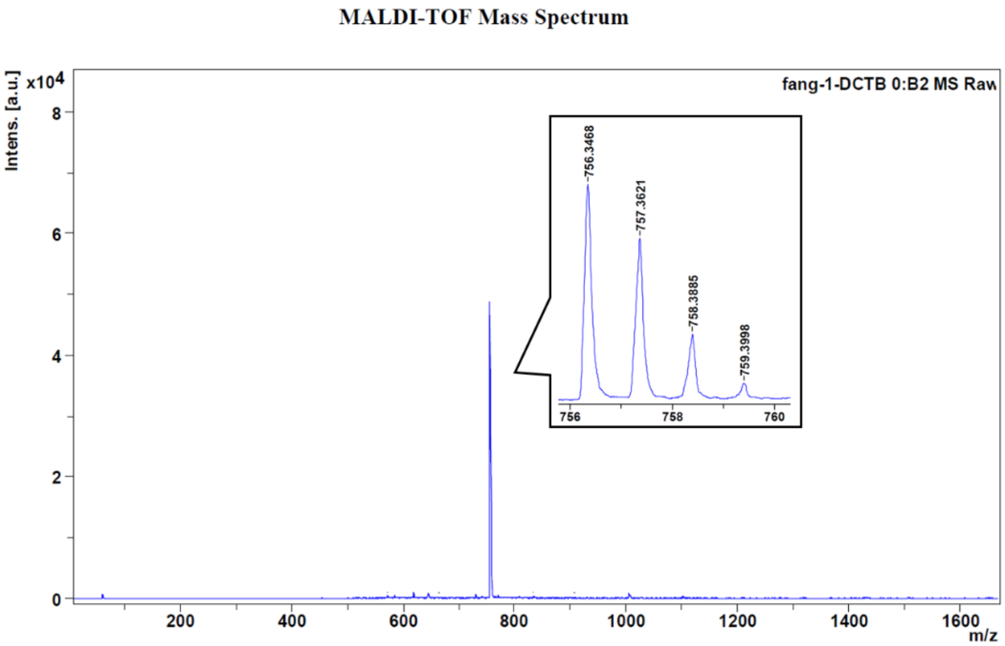


Fig. S3 Mass spectrum of compound **5**.

Cagearene-1: Compound **5** (756 mg, 1.0 mmol) and paraformaldehyde (180 mg, 6.0 mmol) were combined in a reaction flask under the nitrogen protection. Anhydrous dichloroethane (DCE, 100 mL) was added. After the mixture was stirred over half hour at 85 °C, trifluoroacetic acid (CF_3COOH) (1.0 mL) was added to the mixture. The resulting mixture was stirred at 85 °C for 12 h until quenched with water. The organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. The residue was concentrated through reduced pressure distillation, and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 7:1) to give the product as white powder (480 mg, 31%).

Melting point: **cagearene-1** is decomposed above 200 °C. The ^{1}H NMR spectrum of **cagearene-1** is shown in Fig. S4. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.48(s, 6H), 7.37(d, J = 8 Hz, 12H), 7.22 (d, J = 8 Hz, 12H), 6.82 (s, 6H), 6.69 (s, 6H), 3.91 (s, 12H), 3.88 (s, 6H), 3.76 (s, 18H), 3.70 (s, 18H). The ^{13}C NMR spectrum of **cagearene-1** is shown in Fig. S5. ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.36, 151.06, 141.97, 140.64, 138.78, 129.06, 128.36, 127.58, 127.04, 124.64, 114.46, 113.52, 56.15, 56.01, 36.13. The MS spectrum of **cagearene-1** is shown in Fig. S7. MS (MALDI-TOF): m/z calcd for [**M**]$^+$ $C_{105}H_{96}O_{12}^+$, 1548.6902; found 1548.6912 (error: 0.6 ppm).

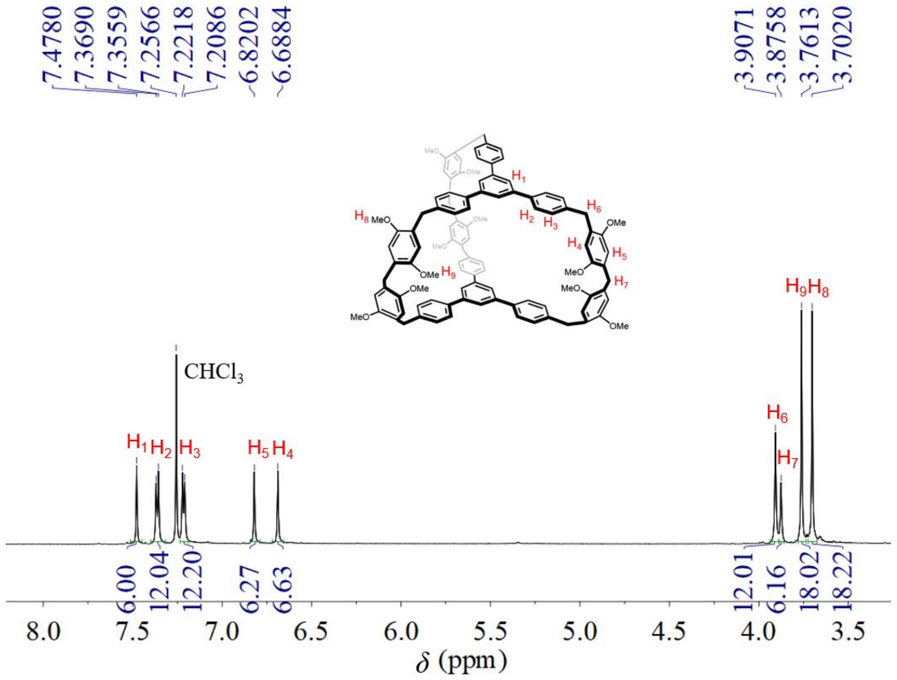


Fig. S4 ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **cagearene-1**.

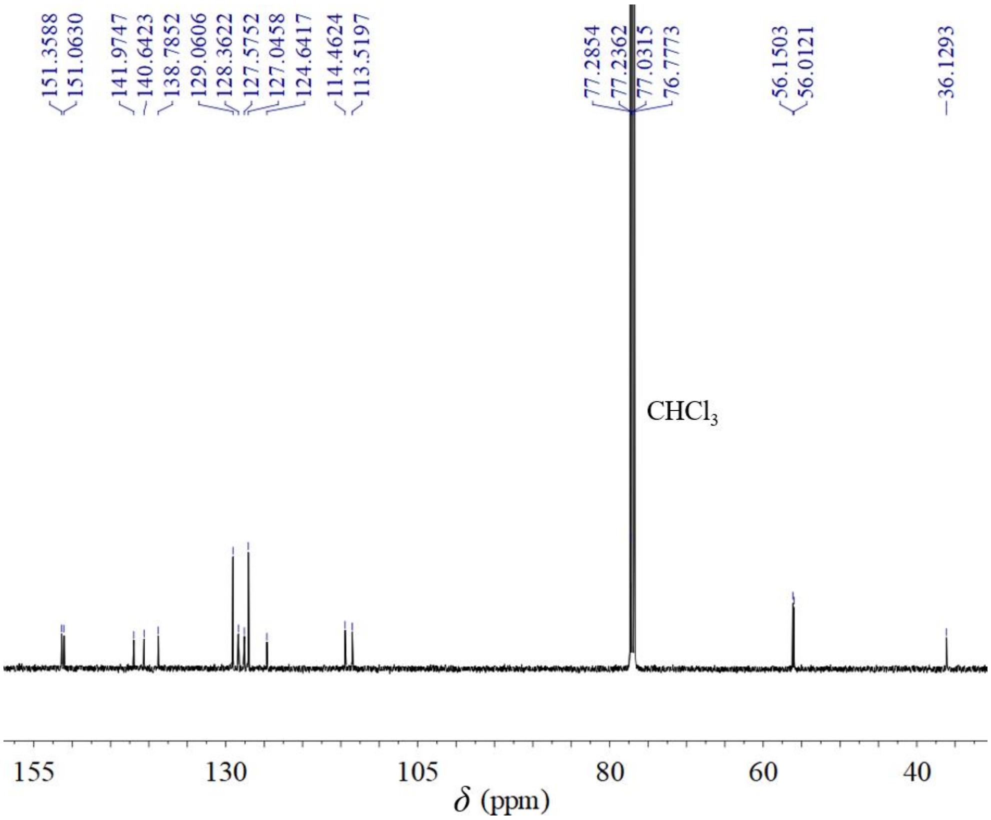


Fig. S5 ^{13}C NMR spectrum (125 MHz, 298 K, CDCl$_3$) of **cagearene-1**.

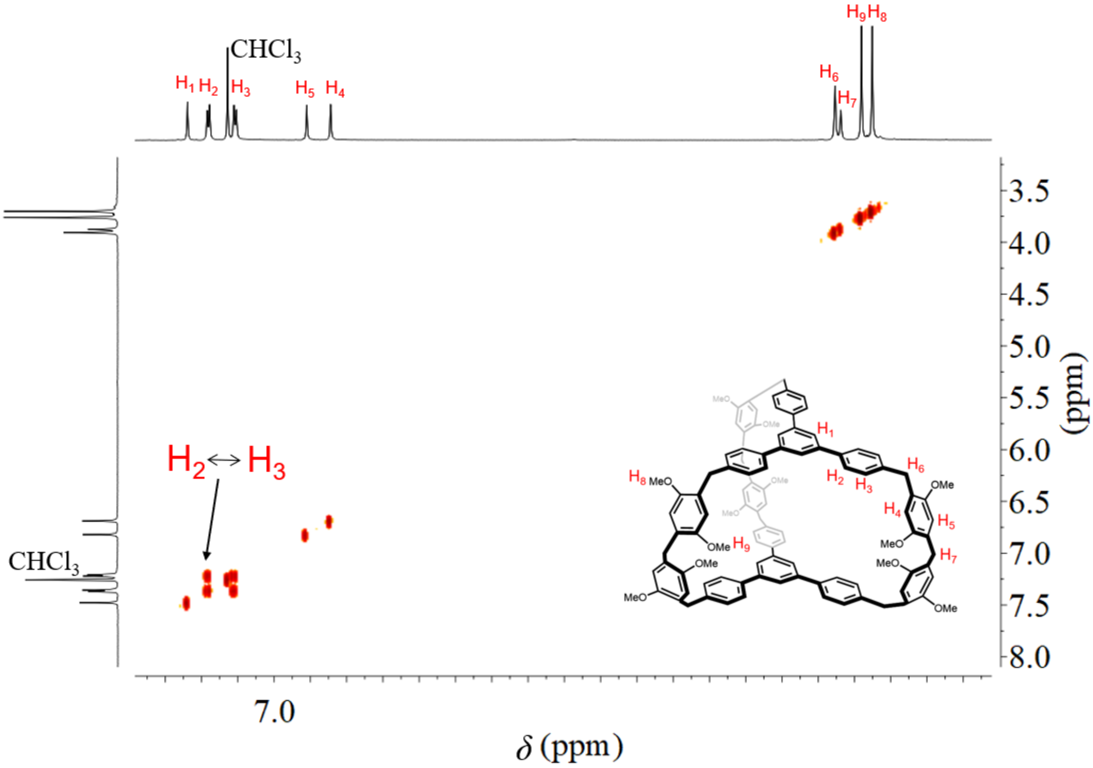


Fig. S6 ^{1}H-^{1}H COSY spectrum (500 MHz, 298 K, CDCl$_3$) of **cagearene-1**.

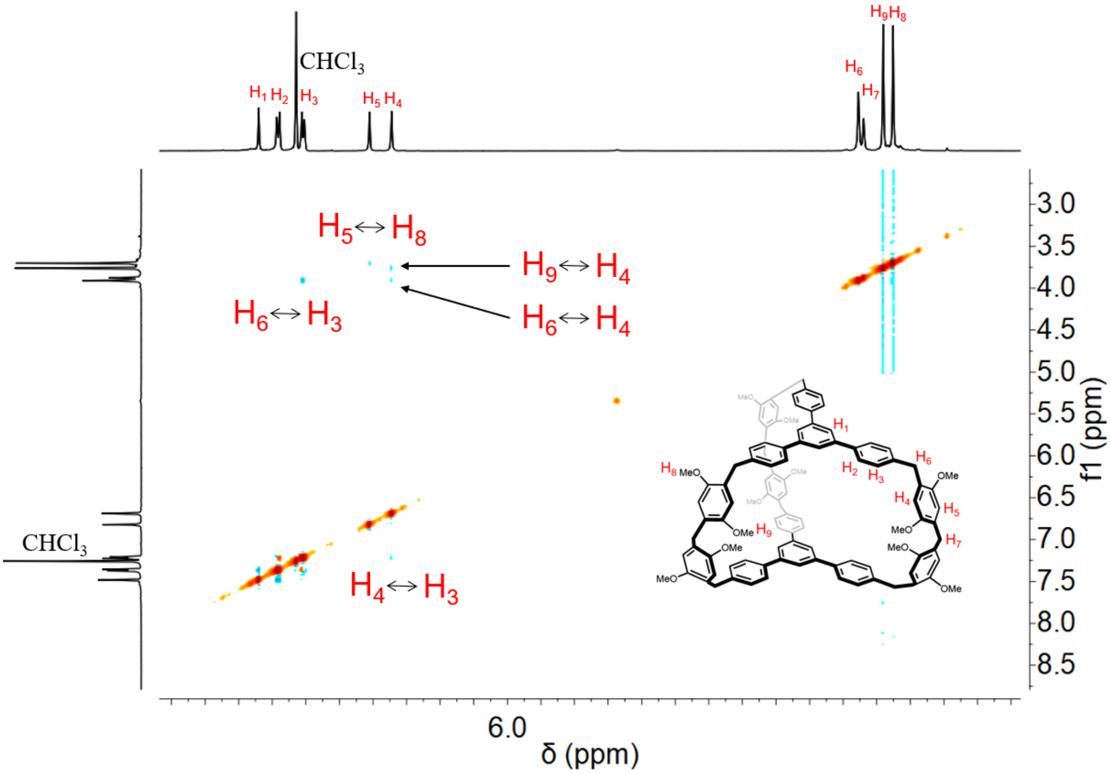


Fig. S7 ^{1}H-^{1}H NOESY spectrum (500 MHz, 298 K, $CDCl_3$) of **cagearene-1**.

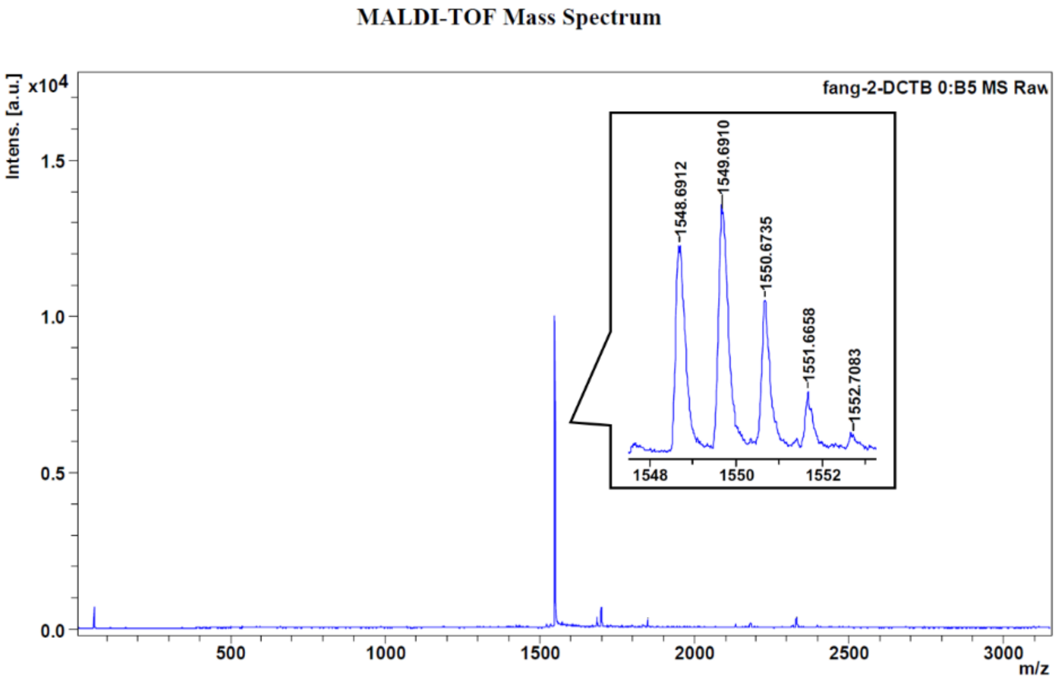
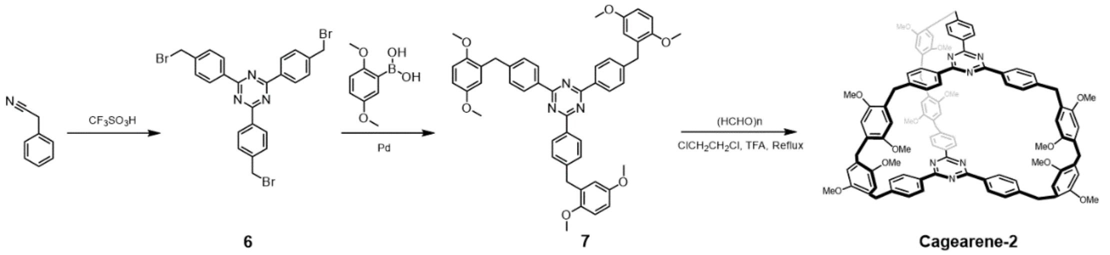


Fig. S8 Mass spectrum of **cagearene-1**.



Scheme S2 Synthesis of **cagearene-2.**

Compound **6** was synthesized according to the literature.[S3]

Compound **7**: 2,4,6-Tris(4*p*-bromomethylphenyl)-1,3,5-triazine **6** (586 mg, 1.0 mmol), (2,5-dimethoxyphenyl)boronic acid (730 mg, 4.0 mmol), and K_2CO_3 (420 mg, 3.0 mmol) were combined in a reaction flask. Toluene (PhMe, 50 mL) and distilled water (H_2O, 15 mL) were added. After the mixture was bubbled under nitrogen for 10 min, tetrakis(triphenylphosphine)palladium(0) ($Pd[P(C_6H_5)_3]_4$) (346 mg, 0.30 mmol) was added to the solution. The resulting mixture was stirred at 90 °C for 12 h under the protection of nitrogen. Then, the solvent was removed by rotary evaporation. The residue was dissolved in CH_2Cl_2 (200 mL), and was washed with water (3 × 150 mL). The organic phase was dried over anhydrous Na_2SO_4, and concentrated through reduced pressure distillation. The residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to give the product as white powder (653 mg, 86%).

Melting point: 164–168 °C. The ^{1}H NMR spectrum of compound **7** is shown in Fig. S8. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.63 (d, $J = 8.1$ Hz, 6H), 7.39 (d, $J = 8.1$ Hz, 6H), 6.80 (m, 3H), 6.70−6.72 (m, 6H), 4.05 (s, 6H), 3.78 (s, 9H), 3.73 (s, 9H). The ^{13}C NMR spectrum of compound **7** is shown in Fig. S9. ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.43, 153.56, 151.72, 145.71, 134.19, 130.28, 129.22, 128.98, 116.82, 111.62, 111.50, 56.04, 55.70, 36.28. The MS spectrum of compound **7** is shown in Fig. S10. MS (MALDI-TOF): *m/z* calcd for [**M**]$^+$ $C_{48}H_{45}N_3O_6^+$, 759.3308; found 759.3314 (error: 0.8 ppm).

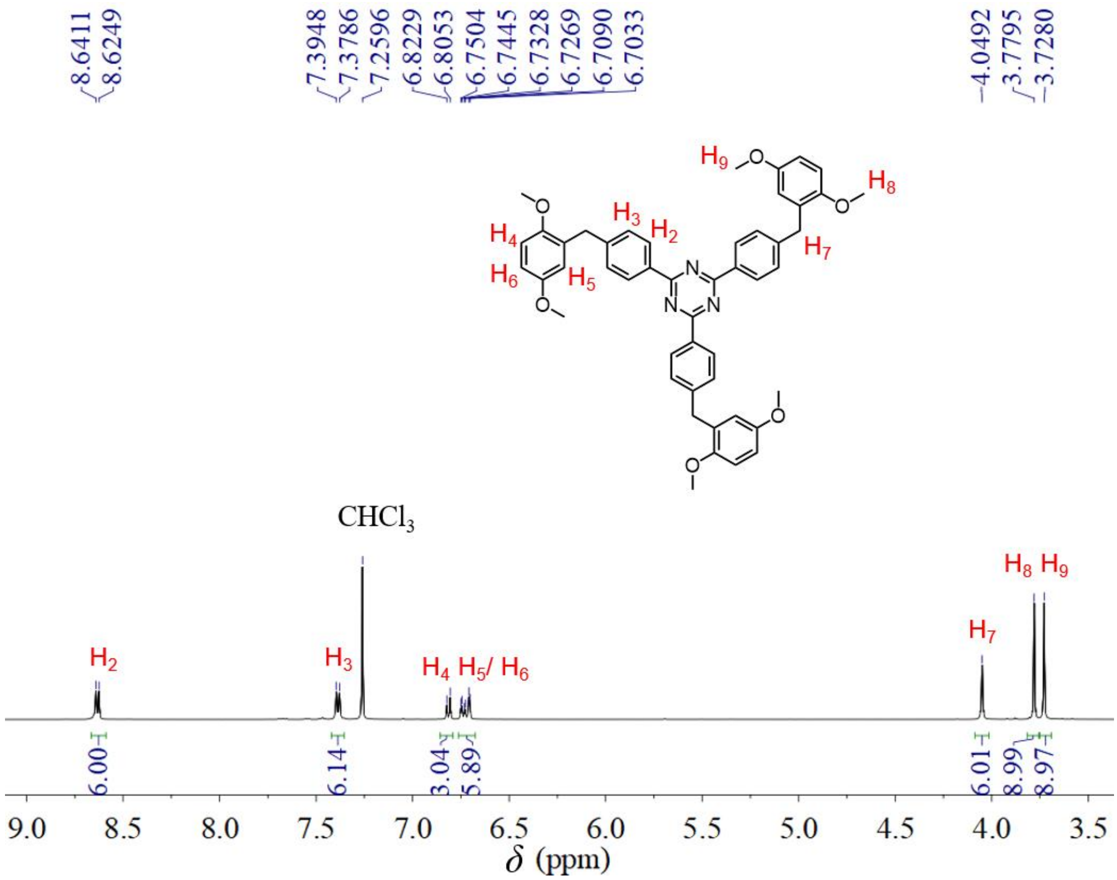


Fig. S9 ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of compound **7**.

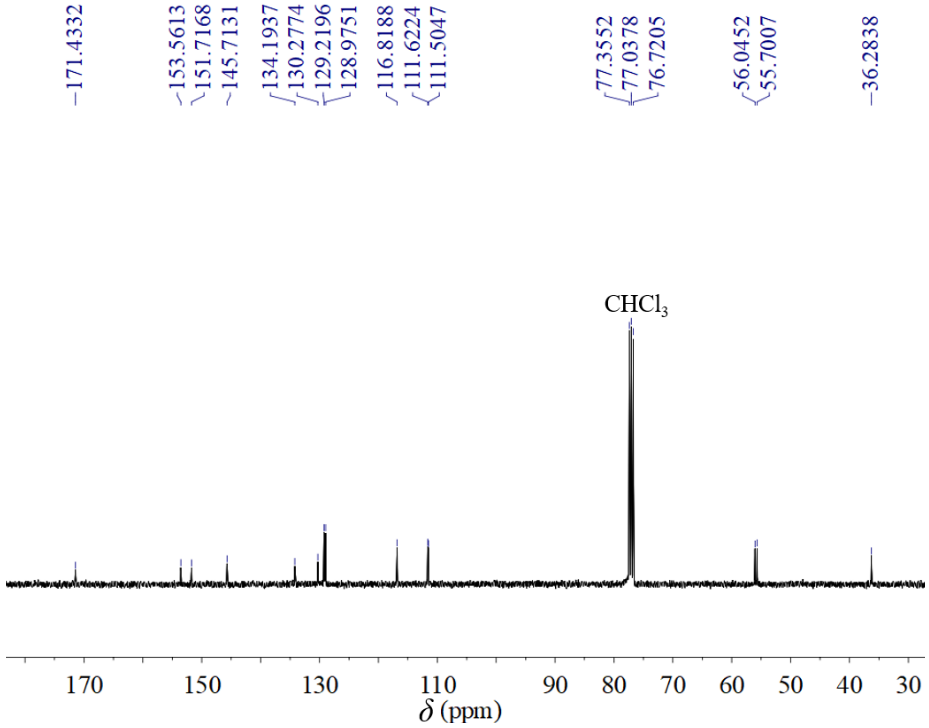


Fig. S10 ^{13}C NMR spectrum (150 MHz, 298 K, $CDCl_3$) of compound **7**.

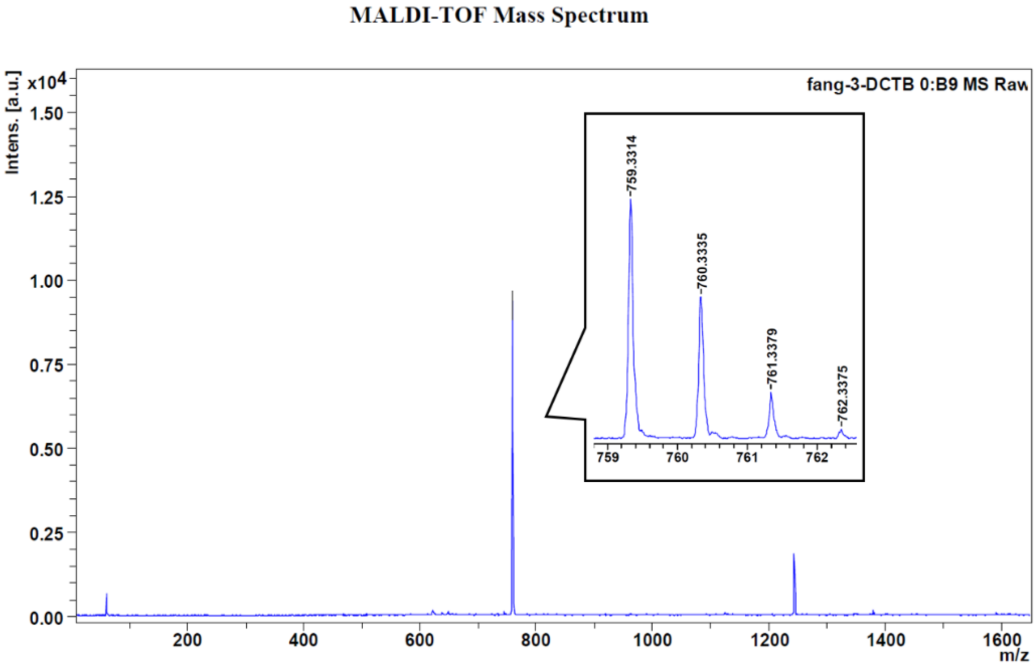


Fig. S11 Mass spectrum of compound **7**.

Cagearene-2: Compound **7** (759 mg, 1.0 mmol) and paraformaldehyde (180 mg, 6.0 mmol) were combined in a reaction flask under the nitrogen protection. Anhydrous dichloroethane (DCE, 150 mL) was added. After the mixture was stirred 0.5 h at 85 °C, trifluoroacetic acid (CF_3COOH) (1.0 mL) was added into the solution. The resulting mixture was stirred at 85 °C for 36 h until quenched with water. The organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. The residue was concentrated through reduced pressure distillation, and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to give the product as white powder (325 mg, 21%).

Melting point: 179–183 °C. The ^{1}H NMR spectrum of **cagearene-2** is shown in Fig. S11. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.32 (d, J = 8.1 Hz, 12H), 7.24 (d, J = 8.1 Hz, 12H), 6.70 (s, 6H), 6.54 (s, 6H), 3.85 (s, 12H), 3.83 (s, 6H), 3.71 (s, 18H), 3.53 (s, 18H). The ^{13}C NMR spectrum of **cagearene-2** is shown in Fig. S12. ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.15, 151.35, 151.18, 146.14, 128.88, 128.62, 127.58, 114.14, 113.71, 56.35, 55.94, 36.96. The MS spectrum of **cagearene-2** is shown in Fig. S14. MS (MALDI-TOF): *m/z* calcd for [**M**]$^+$ $C_{99}H_{91}N_6O_{12}^+$, 1554.6617; found 1554.6574 (error: 2.8 ppm).

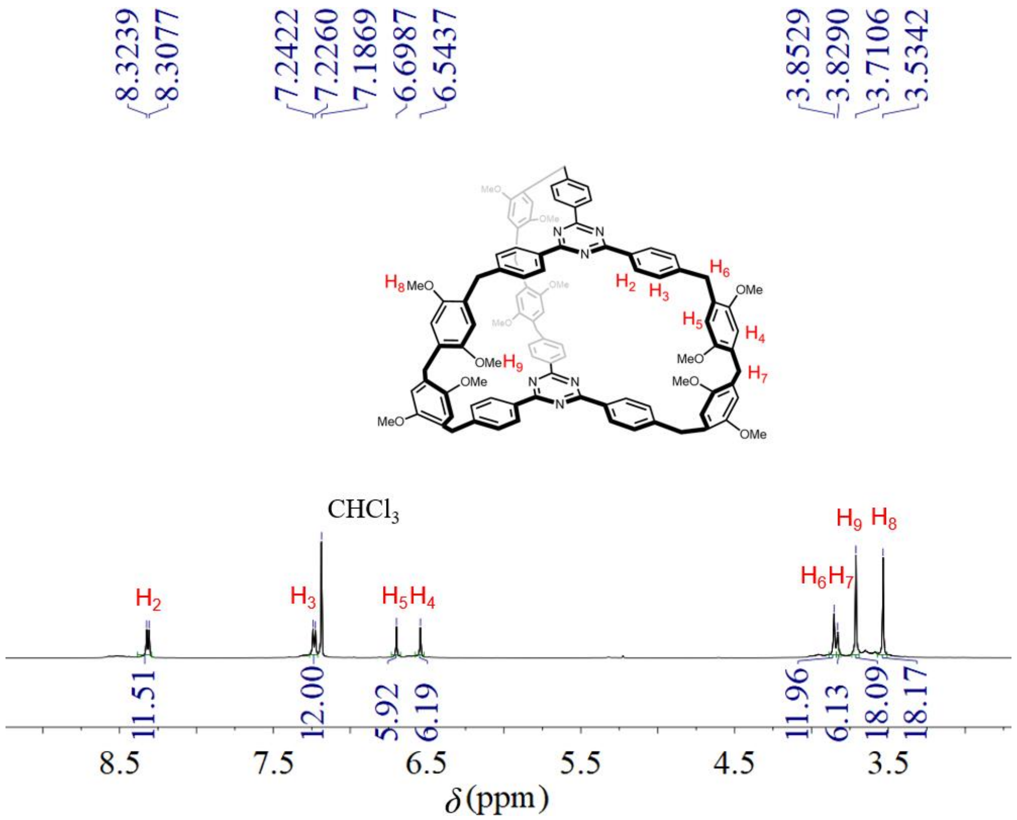


Fig. S12 ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **cagearene-2.**

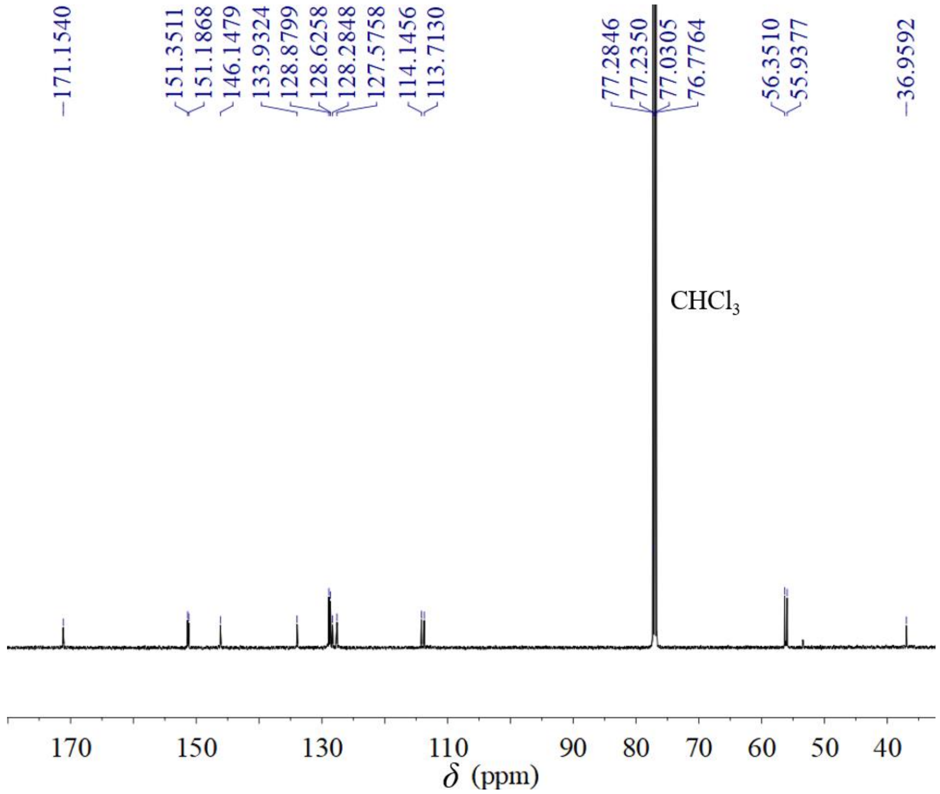


Fig. S13 ^{13}C NMR spectrum (125 MHz, 298 K, $CDCl_3$) of **cagearene-2**.

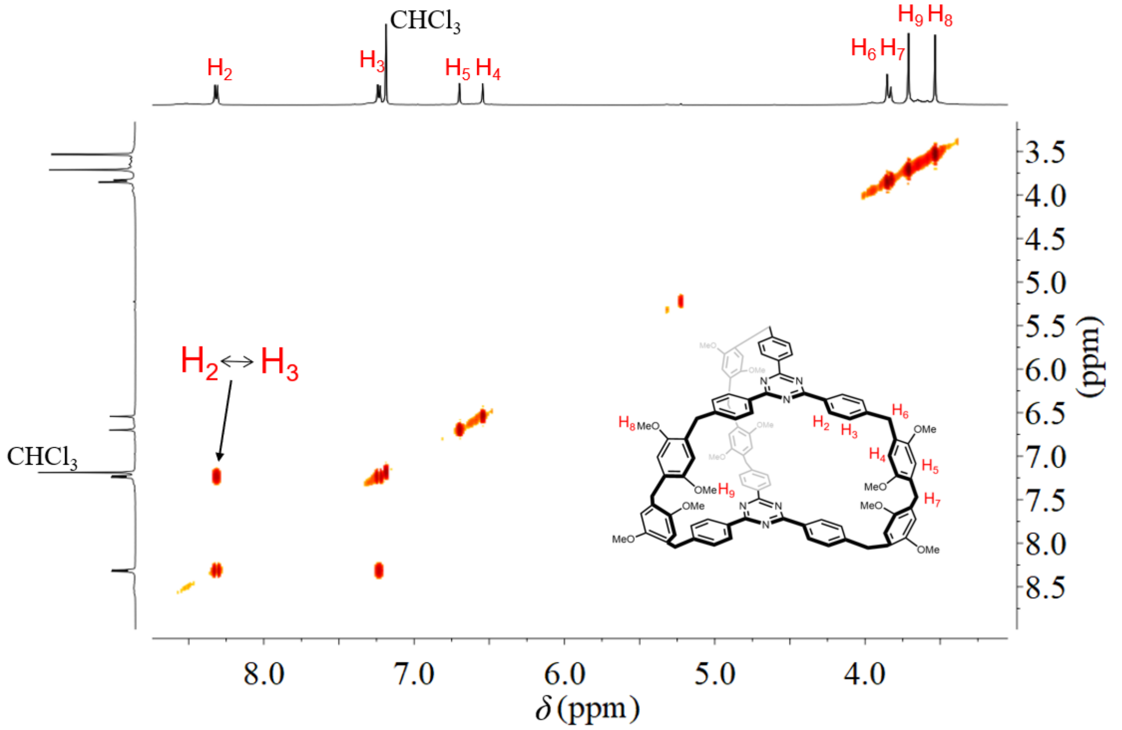


Fig. S14 ^{1}H-^{1}H COSY spectrum (500 MHz, 298 K, CDCl$_3$) of **cagearene-2**.

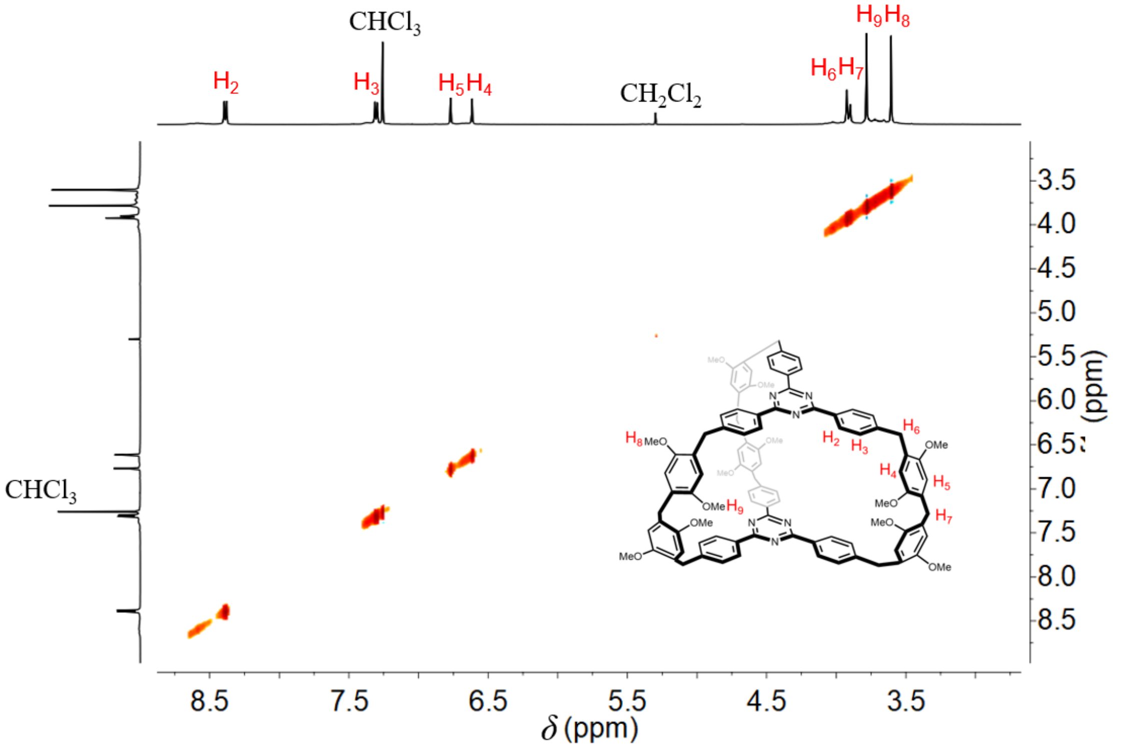


Fig. S15 ^{1}H-^{1}H NOESY spectrum (500 MHz, 298 K, CDCl$_3$) of **cagearene-2**.

MALDI-TOF Mass Spectrum

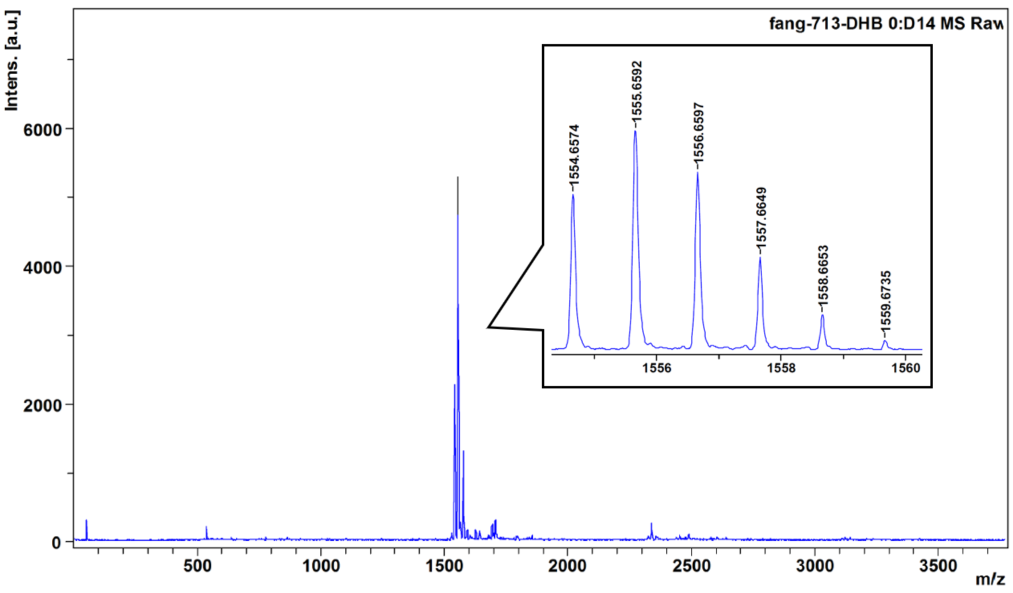


Fig. S16 Mass spectrum of **cagearene-2**.

Table S1 The yields of **cagearene-1** by combining **5** and paraldehyde under different conditions. Most of the reactions were conducted under the protection of nitrogen. The yields presented here are isolated ones. [a]Reaction took place under high humidity environment without nitrogen protection. n.d. = not detected. r.t. = room temperature.

Entry	*T* / °C	Acid	Time / h	Yield / %
1	r.t.	TFA	24	n.d.
2	**85**	**TFA**	**12**	**31**
3	85	TFA	4	18
4[a]	85	TFA	12	n.d.
5	85	$BF_3\cdot OEt_2$	12	11
6	85	CF_3SO_3H	12	0
7	85	*p*-toluenesulfonic acid	12	trace
8	85	$AlCl_3$	12	trace

3. ^{1}H NMR Spectra of Guest Absorption and Desorption

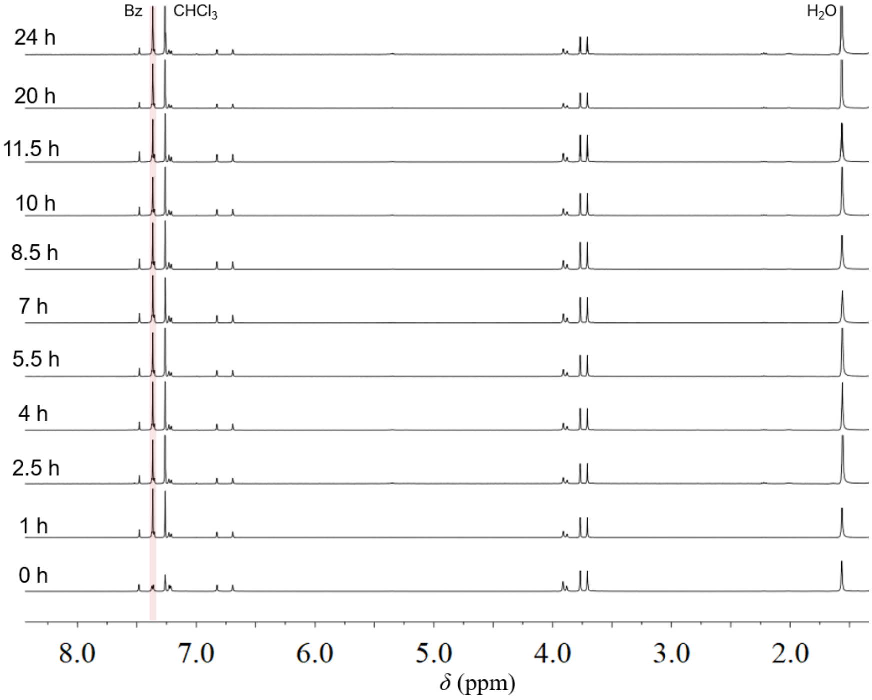


Fig. S17 Time-dependent ^{1}H NMR spectra (400 MHz, 298 K, $CDCl_3$) of **cagearene-1** after Bz vapour adsorption. The peak of Bz is in red region (δ = 7.36 ppm).

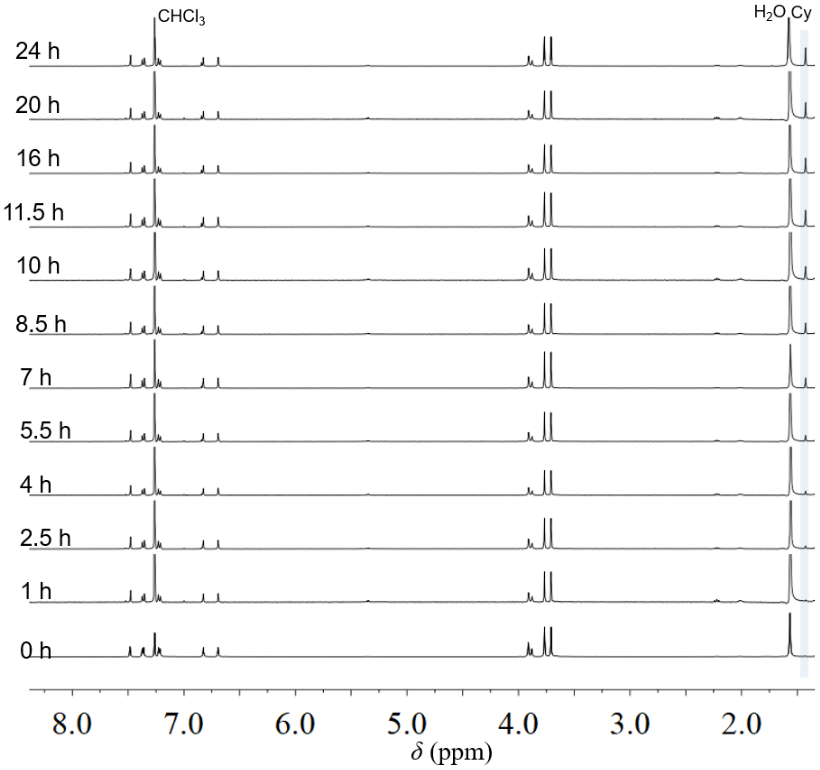


Fig. S18 Time-dependent ^{1}H NMR spectra (400 MHz, 298 K, $CDCl_3$) of **cagearene-1** after Cy vapour adsorption. The peak of Cy is in blue region (δ = 1.43 ppm).

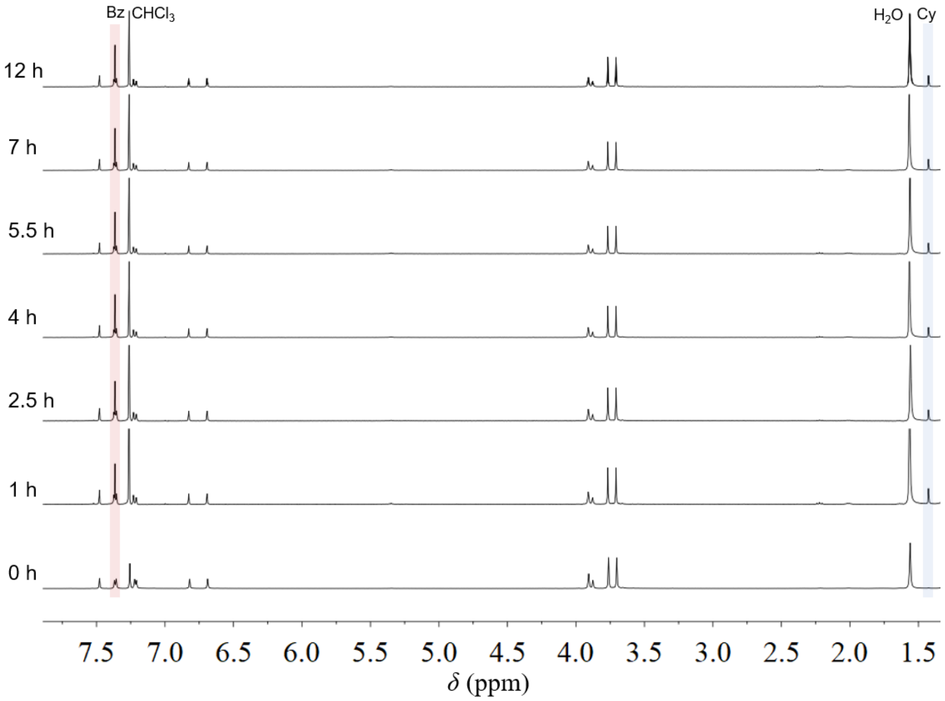


Fig. S19 Time-dependent ^{1}H NMR spectra (400 MHz, 298 K, $CDCl_3$) of **cagearene-1** after Bz/Cy mixture vapour (50:50 *v/v*) adsorption. The peak of Bz is in red region, while the peak of Cy is in blue region (Bz: $\delta = 7.36$ ppm; Cy: $\delta = 1.43$ ppm).

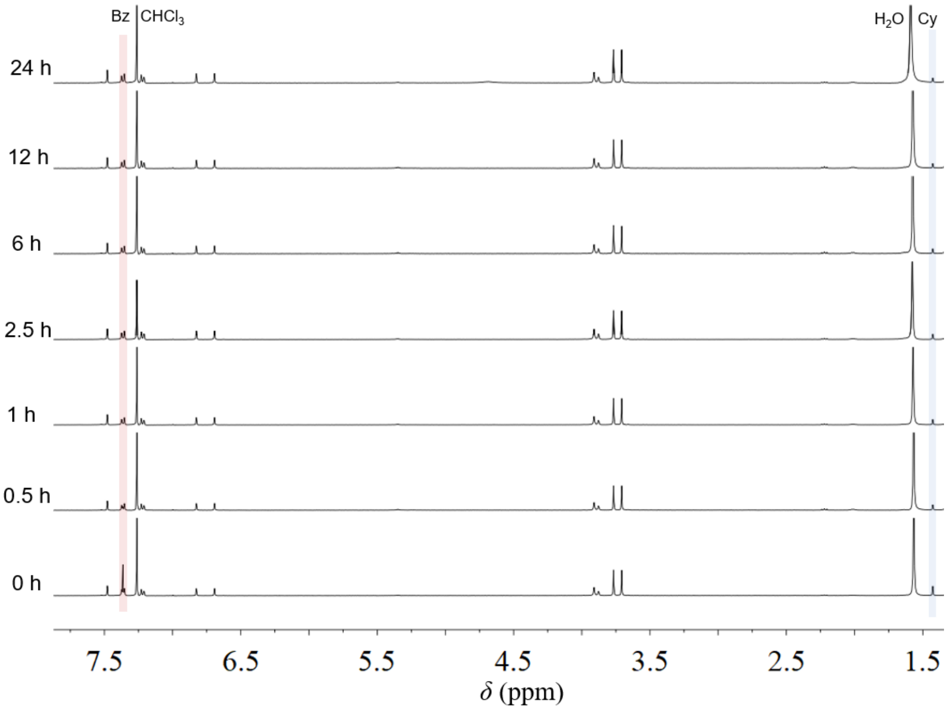


Fig. S20 Time-dependent ^{1}H NMR spectra (400 MHz, 298 K, $CDCl_3$) of desorption of Bz/Cy mixture (50:50 *v/v*) absorbed **cagearene-1** at 70°C. The peak of Bz is in red region, while the peak of Cy is in blue region (Bz: $\delta = 7.36$ ppm; Cy: $\delta = 1.43$ ppm).

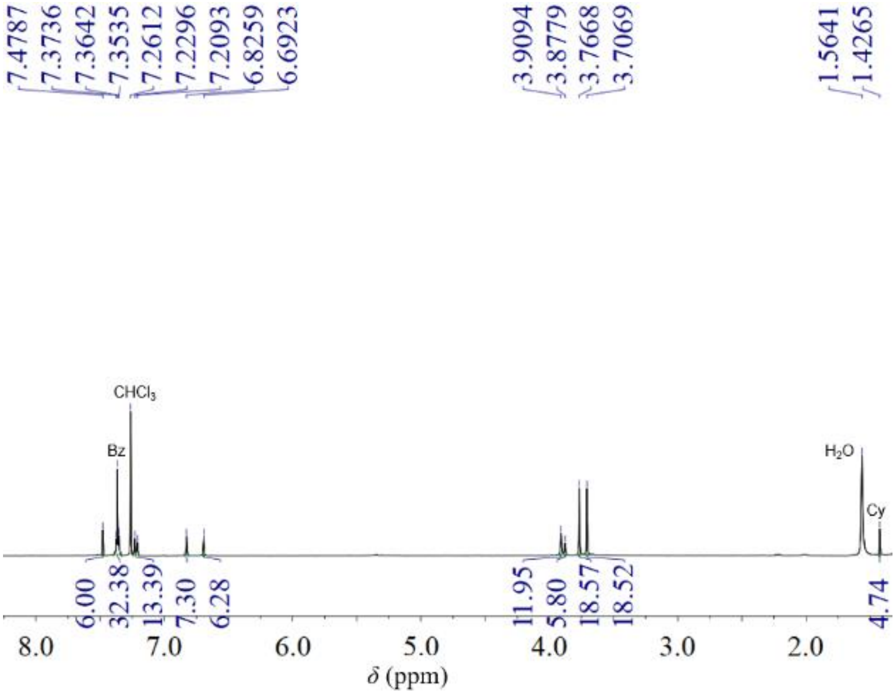


Fig. S21 ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **cagearene-1** after saturated absorption of Bz/Cy mixture vapour (50:50 *v/v*). It was determined that 3 Bz per **cagearene-1** and 0.4 Cy molecule per **cagearene-1** molecule were absorbed by the solid (Bz: δ = 7.36 ppm; Cy: δ = 1.43 ppm).

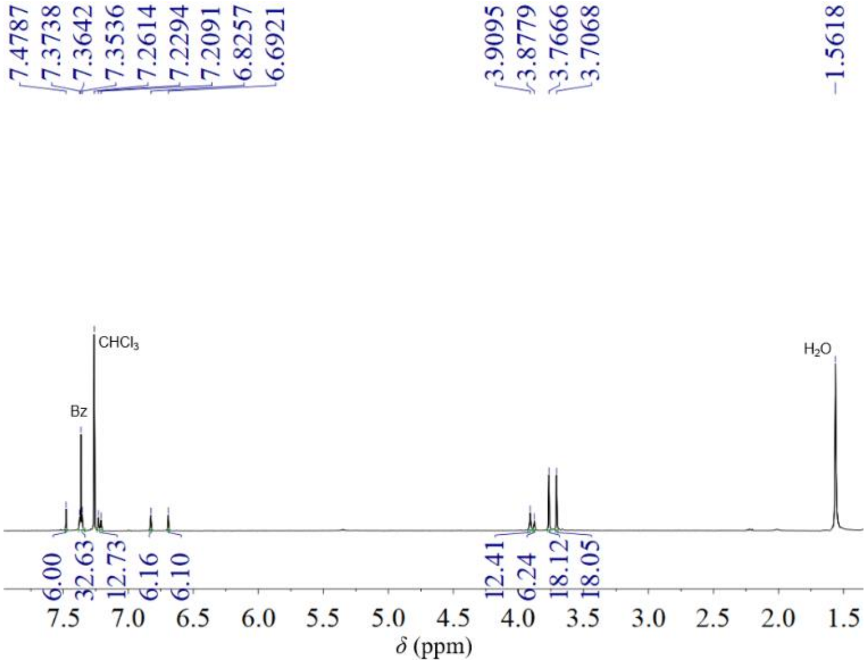


Fig. S22 ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **cagearene-1** after saturated absorption of Bz vapour. It was determined that about 3 Bz molecule per **cagearene-1** molecule were absorbed by the solid (Bz: δ = 7.36 ppm).

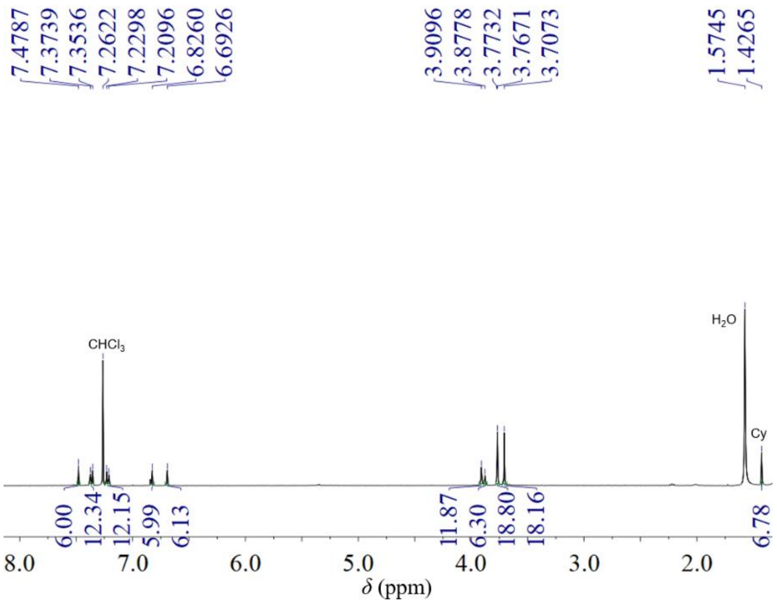


Fig. S23 ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **cagearene-1** after saturated absorption of Cy vapour. It was determined that 0.6 Cy molecule per **cagearene-1** molecule was absorbed by the solid (Cy: δ = 1.43 ppm).

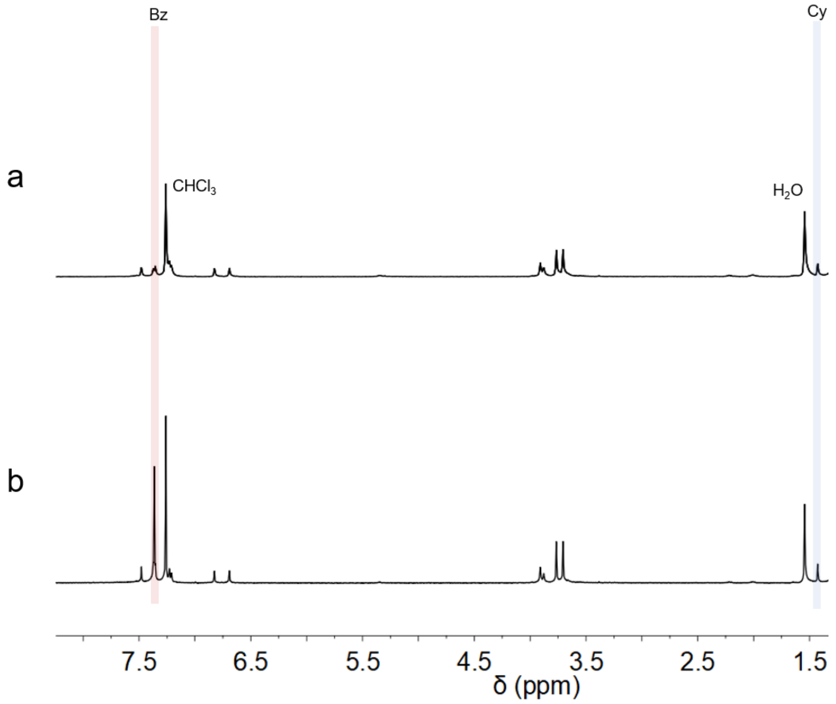


Fig. S24 ^{1}H NMR spectra (400 MHz, 298 K, $CDCl_3$): (a) **cagearene-1** after absorption of Cy vapour for 12 h; (b) Cy-loaded **cagearene-1** after absorption of Bz vapour for 2 h. It was determined that 3.5 Bz molecules per **cagearene-1** molecule and 0.6 Cy molecule per **cagearene-1** molecule were absorbed by the solid (Bz: δ = 7.36 ppm; Cy: δ = 1.43 ppm).

4. Thermogravimetric Analysis (TGA), and Gas Chromatography (GC) Experiments

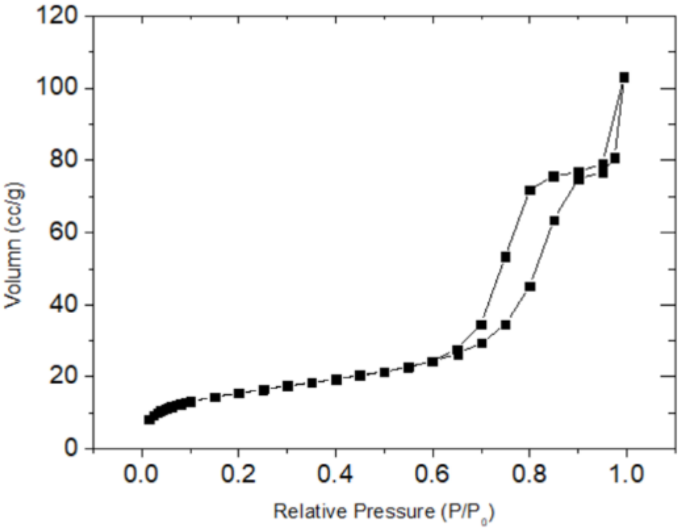


Fig. S25 N_2 adsorption isotherm of the **cagearene-1** solid. The BET surface area is 56 m^2/g.

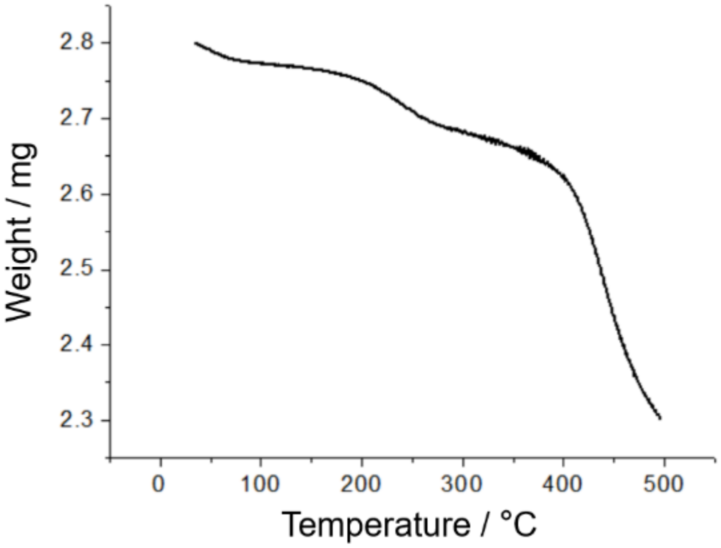


Fig. S26 TGA of the activated **cagearene-1** solid.

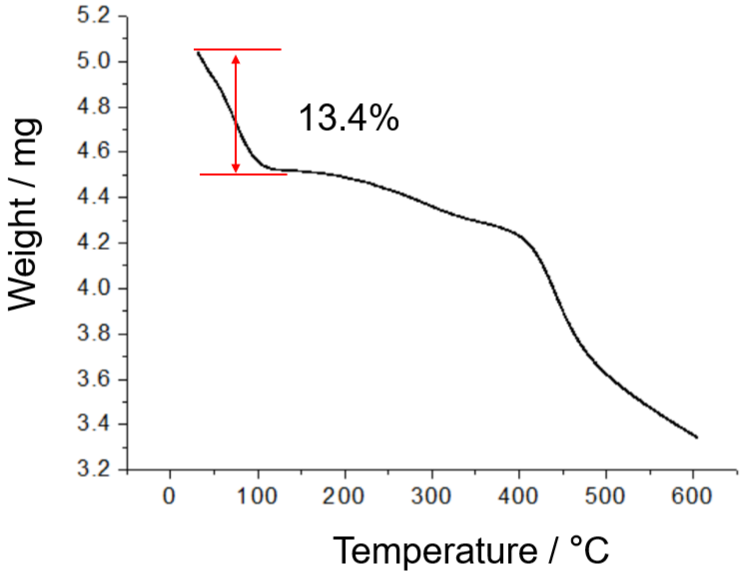


Fig. S27 TGA of the activated **cagearene-1** solid after adsorbing Bz. About 3 Bz molecules per host molecule were lost before 100 °C.

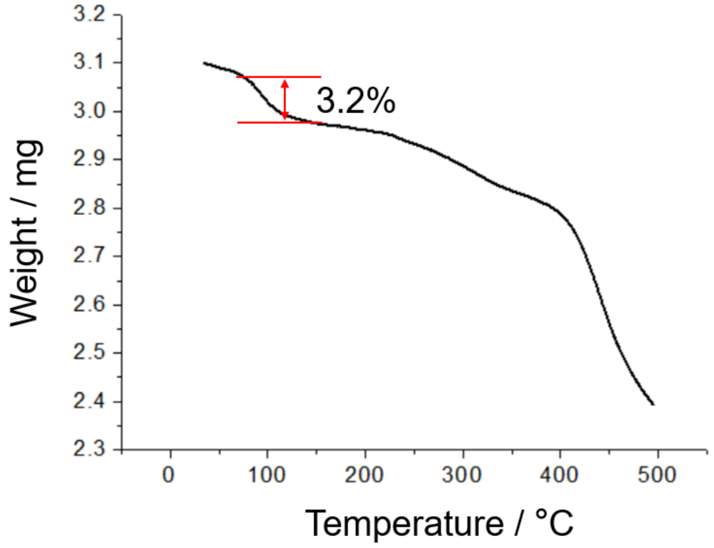


Fig. S28 TGA of the activated **cagearene-1** solid after adsorbing Cy. About 0.7 Cy molecule per host molecule was lost before 130 °C.

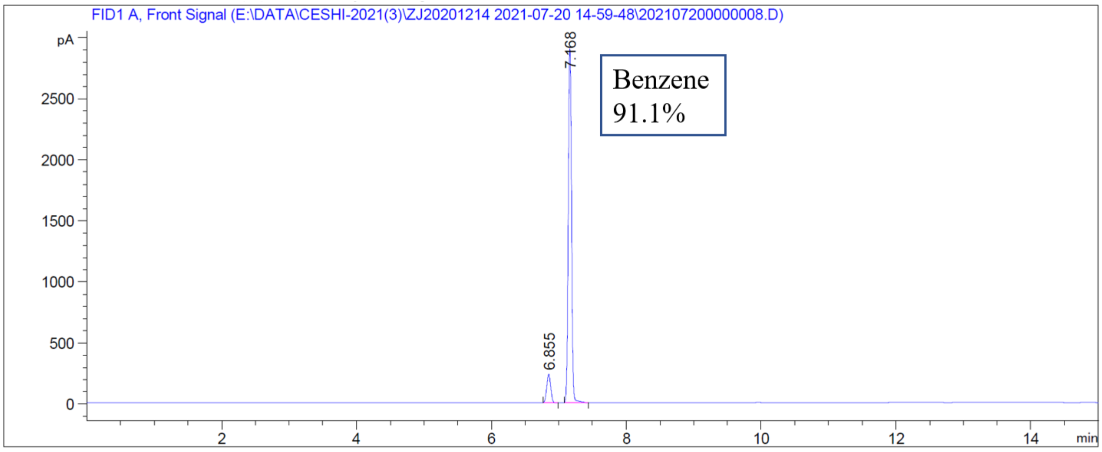


Fig. S29 Percentage of Bz measured by gas chromatography after absorbing a Bz/Cy mixture (50:50 *v/v*) by **cagearene-1** solid for 12 hours.

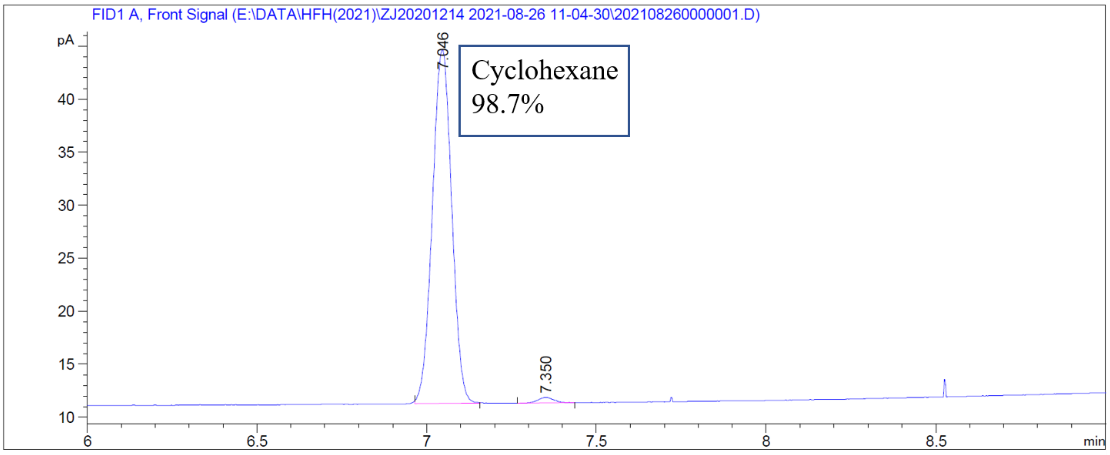


Fig. S30 Percentage of Cy mearsured by gas chromatography after heating **cagearene-1** solid after absorbing Bz/Cy mixture vapour (50:50 *v/v*) for 12 hours at 70 °C.

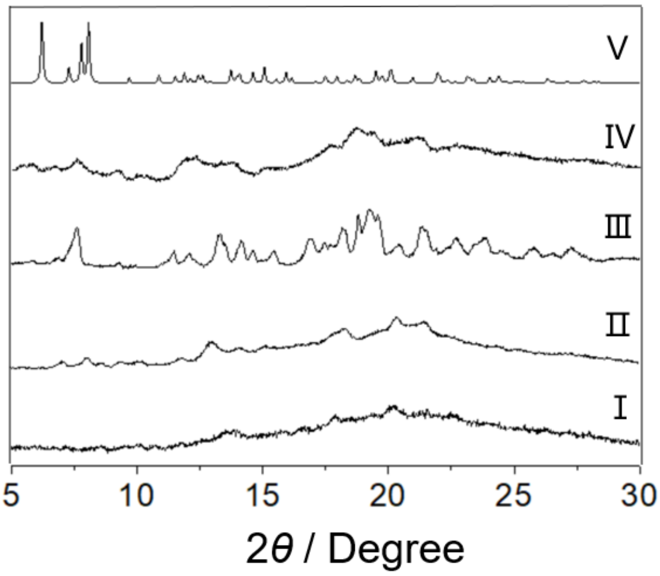


Fig. S31 The PXRD patterns of I) original **cagearene-1**; II) after adsorption of Cy vapour; III) after adsorption of Bz vapour; IV) after adsorption of Bz/Cy (50:50 *v/v*) mixture vapour; V) simulated pattern from the single-crystal structure of **Bz@cagearene-1**.

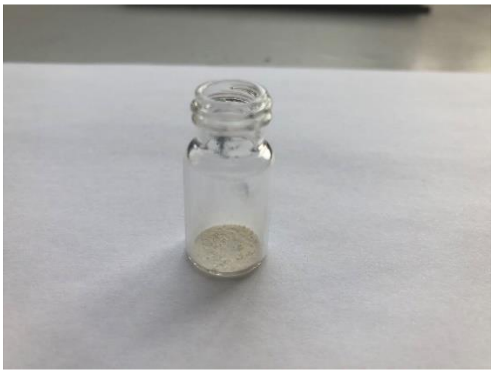


Fig. S32 Picture of the **cagearene-1** solid after adsorbing Bz/Cy (50:50 *v/v*) mixture vapour.

5. Computational Analysis

5.1 Optimization of Cagearene-2

The structure of **cagearene-2** was optimized by density functional theory (DFT) calculation with B3LYP-D3 functionals on the level of 6-31G using the Gaussian 16 program.[S4] All the calculations were performed without solvent.

5.2 Electrostatic Potential (ESP) Calculation

The structure of **cagearene-1** was optimized by DFT calculation with B3LYP functionals on the level of 6-31G using the Gaussian 16 program based on the X-ray single crystal structure of **cagearene-1**. The electrostatic potential map of **cagearene-1** was calculated at the same level. Subsequently, electrostatic potentials (ESP) were calculated by Multiwfn.[S5]

ESP maps of Bz and Cy were obtained using the same method.

5.3 Single Point Energies

The initial structure of **cagearene-1** was created based on the X-ray single crystal structure of empty **cagearene-1** and optimized by a semi-empirical method at the PM7 level[S6] using the MOPAC program.[S7] The optimized structure was used to create the structure of **Cy@cagearene-1**, which was optimized by the same method. Single point energies were calculated using the Gaussian 16 program at B3LYP-D3/6-311+G** level. All the calculations were performed without solvent.

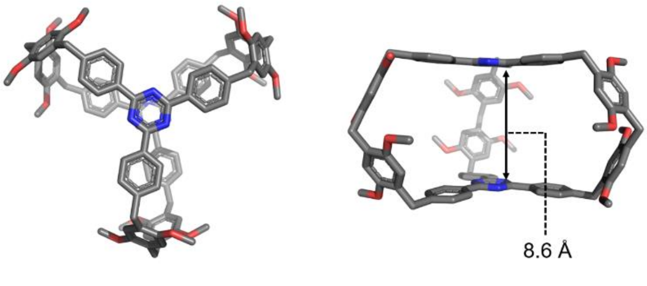


Fig. S33 The optimized structure of **cagearene-2** by means of B3LYP-D3 functionals on the level of 6-31G. Hydrogen atoms are omitted for clarity. The cage is illustrated as a stick representation. Color code: C gray, N blue, O red.

Table S2 The atomic coordinates of **cagearene-2**:

Atom	x	y	z
N	1.26955	4.57163	0.14207
C	0.64467	4.64779	1.324
N	1.18373	4.07127	2.40437
C	2.37549	3.47145	2.31753
N	3.00194	3.3977	1.13907
C	2.46545	3.97561	0.05867
C	3.23737	3.96531	-1.2742
C	0.68726	5.41174	1.45033
C	3.03463	2.87912	3.577
C	4.45664	3.37844	-1.33935
C	5.1678	3.41827	-2.49128
C	4.65915	4.04398	-3.5799
C	3.41765	4.58719	-3.53097
C	2.70639	4.54861	-2.37681
C	1.23797	6.00892	0.36543
C	2.37666	6.73471	0.49629
C	2.96068	6.86334	1.7138
C	2.43885	6.2203	2.78603
C	1.30299	5.49434	2.65405
C	2.41069	2.97268	4.77629
C	3.01864	2.50598	5.89387
C	4.24954	1.94506	5.81146
C	4.85047	1.80394	4.60476
C	4.24326	2.27273	3.48732
C	5.4996	4.14595	-4.86649
C	0.93798	4.36009	-6.86207
C	0.27868	-4.0881	-5.49694

C	0.87565	3.38014	-5.42538
C	1.48729	3.20091	-4.22795
C	0.94291	3.72963	-3.10472
C	0.23861	4.38986	-3.17093
C	0.84949	4.56844	-4.36639
C	1.66623	3.59499	-1.75133
N	2.83915	2.95256	-1.6699
C	3.49403	2.91028	-0.502
N	2.94811	3.45287	0.59106
C	1.77929	4.09393	0.50702
N	1.12276	4.13698	-0.656
C	1.19802	4.79659	1.74692
C	4.88405	2.25401	-0.40882
C	1.86875	4.75579	2.92353
C	1.38912	5.42487	3.99925
C	0.24003	6.13544	3.89678
C	0.45699	6.13436	2.7347
C	0.02204	-5.464	1.65922
C	5.45857	1.70559	-1.50738
C	6.70943	1.18736	-1.42861
C	-7.3825	-1.2192	-0.25208
C	6.78632	1.71915	0.85632
C	5.53762	2.23624	0.77792
C	4.9687	1.48032	7.09149
C	4.61853	0.01555	7.41572
C	5.38282	-0.9919	6.92694
C	5.11405	2.27479	7.27373
C	4.08179	-2.5485	8.10831
C	3.28164	1.54705	8.54731

C	3.55005	0.26491	8.20101
C	3.82607	3.99588	8.56836
C	2.8711	4.71801	7.60004
C	3.3708	5.40282	6.54293
C	2.53716	6.09576	5.73022
C	1.20475	6.10394	5.97546
C	0.69917	5.37307	6.99833
C	1.5327	4.67879	7.81059
C	0.26771	6.95337	5.0977
C	4.20891	7.74959	1.88618
C	5.49677	6.93077	1.67766
C	6.08244	6.3111	2.73162
C	7.25249	5.64641	2.56265
C	-7.8357	5.60419	1.33954
C	7.22129	6.17652	0.27538
C	6.05046	6.83889	0.44425
C	9.20253	4.91813	1.1585
C	9.02453	3.42901	0.80906
C	-8.97611	2.50131	1.79561
C	-8.89124	1.18506	1.48314
C	-8.84977	0.79856	0.18448
C	-8.83722	1.73024	-0.79906
C	-8.92713	3.04569	-0.48646
C	-8.82904	-0.69911	-0.17288
C	5.2454	2.93275	-5.78099
C	4.27009	2.98204	-6.72103
C	4.0911	1.93789	-7.56623
C	4.88829	0.84591	-7.47233
C	5.82695	0.77431	-6.49734

C	6.00566	1.81819	-5.65197
C	4.73625	-0.30712	-8.482
C	3.71388	-1.34428	-7.98039
C	2.40525	-1.21516	-8.30768
C	1.51499	-2.16363	-7.92811
C	1.93401	-3.24162	-7.22239
C	3.2319	-3.34066	-6.84366
C	4.12248	-2.39128	-7.22285
O	-5.46747	6.36428	4.02158
C	-5.78706	5.17776	4.7532
O	-7.81243	6.08618	-1.02348
C	-8.69411	7.19439	-1.22382
O	5.92233	-3.33922	6.76463
C	7.25201	-2.86434	6.53842
O	2.70942	0.79306	8.66912
C	1.37587	0.30417	8.83623
O	-9.02074	2.91142	3.16455
C	-9.62997	1.88517	3.95187
O	-8.73502	1.32565	-2.16618
C	-8.06146	2.34187	-2.91321
O	6.63357	-0.39913	-6.36438
C	5.99768	-1.31745	-5.47166
O	3.4343	4.13733	-6.82606
C	4.02151	5.06637	-7.74117
O	1.96464	-0.08142	-9.05941
C	0.83729	-0.44923	-9.85844
O	3.66239	-4.4492	-6.04938
C	4.75114	-4.04441	-5.21496
O	0.99987	-3.91054	8.89234

C	-0.30698	-3.44459	8.54567
O	3.06368	-6.82313	4.61731
C	4.39123	-7.26051	4.91856
H	4.85969	2.88722	-0.47872
H	6.13295	2.95898	-2.5404
H	3.00081	5.0498	-4.4013
H	1.72877	4.98175	-2.33549
H	-0.77184	5.91132	-0.5927
H	-2.81041	7.20916	-0.35929
H	-2.92132	6.28965	3.73864
H	-0.88904	4.98961	3.50165
H	1.44022	3.41883	4.84154
H	2.52861	2.58409	6.84201
H	5.80563	1.32698	4.53483
H	4.71958	2.16778	2.5351
H	5.23502	5.04126	-5.38922
H	6.53669	4.17531	-4.60483
H	0.17896	-4.40859	-7.61471
H	1.46074	-5.29264	-6.81745
H	-1.30624	-2.96705	-6.31353
H	-2.40081	-2.64668	-4.17079
H	0.68703	-4.77414	-2.27881
H	1.7807	-5.09298	-4.41842
H	-2.77887	-4.19872	3.00162
H	-1.91979	-5.39581	4.92802
H	1.38285	-6.66593	2.66544
H	0.52564	-5.46525	0.74
H	-4.92785	-1.68532	-2.43612
H	-7.16667	-0.75755	-2.29543

H	-7.30369	-1.70921	1.79282
H	-5.06834	-2.63504	1.65282
H	6.02596	1.56515	6.95008
H	4.6639	2.10086	7.90814
H	6.20063	-0.77443	6.2721
H	2.441	-1.7681	9.17131
H	3.38878	-3.98056	9.54483
H	4.75687	-4.52263	8.59899
H	4.42381	-5.40027	6.35287
H	-0.35708	-5.34768	7.16734
H	0.80265	-7.80788	4.7392
H	-0.5688	-7.27275	5.68354
H	-4.21199	8.15873	2.87483
H	-4.17773	8.54239	1.16848
H	-7.71733	5.15955	3.39523
H	-5.56634	7.29338	-0.39497
H	-9.73417	5.40214	0.36575
H	-9.7596	5.00042	2.06824
H	-8.86116	0.45083	2.26141
H	-8.92564	3.78203	-1.26282
H	-9.30567	-0.84087	-1.12028
H	-9.35671	-1.24599	0.5805
H	3.32363	1.9776	-8.31075
H	6.75003	1.76427	-4.88519
H	5.68478	-0.78465	-8.61291
H	4.40057	0.08926	-9.41748
H	0.48241	-2.06375	-8.19019
H	5.14802	-2.47115	-6.9284
H	-5.33483	4.48633	5.43332

H	-5.17281	4.69612	4.02104
H	-5.68712	5.83497	5.59142
H	-9.57039	7.07595	-1.82526
H	-9.2613	6.86357	-0.37869
H	-8.51739	8.11629	-0.71062
H	7.85534	-3.66156	6.15707
H	7.22891	-2.06374	5.82899
H	7.66673	-2.51259	7.4599
H	0.74715	1.09577	9.18687
H	1.00742	-0.05499	7.89802
H	1.3753	-0.49405	9.54877
H	-9.66436	2.19446	4.9757
H	-10.6246	1.70758	3.59939
H	-9.05656	0.98552	3.86996
H	-7.98233	2.03952	-3.93662
H	-8.61561	3.25518	-2.85309
H	-7.08226	2.49132	-2.50876
H	6.60162	-2.19524	-5.37331
H	5.87788	-0.8577	-4.51291
H	5.03796	-1.58654	-5.86062
H	3.39776	5.93211	-7.82009
H	4.98858	5.3547	-7.38552
H	4.11756	4.60711	-8.70292
H	0.50667	0.39894	10.42068
H	1.11653	-1.23489	10.52907
H	0.04517	-0.78708	-9.22342
H	5.07378	-4.87455	-4.62187
H	5.56192	-3.70579	-5.8255
H	4.43214	-3.25003	-4.57294

H	-0.70689	-2.86936	9.3544
H	-0.24696	-2.83386	7.66909
H	-0.94496	-4.28195	8.35391
H	4.78482	-7.80521	4.08593
H	5.01112	-6.41052	5.11387
H	4.37118	-7.89311	5.78128

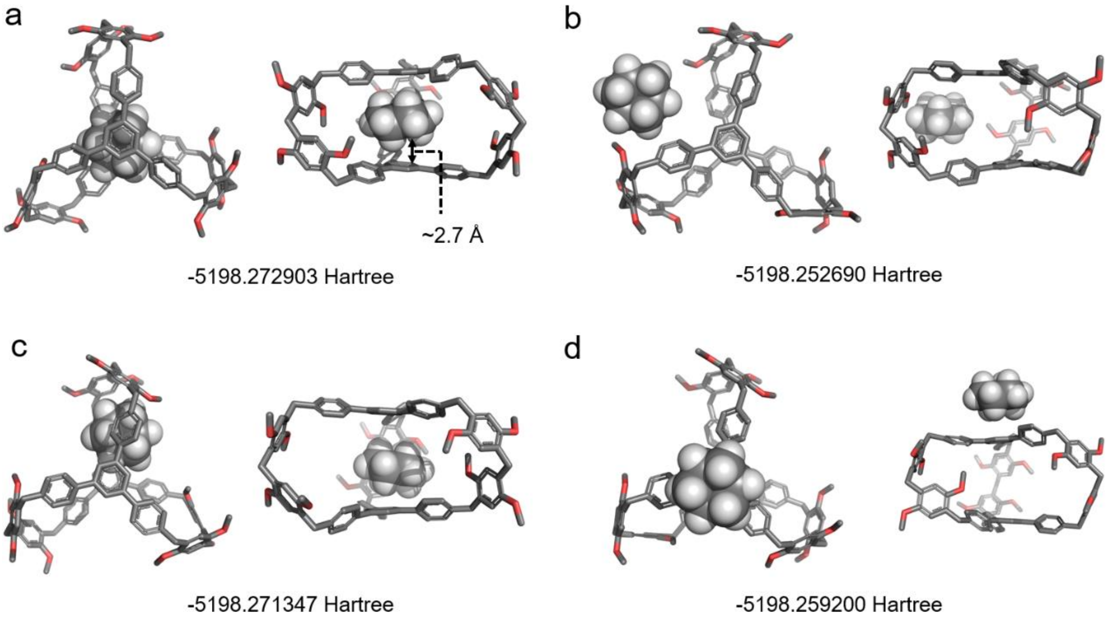


Fig. S34 The structures of **Cy@cagearene-1** complexes, where the Cy molecule is in different positions: a) the center of cavity, b) the window of cavity, c) the lateral side of cavity, and d) the outside of cavity. The structures are optimized by a semi-empirical method at the PM7 level using the MOPAC program. Single point energies are calculated using the Gaussian 16 program at the B3LYP-D3/6-311+G** level. The relative energies are recorded in the corresponding structures. The cages are illustrated as stick representations, while the guest molecules are in space-filling representation. Hydrogen atoms of the cages are omitted for clarity. Color code: C gray, H white, O red.

6. Crystallographic Data

Single crystals suitable for X-ray diffraction were selected, and mounted in inert oil in cold gas stream and their X-ray diffraction intensity data were collected on a Rigaku XtaLAB FRX diffractometer equipped with a Hypix6000HE detector, using Cu Kα radiation (λ = 1.54184 Å) and Mo Kα radiation (λ = 0.71073 Å). By the use of Olex2,[S8] the structure was solved: (i) with the ShelXS structure solution program using Direct Methods, (ii) with the ShelXT structure solution program using Direct Methods or Intrinsic Phasing, or (iii) with the ShelXT refinement package using Least Squares minimisation. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter.

6.1 Cagearene-1

Single crystals, suitable for X-ray crystallography, were obtained as colorless blocks by slow evaporation of a **cagearene-1** (3 mg) solution in $CHCl_3$ (0.5 mL) at room temperature for 3 days. CCDC number: 2116328.

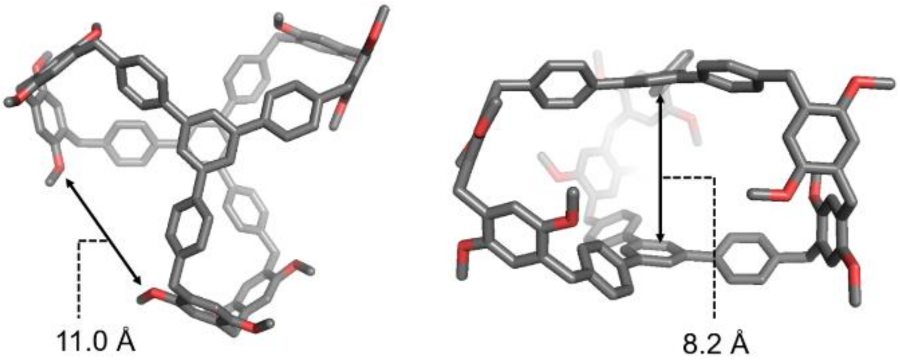


Fig. S35 The crystal structure of **cagearene-1**. Hydrogen atoms are omitted for clarity. The cage is illustrated in a stick representation. Color code: C gray, O red.

6.2 Bz@cagearene-1

Single crystals, suitable for X-ray crystallography, were obtained as colorless blocks by slow evaporation of a **cagearene-1** (3 mg) solution in benzene (0.5 mL) at room temperature for 1 day. CCDC number: 2116330.

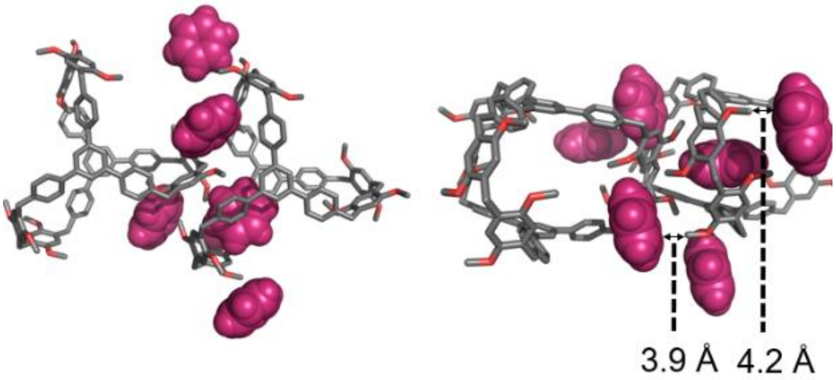


Fig. S36 The crystal structure of **Bz@cagearene-1**. Certain H atoms are omitted for clarity. The cage is illustrated in a stick representation, while the guest molecules are in space-filling representation.

6.3 1,3,5-Trimethylbenzene@cagearene-1

Single crystals, suitable for X-ray crystallography, were obtained as colorless blocks by slow evaporation of a **cagearene-1** (3 mg) solution in the 1,3,5-trimethylbenzene (0.5 mL) at room temperature for 1 day. CCDC number: 2116331.

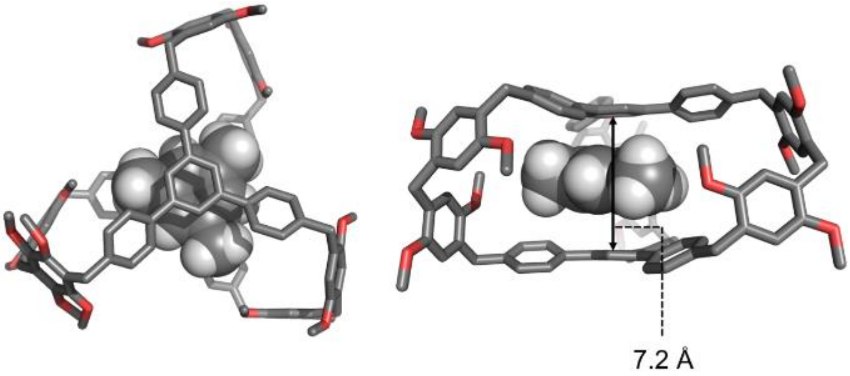


Fig. S37 The crystal structure of **1,3,5-trimethylbenzene@cagearene-1**. Certain H atoms are omitted for clarity. The cage is illustrated in a stick representation, while the guest molecule is in a space-filling representation. Color code: C gray, O red, H white.

6.4 Pentane@cagearene-1

Single crystals, suitable for X-ray crystallography, were obtained as colorless blocks by slowly evaporating pentane into a toluene solution (0.5 mL) of **cagearene-1** (3 mg) at room temperature for 1 day. CCDC number: 2116329.

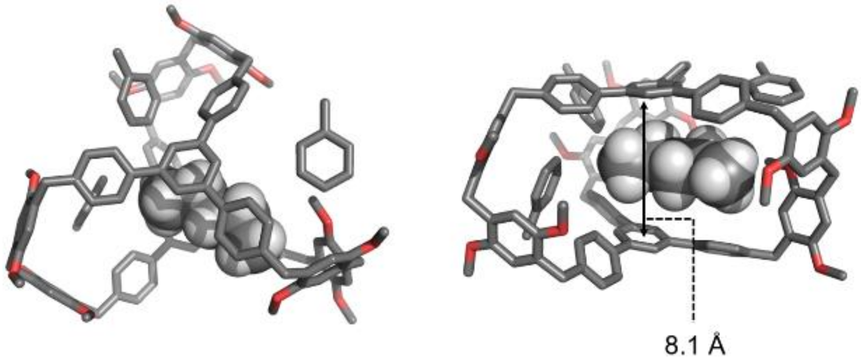


Fig. S38 The crystal structure of **pentane@cagearene-1**. Certain H atoms are omitted for clarity. The cage is illustrated in a stick representation, while the guest molecule is in a space-filling representation. Color code: C gray, O red, H white.

Table S3 Single crystal X-ray data for **Bz@cagearene-1** and **cagearene-1**

Parameter	**Bz@cagearene-1**	**cagearene-1**
Empirical formula	$C_{123}H_{114}O_{12}$	$C_{108}H_{99}Cl_9O_{12}$
Formula weight	1784.14	1907.92
Temperature [K]	192.99	172.99
Crystal system	Monoclinic	Triclinic
Space group	C2/c	P-1
a [Å]	25.7782(7)	14.9569(4)
b [Å]	18.2534(4)	17.9039(5)
c [Å]	27.4389(10)	22.5745(6)
α [°]	90	69.100(2)
β [°]	117.813(2)	74.702(2)
γ [°]	90	88.173(2)
Volume [$Å^3$]	11419.5(6)	5434.3(3)
Z	4	2
ρ_{calc} [g/cm^3]	1.038	1.166
μ / [mm^{-1}]	0.333	1.696
F(000)	3792	1992
Crystal size [mm^3]	0.05 x 0.03 x 0.02	0.07 x 0.06 x 0.05
2θ range for data collection [°]	2.698 to 55.097	3.316 to 54.987

Index ranges	$-31 \leq h \leq 31$, $-22 \leq k \leq 22$, $-33 \leq l \leq 30$	$-18 \leq h \leq 18$, $-21 \leq k \leq 21$, $-27 \leq l \leq 26$
Reflections collected	64386	64089
Independent reflections	10921 [R_{int} = 0.1285]	20496 [R_{int} = 0.0716]
Data restraints parameters	10921/51/603	20496/63/1174
Goodness-of-fit on F^2	0.984	0.947
Final R indexes [$I>2\sigma(I)$]	R_1 = 0.1120, wR_2 = 0.3053	R_1 = 0.1124, wR_2 = 0.2558
Final R indexes [all data]	R_1 = 0.2533, wR_2 = 0.3993	R_1 = 0.1389, wR_2 = 0.2719
Largest diff. peak and hole [e Å^{-3}]	0.389 / -0.366	1.196 / -0.843
CCDC	2116330	2116328

Table S4 Single crystal X-ray data for **pentane@cagearene-1** and **1,3,5-trimethylbenzene@cagearene-1**

Parameter	**pentane@cagearene-1**	**1,3,5-trimethylbenzene @cagearene-1**
Empirical formula	$C_{145}H_{148}O_{12}$	$C_{114}H_{108}O_{12}$
Formula weight	2082.63	1670
Temperature [K]	170	170
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a [Å]	14.1660(6)	13.898(4)
b [Å]	18.6824(10)	19.031(6)
c [Å]	23.8099(13)	24.191(8)
α [°]	82.321(2)	112.073(13)
β [°]	87.364(2)	103.948(14)
γ [°]	74.141(2)	93.107(10)
Volume [Å^3]	6006.9(5)	5680(3)
Z	2	2
ρ_{calc} [g/cm^3]	1.151	0.977
μ / [mm^{-1}]	0.072	0.062
F(000)	2228	1776

Crystal size [mm^3]	0.42 × 0.35 × 0.29	0.35 × 0.25 × 0.09
2θ range for data collection [°]	4.224 to 52.894	4.05 to 54.332
Index ranges	$-17 \leq h \leq 16, -23 \leq k \leq 23, -29 \leq l \leq 29$	$-17 \leq h \leq 17, -24 \leq k \leq 24, -30 \leq l \leq 30$
Reflections collected	125272	157316
Independent reflections	24666 [R_{int} = 0.0604]	25049 [R_{int} = 0.0605]
Data restraints parameters	24666/84/1420	25049/41/1190
Goodness-of-fit on F^2	1.023	0.979
Final R indexes [$I>2\sigma (I)$]	R_1 = 0.0752, wR_2 = 0.2151	R_1 = 0.0550, wR_2 = 0.1430
Final R indexes [all data]	R_1 = 0.0989, wR_2 = 0.2404	R_1 = 0.0799, wR_2 = 0.1620
Largest diff. peak and hole [e Å^{-3}]	0.70 / -0.48	0.54 / -0.28
CCDC	2116329	2116331

7. References

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