Electron Deficient Confined Space within Naphthalene Diimides Cryptophanes

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Supplementary Information

1. Materials and Methods

Starting material and solvents were of commercial grade and were used without further purification. Column chromatography was carried out with Merck 60 Å (0.040 – 0.063 mm) silica gel. Size-exclusion chromatography was performed with JAI Recycling Preparative HLPC LaboACE LC-5060 Plus III with chloroform as mobile phase. TLC was performed with Merck silica gel 60 F 254 plates. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 298 K on a Bruker Avance III HD 300 MHz, 400 MHz, 500 MHz and 600 MHz. Chemical shifts are reported in ppm on the δ scale relative to residual solvent as the internal references. Multiplicities are described with the following standard abbreviations: s= singlet, d= doublet, t= triplet, q= quadruplet, m= multiplet. High-resolution mass spectra (HRMS) were performed on a SYNAPT G2 HDMS (Waters) mass spectrometer equipped with atmospheric pressure ionization source (API) pneumatically assisted. Spectra were obtained with TOF analysis. Measurements were realized with two internal standards. UV spectra were recorded on a JASCO V-730 spectrophotometer. Chiral separations were performed on Agilent 1260 Infinity unit (pump G1311B, autosampler G1329B, DAD G1315D). Optical rotations were measured on a 241 Perkin-Elmer polarimeter with a mercury lamp (578, 546, 436 and 365 nm), a sodium lamp (589 nm) and a double-jacketed 1 cm cell at 25 °C. ECD spectra were recorded on a Jasco J-815 spectrometer equipped with a JASCO Peltier cell holder PTC-423. A CD quartz cell of 1 mm of optical pathlength was used. IR spectra were recorded on a Bruker TENSOR 27 Fourier Transform infrared spectrometer equipped with a single reflection diamond Attenuated Total Reflexion accessory (Bruker A222). Melting points were measured on Büchi Melting Point B-540.

2. Synthesis and characterizations

2-bromoethoxyvanillyl alcohol

K_2CO_3 (45 g, 326 mmol) was added a solution of vanillyl alcohol (45 g, 292 mmol) in ethanol (500 mL). The mixture was stirred and 1,2–dibromoethane (100 mL, 1.155 mol) was added to give a pink reaction mixture which was refluxed for 6 h, giving a pale pink opaque solution. The solvent was evaporated, and water (300 mL) and ethyl acetate (300 mL) were added to the remaining solid. The mixture was stirred overnight at 25 °C, dimers precipitated and were filtered on a frit. The two layers were separated, and the aqueous layer was extracted twice by ethyl acetate (2×150 mL). The organic layers were combined, washed four times with NaOH 10 % (4×100 mL), once with NaCl sat. (100 mL), dried on $MgSO_4$ and the solvent was evaporated under reduced pressure. The remaining solid was recrystallised in diisopropylic ether (200 mL) to give the compound as a white solid (28.5 g, 109 mmol) with a 37 % yield.

^{1}H-NMR ($CDCl_3$, 300 MHz): 6.95 – 6.88 (m, 3H), 4.63 (d, $^{2}J_{H-H}$= 5.6 Hz, 2H), 4.32 (t, $^{3}J_{H-H}$= 6.7 Hz, 2H), 3.88 (s, 3H), 3.67 (t, $^{3}J_{H-H}$= 6.7 Hz, 2H).

The spectroscopic data matched with the reported data.[1]

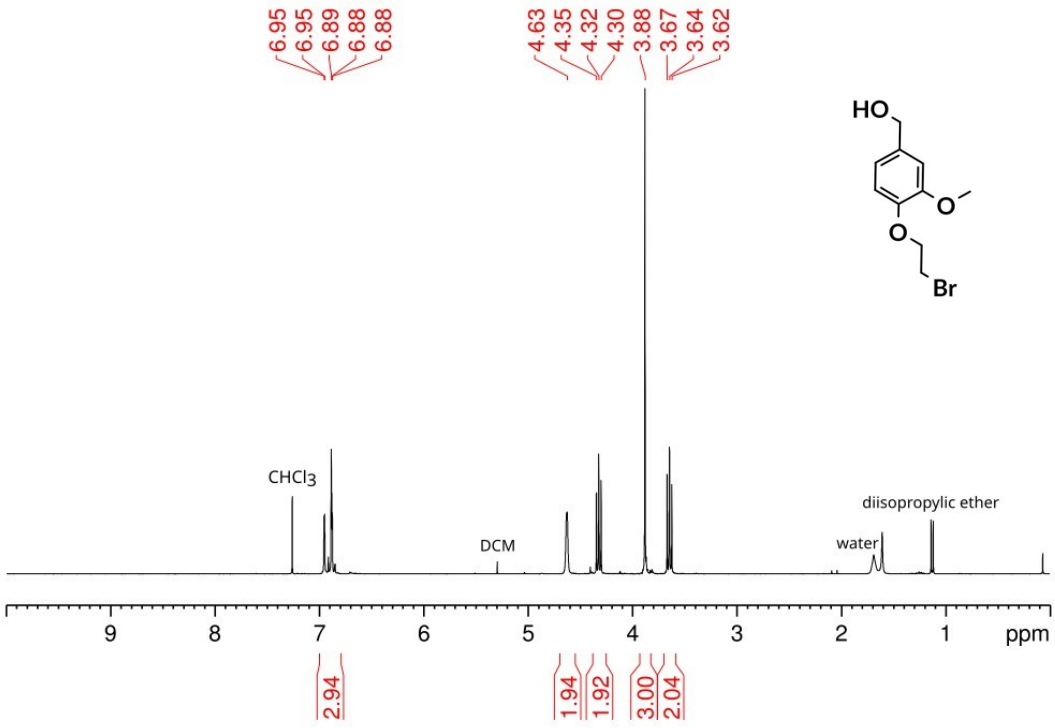


Figure S1. ^{1}H-NMR spectrum of 2-bromoethoxyvanillyl alcohol ($CDCl_3$, 300 MHz, 298 K).

Protected 2-bromoethoxyvanillyl alcohol 2

A solution of PPTS (960 mg, 3.8 mmol) in dry dichloromethane (5 mL) was added to a mixture of 2-bromoethoxyvanillyl alcohol (5.0 g, 19.1 mmol) and DHP (4.4 mL, 48.1 mmol) in dry tetrahydrofuran (25 mL) under argon. The mixture was stirred at room temperature overnight, and the solvent was removed under reduced pressure. The crude was retaken in dichloromethane (50 mL), washed twice with water (2×50 mL), dried on $MgSO_4$ and the solvent was removed under reduced pressure to give compound **2** (6.23 g, 18.1 mmol) as a yellow oil with a 95 % yield.

^{1}H-NMR ($CDCl_3$, 400 MHz): 6.89 (m, 3H), 4.70 (d, $^{3}J_{H-H}$= 11.8 Hz, 1H), 4.66 (t, $^{3}J_{H-H}$= 7.2 Hz, 1H), 4.42 (d, $^{3}J_{H-H}$= 11.8 Hz, 1H), 4.29 (t, $^{3}J_{H-H}$= 13.4 Hz, 2H), 3.93 – 3.87 (m, 1H), 3.85 (s, 3H), 3.61 (t, $^{3}J_{H-H}$= 13.4 Hz, 2H), 3.55 – 3.49 (m, 1H), 1.87 – 1.50 (m, 6H).

The spectroscopic data matched with the reported data.[2]

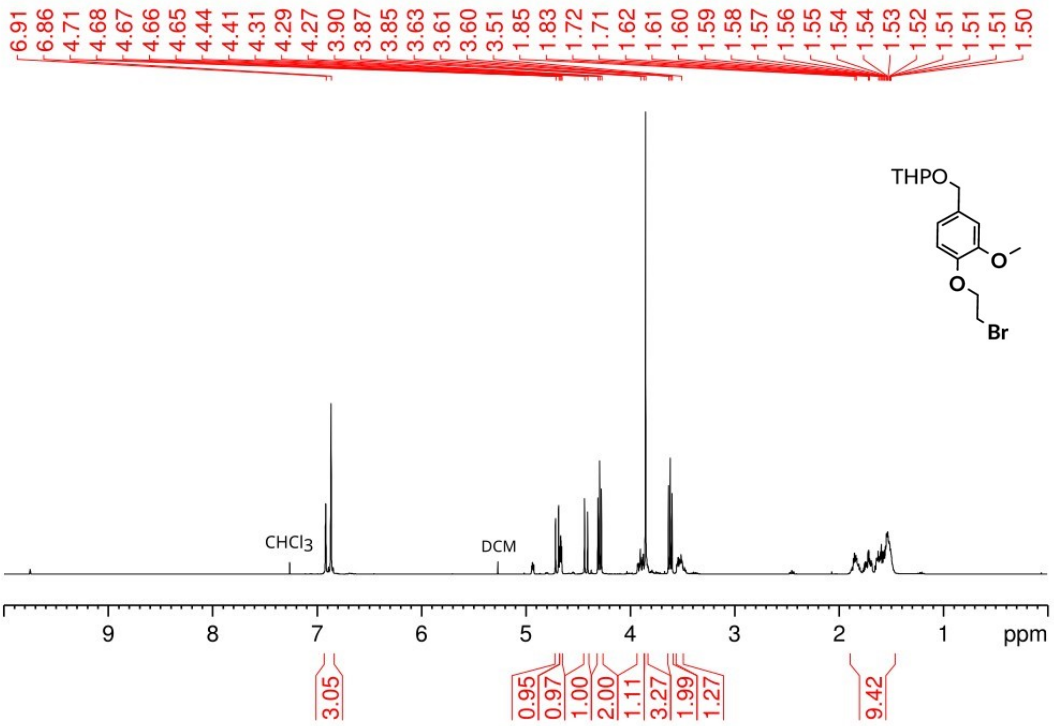


Figure S2. ^{1}H-NMR spectrum of compound **2** ($CDCl_3$, 400 MHz, 298 K).

Compound 3

Potassium phthalimide (1.93 g, 10.4 mmol) was added to a solution of compound **2** (3.00 g, 8.7 mmol) in dimethylformamide (70 mL) in a sealed schlenk. The mixture was stirred at 85 °C for 2 h, let cool to room temperature and the solvent was removed under reduced pressure. The crude was retaken in dichloromethane (100 mL), washed twice with a solution of sodium hydroxide (10 %, 2×75 mL), then twice with water (2×75 mL), dried on $MgSO_4$ and the solvent was removed under reduced pressure to give compound **3** (2.25 g, 5.5 mmol) as a yellow oil with a 63 % yield.

^{1}H-NMR ($CDCl_3$, 400 MHz): 7.85 (q, $^{3}J_{H-H}$= 2.8 Hz, 2H), 7.71 (q, $^{3}J_{H-H}$= 2.8 Hz, 2H), 6.88 (m, 3H), 4.68 (d, $^{2}J_{H-H}$= 11.8 Hz, 1H), 4.65 (t, $^{3}J_{H-H}$= 4.4 Hz, 1H), 4.40 (d, $^{2}J_{H-H}$= 11.8 Hz, 1H), 4.26 (t, $^{3}J_{H-H}$= 6.1 Hz, 2H), 4.11 (t, $^{3}J_{H-H}$= 6.1 Hz, 2H), 3.90 (t, $^{3}J_{H-H}$= 8.2 Hz, 1H), 3.75 (s, 3H), 3.53 (t, $^{3}J_{H-H}$= 10.6 Hz, 1H), 1.69 (m, 6H).

^{13}C-NMR ($CDCl_3$, 100 MHz): 167.1, 148.8, 146.3, 132.9 (CH), 131.1, 131.1, 122.3 (CH), 119.5 (CH), 113.6 (CH), 111.2 (CH), 96.5 (CH), 67.6 (CH_2), 65.2 (CH_2), 61.2 (CH_2), 54.9 (CH_3), 36.2 (CH_2), 29.6 (CH_2), 28.7 (CH_2), 24.4 (CH_2), 18.4 (CH_2).

HRMS: m/z calculated for $[3+NH_4]^+$ ($C_{23}H_{29}N_2O_6^+$) 429.2020, measured 429.2018.

IR: 2939 (w), 1774 (w), 1708 (s), 1512 (m), 1466 (w), 1391 (m), 1261 (w), 1230 (w), 1117 (w), 1075 (w), 1016 (s), 976 (w), 903 (w), 869 (w), 802 (m), 718 (s), 529 (m).

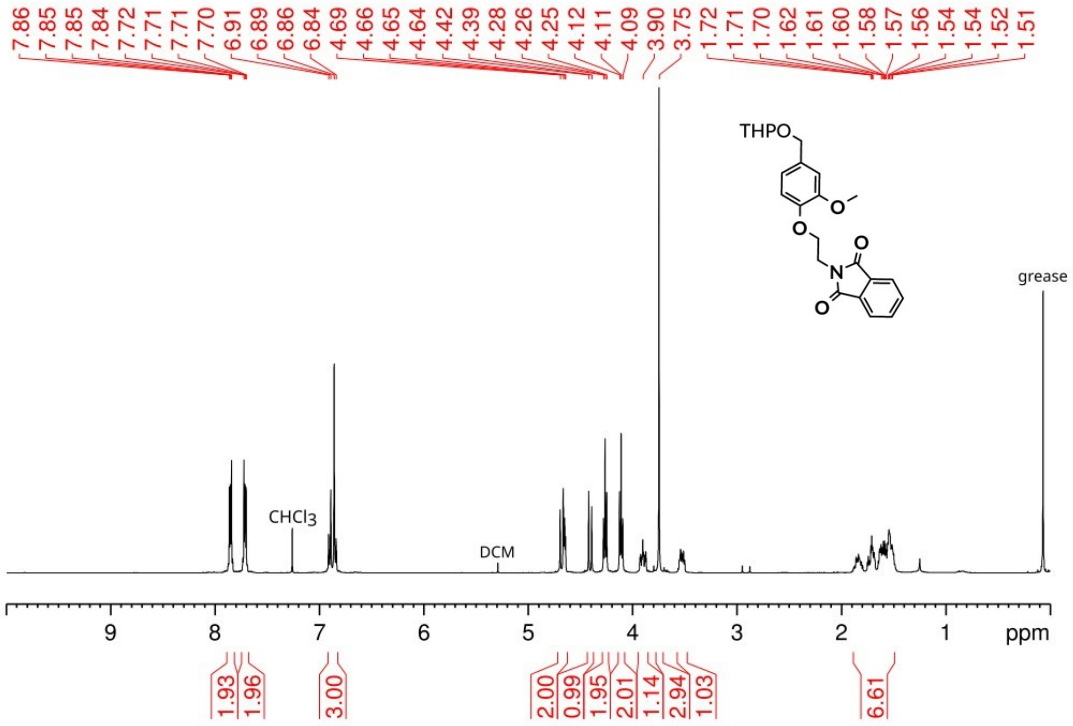


Figure S3. ^{1}H-NMR spectrum of compound **3** ($CDCl_3$, 400 MHz, 298 K).

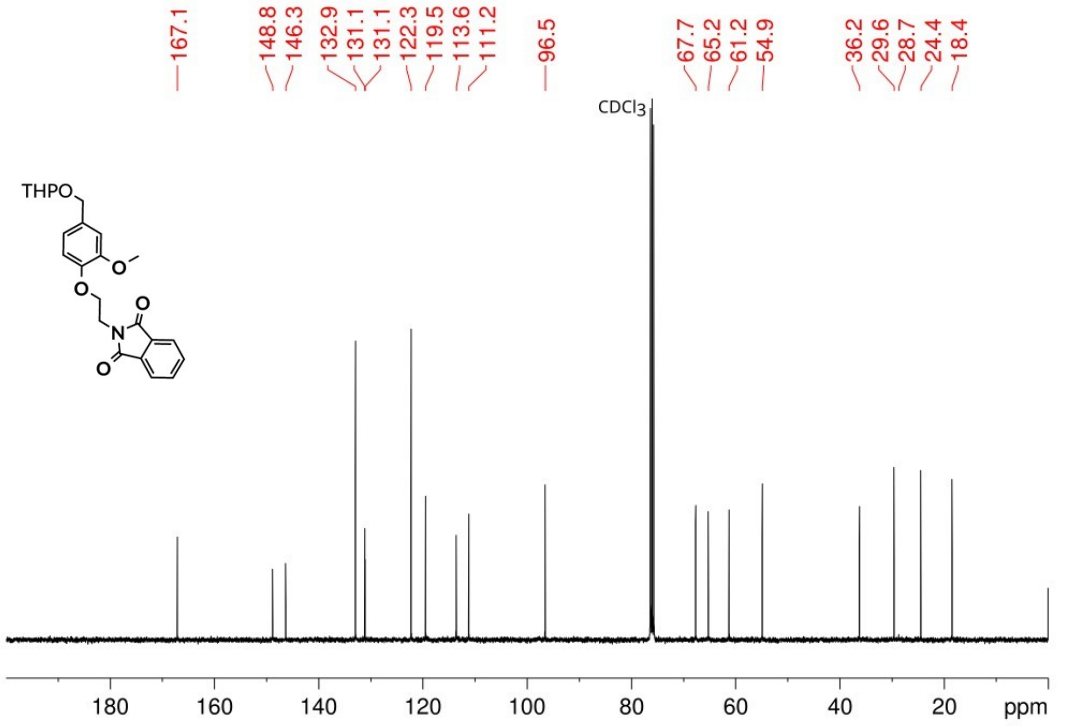


Figure S4. ^{13}C-NMR spectrum of compound **3** ($CDCl_3$, 100 MHz, 298 K).

Compound 4

Hydrazine hydrate (0.6 mL, 12.5 mmol) was added to a mixture of compound **3** (2.04 g, 5.0 mmol) in methanol (50 mL). The mixture was stirred at reflux for 3 h, let cool down at room temperature and filtrated. The solvent was removed under reduced pressure, the crude was retaken in dichloromethane (50 mL) and the white precipitate filtered. The organic phase was washed twice with a solution of sodium hydroxide (10 %, 2×50 mL), then with water (50 mL) and dried on $MgSO_4$. The solvent was removed under reduced pressure to give the amine **4** (915 mg, 3.25 mmol) with a 65 % yield.

^{1}H-NMR ($CDCl_3$, 400 MHz): 6.85 (m, 3H), 4.68 (d, $^3J_{H-H}$= 11.7 Hz, 1H), 4.64 (t, $^3J_{H-H}$= 7.2 Hz, 1H), 4.40 (d, $^3J_{H-H}$= 11.7 Hz, 1H), 3.99 (t, $^3J_{H-H}$= 5.2 Hz, 2H), 3.91 – 3.86 (m, 1H), 3.83 (s, 3H), 3.54 – 3.48 (m, 1H), 3.05 (t, $^3J_{H-H}$= 5.2 Hz, 2H), 1.86 – 1.47 (m, 6H).

The spectroscopic data matched with the reported data.[2]

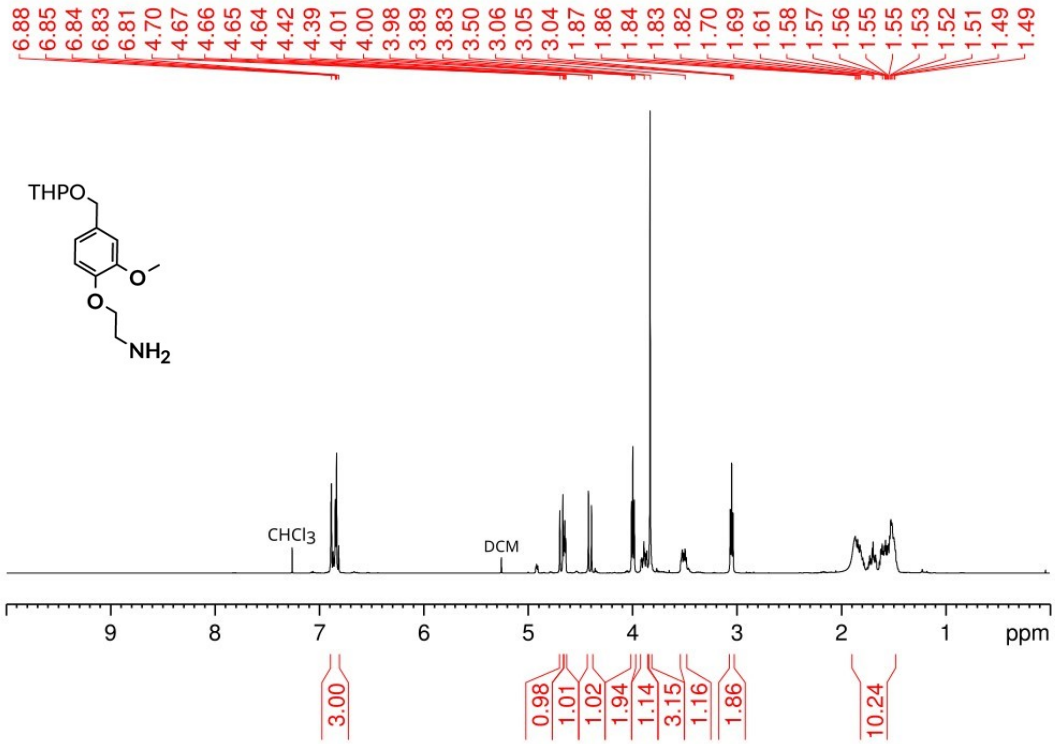


Figure S5. ^{1}H-NMR spectrum of compound **4** ($CDCl_3$, 400 MHz, 298 K).

Compound 5

DIPEA (0.8 mL, 4.74 mmol) was added to a suspension of NTDA (408 mg, 1.52 mmol) and compound **4** (900 mg, 3.2 mmol) in dimethylformamide (15 mL) in a sealed schlenk. The mixture was stirred overnight at 130 °C. The solvent was removed under reduced pressure and the remaining solid was suspended in acetone (10 mL) and precipitated with water (50 mL). The resulting brown solid was washed with water to give precursor **5** (950 mg, 1.2 mmol) with 80 % yield.

^{1}H-NMR ($CDCl_3$, 400 MHz): 8.78 (s, 4H), 6.97 (d, $^{3}J_{H-H}$= 8.1 Hz, 2H), 6.88 – 6.84 (m, 4H), 4.69 – 4.64 (m, 8H), 4.42 – 4.36 (m, 6H), 3.93 – 3.87 (m, 2H), 3.71 (s, 6H), 3.55 – 3.50 (m, 2H), 1.87 – 1.50 (m, 12H).

^{13}C-NMR ($CDCl_3$, 100 MHz): 162.9, 149.6, 147.5, 131.9, 131.1, 126.8, 126.7, 120.6, 114.0, 112.1, 97.6, 68.7, 65.8, 62.3, 55.9, 39.6, 30.6, 25.5, 19.5.

IR: 2940.46 (m), 1704.45 (m), 1664.43 (s), 1581.64 (w), 1513.28 (m), 1453.01 (m), 1420.35 (w), 1372.04 (w), 1341.47 (m), 1262.87 (w), 1244.32 (m), 1161.04 (w), 1137.41 (m), 1032.69 (s), 976.88 (w), 904.53 (w), 869.52 (w), 811.94 (w), 768.73 (m), 734.64 (w).

m.p.: 113.9 °C

HRMS: m/z calculated for $[5+NH_4]^+$ ($C_{44}H_{50}N_3O_{12}$) 812.3389, measured 812.3378.

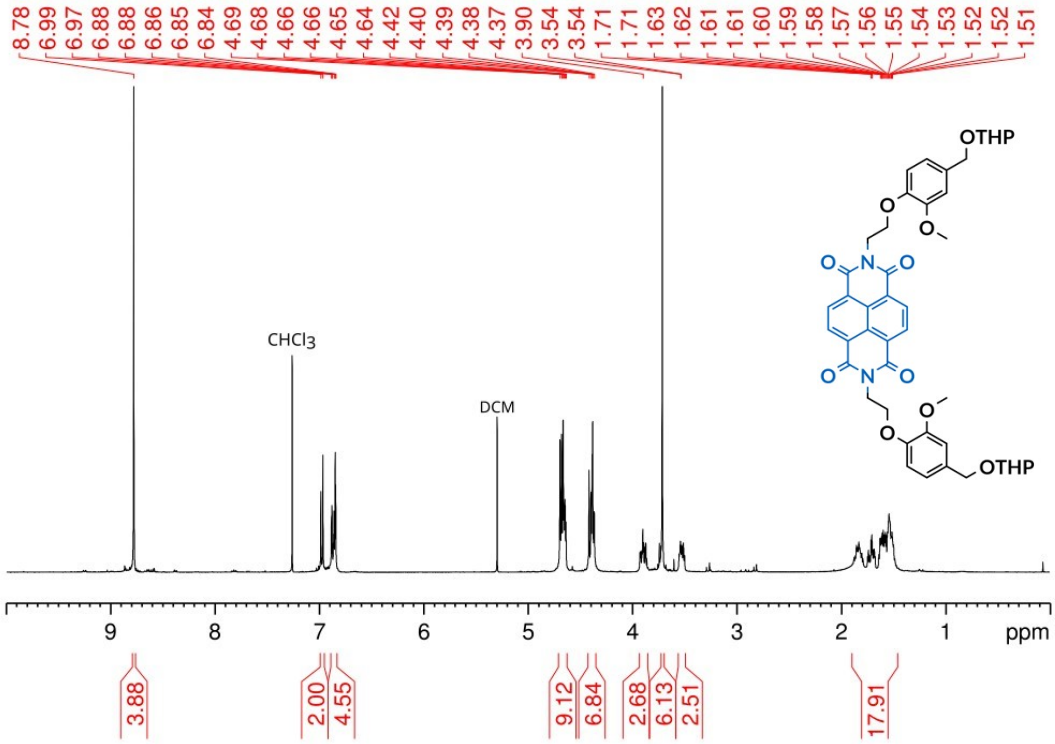


Figure S6. ^{1}H-NMR spectrum of compound **5** ($CDCl_3$, 400 MHz, 298 K).

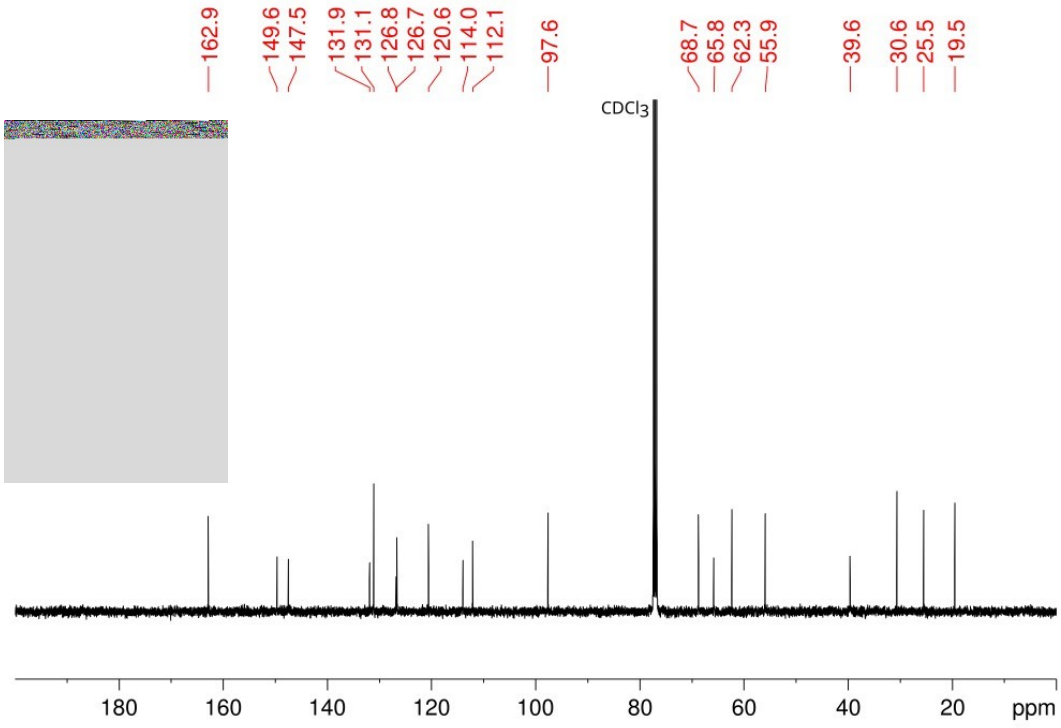


Figure S7. ^{13}C-NMR spectrum of compound **5** ($CDCl_3$, 100 MHz, 298 K).

Cryptophane 1: direct method

HCl (19 µL, 0.23 mmol) was added to a solution of precursor **5** (180 mg, 0.23 mmol) in formic acid (230 mL). The mixture was stirred at room temperature for two weeks and was extracted three times with dichloromethane (3×50 mL). The organic phase was washed three times with water (3×75 mL), dried on $MgSO_4$. The solvent was removed under reduced pressure and the crude was purified by flash silica gel column chromatography with a mixture of chloroform and methanol as eluent (gradient from 100:0 to 95:5, R_f= 0.3 in 100:2 mixture). A second purification by size-exclusion column chromatography in chloroform was performed, and the resulting solid was dissolved in chloroform (0.75 mL) and precipitated with diethyl ether (75 mL). The precipitate was purified by chiral HPLC to give *anti*-cryptophane **1** (2.8 mg, 1.6 µmol) and *syn*-cryptophane **1** (2.8 mg, 1.6 µmol) with a 4.2 % combined yield.

Cryptophane 1: coupling method

A mixture of NTDA **6** (16 mg, 59 µmol) and CTV-NH_2 **7**[3] (21 mg, 39 µmol) in dimethylformamide (20 mL) was heated in the micro-wave (5 min at 45 ◦C then 30 min at 130 °C). The solvent was removed under reduced pressure and the crude was purified by flash silica gel column chromatography with a mixture of chloroform and methanol as eluent (gradient from 100:0 to 100:3, R_f = 0.3 in 100:2 mixture). A second purification by size-exclusion column chromatography in chloroform was performed to give cryptophane **1** (0.5 mg, 0.3 µmol) with a 1.5 % yield.

anti-**1** ^{1}H-NMR ($CDCl_3$, 400 MHz): 8.60 (s, 12H), 6.83 (s, 6H), 6.74 (s, 6H), 4.66 – 4.61 (m, 6H), 4.66 (d, $^{2}J_{H-H}$= 13.7 Hz, 6H), 4.45 (t, $^{3}J_{H-H}$= 5.1 Hz, 3H), 4.41 (t, $^{3}J_{H-H}$= 5.1 Hz, 3H), 4.32 – 4.27 (m, 12H), 3.69 (s, 18H), 3.47 (d, $^{2}J_{H-H}$= 13.7 Hz, 6H).

syn-**1** ^{1}H-NMR ($CDCl_3$, 400 MHz): 8.59 (s, 12H), 6.87 (s, 6H), 6.76 (s, 6H), 4.73 – 4.67 (m, 6H), 4.67 (d, $^{2}J_{H-H}$= 13.7 Hz, 6H), 4.47 (t, $^{3}J_{H-H}$= 5.1 Hz, 3H), 4.44 (t, $^{3}J_{H-H}$= 5.1 Hz, 3H), 4.29 – 4.22 (m, 12H), 3.72 (s, 18H), 3.49 (d, $^{2}J_{H-H}$= 13.7 Hz, 6H).

anti-**1** ^{13}C-NMR ($CDCl_3$, 100 MHz): 161.7, 147.6, 145.5, 132.1, 130.7, 129.8, 125.6, 125.5, 115.6, 113.0, 65.7 (CH_2), 55.1, 38.9 (CH_2), 35.4 (CH_2).

syn-**1** ^{13}C-NMR ($CDCl_3$, 100 MHz): 162.7, 148.7, 146.8, 133.3, 131.7, 130.8, 126.6, 126.5, 117.2, 114.1, 67.1 (CH_2), 56.1, 40.2 (CH_2), 36.4 (CH_2).

MALDI: m/z calculated for $[\mathbf{1}]^{-\bullet}$ ($C_{102}H_{78}N_6O_{24}$) 1771.5, measured 1771.5, and m/z calculated for $[\mathbf{1}+Na]^{+}$ ($C_{102}H_{78}N_6O_{24}Na^{+}$) 1793.5, measured 1794.5, and m/z calculated for $[\mathbf{1}+K]^{+}$ ($C_{102}H_{78}N_6O_{24}K^{+}$) 1809.5, measured 1810.5.

HRMS: m/z calculated for $[syn\text{-}\mathbf{1}]^{+\bullet}$ ($C_{102}H_{78}N_6O_{24}$) 1771.5095, measured 1771.5127. m/z calculated for $[anti\text{-}\mathbf{1}]^{-\bullet}$ ($C_{102}H_{78}N_6O_{24}$) 1771.5106, measured 1771.5111.

anti-**1** IR: 2921.65 (w), 1666.11 (w), 1260.10 (w), 1089.84 (w), 1019.20 (m), 799.65 (m)
syn-**1** IR: 2921.56 (w), 1706.63 (w), 1666.42 (m), 1581.79 (w), 1509.57 (w), 1454.04 (w), 1341.03 (w), 1258.85 (m), 1088.43 (w), 1013.40 (m), 871.01 (w), 793.55 (m), 768.65 (w)

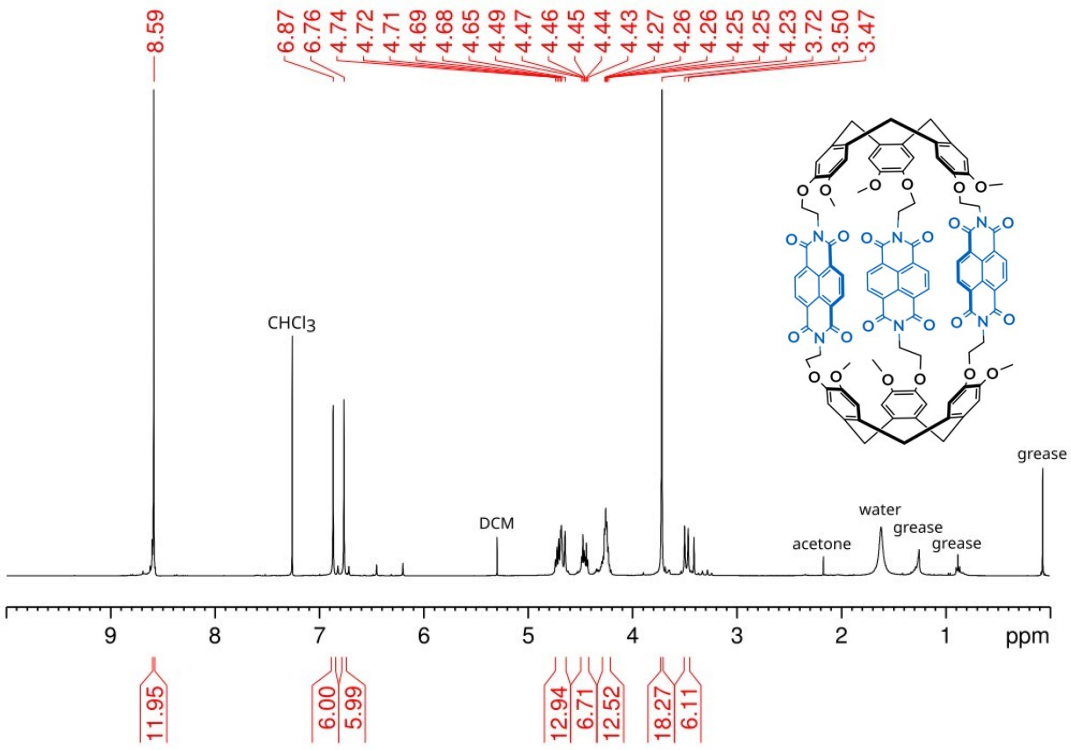


Figure S8. ^{1}H-NMR spectrum of *syn*-cryptophane **1** ($CDCl_3$, 400 MHz, 298 K).

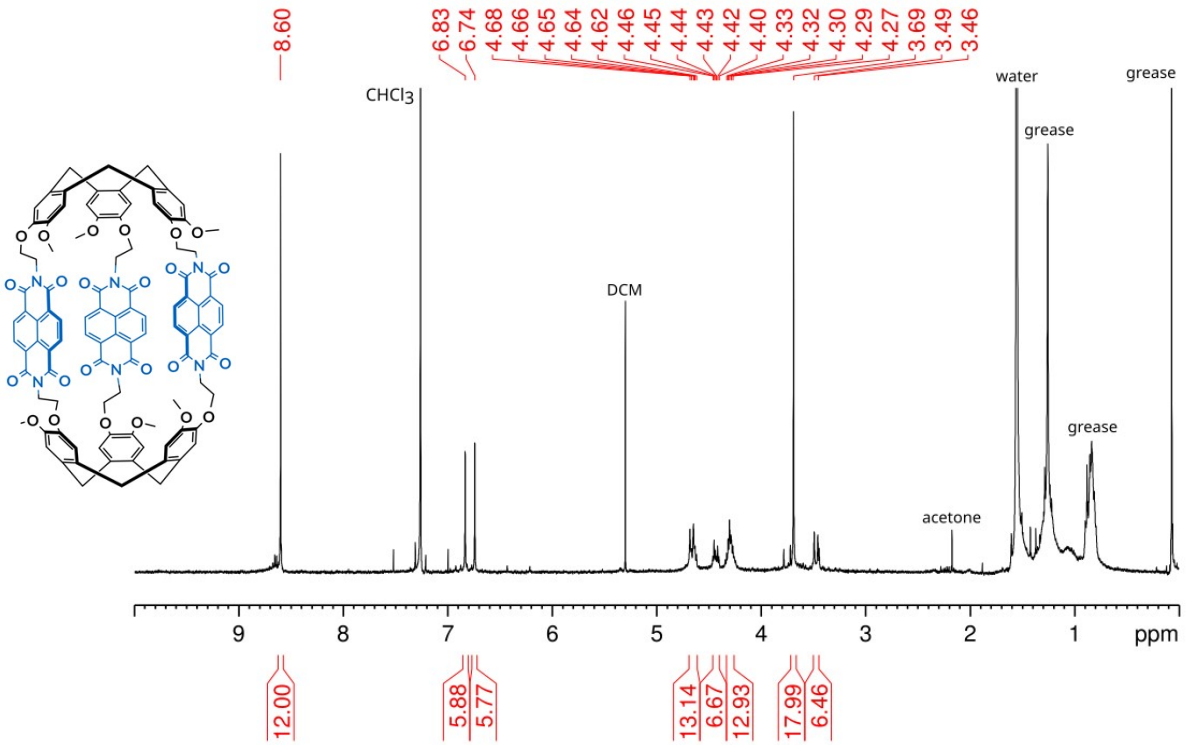


Figure S9. ^{1}H-NMR spectrum of *anti*-cryptophane **1** ($CDCl_3$, 400 MHz, 298 K).

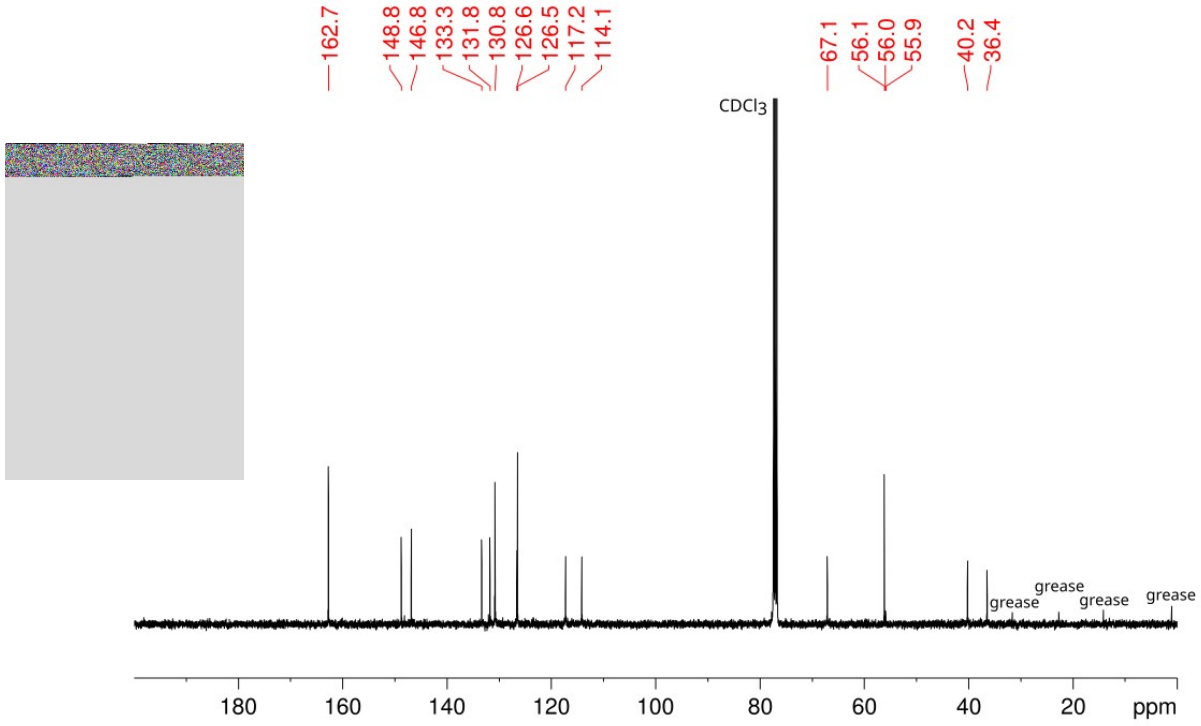


Figure S10. ^{13}C-NMR spectrum of *syn*-cryptophane **1** ($CDCl_3$, 100 MHz, 298 K).

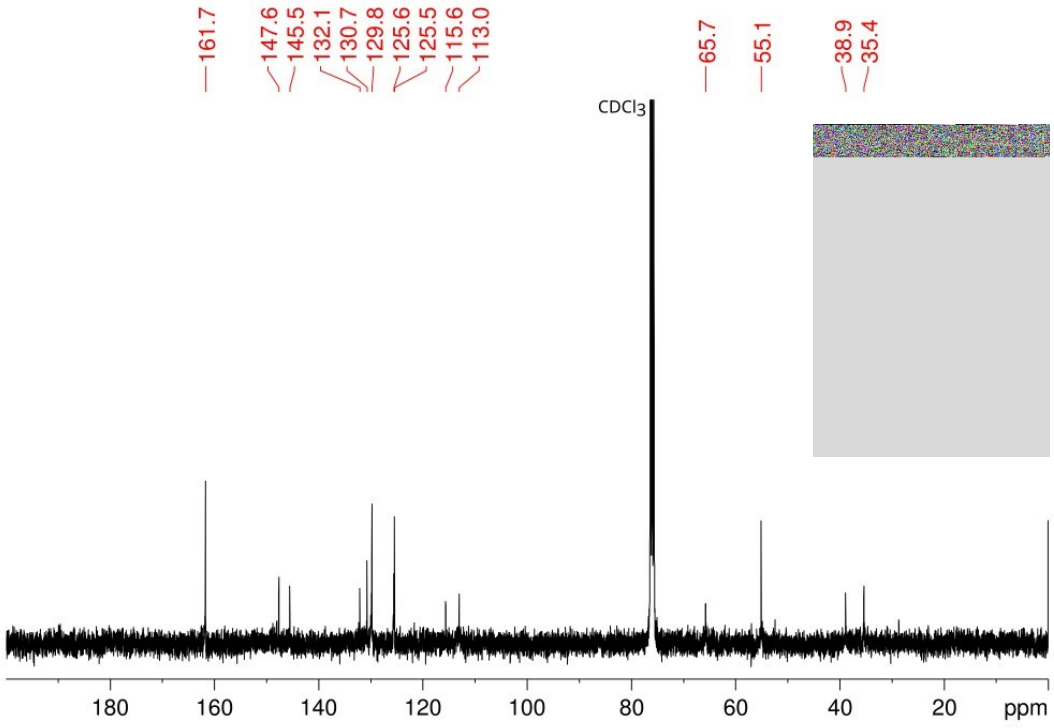
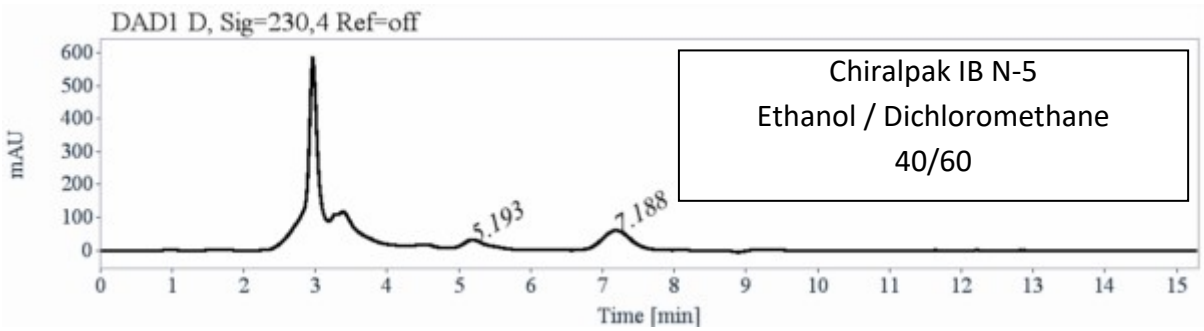


Figure S11. ^{13}C-NMR spectrum of *anti*-cryptophane **1** ($CDCl_3$, 100 MHz, 298 K).

3. Chiral stationary phase HPLC reports for the cryptophane

Purification and separation for **1**

• The sample is dissolved in ethanol, injected on the chiral column, and detected with an UV detector at 230 nm. The flow-rate is 1 mL/min.



RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.19	625	26.98	0.76		
7.19	1691	73.02	1.44	1.89	3.22
Sum	2316	100.00			

Figure S12. Chromatogram obtained by the injection of the racemate on analytical HPLC.

Preparative purification and separation for **1**:

• Sample preparation: About 35 mg of compound **1** are dissolved in 1.5 mL of dichloromethane.

• Chromatographic conditions: Chiralpak IB N-5 (250 x 10 mm), ethanol / dichloromethane (40/60) as mobile phase, flow-rate = 5 mL/min, UV detection at 230 nm.

• Injections (stacked): 22 times 70 µL, every 7.8 minutes.

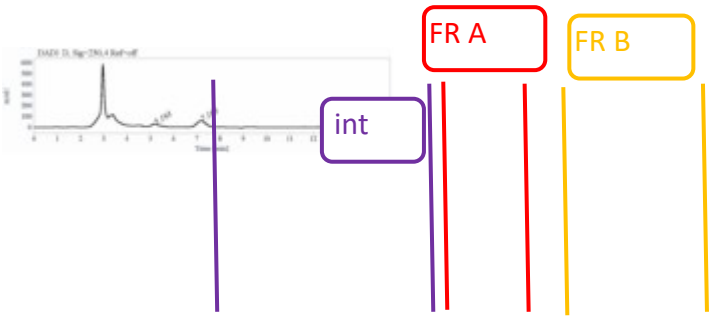


Figure S13. Chromatogram obtained by the injection of the racemate on preparative HPLC.

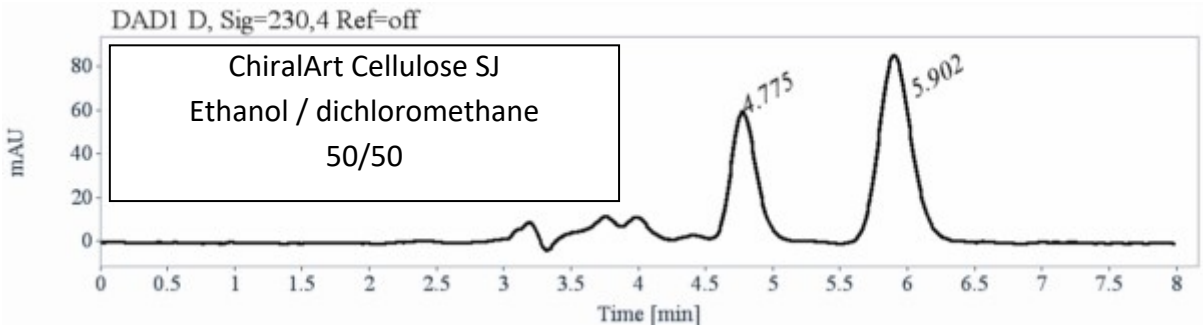
1 mg of FrA: first eluted enantiomer of *anti*-cryptophane **1.**

5 mg of FrB: **mixture of** second eluted enantiomer of *anti*-cryptophane **1** and *syn*-cryptophane **1.**

29 mg of int fraction

Purification and separation for **FrB**

• The sample is dissolved in ethanol, injected on the chiral column, and detected with an UV detector at 290 nm. The flow-rate is 1 mL/min.



RT [min]	Area	Area%	Capacity Factor
4.78	800	34.77	0.62
5.90	1501	65.23	1.00
Sum	2300	100.00	

Figure S14. Chromatogram obtained by the injection of the fraction B obtained above on analytical HPLC.

Preparative purification and separation for **FrB**:

• Sample preparation: About 5 mg of **FrB** are dissolved in 700 µL of dichloromethane.

• Chromatographic conditions: ChiralArt Cellulose SJ (250 x 10 mm), ethanol / dichloromethane (50/50) as mobile phase, flow-rate = 5 mL/min, UV detection at 290 nm.

• Injections (stacked): 30 times 20 µL, every 6.5 minutes.

Figure S15. Chromatogram obtained by the injection of the fraction B obtained above on preparative HPLC.

0.9 mg of FrB1: second eluted enantiomer of *anti*-cryptophane **1.**

1.85 mg of FrB2: *syn*-cryptophane **1.**

4. UV and ECD spectra

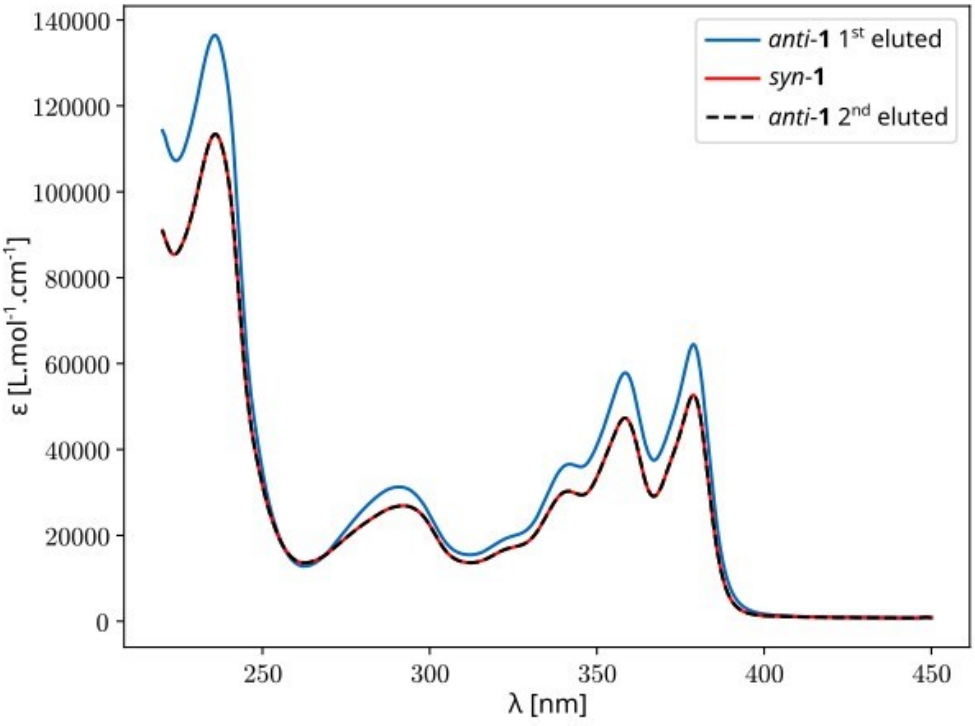


Figure S16. UV spectra of *anti*- and *syn*-cryptophane **1** (DCM, 1.4e-4 M).

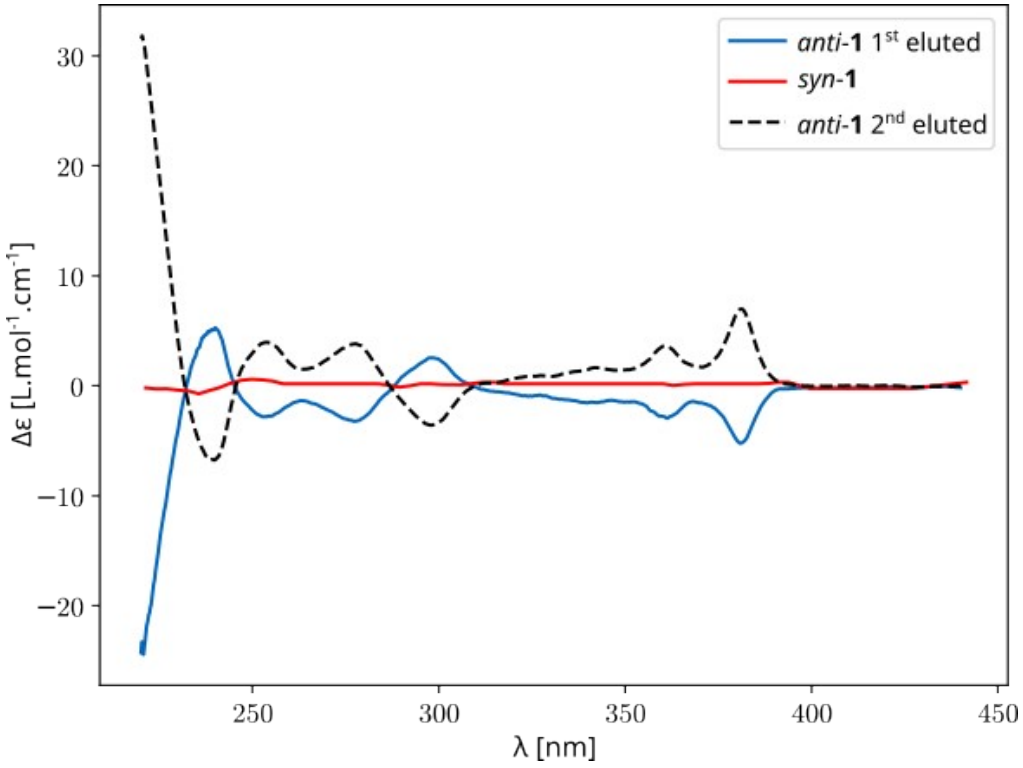


Figure S17. Electronic circular dichroism spectra of *anti*- and *syn*-cryptophane **1** (DCM, 1.4 10^{-4} M).

5. Titration experiments

Titration experiments were conducted using UV-vis spectroscopy according to the following protocol: a solution of the host was prepared, and the guest was dissolved in the same host solution to maintain a constant host concentration. Incremental additions of the guest were then performed. The maximum absorbance (often at λ_{max} = 379 nm) was recorded after each addition and plotted as a function of the $\frac{[Guest]}{[Host]}$ ratio. Despite the relatively small changes in absorbance, the association constant (K_a) was determined using a Python script based on the same equations as those employed by the Bindfit program for a 1:1 binding model.[4] The fitting error in UV measurements corresponds to the root mean square deviation (RMSD) divided by the maximum change in absorbance: $\frac{RMSD}{\max(\Delta A)}$. In this context, an error is considered acceptable up to 5 %.

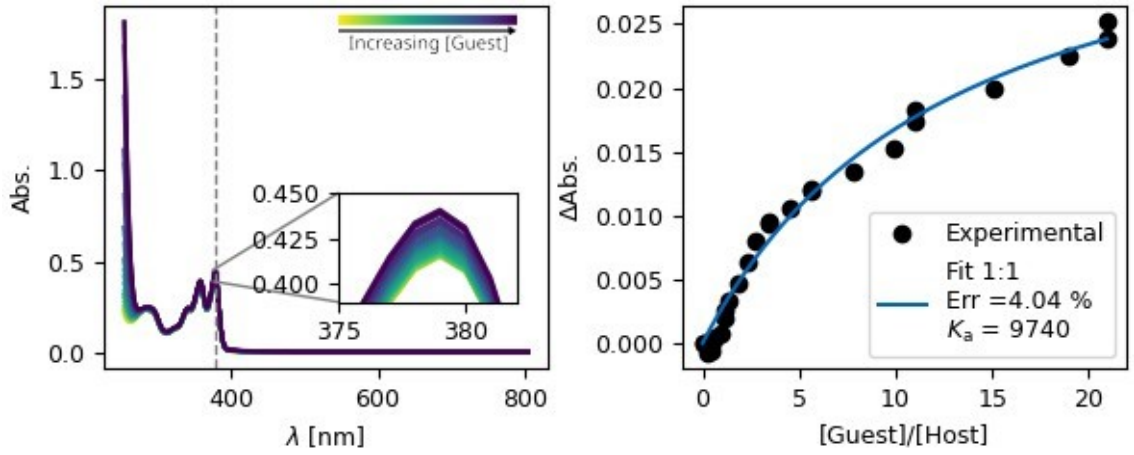


Figure S18. Left: absorption spectra for *syn*-cryptophane **1** (8.4×10^{-6} M, DCM) recorded for each addition of a TBAI solution (1.0×10^{-3} M, DCM) from 0.0 to 20.9 eq. Right: titration curve at λ = 379 nm.

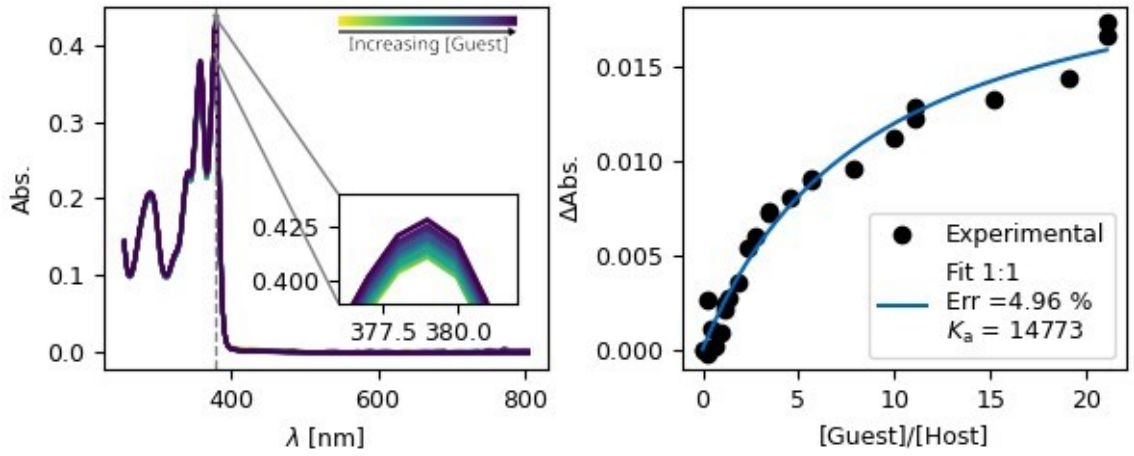


Figure S19. Left: absorption spectra for *syn*-cryptophane **1** (8.5×0^{-6} M, DCM) recorded for each addition of a $TBABF_4$ solution (1.0×10^{-3} M, DCM) from 0.0 to 20.9 eq. Right: titration curve at λ = 379 nm.

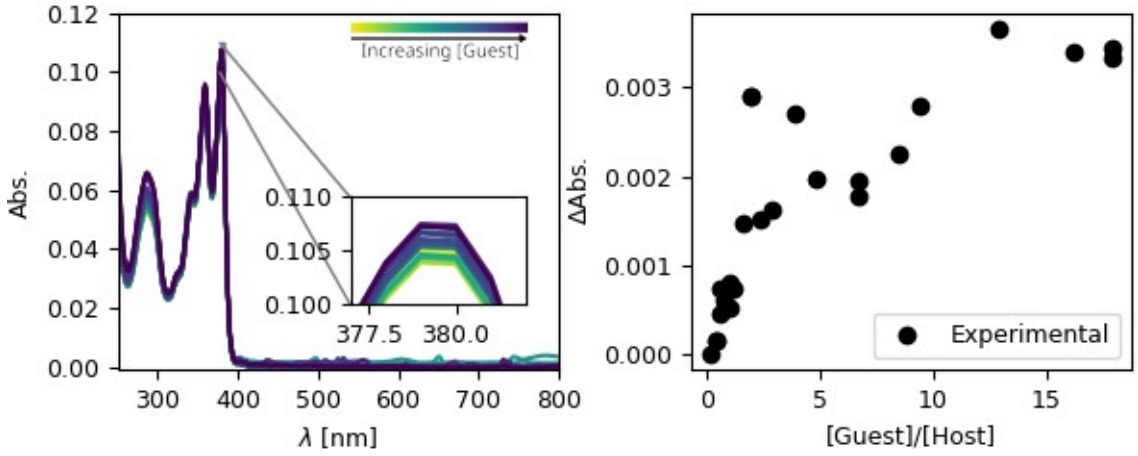


Figure S20. Left: absorption spectra for *syn*-cryptophane **1** (1.5×10^{-6} M, DCM) recorded for each addition of a TBACl solution (1.5×10^{-4} M, DCM) from 0.0 to 17.9 eq. Right: titration curve at λ = 379 nm.

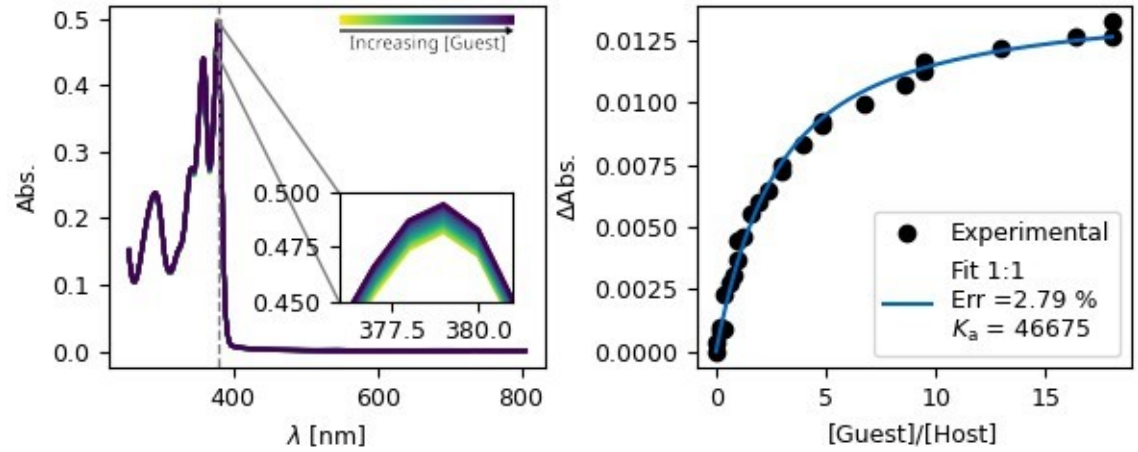


Figure S21. Left: absorption spectra for *syn*-cryptophane **1** (9.9×10^{-6} M, DCM) recorded for each addition of a $TBANO_3$ solution (1.0×10^{-3} M, DCM) from 0.0 to 17.9 eq. Right: titration curve at λ = 379 nm.

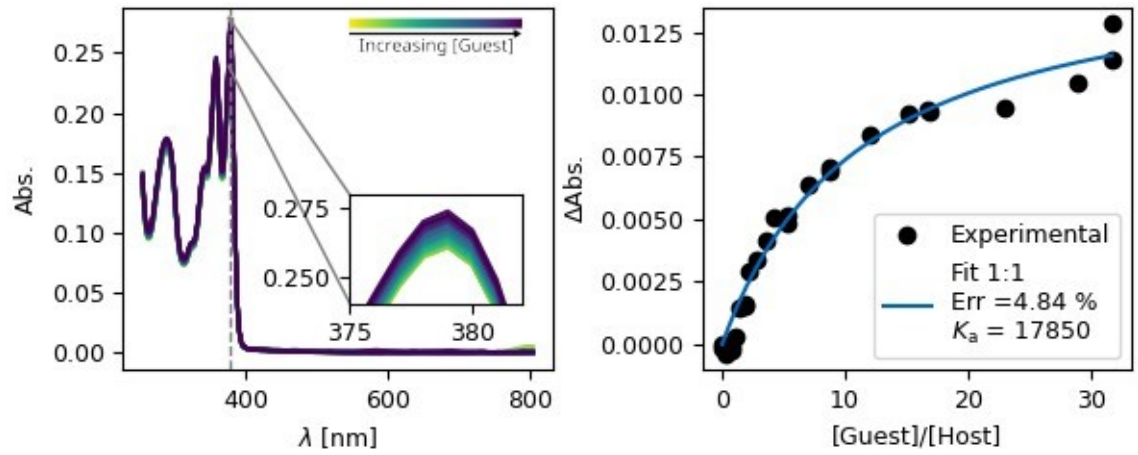


Figure S22. Left: absorption spectra for *syn*-cryptophane **1** (5.4×10^{-6} M, DCM) recorded for each addition of a $TBANO_3$ solution (1.0×10^{-3} M, DCM) from 0.0 to 33.4 eq. Right: titration curve at λ = 379 nm.

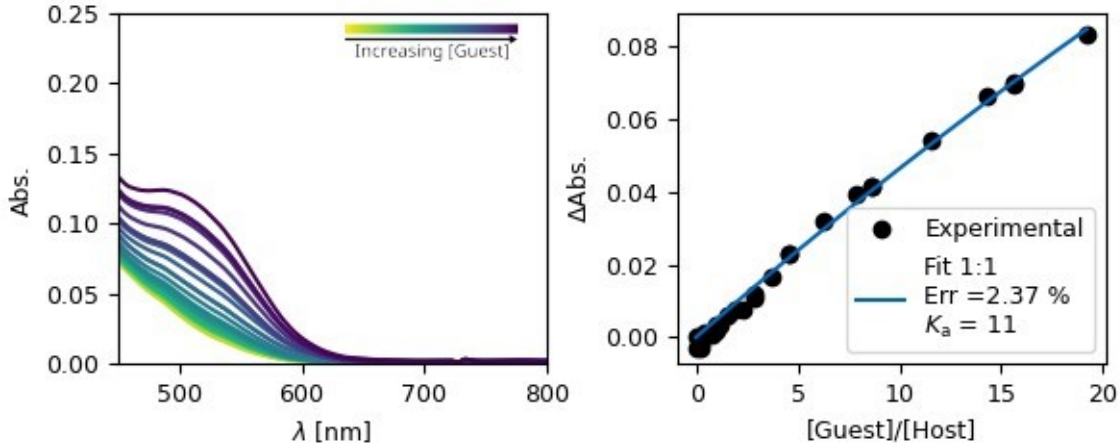


Figure S23. Left: absorption spectra for *syn*-cryptophane **1** (5.0×10^{-4} M, DCM) recorded for each addition of a pyrene solution (5.0×10^{-2} M, DCM) from 0.0 to 18.0 eq. Right: titration curve at λ = 525 nm.

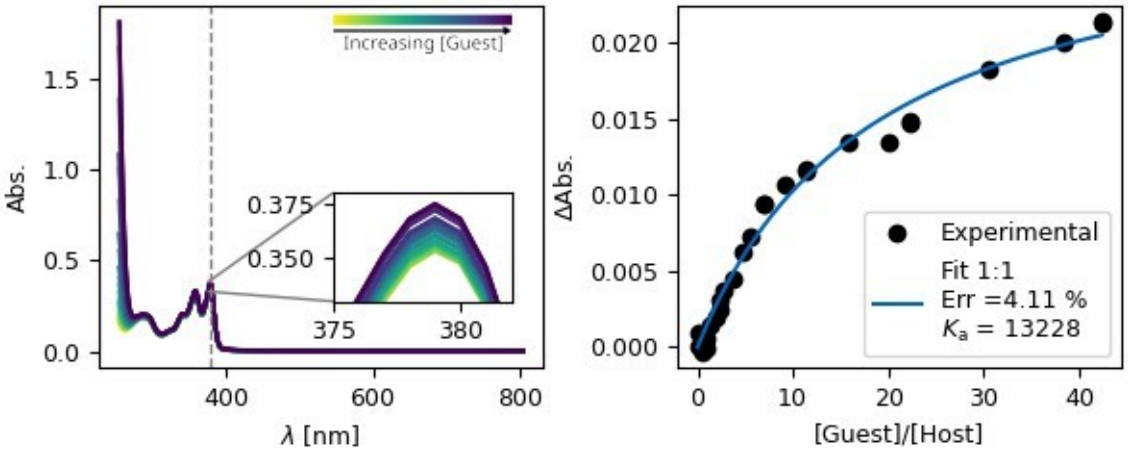


Figure S24. Left: absorption spectra for *anti*-cryptophane **1** (4.2×10^{-6} M, DCM) recorded for each addition of a TBAI solution (1.0×10^{-3} M, DCM) from 0.0 to 42.4 eq. Right: titration curve at λ = 380 nm.

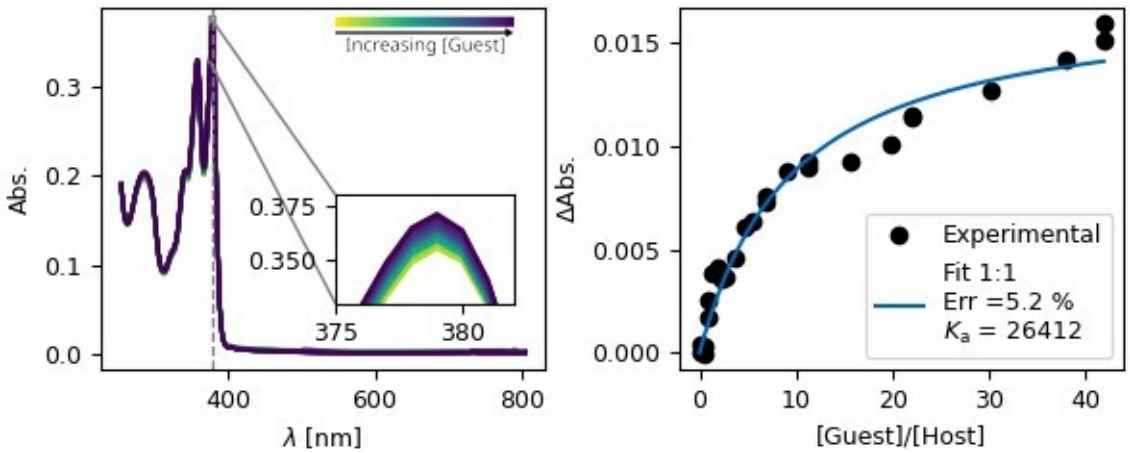


Figure S25. Left: absorption spectra for *anti*-cryptophane **1** (4.3×10^{-6} M, DCM) recorded for each addition of a $TBABF_4$ solution (1.0×10^{-3} M, DCM) from 0.0 to 42.2 eq. Right: titration curve at λ = 380 nm.

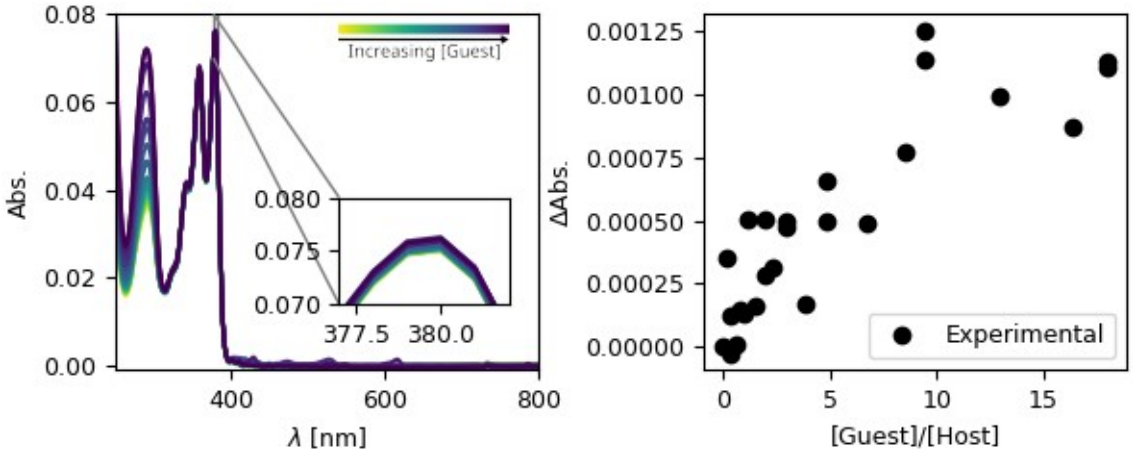


Figure S26. Left: absorption spectra for *anti*-cryptophane **1** (1.5×10^{-6} M, DCM) recorded for each addition of a TBACl solution (1.5×10^{-4} M, DCM) from 0.0 to 17.9 eq. Right: titration curve at λ = 380 nm.

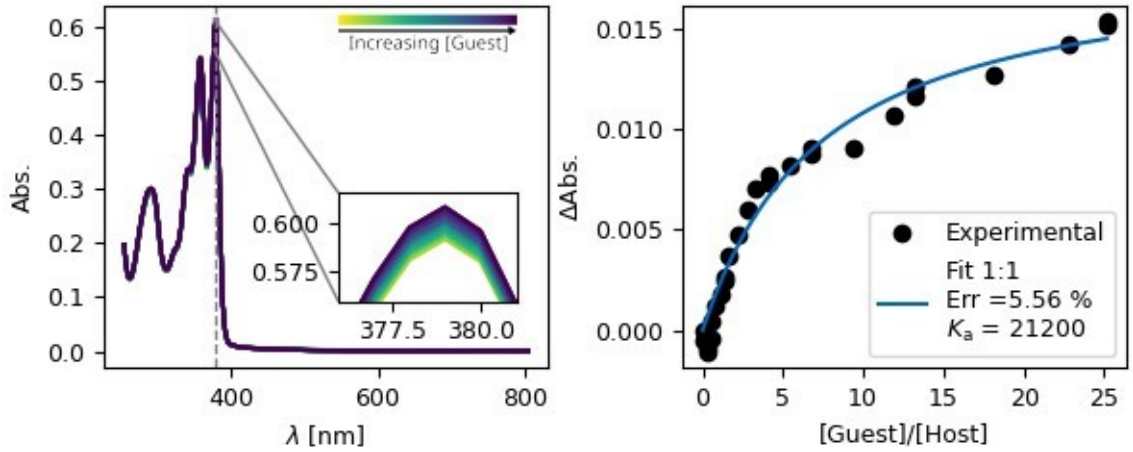


Figure S27. Left: absorption spectra for *anti*-cryptophane **1** (7.1×10^{-6} M, DCM) recorded for each addition of a $TBANO_3$ solution (1.0×10^{-3} M, DCM) from 0.0 to 25.2 eq. Right: titration curve at λ = 380 nm.

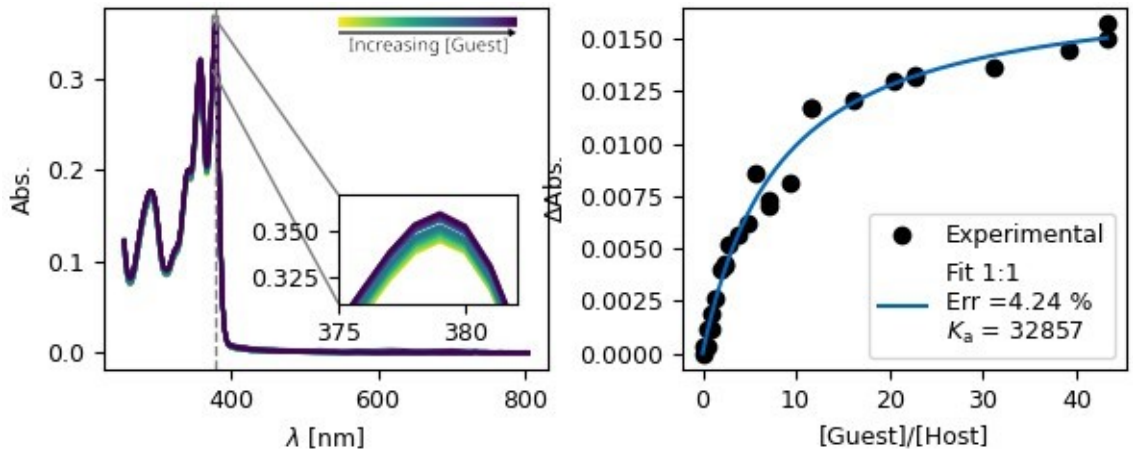


Figure S28. Left: absorption spectra for *anti*-cryptophane **1** (4.1×10^{-6} M, DCM) recorded for each addition of a $TBANO_3$ solution (1.0×10^{-3} M, DCM) from 0.0 to 43.5 eq. Right: titration curve at λ = 380 nm.

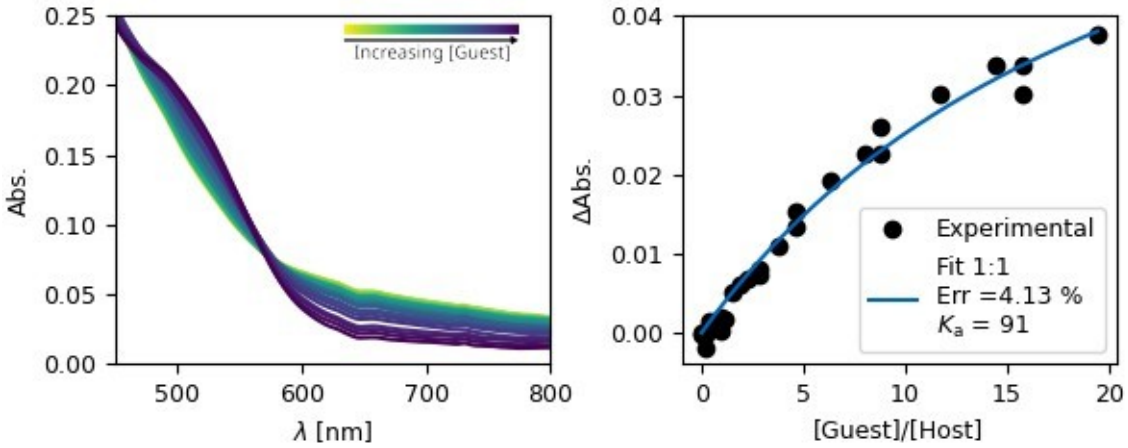


Figure S29. Left: absorption spectra for *anti*-cryptophane **1** (5.0×10^{-4} M, DCM) recorded for each addition of a pyrene solution (5.0×10^{-2} M, DCM) from 0.0 to 18.0 eq. Right: titration curve at λ = 525 nm.

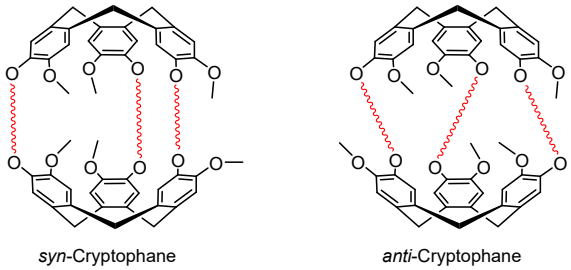


Figure S30. Schematization of *syn* and *anti*-cryptophanes connectivity

6. Calculations

a) Geometry optimization

DFT calculations were performed with the TURBOMOLE program package.[5] The structures of the cages were fully optimized (gas-phase calculations) at the PBE0-D3/def2-TZVP level of theory by imposing a C_3 symmetry, and the structure NO_3^-@*anti*-**1** was optimized at the PBE0-D3/def2-SVP level of theory by including solvent effects with the COSMO implicit solvent model for dichloromethane.[6] The RI approximation was employed, by exploiting the corresponding auxiliary basis sets.[7] Frequency calculations were performed to verify that structures of the cages are minima on their potential energy surface.

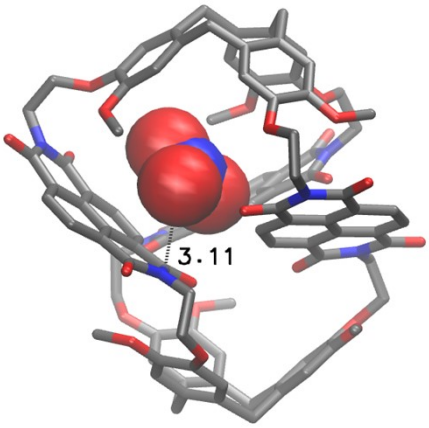
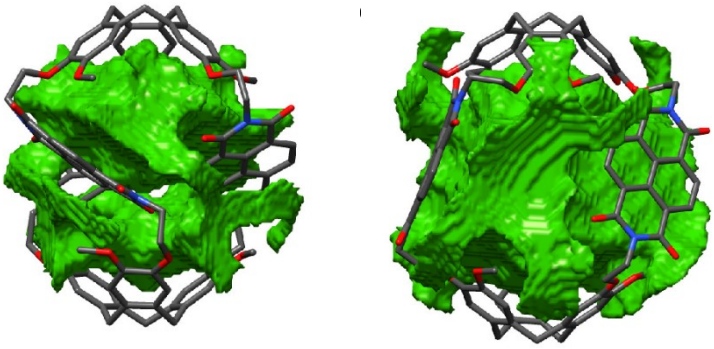


Figure S31. Possible structure of NO_3^-@*anti*-**1**. The distance between the anion and the interaction site of the NDI moiety is 3.11 Å and compatible with anion-π interactions.

Volumes were calculated using the MoloVol software in two-probes mode with a grid resolution of 0.1 Å, a small probe radius of 0.5 Å and a large probe radius of 3.8 Å for the *syn*-cryptophane 1 and 2.6 A for the *anti*-cryptophane **1**.[8] Reports of the calculations are available below. Coordinates of the structures are reported below in the xyz format. Images were rendered with UCSF Chimera, developed by the Resource for Biocomputing, Visualization, and Informatics at the University of California, San Francisco, with support from NIH P41-GM103311.[9]



b) Volume

Calculation par

Crystal unit cel

Probe mode: tv

Small probe radius: 0.5 A

Large probe radius: 2.3 A for *anti*-cryptophane 1 / 3.8 A for *syn*-cryptophane **1**

Grid resolution: 0.1 A

Optimization depth: 4

Elements radii:

O : 1.5 A

N : 1.66 A

H : 1.2 A

C : 1.77 A

c) Cavities data

anti-cryptophane **1**

Cavity ID	Occupied Volume (Å^3)	Accessible Volume (Å^3)	Cavity Type	Cavity center coordinates (A) x	y	z
1	327.105	140.146	Tunnel	0.15	0.15	-0.6

syn-cryptophane **1**

Cavity ID	Occupied Volume (Å^3)	Accessible Volume (Å^3)	Cavity Type	Cavity center coordinates (A) x	y	z
1	766.84	496.24	Tunnel	-0.1	-0.6	-0.3

d) Coordinates

Optimized structure of *syn*-cryptophane **1**

210

Energy = -6063.510065416

C -0.9139184 1.7691875 -7.2254739

C 0.3755451 1.7271780 -8.0096893

C -1.8387783 0.7331161 -7.2070100

C -2.2936098 3.0365509 -5.6720135

C -1.1686227 2.9125736 -6.4597101

C 1.9891205 -0.0931173 -7.2254739

C 1.5542864 1.2258706 -7.2070100

C 3.7765351 0.4680489 -5.6720135

C -1.0752022 -1.6760703 -7.2254739

C 0.2844919 -1.9589868 -7.2070100

C 0.7457917 -3.0029259 -6.3960719

C 1.3080075 -1.1888206 -8.0096893

C -1.4829253 -3.5045998 -5.6720135

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H	1.8069277	-3.2162081	-6.3847264
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C	-2.6123593	-1.8068608	5.9588113
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N	-0.1989010	-6.1611336	3.3087116
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N	-3.6056492	-5.3625962	-2.7819341
O	-2.5721607	-7.2222443	-3.5892173
C	-4.2787833	-5.1607695	-4.0572821
H	-5.3236481	-4.9156094	-3.8674192
H	-4.2084592	-6.1006110	-4.5999556
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H	6.9188667	-2.1526097	-3.8674192
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H	-1.5952186	7.0682192	-3.8674192
H	-3.1790545	6.6949381	-4.5999556
C	1.6558572	-5.0322650	-4.6865328

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H 1.7516566 -5.8445062 -3.9676931

H 2.0920675 -5.3464481 -5.6419162

C 3.5301408 3.9501469 -4.6865328

H 2.4996235 3.9828418 -4.3138357

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H 3.5841261 4.4850076 -5.6419162

C -5.1859979 1.0821181 -4.6865328

H -4.6990539 0.1733165 -4.3138357

H -5.9373191 1.4052740 -3.9676931

H -5.6761936 0.8614404 -5.6419162

Optimized structure of *anti*-cryptophane **1**

210

Energy = -6063.516503312

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C -1.6025227 0.7597214 -7.5648326

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H	-2.6662351	2.7055109	-6.0797951
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C	2.3618606	4.6479119	-4.1961869
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C	-5.2061401	-0.2785246	-4.1961869
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H	-5.9244349	-0.9238023	3.2463938
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H	6.5620787	1.8239588	2.6957689
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H	-0.4238467	-7.7762237	3.0894744
H	-1.7014447	-6.5949063	2.6957689
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C	4.6546553	2.2133915	1.1569097

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C	3.4711169	2.6115941	0.3661222
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C	3.0687272	3.9575905	0.3293084
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C	3.4091292	6.2690011	0.9205367
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H	-0.9979856	-2.9993890	-0.3034584
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Optimized structure of NO_3^-@*anti*-**1**

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H	3.8524729	1.2045921	-6.0664802
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H	-5.8930273	-0.5493832	-3.3401958
H	-5.5581917	-0.0839940	-5.0374429
H	-4.5012429	0.5131860	-3.7113963
C	3.1992487	-4.0212985	-3.8028601
H	3.7754907	-4.5392034	-3.0251030
H	3.1632206	-4.6604362	-4.7016141
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O	-4.3248270	-1.5141654	-4.1566429
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C	-0.7339827	3.9667902	-5.4157380
C	-2.4241063	-2.6862627	-4.9700702
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O	5.0602311	-0.2050807	-4.4897453
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H	4.8877198	2.8744277	3.8679215
C	-5.3793856	3.1028812	4.7312261
H	-5.4730328	3.7784966	5.6017674
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H	6.8240795	2.3205182	2.3086448
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C	0.7725337	3.4636017	-1.2363249
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H	-0.2842754	1.6126920	-0.9432759
H	3.3238952	7.2887238	-1.3119460
C	-0.3668074	4.1442884	-1.8873660
C	0.9832748	6.2137810	-2.0560556
O	-1.4205998	3.5832066	-2.1068551
N	-0.1931196	5.4909625	-2.2178006
O	1.0725796	7.3589124	-2.4588342
N	-5.8946133	2.8687928	2.3642822
C	-4.8097448	3.1029266	1.5095564
C	-6.7641908	1.7882389	2.2848499
C	-4.4584906	2.0078789	0.5840148
O	-4.1955095	4.1489805	1.5478118
C	-6.4280765	0.7275364	1.3083542
O	-7.7286276	1.7088846	3.0249174
C	-5.2378905	0.8303626	0.5606100
C	-3.3439161	2.1152072	-0.2235215
C	-7.2113982	-0.4134014	1.2189359
C	-4.7995142	-0.2745858	-0.2032472
C	-2.9249267	1.0245416	-1.0069133

H	-2.7689453	3.0403403	-0.2235407
C	-6.7747792	-1.5127730	0.4611283
H	-8.1358376	-0.4662999	1.7972721
C	-3.6013760	-0.1767511	-0.9443876
C	-5.5593774	-1.4611839	-0.2047047
H	-2.0438078	1.1058185	-1.6408240
H	-7.3584227	-2.4347304	0.4269163
C	-3.0241148	-1.3827533	-1.5710962
C	-5.0210984	-2.6671384	-0.8743383
O	-1.9658861	-1.3756307	-2.1639537
N	-3.7500580	-2.5678919	-1.4192050
O	-5.6390319	-3.7172665	-0.9223208
N	0.2584172	-5.9607699	1.9671935
C	-0.3646144	-4.9128118	1.2688223
C	1.6091340	-6.2702600	1.9161789
C	0.5312614	-3.9703341	0.5597852
O	-1.5709976	-4.8070157	1.2432606
C	2.4730263	-5.3832384	1.1019973
O	2.0574370	-7.2217091	2.5310556
C	1.9182091	-4.2430936	0.4828641
C	0.0121890	-2.8329783	-0.0288340
C	3.8303065	-5.6449393	0.9971325
C	2.7657810	-3.3463221	-0.2112946
C	0.8514577	-1.9642884	-0.7578673
H	-1.0410305	-2.5848741	0.1147832
C	4.6715897	-4.7557478	0.3106305
H	4.2344839	-6.5385607	1.4767747
C	2.2097866	-2.2078018	-0.8446013
C	4.1503808	-3.6112939	-0.2727514
H	0.4135465	-1.0908313	-1.2390629
H	5.7449738	-4.9415898	0.2411055

C	3.0968210	-1.2748795	-1.5777356
C	5.0530854	-2.6480892	-0.9442940
O	2.6779614	-0.3267434	-2.2061620
N	4.4706747	-1.5226755	-1.4967998
O	6.2584009	-2.8247368	-1.0073115
N	-1.6909030	-0.1087608	1.5635035
O	-0.7250100	0.0446783	0.7870176
O	-1.9590700	0.7536027	2.3996414
O	-2.3870815	-1.1391280	1.4631269

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