Electronic supplementary information

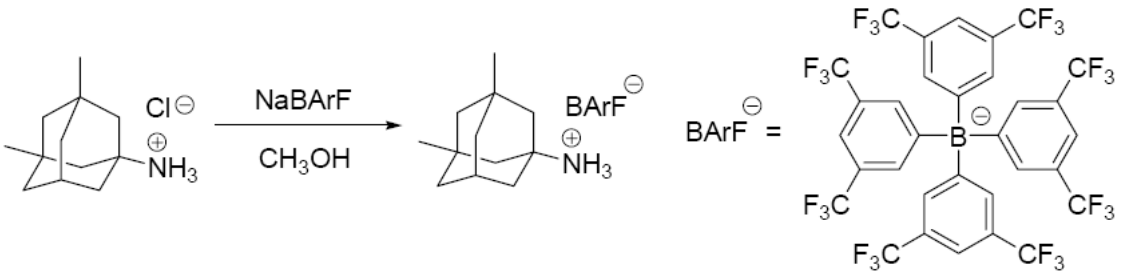
Host-guest properties of pillar[7]arene towards substituted adamantane ammonium cation

Contents

Materials and methods.

per-Ethylated pillar[5,6,7]arenes (EtP5A, EtP6A and EtP7A) [S1] were prepared according to our previously reported method. Sodium tetrakis[3,5-bis(trifluor omethyl)phenyl]borate (NaBArF) [S2] was synthesized according to a literature procedure. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV500 instrument. Electrospray ionization mass spectra (ESI-MS) were recorded on a Bruker Daltonics, Inc. APEXIII7.0 TESLA FTMS instrument.

Synthesis of 1·BArF



1·Cl (72 mg, 0.33 mmol) was added to a solution of NaBArF (300 mg, 0.34 mmol) in dry methanol (5.0 mL). The resulting solution was stirred at room temperature for 9 hours. Then the solvent was removed in vacuo. The residue was suspended in H_2O (5.0 mL), extracted with CH_2Cl_2 (15 mL × 3). The organic layer was collected, washed with H_2O (5.0 mL), dried ($MgSO_4$), and concentrated to give **1**·BArF (310 mg, 90%). ^{1}H NMR (500 MHz, CDCl3, 298 K): δ (ppm): 7.72 (s, 8H), 7.56 (s, 4H), 1.49 (d, J = 1.0 Hz, 2H), 1.38 − 1.22 (m, 10H), 1.08 (d, J = 13.1 Hz, 1H), 0.86 (s, 6H), ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ (ppm): 161.7 (q, $^{1}J_{CB}$ = 49.3 Hz), 134.7, 129.5 (q, $^{2}J_{CF}$ = 31.9 Hz), 124.4 (q, $^{1}J_{CF}$ = 271 Hz), 120.0, 117.7, 58.2, 48.8, 46.8, 40.8, 39.6, 33.0, 29.5, 28.8.

Copies of ^{1}H NMR and ^{13}C NMR spectra of pillararene hosts and gusets.

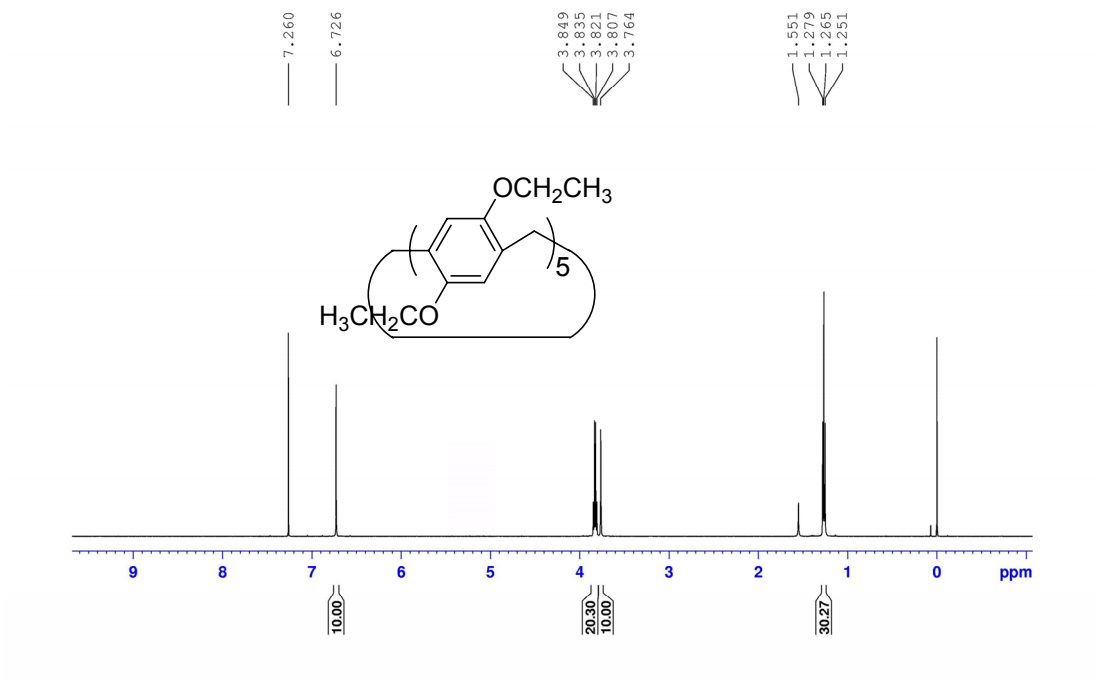


Figure S1. ^{1}H NMR spectrum (500 MHz) of EtP5A in $CDCl_3$.

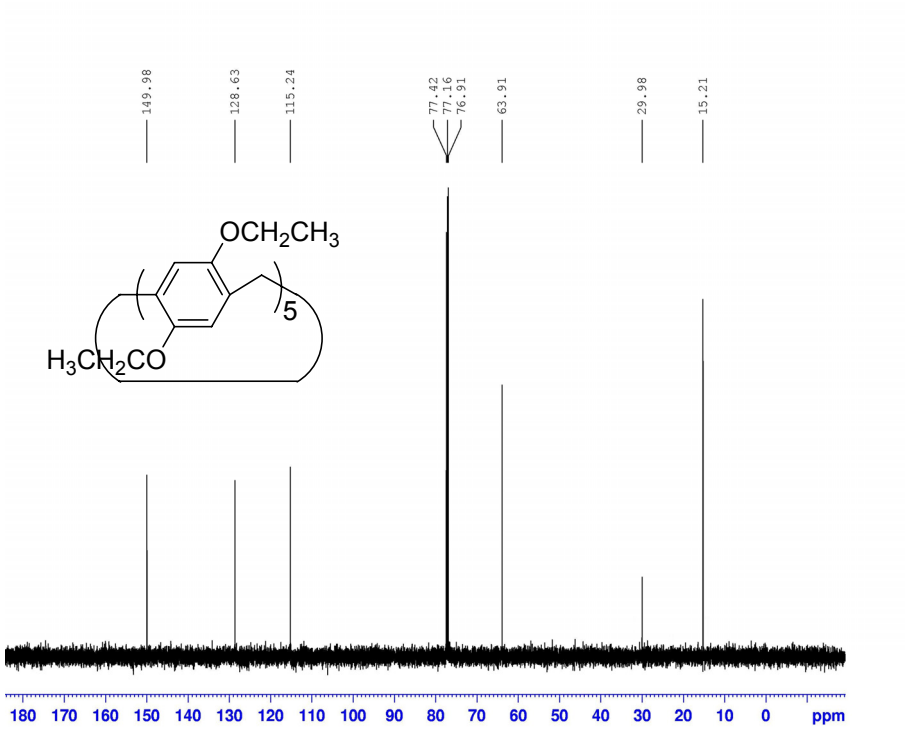


Figure S2. ^{13}C NMR spectrum (125 MHz) of EtP5A in $CDCl_3$.

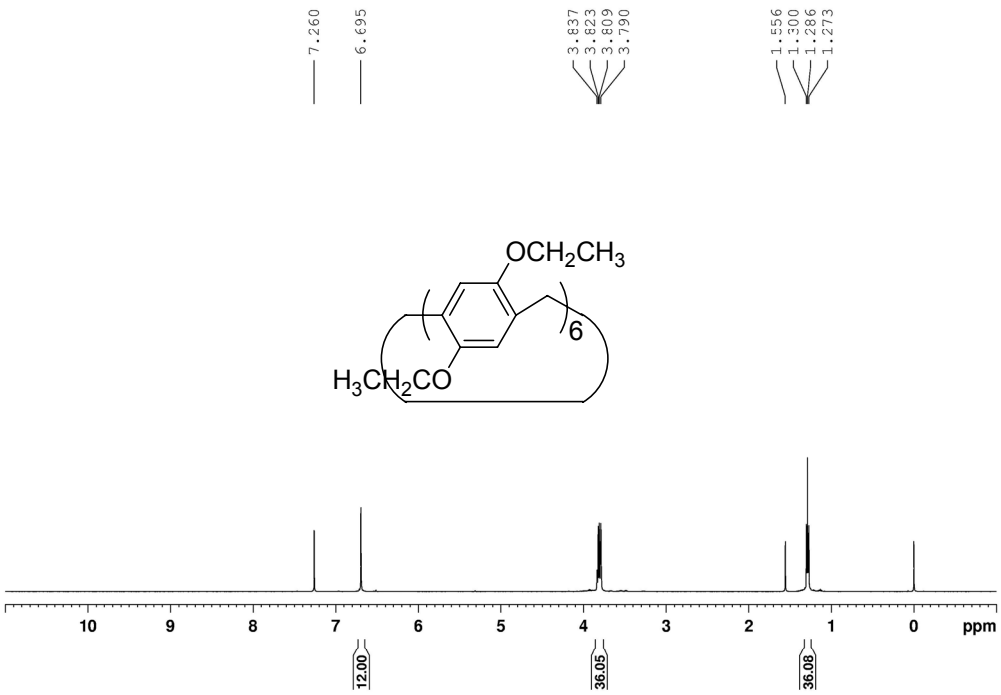


Figure S3. ^{1}H NMR spectrum (500 MHz) of EtP6A in $CDCl_3$.

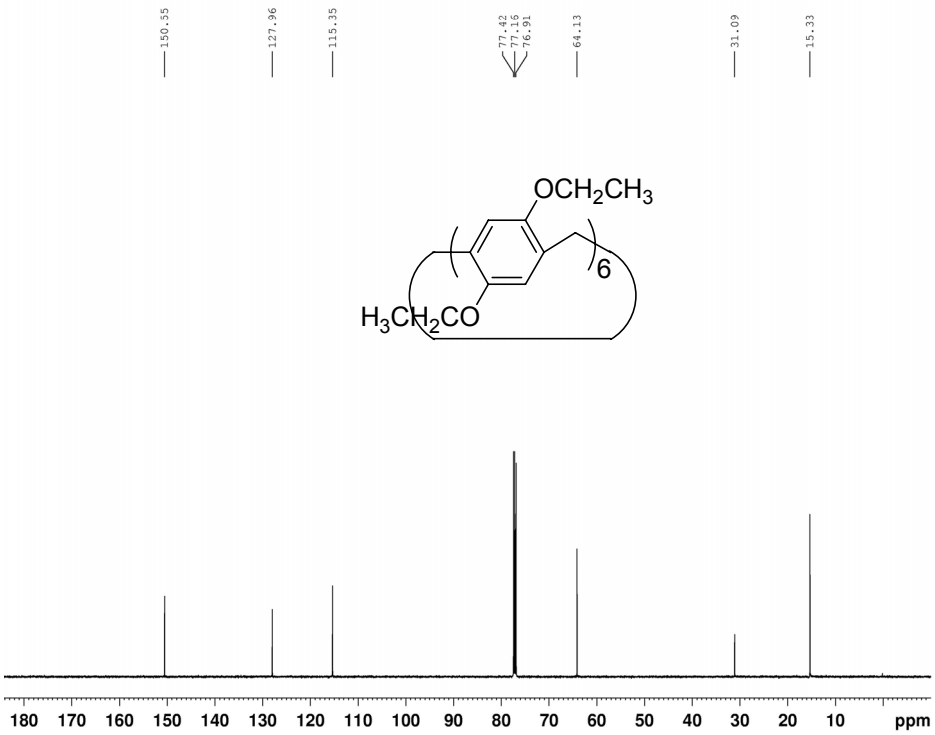


Figure S4. ^{13}C NMR spectrum (125 MHz) of EtP6A in $CDCl_3$.

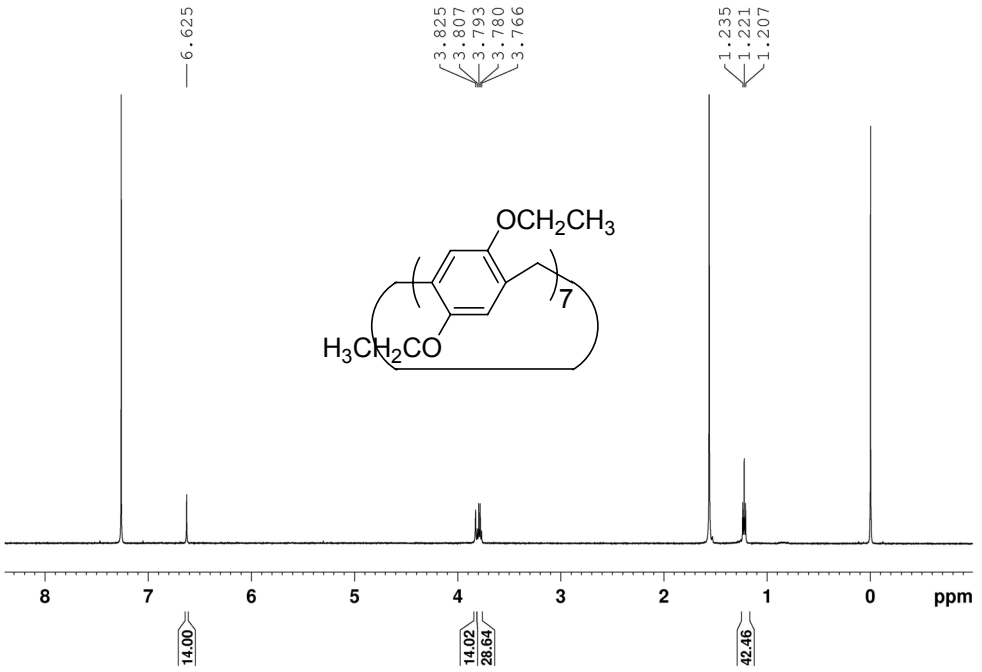


Figure S5. ^{1}H NMR spectrum (500 MHz) of EtP7A in $CDCl_3$.

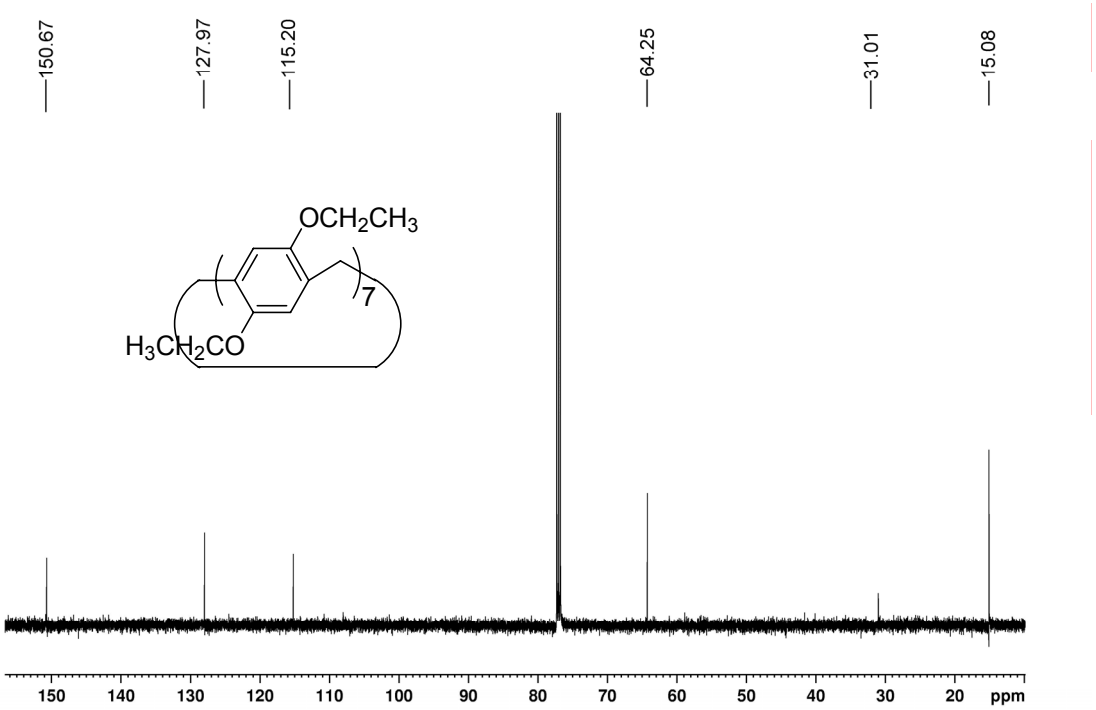


Figure S6. ^{13}C NMR spectrum (125 MHz) of EtP7A in $CDCl_3$.

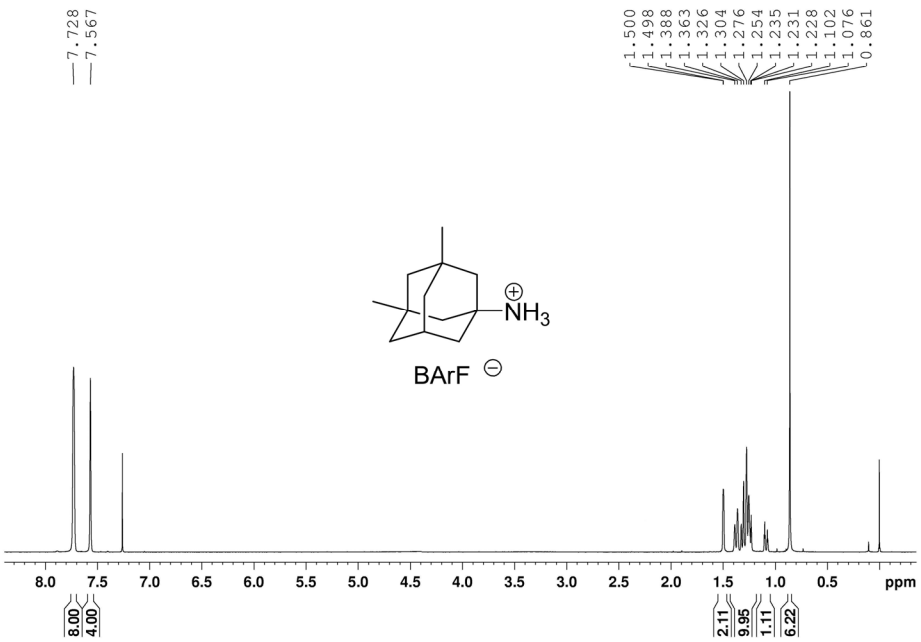


Figure S7. ^{1}H NMR spectrum (500 MHz) of **1**·BArF in $CDCl_3$.

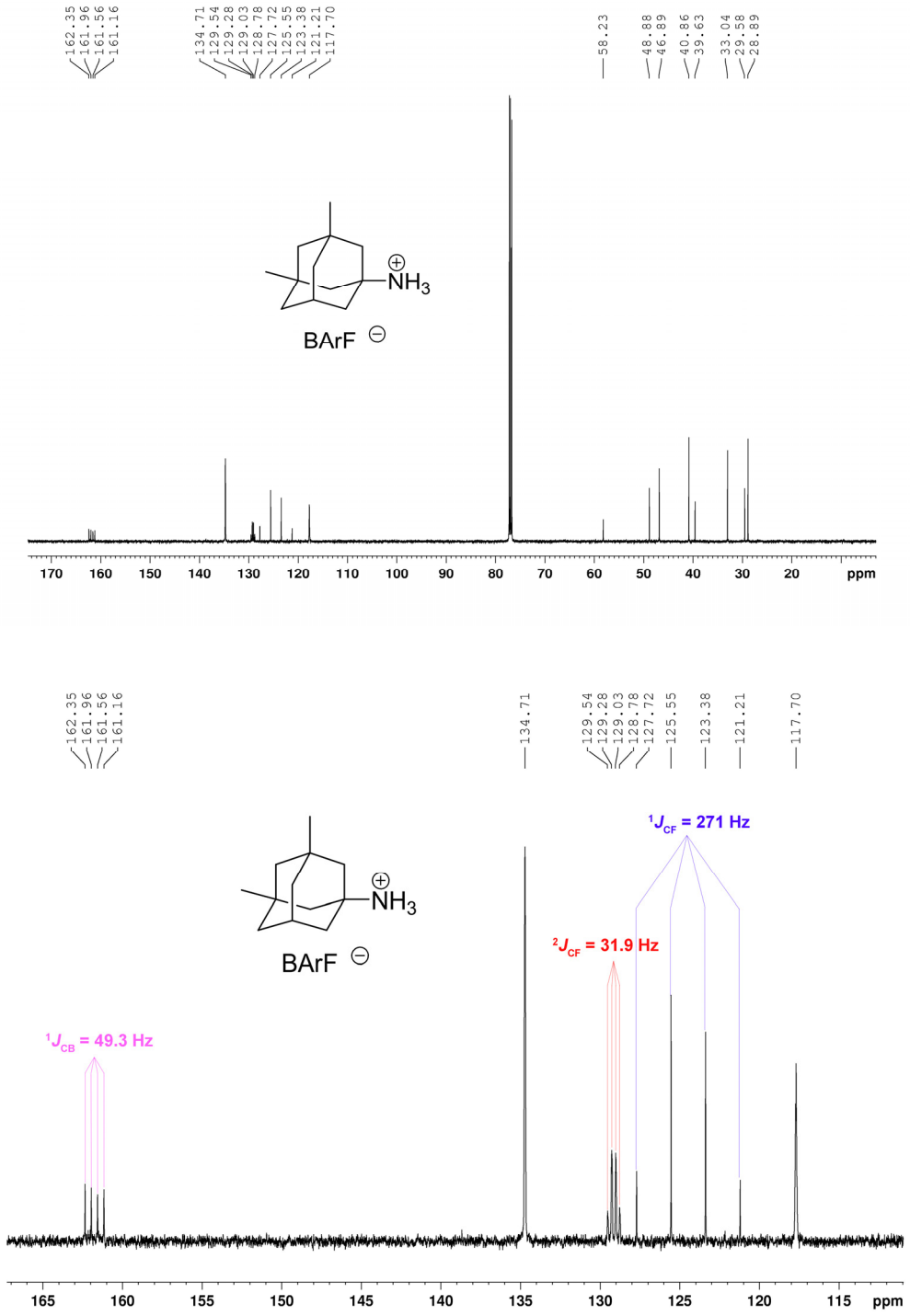


Figure S8. ^{13}C NMR spectrum (125 MHz) of **1**·BArF in $CDCl_3$.

Variable-temperature (VT) ^{1}H NMR spectra of 1·BArF and EtP7A.

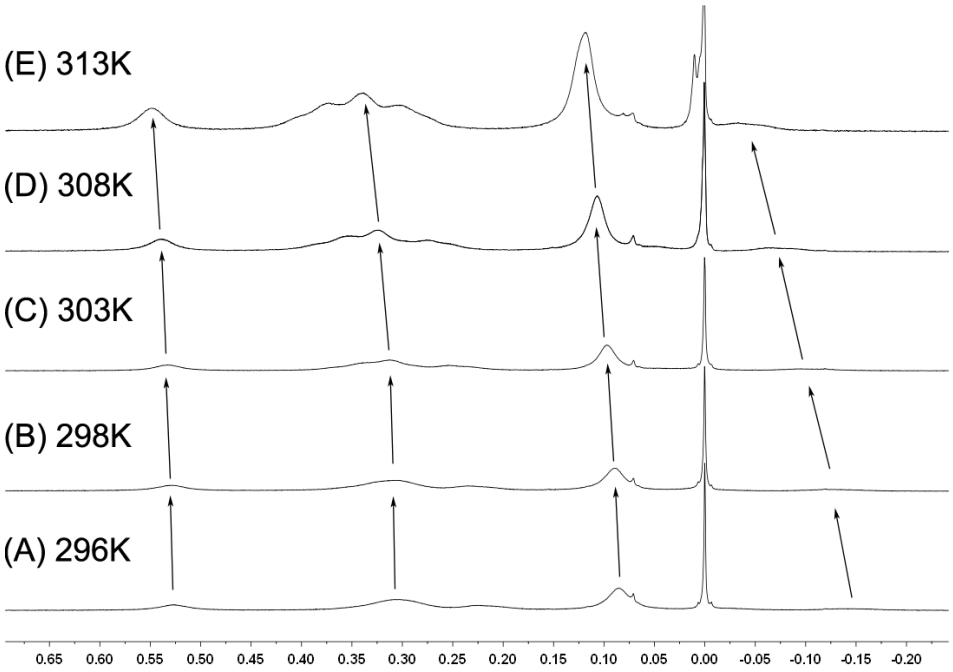


Figure S9. Variable-temperature (VT) ^{1}H NMR spectra of the 1 : 1 mixture of **1**·BArF and EtP7A in $CDCl_3$ (~ 5.0 mM). (A) 296 K, (B) 298 K, (C) 303 K, (D) 308 K, (E) 313 K.

^{1}H NMR spectra of 1·BArF guest in the absence and presence of EtP6A host.

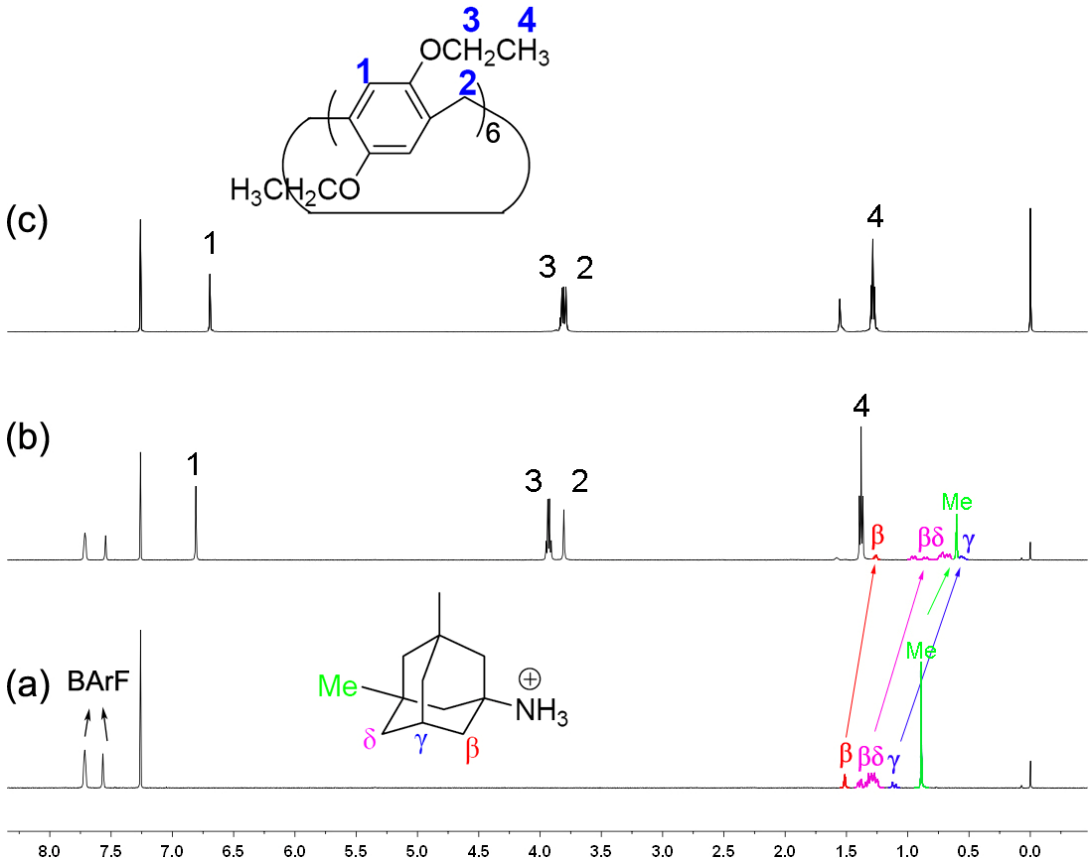


Figure S10.^{1}H NMR spectra (500 MHz, 298 K) of (a) **1**·BArF, (b) **1**·BArF + EtP6A, and (c) EtP6A in $CDCl_3$ at a concentration of 4.8−5.2 mM.

Determination of the association constants.

For the present host-guest system, chemical exchange is fast on the NMR time scale. To determine the association constant, NMR titrations were done with solutions which had a constant concentration of pillararene host and varying concentrations of guest. Using the nonlinear curve-fitting method, the association constant was obtained for each host-guest combination from the following equation[S3]:

$$A = (A_\infty/[H]_0)\ (0.5[G]_0 + 0.5([H]_0+1/K_a) - (0.5\ ([G]_0^2+(2[G]_0(1/K_a - [H]_0)) + (1/K_a + [H]_0)^2)^{0.5}))$$

Where A is the chemical shift change of H_1 on EtP7A (or EtP5A or EtP6A) host at $[G]_0$, A_∞ is the chemical shift change of H_1 when the host is completely complexed, $[H]_0$ is the fixed initial concentration of the EtP7A (or EtP5A or EtP6A) host, and $[G]_0$ is the initial concentration of guest.

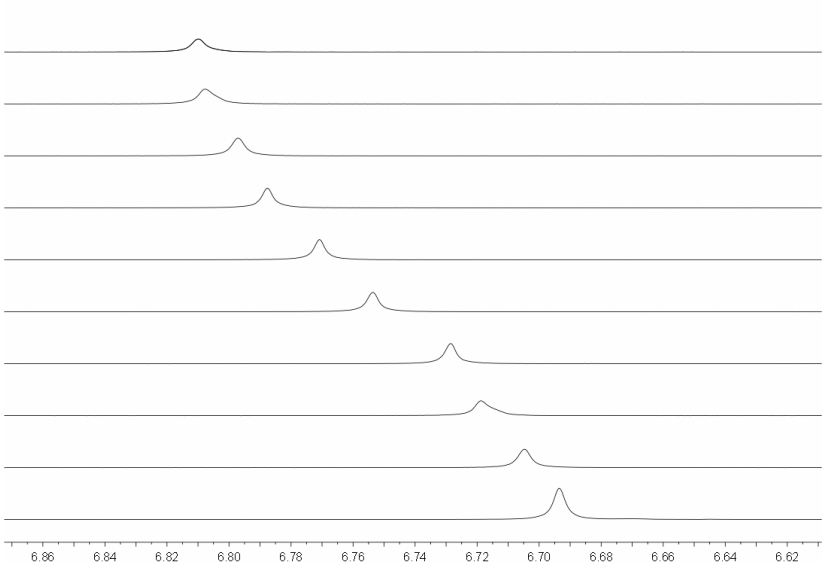


Figure S17. Partial ^{1}H NMR spectra (500 MHz, in $CDCl_3$, 298 K) of EtP6A at a concentration of 1.0 mM upon addition of **1**·BArF. From bottom to top, the concentration of **1**·BArF was 0, 0.10, 0.20, 0.30, 0.60, 0.70, 0.90, 1.4, 3.0 and 4.4 mM.

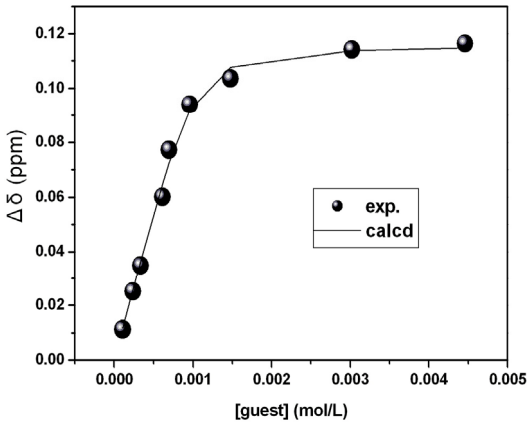


Figure S18. The non-linear curve-fitting (NMR titrations) for the complexation of EtP6A host (1.0 mM) **1**·BArF in $CDCl_3$ at 298 K. The concentration of **1**·BArF was 0.10, 0.20, 0.30, 0.60, 0.70, 0.90, 1.4, 3.0 and 4.4 mM.

References

[S1] (a) D. Cao, Y. Kou, J. Liang, Z. Chen, L. Wang and H. Meier, *Angew. Chem., Int. Ed.*, **2009**, *48*, 9721; (b) Y. Chen, H. Q. Tao, Y. H. Kou, H. Meier, J. L. Fu and D. R. Cao, *Chin. Chem. Lett.*, **2012**, *23*, 509.

[S2] N. A. Yakelis, R. G. Bergman, *Organometallics*, **2005**, *24*, 3579.

[S3] (a) K. A. Connors, Binding Constants; Wiley: New York, **1987**. Corbin, P. S. Ph.D. Dissertation, University of Illinois at Urbana-Champaign, Urbana, IL, 1999; (b) R. P. Ashton, R. Ballardini, V. Balzani, M. Belohradsky, M. T. Gandolfi, D. Philp, L. Prodi, F. M. Raymo, M. V. Reddington, N. Spencer, J. F. Stoddart, M. Venturi , D. J. Williams, *J. Am. Chem. Soc.*, **1996**, *118*, 4931; (c) Y. Inoue, K. Yamamoto, T. Wada, S. Everitt, X.-M. Gao, Z.-J. Hou, L.-H. Tong, S.-K. Jiang, H.-M. Wu, *J. Chem. Soc., Perkin Trans. 2*, **1998**, 1807.