Supplementary Information

Constitutional Isomers of Brominated-Functionalized Copillar[5]arenes: Synthesis, Characterization, and Crystal Structures

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Single crystal X-ray diffraction data:

Table 1S. Summary on the nature of the crystals and various crystallographic parameters of **Pilla-3a, Pillar-3b, Pillar-4a** and **Pillar-4b**.

Crystal Name	**Pillar-3(a)**	**Pillar-3(b)**	**Pillar-4(a)**	**Pillar-4(b)**
Crystal Dimension/mm	0.15 X 0.08 X 0.06	0.20 X 0.16 X0.06	0.17 X 0.11 X0.07	0.20 X 0.17 X0.16
Crystal Color, Habit	Colorless, Block	Colorless, Block	Colorless, Block	Colorless, Block
Formula	$C_{53}H_{62}Br_4Cl_4O_{10}$	C_{54} H_{65} Br_4 Cl_2 O_{10}	C_{53} H_{60} Br_6 Cl_2 O_{10}	C_{55} H_{62} Br_6 N_2 O_1
Crystal system	Monoclinic	Triclinic	Orthorhombic	Triclinic
Space group(no.)	P 21/n	P -1 (2)	P 21 21 21 (19)	P -1 (2)
T/K	150	150	150	150
a/Å	11.639(10)	12.3273(7)	12.3663(6)	11.7192(7)
b//Å	40.03(3)	12.4719(8)	19.9827(7)	11.9722(6)
c/Å	11.802(10)	19.4537(14)	22.6075(16)	22.1105(16)
α	90	91.125(6)	90	94.870(7)
β	92.258(12)	94.226(7)	90	102.695(8)
γ	90	112.641(8)	90	97.465(7)
V/ Å^3	5494.(8)	2749.2(3)	5586.6(5)	2980.0(4)
Z	4	2	4	2
μ(MoKα) / mm^{-1}	3.181	3.080	4.463	4.096
ρ_{calcd}/g cm^{-3}	1.596	1.528	1.673	1.550
θ_{max}/deg	25.030	26.340	26.360	27.450
Reflections collected	23953	22394	26875	28910
Unique reflections	9414	11119	11368	13556
R_{int}	0.1621	0.0375	0.0768	0.0569
R (I > 2σ)	0.1601	0.0764	0.0724	0.0900
R (all data)	0.3000	0.1036	0.1240	0.1599
R_w(all data)	0.4443	0.2782	0.2053	0.3121
$\lvert\Delta\rho\rvert_{max}$e Å^{-3}	0.994	1.897	1.868	1.618

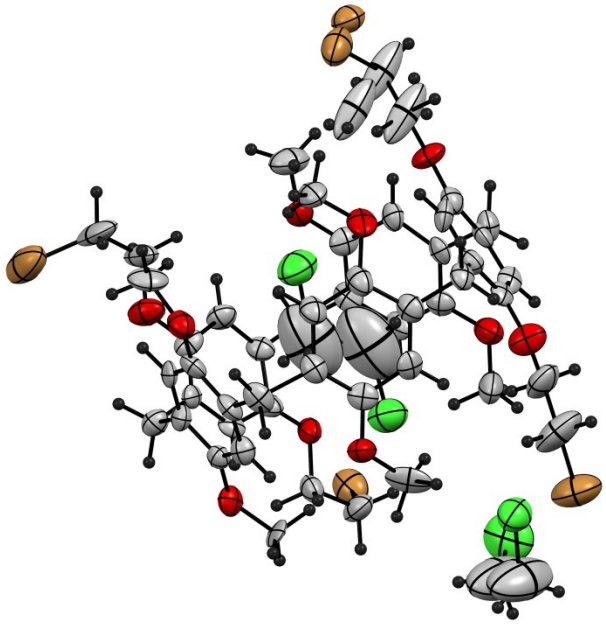

Figure S1. Thermal ellipsoid (50% probability) representation of **3(a)**

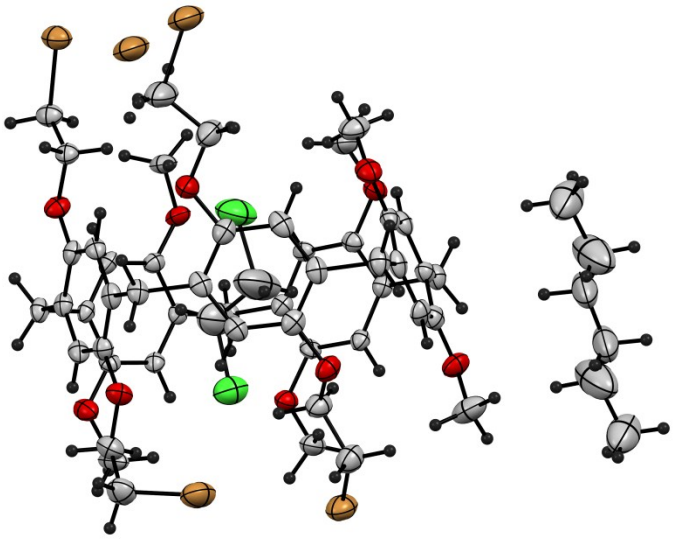

Figure S2. Thermal ellipsoid (50% probability) representation of **3(b)**

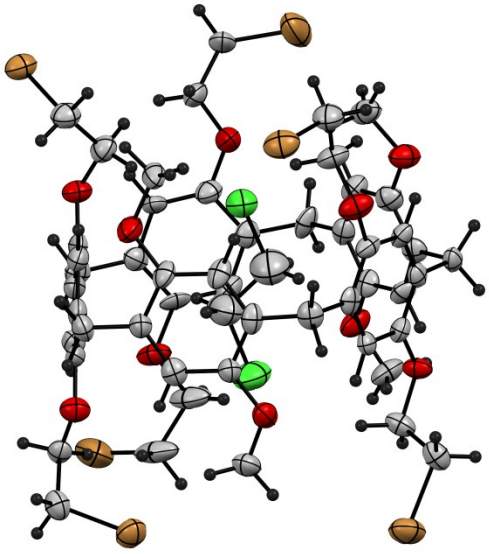

Figure S3. Thermal ellipsoid (50% probability) representation of **4(a)**

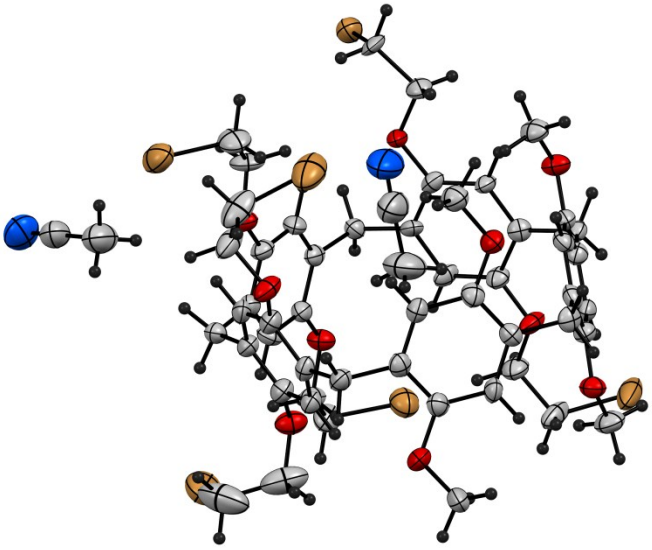

Figure S4. Thermal ellipsoid (50% probability) representation of **4(b)**

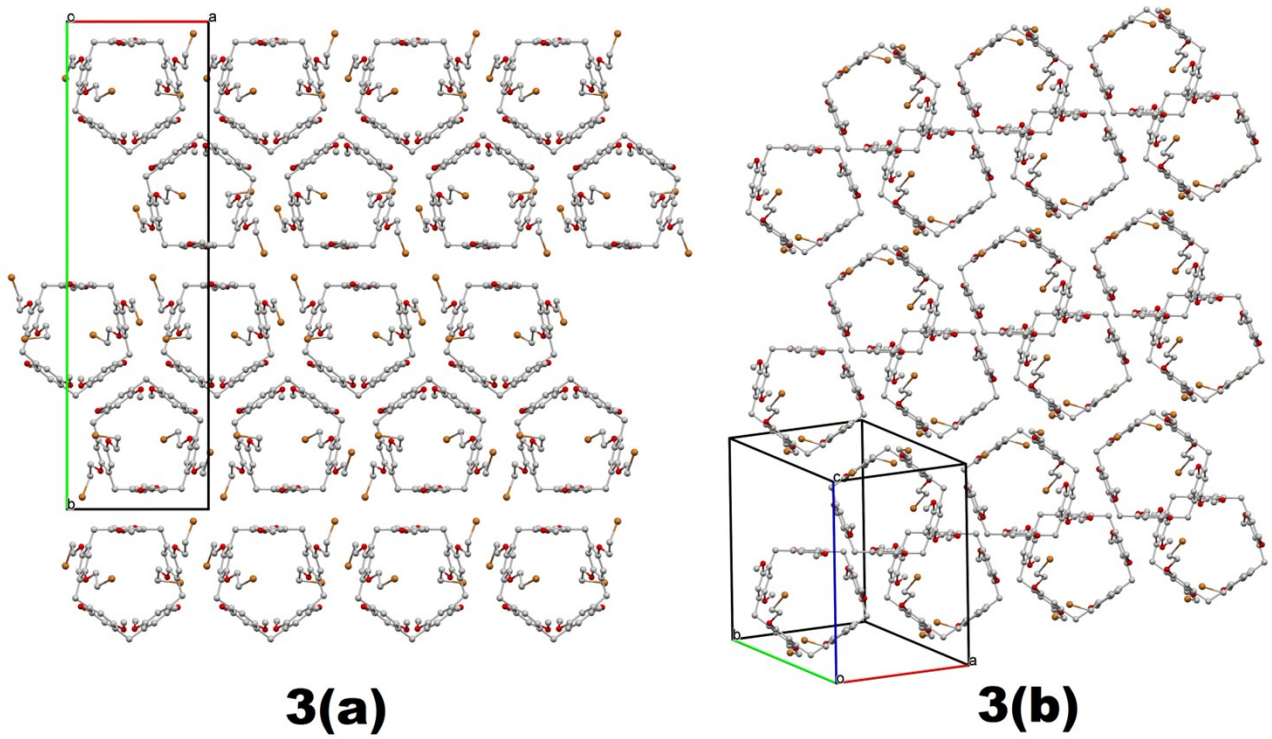

Figure S5. Packing pattern of **3(a)** and **3(b)** in their crystal network

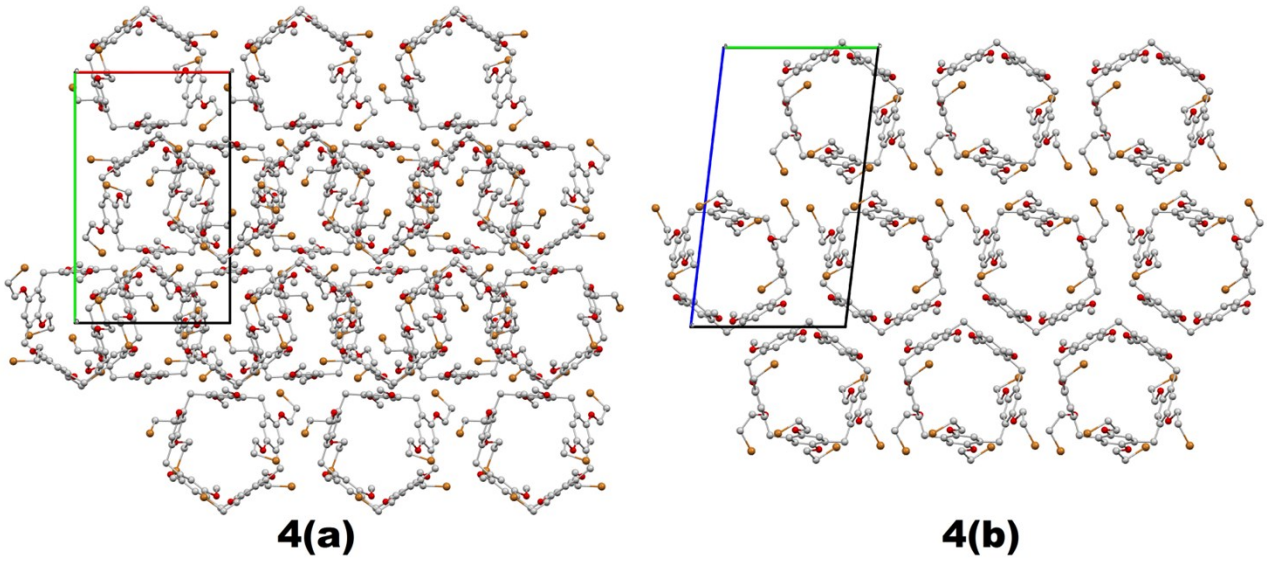

Figure S6. Packing pattern of **4(a)** and **4(b)** in their crystal network

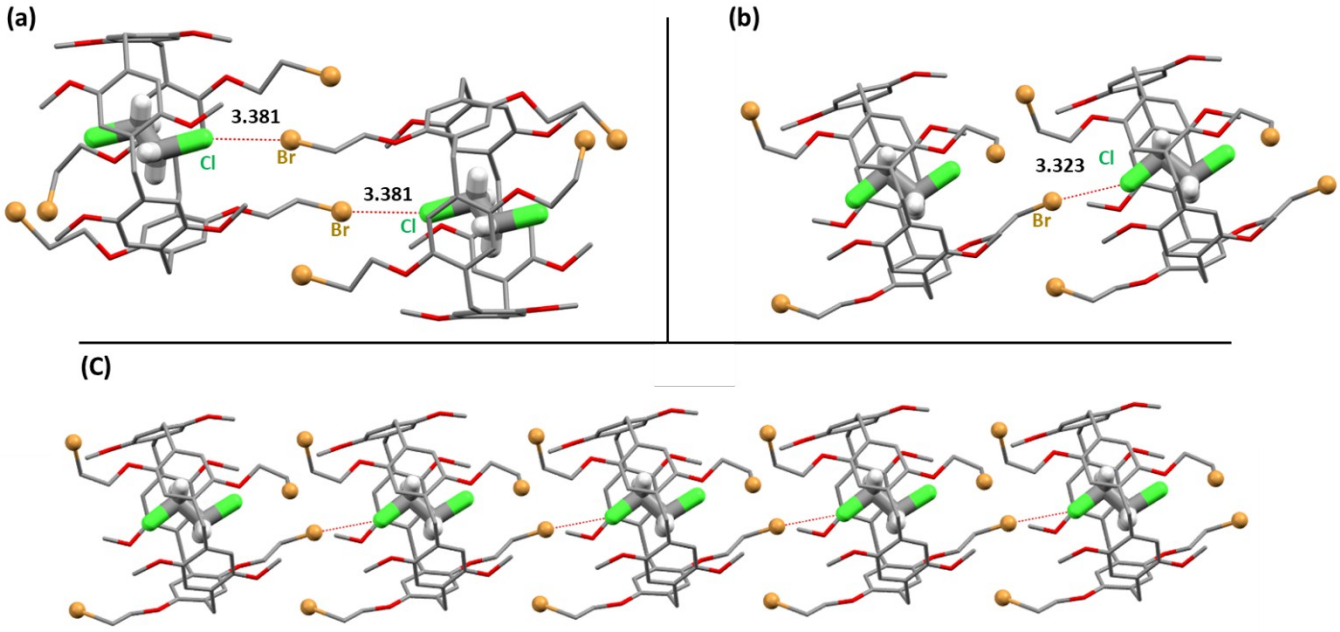

Figure S7. Packing pattern of **4(a)** and **4(b)** in their crystal network

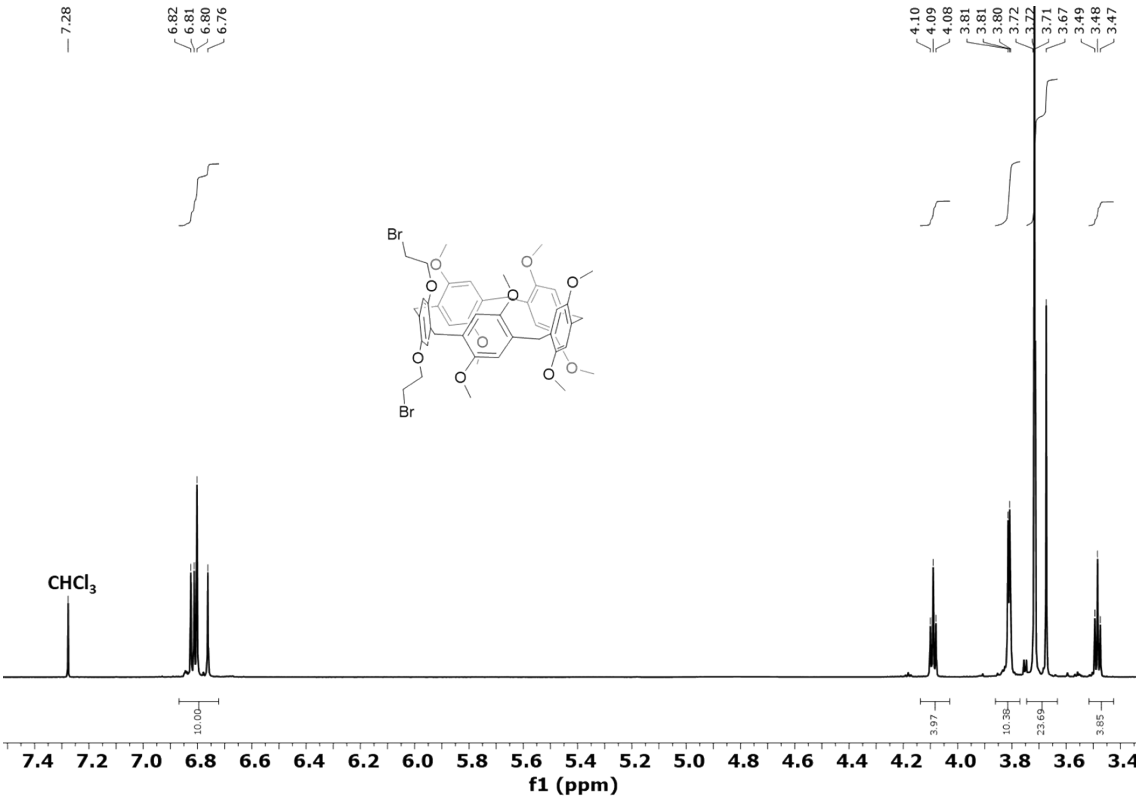

Figure S8. ^{1}HNMR (600 MHz, $CDCl_3$) spectrum of **Pillar-2**.

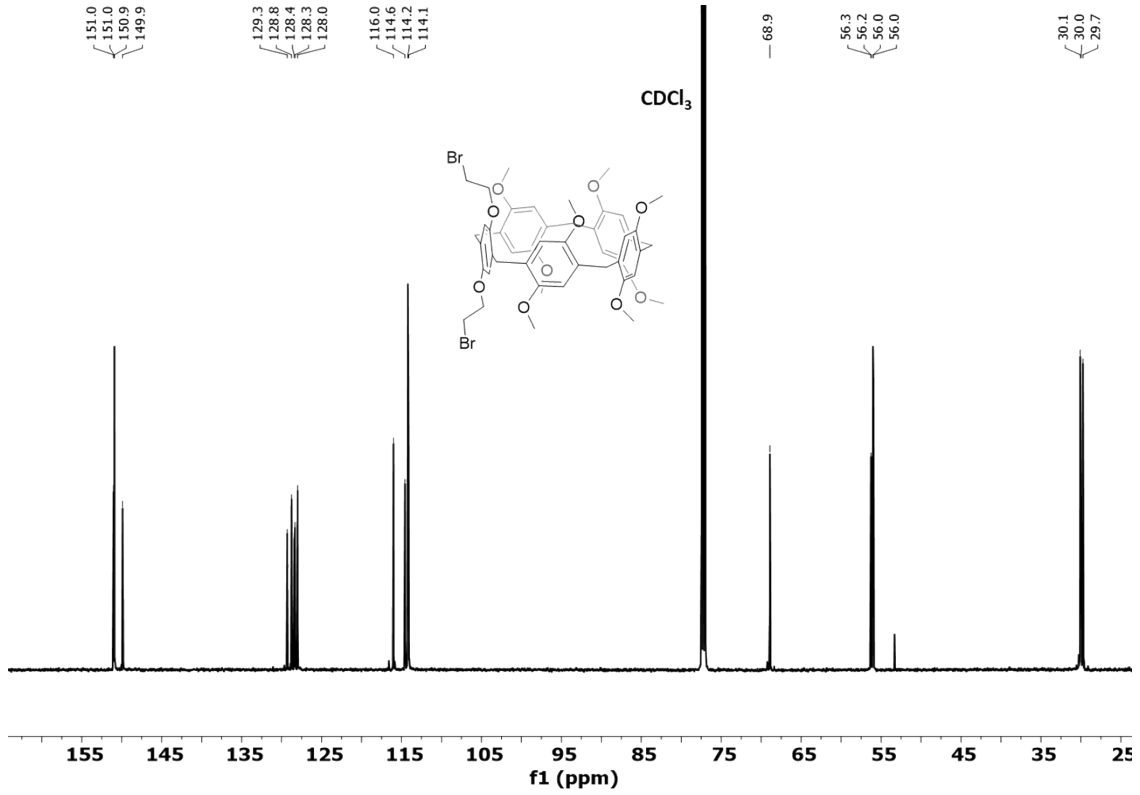

Figure S9. ^{13}CNMR (150 MHz, $CDCl_3$) spectrum of **Pillar-2**.

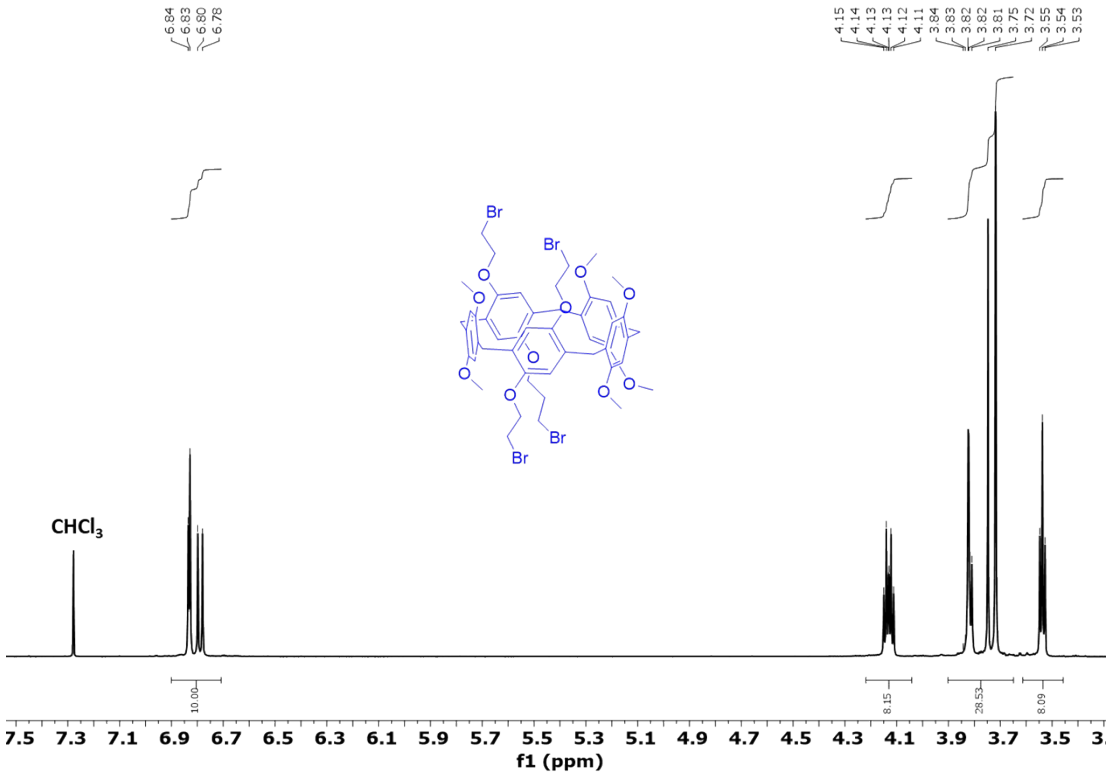

Figure S10. ^{1}HNMR (600 MHz, $CDCl_3$) spectrum of **Pillar-3a**.

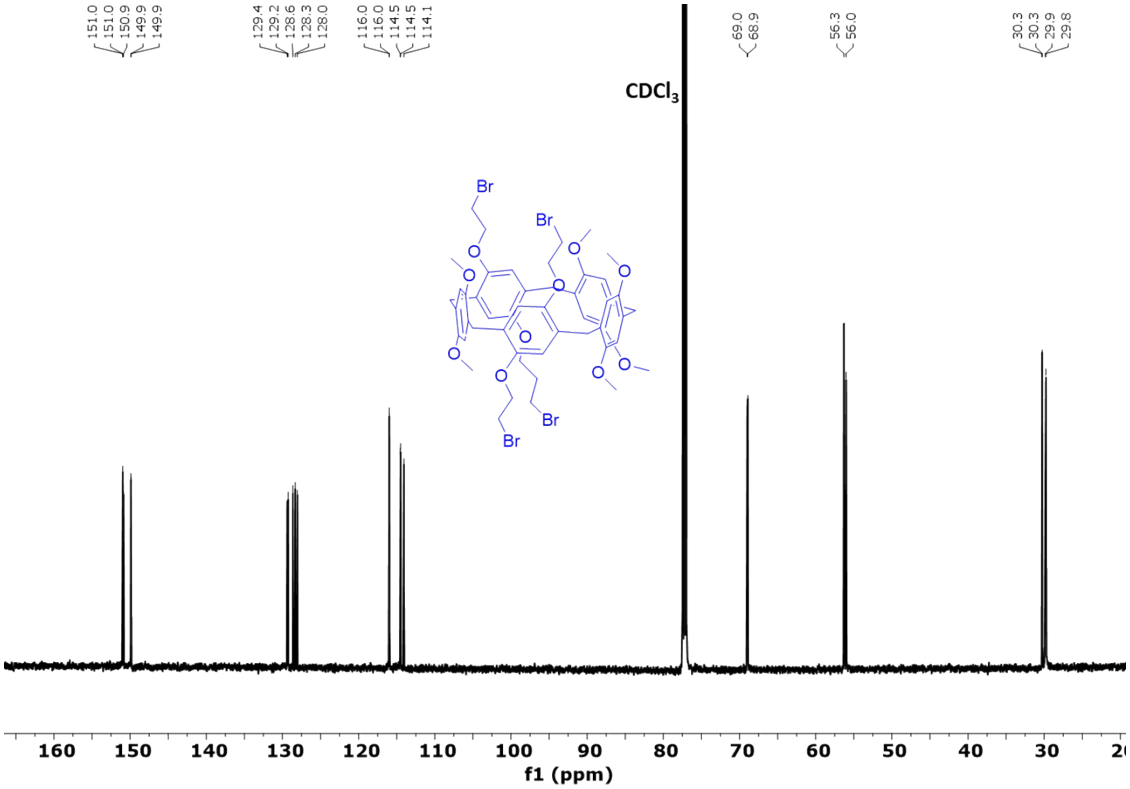

Figure S11. ^{13}CNMR (150 MHz, $CDCl_3$) spectrum of **Pillar-3a**.

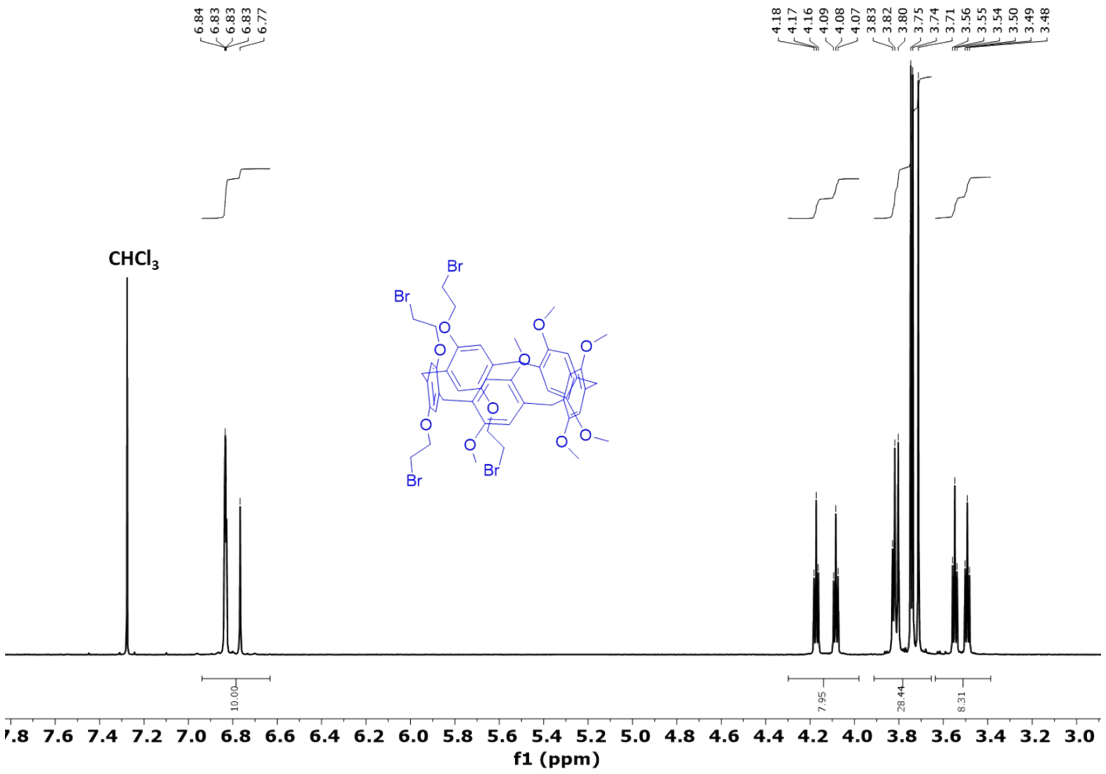

Figure S12. ^{1}HNMR (600 MHz, $CDCl_3$) spectrum of **Pillar-3b**.

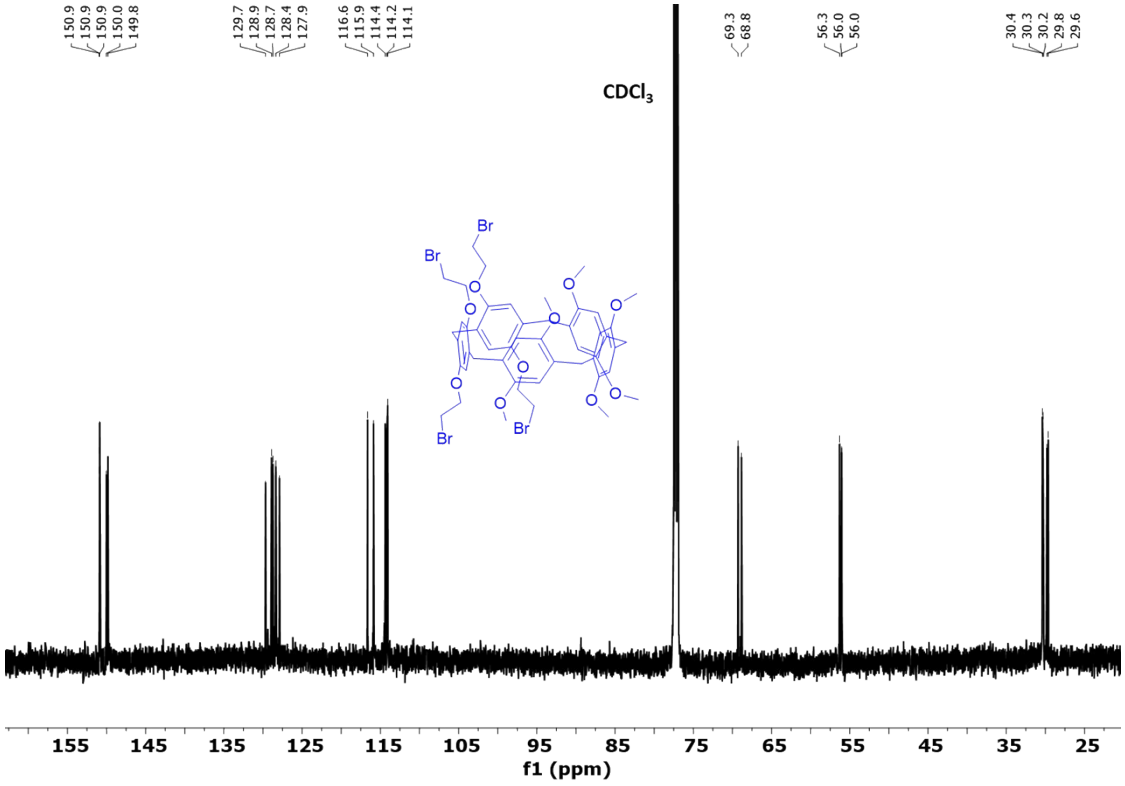

Figure S13. ^{13}CNMR (150 MHz, $CDCl_3$) spectrum of **Pillar-3b**.

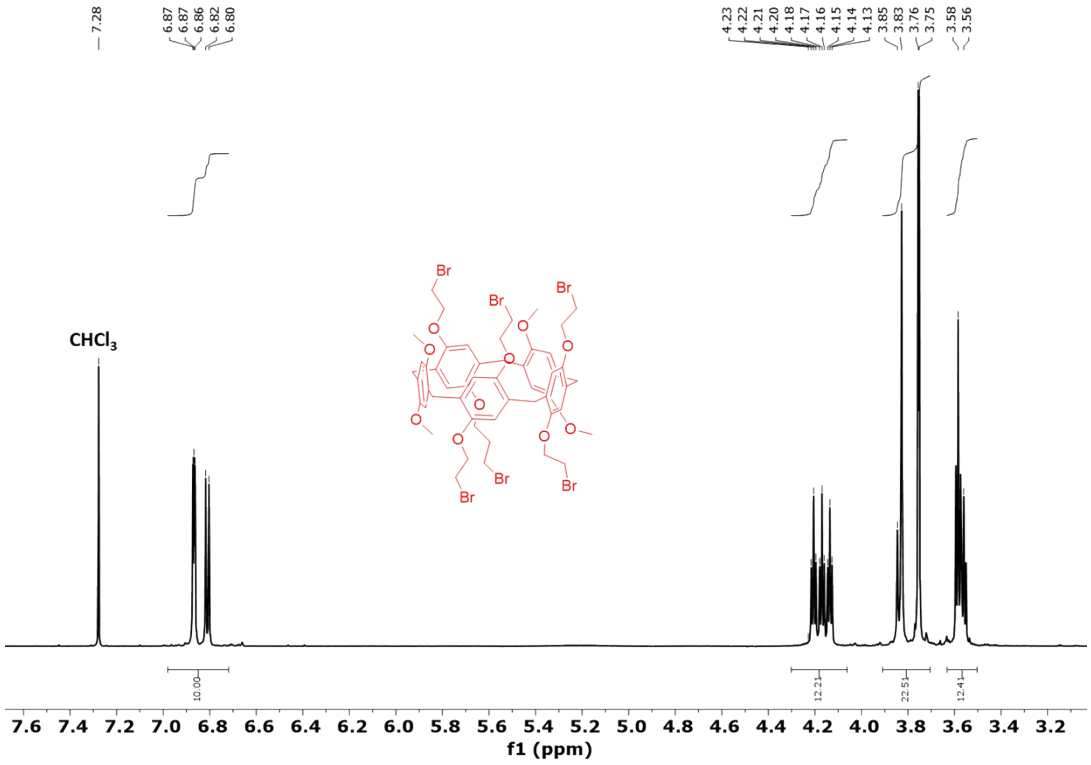

Figure S14. ^{1}HNMR (600 MHz, $CDCl_3$) spectrum of **Pillar-4a**.

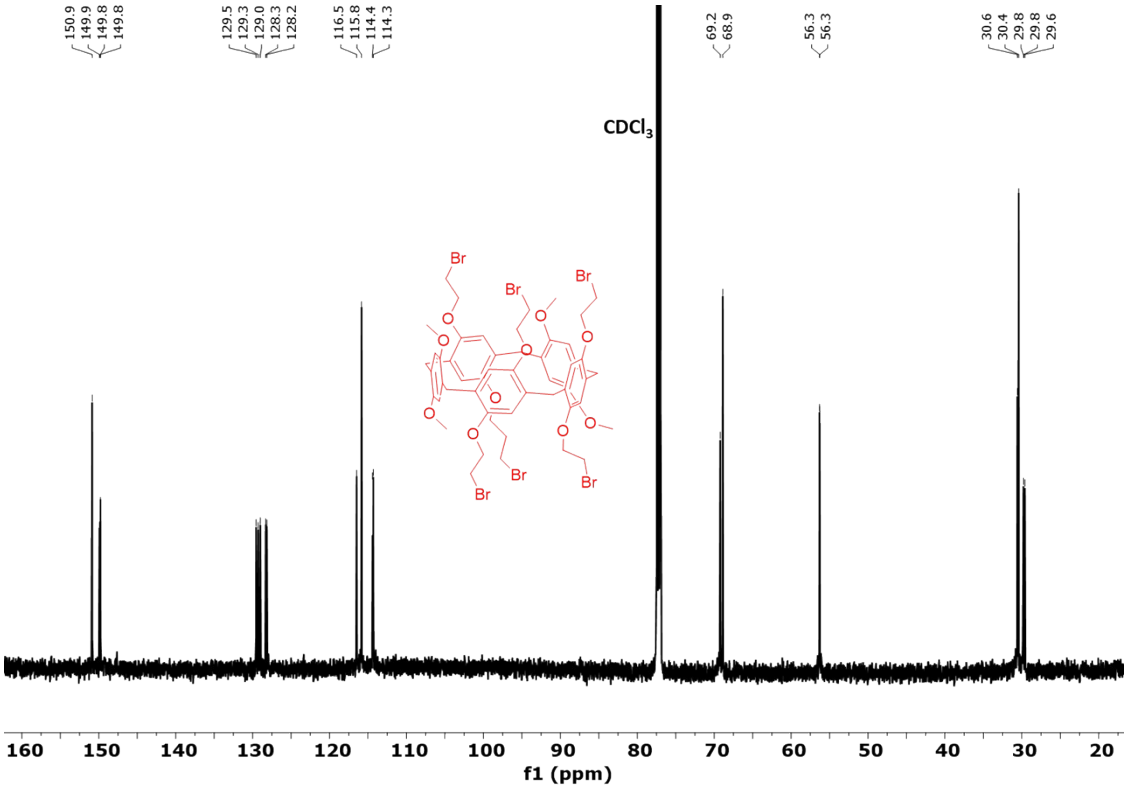

Figure S15. ^{13}CNMR (150 MHz, $CDCl_3$) spectrum of **Pillar-4a**.

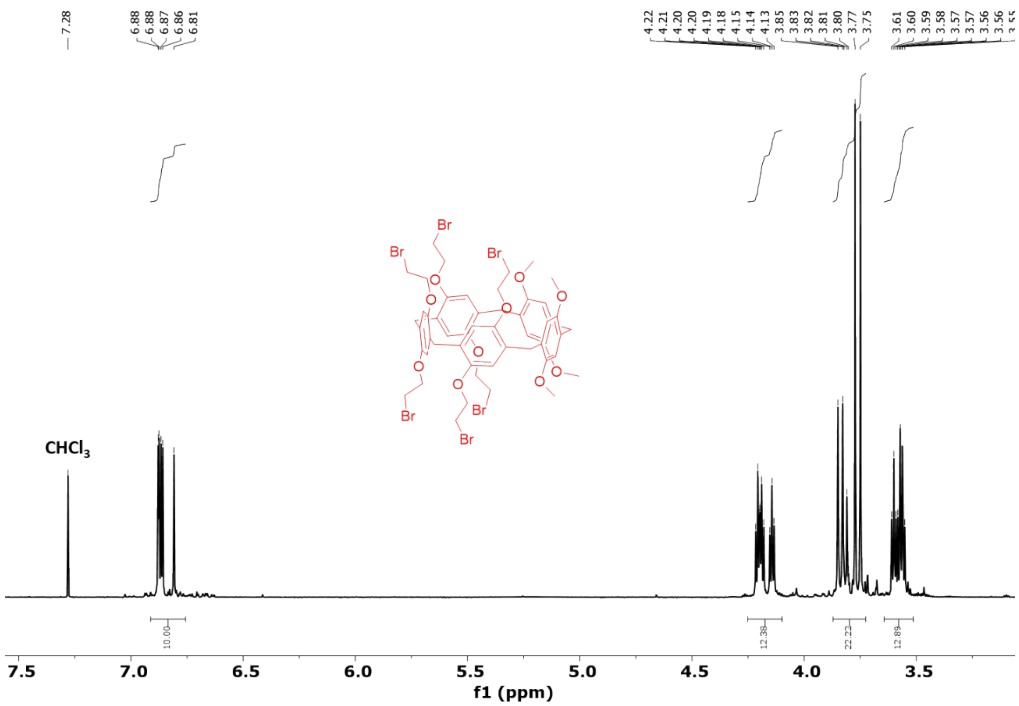

Figure S16. ^{1}HNMR (600 MHz, $CDCl_3$) spectrum of **Pillar-4b**.

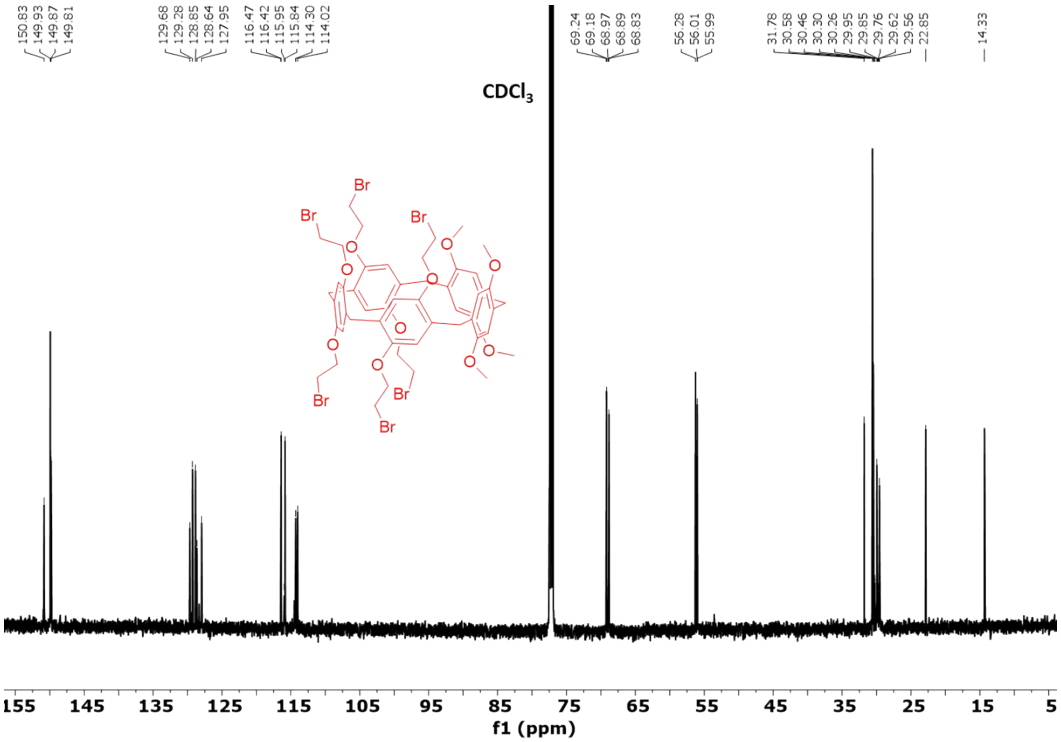

Figure S17. ^{13}CNMR (150 MHz, $CDCl_3$) spectrum of **Pillar-4b**.

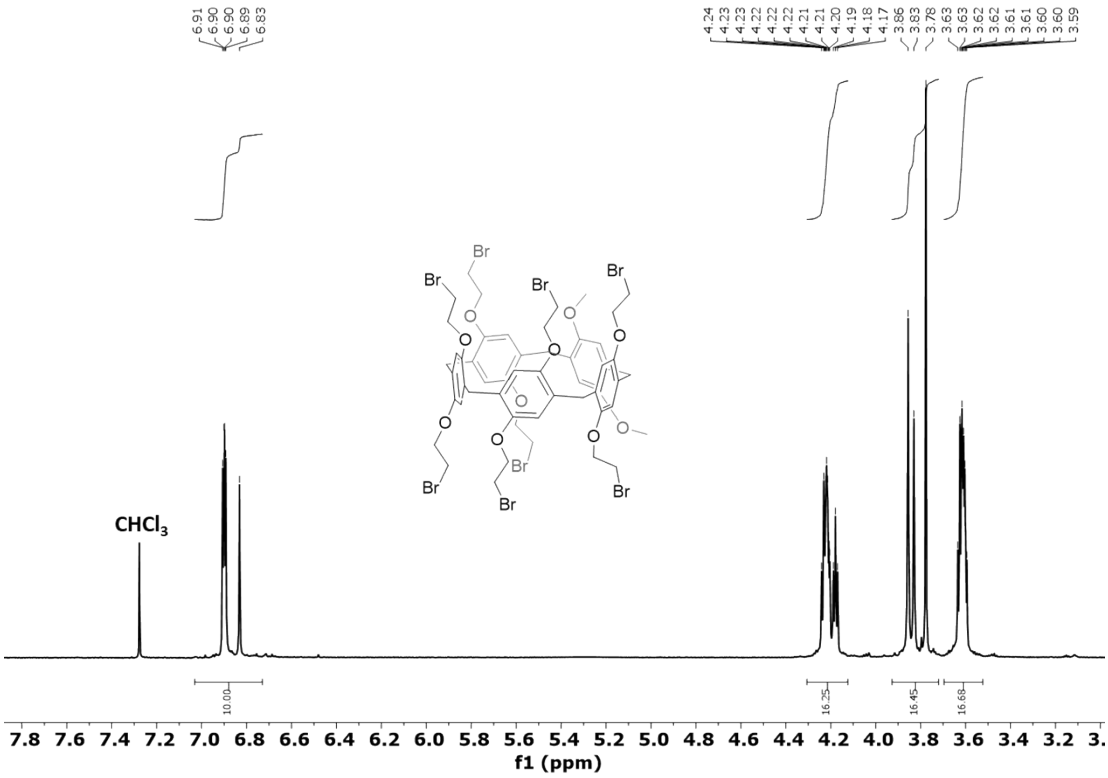

Figure S18. ^{1}HNMR (600 MHz, $CDCl_3$) spectrum of **Pillar-5**.

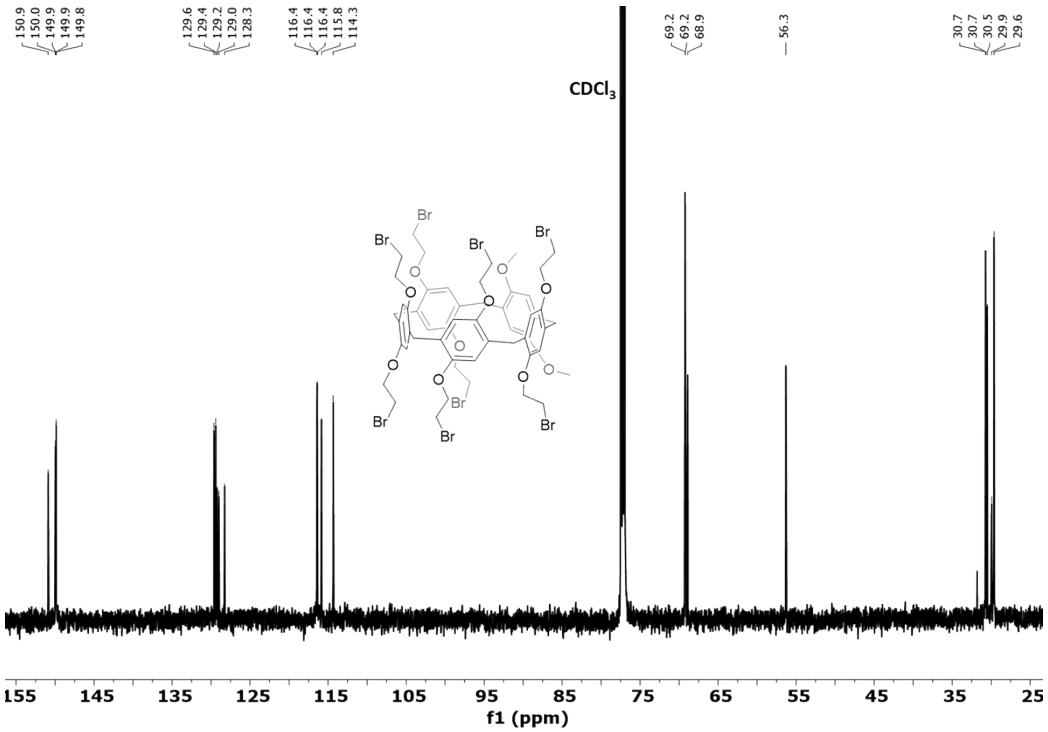

Figure S19. ^{13}CNMR (150 MHz, $CDCl_3$) spectrum of **Pillar-5**.

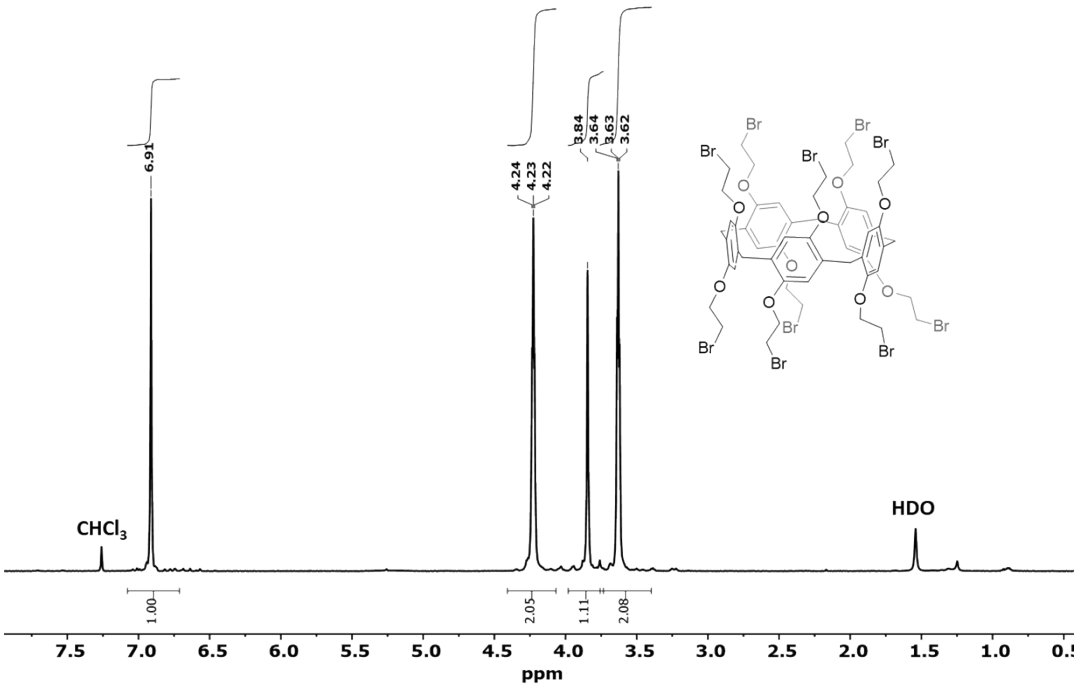

Figure S20. ^{1}HNMR (600 MHz, $CDCl_3$) spectrum of **Pillar-6**.

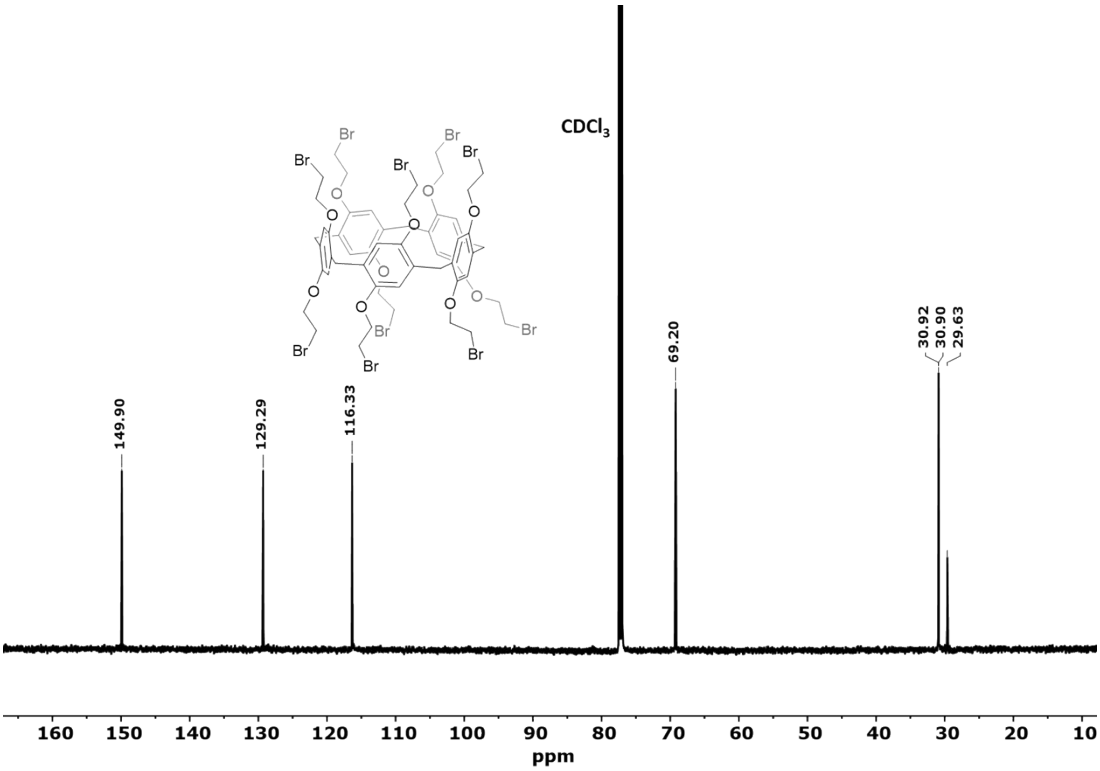

Figure S21. ^{13}CNMR (150 MHz, $CDCl_3$) spectrum of **Pillar-5**.

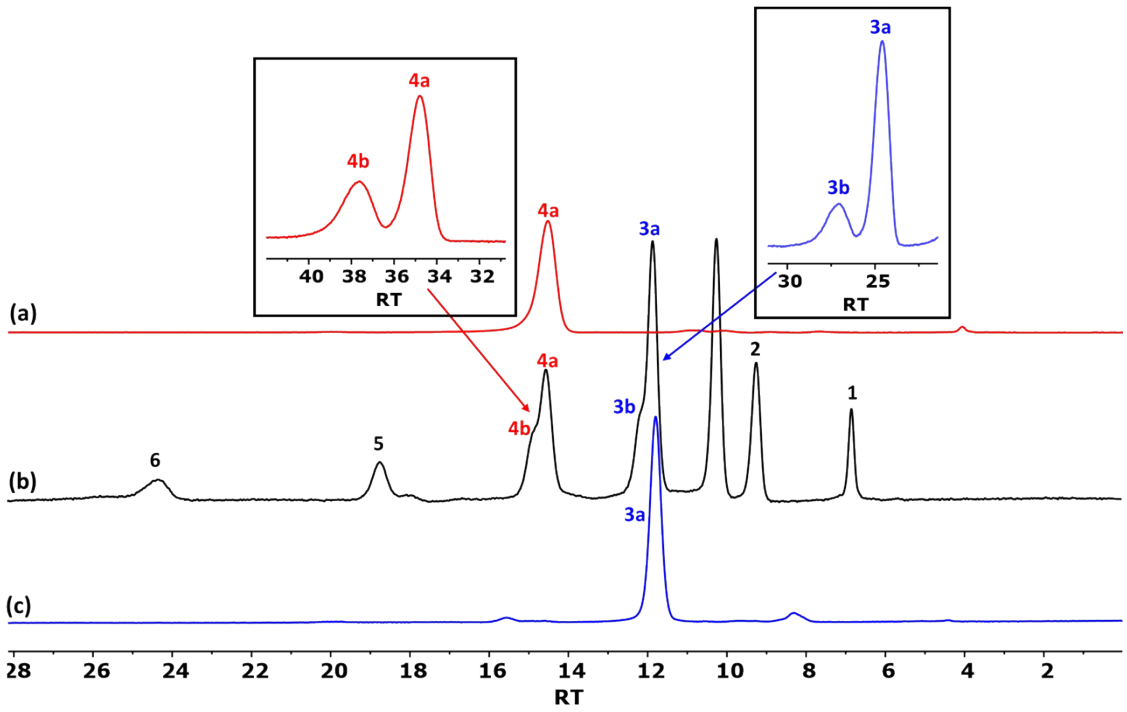

Figure S23. HPLC chromatogram for the for the crude reaction mixtures of the copillar[5]arenes synthesized from monomers 1,4-dimethoxybenzene and 1,4-bis(2-bromoethoxy)benzene and insets showing the separated constitutional isomers, (a) pure 1,3-alternate isomer **Pillar-4a**, (b) crude reaction mixture [Table 1, entry 6) and (c) pure 1,3-alternate isomer **Pillar-3a**.

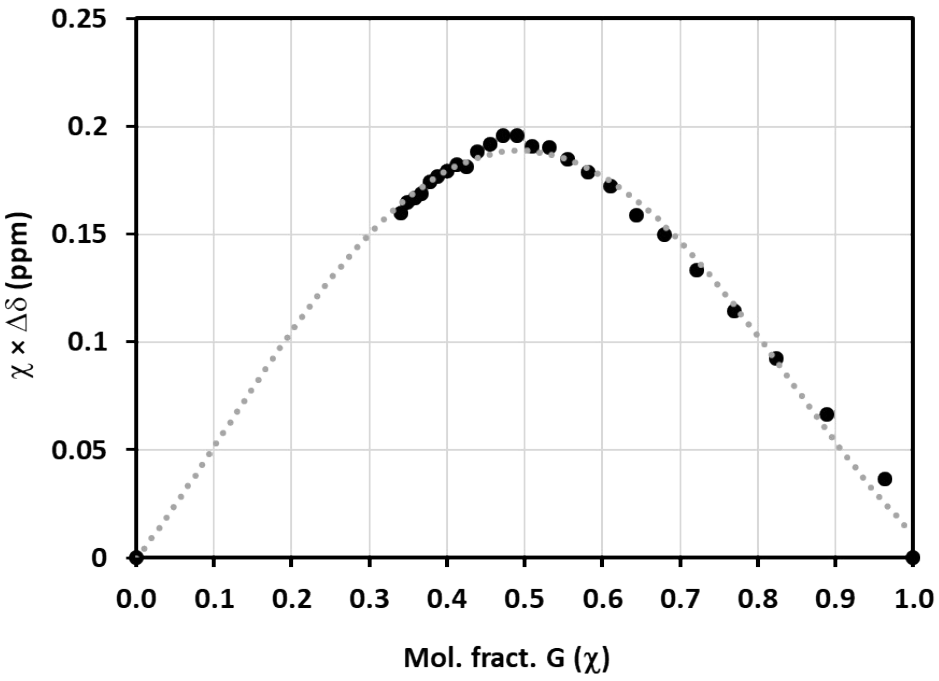

Figure S23. Typical job's plot for complexation of constitutional isomer of with **OMA** guest determined from ^{1}H NMR titration in CDCl3 at 25 °C.

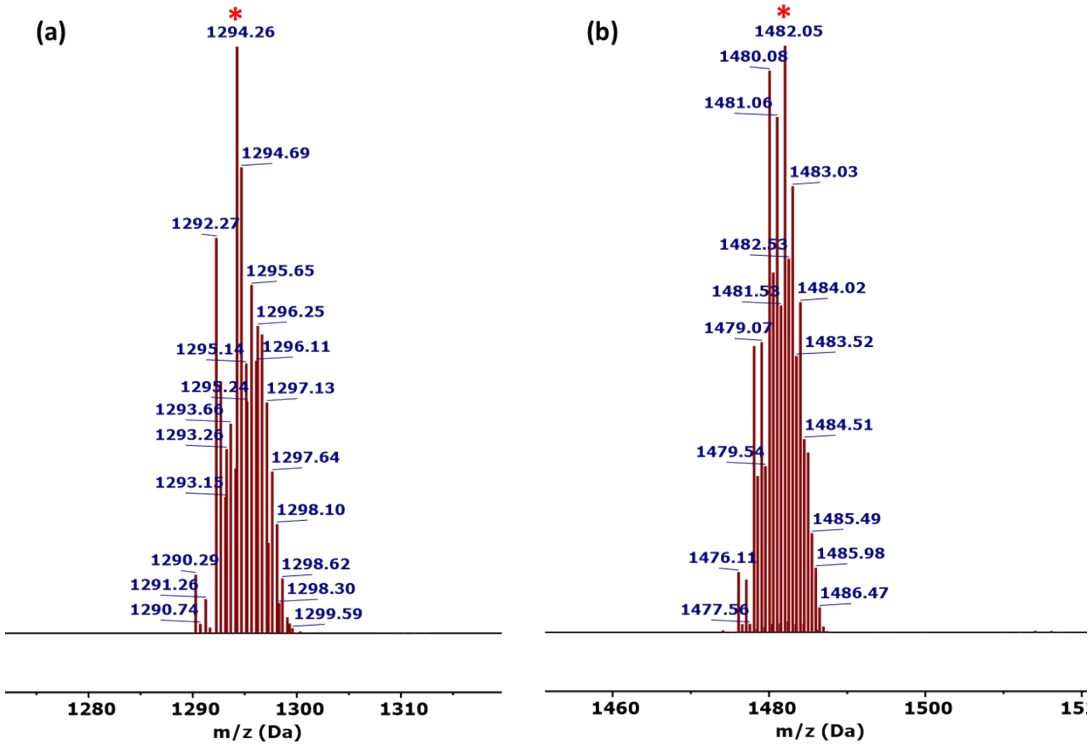

Figure S24. ES-MS spectra of the complex (a) [(**Pillar-3a** + OMA)–PF_6]$^+$ and (b) [(Pillar-4a . OMA)–PF_6]$^+$.

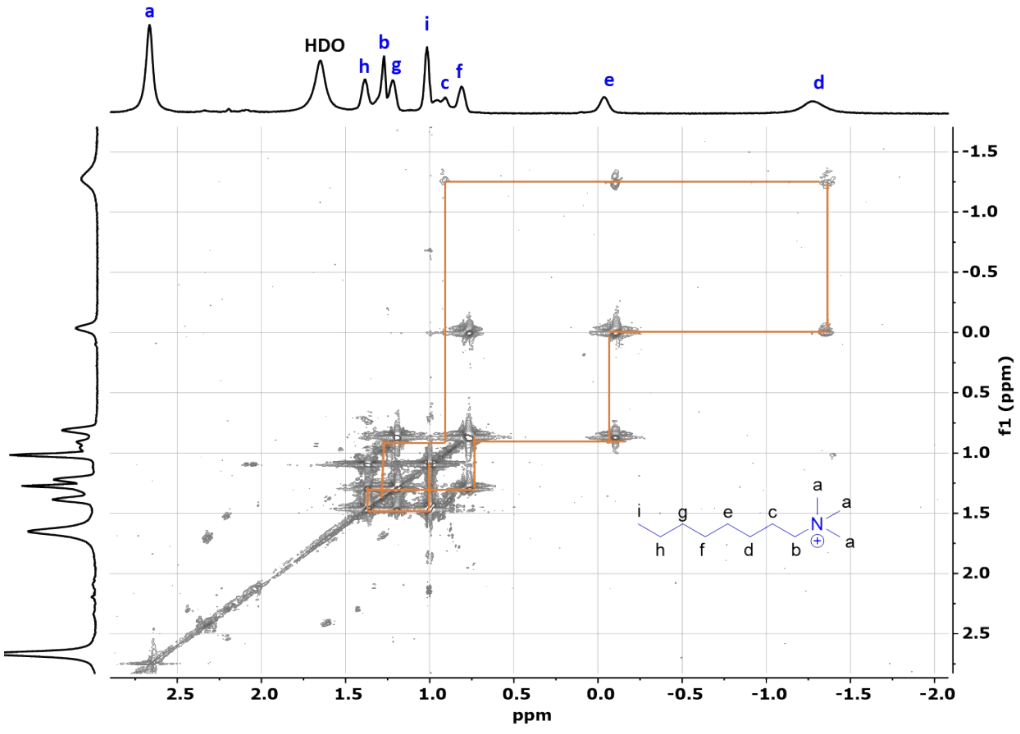

Figure S25. Partial COSY (600 MHz, $CDCl_3$) spectrum of [(**Pillar-3a** + OMA)–PF_6]$^+$.

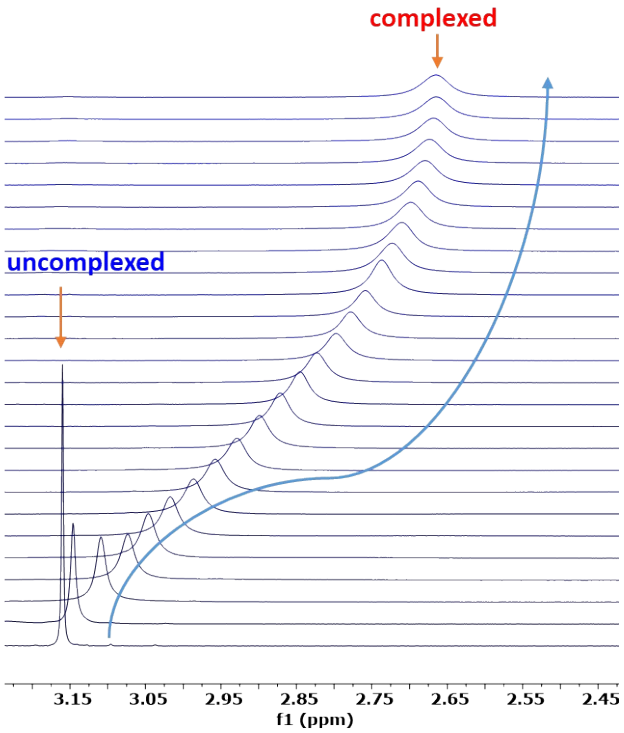

Figure S26. ^{1}HNMR chemical shifts (600 MHz, $CDCl_3$) of *N*-trimethyl protons (Ha) measured upon incremental addition of the host Pillar-3a to a solution of OMA guest (8.4 mM) at 298 K.

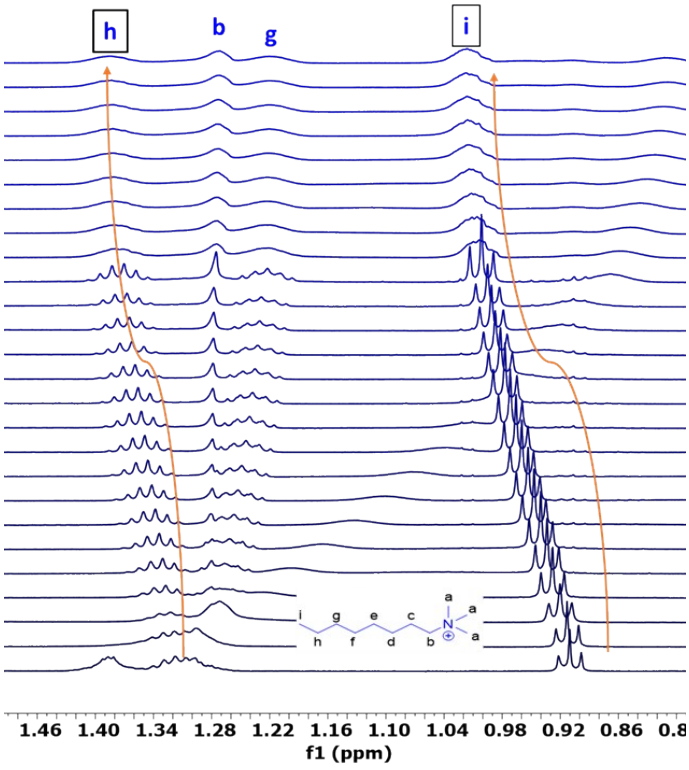

Figure S27. ^{1}HNMR chemical shifts (600 MHz, $CDCl_3$) of protons **Hh** and **Hi** measured upon incremental addition of the host Pillar-3a to a solution of OMA guest (8.4 mM) at 298 K.

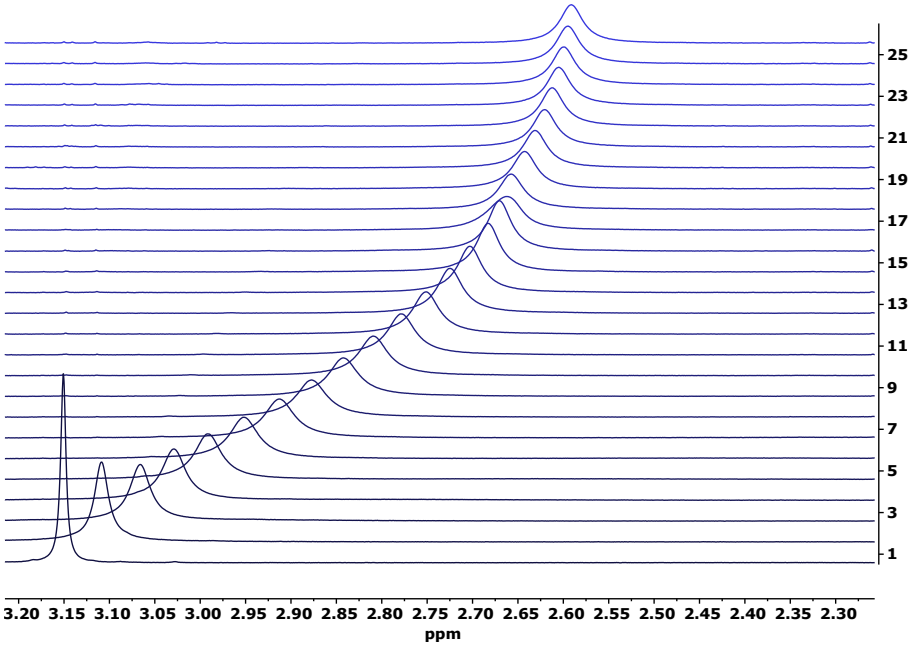

Figure S28. ^{1}HNMR chemical shifts (600 MHz, $CDCl_3$) of *N*-trimethyl protons (Ha) measured upon incremental addition of the host Pillar-3b to a solution of OMA guest (8.4 mM) at 298 K.

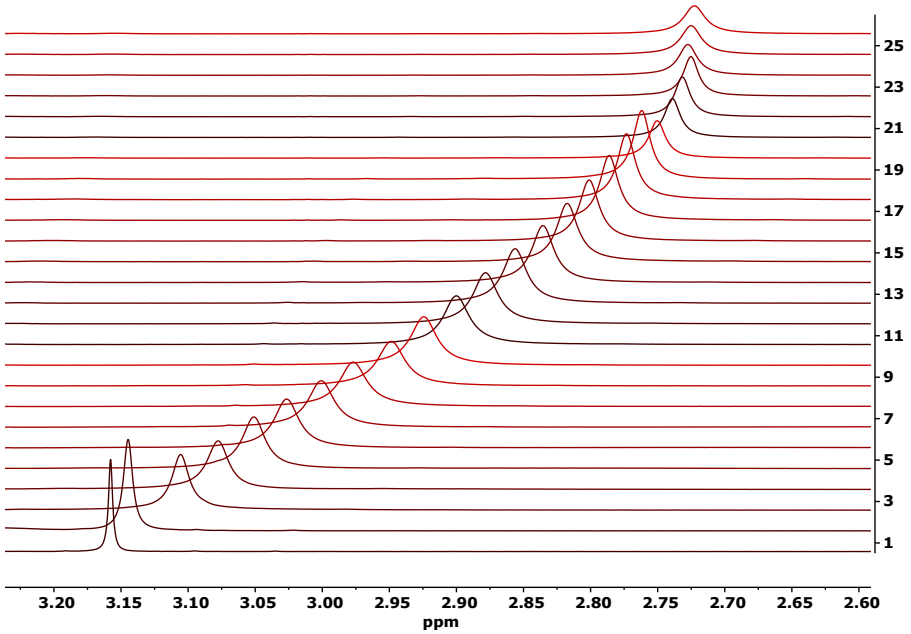

Figure S29. ^{1}HNMR chemical shifts (600 MHz, $CDCl_3$) of *N*-trimethyl protons (Ha) measured upon incremental addition of the host Pillar-4a to a solution of OMA guest (8.4 mM) at 298 K.

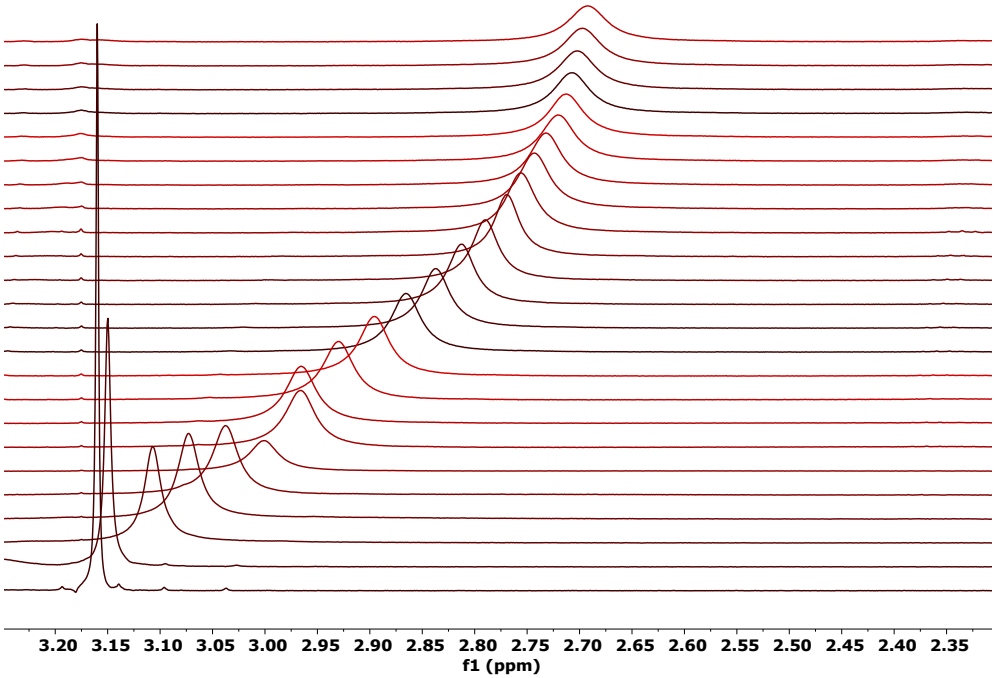

Figure S30. ^{1}HNMR chemical shifts (600 MHz, $CDCl_3$) of *N*-trimethyl protons (Ha) measured upon incremental addition of the host Pillar-4b to a solution of OMA guest (8.4 mM) at 298 K.