Electronic Supplementary Information (ESI)

Template Effect of Solvents for High-Yield Synthesis, co-Cyclization of Pillar[6]arenes and Interconversion between Pillar[5]- and pillar[6]arenes

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Experimental section

Materials. All solvents and reagents were used as supplied. 1,4-Bis(methylcyclohexyl ether)benzene (**M3**), bis(1-bromobutyloxy)benzene (**M4**), **TEO[5]** and **TEO[6]** were synthesized according to the previous papers.[S1-S4] **P3[5]** and **P3[6]** were already synthesized by different method and characterized completely.[S1,S5]

Measurements. The ^{1}H NMR spectra were recorded at 500 MHz and ^{13}C NMR spectra were recorded at 125 MHz with a JEOL-ECA500 spectrometer. Gel permeation chromatography (GPC) analysis was carried out on Shodex GPC LF804 by using THF as an eluent at 25 °C at the flow rate of 1 mL min^{-1}.

High-yield Synthesis of P3[6] in Chlorocyclohexane. To a solution of **M3** (300 mg, 1.00 mmol) in chlorocyclohexane (Cl-CyC6, 10 mL), paraformaldehyde (90 mg, 2.98 mmol) was added under nitrogen atmosphere. Then, $BF_3{\cdot}OEt_2$ (0.125 mL, 1.00 mmol) was added to the solution and the mixture was stirred at 25 °C for 150 min. The solution was poured into methanol and the resulting precipitate was collected by filtration. The filtrate was purified by silica gel column chromatography (dichloromethane/hexane = 1/3) to yield **P3[5]** (8.28 mg, 5.27 μmol, yield 3%) and **P3[6]** (272 mg, 144 μmol, yield 87%) as white solids.

Co-pillar[6]arene, P3[5]P4[1]. To a solution of **M3** (143 mg, 0.375 mmol) and **M4** (1.81 g, 6.00 mmol) in Cl-CyC6 (40 mL), paraformaldehyde (575 mg, 19.1 mmol) was added under nitrogen atmosphere. Then, $BF_3{\cdot}OEt_2$ (0.780 mL, 6.38 mmol) was added to the solution and the mixture was stirred at 25 °C for 1 h. The solution was poured into water. The solution was extracted with dichloromethane and the organic phase was dried over Na_2SO_4 and concentrated. The residue was dissolved in dichloromethane and insoluble part was removed by celite filtration. The filtrate was poured into methanol and the resulting precipitate was collected by filtration. Silica gel column chromatography (dichloromethane/hexane = 1/3) afforded **P3[5]P4[1]** (64.0 mg, 32.7 μmol, yield 9%), **P3[5]** (20.0 mg, 12.7 μmol, yield 1%) and **P3[6]** (150 mg, 79.6 μmol, yield 8%) as white solids. **P3[5]P4[1]:** ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 6.86 (s, 2H, phenyl), 6.84 (s, 2H, phenyl), 6.79 (s, 2H, phenyl), 6.77 (s, 2H, phenyl), 6.55 (s, 2H, phenyl), 6.53 (s, 2H, phenyl), 3.50−3.90 (m, 36H, methylene and methylene bridge), 3.25 (t, 4H, methylene), 0.92−2.00 (m, 118H, methylene and cyclohexyl moiety). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 150.5, 150.4, 128.3, 128.1, 127.9, 127.8, 127.4, 115.0, 114.8, 114.6, 114.5, 74.2, 67.4, 38.3, 38.2, 34.0, 30.3, 30.2, 30.1, 29.4, 27.9, 26.7, 26.6, 26.0. HRESIMS: *m*/*z* Calcd for C120H170Br2NaO12 $[M+Na]^+$: 1984.0957, found 1984.0952.

Interconversion between pillar[5]arene P3[5] and pillar[6]arene P3[6]. Pillar[5]arene or pillar[6]arene (**P3[5] or P3[6]**, 770 μmol) was dissolved in solvent (DCE or Cl-CyC6, 5 mL). To the mixture, BF_3▪OEt_2 (0.100 mL, 7700 μmol) was added. The mixture was heated at 80 ^{o}C. The reaction was monitored by ^{1}H NMR measurements.

^{1}H and ^{13}C NMR spectra of P3[5]P4[1]

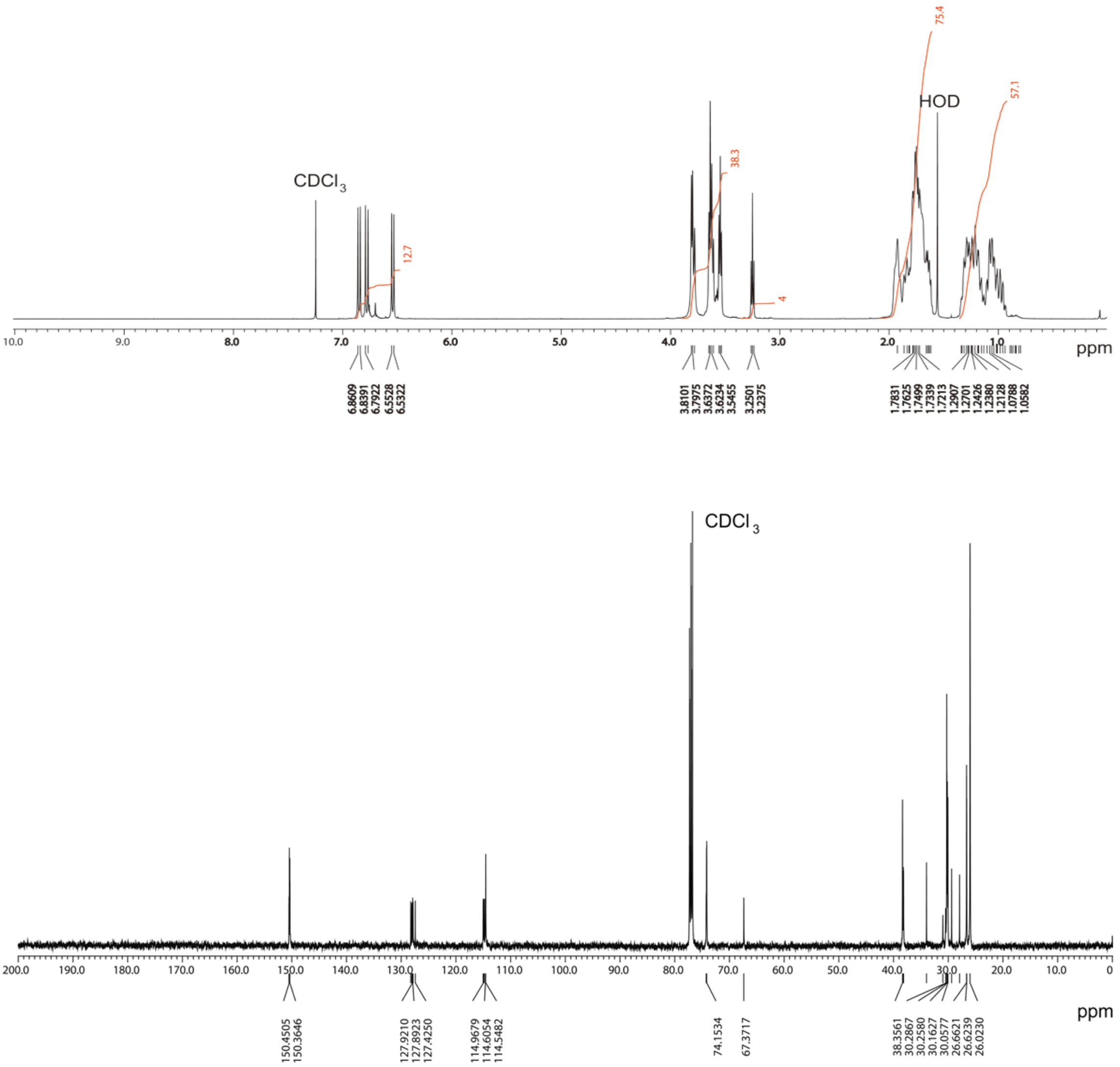


Fig. S1 ^{1}H and ^{13}C NMR spectra of co-pillar[6]arene **P3[5]P4[1]** in $CDCl_3$ at 25 °C.

^{1}H NMR spectrum of a DABCO cation with P3[6] in $CDCl_3$

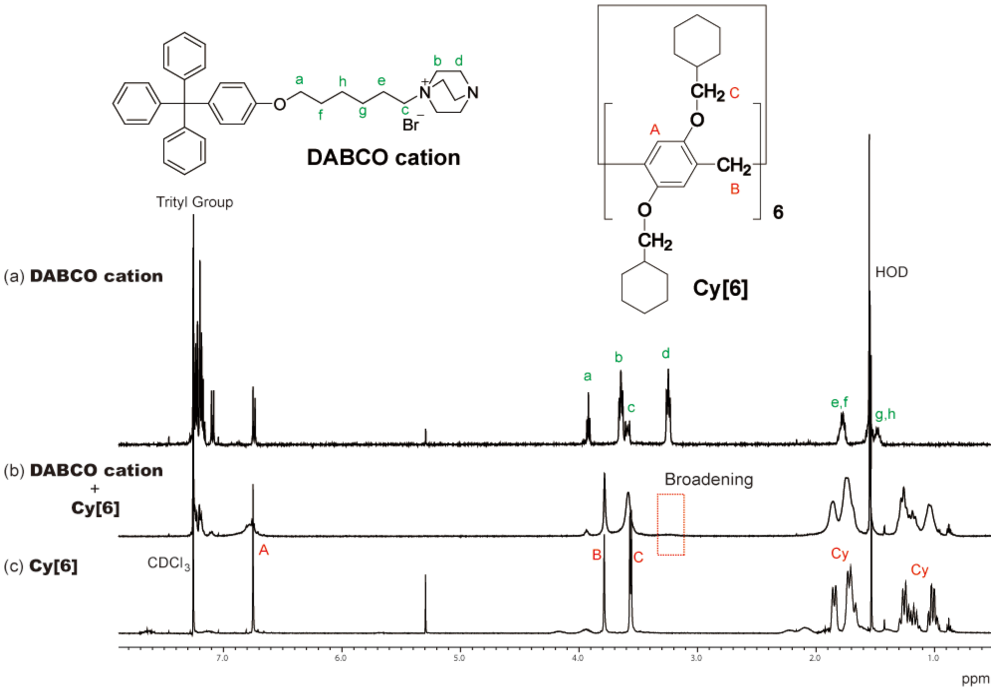


Fig. S2 ^{1}H NMR spectra (2 mM, $CDCl_3$) of (a) DABCO cation, (b) a mixture of DABCO cation and **Cy[6]**, and (c) **Cy[6]**. When **DABCO cation** and **Cy[6]** were mixed in $CDCl_3$, the peaks of DABCO cation were broadening. The trend is same to the host-guest complexation between pillar[6]arenes and **DABCO cation**,[S8] and thus indicates host-guest complexation between **DABCO cation Cy[6]**.

^{1}H NMR spectra of DCE with P3[5] and P3[6]

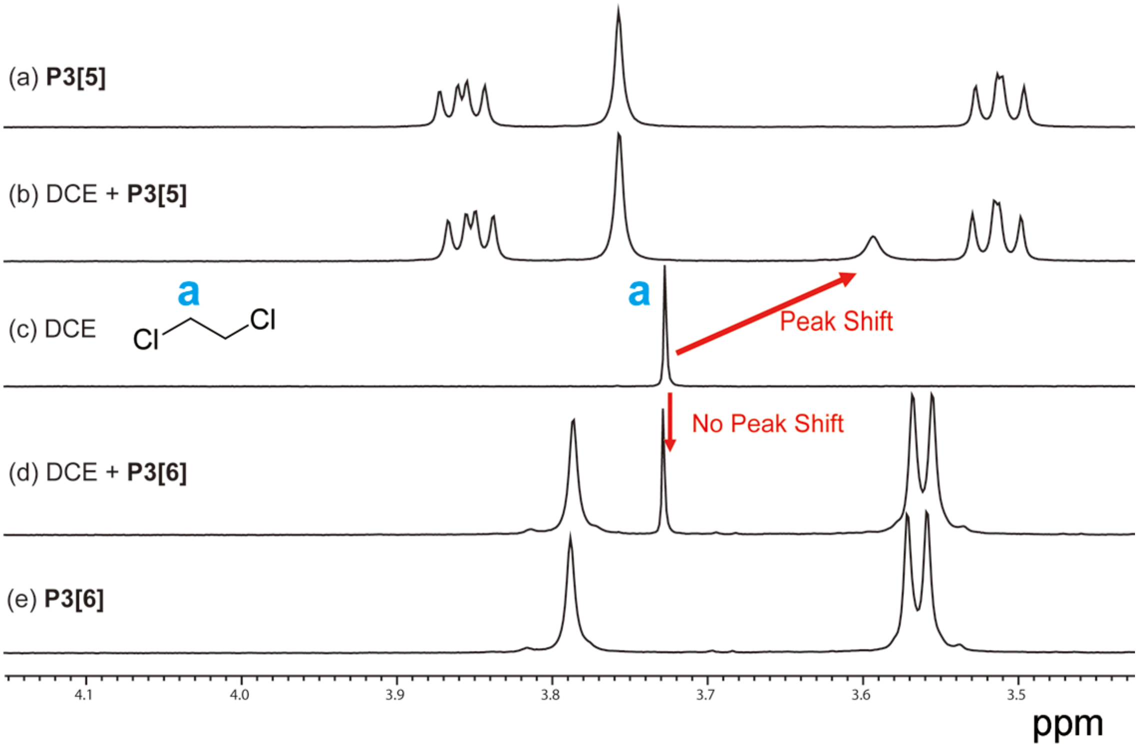


Fig. S3 ^{1}H NMR spectra of (a) **P3[5]**, (b) a mixture of **P3[5]** and DCE, (c) DCE, (d) a mixture of **P3[6]** and DCE and (e) **P3[6]** in $CDCl_3$ in 2 mM at 25 ^oC. The proton signal from ethylene moiety of DCE was observed at 3.73 ppm (Figure S2c). When DCE was mixed with **P3[5]** (Figure S2(b)), upfield shift of 1.32 ppm was observed for the peak. On the other hand, in an equimolar mixture of DCE and **P3[6]** (Figure S2d), no upfield shift of the peak was observed. These results indicate that DCE forms a complex with **P3[5]** but not with **P3[6]**.

^{1}H NMR spectra of Cl-CyC6 with P3[5] and P3[6]

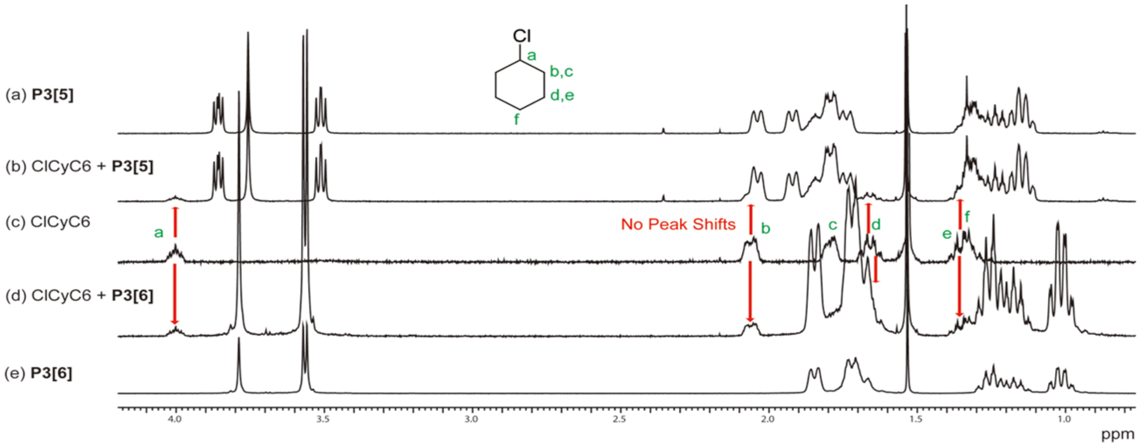


Fig. S4 ^{1}H NMR spectra of (a) **P3[5]**, (b) a mixture of **P3[5]** and Cl-CyC6, (c) Cl-CyC6, (d) a mixture of **P3[6]** and Cl-CyC6 and (e) **P3[6]** in $CDCl_3$ in 2 mM at 25 ^{o}C. The proton signals from ethylene moiety of Cl-CyC6 were not shifted with **P3[5]** (Figure S2(b)) and **P3[6]** (Figure S2(d)). This is due to the weak complexation in $CDCl_3$.

DFT Calculations

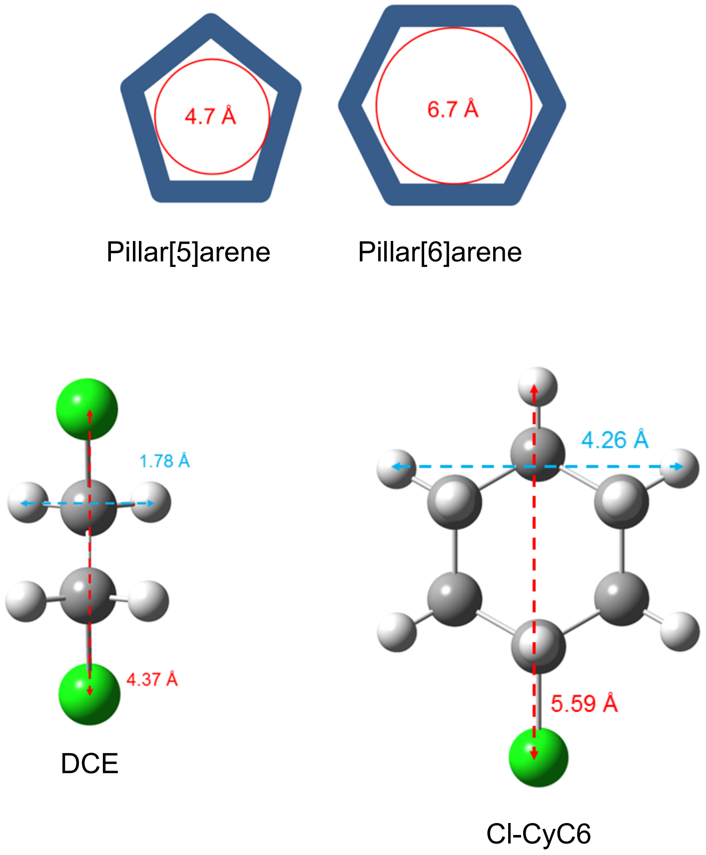
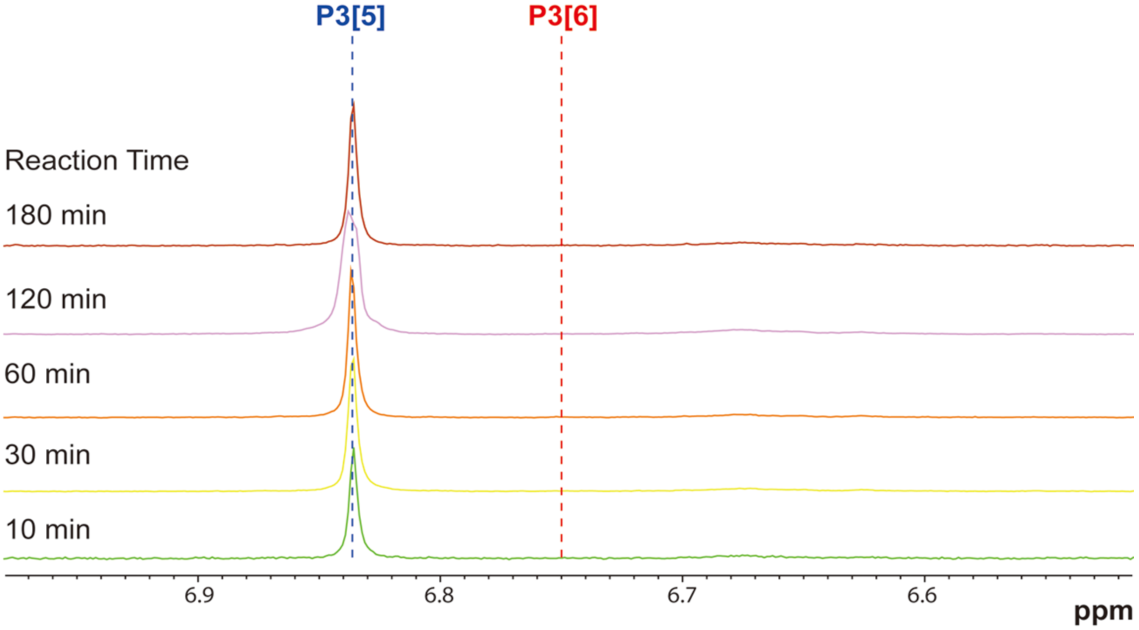


Fig. S5 Cavity sizes of pillar[5]- and pillar[6]arenes were based on X-ray crystal structures.[S6,S7] Molecular models of DCE and Cl-CyC6 were predicted by DFT method (B3LYP, 6-311G, d, p) using Gaussian 09.

Monitoring the reactions of P3[5] in DCE and P3[6] in Cl-CyC6 with BF_3▪OEt_2 at 80 °C by ^{1}H NMR measurements

(a)**P3[5]** in DCE at 80 °C



(b)**P3[6]** in Cl-CyC6 at 80 °C

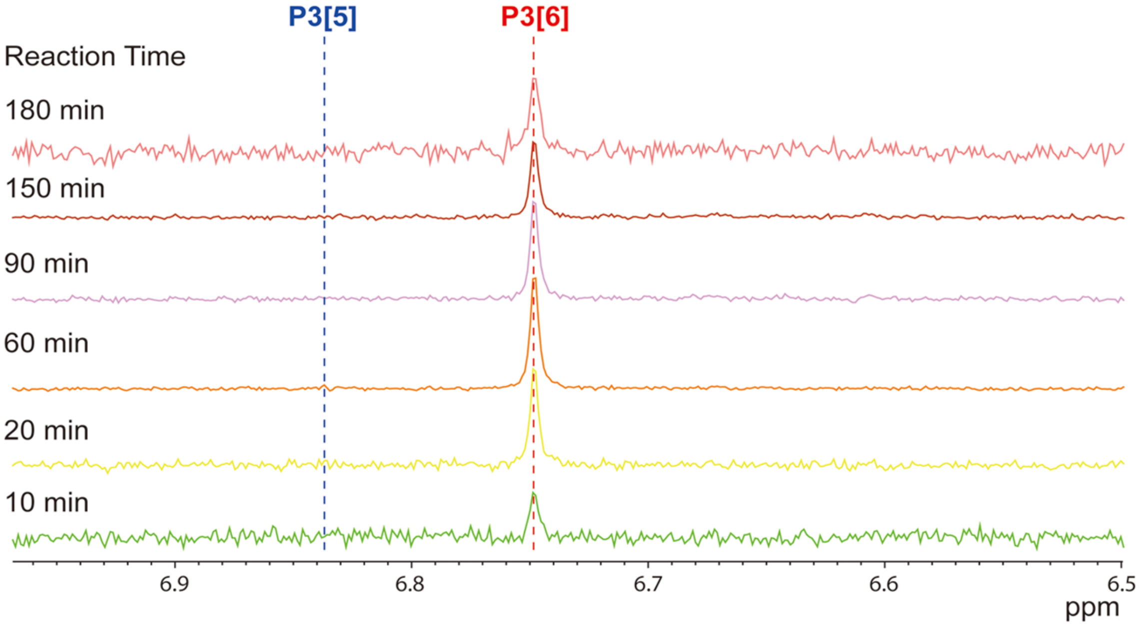


Fig. S6 Monitoring the reactions of (a) **P3[5]** in DCE and (b) **P3[6]** in Cl-CyC6 at 80 °C with BF_3▪OEt_2 by ^{1}H NMR measurements. No peak changes indicate interconversions did not take place by inclusion of the template solvent.

References

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