Electronic Supplementary Information (ESI)

Synthesis and X-ray Crystal Structure of Difunctionalized Pillar[5]arene at A1/B2 Positions by *in-situ* Cyclization and Deprotection

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Experimental Section

Materials. All solvents and reagents were used as supplied.

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.

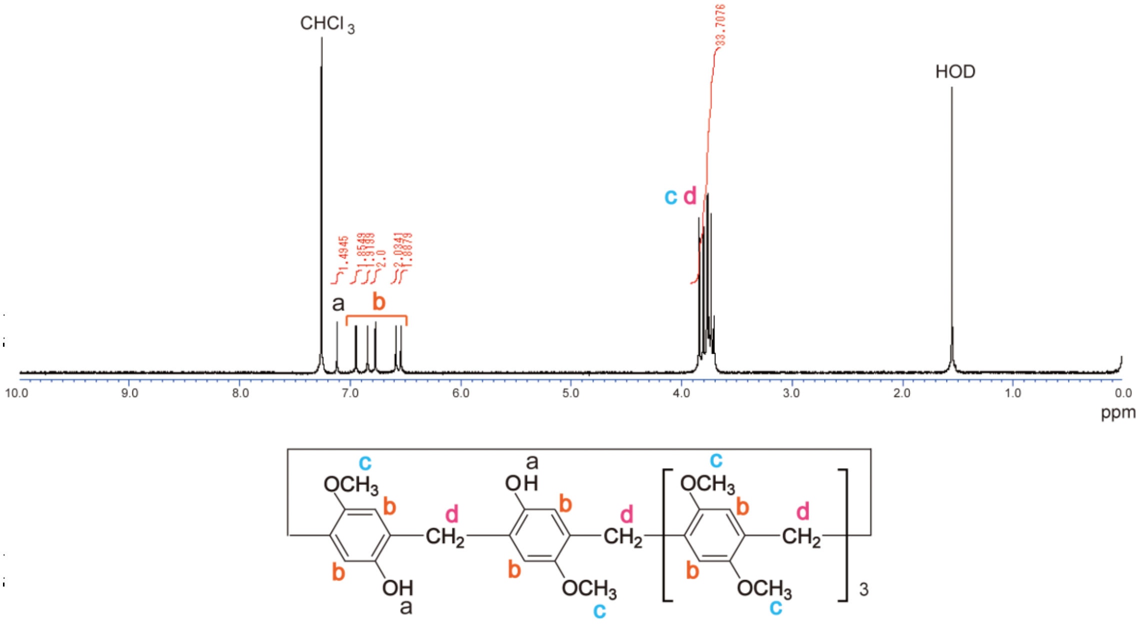
A1/B2. To a solution of 1,4-dimethoxybenzene (1.38 g, 10 mmol) in 1,2-dichloroethane (20 mL), paraformaldehyde (0.31 g, 10 mmol) was added under nitrogen atmosphere. Aluminum bromide (2.67 g, 10 mmol) was added to the solution and the mixture was stirred at 30 ^{o}C for 3 h. The solution was poured into methanol and the solid was filtered off. The filtrate was concentrated, then dissolved in dichloromethane. Insoluble solid was removed by filtration and the filtrate was concentrated. Column chromatography (silica gel; dichloromethane:acetone = 100:0 to 97:3) afforded a mixture of constitutional isomers of di-deprotected pillar[5]arenes. Since solubility of **A1**/**B2** is low, washing with small portion of methanol afforded **A1**/**B2**. (0.0571 g, 0.0790 mmol, Yield: 4%.) ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.12 (s, 2H, OH), 6.95, 6.84, 6.77, 6.59, 6.54 (s, 10H, phenyl), 3.84, 3.80, 3.77, 3.75, 3.73, 3.71 (m, 34H, methylene and methoxy). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 151.9, 150.6, 148.0, 147.5, 130.5, 129.2, 127.4, 126.5, 124.5, 119.0, 114.8, 113.7, 112.9, 112.8 (C of phenyl), 56.5, 56.2, 55.8, 55.6 (C of methoxy), 31.1, 29.8, 27.1 (C of methylene). HRFABMS Calcd for C43H47O10 $[M+H]^{+}$: 723.3169, found 723.3173. FT-IR (KBr) 3268 cm^{-1} (br, -OH). Melting point (T_m): 236.8 ^{o}C.

Pillar[5]arene oligomer. Under a nitrogen atmosphere **A1/B2** (40.4 mg, 0.0559 mmol) was dissolved in DMF (1 mL). Sodium hydride (8.05 mg, 0.335 mmol) was added and the reaction mixture was stirred. Then, 1,4-bis(bromomethyl)benzene (14.8 mg, 0.0559 mmol) was added and the reaction mixture was heated at 80 ^{o}C for 72 h. The solution was poured into methanol and the resulting precipitate was collected by filtration (Pillar[5]arene oligomer, 1.50 mg, Yield: 3%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.30-7.75 (m, phenyl protons from linker), 6.50-6.92 (m, phenyl protons from pillar[5]arene), 4.80-5.00 (s, methylene from linker), 3.30-4.02 (m, methoxy and methylene bridge protons from pillar[5]arene). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 151.1, 150.8, 150.0, 137.5, 128.6, 128.2, 128.0, 127.5, 115.3, 114.3, 114.1 (C of phenyl), 70.5 (C of methylene linker), 55.7, 55.5 (C of methoxy), 30.0, 29.7, 29.6 (C of methylene bridge). GPC analysis (THF, polystyrene standards) : M_w = 1,800, M_w / M_n =

2.1. By using ^{1}H NMR measurement, the average number of repeating units (n) was determined from the peak integration ratio of the methylene protons of linker to the proton peak from the end-group. The average number of repeating units (n) was found to be ca. 15.

^{1}H and ^{13}C NMR spectra of A1/B2

(a) ^{1}H NMR Spectrum



(b) ^{13}C NMR Spectrum

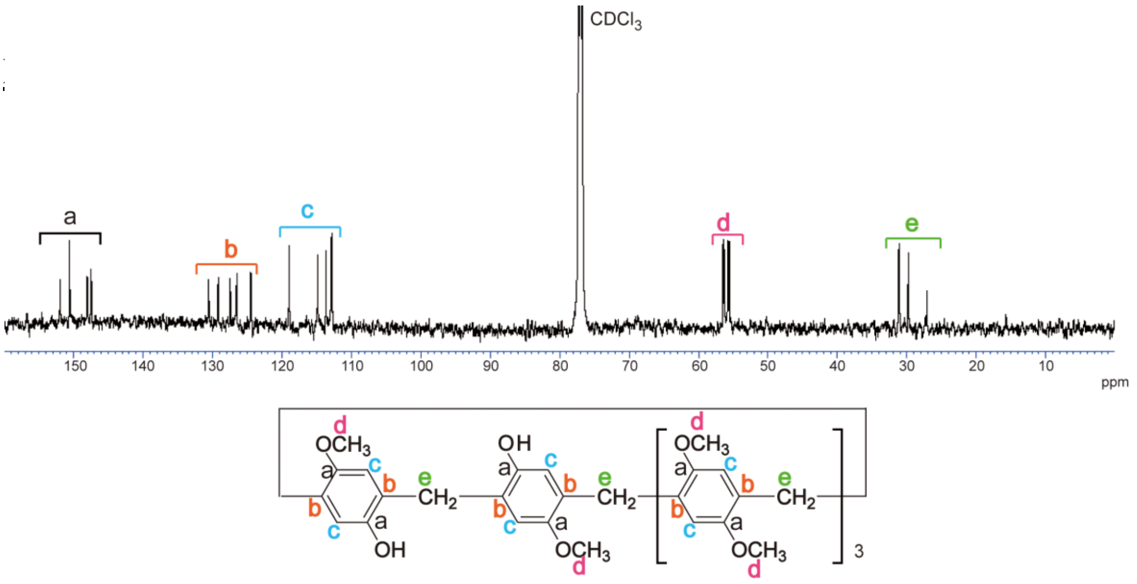
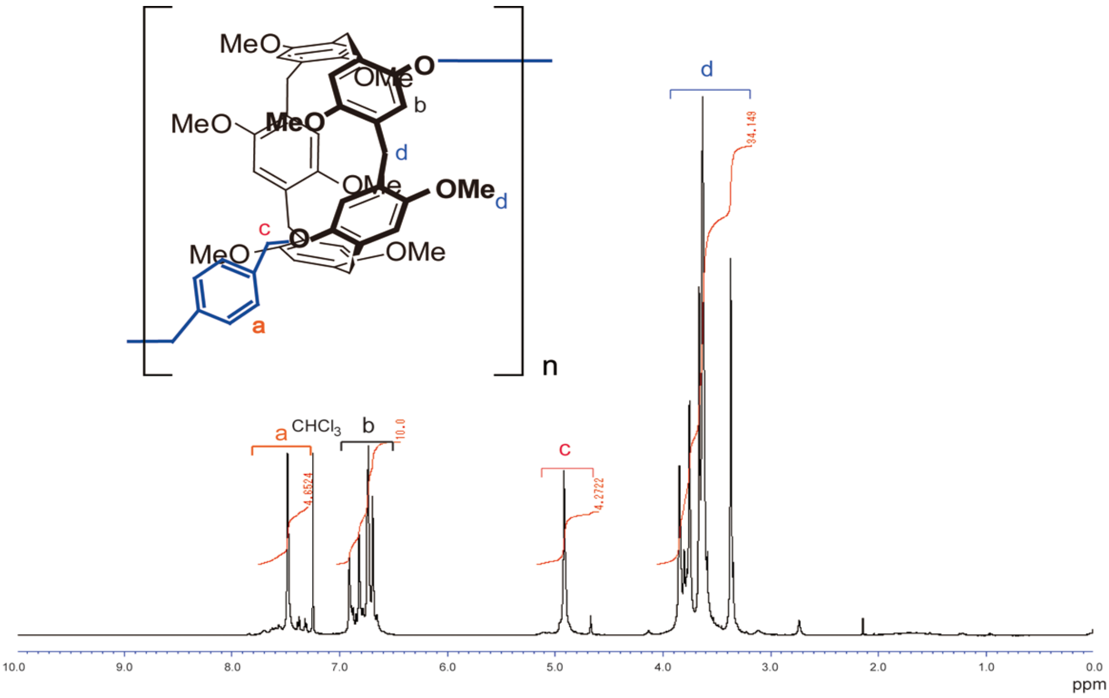


Figure S1. (a) ^{1}H and (b) ^{13}C NMR spectra of **A1/B2** in $CDCl_3$ at 25 °C.

^{1}H and ^{13}C NMR spectra of pillar[5]arene oligomer

(a) ^{1}H NMR Spectrum



(b) ^{13}C NMR Spectrum

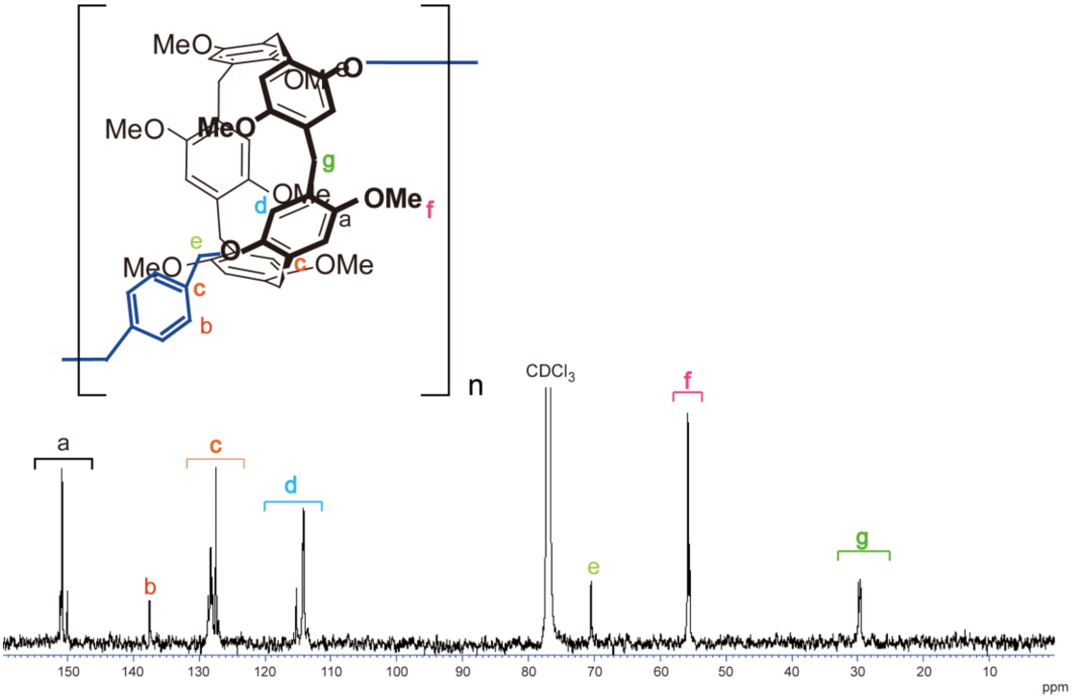


Figure S2. (a) ^{1}H and (b) ^{13}C NMR spectra of pillar[5]arene oligomer in $CDCl_3$ at 25 °C.

GPC traces as a function of time

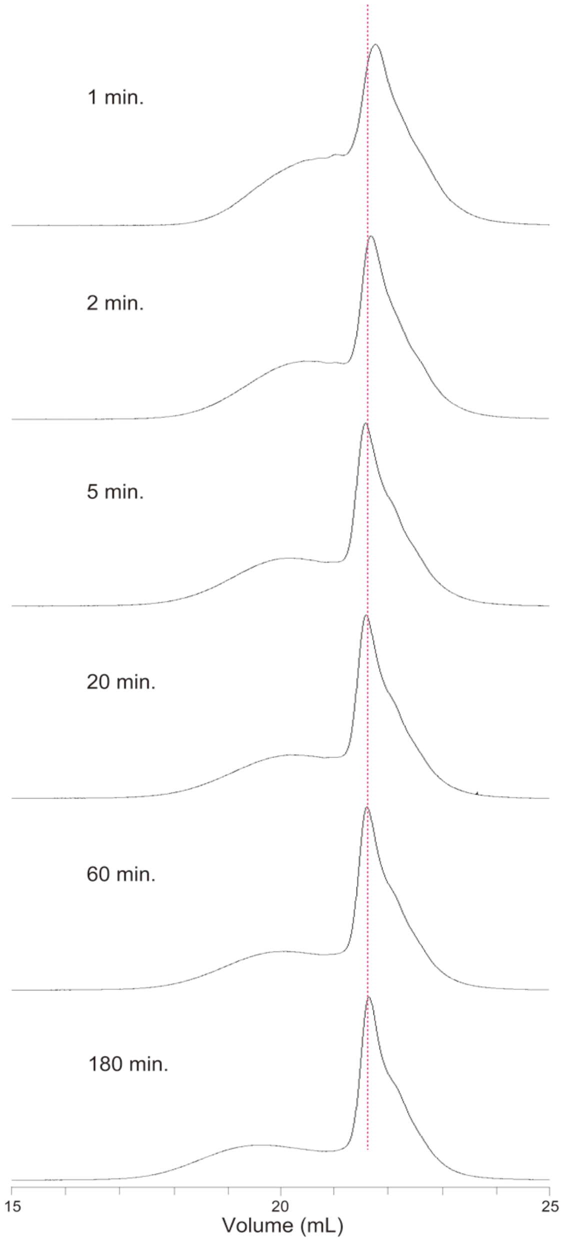


Figure S3. GPC traces of the product obtained using $AlBr_3$ as a function of time. Formation of per-methylated pillar[5]arene took place after 1 min. The observation is same by using $BF_3 \cdot OEt_2$.[S1] However, the peak top was shifted to the retention time of di-deprotected pillar[5]arene as the reaction time increased. It took at least 5 min to complete the di-deprotection.

^{1}H NMR spectrum of the product before washing with methanol

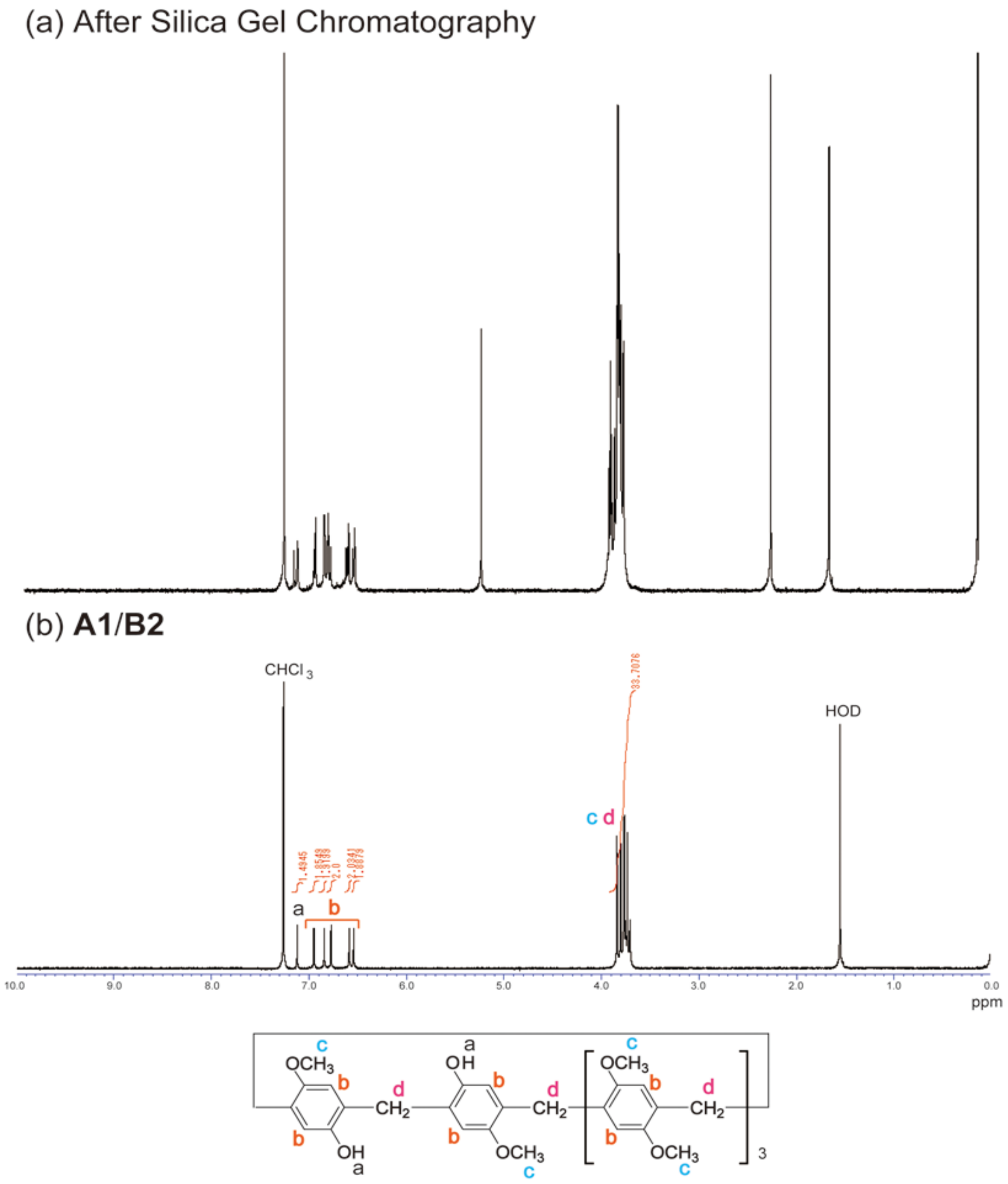


Figure S4. ^{1}H NMR spectra of the product using $AlBr_3$ (a) before and (b) after washing with methanol in $CDCl_3$. Complex split peaks from the phenol and phenyl (protons a and b) indicate that the obtained product was a mixture of constitutional isomers of di-deprotected pillar[5]arene.

FAB mass spectrum of the product before washing with methanol

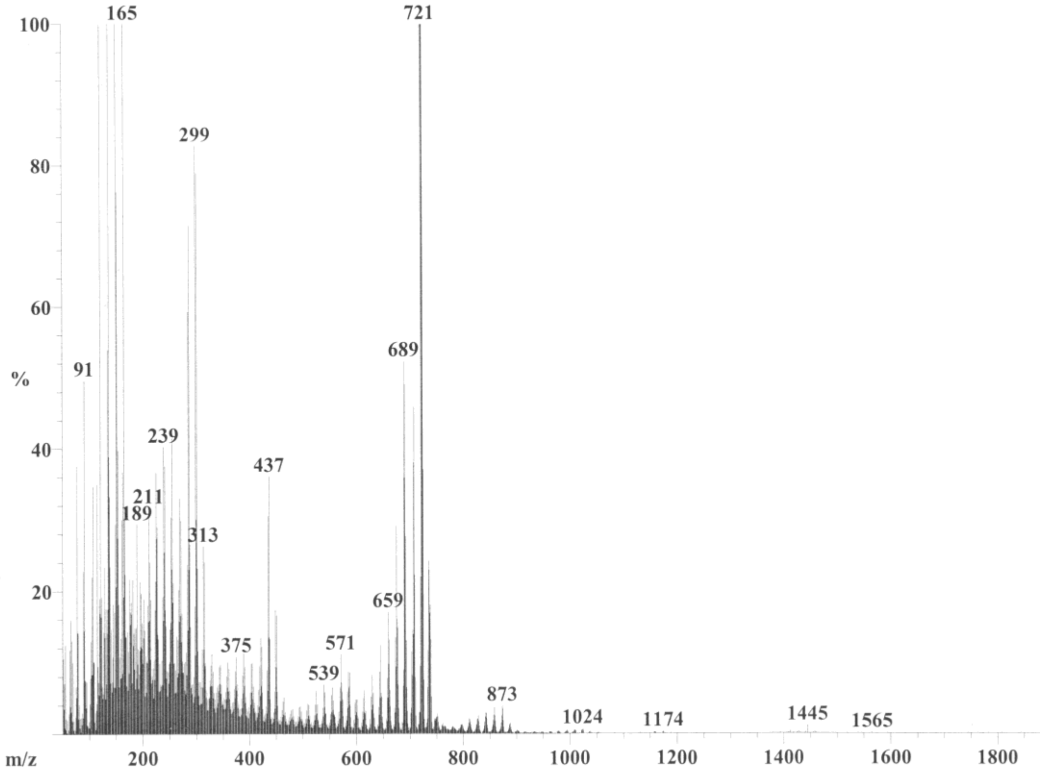


Figure S5. (a) FAB mass spectrum of the product after silica gel chromatography. Peak from di-deprotected pillar[5]arene [m/z = 721 $(M-H)^+$] was observed, whereas the other multiple-deprotected pillar[5]arenes did not detected. This indicates that di-deprotected pillar[5]arenes were isolated by silica gel chromatography.

GPC traces of A1/B2 monomer and pillar[5]arene oligomer

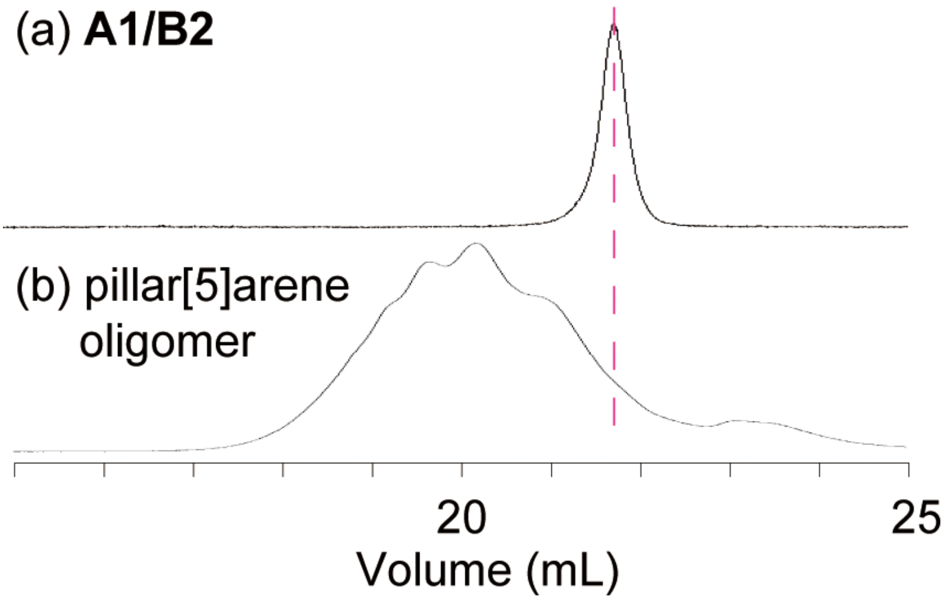


Figure S6. GPC Traces of (a) **A1/B2** and (b) pillar[5]arene oligomer. A number of peaks were observed around 17 mL - 21 mL and the peak from un-reacted **A1/B2** monomer observed in Figure S6 (a) was not detected. The data indicate that pillar[5]arene oligomer was successfully obtained.

Reference

S1) Ogoshi, T. Aoki, K. Kitajima, S. Fujinami, T. Yamagishi and Y. Nakamoto, *J. Org. Chem.*, 2011, **76**, 328.