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Supplementary Information

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The high yielding synthesis of pillar[5]arene under Friedel-Crafts conditions explained by dynamic covalent bond formation

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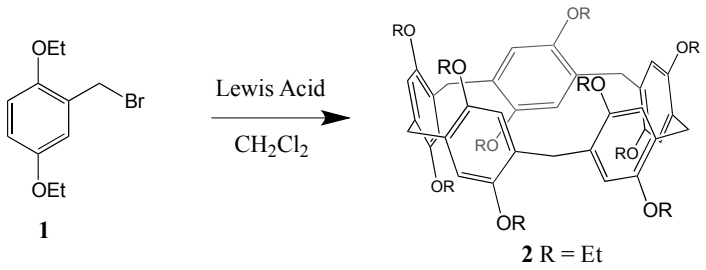
Experimental section

General: Reagents and solvents were purchased as reagent grade and used without further purification. CH_2Cl_2 was distilled over CaH_2. Compounds **6**[1] and **10**[1] were prepared according to previously reported procedures. All reactions were performed in standard glassware under an inert Ar or N_2 atmosphere. Evaporation and concentration were done at water aspirator pressure and drying in vacuo at 10^{-2} Torr. Column chromatography: silica gel 60 (230-400 mesh, 0.040-0.063 mm) was purchased from E. Merck. Thin Layer Chromatography (TLC) was performed on glass sheets coated with silica gel 60 F_{254} purchased from E. Merck, visualization by UV light. NMR spectra were recorded on a Bruker AC 300 or AC 400 with solvent peaks as reference. Elemental analysis were performed by the analytical service at the Laboratoire de Chimie de Coordination (Toulouse, France). MALDI-TOF mass spectra were obtained on a Bruker ULTRAFLEX TOF/TOF mass spectrometer with a dithranol matrix.

Cyclooligomerization of compound 1.



1 **2** R = Et

The appropriate Lewis acid (see Table S1) was added in several portions (over 1 h) to a stirred 11 mM solution of **1** in dry CH_2Cl_2 at room temperature. The reaction mixture turned progressively dark green. After 12 h, H_2O was added. The aqueous layer was extracted with CH_2Cl_2 (3 x) and the combined organic layers dried ($MgSO_4$), filtered and concentrated. Column chromatography (SiO_2, cyclohexane/CH_2Cl_2 1:1) followed by recrystallization

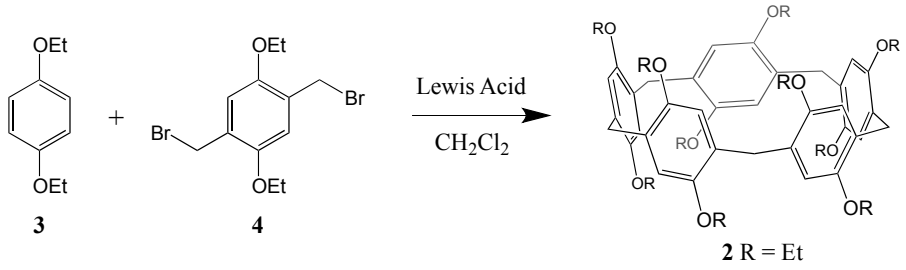
[1] M. J. Gomez-Escalonilla, F. Langa, J.-M. Rueff, L. Oswald and J.-F. Nierengarten, *Tetrahedron Lett.*, 2002, **43**, 7507-7511.

(CH_3CN) gave **2**. The yields are summarized in Table S1. The analytical data were identical to those reported in the literature for compound **2**.[2]

Table S1.

Reagents		Product
Lewis Acid	Compound **1**	(isolated yield)
$AlCl_3$ (616 mg, 4.62 mmol)	400 mg, 1.54 mmol	**2** (194 mg, 71%)
$ZnCl_2$ (470 mg, 3.46 mmol)	300 mg, 1,15 mmol	**2** (86 mg, 42%)
$FeCl_3$ (320 mg, 2.0 mmol)	178 mg, 0.68 mmol	**2** (47 mg, 39%)

Cyclization reaction from compounds 3 and 4.



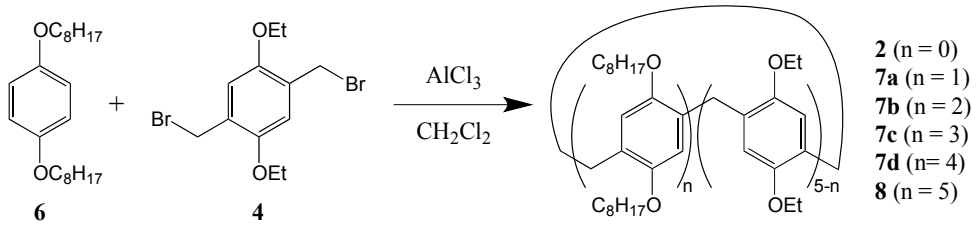
The appropriate Lewis acid (see Table S2) was added in several portions (over 1 h) to a stirred 11 mM solution of **3** (1 equiv.) and **4** (1 equiv.) in dry CH_2Cl_2 at room temperature. The reaction mixture turned progressively dark green. After 12 h, H_2O was added. The aqueous layer was extracted with CH_2Cl_2 (3 x) and the combined organic layers dried ($MgSO_4$), filtered and concentrated. Column chromatography (SiO_2, cyclohexane/CH_2Cl_2 1:1) followed by recrystallization (CH_3CN) gave **2**. The yields are summarized in Table S2. The analytical data were identical to those reported in the literature for compound **2**.[2] As a typical example, the MALDI-TOF mass spectrum of the cyclization product isolated from the reaction of **3** and **4** with $AlCl_3$ as a Lewis acid is depicted in Fig. S1.

[2] T. Ogoshi, T. Aoki, K. Kitajima, S. Fujinami, T. Yamagishi and Y. Nakamoto, *J. Org. Chem*, 2011, **66**, 328-331.

Table S2.

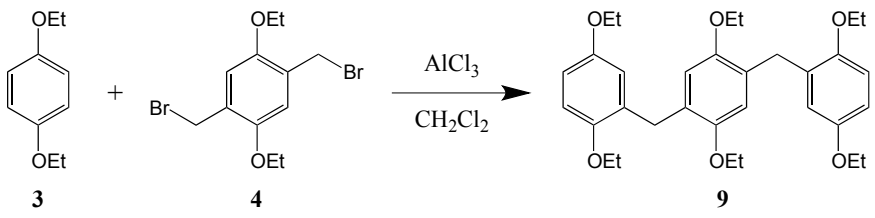
	Reagents		Product
Lewis acid	Compound **3**	Compound **4**	(isolated yield)
$AlCl_3$ (400 mg, 3.0 mmol)	182 mg, 1.1 mmol	400 mg, 1.1 mmol	**2** (239 mg, 61%)
$ZnCl_2$ (400 mg, 2.9 mmol)	182 mg, 1.1 mmol	400 mg, 1.1 mmol	**2** (217 mg, 55%)
$FeCl_3$ (490 mg, 3.0 mmol)	182 mg, 1.1 mmol	400 mg, 1.1 mmol	**2** (245 mg, 63%)

Cyclization reaction from compounds 4 and 6.



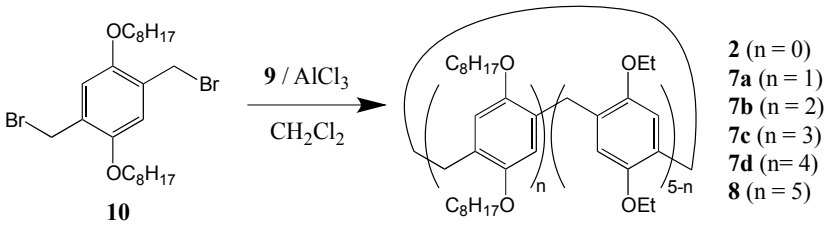
$AlCl_3$ (400 mg, 3.0 mmol) was added in several portions (over 1 h) to a stirred solution of **6** (365 mg, 1.1 mmol) and **4** (400 mg, 1.1 mmol) in dry CH_2Cl_2 (100 mL) at room temperature. The reaction mixture turned progressively dark green. After 12 h, H_2O was added. The aqueous layer was extracted with CH_2Cl_2 (3 x) and the combined organic layers dried ($MgSO_4$), filtered and concentrated. Rapid filtration over SiO_2 (cyclohexane/CH_2Cl_2 1:1) to eliminate the polymers afforded a mixture of pillar[5]arene derivatives that was directly analyzed by MALDI-TOF mass spectrometry (Fig. S2).

Preparation of compound 9.



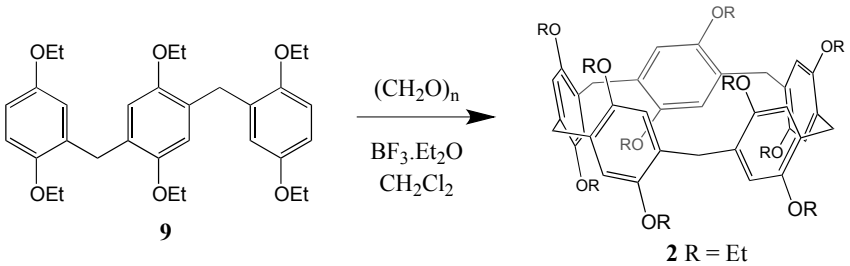
$AlCl_3$ (567 mg, 4.2 mmol) was added in several portions (over 1 h) to a stirred solution of **3** (2.36 g, 14.2 mmol) and **4** (500 mg, 1.4 mmol) in dry CH_2Cl_2 (100 mL) at room temperature. After 12 h, H_2O was added. The aqueous layer was extracted with CH_2Cl_2 (3 x) and the combined organic layers dried ($MgSO_4$), filtered and concentrated. Two successive column chromatographic purifications (SiO_2, cyclohexane/CH_2Cl_2 1:1) afforded compound **9** (358 mg, 48%) as a colorless solid. ^1H NMR ($CDCl_3$, 300 MHz): 6.78-6.64 (m, 6 H), 4.00 (q, J = 7 Hz, 4 H), 3.93 (q, J = 7 Hz, 4 H), 3.92 (s, 4 H), 3.91 (q, J = 7 Hz, 4 H), 1.40 (t, J = 7 Hz, 6 H), 1.35 (t, J = 7 Hz, 6 H), 1.33 (t, J = 7 Hz, 6H). Elemental calcd. for $C_{26}H_{42}O_6$: C 73.53, H 8.10; found: C 73.49, H 8.19. MALDI-TOF MS: 522.2 ($[M]^+$ calcd. for $C_{26}H_{42}O_6$: 522.297).

Cyclization from compounds 9 and 10.



$AlCl_3$ (90 mg, 0.68 mmol) was added in several portions (over 1 h) to a stirred solution of **9** (130 mg, 0.25 mmol) and **10** (129 mg, 0.25 mmol) in dry CH_2Cl_2 (45 mL) at room temperature. The reaction mixture turned progressively dark green. After 12 h, H_2O was added. The aqueous layer was extracted with CH_2Cl_2 (3 x) and the combined organic layers dried ($MgSO_4$), filtered and concentrated. Rapid filtration over SiO_2 (cyclohexane/CH_2Cl_2 1:1) to eliminate the polymers afforded a mixture of pillar[5]arene derivatives that was directly analyzed by MALDI-TOF mass spectrometry (Fig. S3).

Cyclization from compound 9 and paraformaldehyde.



$BF_3.Et_2O$ (40 µL, 0.3 mmol) was added to a stirred solution of **9** (150 mg, 0.3 mmol) and paraformaldehyde (26 mg, 0.9 mmol) in dry CH_2Cl_2 (30 mL) at room temperature. After 3 h, H_2O was added. The aqueous layer was extracted with CH_2Cl_2 (3 x) and the combined organic layers dried ($MgSO_4$), filtered and concentrated. Column chromatography (SiO_2, cyclohexane/CH_2Cl_2 1:1) followed by recrystallization (CH_3CN) gave **2** (40 mg, 20%). The analytical data were identical to those reported in the literature for compound **2**.[2]

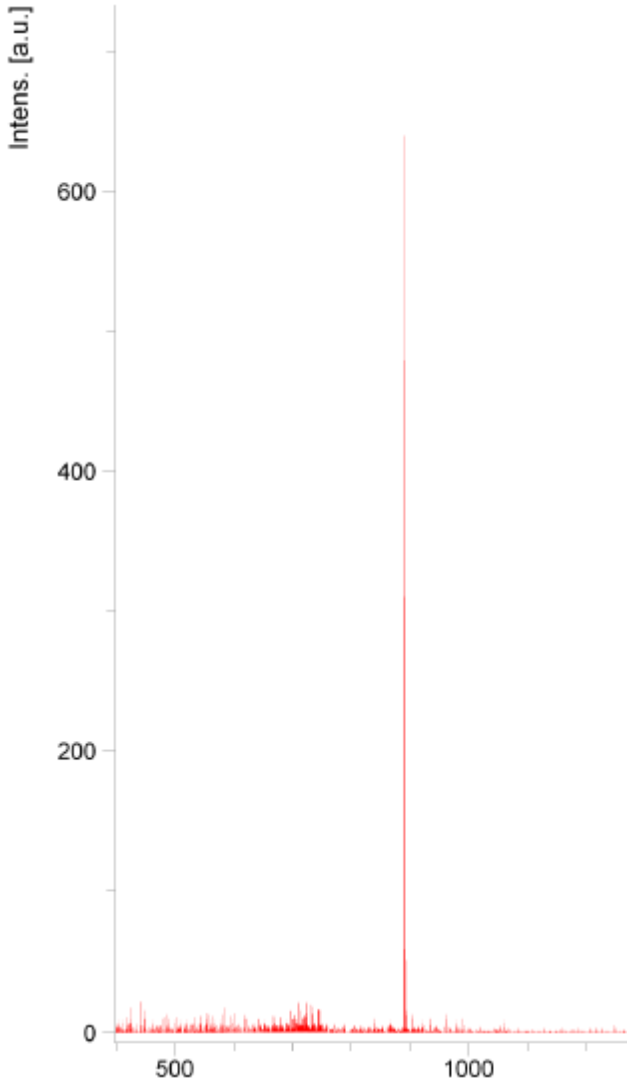


Fig. S1. MALDI-TOF MS of compound **2** obtained from the reaction of **3** and **4** with $AlCl_3$ as a Lewis acid ($[M]^+$ calcd. for $(C_{11}H_{14}O_2)_5$: 890.497; found: 890.4).

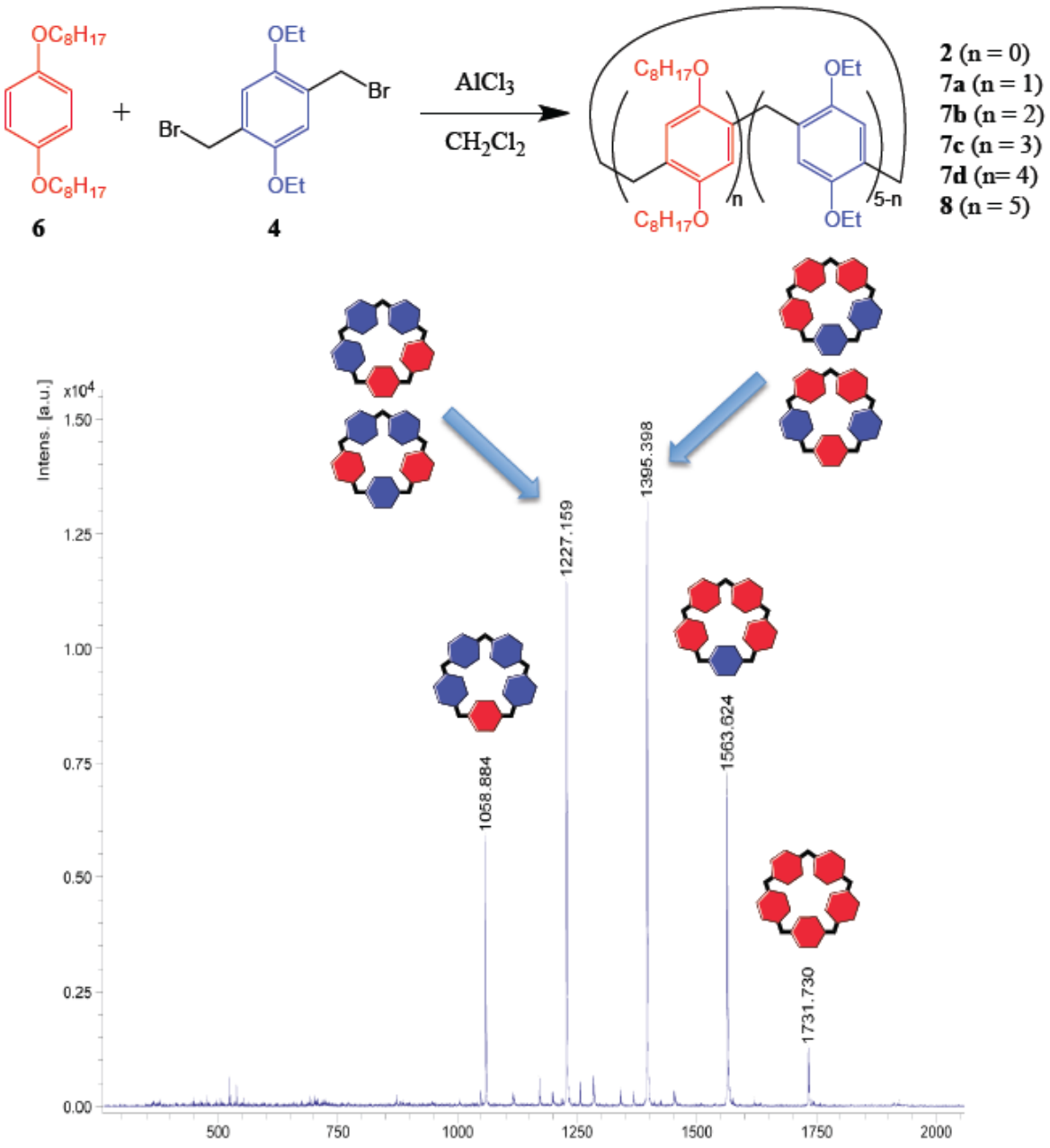


Fig. S2. MALDI-TOF MS of the mixture of pillar[5]arenes obtained from the reaction of **4** and **6** with $AlCl_3$. Out of all the possible cyclopentamers (**2**, **7a-d** and **8**), only compound **2** is not detected.

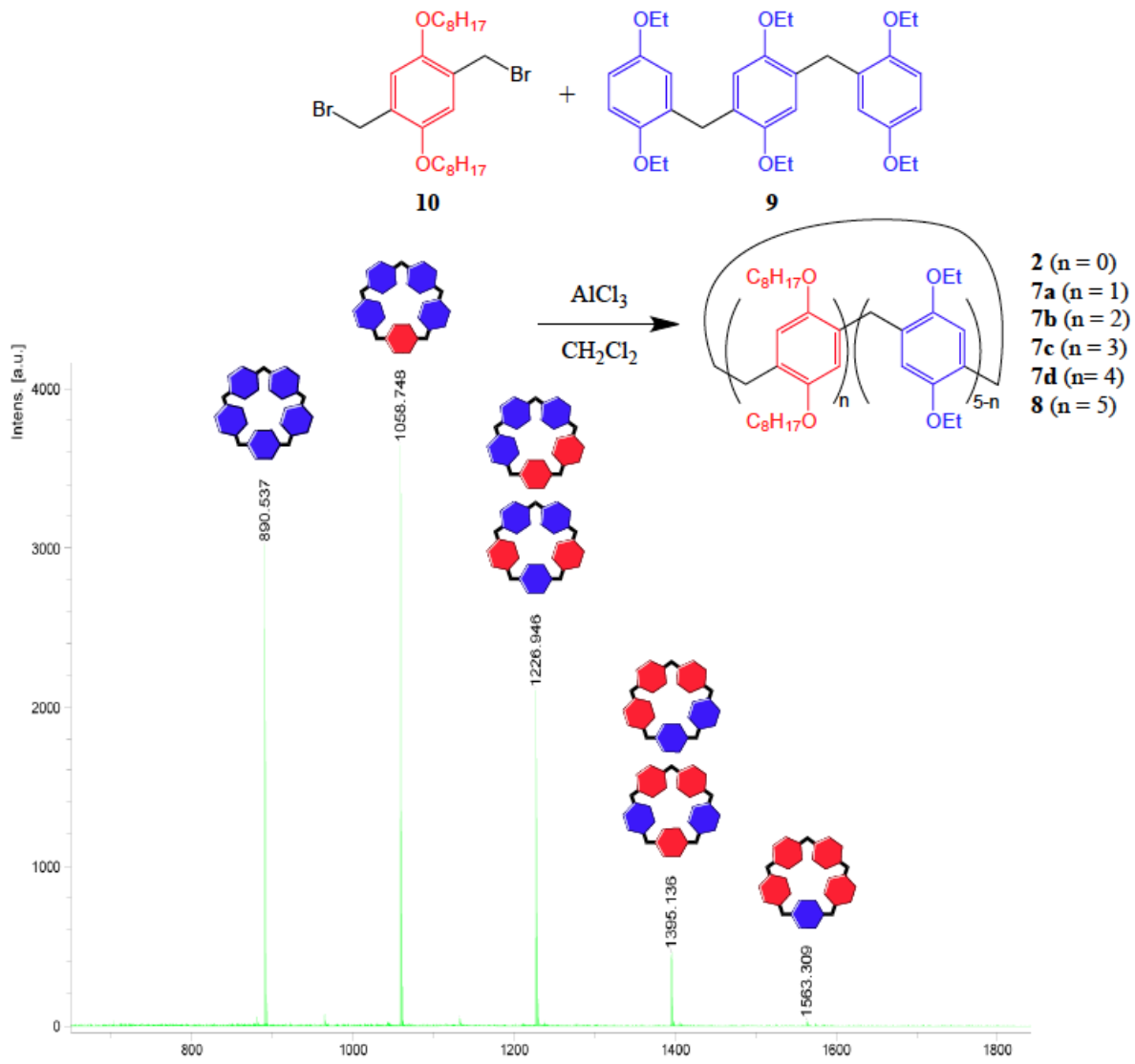


Fig. S3. MALDI-TOF MS of the mixture of pillar[5]arenes obtained from the reaction of **9** and **10** with $AlCl_3$. Out of all the possible cyclopentamers (**2**, **7a-d** and **8**), only compound **8** is not detected.