

# Electronic Supplementary Information

## (ESI)

### Diastereoselective Synthesis of Meso-Pillar[6]arenes by Bridging Between Hydroquinone Units in an Alternating Up-and-Down Manner

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## Experimental section

**Materials.** All solvents and reagents were used as supplied. Per-hydroxylated pillar[5]arene (**H1**), pillar[6]arene (**H2**) and per-ethylated pillar[6]arene (**H7**) were synthesized according to the previous papers.<sup>S1-S3</sup>

**Measurements.** The <sup>1</sup>H NMR spectra were recorded at 500 MHz and <sup>13</sup>C NMR spectra were recorded at 125 MHz with a JEOL-ECA500 spectrometer.

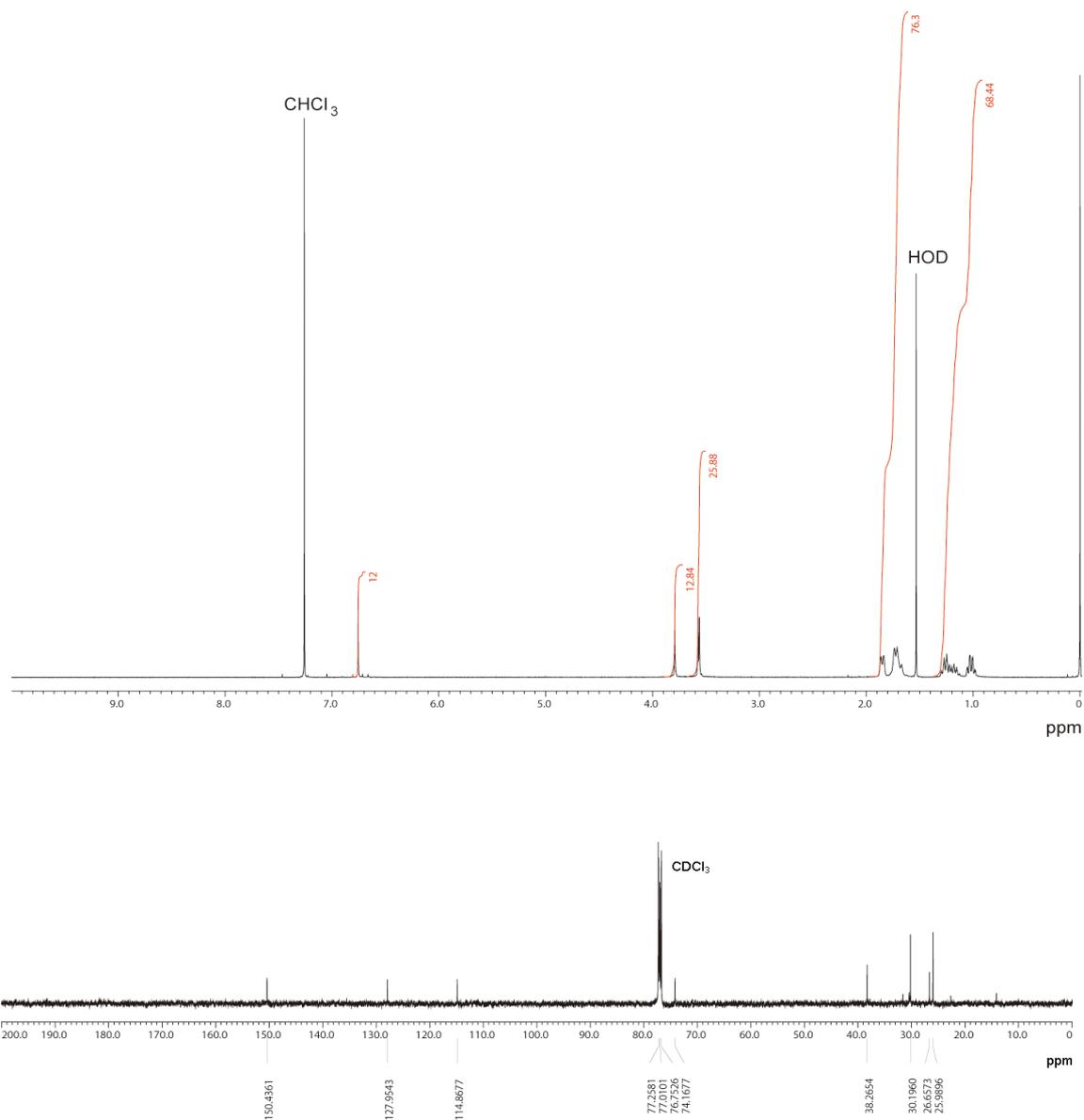
**H4.** To a solution of 1,4-bis(methylcyclohexyl ether)benzene<sup>S4</sup> (1.21 g, 4.00 mmol) in chloroform (160 mL), paraformaldehyde (3.40 g, 12.0 mmol) was added under nitrogen atmosphere. Then, FeCl<sub>3</sub> (60 mg, 368 μmol) was added to the solution and the mixture was stirred at 30 °C for 72 h. The solution was poured into methanol and the resulting precipitate was collected by filtration. The obtained solid was dissolved in hexane and an insoluble solid was filtered off. The filtrate was purified by silica gel column chromatography (dichloromethane/hexane = 1/3, R<sub>f</sub> = 0.30) to yield **4** as a white solid (0.125 g, 66.3 μmol, Yield: 10%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, ppm): δ 6.75 (s, 12H), 3.79 (s, 12H), 3.57, 3.56 (dd, 12H), 0.98-1.86 (m, 132H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm): δ 150.4, 128.0, 114.9, 74.2, 38.3, 30.2, 26.7, 26.0. HRMS (ESI): *m/z* Calcd for C<sub>126</sub>H<sub>180</sub>NaO<sub>12</sub> [M+Na]<sup>+</sup>: 1908.3372, found 1908.3373.

**H5.** To a solution of per-hydroxylated pillar[6]arene (150 mg, 0.200 mmol) in dry pyridine (50 mL), cooled to 0 °C, dichlorodimethylsilane (464 mg, 3.60 mmol) was added. The mixture was stirred at 80 °C for 3 h. The solvent was removed under vacuum and the resulting residue was suspended in methanol (20 mL). The white solid obtained after vacuum filtration, yielding **5** as a white powder (135 mg, 0.126 mmol, 63%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, ppm): δ 6.66 (s, 12H), 4.14 (d, J = 13.2 Hz, 6H), 3.11 (d, J = 13.2 Hz, 6H), 0.48 (s, 18H), -0.50 (s, 18H). <sup>13</sup>C NMR (CDCl<sub>3</sub>/CS<sub>2</sub> = 1/1, 125 MHz, ppm): δ 146.6, 131.6, 121.6, 32.5, -2.19, -5.46. HRMS(ESI): *m/z* Calcd for C<sub>55</sub>H<sub>64</sub>NaO<sub>13</sub>Si<sub>6</sub> [M+Na+MeOH]<sup>+</sup>: 1123.2860, found 1123.2862.

**H6.** To a solution of per-hydroxylated pillar[6]arene (75.0 g, 0.100 mmol) in dry pyridine (30 mL), cooled to 0 °C, dichlorodiethylsilane (283 mg, 1.80 mmol) was added. The mixture was stirred at 80 °C for 3 h. The solvent was removed under vacuum and the resulting residue was suspended in methanol (20 mL). The white solid obtained after vacuum filtration, yielding **6** as a white powder (68.0 mg, 0.0551 mmol, 54%). <sup>1</sup>H NMR

(CDCl<sub>3</sub>, 500 MHz, ppm): δ 6.63 (s, 12H), 4.13 (d, J = 13.2 Hz, 6H), 3.10 (d, J = 13.8 Hz, 6H), 1.18 (t, J = 8.0 Hz, 18H), 0.91 (m, 12H), 0.83 (t, J = 8.0 Hz, 18H), 0.33 (m, 12H).  
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm): δ 146.7, 131.4, 121.7, 32.8, 6.22, 6.12, 4.30, 3.30.  
HRMS(ESI): *m/z* Calcd for C<sub>67</sub>H<sub>88</sub>NaO<sub>13</sub>Si<sub>6</sub> [M+Na+MeOH]<sup>+</sup>: 1291.4738, found 1291.4737.

## $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of H4



**Fig. S1**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **H4** in  $\text{CDCl}_3$  at 25 °C.

## $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of H5

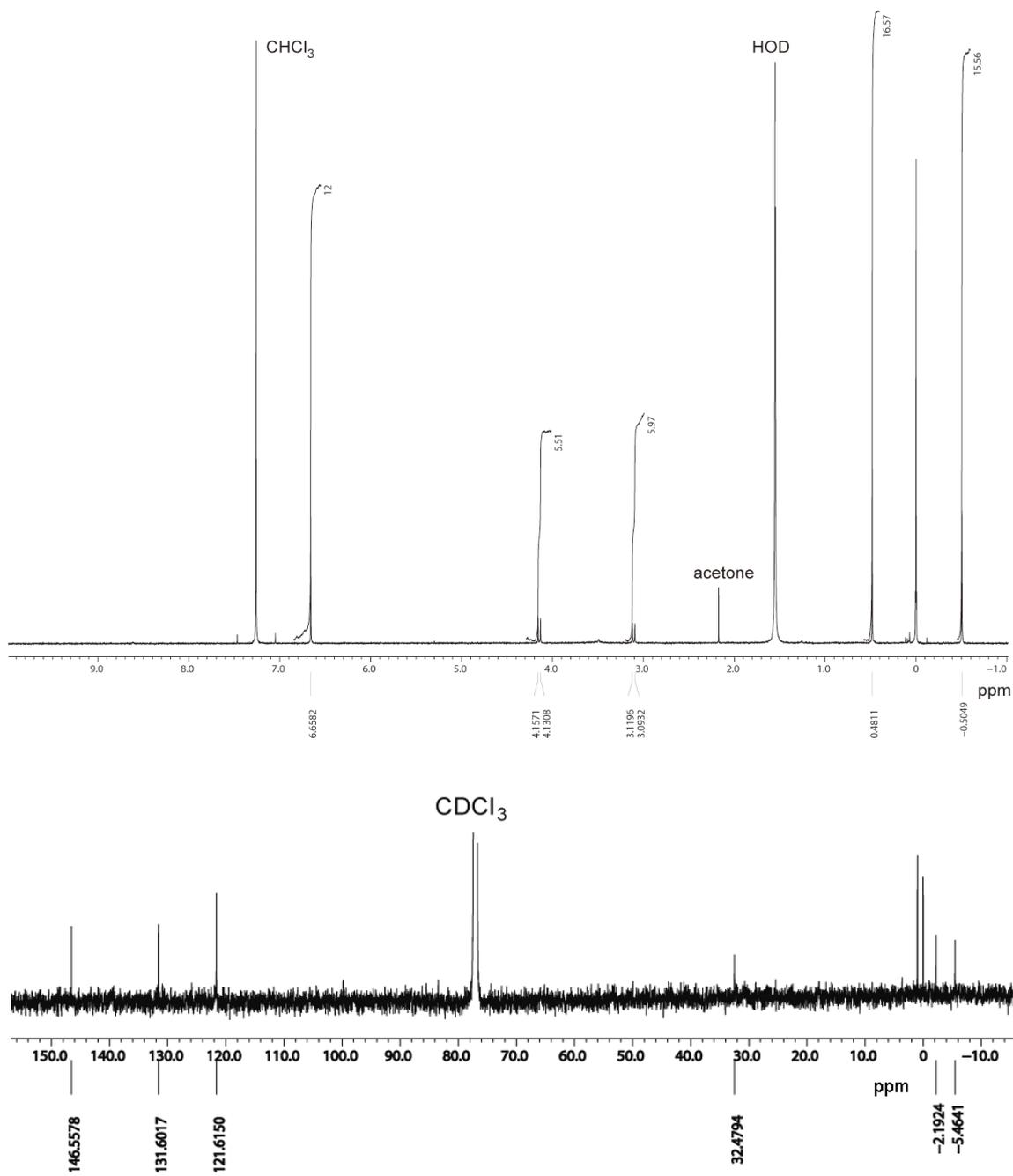
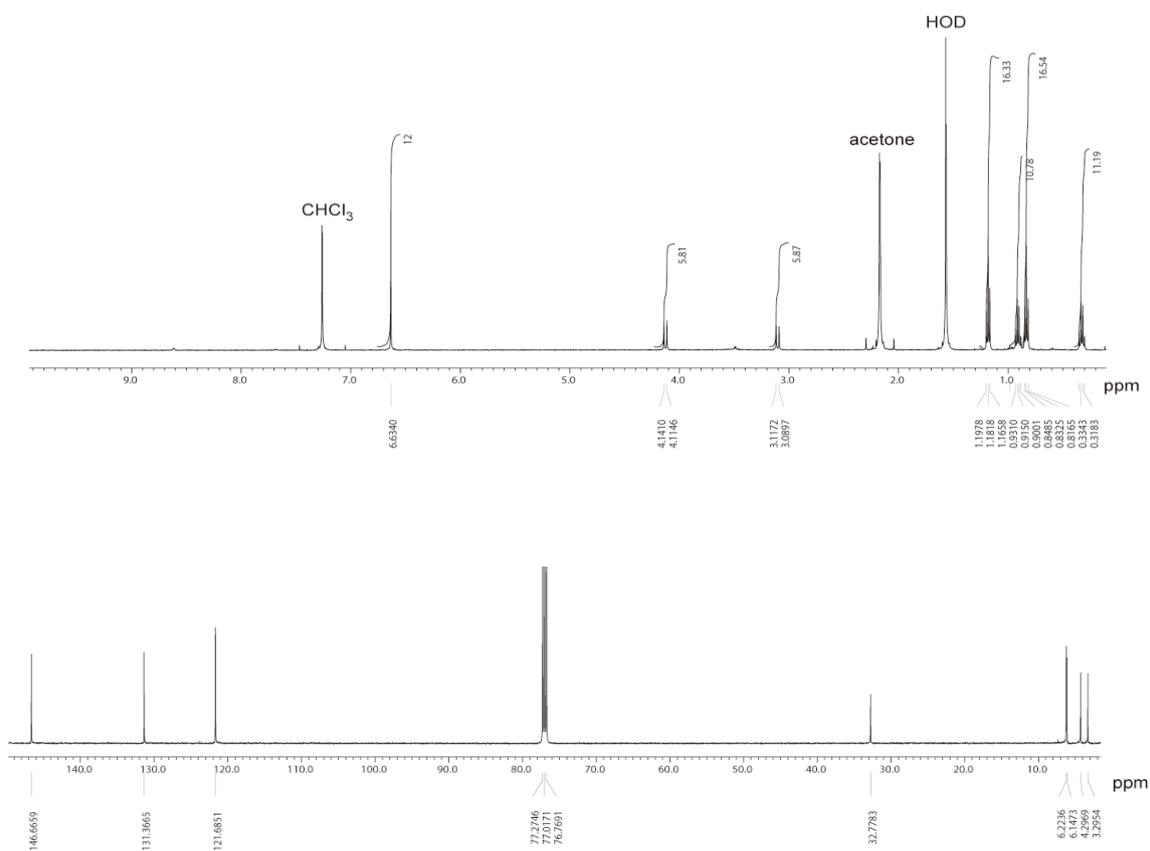


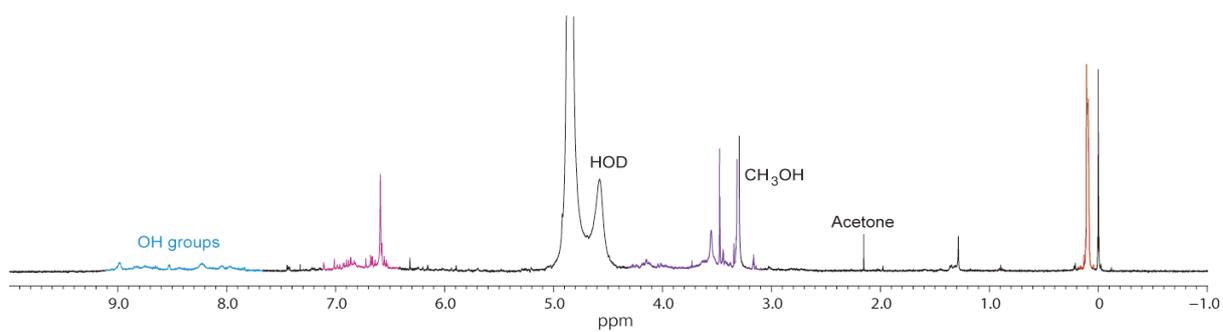
Fig. S2  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of H5 in  $\text{CDCl}_3$  at 25 °C.

## $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of H6



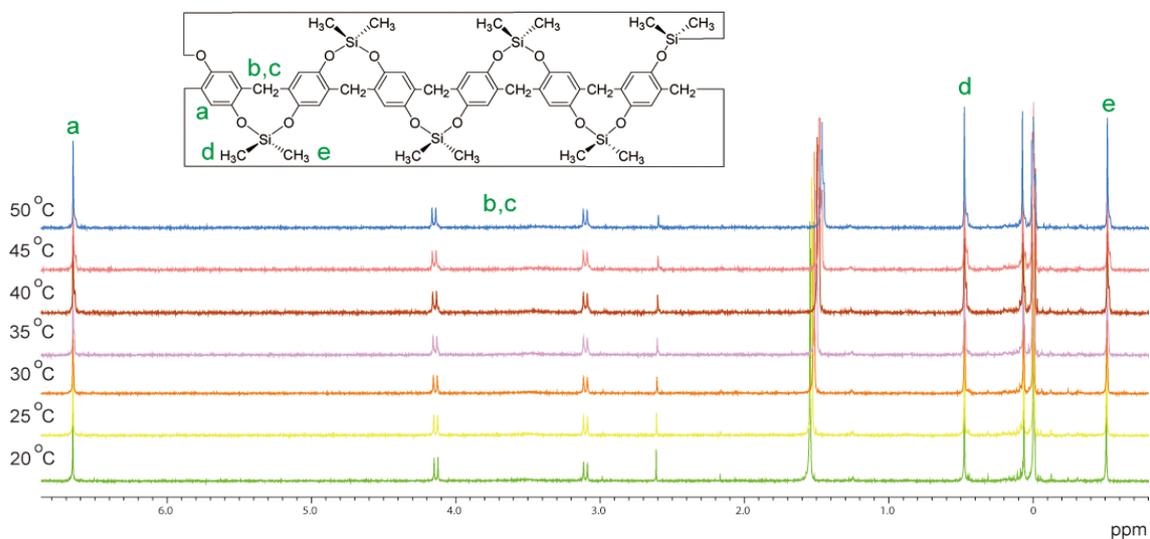
**Fig. S3**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **H6** in  $\text{CDCl}_3$  at 25 °C.

## $^1\text{H}$ NMR spectra of a product of H1 with dichlorodimethylsilane



**Fig. S4**  $^1\text{H}$  NMR spectrum ( $\text{CD}_3\text{OD}$ , 25 °C) of a product by reaction of per-hydroxylated pillar[5]arene **H1** with dichlorodimethylsilane.

## Variable-temperature $^1\text{H}$ NMR spectra of **H5**



**Fig. S5** Variable-temperature  $^1\text{H}$  NMR spectra of **H5** in  $\text{CDCl}_3$ .

## References

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