# Efficient Synthesis of Copillar[5]arenes and Their Host–Guest Properties with Alkyl Bromide

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## **Supporting Information**

#### 1. Materials and methods

The 1,4-bis(ethoxy)pillar[6]arene was synthesized according to the literature procedure<sup>1</sup>. Solvents were either employed as purchased or dried according to the procedures described in the literatures. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded with a Bruker DRX 400 spectrometer by using CDCl<sub>3</sub> as solvent and TMS as an internal standard. Matrix-assisted laser desorption ionization time-off flight (MALDI-TOF) mass measurements were performed with an Autoflex III smart-beam spectrometer. Thin layer chromatography was performed by using commercial Merck silica gel plates (GF254), and visualization was carried out at 254 nm.

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#### 2. General Procedure for the preparation of copillar[5] arenes (3b-i)

<sup>a</sup>isolated yields, calculated with the feed amounts of compounds **2b-i**.

Scheme S1. Preparation of pillar[5] arenes by oligomerization of different 1,4-dialkoxybenzenes.

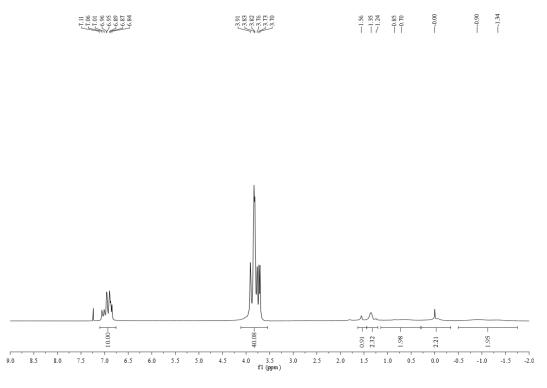


Figure S1 <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of copillar[5]arene **3b**.

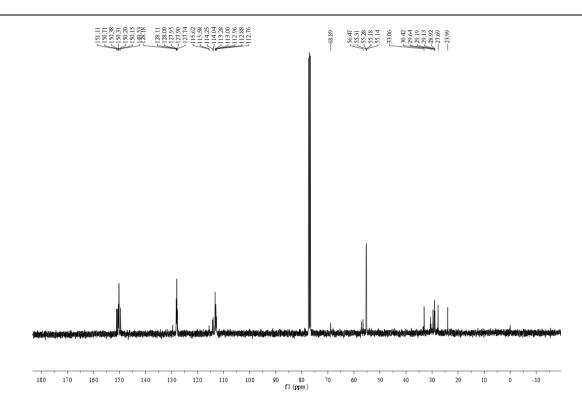


Figure S2 <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>) of copillar[5]arene **3b**.

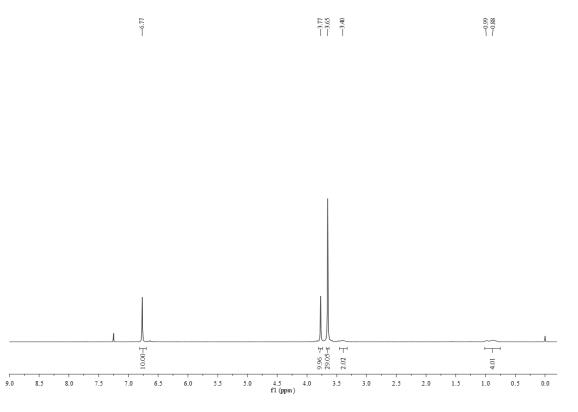


Figure S3 <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of copillar[5]arene **3c** 

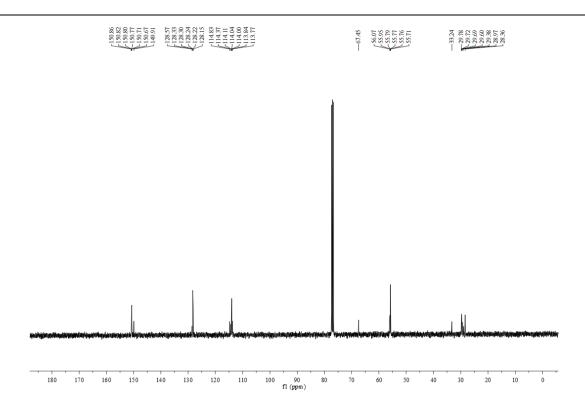


Figure S4 <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>) of copillar[5]arene **3c**.

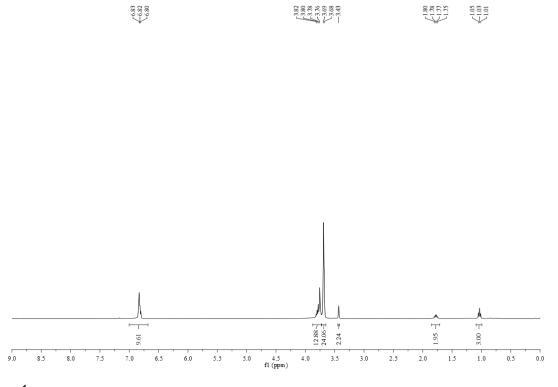


Figure S5 <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of copillar[5]arene **3d**.

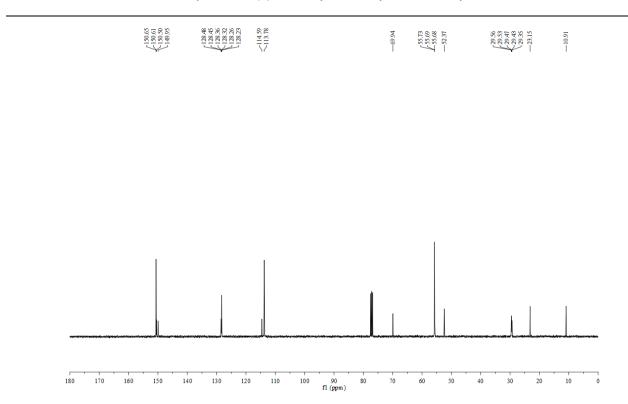


Figure S6 <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>) of copillar[5] arene 3d.

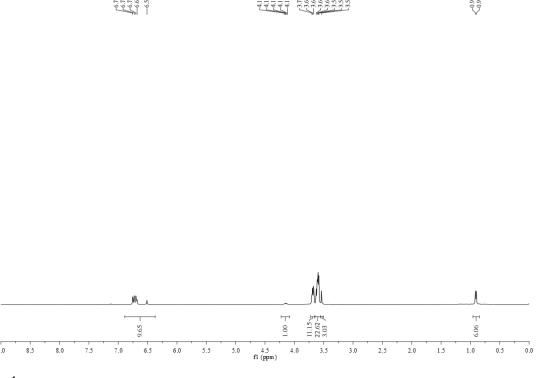


Figure S7 <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of copillar[5]arene **3e**.

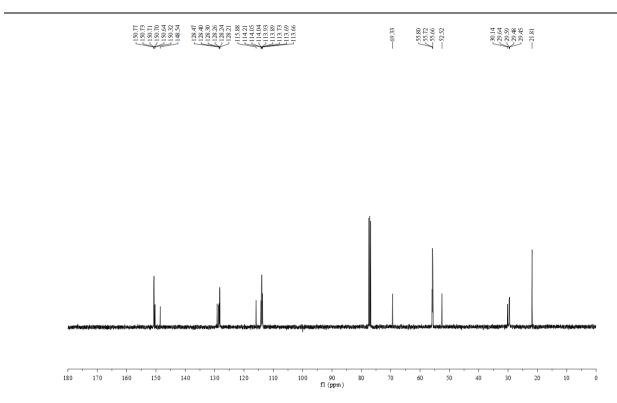


Figure S8 <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>) of copillar[5] arene **3e**.

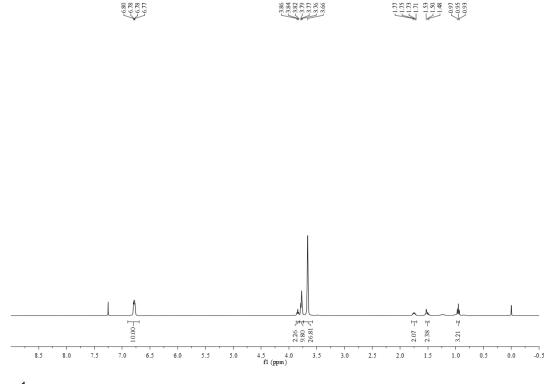


Figure S9 <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of copillar[5] arene 3f.

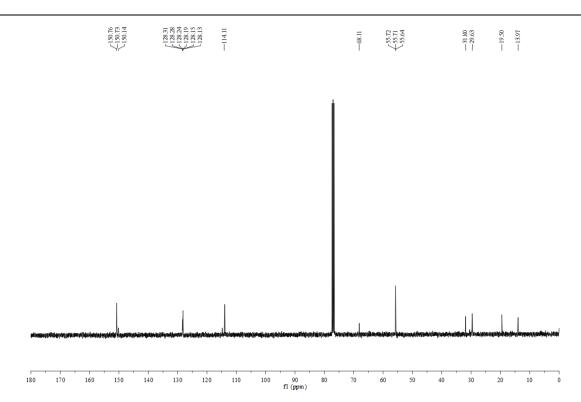


Figure S10 <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>) of copillar[5]arene **3f**.

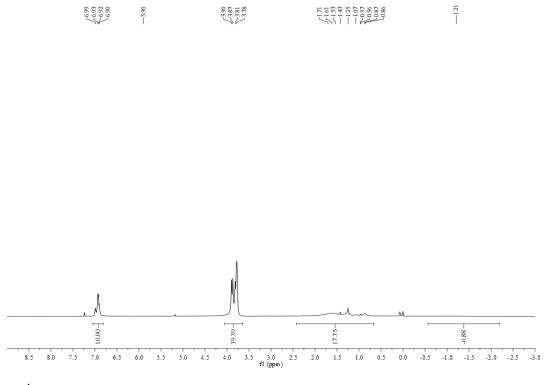


Figure S11 <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of copillar[5]arene **3g**.

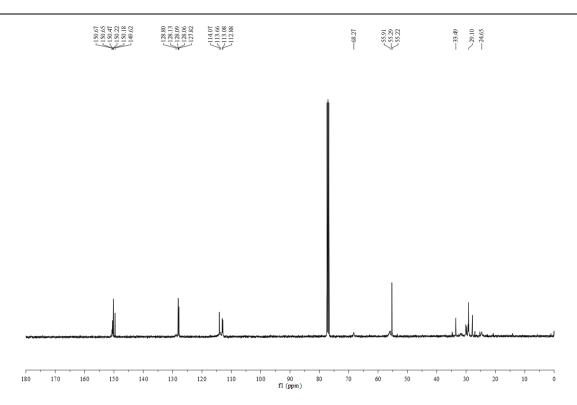


Figure S12  $^{13}$ C NMR spectrum (CDCl3) of copillar[5]arene **3g**.



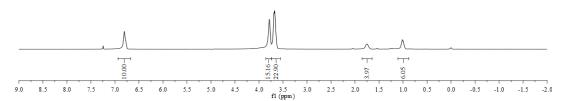


Figure S13 <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of copillar[5]arene **3h**.

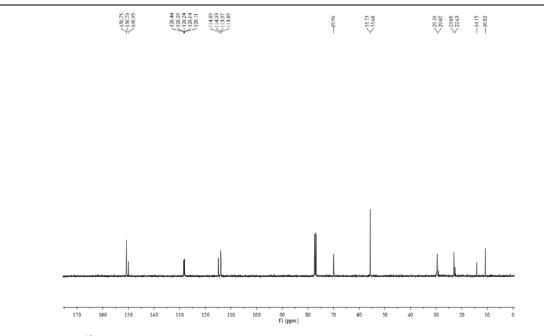


Figure S14 <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>) of copillar[5]arene **3h**.

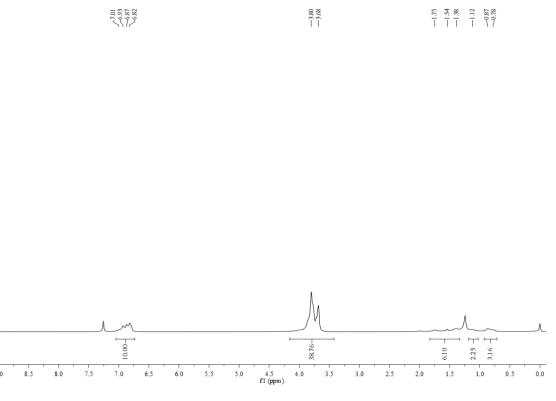


Figure S15 <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of copillar[5]arene 3i.

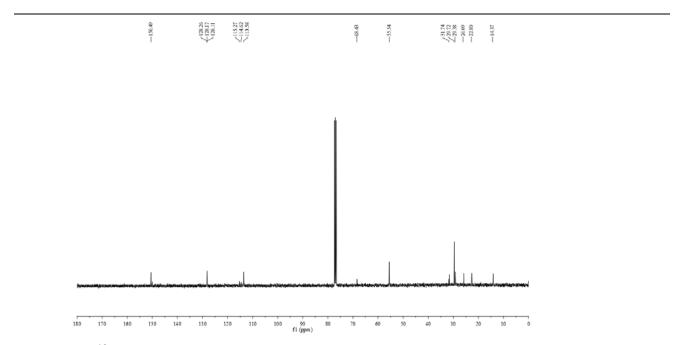


Figure S16 <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>) of copillar[5] arene 3i.

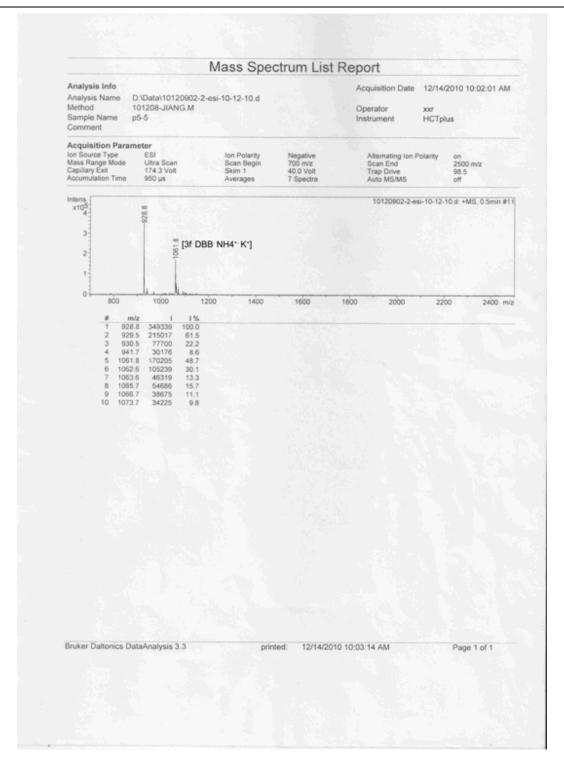


Figure S17 Mass (ESI) spectra of an equimolar mixture of 3f and DBB

#### References

D. Cao, Y. Kou, J. Liang, Z. Chen, L. Wang and H. Meier, *Angew. Chem. Int. Ed.*, 2009, **48**, 9721-9723.