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Electronic Supplementary Information

(ESI)

A monophosphoryl copillar[5]arene: synthesis and host-guest complexation with alkanols

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1. Materials and Methods

Dimethoxypillar[5]arene **2** was prepared according to the literature procedure.[1] All reagents and chromatography grade solvents were obtained from commercial sources and purified prior to use according to standard solvent manual. Melting points were measured with a Tektronix X4 apparatus and are uncorrected. ^{1}H NMR, ^{31}P NMR and ^{13}C NMR spectra were recorded with a Bruker DRX 400 spectrometer. Matrix-assisted laser desorption ionization time-off flight (MALDI-TOF) mass measurements were performed with an Autoflex III smart-beam spectrometer. HR-MS (ESI) was carried out on a Bruker maxis impact.

2. Synthetic procedure and NMR spectra of Compound 4

To a stirred mixture of monohydroxypillar[5]arene (0.5 g, 0.68 mmol), diethyl chlorophosphate (0.393 mL, 2.72 mmol) and TBAB (21.9 mg, 0.068 mmol) in CH_3Cl (34 mL) under a nitrogen atmosphere was added dropwise 50% aqueous NaOH (0.82 mL, 2.04 mmol). The reaction mixture was heated at reflux for 24 h under N_2. The cooled reaction mixture was washed with deionized water, dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography to afford compound **4** (287 mg, 49%). m.p.187 °C. ^{1}H NMR (400Hz, $CDCl_3$, 298K):□ δ (ppm) 7.07−6.58 (m,10H),□3.85 −3.56 (m, 37H), 3.27−3.17 (m, 4H), 0.05 (t, J = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ (ppm) 152.13, 151.07, 150.77, 150.59, 150.50, 150.30, 150.21, 143.11, 129.57, 129.17, 128.95, 128.84, 128.52, 128.33, 128.18, 126.40, 119.94, 114.78, 114.48, 114.13, 114.01, 113.91, 113.76, 113.56, 113.30, 63.49, 63.44, 56.18, 55.94, 55.74, 55.60, 55.53, 32.60, 30.04, 29.70, 29.25, 28.58, 27.17, 14.77, 14.70; MS (MALDI-TOF): *m/z* calcd for $[M]^+$ $C_{48}H_{57}O_{13}P$: 872.354, found 872.299; HR-MS (ESI): *m/z* calcd for $[M + Na]^+$ $C_{48}H_{57}NaO_{13}P$: 895.3429; found 895.3419.

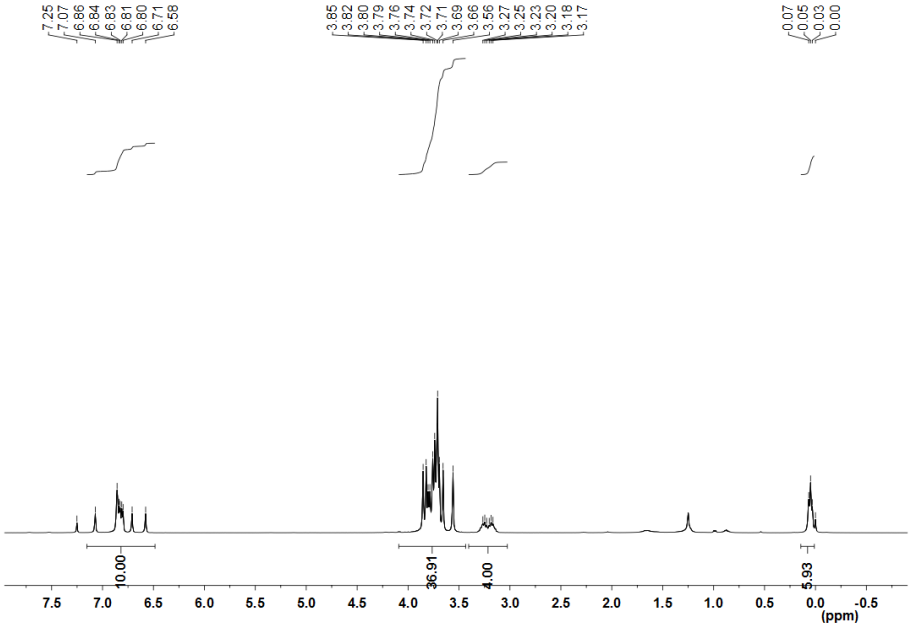

Fig. S1 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **4**.

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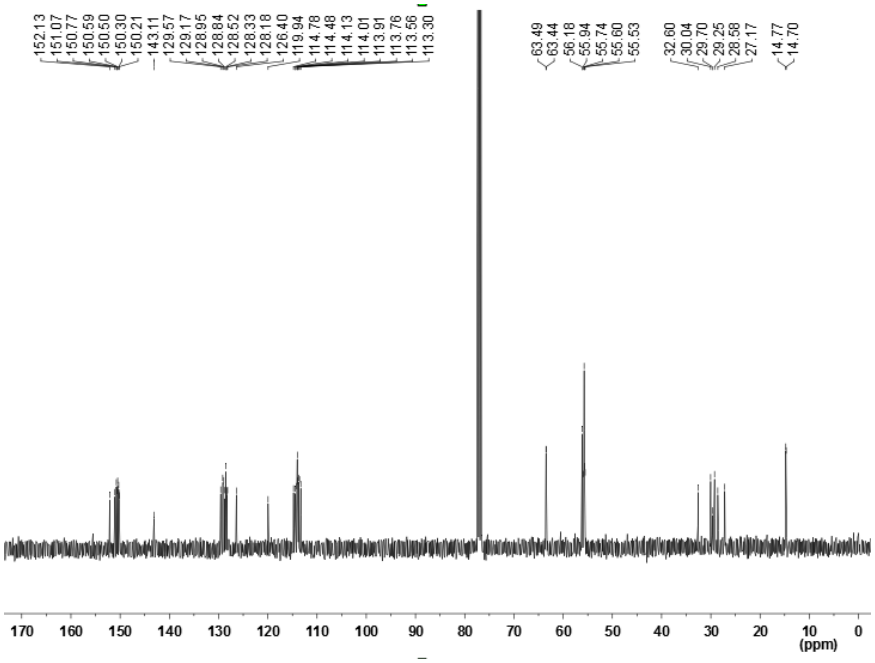

Fig. S2 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **4**.

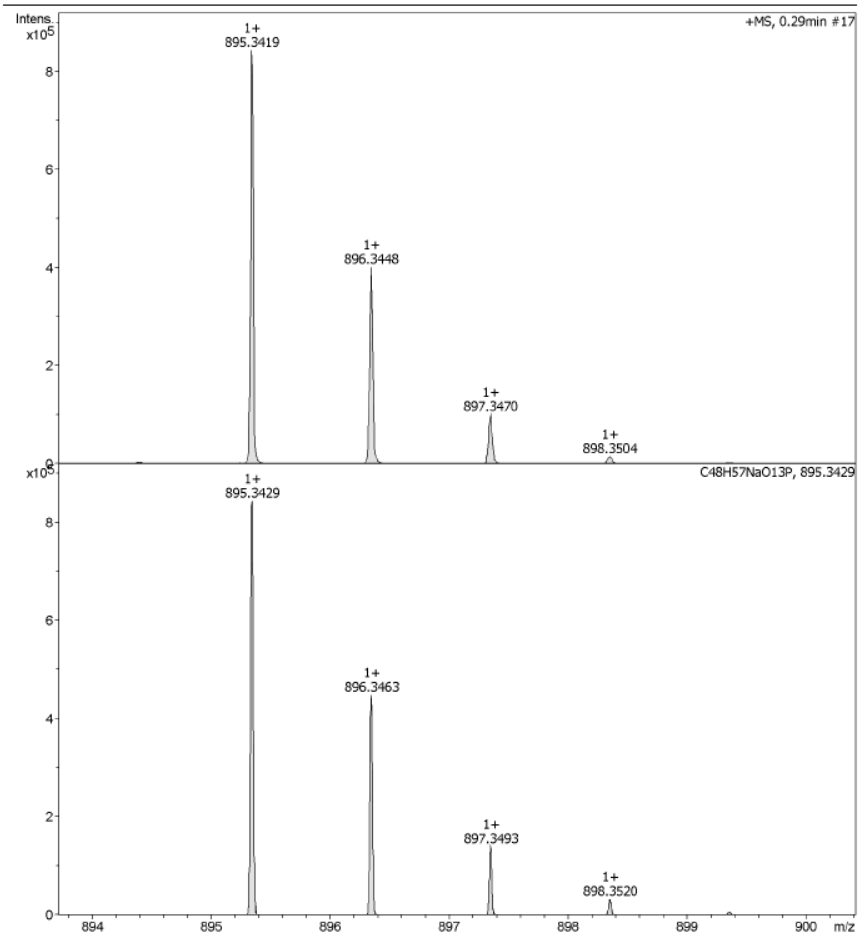

Fig. S3 HR-MS (ESI) of **4**.

3. Synthetic procedure and NMR spectra of Compound 1

To a stirred solution of **4** (200 mg, 0.229 mmol) in freshly distilled $CHCl_3$ (10 mL) was added trimethylsilyl bromide (0.3 mL, 2.29 mmol) at 0 °C for 30 min. The resulting mixture was stirred at room temperature for 20 h

and was then evaporated under reduced pressure. Anhydrous methanol (10 mL) was added to the residue. The methanolic solution was boiled for 2 h and then evaporated. The crude product was recrystallised from methanol/ chloroform to afford **1** as white solid (123.3 mg, 66%). mp 120 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ (ppm) 7.12–6.75 (m, 10H), 3.69–3.63 (m, 37H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ (ppm) 153.33, 150.94, 150.89, 150.84, 150.75, 150.71, 150.68, 128.96, 128.88, 128.81, 128.74, 128.60, 128.57, 128.52, 128.48, 128.40, 127.56, 121.40, 114.54, 114.25, 114.14, 113.58, 56.06, 55.99, 55.95, 55.58, 30.79, 29.79, 29.49, 28.98; ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm) -3.56; MS (MALDI-TOF): *m/z* calcd. for $[M]^+ C_{44}H_{49}O_{13}P$: 816.291; found: 816.202. HR-MS (ESI): *m/z* calcd for $[M + Na]^+ C_{44}H_{49}NaO_{13}P$, 839.2803; found 839.2807.

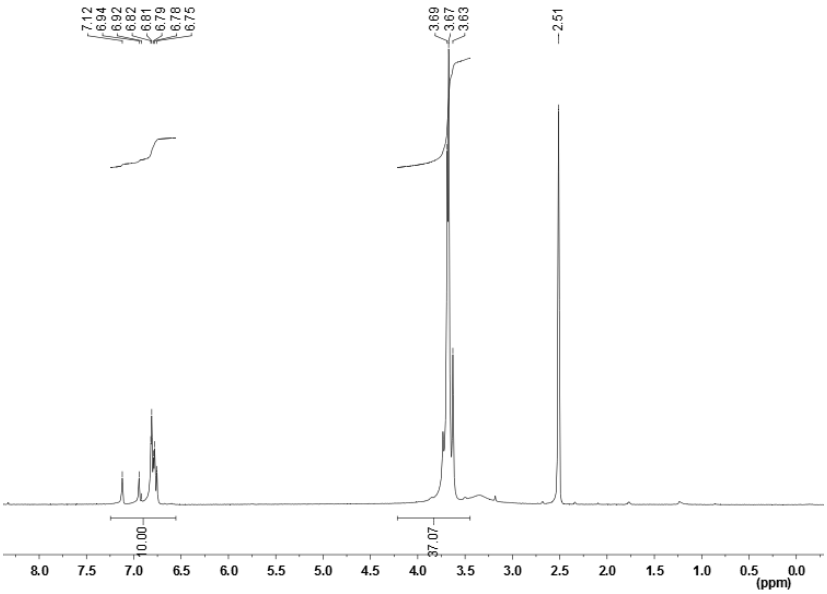

Fig. S4 ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of **1**.

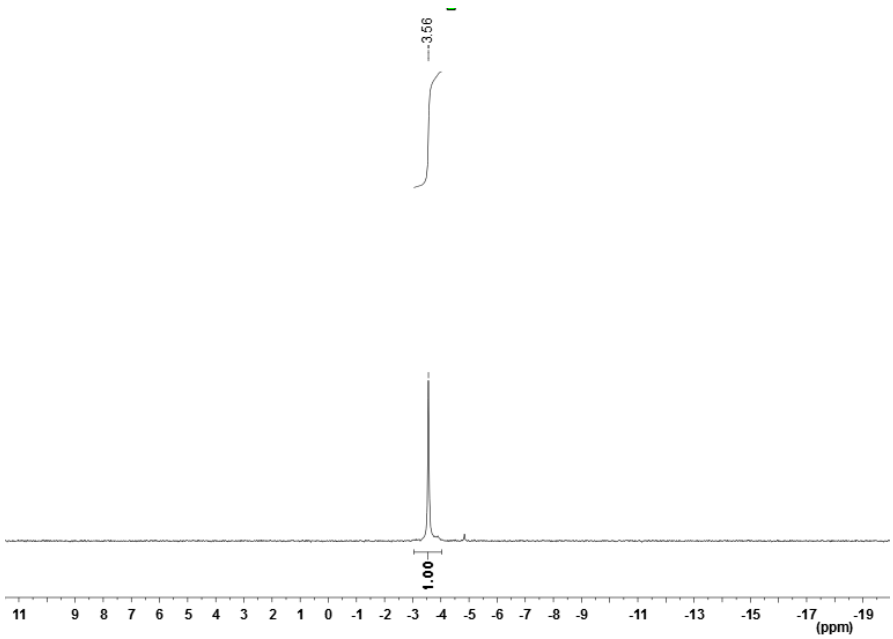

Fig. S5 ^{31}P NMR spectrum (162 MHz, $CDCl_3$, 298 K) of **1**.

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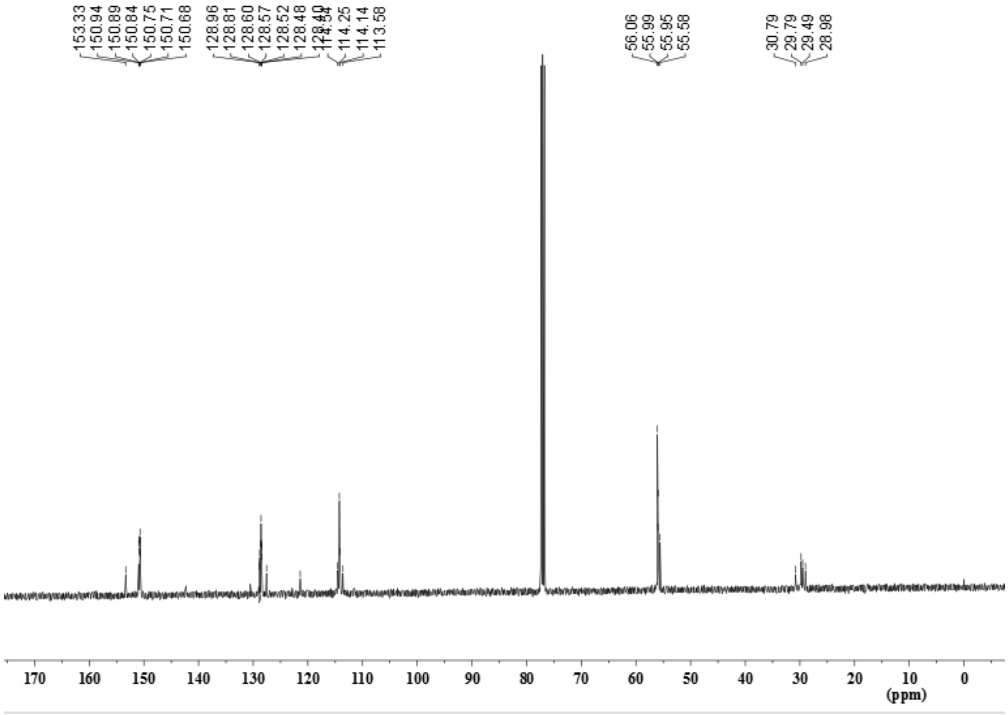


Fig. S6 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **1**.

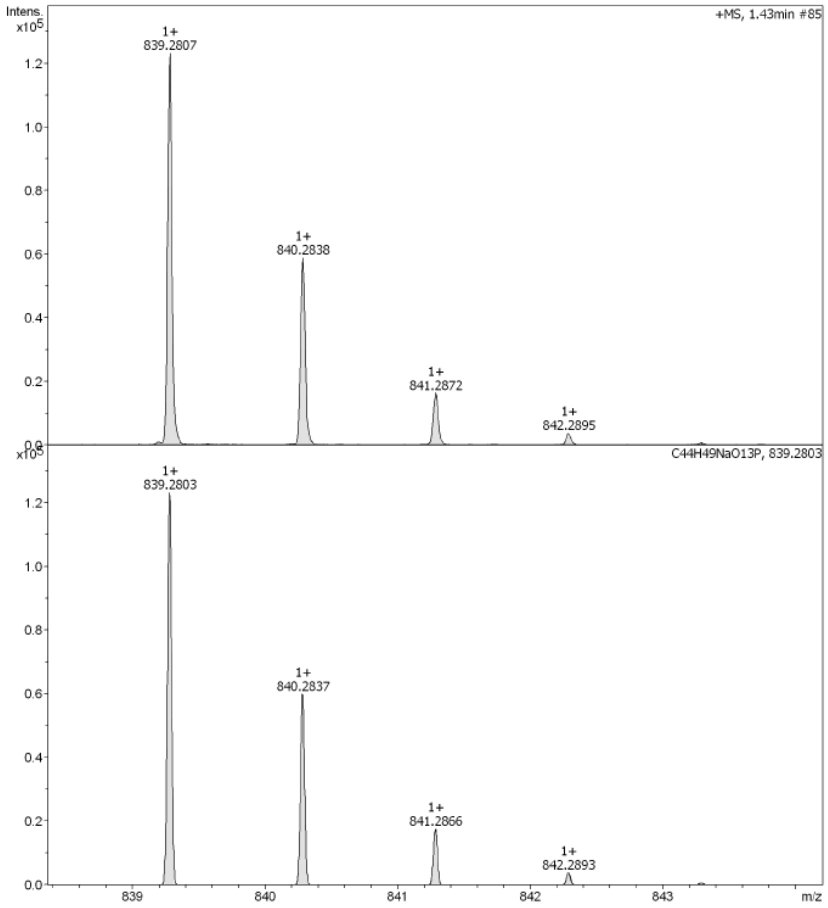
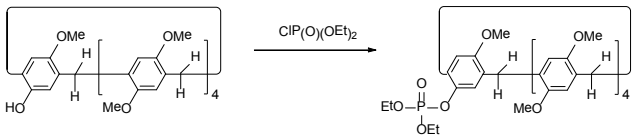


Fig. S7 HR-MS (ESI) of **1**.

4. Optimiztion of reaction condition for the synthesis of the phosphate ester 4

Table S1 Optimiztion of reaction condition for the synthesis of **4**



3 **4**

Entry	Base	Solvent	Time (h)	Temperature (°C)	Yield (%)[b]
1	Et_3N	CH_2Cl_2	12	r.t.	Trace
2	Et_3N	CH_2Cl_2	12	40	Trace
3	Et_3N	$CHCl_3$	12	r.t.	Trace
4	Et_3N	$CHCl_3$	72	62	35
5[c]	NaOH	$CHCl_3$	24	62	49

[a] Reaction conditions: **3** (0.068 mmol), base (0.204 mmol), diethylchlorophosphate (0.408 mmol), N_2, solvent (5 mL). [b] Isolated yield. [c] 10 mol% TBAB was used.

5. ^{1}H NMR spectra of BDO in the absence and presence of 2

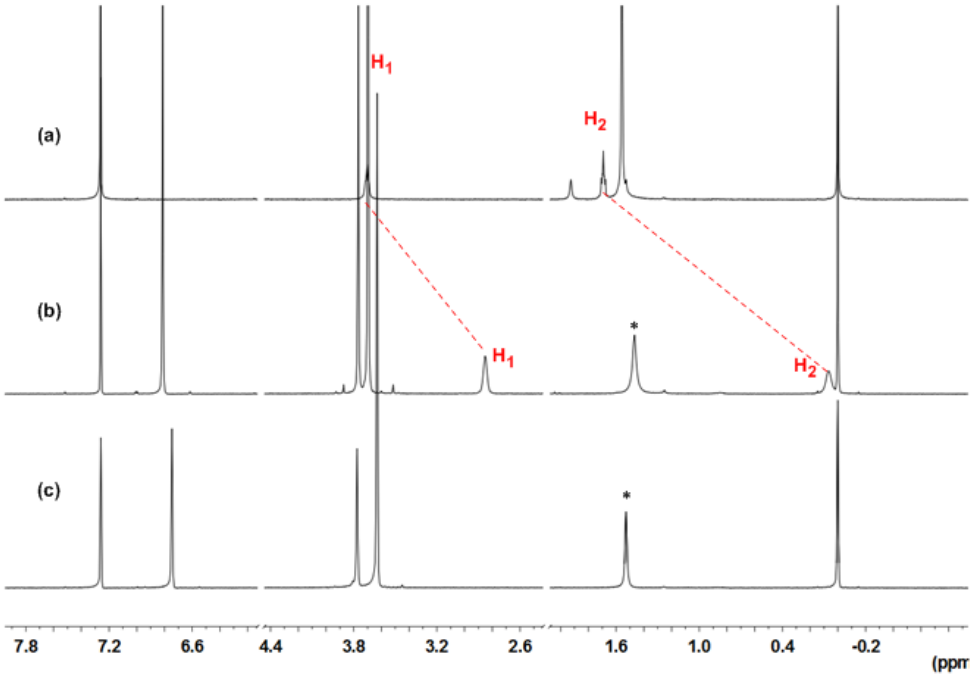


Figure S8 ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of (a) BDO, (b) BDO in the presence of **2**, (c) **2**. [**2**] = [BDO] = 5.6 mM. Asterisk represents water.

6. ^{1}H NMR spectra of BO in the absence and presence of 2

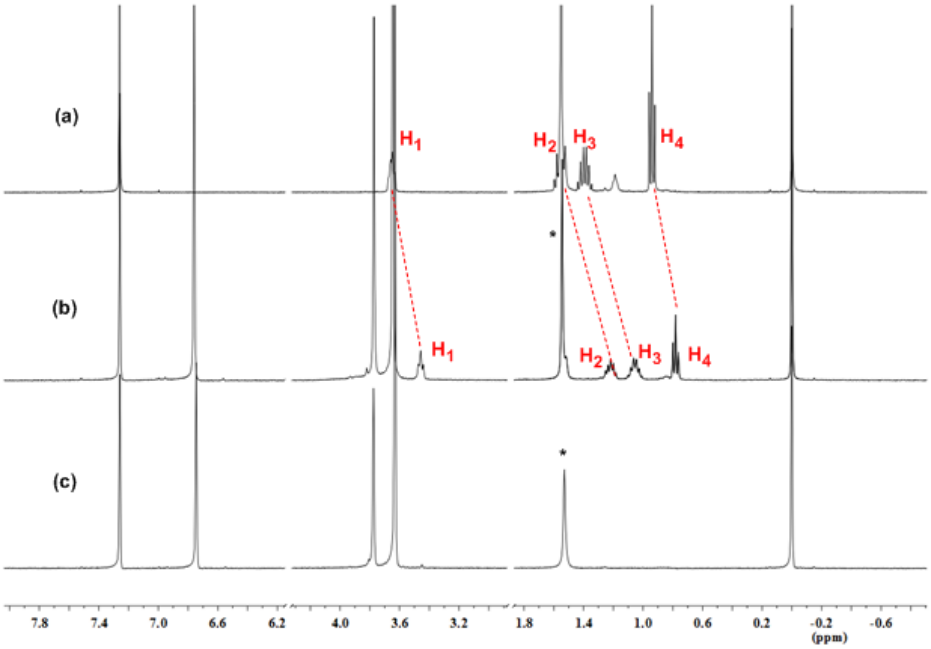


Figure S9 ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of (a) BO, (b) BO in the presence of **2**, (c) **2**. [**2**] = [BO] = 5.0 mM. Asterisk represents water.

7. Determination of association constants

^{1}H NMR titration was done in order to determine the association constant between the host **2** and the guest (BDO and BO). A constant concentration of the guest (5 mM) and varying concentrations of the host in $CDCl_3$ were kept. A nonlinear curve-fitting method was applied to calculate the association constant for complexation between host and the guest, which was based on the equation as follows:[2]

$$\Delta\delta = (\Delta\delta_\infty/[G]_0)\,(0.5[H]_0 + 0.5([G]_0 + 1/Ka) - (0.5([H]_0^2 + (2[H]_0\,(1/Ka - [G]_0)) + (1/Ka + [G]_0)^2)^{0.5}))$$

Where $\Delta\delta$ is the chemical shift change of H_2 of the guest at $[G]_0$, $\Delta\delta_\infty$ is the chemical shift change of H_2 when the guest is completely complexed, $[G]_0$ is the fixed initial concentration of the guest, and $[H]_0$ is the varying concentrations of the host.

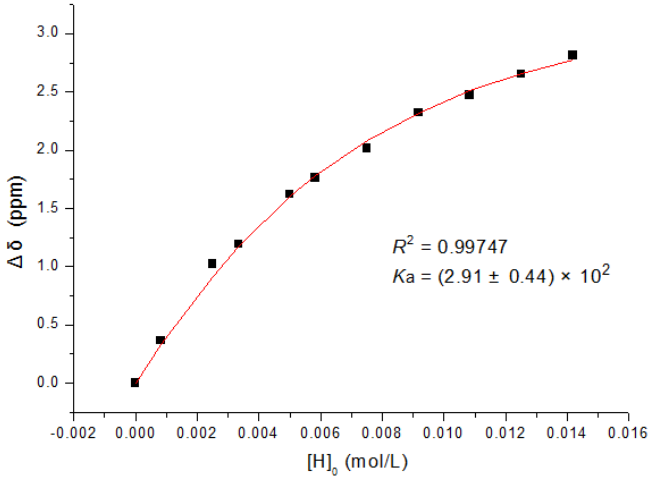


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Fig. S10 The chemical shift changes of H_2 of BDO (5.6 mM) upon the addition of **2** (0–14 mM). The red solid line was obtained from the nonlinear curve-fitting.

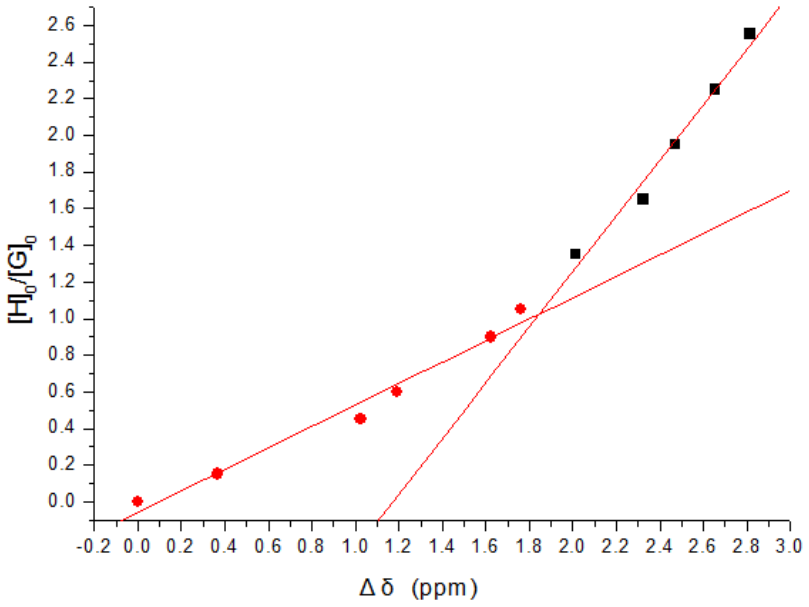

Fig. S11 Mole ratio plot for the complexation between **2** and BDO, indicating a 1:1 stoichiometry.

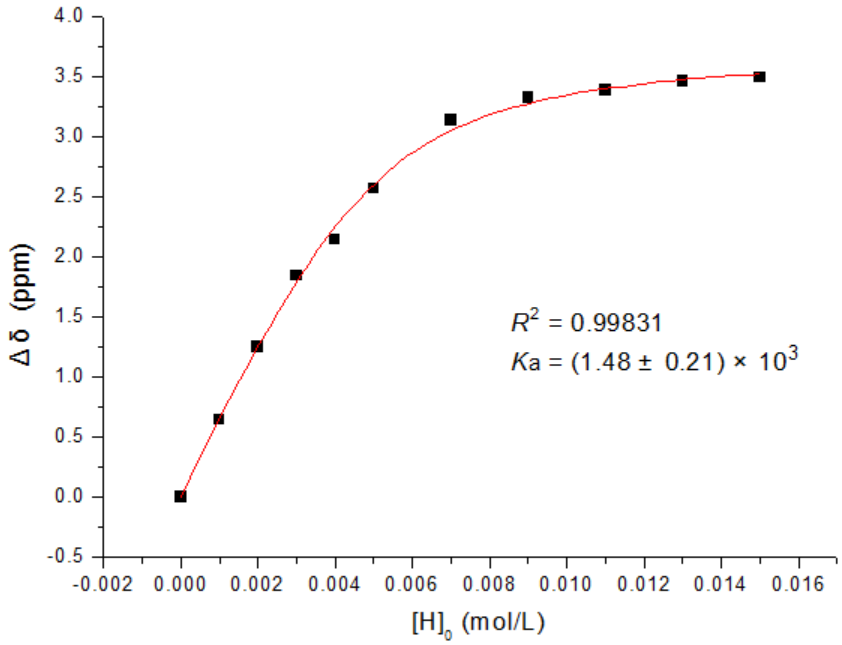

Fig. S12 The chemical shift changes of H_2 of BDO (5.0 mM) upon the addition of **1** (0–14 mM). The red solid line was obtained from the nonlinear curve-fitting.

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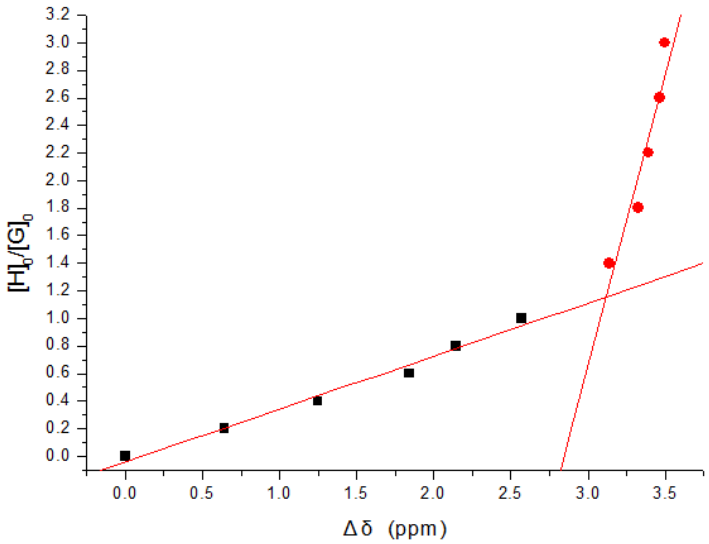

Fig. S13 Mole ratio plot for the complexation between **1** and BDO, indicating a 1:1 stoichiometry.

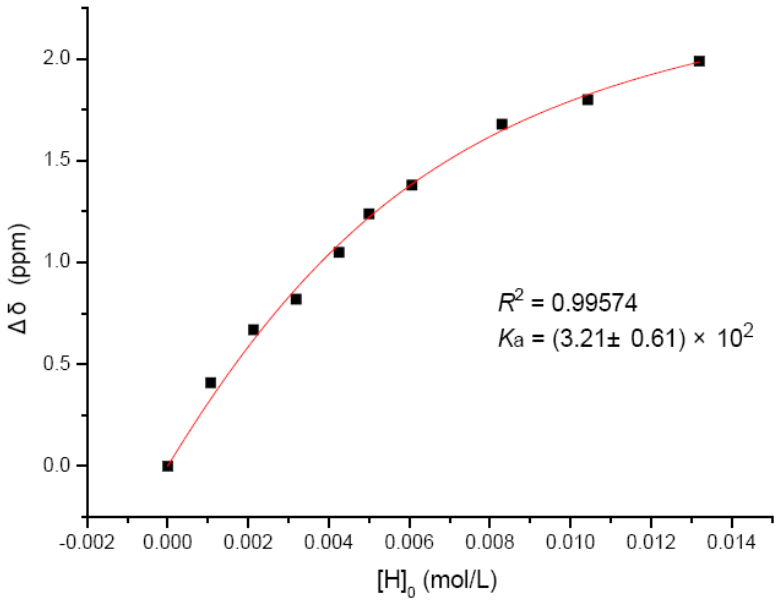

Fig. S14 The chemical shift changes of H_1 of BO (5.0 mM) upon the addition of **1** (0–14 mM). The red solid line was obtained from the nonlinear curve-fitting.

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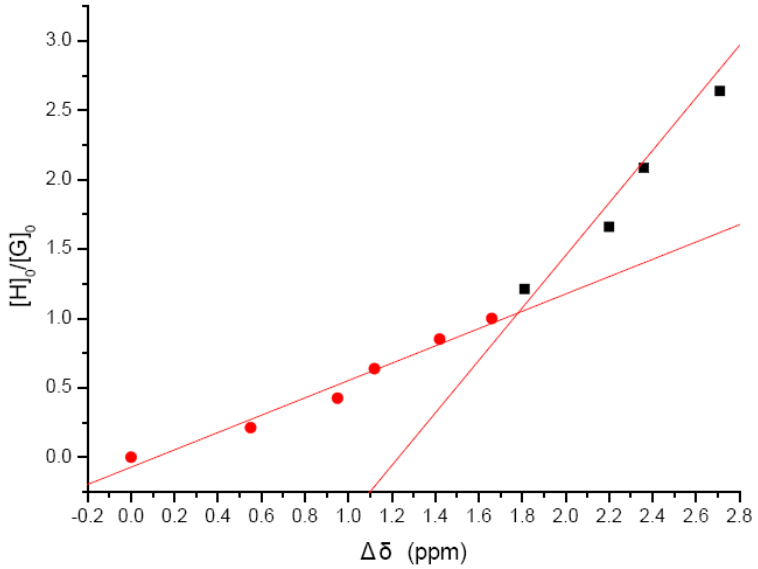

Fig. S15 Mole ratio plot for the complexation between **1** and **BO**, indicating a 1:1 stoichiometry.

8. ^{1}H NMR spectra of the host 1 in the absence and presence of 1,4-butanediamine

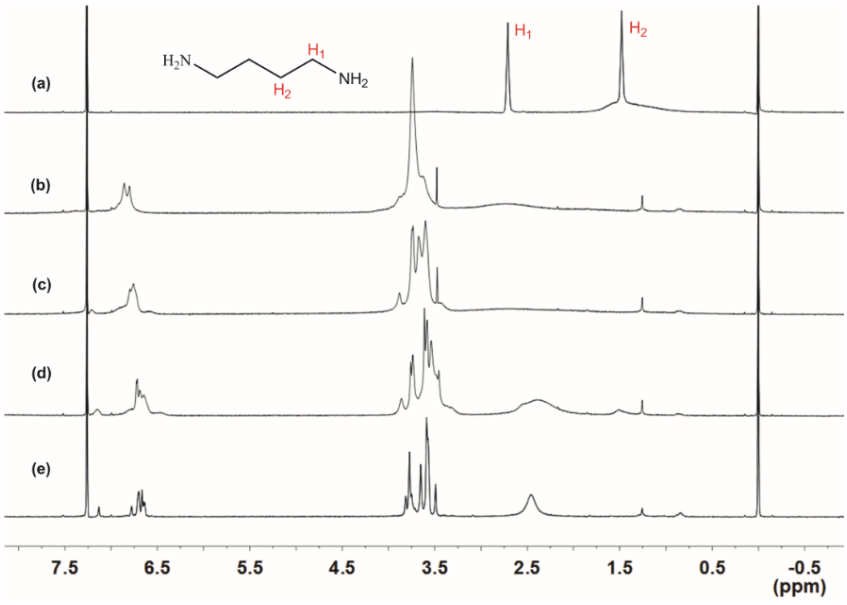

Fig. S16 ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of **1** (5.0 mM) in the presence of increasing amounts of 1,4-butanediamine from (b) to (e): 1.5, 1.0, 0.5 and 0.0 equivalents. For comparison, the spectrum of 1,4-butanediamine (5.0 mM) is shown at the top.

References:

S1 a) D. R. Cao, Y. H. Kou, J. Q. Liang, Z. Z. Chen, L. Y. Wang and H. Meier, *Angew. Chem. Int. Ed.*, 2009, **48**, 9721-9723; b) L. Liu, D. Cao, Y. Jin, H. Tao, Y. Kou and H. Meier, *Org. Biomol. Chem.*, 2011, **9**, 7007-7010.

S2 Y. Ma, X. Chi, X. Yan, J. Liu, Y. Yao, W. Chen, F. Huang and J. L. Hou, *Org. Lett.*, 2012, **14**, 1532-1535.