

## Supporting Information

### A Reversible Reaction Inside a Self-Assembled Capsule

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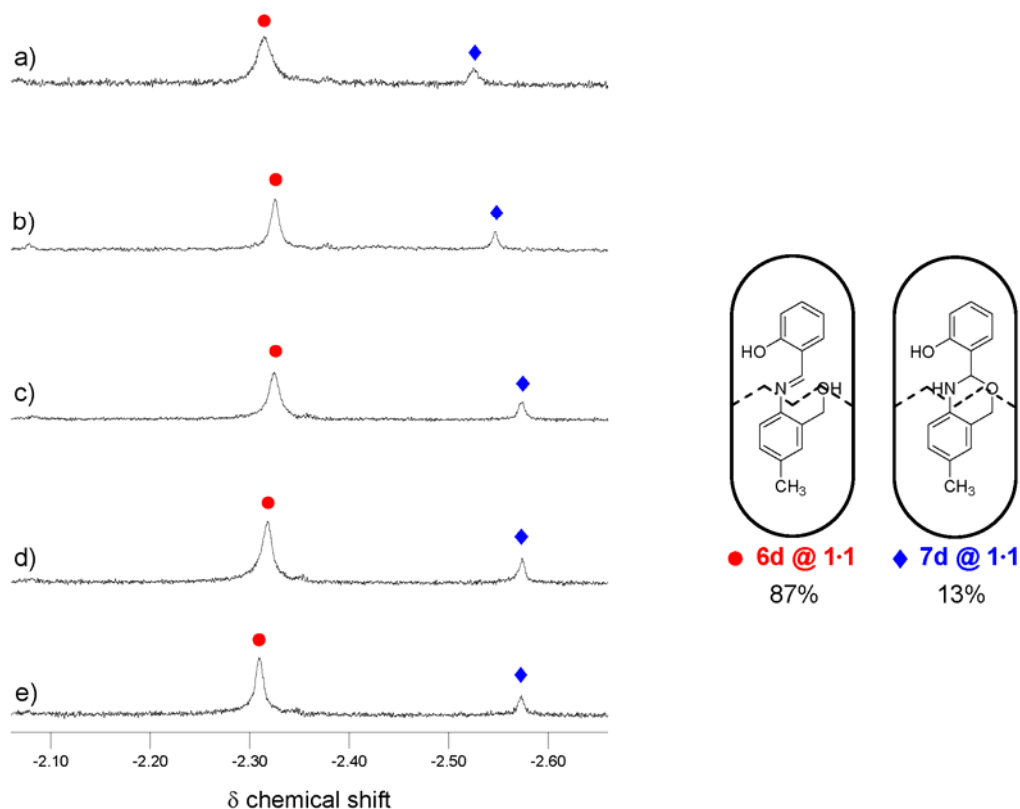
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**(1) General** NMR spectra were recorded on a Bruker DRX-600 spectrometer. Proton ( $^1\text{H}$ ) chemical shifts, reported in parts per million (ppm), were indirectly referenced to external tetramethylsilane employing resonances due to trace protiated-solvent as an internal references. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet. Deuterated NMR solvents were obtained from Cambridge Isotope Laboratories, Inc., and used without further purification. All starting materials for preparing guests are purchased from Aldrich Chemical Company and were used without further purification.

**(2) The temperature dependence of the encapsulated equilibrium between 6d and 7d.**

The temperature dependence of the encapsulated equilibrium showed the equilibrium constant remained unchanged over nearly 100 °C. The upfield portions of  $^1\text{H}$  NMR spectra are shown in Figure 1S.

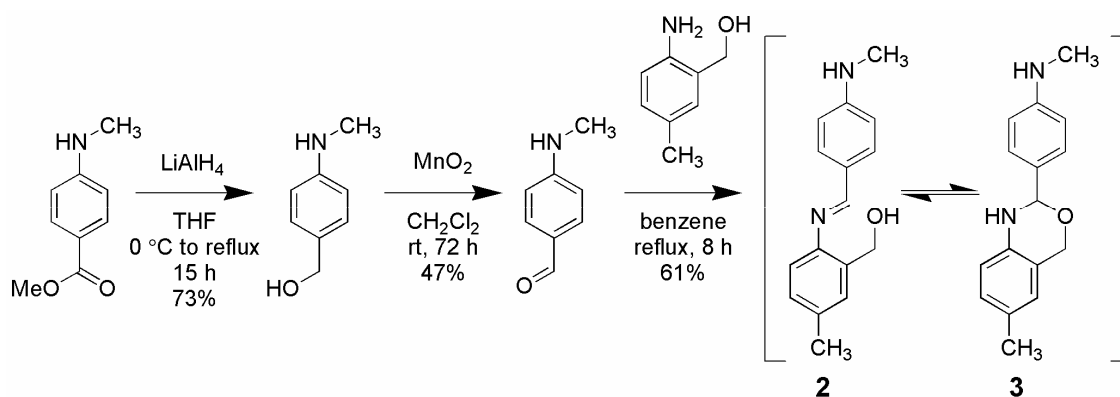


**Figure 1S.** Upfield portions of  $^1\text{H}$  NMR spectra (600 MHz, mesitylene- $\text{d}_{12}$ ) of **6d@1.1** and **7d@1.1** at various temperatures; a) 340 K; b) 320 K; c) 273 K; d) 263 K; e) 253 K. These showed the equilibrium constant ( $K = \mathbf{6d}/\mathbf{7d} = 6.7$ ) remained unchanged over nearly 100 °C.

**(3) Complete assignments of NMR spectra and  $\Delta\delta$  between free and encapsulated species for 2/3 and 4/5 isomerizations.**

**-1) Preparation of 2/3 tautomers.**

**Scheme 1S.** Synthesis of **2** and **3**



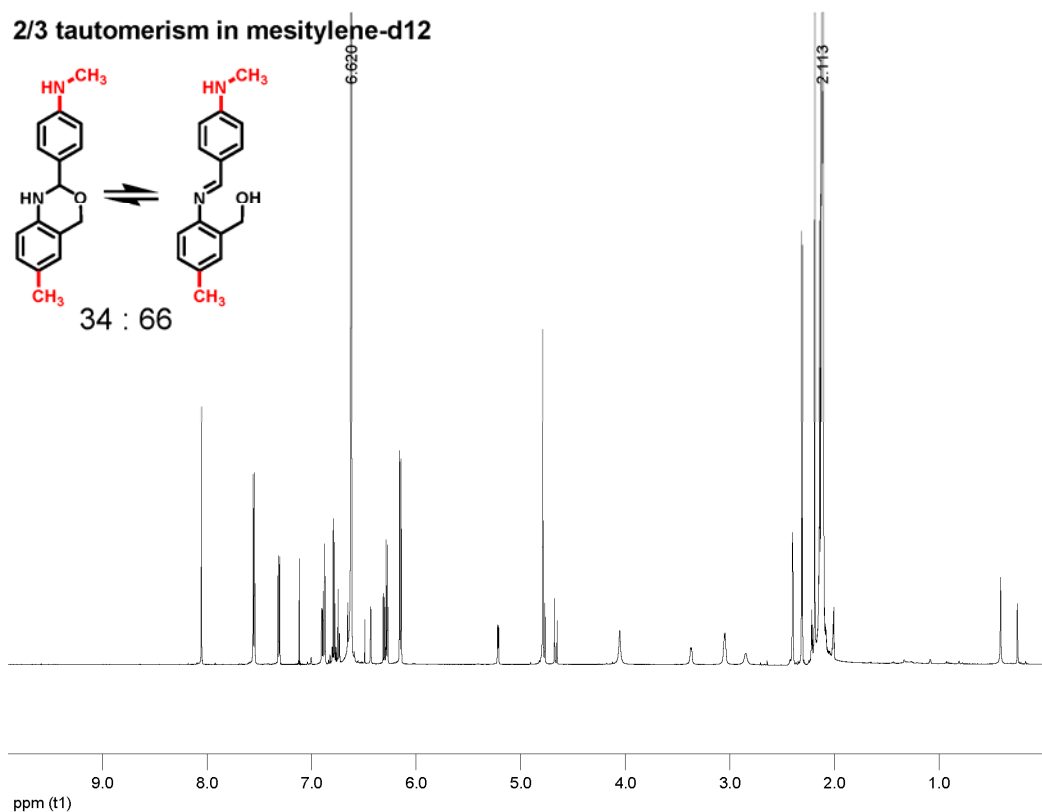
Commercially available methyl 4-(methylamino)benzoate (3.00 g, 18.6 mmol) was dissolved in THF (100 mL) and cooled under nitrogen to 0 °C, and slowly LiAlH<sub>4</sub> (1.41 g, 37.2 mmol) was added. After reflux for 15 h, the reaction mixture was quenched by the sequential slow addition of 3 mL of water, 3 mL of 10% aqueous NaOH, and 3 mL of water. The reaction was stirred for 0.5 h, and filtered. The solvent was removed *in vacuo*, and the crude products were taken up in CH<sub>2</sub>Cl<sub>2</sub> and dried over MgSO<sub>4</sub>. The drying agent was removed by filtration, and the filtrate was concentrated under reduced pressure. Purification of the residue by column chromatography (SiO<sub>2</sub>, 1:1 hexane-ethyl acetate eluent) afforded 4-(methylamino)phenylmethanol (1.86 g, 73%) as a pale yellow solid material. The data of NMR and MS were identical to those previously reported in the literature<sup>1</sup>.

To a solution of (4-(methylamino)phenyl)methanol (1.00 g, 7.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added MnO<sub>2</sub> (2.60 g, 30 mmol). The mixture was stirred at room temperature for 24 h, and then more MnO<sub>2</sub> (2.6 g, 30 mmol) was added. After additional stirring for 48 h, the mixture was filtered through celite, and concentrated *in vacuo*. The residue was purified by column chromatography (SiO<sub>2</sub>, 2:3 ethyl acetate-hexane eluent) to give 4-(methylamino)benzaldehyde (463 mg, 47%) as a red oil which crystallized after one week 4 °C. The data of NMR and MS were identical to those previously reported in the literature<sup>2</sup>.

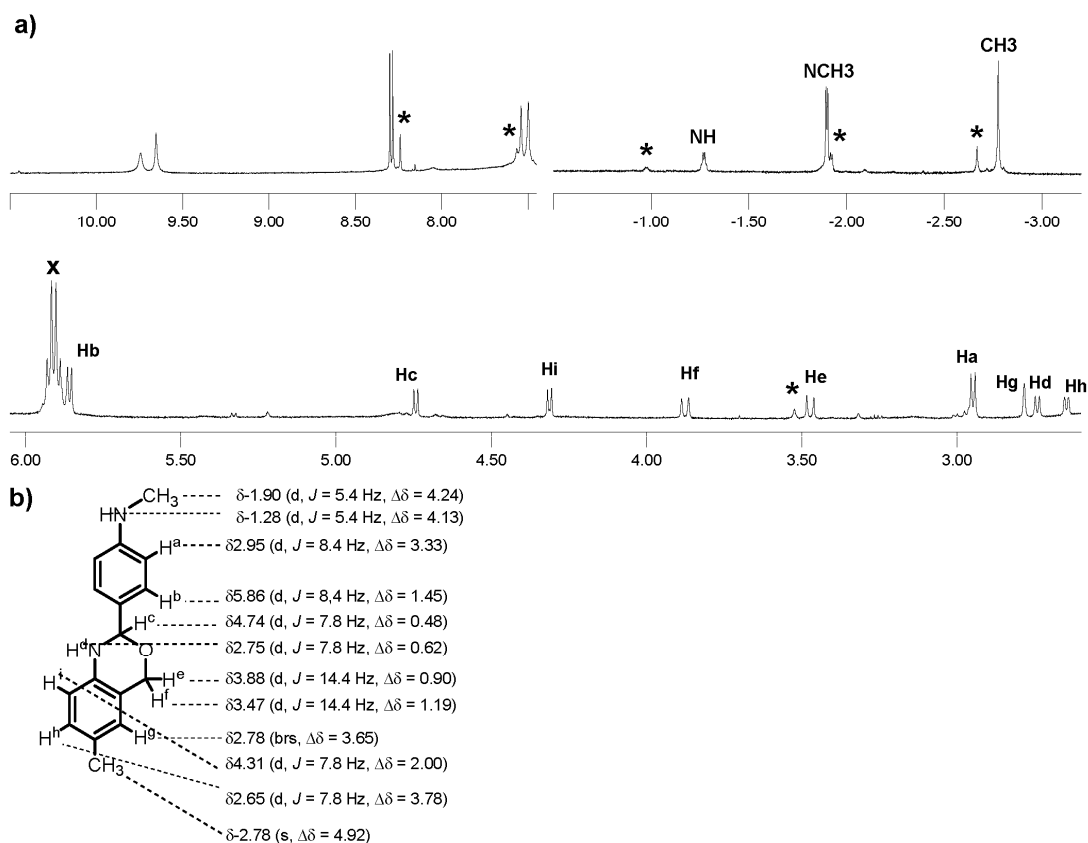
The reaction between 4-(methylamino)benzaldehyde (463 mg, 3.4 mmol) and (5-methyl-2-(methylamino)phenyl)methanol (559 mg, 4.1 mmol) in refluxing benzene (7 mL) with Dean-Stark apparatus and the following recrystallization produced desired

compounds in 61% yield (532 mg) as pale yellow crystals.

**2** and **3**: The tautomerism between **2** and **3** in mesitylene-*d*<sub>12</sub> plateau with 34:66 ratio. The <sup>1</sup>H NMR spectrum is shown below. <sup>1</sup>H NMR (600 MHz, 300 K, mesitylene-*d*<sub>12</sub>) δ (for **3**) 7.31 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.43 (brs, 1H), 6.31 (d, *J* = 8.4 Hz, 1H), 6.28 (d, *J* = 8.4 Hz, 2H), 5.22 (d, *J* = 6.0 Hz, 1H), 4.78 (d, *J* = 14.4 Hz, 1H), 4.66 (d, *J* = 14.4 Hz, 1H), 3.37 (d, *J* = 6.0 Hz, 1H), 2.85 (brs, 1H), 2.34 (s, 3H), 2.14 (s, 3H), δ (for **2**) 8.05 (s, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.88 (s, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.15 (d, *J* = 8.4 Hz, 2H), 4.79 (s, 2H), 4.05 (brs, 1H), 3.05 (brs, 1H), 2.31 (s, 3H), 2.19 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ (for **3**) 149.9, 139.5, 128.9, 127.9, 127.5, 125.2, 124.9, 122.3, 112.1, 85.5, 67.7, 30.6, 20.6, δ (for **2**) 158.4, 152.1, 147.6, 135.2, 134.7, 130.7, 128.8, 128.6, 127.9, 117.1, 111.8, 64.7, 30.1, 20.9. HRMS (ESI, MH<sup>+</sup>): Calcd. For C<sub>16</sub>H<sub>19</sub>N<sub>2</sub>O: 255.1492. Found: 255.1503.



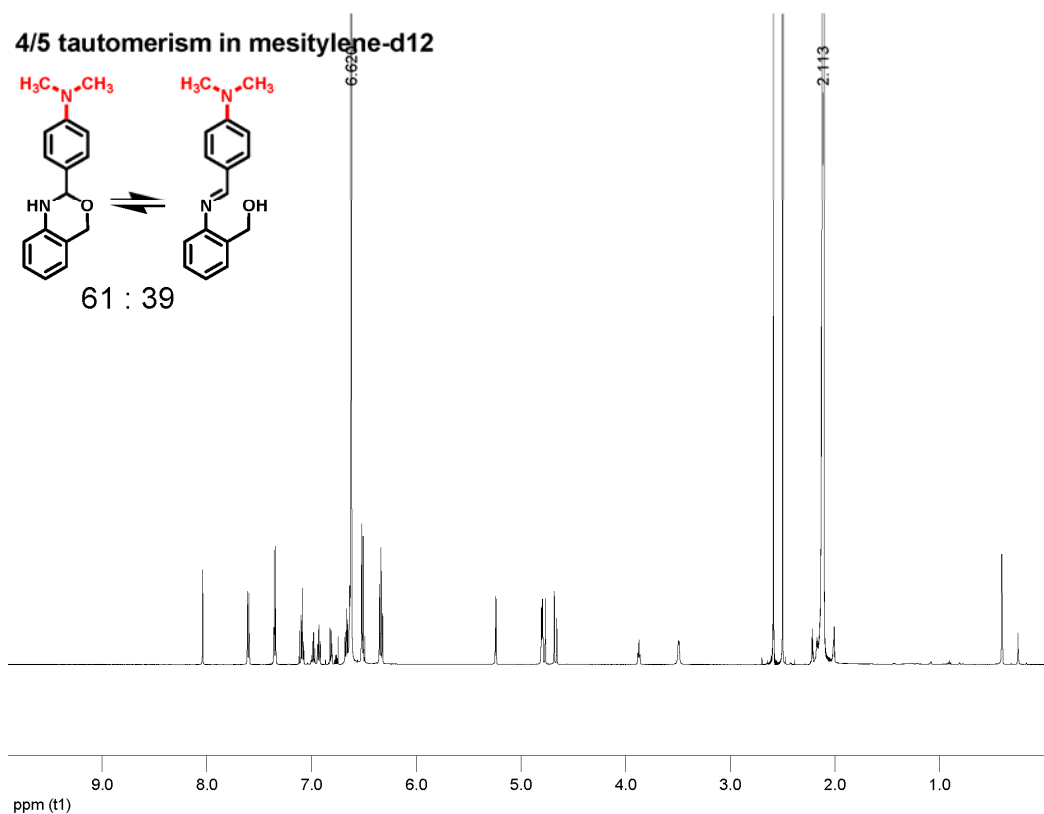
### 3-2) Assignments and $\Delta\delta$ between free and encapsulated species for 2/3 isomerization



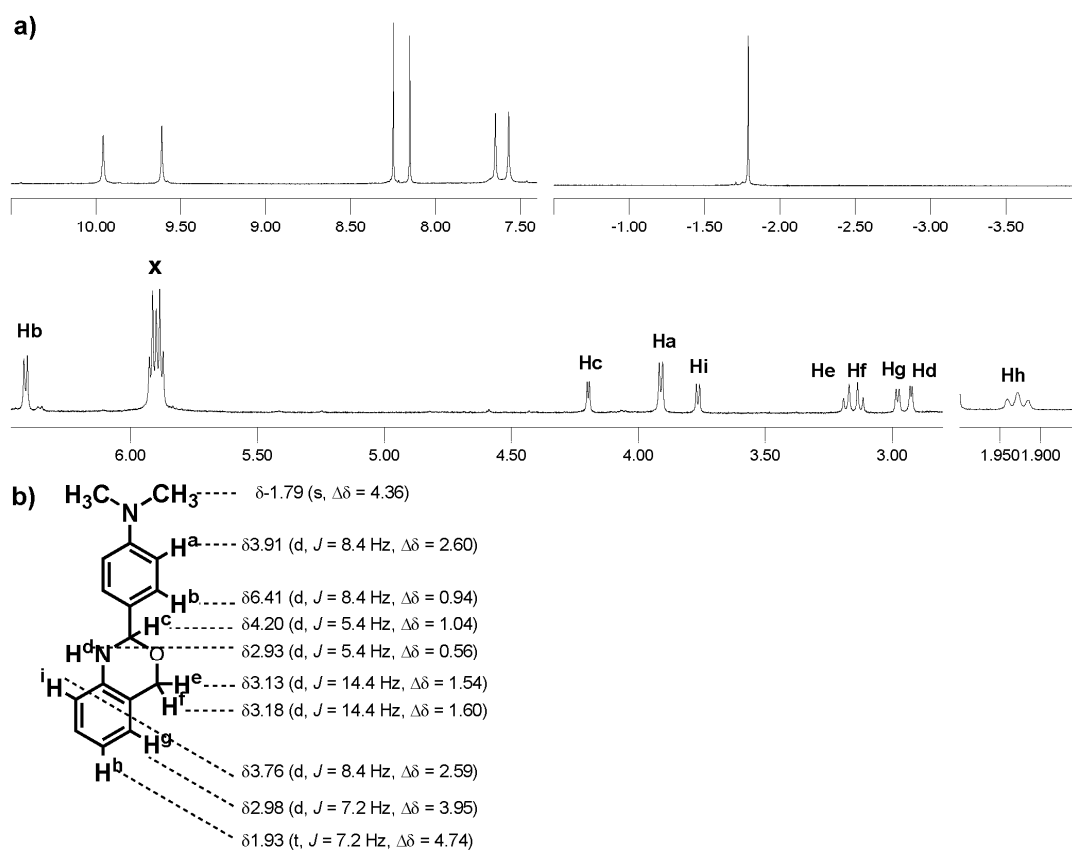
**Figure 2S.** Encapsulation experiments of **2** and **3**. (a) Downfield, mid-field, and upfield portions of  $^1\text{H}$  NMR spectra (600 MHz, 300 K, mesitylene- $d_{12}$ ) of **2@1·1** and **3@1·1**. The peaks labeled with asterisks were estimated to be a detectable amount of **2@1·1**. The peaks in downfield portions are corresponding to those of asymmetrically filled capsule,  $\delta$  (for **3@1·1**) 9.76 (s, 4H, NH), 9.74 (s, 4H, NH), 8.30 (s, 4H, arom), 8.28 (s, 4H, arom), 7.54 (s, 4H, arom), 7.50 (s, 4H, arom). Other signals of **3@1·1** in portions of mid-field and upfield are assigned as shown in (b) with  $\Delta\delta$  values between free and encapsulated species. The peaks labeled x are CH-methines of **1·1**.

### 3-3) Preparation of 4/5 tautomers.

The **4/5** tautomers were prepared according to literature procedure.<sup>3</sup> The **4/5** tautomerism in mesitylene-*d*<sub>12</sub> plateau with 61:39 ratio. The <sup>1</sup>H NMR spectrum is shown below. <sup>1</sup>H NMR (600 MHz, 300 K, mesitylene-*d*<sub>12</sub>) δ (for **5**) 7.35 (d, *J* = 8.4 Hz, 2H), 7.09 (m, 1H), 6.93 (m, 1H), 6.67 (m, 1H), 6.51 (d, *J* = 8.4 Hz, 2H), 6.35 (d, *J* = 8.4 Hz, 1H), 5.24 (d, *J* = 5.4 Hz, 1H), 4.78 (d, *J* = 14.4 Hz, 1H), 4.67 (d, *J* = 14.4 Hz, 1H), 3.49 (d, *J* = 5.4 Hz, 1H), 2.57 (s, 6H), δ (for **4**) 8.04 (s, 1H), 7.61 (d, *J* = 9.0 Hz, 2H), 7.07 (m, 1H), 6.98 (m, 1H), 6.81 (m, 1H), 6.50 (d, *J* = 8.4 Hz, 1H), 6.33 (d, *J* = 9.0 Hz, 2H), 4.80 (d, *J* = 4.8 Hz, 2H), 3.87 (t, *J* = 4.8 Hz, 1H), 2.50 (s, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ (for **5**) 151.0, 142.0, 127.4, 127.2, 126.9, 124.8, 121.8, 119.1, 116.4, 112.2, 85.2, 67.7, 40.4 δ (for **4**) 159.2, 152.7, 150.3, 134.9, 130.6, 128.3, 127.8, 125.3, 123.7, 117.3, 111.5, 64.5, 40.0. HRMS (ESI, MH<sup>+</sup>): Calcd. For C<sub>16</sub>H<sub>19</sub>N<sub>2</sub>O: 255.1492. Found: 255.1498.



### 3-4) Assignments and $\Delta\delta$ between free and encapsulated species for 4/5 isomerization



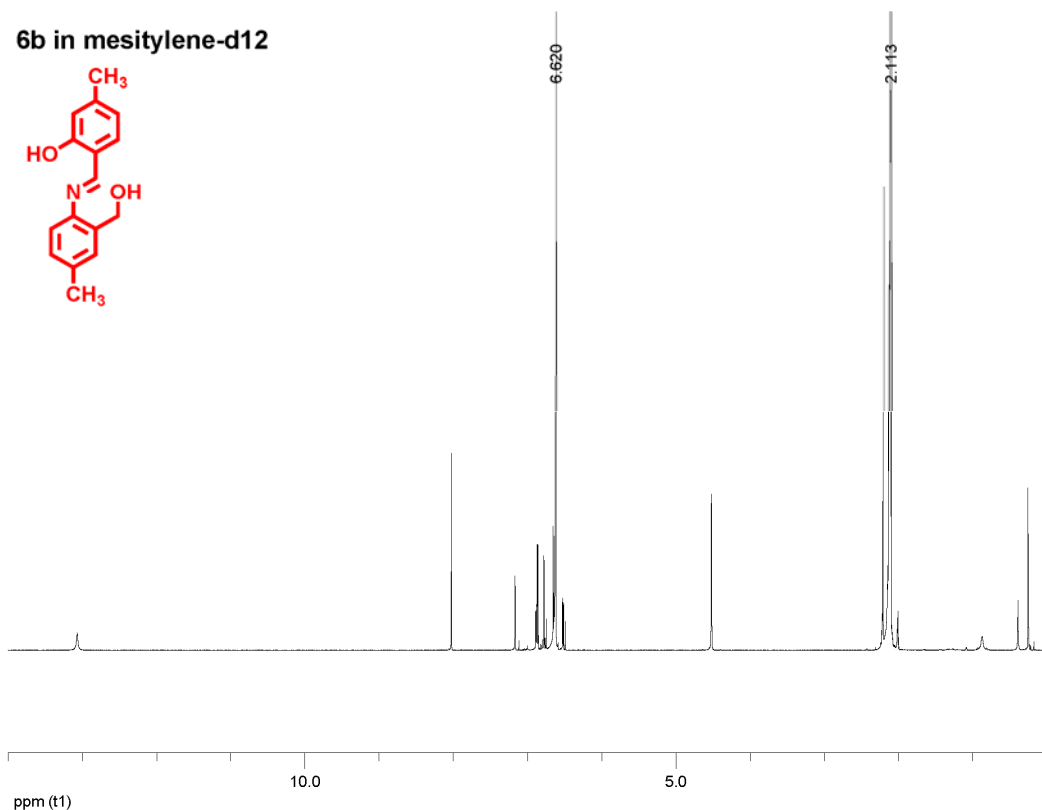
**Figure 3S.** Encapsulation experiments of **4** and **5**. (a) Downfield, mid-field, and upfield portions of  $^1\text{H}$  NMR spectra (600 MHz, 300 K, mesitylene- $d_{12}$ ) of **5@1.1**. A detectable amount of **4@1.1** was not formed. The peaks in downfield portions are corresponding to those of asymmetrically filled capsule,  $\delta$  9.96 (s, 4H, NH), 9.61 (s, 4H, NH), 8.24 (s, 4H, arom), 8.15 (s, 4H, arom), 7.65 (s, 4H, arom), 7.57 (s, 4H, arom). Other signals of **5@1.1** in portions of mid-field and upfield are assigned as shown in (b) with  $\Delta\delta$  values between free and encapsulated species. However, the peak of  $\text{H}_i$  overlapped with peaks of solvent or **1.1**. The peaks labeled x are CH-methines of **1.1**.

#### (4) Encapsulation experiments of 6b, 6c, 6d and 6e.

##### -1) Preparation of 6b, 6c, 6d and 6e.

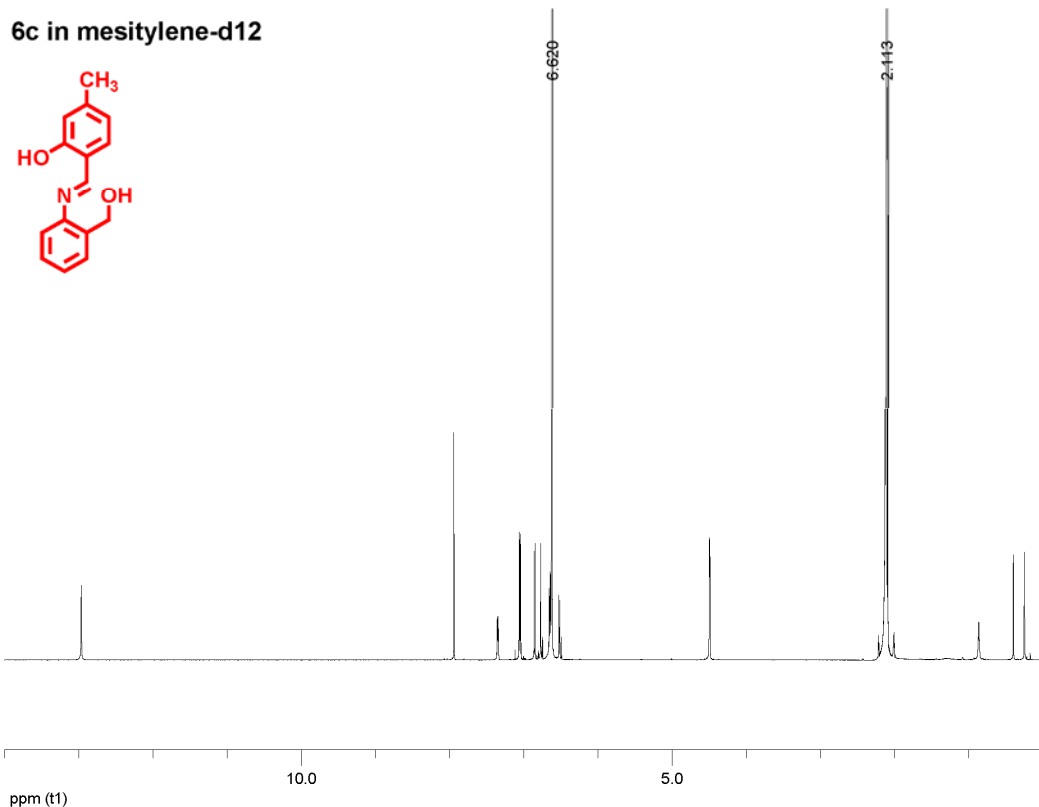
Schiff's bases **6b**, **6c**, **6d**<sup>4</sup> and **6e**<sup>5</sup> were prepared from corresponding aldehydes and anilines through conventional condensation methods. The physical data of them are shown below, as well as <sup>1</sup>H NMR spectra in mesitylene-*d*<sub>12</sub>.

**6b**: <sup>1</sup>H NMR (600 MHz, 300 K, mesitylene-*d*<sub>12</sub>) δ 13.1 (s, 1H), 8.02 (s, 1H), 7.20 (s, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.78 (s, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 6.52 (d, *J* = 8.4 Hz, 1H), 4.52 (d, *J* = 5.4 Hz, 2H), 2.20 (s, 3H), 2.10 (s, 3H), 0.87 (brs, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 161.9, 161.0, 144.4, 144.1, 136.8, 134.3, 132.0, 129.2, 129.0, 120.3, 117.6, 117.5, 117.0, 61.9, 21.9, 21.0. HRMS (ESI, MNa<sup>+</sup>): Calcd. For C<sub>16</sub>H<sub>17</sub>NO<sub>2</sub>Na: 278.1151. Found: 278.1145.



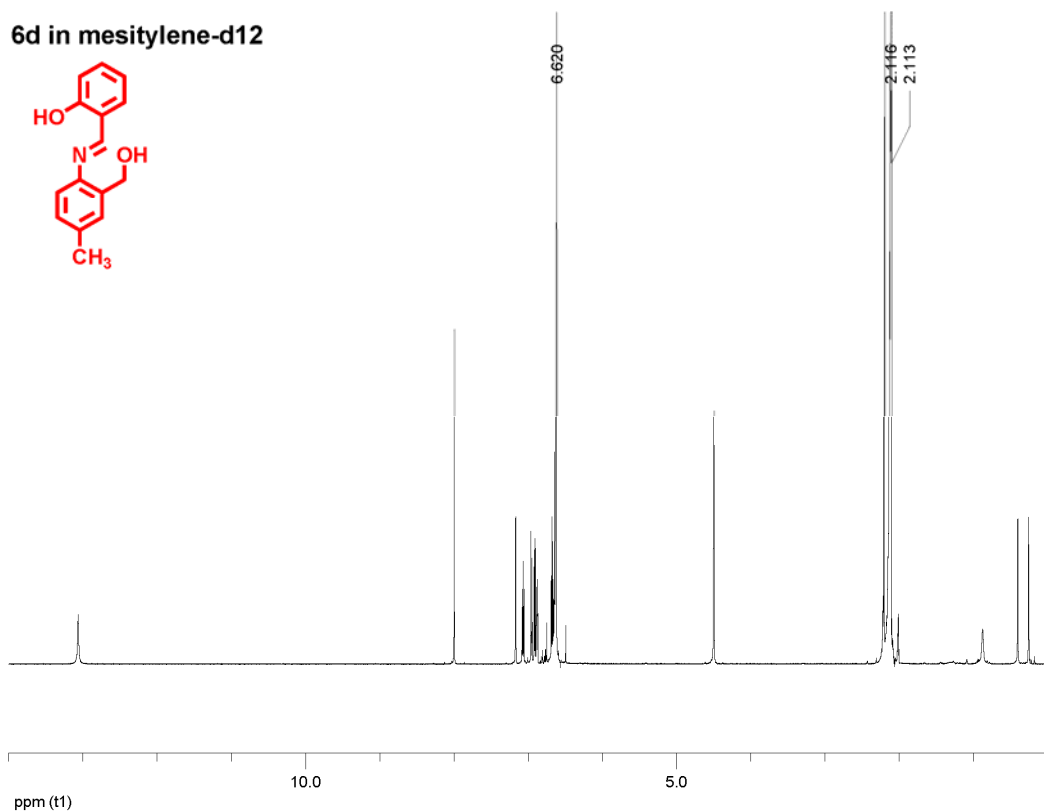


**6c:**  $^1\text{H}$  NMR (600 MHz, 300 K, mesitylene- $d_{12}$ )  $\delta$  12.9 (s, 1H), 7.94 (s, 1H), 7.35 (m, 1H), 7.06-7.04 (m, 2H), 6.86 (d,  $J = 7.8$  Hz, 1H), 6.77 (s, 1H), 6.65 (m, 1H), 6.51 (d,  $J = 7.8$  Hz, 1H), 4.49 (d,  $J = 4.2$  Hz, 2H), 2.09 (s, 3H), 0.86 (brs, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  162.6, 161.0, 146.5, 144.5, 134.4, 132.1, 128.6, 128.1, 126.7, 120.3, 117.8, 117.5, 116.9, 61.6, 21.8. HRMS (ESI,  $\text{MH}^+$ ): Calcd. For  $\text{C}_{15}\text{H}_{16}\text{NO}_2$ : 242.1175. Found: 242.1176.

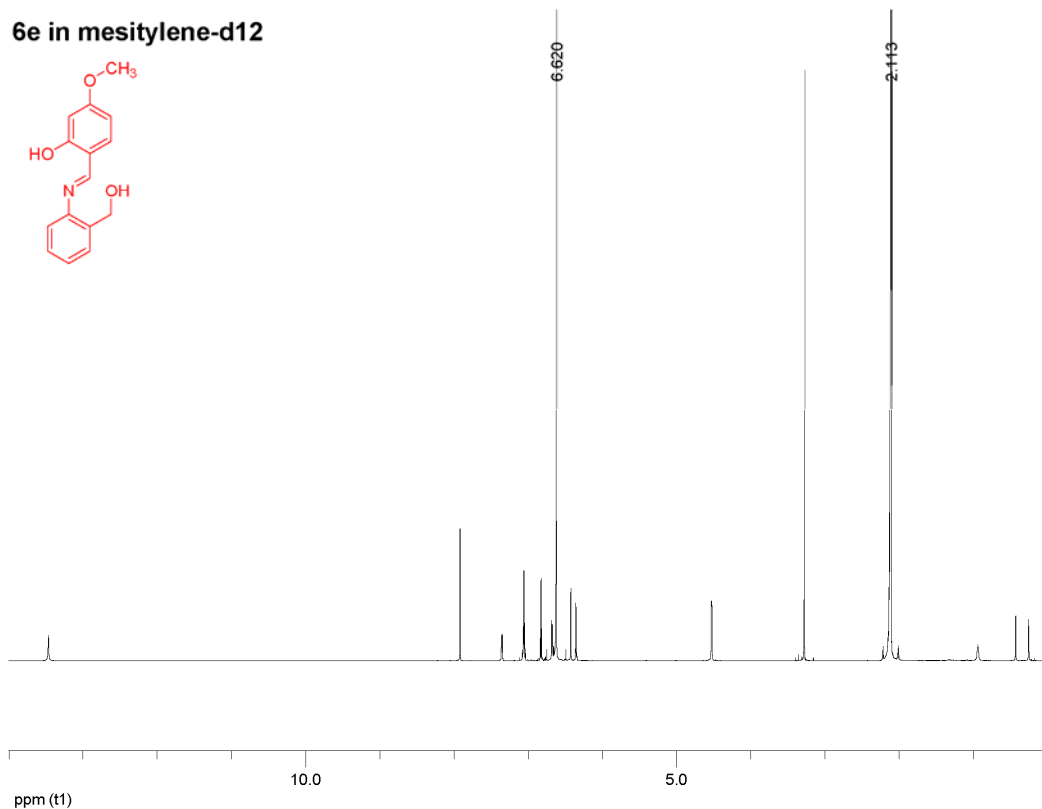


**6d:**  $^1\text{H}$  NMR (600 MHz, 300 K, mesitylene- $d_{12}$ )  $\delta$  13.1 (s, 1H), 8.00 (s, 1H), 7.17 (s, 1H), 7.07 (m, 1H), 6.96 (m, 1H), 6.91 (m, 1H), 6.88 (m, 1H), 6.68 (m, 1H), 6.64 (m, 1H), 4.50 (s, 2H), 2.20 (s, 3H), 0.87 (brs, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  162.1, 161.0, 143.9, 137.1, 134.4, 133.1, 132.2, 129.2, 129.0, 119.2, 119.0, 117.5, 117.2, 61.8, 21.0. HRMS (ESI,  $\text{MH}^+$ ): Calcd. For  $\text{C}_{15}\text{H}_{16}\text{NO}_2$ : 242.1175. Found: 242.1182.

**6d in mesitylene- $d_{12}$**

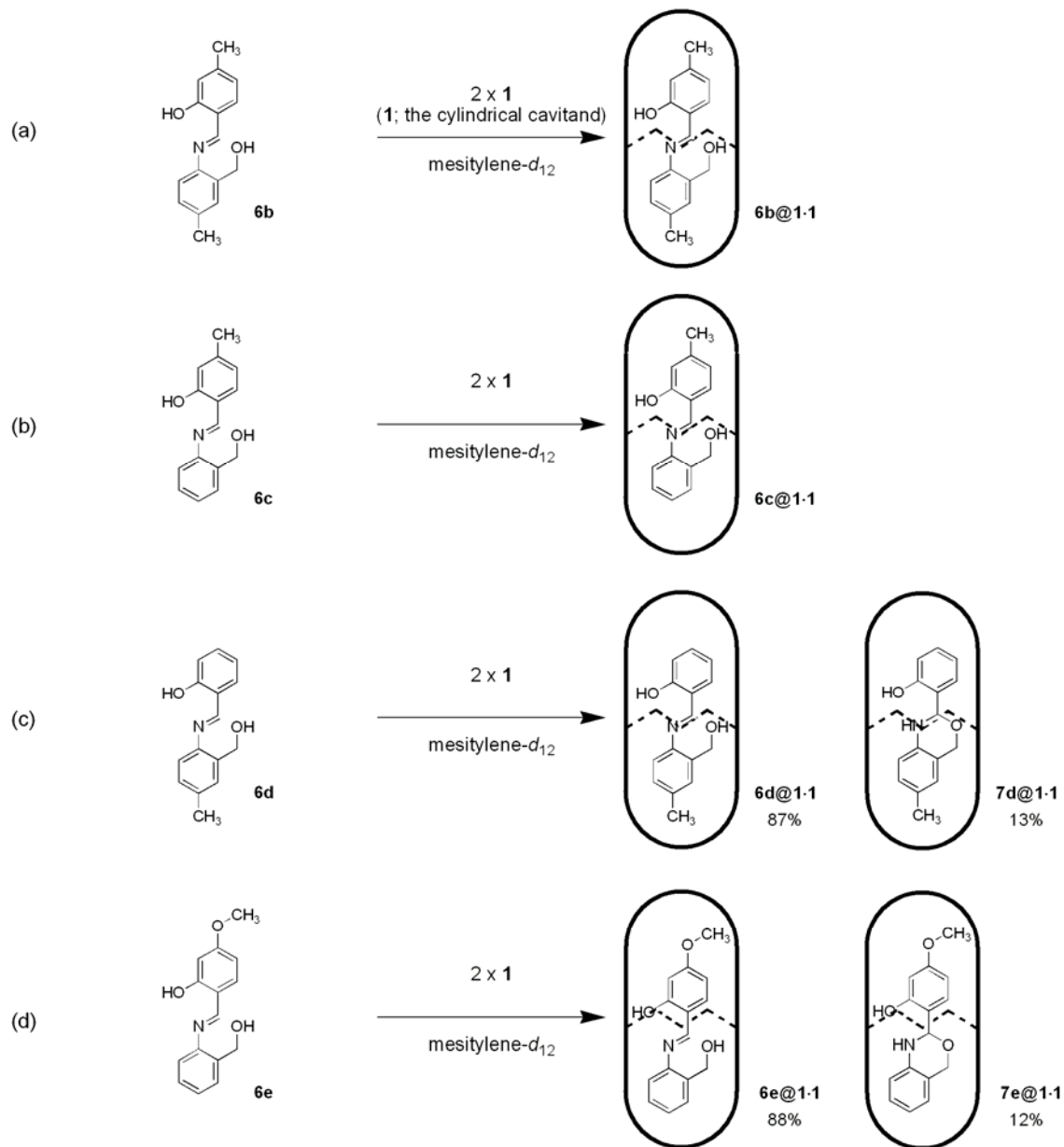


**6e:**  $^1\text{H}$  NMR (600 MHz, 300 K, mesitylene- $d_{12}$ )  $\delta$  13.5 (s, 1H), 7.92 (s, 1H), 7.35 (m, 1H), 7.07-7.05 (m, 2H), 6.82 (d,  $J = 8.4$  Hz, 1H), 6.68 (m, 1H), 6.42 (d,  $J = 3.0$  Hz, 1H), 6.35 (dd,  $J = 8.4$  Hz, 3.0 Hz, 1H), 4.53 (d,  $J = 3.6$  Hz, 2H), 3.28 (s, 3H), 0.94 (t,  $J = 3.6$  Hz, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  164.4, 164.2, 161.4, 145.9, 134.2, 133.6, 128.6, 128.2, 126.4, 117.7, 113.0, 107.2, 101.0, 61.6, 55.3. HRMS (ESI,  $\text{MH}^+$ ): Calcd. For  $\text{C}_{15}\text{H}_{16}\text{NO}_3$ : 258.1125. Found: 258.1126.

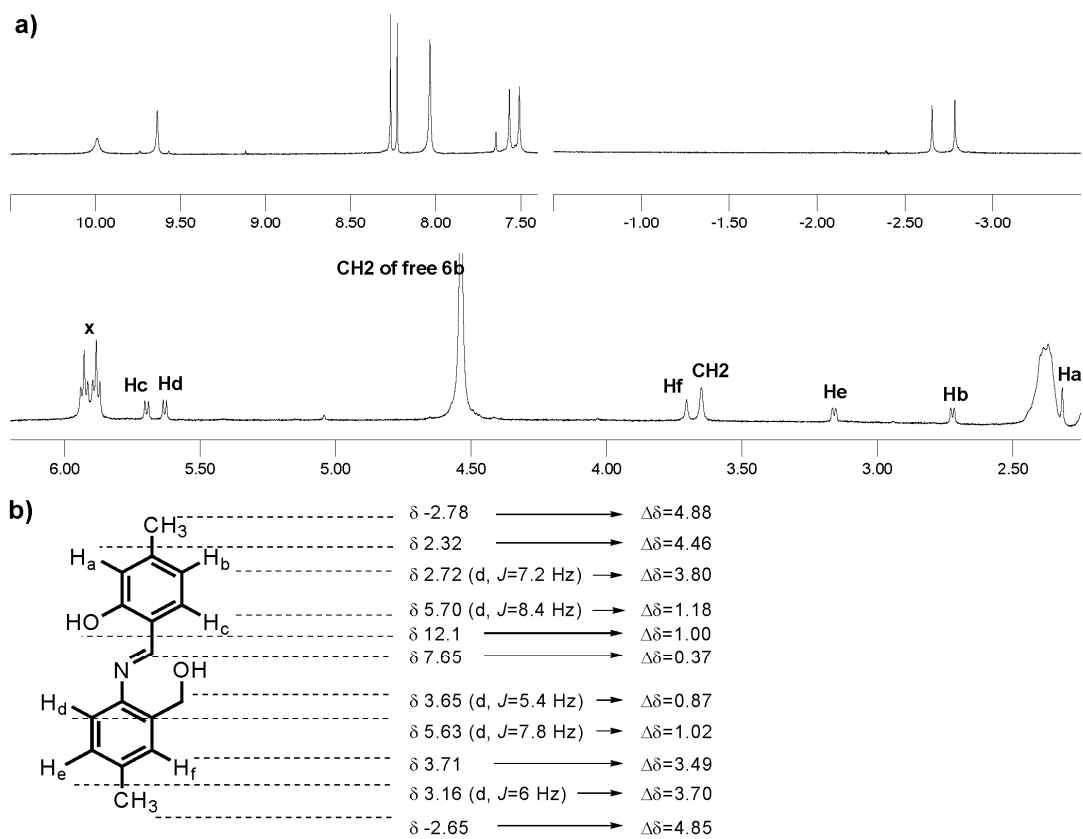


#### 4-2) Encapsulation of **6b**, **6c**, **6d** and **6e** with the cylindrical capsule.

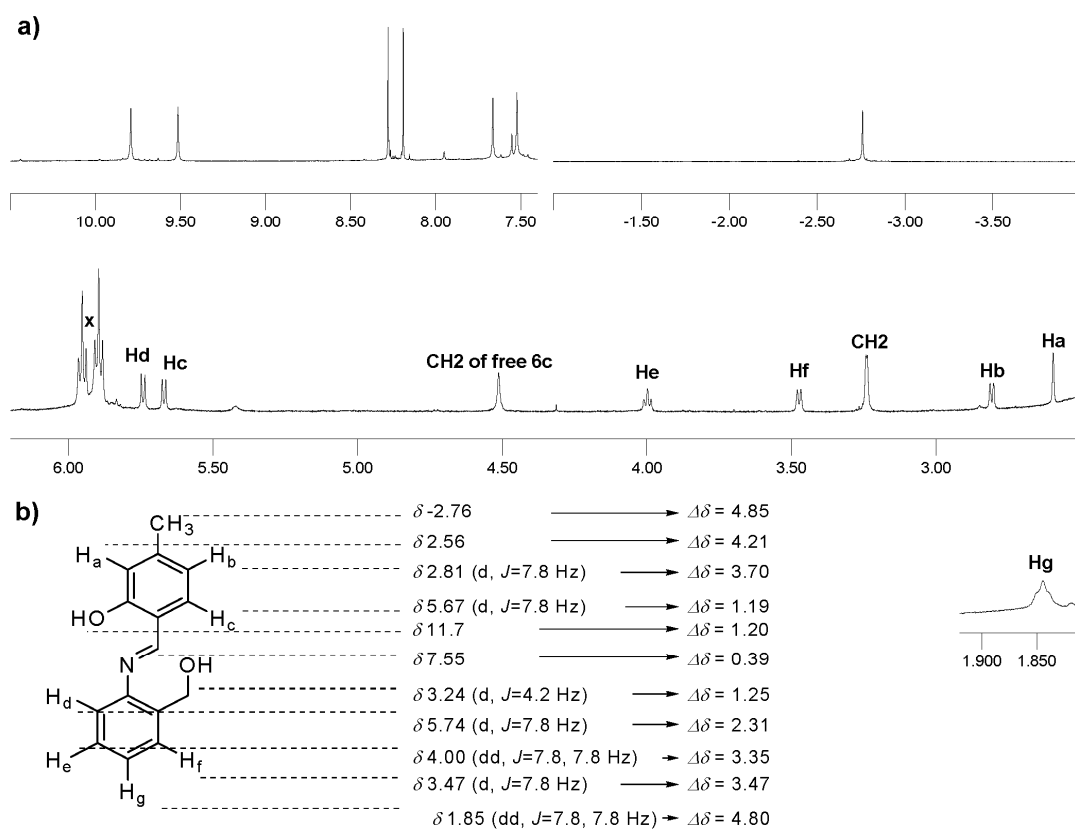
Encapsulation experiments of non-tautomeric Schiff's bases **6b** – **6e** were carried out, which summarize in Figure 4S.  $^1\text{H}$  NMR spectra (600 MHz, 300K, mesitylene- $d_{12}$ ) are shown in Figure 5S – 8S.



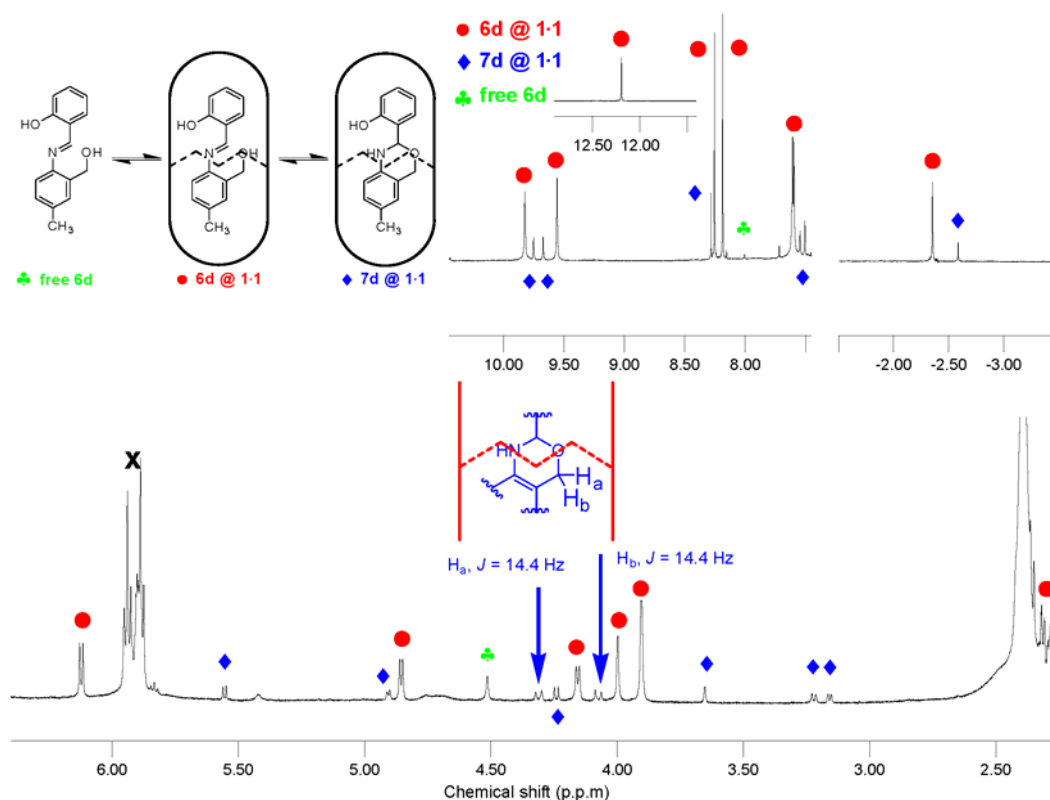
**Figure 4S.** Encapsulations of **6b** – **6e** with **1.1**. They were carried out with the guest (excess over  $2.70 \times 10^{-3}$  mmol) and **1** (10 mg,  $5.94 \times 10^{-3}$  mmol) in mesitylene- $d_{12}$  (1.5 mL).; a) **6b@1.1** was observed in >99% ratio; b) **6c@1.1** was observed in >99% ratio; c) a detectable amount of **7d@1.1** was observed in 13% ratio; d) a detectable amount of **7e@1.1** was observed in 12% ratio.



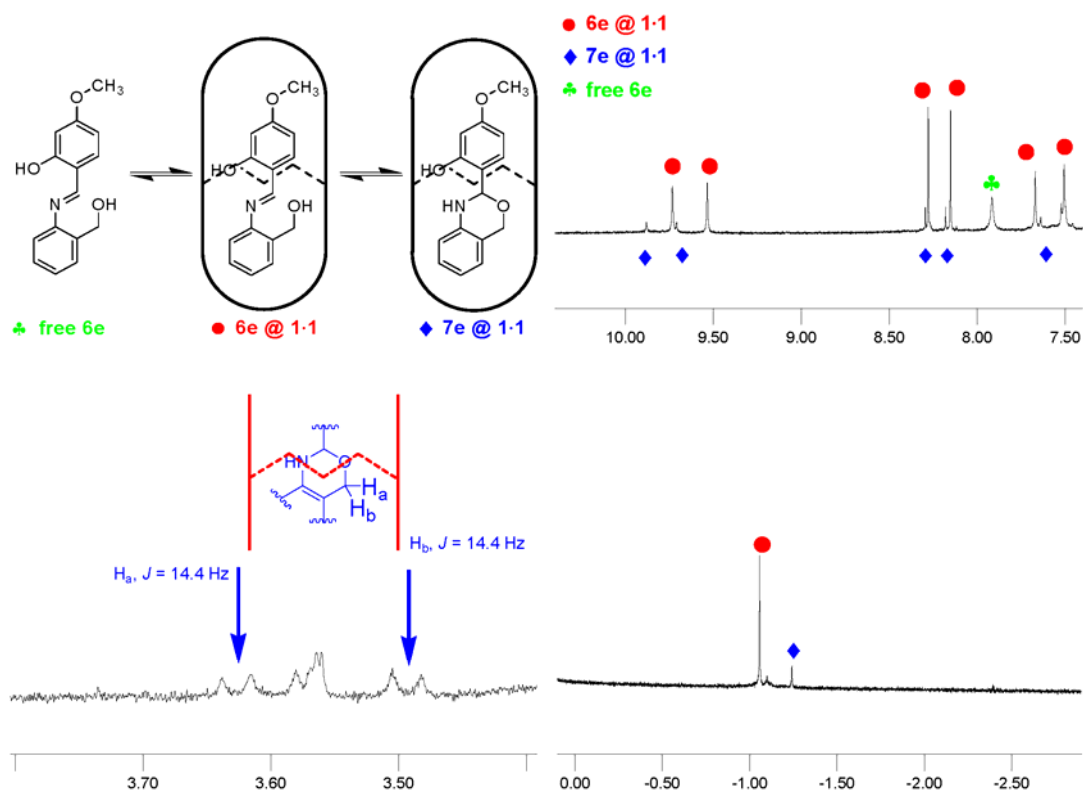
**Figure 5S.** Encapsulation experiments of **6b**. (a) Downfield, mid-field, and upfield portions of  $^1\text{H}$  NMR spectra (600 MHz, 300 K, mesitylene- $d_{12}$ ) of **6b@1.1** and free **6b**. Downfield portions of  $^1\text{H}$  NMR;  $\delta$  9.99 (s, 4H, NH), 9.64 (s, 4H, NH), 8.27 (s, 4H, arom), 8.23 (s, 4H, arom), 8.03 (s, 1H, N=CH of free **6b**), 7.67 (s, 1H, N=CH of **6b@1.1**) 7.57 (s, 4H, arom), 7.51 (s, 4H, arom). Other signals in portions of mid-field and upfield are assigned as shown in (b) with  $\Delta\delta$  values between free and encapsulated **6b**. The peaks labeled x are CH-methines of the cylindrical capsule.



**Figure 6S.** Encapsulation experiments of **6c**. (a) Downfield, mid-field, and upfield portions of  $^1\text{H}$  NMR spectra (600 MHz, 300 K, mesitylene- $d_{12}$ ) of **6c@1.1** and free **6c**. Downfield portions of  $^1\text{H}$  NMR;  $\delta$  9.79 (s, 4H, NH), 9.52 (s, 4H, NH), 8.28 (s, 4H, arom), 8.19 (s, 4H, arom), 7.95 (s, 1H, N=CH of free **6c**), 7.66 (s, 4H, arom), 7.55 (s, 1H, N=CH of **6c@1.1**), 7.52 (s, 4H, arom). Other signals in portions of mid-field and upfield are assigned as shown in (b) with  $\Delta\delta$  values between free and encapsulated **6c**. The peaks labeled x are CH-methines of **1.1**.



**Figure 7S.** Encapsulation experiments of **6d**. Downfield, mid-field, and upfield portions of  $^1\text{H}$  NMR spectra (600 MHz, 300 K, mesitylene- $d_{12}$ ) of **6d@1·1** and **7d@1·1**;  $\delta$  (for **6d@1·1**) 12.2 (s, 1H, OH), 9.82 (s, 4H, NH), 9.56 (s, 4H, NH), 8.25 (s, 4H, arom of **1·1**), 8.19 (s, 4H, arom of **1·1**), 7.62 (s, 1H, N=CH), 7.61 (s, 4H, arom of **1·1**), 7.60 (s, 4H, arom of **1·1**), 6.12 (d, 1H,  $J = 7.2$  Hz), 4.85 (d, 1H,  $J = 7.2$  Hz), 4.16 (d, 1H,  $J = 7.2$  Hz), 4.00 (s, 1H), 3.90 (d, 2H,  $J = 1.2$  Hz), 2.32 - 2.28 (m, 3H), - 2.35 (s, 3H).;  $\delta$  (for **7d@1·1**) 9.75 (s, 4H, NH), 9.67 (s, 4H, NH), 8.28 (s, 4H, arom of **1·1**), 8.19 (s, 4H, arom of **1·1**), 7.55 (s, 4H, arom of **1·1**), 7.51 (s, 4H, arom of **1·1**), 5.55 (d, 1H,  $J = 7.8$  Hz), 4.91 (d, 1H,  $J = 6.0$  Hz), 4.31 (d, 1H,  $J = 14.4$  Hz), 4.24 (d, 1H,  $J = 9.6$  Hz), 4.07 (d, 1H,  $J = 14.4$  Hz), 3.65 (s, 1H), 3.22 (d, 1H,  $J = 9.6$  Hz), 3.16 (s, 1H,  $J = 7.8$  Hz), - 2.59 (s, 3H). The ratio of **6d@1·1** to **7d@1·1** is 87:13 from the integrals of upfield  $\text{CH}_3$  peaks. The peaks labeled x are CH-methines of **1·1**.

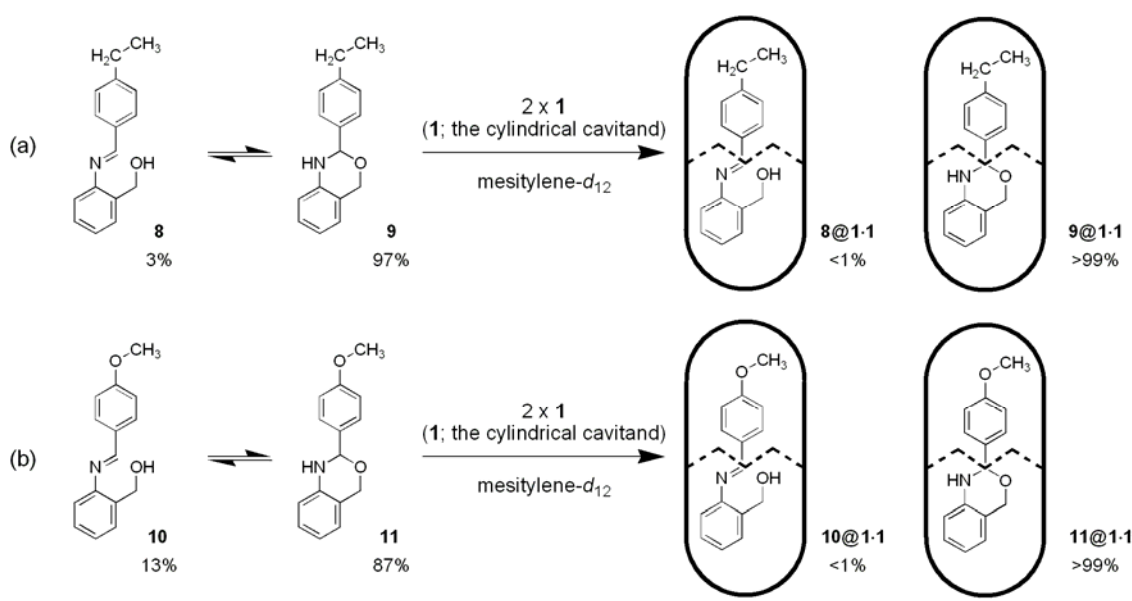


**Figure 8S.** Encapsulation experiments of **6e**. Downfield, mid-field, and upfield portions of  $^1\text{H}$  NMR spectra (600 MHz, 300 K, mesitylene- $d_{12}$ ) of **6e@1:1** and **7e@1:1**;  $\delta$  (for **6e@1:1**) 9.73 (s, 4H, NH), 9.53 (s, 4H, NH), 8.28 (s, 4H, arom of **1:1**), 8.15 (s, 4H, arom of **1:1**), 7.67 (s, 1H, N=CH), 7.51 (s, 4H, arom of **1:1**), - 1.06 (s, 3H);  $\delta$  (for **7e@1:1**) 9.98 (s, 4H, NH), 9.71 (s, 4H, NH), 8.30 (s, 4H, arom of **1:1**), 8.18 (s, 4H, arom of **1:1**), 7.64 (s, 4H, arom of **1:1**), 7.52 (s, 4H, arom of **1:1**), 3.62 (d, 1H,  $J = 14.4$  Hz), 3.49 (d, 1H,  $J = 14.4$  Hz), - 1.24 (s, 3H). The ratio of **6e@1:1** to **7e@1:1** is 88:12 from the integrals of upfield  $\text{CH}_3$  peaks.

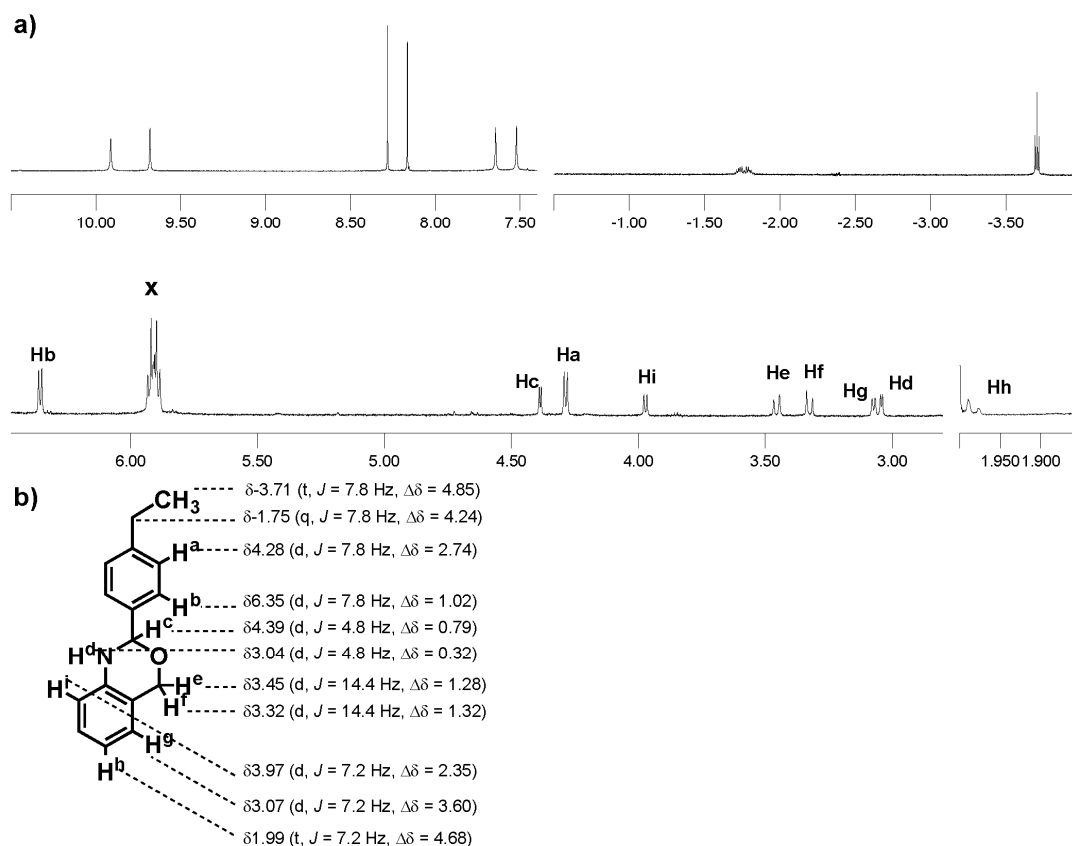


### (5) Corroborative data of encapsulation experiments.

The **8/9** and **10/11** tautomers were prepared and were encapsulated into the host **1·1**. The encapsulation phenomena were summarized in Figure 9S. The  $^1\text{H}$  NMR spectra of encapsulated species were shown in Figure 10S and 11S, as well as the data of free species.

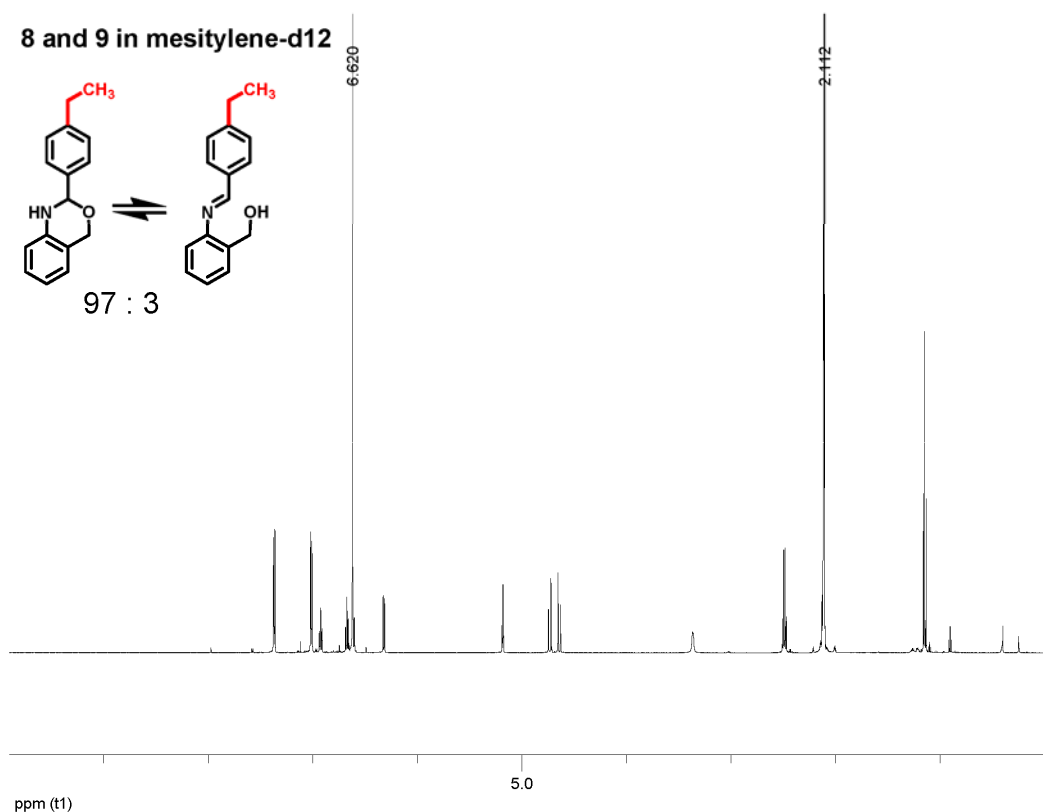


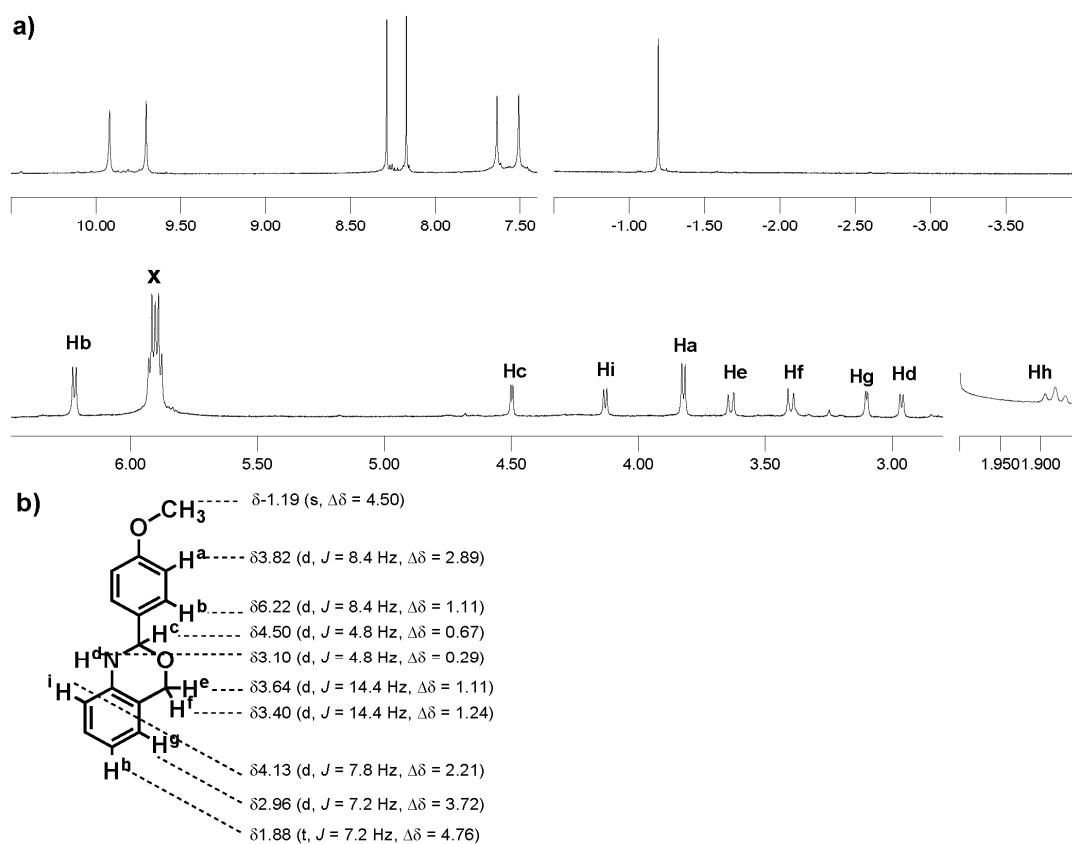
**Figure 9S.** Encapsulation of **8/9** and **10/11** isomerizations with **1·1**. The experiments were carried out with the guest ( $2.70 \times 10^{-3}$  mmol) and **1** (10 mg,  $5.94 \times 10^{-3}$  mmol) in *mesitylene-d*<sub>12</sub> (1.5 mL); a) a detectable amount of **8@1·1** was not formed; b) a detectable amount of **10@1·1** was not formed. The ratios were determined by  $^1\text{H}$  NMR (600 MHz, 300 K, *mesitylene-d*<sub>12</sub>).



**Figure 10S.** Encapsulation experiments of **8** and **9**. (a) Downfield, mid-field, and upfield portions of  $^1\text{H}$  NMR spectra (600 MHz, 300 K, mesitylene- $d_{12}$ ) of **9@1.1**. A detectable amount of **8@1.1** was not formed. The peaks in downfield portions are corresponding to those of asymmetrically filled capsule,  $\delta$  9.91 (s, 4H, NH), 9.68 (s, 4H, NH), 8.28 (s, 4H, arom), 8.16 (s, 4H, arom), 7.64 (s, 4H, arom), 7.52 (s, 4H, arom). Other signals in portions of mid-field and upfield are assigned as shown in (b) with  $\Delta\delta$  values between free and encapsulated **9**. The peaks labeled x are CH-methines of the cylindrical capsule.

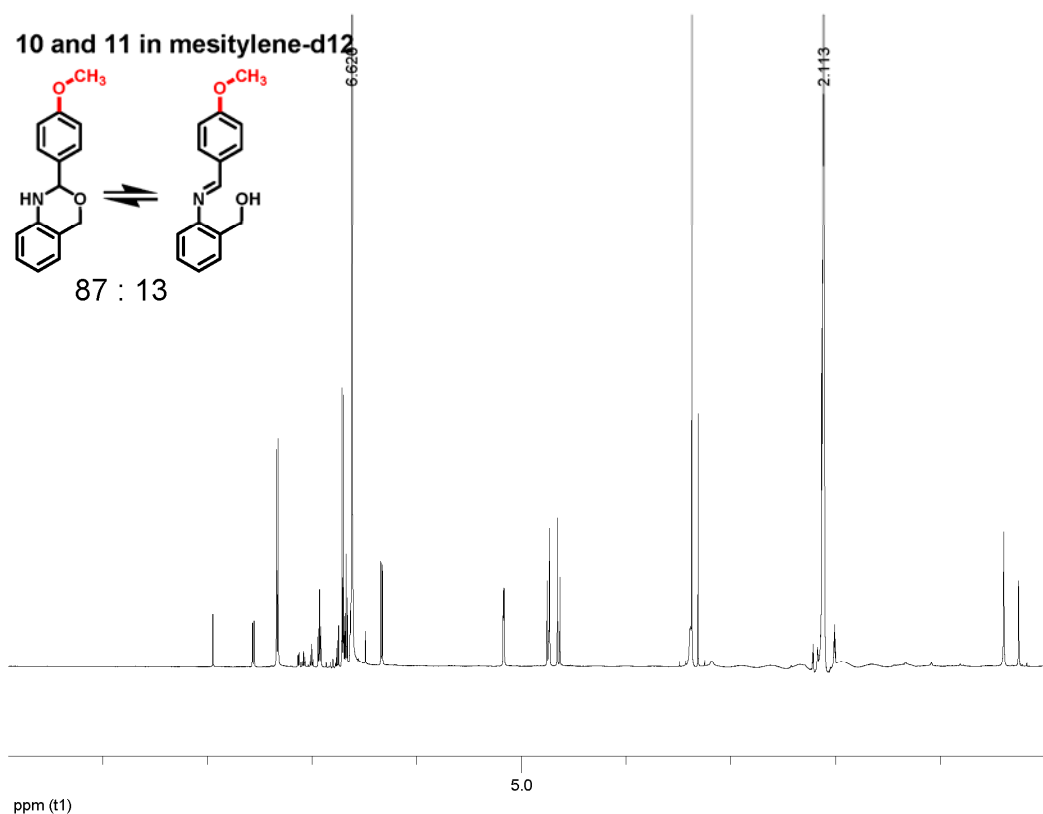
**8** and **9**: The tautomerism between **8** and **9** in mesitylene- $d_{12}$  plateau with 3:97 ratio.  $^1\text{H}$  NMR (600 MHz, 300 K, mesitylene- $d_{12}$ )  $\delta$  (for **9**) 7.37 (d,  $J = 8.4$  Hz, 2H), 7.02 (d,  $J = 8.4$  Hz, 2H), 6.92 (dd,  $J = 8.4$  Hz, 8.4 Hz, 1H), 6.67 (dd,  $J = 8.4$  Hz, 8.4 Hz, 1H), 6.63 (d,  $J = 8.4$  Hz, 1H), 6.32 (d,  $J = 8.4$  Hz, 1H), 5.18 (d,  $J = 6.0$  Hz, 1H), 4.73 (d,  $J = 14.4$  Hz, 1H), 4.64 (d,  $J = 14.4$  Hz, 1H), 3.36 (d,  $J = 6.0$  Hz, 1H), 2.49 (q,  $J = 7.8$  Hz, 2H), 1.14 (t,  $J = 7.8$  Hz, 3H),  $\delta$  (for **8**, four protons of aryl-ring were overlapped and/or too small, so that could not be accurately assigned.) 7.97 (s, 1H), 7.58 (d,  $J = 8.4$  Hz, 2H), 6.96 (d,  $J = 8.4$  Hz, 2H), 4.72 (d,  $J = 6.0$  Hz, 1H), 3.02 (d,  $J = 6.0$  Hz, 1H), 2.44 (q,  $J = 7.8$  Hz, 2H), 1.10 (t,  $J = 7.8$  Hz, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  (for **9**) 145.2, 141.7, 136.5, 129.0, 128.0, 127.3, 126.5, 124.9, 119.6, 116.9, 85.1, 67.7, 28.6, 15.6,  $\delta$  (for **8**) 159.6, 149.6, 148.7, 135.1, 133.4, 128.5, 128.4, 128.03, 126.3, 122.1, 117.4, 64.0, 28.9, 15.3. HRMS (ESI,  $\text{MH}^+$ ): Calcd. For  $\text{C}_{16}\text{H}_{18}\text{NO}$ : 240.1383. Found: 240.1385.





**Figure 11S.** Encapsulation experiments of **10** and **11**. (a) Downfield, mid-field, and upfield portions of  $^1\text{H}$  NMR spectra (600 MHz, 300 K, mesitylene- $d_{12}$ ) of **11@1-1**. A detectable amount of **10@1-1** was not formed. The peaks in downfield portions are corresponding to those of asymmetrically filled capsule,  $\delta$  9.92 (s, 4H, NH), 9.70 (s, 4H, NH), 8.21 (s, 4H, arom), 8.17 (s, 4H, arom), 7.64 (s, 4H, arom), 7.51 (s, 4H, arom). Other signals in portions of mid-field and upfield are assigned as shown in (b) with  $\Delta\delta$  values between free and encapsulated **11**. The peaks labeled x are CH-methines of **1-1**.

**10** and **11**<sup>3,6</sup>: The tautomerism between **10** and **11** in mesitylene-*d*<sub>12</sub> plateau with 13:87 ratio. <sup>1</sup>H NMR (600 MHz, 300 K, mesitylene-*d*<sub>12</sub>) δ (for **11**) 7.33 (d, *J* = 8.4 Hz, 2H), 6.93 (m, 1H), 6.71 (d, *J* = 8.4 Hz, 2H), 6.68 (m, 1H), 6.64 (m, 1H), 6.34 (d, *J* = 8.4 Hz, 1H), 5.17 (d, *J* = 4.8 Hz, 1H), 4.75 (d, *J* = 14.4 Hz, 1H), 4.64 (d, *J* = 14.4 Hz, 1H), 3.39 (d, *J* = 4.8 Hz, 1H), 3.37 (s, 3H), δ (for **10**, one proton of aryl-ring was overlapped and/or too small, so that could not be accurately assigned.) 7.95 (s, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.12 (m, 1H), 7.08 (m, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 2H), 4.74 (brs, 2H), 3.31 (s, 3H), 3.18 (brs, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ (for **11**) 160.1, 159.0, 141.8, 131.5, 127.8, 127.4, 124.9, 119.6, 116.8, 113.9, 84.9, 67.7, 55.3, δ (for **10**) 162.6, 149.8, 135.0, 130.7, 128.7, 128.5, 128.0, 126.1, 122.0, 117.4, 114.3, 64.2, 55.4. HRMS (ESI, MH<sup>+</sup>): Calcd. For C<sub>15</sub>H<sub>16</sub>NO<sub>2</sub>: 242.1175. Found: 242.1181.



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