

## Supporting Information

### LCST Behavior Induced by Size-Matching Selectivity from Low Molecular Weight Monomer Systems

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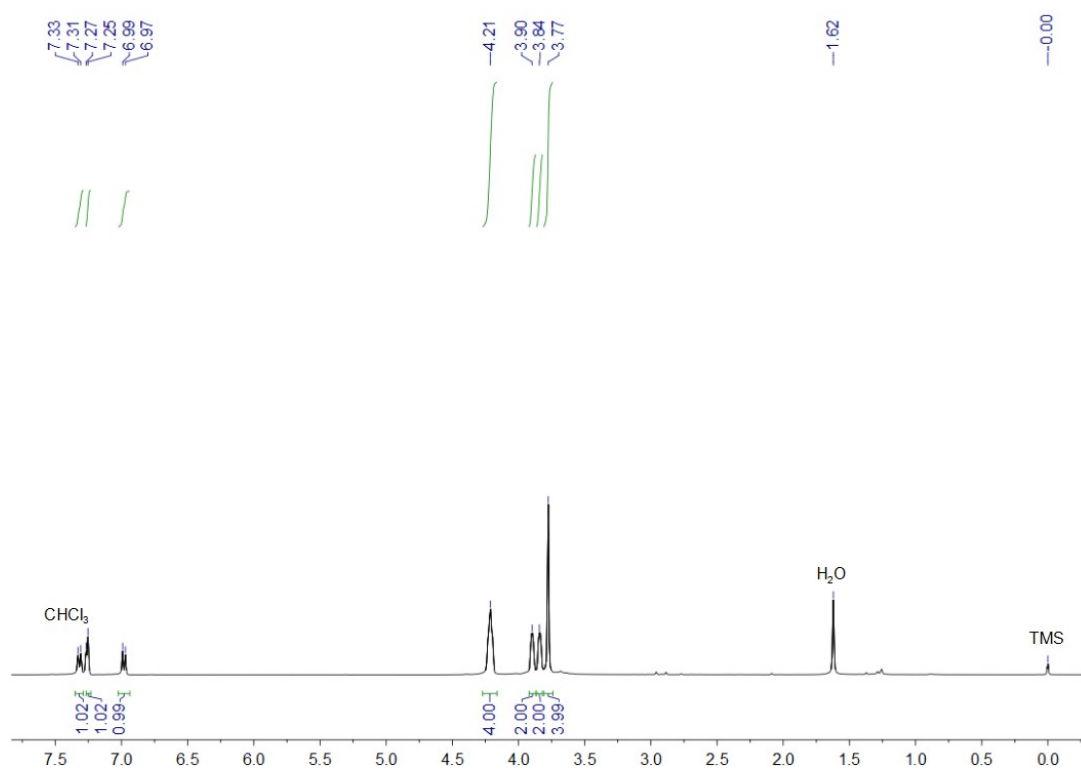
1. Materials and methods .....	S1
2. NMR spectra of <b>BC4-CN</b> , <b>BC5-CN</b> , <b>BC6-CN</b> and <b>BC7-CN</b> .....	S1
3. NMR spectra of <b>TC4</b> , <b>TC5</b> , <b>TC6</b> and <b>TC7</b> .....	S3
4. Partial proton NMR spectra of <b>TC4</b> , <b>TC5</b> , <b>TC6</b> and <b>TC7</b> in D <sub>2</sub> O .....	S7
5. Solubility tests of <b>TC4</b> , <b>TC5</b> , <b>TC6</b> and <b>TC7</b> in water .....	S8
6. Reference .....	S8

## 1. Materials and methods

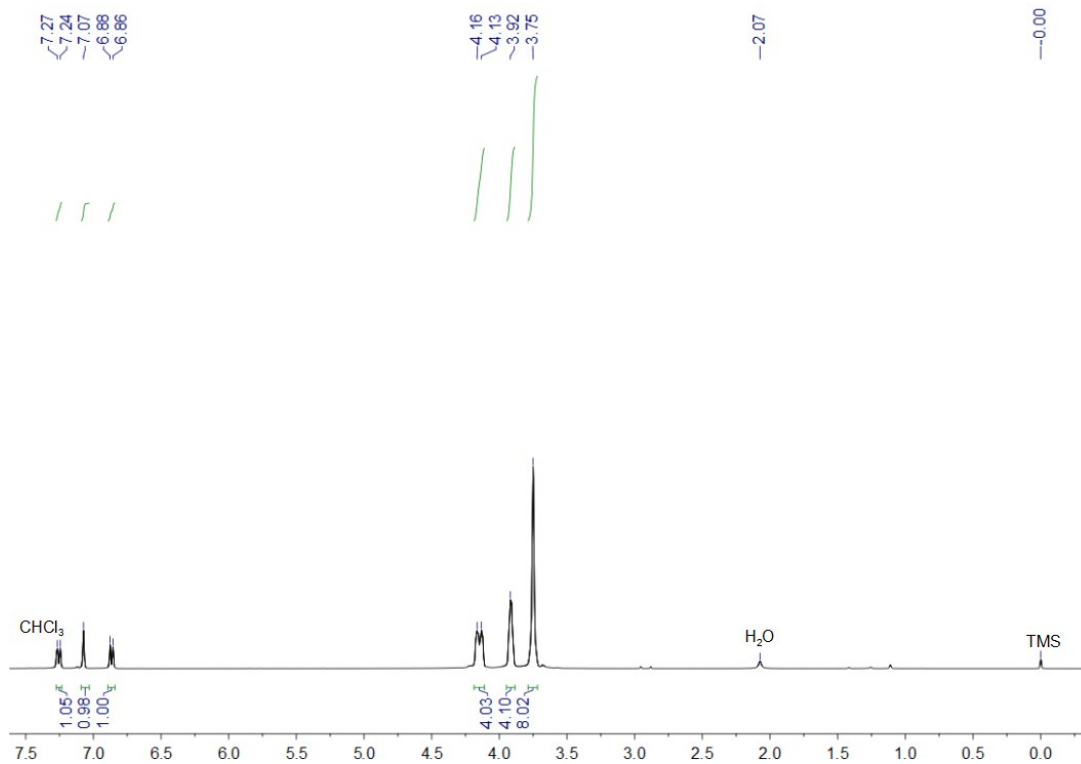
All reagents were commercially available and used as supplied without further purification. **BC4-CN**, **BC5-CN**, **BC6-CN**, **BC7-CN**, **TC7** were prepared according to the reported methods.<sup>1-3</sup> <sup>1</sup>H NMR spectra were collected on a Varian Unity INOVA-400 or Bruker-AV400 with TMS as the internal standard. <sup>13</sup>C NMR spectra were recorded on a Bruker-AV400 spectrometer at 125 MHz. UV/Vis spectra were obtained on a UV2600 spectrometer with a temperature controllable system at a heating rate of 1.0 °C/min or 0.1 °C/min. Unless otherwise stated, samples were dispersed in Milli-Q water. MALDI-TOF mass spectrometry was performed on a Shimadzu Biotech AXIMA Performance instrument.

## 2. NMR spectra of **BC4-CN**, **BC5-CN**, **BC6-CN** and **BC7-CN**

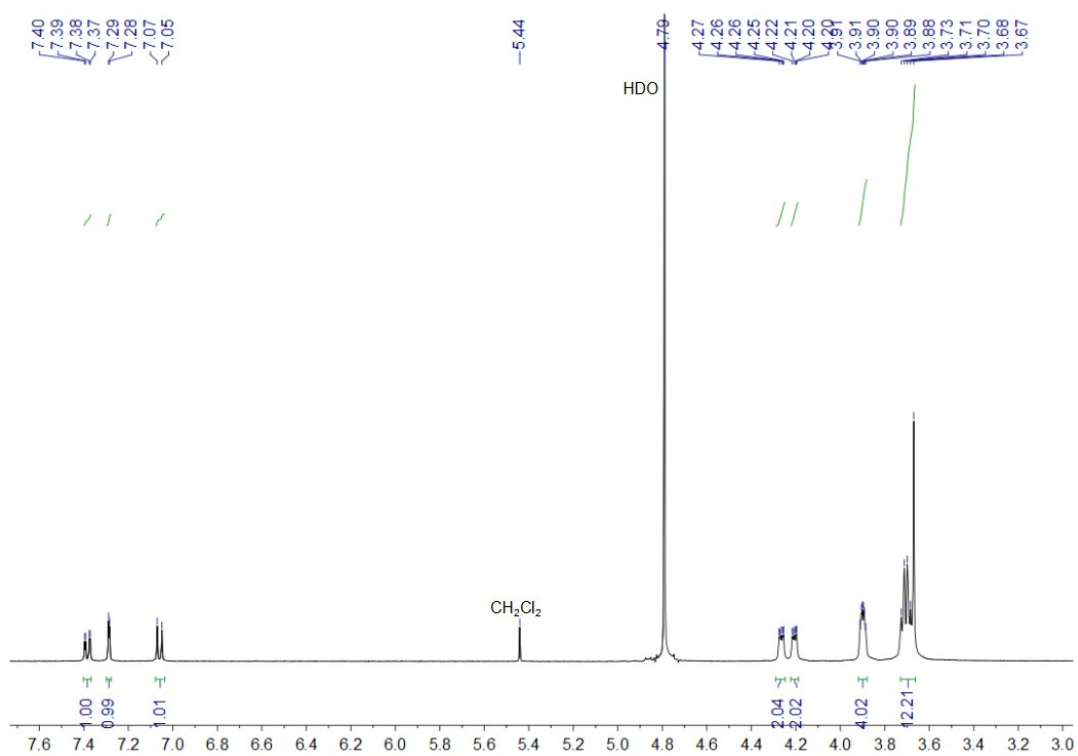
**BC4-CN**, **BC5-CN**, **BC6-CN**, **BC7-CN** were prepared according reported methods,<sup>1,2</sup> and their proton NMR spectras were consistent with reported data.



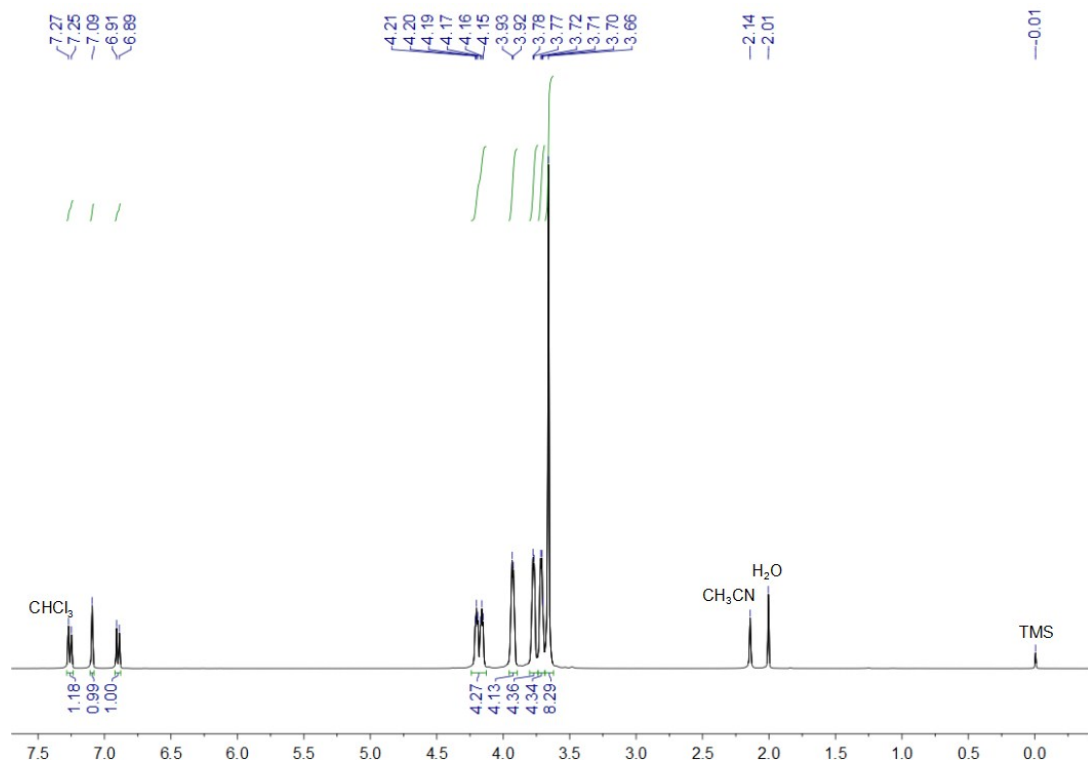
**Figure S1.** <sup>1</sup>H NMR spectrum (400 MHz,  $\text{CDCl}_3$ , room temperature) of **BC4-CN**



**Figure S2.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, room temperature) of BC5-CN



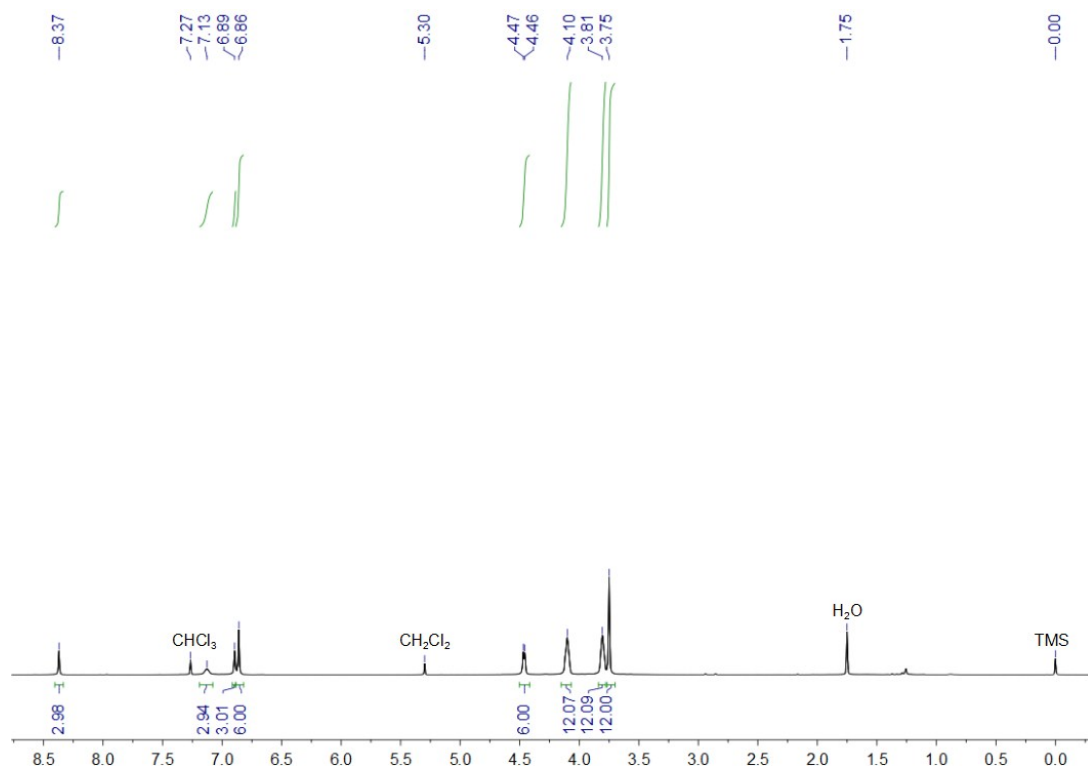
**Figure S3.** <sup>1</sup>H NMR spectrum (400 MHz, D<sub>2</sub>O, room temperature) of BC6-CN



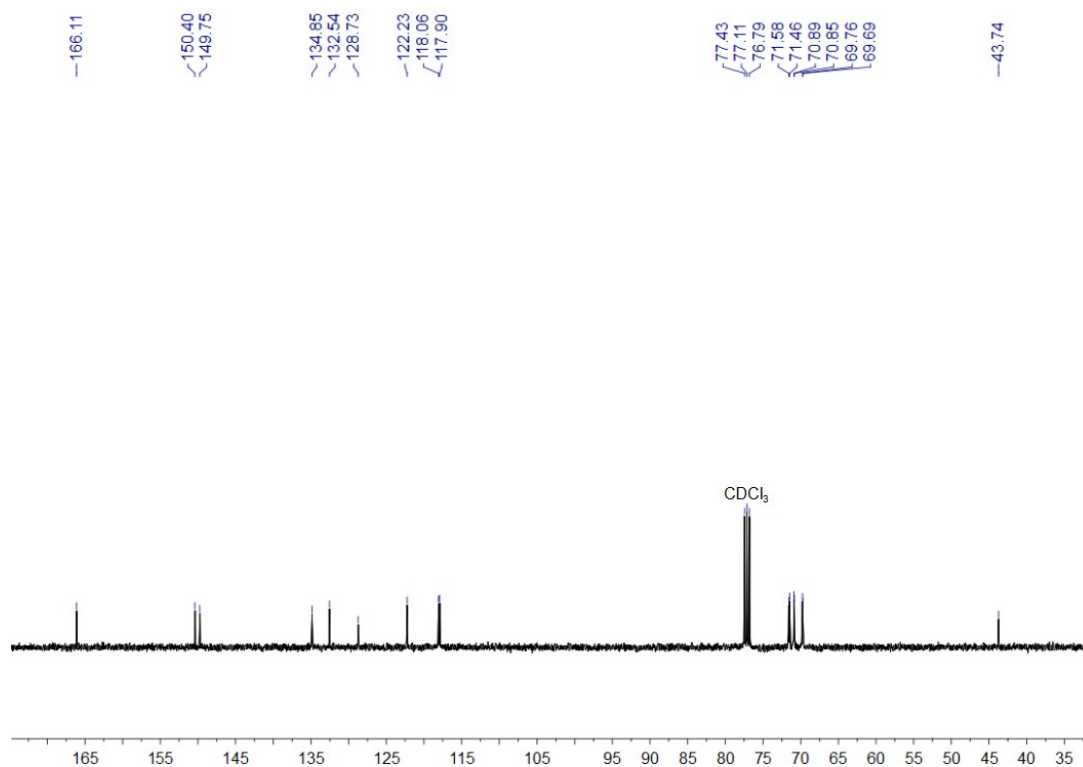
**Figure S4.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, room temperature) of BC7-CN

### 3. NMR spectra of TC4, TC5, TC6 and TC7

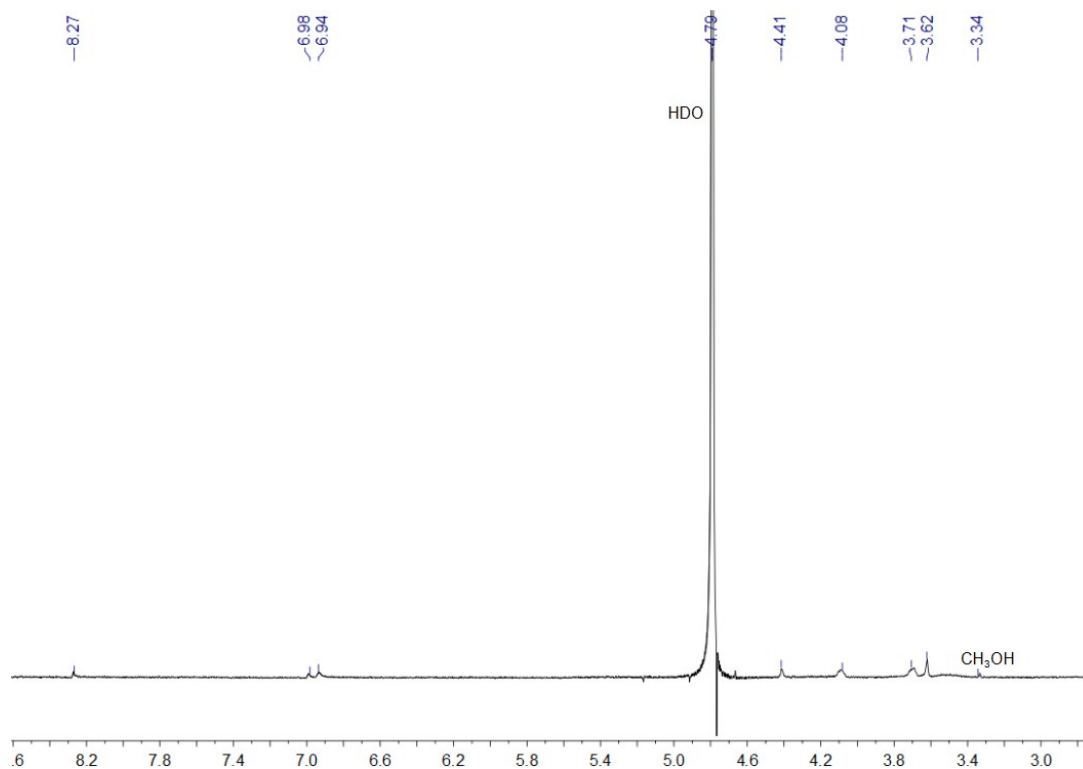
TC7 were prepared according to reported method,<sup>3</sup> and its proton NMR spectrum in D<sub>2</sub>O was additionally prepared.



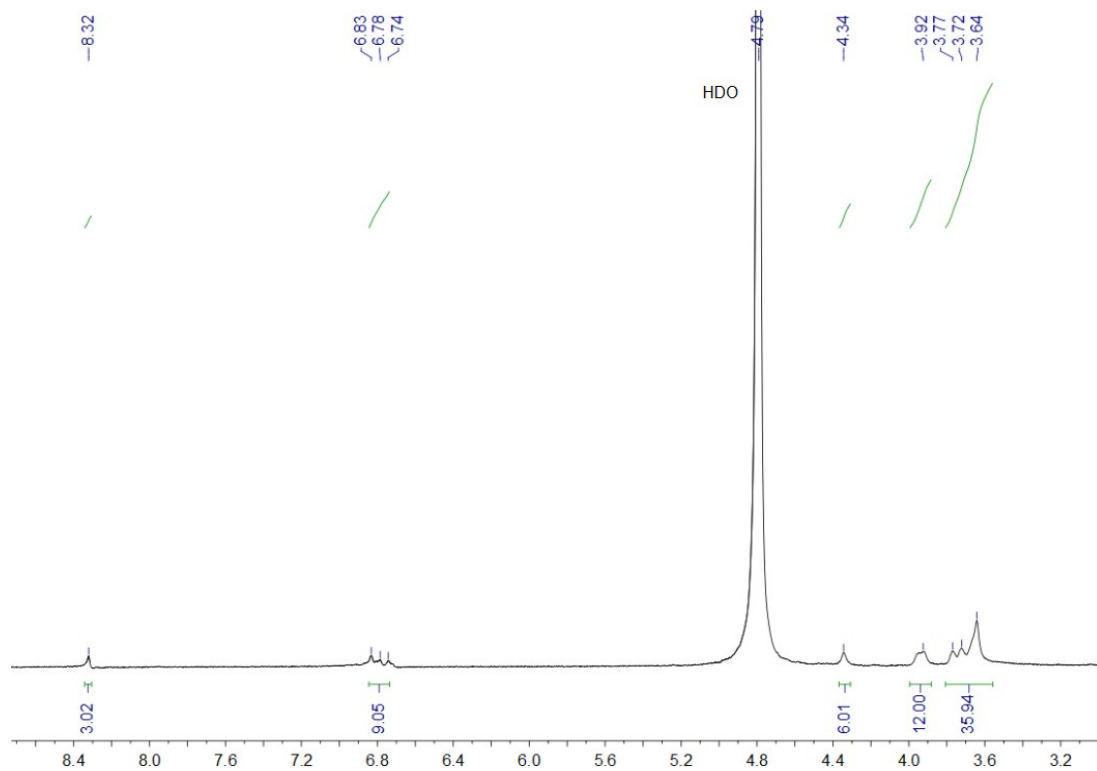
**Figure S5.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , room temperature) of TC4



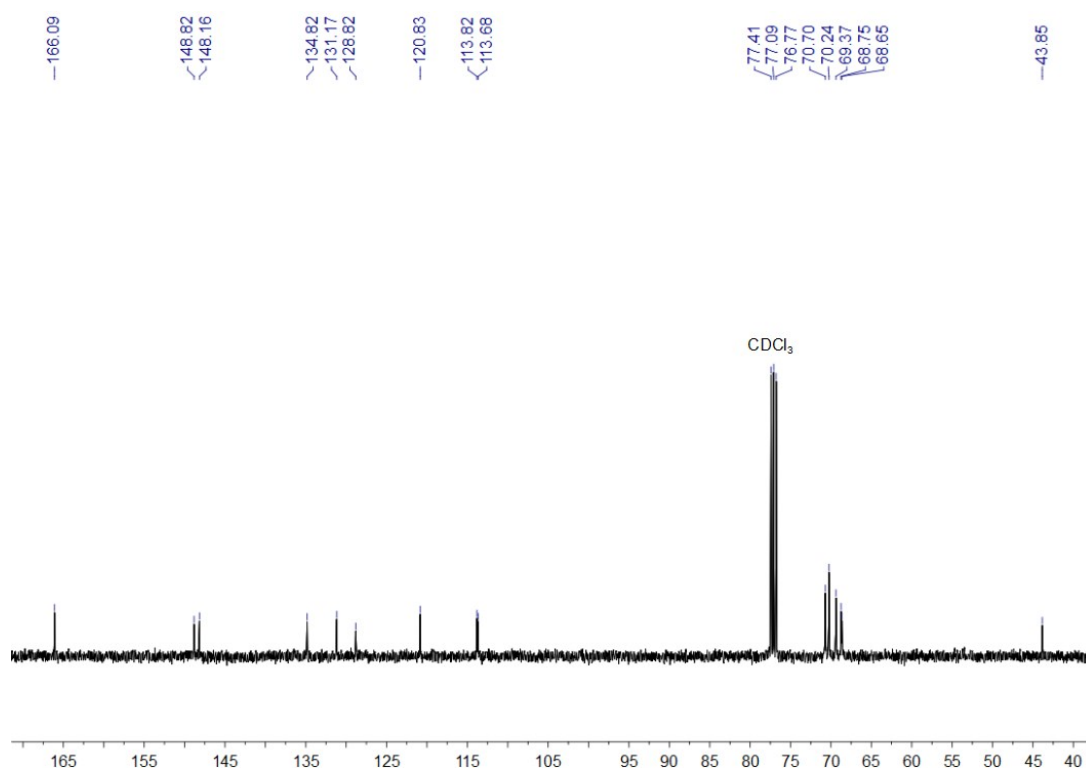
**Figure S6.**  $^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ , room temperature) of TC4



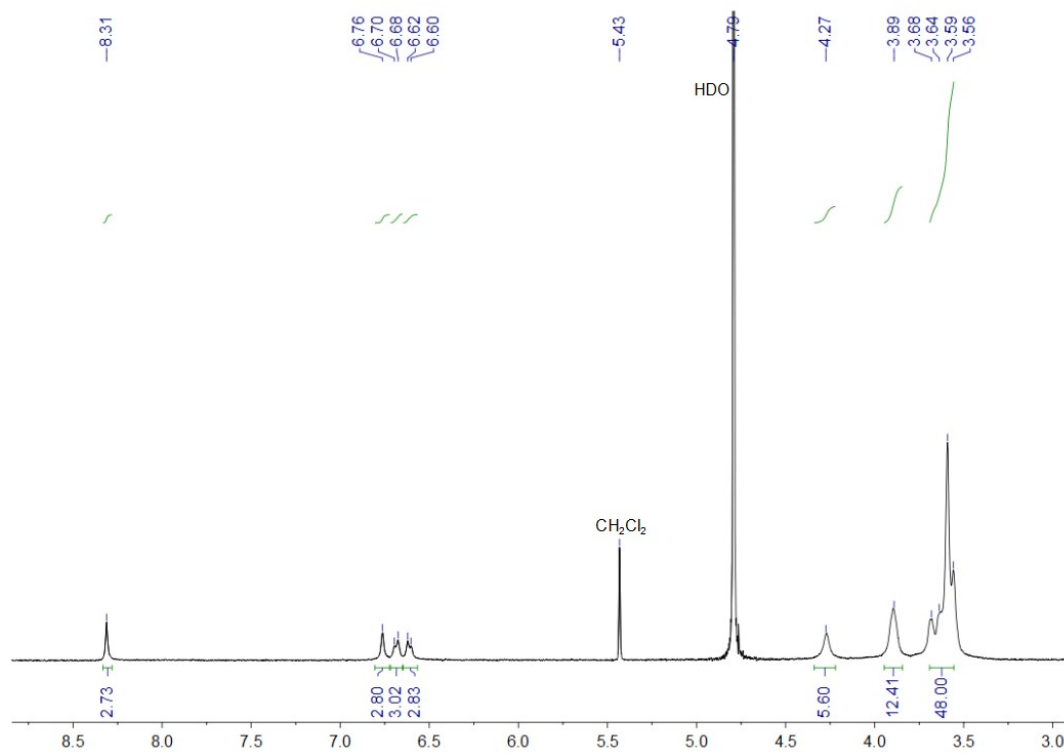
**Figure S7.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{D}_2\text{O}$ , room temperature) of TC4  
Due to the poor solubility in  $\text{D}_2\text{O}$ , it is difficult to get clear integral of each peaks.



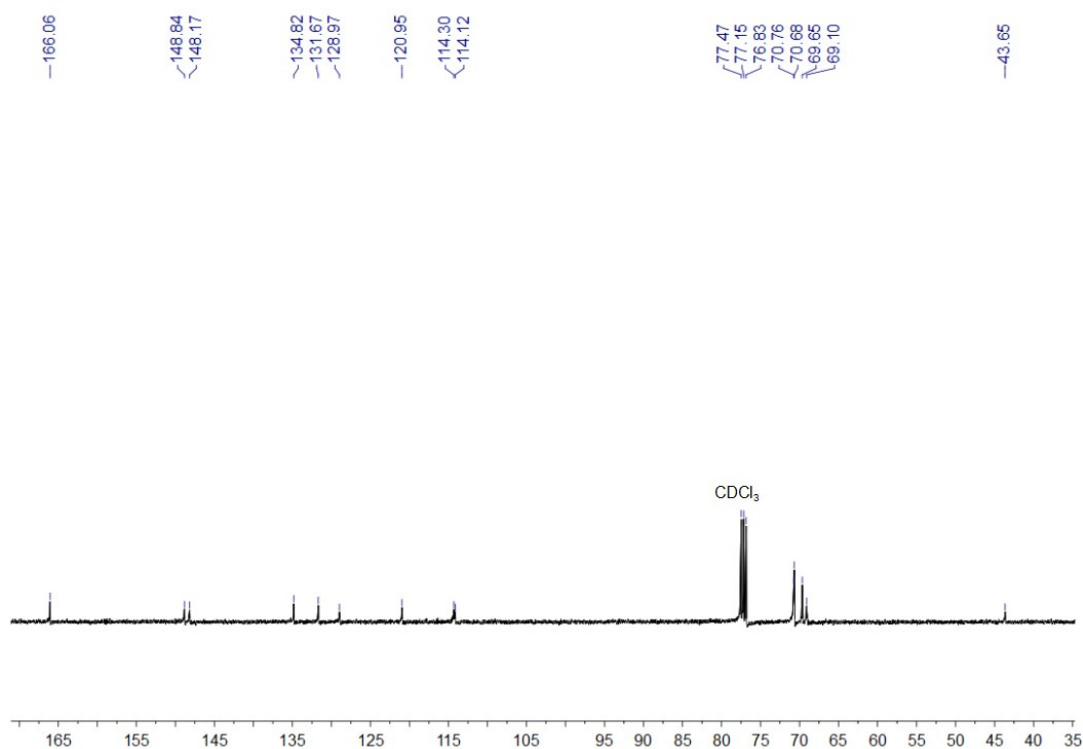
**Figure S8.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{D}_2\text{O}$ , room temperature) of TC5



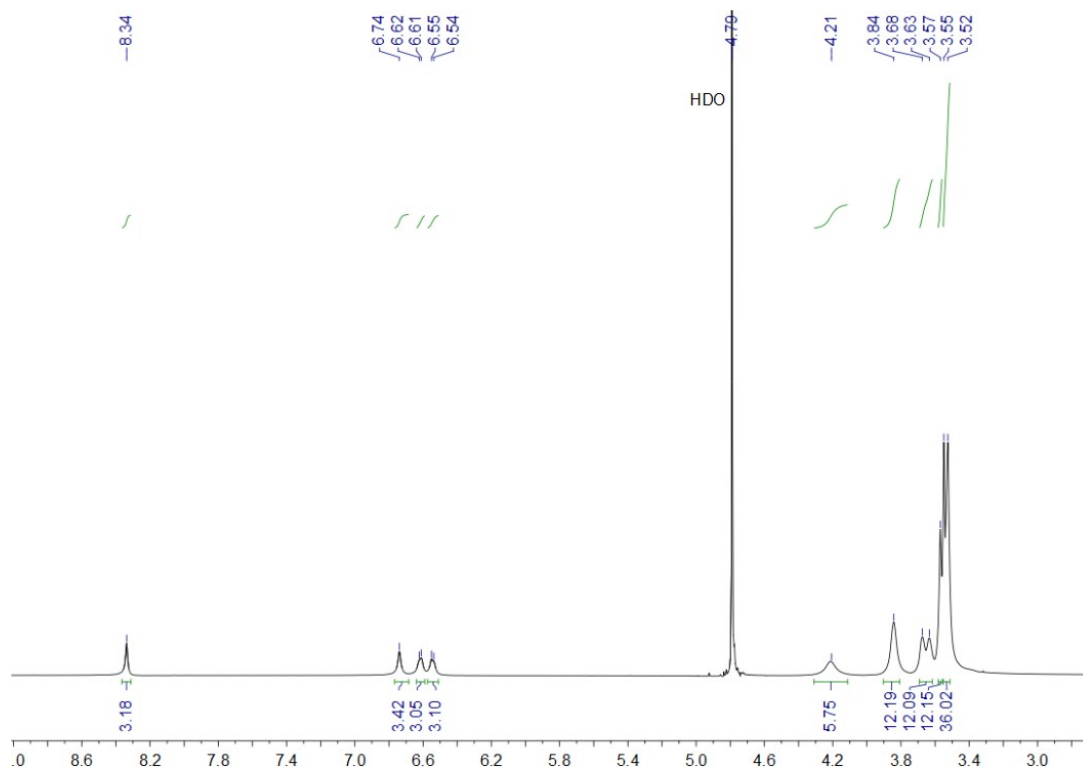
**Figure S9.**  $^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ , room temperature) of TC5



**Figure S10.** <sup>1</sup>H NMR spectrum (400 MHz, D<sub>2</sub>O, room temperature) of TC6

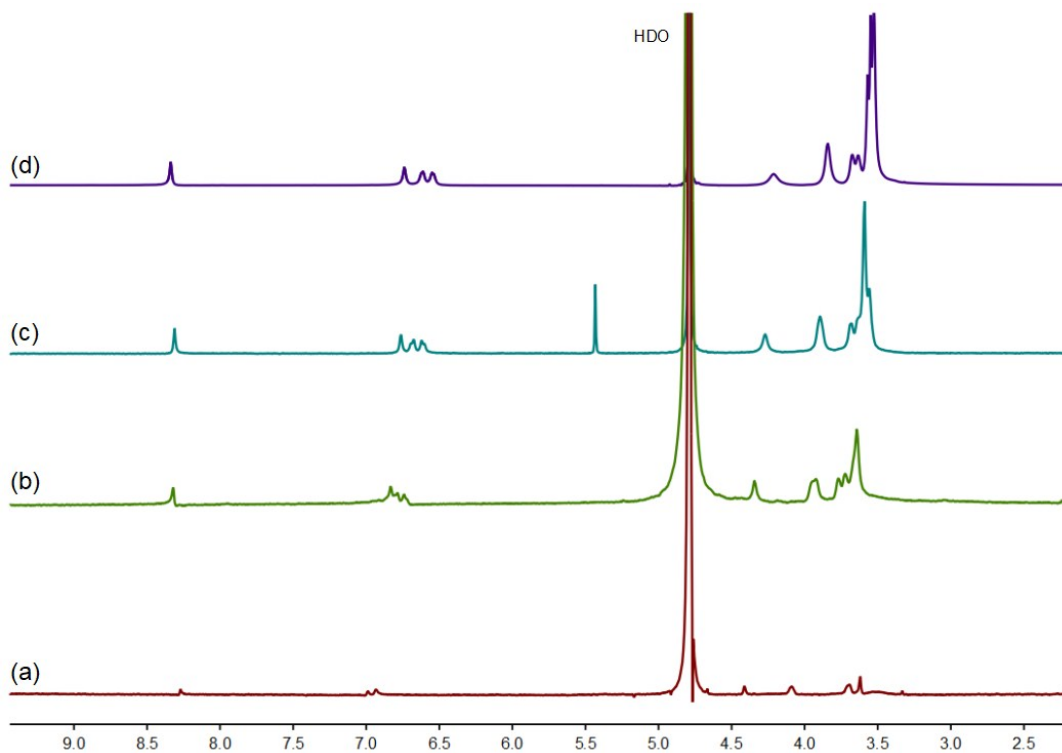


**Figure S11.** <sup>13</sup>C NMR spectrum (125 MHz, CDCl<sub>3</sub>, room temperature) of TC6



**Figure S12.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{D}_2\text{O}$ , room temperature) of TC7

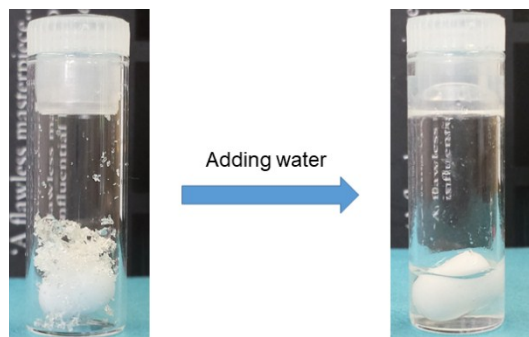
**4. Partial proton NMR spectra of TC4, TC5, TC6 and TC7 in  $\text{D}_2\text{O}$**



**Figure 13.** Partial proton NMR (400 MHz,  $\text{D}_2\text{O}$ , room temperature) spectra of (a) TC4, (b) TC5, (c) TC6 and (d) TC7.



## 5. Solubility tests of TC4, TC5, TC6 and TC7 in water



**Figure S14.** Solubility test of TC7 in water.

Excess TC4/TC5 was added to a vial with 2 mL water. The mixture was stirred for two days. The upper layer solution was removed and water was evaporated to yield TC4/TC5. Based on the weight of the upper layer solution and the obtained TC4/TC5. Their solubility can be calculated. The solubility of TC4 and TC5 in water are 0.8 mg/mL and 2.3 mg/mL, respectively. For TC6/TC7, no matter how much it is added, a viscous but still transparent liquid is prepared, and no insoluble TC6/TC7 is found.

## 6. Reference

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