

## Supporting Informations

### Synthesis of benzo[6]urils and their selective interactions with bipyridines

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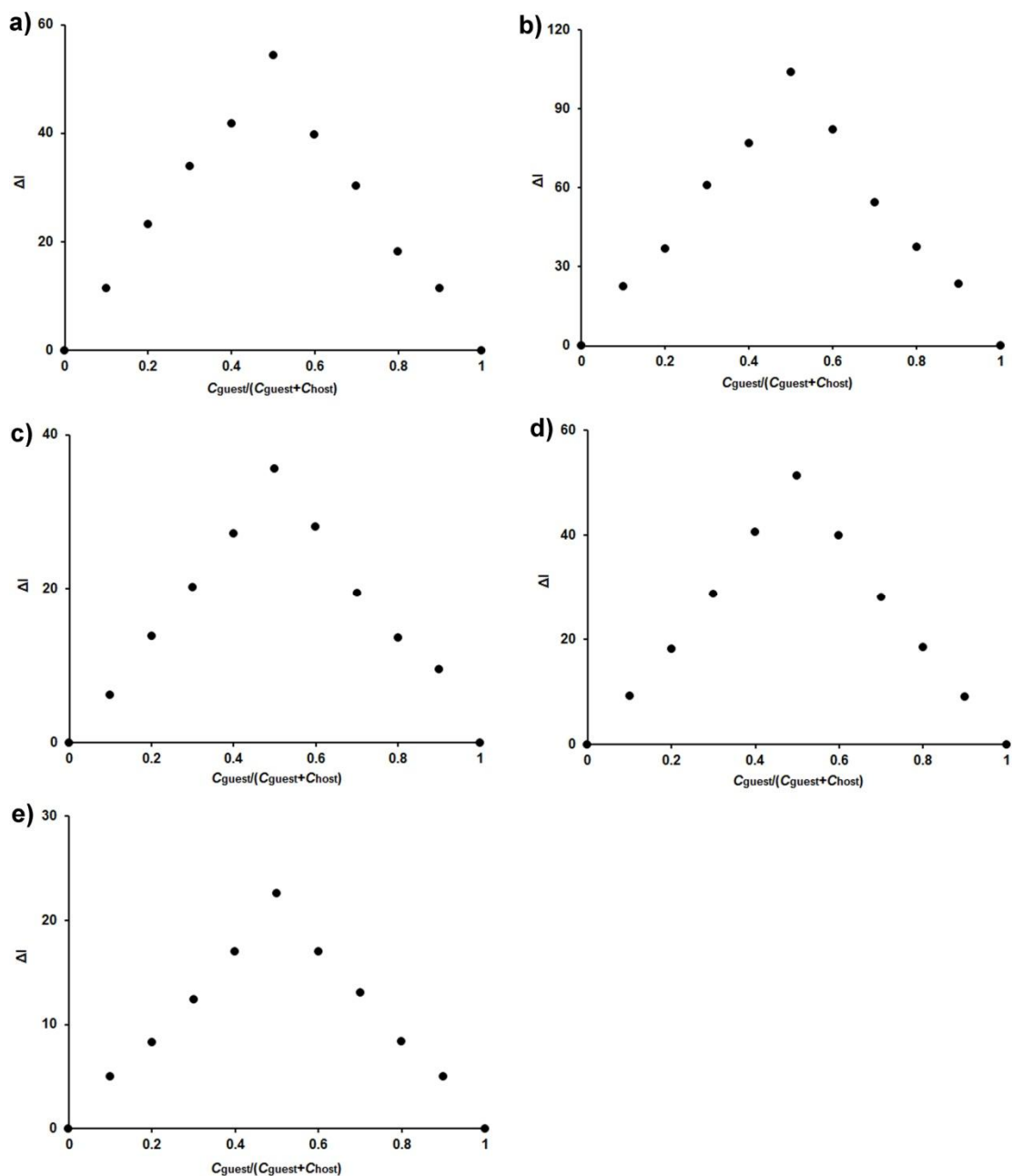


Figure S1 Job's plots of the interaction between benzo[6]uril **1** and a) guest **3**; b) guest **4**; c) guest **5**; d) guest **6**; e) guest **8**. The total concentration was maintained at  $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ , and fluorescence intensities were recorded at  $\lambda_{\text{em}} = 326 \text{ nm}$ ,  $\lambda_{\text{ex}} = 300 \text{ nm}$ .

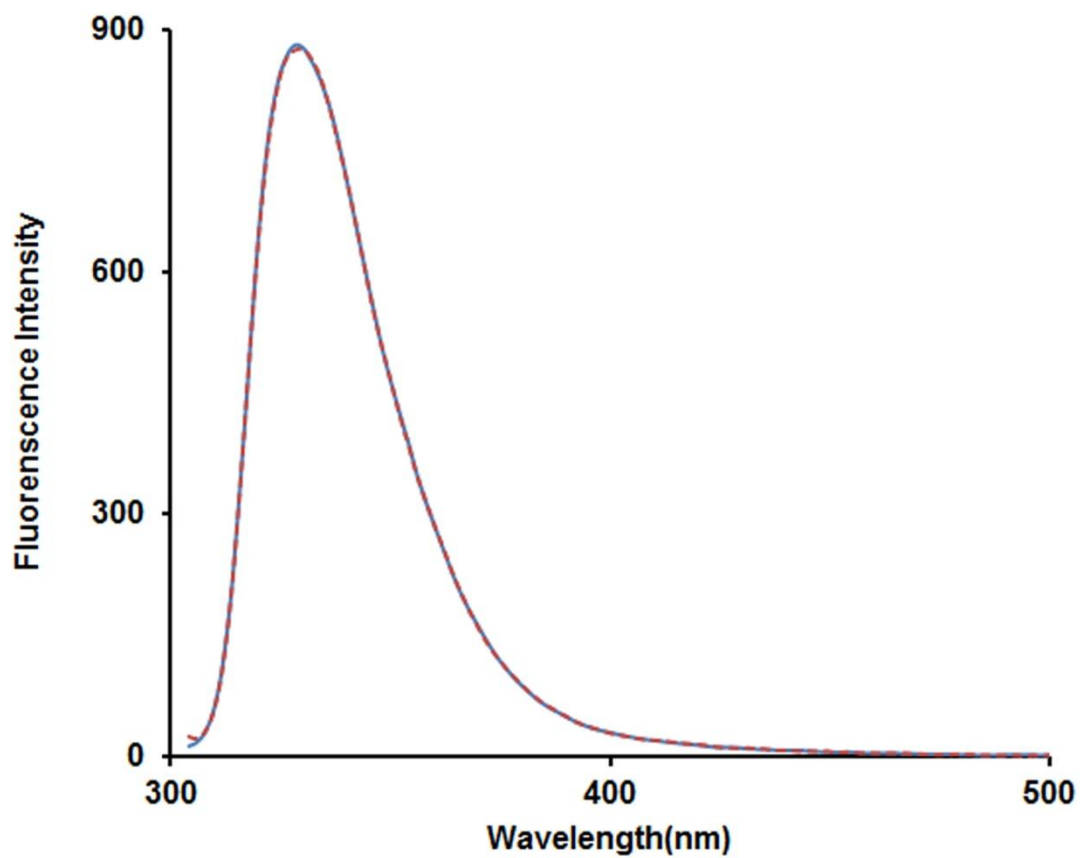


Figure S2 Fluorescence spectra of benzo[6]uril **1** ( $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  in DMSO) in the absence (blue solid) and presence of 1 eq. guest **7** (red dash).

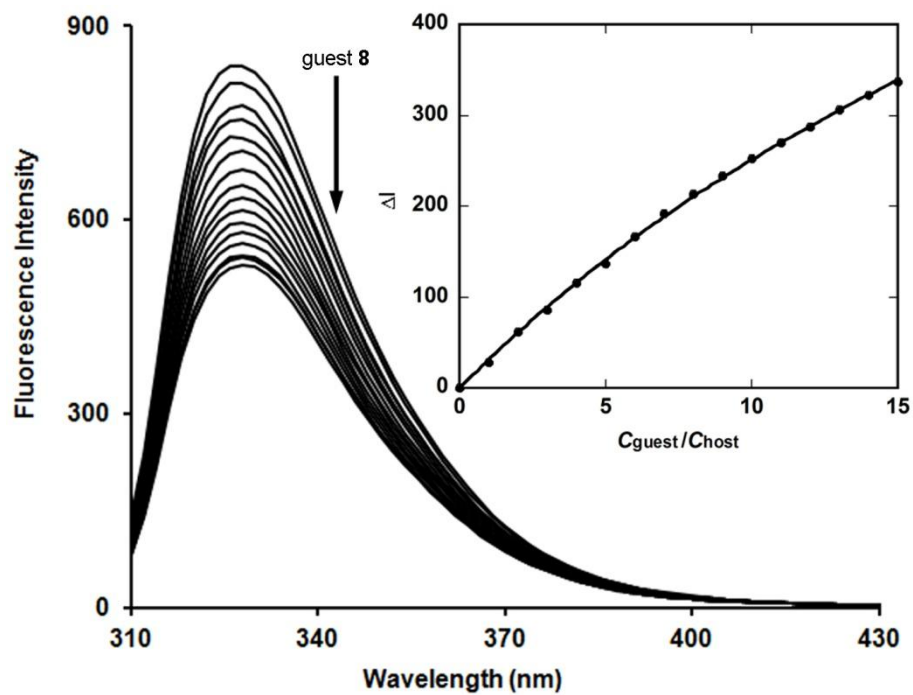


Figure S3 Fluorescence titration spectra of benzo[6]uril **1** with guest **8**. The host concentration was fixed at  $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  in DMSO. Insets: nonlinear fitting of the changes in fluorescence intensity upon addition of the guest ( $\lambda_{\text{em}} = 326 \text{ nm}$ ,  $\lambda_{\text{ex}} = 300 \text{ nm}$ )

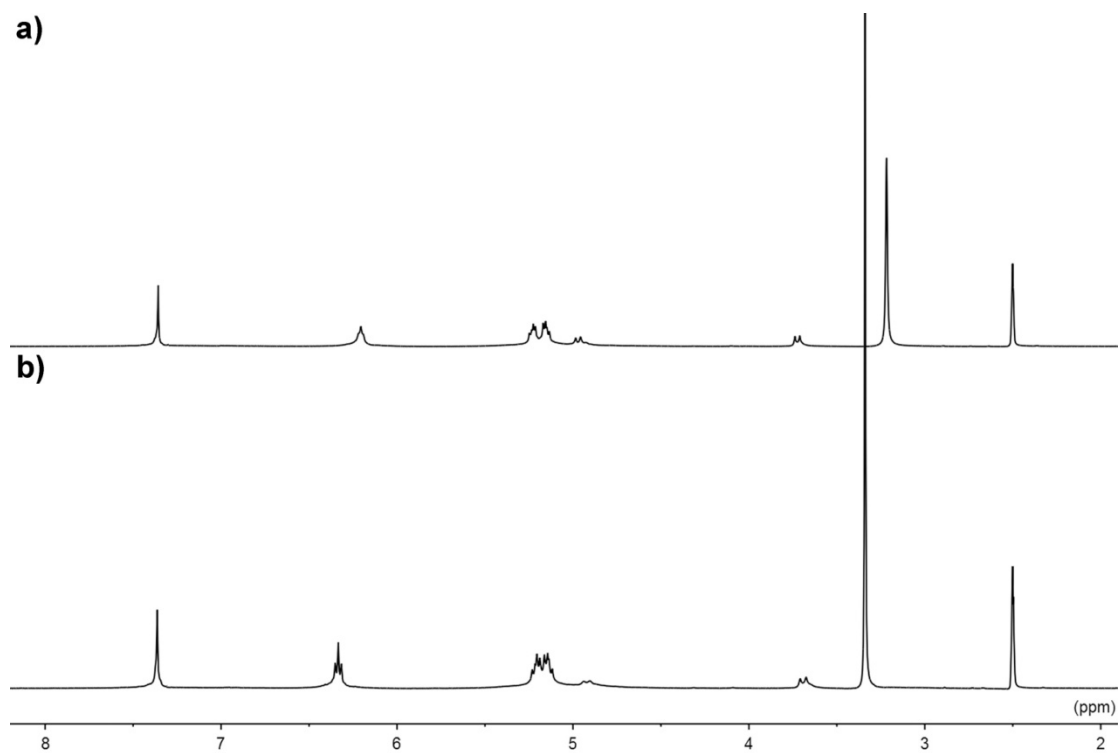


Figure S4  $^1\text{H}$  NMR spectra of benzo[6]uril **1** at a) 50 and b) 25  $^{\circ}\text{C}$

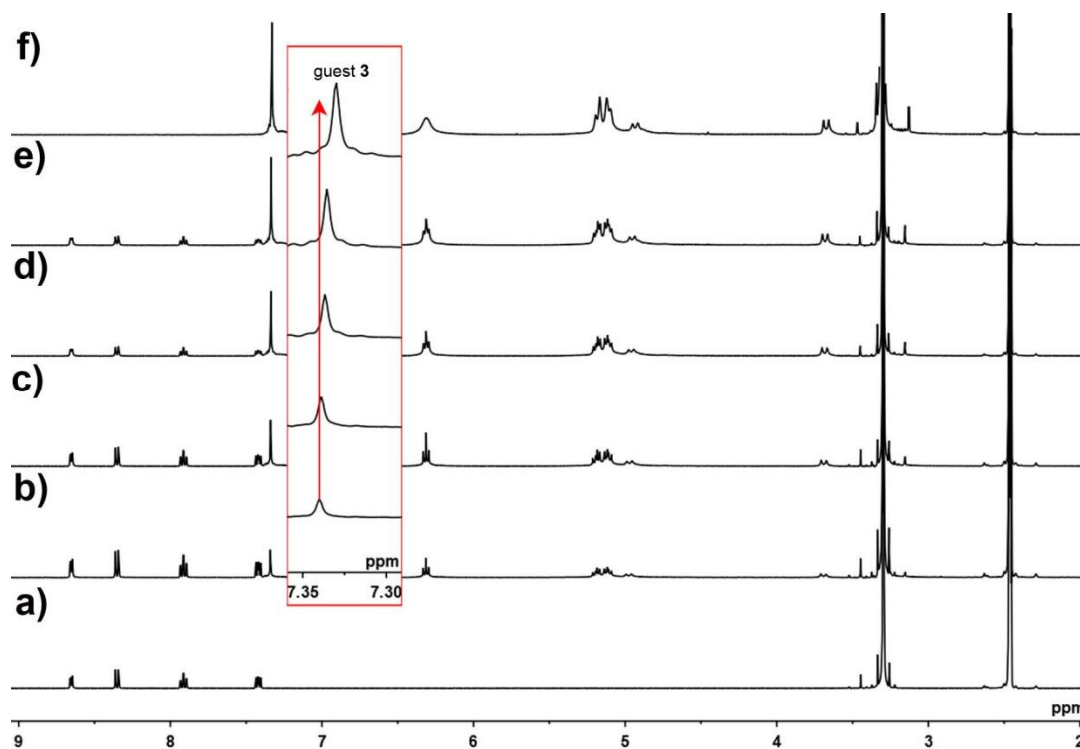


Figure S5  $^1\text{H}$  NMR spectra (400 MHz,  $[\text{D}_6]\text{DMSO}$ ) of a) free guest **3** ( $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ), and in the presence of b) 0.5 equiv.; c) 1.0 equiv.; d) 2.0 equiv.; e) 3.0 equiv. of benzo[6]uril **1**, and f) free benzo[6]uril **1**.

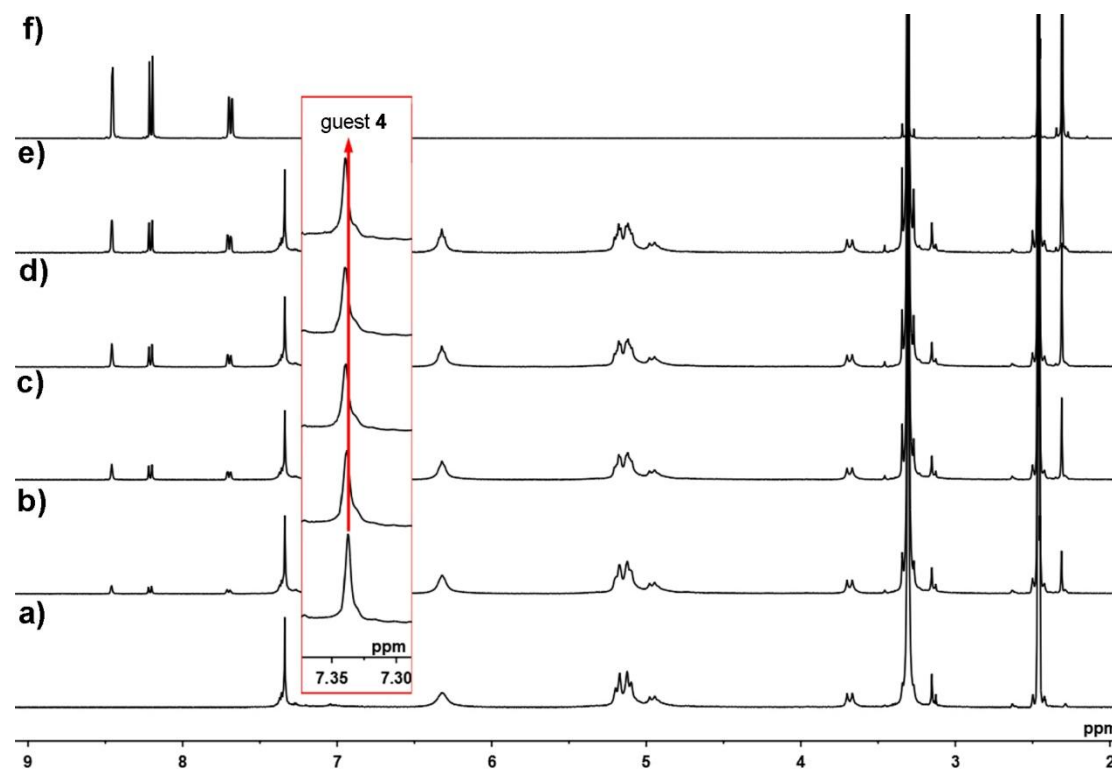


Figure S6  $^1\text{H}$  NMR spectra (400 MHz,  $[\text{D}_6]\text{DMSO}$ ) of a) free benzo[6]uril **1** ( $2.0 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ ), and in the presence of b) 0.5 equiv.; c) 1.0 equiv.; d) 2.0 equiv.; e) 3.0 equiv. of guest **4**, and f) free guest **4**.

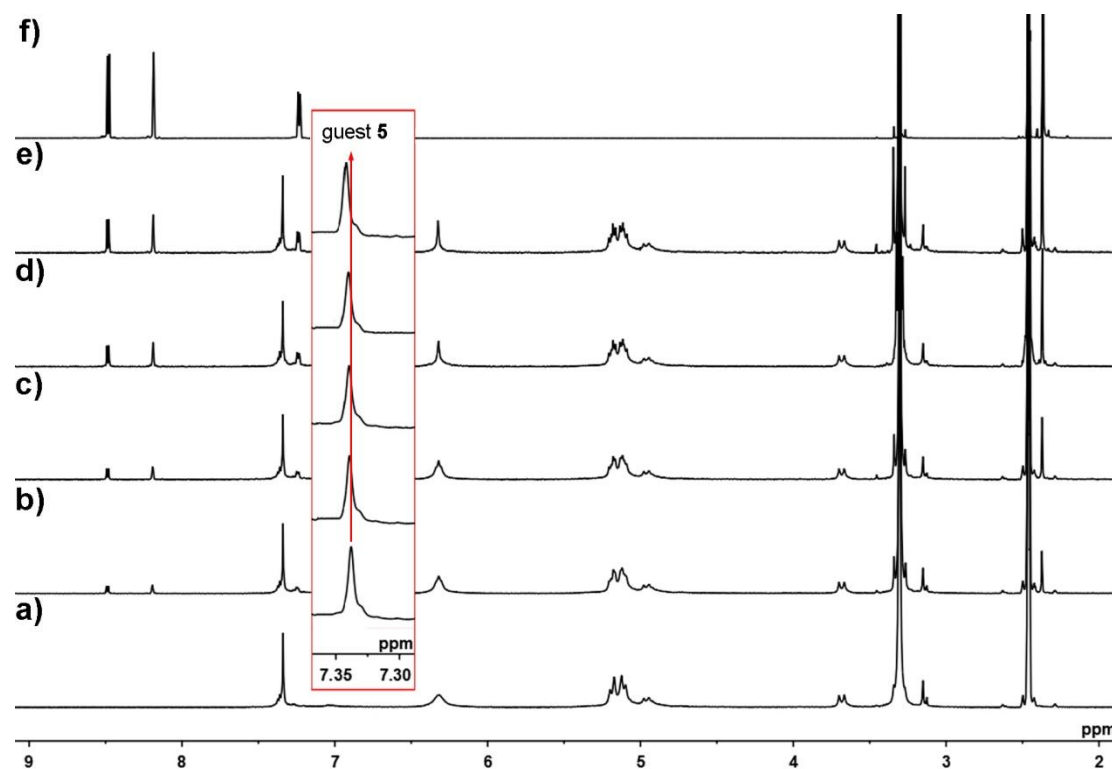


Figure S7  $^1\text{H}$  NMR spectra (400 MHz,  $[\text{D}_6]\text{DMSO}$ ) of a) free benzo[6]uril **1** ( $2.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ), and in the presence of b) 0.5 equiv.; c) 1.0 equiv.; d) 2.0 equiv.; e) 3.0 equiv. of guest **5**, and f) free guest **5**.

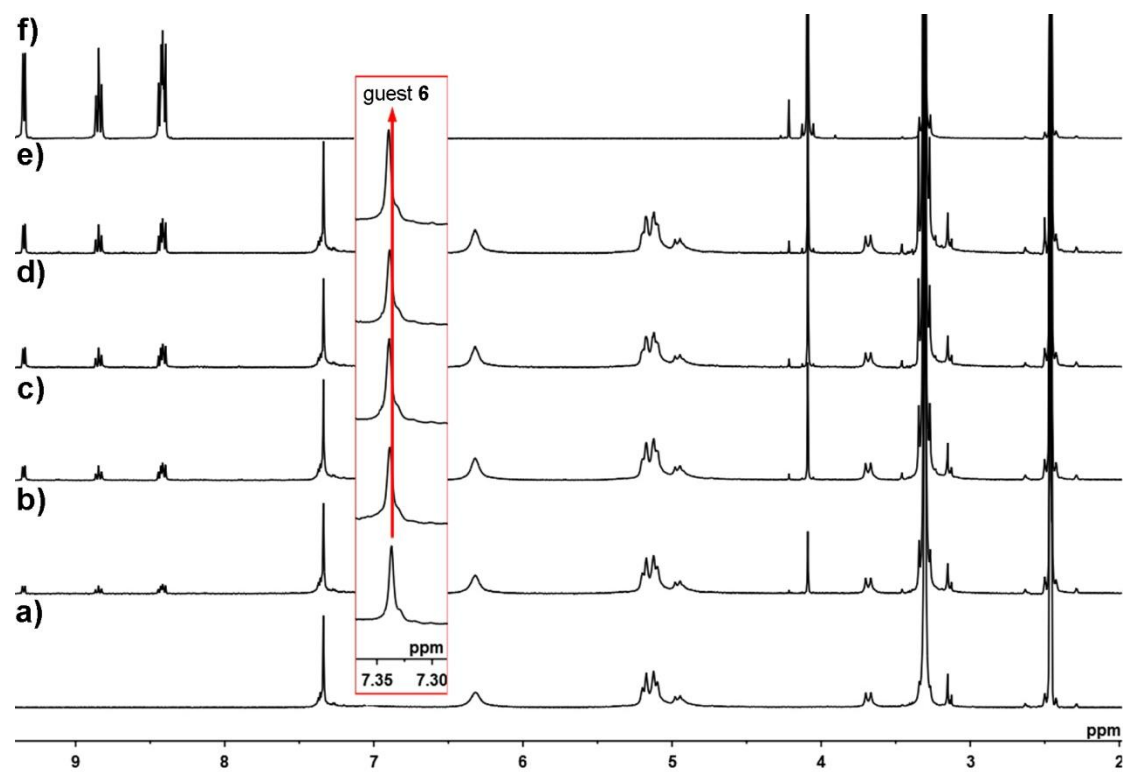


Figure S8  $^1\text{H}$  NMR spectra (400 MHz,  $[\text{D}_6]\text{DMSO}$ ) of a) free benzo[6]uril **1** ( $2.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ), and in the presence of b) 0.5 equiv.; c) 1.0 equiv.; d) 2.0 equiv.; e) 3.0 equiv. of guest **6**, and f) free guest **6**.

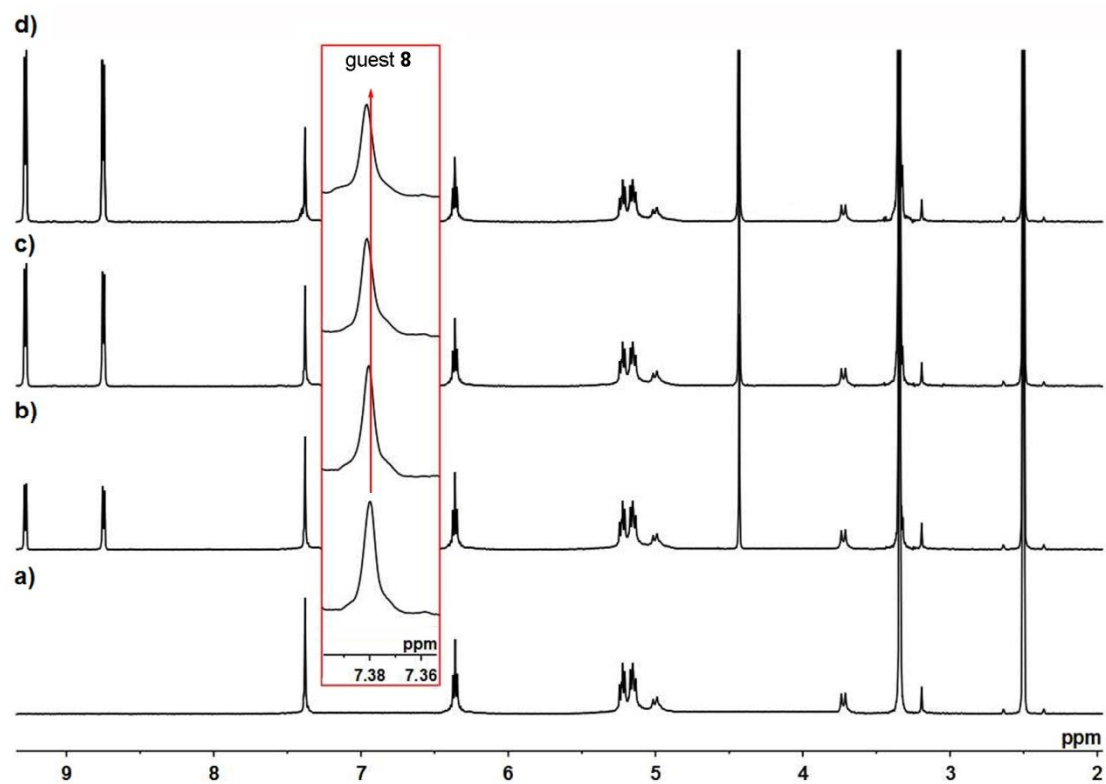


Figure S9 <sup>1</sup>H NMR spectra (400 MHz, [D<sub>6</sub>]DMSO) of a) free benzo[6]juril **1** ( $2.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ), and in the presence of b) 2.0 equiv.; c) 4.0 equiv.; d) 6.0 equiv. of guest **8**.

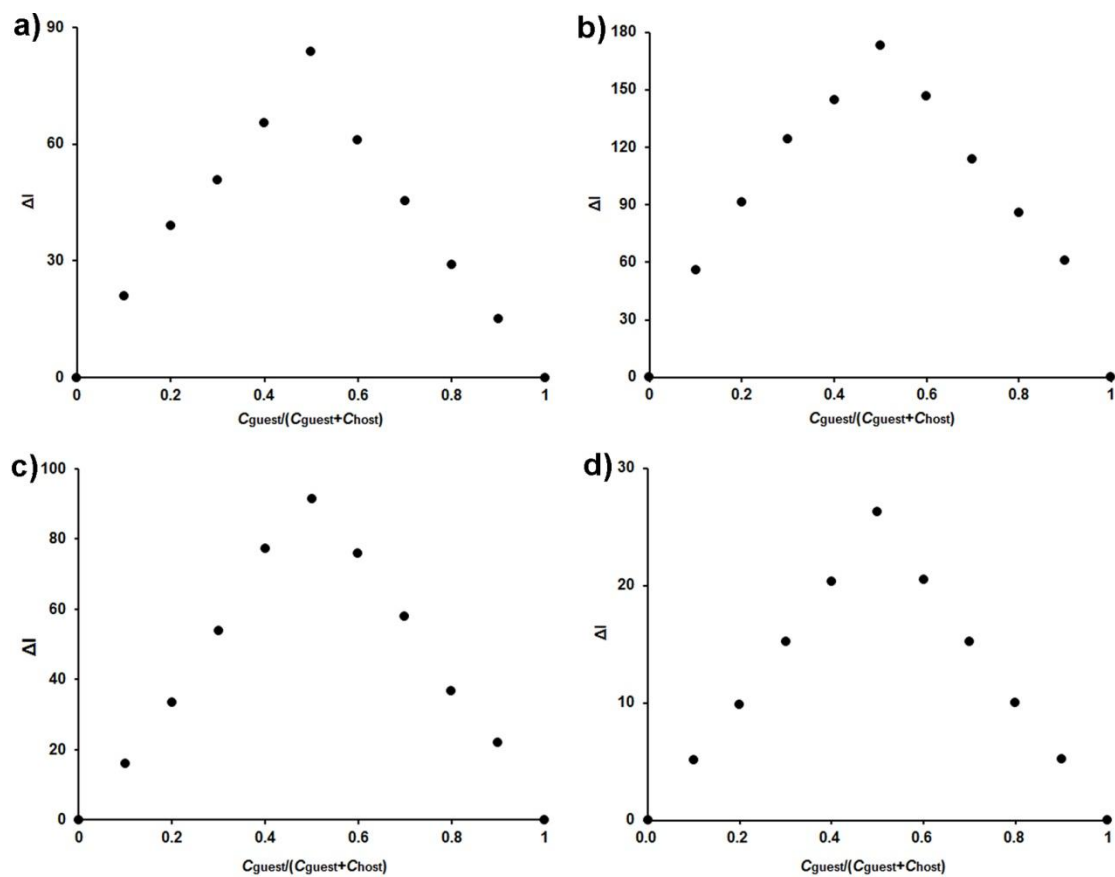


Figure S10 Job's plots of the interaction between benzo[6]uril **2** and a) guest **3**; b) guest **4**; c) guest **5**; d) guest **8**. The total concentration was maintained at  $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ , and fluorescence intensities were recorded at  $\lambda_{\text{em}} = 327 \text{ nm}$ ,  $\lambda_{\text{ex}} = 304 \text{ nm}$  for host **2** system.

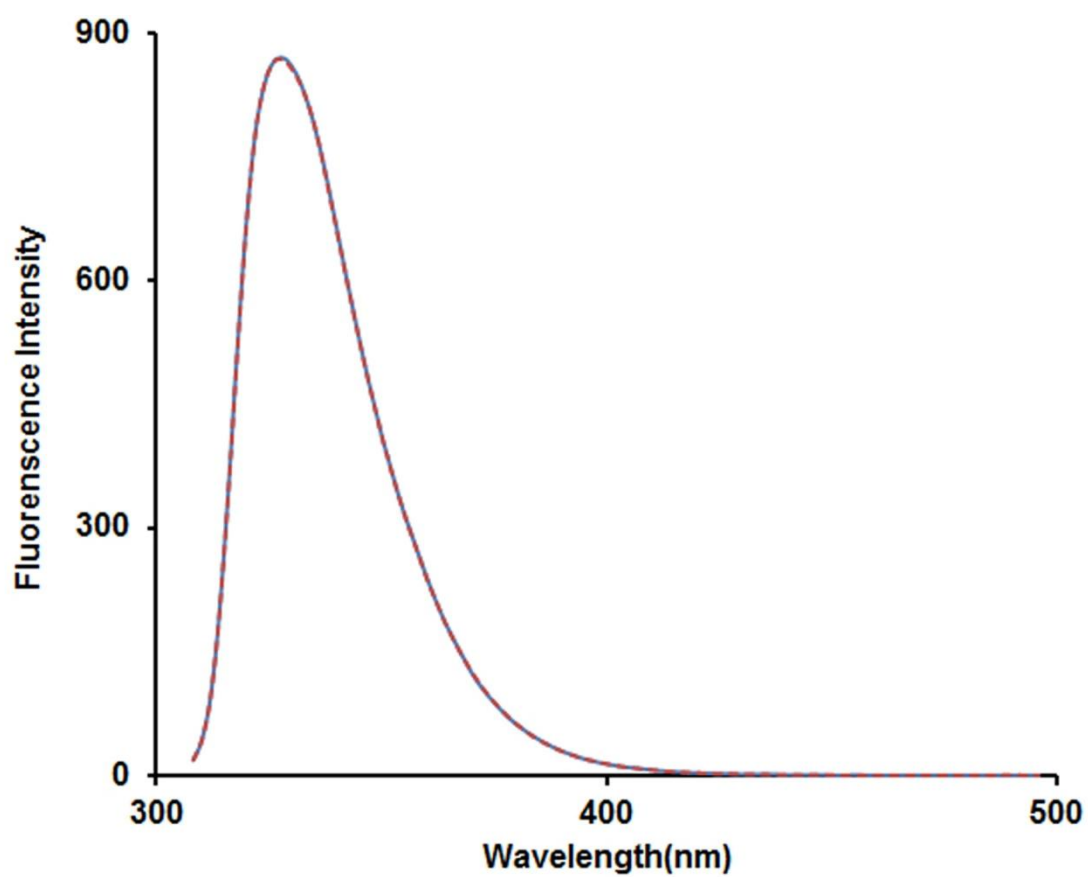


Figure S11 Fluorescence spectra of benzo[6]uril **2** ( $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  in  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ , 5:1, v/v) in the absence (blue solid) and presence of 1 eq. guest **7** (red dash).

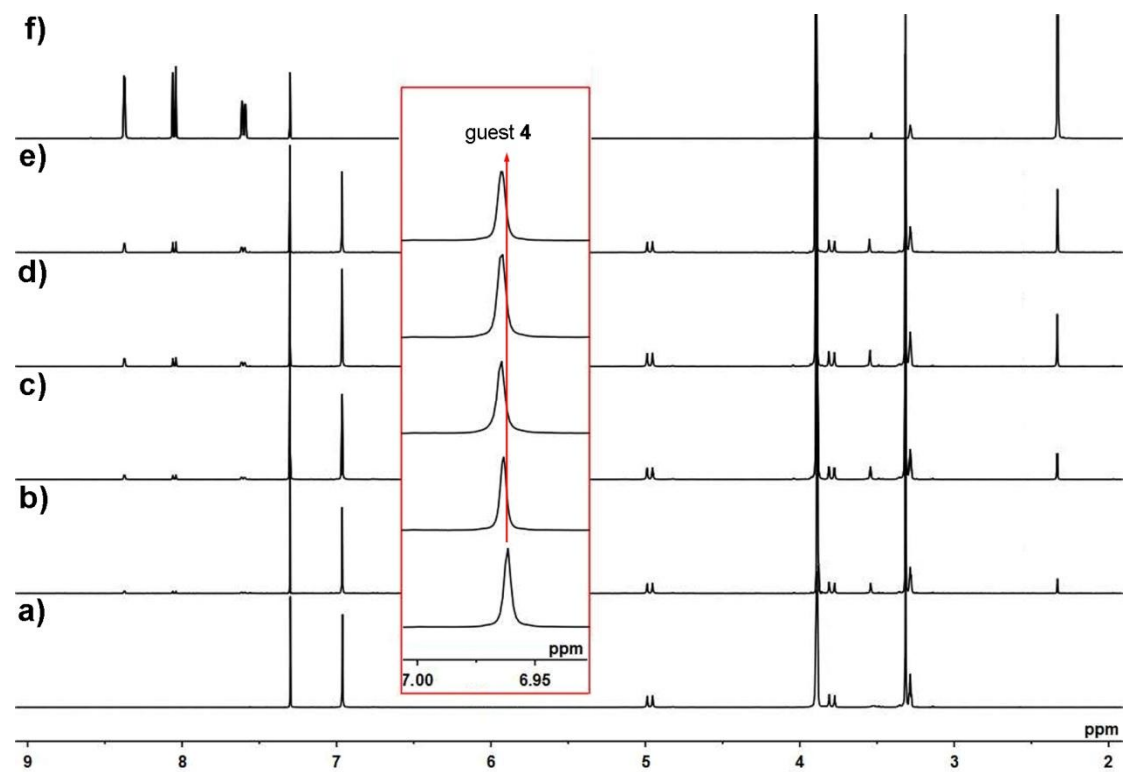


Figure S12  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3/\text{CD}_3\text{OD}$ , 5:1, v/v) of a) benzo[6]uril **2** ( $2.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ), and in the presence of b) 0.5 equiv.; c) 1.0 equiv.; d) 2.0 equiv.; and e) 3.0 equiv. of guest **4**, and f) free guest **4**.

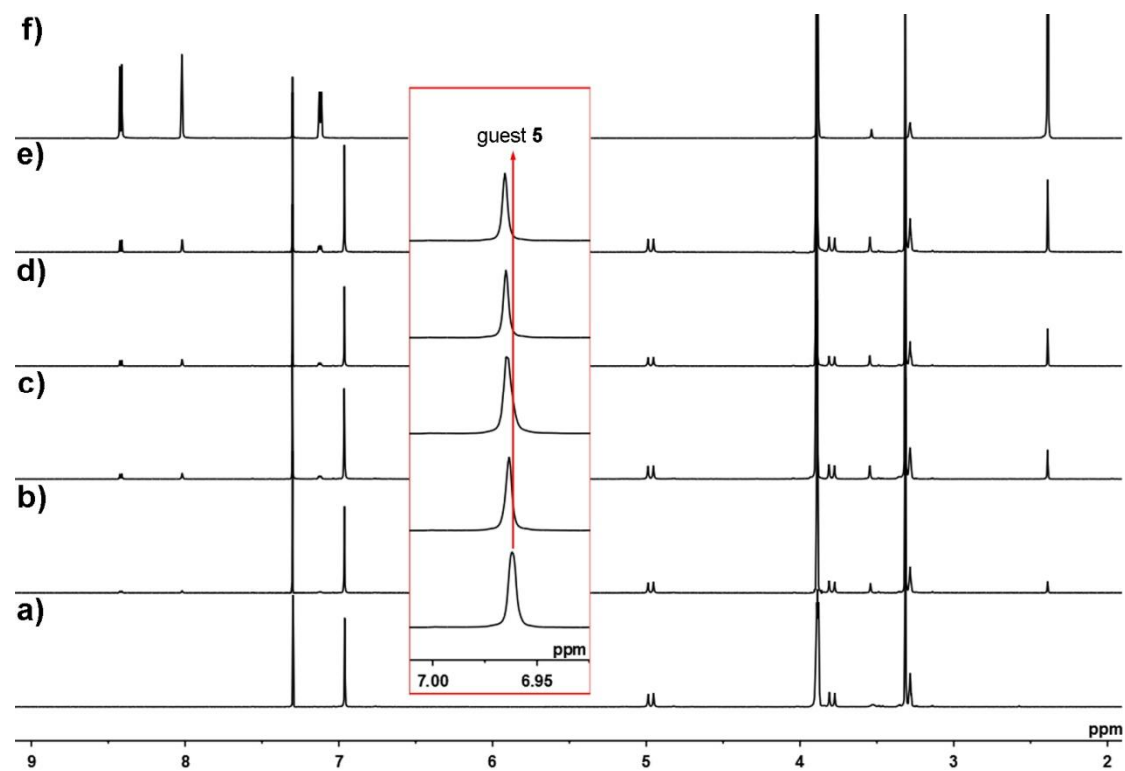


Figure S13  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3/\text{CD}_3\text{OD}$ , 5:1, v/v) of a) benzo[6]uril 2 ( $2.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ), and in the presence of b) 0.5 equiv.; c) 1.0 equiv.; d) 2.0 equiv.; and e) 3.0 equiv. of guest 5, and f) free guest 5.

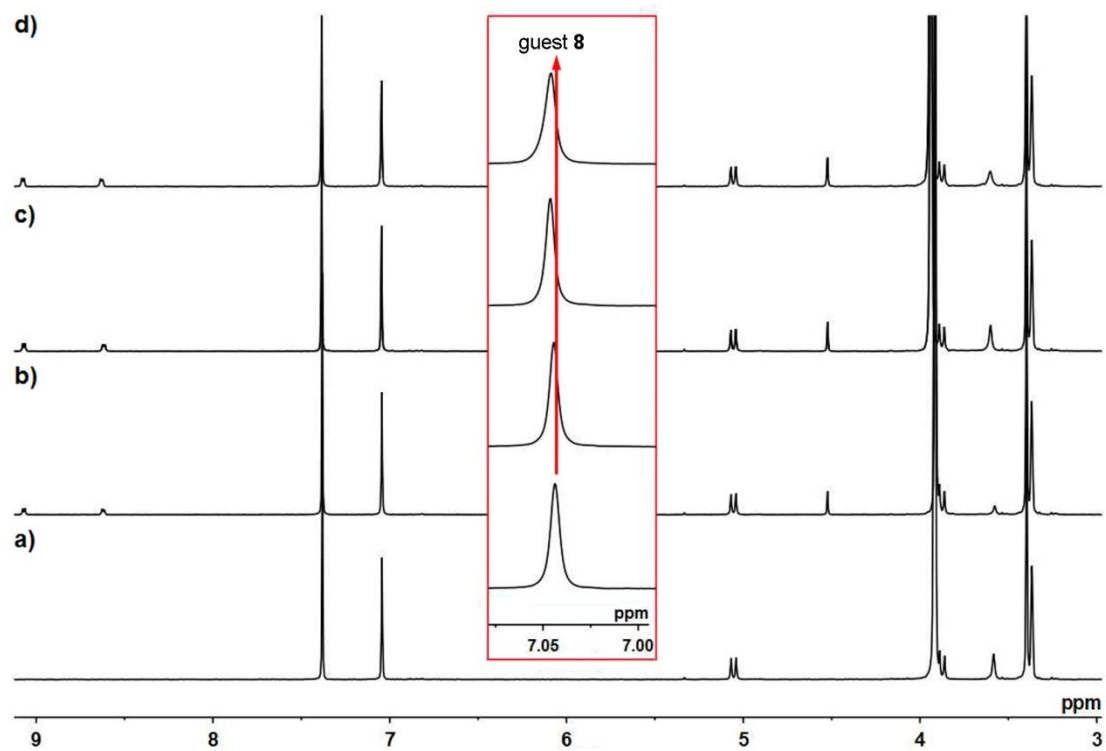


Figure S14 <sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>OD, 5:1, v/v) of a) benzo[6]uril 2 ( $2.0 \times 10^{-3}$  mol · L<sup>-1</sup>), and in the presence of b) 0.2 equiv.; c) 0.4 equiv.; and d) 0.6 equiv. of guest 8.

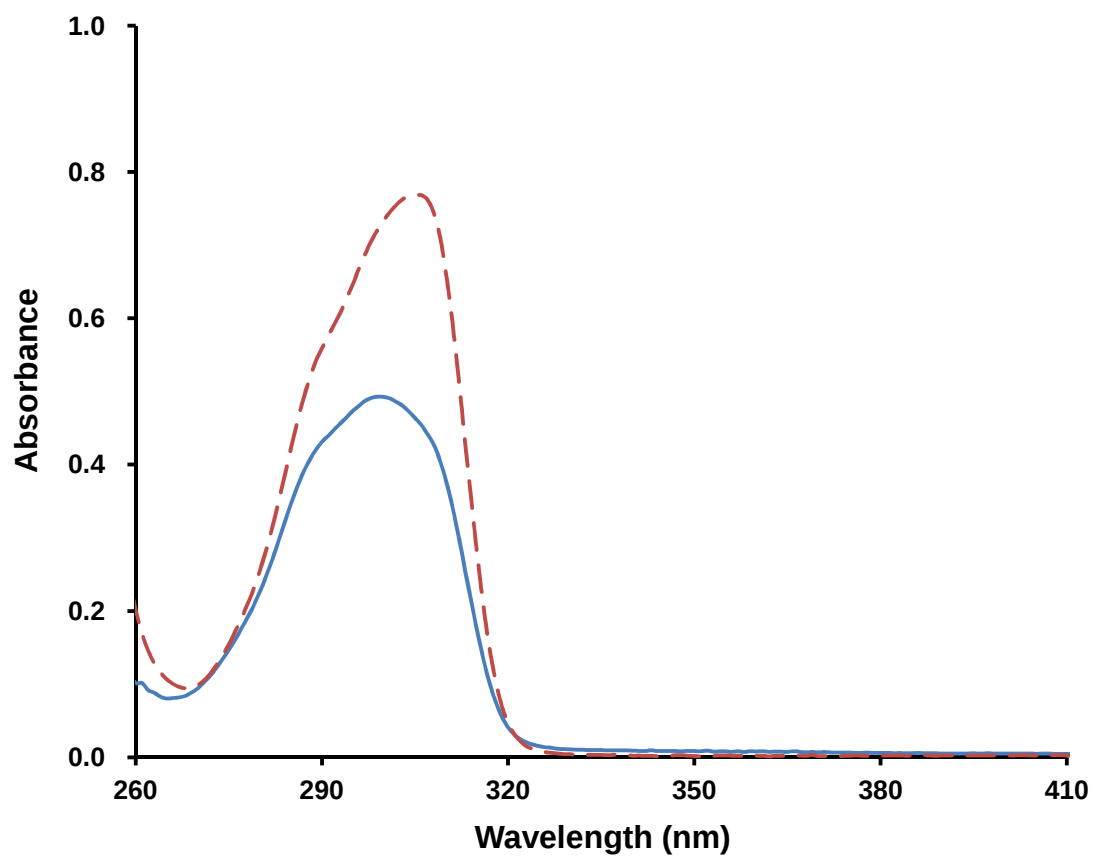


Figure S15 UV-vis spectra of benzo[6]uril **1** in DMSO ( $1.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ , solid line) and benzo[6]uril **2** in  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  (v/v, 5:1;  $1.5 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ , dash line).

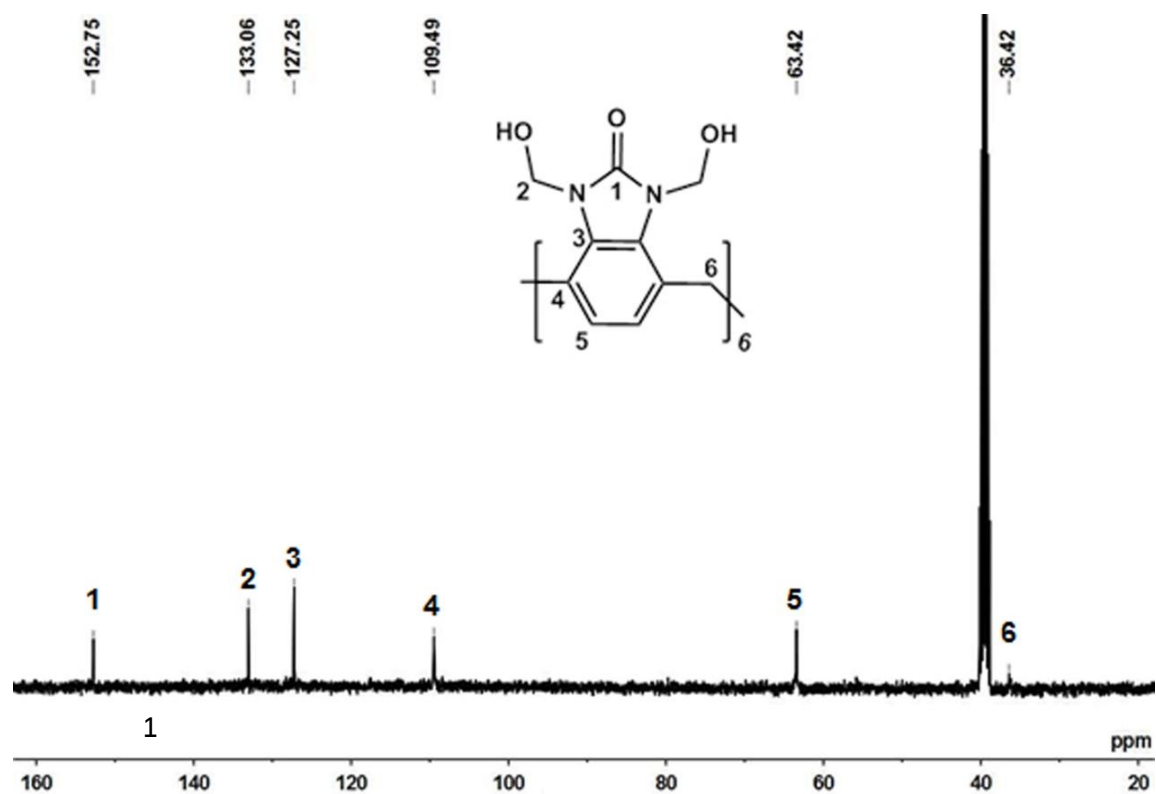


Figure S16  $^{13}\text{C}$  NMR spectrum of benzo[6]uril 1.

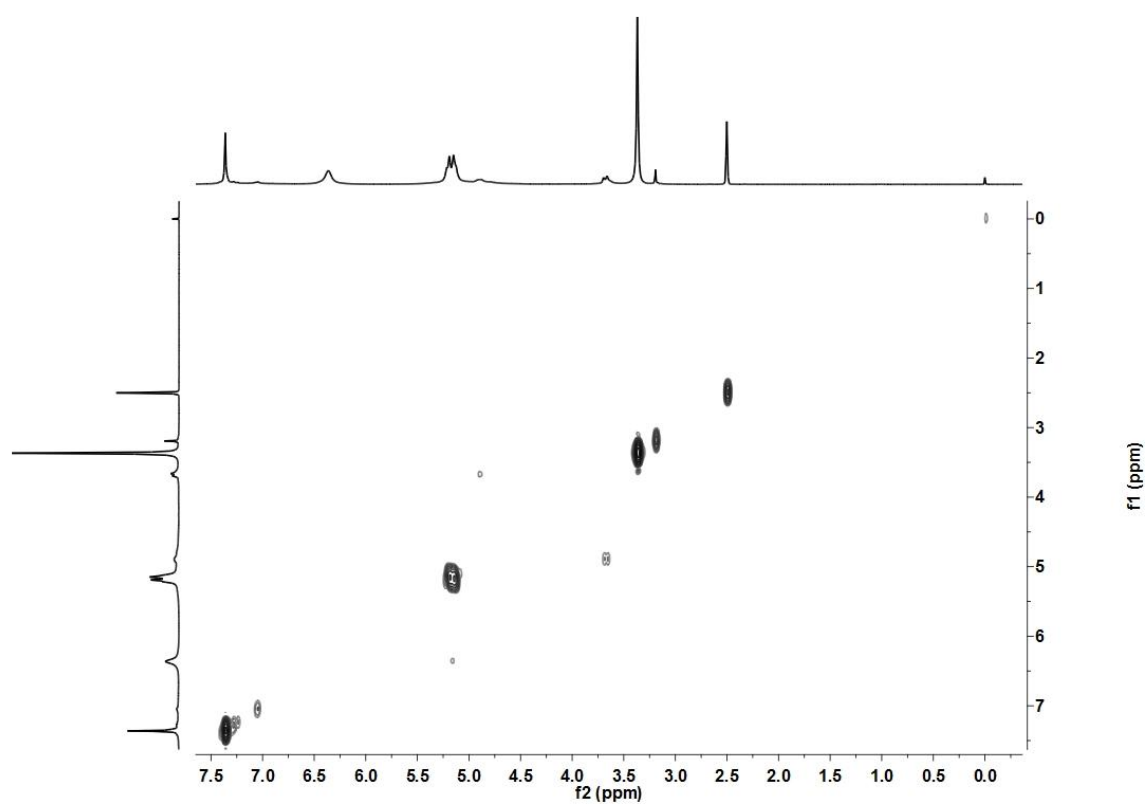


Figure S17 gCOSY NMR spectrum of benzo[6]uril **1**.

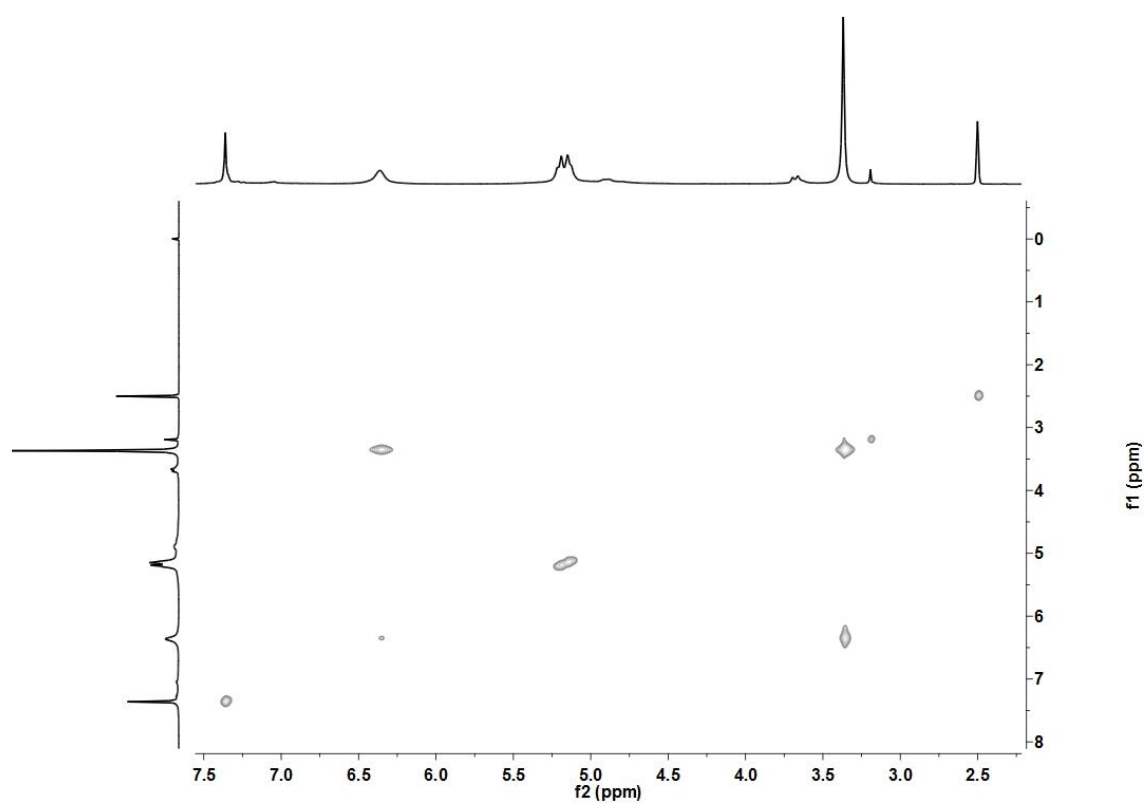


Figure S18 NOESY NMR spectrum of benzo[6]uril **1**.

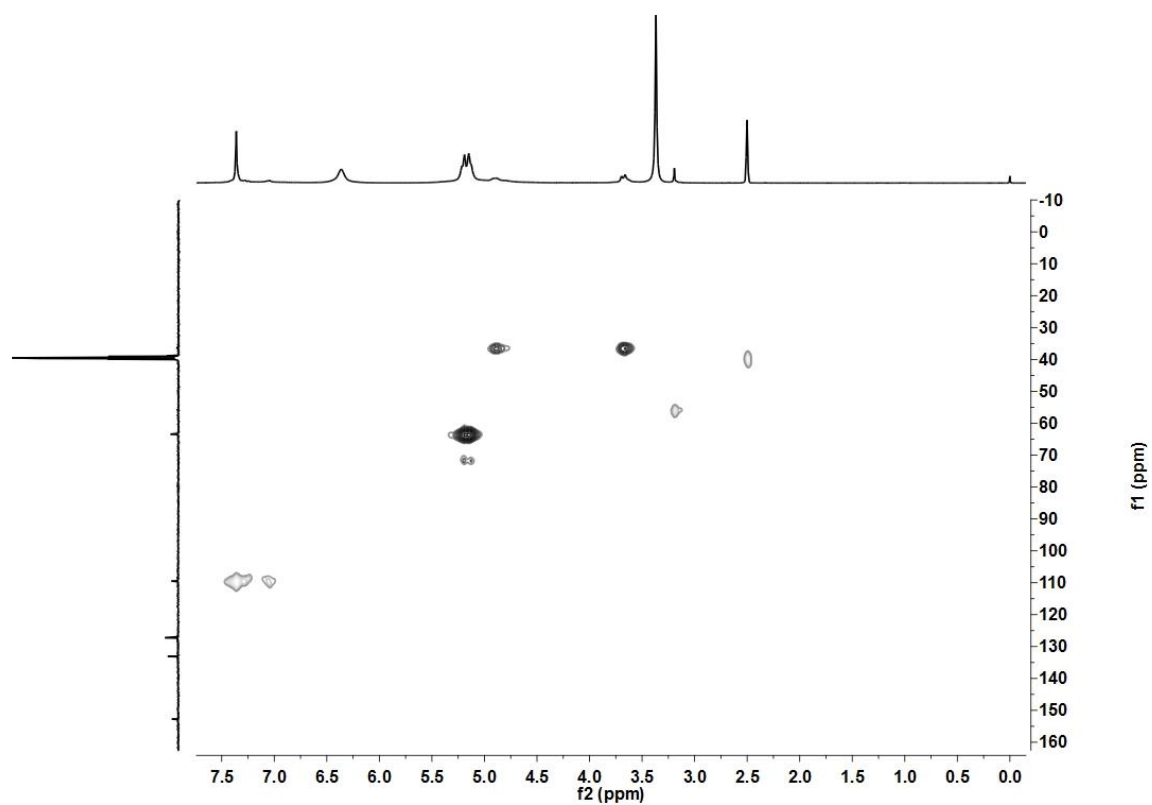


Figure S19 gHSQC (Heteronuclear Single Quantum Correlation) NMR spectrum of benzo[6]uril **1**.

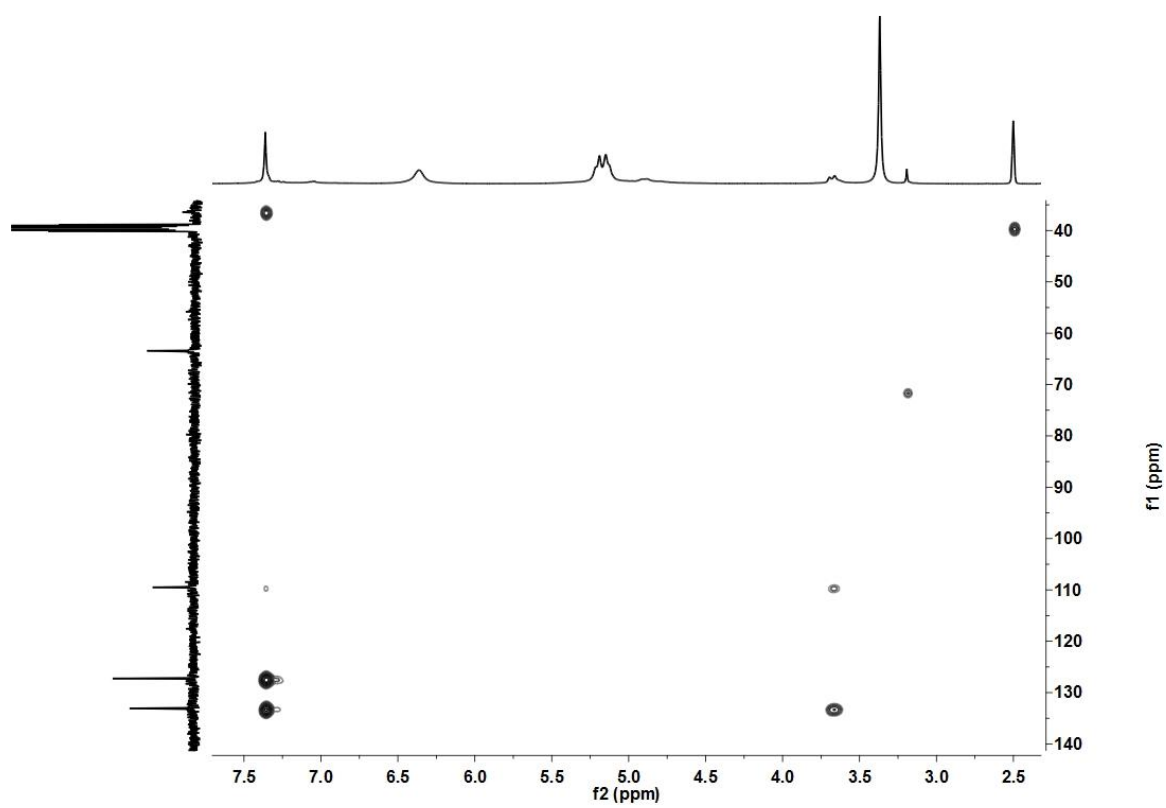


Figure S20 gHMBC (Heteronuclear Multiple Bond Correlation) NMR spectrum of benzo[6]uril **1**.

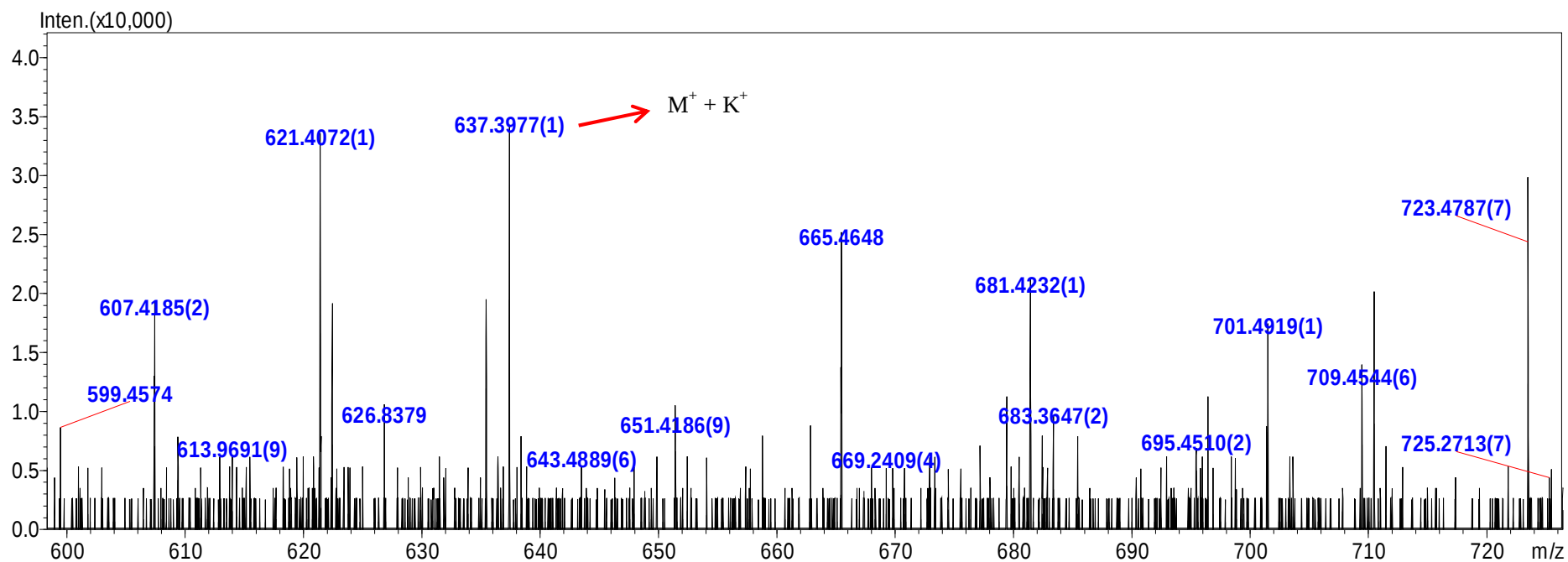


Figure S21 High resolution MS of benzo[6]uril 1.

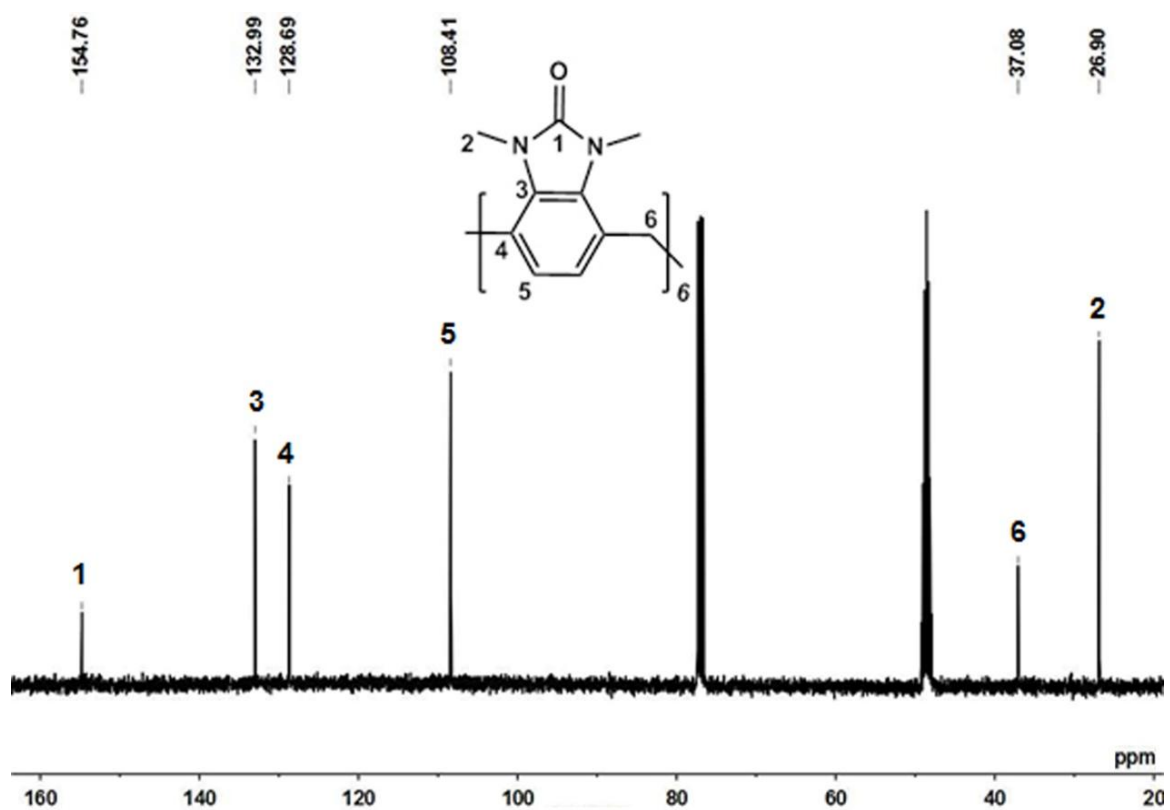


Figure S22  $^{13}\text{C}$  NMR spectrum of benzo[6]uril 2.

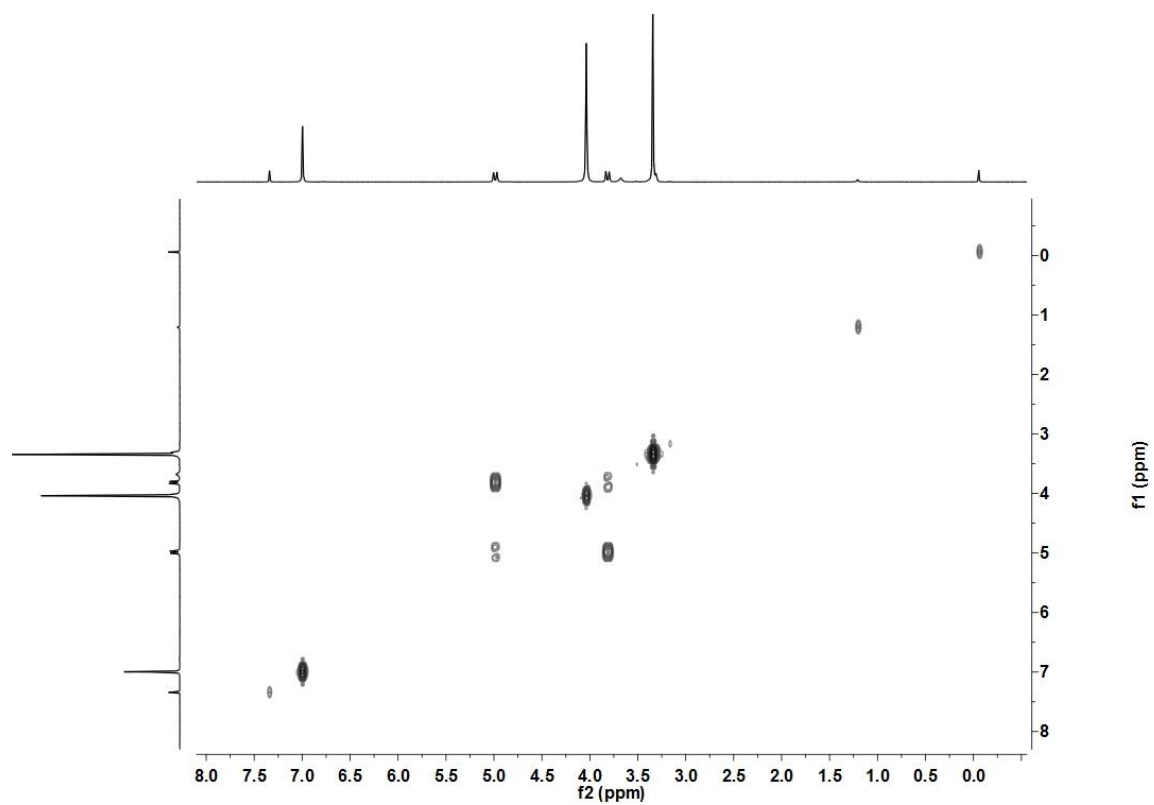


Figure S23 gCOSY NMR spectrum of benzo[6]uril **2**.

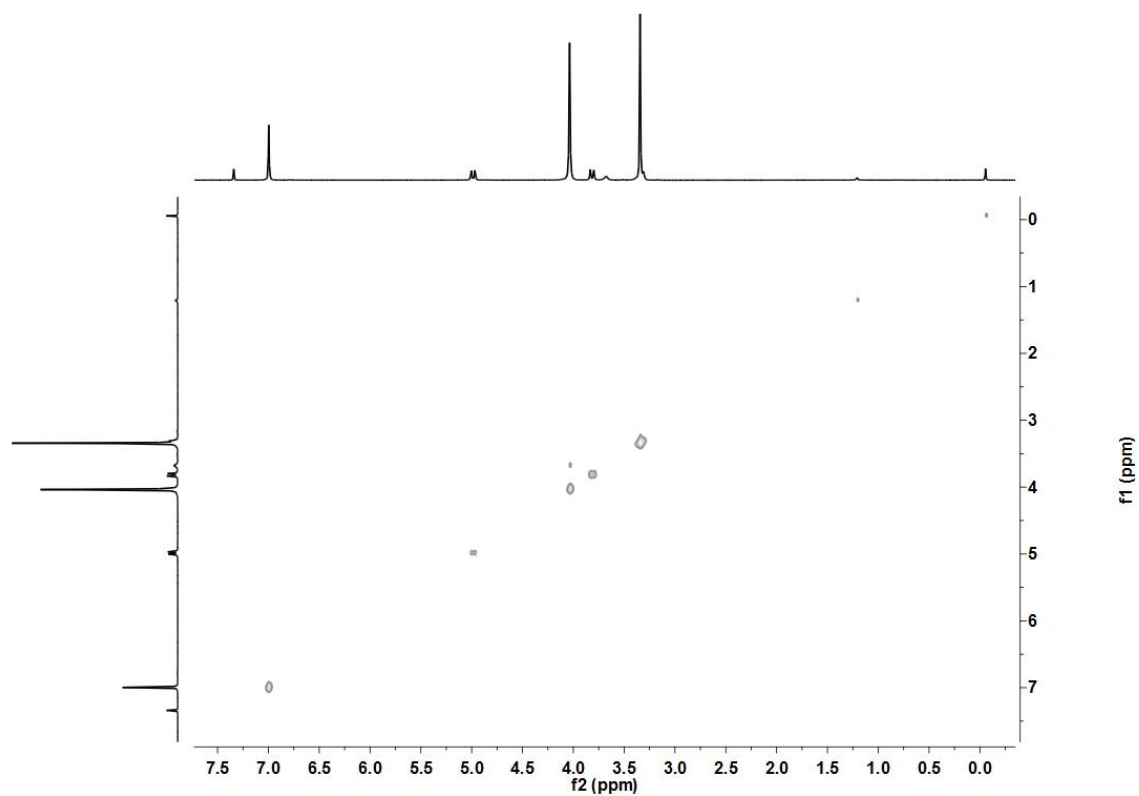


Figure S24 NOESY NMR spectrum of benzo[6]uril 2.

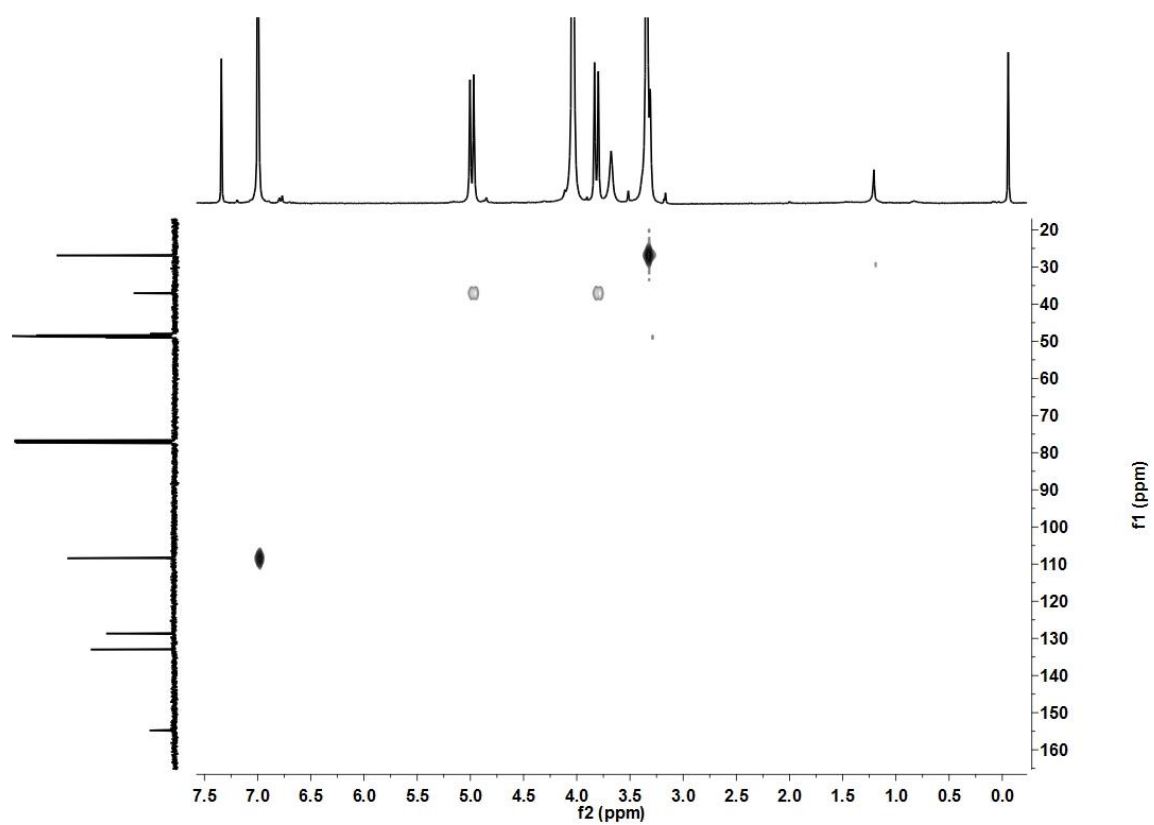


Figure S25 gHSQC (Heteronuclear Single Quantum Correlation) NMR spectrum of benzo[6]uril 2.

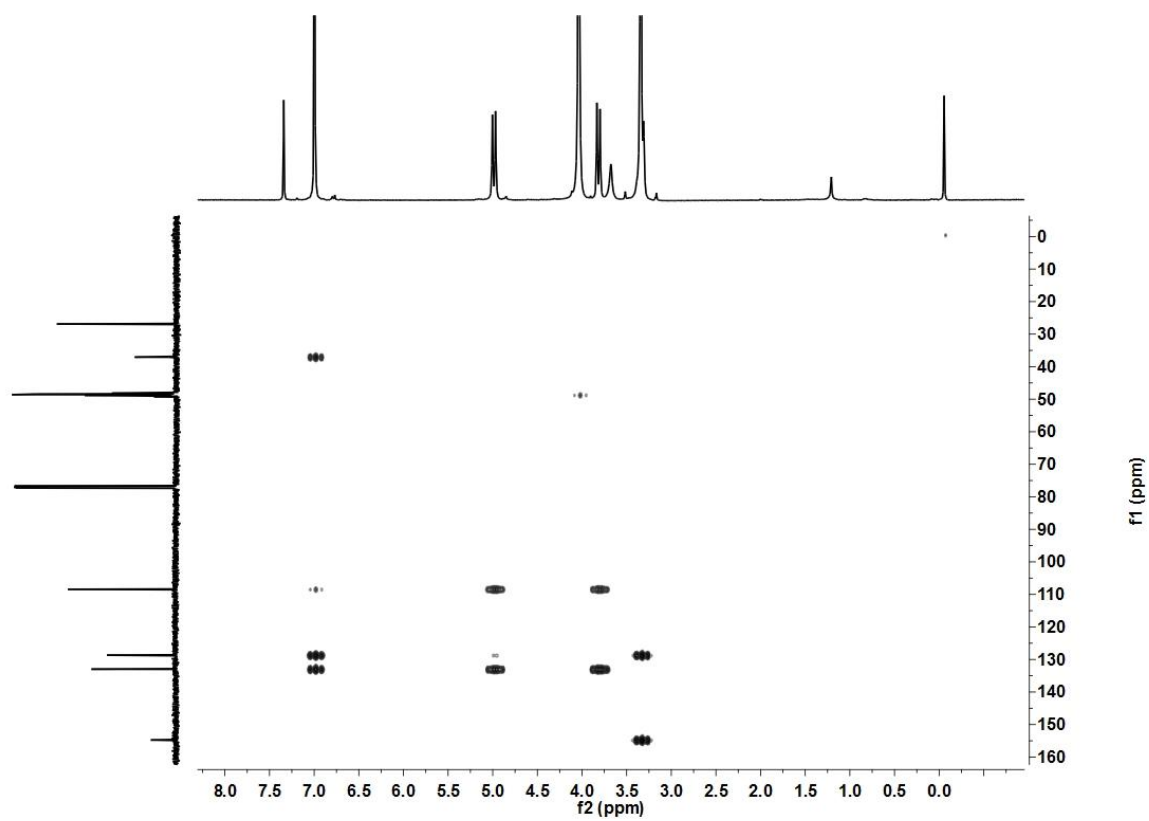


Figure S26 gHMBC (Heteronuclear Multiple Bond Correlation) NMR spectrum of benzo[6]uril 2.

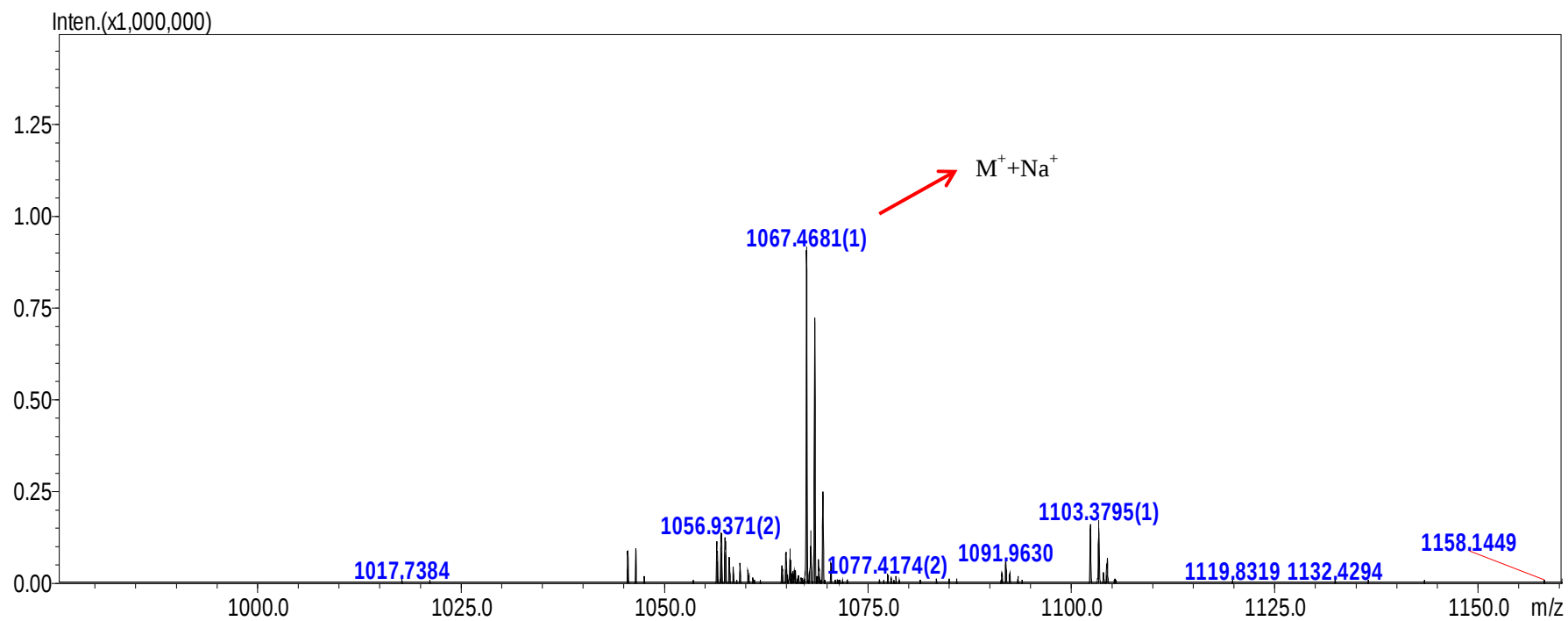


Figure S27 High resolution MS of benzo[6]uril 2.