

## Electronic Supplementary Information

### *Synthetic minimalistic tryptophan zippers as chiroptical switch*

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## 2D NMR spectroscopy

COSY, ROESY, and NOESY were recorded on a Bruker Avance 300 at 25°C. COSY spectrum of **1a-1c** was recorded by collecting 1024 complex data points in the  $t_2$  domain by averaging 16scans and 2048 increments in the  $t_1$  domain with a mixing time 800ms. NOESY spectrum was recorded by collecting 1024 complex data points in the  $t_2$  domain by averaging 16 scans and 1024 increments in the  $t_1$  domain with a mixing time 1000ms.

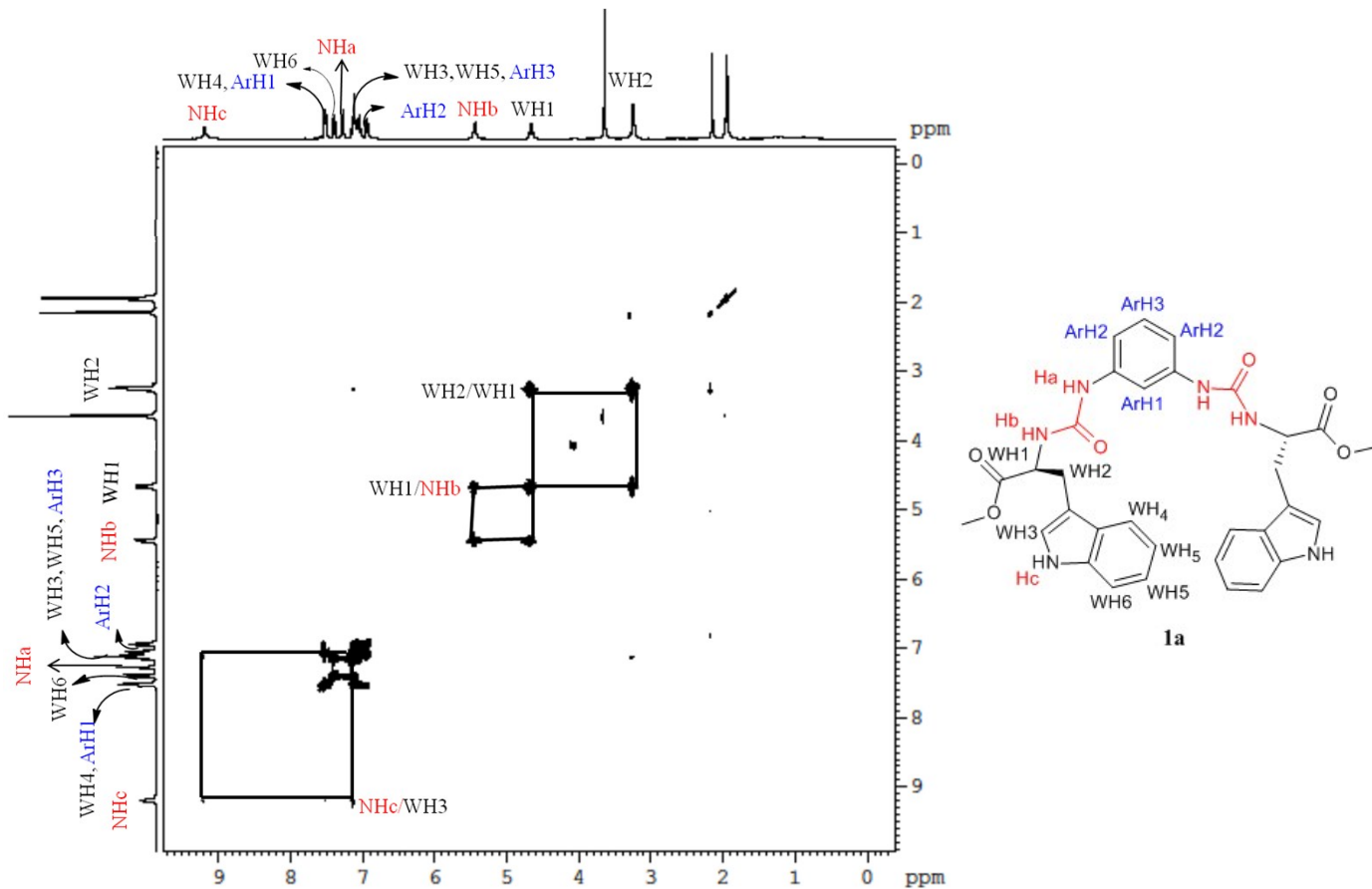
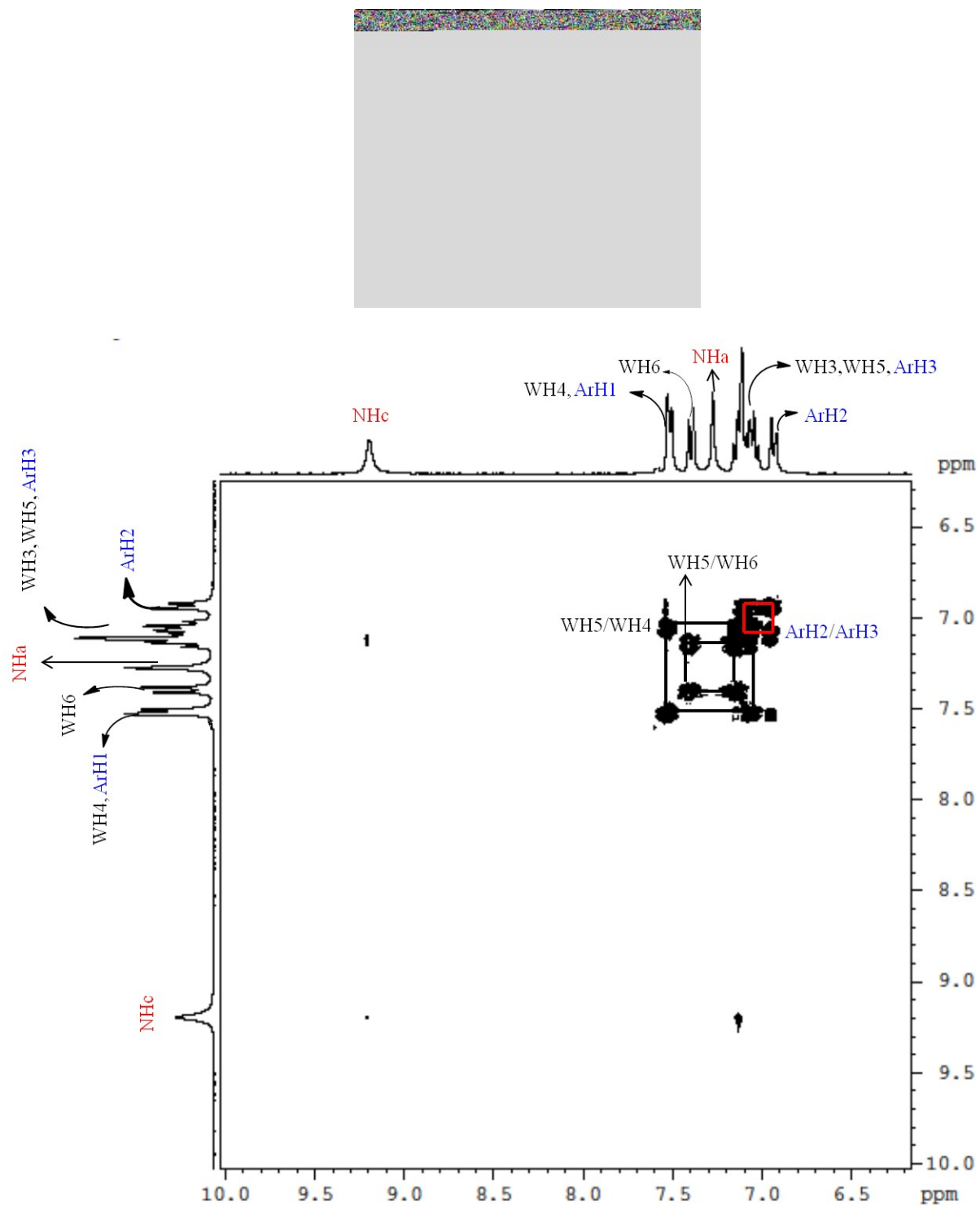


Figure S1. COSY (CD<sub>3</sub>CN, 300MHz) spectrum of **1a**



**Figure S2.** Selected region of COSY (CD<sub>3</sub>CN, 300MHz) spectrum of **1a**

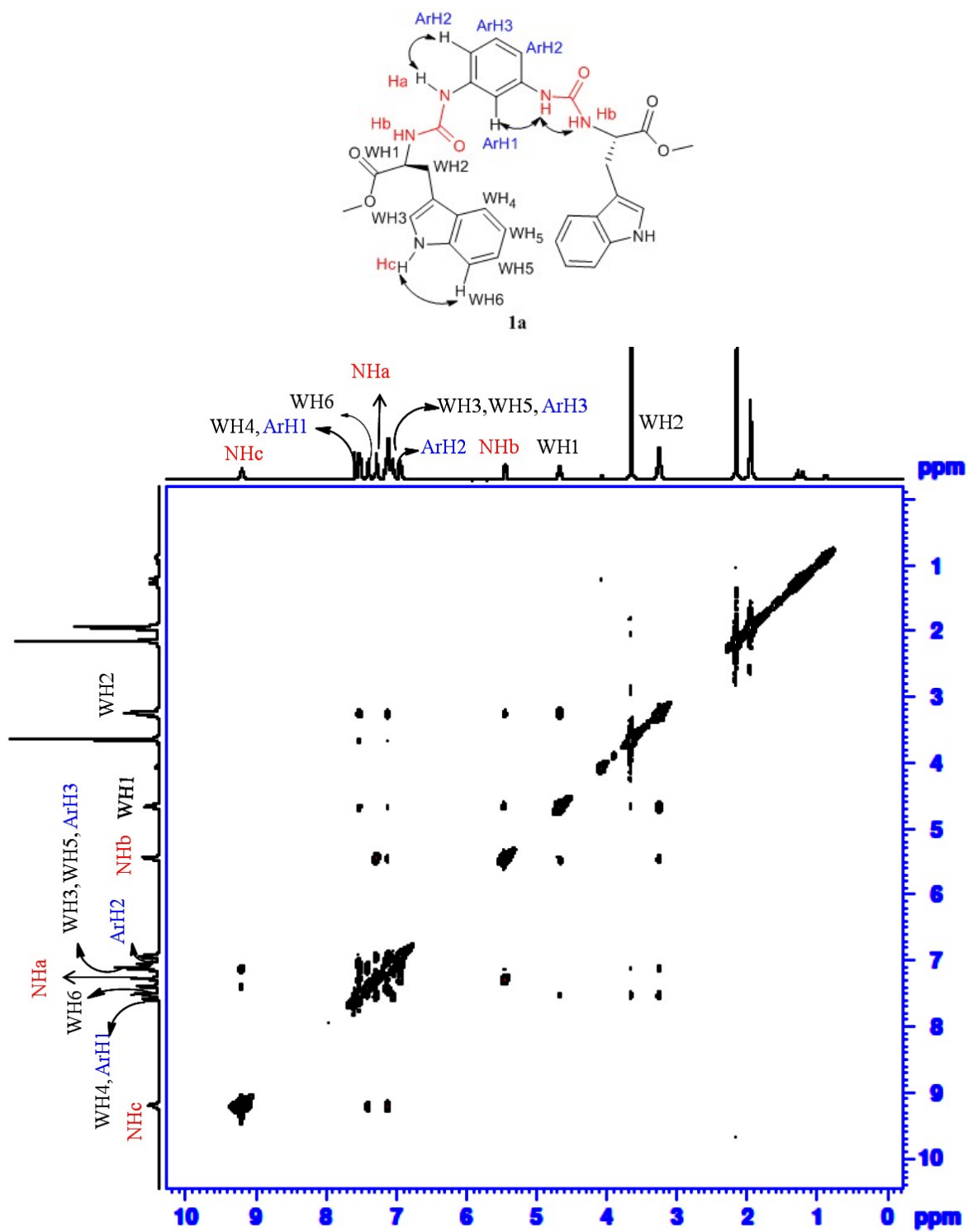
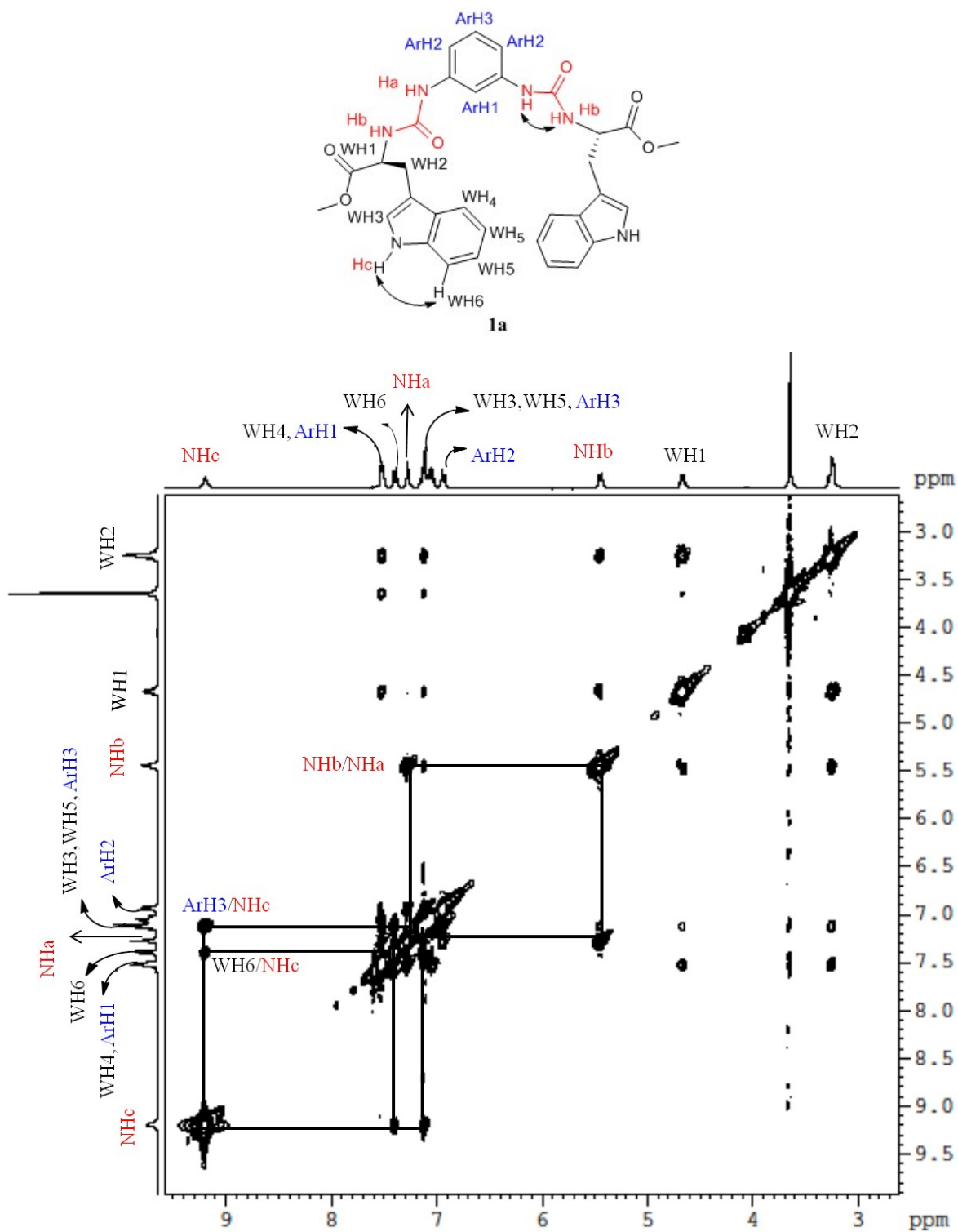
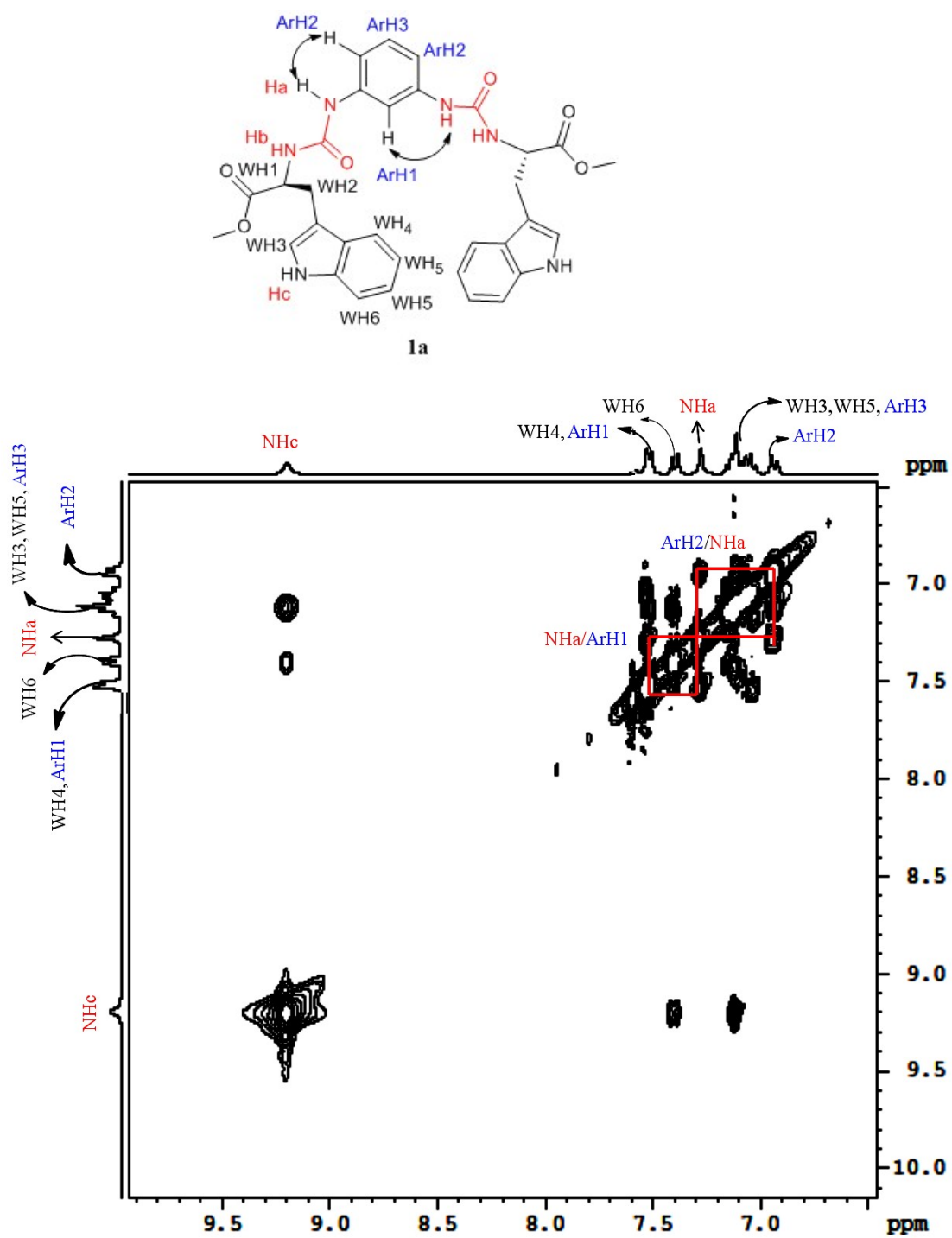


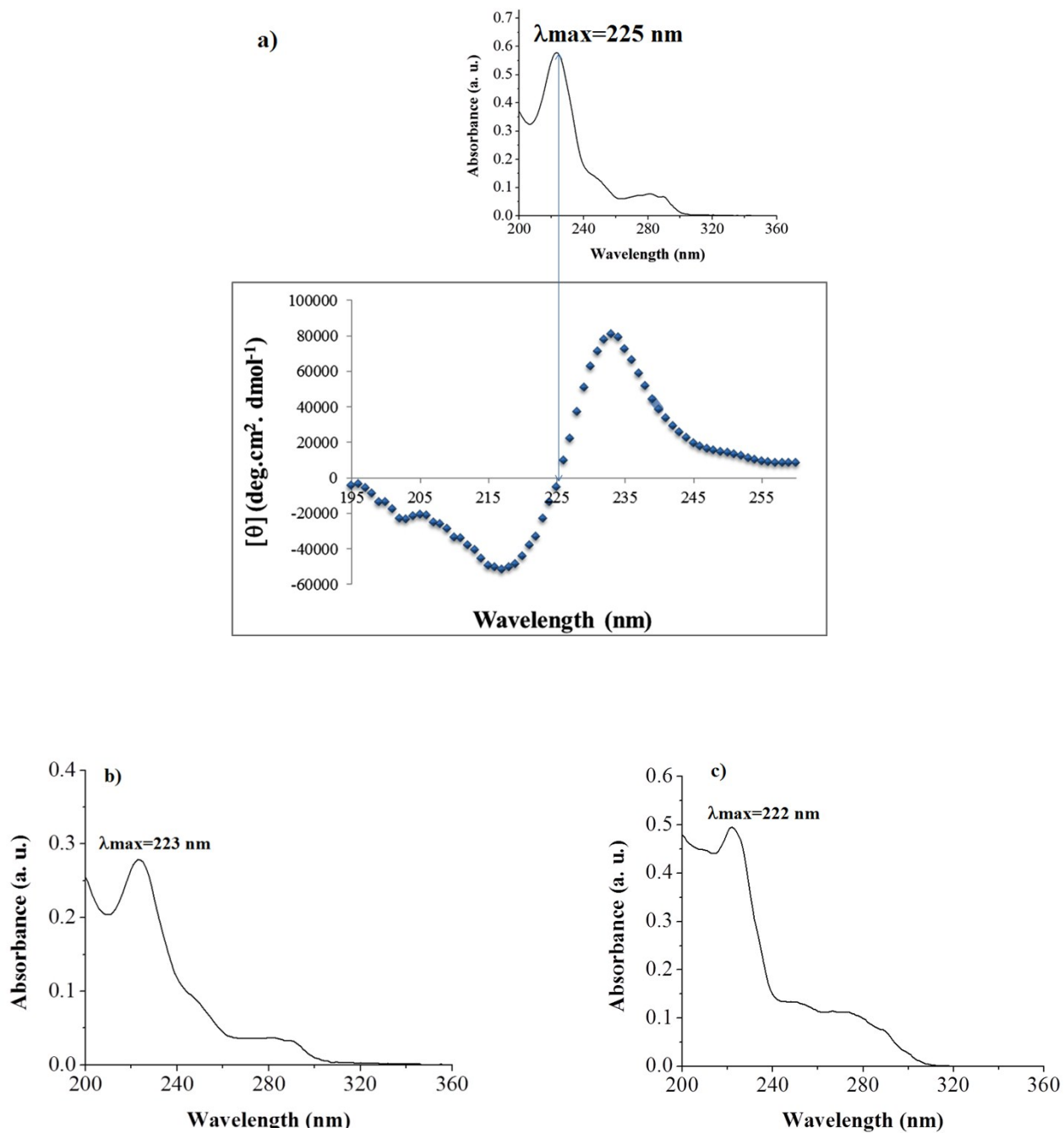
Figure S3. NOESY (CD<sub>3</sub>CN, 300MHz) spectrum of **1a**



**Figure S4.** Selected region of NOESY ( $\text{CD}_3\text{CN}$ , 300MHz) spectrum of **1a**

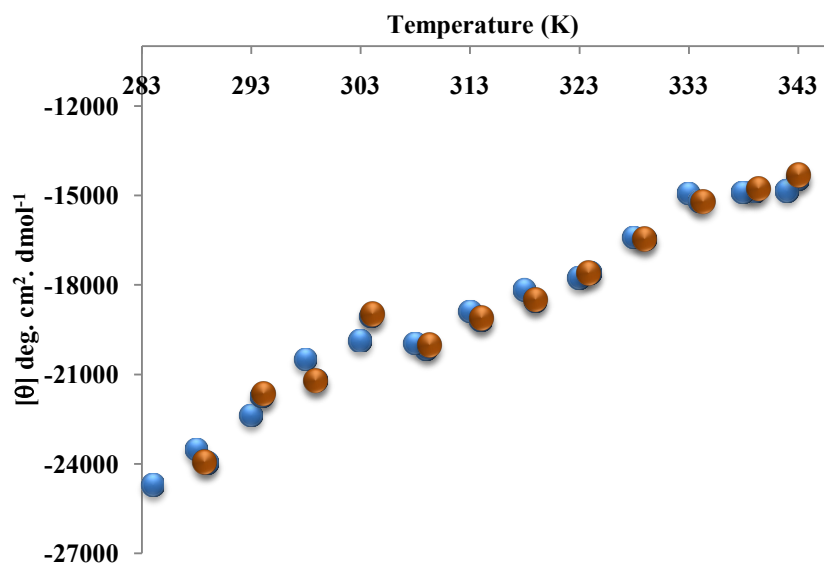


**Figure S5.** Selected region of NOESY (CD<sub>3</sub>CN, 300MHz) spectrum of **1a**

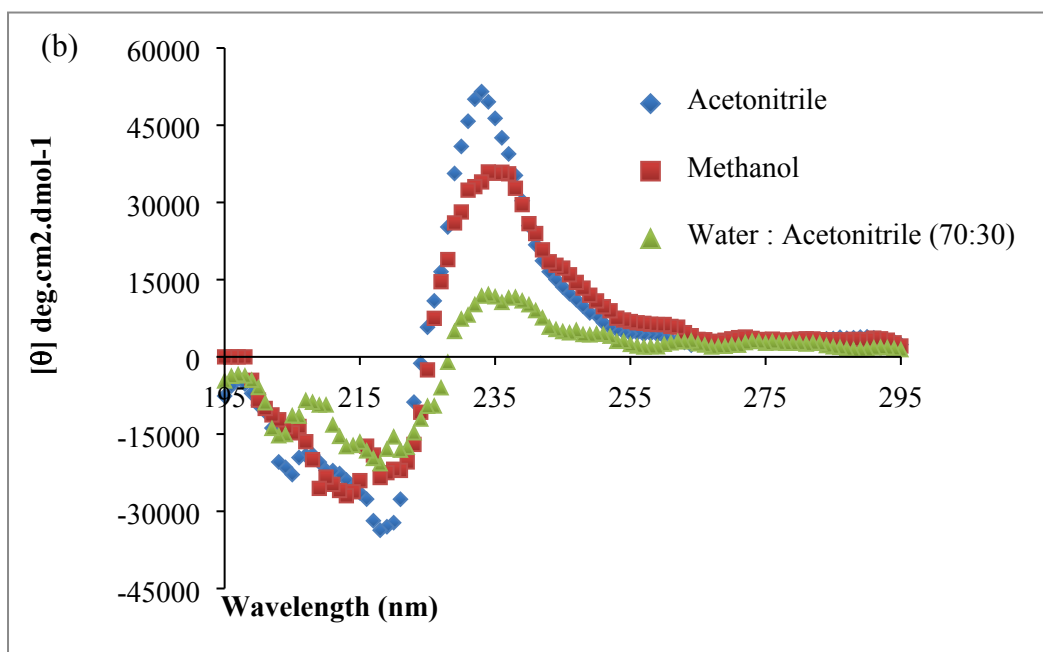
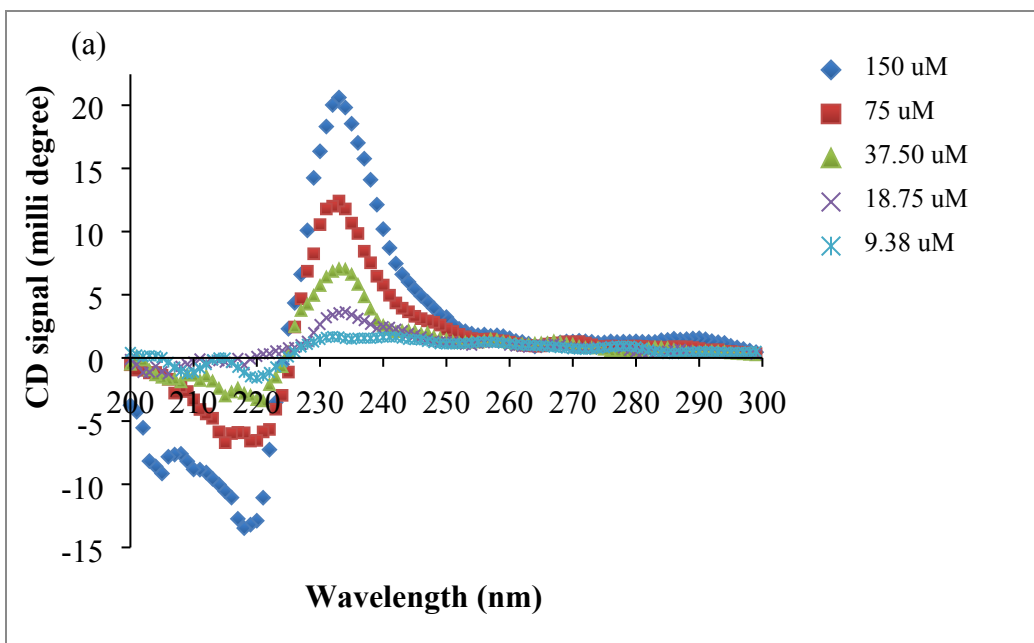


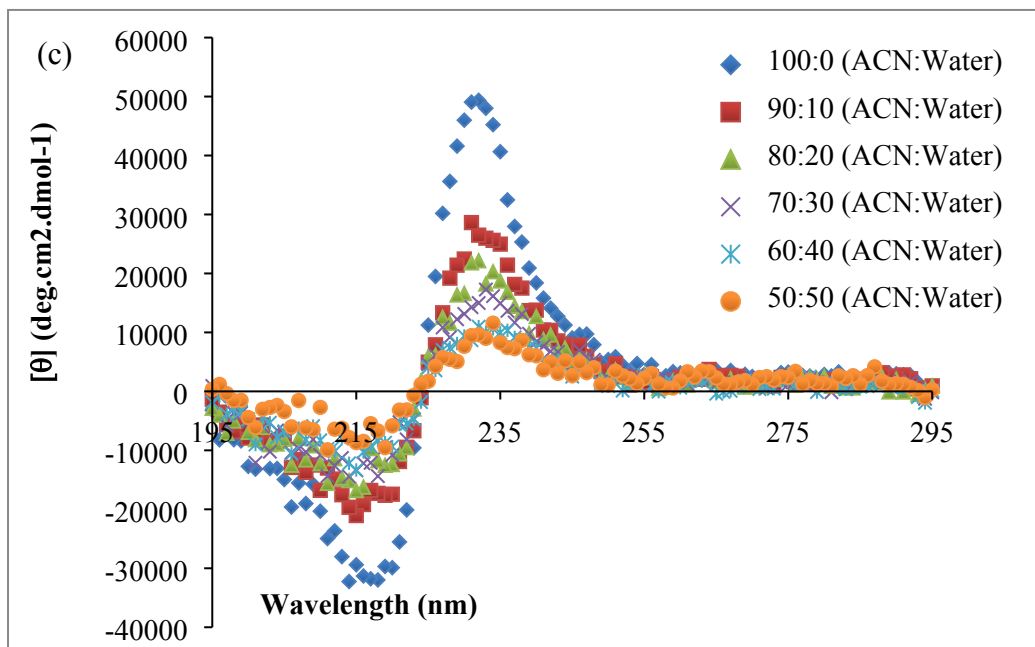
**Figure S6.** UV absorption spectra of a) **1a** (6.3  $\mu\text{M}$ ) showing absorption maximum coincides with zero cross-over point of CD, b) **1b** (6.3  $\mu\text{M}$ ), c) **1c** (6.3  $\mu\text{M}$ ).



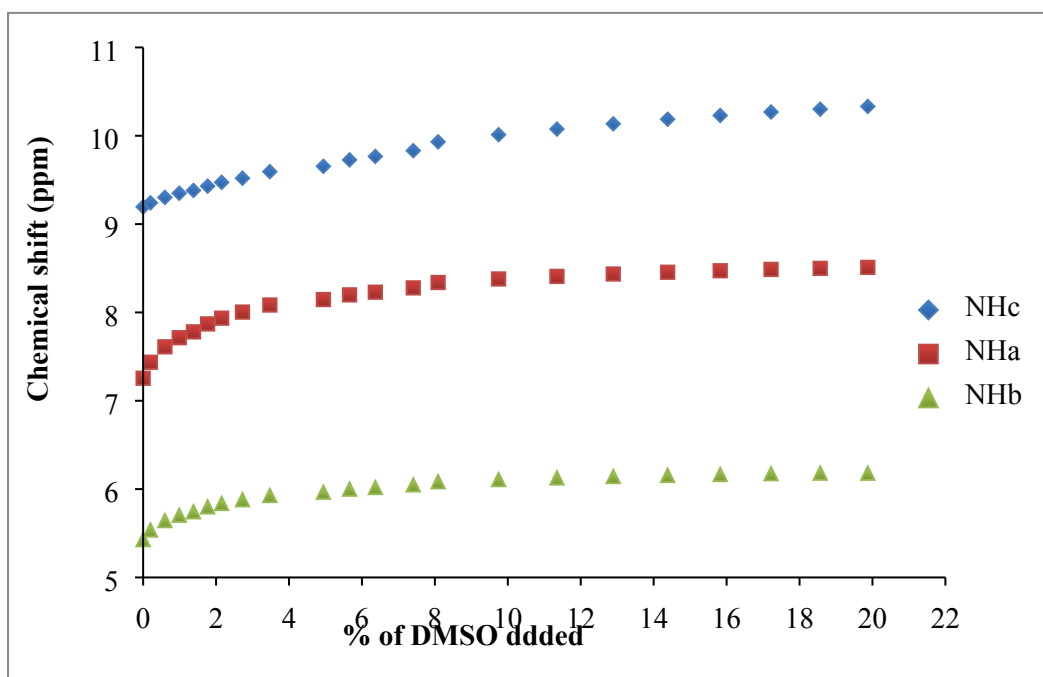


**Figure S7.** Thermal denaturation curve for **1c** at 235 nm (blue circle and red circle represents the forward and reverse melting curves respectively)

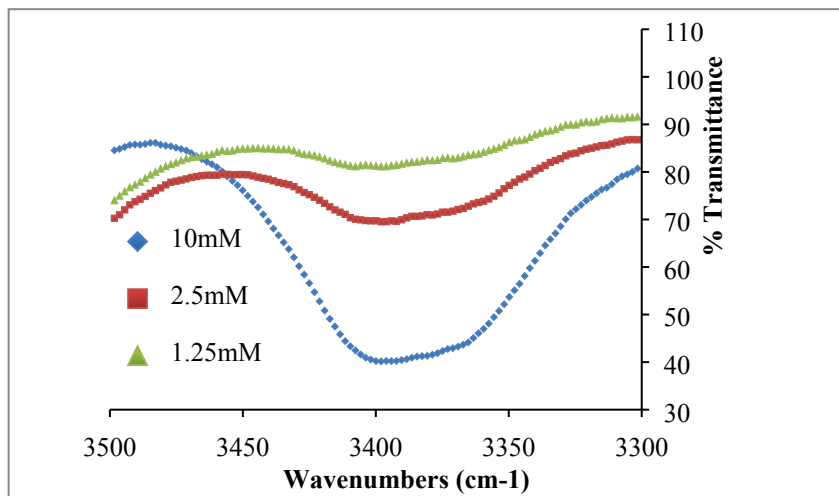




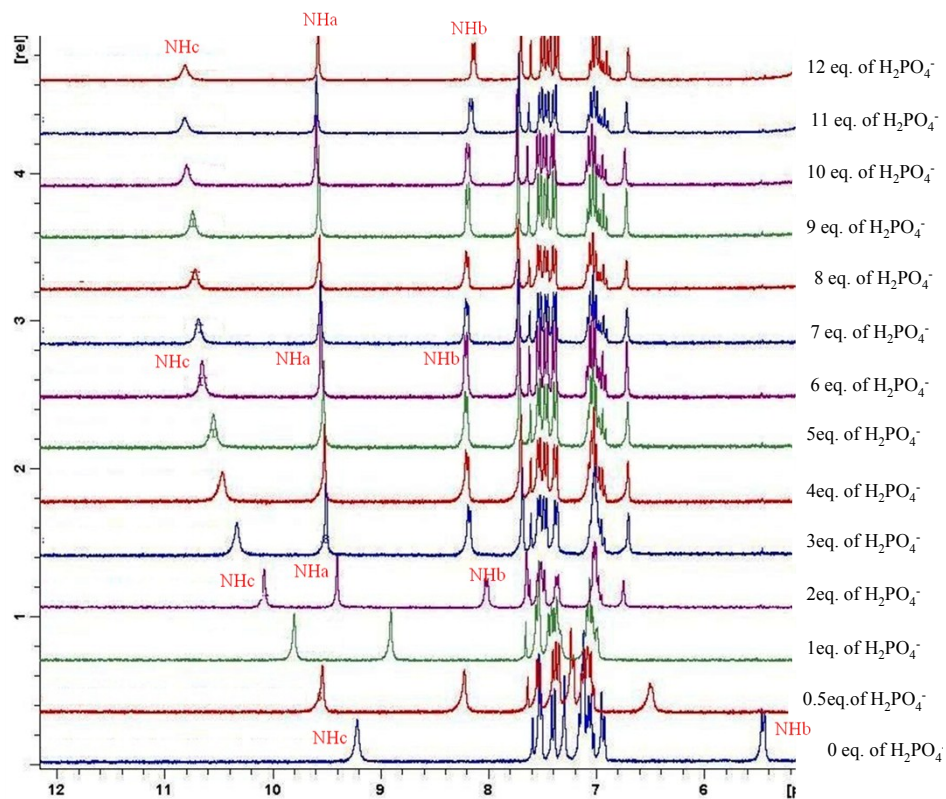
**Figure S8.** CD measurements to establish the intermolecular association in **1a** (a) at different concentrations (b) In different solvent systems (c) at different proportions of ACN: water solvent mixture.



**Figure S9.** Chemical shift of NHs versus % of DMSO added (v/v) to a solution of **1a** in CD<sub>3</sub>CN



**Figure S10.** The NH stretching region in the solution FT-IR spectrum of **1a**. Spectra presented are in acetonitrile after subtraction of the spectrum of pure acetonitrile.



**Figure S11.**  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , 300MHz) overlay spectra of **1a** upon the addition of varying amounts of  $\text{H}_2\text{PO}_4^-$

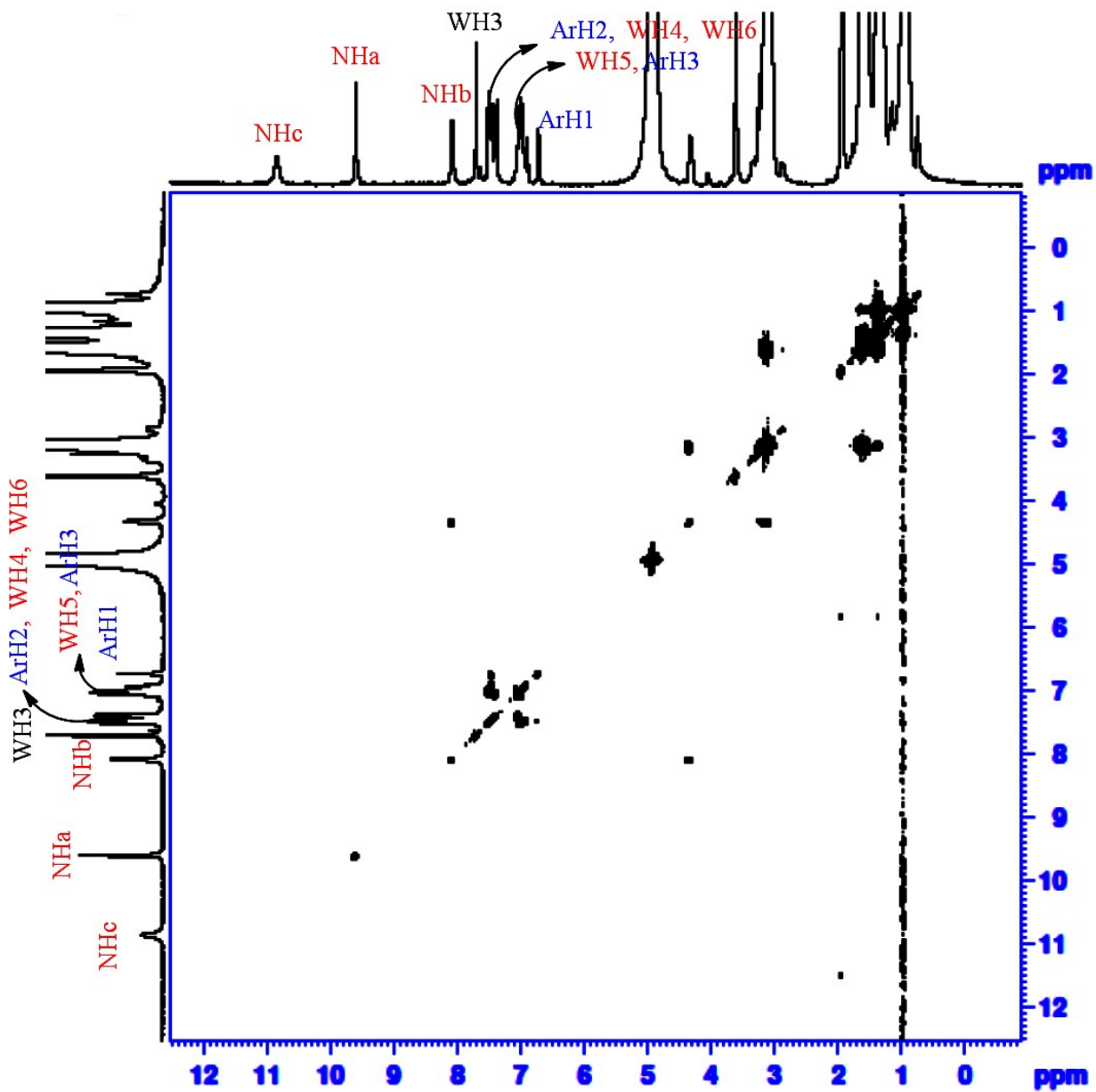


Figure S12. COSY (CD<sub>3</sub>CN, 300MHz) spectrum of **1a** -H<sub>2</sub>PO<sub>4</sub><sup>-</sup> complex

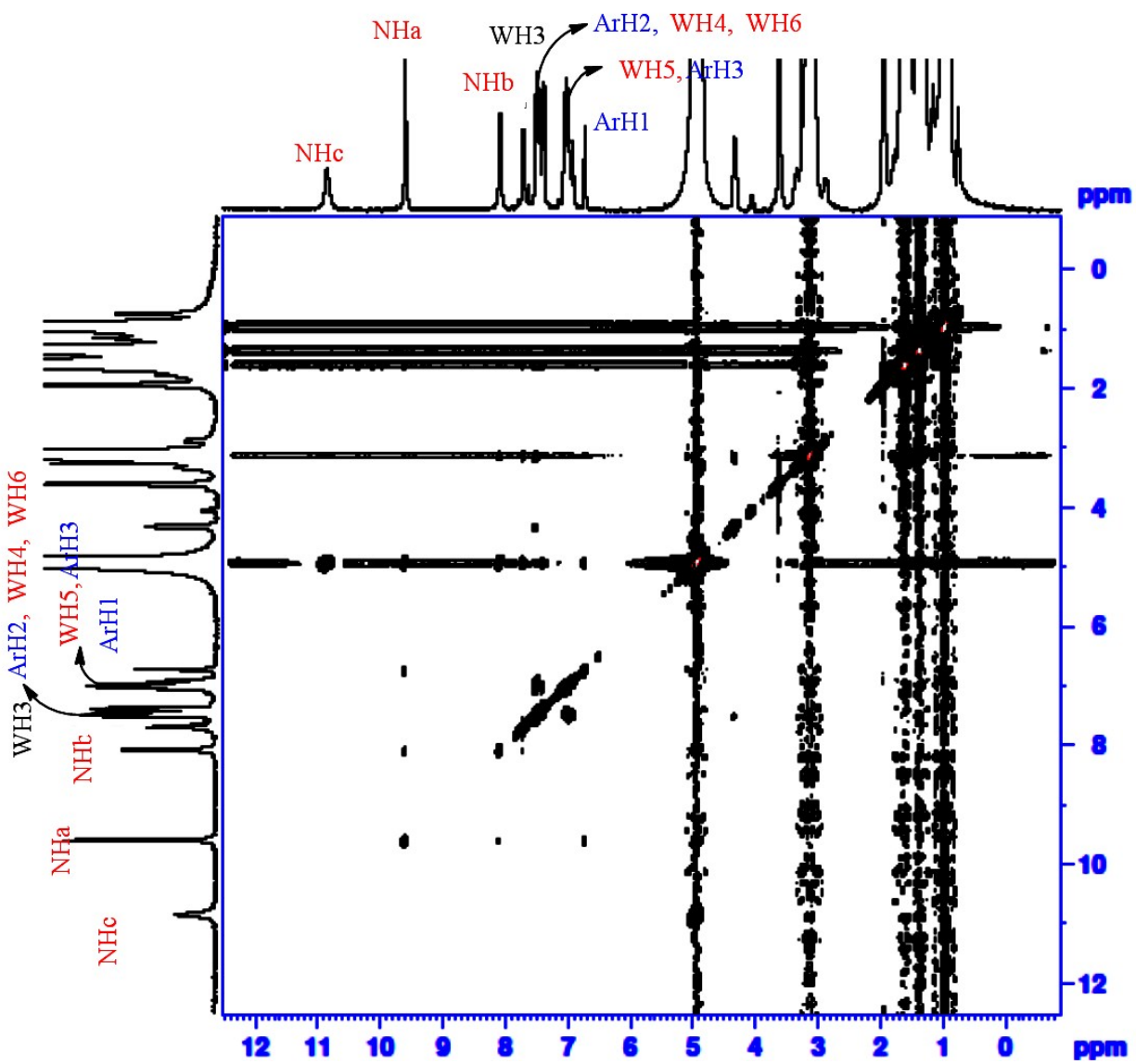
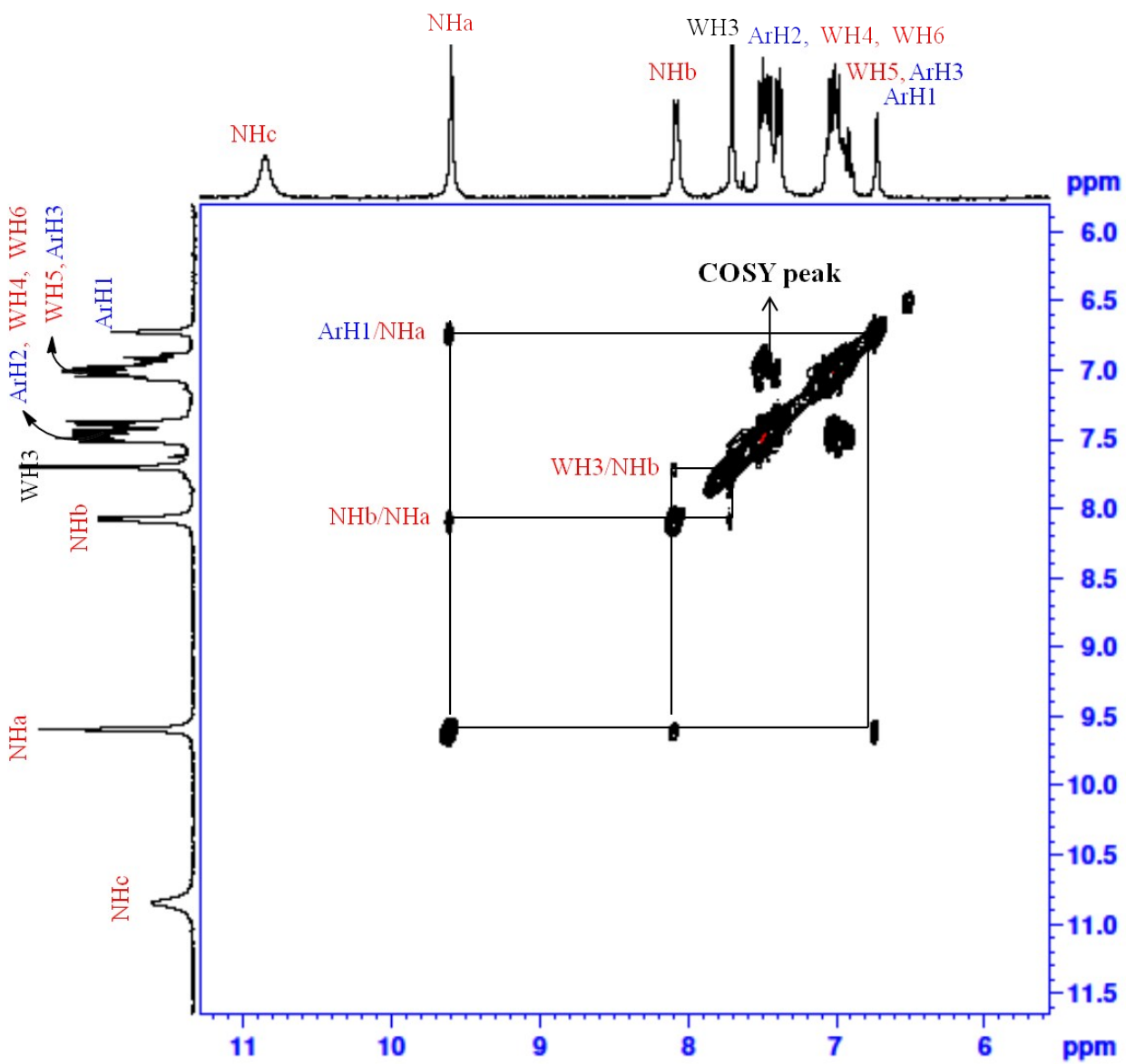
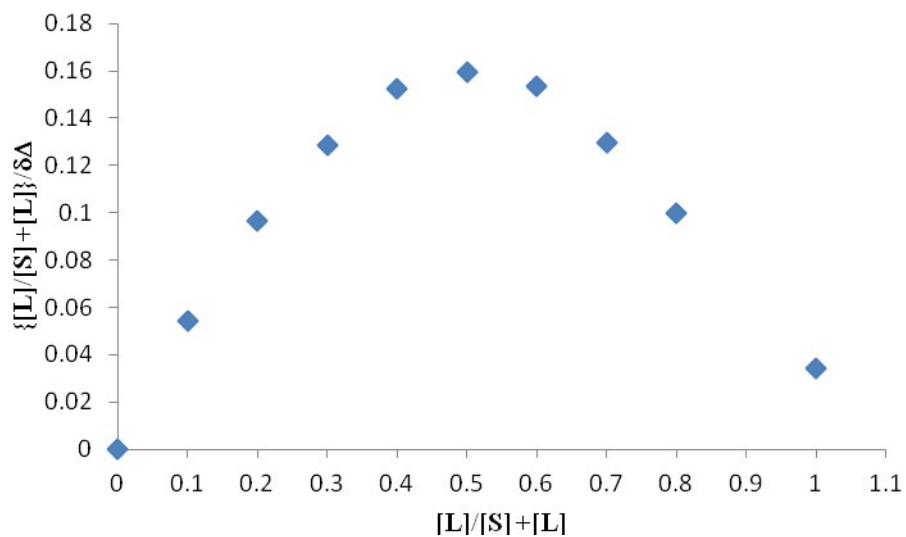


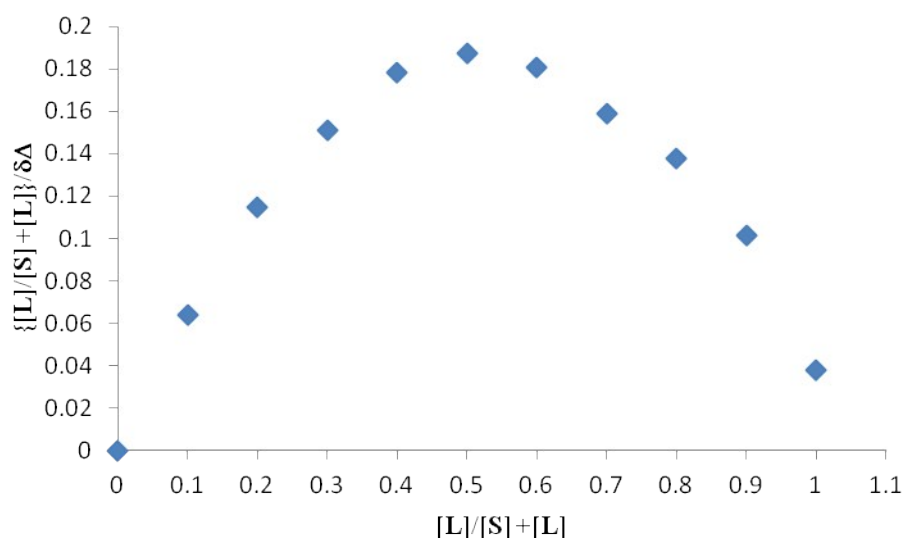
Figure S13a. NOESY (CD<sub>3</sub>CN, 300MHz) spectrum of **1a** -H<sub>2</sub>PO<sub>4</sub><sup>-</sup> complex



**Figure S13b.** Selected region of NOESY (CD<sub>3</sub>CN, 300MHz) spectrum of **1a** -H<sub>2</sub>PO<sub>4</sub><sup>-</sup> complex

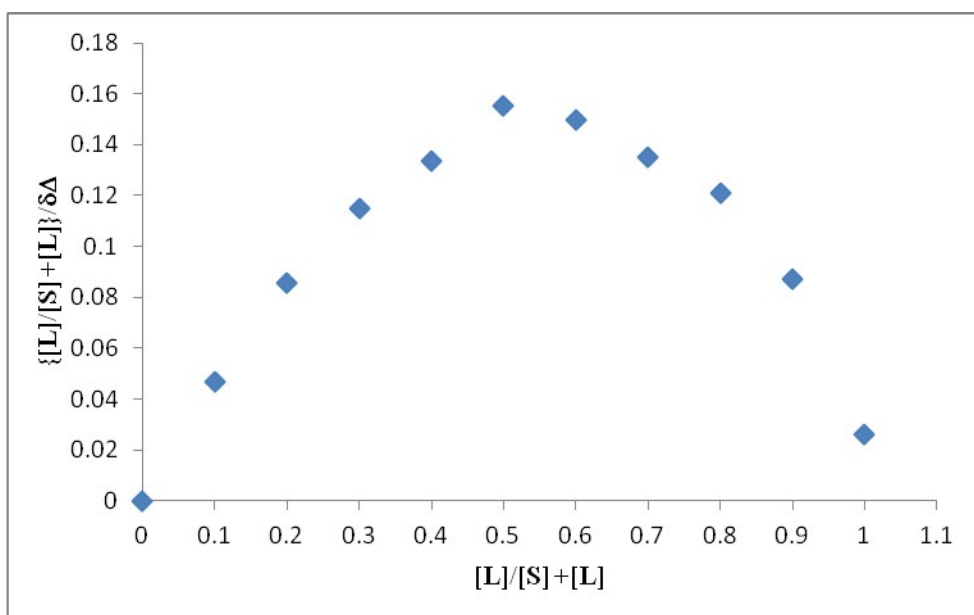


**Figure S14a.** Job plot of **1a** binding with  $\text{H}_2\text{PO}_4^-$  by UV spectroscopy

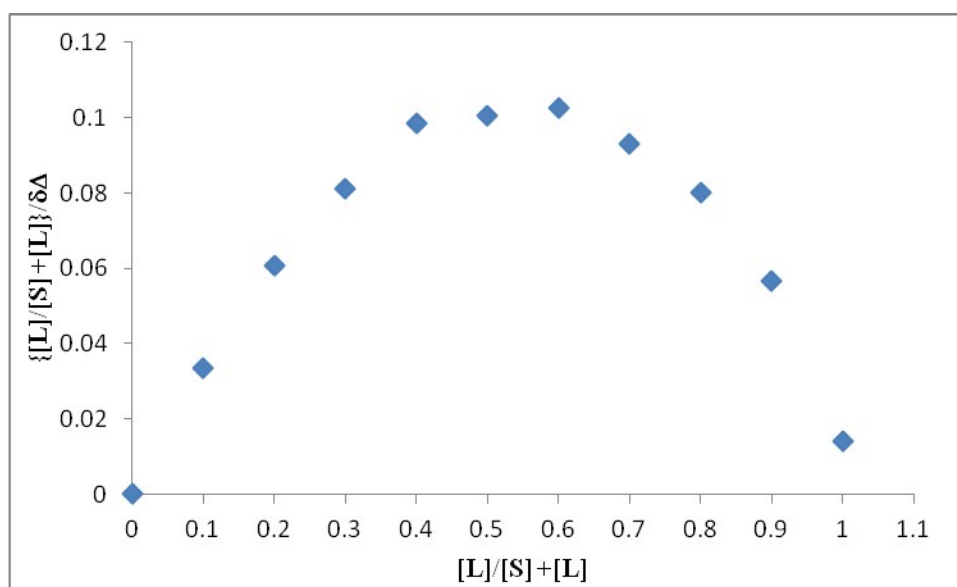


**Figure S14b.** Job plot of **1a** binding with  $\text{HSO}_4^-$  by UV spectroscopy





**Figure S15a.** Job plot for 1c binding with H<sub>2</sub>PO<sub>4</sub><sup>-</sup> by UV spectroscopy



**Figure S15b.** Job plot for 1c binding with HSO<sub>4</sub><sup>-</sup> by UV spectroscopy

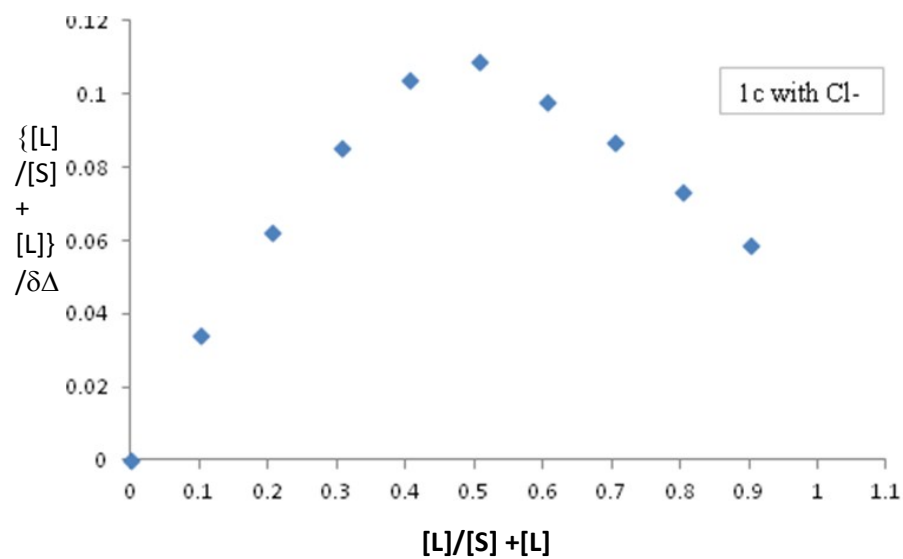


Figure S15c. Job plot for **1c** binding with Cl<sup>-</sup> by UV spectroscopy

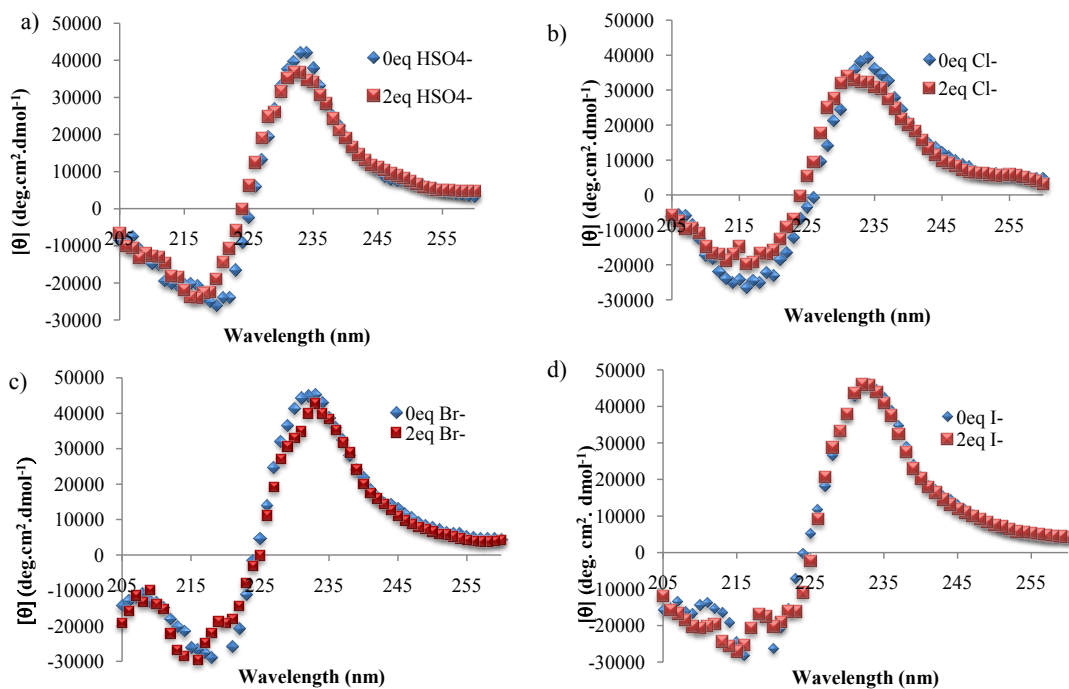
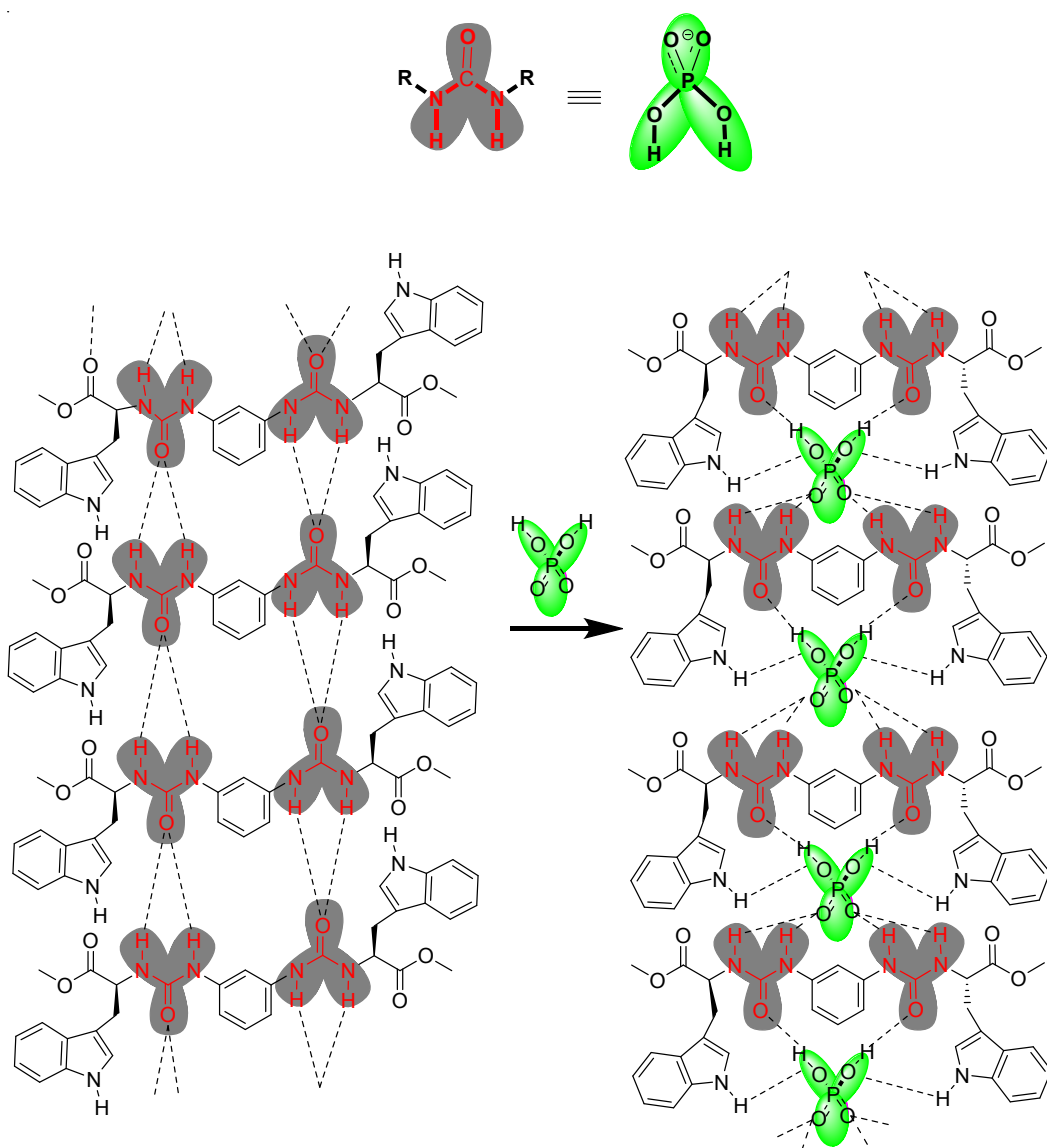
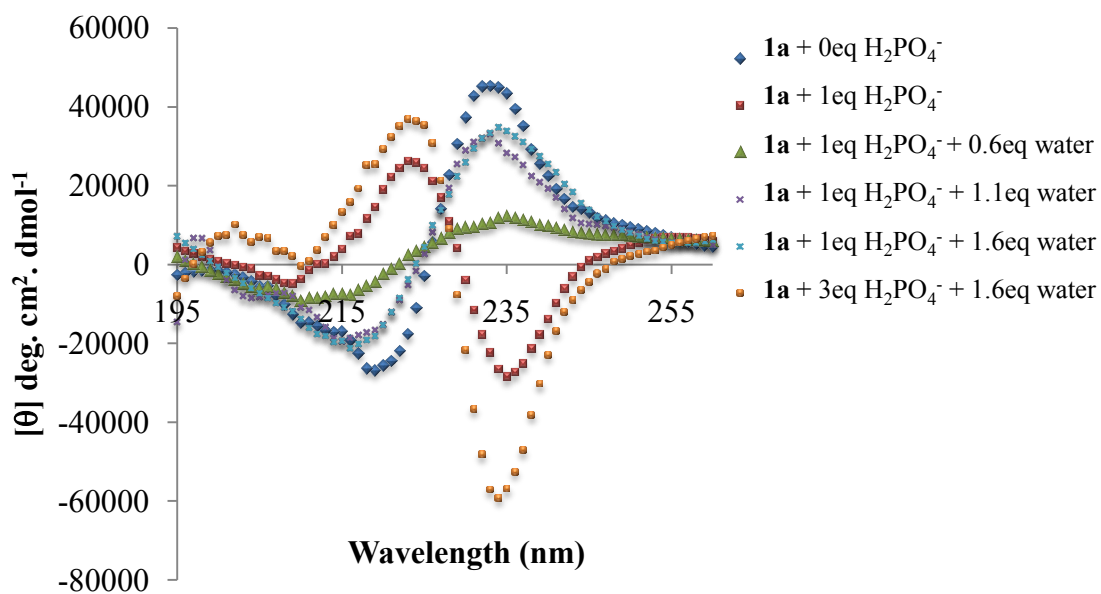


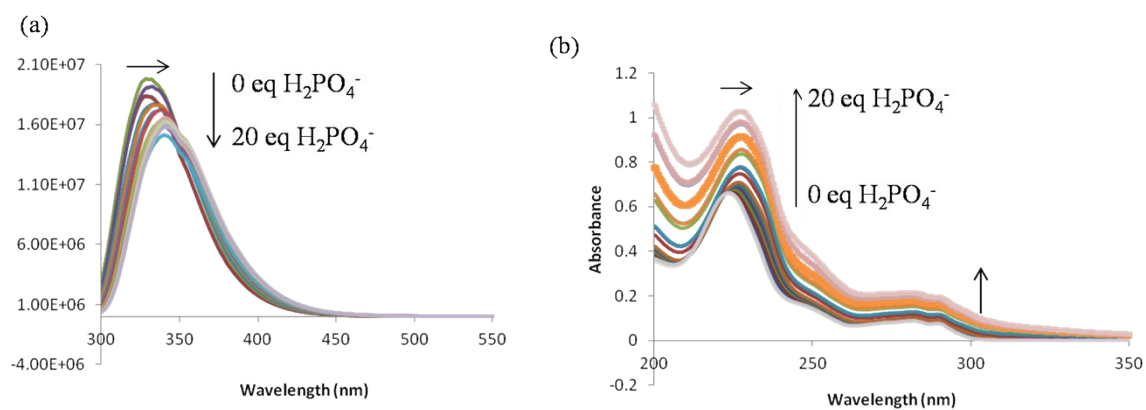
Figure S16. CD titration of **1a** in acetonitrile with a) HSO<sub>4</sub><sup>-</sup>, b) Cl<sup>-</sup>, c) Br<sup>-</sup>, d) I<sup>-</sup>



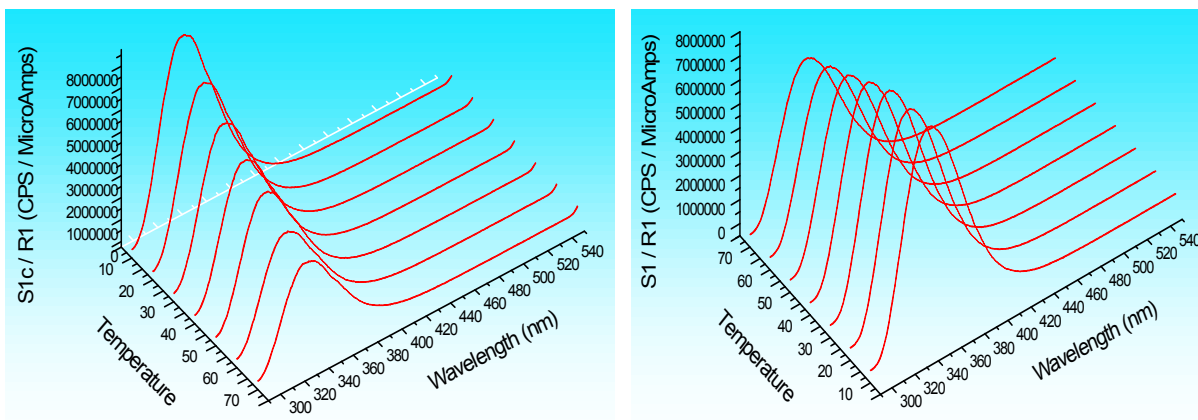
**Figure S17.** Expected intermolecular H-bonding pattern in **1a** and **1a**- $\text{H}_2\text{PO}_4^-$  complex



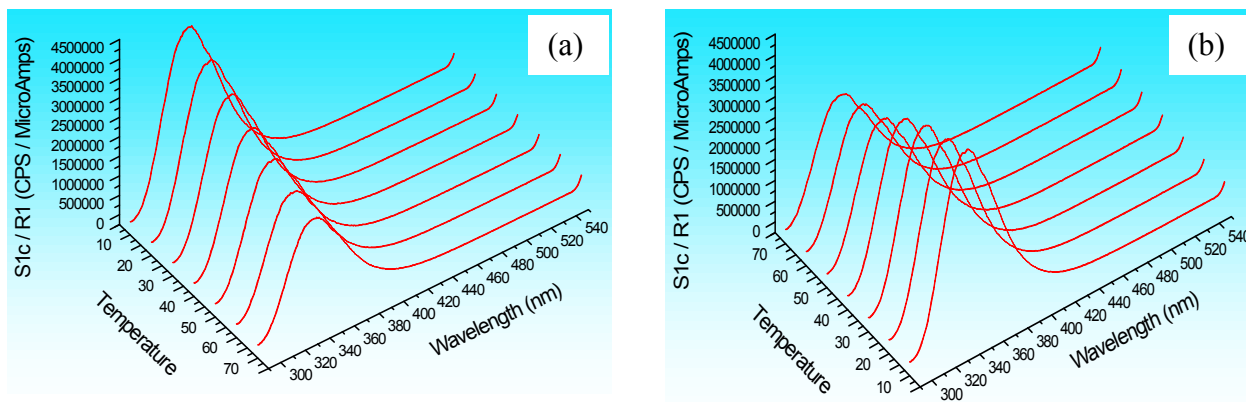
**Figure S18.** Demonstration of chiroptical property of **1a** by CD. Addition of  $\text{H}_2\text{PO}_4^-$  reverses the chirality and the water addition further revert it back to the original state.



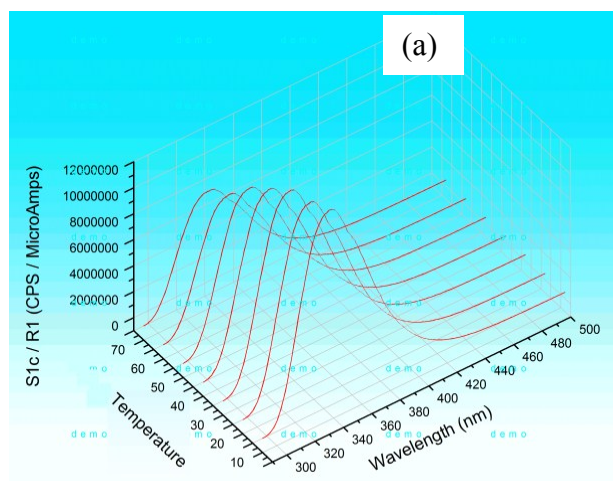
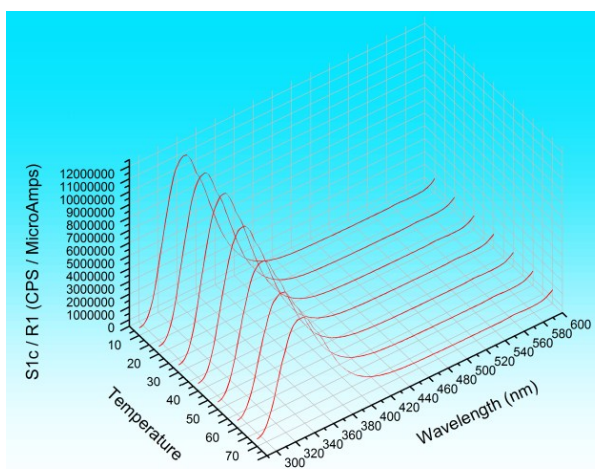
**Figure S19.** Changes in a) fluorescence spectra b) UV spectra of **1a** upon the addition of  $\text{H}_2\text{PO}_4^-$



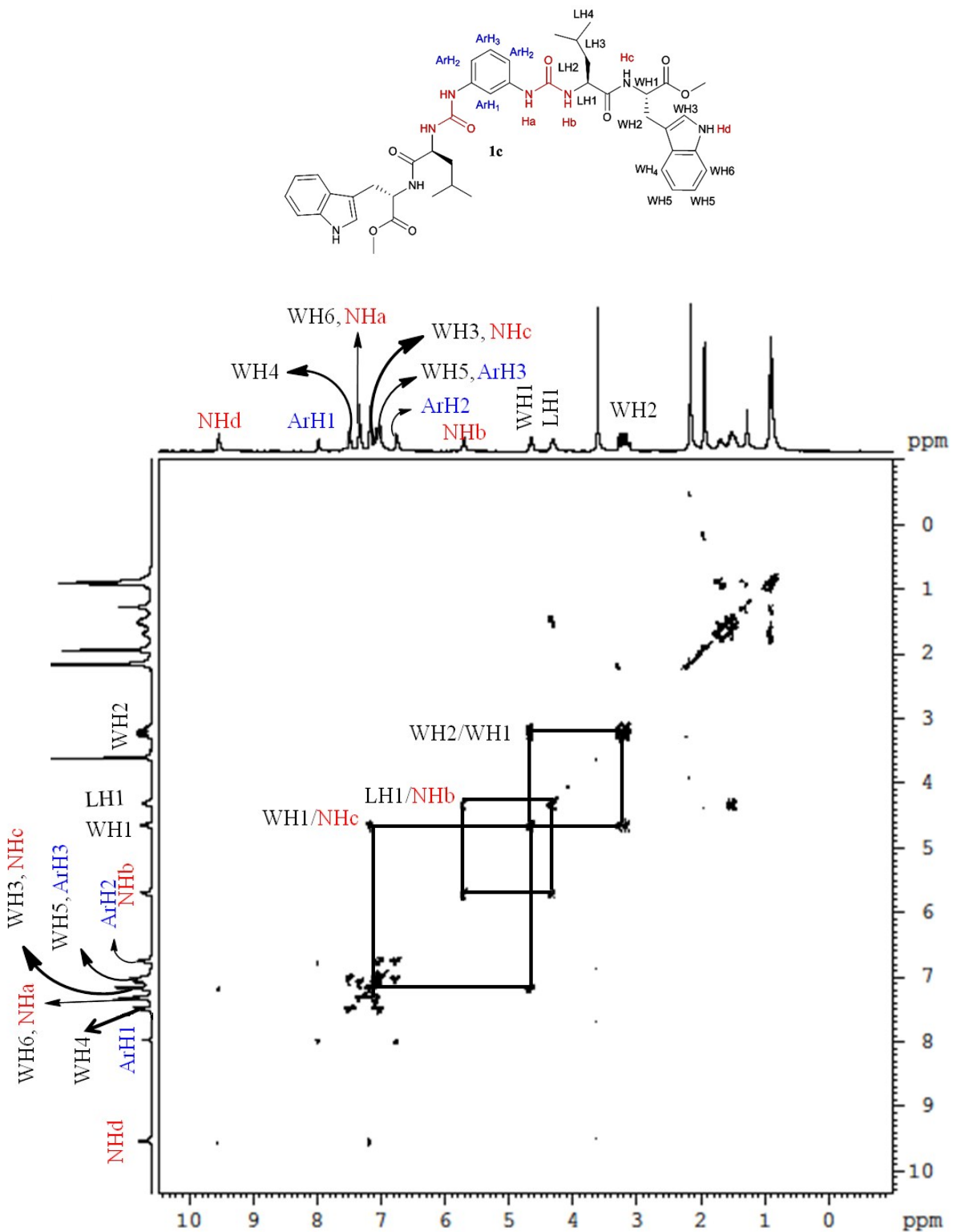
**Figure S20a.** Temperature dependent fluorescence spectra of **1a** (a) upon heating from 10 °C to 70°C (b) upon cooling from 70 °C to 10 °C.



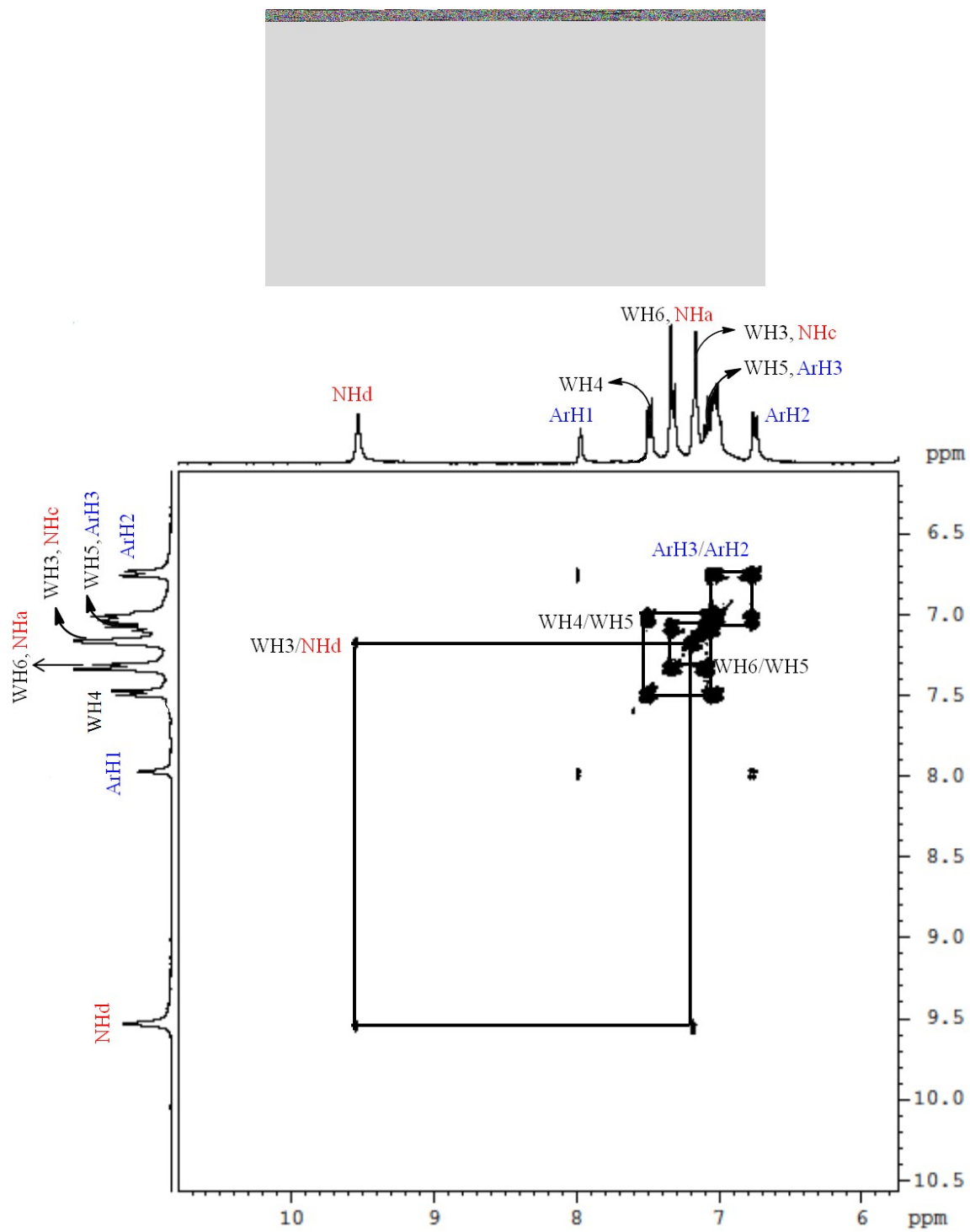
**Figure S20b.** Temperature dependent fluorescence spectra of **1b** (a) upon heating from 10 °C to 70 °C (b) upon cooling from 70 °C to 10 °C



**Figure S20c.** Temperature dependent fluorescence spectra of **1c** (a) upon heating from 10 °C to 70 °C (b) upon cooling from 70 °C to 10 °C



**Figure S21.** COSY (CD<sub>3</sub>CN, 300MHz) spectrum of **1c**



**Figure S22.** Selected region of COSY (CD<sub>3</sub>CN, 300MHz) spectrum of **1c**



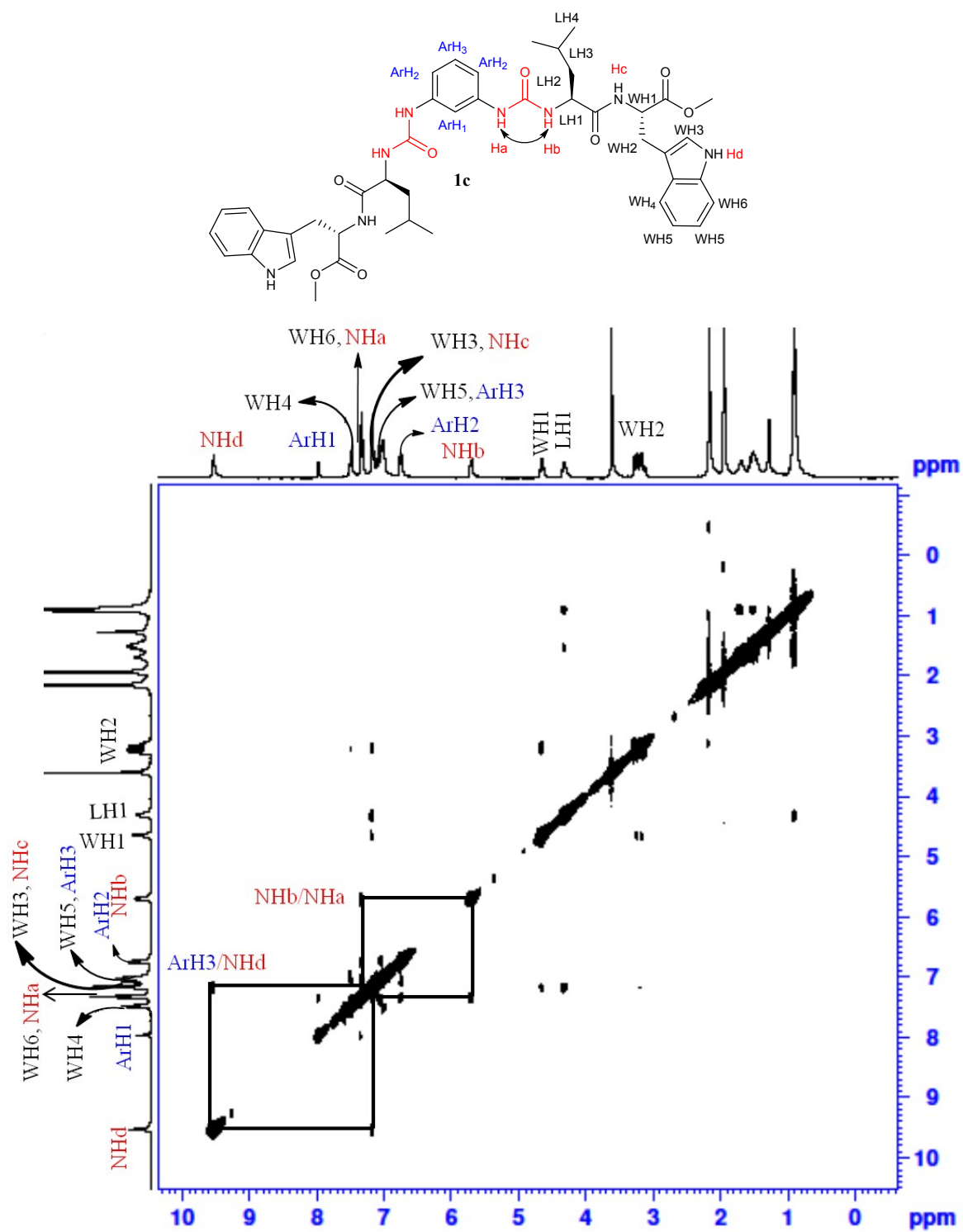
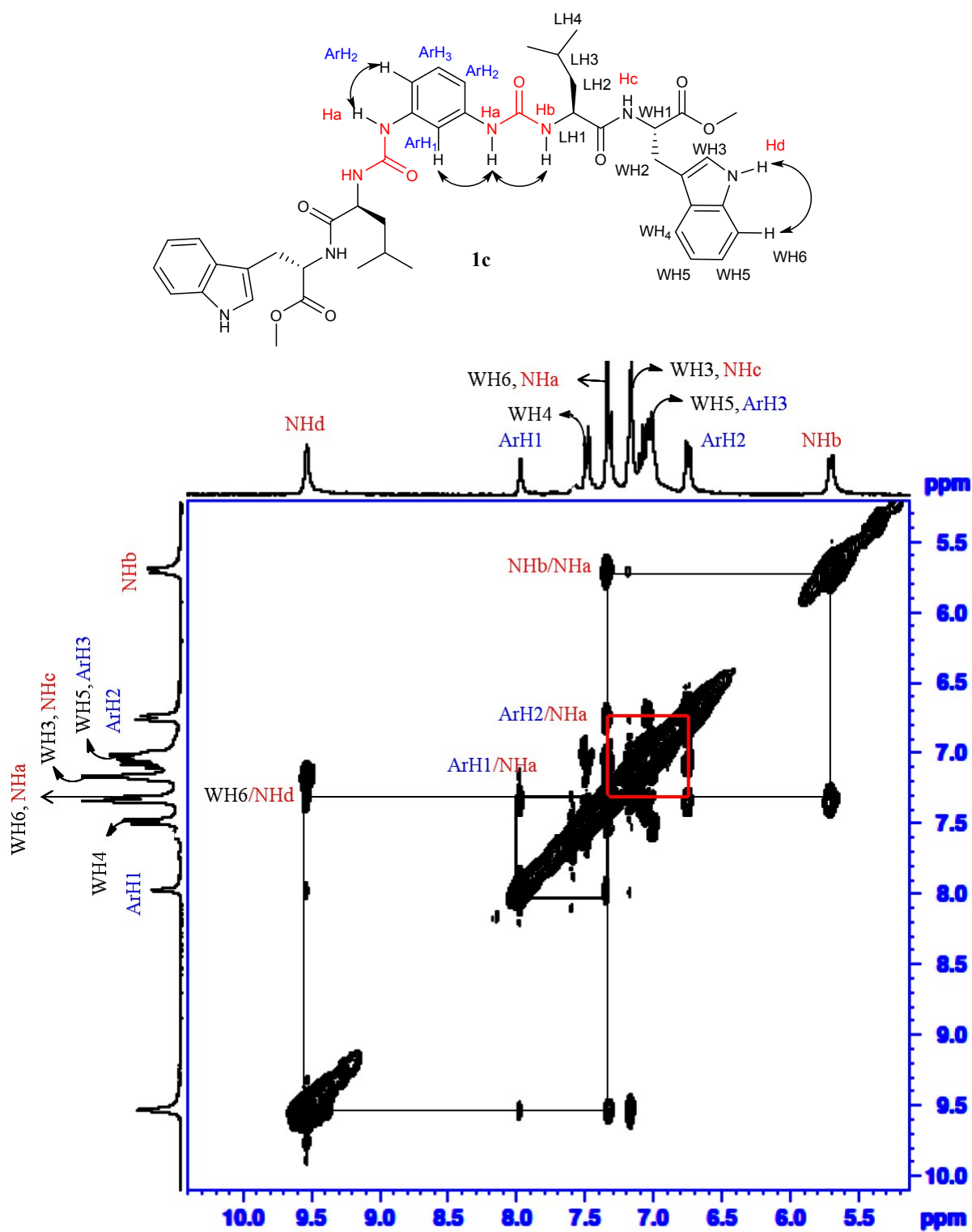


Figure S23. NOESY (CD<sub>3</sub>CN, 300MHz) spectrum of **1c**



**Figure S24.** Selected region of NOESY ( $\text{CD}_3\text{CN}$ , 300MHz) spectrum of **1c**

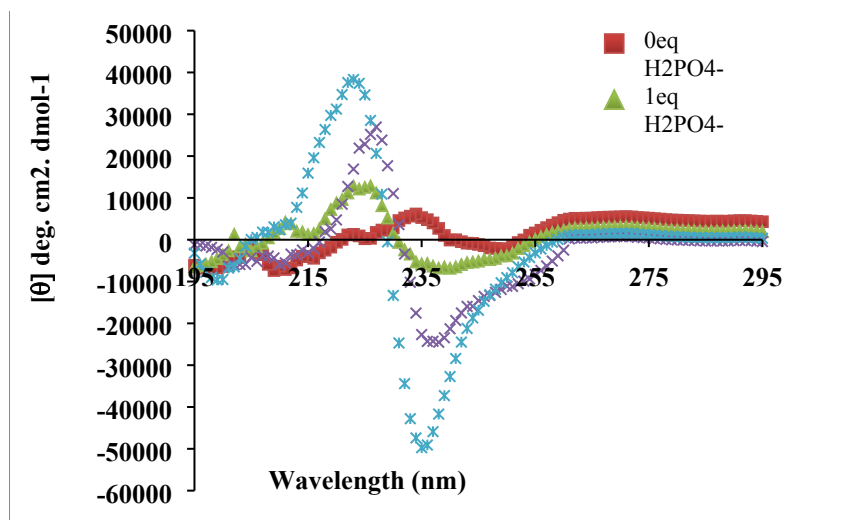
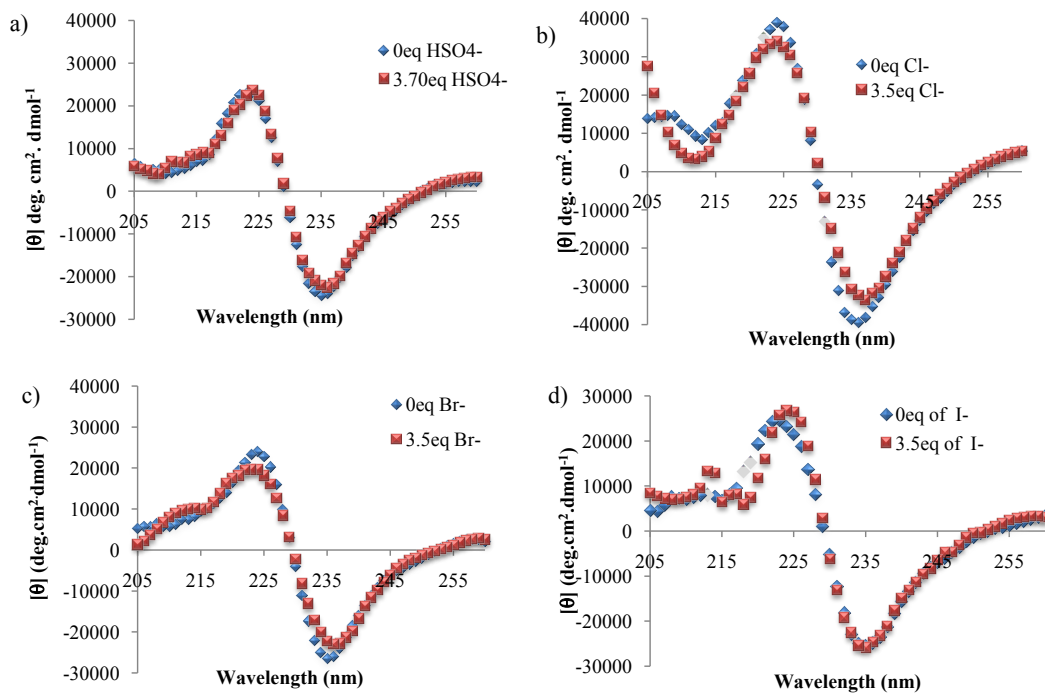
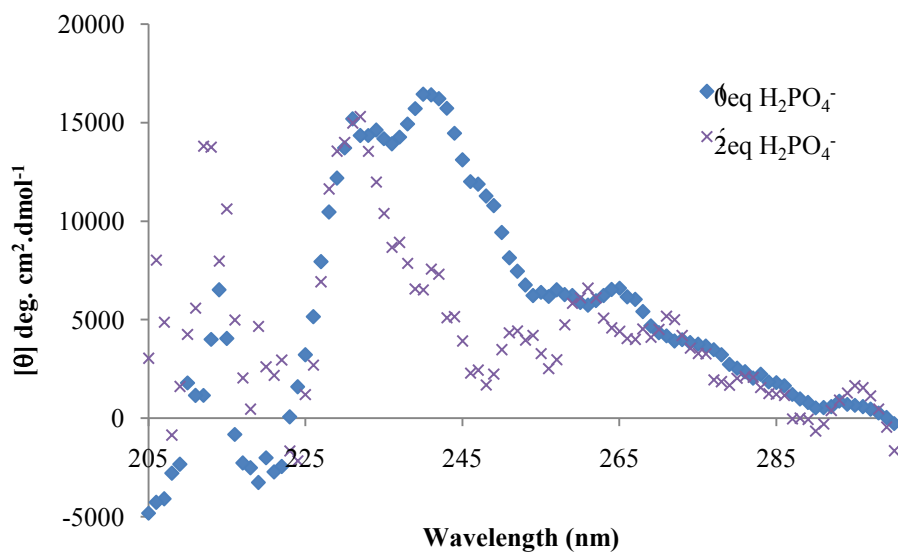


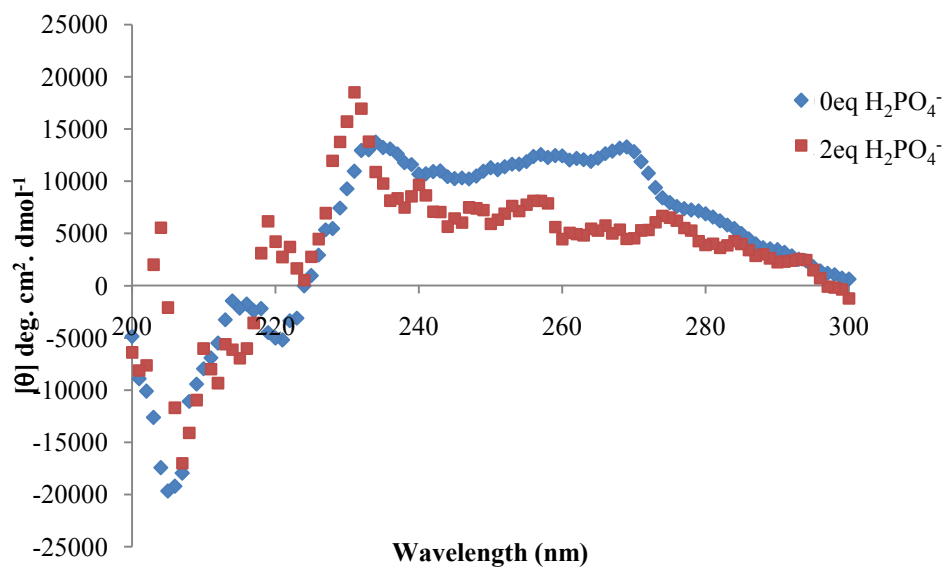
Figure S25. CD titration of **1b** in acetonitrile with H<sub>2</sub>PO<sub>4</sub><sup>-</sup>



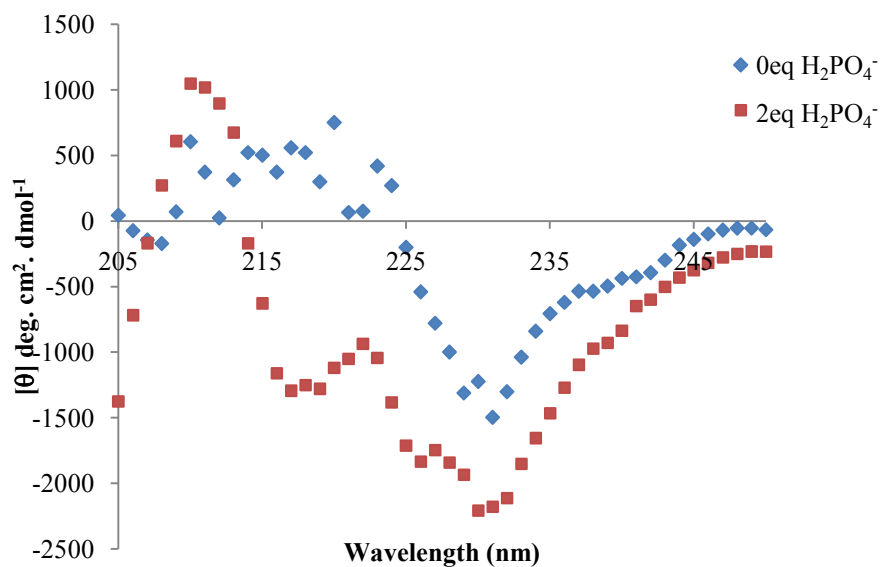
**Figure S26.** CD titration of **1c** in acetonitrile with a) HSO<sub>4</sub><sup>-</sup>, b) Cl<sup>-</sup>, c) Br<sup>-</sup>, d) I<sup>-</sup>



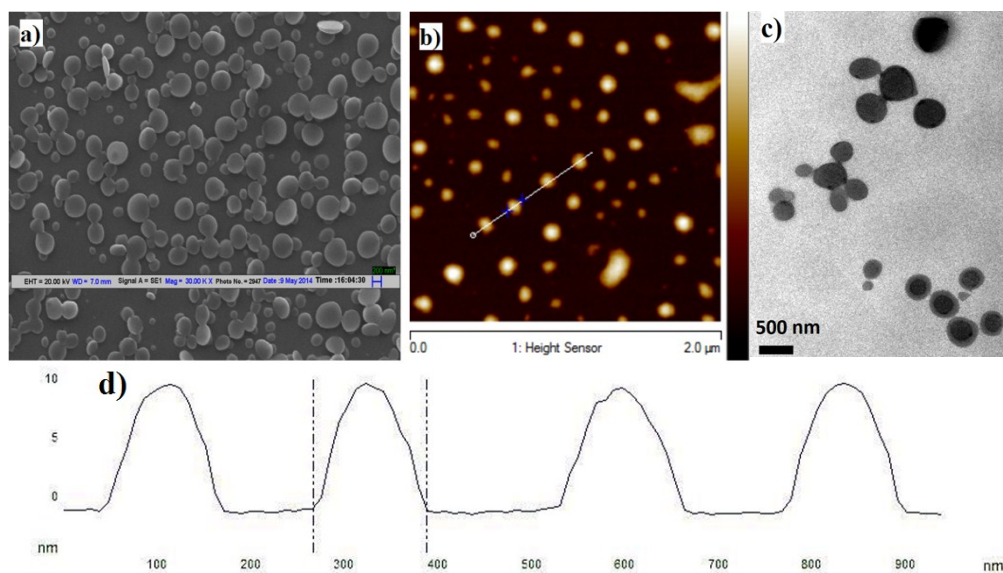
**Figure S27.** CD Titration of **1d** with H<sub>2</sub>PO<sub>4</sub><sup>-</sup>



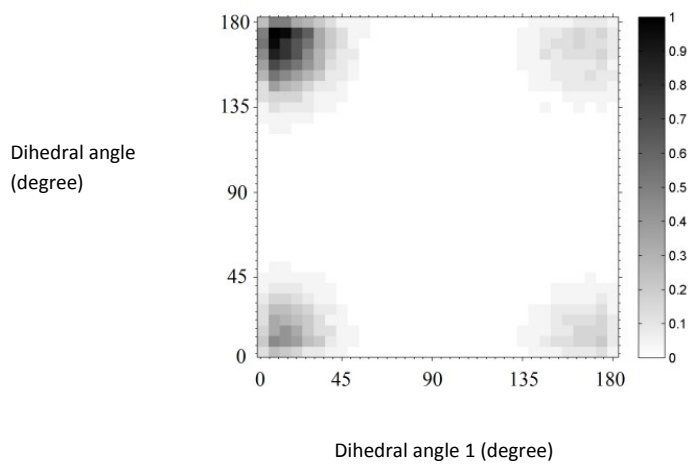
**Figure S28.** CD Titration of **1e** with H<sub>2</sub>PO<sub>4</sub><sup>-</sup>



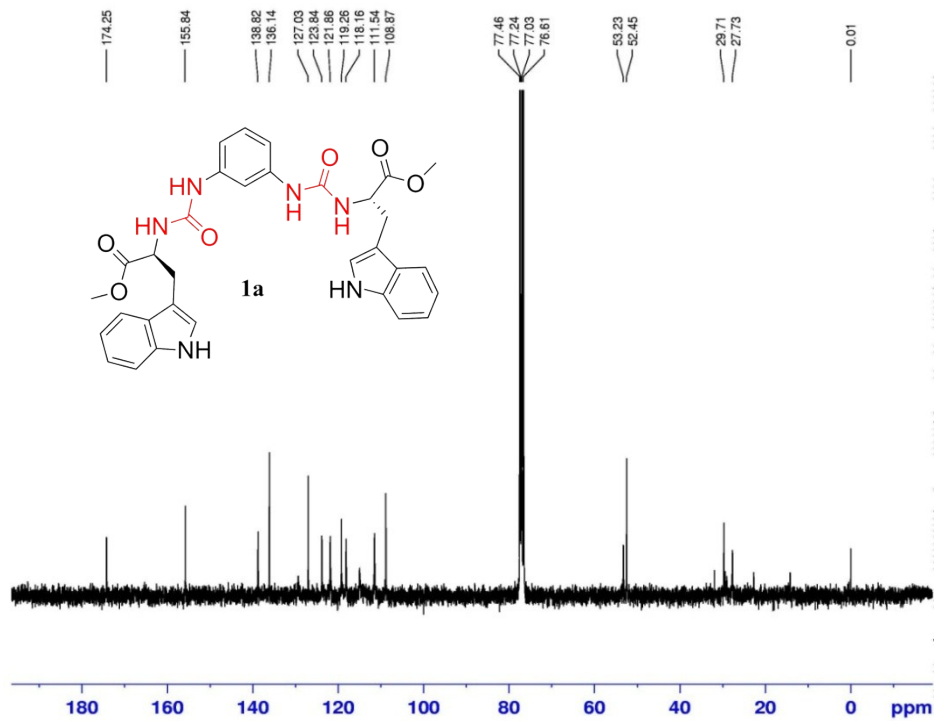
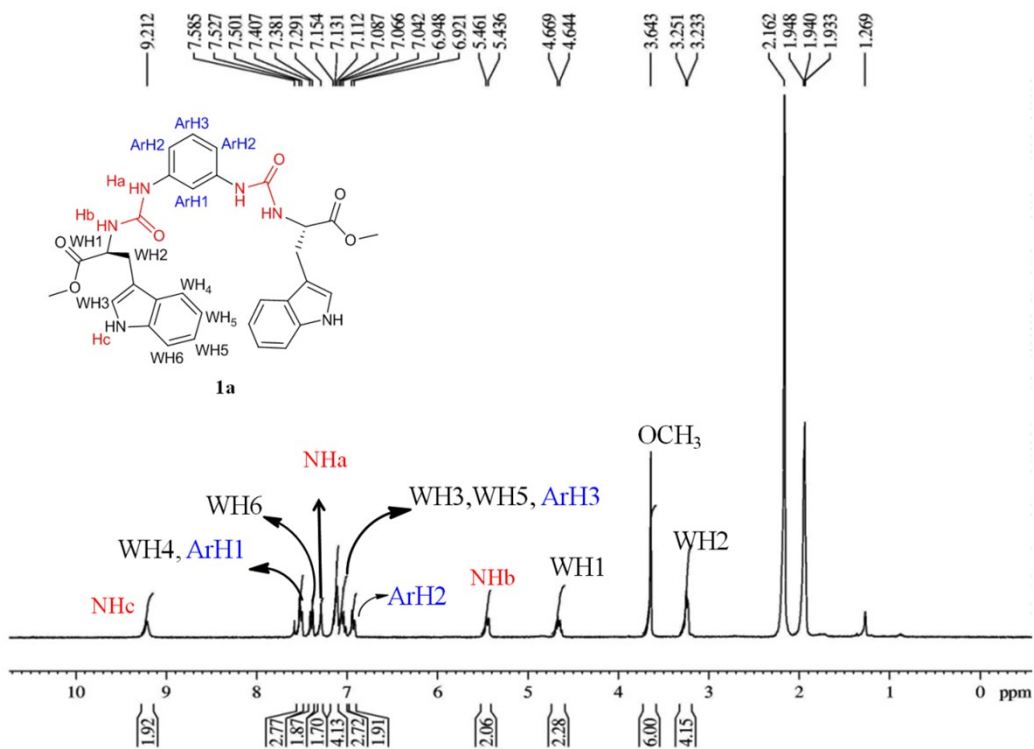
**Figure S29.** CD Titration of **1f** with H<sub>2</sub>PO<sub>4</sub><sup>-</sup>



**Figure S30.** a) SEM b) AFM c) TEM and d) AFM cross sectional analysis of **1c**



**Figure S31.** Dihedral angle distribution of **1a** obtained using MD simulations OPLS-AA.<sup>1,2</sup> Magnitude of dihedral angles is plotted.



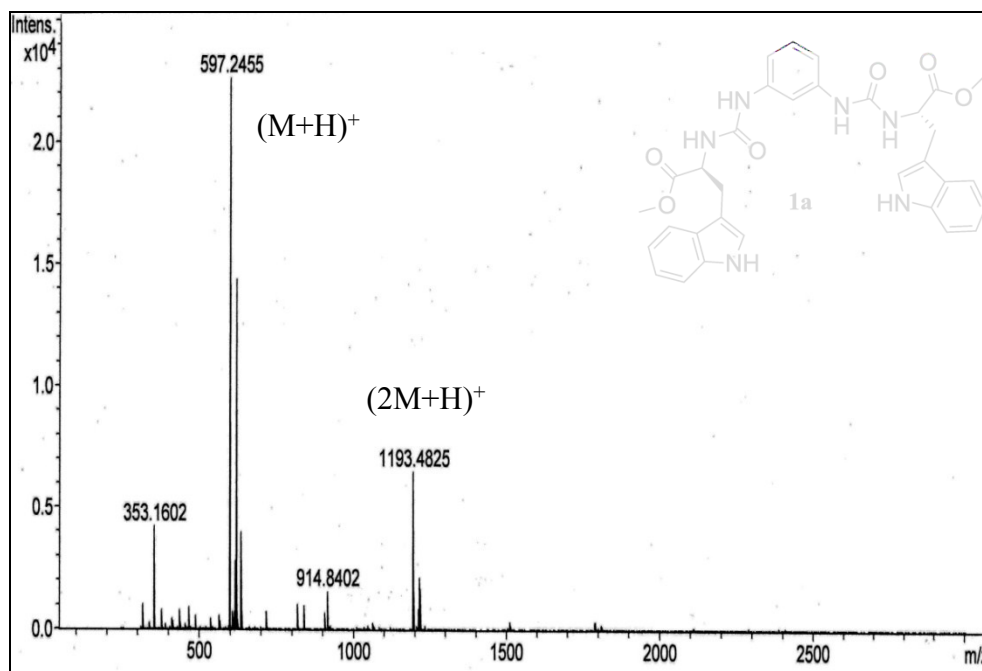


Figure S34. HRMS of 1a

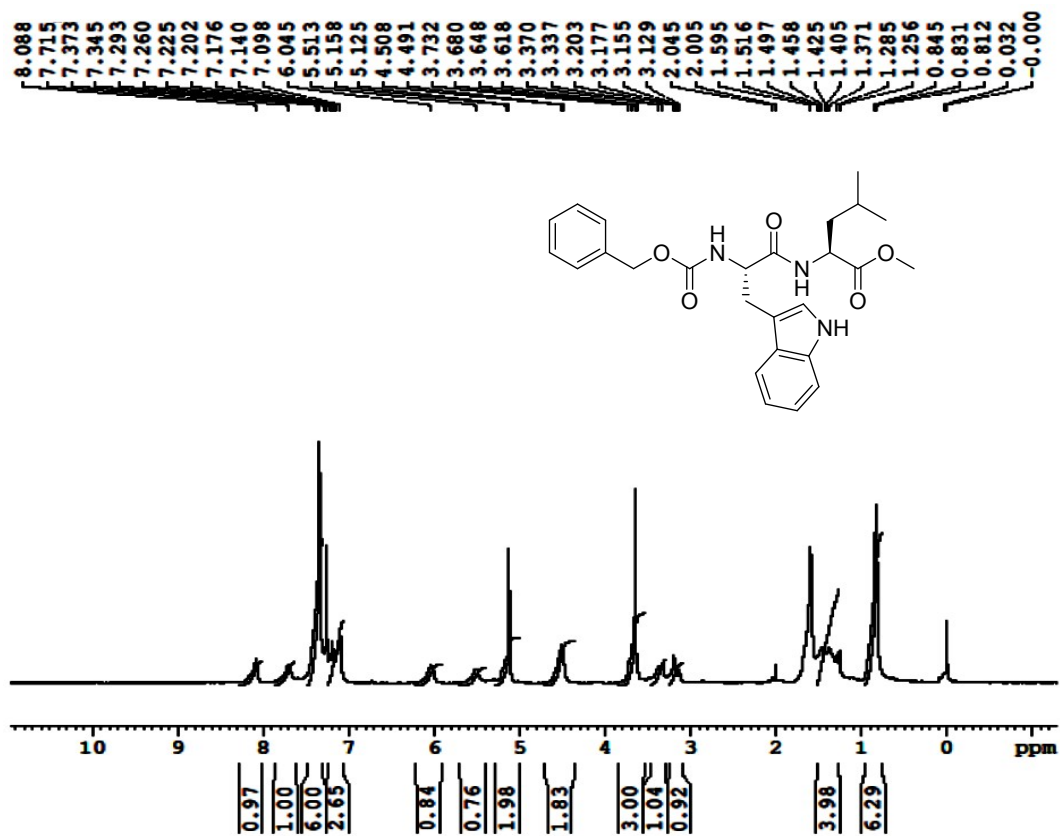


Figure S35. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300MHz) spectrum of Z-Trp-Leu-OMe



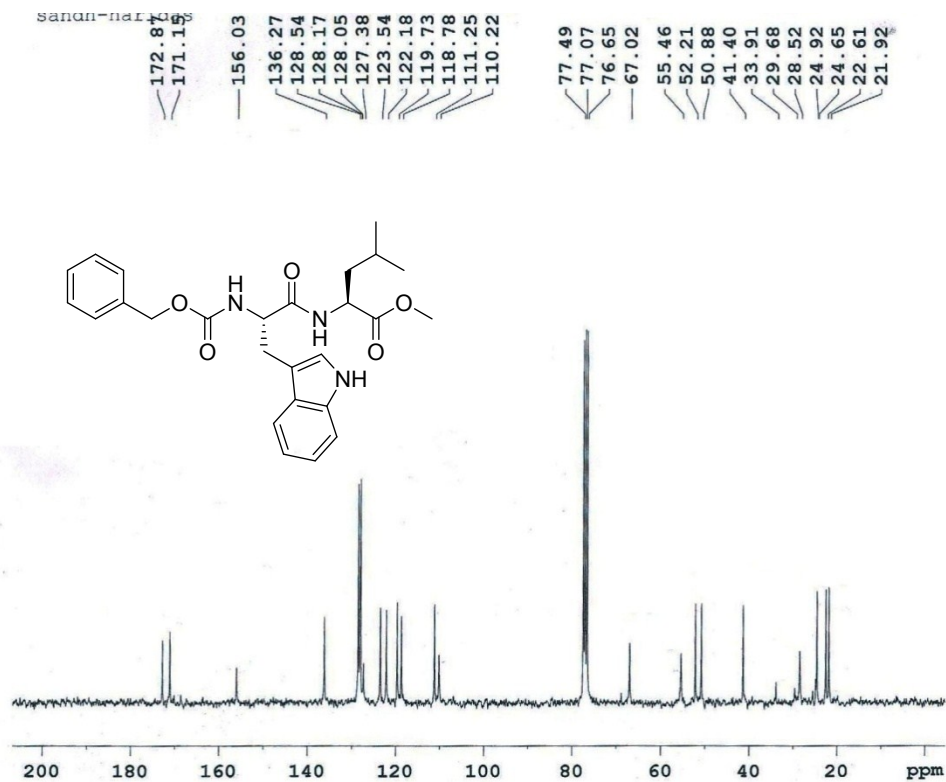


Figure S36.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 300MHz) spectrum of Z-Trp-Leu-OMe

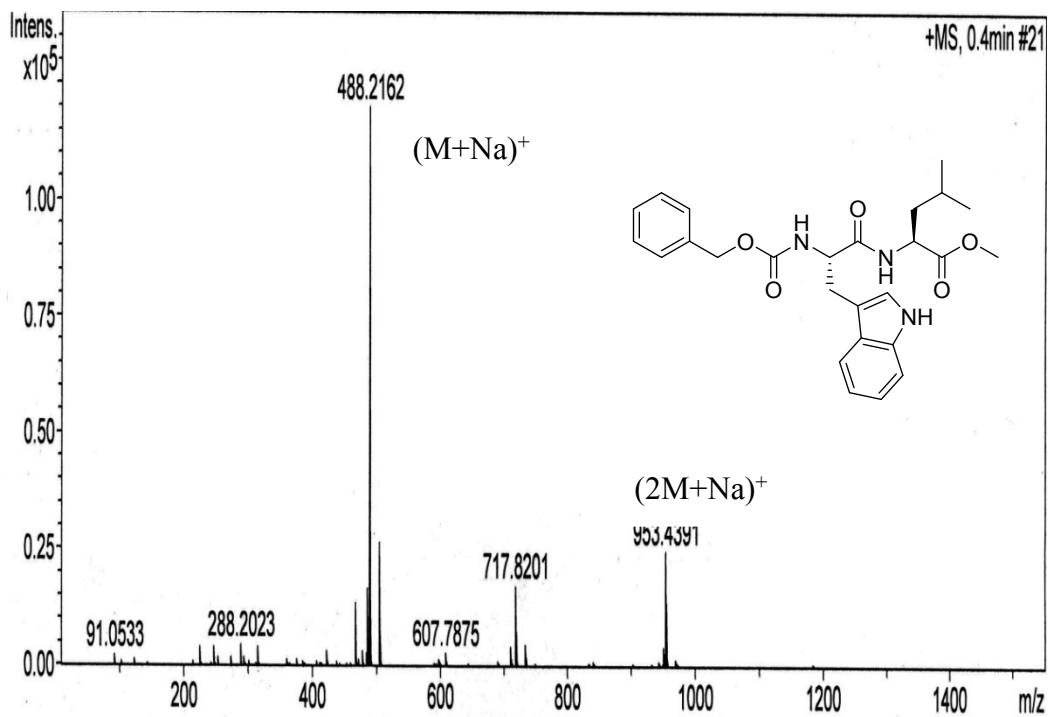
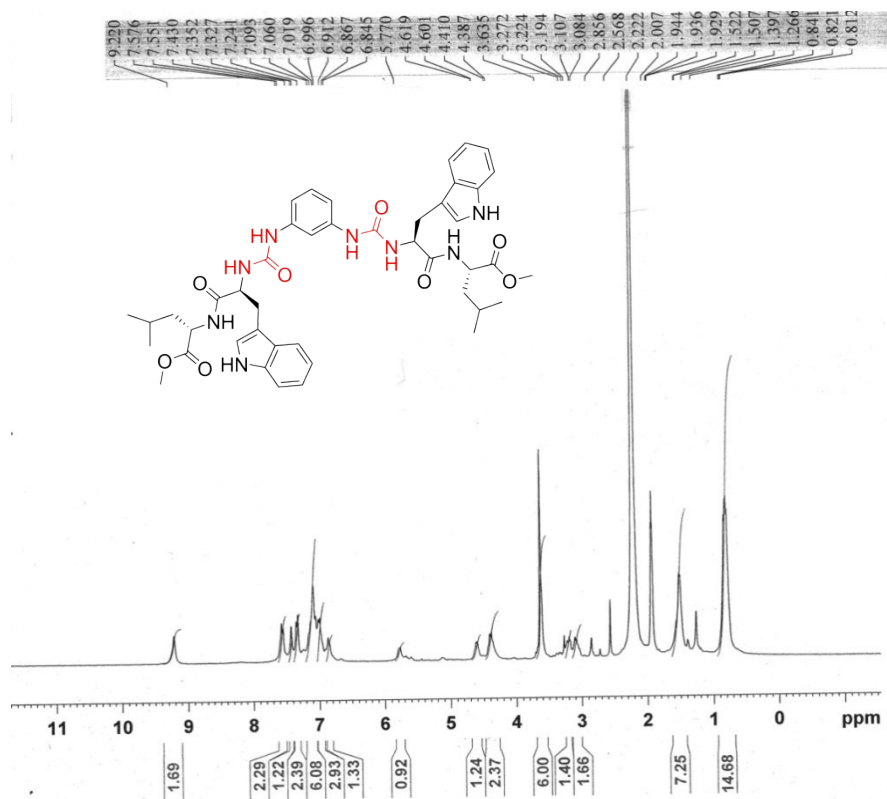
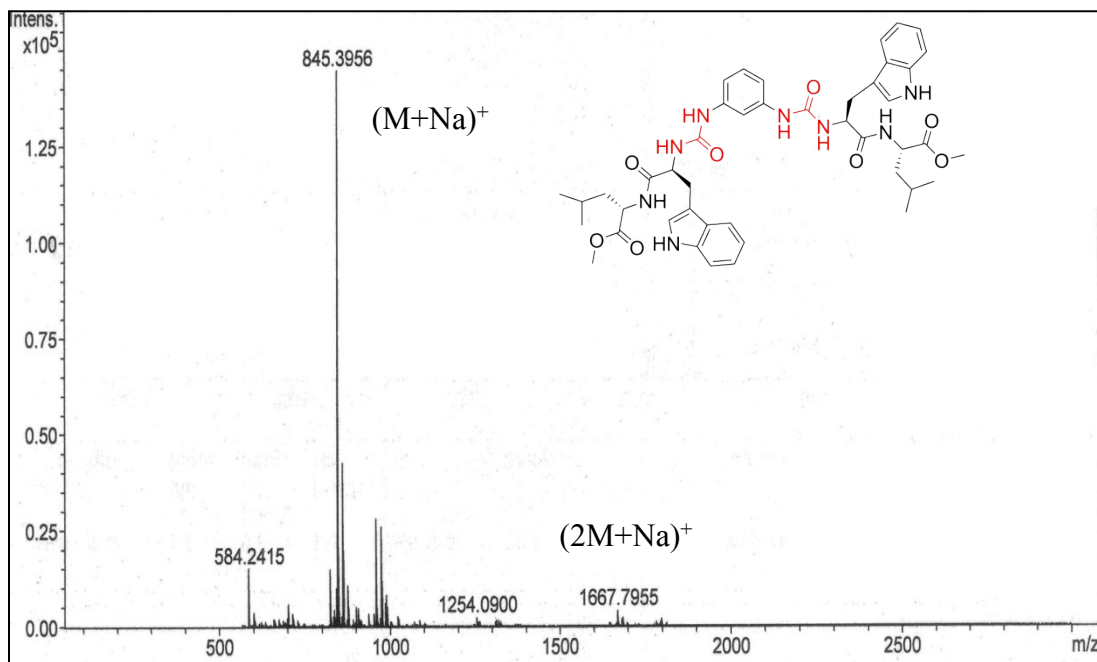


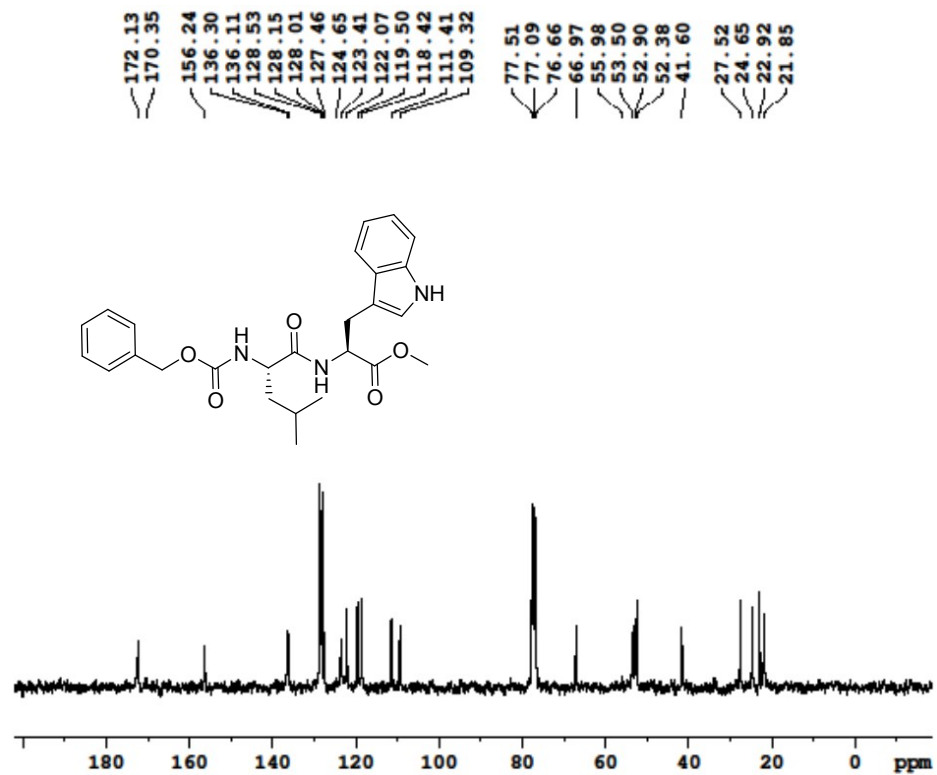
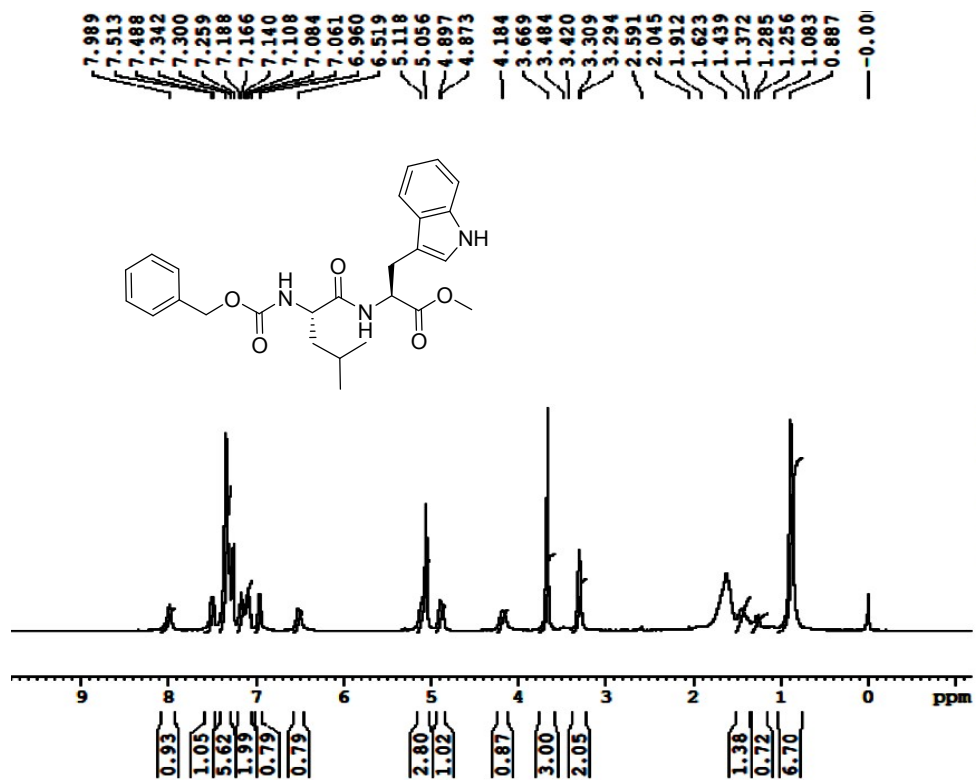
Figure S37. HRMS of Z-Trp-Leu-OMe



**Figure S38.**  $^1\text{H NMR}$  (CD<sub>3</sub>CN, 300MHz) spectrum of **1b**



**Figure S39.** HRMS of **1b**



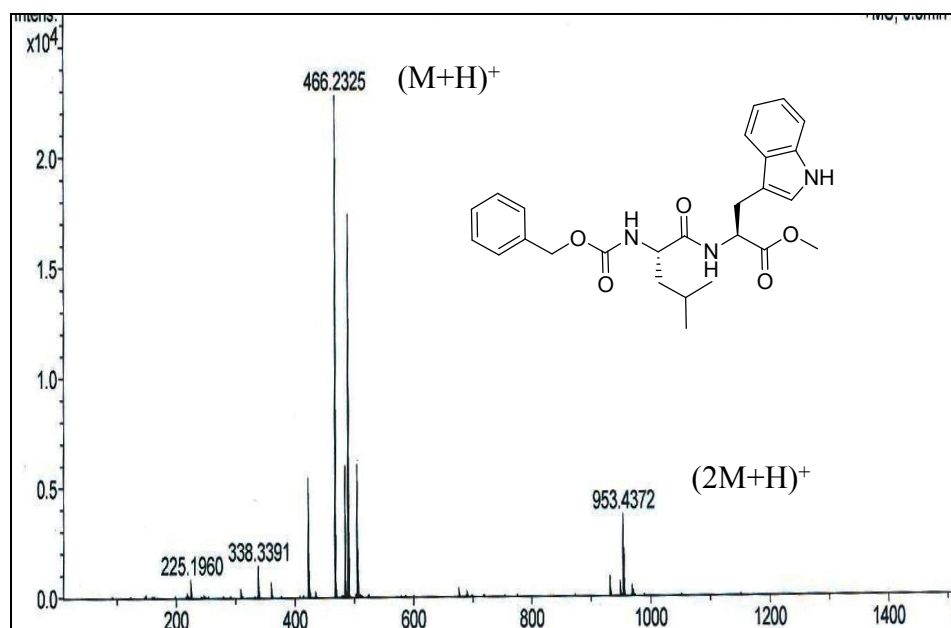


Figure S42. HRMS of Z-Leu-Trp-Ome

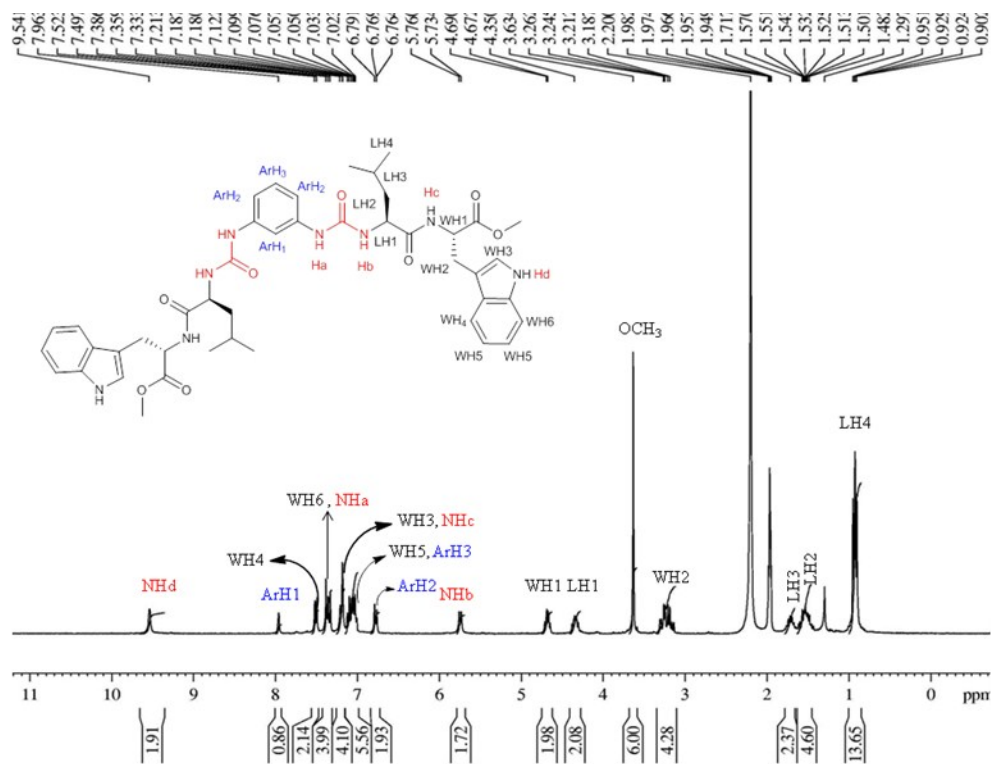


Figure S43.  $^1\text{H}$ NMR ( $\text{CD}_3\text{CN}$ , 300MHz) spectrum of 1c

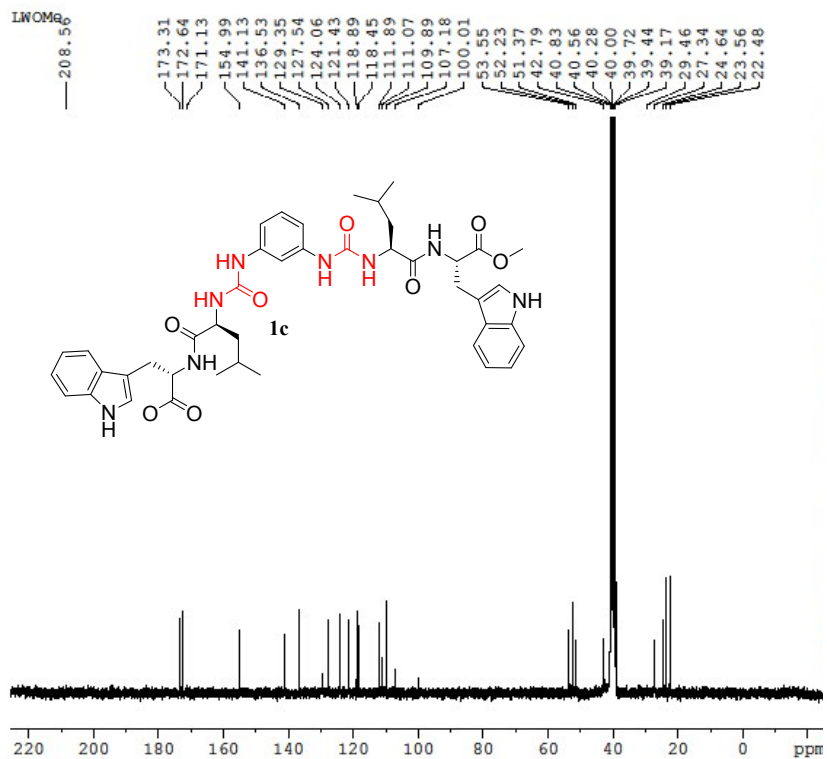


Figure S44.  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 75MHz) spectrum of **1c**

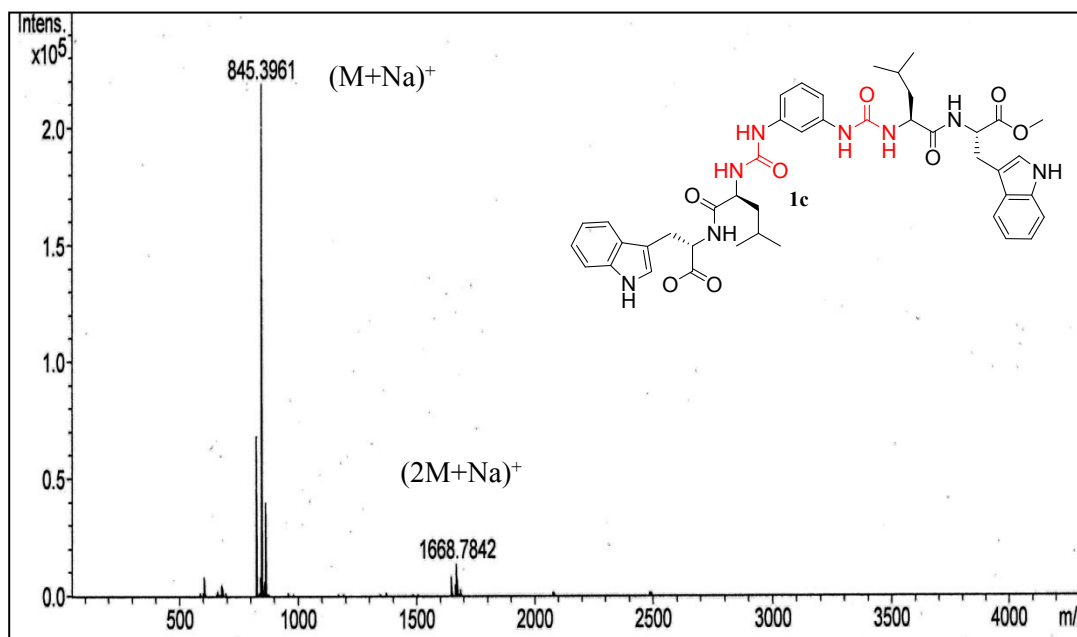
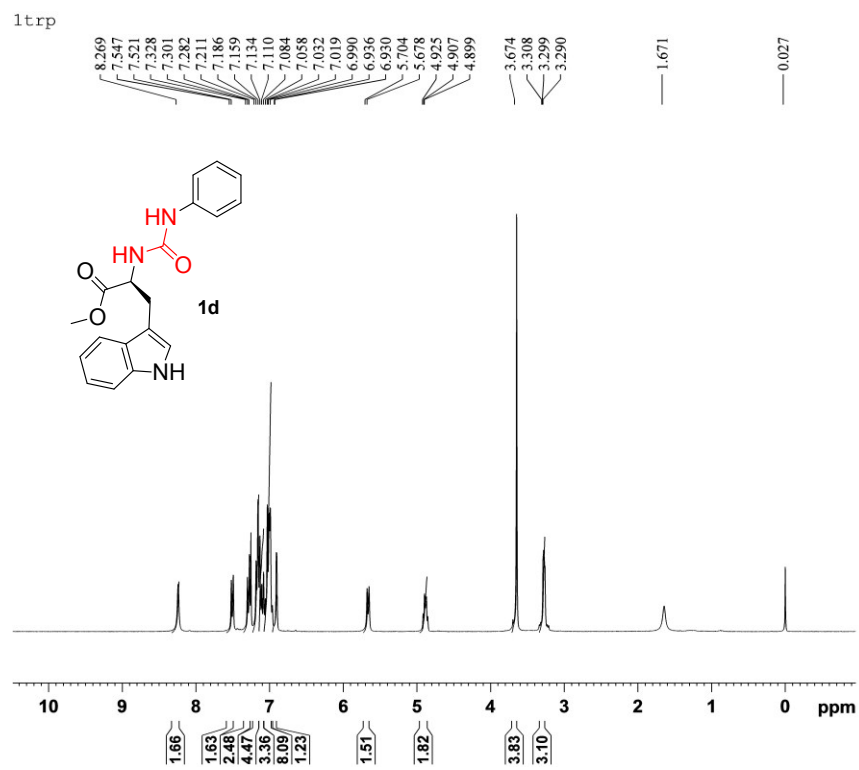
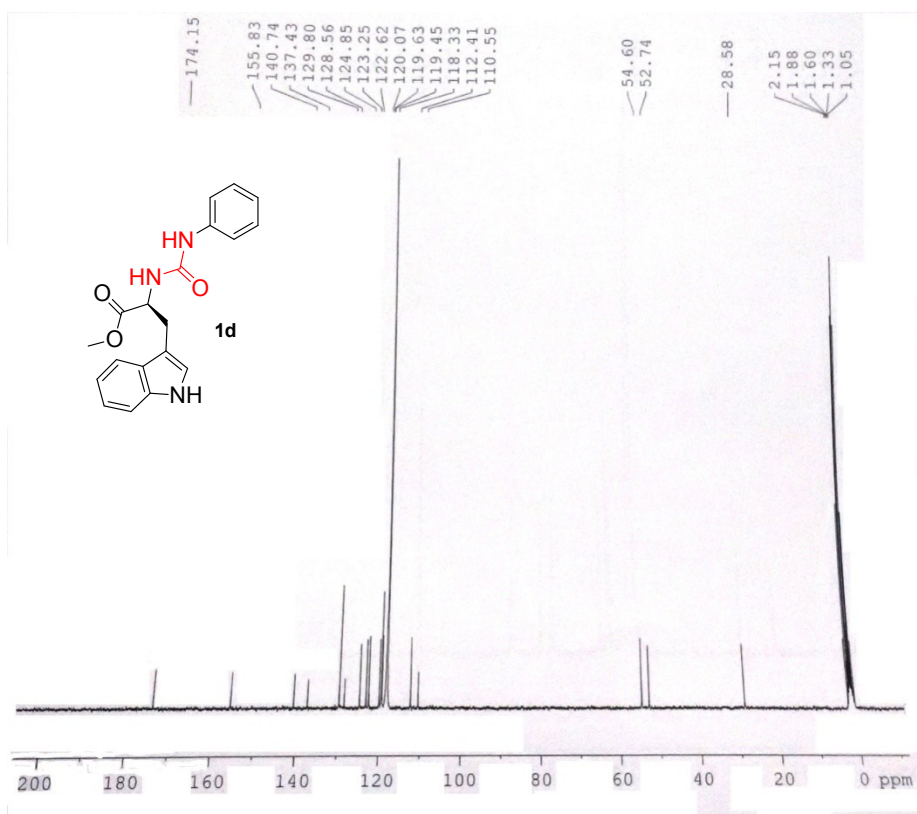


Figure S45. HRMS of **1c**



**Figure S46.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300MHz) spectrum of **1d**



**Figure S47.**  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ , 75MHz) spectrum of **1d**

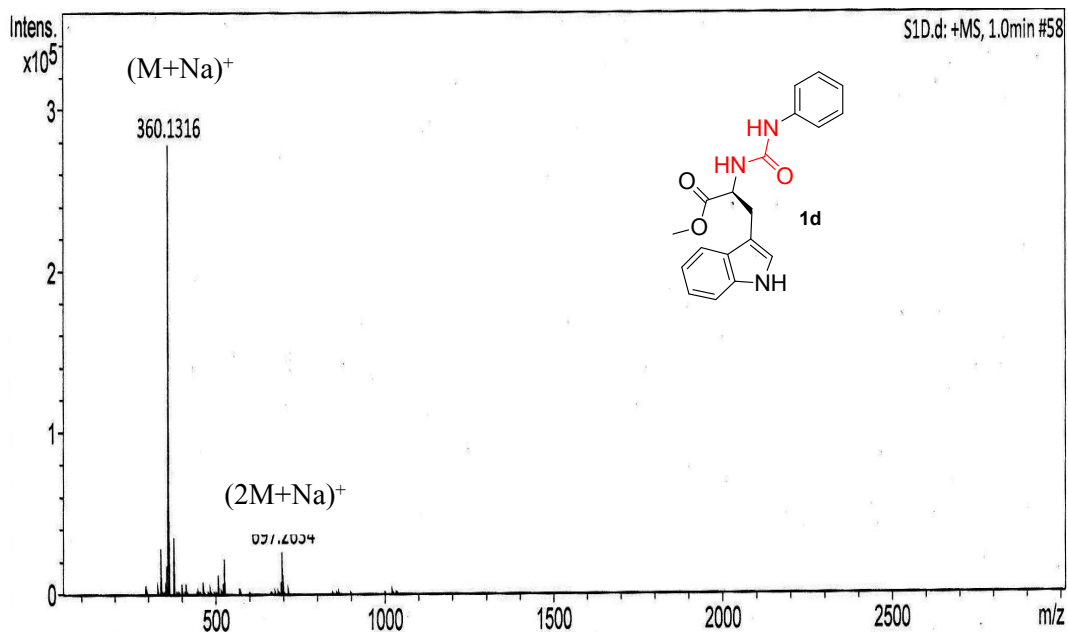


Figure S48. HRMS of **1d**

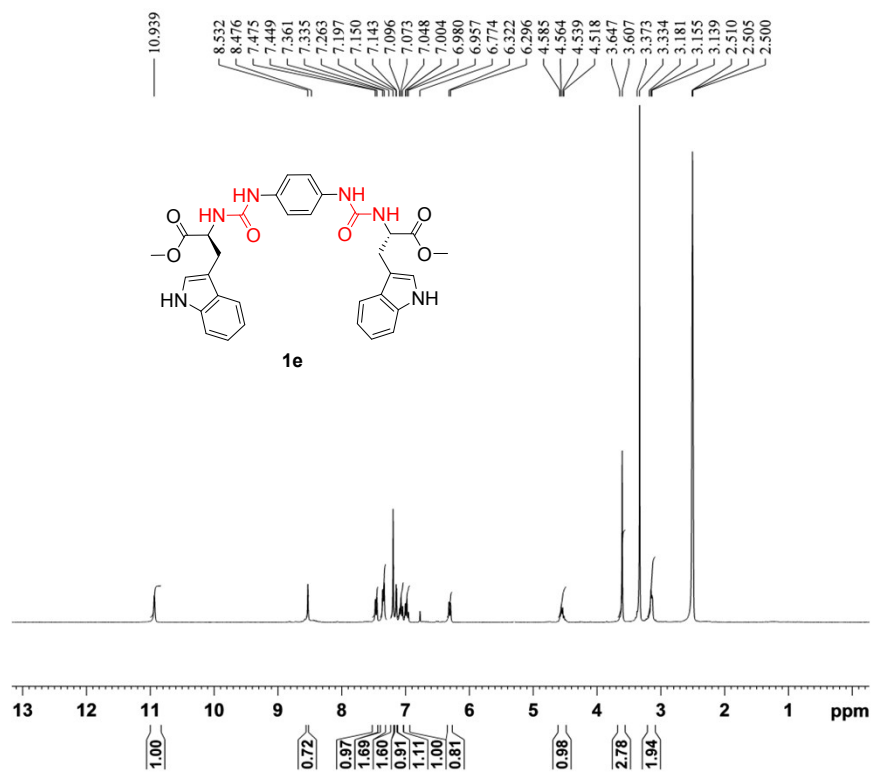
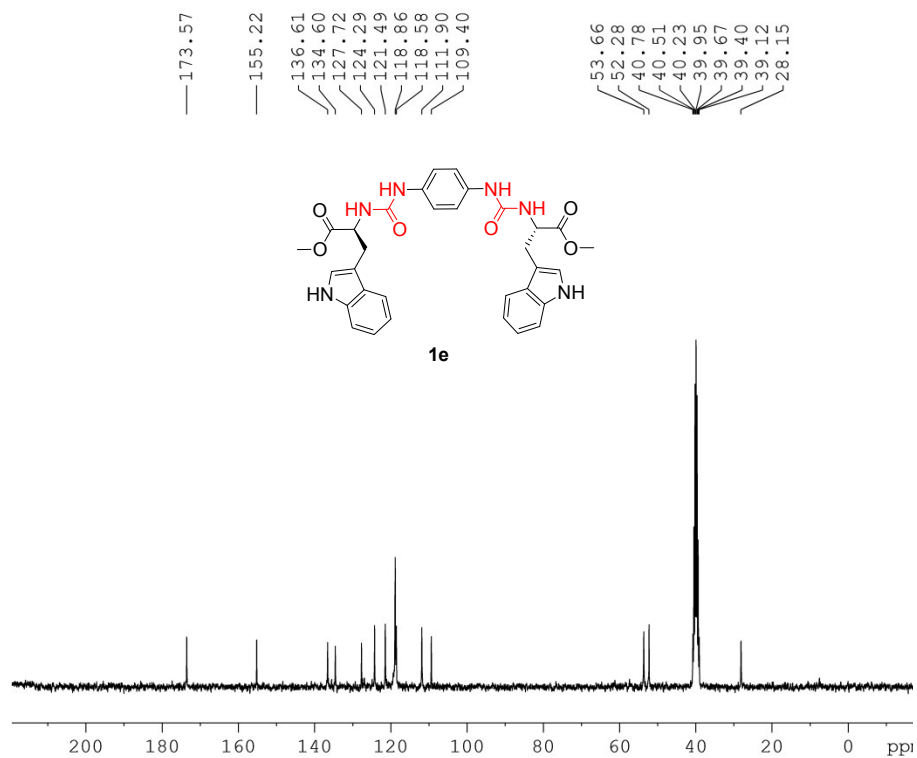
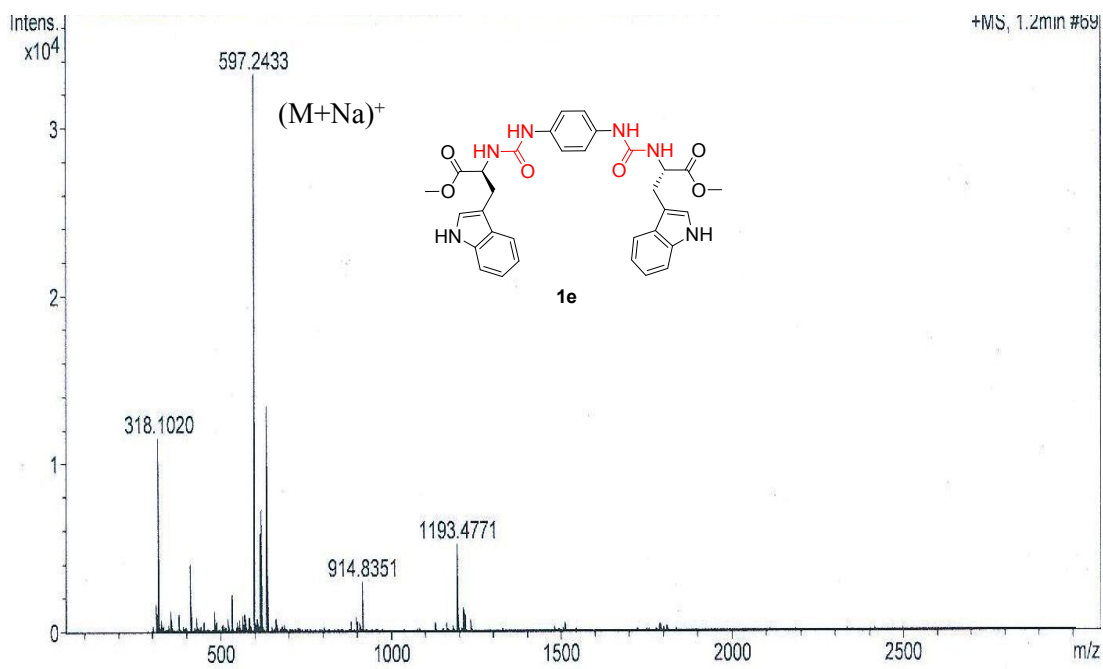


Figure S49.  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 300MHz) spectrum of **1e**

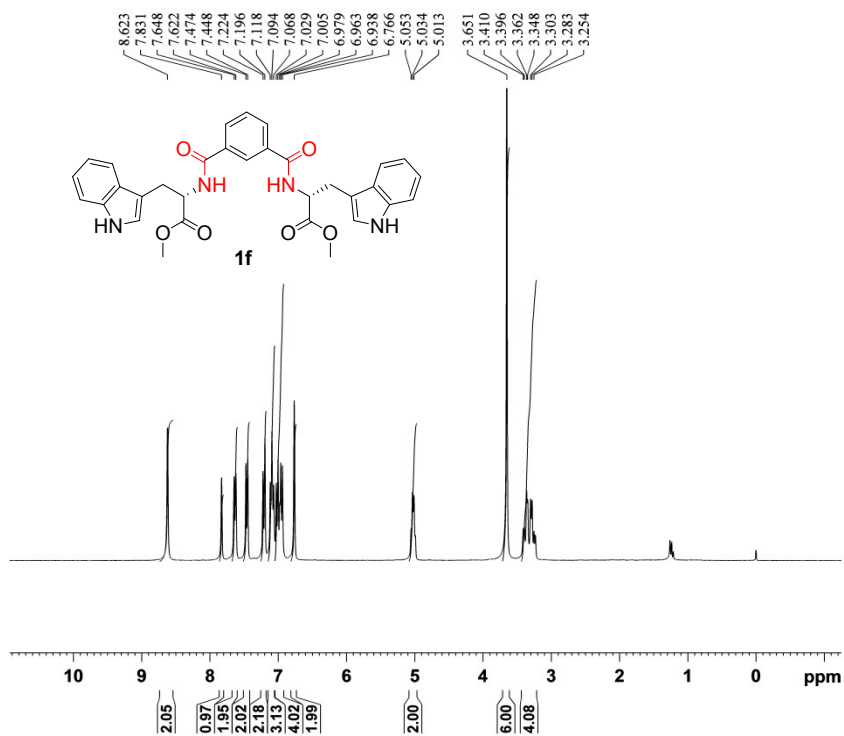


**Figure S50.**  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 75MHz) spectrum of **1e**

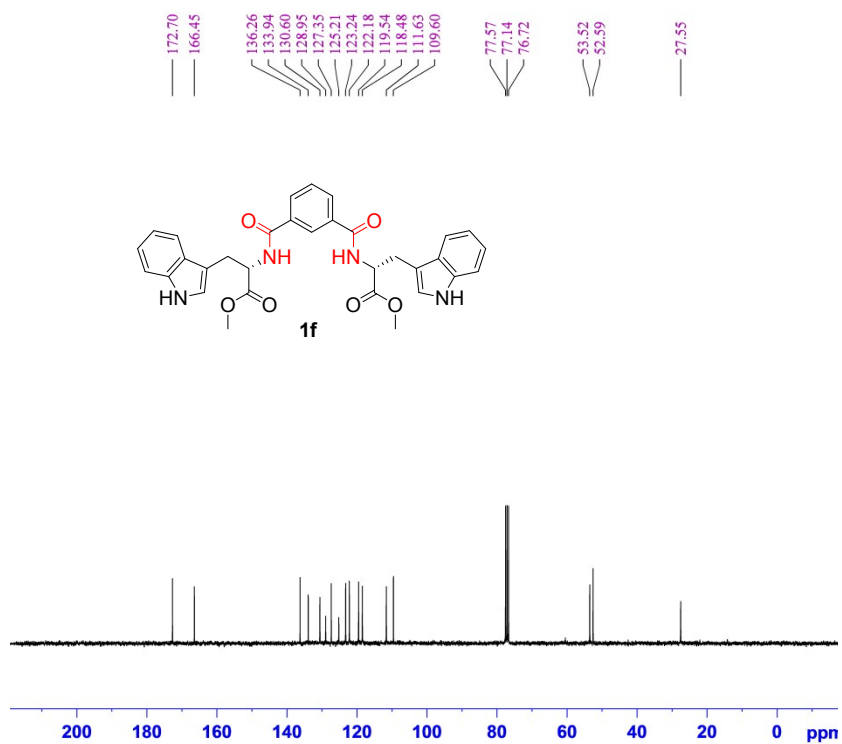


**Figure S51.** HRMS of **1e**





**Figure S52.** <sup>1</sup>H NMR (CD<sub>3</sub>CN, 300MHz) spectrum of **1f**



**Figure S53.** <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz) spectrum of **1f**

## References

1. Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. *J. Am. Chem. Soc.* **1996**, *118*, 11225-11236.
2. Kaminski, G. A.; Friesner, R. A.; Tirado-Rives, J.; Jorgensen, W. L. *J. Phys. Chem. B*, **2001**, *105*, 6474-6487.