

Supporting Information

Stereochemistry and Solid State Structure of an Intrinsically Chiral *meso*-Patterned Porphyrin: a Case Study by NMR and Single-Crystal X-ray Diffraction Analysis

Liguo Yang, Yang Zhou, Mengliang Zhu, Luyang Zhao, Liye Wei, and Yongzhong

Bian*

Beijing Key Laboratory for Science and Application of Functional Molecular and Crystalline Materials, Department of Chemistry, University of Science and Technology Beijing, Beijing 100083, China
College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan, 250014, China

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1. NMR spectra of **1-6**, **1a**•*D*-Phe-OMe and **1b**•*D*-Phe-OMe.

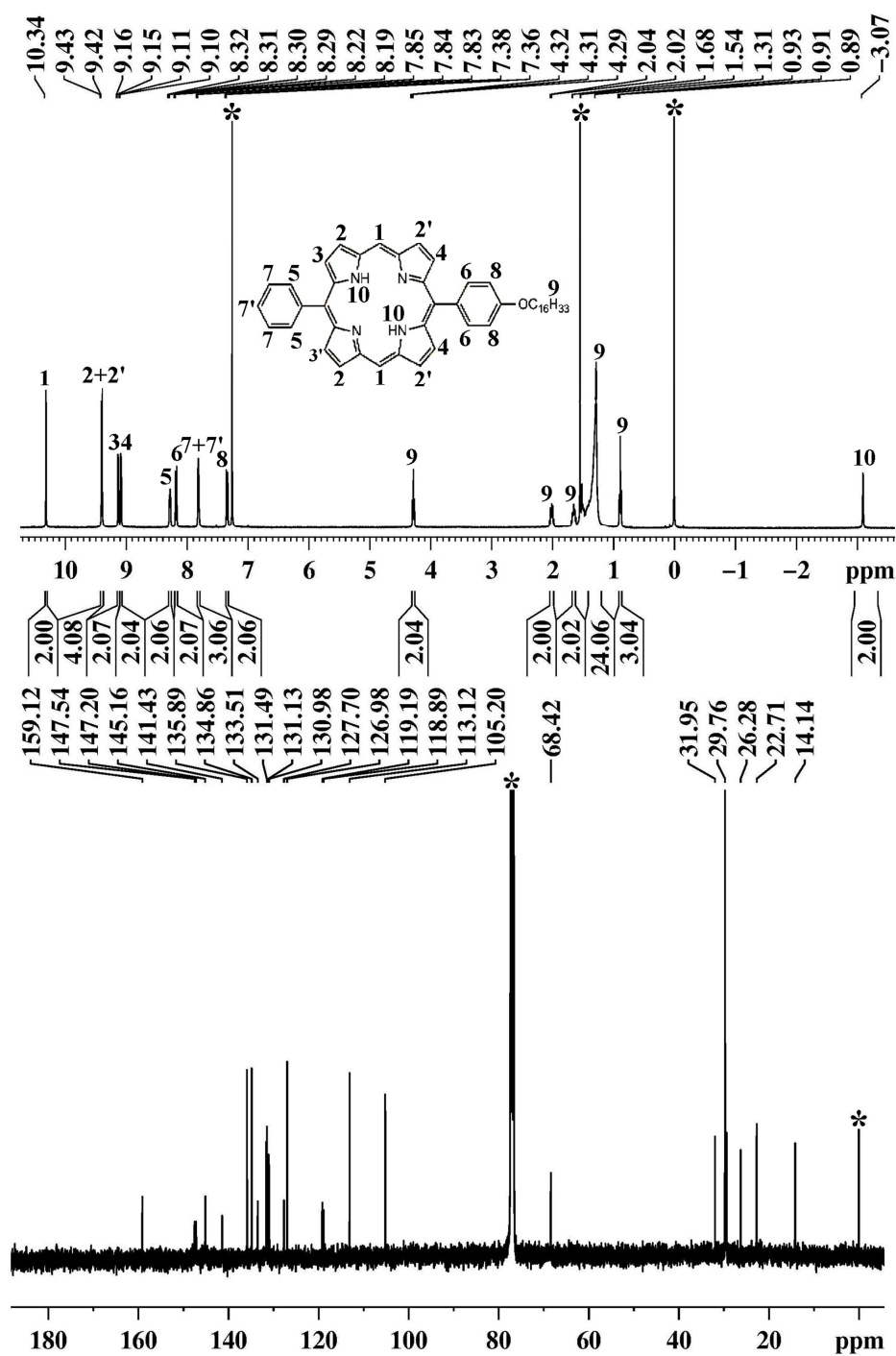


Figure 1. ^1H NMR and ^{13}C NMR spectra of **2** in CDCl_3 at 293 K. * indicate the

residual solvent and H_2O signals.

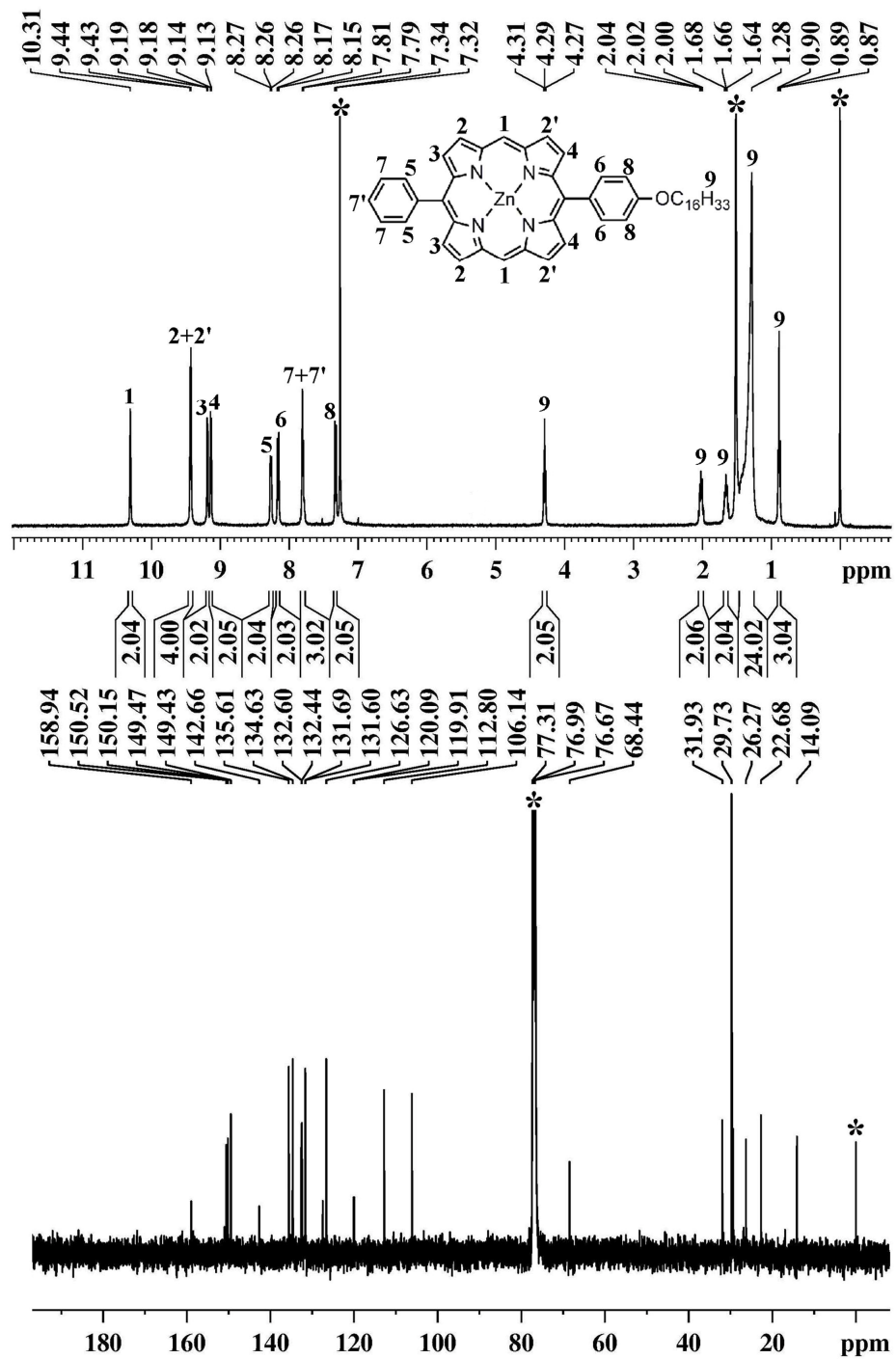


Figure 2. ^1H NMR and ^{13}C NMR spectra of **3** in CDCl_3 at 293 K. * indicate the residual solvent and H_2O signals.

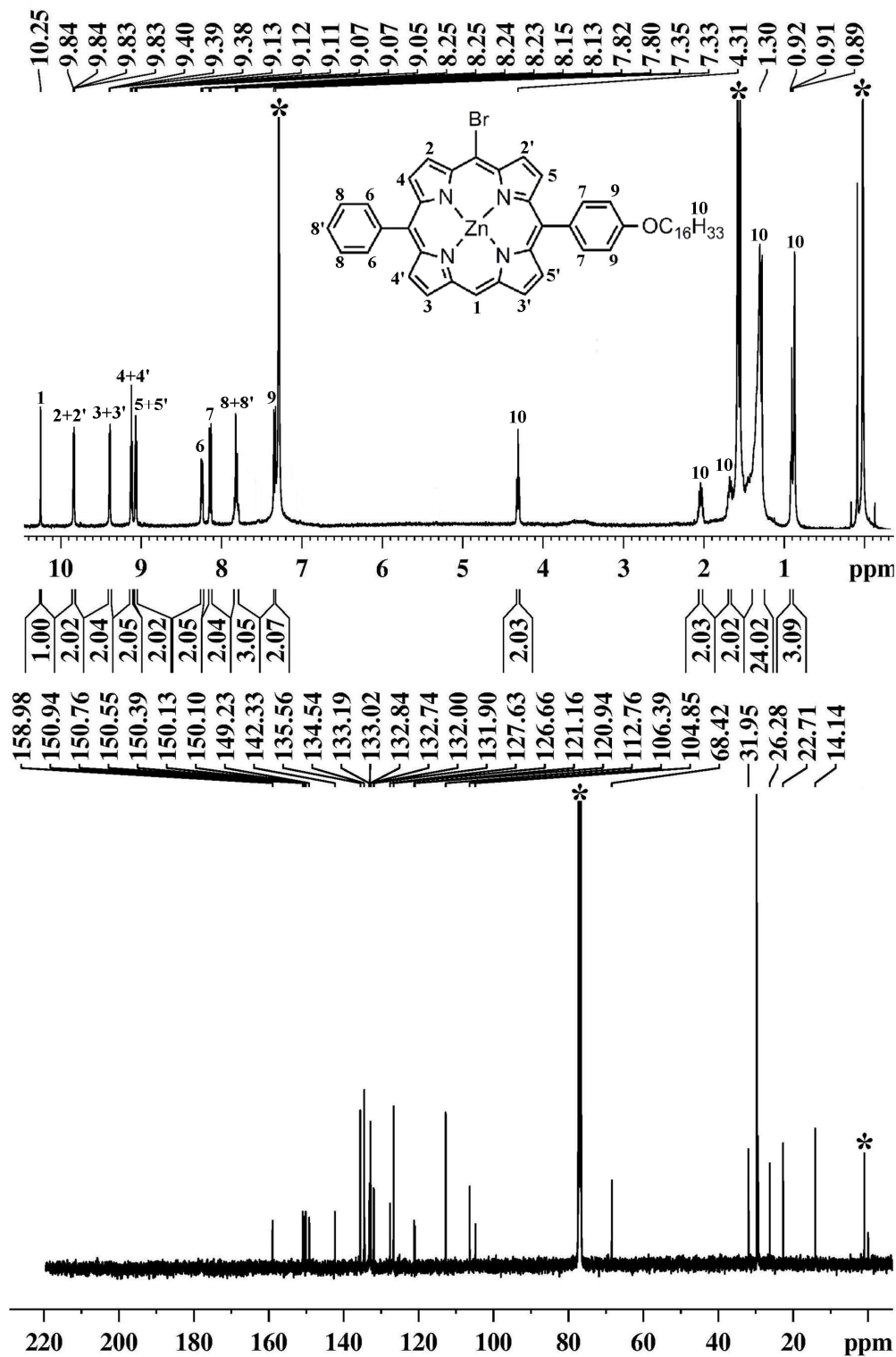
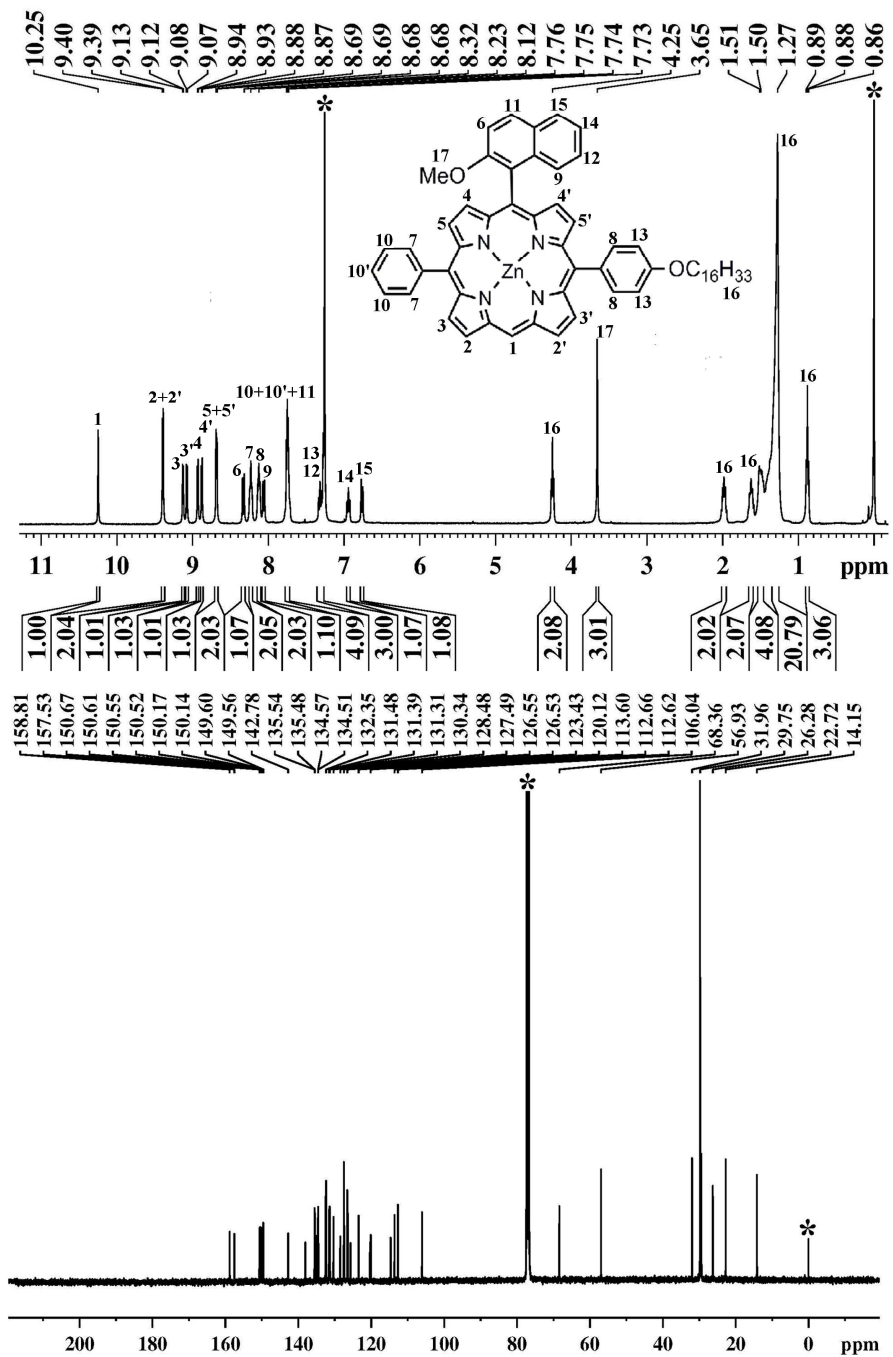


Figure 3. ¹H NMR and ¹³C NMR spectra of **4** in CDCl₃ at 293 K. * indicate the residual solvent and H₂O signals.



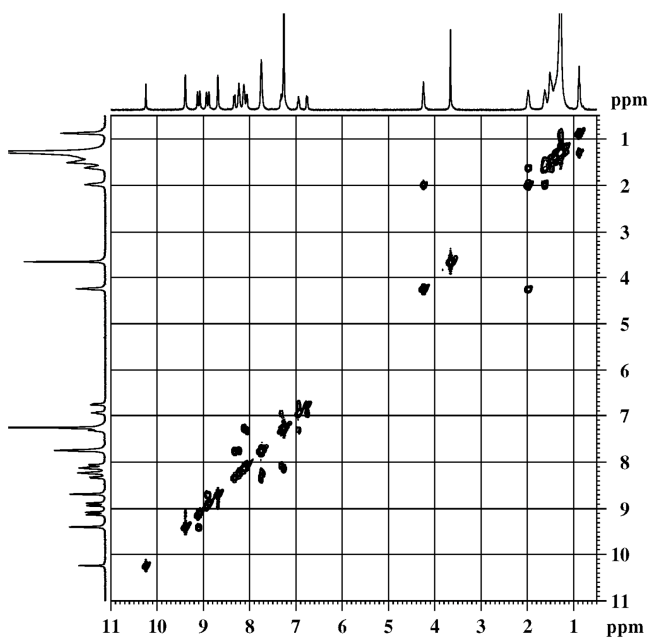
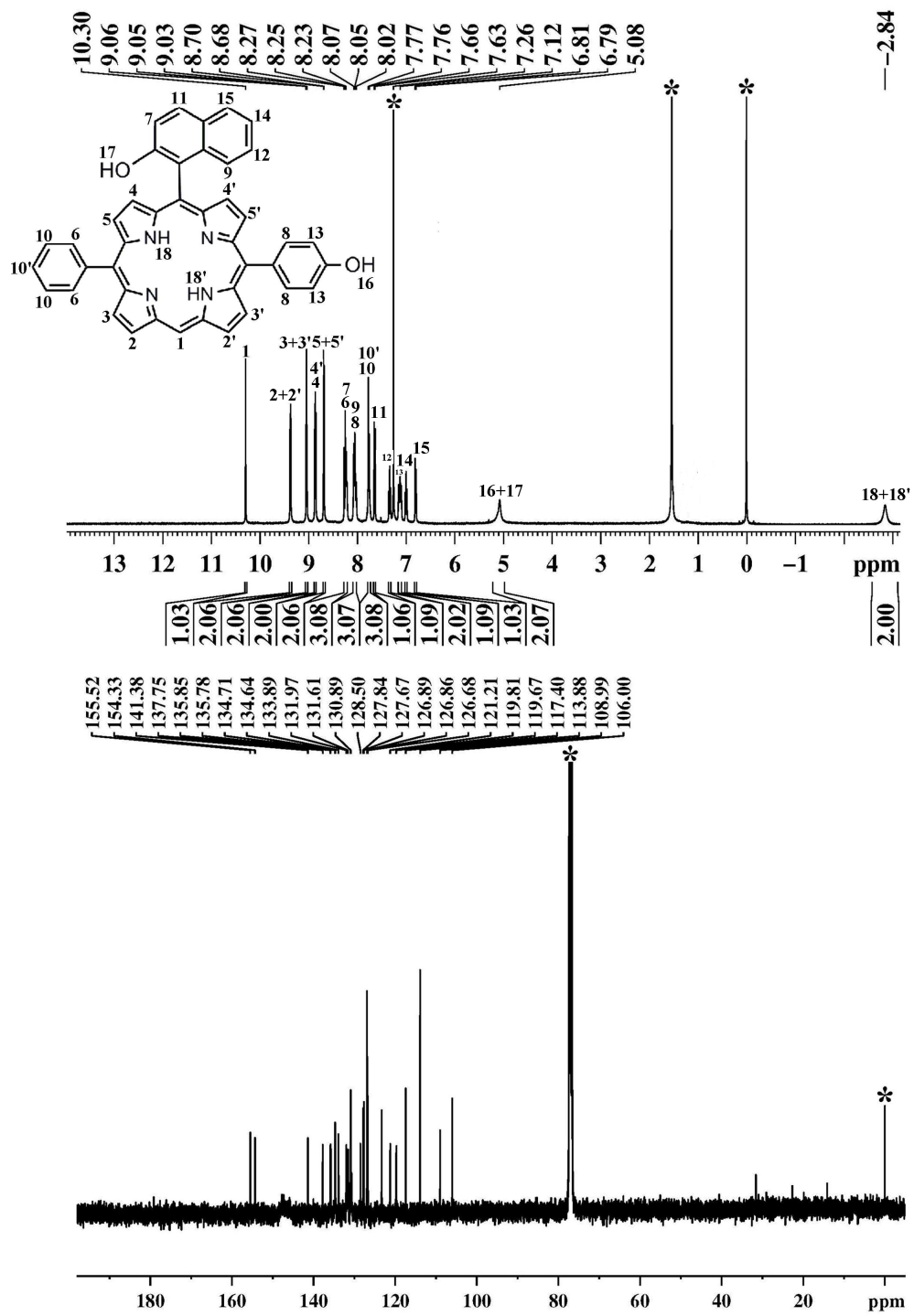


Figure 4. ^1H NMR, ^{13}C NMR and ^1H - ^1H COSY spectra of **5** in CDCl_3 at 293 K. *

indicate the residual solvent and H_2O signals.



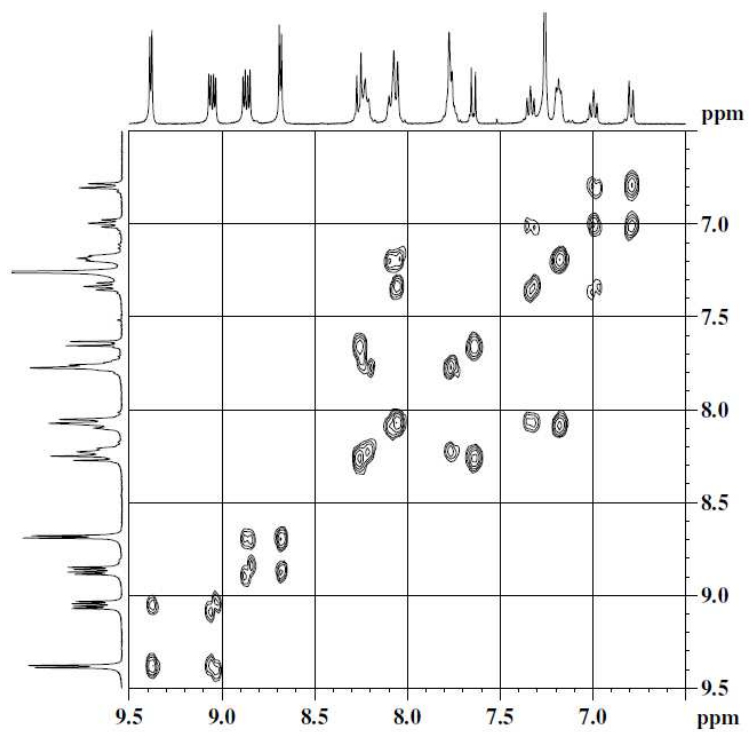
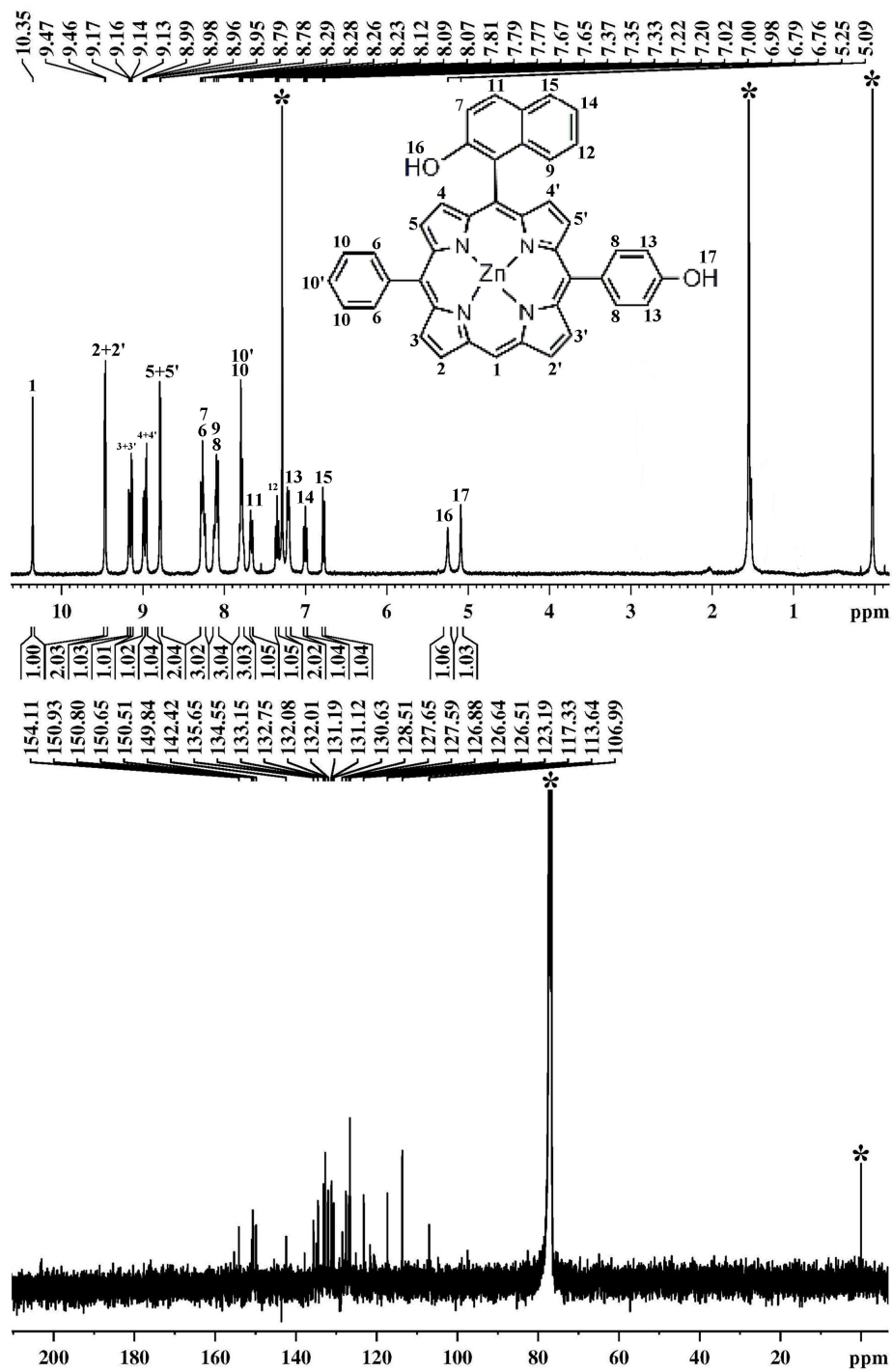


Figure 5. ^1H NMR, ^{13}C NMR and ^1H - ^1H COSY spectra of **6** in CDCl_3 at 293 K. *

indicate the residual solvent and H_2O signals.



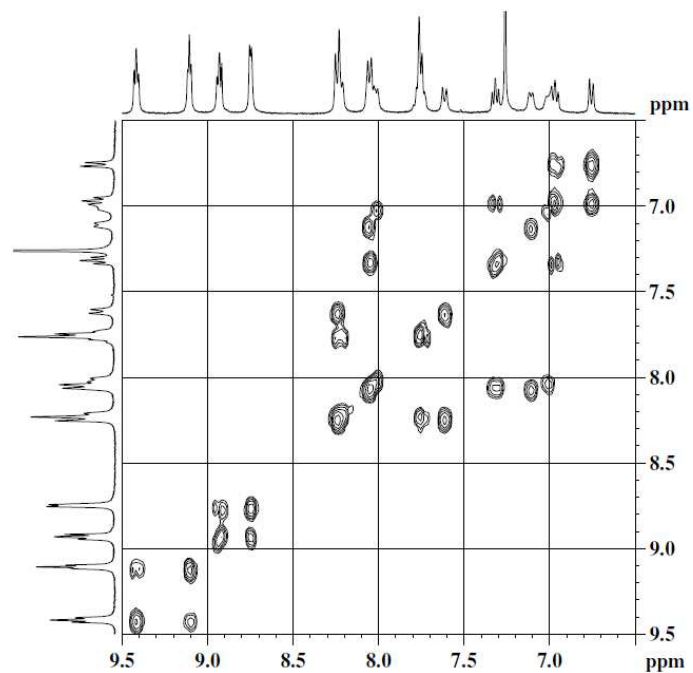


Figure 6. ^1H NMR, ^{13}C NMR and ^1H - ^1H COSY spectra of **1** in CDCl_3 at 293 K. *

indicate the residual solvent and H_2O signals.

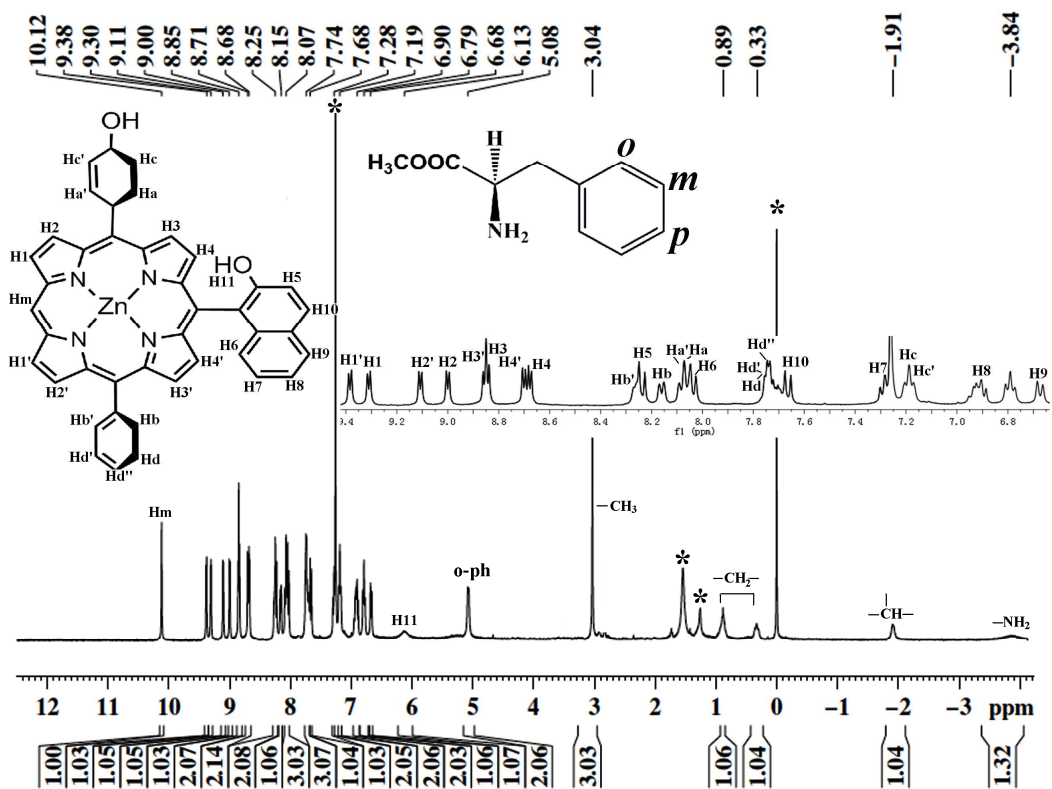


Figure 7. ^1H NMR spectra of **1a**•*D*-Phe-OMe in CDCl_3 at 293 K. * indicate the residual solvent and H_2O signals.

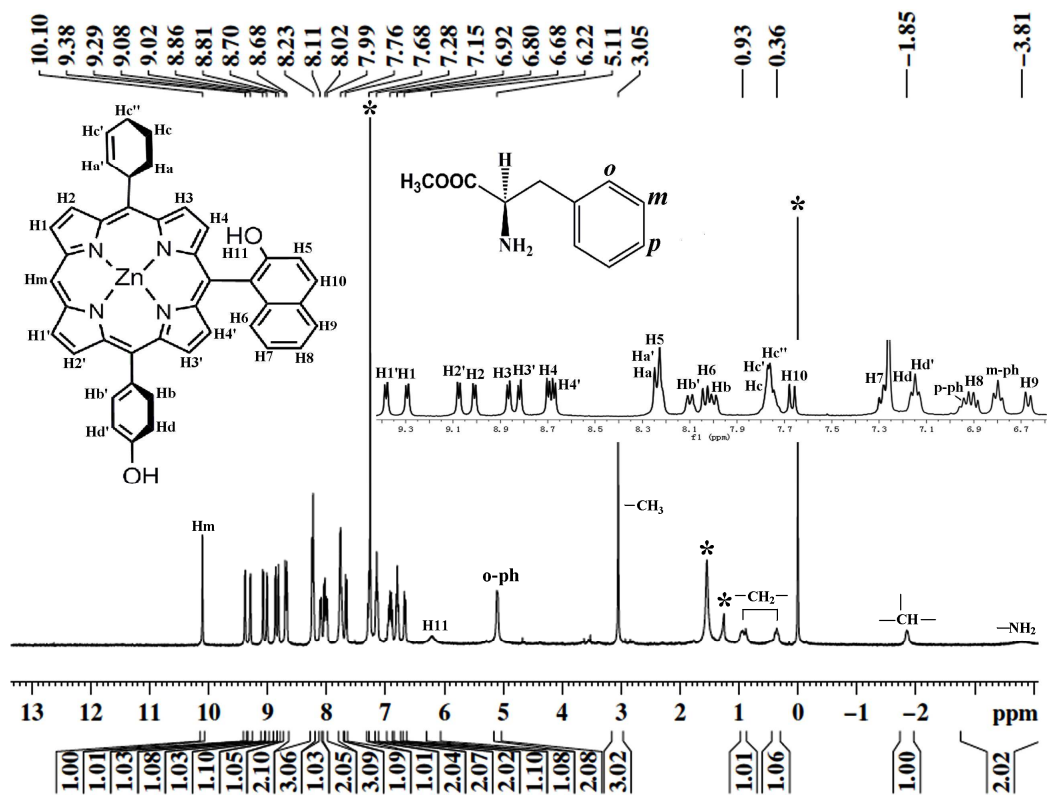


Figure 8. ^1H NMR spectra of $1\mathbf{b}\cdot\text{D-Phe-OME}$ in CDCl_3 at 293 K. * indicate the residual solvent and H_2O signals.

2. Crystallographic data for compound 1 and 1a·L-Phe-OMe (Table S1).

	1 ·2Py·2CHCl ₃	1a ·L-Phe-OMe·CHCl ₃
Formula	C ₅₄ H ₃₈ Cl ₆ N ₆ O ₂ Zn	C ₅₂ H ₃₉ Cl ₃ N ₅ O ₄ Zn
<i>M</i>	1080.97	982.62
Cryst syst	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁
<i>a</i> /Å	12.2680(10)	18.721(3)
<i>b</i> /Å	12.5730(8)	13.4029(11)
<i>c</i> /Å	18.1872(11)	20.590(3)
α /deg	88.879(5)	90
β /deg	77.687(6)	115.365(17)
γ /deg	63.913(7)	90
<i>V</i> /Å ³	2452.7(3)	4668.4(10)
<i>Z</i>	2	4
<i>F</i> (000)	1104	2024
<i>D</i> _c /Mg m ⁻³	1.464	1.398
μ /mm ⁻¹	4.098	0.750
θ range/deg	4.12 to 60.00	2.90 to 25.00
Reflns collected	11838	18407
Independent reflns	7118 [R _{int} = 0.0390]	8587 [R _{int} = 0.1375]
Params	554	1194
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0925	0.0866
w <i>R</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.2593	0.1360
Goodness of fit	1.031	0.936
Flack parameter	----	0.05(2)

3. Method for Evaluation of Association Constants (K_{ass})^[S1]

K_s values were evaluated from the following equation by applying a nonlinear curve-fitting method to the changes in absorbance (ΔAbs) upon titration of host **1b** with *L*- and *D*-Phe-OMe:

$$\Delta Abs = (L(1+K_{ass}X+K_{ass}A)-(L^2(K_{ass}X+K_{ass}A+1)^2-4K_{ass}^2AXL^2)^{0.5})/2K_{ass}A$$

Where X and A represent $[Guest]_{total}$ and $[Host]_{total}$, respectively; L denotes ΔAbs at 100% complexation; L and K_s are parameters.

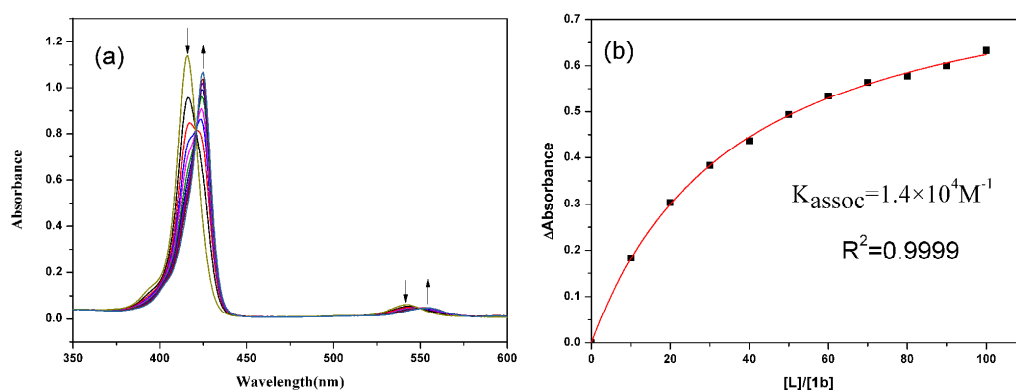


Figure S1. (a) A spectral change upon titration of **1b** with *D*-Phe-OMe in $CHCl_3$ at 25°C. (b) Changes in ΔAbs at 415 nm for evaluating K_{ass} . $[1b] = 2.0 \times 10^{-6} M$; $[L]/[1b] = 0-100$.

4. ^1H NMR spectra of *L*-Phe-OMe, **1a**•*L*-Phe-OMe, **1b**•*L*-Phe-OMe, **1a**•*D*-Phe-OMe and **1b**•*D*-Phe-OMe in CDCl_3 at 293 K.

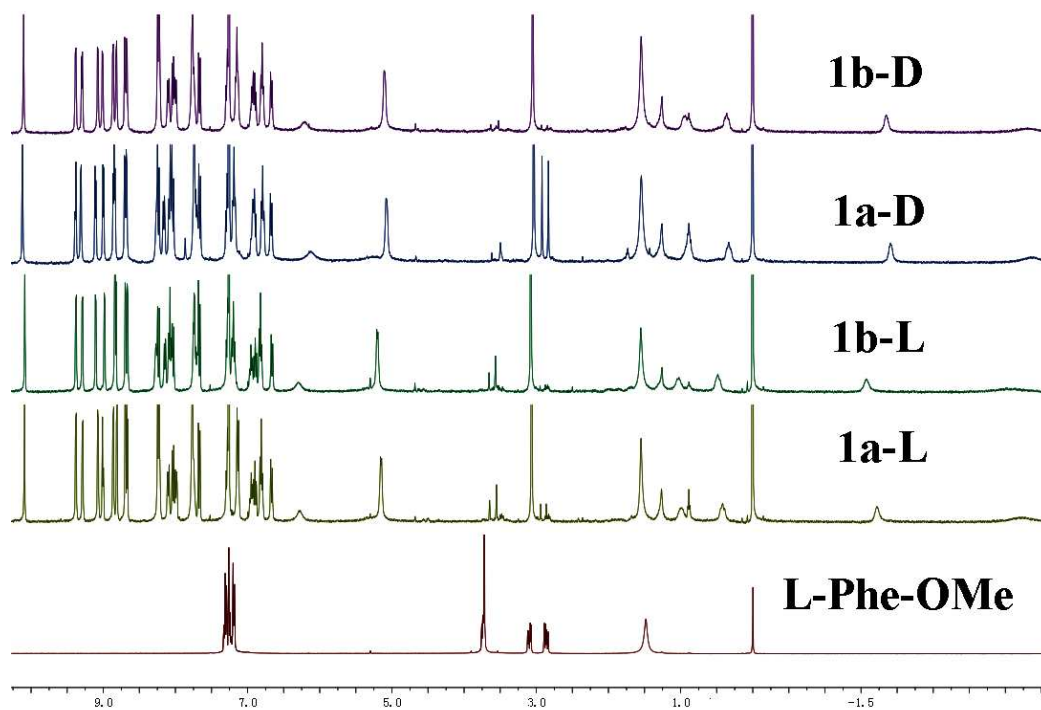


Figure S2. ^1H NMR spectra of *L*-Phe-OMe, **1a**•*L*-Phe-OMe, **1b**•*L*-Phe-OMe, **1a**•*D*-Phe-OMe and **1b**•*D*-Phe-OMe in CDCl_3 at 293 K.

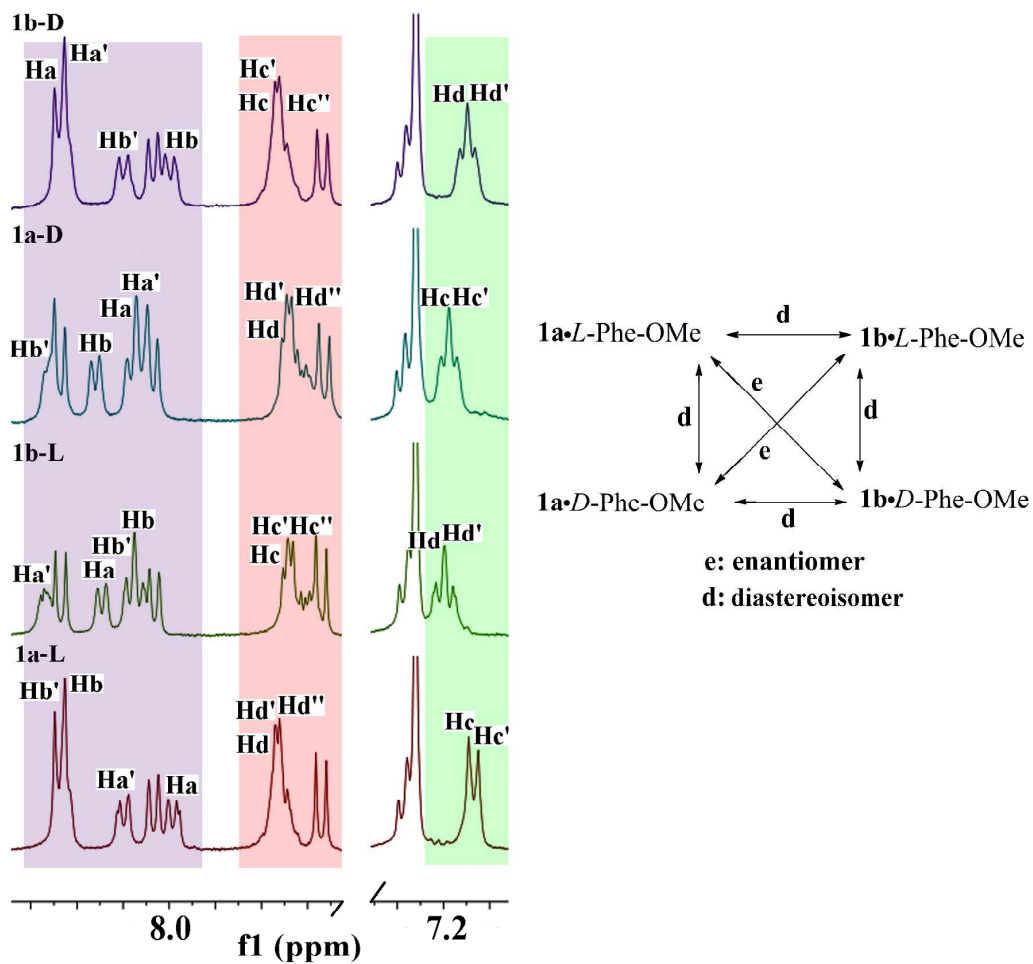


Figure S3. Partial ¹H NMR spectra of *L*-Phen-OMe, **1a•L-Phe-OMe**, **1b•L-Phe-OMe**, **1a•D-Phe-OMe** and **1b•D-Phe-OMe** in CDCl₃ at 293 K.

5. Density functional theory calculation.

The DFT calculation was carried out by ω b97xd^[S21] method with mixed basis sets: 6-311++G(d) for Zn, 6-31+G(d) for O, and 6-31G(d) for other elements. The geometric molecular structure of **S-1•L-Phe-OMe** and **R-1•L-Phe-OMe** with their single point energies E_S , E_R were simulated, and binding energy was calculated according to the formula: $\Delta E = E - E_{\text{Por}} - E_{\text{amo}}$, where E_{Por} stands for the geometry-relaxed energy of porphyrin moiety, E_{amo} for that of amino acid ester moiety, and E for either E_S and E_R . All the calculations were carried out by *Gaussian 09* program^[S3] housed at the School of Chemistry and Chemical Engineering, Shandong University. The optimized molecular structures of **S-1•L-Phe-OMe** and **R-1•L-Phe-OMe** are given below.

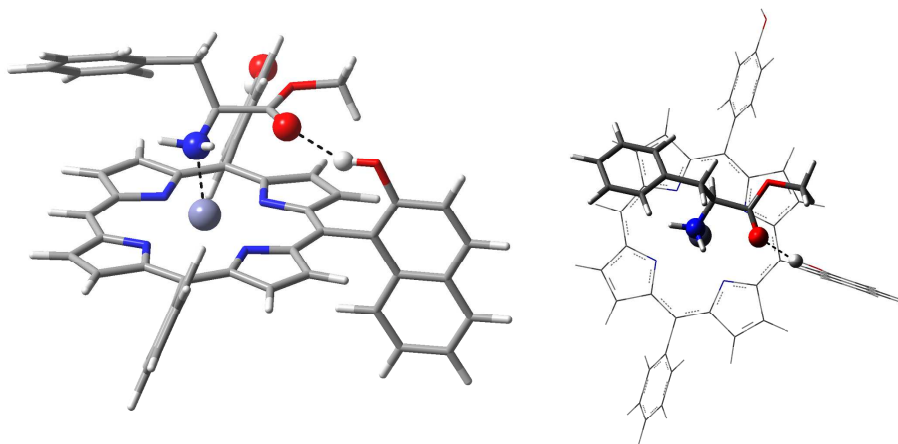


Figure S4. The simulated structure of **S-1•L-Phe-OMe** from two perspectives.

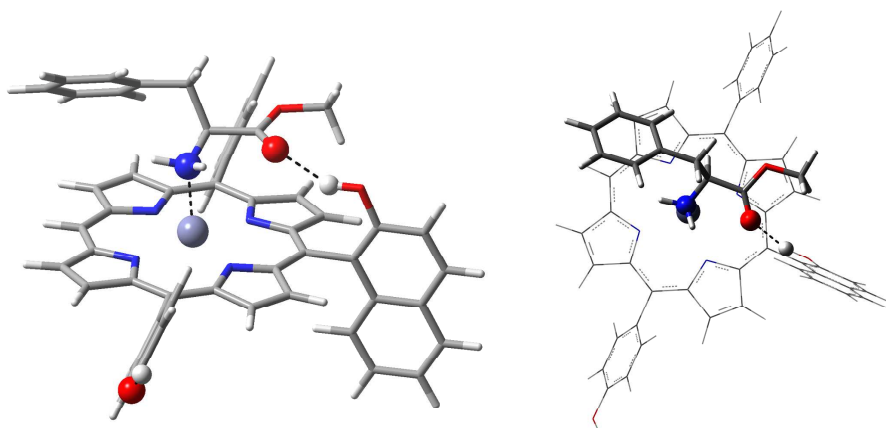


Figure S5. The simulated structure of *R*-1•*L*-Phe-OMe from two perspectives.

6. ^1H NMR titration of **1a** and **1b** with *L*-Phe-OMe.

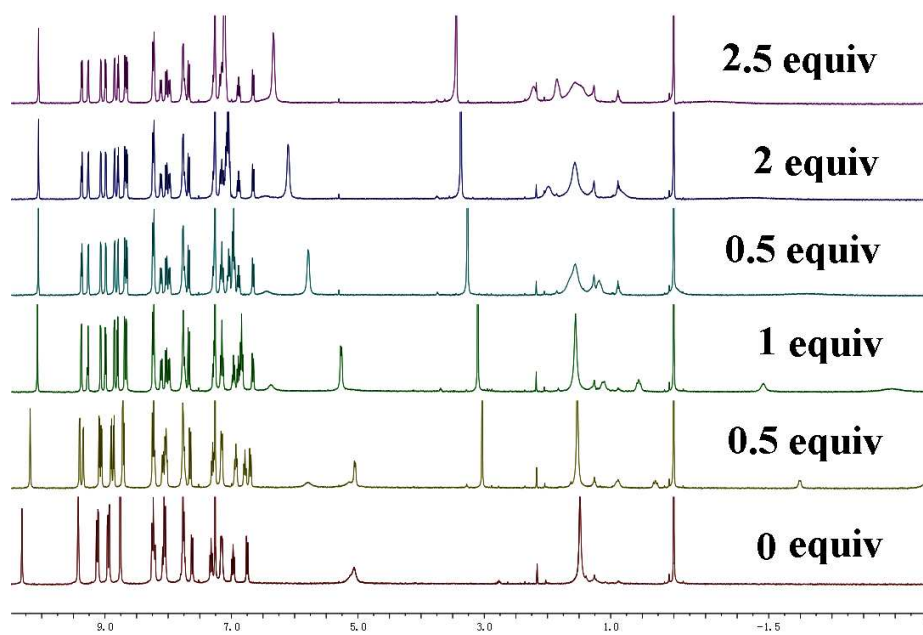


Figure S6. ^1H NMR titration spectra of **1a** with *L*-Phe-OMe (0.5 equiv additions) at 293 K in CDCl_3 .

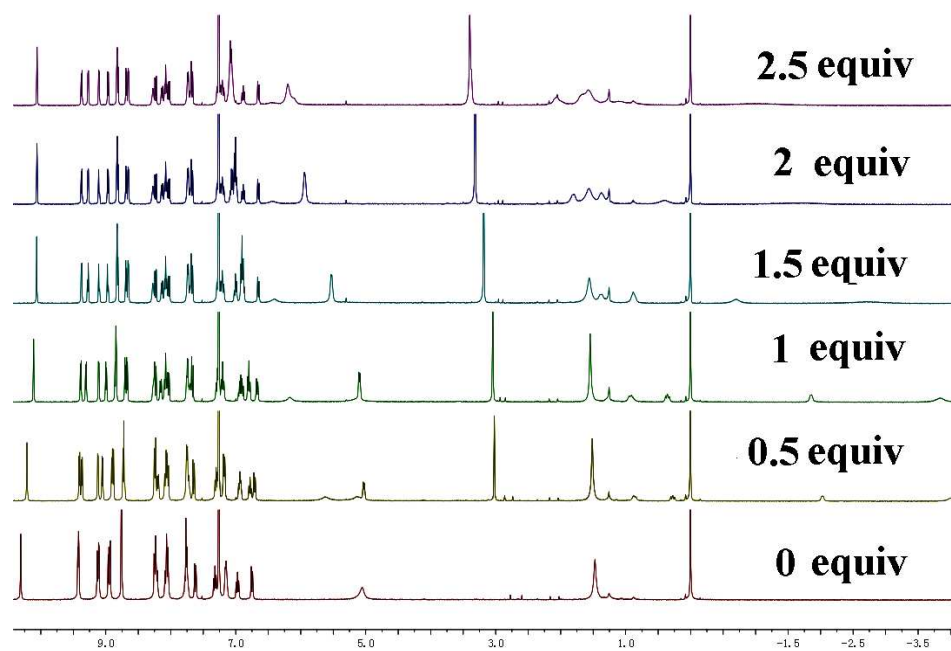


Figure S7. ¹H NMR titration spectra of **1b** with *L*-Phe-OMe (0.5 equiv additions) at 293 K in CDCl₃.

7. ^1H NMR and ^1H - ^1H COSY spectra of **1a**•*L*-Phe-OMe and **1b**•*L*-Phe-OMe.

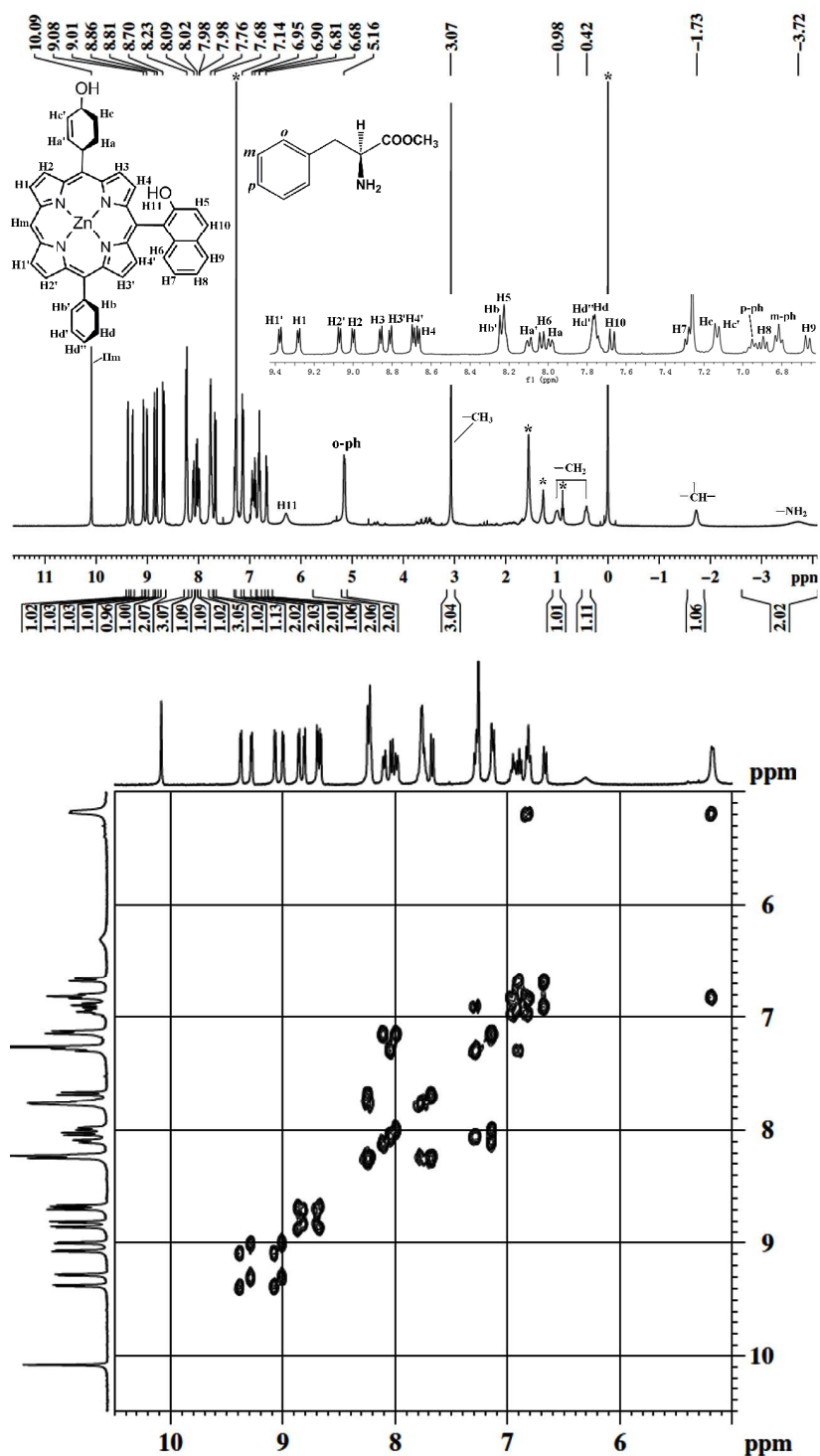


Figure S8. ^1H NMR and ^1H - ^1H COSY spectra of **1a**•*L*-Phe-OMe in CDCl_3 at 293 K.

* indicate the residual solvent and H₂O signals.

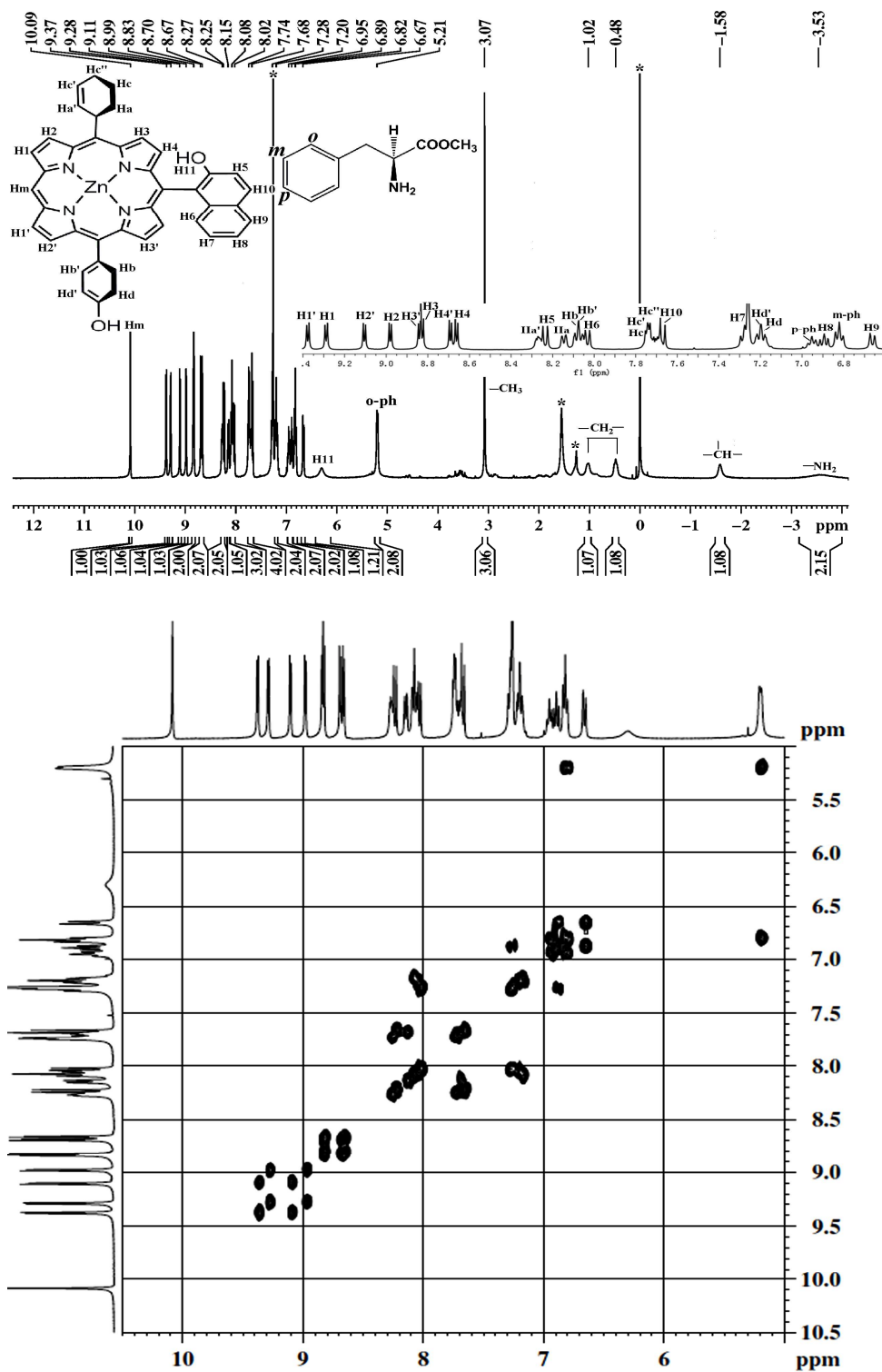


Figure S9. ^1H NMR and ^1H - ^1H COSY spectra of **1b**•L-Phe-OMe in CDCl_3 at 293 K.

* indicate the residual solvent and H_2O signals.

8. ^1H - ^1H NOESY spectra of **1a**•*L*-Phe-OMe and **1b**•*L*-Phe-OMe.

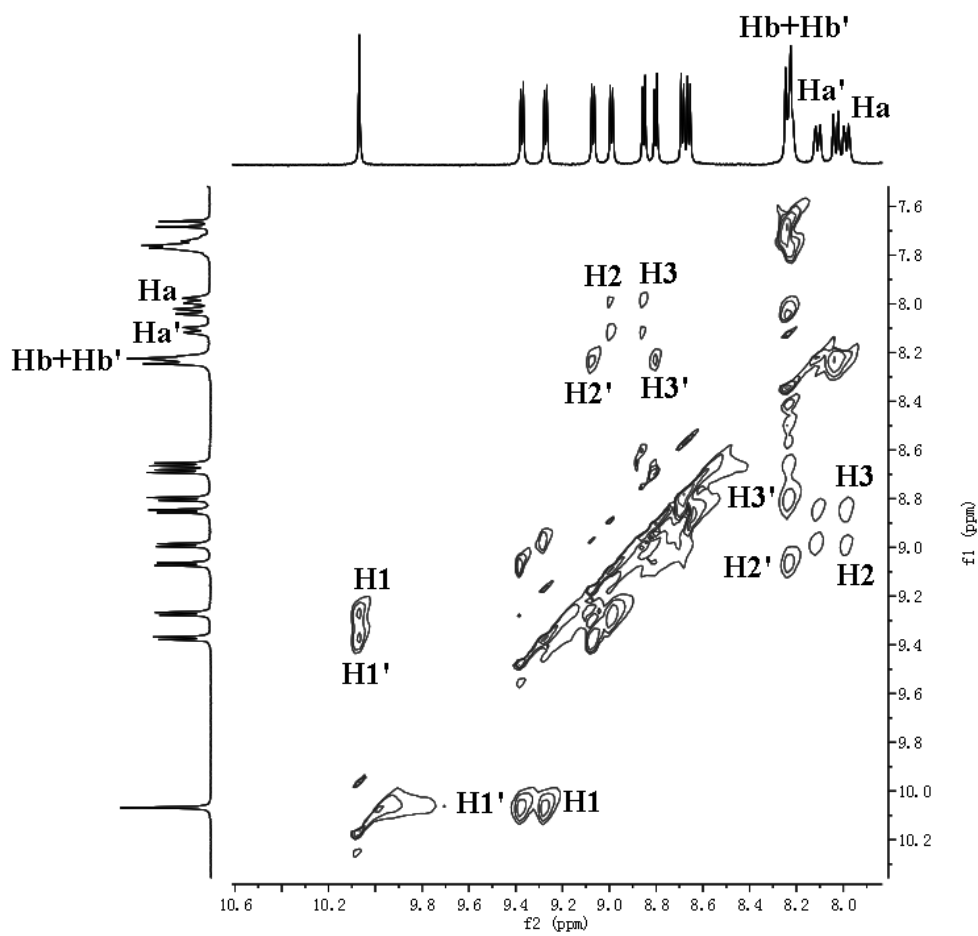


Figure S10. ^1H - ^1H NOESY spectra of **1a**•*L*-Phe-OMe in CDCl_3 at 293K.

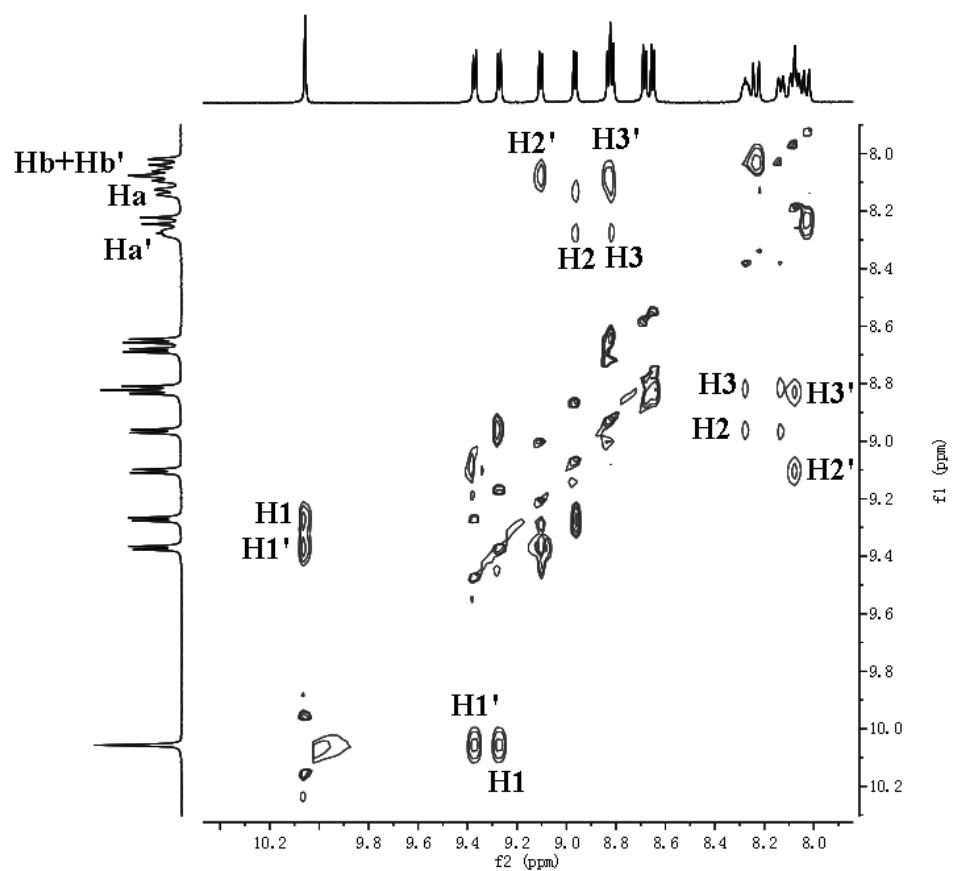


Figure S11. ^1H - ^1H NOESY spectra of **1b**•*L*-Phe-OMe in CDCl_3 at 293K.

9. References

[S1] Shoji, Y.; Tashiro, K.; Aida, T. *J. Am. Chem. Soc.* **2010**, *132*, 5928–5929.

[S2] Chai, J. D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.

[S3] Frisch, M. J. et al. *Gaussian 09 A.02*; Gaussian, Inc., Pittsburgh PA, **2009**.