

## Electronic Supporting Information

# Geometry & Temperature Dependence of *meso*-Aryl Rotation in Strained Metalloporphyrins: Adjustable Turnstile Molecules

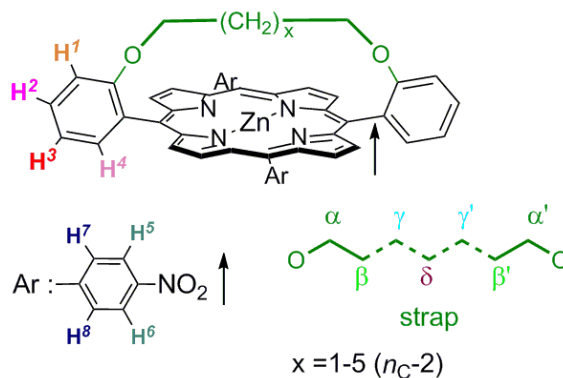
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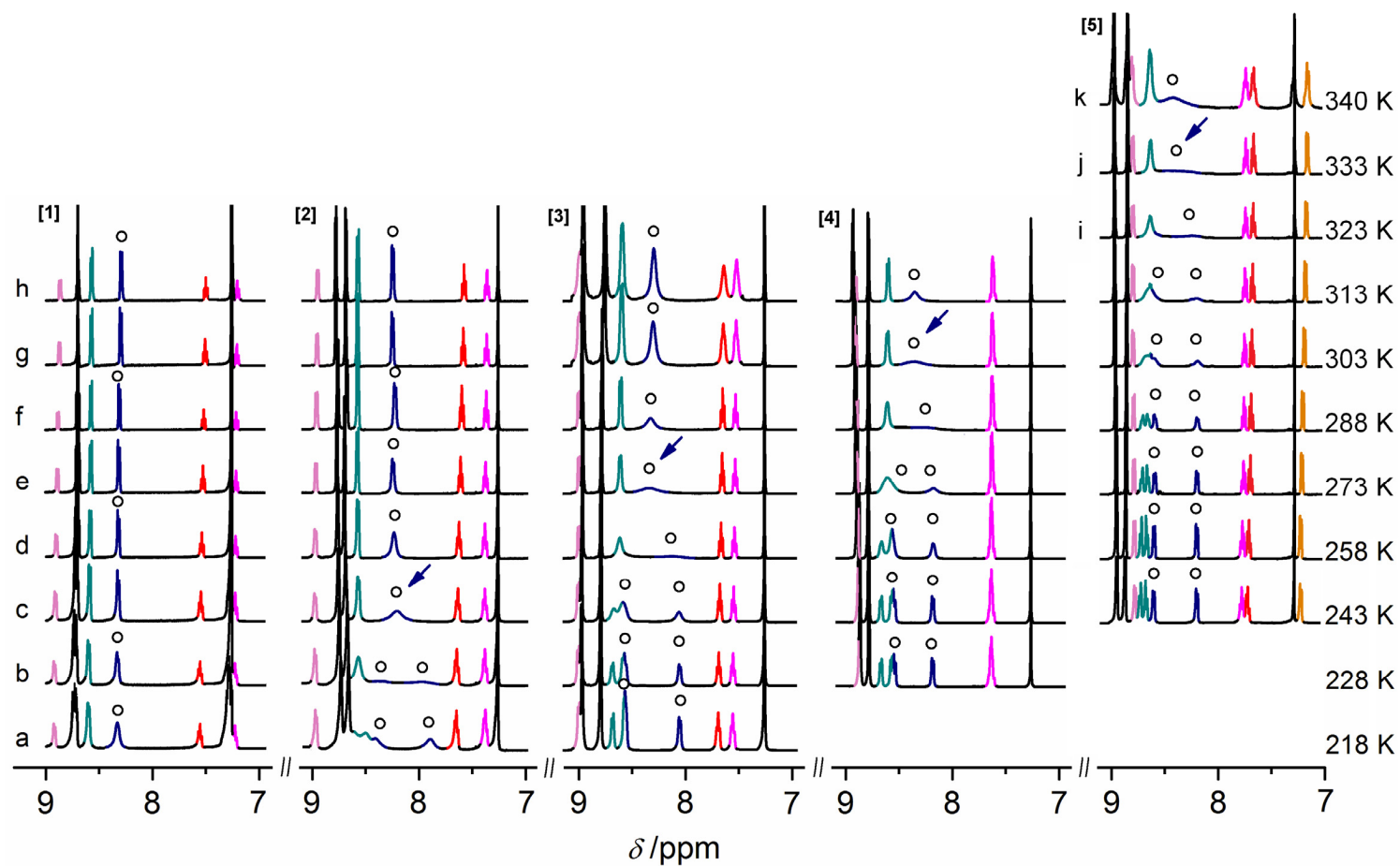
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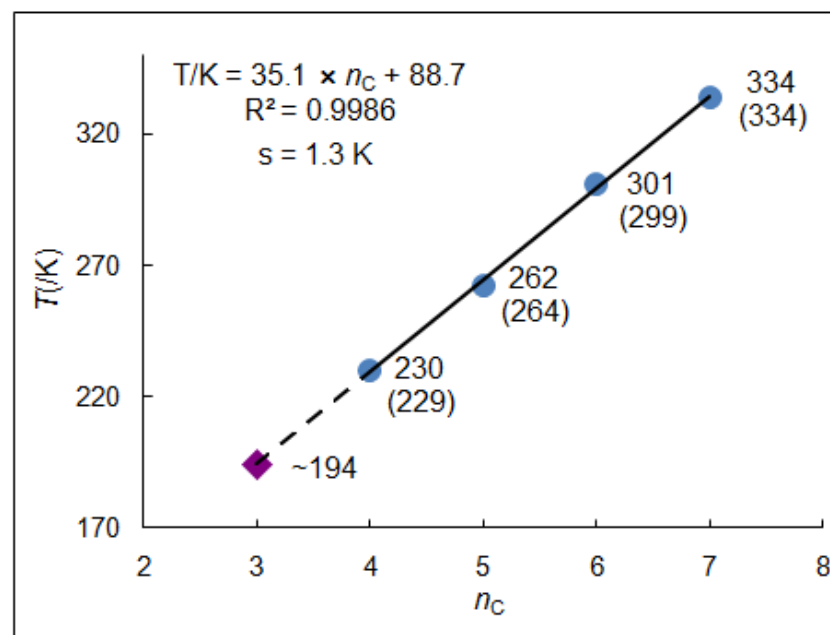
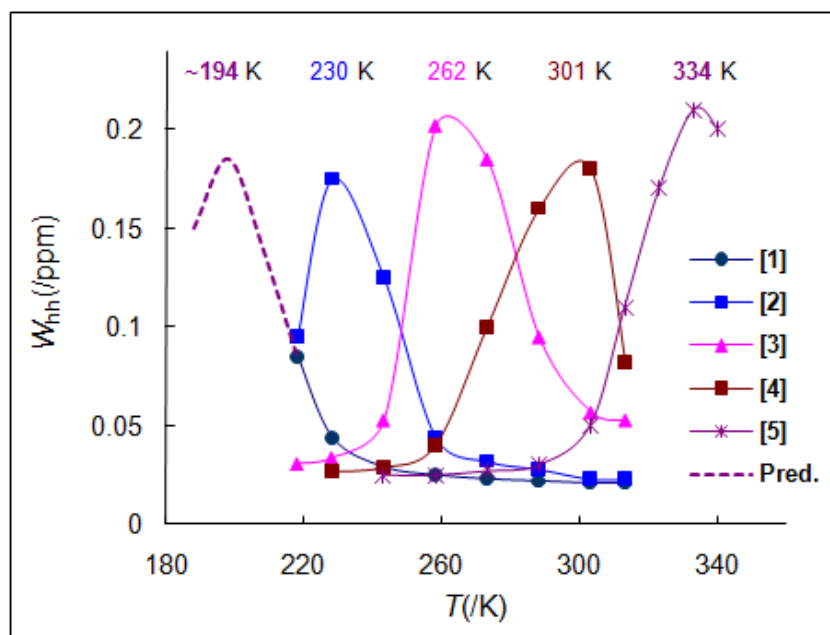


Model compounds

# 1. Acquirement of the coalescence temperature ( $T_C$ ) of the *meso*-aryl rotation



Comparison of low-field signals containing diagnostic protons  $\text{H}^7$  and  $\text{H}^8$ .



The relationship of  $T_C$  to  $W_{hh}$  of diagnostic protons  $H^7$  (left) and that of  $T_C$  to  $n_C$  in straps (right)

The coalescence temperature,  $T_C$ , of compound **1** is obtained according to the Equation 1, and the Equation is acquired through linear fitting of 4 experimental  $T_C$  to their relative  $n_C$  in straps ( $n_C$  is the number of carbon atom in the strap). The numbers denote  $T_C$  and their relative fitted values (in brackets)

$$T/K = 35.1 \times n_C + 88.7 \quad (1)$$

The predictive  $T_C$  of compound **1** ( $n_C = 3$ ) was not verified due to the poor solubility at thus low temperature (194 K).  $W_{hh}$  presents the peak width at half-height.

## 2. Calculation of the rotational barrier ( $\Delta G^\ddagger$ ) of the meso-aryl groups

| $n_c(\text{Compd.})$                                  | 3(1)        | 4(2)         | 5(3)         | 6(4)         | 7(5)         |
|-------------------------------------------------------|-------------|--------------|--------------|--------------|--------------|
| $\Delta G^\ddagger/(\text{kJ}\cdot\text{mol}^{-1})^a$ | $\sim 37^b$ | 45.0         | 51.6         | 60.5         | 67.1         |
| $\Delta\nu(\text{Hz})$                                | —           | 127.8        | 123.8        | 87.5         | 100.3        |
| $T_c(\text{K})$                                       | $\sim 194$  | 230<br>(229) | 262<br>(264) | 301<br>(299) | 334<br>(334) |

$$\frac{\Delta G^\ddagger}{RT_c} = 22.96 + \ln \frac{T_c}{\Delta\nu} \quad (2)$$

a). the value of  $\Delta G^\ddagger$  is obtained by using Equation (2) <sup>1</sup> b) the value of rotational barrier ( $\Delta G^\ddagger$ ) is also calculated by linear extension.

The value of rotational barrier ( $\Delta G^\ddagger$ ) can be also calculated by linear treatment. Because for complex, **1**, the value,  $T_c/\Delta\nu$ , is near or less than 2, and the exponential term is less than 1, the term,  $(22.96 + \ln(T_c/\Delta\nu))R$ , can be viewed as a constant.

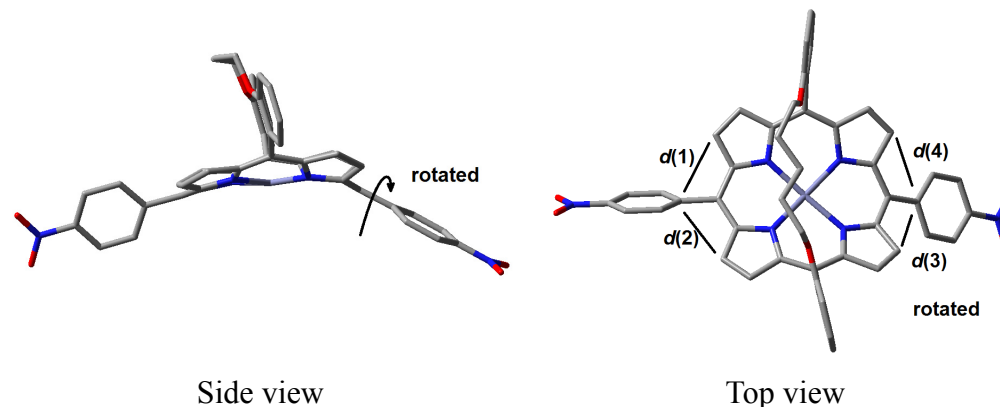
$$\text{Equation 2:} \quad \Delta G^\ddagger = (22.96 + \ln(T_c/\Delta\nu)) RT_c$$

$$\Rightarrow \Delta G^\ddagger \propto T_c$$

(1) Medforth, C. J.; Haddad, R. E.; Muzzi, C. M.; Dooley, N. R.; Jaquinod, L.; Shyr, D. C.; Nurco, D. J.; Olmstead, M. M.; Smith, K. M.; Ma, J. G.; Shelnut, J. A. *Inorg. Chem.* **2003**, 42, 2227–2241

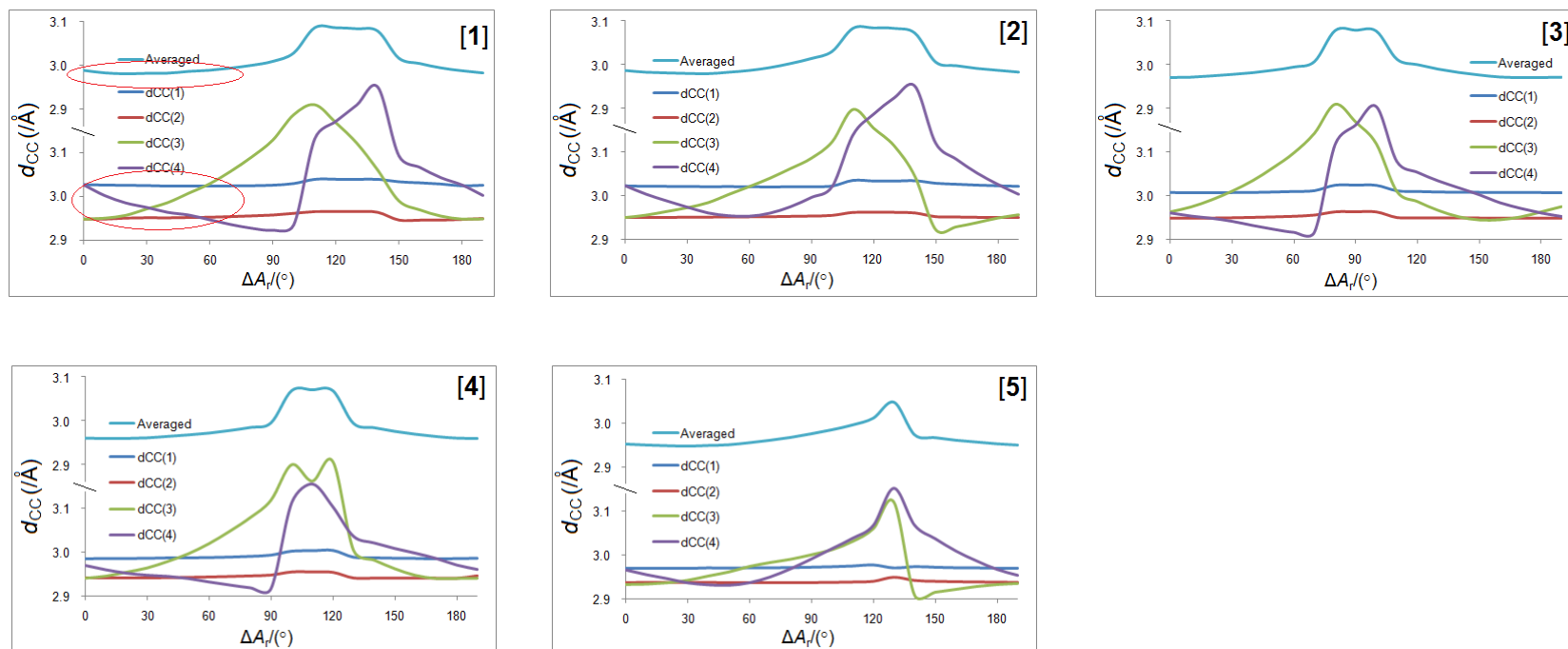
### 3. The account to parameter, $d_{CC}$

In solid state, these complexes adopt a dominant arc type (or ruffle-like type) deformation, but the folding of C-O-C component in strap makes the phenyls modified by ether shift between  $\beta$ -Cs, which makes the other phenyls containing  $-\text{NO}_2$  also slightly shift from one  $\beta$ -C to another one. The 4 distances,  $d_{CC}$ , appear as four individual values,  $d_{CC}(1)$ ,  $d_{CC}(2)$ ,  $d_{CC}(3)$  and  $d_{CC}(4)$  (below Figure), the difference among them is not the deviation from error but the shift of phenyl due to macrocyclic extra deformation.



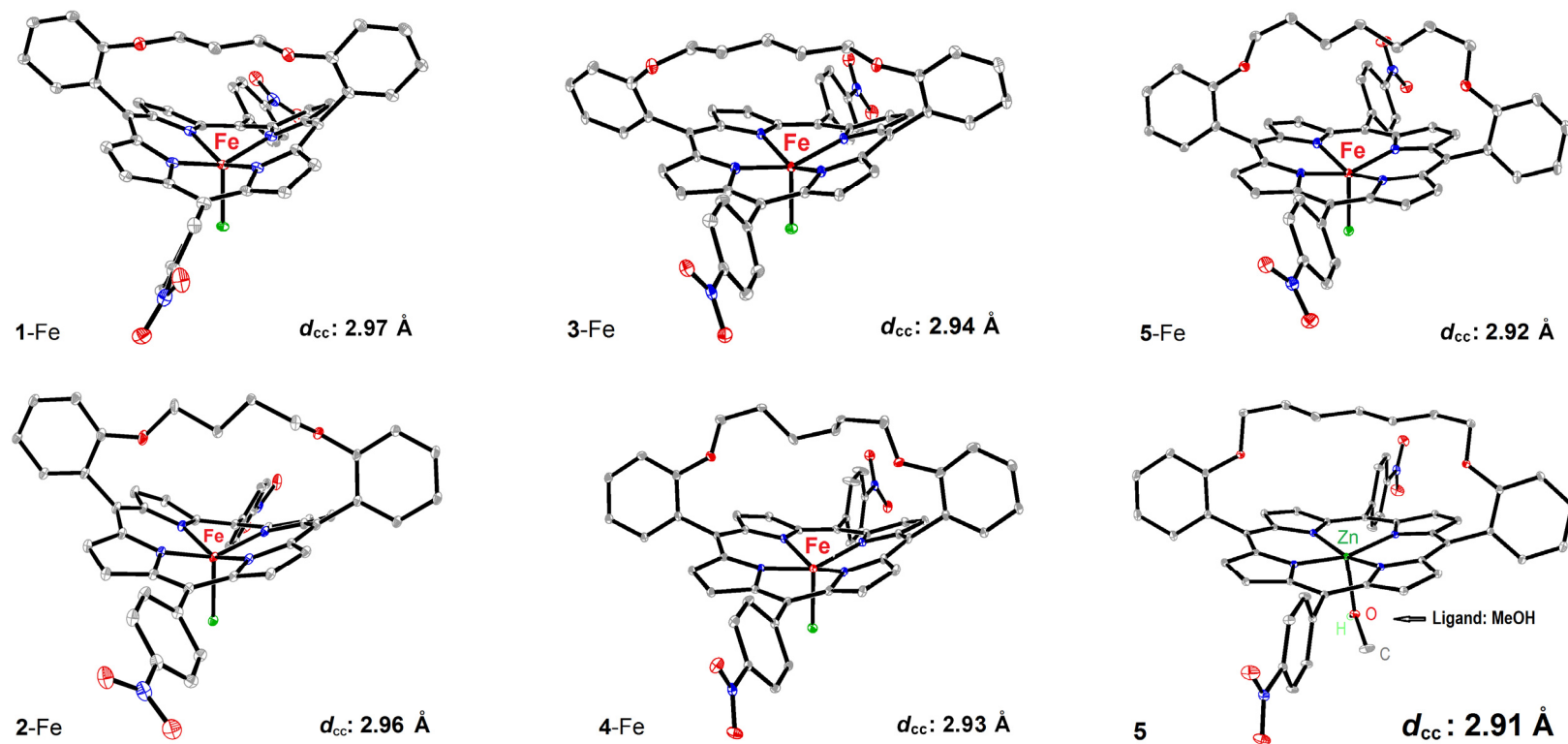
The relationship of 4  $d_{CC}$  distances can be directly reflected in computation results of rotational potential energy surface to the 5 model complexes. The 4 individual distances completely correlate each other. The computation was carried out under Gaussian 03 circumstance, and the calculation set: DFT/B3LYP/6-31G step  $10^\circ$ .

The computation results show that the  $d_{CC}(1)$  and  $d_{CC}(2)$  are not be visibly changed and the difference between both is also invariable under the rotation forced of another aryl (below Figure). On the other hand, the mean value of 4  $d_{CC}$  is also invariable near the ground state of these complexes when the aryl is rotated. The deviation of  $d_{CC}(1)$ ,  $d_{CC}(2)$  and mean value of 4  $d_{CC}$  is very small,  $\sim 0.001$  Å around their ground states (e.g those in red cycle).



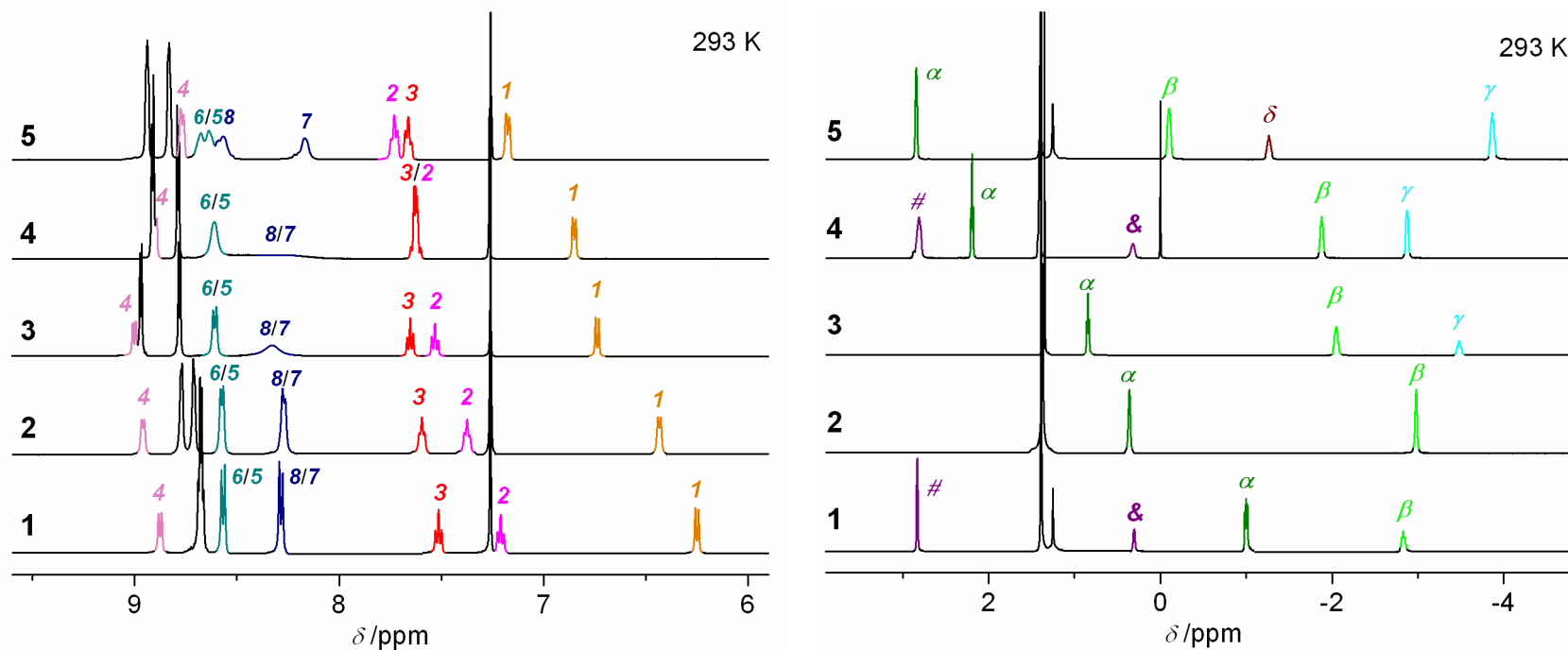
Plot of the independent  $d_{CC}$  distance to aryl rotation, step is  $10^\circ$ .

The  $d_{CC}$  values of strapped metalloporphyrins **1-Fe** to **5-Fe** and **5**.



Crystal structure and parameter,  $d_{CC}$ , of strapped metalloporphyrins **1-Fe** to **5-Fe** and **5**.  
The substituents, *tert*-butyl groups, protons and solvents have been omitted for clarity.

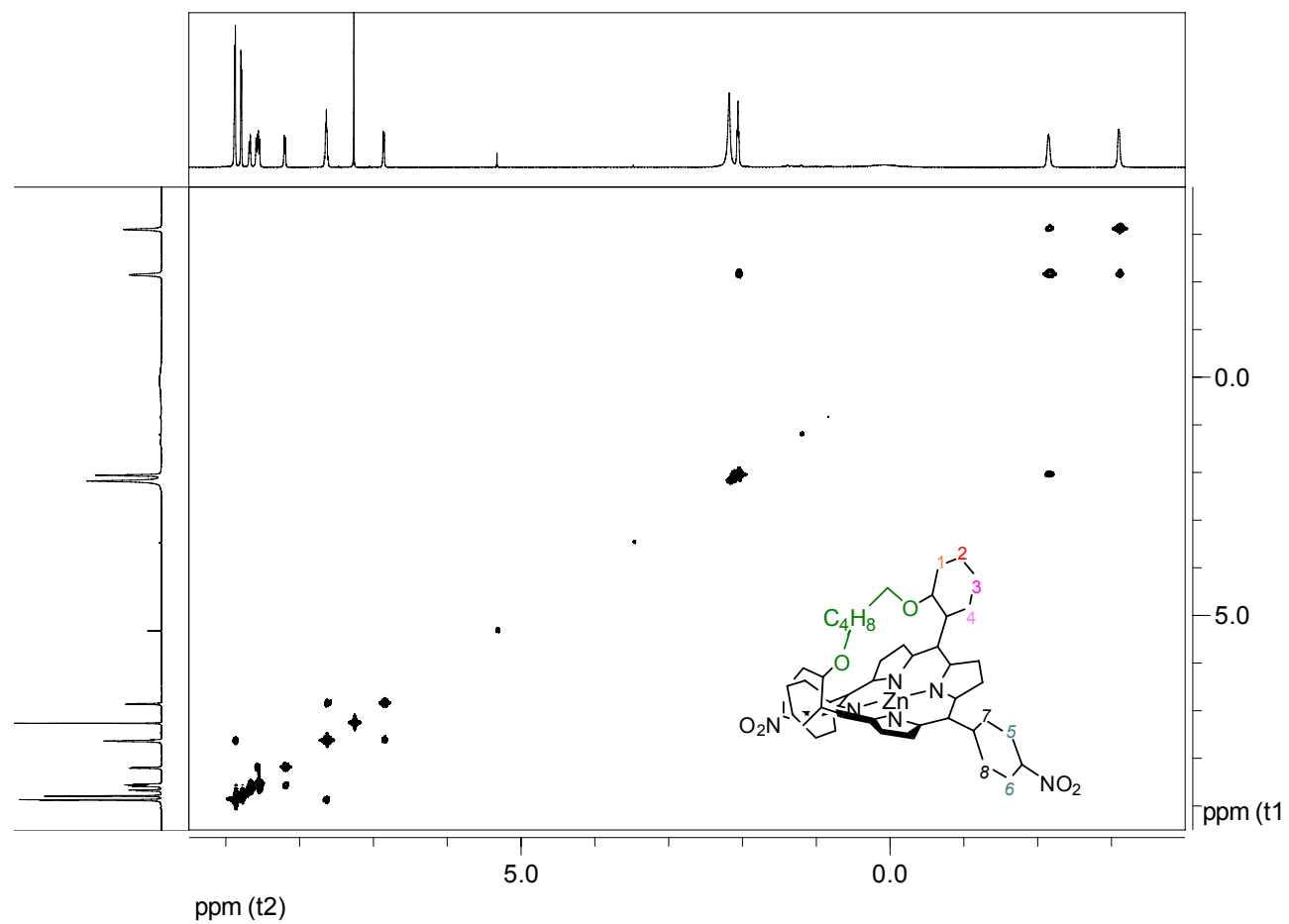
#### 4. The accounts to the $^1\text{H}$ NMR spectra of model compounds **1** to **5**



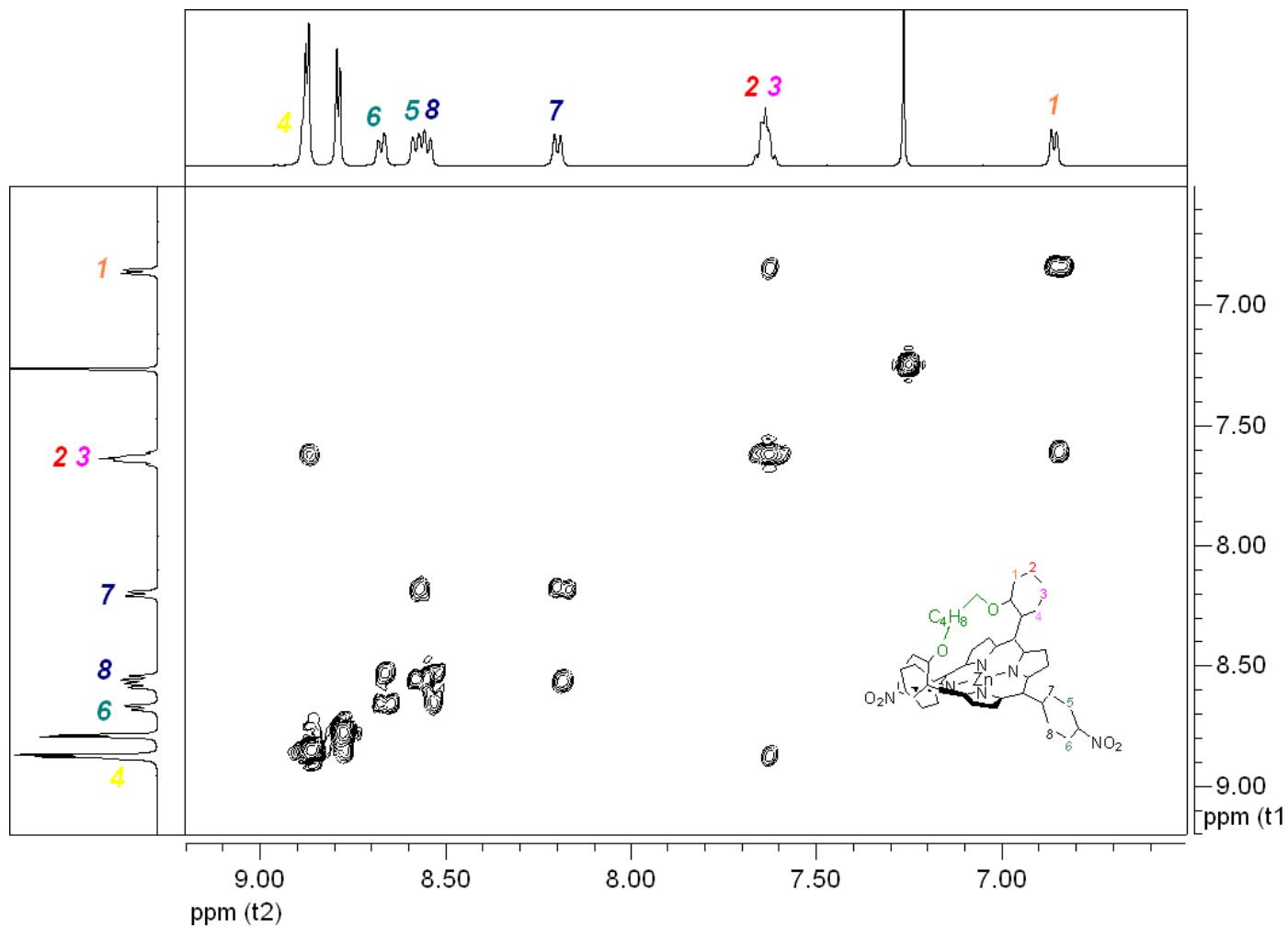
An inspection of the  $^1\text{H}$  NMR spectra of model compounds **1** to **5** reveals that there are several broad peaks at the determined temperature 293 K, especially the diagnostic signals  $\text{H}^7$  and  $\text{H}^8$  in compound **3**, **4** and **5** (above Figure). These phenomena indicate the aryl rotation has geometry dependence at a temperature.



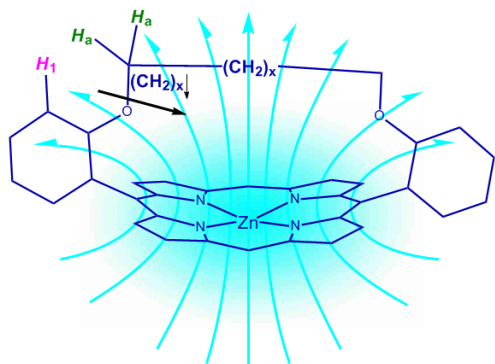
HH COSY spectra of model compounds 4 at 228 K



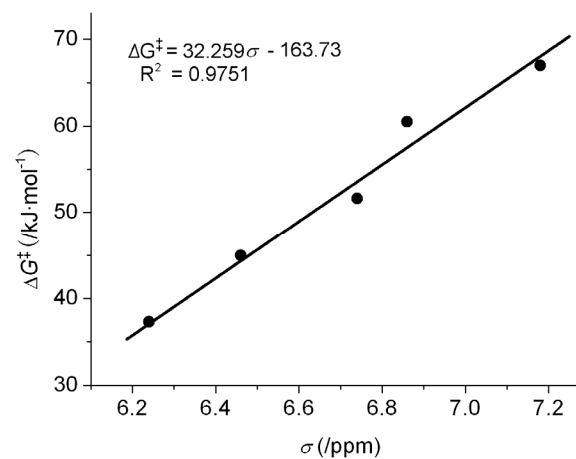
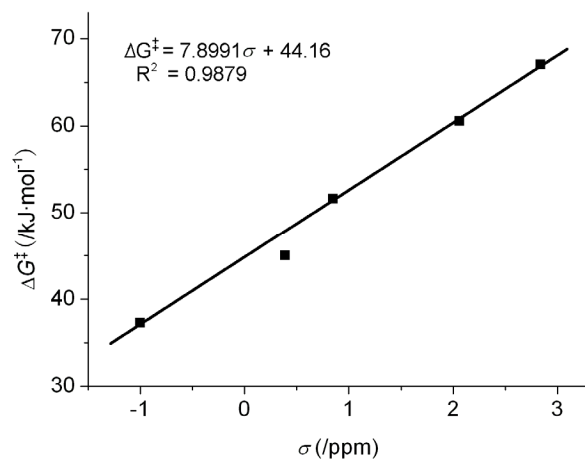
Magnification of HH COSY spectra of model compounds 4 at 228 K



## 5. Correlation analysis of $\Delta G^\ddagger$ to chemical shift of the protons in phenyl bridged and straps



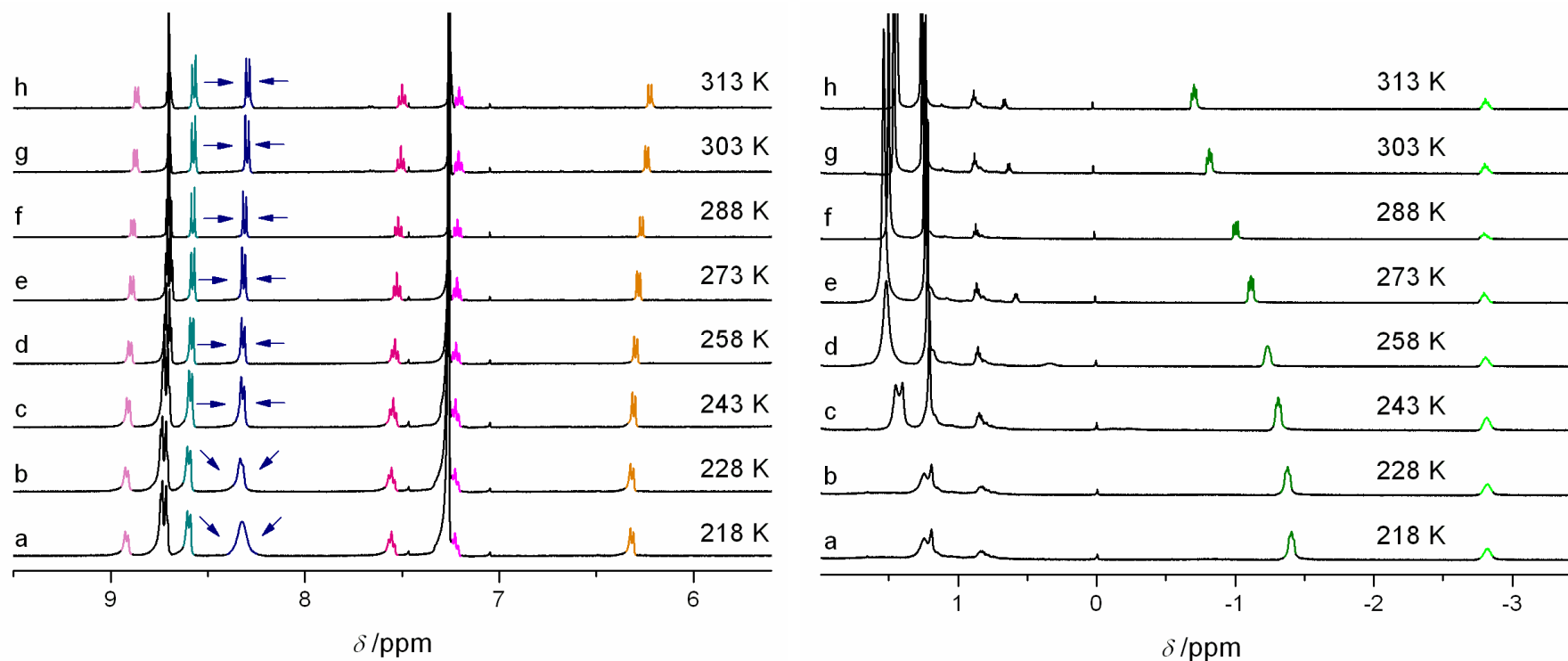
| Compd. | $\Delta G^\ddagger$ /(kJ/mol) | $\delta H_1$ (/ppm) | $\delta OCH_2$ (/ppm) |
|--------|-------------------------------|---------------------|-----------------------|
| 1      | 37.3                          | 6.24                | -1.00                 |
| 2      | 45.0                          | 6.46                | 0.39                  |
| 3      | 51.6                          | 6.74                | 0.85                  |
| 4      | 60.5                          | 6.84                | 2.06                  |
| 5      | 67.0                          | 7.18                | 2.84                  |



Correlation analysis of  $\Delta G^\ddagger$  to  $\delta OCH_2$  (left) and to  $\delta H_1$  (right). Inserts are the empirical equation

## 6. Variable-temperature $^1\text{H}$ NMR spectra of model compounds 1 to 5

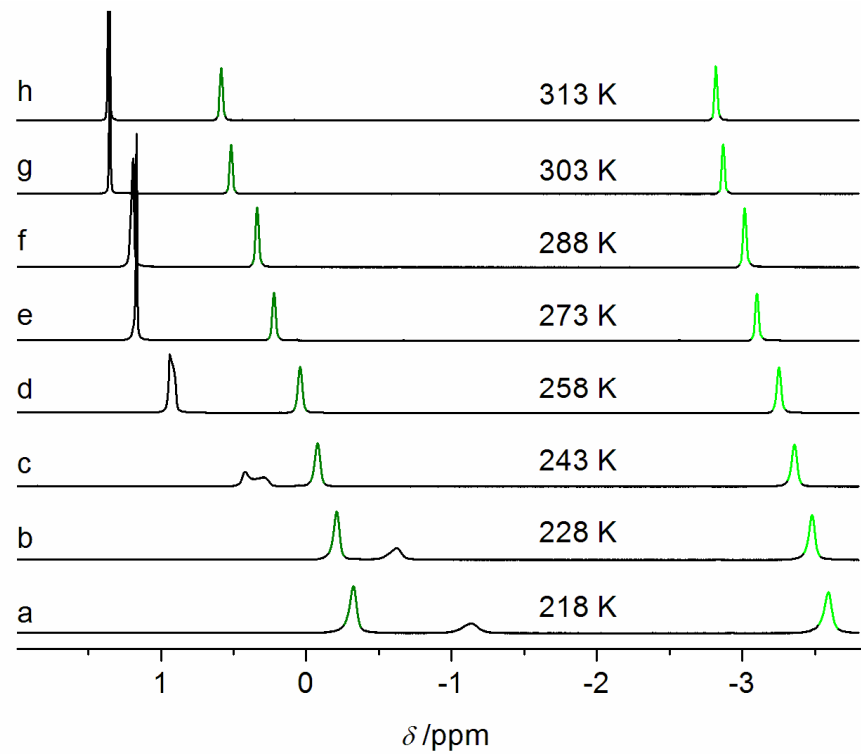
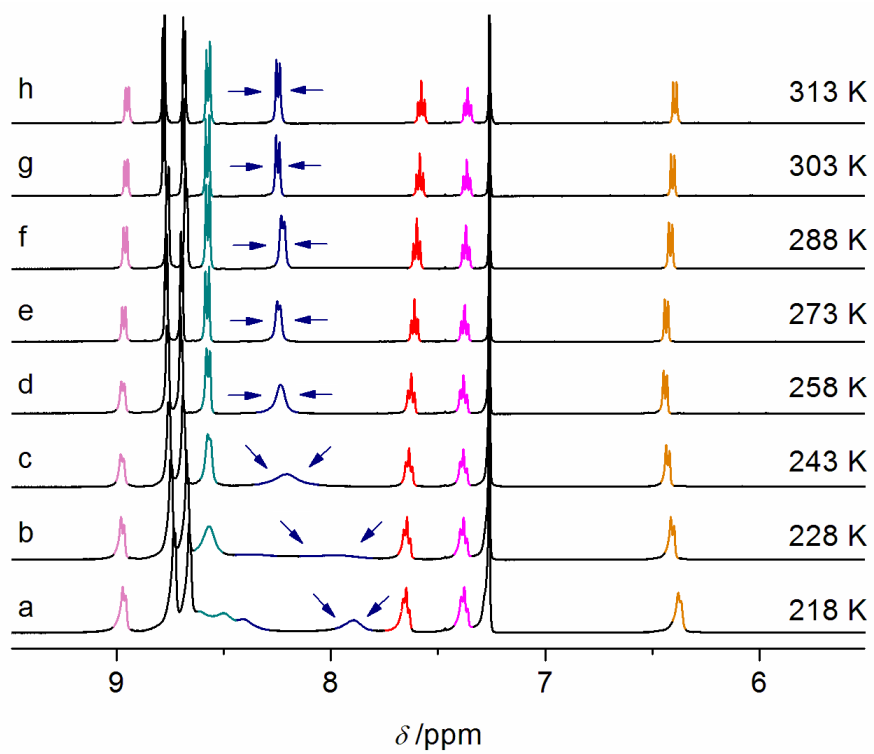
### 6.1 VT-NMR of compounds 1 ( $n_{\text{C}} = 3$ )



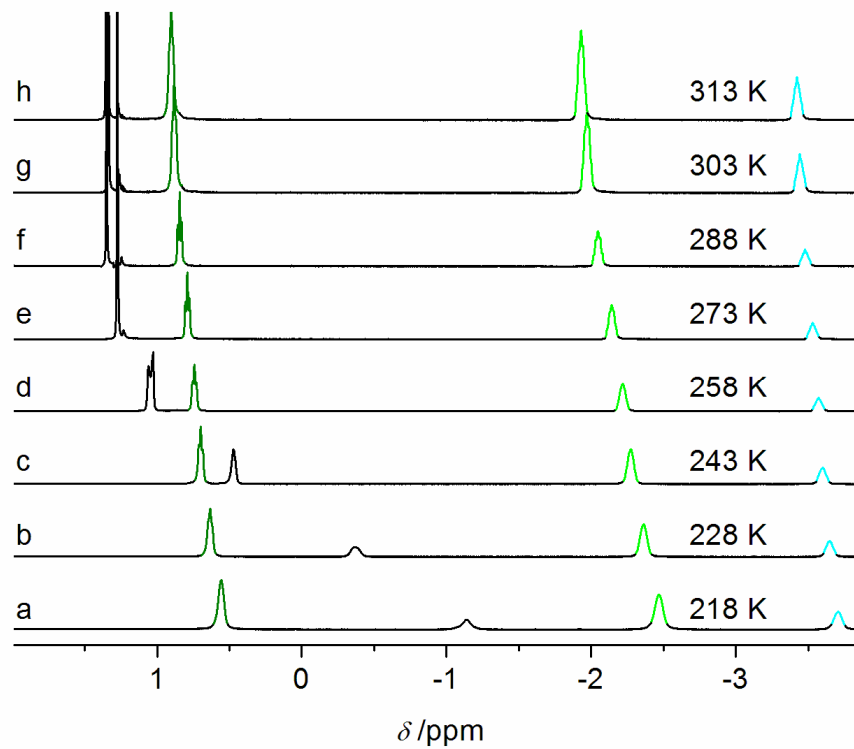
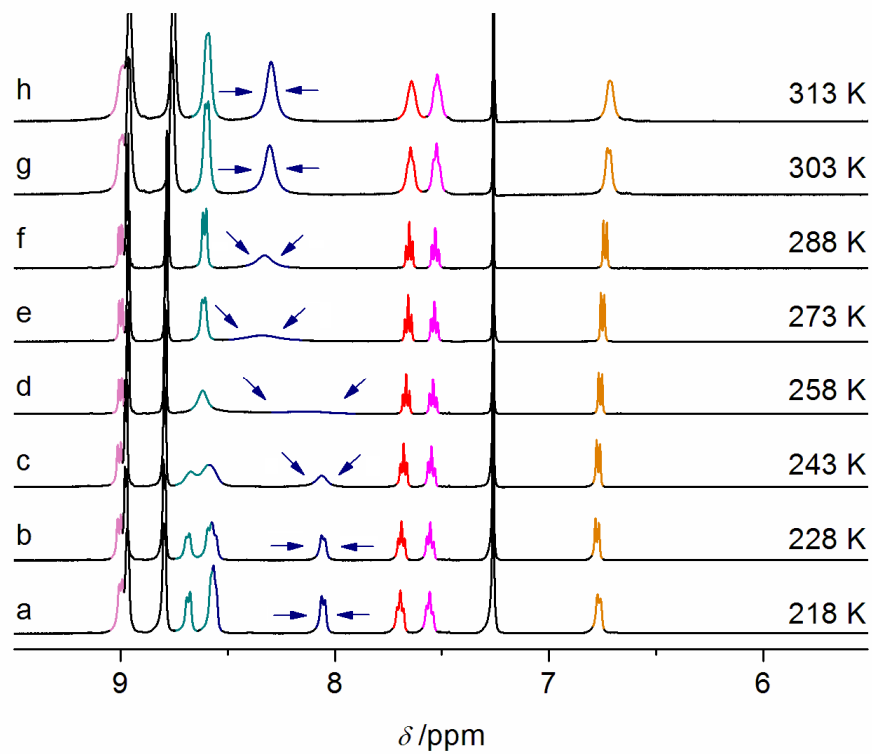
The solubility of compound 1 is very poor below 218 K, which is not convenient to acquire its exact shift value at the low temperature.

The arrows denote the half-height positions of peak diagnostic proton  $\text{H}^7$ , the same as below.

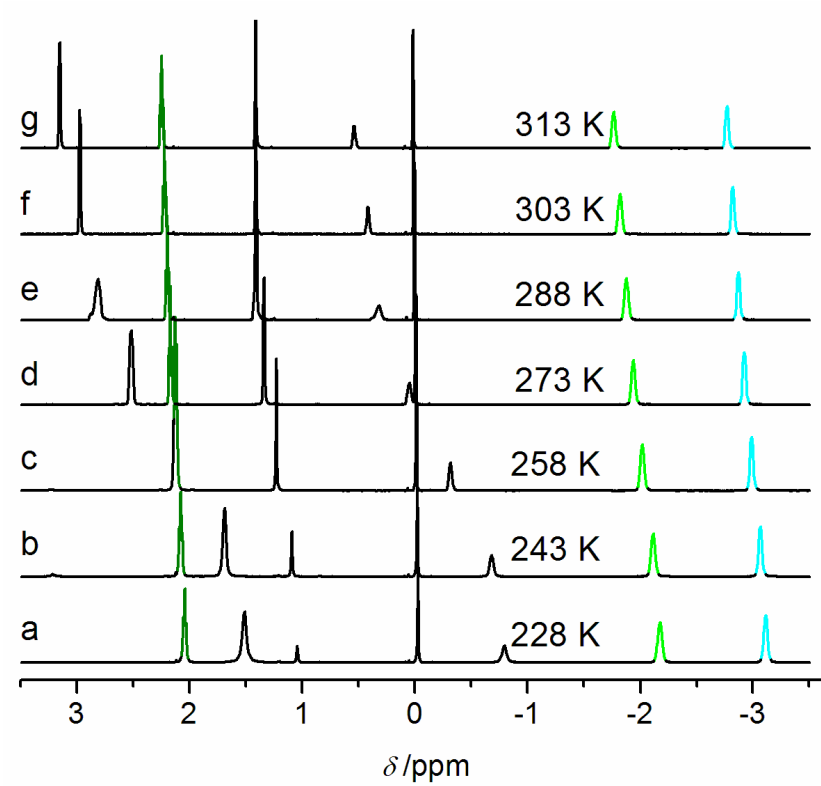
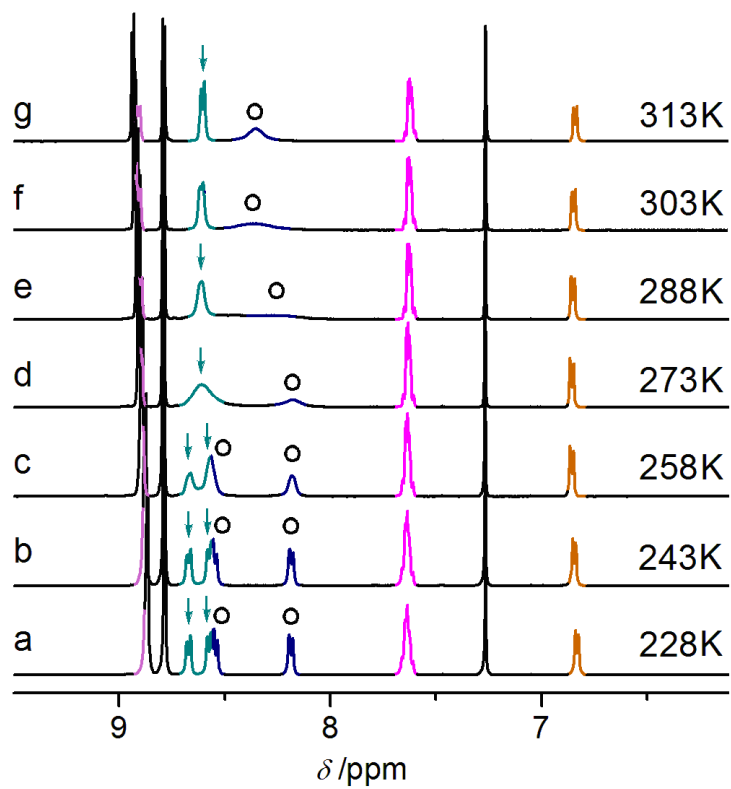
6.2 VT-NMR of compounds 2. ( $n_C = 4$ )



### 6.3 VT-NMR of compounds 3. ( $n_C = 5$ )



6.4 VT-NMR of compounds 4. ( $n_C = 6$ )



6.5 VT-NMR of compounds 5. ( $n_C = 7$ ).

