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Supporting Information

Metal-Cation Recognition in Water by a Tetrapyrazinoporphyrazine-Based Tweezer Receptor

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Content:

Content: S1
Methods used for photophysical studies S2
Dependences of Φ_F of target sensors on the concentration of added analyte S3
The effect of water in THF solution S5
Fluorescence titration experiments in water S5
Competition experiments S6
Characterization of silica nanoparticles S7
NMR spectra S8
References S13

Methods used for photophysical studies

Fluorescence measurements

Fluorescence quantum yields (Φ_F) were determined by the comparative method using unsubstituted ZnPc (Φ_F = 0.32 in THF[1]). Samples were excited at 595 nm. Φ_F was calculated using Equation (Eq. 1) where *F* is the integrated area under the emission spectrum, *A* is the absorbance at the excitation wavelength, and *n* is the refractive index of the solvent. The superscripts *R* and *S* correspond to the reference and sample, respectively. Estimated error ± 15%.

$$\Phi_F^S = \Phi_F^R \left(\frac{F^S}{F^R}\right)\left(\frac{1-10^{-A^R}}{1-10^{-A^S}}\right)\left(\frac{n^S}{n^R}\right)^2 \qquad \text{(Eq. 1)}$$

Determination of binding constant

A dye stock solution in THF (15 - 20 µL) was added to a 10 × 10 mm fluorescence quartz cell with 2.5 mL of THF (HPLC, <0.05% H_2O) to reach a final concertation of 1 µM. The absorption and emission spectra (λ_{exc} = 595 nm) were recorded. Then, defined amounts (typically 10 - 100 µL) of a stock solution (typically 0.01 M, 0.1 M or 1 M) containing the analyte in the form of a perchlorate (in the case of Li^+, Na^+, Mg^{2+}, Ca^{2+}, and Ba^{2+}) or thiocyanate (in the case of K^+) salt in MeOH (<0.03 % H_2O) were added. The absorption and emission spectra were recorded after each addition, and the fluorescence quantum yields were determined for each point. The fluorescence quantum yields were calculated as mentioned above and plotted as a function of the analyte concentration. Association constants (K_A) were calculated by non-linear regression analysis using the Prism 5 software for Windows (GraphPad Software, Inc.). In the cases of biphasic titration curves, the first part of the titration curves was analysed separately.

Fluorescence enhancement factor

The fluorescence enhancement factor (FEF) was calculated as follows: FEF = $\Phi_F(M^+)$ / Φ_F(Free), where Φ_F(Free) is Φ_F in THF (1 µM) before the addition of any analyte, Φ_F(M+) is Φ_F at complete saturation of the analyte in the cavity of the recognition moiety (i.e., when the titration curve from the "Determination of binding constant" reached an apparent plateau). In the cases of biphasic titration isotherms, FEF_1 corresponds to the increase of fluorescence intensity of the first step, total FEF corresponds to the increase of fluorescence intensity for both steps together.

Fluorescence titration experiments of 1bZn@NP

A total of 2.5 mL of a **1bZn@NP** (c ~ 1 µM) stock solution in water/acetic acid = 3:1 (v/v) was transferred to a 10 × 10 mm fluorescence quartz cell, and absorption and emission spectra (λ_{exc} = 599 nm) were recorded. Then, defined amounts (typically 5-50 µL) of stock solution (1 M) of analyte in H_2O/acetic acid = 3:1 (v/v) were subsequently added and absorption and emission spectra were measured after each addition. The fluorescence intensity was corrected to the same absorption at the excitation wavelength and plotted as a function of the analyte concentration.

Job's method of continuous variation

Stock solutions of **1bZn** (100 µM) in THF and of 1 mM for KSCN in MeOH were prepared. A series of fluorescence measurements with different **1bZn**/KSCN (13 or 15 measurements ranging between 1:5 to 5:1 ratios) were performed as follows: an appropriate amount of THF that resulted in a the total volume of the solution being 1.00 mL after the addition of stock solutions of **1bZn** and analyte was transferred to a 10 × 4 mm fluorescence quartz optical cell. A stock solution containing **1bZn** was added, and the fluorescence emission spectrum was recorded (λ_{exc} = 595 nm). The fluorescence intensity at maximum was considered to be F_0. An appropriate amount of analyte stock solution was added to yield a total concentration of components of 10 µM ([**1bZn**] + [K^+] = 10 µM). The fluorescence emission spectrum was recorded and F_{max} was found as the fluorescence intensity at maximum. The final stoichiometry of the **1bZn**/K^+ complex was determined from the Job´s plot constructed from the dependence of F_{max}-F_0 on [K^+]/([K^+]+[**1bZn**]).

Dependences of Φ_F of target sensors on the concentration of added analyte

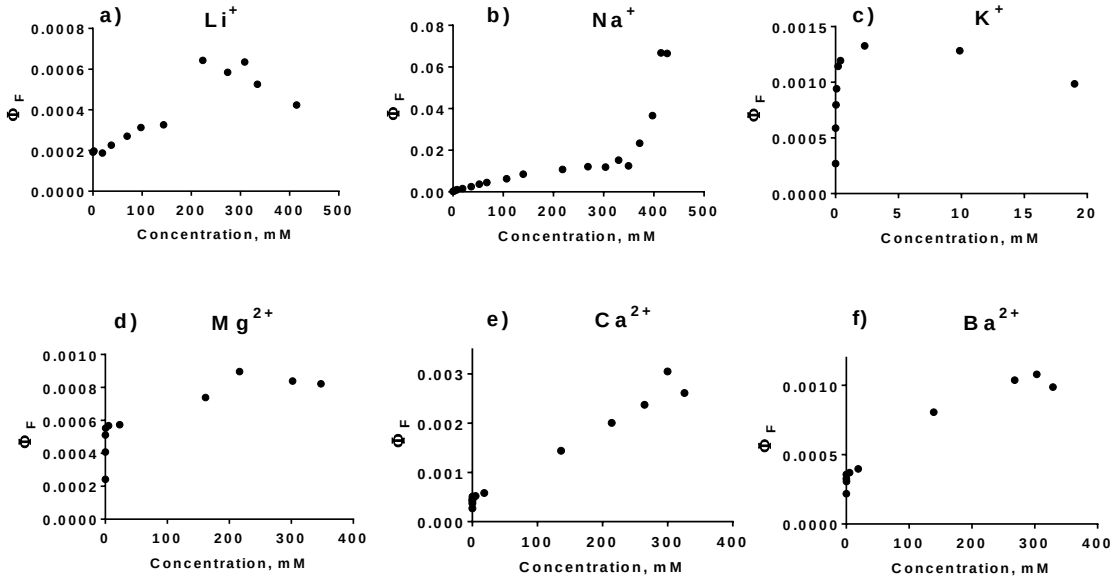

Fig. S1. Fluorescence titration experiments of **1aZn** in THF ($c_{(TPyzPz)}$ = 1 μM) by Li^+ (a), Na^+ (b), K^+ (c), Mg^{2+} (d), Ca^{2+} (e), Ba^{2+} (f) in MeOH.

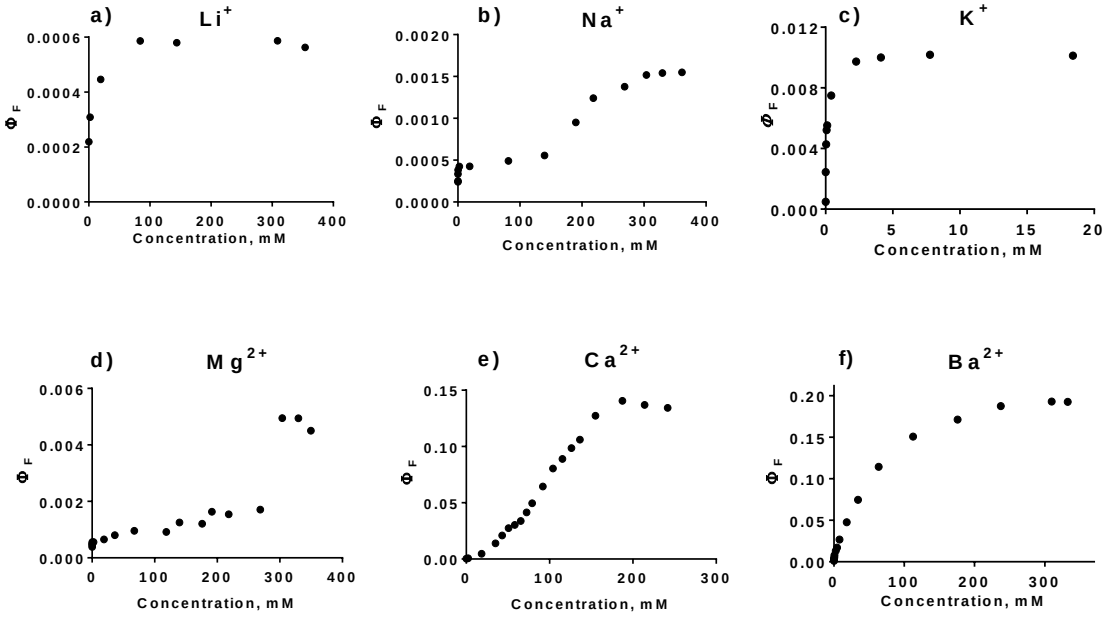

Fig. S2. Fluorescence titration experiments of **1bZn** in THF ($c_{(TPyzPz)}$ = 1 μM) by Li^+ (a), Na^+ (b), K^+ (c), Mg^{2+} (d), Ca^{2+} (e), Ba^{2+} (f) in MeOH.

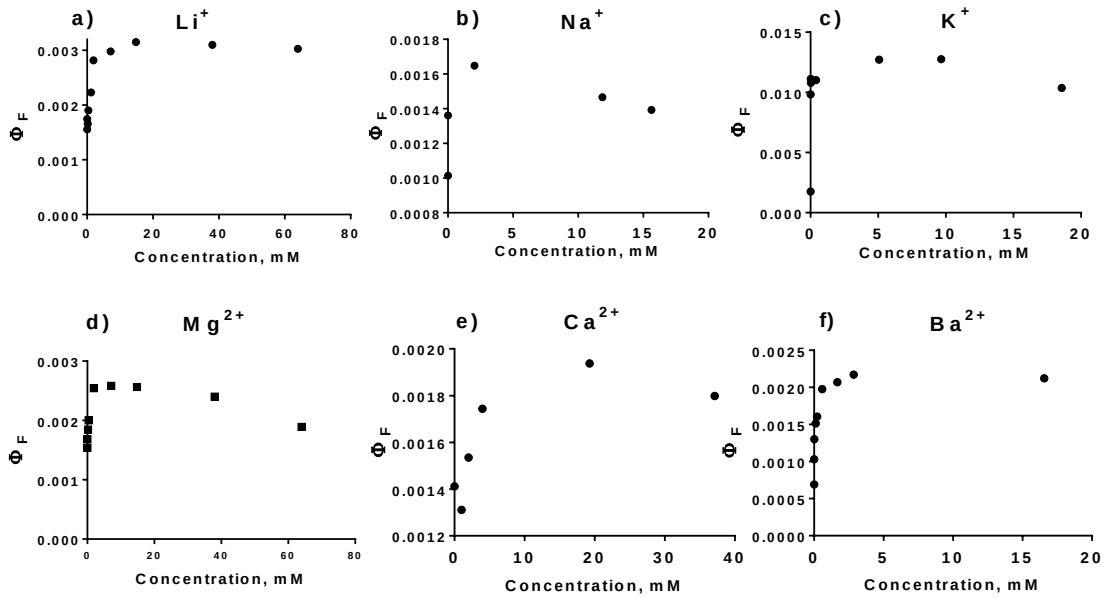

Fig. S3. Fluorescence titration experiments of **1cZn** in THF ($c_{(TPyzPz)}$ = 1 μM) by Li^+ (a), Na^+ (b), K^+ (c), Mg^{2+} (d), Ca^{2+} (e), Ba^{2+} (f) in MeOH.

The effect of water in THF solution

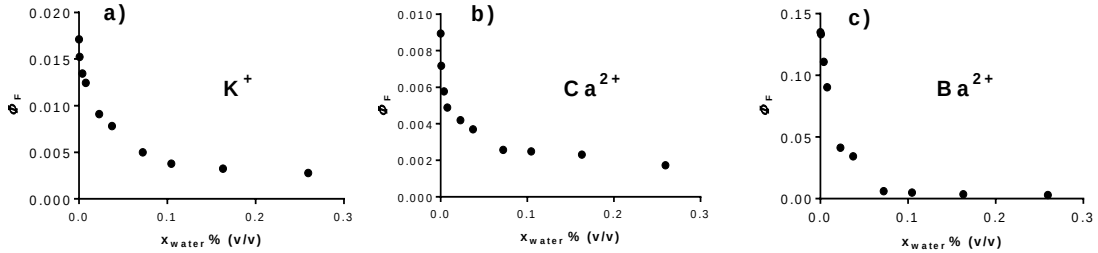

Fig. S4. Fluorescence titration experiments with water. Original solutions consisted of **1bZn** in anhydrous THF ($c_{(TPyzPz)}$ = 1 µM) and K^+ (a), $Ca2^+$ (b) and Ba^{2+} (c) (dissolved in anhydrous MeOH) at their complete binding.

Fluorescence titration experiments in water

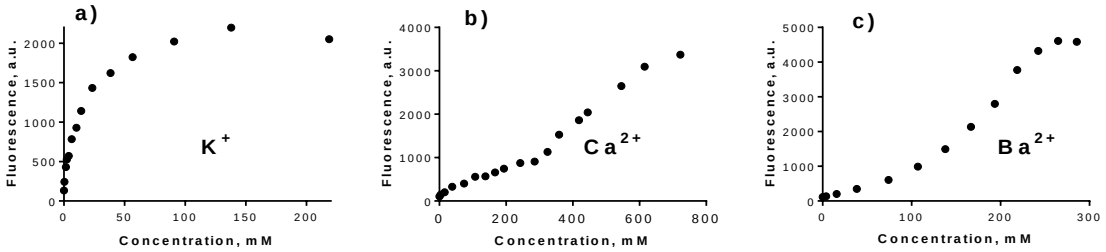

Fig. S5. Titration of **1bZn@NP** in water/acetic acid 3:1 ($c_{(TPyzPz)}$ = 1 µM) with K^+ (a), Ca^{2+} (b) and Ba^{2+} (c). Fluorescence intensity was corrected for changes of absorbance at excitation wavelength.

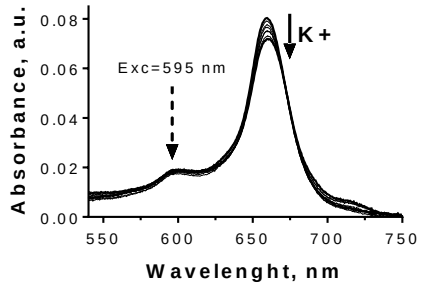

Fig. S6. Changes in absorption spectra of **1bZn@NP** upon titration with K^+ (concentration of K^+ ranges from 0 to 220 mM).

Competition experiments

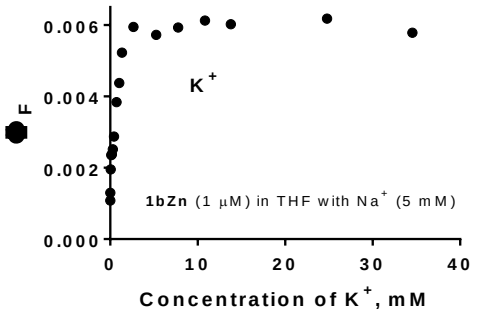

Fig. S7. Fluorescence titration experiment of **1bZn** in THF ($c_{(TPyzPz)}$ = 1 μM) titrated with KSCN (in MeOH) in the presence of 5 mM Na^+.

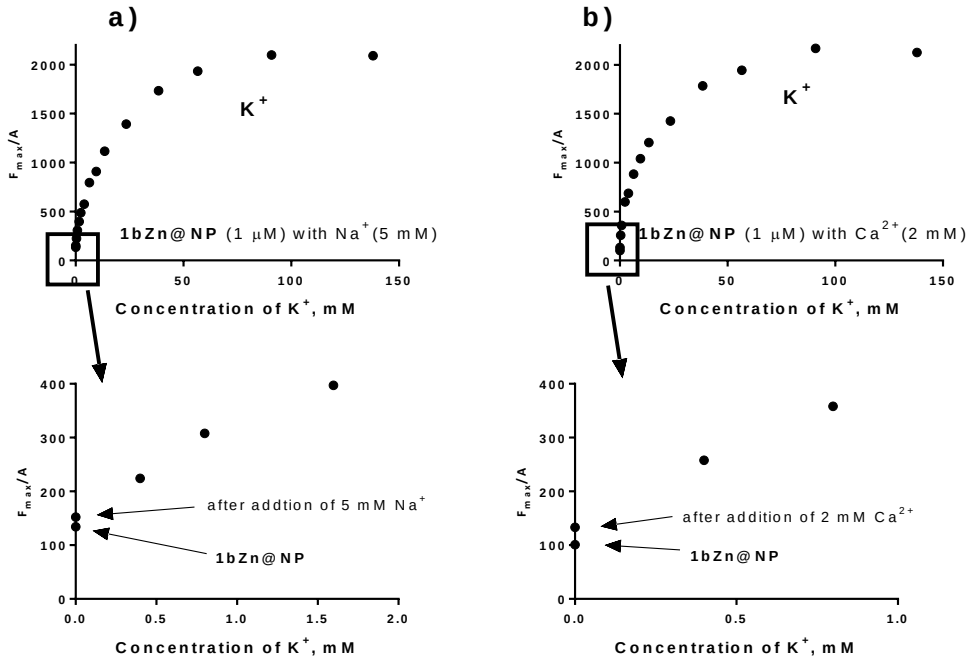

Fig. S8. Titration of **1bZn@NP** in water/acetic acid 3:1 ($c_{(TPyzPz)}$ = 1 μM) with K^+ (a) in the presence of Na^+ (5 mM) (a) or Ca^{2+} (2 mM) (b). Enlarged areas of graphs show the negligible increase of fluorescence after addition of competitive cations.

Characterization of silica nanoparticles

The size of particles in water was determined on a particle size analyzer Zetasizer Nano ZS from Malvern (United Kingdom). In addition, nanoparticles were also investigated by high-resolution transmission electron microscopy (HRTEM) using a JEM-3010 (JEOL, Japan) operating at 300 kV in conjunction with an EDX detector (Oxford Instruments, United Kingdom).

			Diam. (nm)	% Number	Width (nm)
Z-Average (d.nm):	13,05	Peak 1:	8,194	100,0	1,645
PdI:	0,391	Peak 2:	0,000	0,0	0,000
Intercept:	0,788	Peak 3:	0,000	0,0	0,000
Result quality :	Good				

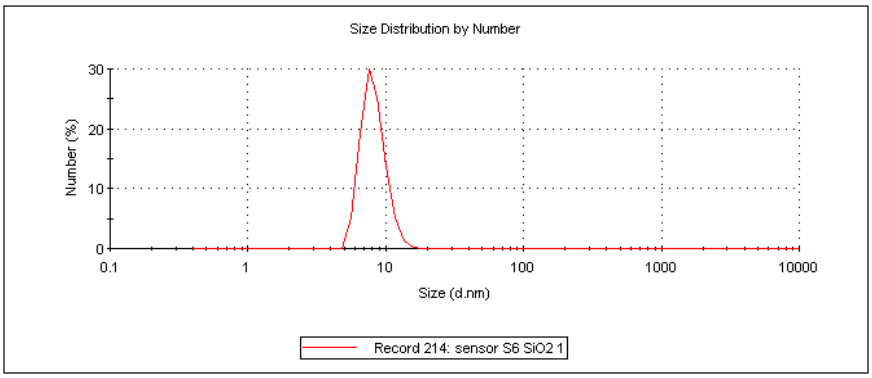

Fig. S9. Size distribution of **1bZn@NP** silica nanoparticles in water dispersions at room temperature.

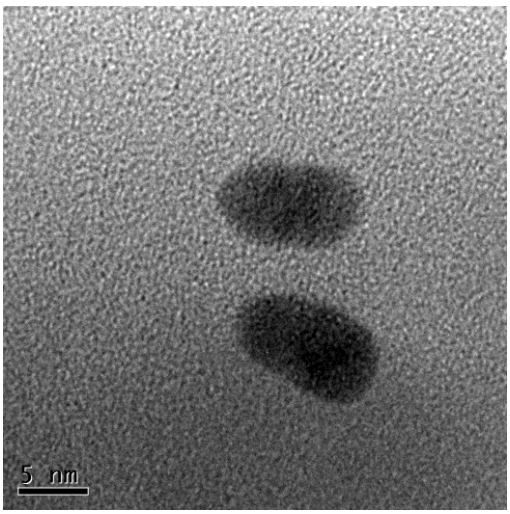

Fig. S10. HRTEM images of **1bZn@NP** silica nanoparticles.

NMR spectra

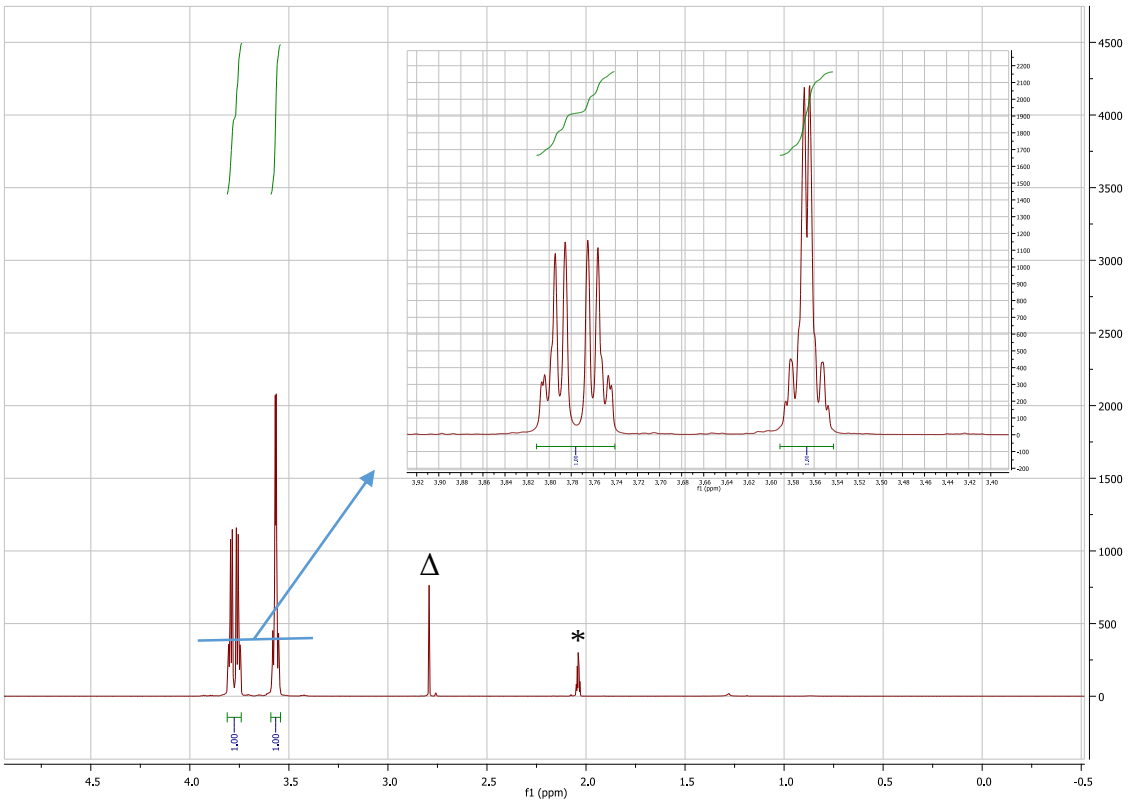

Fig. S11. ^{1}H NMR spectrum of **3a** in acetone-d_6. Asterisks indicate residuals of non-deuterated solvent (acetone), triangle indicates water.

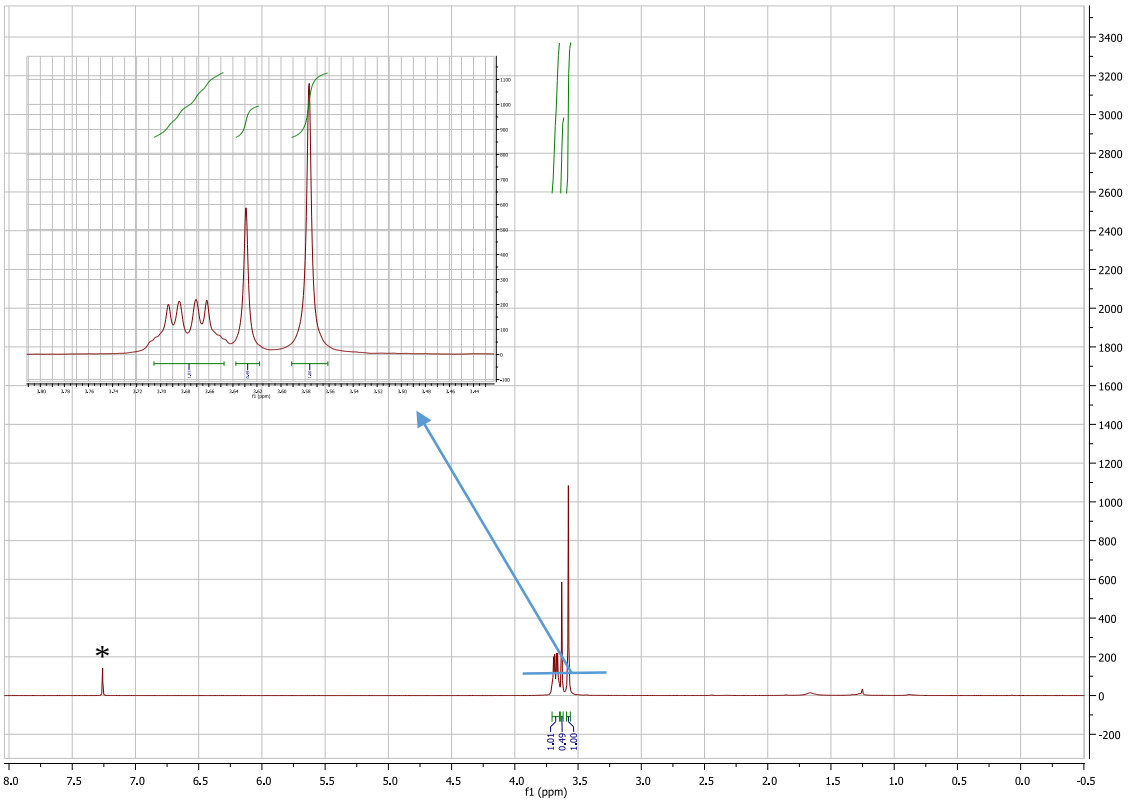

Fig. S12. ^{1}H NMR spectrum of **3b** in $CDCl_3$. Asterisk indicates residuals of non-deuterated solvent.

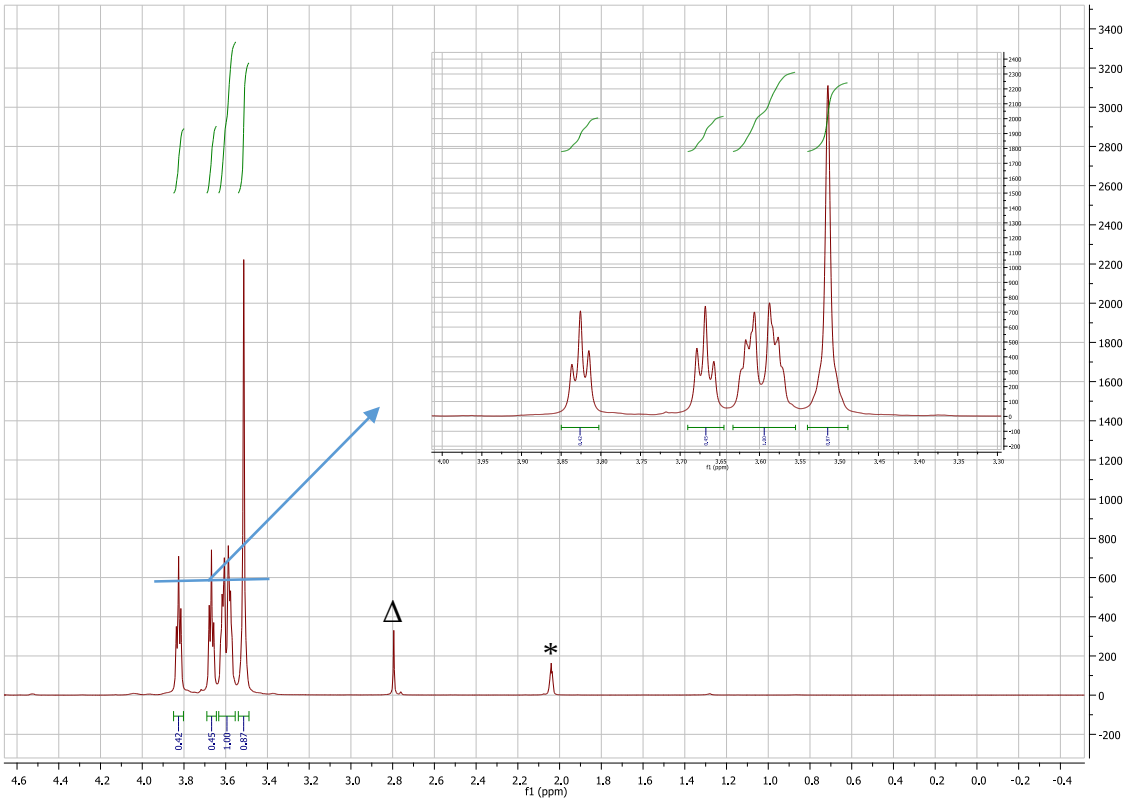

Fig. S13. ^{1}H NMR spectrum of **3c** in acetone-d_6. Asterisk indicates residuals of non-deuterated solvent, triangle indicates water.

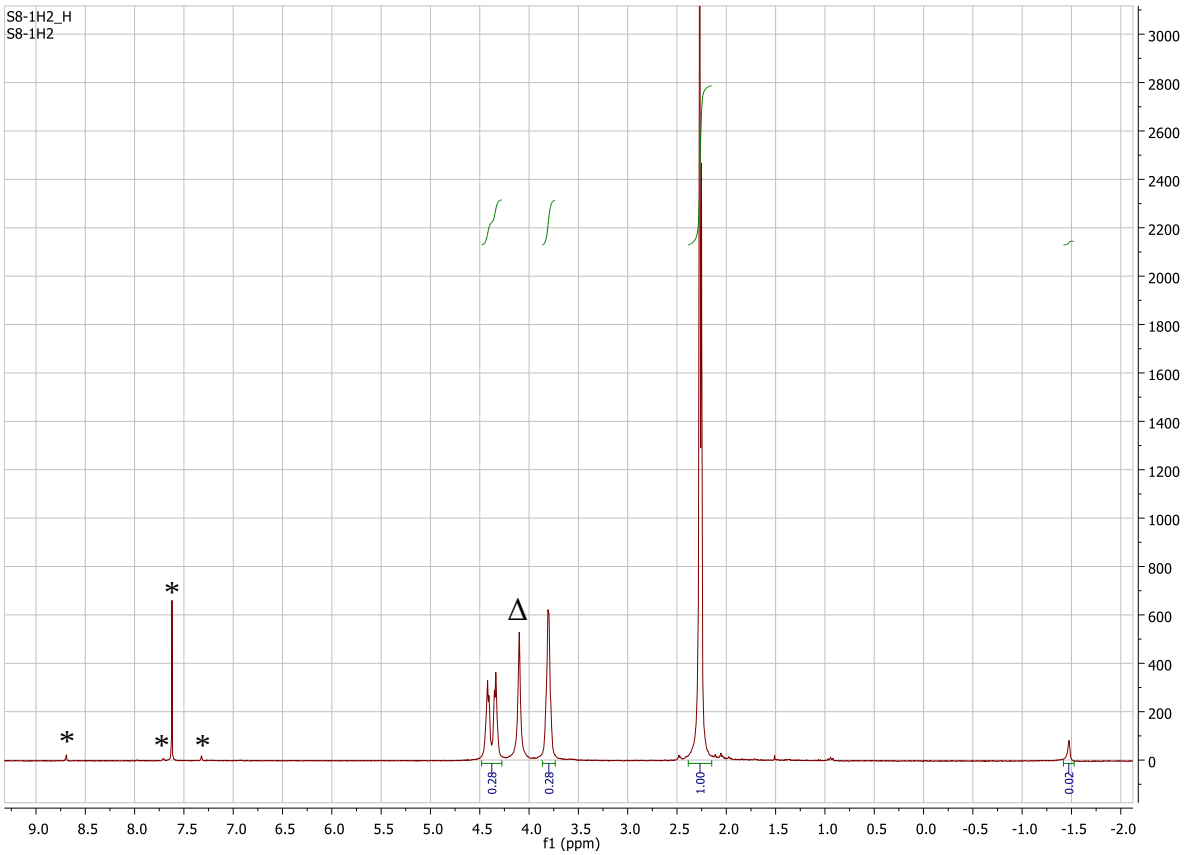

Fig. S14. ^{1}H NMR spectrum of **1aH** in $CDCl_3$/pyridine-d_5. Asterisks indicate residuals of non-deuterated solvent, triangle indicates water.

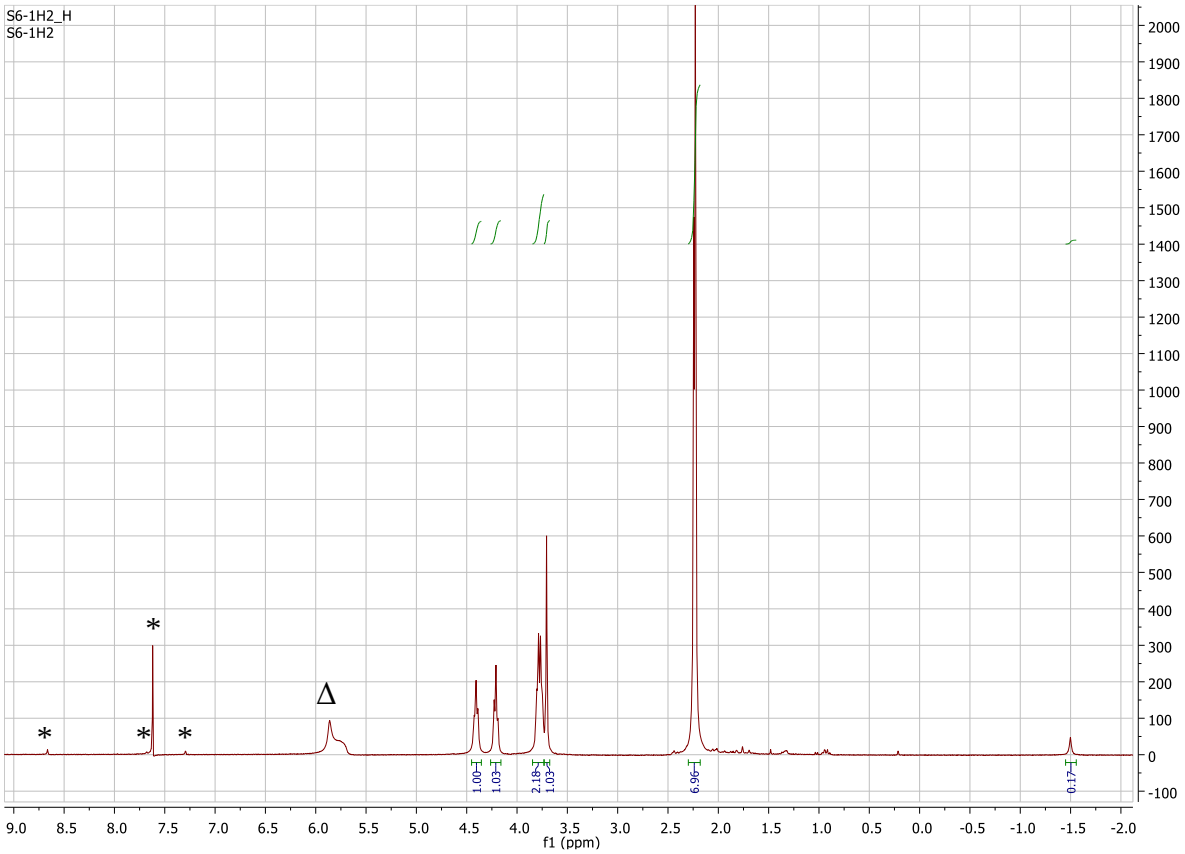

Fig. S15. ^{1}H NMR spectrum of **1bH** in $CDCl_3$/pyridine-d_5. Asterisk indicates residuals of non-deuterated solvent, triangle indicates water.

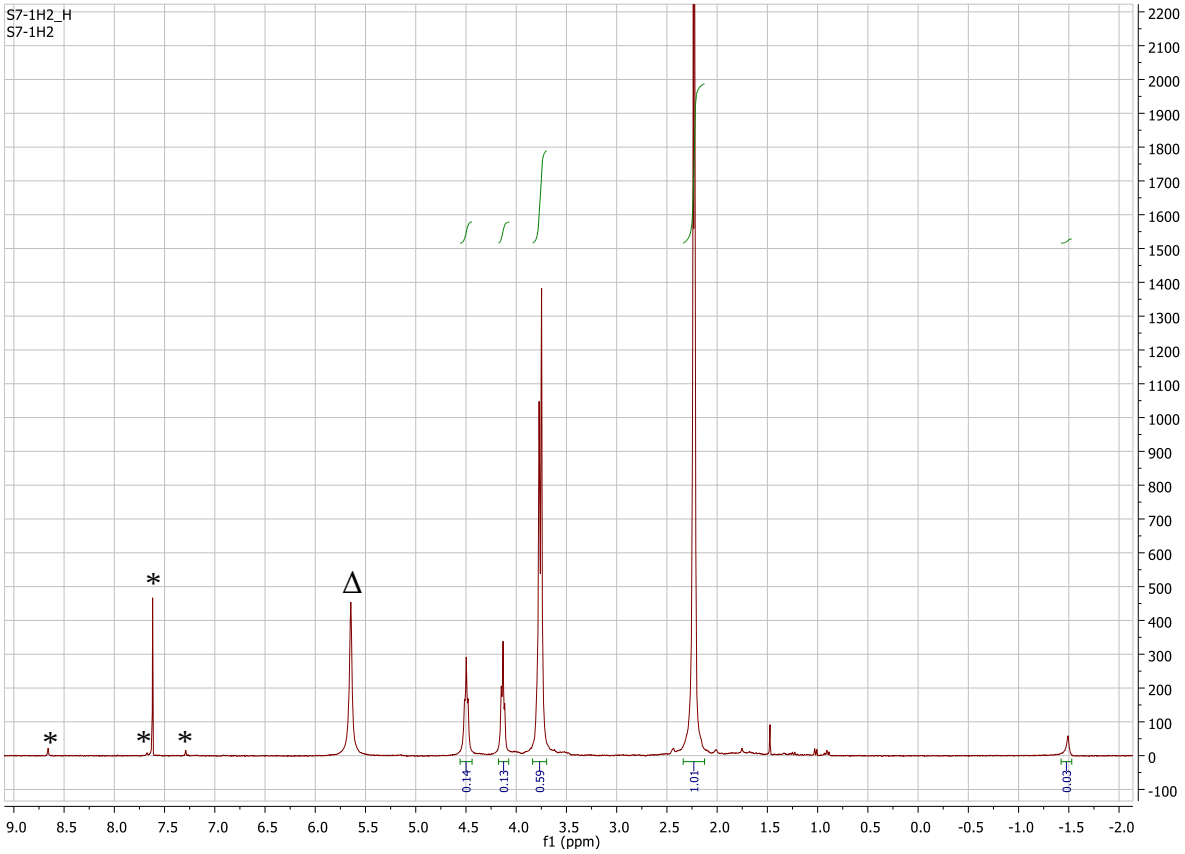

Fig. S16. ^{1}H NMR spectrum of **1cH** in $CDCl_3$/pyridine-d_5. Asterisk indicates residuals of non-deuterated solvent, triangle indicates water.

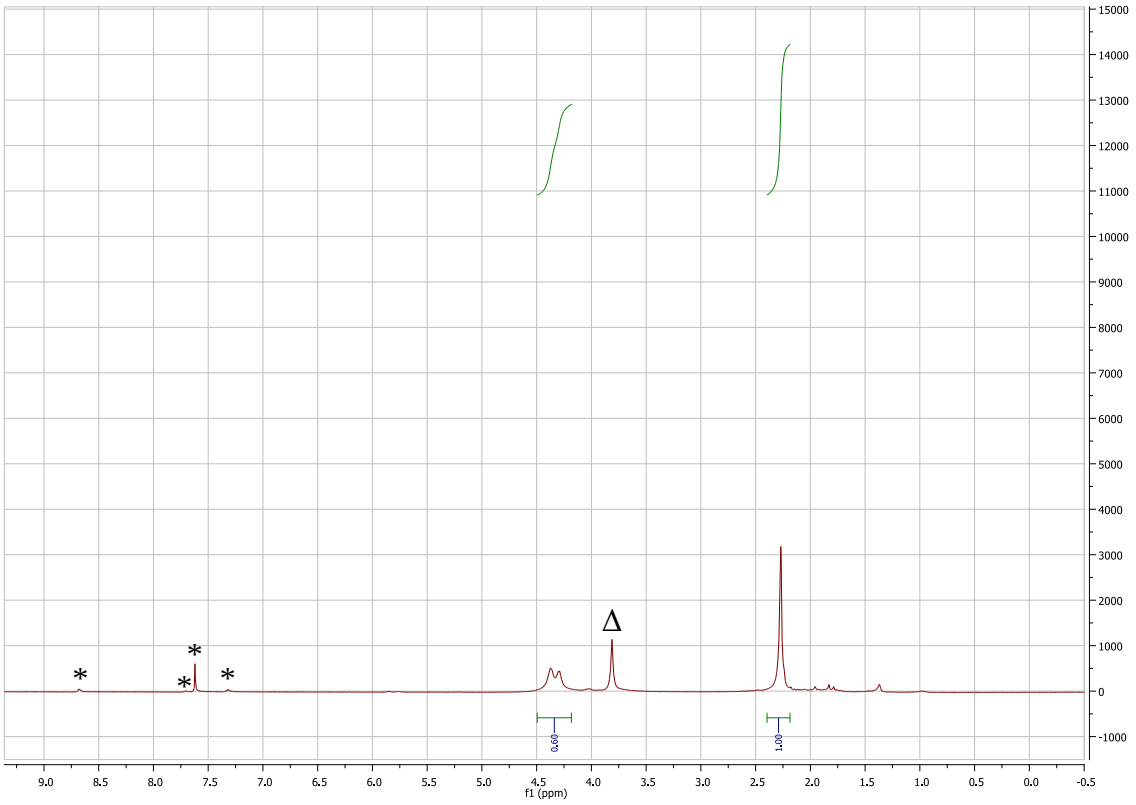

Fig. S17. ^{1}H NMR spectrum of **1aZn** in $CDCl_3$/pyridine-d_5. Asterisks indicate residuals of non-deuterated solvents, triangle indicates water.

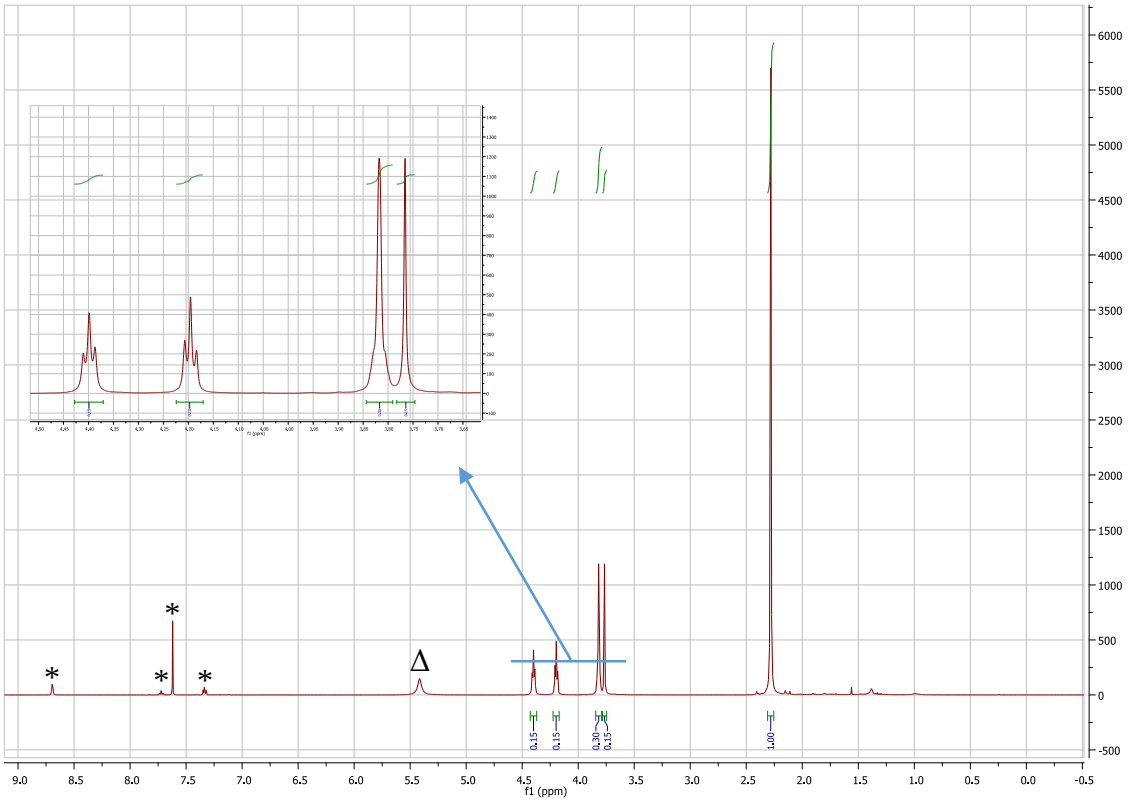

Fig. S18. ^{1}H NMR spectrum of **1bZn** in $CDCl_3$/pyridine-d_5. Asterisks indicate residuals of non-deuterated solvents, triangle indicates water.

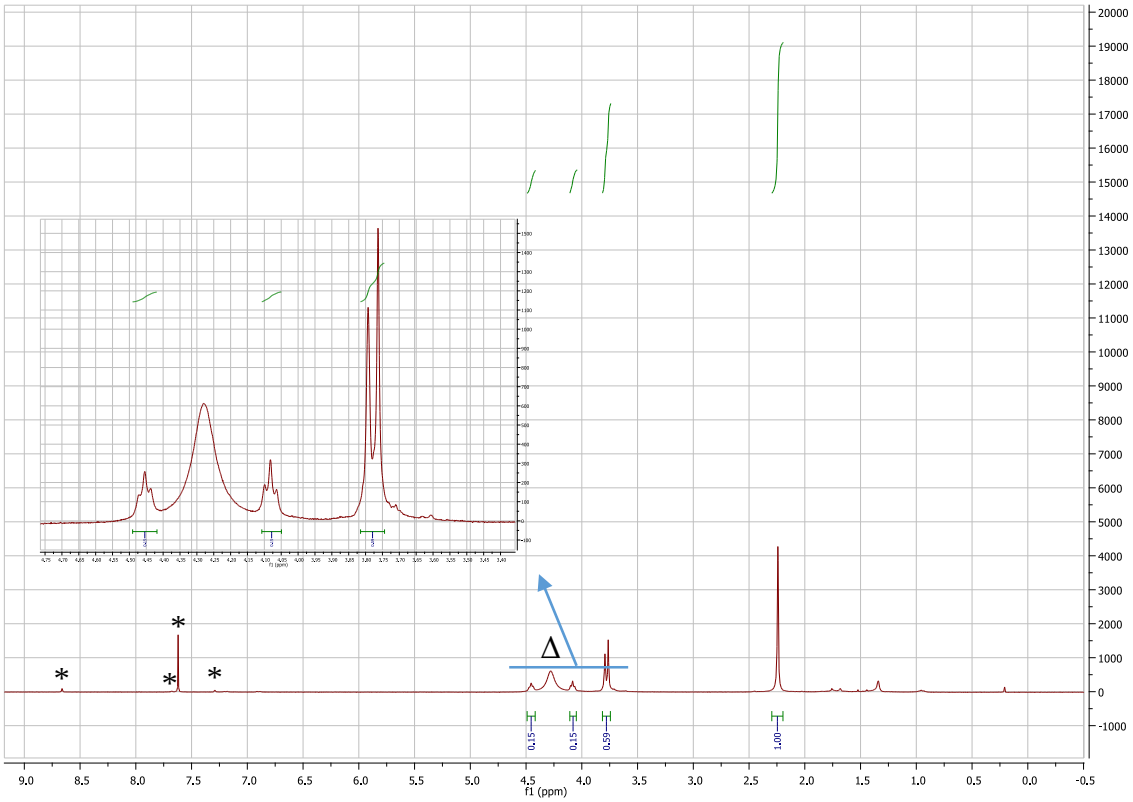

Fig. S19. ^{1}H NMR spectrum of **1cZn** in $CDCl_3$/pyridine-d_5. Asterisks indicate residuals of non-deuterated solvents, triangle indicates water.

References

[1] P. Zimcik, V. Novakova, K. Kopecky, M. Miletin, R. Z. Uslu Kobak, E. Svandrlikova, L. Váchová, K. Lang, *Inorg. Chem.* **2012**, *51*, 4215-4223.