Electronic Supplementary Information

Control over the Oxidative Reactivity of Metalloporphyrins. Efficient Electrosynthesis of *meso*,*meso*-Linked Zinc Porphyrin Dimer

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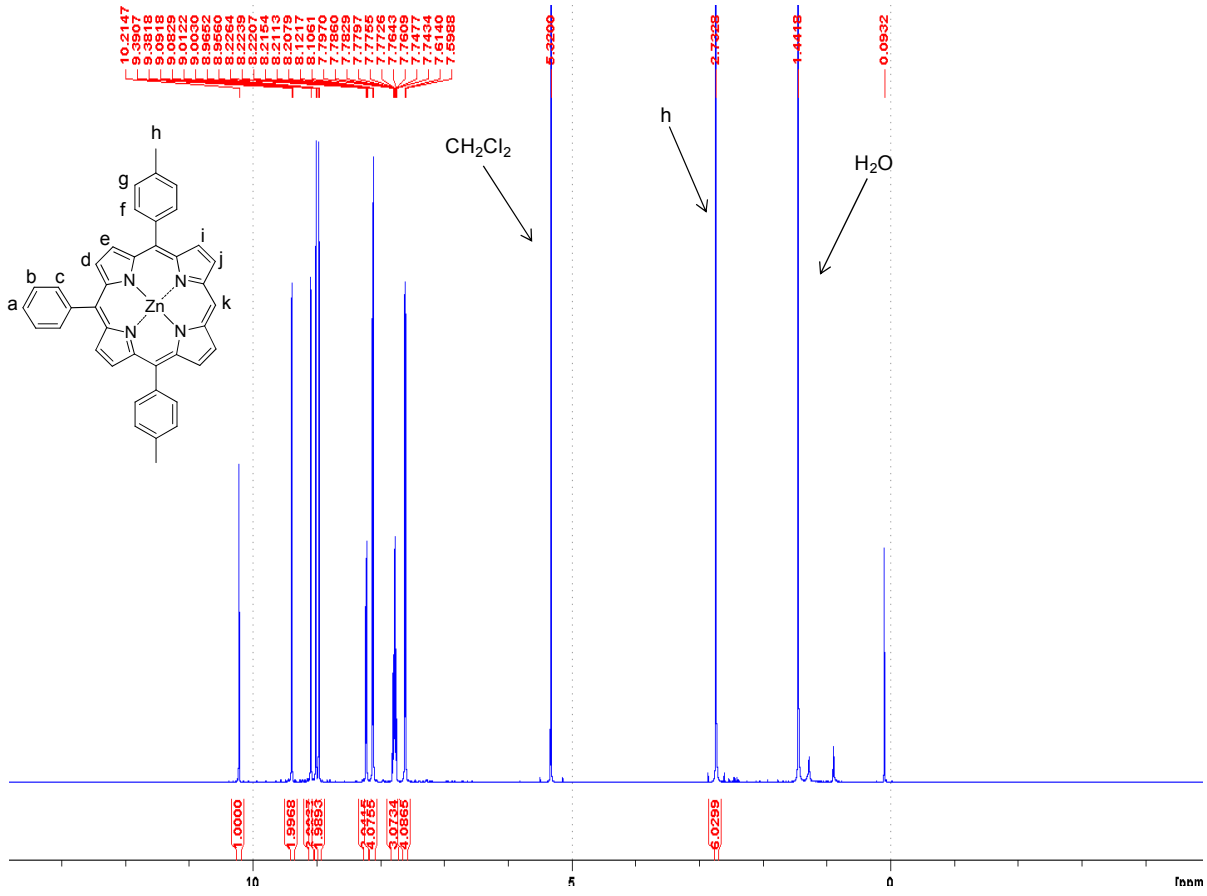

Fig. 1 ^{1}H NMR spectrum of **1-Zn** in CD_2Cl_2, 500 MHz, 300 K.

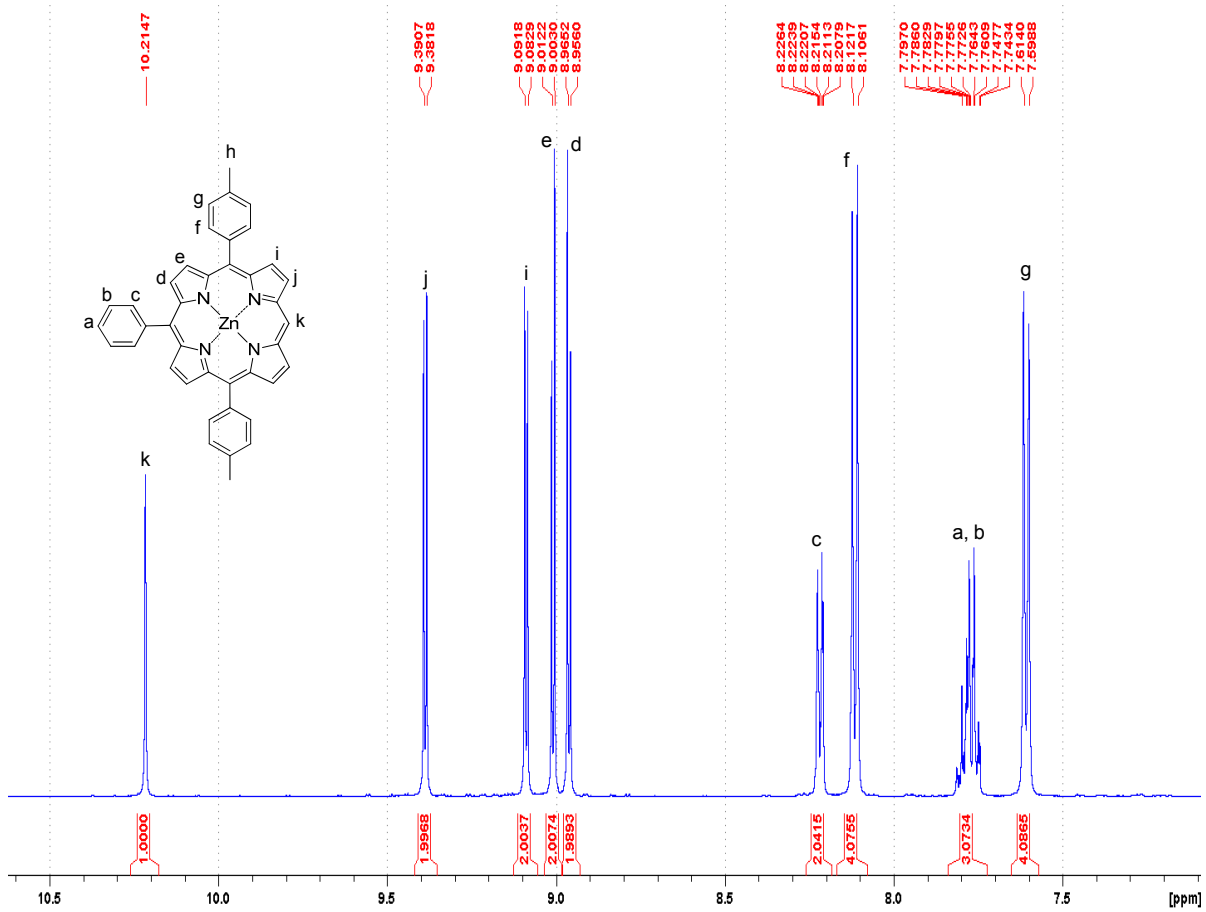

Fig. 2 Partial ^{1}H NMR spectrum of **1-Zn** in CD_2Cl_2, 500 MHz, 300 K. δ (ppm) 2.73 (s, CH_3, 6H), 7.61 (d, ^{3}J = 7.7 Hz, *m*-tol, 2H), 7.74-7.80 (m, *p,m*-Ph, 3H), 8.11 (d, ^{3}J = 7.9 Hz, *o*-tol, 2H),, 8.21-8.23 (m, *o*-Ph, 2H), 8.96 (d, ^{3}J = 4.7 Hz, β-Pyrr, 2H), 9.01 (d, ^{3}J = 4.7 Hz, β-Pyrr, 2H), 9.09 (d, ^{3}J = 4.5 Hz, β-Pyrr, 2H), 9.39 (d, ^{3}J = 4.5 Hz, β-Pyrr, 2H), 10.21 (s, β-Pyrr, 1H).

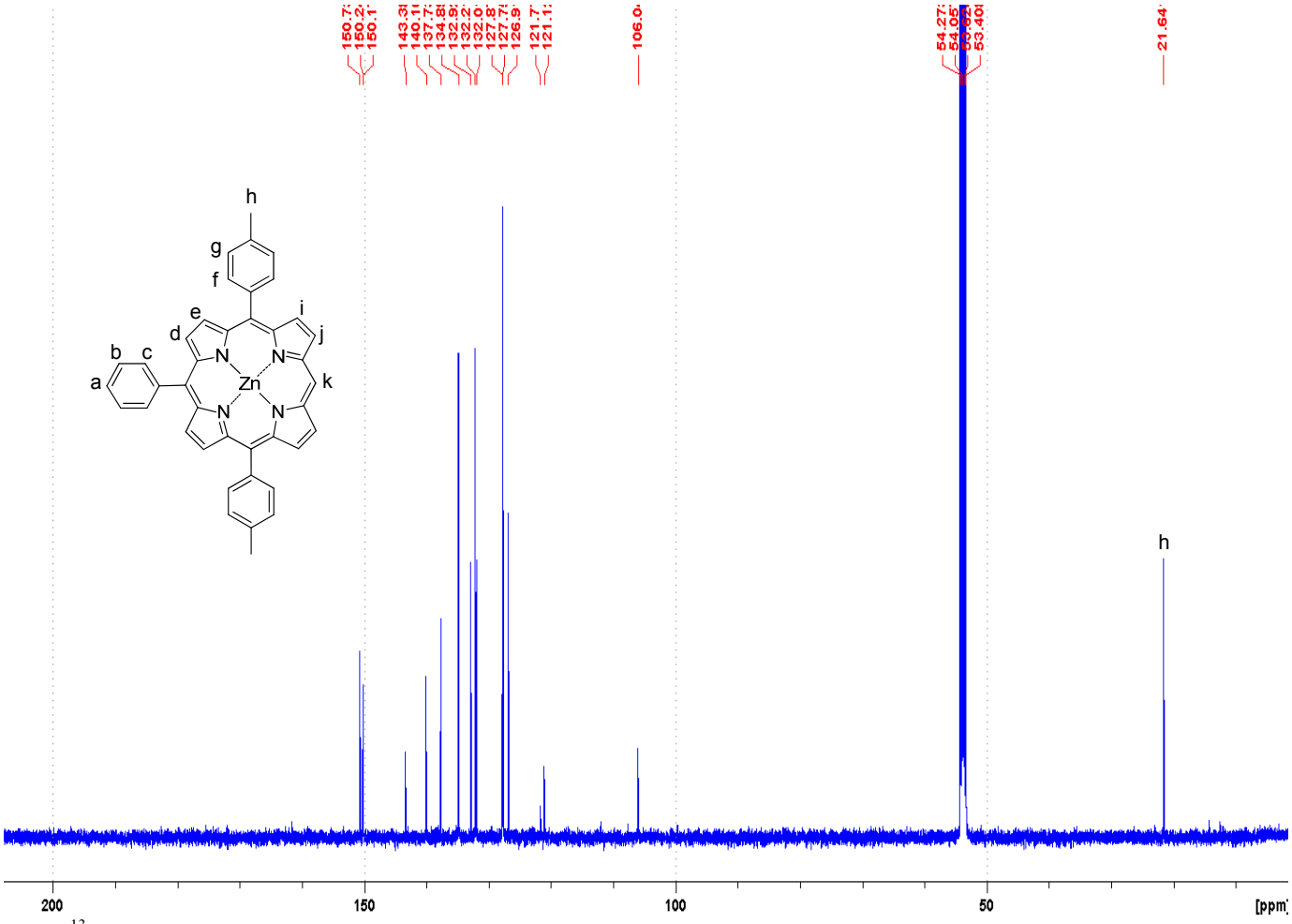

Fig. 3 ^{13}C NMR spectrum of **1-Zn** in CD_2Cl_2, 125.7574 MHz, 300 K.

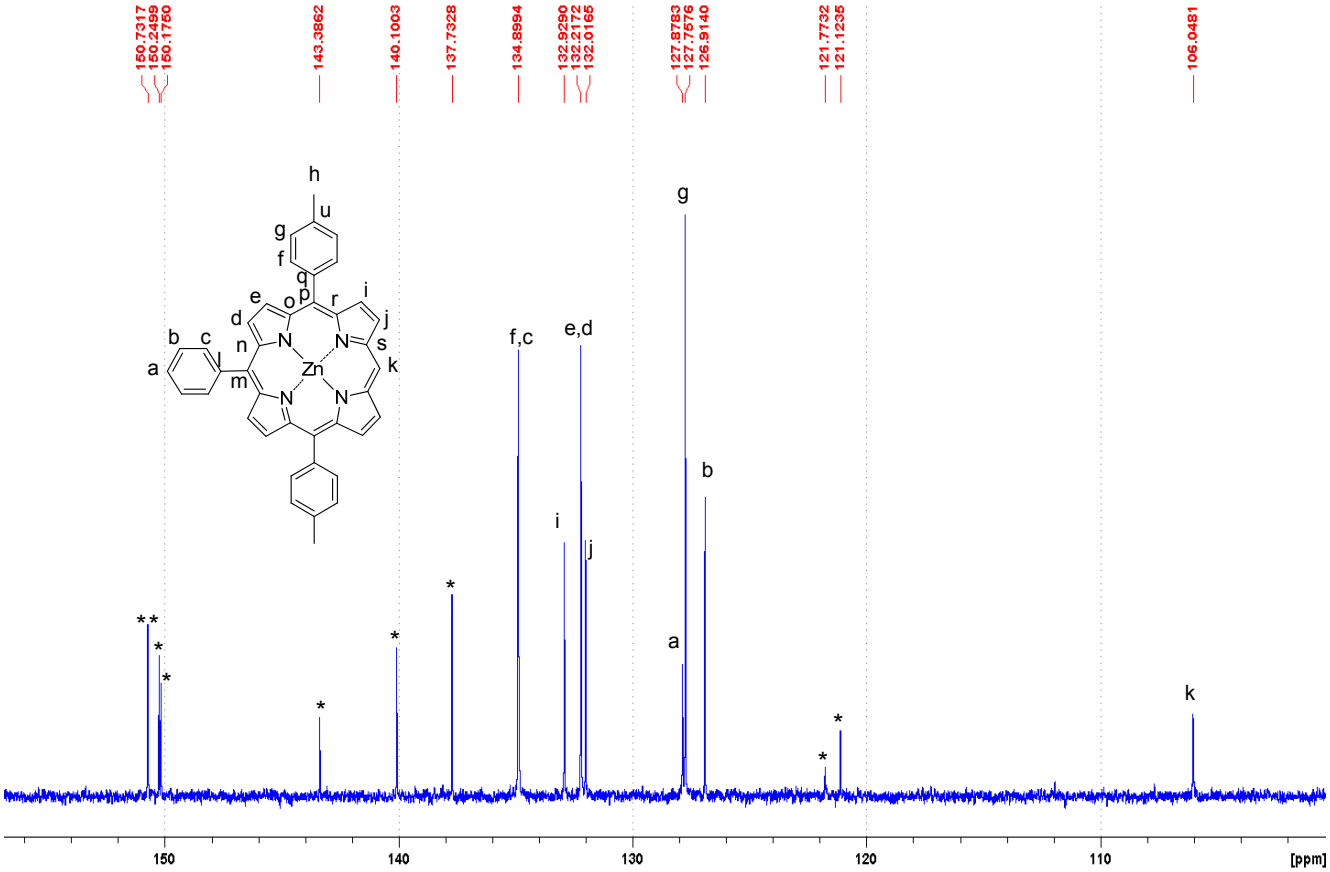

Fig. 4 Partial ^{13}C NMR spectrum of **1-Zn** in CD_2Cl_2, 125.7475 MHz, 300 K.
(*): non attributed signals. These signals could be: l, m, n, o, p, q, u, r, and s (these 9 C are uncoupled with proton signals in the ^{1}H-^{13}C HSQC experiment).

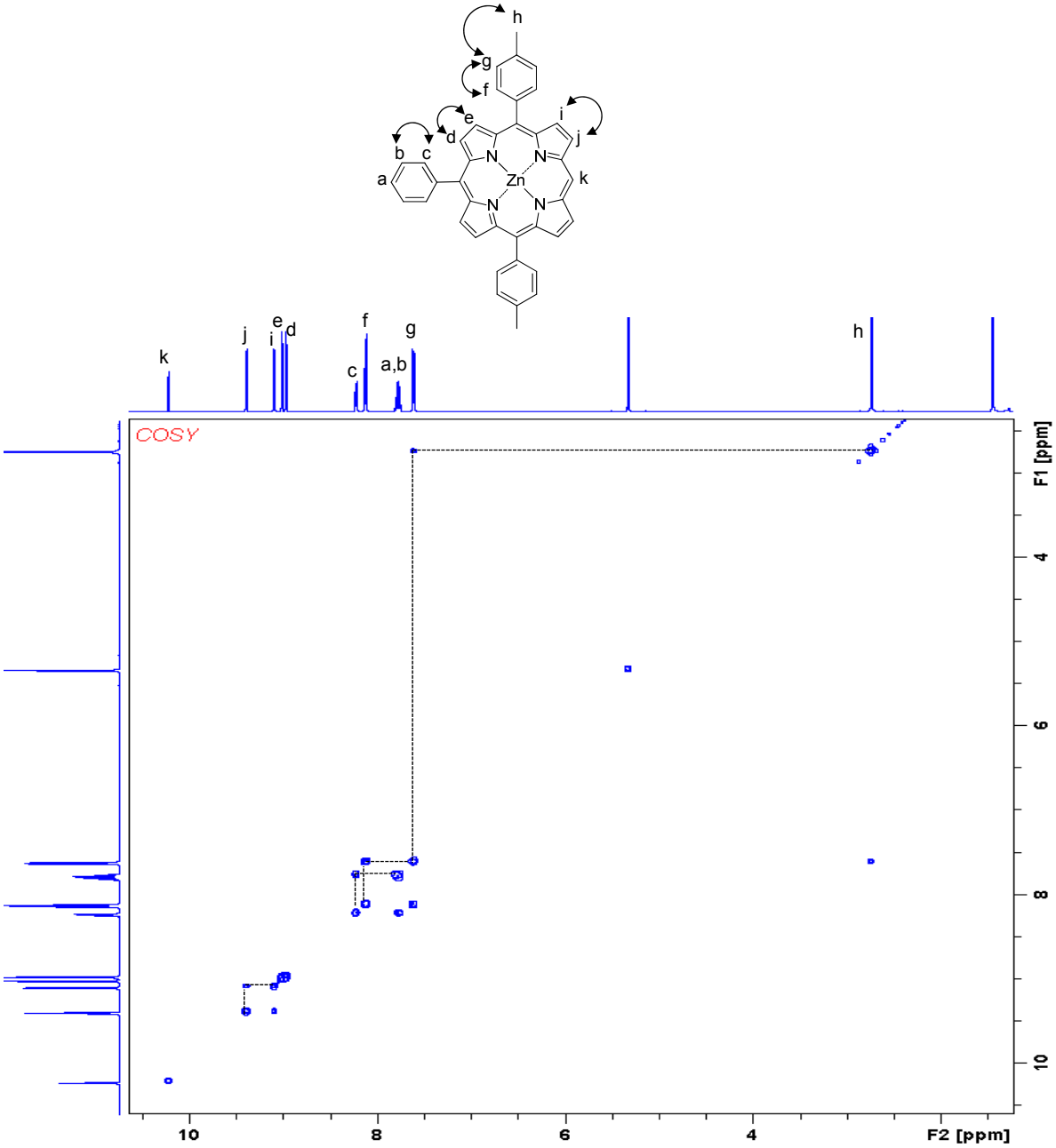

Fig. 5 ^{1}H-^{1}H COSY NMR spectrum of **1-Zn** in CD_2Cl_2, 500 MHz, 300 K.

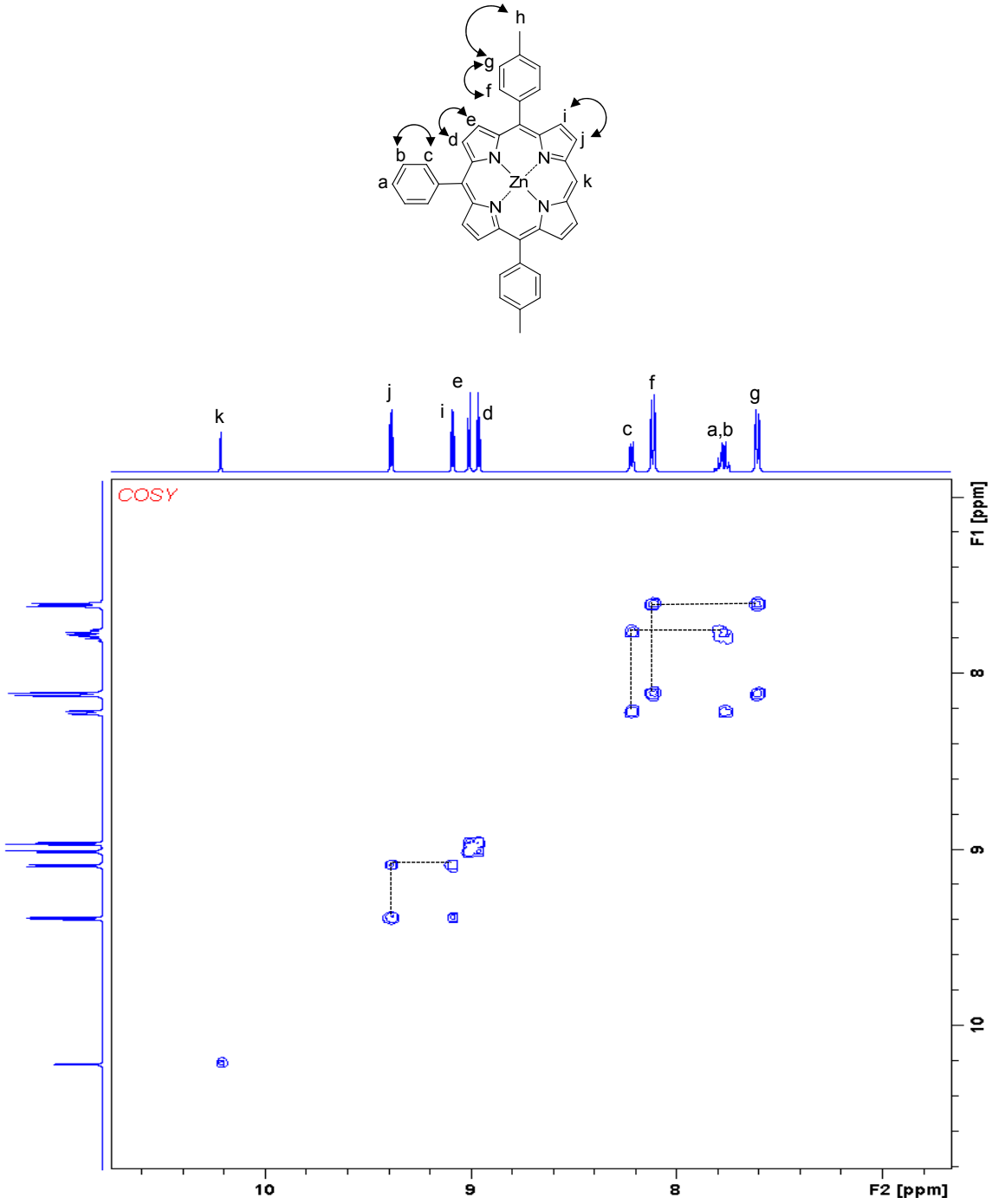

Fig. 6 Partial ^{1}H-^{1}H COSY NMR spectrum of **1-Zn** in CD_2Cl_2, 500 MHz, 300 K.

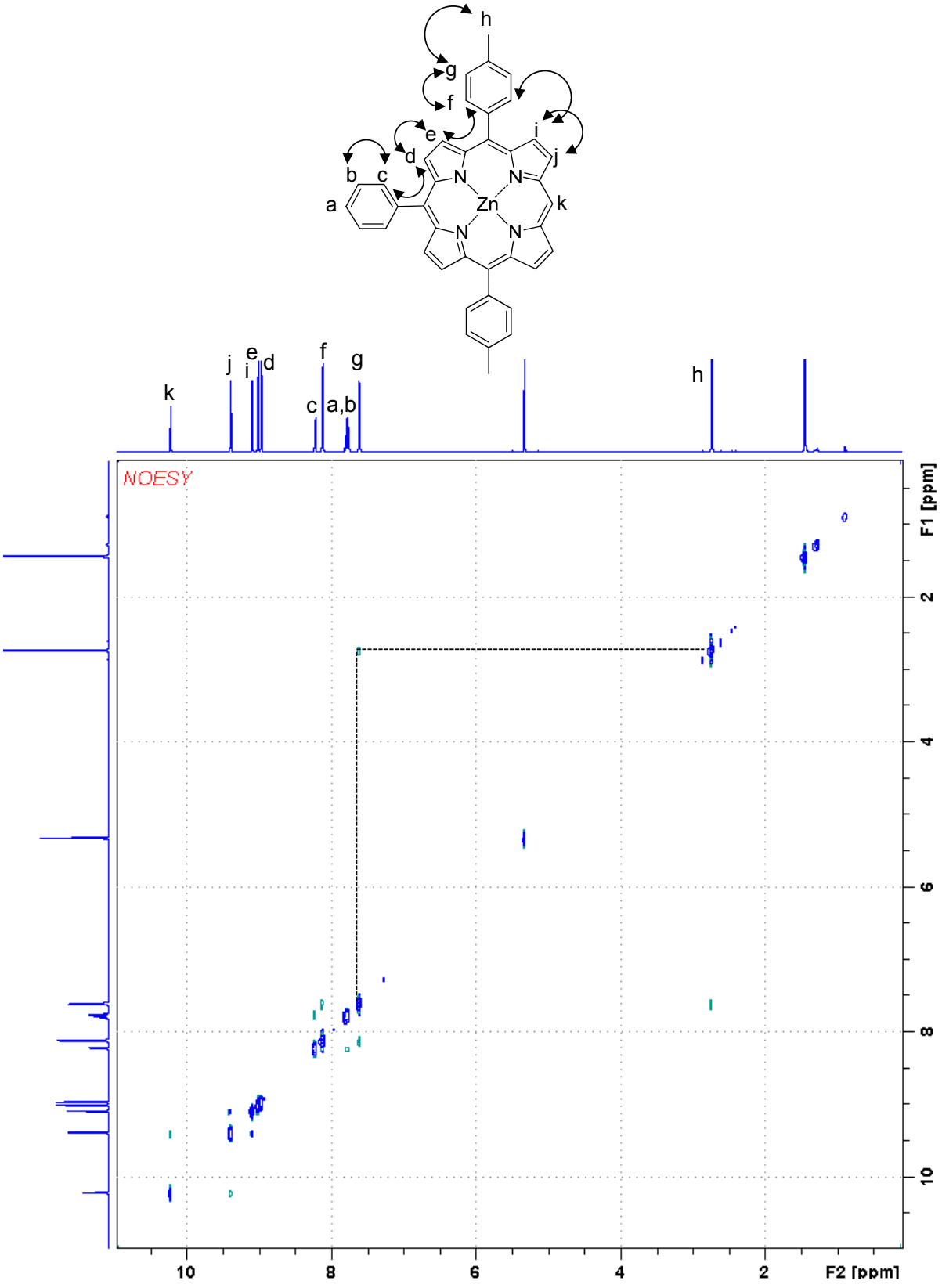

Fig. 7 ^{1}H-^{1}H NOESY NMR spectrum of **1-Zn** in CD_2Cl_2, 500 MHz, 300 K

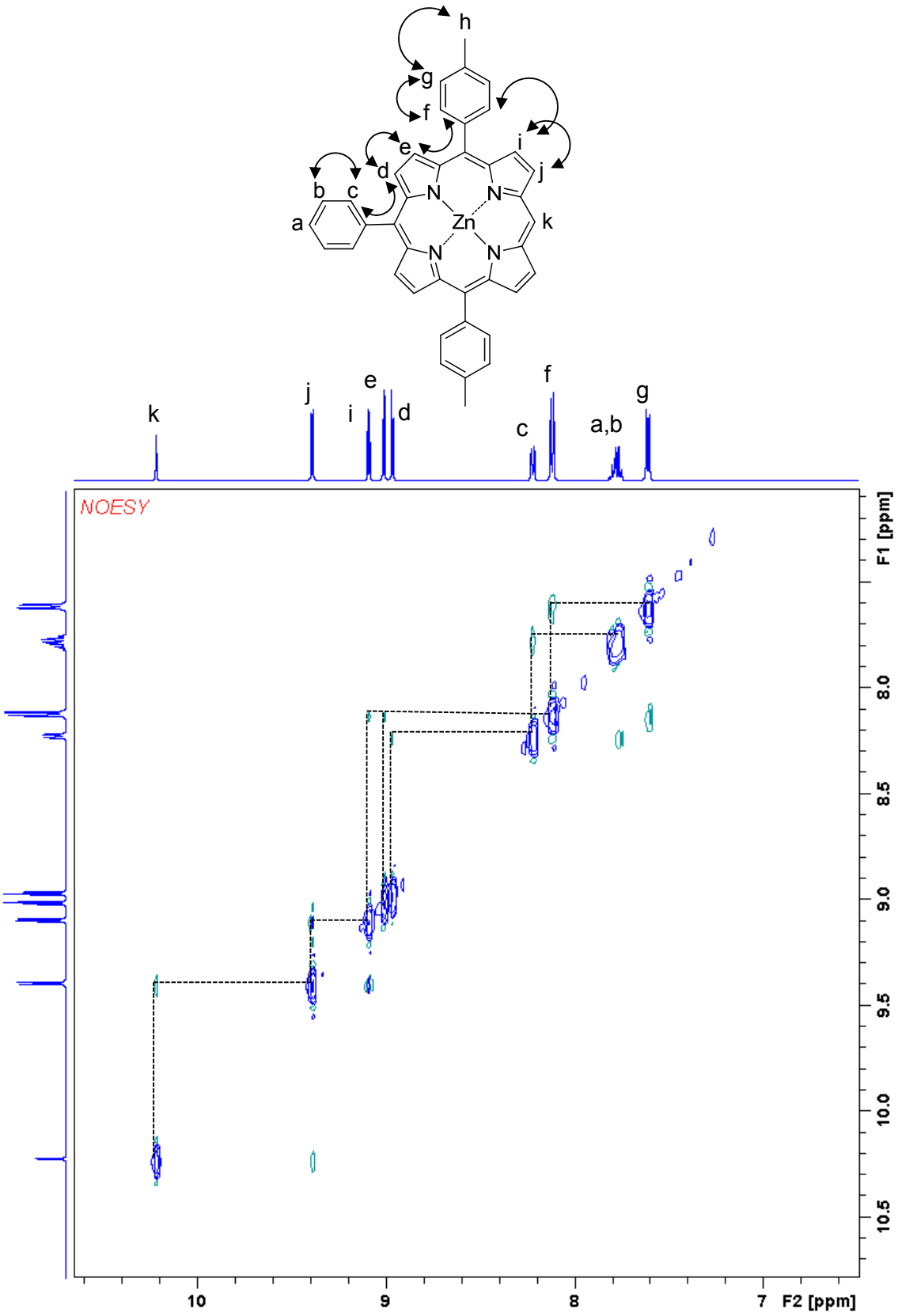

Fig. 8 Partial ^{1}H-^{1}H NOESY NMR spectrum of **1-Zn** in CD_2Cl_2, 500 MHz, 300 K.

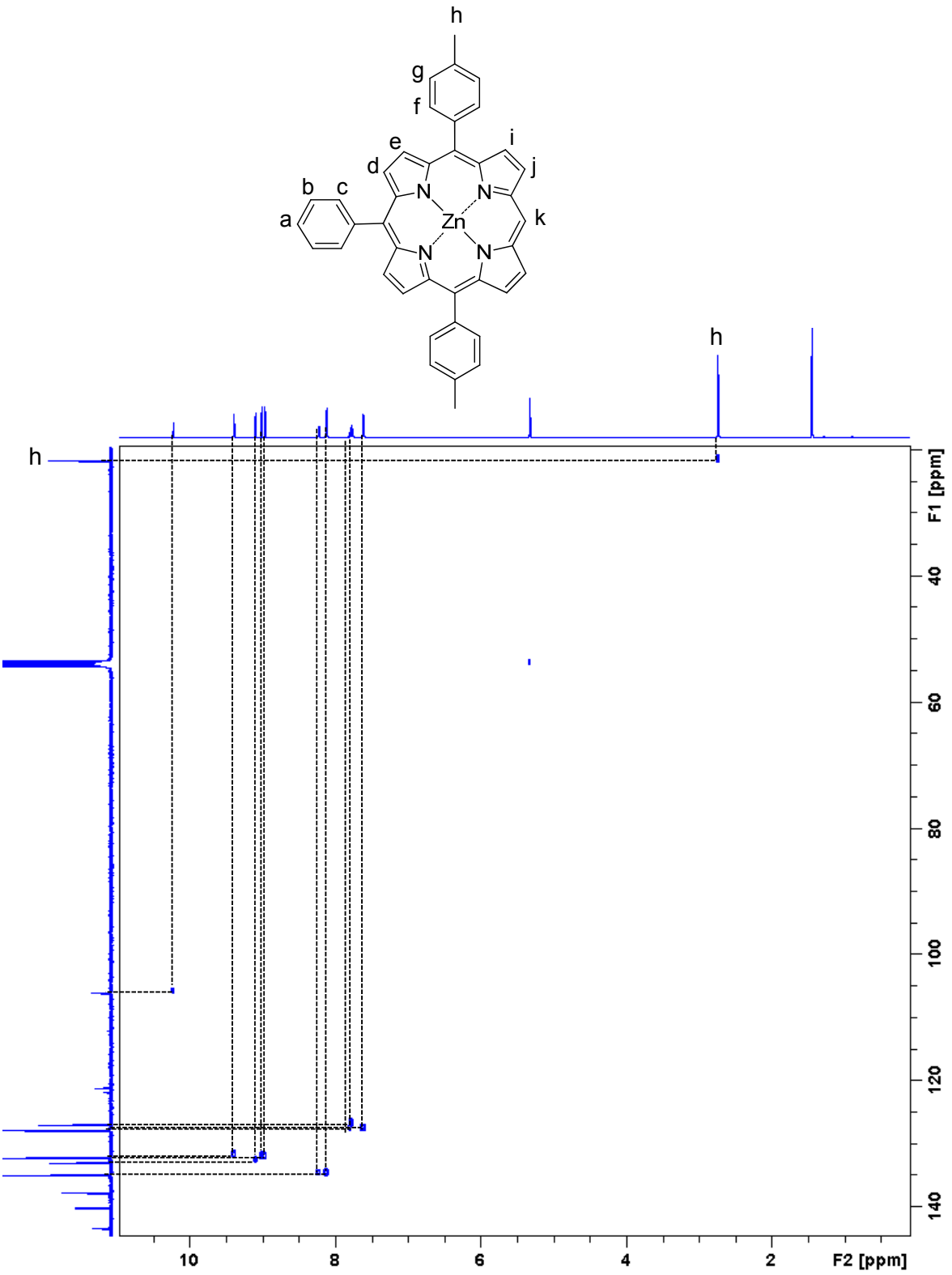

Fig. 9 ^{1}H-^{13}C HSQC NMR spectrum of **1-Zn** in CD_2Cl_2, 500 MHz, 300 K.

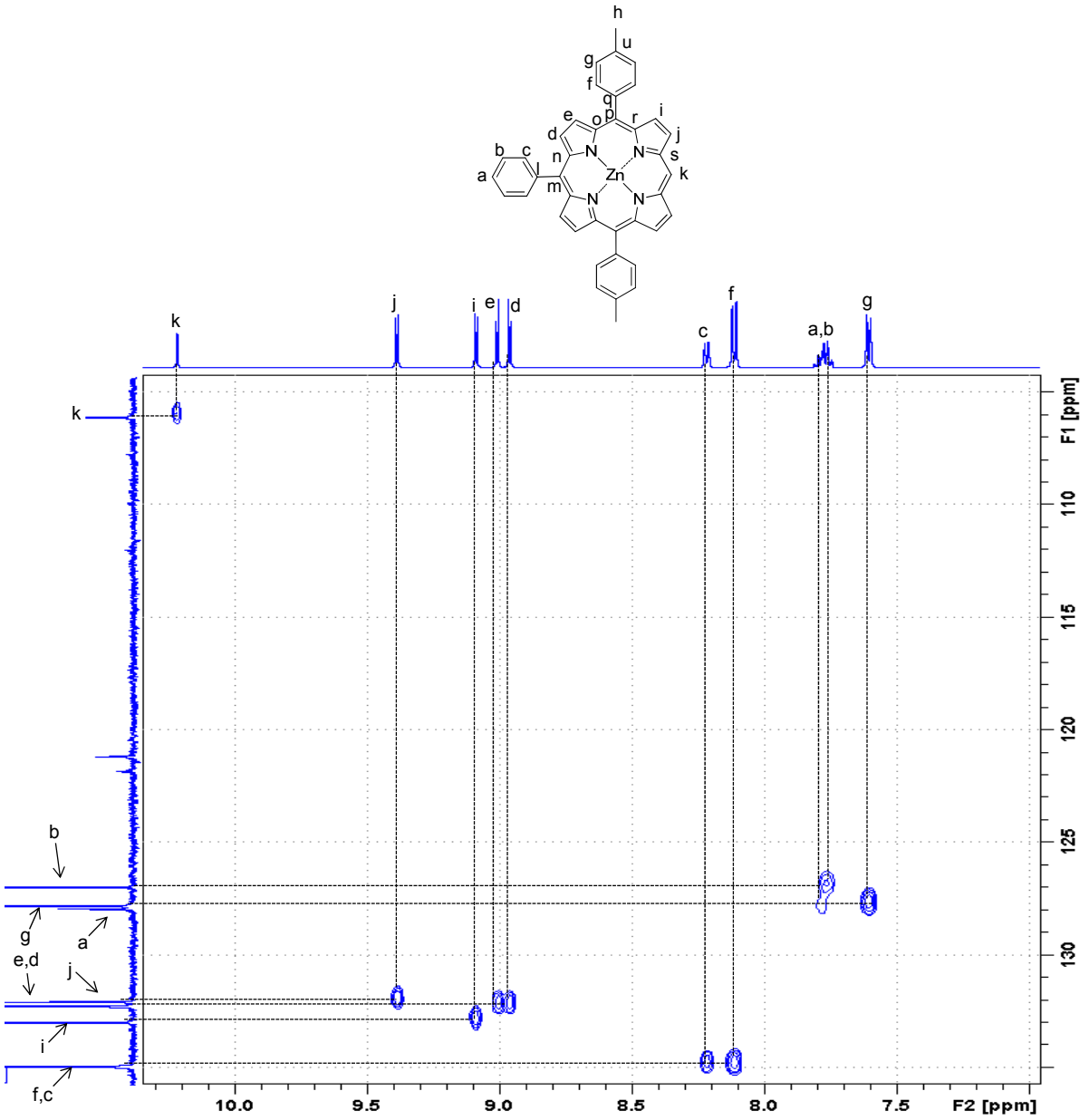

Fig. 10 Partial ^{1}H-^{13}C HSQC NMR spectrum of **1-Zn** in CD_2Cl_2, 500 MHz, 300 K.

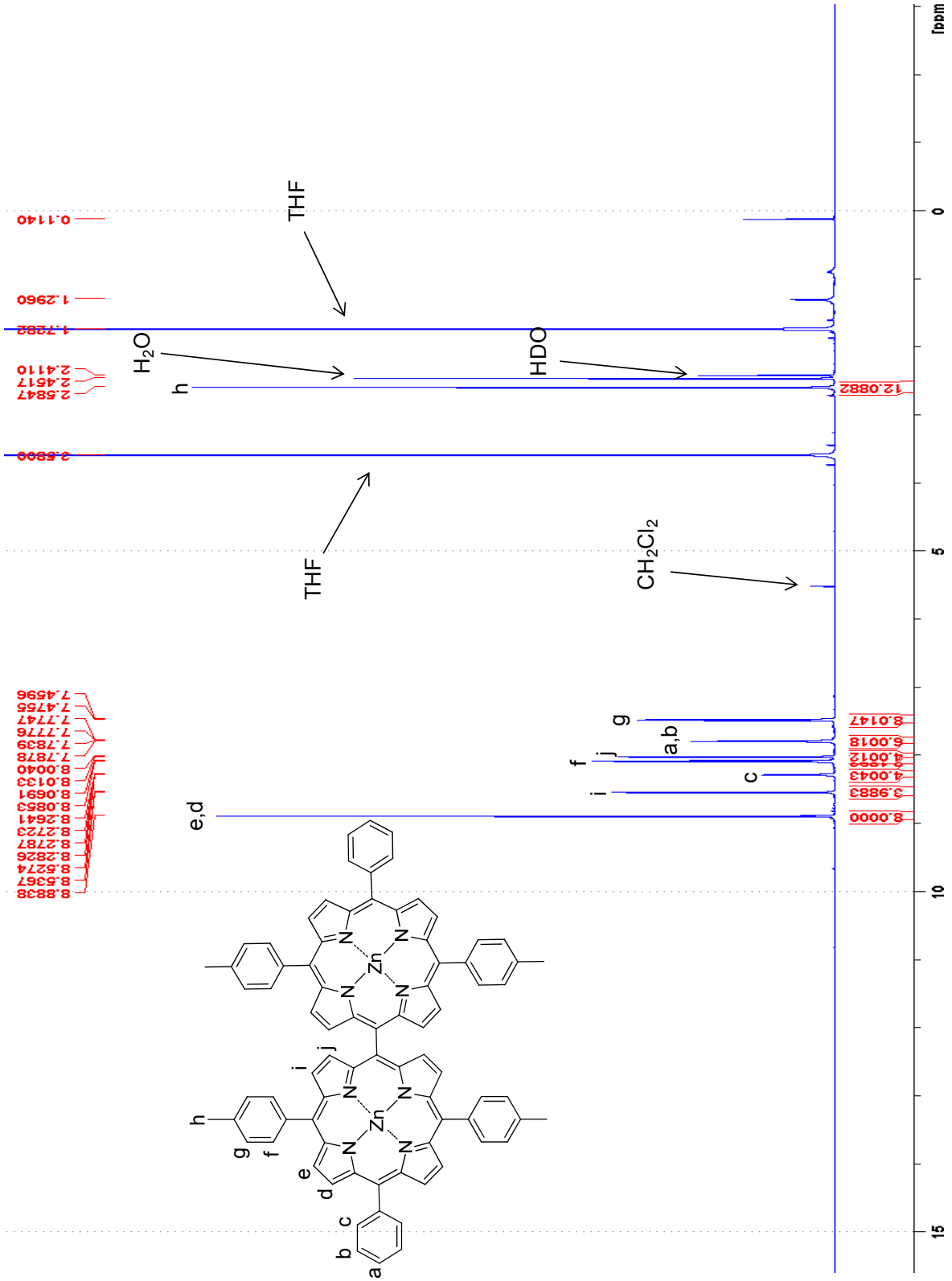

Fig. 11 ^{1}H NMR spectrum of **2-Zn** in THF-d8, 500 MHz, 295 K.

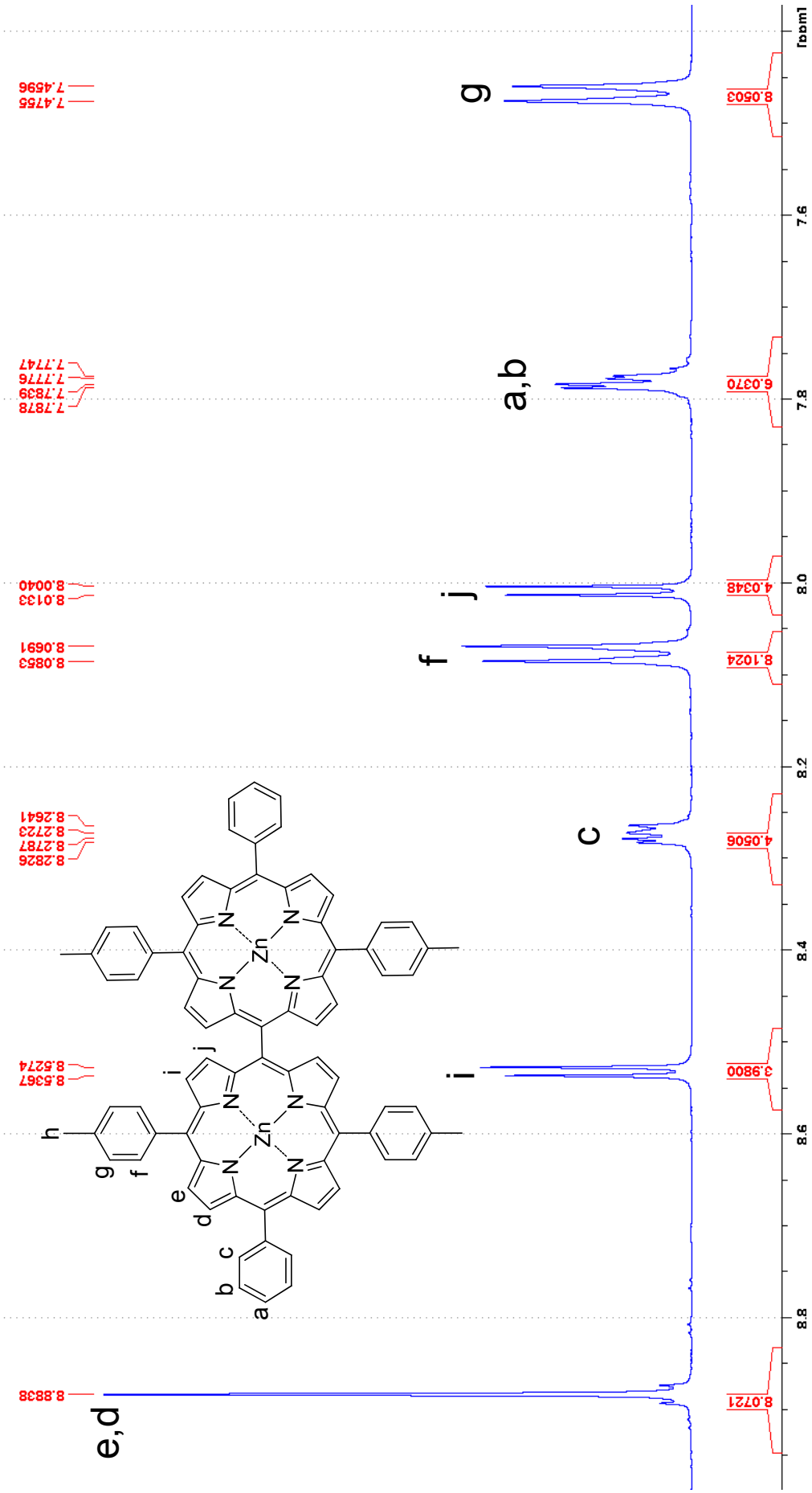

Fig. 12 Partial ^{1}H NMR spectrum of **2-Zn** in THF-d8, 500 MHz, 300 K. δ (ppm) 2.58 (s, CH_3, 12H), 7.47 (d, ^{3}J = 8.1 Hz, *m* -tol, 8H), 7.76-7.80 (m, *p*,*m*-Ph, 6H), 8.01 (d, ^{3}J = 4.6 Hz, β-Pyrr, 4H) 8.08 (d, ^{3}J = 8.2 Hz, *o*-tol, 8H), 8.26-8.29 (m, *o*-Ph, 4H), , 8.53 (d, ^{3}J = 4.6 Hz, β-Pyrr, 4H), 8.88 (s, β-Pyrr, 8H).

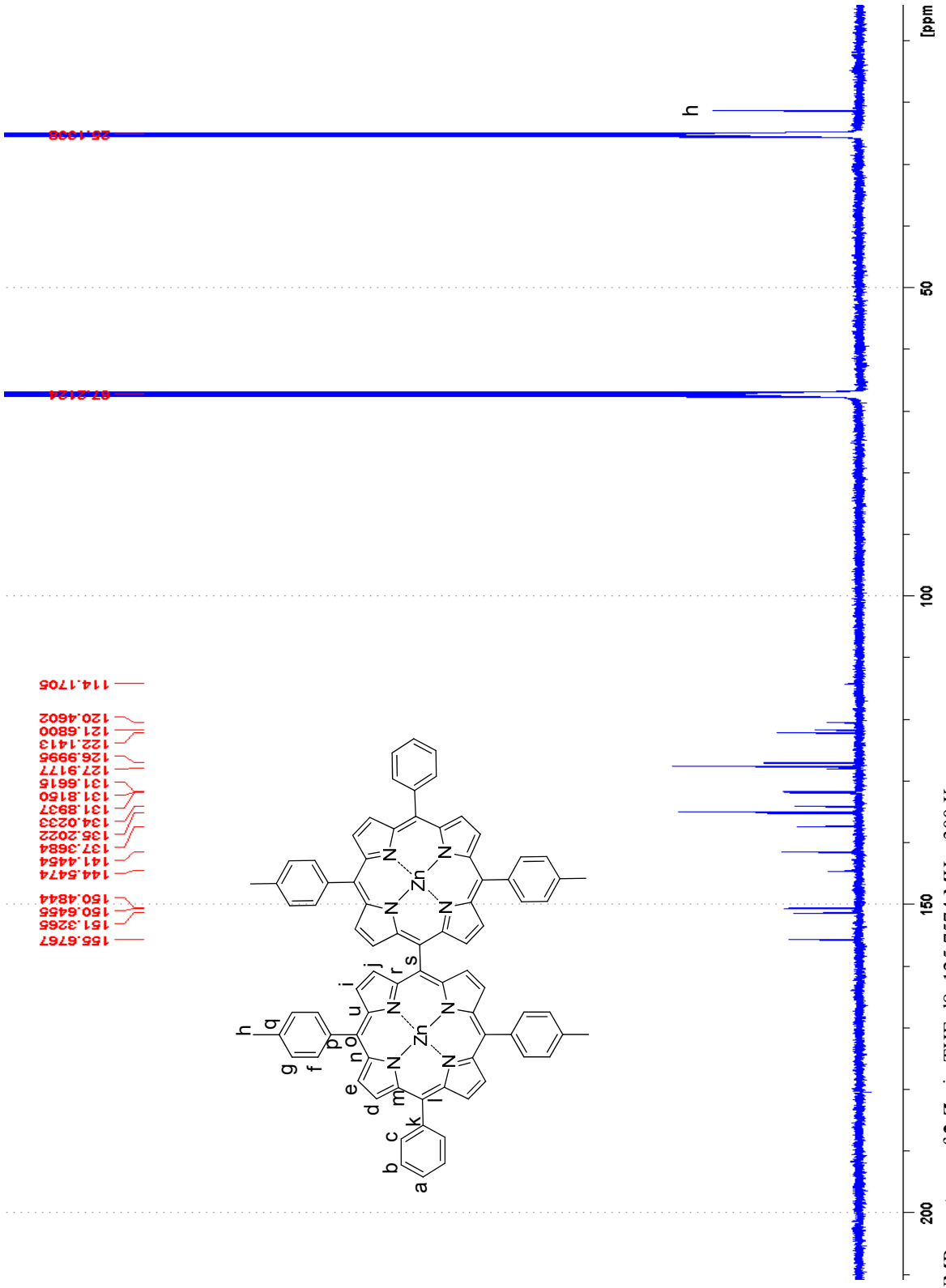

Fig. 13 ^{13}C NMR spectrum of **2-Zn** in THF-d8, 125.7574 MHz, 300 K.

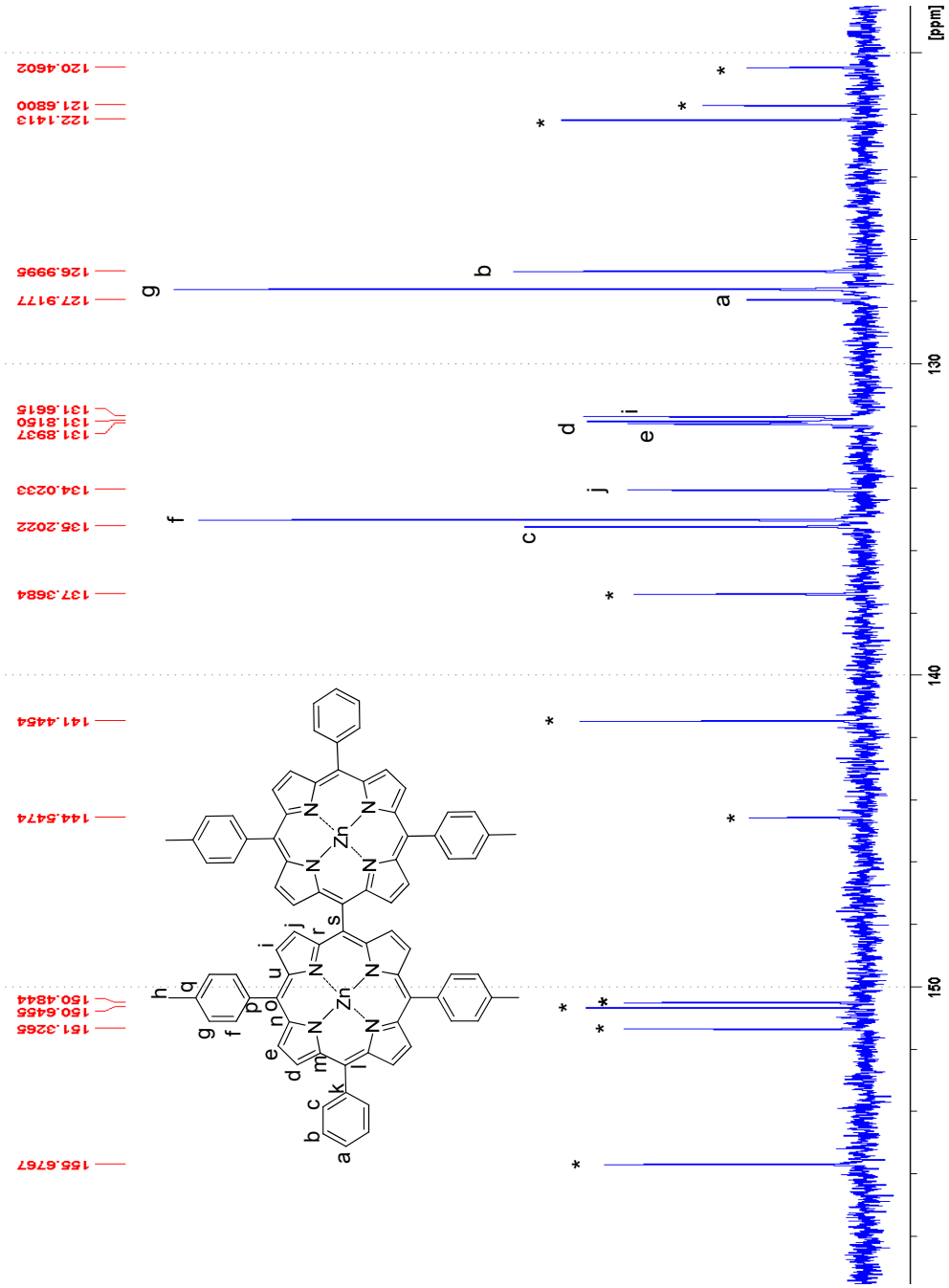

Fig. 14 Partial ^{13}C NMR spectrum of **2-Zn** in THF-d8, 125.7475 MHz, 300 K.
(*): non attributed signals. These signals could be: k, l, m, n, o, p, q, u, r, and s (these 10 C are uncoupled with proton signals in the ^{1}H-^{13}C HSQC experiment).

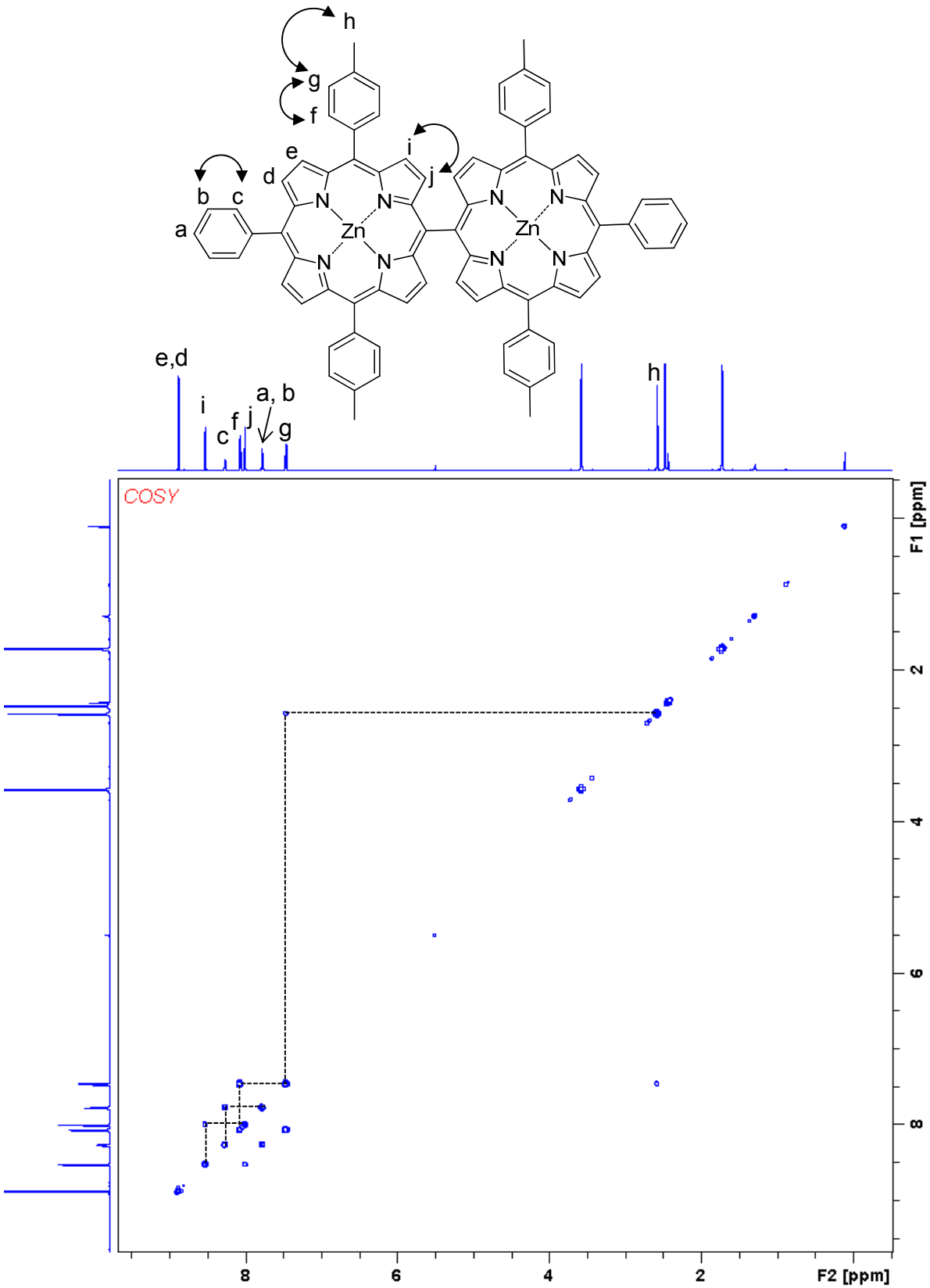

Fig. 15 ^{1}H-^{1}H COSY NMR spectrum of **2-Zn** in THF-d8, 500 MHz, 300 K.

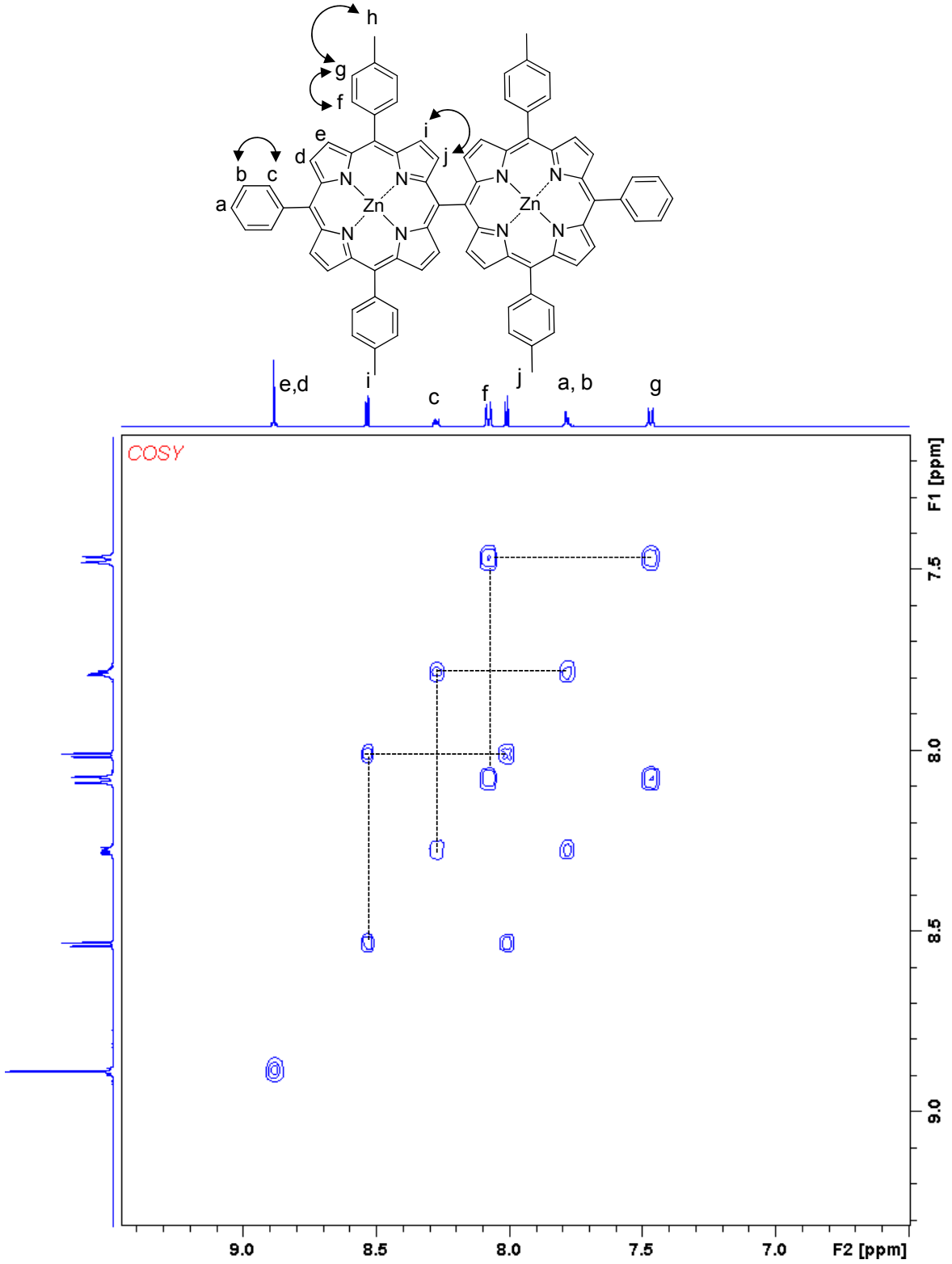

Fig. 16 Partial ^{1}H-^{1}H COSY NMR spectrum of **2-Zn** in THF-d8, 500 MHz, 300 K.

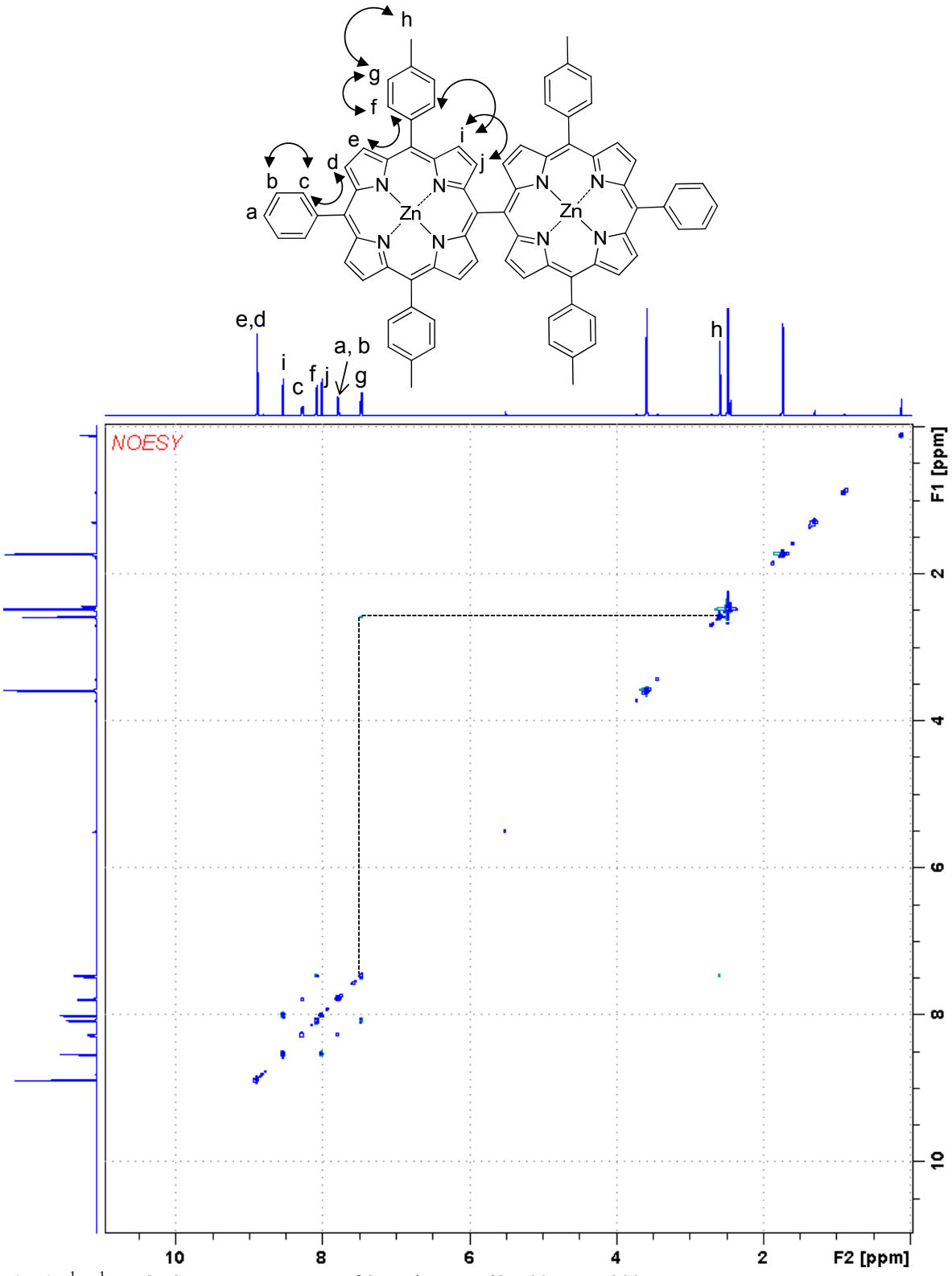

Fig. 17 ^{1}H-^{1}H NOESY NMR spectrum of **2-Zn** in THF-d8, 500 MHz, 300 K.

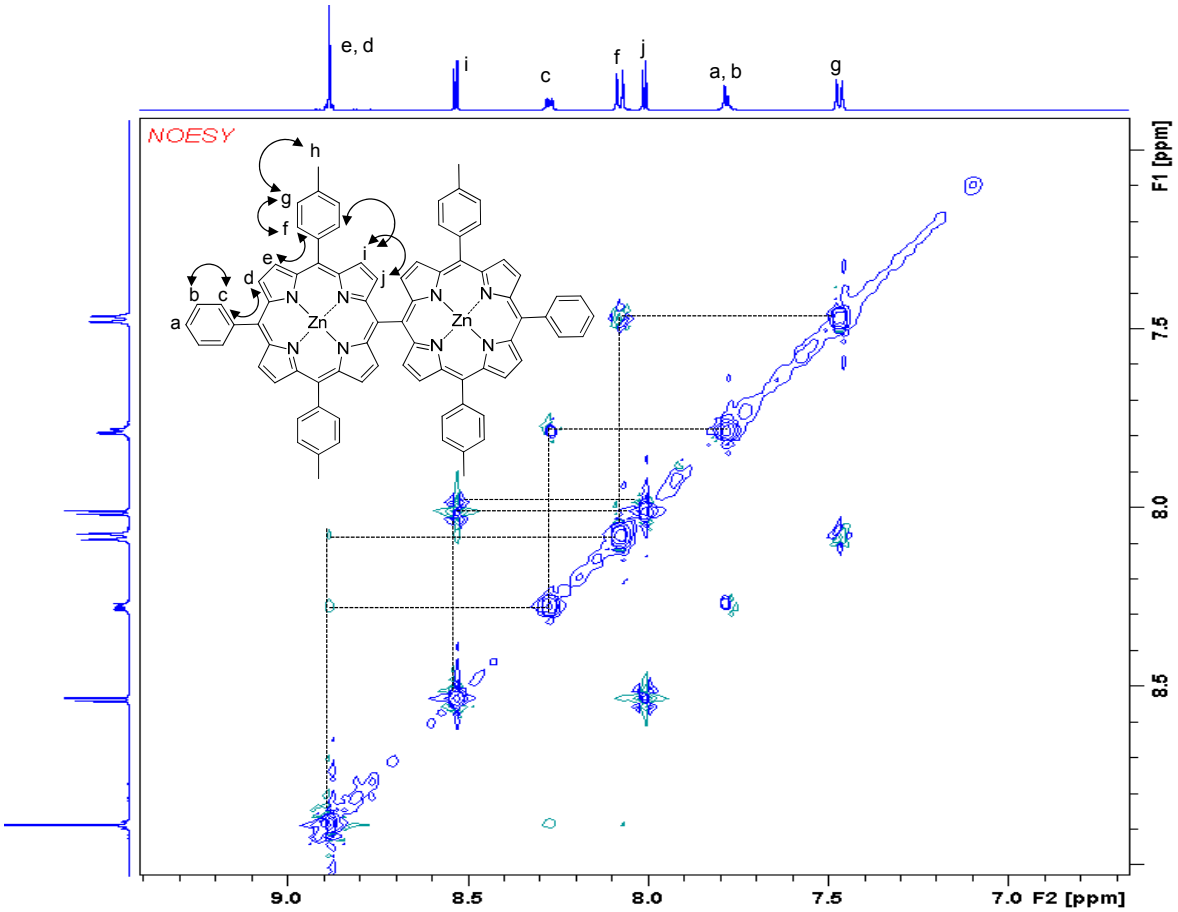

Fig. 18 Partial ^{1}H-^{1}H NOESY NMR spectrum of **2-Zn** in THF-d8, 500 MHz, 300 K.

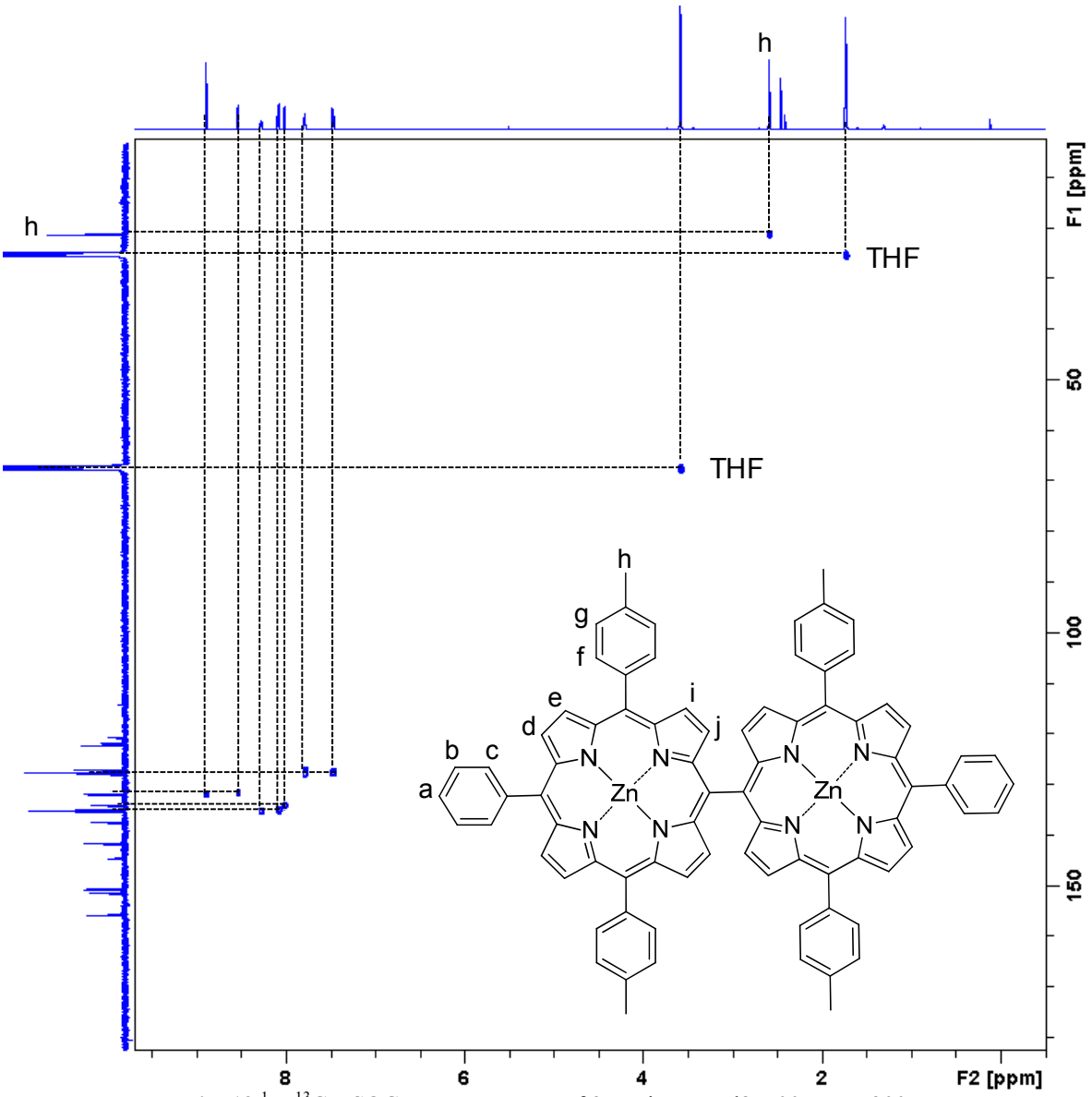

Fig. 19 ^{1}H-^{13}C HSQC NMR spectrum of **2-Zn** in THF-d8, 500 MHz, 300 K.

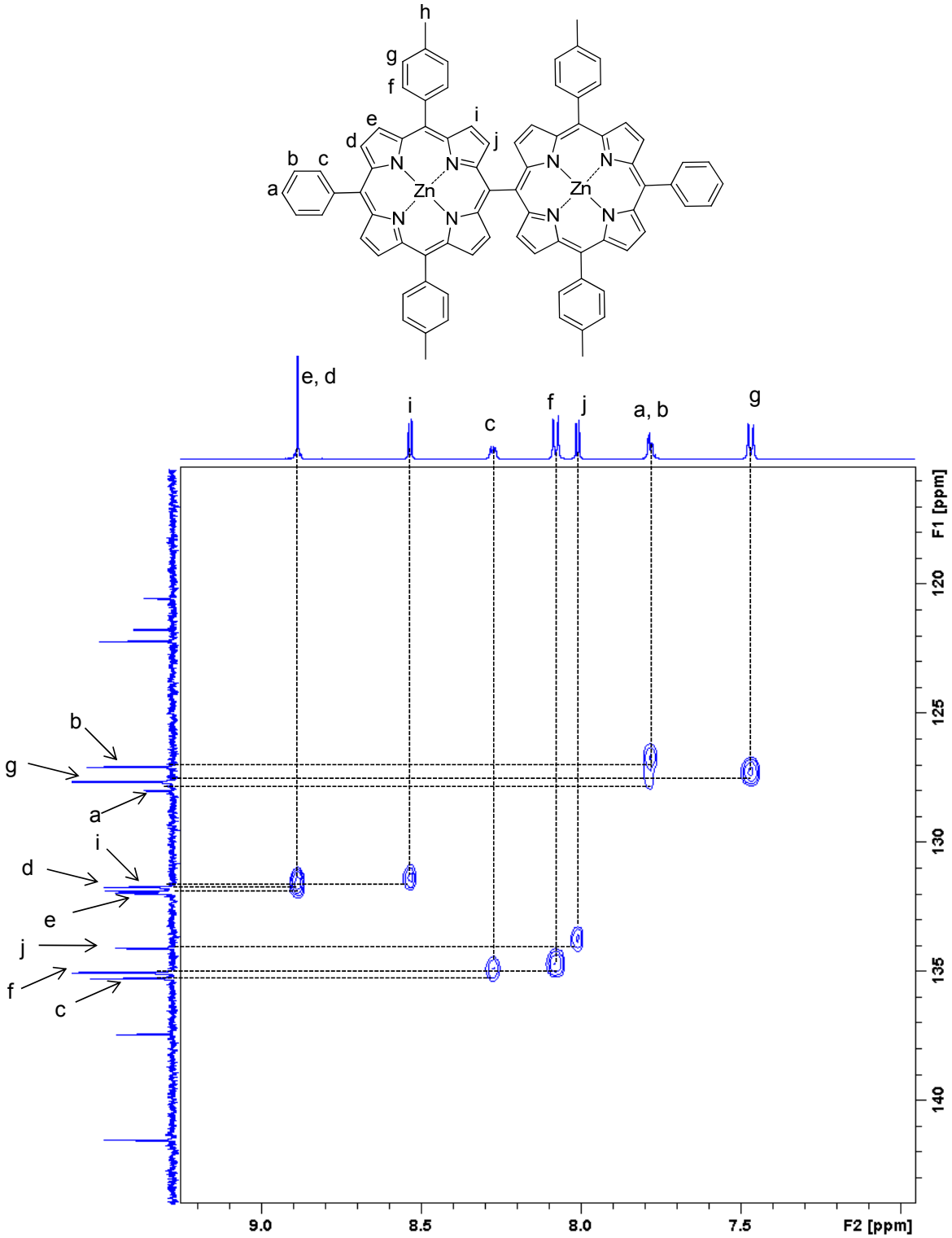

Fig. 20 Partial ^{1}H-^{13}C HSQC NMR spectrum of **2-Zn** in THF-d8, 500 MHz, 300 K.

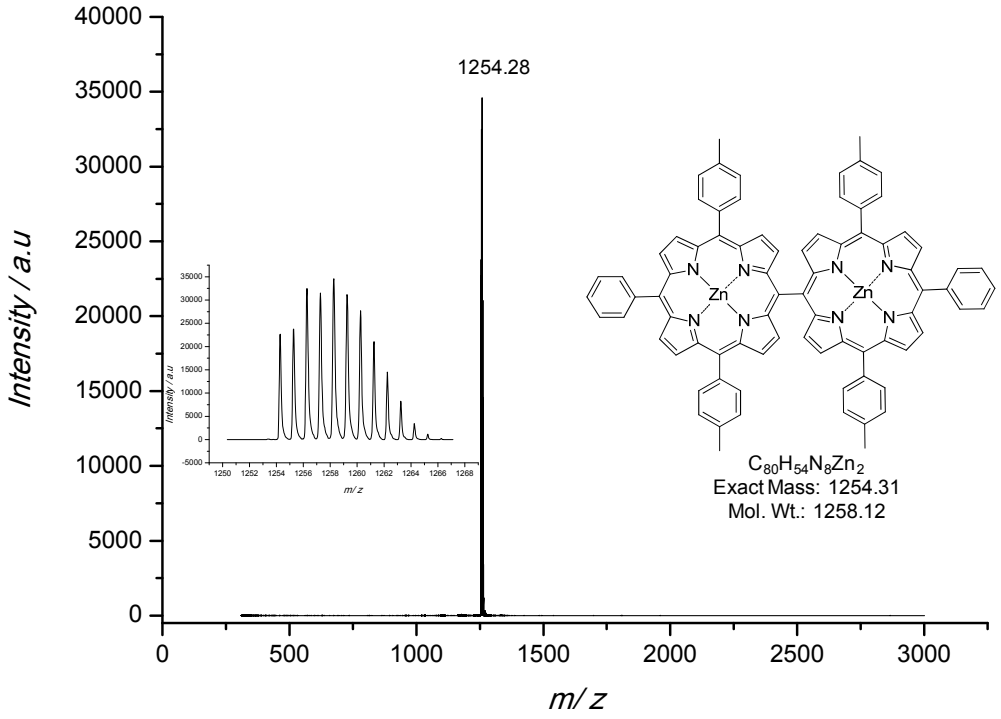

Fig. 21 MALDI-TOF mass spectrum of **2-Zn**.

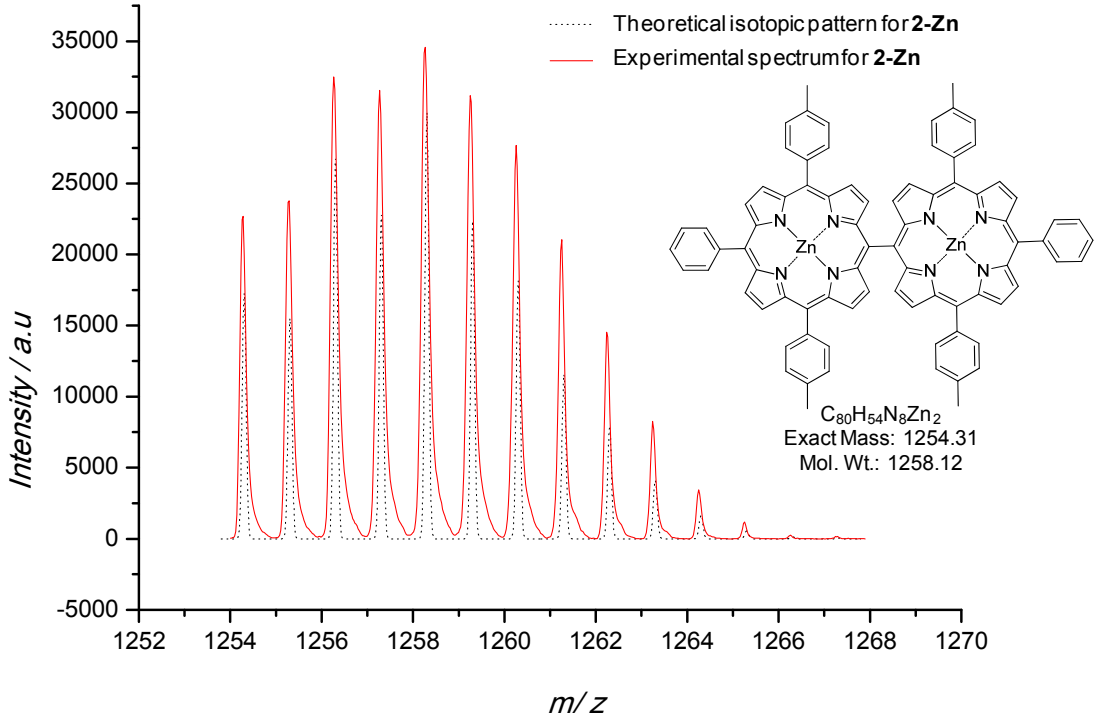

Fig. 22 Partial MALDI-TOF mass spectrum of **2-Zn** centered on its isotopic pattern (red/solid curve) and simulated isotopic pattern for a formula corresponding to **2-Zn** (black/dotted curve).

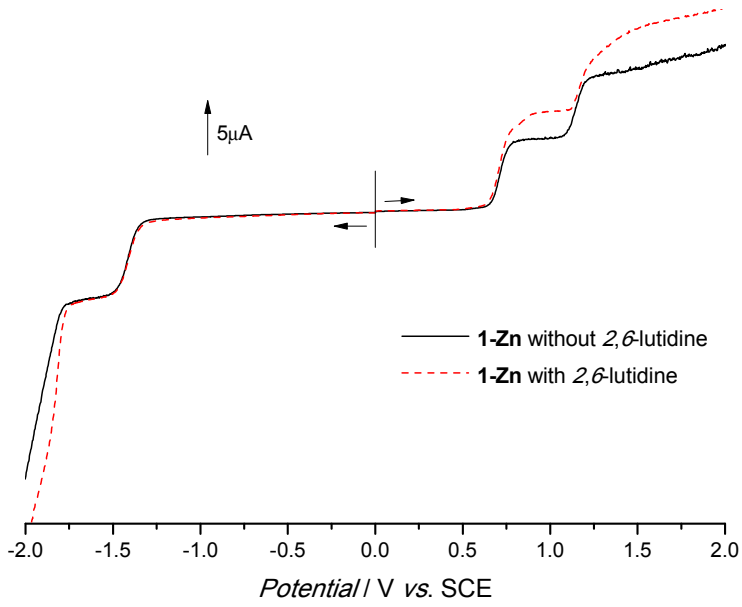

Fig. 23 RDE voltammograms of **1-Zn** without (black/solid line) and with (red/dashed line) *2,6*-lutidine in DCM/ACN (4/1 v/v) containing 0.1 M $TBAPF_6$ (WE: Pt, $\varnothing$ = 2 mm, 10 mV s^{-1}, ω = 500 rpm, [**1-Zn**] = 5.0×10^{-4} M).

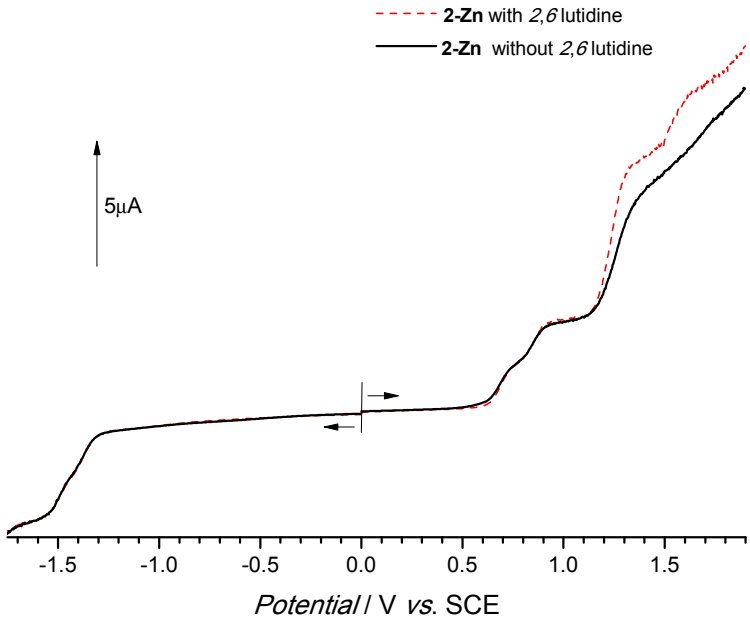

Fig. 24 RDE voltammograms of **2-Zn** without (black/solid line) and with (red/dashed line) *2,6*-lutidine in CH_2Cl_2/CH_3CN (4/1 v/v) containing 0.1 M $TBAPF_6$ (WE: Pt, $\varnothing$ = 2 mm, 10 mV s^{-1}, ω = 500 rpm, [**2-Zn**] = 2.5×10^{-4} M).

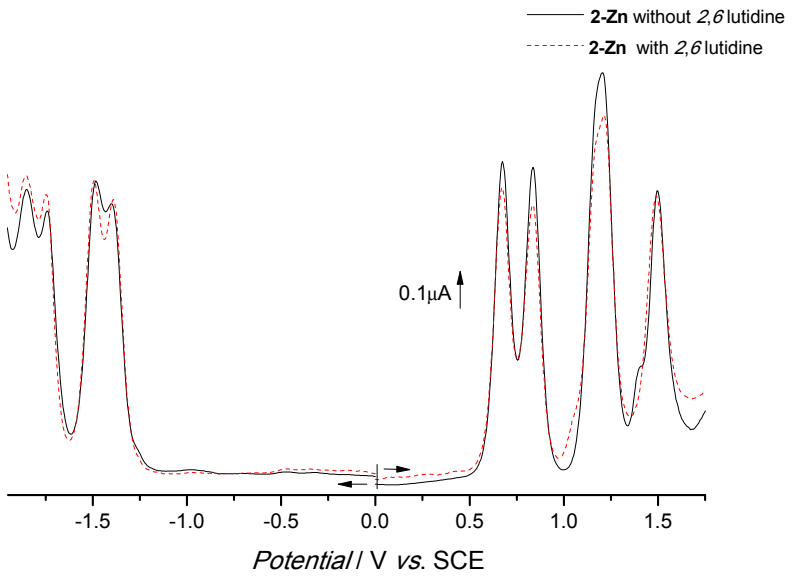

Fig. 25 DPV voltammograms of **2-Zn** without (black/solid line) and with (red/dashed line) *2,6*-lutidine in CH_2Cl_2/CH_3CN (4/1 v/v) containing 0.1 M $TBAPF_6$ (WE: Pt, Ø = 2 mm, 10 mV s^{-1}, [**2-Zn**] = 2.5×10^{-4} M).

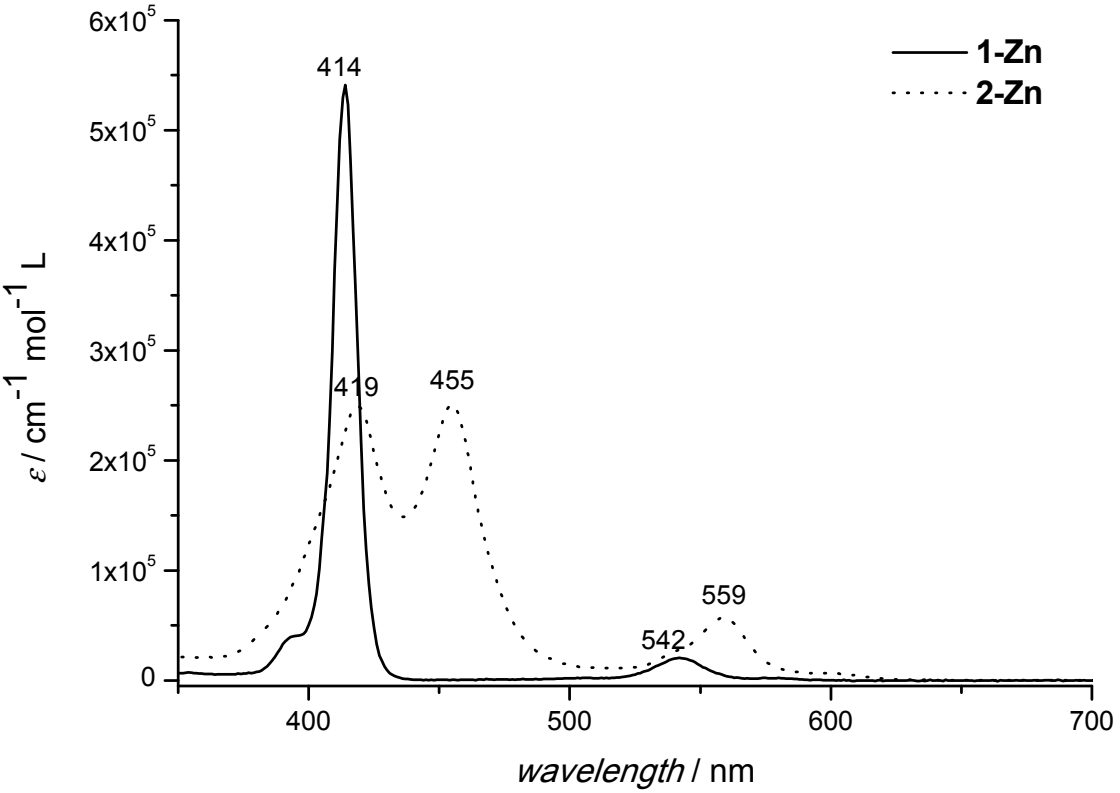

Fig. 26 UV-visible absorption spectra of **1-Zn** and **2-Zn** in CH_2Cl_2.

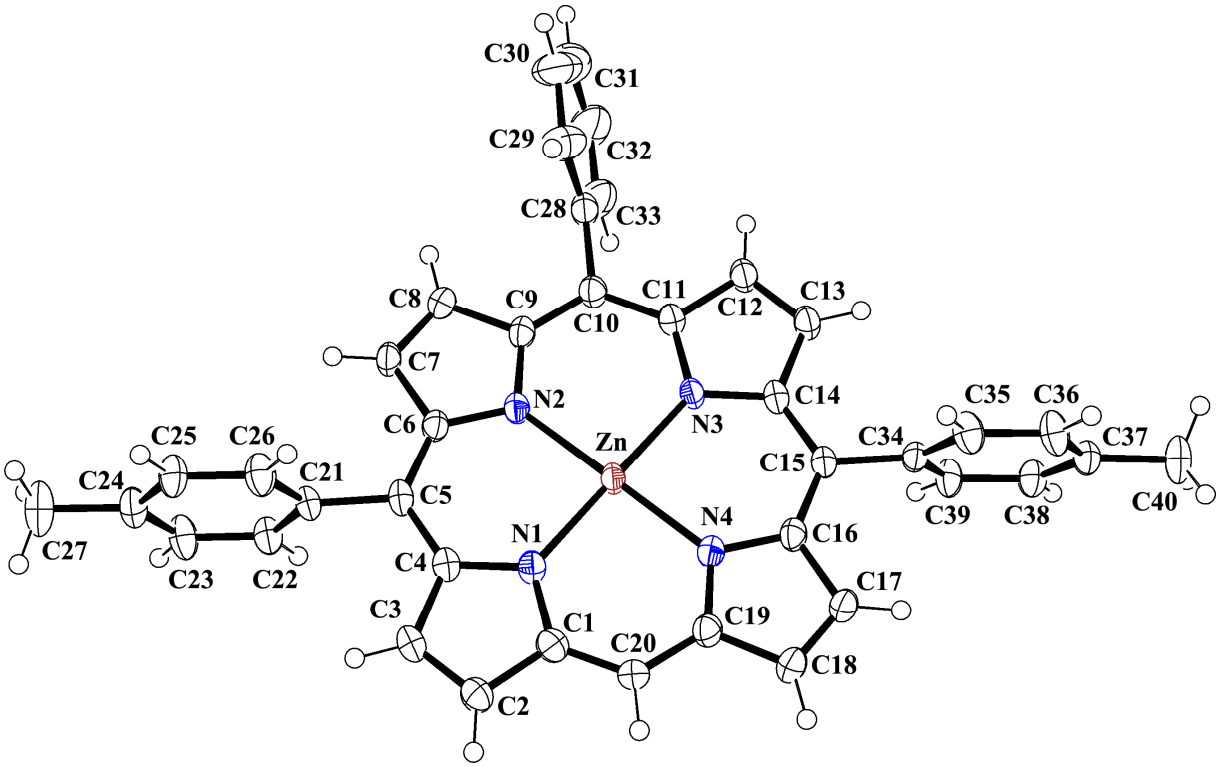

Fig. 27: Ortep view of **1-Zn** crystallographic structure (plot of metallo-ligand with 30% probability)

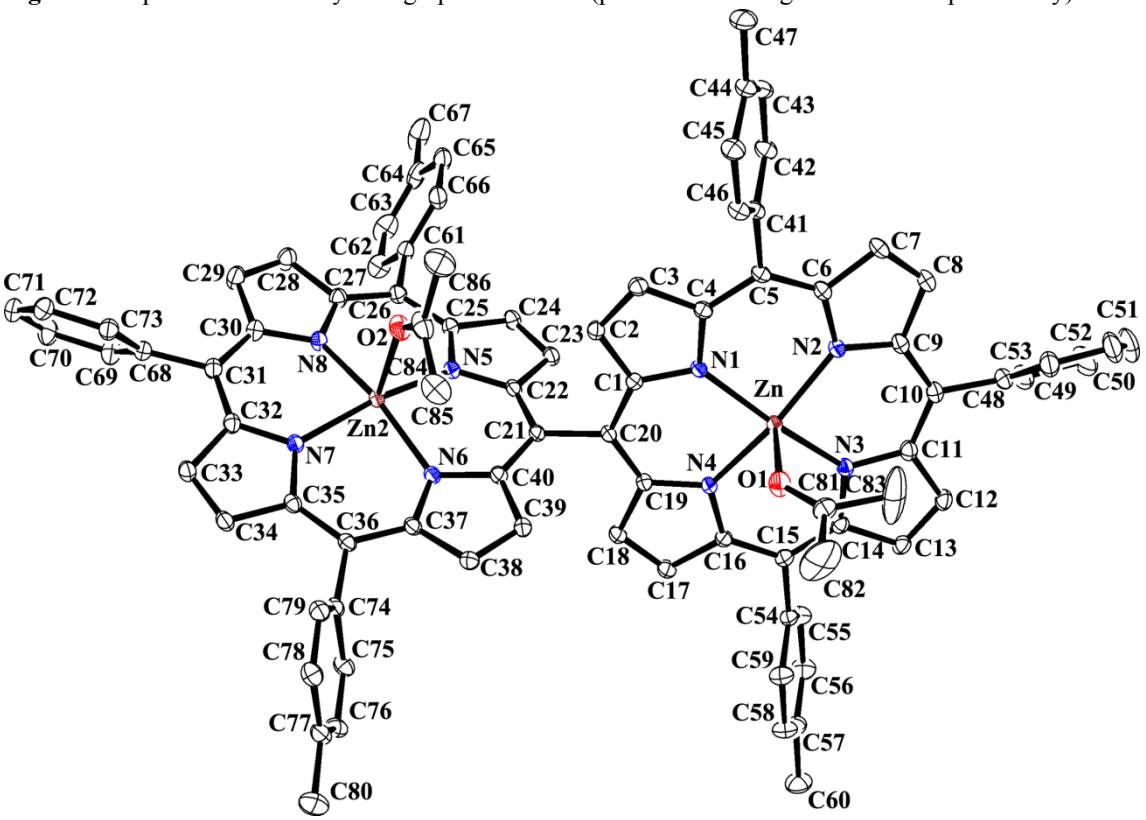

Fig 28: Ortep view of **2-Zn** crystallographic structure (plot of metallo-ligand with 30% probability)

Table 1. Crystal data and structure refinement for **1-Zn** and **2-Zn** complexes.

Compounds	**cd8=1-Zn**	**cd4=2-Zn**
Empirical formula	$C_{40}H_{28}ZnN_4$	$C_{86}H_{66}N_8O_2Zn_2$, C_3H_6O
Formula weight	630.03	1432.29
Temperature (K)	115(2)	115(2)
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	P -1
a (Å)	22.8237(7)	10.9880(2)
b (Å)	9.3135(3)	16.0826(4)
c (Å)	15.0499(5)	22.0181(5)
α (°)		73.0542(8)
β (°)	107.2963(14)	81.9980(12)
γ (°)		74.2166(12)
Volume (Å^3)	3054.47(17)	3577.32(14)
Z	4	2
$\rho_{calc.}$ (g/cm^3)	1.370	1.330
μ (mm^{-1})	0.840	0.729
F(000)	1304	1492
Crystal size (mm^3)	0.18 x 0.15 x 0.15	0.23 x 0.13 x 0.1
sin(θ)/λ max (Å^{-1})	0.65	0.65
Index ranges	*h*: -29; 29 *k*: -11; 12 *l*: -19; 19	*h*: -14; 14 *k*: -20; 20 *l*: -28; 28
Reflections collected	12577	28953
R_{int}	0.0354	0.0237
Reflections with $I \geq 2\sigma(I)$	5272	13792
Data / restraints / parameters	6935 / 0 / 408	16167 / 18 / 943
Final *R* indices [$I \geq 2\sigma(I)$]	$R1^a$ = 0.0612 $wR2^b$ = 0.1067	$R1^a$ =0.0451 $wR2^b$ = 0.1038
R indices (all data)	$R1^a$ = 0.0866 $wR2^b$ = 0.1169	$R1^a$ = 0.0572 $wR2^b$ = 0.1120
Goodness-of-fit[c] on F^2	1.155	1.080
Largest difference, peak and hole (e Å^{-3})	0.355 and -0.476	0.625 and -0.557
CCDC deposition no.		

[a] $R1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$.
[b] $wR2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma[w(F_o^2)^2]^{1/2}$ where w=1/[σ^2(Fo^2+(7.6974P)] for **1-Zn,** w=1/[σ^2(Fo^2+(0.0344P)^2+4.7907P] for **2-Zn** where P=(Max(Fo^2.0)+2*Fc^2)/3
[c] $S=[\Sigma w(F_o^2-F_c^2)^2/(n-p)]^{1/2}$ (*n* = number of reflections. *p* = number of parameters).

Table 2. Selected bond lengths (Å) and angles (°) for **1-Zn**

Zn-N1	2.039(3)	C5-C21	1.502(4)
Zn-N2	2.034(3)	C10-C28	1.504(5)
Zn-N3	2.039(3)	C15-C34	1.501(4)
Zn-N4	2.035(3)		

Table 3. Selected bond lengths (Å) and angles (°) for **2-Zn**

Zn1-O1	2.2113(34)	C5-C41	1.496(3)
Zn1-O1b	2.2303(100)	C10-C48	1.499(3)
Zn1-N1	2.0450(18)	C15-C54	1.497(3)
Zn1-N2	2.0610(19)	C26-C61	1.494(3)
Zn1-N3	2.0516(19)	C31-C68	1.503(3)
Zn1-N4	2.0745(18)	C36-C74	1.495(3)
Zn2-O2	2.1823(24)	C20-C21	1.507(3)
Zn2-N5	2.0631(18)		
Zn2-N6	2.048(2)	Zn1-Zn2	8.3037(4)
Zn2-N7	2.0621(18)		
Zn2-N8	2.0544(19)	C1-C20-C21-C22	72.76(26)

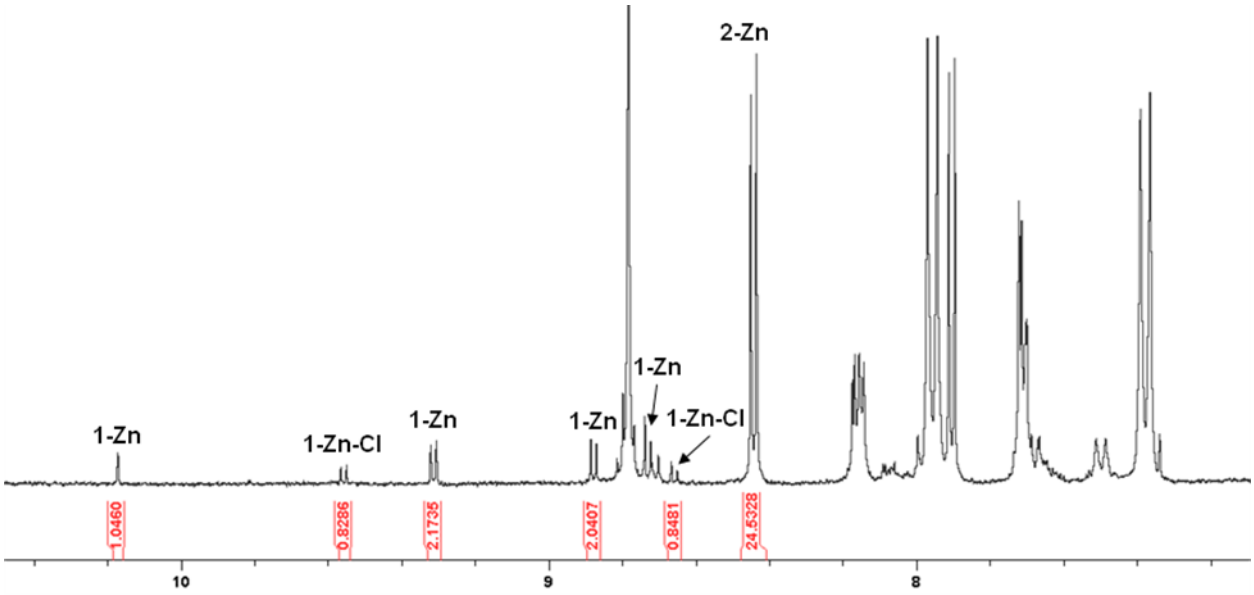

Fig. 29 ^{1}H NMR spectrum (300 MHz, CD_3COCD_3, 300 K) of a crude solution resulting from electrosynthesis performed using experimental conditions of entry 3, Table 2 of the manuscript. The product's distribution was calculated using integration of each product as exemplified below.

Total amount of products:
(2.1735/2H) = 1.08675 for **1-Zn** (signal at 9.30 ppm integrating for 2 H) + (0.8286/2H) = 0.4143 for **1-Zn-Cl** (signal at 9.55 ppm integrating for 2 H) + (24.5328/4H) = 6.1332 for **2-Zn** (signal at 8.44 ppm integrating for 4 H) thus the double for monomer units of **2-Zn** = 12.2664. Total amount of products =1.08675 + 0.4143 + 12.2664 = 13.7674.

Product's distribution:
For **1-Zn**: 1.08675/13.7674 = 7.9%; for **1-Zn-Cl**: 0.4143/13.7674 = 3.0%; for **2-Zn**: 12.2664/13.7674 = 89.1%.

Synthesis of **1-H_2**

After dissolution of **1-Zn** (15.0 mg, 23.8 µmol) in 80 mL of acetone, 20 mL of concentrated hydrochloric acid was added and this mixture was stirred for 1 min at room temperature. The organic layer was washed with 2× 200 ml of distilled water and neutralized with 100 ml of saturated sodium acetate solution. The organic phase was washed again with 3×250 ml of distilled water. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel (CH_2Cl_2), affording the porphyrin **1-H_2** (12.1 mg, 21.35 µmol, 89% yield).
λ_{max} (CH_2Cl_2)/nm (relative absorbance/ %) = 413 (100), 509 (4.24), 544 (1.39), 583 (1.21), 639 (0.56).

Synthesis of **1-Zn-Cl**

1-Zn (10.0 mg, 15.87 µmol) was dissolved in 5 mL of CH_2Cl_2 containing 2.2 eq. of *2,6*-lutidine (4 µL). *N*-chlorosuccinimide (10.0 mg, 4.98 eq.) was then added and the reaction mixture was stirred for 12 min. at room temperature. The solution was washed with 3×250 ml of distilled water. After evaporation of the solvent, the crude product was purified by column chromatography on alumina (CH_2Cl_2/*n*-heptane (7/3)) affording **1-Zn-Cl** (8.7 mg, 82% yield).
λ_{max} (CH_2Cl_2)/nm (relative absorbance/ %)= 423 (100), 555 (3.35), 598 (0.84).

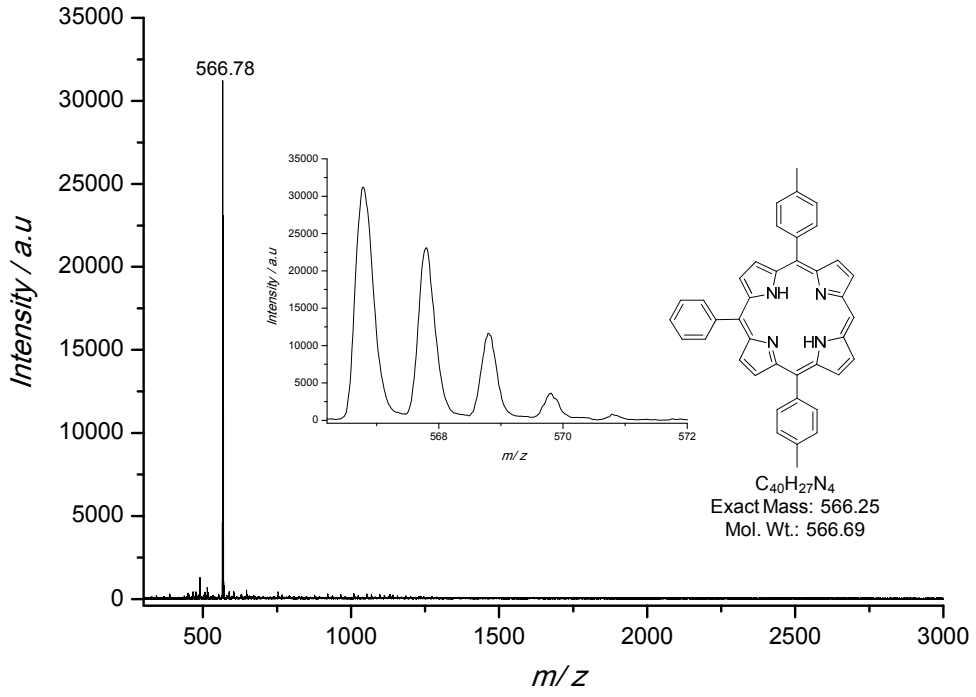

Fig. 30 MALDI-TOF mass spectrum of **1-H_2**.

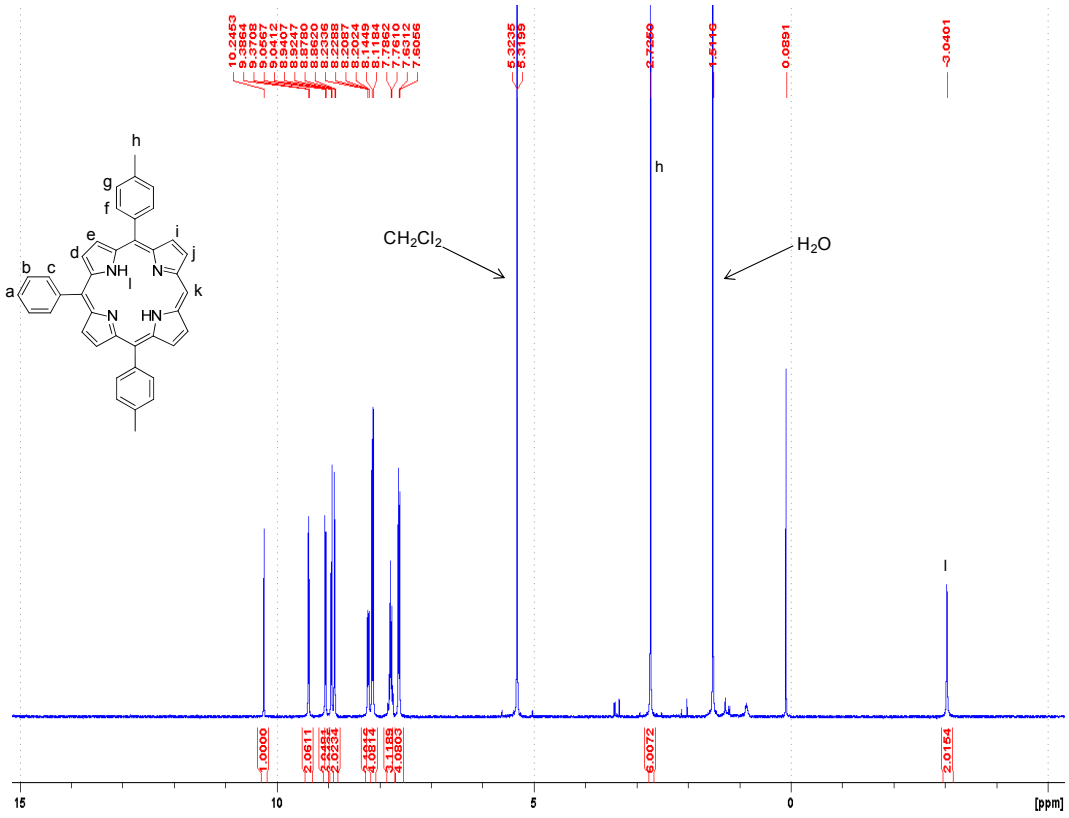

Fig. 31 ^{1}H NMR spectrum of **1-H$_2$** in CD_2Cl_2, 300 MHz, 300 K.

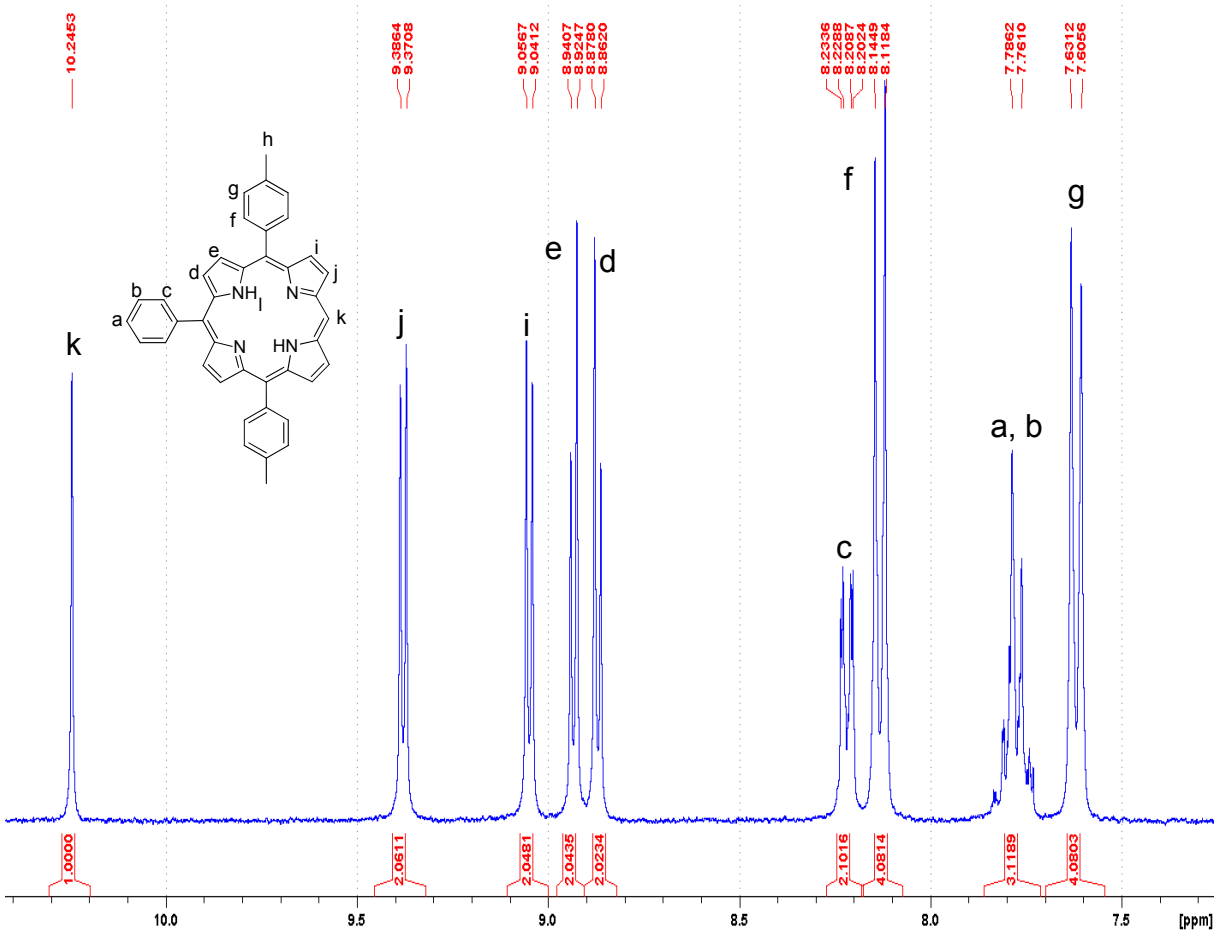

Fig. 32 Partial ^{1}H NMR spectrum of **1-H$_2$** in CD_2Cl_2, 300 MHz, 300 K. δ (ppm) -3.04 (s, NH, 2H), 2.73 (s, CH_3, 6H), 7.62 (d, ^{3}J = 7.7 Hz, *m*-tol, 2H), 7.73-7.84 (m, *p,m*-Ph, 3H), 8.13 (d, ^{3}J = 7.9 Hz, *o*-tol, 2H),, 8.20-8.23 (m, *o*-Ph, 2H), 8.87 (d, ^{3}J = 4.8 Hz, β-Pyrr, 2H), 8.93 (d, ^{3}J = 4.8 Hz, β-Pyrr, 2H), 9.05 (d, ^{3}J = 4.6 Hz, β-Pyrr, 2H), 9.38 (d, ^{3}J = 4.6 Hz, β-Pyrr, 2H), 10.25 (s, β-Pyrr, 1H).

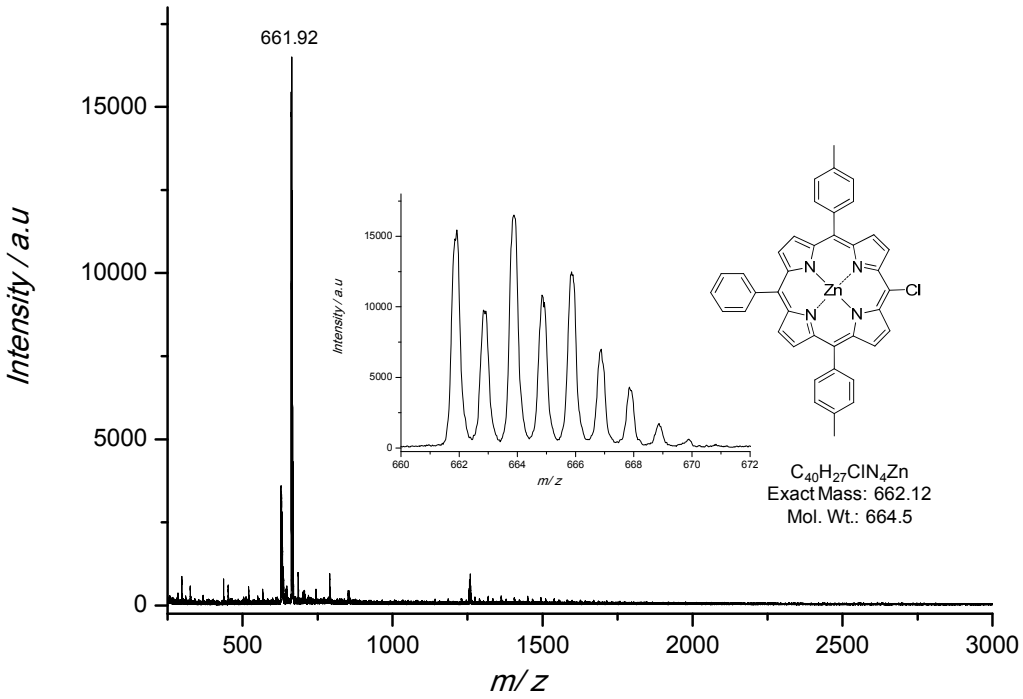

Fig. 33 MALDI-TOF mass spectrum of **1-Zn-Cl**.

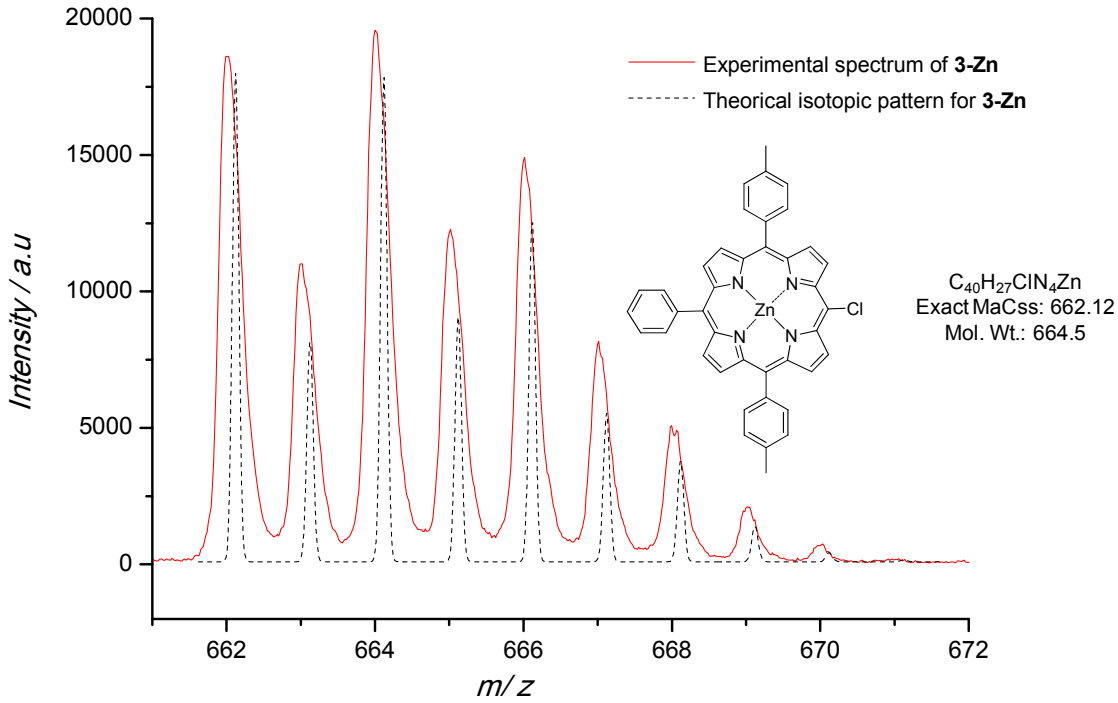

Fig. 34 Partial MALDI-TOF mass spectrum of **1-Zn-Cl** centered on its isotopic pattern (red/solid curve) and simulated isotopic pattern for a formula corresponding to **1-Zn-Cl** (black/dotted curve).

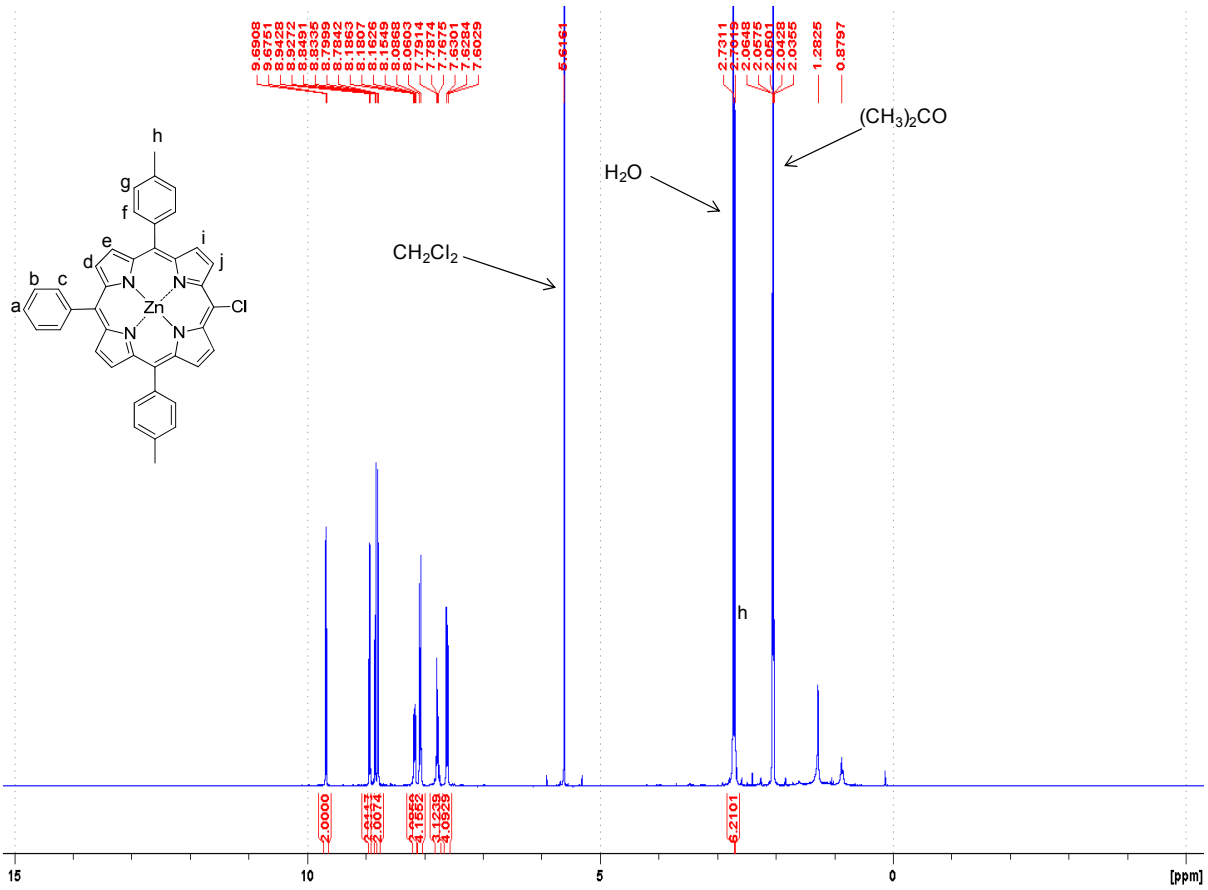

Fig. 35 ^{1}H NMR spectrum of **1-Zn-Cl** in $(CD_3)_2CO$, 300 MHz, 300 K.

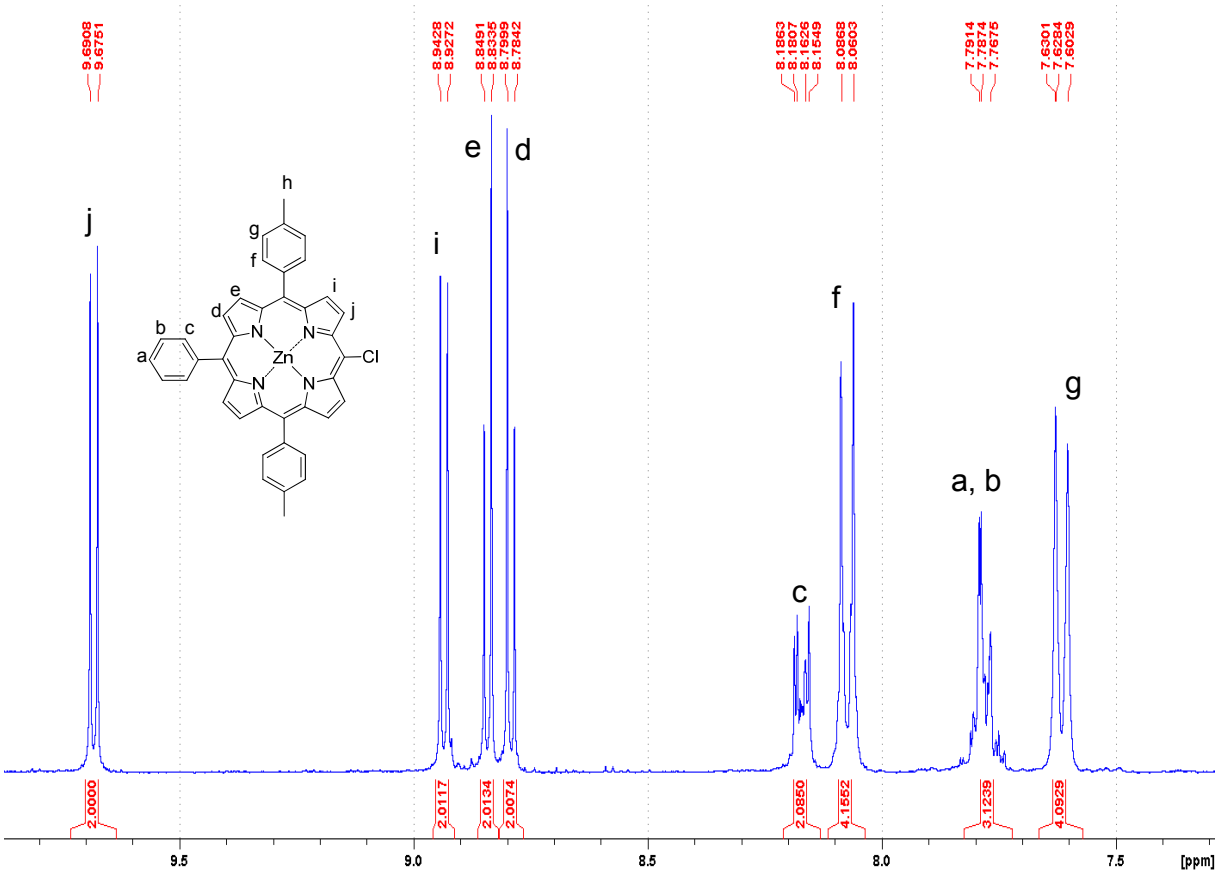

Fig. 36 Partial ^{1}H NMR spectrum of **1-Zn-Cl** (CD_3COCD_3, 300 MHz, 300 K). δ (ppm) 2.70 (s, CH_3, 6H), 7.62 (d, ^{3}J = 7.7 Hz, *m*-tol, 2H), 7.74-7.83 (m, *p,m*-Ph, 3H), 8.07 (d, ^{3}J = 7.9 Hz, *o*-tol, 2H),, 8.15-8.19 (m, *o*-Ph, 2H), 8.79 (d, ^{3}J = 4.7 Hz, β-Pyrr, 2H), 8.84 (d, ^{3}J = 4.7 Hz, β-Pyrr, 2H), 8.94 (d, ^{3}J = 4.7 Hz, β-Pyrr, 2H), 9.68 (d, ^{3}J = 4.7 Hz, β-Pyrr, 2H).