Supporting information

Synthesis of Ni(II) & Zn(II) Complexes of Pyrrolyl Dipyrrins and Their Biomimetic Role in Catalyzing Hydrolysis of Phospho-Ester Bond

Pinky Chauhan, Abani Sarkar and Mangalampalli Ravikanth*

Department of Chemistry, IIT Bombay, Powai, Mumbai. India

Email: ravikanth@chem.iitb.ac.in

Content

Sl. No.	*Descriptions*	*Page No.*
1.	**Materials, methods and schemes**	**S2-S3**
2.	**Fig. S1-S14** Characterization (HRMS, ^{1}H, ^{13}C, ^{31}P NMR, NOESY and COSY) data for compounds **1-Zn**, **4-Zn** and **4-Ni**.	**S4-S12**
3.	**Table S1-S7.** X-ray crystal data, bond lengths, and bond angles for complexes **1-Zn**, **4-Zn** and **4-Ni**.	**S13-S21**
4.	**Fig. S15-S16** Crystal structures of **1-Zn** and **4-Zn.**	**S21-S22**
5.	**Fig. S17-S18** Comparison of fluorescence and absorption spectra for the pH-dependent phosphatase-like activity of **4-Ni** in various buffer solutions.	**S22-S23**
6.	**Fig. S19-S23.** Time-dependent UV for hydrolysis of PNPP at different pH of **4-Ni,** for hydrolysis of PNPA, time dependent UV and cyclic volatammetry in DMF for compounds **1-Zn**, **4-Zn** and **4-Ni** and B3LYP/6-31G(d,p) calculated free energy changes along the phosphate hydrolysis pathway of **4-Ni (Fig. S23)**	**S23-S25**
7.	**Table S8-S11.** First-order kinetic parameters for phosphatase activity of **1-Zn**, **4-Zn**, and **4-Ni** in presence of PNPA substrate (**Table S8)** and Cartesian coordinates of the optimized (S_0) geometry of compounds **1-Zn**, **4-Zn** and **4-Ni**.	**S26-S31**
8.	**Table S12**. First-order rate constants for the hydrolysis of various phosphate esters by previously reported Ni((II) complexes.	**S32**
9.	References	**S32-S33**

MATERIALS AND METHODS

Materials: The chemicals were obtained from reliable vendors like Merck and TCI. These suppliers supplied $BF3.OEt_2$, $AlCl_3$, $ZnCl_2.2H2o$, $NiCl_2.6H_2O$ and so on. All other compounds used in the synthesis were of reagent grade quality unless specified differently. To ensure the purity and separation of chemicals throughout the purification process, column chromatography was carried out using silica gel (100-200 mesh) and basic alumina.

Methods:

- All the ^{1}H and ^{13}C NMR spectra were recorded in CDCl3 on Bruker 400 and 500 MHz instruments. The frequencies for the ^{13}C nucleus are 100.06 and 125.77 MHz for 400 and 500 MHz instruments, respectively.
- Absorption spectra were obtained with PerkinElmer Lambda-35
- Single crystals of compounds **1-Zn**, **4-Zn** and **4-Ni** were picked up with nylon loops and were mounted on Bruker Bruker APEX-II CCD diffractometer equipped with a Mo-target rotating-anode X-ray source and a graphite monochromator (Mo-Kα, λ = 0.71073 Å). The structures were solved by direct methods and subsequent difference Fourier techniques. Low angle, poor intensity diffraction and twin nature of single crystal resulted slightly higher R1 and wR2 value than normal range for all the compound. The structures were solved using the Olex2 Solve 1.5 program (Bourhis et al., 2015) with dual-space methods, employing Olex2 1.5-dev (Dolomanov et al., 2009) as the graphical interface. The model was refined using olex2.refine 1.5-dev (Bourhis et al., 2015) with full matrix least squares minimization on F^2. All the crystal parameter of [S2] compounds **1-Zn**, **4-Zn** and **4-Ni** are given in the main manuscript. All the relevant bond angle and bond distance parameters are given in Table S2-S12 in the supporting information file. [S1-S2]

- Studies on cyclic voltammetry (CV) were conducted using the BAS electrochemical system, employing a three-electrode configuration: platinum wire for the auxiliary electrode, silver electrode for the reference electrode, and glassy carbon for the working electrode at scan rates of 100 mV s−1. As a supporting electrolyte, tetrabutylammonium perchlorate was used in the dry dichloromethane studies. Mass spectra were recorded with a Q-TOF micro mass spectrometer.
- DFT was used in a Gaussian 09W programme package to perform quantum chemistry calculations (gas phase/vacuum) for ground state energy minimized structures for **1-Zn**, **4-Zn** and **4-Ni**. The optimization process for the ground state structure elucidation utilizes 6-311G basis sets and a DFT-based Beck-3 Lee Young Parr (B3LYP) functional.[S3]
- Distortion parameter τ_4 around the Ni(II) center in **4-Ni** parameter was calculated by following following Yang, Powell, and Houser.[S4]

  The two largest N–Ni–O and N-Ni-N bond angles for **4-Ni** are α = 173.67°, β = 173.51°

  Formula:

$$\tau_4 = \frac{360 - (\alpha + \beta)}{141}$$

$$\alpha + \beta = 173.67 + 173.51 = 347.18$$

$$360 - 347.18 = 12.82$$

$$\tau_4 = \frac{12.82}{141} = 0.091$$

τ_4 = 0.00 → ideal square planar

τ_4 = 0.091 → distorted square planar

Experimental section of PNPA hydrolysis:

Para-nitrophenyl acetate (PNPA) was used as a model substrate to investigate phosphatase-like activity. The hydrolysis of PNPA was monitored using time-dependent UV-Vis spectroscopy. During the reaction, the ester bond in PNPA was cleaved, resulting in the formation of 4-nitrophenolate ions. This process was monitored with the increase in the absorption band at λ_{max} ~ 420 nm in the presence of the catalyst **4-Ni** at room temperature. To evaluate hydrolysis activity, a PNPA solution (1×10^{-3} M) was prepared in a

97.5% (v/v) DMF-H_2O mixture, and a catalyst solution (5×10^{-5} M) was prepared in DMF. In a 3 mL cuvette, 30 µL of catalyst solution was added, and the remaining volume was filled with different concentrations of the substrate solution ($5 \times 10^{-4} - 20 \times 10^{-4}$ M), while the catalyst concentration remained constant at 5×10^{-6} M in every case. The substrate (PNPA) and catalyst (**4-Ni**) were mixed, and changes in UV-Vis absorption were recorded over one hour at 25°C. The reaction kinetics were studied using the steady-state kinetics method, monitoring the increase in absorption at λ_{max} ~ 420 nm as the concentration of 4-nitrophenolate increased. The reaction followed Michaelis–Menten kinetics, exhibiting saturation behavior. Using the Michaelis–Menten equation, the kinetic parameters (k_{cat}, V_{max}, and K_M) were determined for the hydrolysis of the ester bond in PNPA.

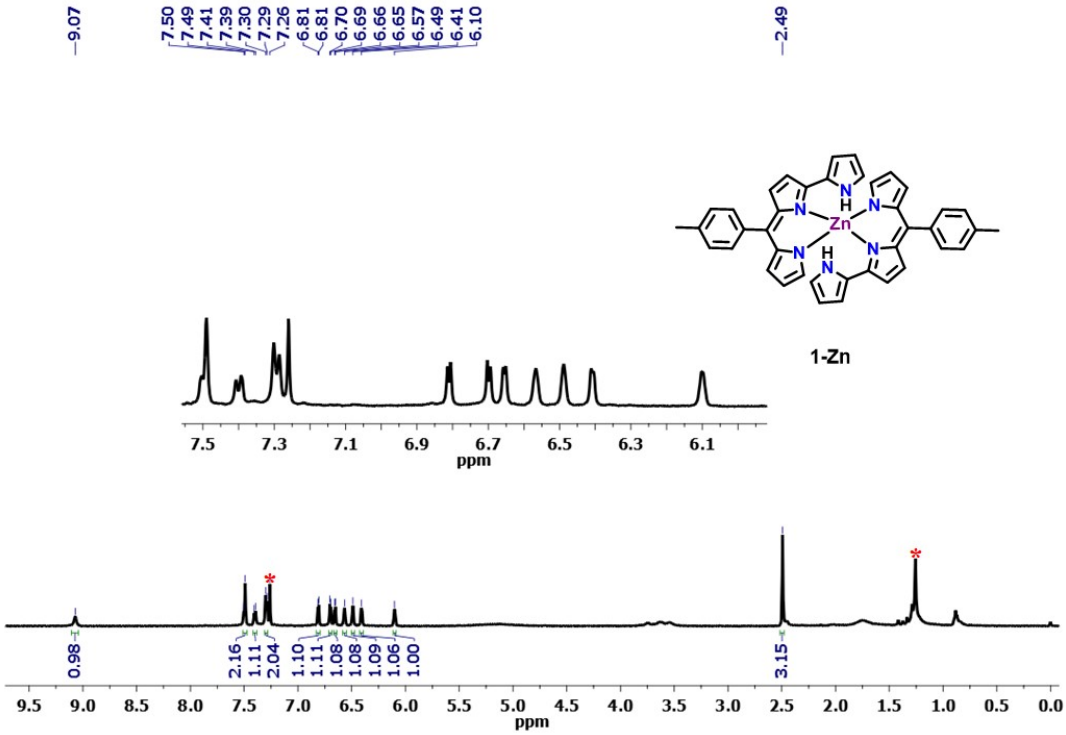

Fig. S1 ^{1}H NMR spectrum of the compound **1-Zn** recorded in $CDCl_3$ at 25 °C; Note: Peaks marked with asterisk (*) are due to residual solvents.

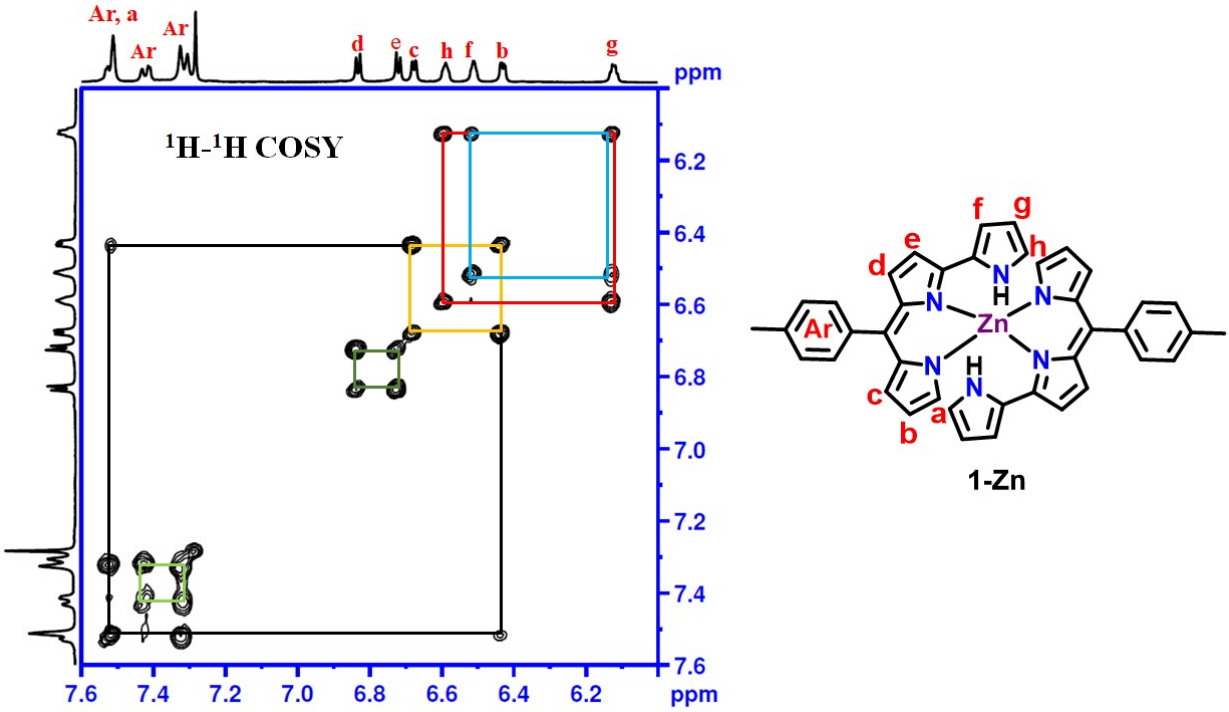

Fig. S2 Partial ^{1}H-^{1}H COSY spectrum of compound **1-Zn** in $CDCl_3$ at 25 ˚C.

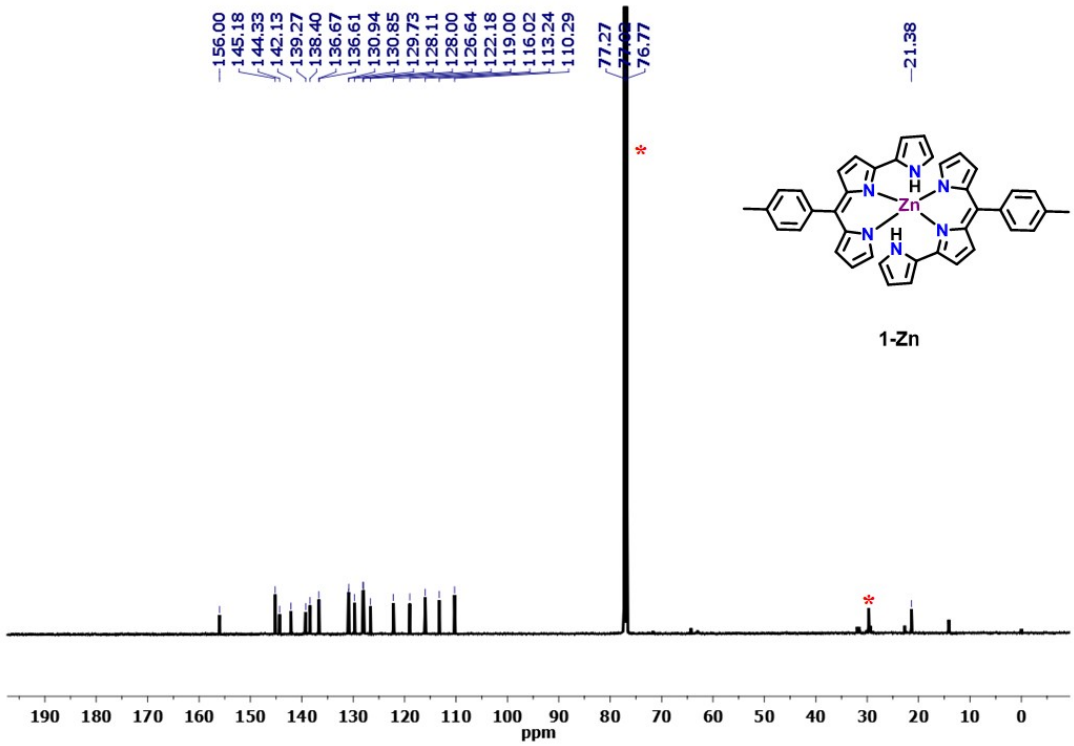

Fig. S3 ^{13}C NMR spectrum of the compound **1-Zn** recorded in $CDCl_3$. Note: Peaks marked with asterisk (*) are due to residual solvents.

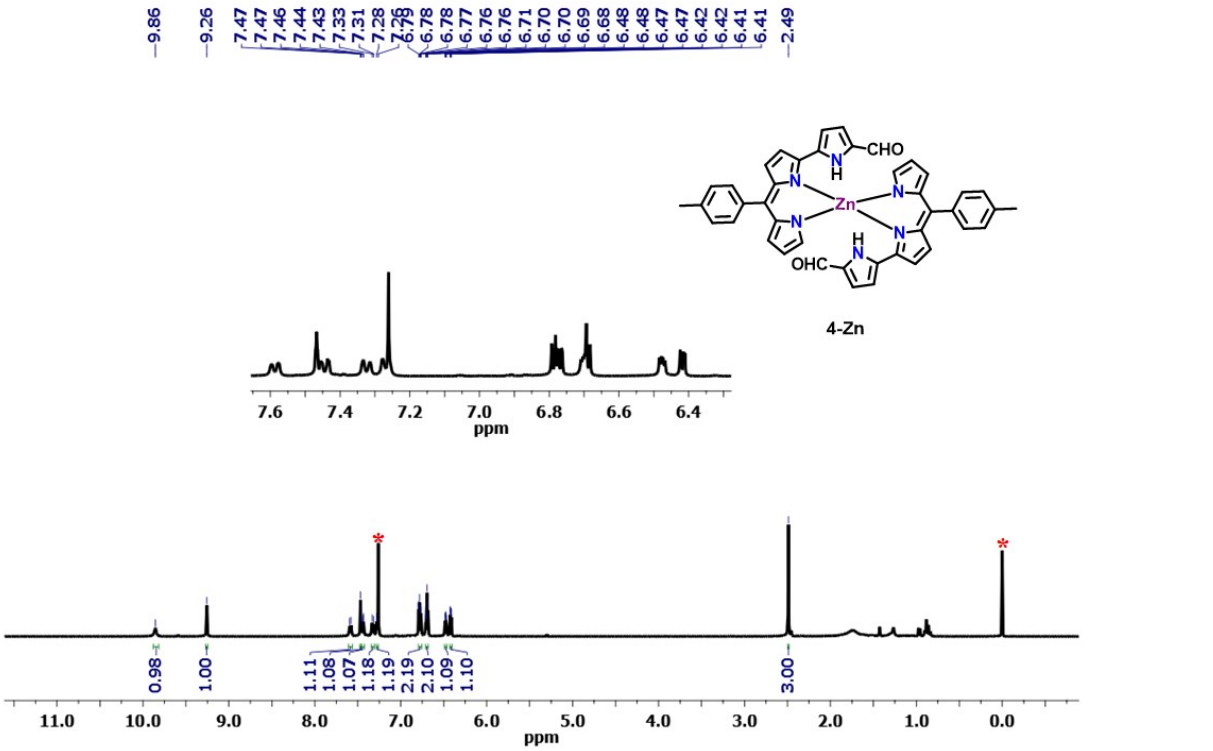

Fig. S4 ^{1}H NMR spectrum of the compound **4-Zn** recorded in $CDCl_3$ at 25 °C; Note: Peaks marked with asterisk (*) are due to residual solvents.

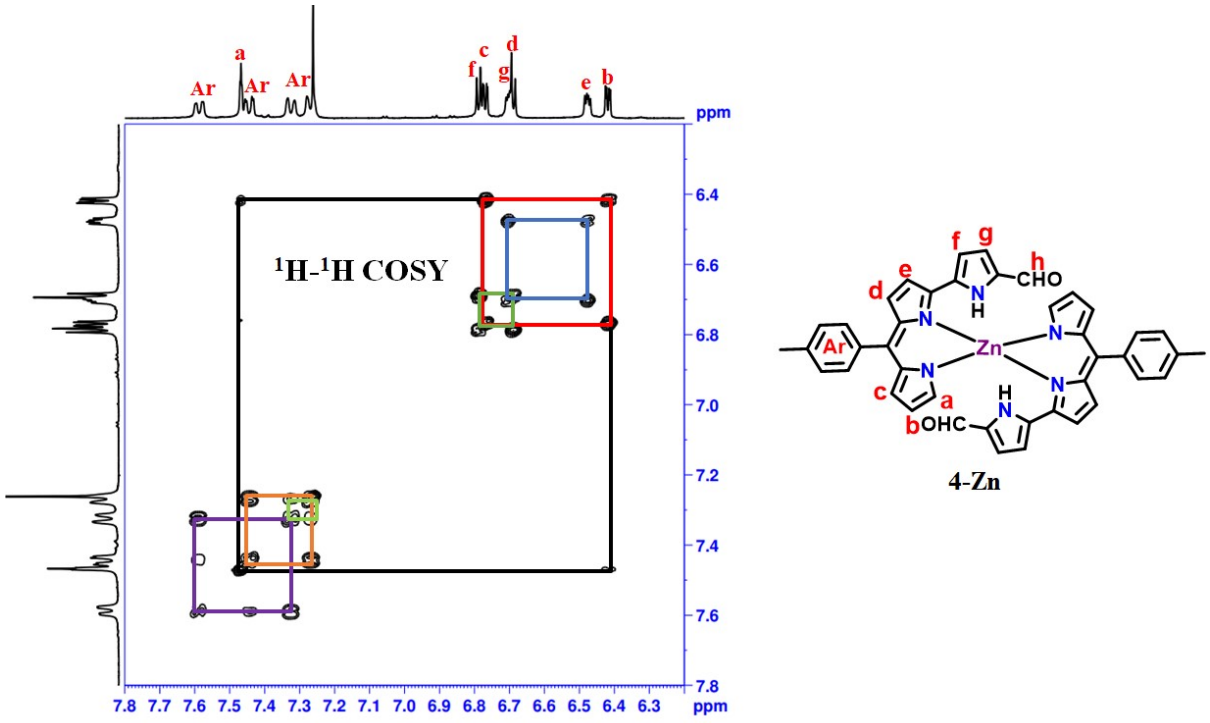

Fig. S5 Partial ^{1}H-^{1}H COSY spectrum of compound **4-Zn** in $CDCl_3$ at 25 ˚C.

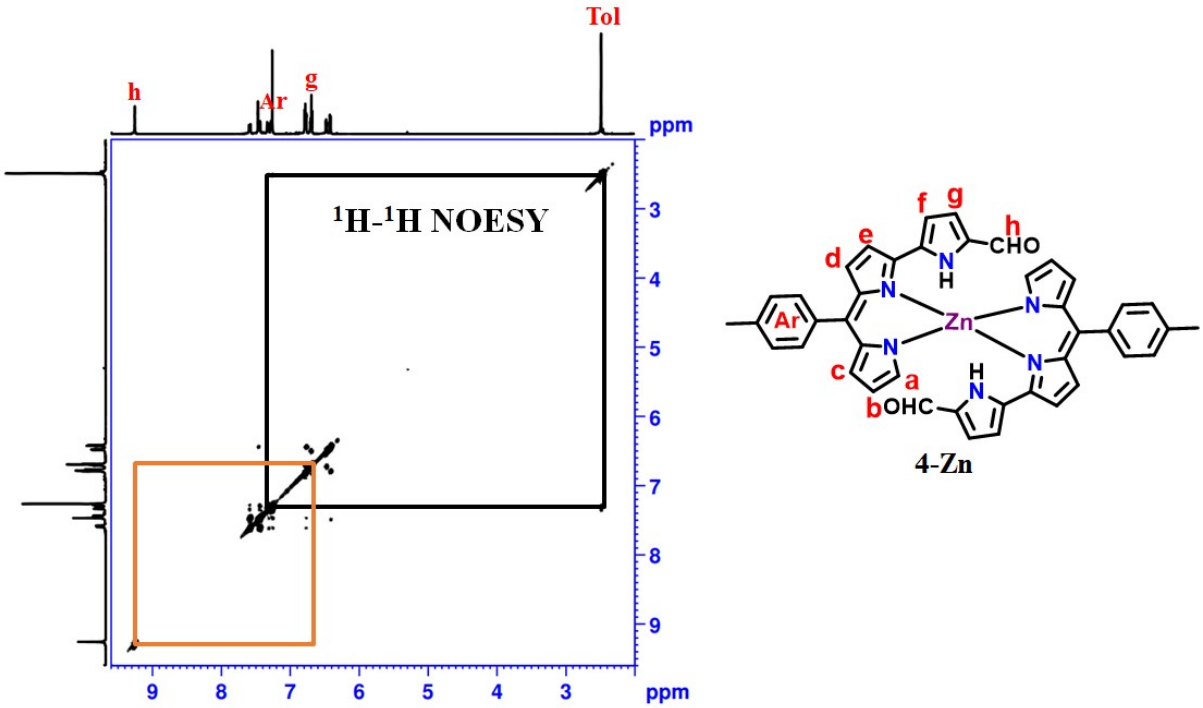

Fig. S6 ^{1}H-^{1}H NOESY spectrum of compound **4-Zn** in $CDCl_3$ at 25 ˚C.

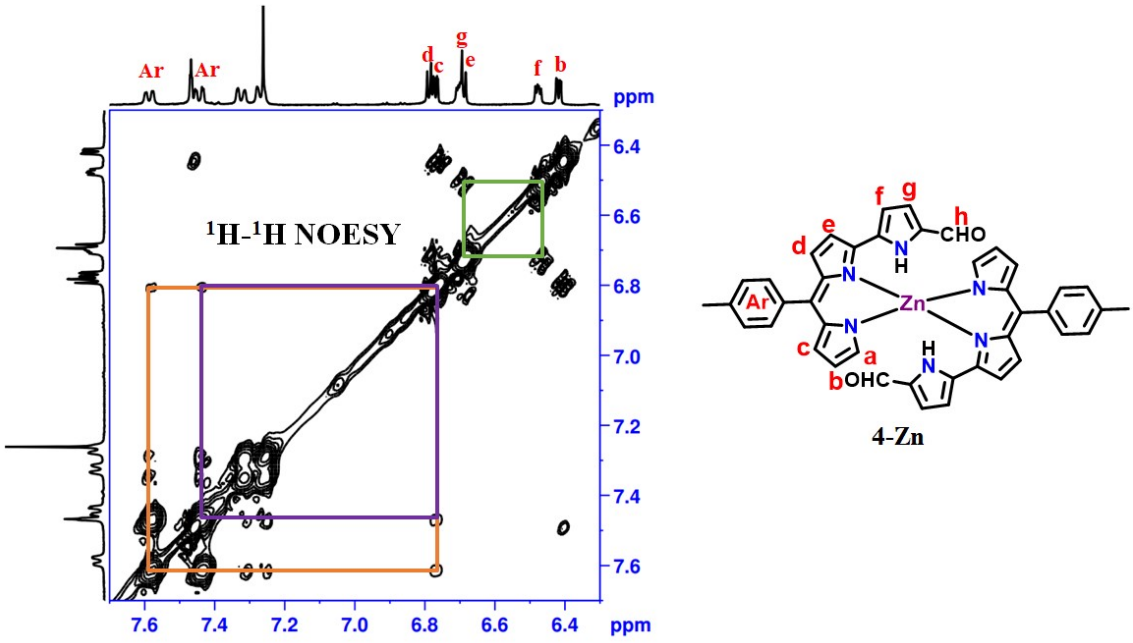

Fig. S7 Partial ^{1}H-^{1}H NOESY spectrum of compound **4-Zn** in $CDCl_3$ at 25 ˚C.

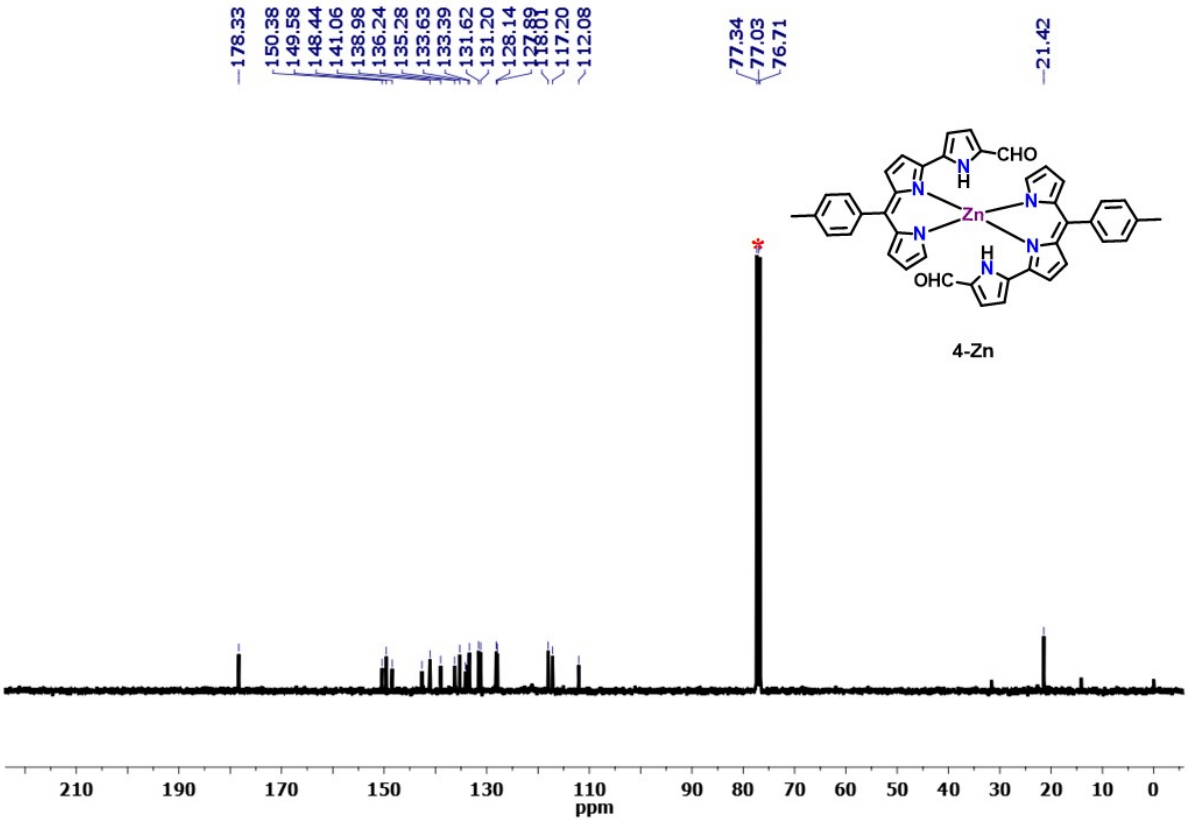

Fig. S8 ^{13}C NMR spectrum of the compound **4-Zn** recorded in $CDCl_3$. Note: Peaks marked with asterisk (*) are due to residual solvents.

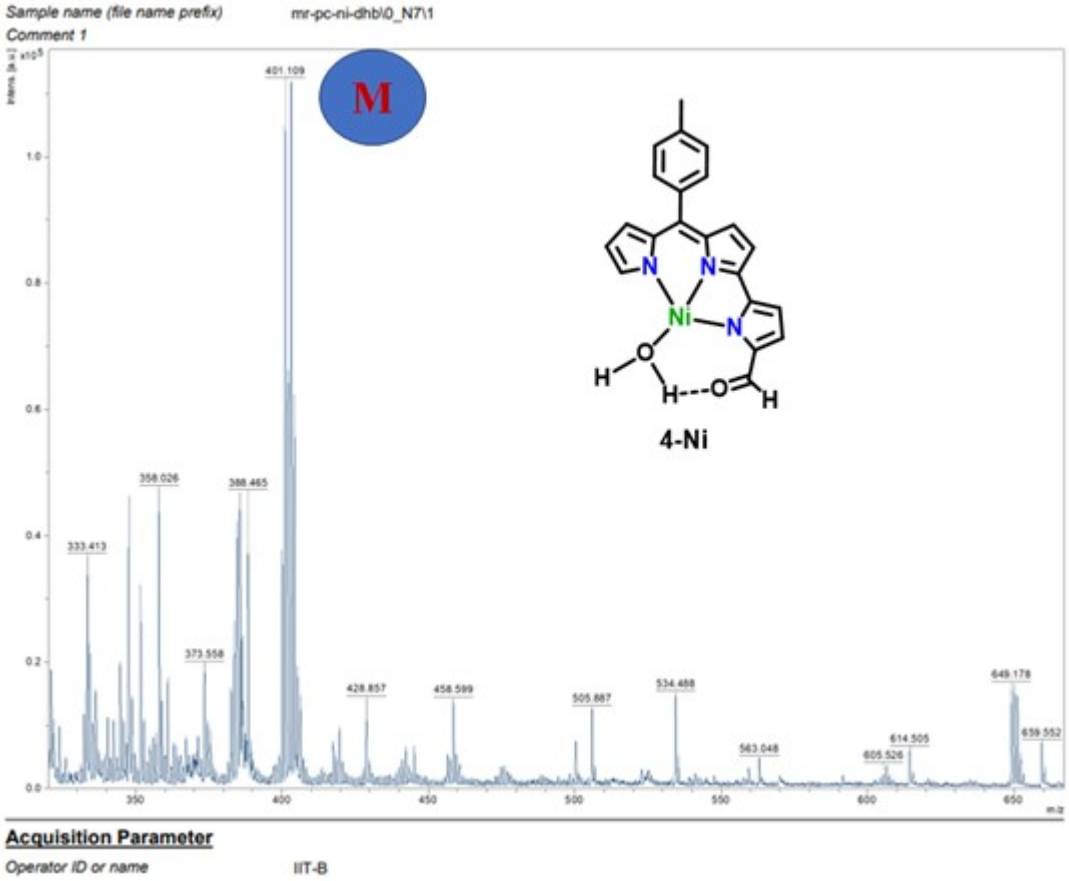

Fig. S9 MALDI-TOF of compound **4-Ni**.

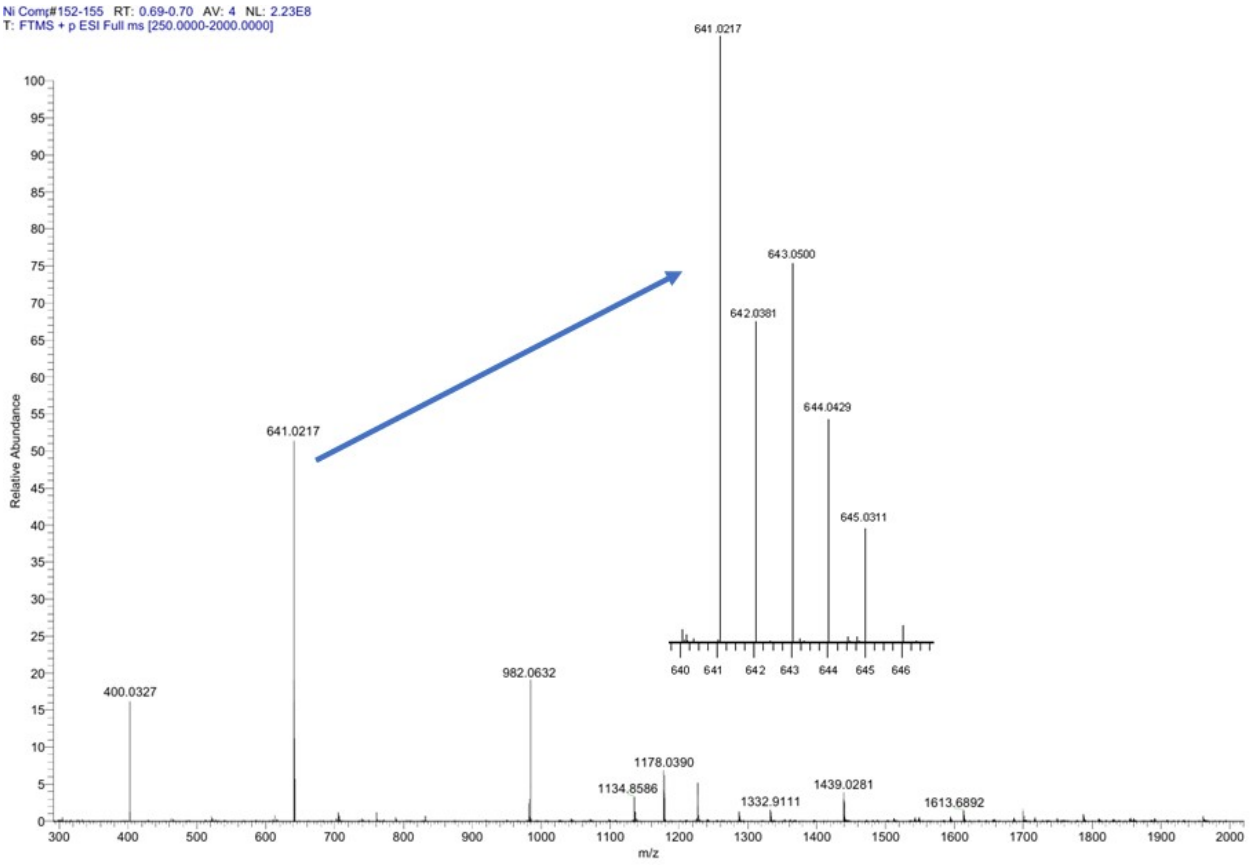

Fig. S10 HR mass spectrum of compound **4-Ni (I)** in presence of PNPP.

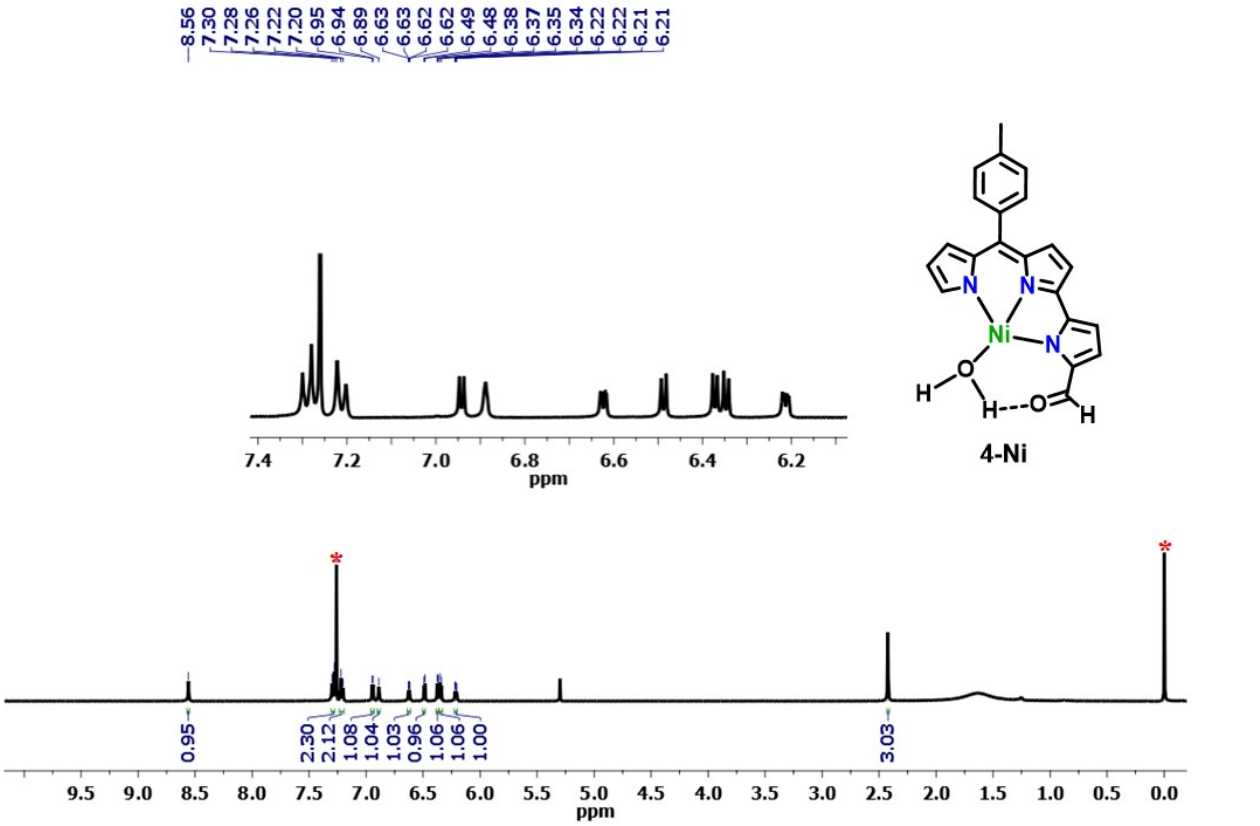

Fig. S11 ^{1}H NMR spectrum of the compound **4-Ni** recorded in $CDCl_3$ at 25 °C; Note: Peaks marked with asterisk (*) are due to residual solvents.

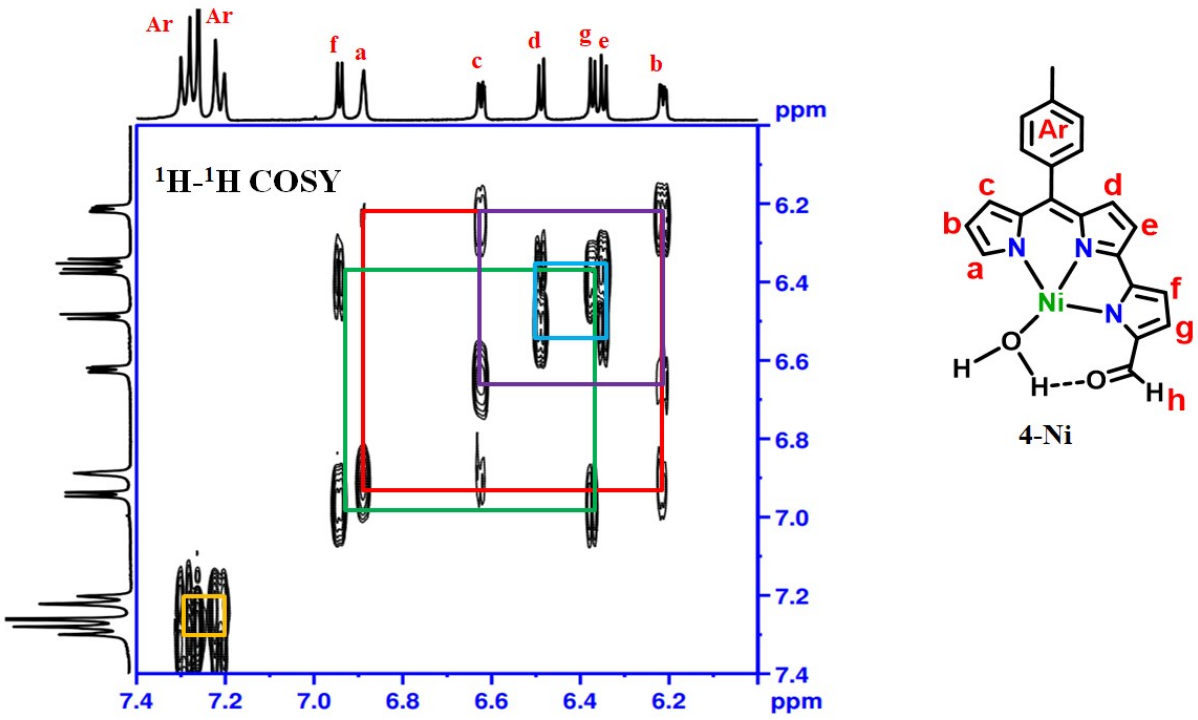

Fig. S12 Partial ^{1}H-^{1}H COSY spectrum of compound **4-Ni** in $CDCl_3$ at 25 °C.

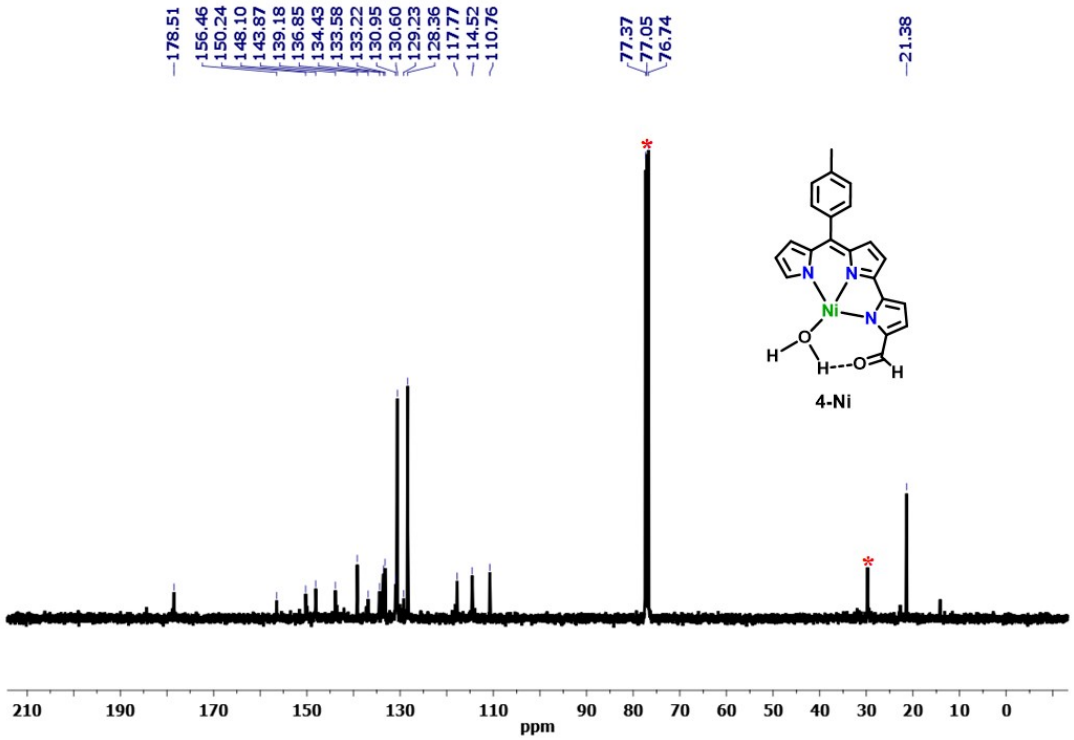

Fig. S13 ^{13}C NMR spectrum of the compound **4-Zn** recorded in $CDCl_3$. Note: Peaks marked with asterisk (*) are due to residual solvents.

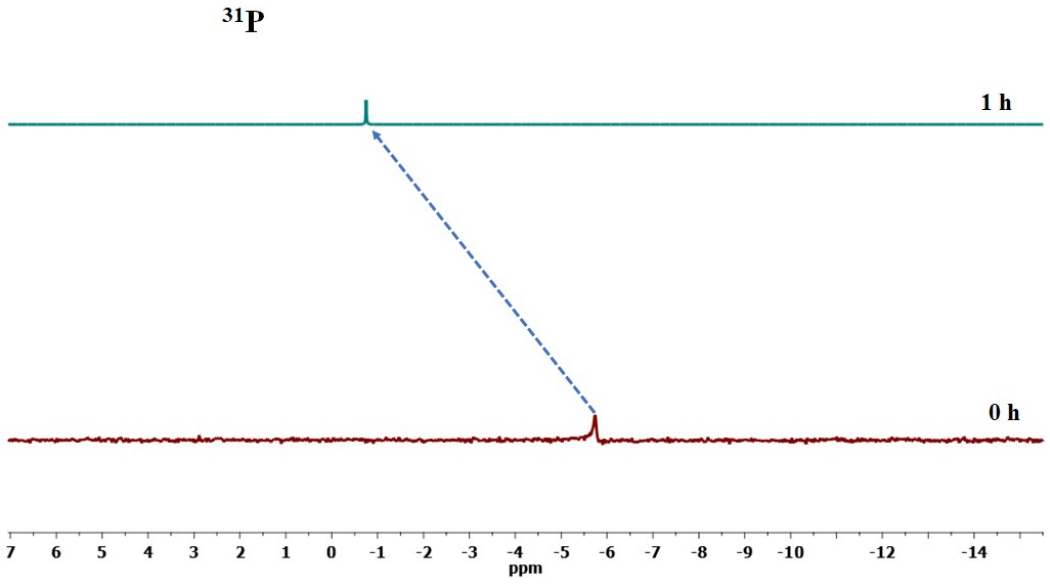

Fig. S14 ^{31}P NMR spectra showing the generation of H_3PO4 generated during hydrolysis of PNPP using **4-Ni** catalyst in DMSO-*d6*: D_2O (95.5 : 2.5) medium at 25 ºC.

Table S1. Crystal data and structure refinement for compounds **1-Zn**, **4-Zn** and **4-Ni**.

Parameters	**1-Zn**	**4-Zn**	**4-Ni**
CCDC No.	**2451682**	**2447018**	**2447021**
Empirical formula	**$C_{40}H_{32}N_6Zn$**	**$C_{43}H_{34}Cl_2O_2N_6$ Zn**	**$C_{21}H_{18}N_3NiO_2$**
Formula weight	**662.136**	**803.089**	**403.089**
Temperature/K	**150.15**	**150.15**	**150.00**
Crystal system	**Monoclinic**	**orthorhombic**	**triclinic**
Space group	**C2 /c**	**Fddd**	**P-1**
a/Å	**32.7458(4)**	**20.0126(5)**	**8.447(8)**
b/Å	**12.4657(2)**	**20.9012(4)**	**8.757(8)**
c/Å	**33.4685(5)**	**35.8631(5)**	**13.826(12)**
α/°	**90**	**90**	**74.579(19)**
β/°	**90.865(1)**	**90**	**74.53(2)**
γ/°	**90**	**90**	**65.03(2)**
Volume/Å3	**13660.3(3)**	**15001.1(5)**	**879.7(14)**
Z	**8**	**16**	**2**
ρcalc [g/cm³]	**1.288**	**1.422**	**1.522**
μ/mm⁻¹	**0.757**	**0.844**	**1.124**
F(000)	**5512.4**	**6637.7**	**419.0**
Crystal size/mm³	**0.3 × 0.2 × 0.1**	**0.3 × 0.2 × 0.1**	**0.3 × 0.2 × 0.1**
Radiation	**Mo Kα (λ = 0.71073)**	**MoKα (λ = 0.71073)**	**MoKα (λ = 0.71073)**
2Θ range for data collection/°	**3.7 to 50**	**3.04 to 50**	**5.22 to 50**
Reflections collected	**133845**	**34275**	**27887**
Independent reflections	**12014 [R_{int} = 0.0685, R_{sigma} = 0.0483]**	**3300 [Rint=0.0629, Rsigma= 0.0367]**	**3074 [R_{int} = 0.2295, R_{sigma} = 0.1387]**
Data/restraints/parameters	**12014/0/851**	**3300/0/250**	**3074/0/247**
Goodness-of-fit on F²	**1.049**	**1.044**	**1.031**
Final R indexes [I>=2σ (I)]	**R_1 = 0.0397, wR_2 = 0.1091**	**R1 = 0.0347, wR2 = 0.0929**	**R_1 = 0.0759, wR_2 = 0.1809**
Final R indexes [all data]	**R_1 = 0.0449, wR_2 = 0.1134**	**R1 = 0.0370, wR2 = 0.0956**	**R_1 = 0.1286, wR_2 = 0.2227**
Largest diff. peak/hole / e Å⁻³	**0.45/-0.39**	**0.41/-0.46**	**0.89/-0.84**

Table S2. Bond Lengths for compound **1-Zn**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn1	N1	1.9564(19)	Zn2	N7	1.963(2)
Zn1	N2	2.0248(19)	Zn2	N8	2.0216(18)
Zn1	N4	1.958(2)	Zn2	N10	1.963(2)
Zn1	N5	2.0200(18)	Zn2	N11	2.0265(19)
N1	C9	1.395(3)	N7	C49	1.389(3)
N1	C12	1.340(3)	N7	C52	1.343(3)
N2	C13	1.413(3)	N8	C53	1.411(3)
N2	C16	1.357(3)	N8	C56	1.356(3)
N3	C17	1.363(3)	N9	C57	1.378(3)
N3	C20	1.356(3)	N9	C60	1.356(3)
N4	C29	1.394(3)	N10	C69	1.394(3)
N4	C32	1.341(3)	N10	C72	1.342(3)
N5	C33	1.411(3)	N11	C73	1.408(3)
N5	C36	1.352(3)	N11	C76	1.358(3)
N6	C37	1.379(3)	N12	C77	1.369(3)
N6	C40	1.361(3)	N12	C80	1.362(3)
C1	C2	1.512(4)	C41	C42	1.506(4)
C2	C3	1.389(4)	C42	C43	1.372(4)
C2	C6	1.391(4)	C42	C47	1.385(4)
C3	C4	1.385(4)	C43	C44	1.393(4)
C4	C5	1.390(3)	C44	C45	1.374(4)
C5	C7	1.391(4)	C45	C46	1.381(4)
C5	C8	1.499(3)	C45	C48	1.502(3)
C6	C7	1.386(4)	C46	C47	1.389(4)
C8	C9	1.416(3)	C48	C49	1.420(3)
C8	C13	1.401(3)	C48	C53	1.389(3)
C9	C10	1.422(3)	C49	C50	1.408(3)
C10	C11	1.383(4)	C50	C51	1.375(4)
C11	C12	1.398(4)	C51	C52	1.394(4)
C13	C14	1.422(3)	C53	C54	1.431(3)
C14	C15	1.360(4)	C54	C55	1.357(4)
C15	C16	1.421(3)	C55	C56	1.427(3)
C16	C17	1.447(3)	C56	C57	1.439(3)
C17	C18	1.373(4)	C57	C58	1.382(4)
C18	C19	1.402(4)	C58	C59	1.408(4)
C19	C20	1.350(4)	C59	C60	1.362(4)
C21	C22	1.510(4)	C61	C62	1.514(4)
C22	C23	1.381(4)	C62	C63	1.396(6)
C22	C27	1.387(4)	C62	C67	1.354(6)
C23	C24	1.393(4)	C63	C64	1.400(4)

C24	C25	1.386(4)	C64	C65	1.383(4)
C25	C26	1.383(4)	C65	C66	1.376(4)
C25	C28	1.501(3)	C65	C68	1.496(3)
C26	C27	1.382(4)	C66	C67	1.387(5)
C28	C29	1.413(3)	C68	C69	1.411(3)
C28	C33	1.399(3)	C68	C73	1.398(3)
C29	C30	1.420(3)	C69	C70	1.422(3)
C30	C31	1.380(4)	C70	C71	1.369(4)
C31	C32	1.397(4)	C71	C72	1.396(4)
C33	C34	1.430(3)	C73	C74	1.422(3)
C34	C35	1.360(4)	C74	C75	1.362(4)
C35	C36	1.427(3)	C75	C76	1.422(3)
C36	C37	1.439(3)	C76	C77	1.438(3)
C37	C38	1.390(4)	C77	C78	1.379(3)
C38	C39	1.404(4)	C78	C79	1.400(4)
C39	C40	1.362(4)	C79	C80	1.354(4)

Table S3. Bond angles for compound **1-Zn**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N2	Zn1	N1	95.56(8)	N8	Zn2	N7	95.96(8)
N4	Zn1	N1	116.68(8)	N10	Zn2	N7	120.43(8)
N4	Zn1	N2	119.68(8)	N10	Zn2	N8	116.66(8)
N5	Zn1	N1	117.76(8)	N11	Zn2	N7	116.70(8)
N5	Zn1	N2	112.56(7)	N11	Zn2	N8	112.17(7)
N5	Zn1	N4	96.16(8)	N11	Zn2	N10	96.13(8)
C9	N1	Zn1	124.99(15)	C49	N7	Zn2	124.29(16)
C12	N1	Zn1	127.48(17)	C52	N7	Zn2	128.73(18)
C12	N1	C9	106.9(2)	C52	N7	C49	106.7(2)
C13	N2	Zn1	121.54(15)	C53	N8	Zn2	121.24(15)
C16	N2	Zn1	131.44(16)	C56	N8	Zn2	131.60(16)
C16	N2	C13	106.31(19)	C56	N8	C53	106.45(19)
C20	N3	C17	110.1(2)	C60	N9	C57	110.0(2)
C29	N4	Zn1	124.75(16)	C69	N10	Zn2	124.25(15)
C32	N4	Zn1	128.90(17)	C72	N10	Zn2	129.07(17)
C32	N4	C29	106.3(2)	C72	N10	C69	106.3(2)
C33	N5	Zn1	121.11(15)	C73	N11	Zn2	120.76(15)

C36	N5	Zn1	132.35(16)	C76	N11	Zn2	132.52(16)
C36	N5	C33	106.43(19)	C76	N11	C73	106.32(19)
C40	N6	C37	109.9(2)	C80	N12	C77	109.7(2)
C3	C2	C1	121.5(3)	C43	C42	C41	121.7(3)
C6	C2	C1	120.8(3)	C47	C42	C41	120.8(3)
C6	C2	C3	117.6(2)	C47	C42	C43	117.5(2)
C4	C3	C2	121.2(3)	C44	C43	C42	121.6(3)
C5	C4	C3	121.2(3)	C45	C44	C43	120.8(3)
C7	C5	C4	117.6(2)	C46	C45	C44	118.0(2)
C8	C5	C4	121.4(2)	C48	C45	C44	121.5(2)
C8	C5	C7	121.1(2)	C48	C45	C46	120.5(2)
C7	C6	C2	121.1(2)	C47	C46	C45	121.0(3)
C6	C7	C5	121.2(2)	C46	C47	C42	121.0(3)
C9	C8	C5	115.9(2)	C49	C48	C45	115.8(2)
C13	C8	C5	116.8(2)	C53	C48	C45	116.8(2)
C13	C8	C9	127.3(2)	C53	C48	C49	127.5(2)
C8	C9	N1	124.2(2)	C48	C49	N7	124.5(2)
C10	C9	N1	108.0(2)	C50	C49	N7	108.3(2)
C10	C9	C8	127.8(2)	C50	C49	C48	127.2(2)
C11	C10	C9	107.2(2)	C51	C50	C49	107.5(2)
C12	C11	C10	106.3(2)	C52	C51	C50	106.4(2)
C11	C12	N1	111.5(2)	C51	C52	N7	111.1(2)
C8	C13	N2	125.5(2)	C48	C53	N8	125.8(2)
C14	C13	N2	107.9(2)	C54	C53	N8	108.1(2)
C14	C13	C8	126.5(2)	C54	C53	C48	126.2(2)
C15	C14	C13	108.3(2)	C55	C54	C53	107.9(2)
C16	C15	C14	106.8(2)	C56	C55	C54	107.1(2)
C15	C16	N2	110.6(2)	C55	C56	N8	110.5(2)
C17	C16	N2	124.5(2)	C57	C56	N8	124.9(2)
C17	C16	C15	124.8(2)	C57	C56	C55	124.5(2)
C16	C17	N3	124.9(2)	C56	C57	N9	124.6(2)

C18	C17	N3	106.3(2)	C58	C57	N9	106.6(2)
C18	C17	C16	128.7(2)	C58	C57	C56	128.6(2)
C19	C18	C17	108.1(3)	C59	C58	C57	107.5(2)
C20	C19	C18	107.3(2)	C60	C59	C58	107.7(2)
C19	C20	N3	108.2(2)	C59	C60	N9	108.1(2)
C23	C22	C21	122.2(3)	C63	C62	C61	120.9(4)
C27	C22	C21	120.4(3)	C67	C62	C61	121.2(4)
C27	C22	C23	117.4(2)	C67	C62	C63	117.9(3)
C24	C23	C22	121.8(3)	C64	C63	C62	120.8(3)
C25	C24	C23	120.0(3)	C65	C64	C63	120.3(3)
C26	C25	C24	118.5(2)	C66	C65	C64	118.0(3)
C28	C25	C24	121.3(2)	C68	C65	C64	121.0(3)
C28	C25	C26	120.2(2)	C68	C65	C66	121.0(3)
C27	C26	C25	120.9(3)	C67	C66	C65	121.4(3)
C26	C27	C22	121.3(3)	C66	C67	C62	121.6(4)
C29	C28	C25	115.9(2)	C69	C68	C65	116.0(2)
C33	C28	C25	116.4(2)	C73	C68	C65	116.2(2)
C33	C28	C29	127.6(2)	C73	C68	C69	127.8(2)
C28	C29	N4	124.2(2)	C68	C69	N10	124.2(2)
C30	C29	N4	108.6(2)	C70	C69	N10	108.3(2)
C30	C29	C28	127.1(2)	C70	C69	C68	127.4(2)
C31	C30	C29	107.0(2)	C71	C70	C69	107.1(2)
C32	C31	C30	106.4(2)	C72	C71	C70	106.7(2)
C31	C32	N4	111.8(2)	C71	C72	N10	111.5(2)
C28	C33	N5	126.0(2)	C68	C73	N11	125.8(2)
C34	C33	N5	108.2(2)	C74	C73	N11	108.4(2)
C34	C33	C28	125.8(2)	C74	C73	C68	125.7(2)
C35	C34	C33	107.7(2)	C75	C74	C73	107.8(2)
C36	C35	C34	107.0(2)	C76	C75	C74	107.1(2)
C35	C36	N5	110.6(2)	C75	C76	N11	110.4(2)
C37	C36	N5	125.5(2)	C77	C76	N11	126.0(2)
C37	C36	C35	123.8(2)	C77	C76	C75	123.5(2)
C36	C37	N6	124.2(2)	C76	C77	N12	125.4(2)
C38	C37	N6	106.5(2)	C78	C77	N12	106.5(2)
C38	C37	C36	129.2(2)	C78	C77	C76	128.0(2)
C39	C38	C37	107.5(2)	C79	C78	C77	108.1(2)
C40	C39	C38	108.0(2)	C80	C79	C78	107.4(2)
C39	C40	N6	108.1(2)	C79	C80	N12	108.4(2)

Table S4. Bond Lengths for compound **4-Zn**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn1	N1	1.9803(16)	C5	C8	1.505(3)
Zn1	N1[1]	1.9803(16)	C6	C7	1.393(3)
Zn1	N2[1]	1.9848(15)	C8	C9	1.402(3)
Zn1	N2	1.9848(15)	C8	C13	1.415(3)
O1	C21	1.221(3)	C9	C10	1.429(3)
N1	C9	1.401(2)	C10	C11	1.372(3)
N1	C12	1.333(3)	C11	C12	1.415(3)
N2	C13	1.403(2)	C13	C14	1.421(3)
N2	C16	1.351(2)	C14	C15	1.376(3)
N3	C17	1.363(2)	C15	C16	1.418(3)
N3	C20	1.385(2)	C16	C17	1.458(3)
C1	C2	1.514(3)	C17	C18	1.399(3)
C2	C3	1.390(3)	C18	C19	1.400(3)
C2	C7	1.389(3)	C19	C20	1.390(3)
C3	C4	1.393(3)	C20	C21	1.434(3)
C4	C5	1.396(3)	Cl1	C22	1.751(2)
C5	C6	1.396(3)			

Table S5. Bond angles for compound **4-Zn**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1[1]	Zn1	N1	105.72(10)	C13	C8	C9	127.07(18)
N2	Zn1	N1	95.11(7)	C8	C9	N1	124.09(17)
N2	Zn1	N1[1]	124.45(7)	C10	C9	N1	108.08(17)
N2[1]	Zn1	N1	124.45(7)	C10	C9	C8	127.77(18)
N2[1]	Zn1	N1[1]	95.11(7)	C11	C10	C9	107.55(18)
N2[1]	Zn1	N2	114.33(9)	C12	C11	C10	105.96(19)
C9	N1	Zn1[1]	124.41(13)	C11	C12	N1	111.86(18)
C12	N1	Zn1[1]	128.54(14)	C8	C13	N2	124.91(17)
C12	N1	C9	106.55(16)	C14	C13	N2	108.33(16)

C13	N2	Zn1	123.36(13)	C14	C13	C8	126.66(17)
C16	N2	Zn1	128.50(13)	C15	C14	C13	107.91(17)
C16	N2	C13	106.44(15)	C16	C15	C14	106.09(17)
C20	N3	C17	109.35(17)	C15	C16	N2	111.20(17)
C3	C2	C1	121.2(2)	C17	C16	N2	120.68(17)
C7	C2	C1	121.0(2)	C17	C16	C15	128.08(18)
C7	C2	C3	117.87(19)	C16	C17	N3	121.95(17)
C4	C3	C2	121.3(2)	C18	C17	N3	108.04(16)
C5	C4	C3	120.5(2)	C18	C17	C16	129.86(18)
C6	C5	C4	118.37(18)	C19	C18	C17	107.28(18)
C8	C5	C4	119.96(18)	C20	C19	C18	107.87(18)
C8	C5	C6	121.54(18)	C19	C20	N3	107.45(18)
C7	C6	C5	120.4(2)	C21	C20	N3	123.36(19)
C6	C7	C2	121.5(2)	C21	C20	C19	129.11(19)
C9	C8	C5	115.45(17)	C20	C21	O1	126.39(19)
C13	C8	C5	117.46(17)	Cl1[2]	C22	Cl1	112.90(19)

Table S6. Bond Lengths for compound **4-Ni**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ni1	O2	1.876(5)	C5	C6	1.399(9)
Ni1	N1	1.892(5)	C5	C8	1.490(8)
Ni1	N2	1.840(5)	C6	C7	1.391(9)
Ni1	N3	1.949(5)	C8	C9	1.401(9)
O1	C21	1.256(10)	C8	C13	1.378(9)
N1	C9	1.418(8)	C9	C10	1.424(9)
N1	C12	1.346(9)	C10	C11	1.366(9)
N2	C13	1.395(8)	C11	C12	1.408(9)
N2	C16	1.336(8)	C13	C14	1.423(9)
N3	C17	1.366(9)	C14	C15	1.396(9)
N3	C20	1.409(8)	C15	C16	1.414(9)

C1	C2	1.522(9)	C16	C17	1.435(9)
C2	C3	1.379(9)	C17	C18	1.410(9)
C2	C7	1.371(9)	C18	C19	1.374(10)
C3	C4	1.378(8)	C19	C20	1.392(10)
C4	C5	1.394(8)	C20	C21	1.412(10)

Table S7. Bond angles for compound **4-Ni**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N1	Ni1	O2	92.4(2)	C13	C8	C5	117.9(6)
N2	Ni1	O2	173.52(19)	C13	C8	C9	122.2(6)
N2	Ni1	N1	90.6(2)	C8	C9	N1	125.1(6)
N3	Ni1	O2	93.9(2)	C10	C9	N1	107.6(6)
N3	Ni1	N1	173.7(2)	C10	C9	C8	127.2(6)
N3	Ni1	N2	83.2(2)	C11	C10	C9	108.3(6)
C9	N1	Ni1	126.8(5)	C12	C11	C10	106.2(6)
C12	N1	Ni1	127.2(5)	C11	C12	N1	111.9(7)
C12	N1	C9	106.0(5)	C8	C13	N2	121.5(6)
C13	N2	Ni1	133.3(5)	C14	C13	N2	106.4(6)
C16	N2	Ni1	118.1(4)	C14	C13	C8	131.9(6)
C16	N2	C13	108.5(6)	C15	C14	C13	109.1(6)
C17	N3	Ni1	111.4(4)	C16	C15	C14	104.6(6)
C20	N3	Ni1	142.3(5)	C15	C16	N2	111.4(6)
C20	N3	C17	105.5(6)	C17	C16	N2	112.1(6)

C3	C2	C1	120.3(6)	C17	C16	C15	136.2(7)
C7	C2	C1	122.1(6)	C16	C17	N3	115.1(6)
C7	C2	C3	117.6(6)	C18	C17	N3	110.9(6)
C4	C3	C2	122.1(6)	C18	C17	C16	133.8(7)
C5	C4	C3	120.8(6)	C19	C18	C17	106.2(7)
C6	C5	C4	117.2(6)	C20	C19	C18	108.5(6)
C8	C5	C4	121.2(5)	C19	C20	N3	109.0(7)
C8	C5	C6	121.5(5)	C21	C20	N3	126.4(7)
C7	C6	C5	120.6(6)	C21	C20	C19	124.5(7)
C6	C7	C2	121.7(6)	C20	C21	O1	129.7(7)
C9	C8	C5	119.9(6)				

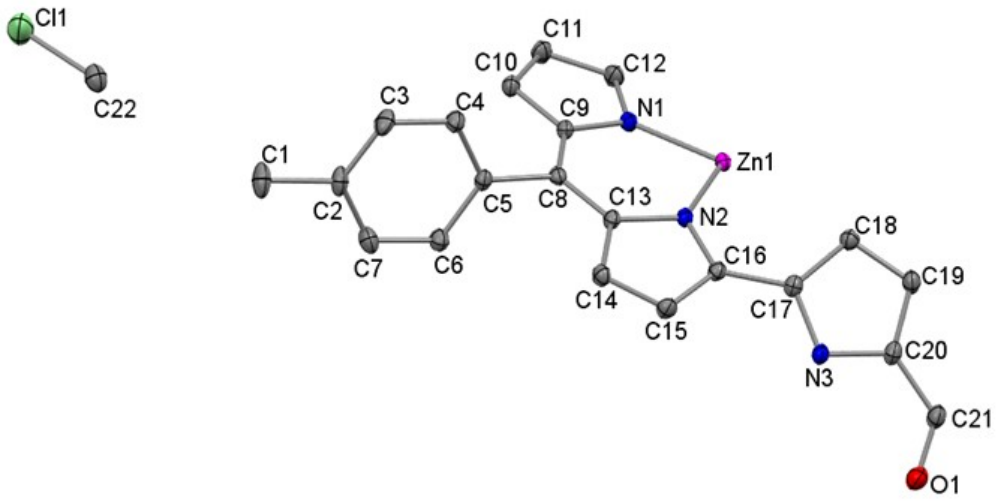

Fig. S15 The asymmetric unit of compound **4-Zn.**

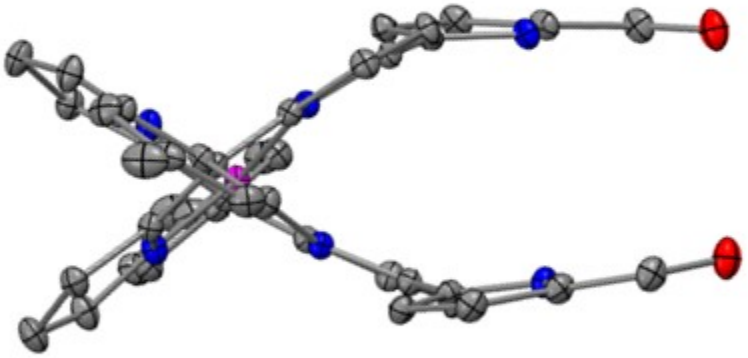

Fig. S16 The Side view structure of compound **4-Zn.**

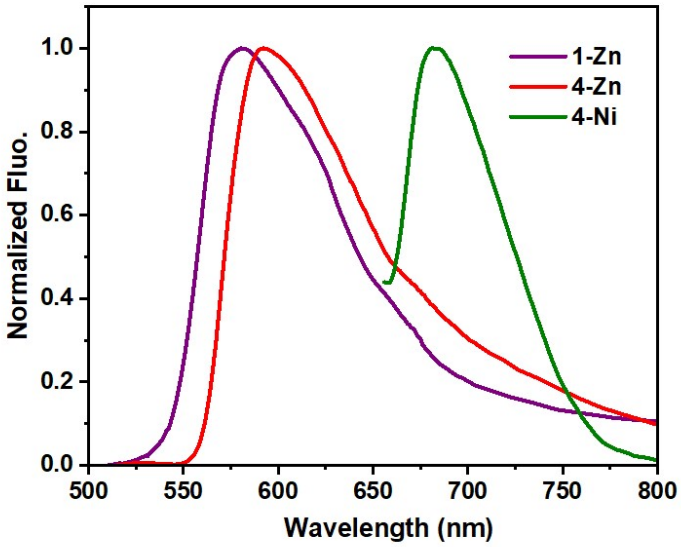

Fig. S17 Comparison of normalized fluorescence spectra of compounds **1-Zn**, **4-Zn** and **4-Ni** recorded in $CHCl_3$.

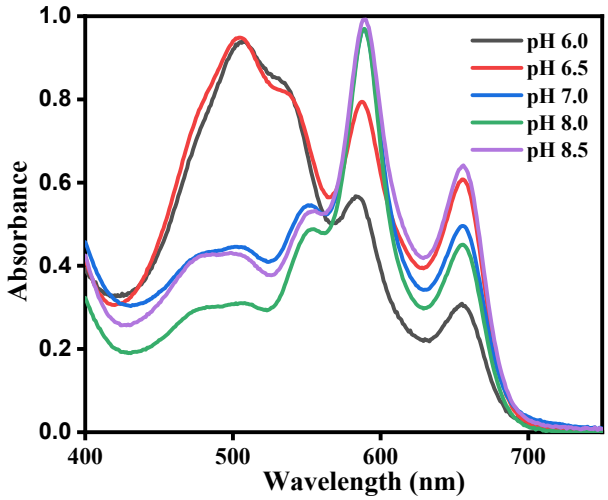

Fig. S18 Comparison of absorption spectra for the pH-dependent phosphatase-like activity of **4-Ni** in various buffer solutions.

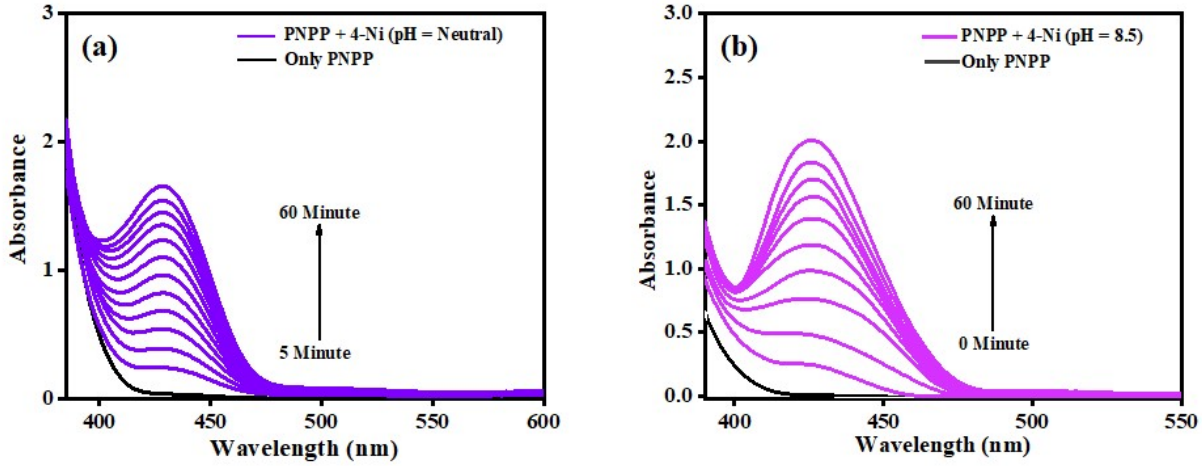

Fig. S19 Time-dependent UV–Vis spectral changes during the hydrolysis of PNPP catalyzed by compounds **4-Ni**, recorded at 5-minute intervals over 1 hour at 25 °C (substrate-to-catalyst ratio = 20:1). at neutral pH (a) and at basic medium *p*H=8.5 (b).

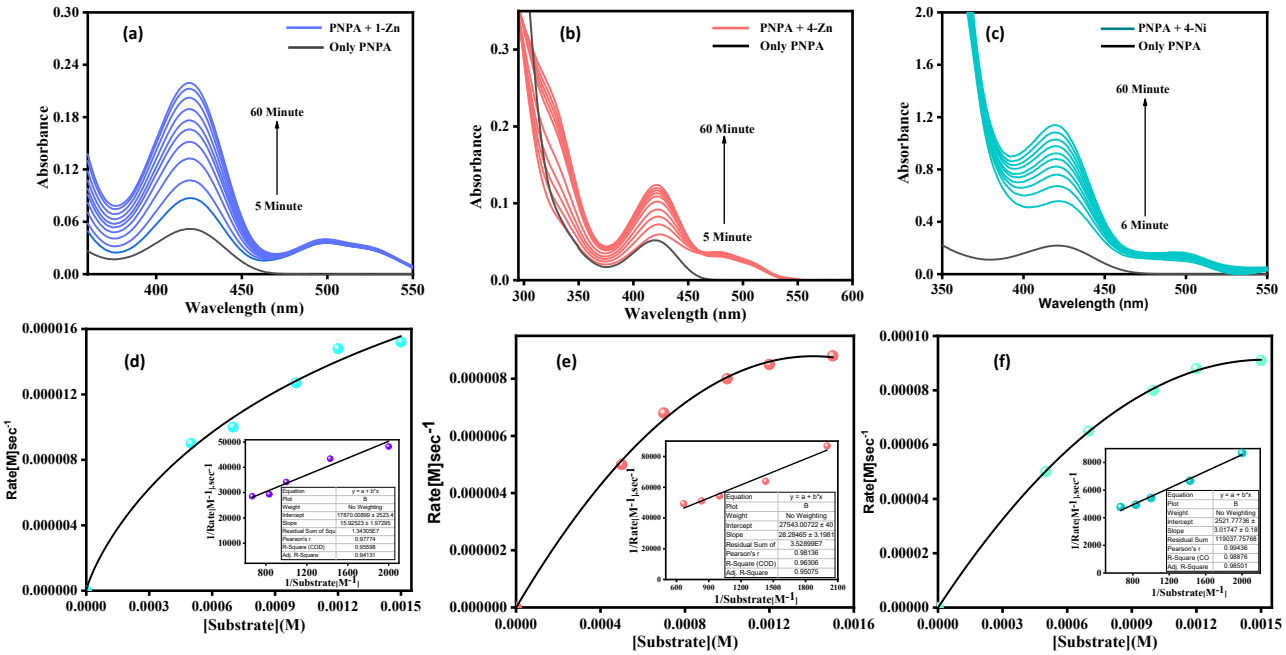

Fig. S20 (a-c) Time-dependent UV–Vis spectral changes during the hydrolysis of 4-nitrophenyl acetate (PNPA) catalyzed by compounds **1-Zn**, **4-Zn**, and **4-Ni**, respectively, recorded at 6-minute intervals over 1 hour at 25 °C (substrate-to-catalyst ratio = 20:1)

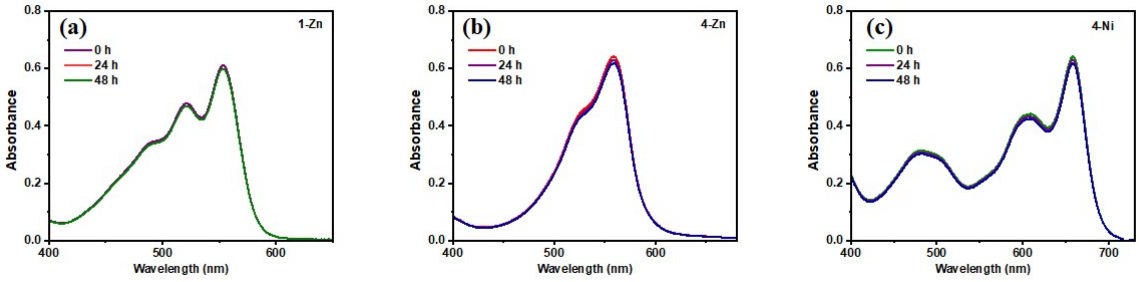

Fig. S21 Time-dependent UV–Vis spectra of compounds **1-Zn**, **4-Zn**, and **4-Ni** (2×10^{-5} M) recorded in a DMF/H_2O (97.5:2.5) solvent mixture at 25 °C.

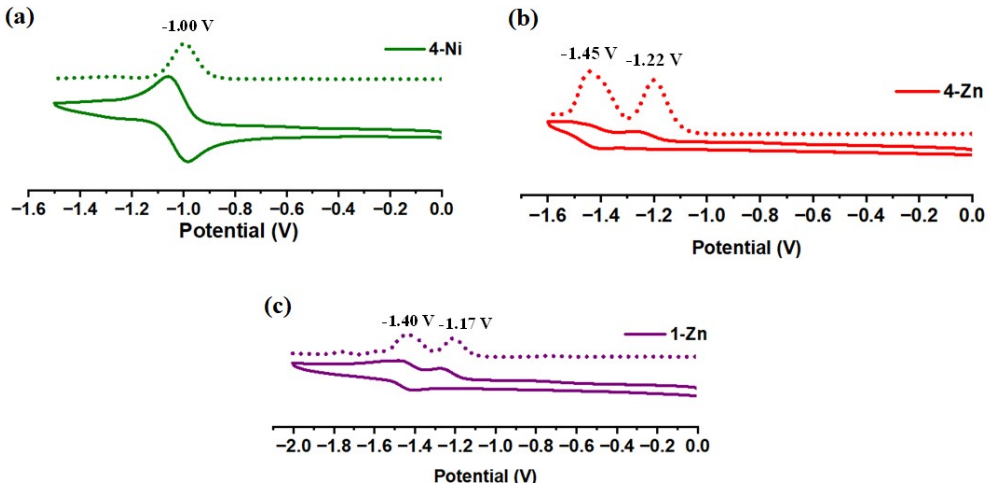

Fig. S22 Comparison of cyclic voltammograms of compounds (a) **4-Ni**, (b) **4-Zn** and (c) **1-Zn** recorded in DMF containing 0.1 M TBAP as the supporting electrolyte recorded at 100 mV s^{-1} scan speed.

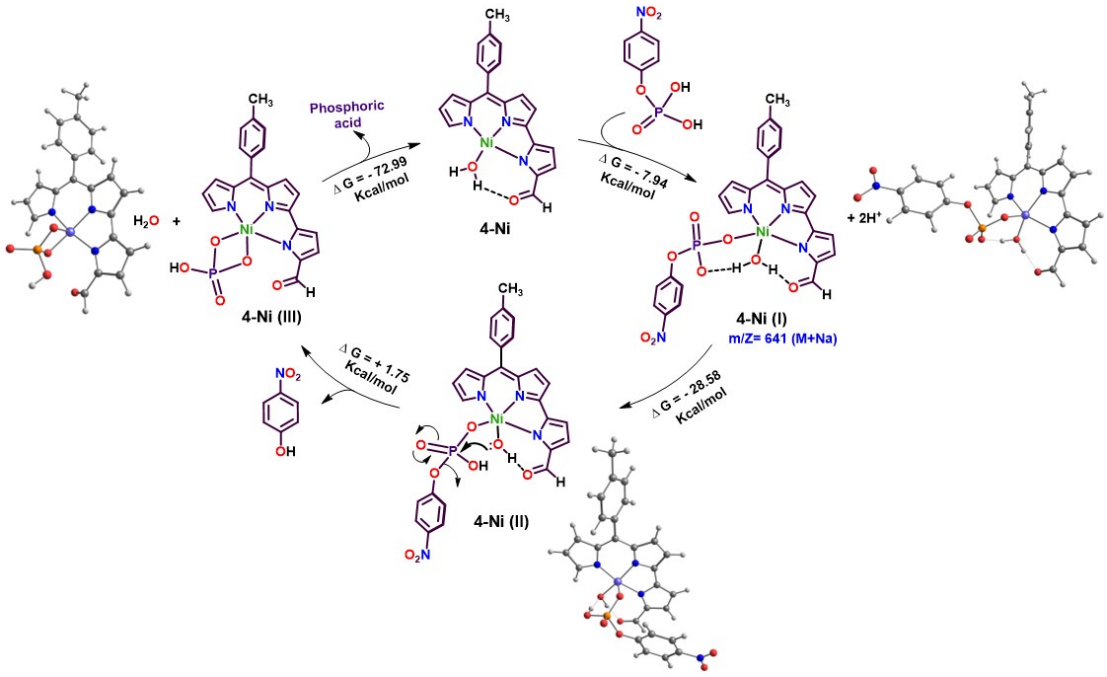

Fig. S23 B3LYP/6-31G(d,p) calculated free energy changes along the phosphate hydrolysis pathway of **4-Ni**. The values in parentheses indicate the free energy change obtained without dispersion.

Table S8. First-order kinetic parameters for phosphatase activity of **1-Zn**, **4-Zn**, and **4-Ni** in presence of PNPA substrate.

Compounds	K_{cat}	V_{max}	K_M
1-Zn	1.11	5.6×10^{-5}	8.8×10^{-4}
4-Zn	0.72	3.6×10^{-5}	10.2×10^{-4}
4-Ni	7.8	3.9×10^{-4}	11.9×10^{-4}

Table S9. S_0 optimized geometry of the compound **1-Zn** at B3LYP/6-31g (d,p) level of theory.

Total Energy (hartree) = -2164.378788

Atoms	X	Y	Z
Zn	-0.010376918939	-0.490403932422	-0.054250060919
N	1.334262202689	-1.559988875539	1.021652774883
N	-1.073627781097	2.314550456751	-1.524897756297
H	-1.218152702515	1.804897414024	-0.655598238839
N	1.438020176694	0.710068246989	-0.957158964279
N	-1.376906745066	-1.377231506435	-1.258595179605
N	-1.442514664282	0.605729818459	1.009152967957
N	1.077151138473	2.084967304156	1.788832920979
H	1.194195573135	1.717975849208	0.848599225333
C	4.863433543035	-0.792591152925	-0.164231830369
C	0.114674746662	2.396407895838	-2.227321461121
C	2.799585972768	0.351898621821	-0.899362823114
C	-2.758601745177	-1.270155257697	-1.095628706232
C	-3.390424298931	-1.922792839788	-2.196737249257
H	-4.455950582726	-1.987073915845	-2.360509897710
C	-4.879603654567	-0.776918811972	0.072901358098
C	-2.789082180091	0.189781471053	0.975868316965
C	3.373009520176	-0.641797439063	-0.080543326345
C	-3.396906445059	-0.606342711549	-0.018701050265
C	1.332250307831	1.710636361852	-1.874525598637
C	2.714728490271	-1.515193566319	0.817125164882
C	3.519850015399	1.188900853128	-1.809579955331
H	4.588074796241	1.165577424088	-1.965731154914
C	3.321494517160	-2.510143448663	1.642200799881
H	4.379045343089	-2.722603055202	1.693240723437
C	-1.287092549237	1.342800414100	2.144812393170
C	-3.441397715491	0.695323442627	2.144089092539
H	-4.476281133415	0.527756863708	2.402474939456
C	-0.068867787069	1.993291404556	2.556504894994
C	2.612224729847	2.019850958853	-2.422217590097
H	2.814388917834	2.792670679186	-3.150206646878
C	2.305099472795	-3.137011157082	2.346566844506
H	2.397835780100	-3.938187946283	3.066818155133
C	-2.020076473029	3.093904187875	-2.124269028558
H	-3.016049773590	3.168860711125	-1.713484584310
C	-5.743473744658	0.328067274698	0.025038295280
H	-5.326403542542	1.324338240107	-0.085002438433
C	5.474601165738	-1.343402723645	-1.298524857482
H	4.858102701389	-1.670162811474	-2.130692044421
C	1.104592402611	-2.523408964485	1.929326638907
H	0.094792677395	-2.750803879196	2.251049440876
C	-7.693944406688	-1.112155626108	0.246945860310
C	-7.125075106855	0.159969129295	0.106178186262
H	-7.771862052363	1.032597022951	0.057907069946

C	-1.168444501131	-2.064305213336	-2.394830196204
H	-0.162067845207	-2.280854619162	-2.734131303282
C	-5.448518548312	-2.054053060316	0.208376615118
H	-4.797799350168	-2.921593671976	0.255179660392
C	-2.513718956457	1.407332590054	2.867482414249
H	-2.670647236955	1.934796929342	3.797614507803
C	-2.385422107355	-2.421285751296	-3.012398693993
H	-2.497343889285	-2.968679122743	-3.938195629937
C	-0.113023303003	3.258119217924	-3.304319027065
H	0.613944136352	3.517435660076	-4.060779671962
C	7.681936634060	-1.080761995307	-0.302641757301
C	-6.828977734335	-2.214130659835	0.302369816287
H	-7.242162558336	-3.212641116591	0.423654767325
C	6.861022221402	-1.486506539560	-1.362005785789
H	7.310947186787	-1.925165792283	-2.249340558203
C	5.681062156569	-0.392332145232	0.903238189196
H	5.224431562919	0.030835211958	1.793066735854
C	-1.454558293960	3.690813589988	-3.239418310907
H	-1.956917543787	4.357365633836	-3.925824439542
C	2.041164440407	2.768530491521	2.471400186178
H	3.009531214775	2.948314614750	2.028267893422
C	7.065648872216	-0.533078031465	0.831118643387
H	7.677846305596	-0.212603320496	1.670845444833
C	1.527126211653	3.132024841575	3.705828814508
H	2.051435479762	3.681299057135	4.474743963467
C	-9.191466119944	-1.296541702240	0.310757672038
H	-9.693540233193	-0.386953464904	0.652963587027
H	-9.465917073751	-2.111393897377	0.987936135336
H	-9.601765975418	-1.544547610416	-0.676299414690
C	9.184964489509	-1.207003419430	-0.384302832998
H	9.484467170544	-1.947677384046	-1.131333390619
H	9.615210940536	-1.502980324748	0.577810262757
H	9.648381199282	-0.252801004425	-0.664893300719
C	0.202384917343	2.649274995559	3.761146913868
H	-0.486227158092	2.747358321459	4.588142610305

Table S10. S_0 optimized geometry of the compound **4-Zn** at B3LYP/6-31g (d,p) level of theory.

Total Energy (hartree) = -1937.726043

Atoms	X	Y	Z
Zn	-0.000001383906	-1.028112732609	-0.000008815883
N	1.260709507304	0.046144273787	1.245170159177
O	-1.742331443764	5.151436376932	3.814034179326
N	1.518236975805	-2.253190539652	-0.638368211736
N	-0.607894894256	2.741264496180	2.896488418470
H	0.040436954861	3.515167474093	2.928674179986
C	2.652155593081	-0.073750394947	1.194081175598
C	3.388244030456	-1.009198614787	0.428256129667
C	2.876995375445	-2.021172483780	-0.411130757949
C	-0.354565931278	1.468994408066	2.459460846752
C	3.225512199567	0.902114814689	2.069791363213
H	4.279888078420	1.026877669952	2.264708108935
C	4.880254219785	-0.913751872195	0.516185465457
C	0.987748589627	1.052487028289	2.105052903988
C	3.628553865186	-2.967480615651	-1.178655558246
H	4.705884267744	-3.029572522472	-1.218394081425
C	-1.568353950738	0.766375950139	2.514090851644
H	-1.697598778547	-0.280290938581	2.283801067501
C	2.187354275160	1.612664422471	2.629947447427
H	2.253249627583	2.398645675296	3.370307123092
C	-1.938116786315	2.883827831620	3.213545295298
C	-2.553502089278	1.651529300471	2.984423225423
H	-3.596461397618	1.426676262217	3.161636166359
C	5.635807182823	-1.938157919262	1.104847069162
H	5.128321909404	-2.806373327166	1.514075774632
C	1.437094021257	-3.292074849793	-1.482094180282
H	0.472283841887	-3.661397753863	-1.810466480684
C	7.024529524507	-1.842334323093	1.183915135592
H	7.587188347228	-2.643147456397	1.657444983521
C	7.706577190565	-0.732001622648	0.669250286890
C	2.718461978640	-3.772023395498	-1.842188190796
H	2.929182994495	-4.597739340259	-2.507803268115
C	-2.445045169472	4.155428282968	3.679711493638
H	-3.529760272290	4.172896270496	3.911354452800
C	6.947316795845	0.288565599614	0.081046423622
H	7.450231824661	1.163327616430	-0.324180518606
C	5.557976533888	0.204572178367	0.007181789626
H	4.988800882762	1.007485826785	-0.451782730491
C	9.213530271176	-0.648004799321	0.723505136863
H	9.615962319312	-1.211037999070	1.570766363981
H	9.554010480417	0.388141829256	0.811433355559
H	9.665515746934	-1.061876664727	-0.186718050200

N	**-1.260702993132**	**0.046178626916**	**-1.245170201511**
O	**1.742341519299**	**5.151512663125**	**-3.813949881390**
N	**-1.518252470115**	**-2.253182072816**	**0.638335095824**
N	**0.607909504840**	**2.741325579110**	**-2.896437823833**
H	**-0.040422107629**	**3.515229551876**	**-2.928604915976**
C	**-2.652150893987**	**-0.073697426951**	**-1.194074396837**
C	**-3.388247120851**	**-1.009142061614**	**-0.428251800997**
C	**-2.877008245036**	**-2.021137976132**	**0.411111581094**
C	**0.354580718607**	**1.469046442065**	**-2.459436494015**
C	**-3.225497975282**	**0.902157815632**	**-2.069801830339**
H	**-4.279871451671**	**1.026918908735**	**-2.264732419338**
C	**-4.880256939756**	**-0.913708955920**	**-0.516197350248**
C	**-0.987734577013**	**1.052534543114**	**-2.105036298406**
C	**-3.628578646556**	**-2.967492045880**	**1.178567307356**
H	**-4.705909758212**	**-3.029598997210**	**1.218268893963**
C	**1.568363576472**	**0.766422401318**	**-2.514107309056**
H	**1.697604895836**	**-0.280254335920**	**-2.283861055033**
C	**-2.187336447179**	**1.612738803625**	**-2.629910648441**
H	**-2.253225322472**	**2.398742308354**	**-3.370247262562**
C	**1.938131587402**	**2.883896714623**	**-3.213490303198**
C	**2.553519742631**	**1.651597035159**	**-2.984382436440**
H	**3.596481310558**	**1.426750886793**	**-3.161590773535**
C	**-5.635794535487**	**-1.938136201828**	**-1.104841428132**
H	**-5.128296588273**	**-2.806354742461**	**-1.514047934617**
C	**-1.437122475117**	**-3.292072780709**	**1.482054253858**
H	**-0.472316855139**	**-3.661402235995**	**1.810432544547**
C	**-7.024517459265**	**-1.842330317221**	**-1.183919654766**
H	**-7.587164322581**	**-2.643159278217**	**-1.657436945319**
C	**-7.706581000641**	**-0.731996150955**	**-0.669278952422**
C	**-2.718497237720**	**-3.771981653996**	**1.842178903735**
H	**-2.929228561948**	**-4.597675955409**	**2.507817561192**
C	**2.445059769472**	**4.155507596054**	**-3.679628206431**
H	**3.529772760873**	**4.172978070715**	**-3.911280706659**
C	**-6.947336216650**	**0.288588969139**	**-0.081085769538**
H	**-7.450264104473**	**1.163350990189**	**0.324125228579**
C	**-5.557995372598**	**0.204613093293**	**-0.007210929935**
H	**-4.988832040718**	**1.007539898116**	**0.451745808736**
C	**-9.213534769183**	**-0.648018579096**	**-0.723543539256**
H	**-9.615954540407**	**-1.211062531728**	**-1.570803512224**
H	**-9.554027414089**	**0.388123170466**	**-0.811480711631**
H	**-9.665520668282**	**-1.061890269874**	**0.186679520275**

Table S11. S_0 optimized geometry of the compound **4-Ni** at B3LYP/6-31g (d,p) level of theory.

Total Energy (hartree) = -1294.574771

Atoms	X	Y	Z
Ni	1.706575116970	0.665603541255	0.002707393744
O	2.891058567760	2.161005740875	0.214318573406
H	3.895939164988	1.878056655541	0.131197217215
H	2.779790991788	2.526118510753	1.102630372124
N	0.185637657057	1.814293887432	-0.099191375963
N	0.588065485005	-0.811231786653	-0.087589754811
O	5.263064703618	1.461174057344	0.074557164823
N	3.116284183840	-0.689795805253	0.024992622468
C	1.176884735375	-2.020310263538	-0.013474643919
C	-1.648224773763	0.132188880562	-0.039211453432
C	2.614271000059	-1.955388216245	0.010851028045
C	-1.167271701470	1.457186844359	-0.104517752941
C	-5.286508525774	0.246981826371	1.037311801736
H	-5.883072396311	0.712385916337	1.818093919841
C	4.495353988537	-0.818554229210	0.041284238070
C	0.182534772282	-3.031454737154	0.078450794928
H	0.357074510314	-4.095887836003	0.150924380425
C	0.240567019106	3.144696689317	-0.287859830625
H	1.194390336822	3.648296944460	-0.353338803634
C	-1.938767393867	2.643367763469	-0.295922986920
H	-3.015746867241	2.679324145723	-0.369514978478
C	-3.914813917315	0.485688112217	0.993494237443
H	-3.451876091785	1.125931242338	1.737688580168
C	-0.777284658663	-0.971490110786	-0.028308031335
C	-3.113632656566	-0.108947417903	0.004418049580
C	-1.051633280174	3.700341643319	-0.407217731910
H	-1.281789981531	4.744009366533	-0.571128182881
C	4.834281321849	-2.198067177519	0.038289688525
H	5.842670665869	-2.591545641854	0.046281440340
C	3.648011987804	-2.917719094368	0.022132578825
H	3.523128665340	-3.991602087069	0.014101216452
C	-1.038761472226	-2.376026861639	0.080627382976
C	-5.910561143523	-0.582688768983	0.095766967324
C	-3.736162000560	-0.942149322579	-0.940036476577
H	-3.139349829475	-1.392688011863	-1.726715063306
C	5.457220180242	0.222936211147	0.055774086104
H	6.502867756632	-0.125723536341	0.050735448779
C	-5.110398316140	-1.166426647737	-0.895621450003
H	-5.570473530883	-1.801375273756	-1.648793290049
C	-7.393544188122	-0.858656365953	0.162454776436
H	-7.603533415342	-1.739020185922	0.782968170487
H	-7.938714496529	-0.016646779634	0.599261002306
H	-7.809443638492	-1.054991253784	-0.830246649240
H	-2.018228152150	-2.824896409460	0.159450221260

Table S12. First-order rate constants for the hydrolysis of various phosphate esters by previously reported Ni((II) complexes. [S5-S9]

Catalyst	Substrate	Solvent	kcat(s-1)	Ref
$[Ni_2(L^1)(NCS)_3(H_2O)_2]$	PNPP	$MeCN/H_2O$	0.841	4
$[Ni_2(L^2)(CH3COO)(NCS)_2(H_2O)]$	PNPP	$MeCN/H_2O$	0.941	4
$[Ni_2(L^3)(NCS)_3]$ $L^{1,2,3}$=Schiff-base	PNPP	$MeCN/H_2O$	0.742	4
$[Ni_2L(\mu\text{-}OH)]$ $(ClO_4)_2$ L=Schiff-base	BNPP	$EtOH/H_2O$	1.49×10-4	5
$[Ni_2L^{1-5}(\mu\text{-}NO_3)(NO_3)2]$L=Mannich-base	PNPP	$DMSO/H_2O$	6.66-80.6	6
$[Ni_2L^2(NCS)(Ac)(H_2O)_{0.5}(MeOH)_{0.5}]$. $1.25H_2O$ L=Schiff-base	PNPP	$DMSO/H_2O$	8.18	7
$[Ni_2(HL^1)(OAc)_2]$	HNPP	$DMSO/H_2O$	6.38×10-4	8

PNPP=*para*-nitrophenyl-phosphate, BNPP=bis(4 nitrophenyl)phosphate, HPNP= 2-hydroxypropyl(4-nitrophenyl)phosphate.

References:

S1. L. J. Bournias, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Acta Crystallogr. A Found. Adv.*, 2015, **71**, 59–75.

S2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.

S3. S. Gilb, K. Jacobsen, D. Schooss, F. Furche, R. Ahlrichs and M. M. Kappes, *J. Chem. Phys.*, 2004, **121**, 4619–4627.

S4. L. Yang, D. R. Powell and R. P. Houser, *Coord. Chem. Rev.*, 2007, **251**, 289–325.

S5. A. Banerjee, A. Guha, P. Maiti, S. Goswami, T. Chattopadhyay, T. K. Mondal, S. Bhattacharya, E. Zangrando and D. Das, *Transition Met. Chem.*, 2011, **36**, 829–839.

S6. Y. Ren, J. Lu, B. Cai, D. Shi, H. Jiang, J. Chen, D. Zheng and B. Liu, *Dalton Trans.*, 2011, **40**, 1372–1381.

S7. R. Sanyal, X. Zhang, P. Chakraborty, F. A. Mautner, C. Zhao and D. Das, *RSC Adv.*, 2016, **6**, 73534.

S8. R. Sanyal, X. Zhang, P. Chakraborty, S. Giri, S. K. Chattopadhyay, C. Zhao and D. Das, *New J. Chem.*, 2016, **40**, 7388.

S9. V. K. Bhardwaj and A. Singh, *Inorg. Chem.*, 2014, **53**, 10731–10742.