Electronic Supplementary Material (ESI) for Dalton Transactions.

Hydrolysis of the RNA model substrate catalyzed by a binuclear Zr^{IV}-substituted Keggin polyoxometalate

Thi Kim Nga Luong,[a] Gregory Absillis,[a] Pavletta Shestakova,[a,b] and Tatjana N. Parac-Vogt [a]

[a]Department of Chemistry, KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium
E-mail: Tatjana.Vogt@chem.kuleuven.be
www.chem.kuleuven.be/lbc/
[b]NMR Laboratory, Institute of Organic Chemistrywith Centre of Phytochemistry
Bulgarian Academy of Sciences, Acad. G. Bontchev Str., B1.9, 1113 Sofia, Bulgaria

Supporting Information

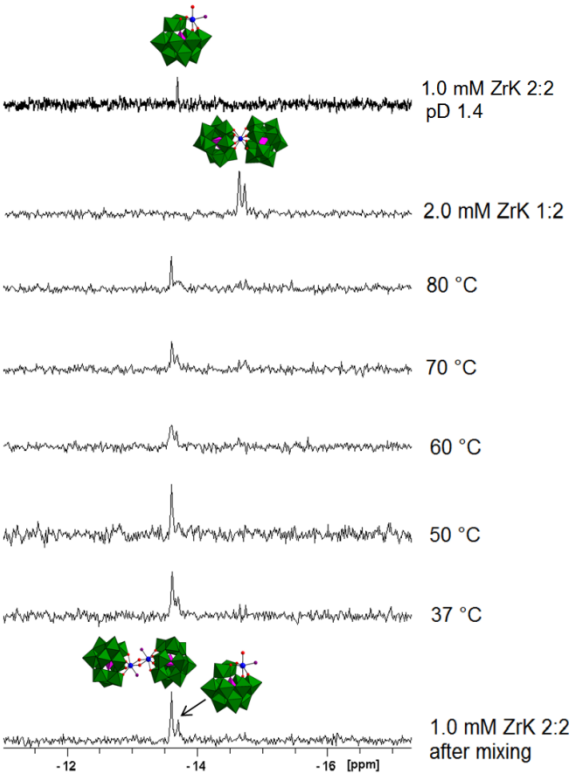


Figure S1. Temperature dependence of the ^{31}P NMR spectra of 1.0 mM of ZrK 2:2 at pD 6.4. The spectra were recorded 1 h after mixing and heating at temperatures ranging from 37 °C to 80 °C. The ^{31}P NMR spectra of 2.0 mM ZrK 1:2 at pD 6.4 and of 1.0 mM ZrK 2:2 at pD 1.4 were added for comparison. (400 MHz, D_2O, 293 K, NS = 1024, 25% H_3PO_4).

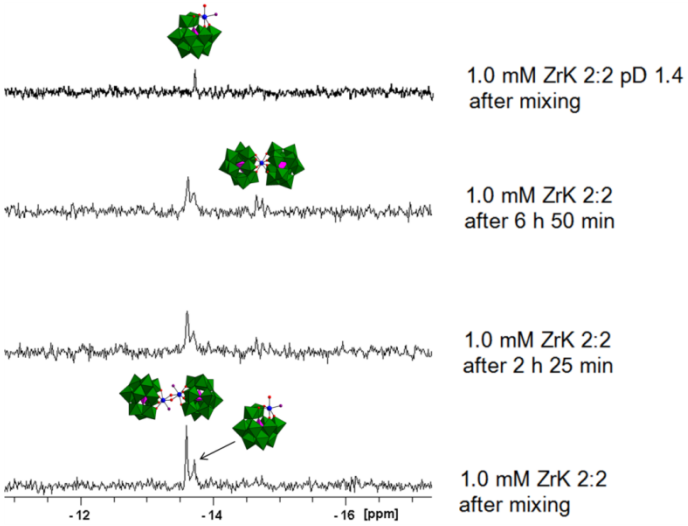


Figure S2. Time dependence of the ^{31}P NMR spectra of 1.0 mM of ZrK 2:2. The spectra were recorded after mixing, 2 h 25 min, 6 h 50 min at pD 6.4 and 50 °C (600 MHz, D_2O, 293 K, NS = 1024, 25% H_3PO_4).

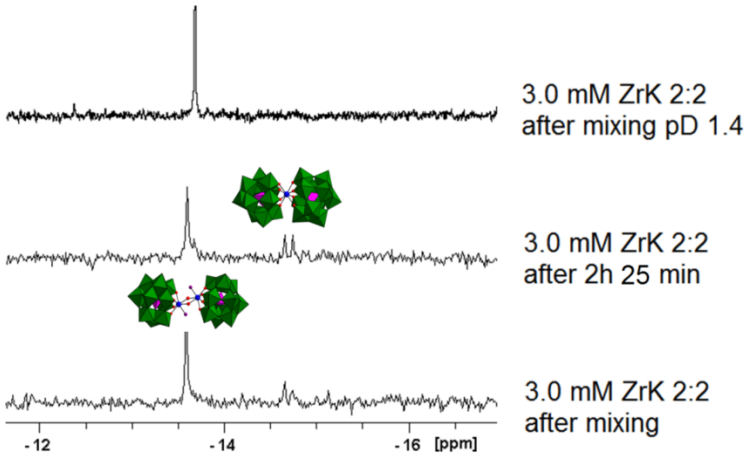


Figure S3. Time dependence of the ^{31}P NMR spectra of 3.0 mM of ZrK 2:2. The spectra were recorded after mixing, 2 h 25 min at pD 6.4 and 50 °C (400 MHz, D_2O, 293 K, NS = 1024, 25% H_3PO_4).

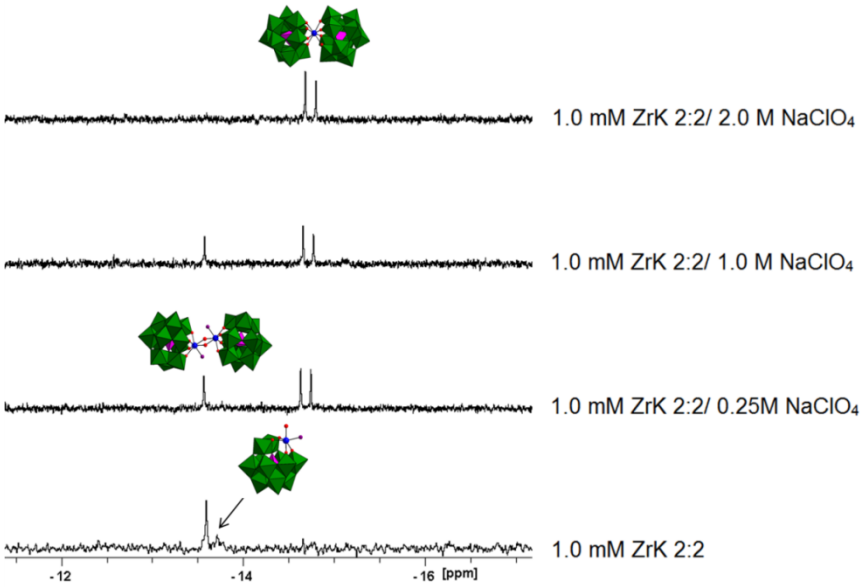


Figure S4. ^{31}P NMR spectra of 1.0 mM of ZrK 2:2 in the presence of different (0.25 M to 2.0 M) $NaClO_4$ concentrations (600 MHz, D_2O, 293 K, NS = 1024, 25% H_3PO_4).

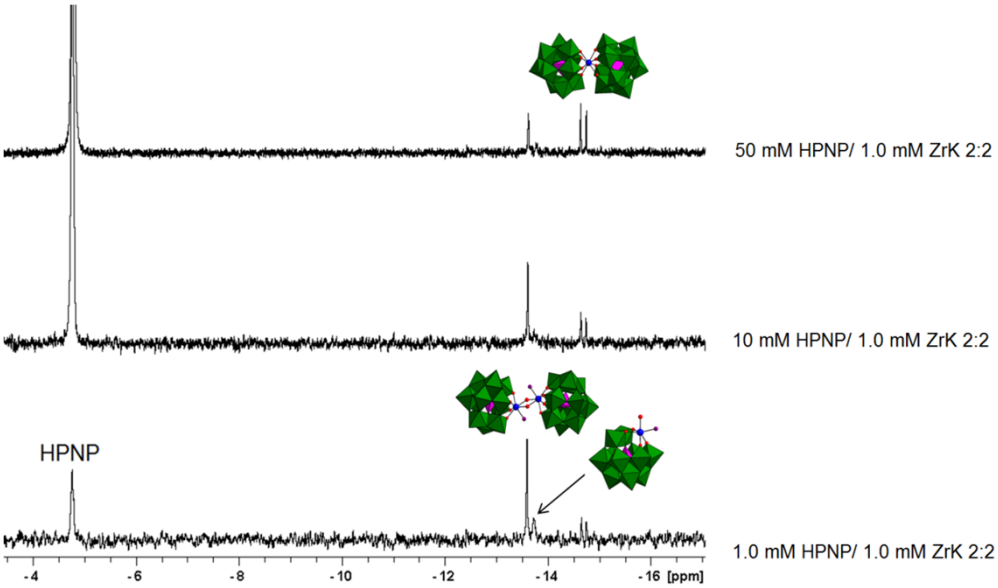


Figure S5. ^{31}P NMR spectra of the reaction mixture of different concentrations (1 mM - 50 mM) of HPNP and 1.0 mM of ZrK 2:2 after mixing at pD 6.4. (600 MHz, D_2O, 293 K, NS = 1024, 25% H_3PO_4).

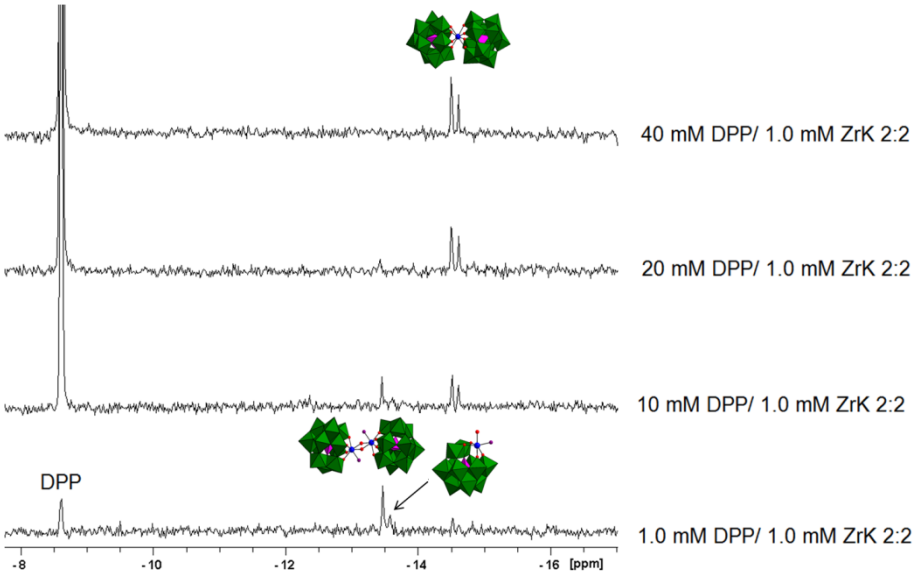


Figure S6. ^{31}P NMR spectra of the reaction mixture of different concentrations (1 mM - 40 mM) of DPP and 1.0 mM of ZrK 2:2 after mixing at pD 6.4. (600 MHz, D_2O, 293 K, NS = 1024, 25% H_3PO_4).

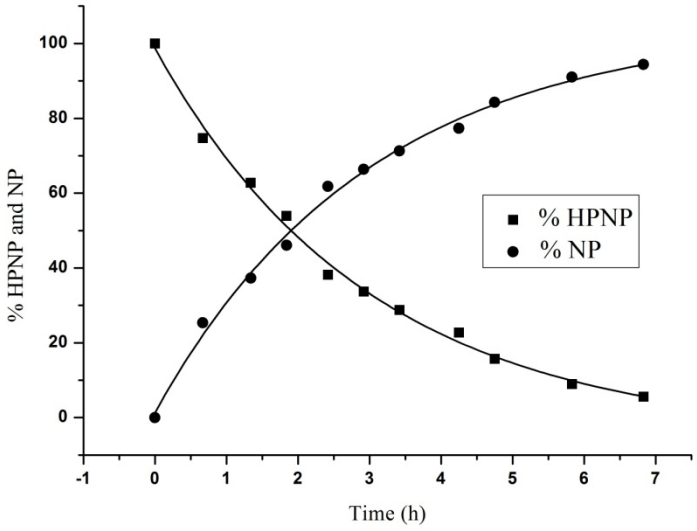


Figure S7. Percentage of HPNP and NP as a function of reaction time for the reaction between 1.0 mM of HPNP and 1.0 mM of ZrK 2:2 at pD 6.4 and 50 °C.

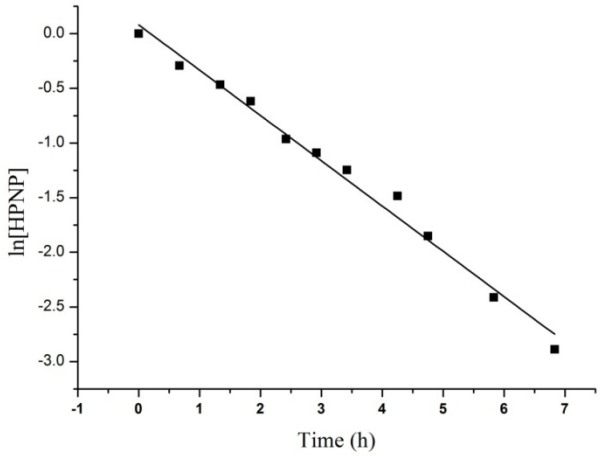


Figure S8. ln[HPNP] as a function of time (linear fit with $R^2 = 0.98$) for the reaction between 1.0 mM of HPNP and 1.0 mM of ZrK 2:2 at pD 6.4 and 50 °C.

Table 1: pD dependence of the reaction rate constant for the hydrolysis of 1.0 mM of HPNP in the presence of 1.0 mM of ZrK 2:2 at 50 °C.

pD	k_{obs}[a] (10^{-5} s^{-1})	k_{obs}[b] (10^{-7} s^{-1})	Δk_{obs}(10^{-5} s^{-1})
4.5	5.85 ± 0.57	No hydrolysis after 3 months	/
5.5	9.60 ± 0.41	No hydrolysis after 3 months	/
6.4	11.5 ± 0.42	2.17 ± 0.11	11.48
6.9	11 ± 0.73	Not determined	/
7.5	9.69 ± 0.34	1.50 ± 0.09	9.68
8.0	8.48 ± 0.36	Not determined	/
8.5	6.09 ± 0.58	1.47 ± 0.14	6.08
9.5	0.16 ± 0.01	1.47 ± 0.08	0.15

[a] in the presence of ZrK 2:2
[b] in the absence of ZrK 2:2

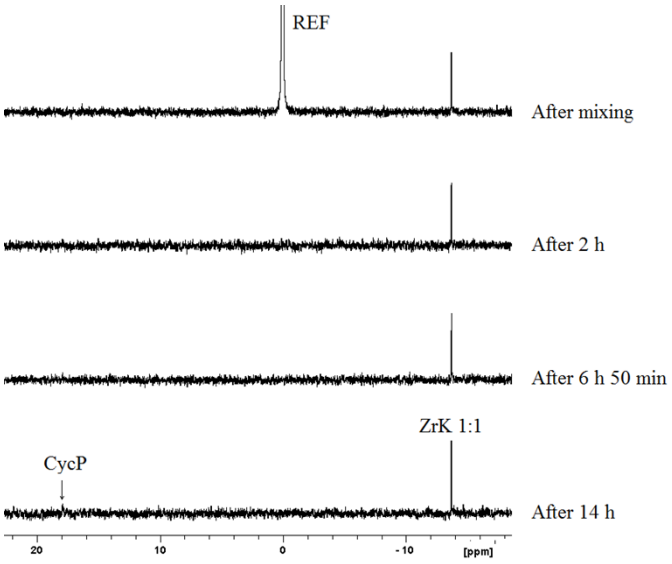


Figure S9. ^{31}P NMR of the hydrolysis reaction between 1.0 mM of HPNP in the presence of 1.0 mM of ZrK 2:2 at different time intervals at pD 4.5 and 50 °C. (400 MHz, D_2O, 293 K, NS = 1024, 25% H_3PO_4). The resonance of HPNP at -4.61 ppm disappeared after the addition of ZrK 2:2, suggesting that the strong binding between HPNP and this POM took place at acidic invironment.

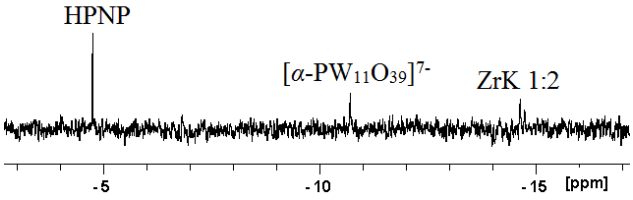


Figure S10. ^{31}P NMR of the hydrolysis reaction between 1.0 mM of HPNP in the presence of 1.0 mM of ZrK 2:2 at different time intervals at pD 9.5 and 50 °C. (400 MHz, D_2O, 293 K, NS = 1024, 25% H_3PO_4).

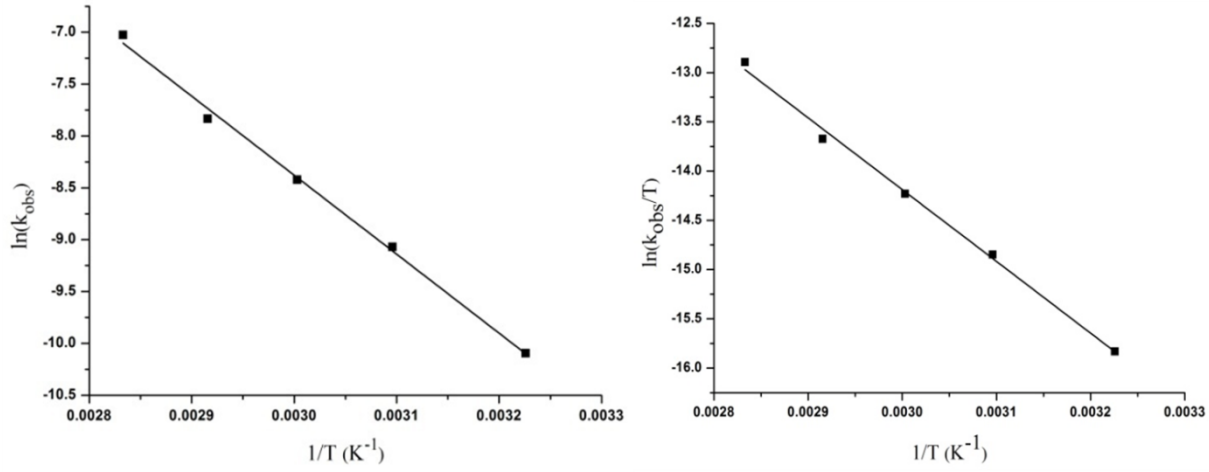


Figure S11: a: Arrhenius plot of $\ln(k_{obs})$ as a function of 1/T ($Arrhenius\ equation: lnk_{obs} = lnA - \frac{E_a}{R}\frac{1}{T}$) and b: Eyring plot of $\ln(k_{obs}/T)$ as a function of 1/T (Eyring equation: $ln\frac{k_{obs}}{T} = \frac{-\Delta H^{\ddagger}}{R}\frac{1}{T} + ln\frac{k_b}{h} + \frac{\Delta S^{\ddagger}}{R}$) for the hydrolysis of 1.0 mM of HPNP in the presence of 1.0 mM of ZrK 2:2 at pD 6.4.

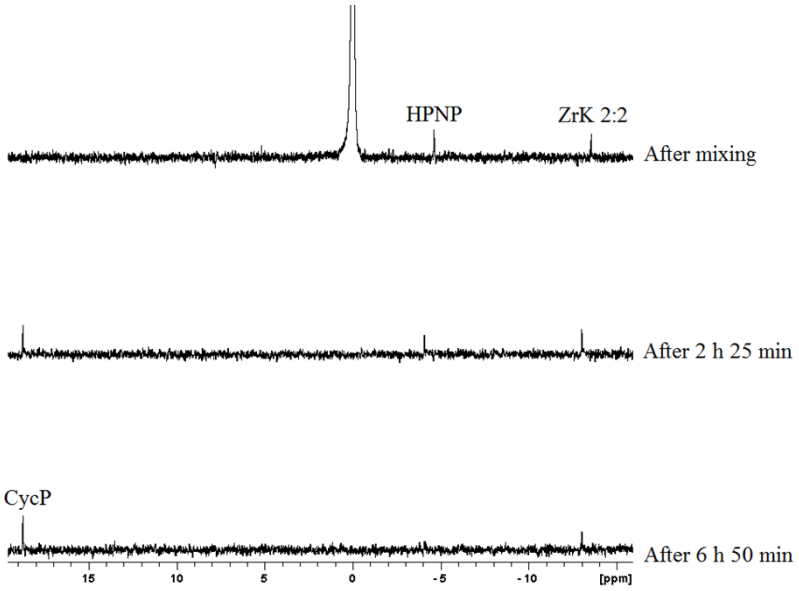


Figure S12. ^{31}P NMR of the hydrolysis reaction between 1.0 mM of HPNP in the presence of 0.25 mM of ZrK 2:2 at different time intervals at pD 6.4 and 50 ^{o}C. (400 MHz, D_2O, 293 K, NS = 1024, 25% H_3PO_4).

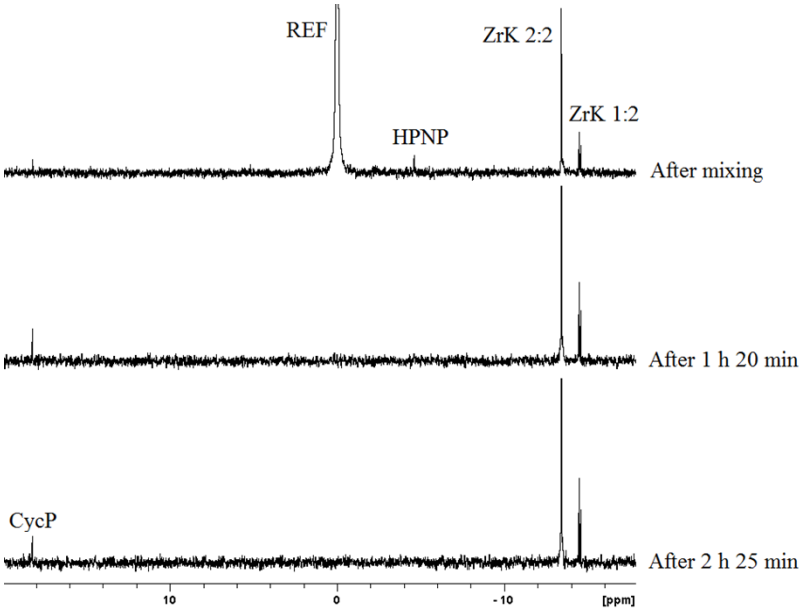


Figure S13. ^{31}P NMR of the hydrolysis reaction between 1.0 mM of HPNP in the presence of 3.0 mM of ZrK 2:2 at different time intervals at pD 6.4 and 50 ^{o}C. (400 MHz, D_2O, 293 K, NS = 1024, 25% H_3PO_4).

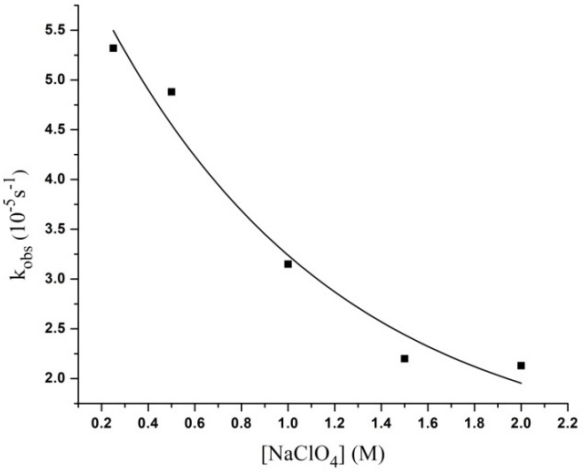


Figure S14. $NaClO_4$ concentration dependence on the observed rate constant for the hydrolysis of 1.0 mM of HPNP in the presence of 1.0 mM of ZrK 2:2 at pD 6.4 and 50 °C.

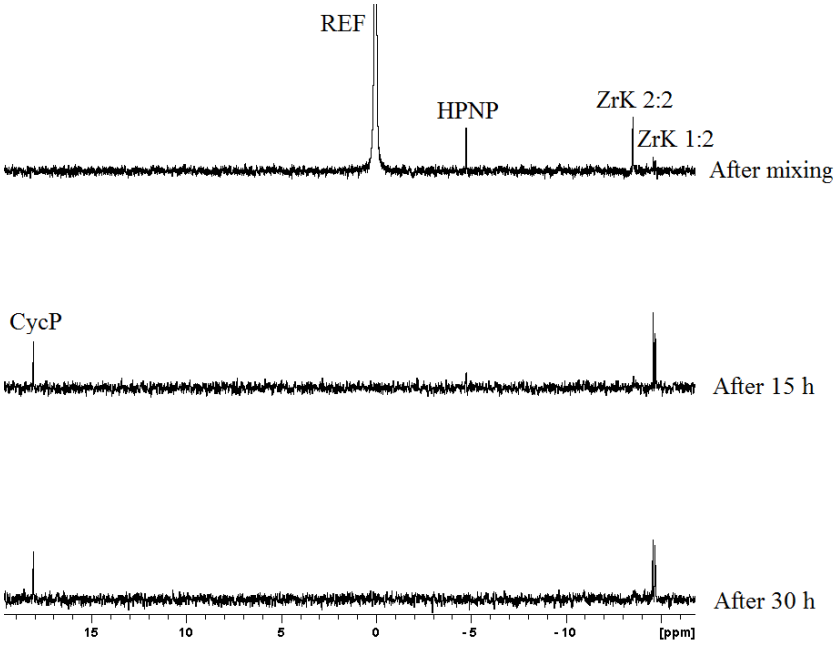


Figure S15. ^{31}P NMR of the hydrolysis reaction between 1.0 mM of HPNP in the presence of 1.0 mM of ZrK 2:2 and 0.25 M $NaClO_4$ at different time intervals at pD 6.4 and 50 ^{o}C. (400 MHz, D_2O, 293 K, NS = 1024, 25% H_3PO_4).

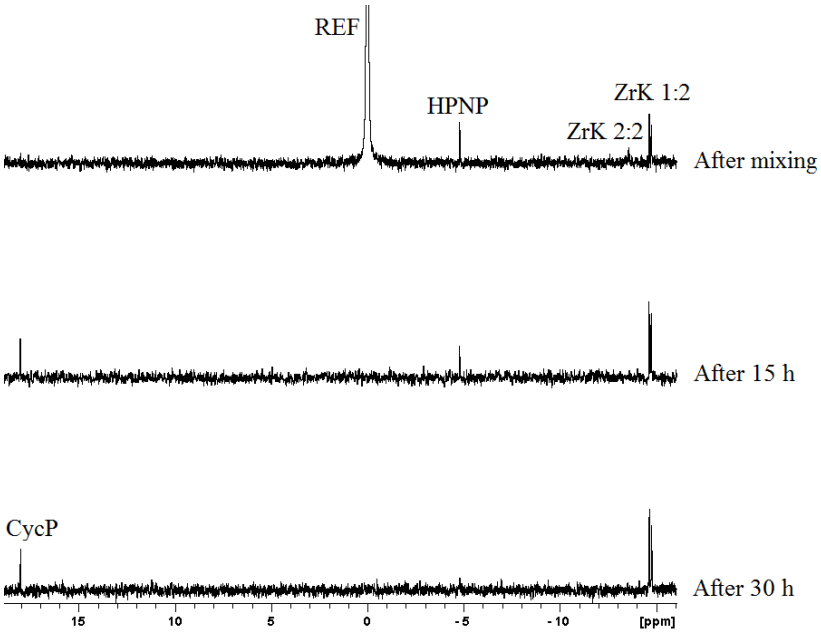


Figure S16. ^{31}P NMR of the hydrolysis reaction between 1.0 mM of HPNP in the presence of 1.0 mM of ZrK 2:2 and 1.0 M $NaClO_4$ at different time intervals at pD 6.4 and 50 ^{o}C. (400 MHz, D_2O, 293 K, NS = 1024, 25% H_3PO_4).

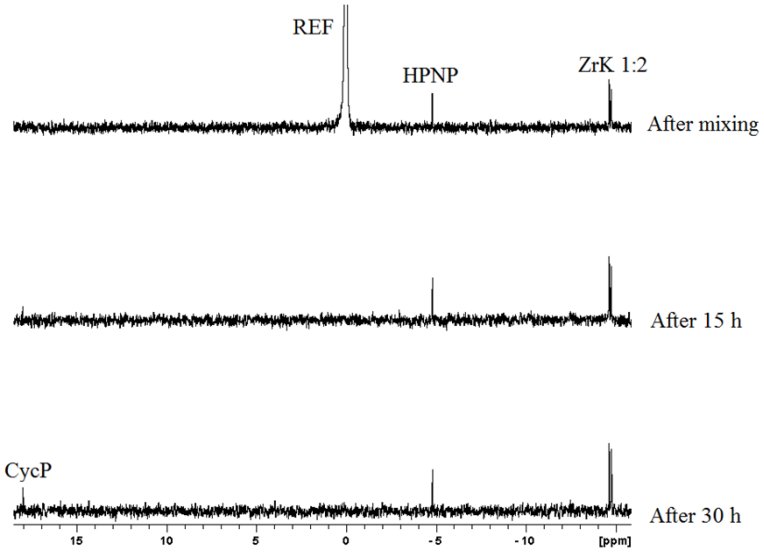


Figure S17. ^{31}P NMR of the hydrolysis reaction between 1.0 mM of HPNP in the presence of 1.0 mM of ZrK 2:2 and 2.0 M $NaClO_4$ at different time intervals at pD 6.4 and 50 ^{o}C. (400 MHz, D_2O, 293 K, NS = 1024, 25% H_3PO_4).

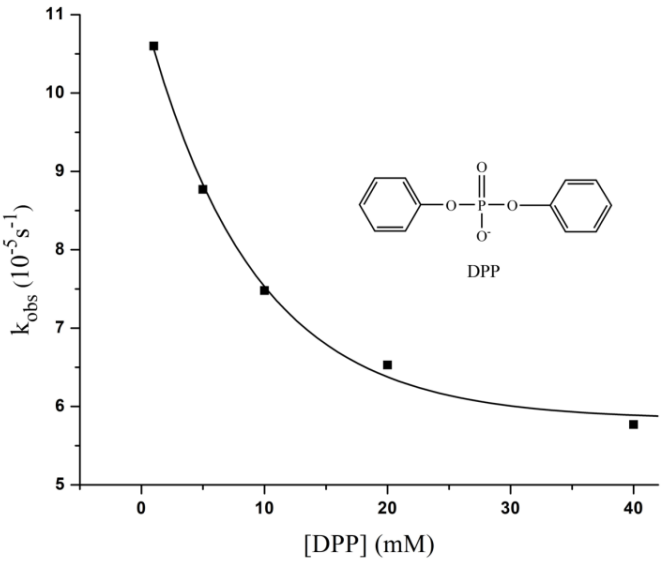


Figure S18. Influence of DPP concentration on the observed rate constant for the hydrolysis of 1.0 mM of HPNP in the presence of 1.0 mM of ZrK 2:2 at pD 6.4 and 50 °C.

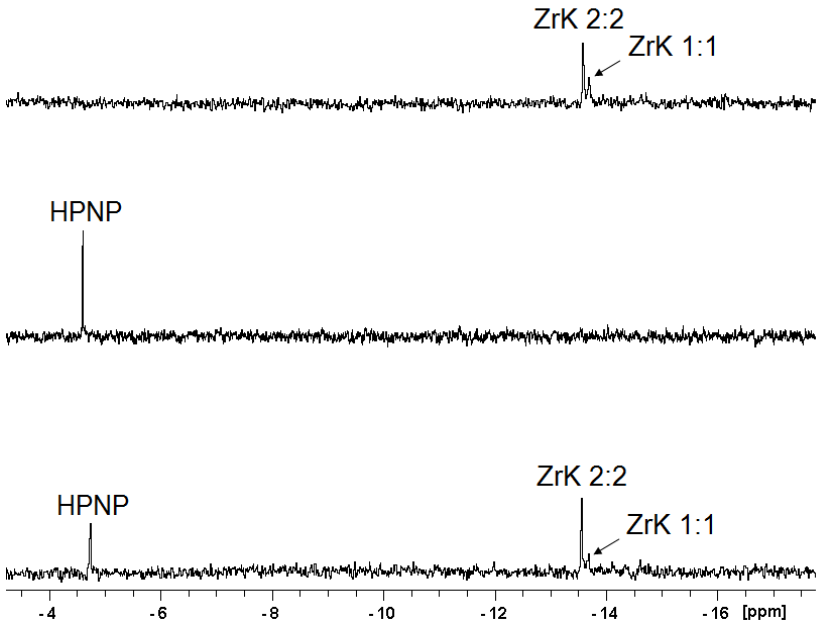
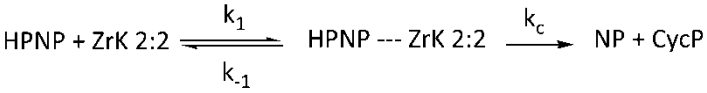


Figure S19. ^{31}P NMR spectra (from the top to the bottom) of 1.0 mM of ZrK 2:2, 1.0 mM of HPNP, 1.0 mM of HPNP and 1.0 mM of ZrK 2:2 after mixing, at pD 6.4 and 50 °C. (400 MHz, D_2O, 293 K, NS = 1024, 25% H_3PO_4).

Deriving the Equation 1 from the mechanism given in scheme 2

Based on Scheme 2:



when the concentration of ZrK 2:2 is higher than the concentration of HPNP, the approximate k_{obs} is calculated by the equation:[1]

$$k_{obs} = \frac{k_1 k_c [ZrK\ 2{:}2]_0}{k_1 [ZrK\ 2{:}2]_0 + k_{-1} + k_c}$$

Considering the case $k_1 [ZrK\ 2{:}2]_0 + k_{-1} \gg k_c$, the approximate k_{obs} is:

$$k_{obs} = \frac{k_1 k_c [ZrK\ 2{:}2]_0}{k_1 [ZrK\ 2{:}2]_0 + k_{-1}}$$

or

$$k_{obs} = \frac{k_c [ZrK\ 2{:}2]_0}{[ZrK\ 2{:}2]_0 + {k_{-1}}/{k_1}}$$

[1] E. J. H., Mc Graw-Hill, New York, **1994**.