Electronic Supplementary Information

Discovering the Precise pH-Controlled Biomimetic Catalysts: Defective Zirconium Metal-Organic Frameworks as Alkaline Phosphatase

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1. Materials and Instrumentation

All reagents employed were of at least of analytical grade and used without further purification. Zirconium chloride ($ZrCl_4$), 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES), sodium sulfate (Na_2SO_4), trifluoroacetic acid (TFA), acetonitrile (ACN), p-nitrophenyl phosphate (PNPP) and p-nitrophenol (PNP) were purchased from Aladdin Industrial Inc (Shanghai, China). Biphenyldicarboxylic acid (H_2BPDC) were purchased from Henghua Sci. & Tec. Co., Ltd. (Jinan, China). Terephthalic acid (H_2BDC) were purchased from Ourchem (Shanghai, China). Acetic acid, sulfuric acid (H_2SO_4), N,N-dimethylformamide (DMF) and ethanol (EtOH) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

Activity assays were measured using a Hitachi UH5300 spectrophotometer using a quartz cell with 1 cm optical path. X-ray diffraction (XRD) patterns were obtained from a high brightness source Rigaku SmartLab 9 Kw instrument, with data recorded from 5° to 50°. Transmission electron microscopy (TEM) analyses were performed on an H7650 transmission electron microscopy operated at an accelerating voltage of 200 kV. The acetate concentrations were recorded on a Waters high-performance liquid chromatography (HPLC) on a C18 column (250 × 4.6 mm i.d., 5 μm particle size) at room temperature. Scanning electron microscope (SEM) images were collected on a JSM-7600F (JEOL Ltd) scanning electron microscope. The potentiometric titrations were completed with a STARTER3100 pH meter (Ohaus Co.). Thermogravimetric analysis (TGA) was collected on a Perkin-Elmer Pyris Diamond 1 TGA analyzer. The diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) of the MOFs during biomimetic catalysis was conducted under controlled atmosphere and temperature on a Thermo Fisher Nicolet iS 50 ATR-FTIR spectrometer.

2. Synthesis and Characterization of Zr-based MOFs

Synthesis of UiO-66

UiO-66 was synthesized according to the literature procedure with few changes.[1] $ZrCl_4$ (159 mg) and H_2BDC (102 mg) were mixed with 20 mL DMF in a 25 mL teflon reaction kettle under ultrasonication for 5 min. Then, 0.3 mL acetic acid was added into the aforementioned solution and was stirred for 1 min. The reaction kettle was put into an oven at 120 ºC for 24 h. After cooling to room temperature, the products were collected by centrifugation and washed with DMF and EtOH three times, respectively. After that, the UiO-66 was dried at 80 ºC overnight in a vacuum oven.

Synthesis of UiO-67

UiO-67 was synthesized according to the literature procedure.[2] $ZrCl_4$ (100 mg) and H_2BPDC (100 mg) were mixed with 20 mL DMF in a 25 mL teflon reaction kettle under ultrasonication for 5 min. Then, 2 mL acetic acid was added into the aforementioned solution and was stirred for 1 min. The reaction kettle was put into an oven at 120 ºC for 24 h. After cooling to room temperature, the products were collected by centrifugation and washed with DMF and EtOH three times, respectively. After that, the UiO-67 was dried at 80 ºC overnight in a vacuum oven.

Synthesis of PCN-700

The ligand dimethyl 2,2'-dimethylbiphenyl-4,4'-dicarboxylate (H_2Me_2-BPDC) was synthesized according to a reported procedure.[2] $ZrCl_4$ (100 mg) and H_2Me_2-BPDC (100 mg) were dispersed into 20 mL DMF in a vial alongside 1 mL TFA. The solution was put into an oven at 120 ºC for 72 h. The PCN-700 crystals were then collected by centrifugation and washed with fresh DMF 3 times.

Synthesis of PCN-701

PCN-701 was synthesized according to the literature procedure.[2] PCN-700 (100mg) and H_2BDC (200 mg) were dispersed in 40 mL of DMF in a vial. Then, the vial was put into an oven at 75 ºC for 24 h. The PCN-701 crystals were collected by filtration and washed with DMF three times.

Synthesis of PCN-703

The ligand H_2Me_2-TPDC (TPDC: p-terphenyl-4,4″-dicarboxylate) was synthesized according to a reported procedure.[2] PCN-701 (100 mg) and H_2Me_2-TPDC (300 mg) were dispersed into 40 mL of DMF in a vial. The vial was then heated in a 75 ºC oven for 24 h. The PCN-703 crystals were collected by filtration and washed with DMF three times.

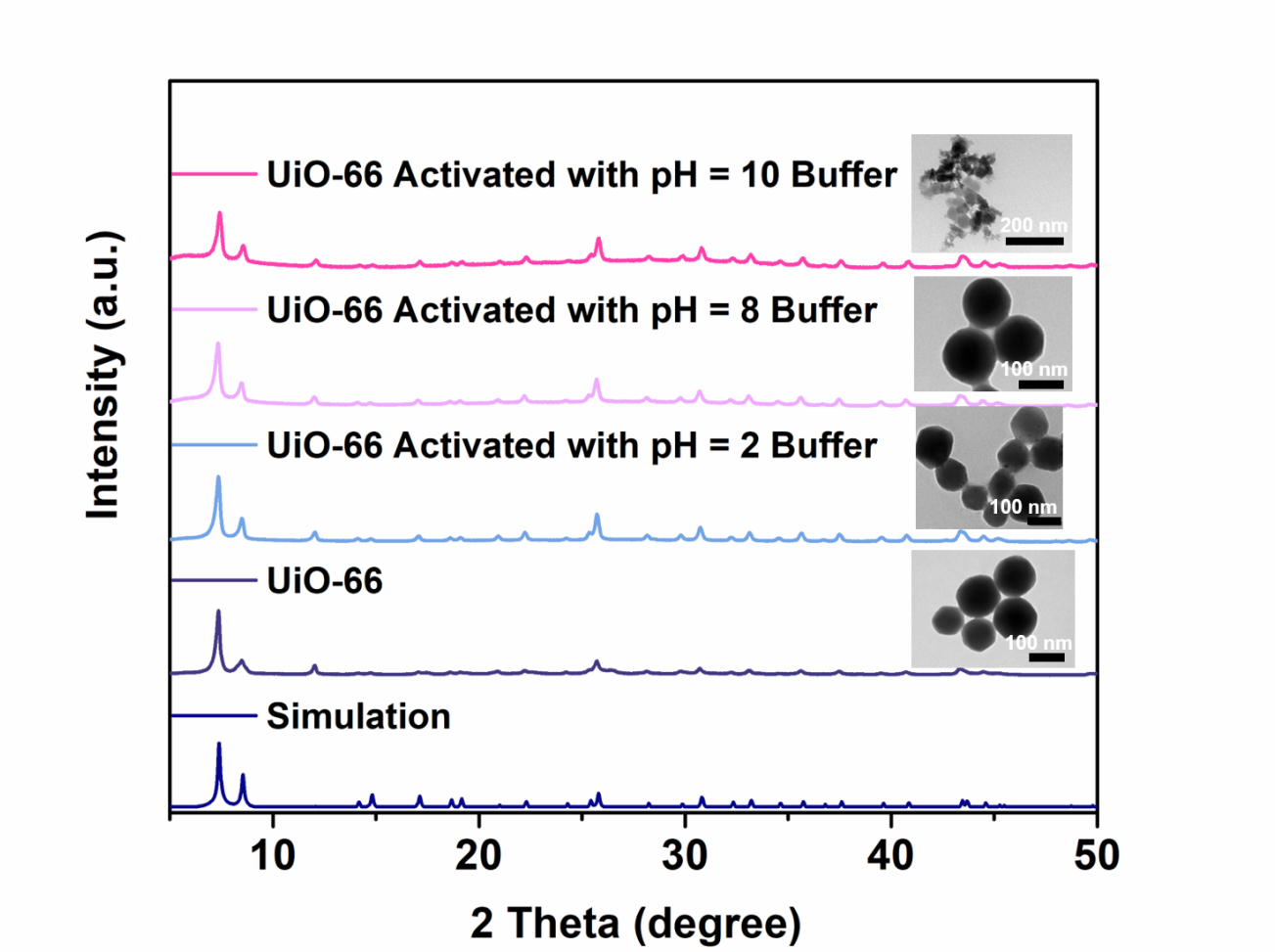

Figure S1. The XRD patterns and TEM images of UiO-66 with the activation of different pH.

The successful synthesis of UiO-66 was confirmed through the comparison of the experimental and simulated powder X-ray diffraction (PXRD) patterns. The stability of UiO-66 under a broad pH range of 2 to 10 was first investigated using both PXRD patterns and TEM morphologies. UiO-66 exhibited outstanding water stability over a wide range of pH from 2 to 8, confirmed by a well-maintained PXRD pattern and morphology. However, after activation with a buffer of pH = 10, the stability of UiO-66 was partially compromised with the decreasing crystallinity and the partial particle decomposition seen in the TEM images. The average size of UiO-66 after activation with pH of 2 and 8 performed almost no difference (110 ± 18 nm for pH = 2 and 117 ± 17 nm, calculated from TEM images by ImageJ).

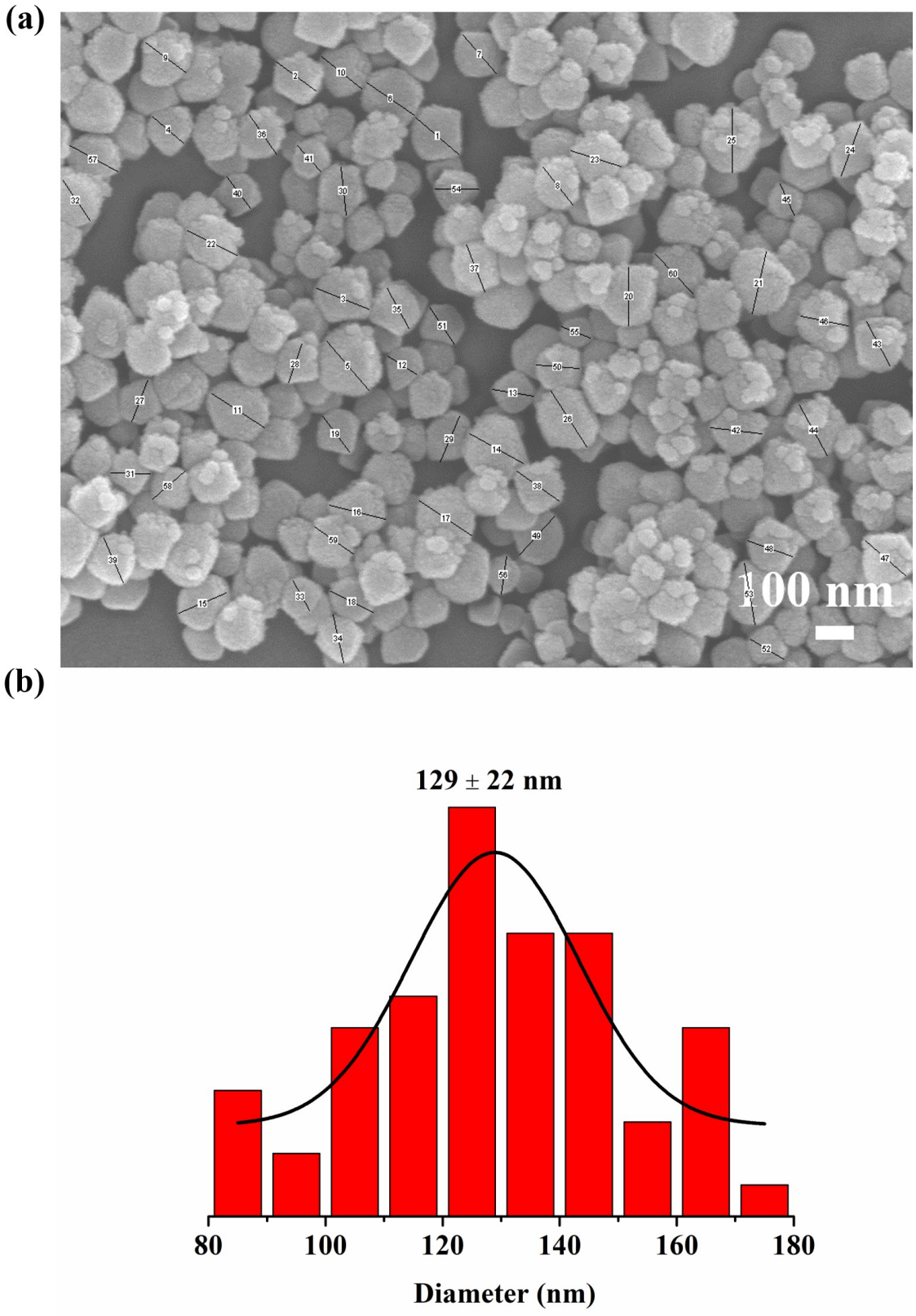

Figure S2. a. SEM image of UiO-66 with the size 129 ± 22 nm measured by ImageJ. b. The size distribution of the as-synthesized UiO-66.

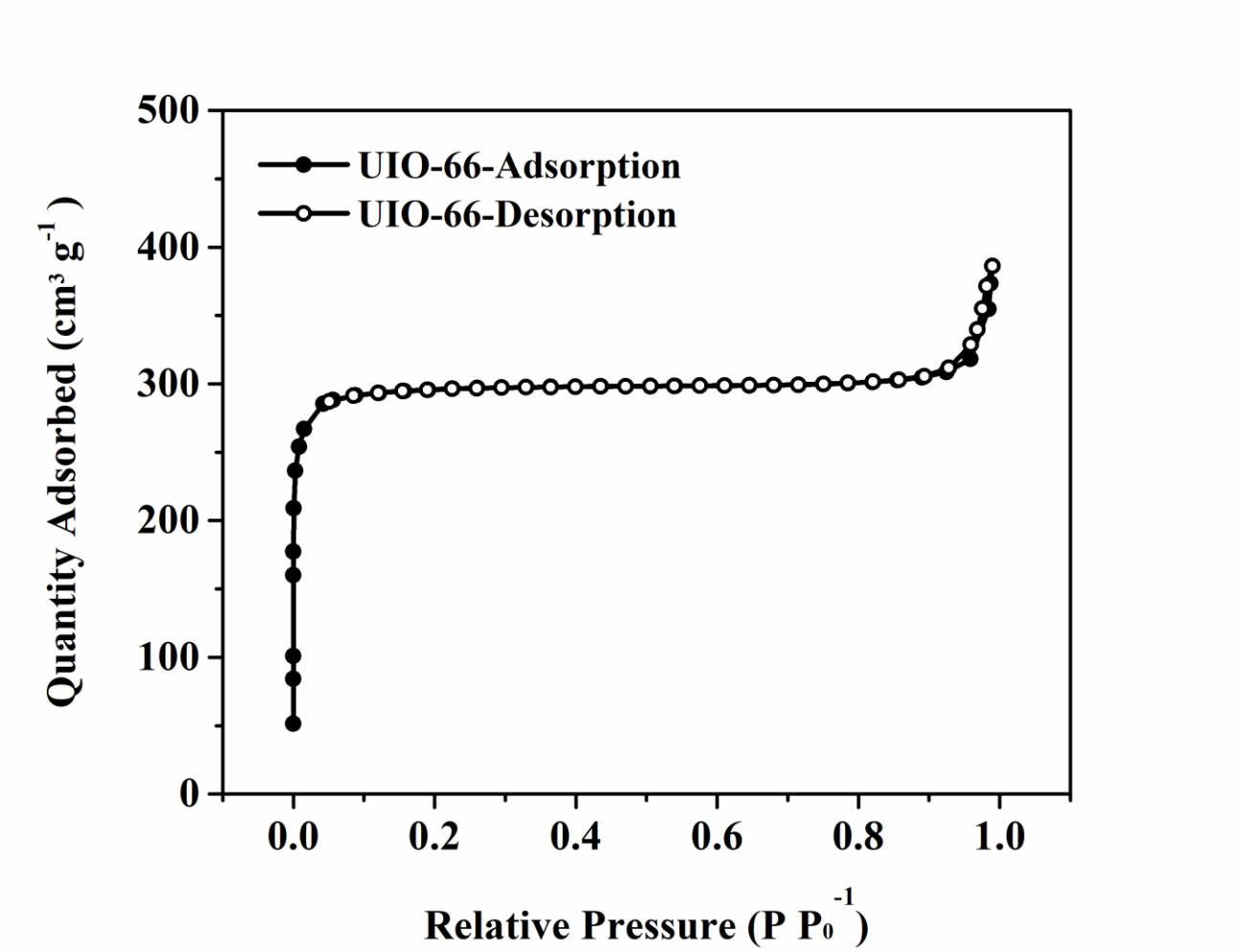

Figure S3. The N_2 sorption isotherms of UiO-66 at 77 K.

The as-synthesized microporous UiO-66 with 129 ± 22 nm exhibited a type I nitrogen adsorption isotherm at 77 K with Brunauer–Emmett–Teller (BET) surface area of 893 $m^2 \cdot g^{-1}$ and a total pore volume of 0.50 $cm^3 \cdot g^{-1}$.

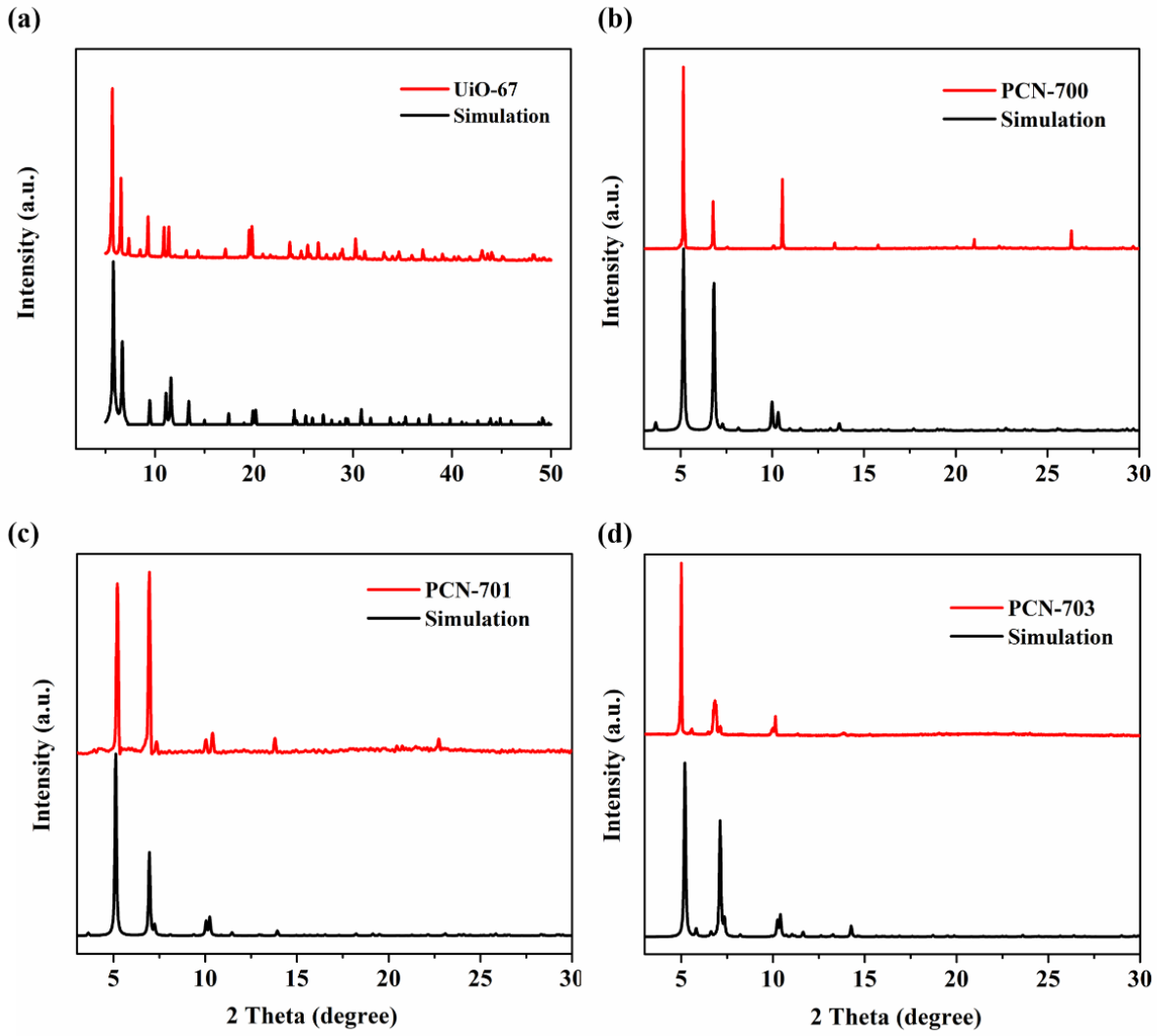

Figure S4. The XRD patterns of different Zr-based MOFs. a. UiO-67, b. PCN-700, c. PCN-701 and d. PCN-703

The PXRD patterns of the as-synthesized UiO-67, PCN-700, PCN-701, and PCN-703 were also consistent with the simulated ones, indicating that these MOFs were successfully prepared with high crystallinity.

3. Catalytic Activity of Zr-based MOFs

Catalytic activity of UiO-66 and UiO-67. Catalytic activity measurements were performed in HEPES buffer (100 mM, pH = 8) at 37 °C. To evaluate the activity of different Zr-MOFs, 30 μL of a 0.1 mM of PNPP was added into a 2970 μL MOF suspensions. The hydrolysis reaction rate was calculated by monitoring the absorbance of p-nitrophenol (PNP) every 2 min for a total of 18 min at 405 nm with a Hitachi UH5300 spectrophotometer. The concentrations of UiO-66 and UiO-67 were 80 $\mu g \cdot mL^{-1}$.

Catalytic activity of PCN-700, 701 and 703. The activity measurements of PCN series were similar as UiO-66 and UiO-67. While, due to the instability of PCN-700, the three MOFs were not dried after synthesis. The concentrations of them were calculated gravimetrically. The experimental solutions were prepared by solvent exchanging. The 1 mL DMF with about 5 mg MOFs was collected by centrifugation, and the supernatant was removed. Then, 1 mL HEPES (pH = 8, 100 mM) was added, and the suspension was sealed up overnight. After that, the MOFs were washed with the same buffer 3 times. The wet MOFs were then dispersed into 1 mL of buffer. 100 μL the above solution was added into 3.4 mL of HEPES buffer and used for activity detection. 30 μL PNPP (0.1 mM) was added into 2.970 mL of the MOF solutions and the product was detected by a UV-Vis spectrophotometer at 405 nm. The concentration of the MOF solution was calculated by removing 100 μL of this solution, placing it on a cover glass, and drying it in a vacuum oven. The weight difference of the cover glass (Δm) before and after the added the MOF was recognized as the weight of the MOF and HEPES molecules in 100 μL water. So, the concentration of the MOF solution could be obtained as $C_{MOF} = \frac{\Delta m - (0.1\times10^{-3}\times100\times238.3)}{0.1}$ (C_{MOF} is the mass concentration of MOF).

Catalytic activity of ZrO_2 and $Zr(OH)_4$. The biomimetic activities of ZrO_2 and $Zr(OH)_4$ were also evaluated to eliminate the possibility of UiO-66 synthesis or activation impurities being responsible for the catalysis. The molar concentrations of ZrO_2 and $Zr(OH)_4$ were 0.048 mM.

General pH activation. To remove the coordinated acetate on the defects of Zr-based MOFs, the material was soaked in HEPES buffer at pH 2, 3, 4, 5, 6, 7 and 8 for 24 h and washed with water two times. The activated Zr-based MOFs were further dried at 80 °C overnight in a vacuum oven before the hydrolysis of PNPP. To distinguish the roles of activation pH and reaction pH, the measurements of the above pH-activated MOFs were performed in the same HEPES buffer (pH = 8, 37 °C). Due to the short reaction time of 20 min comparing with a 24 h activation, the re-activation during the reaction

process was omitted. Meanwhile, the quantity of acetate dissociated from Zr-based MOFs was detected by measuring their concentrations in the corresponding activation buffers with HPLC (Waters model 510). Before detection, 40 μL of HCl (1 $mol \cdot L^{-1}$) was added to 200 μL of the acetate solution. Then, the acetate was detected in its acidic form after eluting through a C18 column (250 × 4.6 mm i.d., 5 μm) with 1 mM sulfuric acid and 8 mM sodium sulfate (pH 2.8) solution as the mobile phase at a flow rate of 1 $mL \cdot min^{-1}$, the concentration was evaluated by UV detection at 210 nm.

General and precise control of reaction pH. The general effects of reaction pH on the hydrolysis of PNPP was also investigated by examining the reaction at pH = 2, 3, 4, 5, 6, 7, 7.5, 7.8, 8, 8.2, 8.5, 9 and 10. As the product, PNP, could not be detected by the UV-Vis spectrophotometer at low pH, the catalytic kinetics was monitored by HPLC on a C18 column with 22 % acetonitrile, 0.1 % trifluoroacetic acid (TFA) and 0.5 % triethylamine solution as the mobile phase at a flow rate of 1 $mL \cdot min^{-1}$ using a UV detector at 405 nm.[3]

The precise control of the reaction pH was achieved through finely tuning the pH from the optimal pH by adding the same volume of NaOH (or HCl) at different concentrations into the 10 mL UiO-66 (80 $\mu g \cdot mL^{-1}$) suspensions. The reaction kinetics were then monitored by UV-Vis spectrophotometry. The precise control of reaction pH with UiO-67 and PCN-700 were also demonstrated by following the above procedure.

DRIFTS measurements. The DRIFTS of the MOFs during biomimetic catalysis was conducted under controlled atmosphere and temperature on a Thermo Fisher Nicolet iS 50 ATR-FTIR spectrometer. All DRIFTS spectra of the MOF catalysts were obtained with following procedure: after a specific reaction time, the MOF catalysts were prepared by the immediate centrifugation at 12000 rpm followed by pre-drying. The solvent was further removed with in-situ heating at a specific temperature (100 or 150 ^{o}C) for 1 h under N_2.

4. The Catalytic Performance under Different Conditions

To study the relationship between substrate and enzyme mimics, the concentrations of UiO-66 were changed from 0 to 120 μg·mL^{-1} with a fixed PNPP concentration of 0.1 mM. Meanwhile, the concentrations of PNPP were changed from 0.01 to 0.4 mmol·L^{-1} with a fixed UiO-66 concentration of 80 μg·mL^{-1}.

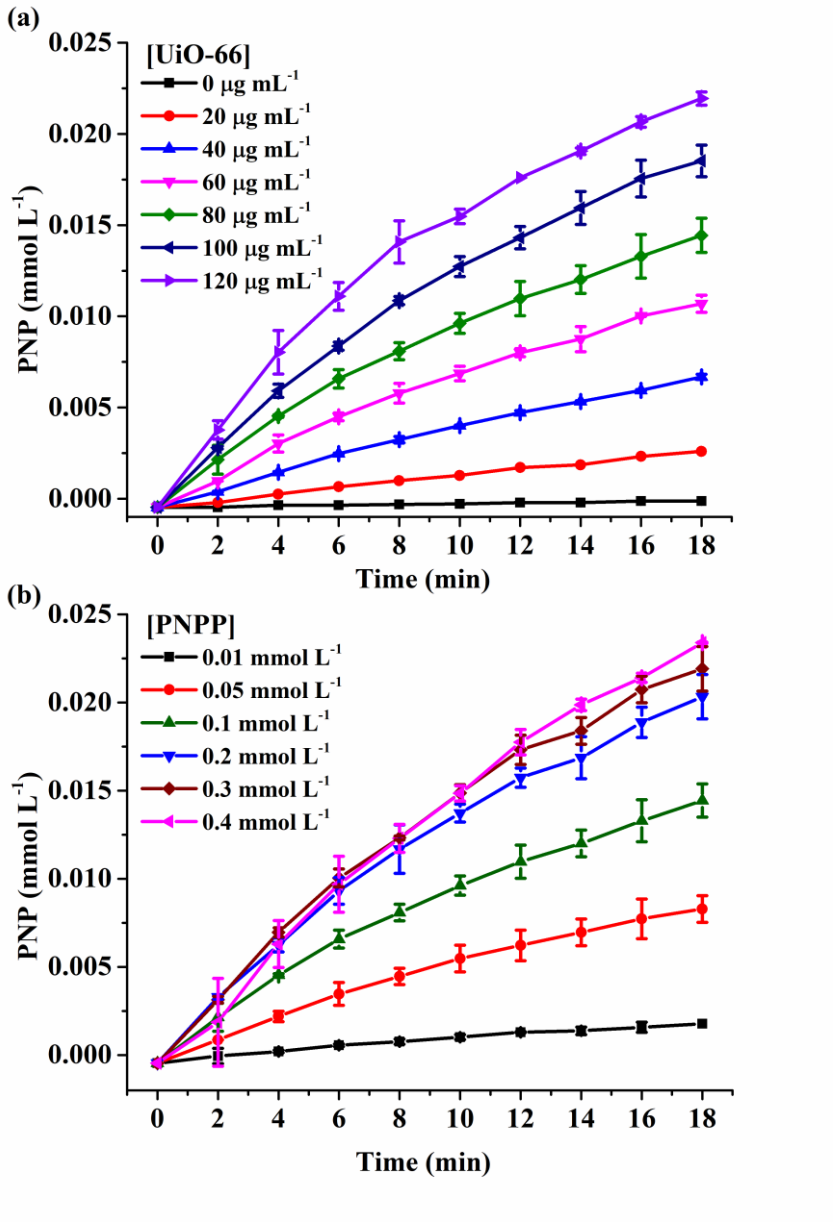

Figure S5. The catalytic activity of UiO-66 in different conditions. a. The catalytic activity of UiO-66 at different UiO-66 concentrations (from 0 to 120 μg·mL^{-1}) at the fixed PNPP concentration (0.1 mM). b. The catalytic activity of UiO-66 with different PNPP concentrations (from 0.01 to 0.4 mM) at the fixed UiO-66 concentration (80 μg·mL^{-1}).

The Standard Curve of PNP Detected by UV. The standard curve was measured by dissolving PNP into pH = 8 HEPES buffers. The concentrations of PNP were 0.0025 mM, 0.005 mM, 0.01 mM, 0.02 mM, and 0.04 mM. The signal was record at 405 nm. The standard curve equation was $\text{Absorbance} = 19.59[PNP] + 0.009$ ([PNP] is the concentration of PNP)

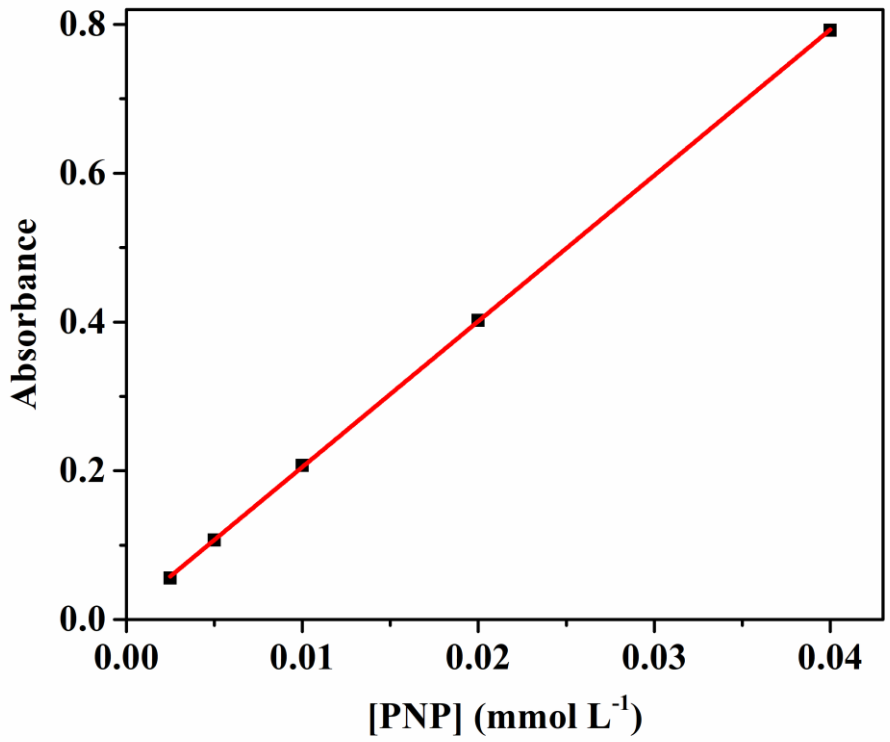

Figure S6. The standard curve of PNP detected by UV in pH = 8.

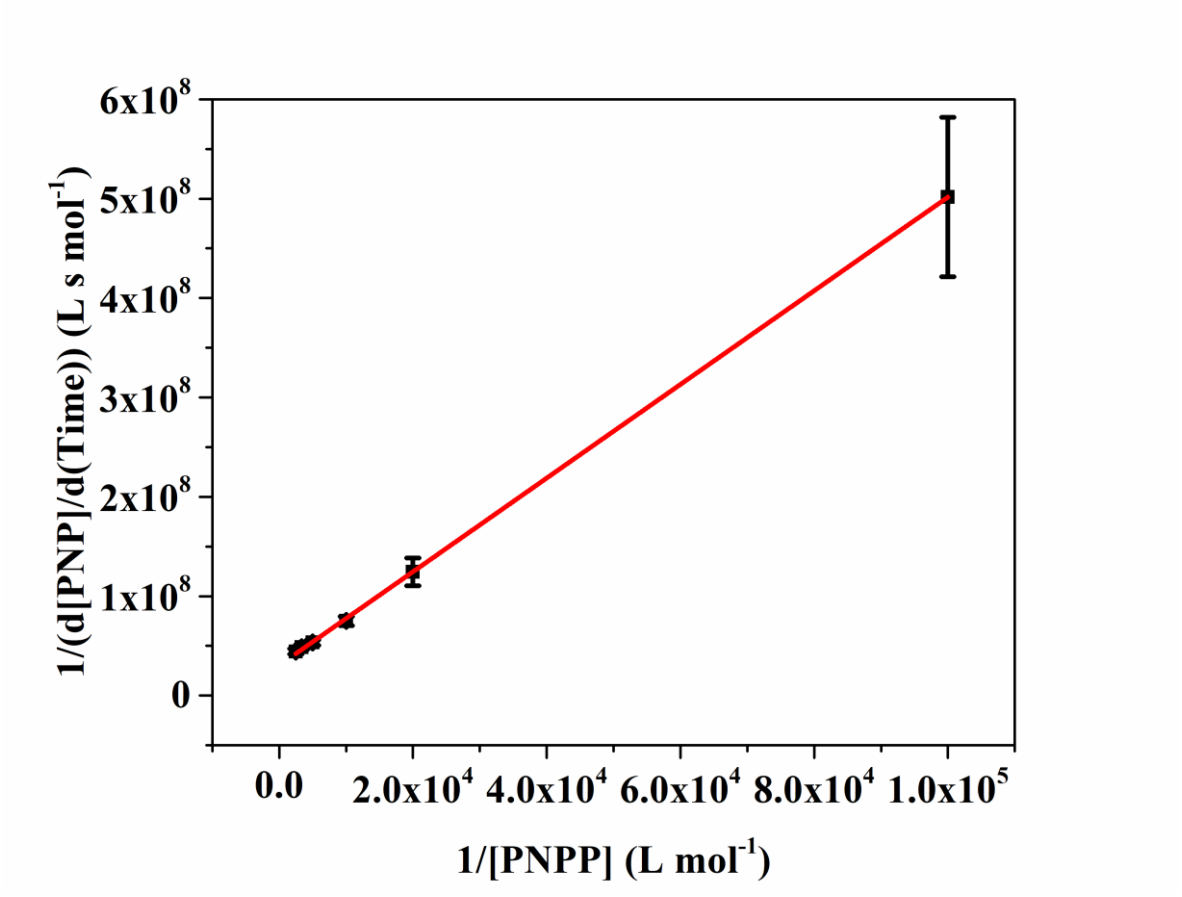

Figure S7. The Lineweaver−Burk plot of UiO-66 (80 μg mL^{-1}) as ALP mimic (K_m=1.55×10^{-4} M).

5. Recyclability and Reusability of UiO-66

After each hydrolysis reaction, UiO-66 was re-collected by centrifugation, washed with water, and dried at 80 °C in a vacuum oven overnight. The concentration of UiO-66 was 1 mg·mL^{-1}. The concentration of PNPP was 0.1 mM.

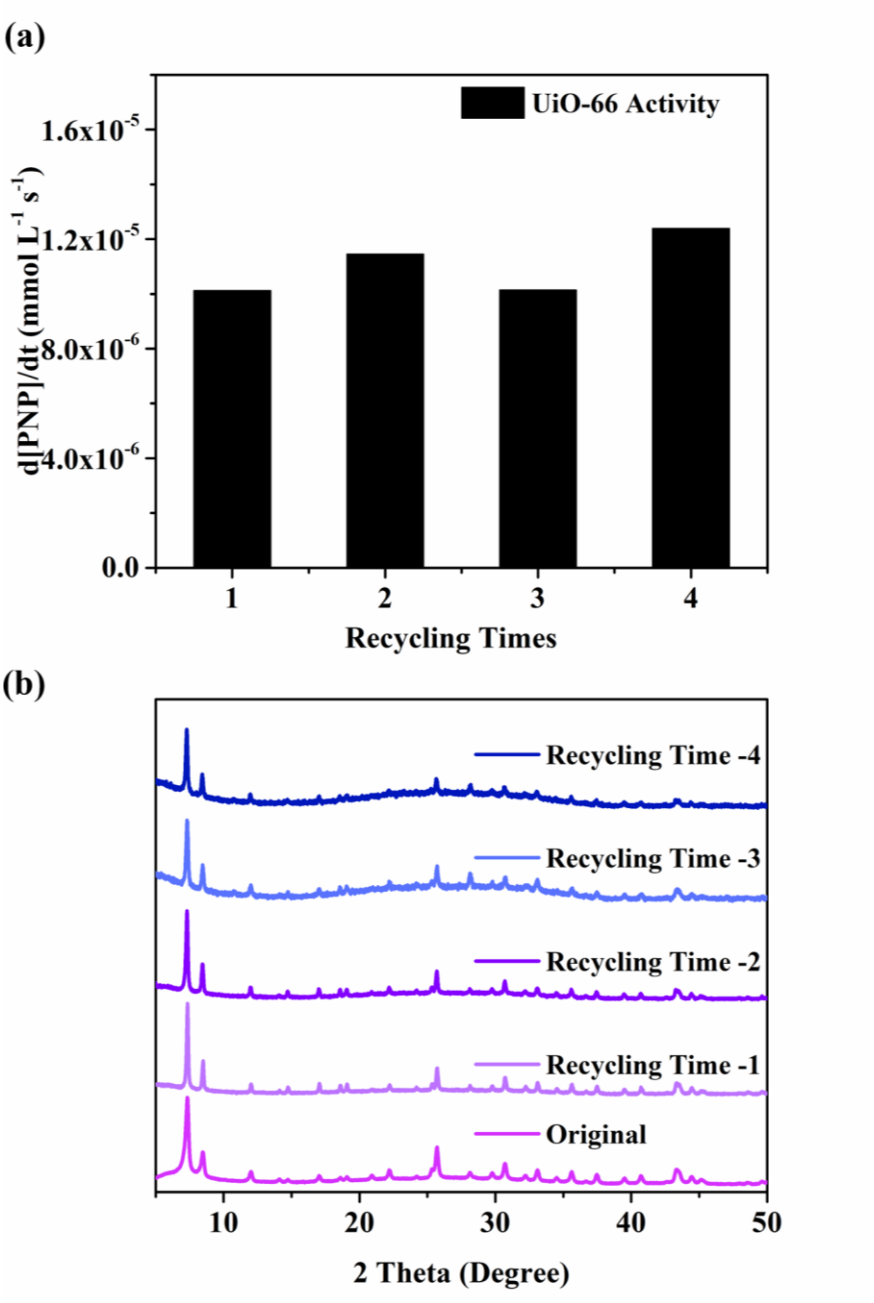

Figure S8. a. The activity of UiO-66 recycled for four times. The performance fluctuation was due to highly pH-sensitive feature of the catalysis reaction. b. The XRD of UiO-66 recycled for four times.

7. The Calculation about the Number of the Total Defects by TGA without the Consideration of Acetate (N_{total})

The calculation method was similar as the reported one.[4] For charity, the residue in each TGA experiment is recognized as pure ZrO_2. Then, the defect-free UiO-66 was recognized as $Zr_6O_6(BDC)_6$

before the last weight loss. Then, the heating procedure could be considered as:

$$Zr_6O_6BDC_6(s) + 45O_2(g) \rightarrow 6ZrO_2(g) + 48CO_2(g) + 12H_2O(g)$$

In a defect-free UiO-66, if the end weight of a TGA is normalized to 100 %, the TGA plateau (representing the empty, solvent free, and dehydroxylated MOF) should ideally be found at 220.2 % ($W_{Theo.plat}$) on the TGA trace (MW($Zr_6O_6(BDC)_6$) / MW($6ZrO_2$)). Then, the weight contribution per BDC linker ($Wt.PL_{Theo}$) could be calculated as:

$$Wt.PL_{Theo} = \frac{W_{Theo.plat} - 100\ \%}{6} = 20.03\ \%$$

Usually, the plateau could not be obtained because of the existence of defects. Assuming that each missing linker is charge compensated by an extra oxide anion on the cluster, giving the material the following average composition:

$$Zr_6O_{6+0.5x}BDC_{6-0.5x}$$

Where x is the number of defects per $Zr_6O_6(BDC)_6$ which have been defined as the number of missing monocarboxylate linkers in the manuscript.

Then, the number (6-0.5x) cold be calculated as: $6 - 0.5x = \frac{W_{Exp.plat} - 100\%}{20.03\%}$

Where the $W_{Exp.plat}$ is the experimental TGA plateau.

Example: The UiO-66 with 129 nm pre-activated with pH = 8 buffer.

The TGA measurements were run up to 800 °C under a flow of air and with a temperature ramp of 10 °C min^{-1}.

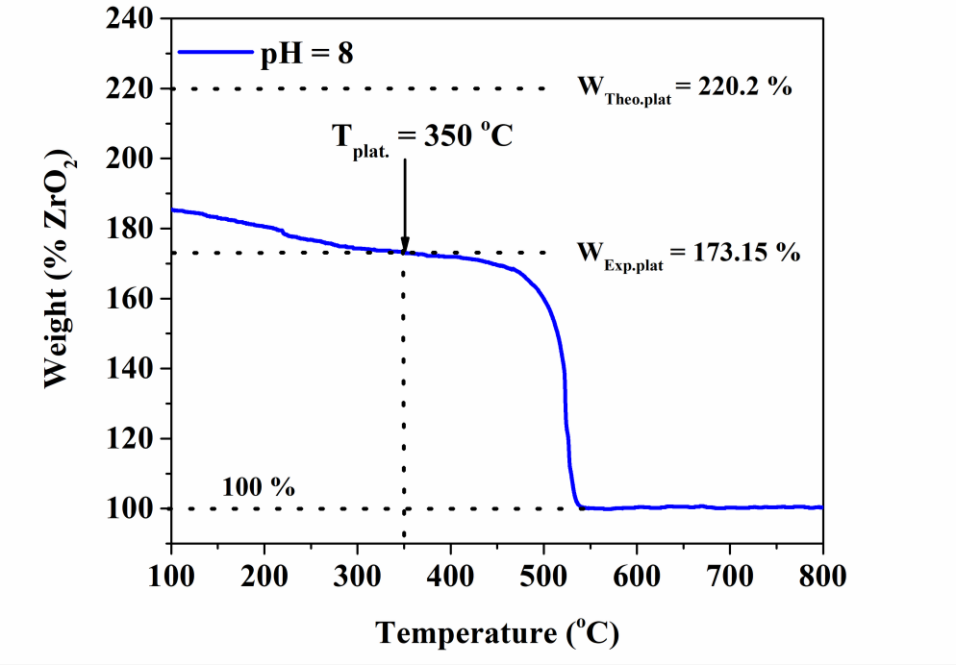

Figure S9. TGA performed on UiO-66 with 129 nm. Sample was activated with pH = 8 HEPES buffer prior to measurement TGA trace (normalized such that end weight = 100%).

$$6 - 0.5x = \frac{W_{Exp.plat} - 100\%}{20.03\%} = \frac{173.15\% - 100\%}{20.03\%} = 3.652$$

Then, the number of missing linkers per $Zr_6O_6(BDC)_6$ is equal to 2.348 and the N_{total} is equal to 4.696.

Table S1. The defects of UiO-66 in different conditions (per $Zr_6O_6(BDC)_6$) without the consideration of acetate (N_{total}).

Size nm	Activation pH	Number of missing linkers	Average number of missing linkers	N_{total}	Average N_{total}
129	2	2.420		4.840	
129	3	2.462		4.924	
129	4	2.342		4.684	
129	5	2.166	2.320 ± 0.121	4.332	4.649± 0.245
129	6	2.383		4.766	
129	7	2.149		4.298	
129	8	2.348		4.696	
407	8	2.569	/	5.138	/
671	8	2.745	/	5.490	/

8. The Calculation about the Number of the Modified Defects by HPLC with the Consideration of Acetate (N_{modif})

Usually, the defects calculated by TGA are partly occupied by the modulators in the synthesis to restrict the amorphous growth. Thus, the measured total number of defects were overestimated, while the existence of monocarboxylate modulators must be considered. The modified total defect number N_{modif} under different activation pH was calculated by quantifying the total and dissociated monocarboxylates with HPLC. First of all, the acetate should be removed from the UiO-66 and be quantified. The acetate was detected in its acidic form after eluting through a C18 column (250 × 4.6 mm i.d., 5 μm) with 1 mM sulfuric acid and 8 mM sodium sulfate (pH 2.8) solution as the mobile phase at a flow rate of 1 $mL \cdot min^{-1}$, the concentration was evaluated by UV detection at 210 nm. Before detection, 40 μL HCl (1 $mol \cdot L^{-1}$) was added to 200 μL of the acetate solution. The standard curve equation was $\text{Peak Area} = 501.13[CH_3COOH] + 987.37$ ([CH_3COOH] is the concentration of the dissociated acetate)

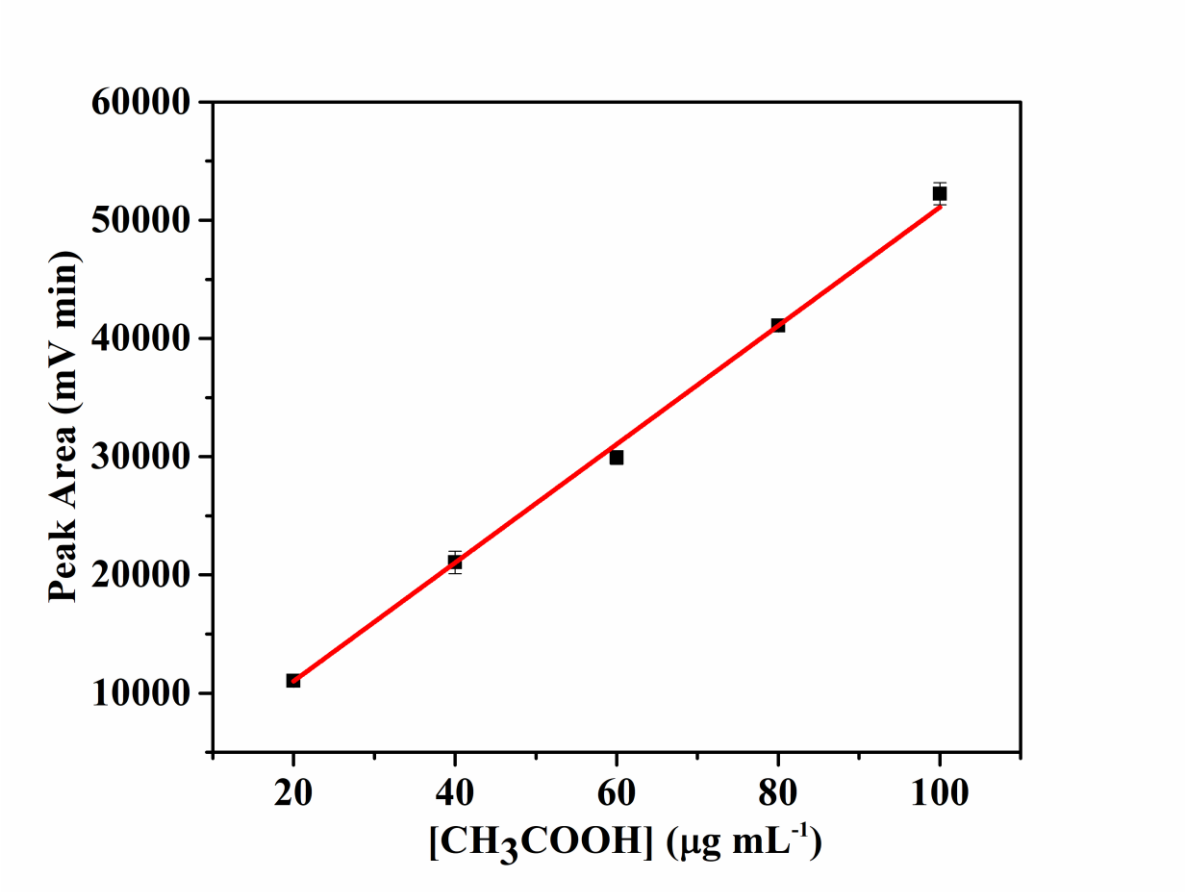

Figure S10. The standard curve of CH_3COOH detected by HPLC.

Then, the quantity of acetate dissociated from UiO-66 by the activation procedure was detected by measuring their concentrations in the corresponding activation buffers with the HPLC method.

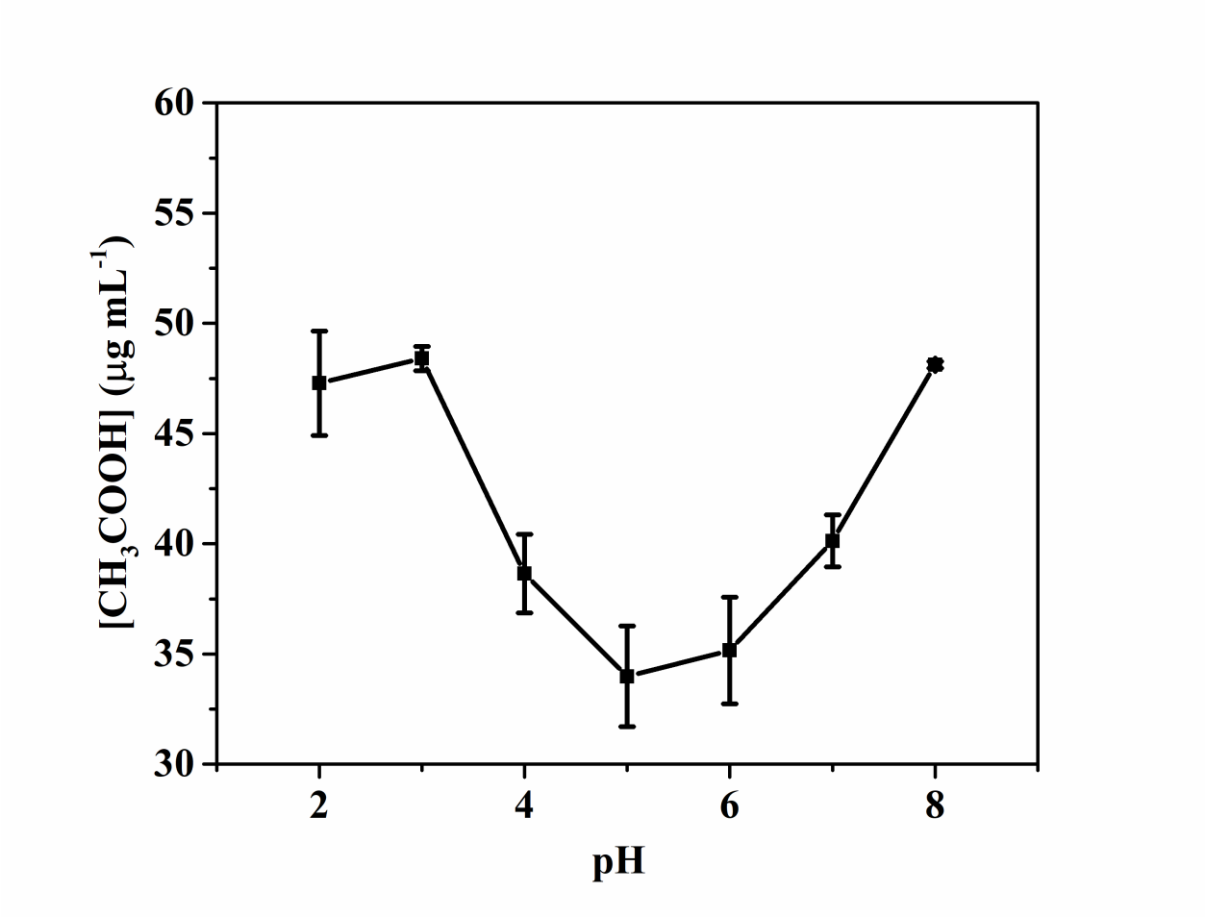

Figure S11. The concentration of dissociative acetate modulator after the activation procedure.

Calculation of N_{modif} by HPLC:

The calculation method was derived from the titration method to calculate the number of the missing linkers.[5] Firstly, the number of missing BDC had been calculated by the methods in **Section 7**. The average number of these missing BDC was calculated as 2.320 in Table S1. We assumed that these defects were partly occupied by several acetates before activation. Herein, the number of acetates was recorded as *y*, then, UiO-66 could be recorded as: $Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_y(OH/H_2O)_{4.64-y}$. Then, the concentration of CH_3COOH which dissociated from the UiO-66 entirely could be calculated as:

$$MW_{(UiO-66)_y} = 1443.92 + 24y \ \ Da$$

$$[CH_3COOH] = \frac{4y}{MW_{(UiO-66)_y}}$$

Where 4 $g \cdot L^{-1}$ is the concentration of UiO-66 we used.

Herein, the UiO-66 was destroyed by adding 4 mg material into 1 mL 20 $mg \cdot mL^{-1}$ K_3PO_4.[6] Then, the solution was collected by filtering out the solid and acidated by adding 40 μL HCl (1 $mol \cdot L^{-1}$) to 200 μL the above solution. The concentration of CH_3COOH was detected by HPLC as 0.926 mM.

Table S2. Calculations for the number of the dissociated CH_3COOH from the original UiO-66 (per $Zr_6O_4(OH)_4(BDC)_6$).

Value of *y*	Molecular formula	MW Da	[CH_3COOH] mM
0.300	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.300}(OH/H_2O)_{4.340}$	1451.12	0.827
0.320	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.320}(OH/H_2O)_{4.320}$	1451.60	0.882
0.330	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.330}(OH/H_2O)_{4.310}$	1451.84	0.909
0.340	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.340}(OH/H_2O)_{4.300}$	1452.08	0.937
0.335	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.335}(OH/H_2O)_{4.305}$	1451.96	0.923
0.336	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.336}(OH/H_2O)_{4.304}$	1451.98	**0.926**
0.337	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.337}(OH/H_2O)_{4.303}$	1452.01	0.928

From Table S2, the conclusion could be made that the number of acetate per Zr_6 cluster was 0.336. As a result, the original molecular formula of the UiO-66 we synthesized here was $Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.336}(OH/H_2O)_{4.304}$.

Subsequently, the molecular formula of the activated UiO-66 under different activation pH could also be calculated by the same method. Herein, the molecular formula of UiO-66 could be recognized as $Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.336-z}(OH/H_2O)_{4.304+z}$. While, *z* is the number of the dissociated CH_3COOH in the activation solution and N_{modif} is equal to 4.304+z.

Table S3. Calculations for the number of the dissociated CH_3COOH from the activated UiO-66 (per $Zr_6O_4(OH)_4(BDC)_6$).

Value of *z*	Molecular formula	MW Da	[CH_3COOH] mM
0.200	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.136}(OH/H_2O)_{4.504}$	1447.86	0.552
0.205	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.131}(OH/H_2O)_{4.509}$	1447.72	0.566
0.208	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.128}(OH/H_2O)_{4.512}$	1447.63	0.575
0.209	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.127}(OH/H_2O)_{4.513}$	1447.60	**0.578**
0.215	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.121}(OH/H_2O)_{4.519}$	1447.43	0.594
0.216	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.120}(OH/H_2O)_{4.520}$	1447.40	**0.597**
0.217	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.119}(OH/H_2O)_{4.521}$	1447.37	0.600
0.236	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.100}(OH/H_2O)_{4.540}$	1446.82	0.652
0.237	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.099}(OH/H_2O)_{4.541}$	1446.79	**0.655**
0.238	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.098}(OH/H_2O)_{4.542}$	1446.76	0.658
0.245	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.091}(OH/H_2O)_{4.549}$	1446.56	0.677
0.246	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.090}(OH/H_2O)_{4.550}$	1446.53	**0.680**
0.247	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.089}(OH/H_2O)_{4.551}$	1446.50	0.683
0.288	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.048}(OH/H_2O)_{4.592}$	1445.31	0.797
0.289	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.047}(OH/H_2O)_{4.593}$	1445.28	**0.800**
0.290	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.046}(OH/H_2O)_{4.594}$	1445.25	0.803
0.293	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.043}(OH/H_2O)_{4.597}$	1445.17	0.811
0.294	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.042}(OH/H_2O)_{4.598}$	1445.14	0.813
0.295	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.041}(OH/H_2O)_{4.599}$	1445.11	**0.816**
0.296	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.040}(OH/H_2O)_{4.600}$	1445.08	**0.819**
0.297	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.039}(OH/H_2O)_{4.601}$	1445.05	0.822
0.300	$Zr_6O_4(OH)_4(BDC)_{3.680}(CH_3COO)_{0.036}(OH/H_2O)_{4.604}$	1444.96	0.830

Then, the number of the dissociated acetate and the N_{modif} were calculated in Table S4.

Table S4. The number of the dissociated acetate and the modified total defects of the activated UiO-66 (per $Zr_6O_4(OH)_4(BDC)_6$) (Nmodif).

Activation pH	Number of the entire acetate	Number of the dissociated acetate	N_{modif}
2		0.289	4.593
3		0.296	4.600
4		0.237	4.541
5	0.336	0.209	4.513
6		0.216	4.520
7		0.246	4.550
8		0.295	4.599

9. The Calculation about the Number of the catalytically effective defects (N_{eff})

Considering about the complicacy of MOF structures, the modified total defects do not work entirely due to the accessibility issue. Besides, we hypothesized that the catalytic efficacy should be proportional to the number of the catalytically effective defects (N_{eff}).

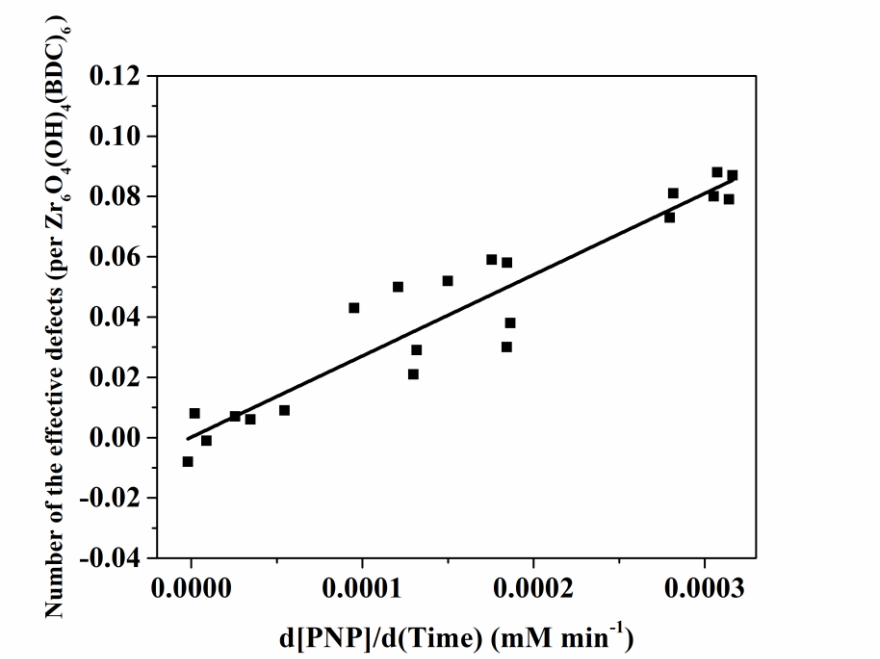

Figure S12. The plots between the differential defects numbers and differential catalytic activity. The slope calculated here is 272.5.

Then (N_{eff}) could be calculated through its catalytic activity.

Table S5. The number of the catalytically effective defects of the activated UiO-66 (per $Zr_6O_4(OH)_4(BDC)_6$) with different activation pH (N_{eff}).

Activation pH	N_{eff}
2	0.214
3	0.221
4	0.174
5	0.138
6	0.138
7	0.188
8	0.224

10. The Catalytic Activity of the Activated UiO-66 with Different Activation pH.

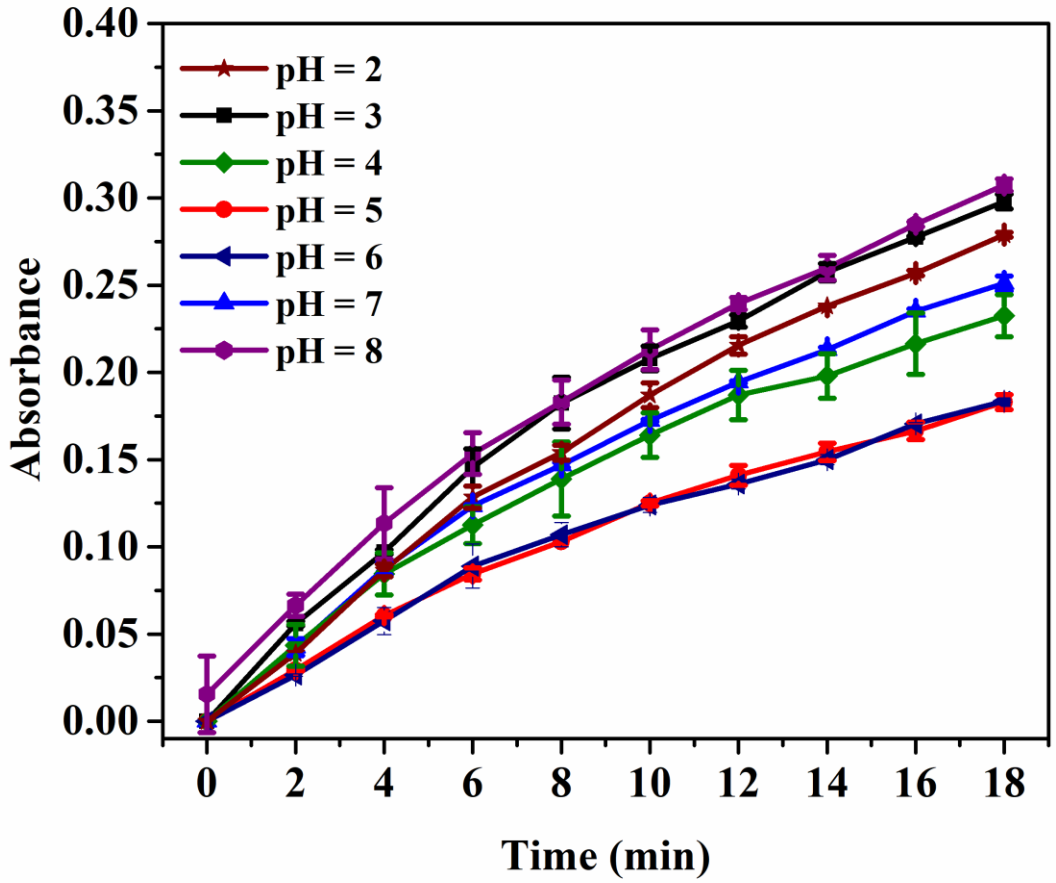

Figure S13. The catalytic activity of UiO-66 activated at pH = 2, 3, 4, 5, 6, 7 and 8.

11. pH Optimization Detected by HPLC

The reaction pH was changed from 2 to 10 and the product was measured by HPLC on a C18 column (250 × 4.6 mm i.d., 5 μm particle size) with a 22 % ACN, 0.1 % TFA and 0.5 % triethylamine solution as the mobile phase with a flow rate of 1 $mL \cdot min^{-1}$. The signal was recorded at 405 nm.[3]

Table S6. The standard curve of PNP detected by HPLC in different pH.

Reaction pH	Standard curve
2	$\text{Peak Aera} = 2.36 \times 10^7 x + 8.21 \times 10^4$
3	$\text{Peak Aera} = 2.74 \times 10^7 x + 2.14 \times 10^4$
4	$\text{Peak Aera} = 2.07 \times 10^7 x - 18.5 \times 10^4$
5	$\text{Peak Aera} = 2.06 \times 10^7 x + 9.14 \times 10^4$
6	$\text{Peak Aera} = 4.04 \times 10^7 x + 6.46 \times 10^4$
7	$\text{Peak Aera} = 2.49 \times 10^7 x + 1.12 \times 10^4$
7.5	$\text{Peak Aera} = 1.34 \times 10^7 x - 2.17 \times 10^4$
7.8	$\text{Peak Aera} = 1.82 \times 10^7 x + 4.27 \times 10^4$
8	$\text{Peak Aera} = 0.94 \times 10^7 x + 0.62 \times 10^4$
8.2	$\text{Peak Aera} = 1.13 \times 10^7 x + 3.93 \times 10^4$
8.5	$\text{Peak Aera} = 1.43 \times 10^7 x - 3.71 \times 10^4$
9	$\text{Peak Aera} = 1.01 \times 10^7 x + 1.04 \times 10^4$
10	$\text{Peak Aera} = 5.39 \times 10^7 x - 1.44 \times 10^4$

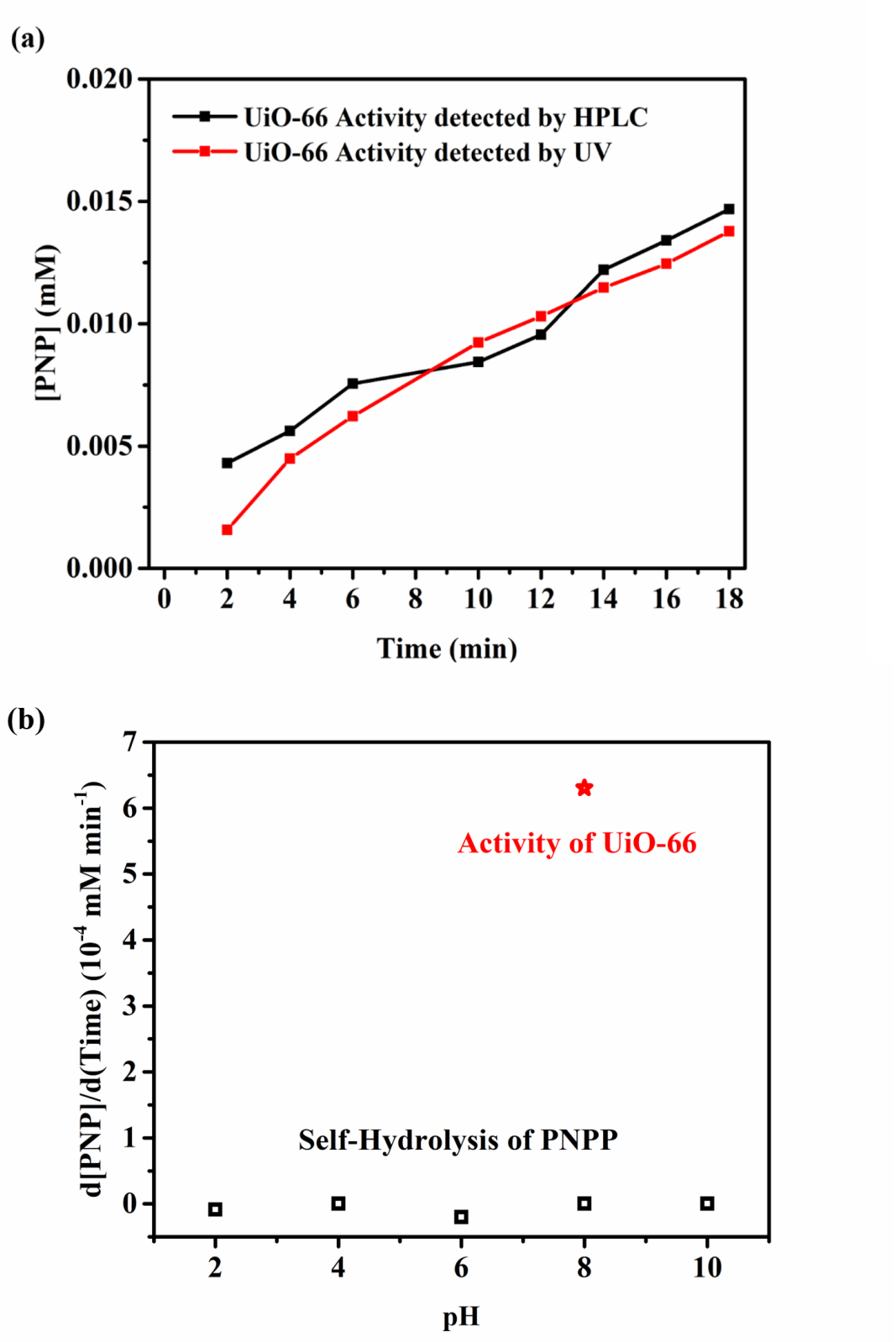

Figure S14. a. Comparison of the detection results between UV and HPLC. b. The self-hydrolysis of PNPP in different pH at 37 °C. The self-hydrolysis of PNPP in pH =2, 4, 6 and 10 was monitored by HPLC, while the self-hydrolysis of PNPP in pH =8 was monitored by UV.

12. Titration of Activated UiO-66

Titration experiments were conducted according to a reported procedure with a few changes. UiO-66 (49 mg) was dispersed into 200 mL water and the pH of the solution was adjusted to 3 with 0.1 M HCl. Then, the sample was titrated with 0.1 M NaOH until the pH reached approximately 10.3.[5]

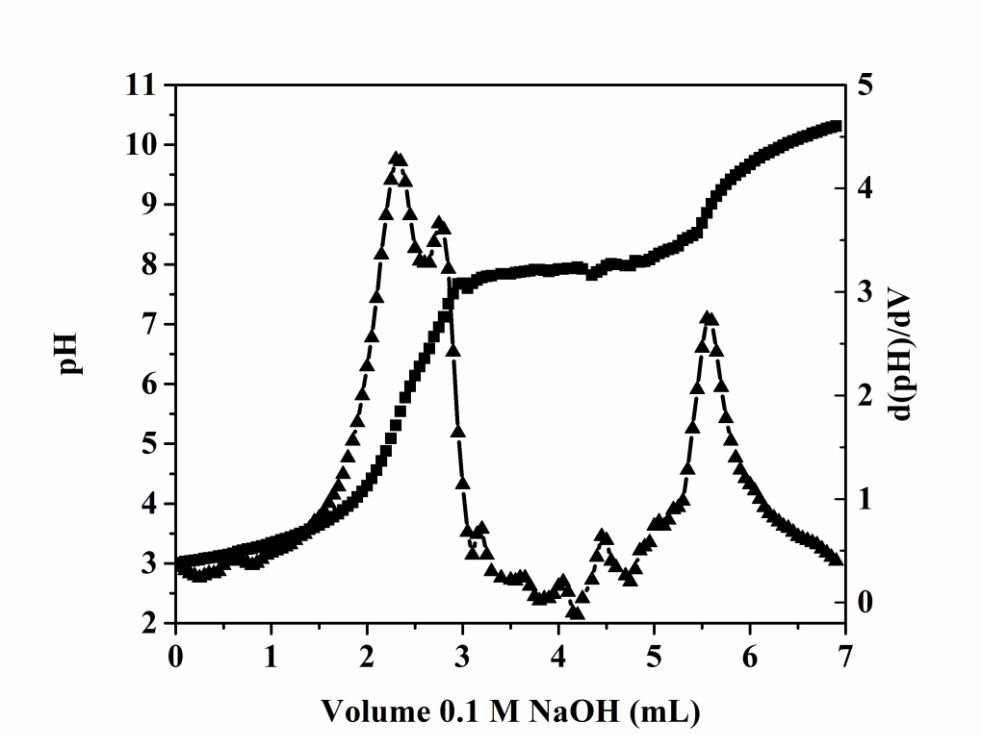

Figure S15. The acid–base titration curve of UiO-66 (square) and first derivative curve (triangle).

13. Activation Energy Calculation

To compare the activation energy, the reaction temperature was changed for the hydrolysis of PNPP (0.1 mM) by UiO-66 (80 μg·mL^{-1}). The activation energy was calculated according to the Arrhenius equation: $k = Ae^{\frac{-E_a}{RT}}$. The k value we used here is the initial velocity of the activity.

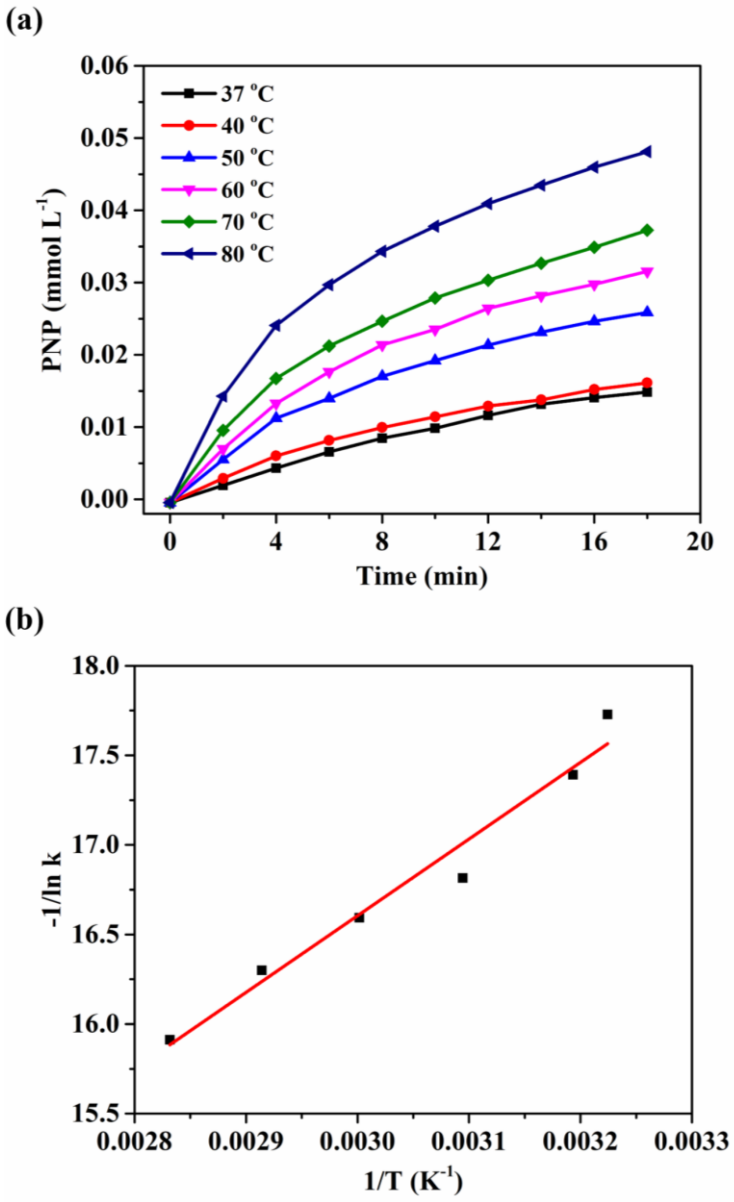

Figure S16. The activation energy calculation. a. The activity curve of the hydrolytic reaction catalyzed by UiO-66 (80 μg·mL^{-1}). b. Calculation method for the activation energy for the hydrolytic reaction. The equation was $-\ln K = 4279.91\frac{1}{T} + 3.76$ and E_a = 35.58 kJ·mol^{-1} = 8.5 kcal·mol^{-1}. It is worth noting that the self-hydrolysis of PNPP could not be ignored at high temperature.

14. Theoretical Investigation.

All molecular geometries of the model complexes were optimized at the DFT M06-L level, which was implemented in Gaussian 09. The effective core potentials (ECPs) of Hay and Wadt with double-ζ valence basis sets (LanL2DZ) were used to describe the Zr atoms. In addition, polarization functions were added for Zr (ζf = 0.875). The 6-31 G(d,p) basis set was used for all other atoms, such as C, H, O, N and P. The transition states found were further confirmed by calculating the intrinsic reaction coordinate routes toward the corresponding minima and reoptimizing from the final phase of the intrinsic reaction coordinate (IRC) paths to reach each minimum. Solvent effects were computed with the SMD model using gas phase optimized structures. The values for ΔG_{sol} reported in this paper are relative Gibbs free energies calculated at 298 K in solution. Detailed comparisons of the different basis set levels and functionals (B3LYP, B3LYP-D, and M06L) are given below The geometries were displayed using CYLview.[7]

Table S7. **The relative free energies of the intermediates and transition states**. These data obtained at B3LYP(6-31G(d,p)+ LANL2DZ), B3LYP-D(6-31G(d,p)+ LANL2DZ) , M06L(6-31G(d,p)+ LANL2DZ) and SMD//B3LYP-D(6-31G(d,p)+ LANL2DZ) and SMD// M06L(6-31G(d,p)+ LANL2DZ) calculation level for the hydrolysis of p-nitrophenyl phosphate (PNPP**) by MOF UiO-66** are shown.

MOF-node	**species**	**B3LYP (gas)**	**B3LYP-D (gas)**	**M06L(gas)**	**B3LYP-D (sol)**	**M06L (sol)**
OH-Zr(OH)Zr-H_2O	1''	-29.2	-41.3	-39.3	-0.2	-5.1
	2	-104.2	-119.7	-116.6	-59.0	-44.4
	TS2	-73.8	-90.8	-92.8	-24.4	-24.5
	Pro-2	-177.6	-190.4	-191.0	-60.1	-59.8
OH-Zr(O)Zr-H_2O	1	-130.8	-137.2	-140.0	-25.5	-34.8
	3	-108.5	-120.3	-112.2	-45.0	-30.7
	TS3	-87.8	-103.6	-99.9	-20.8	-16.9
	Pro-3	-176.3	-190.9	-190.6	-50.2	-49.8
OH-Zr(O)Zr-OH	1'	-201.6	-206.0	-193.6	-89.8	-75.8
	4	-60.0	-69.2	-69.5	-68.8	-57.8
	TS4	-59.3	-68.4	-68.0	-59.1	-53.5
	Pro-4	-171.6	-177.5	-178.4	-69.6	-70.1

Cartesian coordinates for all optimized structures in XYZ format.

State **ZrZr**

C	2.222217	3.119773	-2.401085
O	2.702481	2.791531	-1.270643
Zr	2.059617	1.107206	-0.020278
O	0.501126	0.480016	1.219980
Zr	-1.309826	1.210949	0.480567
O	-3.554763	0.767516	0.476456
C	-4.204184	-0.224562	0.047667
O	-3.744554	-1.311138	-0.421672
Zr	-1.688019	-1.957978	-0.954873
O	-0.117874	-1.546534	-2.529056
Zr	1.814139	-2.066170	-1.475049
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O	1.595965	-0.004775	-1.625493
O	-1.464439	2.574565	-2.661330
C	-2.035624	3.251612	-1.766196
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O	-1.249677	-3.917479	-1.918105
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O	0.994215	-3.987233	-2.251330
O	0.219946	-2.136474	-0.131808
Zr	0.531247	-1.457800	1.819693
O	1.873187	-3.240202	1.975734
C	2.511937	-3.908009	1.109601
O	2.640341	-3.659208	-0.122715
O	-2.179688	-3.510595	0.593777
C	-1.713459	-3.777910	1.737444
O	-0.810381	-3.158354	2.373773
O	-1.570899	-0.940250	1.109343
O	2.362168	-1.061274	0.523911
O	3.971917	-1.547258	-1.567724
C	4.612329	-0.494584	-1.261292
O	4.176154	0.530967	-0.671411
O	2.160772	-0.540670	3.142830
C	2.820783	0.527123	3.029338
O	2.961772	1.257076	1.993648
O	-0.584541	-0.456664	3.551650
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H	-2.287210	-1.133466	1.724941
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H	-3.369955	-0.758345	-4.614661
H	-2.473517	4.212158	-2.076870
H	2.430133	-0.942284	-5.475351
H	2.607936	4.054572	-2.834985
H	-2.151651	-4.649682	2.248218
H	-1.409274	1.018676	4.638256

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H	5.679434	-0.489317	-1.535120
H	3.355150	0.871125	3.928905
H	-0.266714	-5.487183	-2.699088

State **1**

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O	-1.430409	0.361197	-1.091083
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O	-0.707681	3.214402	1.595980
O	2.767363	2.721926	-1.414886
Zr	2.100754	1.204617	0.083715
O	1.817777	3.153308	1.267168
O	4.140840	0.560614	-0.588546
C	4.527812	-0.425563	-1.281124
O	3.837363	-1.402270	-1.689141
Zr	1.644204	-1.876465	-1.575104
O	2.268301	-1.015022	0.453205
Zr	0.437964	-1.441611	1.732562
O	-0.551733	-0.675856	3.584053
C	-1.282736	0.331112	3.813382
O	-1.727287	1.173466	2.983427
O	0.219128	2.224800	-0.667755
O	1.449505	0.198248	-1.584077
O	3.120924	0.992448	2.102397
C	2.937060	0.172944	3.056199
O	2.112948	-0.777212	3.111920

O	0.452484	0.549984	1.166347
O	-0.296057	-1.282330	-2.589383
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O	-1.650481	-0.798540	1.132472
O	2.098752	-1.579474	-3.744125
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O	0.930218	0.251699	-4.409818
O	0.749020	-3.742587	-2.418028
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O	0.072423	-2.013400	-0.227232
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O	-1.896244	0.393642	-3.933168
O	-2.410899	-3.283412	0.477293
C	-1.898306	-3.674776	1.564904
O	-0.939132	-3.151449	2.201847
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H	3.583927	0.310504	3.937948
H	-0.566138	-5.196621	-2.858328
H	2.291950	3.077362	2.106961
H	-1.008351	3.325473	2.507906
H	0.236646	3.185916	-0.762794
H	0.807353	3.263429	1.476261

State **2**

C	6.111977	9.812529	-14.126132
C	6.079767	8.531156	-14.639012
C	7.193720	7.660546	-14.459291
C	8.315366	8.143015	-13.724859
C	8.339851	9.422643	-13.213224
C	7.237144	10.272808	-13.415570
O	7.265844	6.432082	-14.914131
P	6.142931	5.703660	-16.099597
O	4.762961	5.950713	-15.529197
N	7.263354	11.604087	-12.892651
O	6.283149	12.348640	-13.084757
O	6.556434	6.329783	-17.404576
O	6.643309	4.227050	-15.910751

Zr	6.633524	2.195144	-15.768841
O	5.228494	2.182460	-17.389694
Zr	5.407068	0.210661	-18.308269
O	6.609723	0.211313	-16.635084
Zr	6.554180	-1.385359	-15.404734
O	6.529997	0.462941	-14.154267
Zr	4.365152	0.648195	-13.493749
O	2.826959	-0.942654	-12.615758
C	2.020466	-1.723077	-13.166929
O	1.870680	-1.977302	-14.400475
Zr	3.086605	-1.317502	-16.160393
O	1.002073	-0.679250	-16.724221
C	0.530449	0.475742	-16.957577
O	1.099924	1.591889	-16.930100
Zr	3.317147	2.207473	-16.537408
O	2.878337	4.032687	-16.061749
O	8.269578	11.983086	-12.259129
O	7.106733	2.989606	-13.562934
C	6.468274	2.879645	-12.492084
O	5.540765	2.063378	-12.193139
O	4.730077	2.056430	-14.921195
O	8.001698	2.476365	-17.604898
C	7.875617	2.134094	-18.802839
O	7.069301	1.284518	-19.294041
O	8.809116	1.429341	-15.252283
C	9.303710	0.288680	-15.103280
O	8.728013	-0.842768	-15.034569
O	2.884617	1.747715	-12.324389
C	1.604422	1.836387	-12.316520

O	0.794943	1.385527	-13.140041
O	5.447599	-0.773461	-11.998184
C	6.283466	-1.694680	-12.173291
O	6.848790	-2.075547	-13.239116
O	4.606912	-0.992289	-14.790896
O	2.666719	0.662606	-14.945561
O	3.595164	0.206722	-17.338452
O	2.883634	2.659359	-18.744834
C	3.457367	2.252688	-19.782887
O	4.324414	1.334509	-19.894724
O	5.125574	-1.752766	-17.103357
O	5.856275	-3.588666	-15.261234
C	4.708144	-4.096127	-15.397401
O	3.624952	-3.554182	-15.742336
O	7.754706	-2.392978	-17.066466
C	7.763162	-2.156107	-18.312716
O	7.019476	-1.405100	-18.988960
O	2.694316	-2.338967	-18.160992
C	3.204164	-2.101690	-19.298852
O	4.187792	-1.384583	-19.605459
O	5.882730	4.367941	-19.388215
H	5.225146	-2.564594	-17.608511
H	1.818902	0.817131	-14.460621
H	7.196365	0.566174	-13.468424
H	2.710555	-2.628691	-20.143146
H	3.161948	2.740343	-20.729839
H	8.535633	-2.712955	-18.884449
H	8.566803	2.601338	-19.525606
H	1.337044	-2.278551	-12.492209

H	1.206805	2.400626	-11.443406
H	-0.547065	0.488945	-17.220815
H	6.580525	-2.252091	-11.260301
H	10.408050	0.250110	-14.997148
H	6.759147	3.569472	-11.674377
H	4.648711	-5.186345	-15.191902
H	3.477133	4.787663	-15.830284
H	9.152342	7.465518	-13.590015
H	9.193501	9.794999	-12.659497
H	5.270483	10.482910	-14.256136
H	5.212008	8.143097	-15.160538
H	6.134922	5.096110	-18.783901
H	5.635735	3.656502	-18.773132

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C	6.301813	10.166751	-14.235060
C	6.322384	8.850693	-14.614309
C	7.291511	7.905037	-14.069942
C	8.219061	8.467903	-13.091492
C	8.189113	9.786455	-12.721357
C	7.232081	10.671350	-13.283597
O	7.337879	6.695552	-14.400953
P	6.265157	5.529280	-16.589851
O	4.924383	6.116964	-16.270337
N	7.208703	12.021908	-12.902337
O	6.355848	12.797403	-13.410098
O	7.367793	6.163341	-17.358749
O	6.564131	4.153975	-15.904248
Zr	6.523987	2.110056	-15.733177
O	5.091658	2.133754	-17.321983

Zr	5.259288	0.197720	-18.282126
O	6.533437	0.170502	-16.655695
Zr	6.562508	-1.474824	-15.478225
O	6.510097	0.336076	-14.162868
Zr	4.374419	0.431521	-13.444363
O	2.852601	-1.090254	-12.528773
C	2.121564	-1.965041	-13.058012
O	1.971487	-2.255512	-14.279936
Zr	3.078060	-1.477087	-16.128995
O	0.933591	-0.892919	-16.590372
C	0.425141	0.250437	-16.809979
O	0.939529	1.388416	-16.704094
Zr	3.128559	2.141083	-16.346746
O	3.129281	4.050798	-16.339741
O	8.043348	12.444045	-12.055293
O	6.951262	2.880387	-13.558035
C	6.381046	2.716394	-12.457614
O	5.519512	1.833032	-12.133254
O	4.626856	1.876574	-14.855298
O	7.895924	2.419192	-17.625126
C	7.798877	2.028442	-18.808709
O	6.907402	1.290391	-19.327967
O	8.716862	1.402257	-15.274965
C	9.255733	0.275897	-15.181554
O	8.717659	-0.876559	-15.149636
O	2.847939	1.728269	-12.525383
C	2.050207	2.578353	-13.057449
O	1.812262	2.770552	-14.262389
O	5.512991	-1.014401	-12.028043

C	6.379027	-1.898233	-12.254221
O	6.933049	-2.218497	-13.344756
O	4.633130	-1.170549	-14.785727
O	2.638052	0.313294	-14.862507
O	3.508283	0.145698	-17.226953
O	2.586042	2.446060	-18.602089
C	3.162234	2.126336	-19.662388
O	4.145923	1.338174	-19.826354
O	5.074196	-1.810463	-17.149873
O	5.918314	-3.694879	-15.393717
C	4.782272	-4.230616	-15.519162
O	3.676156	-3.706397	-15.819208
O	7.720913	-2.393950	-17.201600
C	7.677289	-2.129500	-18.442954
O	6.890443	-1.381958	-19.070635
O	2.619165	-2.412323	-18.152742
C	3.089359	-2.128808	-19.296808
O	4.038714	-1.367315	-19.603099
O	5.551505	4.462412	-18.448662
H	5.177440	-2.595638	-17.695135
H	1.761013	0.412416	-14.479743
H	7.192077	0.444945	-13.493015
H	2.593086	-2.648309	-20.143141
H	2.766843	2.576584	-20.594293
H	8.441129	-2.654634	-19.053901
H	8.587171	2.375998	-19.506758
H	1.509580	-2.567151	-12.354377
H	1.496425	3.197098	-12.322075
H	-0.638236	0.228910	-17.126134

H	6.714532	-2.476469	-11.368977
H	10.361084	0.272189	-15.096819
H	6.671211	3.407254	-11.644921
H	4.757403	-5.327767	-15.350966
H	3.697859	4.859162	-16.329053
H	8.950099	7.783626	-12.667015
H	8.888337	10.190390	-11.996344
H	5.575654	10.859422	-14.647698
H	5.612538	8.453217	-15.333444
H	6.444379	4.403595	-18.812991
H	5.326865	3.540981	-18.114146

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C	8.605612	10.178416	-13.830547
O	7.465065	10.060802	-14.341919
Zr	6.293577	8.257256	-15.178349
O	5.599006	6.369304	-14.498441
Zr	6.235106	5.723354	-12.669660
O	6.701776	3.830575	-11.400618
C	7.422141	2.824922	-11.630611
O	8.064334	2.526317	-12.679233
Zr	8.421320	3.727767	-14.586606
O	7.527231	4.675919	-16.131675
Zr	8.533630	6.207381	-17.040988
O	7.666755	5.423262	-18.917614
C	6.615408	4.736301	-19.112266
O	5.731925	4.407154	-18.292724
Zr	5.316061	4.912959	-16.034297
O	6.253855	3.964072	-14.068603
O	9.421534	9.272559	-13.478067

Zr	9.340431	7.027084	-13.721200
O	8.193479	5.353835	-13.319638
O	11.027473	5.687639	-12.914026
C	11.158937	4.431372	-12.915426
O	10.440670	3.555462	-13.470024
O	8.284434	7.442617	-15.406080
O	7.274358	7.671982	-13.118854
O	11.132247	7.730404	-14.927057
C	11.339403	7.712707	-16.176540
O	10.645871	7.191139	-17.087060
O	9.759513	5.427727	-15.272303
O	9.349356	7.234887	-11.448575
C	8.503127	6.868683	-10.582597
O	7.358684	6.372164	-10.751857
O	7.373147	1.891256	-15.396270
C	6.273877	1.757172	-16.014469
O	5.396760	2.618290	-16.273080
O	9.795373	2.873750	-16.184588
C	10.152599	3.354375	-17.300030
O	9.921627	4.493461	-17.782636
O	3.710963	5.600036	-16.778183
O	6.324802	6.784617	-16.886291
O	3.634809	4.096330	-14.490741
C	3.446381	4.286167	-13.272334
O	4.244869	4.787518	-12.412070
O	7.191647	9.468010	-16.948541
C	7.837549	9.158318	-17.971262
O	8.371780	8.038365	-18.256380
O	4.660160	8.871383	-16.105269

P	3.657432	8.890281	-17.377468
O	2.551921	7.857306	-17.163044
O	4.960975	8.987161	-13.398963
C	4.548427	8.434598	-12.353522
O	4.913234	7.329561	-11.840889
O	4.666339	8.113168	-18.530433
O	3.351722	10.278705	-17.831298
H	10.682274	5.218731	-15.445979
H	5.785265	3.179802	-13.766690
H	7.201478	8.351992	-12.442012
H	10.765348	2.679836	-17.929259
H	6.474408	4.391795	-20.155382
H	12.269135	8.215889	-16.506222
H	7.973945	9.949321	-18.730206
H	7.498150	2.089363	-10.805573
H	2.468846	3.968378	-12.860229
H	6.055856	0.728105	-16.360635
H	8.810664	7.017814	-9.529069
H	8.947586	11.214477	-13.644611
H	3.776160	8.982363	-11.781194
H	12.037858	4.046343	-12.361464
H	3.164568	6.456513	-16.893993
H	5.823275	7.204989	-17.632357
H	4.115175	7.387057	-18.858406

State **1'**

C	2.191087	3.104199	-2.644546
O	1.142527	2.640832	-3.197530
Zr	-0.157975	1.019197	-2.528520
O	-1.912706	0.375970	-3.916129

C	-2.823974	-0.479817	-3.782668
O	-2.960342	-1.366887	-2.883163
Zr	-1.836383	-1.708967	-0.970184
O	-1.458423	-3.664933	-2.019108
C	-0.390653	-4.212377	-2.424430
O	0.782254	-3.753499	-2.411243
Zr	1.669540	-1.810586	-1.569395
O	0.077205	-1.992919	-0.218780
Zr	0.449347	-1.435051	1.760804
O	-0.944686	-3.167434	2.236638
C	-1.898177	-3.690669	1.598176
O	-2.402703	-3.327818	0.496850
O	2.729887	2.738606	-1.579867
Zr	2.055842	1.333842	0.137061
O	2.236173	-0.966633	0.472656
O	3.206085	0.746339	2.331358
C	2.913725	-0.062478	3.236958
O	2.038165	-0.990866	3.215607
O	0.183330	2.090935	-0.602702
Zr	-1.279385	1.373021	0.601671
O	-1.627445	-0.808289	1.116582
O	1.491791	0.197483	-1.651589
O	0.474839	0.589633	1.372503
O	2.503944	3.001490	1.119647
O	4.135297	0.625096	-0.553751
C	4.523874	-0.340806	-1.258195
O	3.862040	-1.344355	-1.666917
O	-0.639924	-0.701438	3.627150
C	-1.290321	0.359362	3.837440

O	-1.734312	1.189073	2.993794
O	1.706531	-3.330927	1.725950
C	2.366825	-3.900735	0.814560
O	2.547422	-3.525174	-0.377725
O	-1.579425	3.407250	1.769520
O	-2.399694	3.083117	-0.609293
C	-2.232955	3.386982	-1.824734
O	-1.572110	2.764563	-2.693616
O	-1.546160	0.318817	-1.126609
O	-3.589803	0.995153	0.714984
C	-4.280718	0.063100	0.223538
O	-3.890035	-1.011106	-0.325418
O	0.917967	0.236172	-4.423449
C	1.746035	-0.697448	-4.587093
O	2.103965	-1.594282	-3.764046
O	-0.297175	-1.294317	-2.571915
H	-0.458478	-1.674534	-3.441453
H	-2.342599	-0.955146	1.744265
H	3.097132	-1.218316	0.823623
H	-3.610283	-0.477683	-4.559448
H	-2.741409	4.305765	-2.170684
H	2.215533	-0.760148	-5.585430
H	2.680910	3.928710	-3.193658
H	-2.361472	-4.577465	2.065937
H	-1.516203	0.576594	4.898558
H	-5.377759	0.182691	0.292402
H	2.859927	-4.847671	1.098844
H	5.589532	-0.331659	-1.550653
H	3.483897	0.006315	4.183239

H	-0.510144	-5.223077	-2.854374
H	2.888807	2.832836	1.990234
H	-2.023960	3.106784	2.580192
H	-2.209561	3.847507	1.171628

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C	12.483530	-5.789651	-6.856289
C	12.201127	-4.895118	-5.781525
C	12.176690	-3.530360	-5.972088
C	12.432855	-3.001894	-7.251165
C	12.710941	-3.866355	-8.326964
C	12.738741	-5.234437	-8.144964
N	12.413794	-1.586429	-7.453441
O	12.641824	-1.135622	-8.593290
O	12.489453	-7.069029	-6.569407
O	12.170907	-0.841385	-6.482874
P	12.725240	-8.481229	-7.659111
O	13.803319	-9.230152	-6.739949
O	13.385681	-7.953143	-8.896491
O	11.366631	-9.119813	-7.639258
O	10.547499	-11.815312	-8.486201
O	13.390541	-11.114352	-4.869714
Zr	12.234122	-11.674067	-3.296056
O	11.213046	-9.842030	-4.219296
C	10.071782	-9.671432	-4.722458
O	9.010279	-10.326647	-4.460374
Zr	8.742053	-12.365053	-3.608155
O	7.670357	-12.421881	-5.482541
C	7.159852	-13.320384	-6.243658
O	7.232807	-14.553973	-6.121354

Zr	11.243118	-14.545167	-4.811500
O	12.982833	-16.038952	-5.149162
C	13.846937	-16.420085	-4.322007
O	13.924367	-16.183186	-3.082754
Zr	12.704178	-14.754342	-1.827261
O	13.250250	-14.520050	0.482026
C	12.743678	-13.793889	1.372422
O	11.681344	-13.102050	1.342637
Zr	10.318261	-12.605218	-0.420566
O	8.494320	-11.265507	-0.098365
C	7.601159	-10.877879	-0.906119
O	7.498523	-11.089662	-2.141039
O	11.266125	-14.244393	-6.779747
O	11.119385	-15.490991	-2.938914
Zr	9.277819	-15.558594	-2.102891
O	7.086750	-15.525966	-2.467199
C	6.333749	-14.574180	-2.842652
O	6.646525	-13.416233	-3.190588
O	10.267112	-16.636896	-5.389790
C	9.507584	-17.387447	-4.735974
O	9.011628	-17.225329	-3.577389
O	10.638552	-12.586162	-4.351759
O	9.058128	-14.517712	-4.183339
O	12.796086	-13.713510	-3.711598
O	10.777418	-14.814548	-0.552250
O	9.135796	-13.509010	-1.868353
O	10.198250	-17.395959	-1.089973
C	11.413424	-17.662482	-0.846177
O	12.427590	-16.922065	-0.906401

O	8.240295	-15.597282	-0.028950
C	8.241944	-14.762433	0.915687
O	8.896104	-13.690844	1.038924
O	14.493094	-11.817193	-2.487957
C	15.152241	-12.762383	-2.008050
O	14.760665	-13.924944	-1.678689
O	12.025716	-12.846187	-1.481455
O	12.549423	-10.056526	-1.639287
C	12.136851	-9.941660	-0.461654
O	11.294269	-10.651563	0.172569
O	10.191854	-11.283857	-2.213627
H	10.853883	-15.309641	0.268435
H	8.382920	-14.776030	-4.865594
H	10.019602	-10.342819	-2.108065
H	11.600034	-18.704327	-0.510048
H	14.653602	-17.065066	-4.728027
H	13.291326	-13.760821	2.337764
H	16.232889	-12.573975	-1.836996
H	5.252266	-14.817317	-2.854047
H	6.593160	-12.905152	-7.101766
H	9.213924	-18.336037	-5.230853
H	6.800603	-10.254410	-0.459357
H	12.550854	-9.090047	0.115126
H	9.977747	-8.862082	-5.459952
H	7.578225	-15.011958	1.769490
H	12.007823	-5.331211	-4.806808
H	11.963735	-2.849622	-5.156460
H	12.905432	-3.432522	-9.301095
H	12.966765	-5.929388	-8.946041

H	13.444167	-9.858194	-6.054462
H	14.197383	-11.637370	-4.958685
H	11.179641	-14.870292	-7.504619
H	10.804968	-12.408330	-7.762879
H	10.826281	-10.927422	-8.191326

State **TS3**

C	14.156414	-5.371564	-7.751251
C	13.971500	-4.046962	-8.048068
C	12.663136	-3.503240	-8.126124
C	11.547082	-4.352094	-7.886421
C	11.719648	-5.678413	-7.589254
C	13.043488	-6.285344	-7.507134
N	12.479680	-2.145335	-8.435092
O	13.486095	-1.413987	-8.641829
O	13.235200	-7.497667	-7.244475
O	11.313916	-1.675441	-8.502588
P	11.502925	-9.550616	-7.367162
O	11.685779	-9.567052	-8.834317
O	10.497762	-8.824743	-6.542785
O	12.642641	-10.331882	-6.584547
O	10.179042	-11.470991	-7.299639
O	11.237930	-13.958399	-6.641358
Zr	11.011707	-14.633802	-4.752517
O	10.736528	-15.904720	-3.114281
Zr	8.812736	-16.245734	-2.576614
O	8.883017	-17.622758	-4.336813
C	9.540355	-17.541747	-5.421743
O	10.313942	-16.639358	-5.816311
Zr	11.534116	-12.012150	-2.664221

O	10.180568	-12.820415	-4.087262
Zr	8.192531	-12.871484	-3.569425
O	8.780050	-14.861182	-4.452330
O	12.765671	-11.136989	-4.025364
O	12.325009	-13.909589	-3.338995
Zr	12.099019	-15.279373	-1.682784
O	10.033844	-15.698719	-0.725268
Zr	9.365338	-13.590027	-0.282931
O	8.457740	-14.285580	-2.019657
O	13.661744	-12.131538	-1.639320
C	14.346439	-13.093364	-1.228171
O	14.024912	-14.316716	-1.127076
O	11.201551	-13.517216	-1.132442
O	11.493765	-10.721665	-0.718089
C	10.925851	-10.852564	0.391177
O	10.074027	-11.720303	0.762966
O	9.344534	-11.977023	-1.828027
O	10.457940	-10.098589	-3.331762
C	9.363777	-9.889507	-3.915879
O	8.373655	-10.690615	-4.005344
O	12.904253	-15.901785	-5.112117
C	13.695356	-16.362337	-4.251160
O	13.590605	-16.356322	-2.991579
O	12.331248	-15.424130	0.667162
C	11.651151	-14.916239	1.593612
O	10.540144	-14.308335	1.536889
O	11.901534	-17.585723	-1.203540
C	10.960040	-18.391978	-1.415933
O	9.765789	-18.166800	-1.777279

O	7.872262	-15.020233	0.746813
C	7.333189	-16.086912	0.344342
O	7.525263	-16.727255	-0.725728
O	7.403940	-12.459546	0.003424
C	6.585544	-11.991958	-0.840176
O	6.658469	-11.980362	-2.095817
O	6.685748	-16.251816	-3.252618
C	5.925680	-15.297903	-3.599393
O	6.193611	-14.080049	-3.713556
O	7.509779	-12.628817	-5.623247
C	7.154490	-13.413898	-6.578737
O	7.261064	-14.648852	-6.626683
H	10.044447	-16.327994	0.001793
H	8.228744	-15.034560	-5.260621
H	9.078911	-11.086642	-1.576768
H	11.197746	-19.462262	-1.243662
H	14.607584	-16.852979	-4.646180
H	12.069303	-15.027103	2.615268
H	15.378454	-12.855957	-0.898996
H	4.882406	-15.591692	-3.826557
H	6.708408	-12.885027	-7.444758
H	9.396485	-18.398622	-6.110200
H	5.681765	-11.518095	-0.408415
H	11.185745	-10.099370	1.161210
H	9.241514	-8.913185	-4.401830
H	6.589593	-16.533115	1.035693
H	15.155098	-5.797965	-7.690906
H	14.809117	-3.381812	-8.231416
H	10.556692	-3.912934	-7.945689

H	10.875383	-6.333686	-7.396454
H	12.521149	-10.449123	-5.602549
H	13.615838	-11.587738	-4.113750
H	11.382476	-14.498945	-7.424675
H	10.655707	-12.300577	-7.063554
H	9.548277	-11.325568	-6.579981

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C	13.843114	-4.767423	-6.846855
O	13.822678	-3.742523	-7.590652
Zr	12.508515	-3.260886	-9.356280
O	11.155587	-4.117852	-7.751113
Zr	9.074267	-3.612713	-8.475182
O	8.866552	-4.307285	-6.332481
C	9.379236	-5.311536	-5.756811
O	10.258193	-6.107725	-6.160306
Zr	11.280495	-6.410265	-8.217092
O	9.367868	-5.591082	-8.784806
Zr	8.880280	-6.370137	-10.646241
O	8.357694	-8.241478	-9.541323
C	8.911705	-8.699780	-8.504207
O	9.850854	-8.222676	-7.829219
O	12.518990	-8.020990	-8.116406
O	13.058245	-5.739570	-6.808225
Zr	12.121569	-6.105861	-11.518342
O	10.821502	-7.112934	-10.197981
O	12.497313	-5.308373	-9.575522
O	14.578035	-2.960397	-10.024747
C	15.111685	-2.556391	-11.109478
O	14.840582	-2.914641	-12.269635

O	12.027276	-1.569776	-7.891330
C	10.961504	-1.238085	-7.315133
O	9.833162	-1.799696	-7.327962
O	12.590964	-1.220986	-10.509286
C	11.998166	-0.783646	-11.520448
O	11.100583	-1.332187	-12.219679
Zr	10.019141	-3.259066	-11.895267
O	8.521535	-1.579046	-11.461692
C	7.932061	-1.245151	-10.401419
O	7.935515	-1.798475	-9.270911
O	12.255407	-3.752405	-11.540104
O	10.491326	-3.004913	-9.885645
O	11.332882	-7.748811	-12.822898
C	10.205366	-8.300884	-12.828841
O	9.156939	-7.968129	-12.216119
O	14.292016	-5.641120	-11.932128
O	10.227102	-5.281797	-11.828924
O	12.250227	-5.367553	-13.715384
C	11.696556	-4.439866	-14.344827
O	10.921675	-3.529342	-13.925861
O	6.754951	-6.074710	-9.698619
C	6.344737	-5.280379	-8.820360
O	6.921034	-4.283627	-8.294638
O	8.368003	-4.118984	-10.572959
O	7.535735	-5.821274	-12.463440
C	7.574921	-4.860194	-13.268750
O	8.278369	-3.809728	-13.243402
O	13.335135	-7.906066	-10.758435
P	14.955475	-8.499230	-10.784465

O	15.655387	-7.097258	-10.133716
O	15.389463	-8.545886	-12.202050
O	14.996506	-9.588967	-9.769828
H	7.460092	-3.908021	-10.804521
H	12.942359	-3.356942	-12.103255
H	11.384945	-3.897294	-6.844697
H	6.874716	-4.926935	-14.128058
H	10.117439	-9.196673	-13.475415
H	5.311162	-5.460148	-8.454577
H	8.495565	-9.664555	-8.141955
H	12.301615	0.227967	-11.861784
H	15.927936	-1.812994	-10.968688
H	11.920047	-4.392105	-15.430352
H	11.023085	-0.320668	-6.692578
H	8.998541	-5.497389	-4.730075
H	14.679849	-4.787529	-6.116457
H	7.306819	-0.330262	-10.476178
H	12.976040	-8.108823	-9.857078
H	12.095260	-8.884508	-8.121776
H	14.529109	-4.712597	-12.127426
H	15.303954	-6.987518	-9.239757
H	14.935528	-6.010975	-11.279799

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C	2.124062	3.254442	-2.832400
O	2.646642	3.015104	-1.718711
Zr	1.956044	1.511660	-0.069248
O	4.104650	-1.019482	2.370415
C	3.340325	-0.838515	3.334625
O	2.064612	-0.741361	3.328826

Zr	0.456352	-1.046744	1.856786
O	-0.542698	-0.620951	3.770848
C	-1.749526	-0.597878	4.195507
O	-2.800842	-0.685137	3.537036
Zr	-1.341748	1.672467	0.486988
O	-1.843897	2.937838	1.945333
O	1.157998	2.667626	-3.403500
Zr	-0.197316	1.064111	-2.632920
O	-1.574619	2.799544	-2.941910
C	-2.240675	3.466293	-2.096081
O	-2.389125	3.261470	-0.868543
O	-1.583379	0.470903	-1.230422
Zr	-1.829949	-1.512219	-0.858800
O	-3.898657	-0.865444	-0.330015
C	-4.323162	0.223244	0.168759
O	-3.677505	1.231900	0.534914
O	0.170541	2.282685	-0.804287
O	1.507316	0.319457	-1.751950
Zr	1.672704	-1.683849	-1.448999
O	2.089424	-1.623161	-3.704062
C	1.734615	-0.775130	-4.574157
O	0.902743	0.166768	-4.485047
O	-0.288811	-1.240979	-2.508712
O	-1.921571	0.303909	-4.010422
C	-2.822752	-0.552395	-3.806347
O	-2.952434	-1.375760	-2.853811
O	0.468321	0.970977	1.342197
O	-1.625319	-0.432115	1.189252
O	3.024060	2.702403	1.123891

O	4.124845	0.849735	-0.780270
C	4.516684	-0.208787	-1.322698
O	3.851508	-1.244253	-1.638160
O	2.252989	-0.622254	0.533828
O	1.711710	-3.004289	1.878544
C	2.420399	-3.580058	1.022102
O	2.584742	-3.285289	-0.199869
O	-0.901509	-2.879594	2.316403
C	-1.902410	-3.371516	1.747743
O	-2.430532	-3.040312	0.643816
O	0.090420	-1.738467	-0.107675
O	0.803793	-3.684010	-2.179442
C	-0.373141	-4.138138	-2.163374
O	-1.441824	-3.573831	-1.801342
H	-0.451314	-1.692209	-3.342321
H	-2.261381	-0.564204	1.945791
H	3.086474	-0.825073	1.042222
H	-3.611108	-0.609063	-4.583998
H	-2.770522	4.347633	-2.511086
H	2.215730	-0.893592	-5.566096
H	2.568796	4.089613	-3.410663
H	-2.397428	-4.212491	2.269791
H	-1.833703	-0.482445	5.298021
H	-5.423138	0.272744	0.294571
H	2.979317	-4.470289	1.368277
H	5.596587	-0.264981	-1.565286
H	3.791788	-0.743005	4.346079
H	-0.485679	-5.178235	-2.528706
H	3.912974	2.969953	0.864118

H	-2.739601	3.291926	1.985216

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C	15.824571	-14.797051	-6.555914
C	15.381012	-13.995178	-7.677054
C	15.548125	-14.579857	-8.992253
C	16.098827	-15.823181	-9.173204
C	16.526043	-16.583355	-8.056273
C	16.373647	-16.039346	-6.752452
O	14.863511	-12.835092	-7.580075
N	17.090287	-17.859110	-8.243900
O	17.212440	-18.319280	-9.411002
O	17.465870	-18.525937	-7.244981
P	14.580795	-11.645797	-5.922763
O	14.748500	-12.675495	-4.828768
O	13.176295	-11.194434	-6.286966
O	15.724917	-10.686420	-6.201213
O	12.133157	-8.792717	-6.805637
Zr	10.892497	-7.354857	-6.549192
O	9.616950	-6.217832	-4.849966
Zr	11.216280	-4.899122	-3.951051
O	9.918850	-3.775385	-5.181379
Zr	10.776454	-2.286125	-6.327338
O	8.762658	-1.170407	-5.845770
C	7.611875	-1.620694	-5.600137
O	7.181792	-2.805038	-5.624672
Zr	8.311173	-4.828560	-5.994264
O	6.782199	-4.741938	-7.708290
C	6.995979	-4.759074	-8.958715
O	8.072609	-4.654209	-9.592542

Zr	10.361001	-4.738614	-8.788186
O	9.093485	-3.316332	-7.475596
O	11.971910	-4.539479	-10.348799
C	13.227486	-4.549901	-10.180307
O	13.883548	-4.554173	-9.115601
Zr	13.169924	-4.838415	-6.911858
O	14.824075	-5.789266	-6.615178
O	9.417205	-5.807914	-7.330912
O	11.851527	-6.051621	-7.958852
O	10.029737	-6.490398	-10.109528
C	9.982771	-7.715407	-9.762462
O	10.106925	-8.216278	-8.630887
O	11.585355	-3.528169	-7.653356
O	7.504817	-4.820773	-3.831834
C	8.127339	-4.801872	-2.731104
O	9.360749	-4.849576	-2.505395
O	7.176741	-6.793744	-5.895632
C	7.604853	-7.975792	-6.101718
O	8.773032	-8.392133	-6.250910
O	12.984769	-4.688268	-2.654341
C	13.919655	-3.827896	-2.503395
O	14.188825	-2.839650	-3.204841
O	12.077559	-5.958833	-5.441827
O	11.069729	-2.777413	-2.797851
C	11.087151	-1.599816	-3.210918
O	11.061277	-1.164723	-4.402986
O	11.364643	-6.820057	-2.821942
C	11.312231	-8.023680	-3.245165
O	10.972318	-8.441802	-4.369357

O	12.449562	-3.489316	-5.182520
O	14.278011	-2.749166	-7.024959
C	13.860574	-1.574097	-6.926563
O	12.693250	-1.141006	-6.674476
O	10.376540	-1.030931	-8.207044
C	10.246539	-1.419882	-9.408509
O	10.096819	-2.574547	-9.872970
O	15.012079	-8.333944	-7.388012
H	8.463060	-2.774340	-7.957313
H	13.123531	-3.044950	-4.613179
H	9.216352	-6.866903	-4.263986
H	10.246615	-0.595403	-10.157663
H	13.823147	-4.541555	-11.118445
H	6.078113	-4.864942	-9.580346
H	9.794123	-8.421571	-10.599216
H	11.127991	-0.806672	-2.432614
H	14.561342	-4.024314	-1.612635
H	14.620243	-0.776174	-7.077122
H	7.478396	-4.743512	-1.829035
H	6.806972	-8.749502	-6.133449
H	11.586368	-8.788211	-2.490624
H	6.853837	-0.850849	-5.328820
H	14.045027	-8.452875	-7.401324
H	12.495786	-9.703351	-6.576649
H	15.328420	-9.151290	-6.916313
H	15.040066	-6.748381	-6.813454
H	15.216733	-13.982610	-9.837088
H	16.221270	-16.251375	-10.162318
H	16.704900	-16.640718	-5.912174

H	15.680911	-14.351197	-5.574047

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C	13.115535	-4.000324	-9.995659
O	11.856052	-3.972620	-10.129675
Zr	10.284236	-4.268998	-8.547641
O	9.376166	-5.433567	-7.137279
Zr	8.305183	-4.541855	-5.710559
O	7.560014	-4.679667	-3.533236
C	8.210818	-4.737452	-2.450428
O	9.449868	-4.805434	-2.262249
Zr	11.263019	-4.755110	-3.751028
O	13.064309	-4.640634	-2.496461
C	14.009277	-3.796289	-2.314780
O	14.261785	-2.763428	-2.955013
O	12.080035	-5.715092	-5.334948
Zr	13.140502	-4.501876	-6.754711
O	14.252733	-2.417764	-6.759100
C	13.843993	-1.250303	-6.570541
O	12.685942	-0.832303	-6.258036
Zr	10.773721	-1.990516	-5.937896
O	11.113577	-1.003013	-3.950900
C	11.169486	-1.517571	-2.792163
O	11.157343	-2.720962	-2.460101
Zr	10.856327	-7.019973	-6.496704
O	11.019102	-8.258632	-4.431460
C	11.378354	-7.925662	-3.283344
O	11.432761	-6.758408	-2.771062
O	12.104587	-8.444135	-6.902965
O	11.788942	-5.640533	-7.844537

O	10.020965	-7.749957	-8.609073
C	9.871846	-7.176241	-9.702665
O	9.913986	-5.931188	-9.969581
O	8.752072	-8.080105	-6.216677
C	7.588368	-7.674372	-6.009996
O	7.169436	-6.508232	-5.715386
O	9.636901	-6.011714	-4.697823
O	12.468296	-3.271014	-4.922788
O	9.939606	-3.553374	-4.872043
O	11.543136	-3.142503	-7.366182
O	9.057321	-2.936942	-7.107137
O	10.330316	-0.612574	-7.718086
C	10.167730	-0.919961	-8.939010
O	10.001967	-2.041307	-9.474883
O	8.777855	-0.906985	-5.328751
C	7.631956	-1.369402	-5.083479
O	7.196723	-2.548779	-5.176706
O	6.737520	-4.340263	-7.375560
C	6.919322	-4.273567	-8.629452
O	7.980619	-4.129686	-9.281447
O	13.798629	-4.079538	-8.950921
O	14.796303	-5.477157	-6.560929
O	13.178491	-10.944033	-6.304462
P	14.584813	-11.291889	-5.872790
O	15.718710	-10.389805	-6.307012
O	14.808710	-12.293908	-4.773019
O	14.956144	-7.989089	-7.469074
H	8.417757	-2.360818	-7.534178
H	13.158693	-2.866780	-4.342891

H	9.247221	-6.693770	-4.142641
H	10.151164	-0.047939	-9.631415
H	13.686636	-3.931680	-10.946157
H	5.986082	-4.334422	-9.233214
H	9.661882	-7.825895	-10.578875
H	11.235137	-0.779966	-1.963221
H	14.675946	-4.056493	-1.460221
H	14.603102	-0.446839	-6.687907
H	7.586858	-4.737503	-1.529701
H	6.788942	-8.443935	-6.072118
H	11.669801	-8.745235	-2.597316
H	6.884643	-0.618349	-4.740781
H	13.987554	-8.107484	-7.473121
H	12.420208	-9.345379	-6.636371
H	15.283751	-8.812527	-7.028517
H	15.005074	-6.422556	-6.814502
O	14.974062	-12.941242	-7.696582
C	15.470092	-14.094048	-7.644509
C	15.683757	-14.874969	-8.861424
C	16.225102	-16.132712	-8.842823
C	16.604880	-16.735854	-7.613781
C	16.410733	-16.009618	-6.402394
C	15.870294	-14.751389	-6.404367
H	15.390530	-14.403689	-9.796518
H	16.378898	-16.700055	-9.755230
N	17.158565	-18.022364	-7.601382
H	16.706277	-16.490885	-5.475521
H	15.706272	-14.178859	-5.494587
O	17.494464	-18.549108	-6.504866

O	17.317614	-18.646701	-8.689559

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C	13.099042	-3.984206	-10.013695
O	11.839057	-3.953744	-10.143113
Zr	10.267828	-4.238399	-8.567624
O	9.902030	-5.913132	-9.981531
C	9.871076	-7.157580	-9.719817
O	10.027380	-7.735671	-8.627730
Zr	10.824478	-6.973319	-6.516653
O	12.123300	-8.413796	-6.949249
O	13.784262	-4.070682	-8.970669
Zr	13.128192	-4.486882	-6.775611
O	14.240367	-2.417550	-6.775631
C	13.836536	-1.248908	-6.577516
O	12.679774	-0.832808	-6.258758
Zr	10.768690	-1.978993	-5.938752
O	10.326920	-0.605575	-7.713661
C	10.161011	-0.906736	-8.935339
O	9.996120	-2.028551	-9.473411
O	14.790102	-5.466696	-6.590711
O	11.777711	-5.627708	-7.865130
O	11.530796	-3.134343	-7.374713
O	12.070332	-5.707482	-5.359263
Zr	11.259638	-4.753305	-3.761983
O	12.464851	-3.272574	-4.935512
O	9.048602	-2.920969	-7.109400
Zr	8.293623	-4.524310	-5.716896
O	7.162225	-6.493291	-5.732947
C	7.575170	-7.658517	-6.033395

O	8.739154	-8.065636	-6.245774
O	7.980983	-4.110120	-9.287222
C	6.917791	-4.251794	-8.636344
O	6.737866	-4.322290	-7.382358
O	9.368683	-5.414870	-7.152898
O	8.783324	-0.906796	-5.319605
C	7.636692	-1.366238	-5.072079
O	7.201427	-2.546295	-5.170650
O	9.937215	-3.553820	-4.880471
O	11.116027	-1.017904	-3.945770
C	11.178642	-1.539564	-2.791293
O	11.168994	-2.747543	-2.470609
O	9.633063	-6.014421	-4.721394
O	7.567754	-4.685032	-3.542813
C	8.219758	-4.753058	-2.461469
O	9.460363	-4.828643	-2.280028
O	11.041122	-8.261490	-4.508445
C	11.388060	-7.944694	-3.348551
O	11.428607	-6.790582	-2.815237
O	13.066080	-4.675007	-2.527200
C	14.017626	-3.835702	-2.343262
O	14.269933	-2.801129	-2.978865
O	14.897036	-8.023972	-7.486520
O	15.760392	-10.356953	-6.068752
P	14.677265	-11.320456	-5.649506
O	13.236368	-10.892687	-5.702748
O	15.048469	-12.701268	-5.188424
H	8.407221	-2.338198	-7.525113
H	13.160311	-2.875509	-4.355871

H	9.236408	-6.690629	-4.163880
H	10.140305	-0.034549	-9.624573
H	13.666857	-3.912085	-10.965121
H	5.985810	-4.306889	-9.239825
H	9.665613	-7.806440	-10.597772
H	11.248435	-0.811048	-1.956833
H	14.686484	-4.105579	-1.494722
H	14.596654	-0.447811	-6.691082
H	7.600216	-4.756988	-1.539612
H	6.774693	-8.426023	-6.096277
H	11.679855	-8.777618	-2.678763
H	6.892449	-0.617676	-4.723452
H	13.921366	-8.124887	-7.451524
H	12.353269	-9.182285	-6.391177
H	15.228744	-8.759158	-6.929943
H	14.979297	-6.406220	-6.858088

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