Supporting Information

A Hydrophilic Inorganic Framework based on Sandwich Polyoxometalate: Unusual Chemoselectivity for Ketones/Aldehydes with *in-situ* Generated Hydroxylamine

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Contents

1.Experimental Section.

1.1 Supplementary Materials and Methods

All reagents were commercially purchased and used without further purification. The zinc(II)-substituted polyoxometalate $K_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$ $48H_2O$ was prepared according to the literature and characterized by IR spectroscopy.[s1] It was synthesized by adopting a reported procedure, easily self-assembled from Na_2WO_4 and $Zn(NO_3)_2$, by dropwise addition of zinc nitrate to a nitric acid solution of sodium tungstate over 2-3h at 90 °C. The elemental analyses of C, H and N were performed on a Vario EL III elemental analyzer. The infrared spectra (IR) were recorded from a sample powder palletized with KBr on a Nicolet170 SXFT-IR spectrometer over a range of 4000–400 cm^{-1}. Powder X-ray diffraction (PXRD) data were obtained on a Rigaku Model D/Max-2400 X-ray diffractometer with a sealed copper tube (λ = 1.54178 Å). Water contents were determined by TG analyses on a Mettler-Toledo TGA/SDTA 851^e instrument with a heating rate of 10 °C min^{-1} heated from 25 to 800 °C under nitrogen. ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 MHz type (^1H, 400 MHz; ^{13}C, 400 MHz) spectrometer. Their peak frequencies were referenced versus an internal standard (TMS) shifts at 0 ppm for ^1H NMR and against the solvent, chloroform-d at 77.0 ppm for ^{13}C NMR, respectively.

1.2 Supplementary Synthesis and Characterization

$\{K_2Co_4[WZn_3(H_2O)_2][ZnW_9O_{34}]_2\cdot 53H_2O\}$ ($Co_4Zn_5W_{19}$): The cobalt containing polyoxometalate **$Co_4Zn_5W_{19}$** was prepared by the self-assembly approach under hydrothermal conditions: $K_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$ (60 mg, 0.02 mmol), $Co(NO_3)_2\cdot 3H_2O$ (40 mg, 0.19 mmol), were mixed in 4 mL of water and 2 mL of methanol solution at pH 3-6. The resultant mixture was stirred for 12 h, then sealed in a 25 mL Teflon-lined autoclave, and maintained at 130 °C for 5 days. After cooling the autoclave to room temperature, pink cubic single crystals were separated, washed with water, and air-dried. The crystals were obtained with a moderate yield of 40% based on $K_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$. EA and ICP (%). Calcd for $K_2Co_4Zn_5W_{19}H_{110}O_{123}$: K 1.26, H 1.78, Co 3.79, Zn 5.26, W 56.22; Found: K 1.22, H 1.80, Co 3.75, Zn 5.30, W 56.28. IR (KBr; ν): 3401 (br, s), 1706 (s), 1623 (s), 1419 (m), 1184 (w), 925 (s, $W=O_t$), 876 (s, W–O–W), 769 (s, W–O–W) cm^{-1}.

1.3. Single–crystal X–ray Crystallography

A good single crystal of **$Co_4Zn_5W_{19}$** with dimensions of 0.26 × 0.20 × 0.18 mm^3 was prudentially picked under an optical microscope and sealed to a glass tube closed at both ends. Intensity data were collected on Bruker APEX–II CCD detector at 296(2) K with Mo *K*α radiation (λ = 0.71073 Å). Direct methods were used to solve the structures and to locate the heavy atoms using the *SHELXTL–97* program package. The remaining atoms were found from successive full–matrix least–squares refinements on F^2 and Fourier syntheses. [s2] Lorentz polarization and multi-scan absorption corrections were applied.[s3] The cations and lattice water molecules were all determinated by the results of the element analysis and TGA. All H atoms on water molecules were directly included in the molecular formula. A summary of crystal data and structure refinements for compound **$Co_4Zn_5W_{19}$** is provided in **Table S1**.

Table S1. Crystal Data and Structure Refinement for $Co_4Zn_5W_{19}$.

	$Co_4Zn_5W_{19}$
Empirical formula	$K_2Co_4Zn_5W_{19}H_{110}O_{123}$
Formula weight	6212.80
Crystal system	monoclinic
Space group	C2/c
a [Å]	32.285
b [Å]	14.674
c [Å]	21.768
β [°]	95.18
V [$Å^3$]	10270.6
Z	4
ρ_{calcd} [$g\cdot cm^{-3}$]	4.018
μ [mm^{-1}]	23.169
data/parameters	26009/9054
F(000)	11184
R_{int}	0.0472
GOF	1.045
R_1^a, wR_2^b [$I > 2\sigma(I)$]	0.0337, 0.0839
R_1, wR_2 [all data]	0.0452, 0.0934
diff peak and hole, $eÅ^{-3}$	2.671/ -2.406

[a] $R_1 = \sum||Fo| - |Fc||/\sum|Fo|$, [b] $wR_2 = [\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2]^{1/2}$; $w = 1/[\sigma^2(Fo^2) + (xP)^2 + yP]$, $P = (Fo^2 + 2Fc^2)/3$, where x = 0.0497, y = 0 for **$Co_4Zn_5W_{19}$**.

2. Supplementary Structural Figures and characterizations.

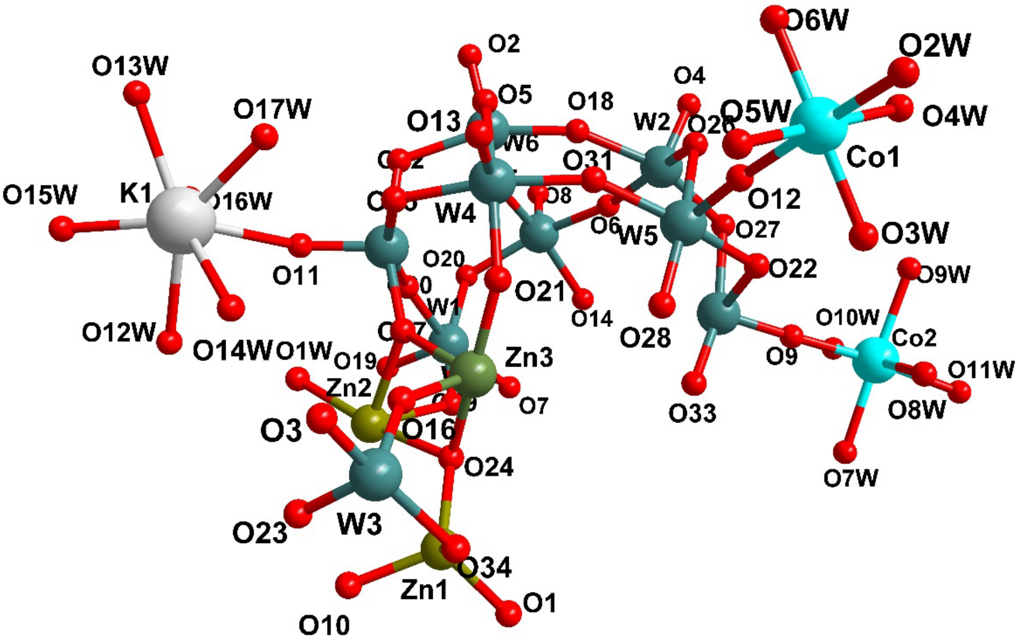


Figure S1. Ball and stick diagram of $\mathbf{Co_4Zn_5W_{19}}$ in an asymmetric unit with the labeled atoms. The crystallization water molecules were omitted for clarify.

The asymmetric unit of $\mathbf{Co_4Zn_5W_{19}}$ consists of half a Zn-substituted sandwich-type $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ unit, two hexa-coordinate cobalt cations ($[Co(H_2O)_5(O_t)]^{2+}$), one eight-coordinate potassium cations ($[K(H_2O)_6(O_t)_2]^{+}$), one protonated water molecules and 9.5 crystallization water. In $[Co(1)(H_2O)_5(O_t)]^{2+}$, the Co(1) atom is defined by five oxygen atoms from coordinated water [Co(1)−O_w, 2.064(10)−2.138(11) Å], one bridging oxygen atom from $\{Zn_5W_{19}\}$ [Co(1)−O(12), 2.078(8) Å], and in $[Co(2)(H_2O)_5(O_t)]^{2+}$, the Co(2) atom is defined by five water oxygen atoms from coordinated water [Co(2)−O_w, 2.079(10)−2.128(8) Å], one oxygen atoms from $\{Zn_5W_{19}\}$ [Co(2)−O(9), 2.051(8) Å]. And in $[K(1)(H_2O)_6(O_t)]^{+}$, the K(1) atom is defined by six oxygen atoms from coordinated water [K(1)−O_w, 2.420(10)−2.588(9) Å], one bridging oxygen atom from $\{Zn_5W_{19}\}$ [K(1)−O(11), 2.478(8) Å].

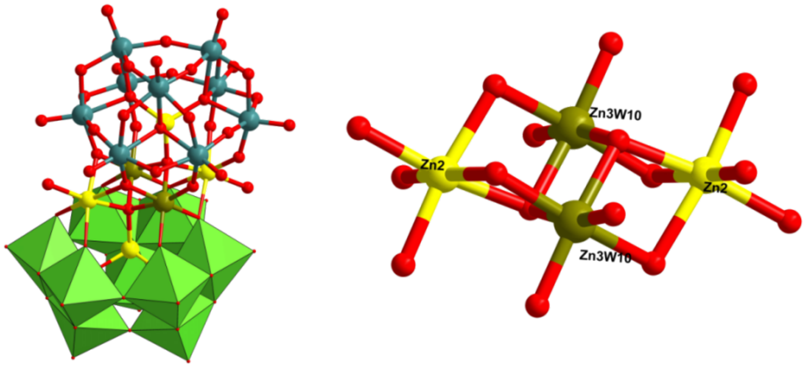


Figure S2. The crystal structure of the $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ polyoxoanion.

The two trivacant subunits can be formally derived from the Keggin structure by removing three adjacent edge-sharing WO_6 octahedra. The crystal structure indicates that the $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ polyoxoanion contains two trivacant Keggin $[B\text{-}\alpha\text{-}ZnW_9O_{34}]^{12-}$ fragments in a staggered fashion linked via a rhomb-like Zn_3O_{16} group in a centrosymmetric arrangement (C2h symmetry) leading to a sandwich-type structure. The two trivacant subunits can be formally derived from the Keggin structure by removing three adjacent edge-sharing WO6 octahedra. Zn(1) is coordinated to three bridge oxygen atoms (O(10), O(1), O(34)) and one μ_4-oxygen atoms (O(24)) from one $[B\text{-}\alpha\text{-}ZnW_9O_{34}]^{12-}$ units [Zn(1)−O_a, 1.911(8)−1.927(8) Å; Zn(1)−O(24), 1.940(7) Å]. The Zn(2) atom is coordinated to one water oxygen atom O(1W), five oxygen atoms (O(33), O(17), O(24), O(28),) of two $[B\text{-}\alpha\text{-}ZnW_9O_{34}]^{12-}$ units.[Zn(2)−O_w, 2.077(7) Å] and [Zn(2)−Ow, 2.044(7)−2.182(8) Å]. The μ_4-oxygen (O(24)) of the Zn_3O_{16} group in each $[ZnW_9O_{34}]^{12-}$ simultaneously coordinates to three Zn atoms on each side of the plane, resulting in the formation of central Zn_3O_{16} cluster through four edge-sharing ZnO_6 octahedra. W(10) and Zn(3) are disordered and refined with constrained site-occupancy factors of 0.5.

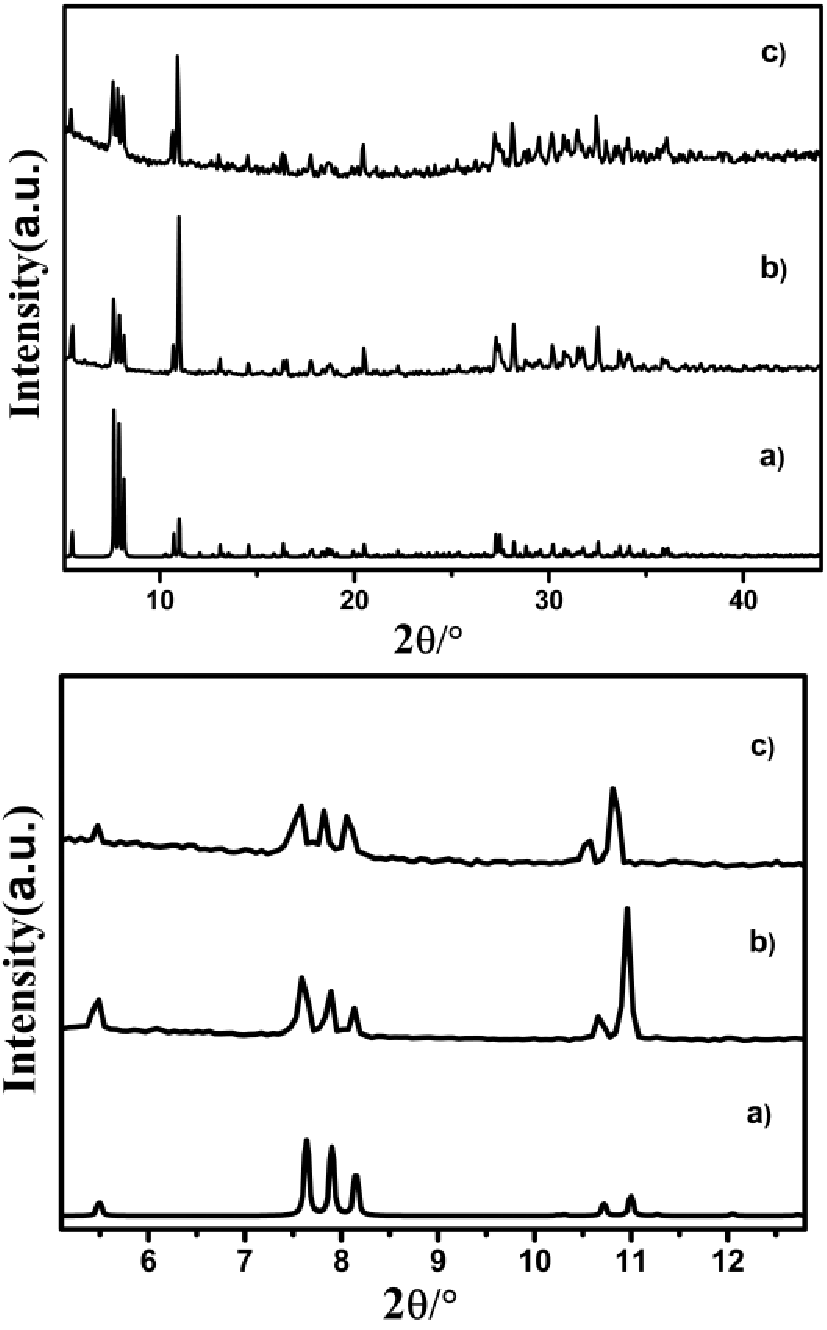
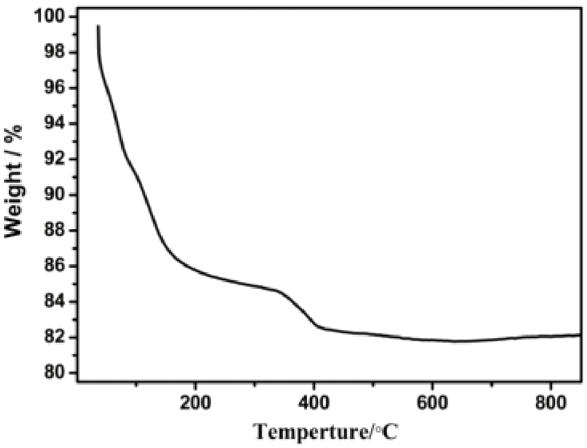


Figure S3. PXRD pattern of **$Co_4Zn_5W_{19}$** (a- Simulated, b- Experimental, c- Recovery catalyst after three runs). [top: 5~43°, bottom: 5~13°]

The very good correspondence between the simulated and the experimental suggests the high purity of the bulk sample. This conclusion is in agreement with the results of the single-crystal X-ray analysis. The index of PXRD patterns of the **$Co_4Zn_5W_{19}$** bulky sample filtrated off from the catalytic reaction showed that five intense peaks ranging from 5 to 11° (200), (111), (002), (112) and (311) of **$Co_4Zn_5W_{19}$** that nearly identical with the experimental, which evidenced the maintenance of the crystallinity.



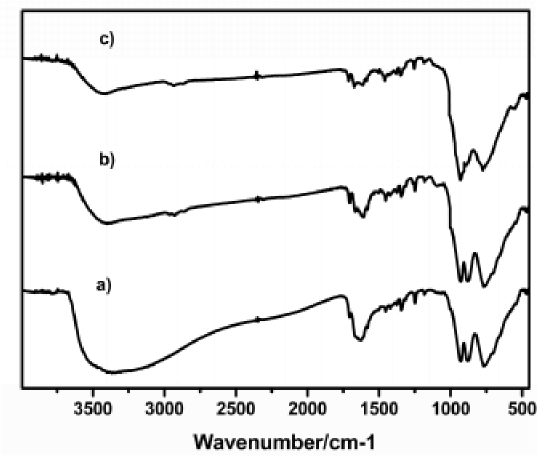


Figure S4. Thermogravimetric analysis (TGA) curve of **$Co_4Zn_5W_{19}$** (Top). Variable temperature infrared (a :25 °C, b :300 °C, c :400 °C) (Bottom).

The thermal behavior of **$Co_4Zn_5W_{19}$** has been investigated under nitrogen atmospheres between 25 and 800 °C by thermogravimetric analysis (TGA). The TG curve of **$Co_4Zn_5W_{19}$** indicates two weight-loss steps, which are associated with the loss of lattice water molecules, coordination water molecules, constitutional water molecules with a total loss of 14.88% (calcd. 15.35%)(top). The weight loss of 14.88% between 25 and 222 °C corresponds to the loss of 21 free water molecules and 32 coordination water molecules (calcd. 15.35%). As the same time, the water molecules could be readily removed in the temperature. In all, TGA revealed that the frameworks are stable up to ~300 °C. It is also confirmed by the variable temperature infrared (bottom). As can be seen from Figure S4 (bottom), the typical vibration bands of {Zn_5W_{19}} near 925 and 876, 769 cm^{-1} basically remain unchanged in the IR spectra of the sample of **$Co_4Zn_5W_{19}$** when temperature gradually increases from 25 to 300 °C, demonstrating that the crystalline structure of **$Co_4Zn_5W_{19}$**

remain almost unchanged in spite of the liberation of some lattice and coordinated water molecules. When the temperature is elevated to 400 °C, the characteristic vibration bands of ν(W–Ob) of the polyoxoanionic skeletons have disappeared, which indicates that the polyoxoanionic skeleton begin to decompose. Meanwhile, the broad peak at 3423 cm^{-1} of the characteristic vibration peak of H_2O and the vibration peaks from 1200 to 1600 cm^{-1} also have great changes.

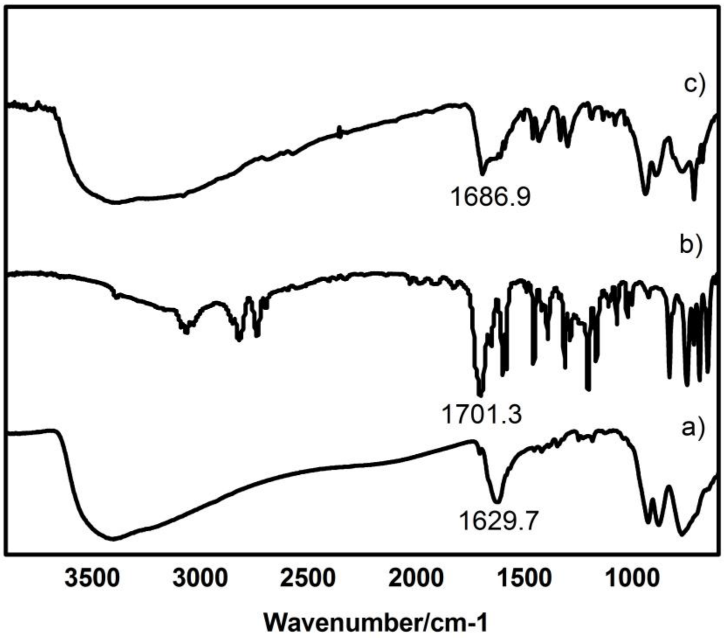
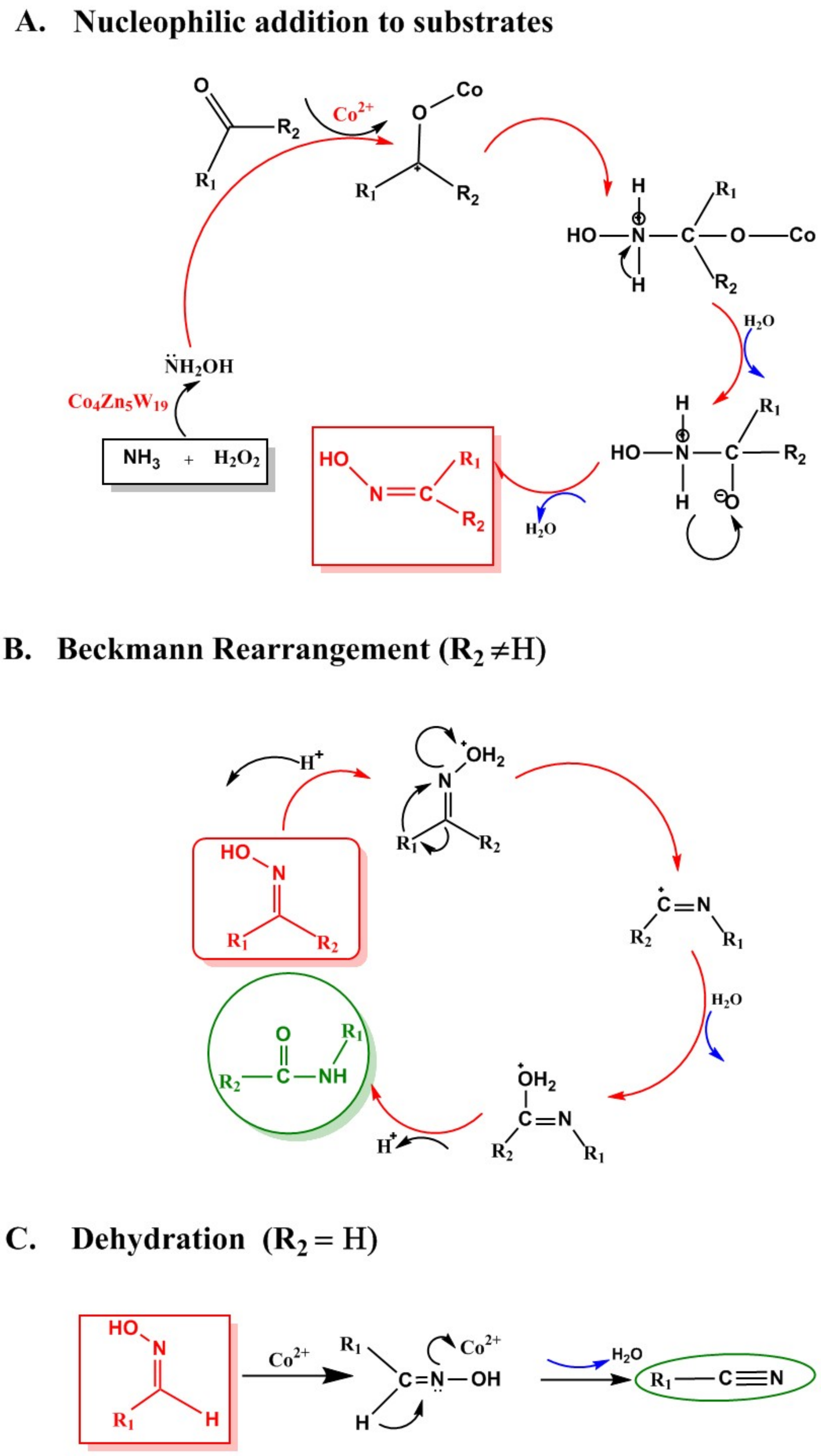


Figure S5. The IR spectra of **$Co_4Zn_5W_{19}$** (a), benzaldehyde (b) and the catalyst **$Co_4Zn_5W_{19}$** impregnated with benzaldehyde in water solution (c).

The IR spectrum of (a) shows three very strong absorption peaks near 925 and 876, 769 cm^{-1} that are assigned to the vibration bands of Zn-polyoxometalate. One broad C-O stretching vibration at 1686 cm^{-1} (c) was presented in the IR spectrum of the catalyst **$Co_4Zn_5W_{19}$** impregnated with benzaldehyde in water solution, which had a red shift of 15 cm^{-1} from 1701 cm^{-1} of the free benzaldehyde (b).

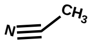
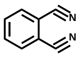
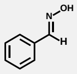
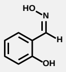
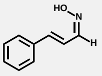
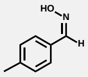
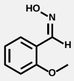
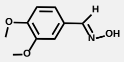
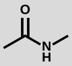
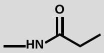
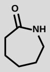
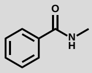
3. Supplementary catalytic reaction

Typical procedure for the catalytic reaction. The heterogeneously catalytic reactions of aldehyde/ketone oxidated by H_2O_2 with NH_3 in 2 mL H_2O using 0.01 mmol of **$Co_4Zn_5W_{19}$**, 10 mmol aldehyde/ketone, 18 mmol H_2O_2 (30%), 16 mmol NH_3 (25%) under stirring in a round bottom flask fitted at 20 °C for 6 h. After completion of the reaction, the mixture was filtered and extracted. The organic extracts were dried by Na_2SO_4 and evaporated to dryness. The yields were directly determined by ^1H NMR analysis of the reaction solution.



Scheme S1. The diagram for potential mechanism of synergistical catalytic process. Oximation of aldehyde/ketone with *in-situ* generated hydroxylamine, and further either dehydrate into nitrile or undergo Beckmann rearrangement into amide by **$Co_4Zn_5W_{19}$**.

Table S2. ^{1}H NMR chemical shift of Products.

Entry	Pro.	Nam.	^{1}H NMR chemical shift
1		**acetonitrile**	1.92
2		**phthalonitrile**	7.57~7.68
3		**(Z)-benzaldehyde oxime**	7.37~7.86, 8.59, 10.03
4		**(Z)-2-hydroxybenzaldehyde oxime**	6.89~7.57, 8.44, 9.88, 10.04
5		**(1E,2Z)-3-phenylacrylaldehyde oxime**	7.34~7.64, 6.89, 5.30, 8.14, 10.01
6		**(Z)-4-methylbenzaldehyde oxime**	2.60, 7.17~7.72, 8.52, 9.94
7		**(Z)-2-methoxybenzaldehyde oxime**	3.87~3.98, 7.56~7.84, 8.53, 10.48
8		**(Z)-3,4-dimethoxybenzaldehyde oxime**	3.44, 3.89, 7.02~7.63, 7.99, 9.84
9		**N-methylacetamide**	1.98~2.16, 2.64, 7.55
10		**N-methylpropionamide**	1.18, 2.10, 3.62, 7.55
11		**azepan-2-one**	1.30~2.34, 7.35
12		**N-methylbenzamide**	2.37, 7.22~7.74, 8.07

The ^1H NMR spectra Figures of the selected products. The yields were directly determined by ^1H NMR analysis of the reaction solution.

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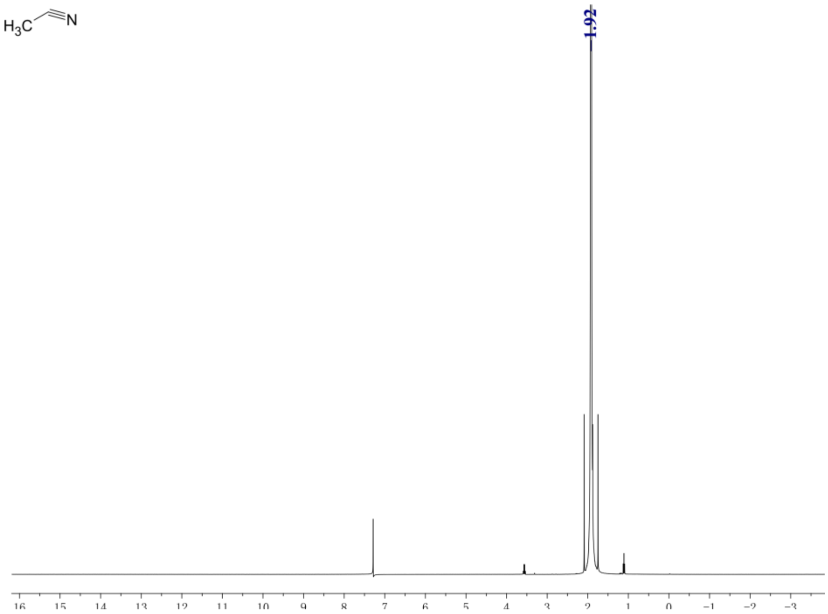

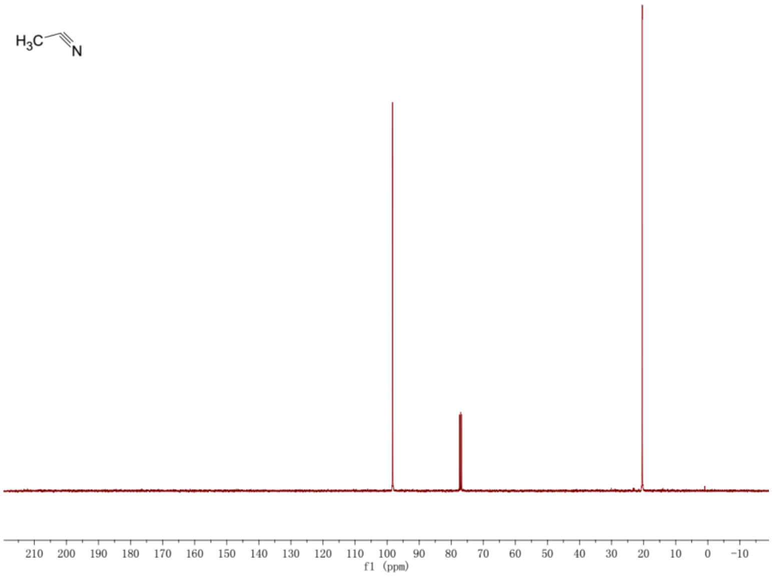

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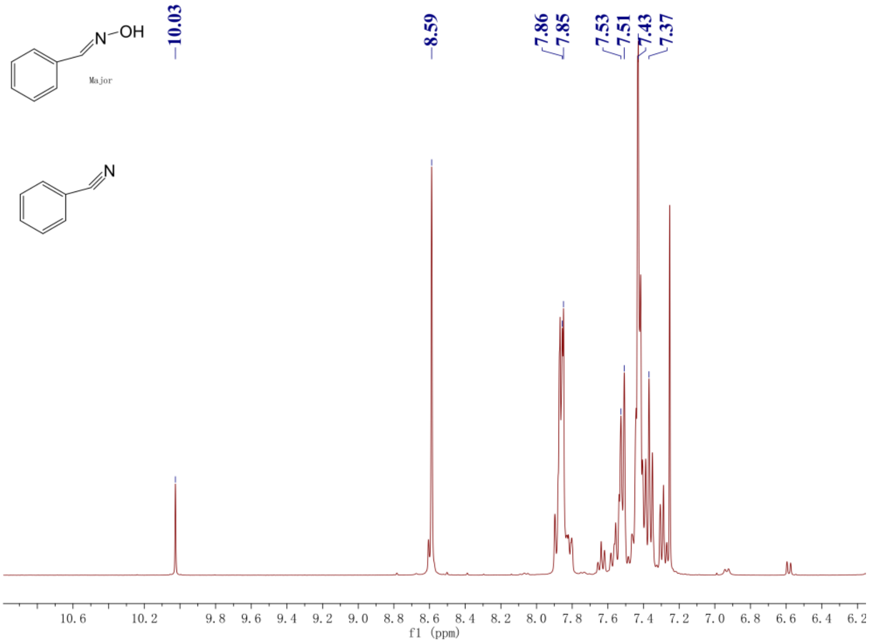

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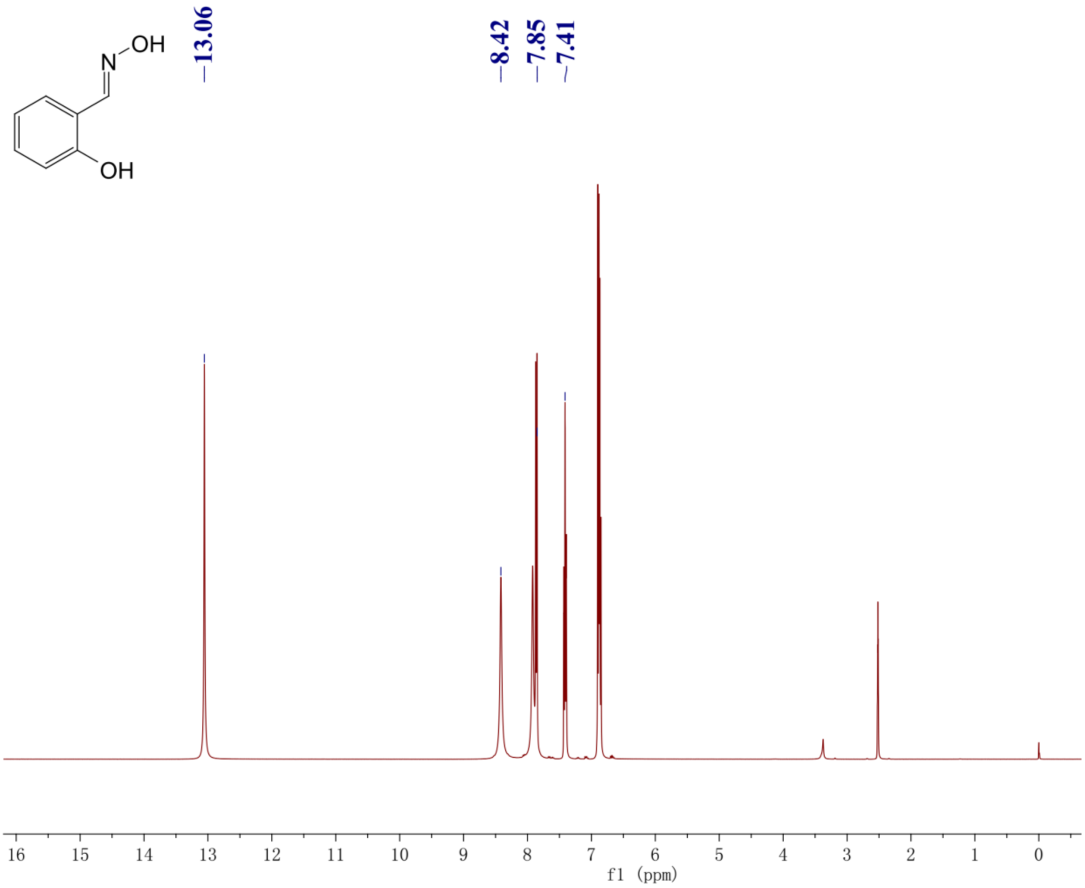

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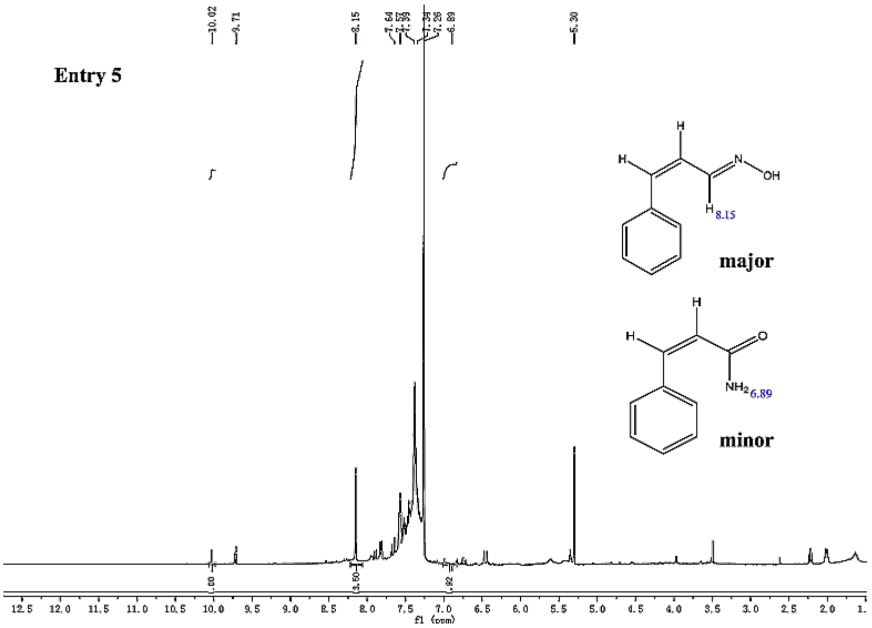

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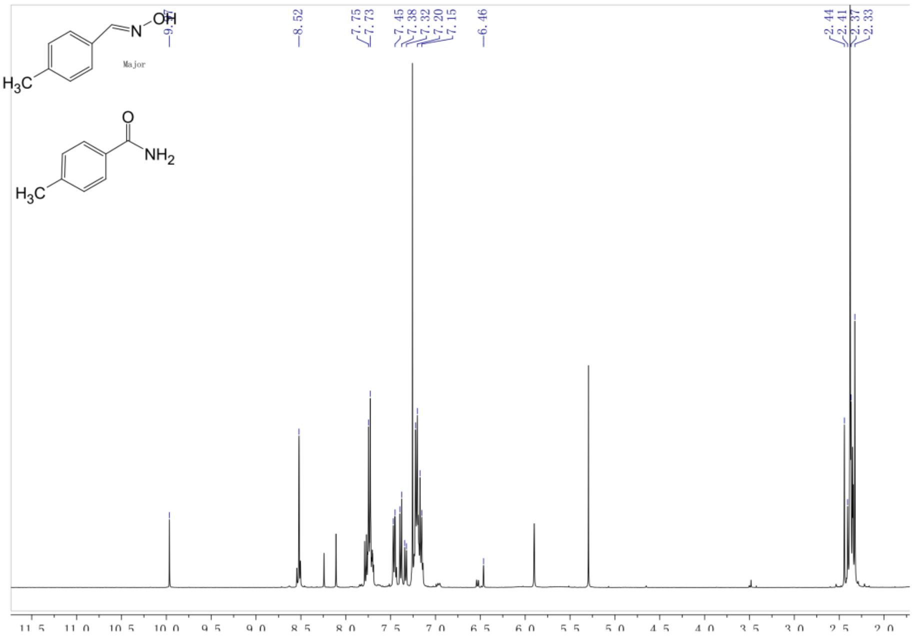

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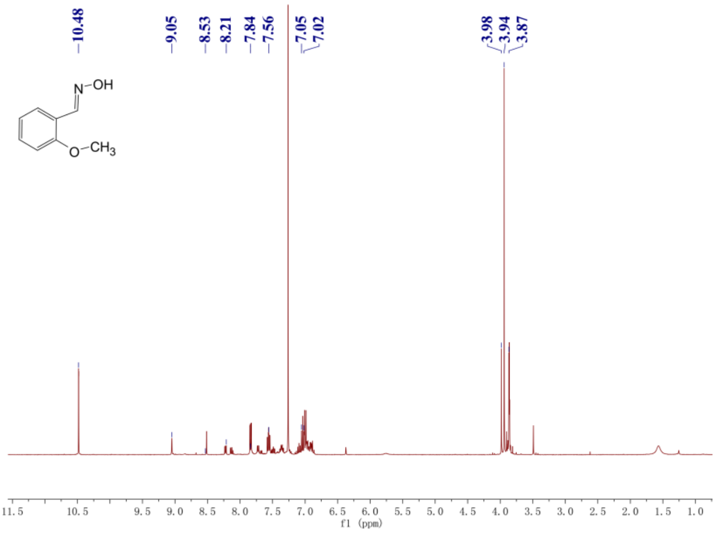

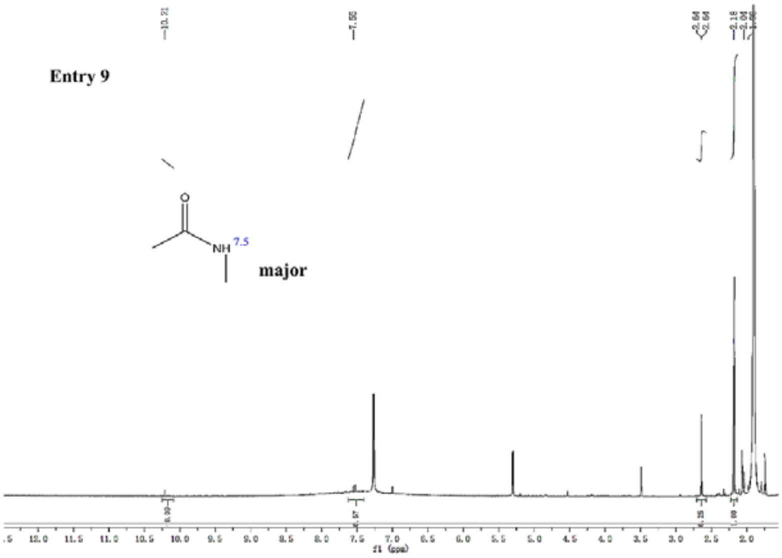

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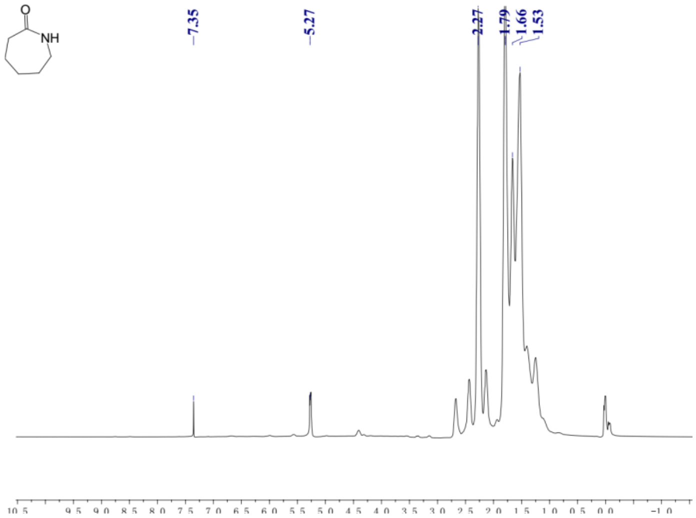

References:

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[3] G. Sheldrick, *SADABS–Bruker AXS area detector scaling and absorption*, version 2008/2001; University of Göttingen: Germany, 2008.