Supporting Information

Multinuclear transition metal-containing polyoxometalates constructed from Nb/W mixed-addendum precursor: synthesis, structures and catalytic performance

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SI-1 Materials and Methods

The precursor $K_8H[P_2W_{15}(NbO_2)_3O_{59}]\cdot 12H_2O$ was synthesized according to the procedure described in the literature.[1] All other reagents were obtained commercially and used without further purification. The FT-IR analysis in ATR mode was performed by a Perkin Elmer Spectrum 400 FT-IR/FT-FIR Spectrometer equipped with ATR objective lens in the range of 400-4000 cm^{-1} at room temperature. Powder X-ray diffraction (PXRD) measurements were performed on a Panalytical X'Pert3 Powder diffractometer with graphite monochromatized Cu *Kα* radiation at 298 K. Thermal analyses were performed on a Netzsch 449C thermal analyzer. The sample was heated to 800 °C with a heating rate of 5 °C/min, under an N_2 atmosphere. Elemental analyses were determined with a PLASMASPEC (I) ICP atomic emission spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on Thermo Fisher Scientific ESCALAB250Xi X-ray photoelectron spectroscopy. GC analyses were performed using Agilent GC6890. ^1H NMR spectra were recorded on a Bruker AVANCE III HD 600MHZ spectrometer.

SI-2 Synthesis of the title compounds

Synthesis of $H_{19}[Cu_4(H_2O)_{15}(P_2W_{15}Nb_3O_{62})_3]\cdot 21H_2O$ (Cu-POM):

$K_8H[P_2W_{15}(NbO_2)_3O_{59}]\cdot 12H_2O$ (0.25 g, 0.05 mmol), $NaHSO_3$ (0.05 g, 0.48 mmol) and $Cu(NO_3)_2\cdot 3H_2O$ (0.12 g, 0.5 mmol) were dispersed in a mixture of 7 mL H_2O and 3.5 mL ethanol in a 25-mL vial. Then, 2.5 mL formic acid was added. The tightly capped vial was placed in an oven at 100 °C for 3 days, and light green single crystals were obtained. Yield: 0.15 g (68.2% based on $K_8H[P_2W_{15}(NbO_2)_3O_{59}]\cdot 12H_2O$). Anal. Calcd (%): Cu 1.93, P 1.41, W 62.71, Nb 6.34; found Cu 1.95, P 1.39, W 63.12, Nb 6.30. IR (KBr disks): 1578 (m), 1462 (m), 1083 (vs), 1014 (m), 944 (m), 894 (m), 723 (vs), 595 (w), 561 (w), 515 (s), 456 (w).

Synthesis of $H_{19}[Co_4(H_2O)_7(P_2W_{15}Nb_3O_{62})_3]\cdot 15H_2O$ (Co-POM):

$K_8H[P_2W_{15}(NbO_2)_3O_{59}]\cdot 12H_2O$ (0.25 g, 0.05 mmol), $NaHSO_3$ (0.05 g, 0.48 mmol) and $CoCl_2\cdot 6H_2O$ (0.12 g, 0.5 mmol) were dispersed in a mixture of 7 mL H_2O and 3.5 mL ethanol in a 25-mL vial. Then, 7 mL formic acid was added. The tightly capped vial was placed in an oven at 100 °C for 3 days, and light pink single crystals were obtained. Yield: 0.08 g (37.2% based on $K_8H[P_2W_{15}(NbO_2)_3O_{59}]\cdot 12H_2O$). Anal. Calcd (%): Co 1.82, P 1.44, W 64.02, Nb 6.47; found Co 1.81, P 1.43, W 64.57, Nb 6.45. IR (KBr disks): 1615 (m), 1466 (m), 1083 (vs), 1014 (m), 944 (m), 889 (m), 726 (vs), 596 (m), 562 (vw), 516 (s), 460 (w).

Synthesis of $H_{19}[Mn_4(H_2O)_7(P_2W_{15}Nb_3O_{62})_3]\cdot 6(HCOOH)\cdot 18H_2O$ (Mn-POM):

$K_8H[P_2W_{15}(NbO_2)_3O_{59}]\cdot 12H_2O$ (0.25 g, 0.05 mmol), $NaHSO_3$ (0.05 g, 0.48 mmol) and $MnCl_2$ (0.12 g, 0.9 mmol) were dispersed in a mixture of 7 mL H_2O and 3.5 mL ethanol in a 25-mL vial. Then, 4.5 mL formic acid was added. The tightly capped vial was placed in an oven at 100 °C for 3 days, and colorless single crystals were obtained. Yield: 0.13 g (58.9% based on $K_8H[P_2W_{15}(NbO_2)_3O_{59}]\cdot 12H_2O$). Anal. Calcd (%): Mn 1.66, P 1.40, W 62.50, Nb 6.32; found Mn 1.68, P 1.40, W 62.98, Nb 6.30. IR (KBr disks): 1579 (m), 1463 (m), 1083 (vs), 1014 (m), 944 (s), 910 (m), 740 (vs), 597 (w), 562 (w), 518 (s), 460 (w).

Synthesis of $H_{19}[Zn_4(H_2O)_7(P_2W_{15}Nb_3O_{62})_3]\cdot 23H_2O$ (Zn-POM):

$K_8H[P_2W_{15}(NbO_2)_3O_{59}]\cdot 12H_2O$ (0.25 g, 0.05 mmol), $NaHSO_3$ (0.05 g, 0.48 mmol) and $Zn(NO_3)_2\cdot 6H_2O$ (0.30 g, 1.0 mmol) were dispersed in a mixture of 7 mL H_2O and 3.5 mL ethanol in a 25-mL vial. Then, 5 mL acetic acid was added. The tightly capped vial was placed in an oven at 100 °C for 3 days, and colorless single crystals were obtained. Yield: 0.10 g (45.8% based on $K_8H[P_2W_{15}(NbO_2)_3O_{59}]\cdot12H_2O$). Anal. Calcd (%): Zn 2.00, P 1.42, W 63.19, Nb 6.39; found Zn 1.99, P 1.41, W 63.60, Nb 6.42. IR (KBr disks): 1582 (s), 1463 (s), 1082 (vs), 1015 (s), 943 (m), 893 (s), 724 (vs), 596 (vw), 562 (vw), 516 (m), 459 (w).

SI-3 Single-crystal X-ray Crystallography

Single crystal XRD analysis of **Cu-POM**, **Co-POM**, **Mn-POM** and **Zn-POM** were recorded on a SuperNova Dual diffractometer using graphite-monochromated Cu *Kα* radiation, λ = 1.54184 Å. The linear absorption coefficients, scattering factors for the atoms, and anomalous dispersion corrections were taken from the International Tables for X-Ray Crystallography. Empirical absorption corrections were applied. Structures were solved using direct methods (SHELXT)[2] and refined by full-matrix least-squares (SHELXL) interfaced with the programme OLEX2.[3] Anisotropic thermal parameters were used to refine all non-hydrogen atoms, with the exception for a few oxygen atoms. Those hydrogen atoms attached to lattice water molecules were not located. Crystallization water molecules and guest molecules were estimated by thermogravimetry and only partial guest molecules were achieved with the X-ray structure analysis. The crystal data and structure refinement results are summarized in Table S1. Further details on the crystal structure investigations can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/ by quoting the depository numbers CCDC-2044367 (**Cu-POM**), CCDC-2044368 (**Co-POM**), CCDC-2044369 (**Mn-POM**), CCDC-2044370 (**Zn-POM**).

Table S1. Crystal data and structural refinements.

Compounds	**Cu-POM**	**Co-POM**	**Mn-POM**	**Zn-POM**
Formula	$H_{91}Cu_4O_{222}Nb_9P_6W_{45}$	$H_{63}Co_4O_{208}Nb_9P_6W_{45}$	$C_6H_{81}Mn_4O_{223}Nb_9P_6W_{45}$	$H_{79}Zn_4O_{216}Nb_9P_6W_{45}$
Formula weight (g·mol^{-1})	13192.57	12921.90	13236.12	13091.93
T (K)	293(2)	170.00(10)	150.00(10)	149.99(10)
Wavelength Cu-K (Å)	1.54184	1.54184	1.54184	1.54184
Crystal system	trigonal	trigonal	trigonal	trigonal
Space group	P-3	P-3	P-3	P-3
a (Å)	34.2443(4)	33.8321(5)	34.5750(3)	34.2369(4)
b (Å)	34.2443(4)	33.8321(5)	34.5750(3)	34.2369(4)
c (Å)	13.7584(2)	13.5769(3)	13.6491(2)	13.7551(2)
α (°)	90	90	90	90
β (°)	90	90	90	90
γ (°)	120	120	120	120
V (Å^3)	13972.5(4)	13458.3(5)	14130.5(3)	13963.1(4)
Z	6	2	2	2
D_{calc} (mg m^{-3})	3.084	3.118	3.041	3.080
μ (mm^{-1})	37.494	40.378	38.144	37.557
F (000)	11234.0	10898.0	11206.0	11210.0
Crystalsize (mm)	0.1 × 0.05 × 0.05	0.1 × 0.05 × 0.05	0.1 × 0.05 × 0.05	0.15 × 0.05 × 0.05
Goodness−of−fit on F^2	1.062	1.023	1.062	1.045
Final R indices	$R_1 = 0.0805$,	$R_1 = 0.0647$	$R_1 = 0.0899$	$R_1 = 0.0877$
$[I>2\sigma(I)]$[a]	$wR_2 = 0.2105$	$wR_2 = 0.1728$	$wR_2 = 0.2073$	$wR_2 = 0.2130$
R indices[a]	$R_1 = 0.0998$,	$R_1 = 0.0848$	$R_1 = 0.1223$	$R_1 = 0.1023$
(all data)	$wR_2 = 0.2266$	$wR_2 = 0.1876$	$wR_2 = 0.2226$	$wR_2 = 0.2234$

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

SI-4 Structure figures

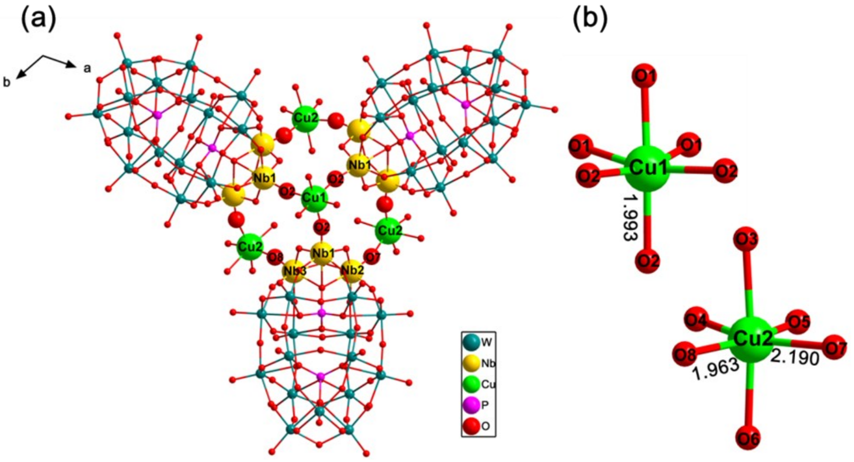


Figure S1. Ball-and-stick representation of connection between Cu ion and POM in **Cu-POM** (a), and the coordination environment of Cu1 and Cu2 ion (b).

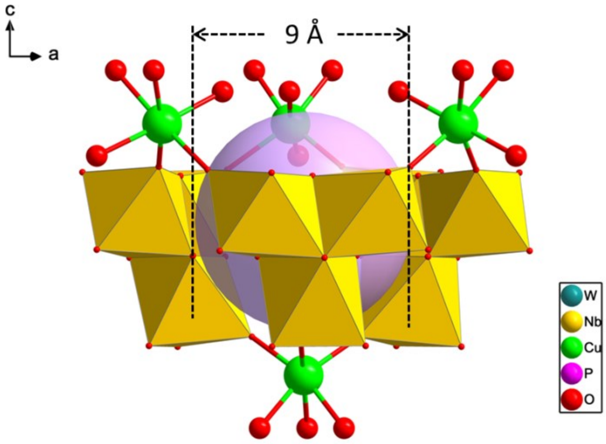


Figure S2. The structure of bowl-shape in **Cu-POM**.

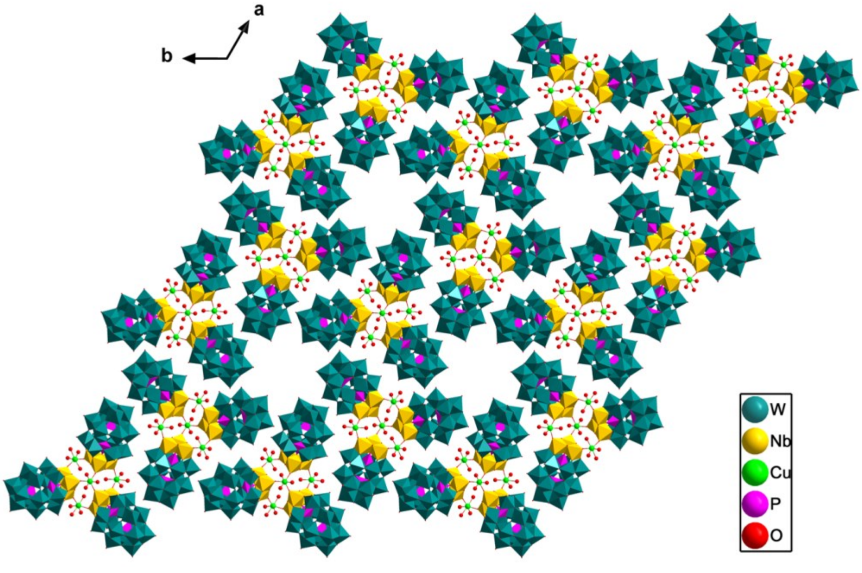


Figure S3. The packing structure of **Cu-POM** viewing along the *c* axis.

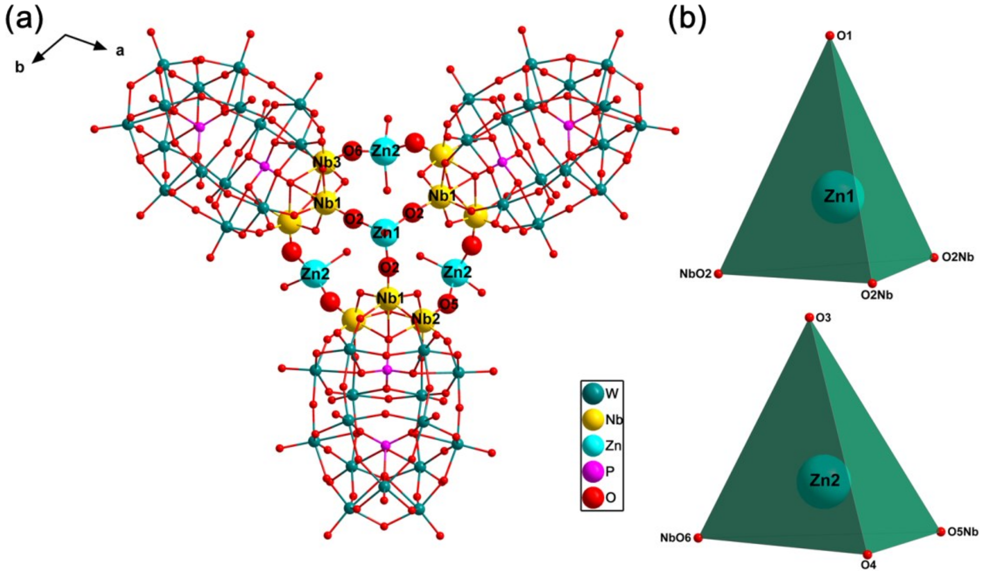


Figure S4. Ball-and-stick representation of connection between Zn ion and POM in **Zn-POM** (a); and the coordination environment of Zn1 and Zn2 ion (b).

Table S2. Bond valence calculations of select O atoms of four compounds.

Atom	Bond	Distance / Å	Bond Valence
O1	O1-Cu1	1.973	0.452
O3	O3-Cu2	2.146	0.283
O4	O4-Cu2	2.024	0.394
O5	O5-Cu2	1.957	0.472
O6	O6-Cu2	2.093	0.327
O1	O1-Co1	2.111	0.322
O3	O3-Co2	2.090	0.341
O4	O4-Co2	2.078	0.352
O1	O1-Mn1	2.101	0.431
O3	O3-Mn2	2.133	0.369
O4	O4-Mn2	2.087	0.448
O1	O1-Zn1	2.129	0.317
O3	O3-Zn2	2.097	0.346
O4	O4-Zn2	2.081	0.361

Table S3. Bond valence sum calculations of Cu, Co, Mn and Zn ions of four compounds.

Atom	Bond	Distance / Å	Bond Valence	Bond Valence Sum (BVS)
Cu1	Cu1-O1(1)	1.973	0.365	2.130
	Cu1-O1(2)	1.973	0.365	
	Cu1-O1(3)	1.973	0.365	
	Cu1-O2(1)	1.994	0.345	
	Cu1-O2(2)	1.994	0.345	
	Cu1-O2(3)	1.994	0.345	
Cu2	Cu2-O3	2.146	0.229	1.771
	Cu2-O4	2.024	0.318	
	Cu2-O5	1.957	0.381	
	Cu2-O6	2.093	0.264	
	Cu2-O7	2.187	0.205	
	Cu2-O8	1.964	0.374	
Co1	Co1-O1	2.111	0.322	1.837
	Co1-O2(1)	1.945	0.505	
	Co1-O2(2)	1.945	0.505	
	Co1-O2(3)	1.945	0.505	
Co2	Co2-O3	2.090	0.341	1.626
	Co2-O4	2.078	0.344	
	Co2-O5	1.956	0.490	
	Co2-O6	1.987	0.451	
Mn1	Mn1-O1	2.101	0.431	2.537
	Mn1-O2(1)	1.921	0.702	
	Mn1-O2(2)	1.921	0.702	
	Mn1-O2(3)	1.921	0.702	
Mn2	Mn2-O3	2.133	0.396	2.263
	Mn2-O4	2.087	0.448	
	Mn2-O5	1.918	0.708	
	Mn2-O6	1.916	0.711	
Zn1	Zn1-O1	2.129	0.317	1.856
	Zn1-O2(1)	1.951	0.513	
	Zn1-O2(2)	1.951	0.513	
	Zn1-O2(3)	1.951	0.513	
Zn2	Zn2-O3	2.097	0.346	1.669
	Zn2-O4	2.081	0.361	
	Zn2-O5	2.001	0.448	
	Zn2-O6	1.950	0.514	

SI-5 Powder X-ray diffraction patterns

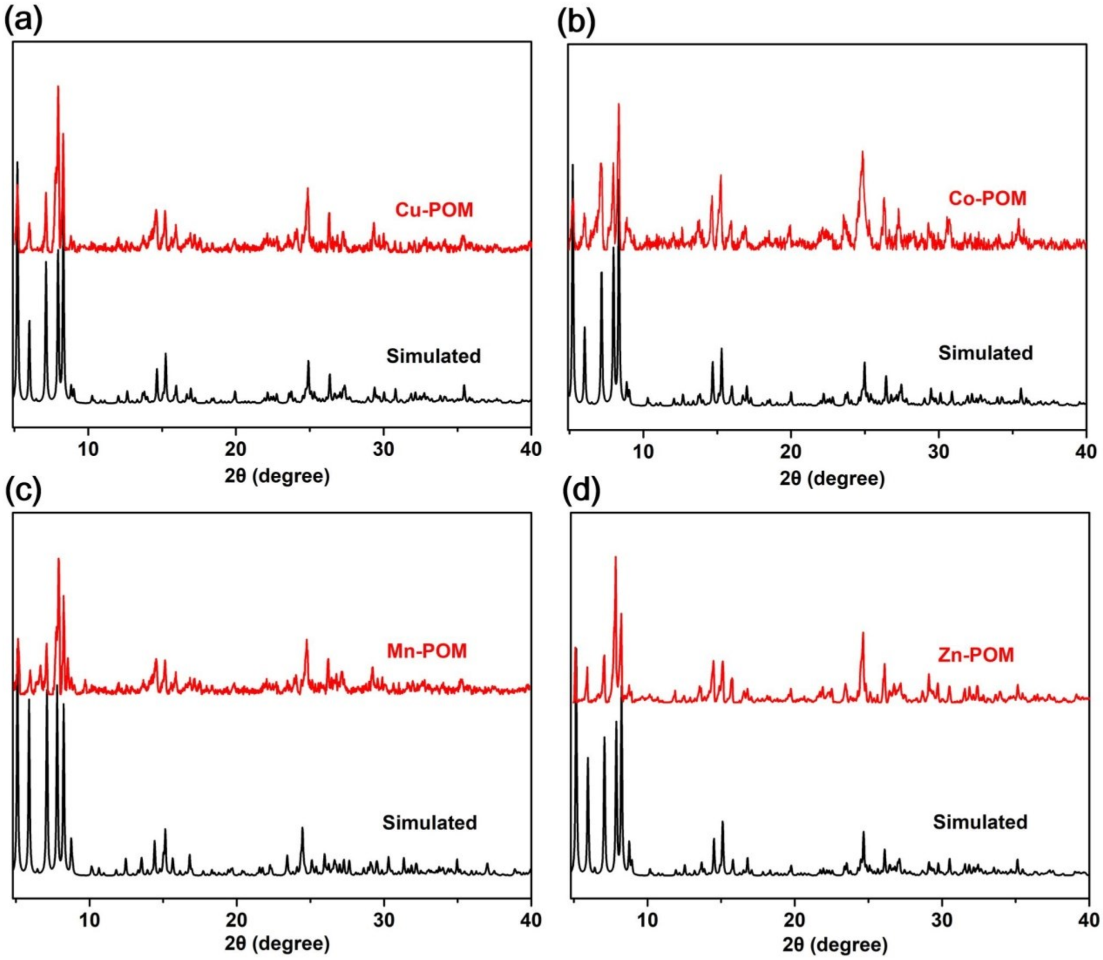


Figure S5. Simulated (black) and experimental (red) PXRD patterns of four compounds.

SI-6 FTIR Spectroscopy

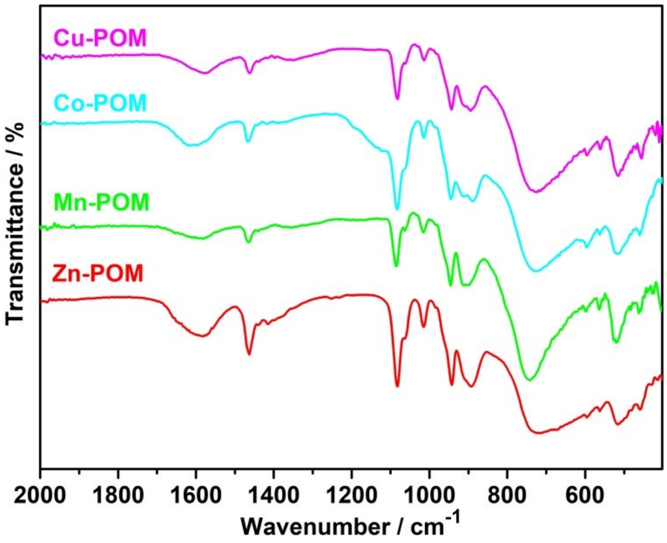


Figure S6. IR spectra of the four compounds.

The four compounds exhibit similar characteristic peak. The signals at 1083 cm^{-1} and 1014 cm^{-1} are attributed to vibrations of P-O$_a$; the absorption peaks at the range of 946-943 cm^{-1}, 892-889 cm^{-1}, 740-728 cm^{-1} are attributed to the W-O$_t$, W-O$_b$-W, W-O$_c$-W vibrations in the Dawson framework of four compounds.

SI-7 Thermal analyses

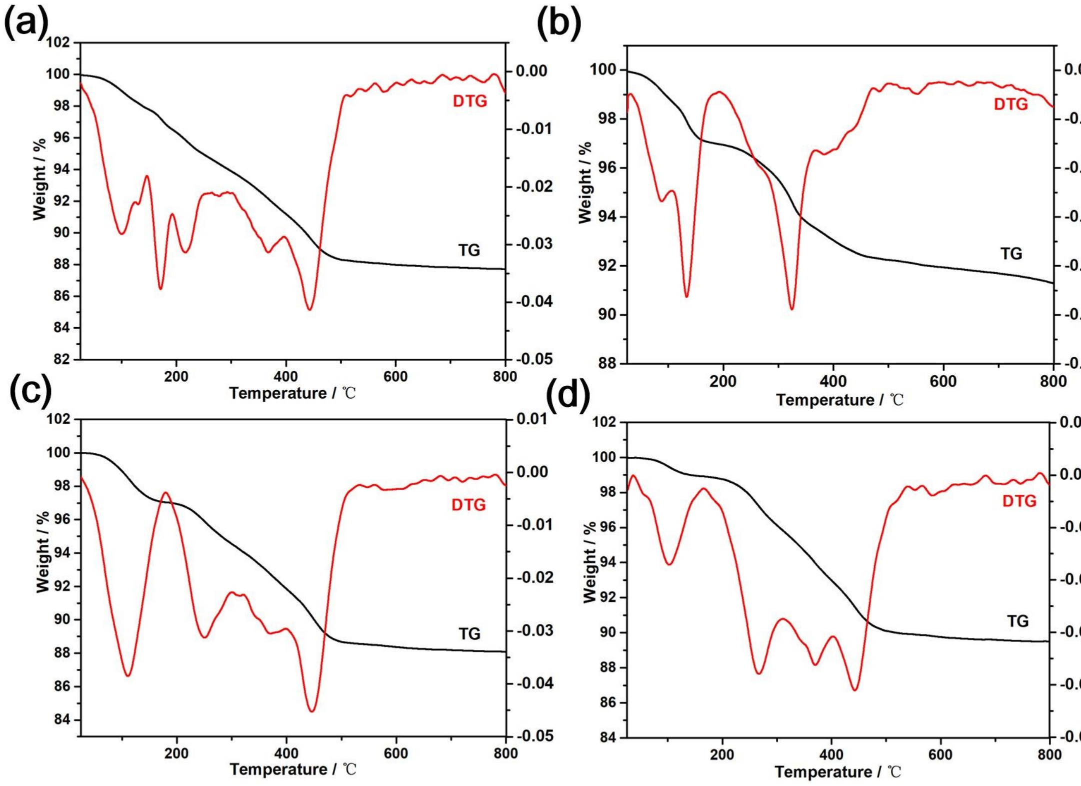


Figure S7. Thermogravimetric curves of **Cu-POM** (a), **Co-POM** (b), **Mn-POM** (c) and **Zn-POM** (d).

The thermal behavior of four compounds has been investigated under nitrogen atmospheres between 25 and 800 °C by thermogravimetric analysis (TGA) and the first derivative of the thermogravimetric (DTG). The TG curve of four compounds exhibits similar continuous weight loss process. For **Cu-POM**, the weight loss of 4.89% (4.91% calculated) from 25 to 243 °C is attributed to the loss of 21 lattice water molecules and 15 coordinated water molecules. The weight loss of 3.00% (3.06% calculated) from 25 to 185 °C for **Co-POM** is attributed to the loss of 15 lattice water molecules and 7 coordinated water molecules. The weight loss of 5.48% (5.49% calculated) from 25 to 301 °C for **Mn-POM** is attributed to the loss of 18 lattice water molecules, 6 formic acid molecule and 7 coordinated water molecules. The weight loss of 4.18% (4.13% calculated) from 25 to 311 °C for **Zn-POM** is attributed to the loss of 23 lattice water molecules and 7 coordinated water molecules. The rest weight losses before 800 °C of four compounds e.g. 6.92% (5.82% calculated) for **Cu-POM**, 5.05% (5.94% calculated) for **Co-POM**, 6.04% (5.75% calculated) for **Mn-POM**, and 5.93% (5.86% calculated) for **Zn-POM** can be ascribed to the dehydration of protons and the partial decomposition of polyoxoanions.[4]

SI-8 Cyanosilylation reaction

A typical procedure for cyanosilylation reaction was performed as follows: 1.5 mmol TMSCN, 0.5 mmol aldehydes/ketones, and 0.5 mol% catalysts were added to a 10 mL Schlenk tube in the absence of solvent. The reaction mixture was stirred at 25 °C under nitrogen atmosphere. The progress of the reaction of the aldehydes or ketones with TMSCN was qualitatively analyzed by GC analyses. Yields were determined using ^{1}H NMR by tracing the change of characteristic hydrogen resonance of in substrate aldehydes/ketones and products using $CDCl_3$ as solvent. Before the catalytic test, the catalysts were activated at 100 °C under vacuum conditions to expose coordination unsaturated active sites .[5,6] After the reaction was completed, the catalysts were recovered by centrifugation and purified by washing with ethanol and then air-dried for the next cycle.

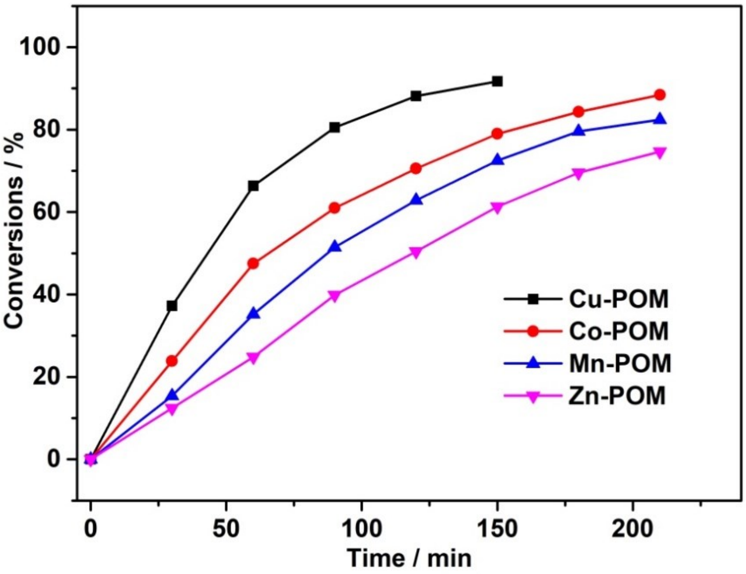


Figure S8. Conversions curves of cyanosilylation reaction of benzaldehyde catalyzed by four compounds.

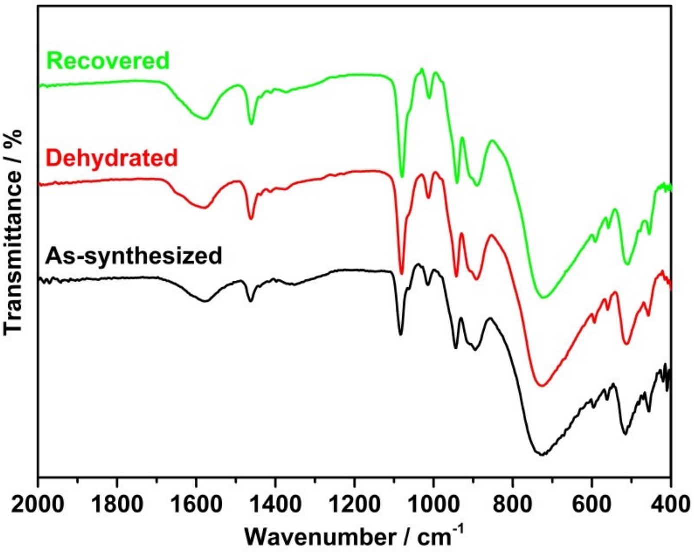
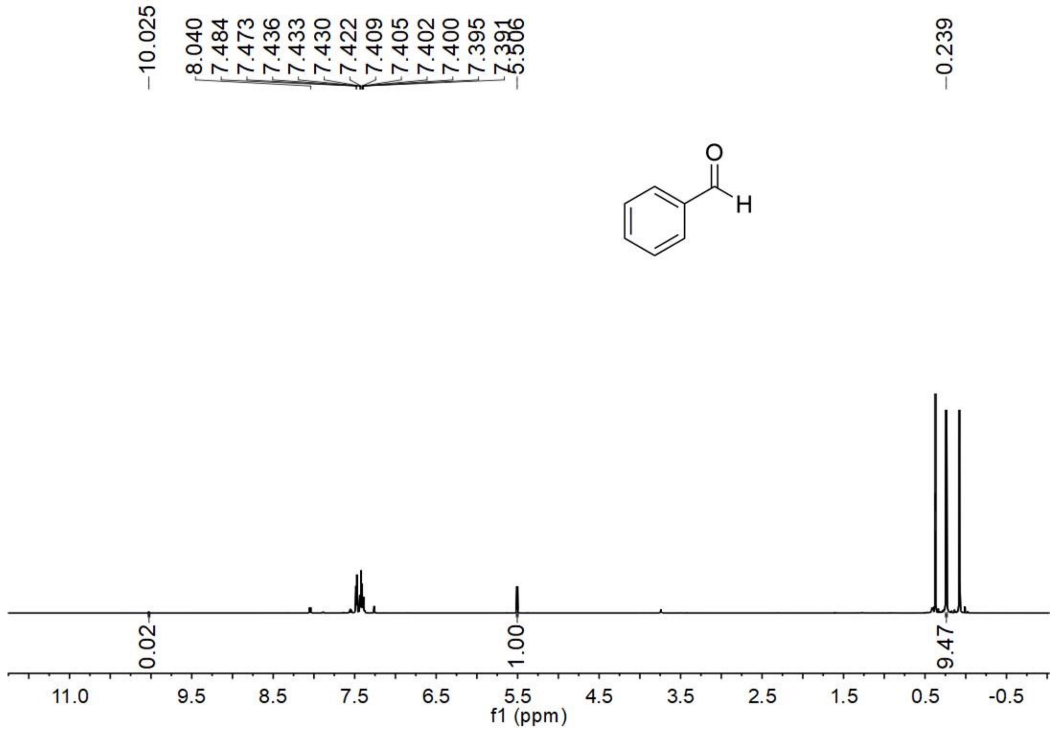
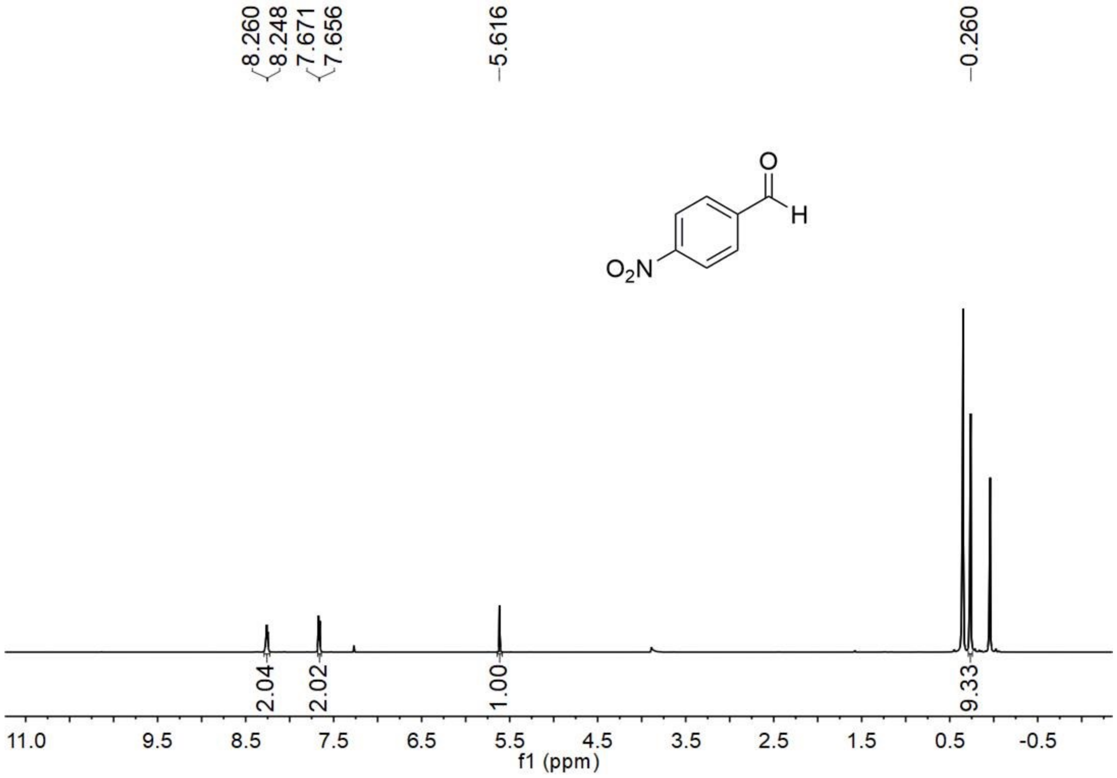
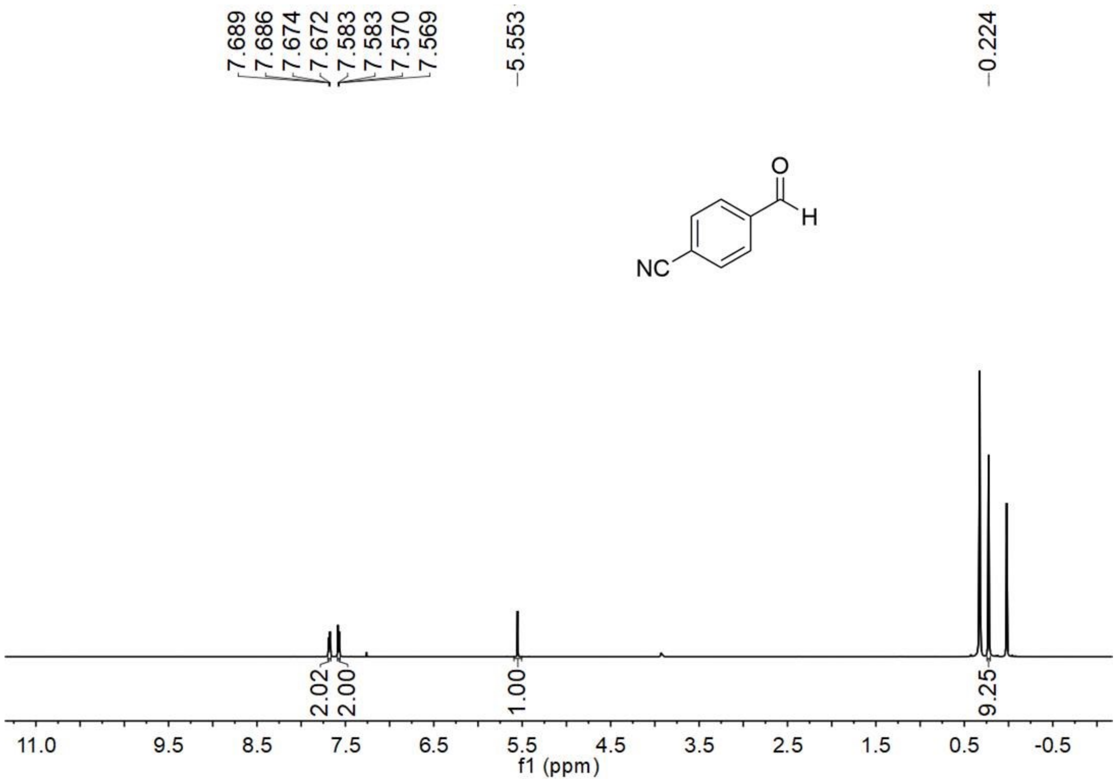


Figure S9. The IR spectra of **Cu-POM** before and after catalysis.

^{1}H NMR Spectra of Cyanosilylation Products[7-9]



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2.00
1.00
9.25
11.0
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6.5
5.5
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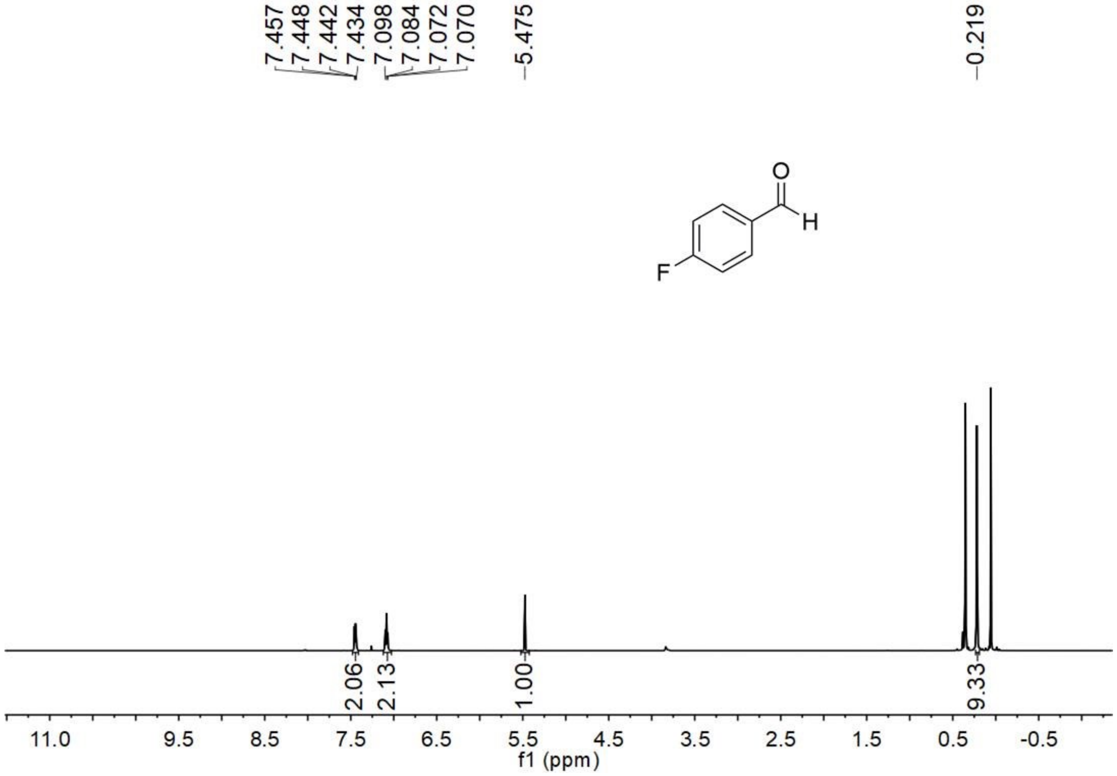
1.5
0.5
-0.5
f1 (ppm)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1.00
9.33
11.0
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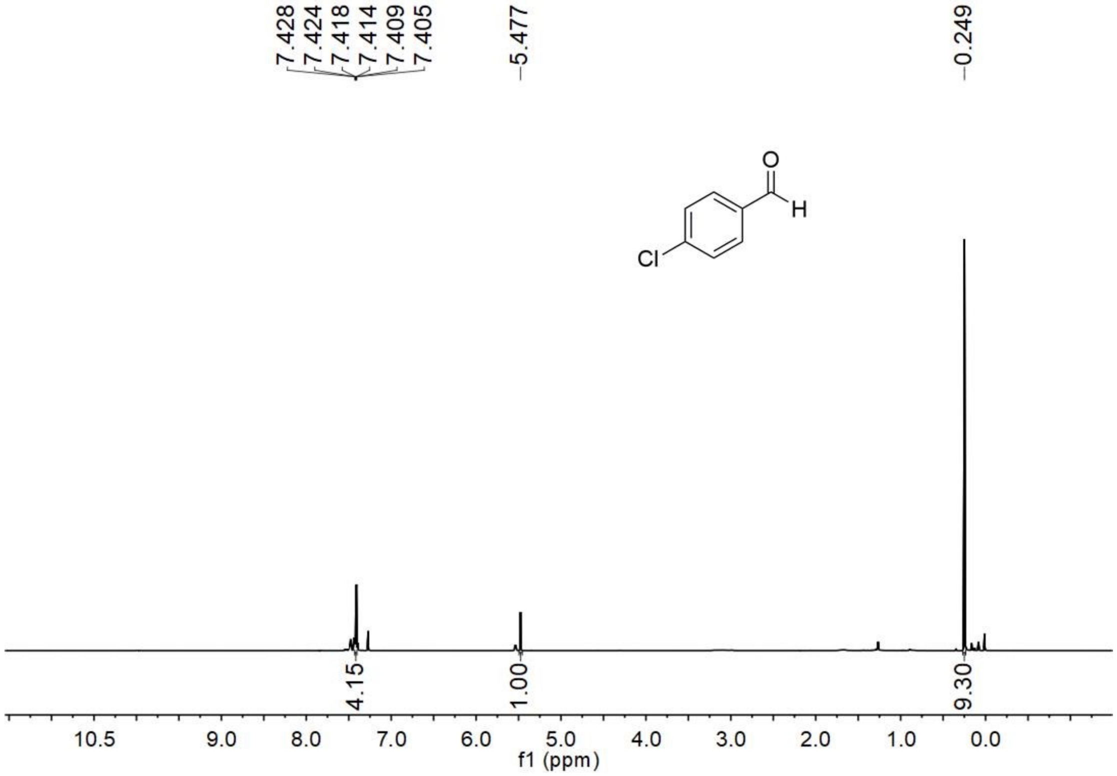
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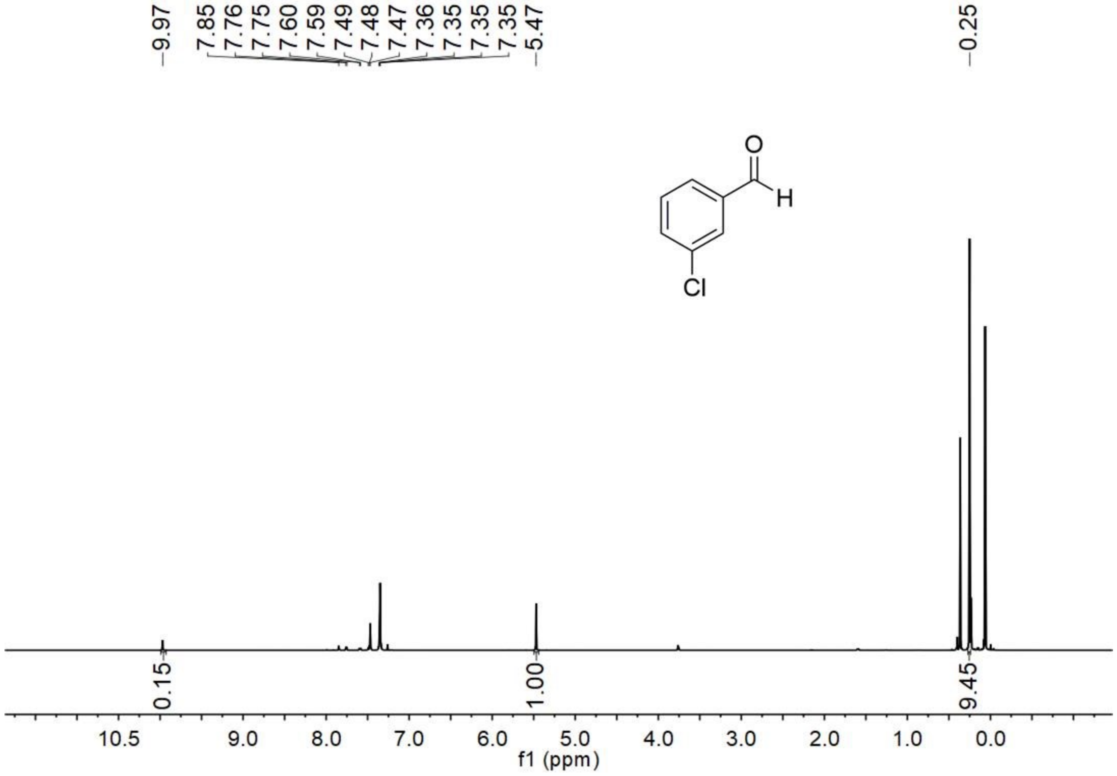
f1 (ppm)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O
H
Cl
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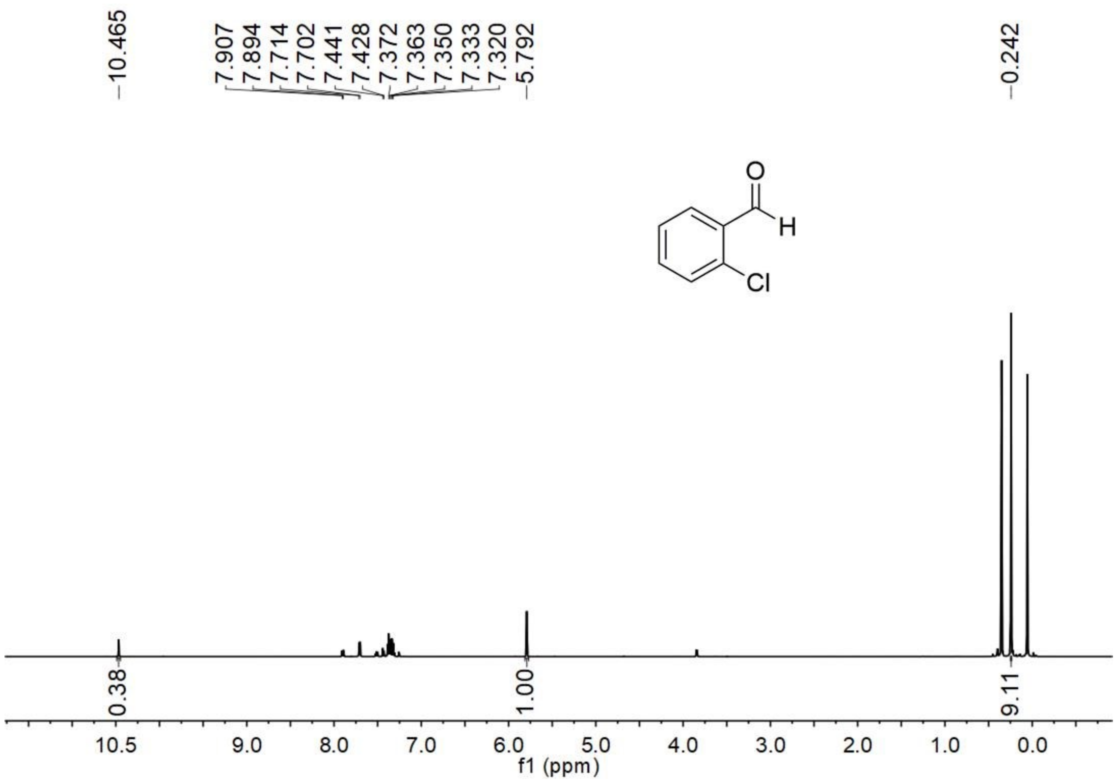
f1 (ppm)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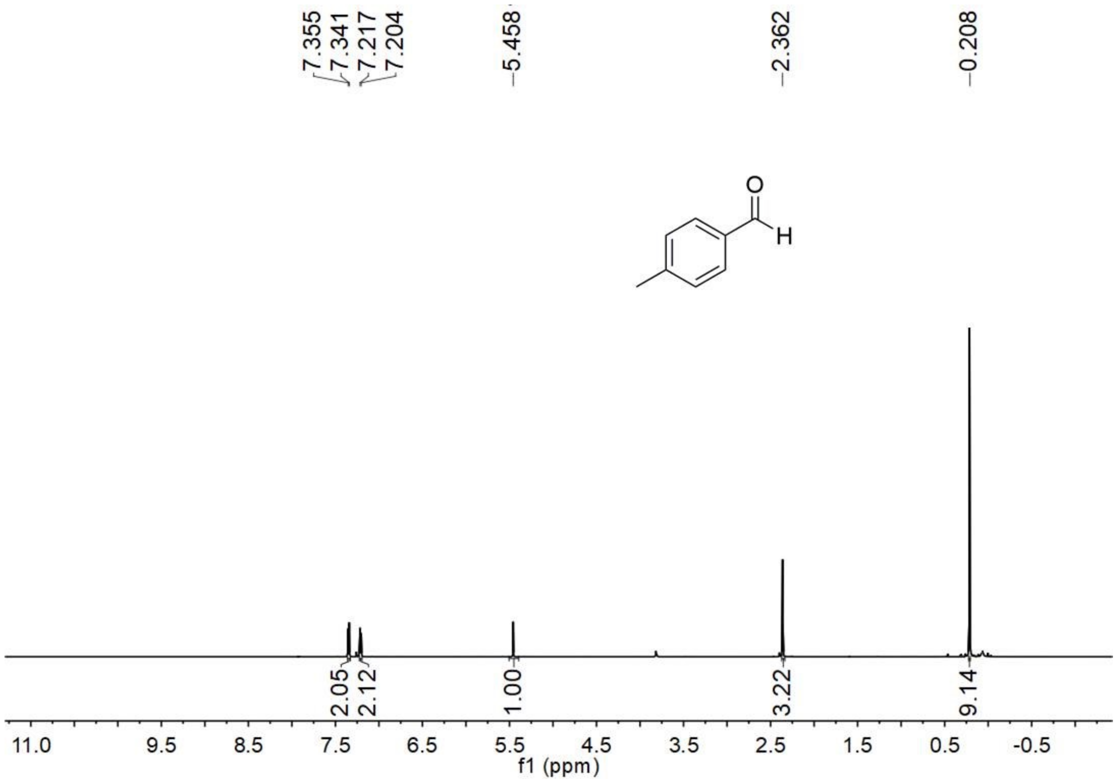
f1 (ppm)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1.5
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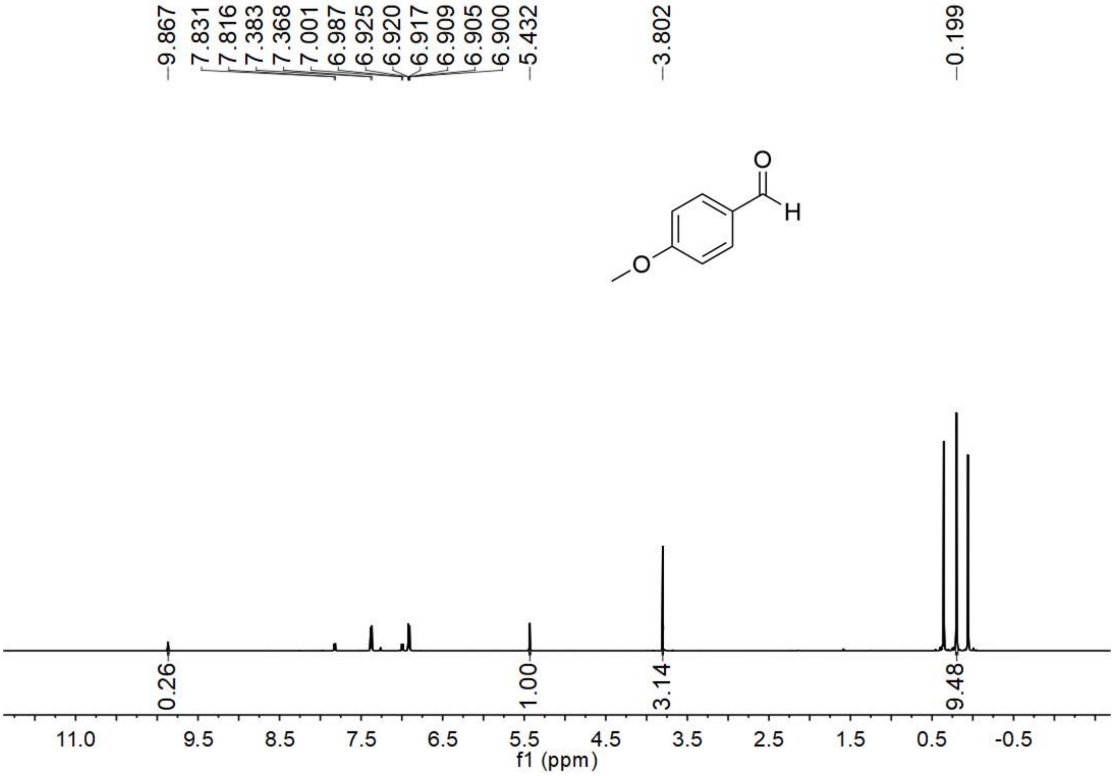
f1 (ppm)



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6.900
5.432
3.802
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O
H
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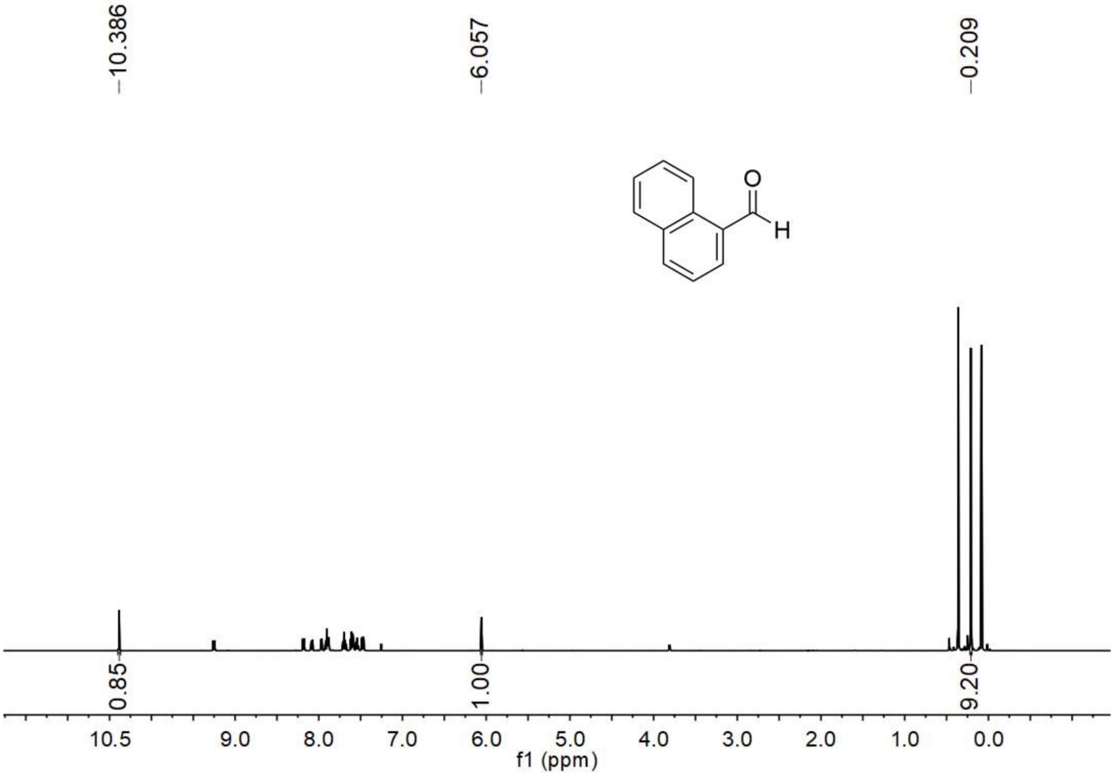
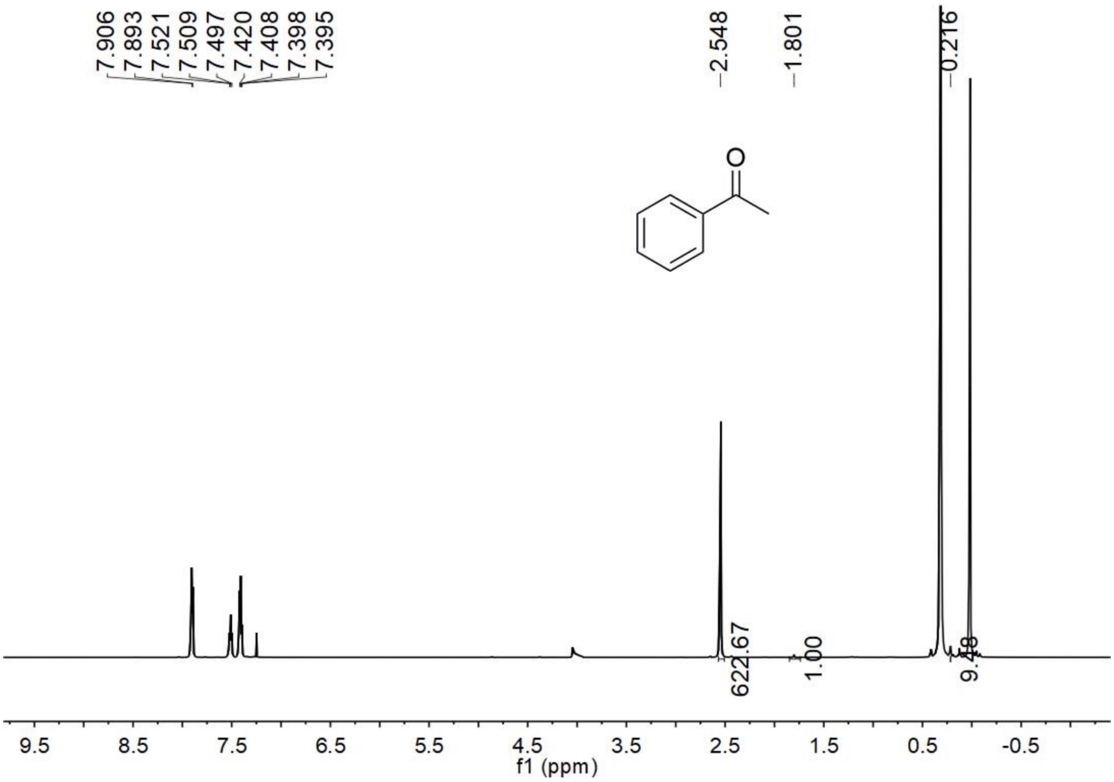
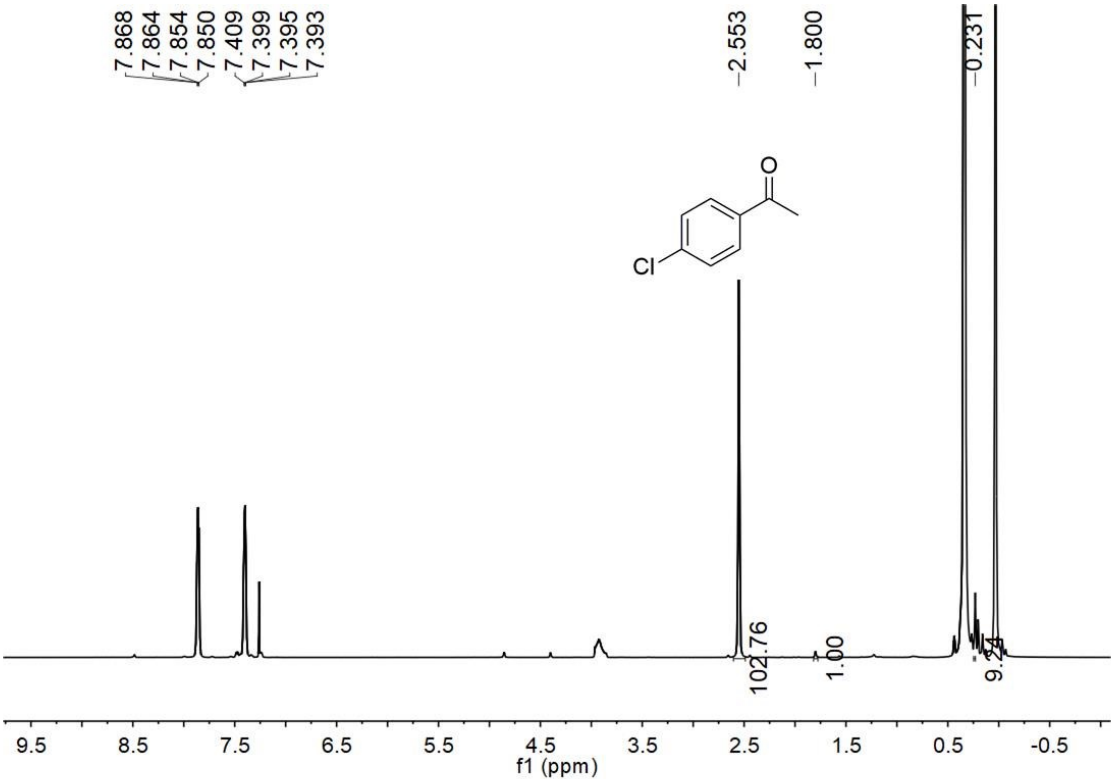
9.48
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)



10.386
6.057
0.209
O
H
0.85
1.00
9.20
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


7.906
7.893
7.521
7.509
7.497
7.420
7.408
7.398
7.395
2.548
1.801
0.216
O
622.67
1.00
9.48
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


7.868
7.864
7.854
7.850
7.409
7.399
7.395
7.393
2.553
1.800
0.231
O
Cl
102.76
1.00
9.24
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

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