

Supporting Information

Efficient catalysis of Knoevenagel condensation by 1D copper-containing heteropolyoxoniobate at room temperature

Ya-Kun Zuo, Yan-Ru Li, Yan-Qiong Sun, Xin-Xiong Li, Cai Sun* and Shou-Tian Zheng*

Fujian Provincial Key Laboratory of Advanced Inorganic Oxygenated-Materials, College of Chemistry, Fuzhou University, Fuzhou, Fujian 350108, China.

*Email: csun@fzu.edu.cn; stzheng@fzu.edu.cn

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1. Materials and Methods

Materials and measurements. All chemicals used for syntheses were purchased from commercial sources, and no further purifications were conducted before their usages. $K_7\text{HfNb}_6\text{O}_{19}\cdot 13\text{H}_2\text{O}$ was prepared according to the literature procedure.¹ Infrared (IR) spectra (KBr pellet) was performed on an Opus Vetex 70 FTIR infrared spectrophotometer in the range of 400–4000 cm^{-1} . Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku DMAX 2500 diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). Thermogravimetric analysis was conducted using a Mettler Toledo TGA/SDTA 851e analyzer in an N_2 flow atmosphere with a heating rate of 10 $^\circ\text{C}/\text{min}$ at a temperature of 25–1000 $^\circ\text{C}$. The UV-vis spectrum was measured on a SHIMADZU UV-2600 UV-visible spectrophotometer. Simulated XRD data was simulated by the Mercury Software with the step of 0.02 $^\circ$ from 5 $^\circ$ to 50 $^\circ$ ($\lambda = 1.54056 \text{ \AA}$).

Synthesis of $\text{H}_3[\text{K}(\text{H}_2\text{O})_6][\text{K}_2(\text{H}_2\text{O})_{10}]_2[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2][\text{Cu}(\text{en})_2(\text{Nb}_6\text{O}_{19}\text{Cu}(\text{en}))_2]\cdot 24\text{H}_2\text{O}$ (HPONb 1). A mixture of $K_7\text{HfNb}_6\text{O}_{19}\cdot 13\text{H}_2\text{O}$ (0.274 g, 0.2 mmol), $\text{Cu}(\text{Ac})_2\cdot \text{H}_2\text{O}$ (0.040 g, 0.2 mmol), $\text{Cr}(\text{Ac})_3\cdot \text{H}_2\text{O}$ (0.050 g, 0.2 mmol), $\text{Na}_4\text{P}_2\text{O}_7\cdot 10\text{H}_2\text{O}$ (0.090 g, 0.2 mmol) and 0.5 mL en (en = ethylenediamine) were mixed in 5 mL deionized water in a 20 mL glass bottle. After stirred 1 hour, the resulting mixture was heated at 80 $^\circ\text{C}$ for 72 h. After cooling down to room temperature, kept at room temperature for slow evaporation. After 1 day, purple crystals were obtained. Yield: ~250mg (86%, based on Nb). The pH values before and after reaction were 11.1 and 11.9, respectively. IR (Fig. S4) (KBr pellet, ν/cm^{-1}): 3220(s), 3140(s), 2960(w), 2891(w), 1646(w), 1580(s), 1450(w), 1401(w), 1288(w), 1115(m), 1040(s), 955(m), 845(m), 653(s), 500(s). UV-Vis (Fig. S5) (λ/nm): 200–400: the charge transfer transitions from O to Nb; 400–800: the d–d transition of the 3d metal ion Cu^{2+} .

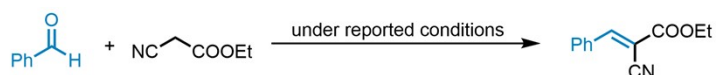
Single-crystal X-ray diffraction. The structure of HPONb 1 was determined at 100 K under nitrogen atmosphere by single-crystal X-ray diffraction method. The apparatus is a Bruker Apex Duo CCD diffractometer and the X-ray

resource is a graphite-monochromatized Cu K α radiation with wavelength of 1.54178 Å. The crystal structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 according to the SHELX and OLEX. Crystal data for HPONb **1**: $M_r = 2872.329$ g/mol, triclinic, $P-1$, $a = 13.1904(13)$ Å, $b = 14.1814(13)$ Å, $c = 15.3343(14)$ Å, $\alpha = 90.693(2)^\circ$, $\beta = 100.806(2)^\circ$, $\gamma = 110.263(4)^\circ$, $V = 2633.9(4)$ Å³, $Z = 1$, $\rho_{(calc)} = 1.811$ g·cm⁻³, $GOF = 1.076$. A total of 66328 reflections ($2.72^\circ \leq 2\theta \leq 50.14^\circ$) were collected, 9174 of which were unique $R_{int} = 0.0289$ $R_{sigma} = 0.0201$, $R_1 (wR_2) = 0.0601 (0.1845)$ for 514 parameters ($I \geq 2\sigma(I)$), $R_1 (wR_2) = 0.0710 (0.2077)$ (all data). The crystallographic data can be queried with CCDC number of [2301263](https://www.ccdc.cam.ac.uk/structures/StructureSearch.do?search=2301263) at the Cambridge Crystallographic Data Centre.

Procedure of the HPONb 1 catalyzed condensation reaction. Aldehyde substrate (2 mmol), methylene substrate (2 mmol), HPONb **1** as catalyst, and ethanol (2 mL) were added to a 25 mL Schlenk tube. Then the reaction was carried out in water bath kettle at predetermined time and temperature. After reaction, the yields were determined by GC with n-dodecane as the internal standard. The gram-scale reactions and cycle experiments were conducted in the same way. The reusability of HPONb **1** was evaluated by the condensation of 2 mmol benzaldehyde and 2 mmol ethyl cyanoacetate. After each cycle of reaction, the catalyst **1** was filtered out and washed with 10 mL ethanol for five times, and it was dried at 45 °C under vacuum for 2 h, then, it was used for the next run.

2. Additional tables

Table S1 A summary of known POM catalysts for Knoevenagel condensation



Entry	Catalysts	Temp. (°C)	Time (h)	a: b	Phase	Yield (%)	Ref
1	HPONb 1	rt	1	1: 1	Hetero-	99	This work
7	K ₈ SiW ₁₀	60	2	1: 1	Hetero-	84	²
8	H ₃ PW ₁₂ O ₄₀	60	2	1: 1	Hetero-	11	²
9	K ₃ AsW ₁₂ O ₄₀	60	2	1: 1	Hetero-	11	²
10	Na ₁₂ P ₂ W ₁₅ O ₅₆	60	2	1: 1	Hetero-	68	²
11	Na ₆ PW ₁₂ O ₄₂	60	2	1: 1	Hetero-	84	²
12	Na-B-PW ₉	25	6	1: 1.5	Hetero-	83	³
13	Na-A-PW ₉	25	6	1: 1.5	Hetero-	80	³
14	Na ₃ PW ₁₂ O ₄₀	70	2	1: 1	Hetero-	23	⁴
15	Mg ₃ Al-PW ₁₂	60	6	1: 1.5	Hetero-	99	⁵
16	[PySalm] ₃ PW ₁₂	70	4	1: 1	Hetero-	96	⁶
17	K ₇ HNb ₆ O ₁₉ ·13H ₂ O	60	2	1: 1	Hetero-	98	²
18	Na ₁₆ SiNb ₁₂ O ₄₀	70	2	1: 1	Hetero-	97	⁴
19	Tris-LDH Zn ₄ (PW ₉) ₂	80	6	1: 1	Hetero-	99	⁷
20	Cd ₃ Cu ₉ Nb ₅₄	60	1.5	1: 1	Hetero-	99	⁸

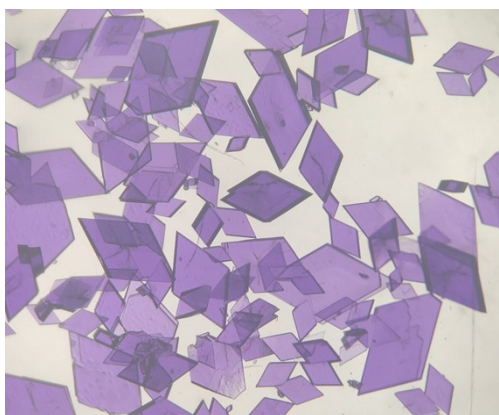
(Hetero = Heterogeneous)

Table S2 Crystallographic data for **1**

<i>Empirical formula</i>	H ₁₅₅ C ₁₂ Cu ₄ K ₅ N ₁₂ Nb ₁₂ O ₉₀
<i>Formula weight</i>	3473.5
<i>Temperature/K</i>	170
<i>Crystal system</i>	Triclinic
<i>Space group</i>	<i>P</i> -1
<i>a/Å</i>	13.1904(13)
<i>b/Å</i>	14.1814(13)
<i>c/Å</i>	15.3343(14)
<i>α/°</i>	90.693(2)
<i>β/°</i>	100.806(2)
<i>γ/°</i>	110.263(2)
<i>V/Å³</i>	2633.9(4)
<i>Z</i>	1
<i>ρ_{calc} g/cm³</i>	1.811
<i>μ/mm⁻¹</i>	2.174
<i>F(000)</i>	1336.6
<i>Radiation</i>	Mo Kα (λ = 0.71073)
<i>2θ range for data collection/°</i>	2.72 to 50.14
<i>Index ranges</i>	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -18 ≤ l ≤ 17
<i>Reflections collected</i>	66328
<i>Independent reflections</i>	9174 [<i>R_{int}</i> = 0.0289, <i>R_{sigma}</i> = 0.0201]
<i>Data/restraints/parameters</i>	9174/0/514
<i>Goodness-of-fit on F²</i>	1.076
<i>Final R indexes [I ≥ 2σ (I)]</i>	<i>R</i> ₁ = 0.0601, <i>wR</i> ₂ = 0.1845
<i>Final R indexes [all data]</i>	<i>R</i> ₁ = 0.0710, <i>wR</i> ₂ = 0.2077
<i>Data completeness</i>	0.958

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

3. Additional figures

**Fig. S1** Crystal morphology of HPONb 1.

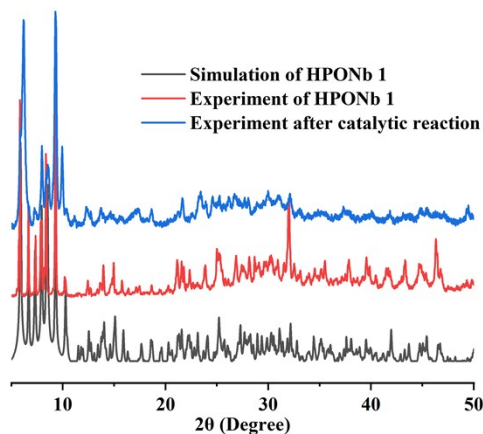


Fig. S2 The simulated and experimented powder XRD patterns for HPONb 1. the loss or gain of moisture during the test makes the actual test diffraction pattern slightly changed; and the preferred orientation of the powder makes some crystal plane peaks in the actual diffraction pattern may not appear. The phenomenon is common in the comparison of powder fitting patterns and actual patterns for clusters.⁹ It is worth mentioning that the powder fitting patterns before and after the catalytic test are consistent, indicating that structure of HPONb 1 remains stable. Diffraction peak analysis for $< 10^\circ$: 5.883° (001), 6.662° (010), 7.292° (100), 7.943° (-110), 8.384° (-101), 8.515° (0-11), 9.255° (011), 9.317° (-111).

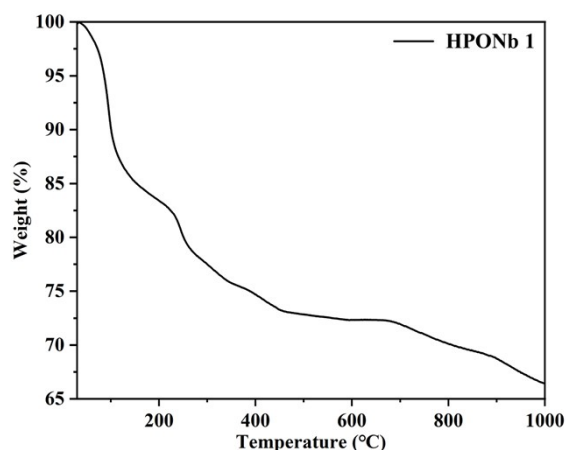


Fig. S3 TGA curve of HPONb 1. The thermogravimetric curve of HPONb 1 was measured at a heating rate of 10 °C/min in a N₂-flow atmosphere, and the temperature range of the test was from 25 °C to 1000 °C. As shown in Figure S3, HPONb 1 has a continuous weight loss process in the temperature range of 25 °C to 800 °C. The first weight-loss stage within the range of 25 °C to 120 °C should be ascribed to the loss of lattice water. Based on the first weight-loss of about 13% for HPONb 1, there are about 24 lattice waters.

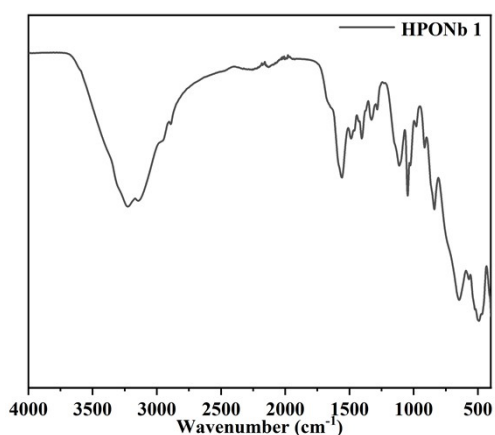


Fig. S4 IR curves of HPONb 1. In the IR spectrum, the broad absorption peak at about 3220 cm⁻¹ is attributed to the $\nu(\text{O-H})$ stretching vibration of water and the bending vibration adsorption of water appears at about 1567 cm⁻¹. The $\nu(\text{N-H})$ and $\nu(\text{C-H})$ stretching vibrations appear at about 3140 cm⁻¹ and 2960 cm⁻¹. The $\nu(\text{C-N})$ stretching vibrations appear at about 1288 cm⁻¹ and 1040 cm⁻¹. The peaks that appear in the range of 400 to 1000 cm⁻¹ can be attributed to the characteristic absorption peak of Nb-O, of which 845 cm⁻¹ is the stretching vibration peak of $\nu(\text{Nb-O}_i)$ and 653 cm⁻¹ and 500 cm⁻¹ are the stretching vibration peaks of $\nu(\text{Nb-O}_b\text{-Nb})$.

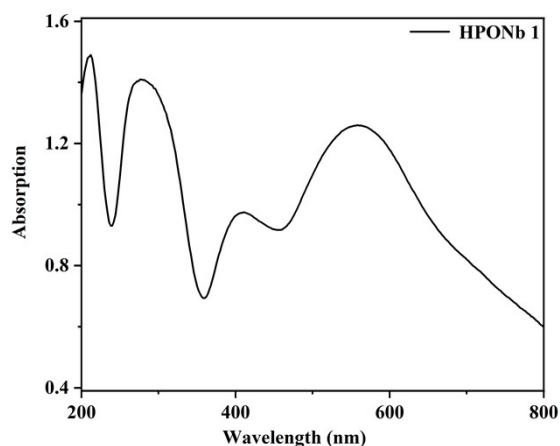


Fig. S5 The solid-state diffuse reflectance UV-vis spectrum of HPONb **1**. The broad absorption bands at 210 and 280 nm are attributed to the local excitation of O and charge-transfer transition of O to Nb, respectively. These absorption bands in the range of 400 and 800 nm can be attributed to d-d transition of Cu complexes. The coordination field parameter of en being greater than that of ligand oxo and water, therefore the peak with absorption center around 410 nm is attributed to $\text{Cu(en)}_2\text{O}_2$ and $\text{Cu(en)}_2(\text{H}_2\text{O})_2$ for Cu2 and Cu3 complexes, respectively; the peak with absorption center around 560 nm is attributed to $\text{Cu(en)}\text{O}_4$ for Cu1 complexes.

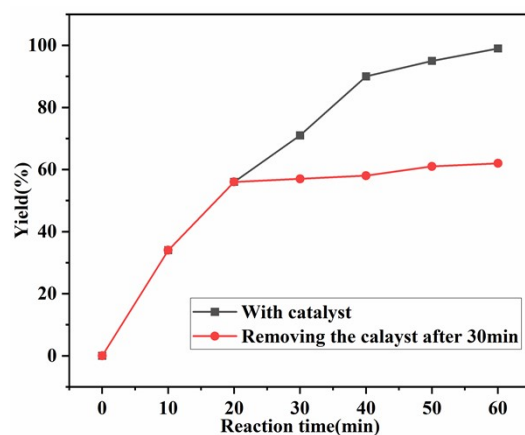


Fig. S6 Hot filtration test for HPONb **1**. The experimental data proved that the catalytic reaction was heterogeneously catalyzed and that the reaction rate decreased dramatically when the catalyst was removed after 30 min, this data proved that there was no catalytic center leakage during the catalytic reaction.

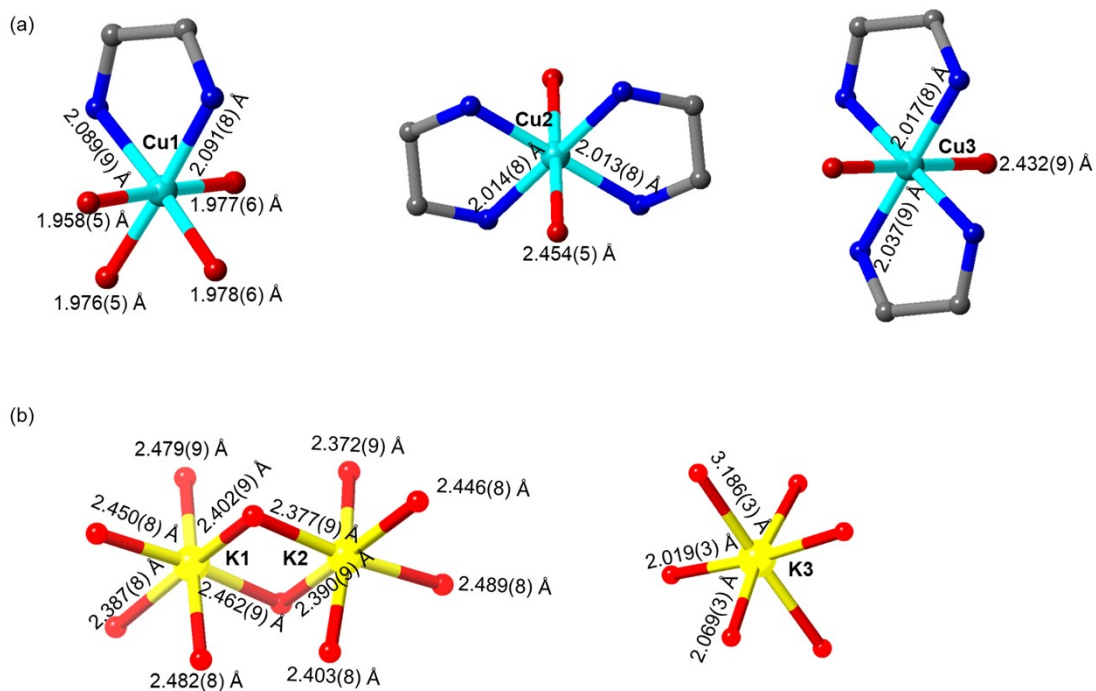


Fig. S7 Coordination pattern for (a) Cu and (b) K. Colour code: O, red; C, grey; N, blue.

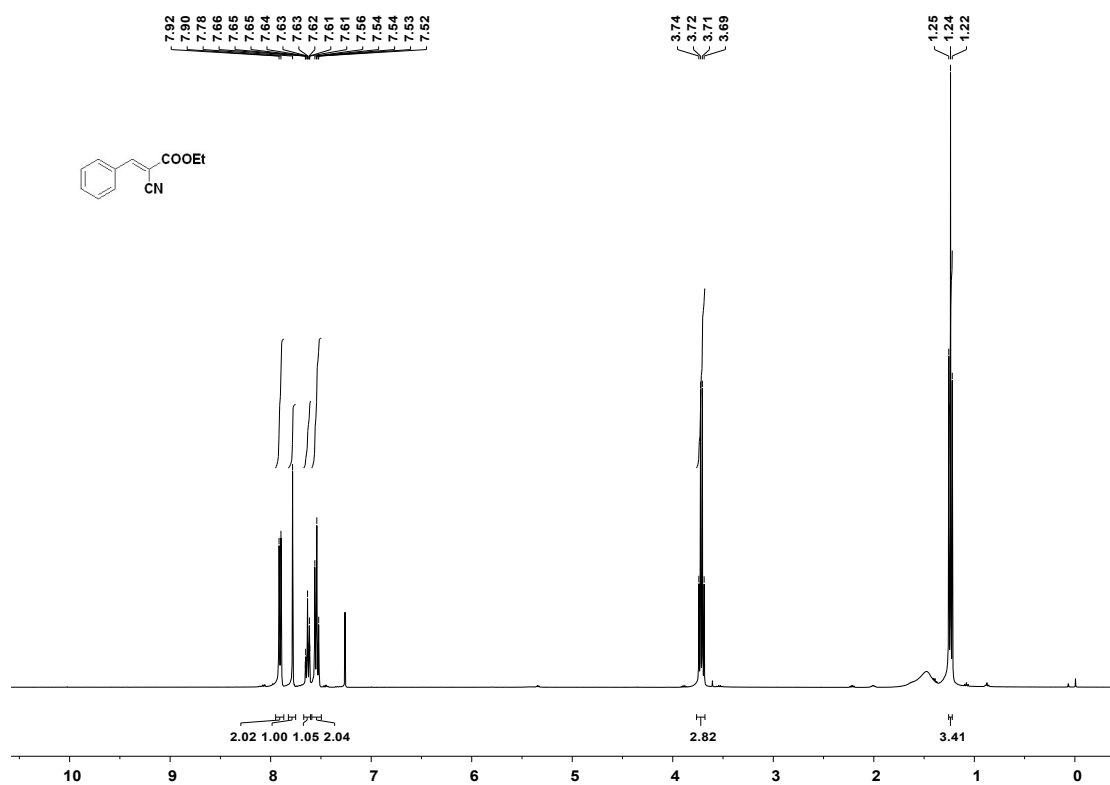


Fig. S8 ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, $J = 7.5$ Hz, 2H), 7.78 (s, 1H), 7.63 (t, $J = 7.5$ Hz, 1H), 7.54 (t, $J = 7.7$ Hz, 2H), 3.71 (q, $J = 7.0$ Hz, 3H), 1.25 (t, $J = 7.0$ Hz, 3H).

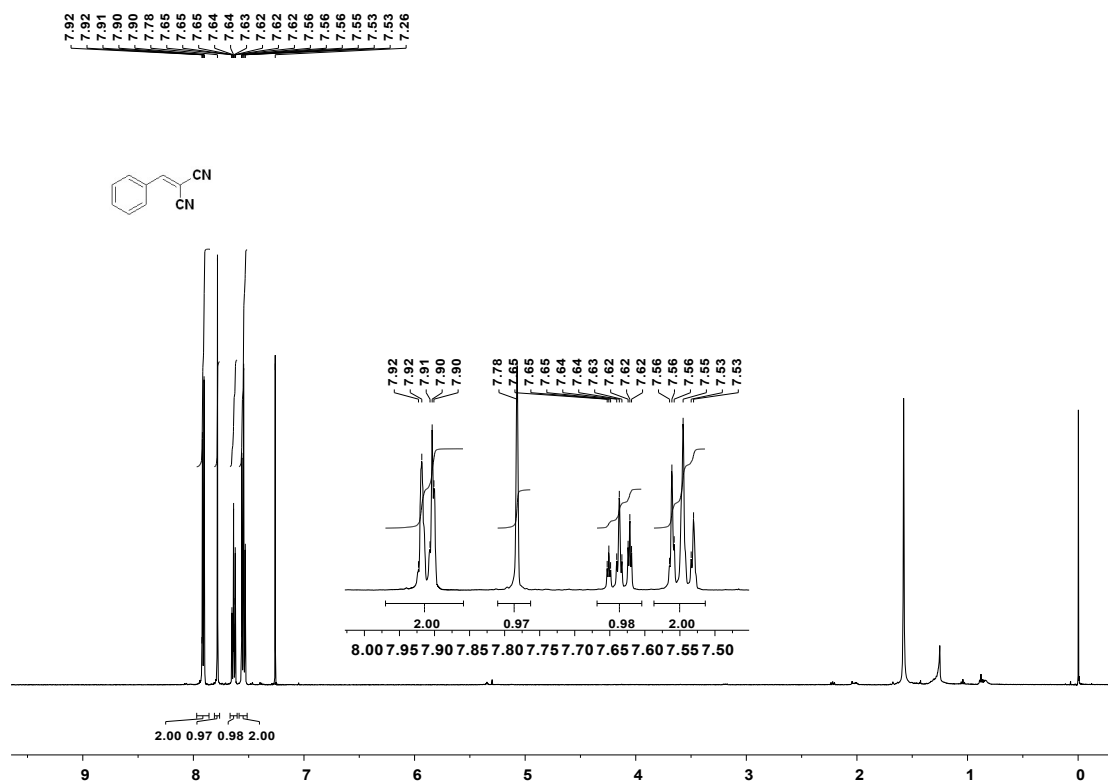


Fig. S9 ^1H NMR (400 MHz, CDCl_3) δ 7.97 – 7.86 (m, 2H), 7.78 (s, 1H), 7.67 – 7.60 (m, 1H), 7.59 – 7.51 (m, 2H).

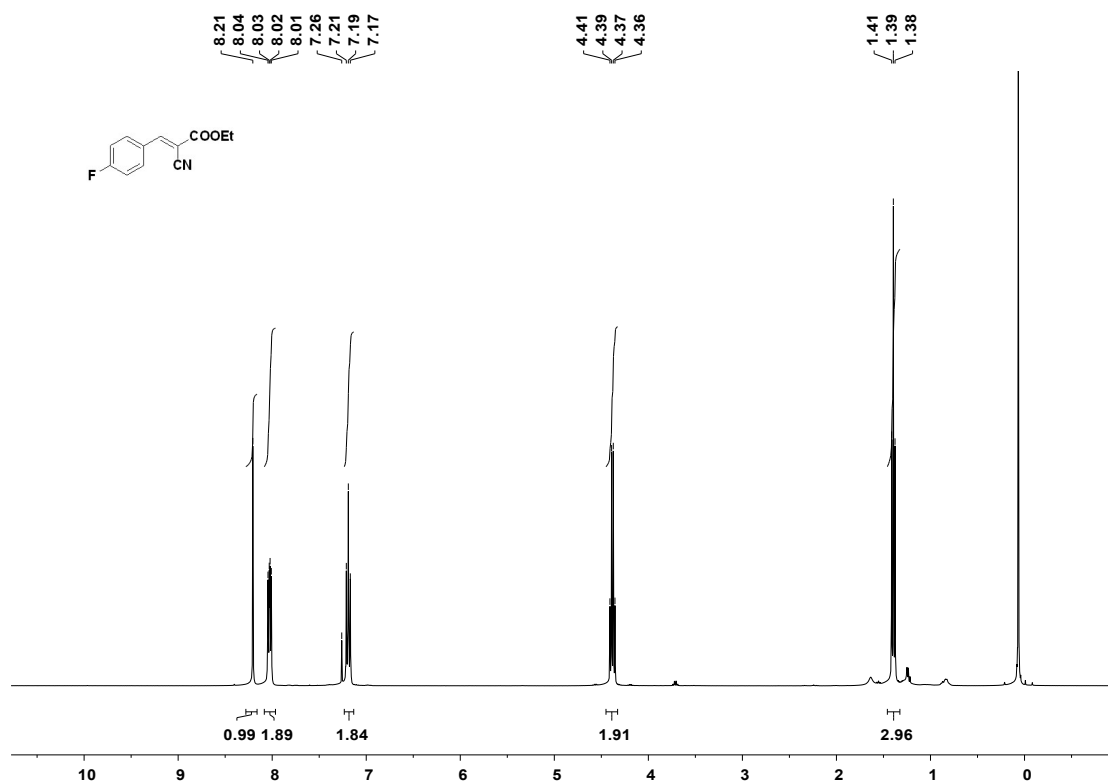


Fig. S10 ^1H NMR (400 MHz, CDCl_3) δ 8.21 (s, 1H), 8.03 (dd, $J = 8.9, 5.3$ Hz, 2H), 7.19 (t, $J = 8.5$ Hz, 2H), 4.38 (q, $J = 7.1$ Hz, 2H), 1.39 (t, $J = 7.1$ Hz, 3H).

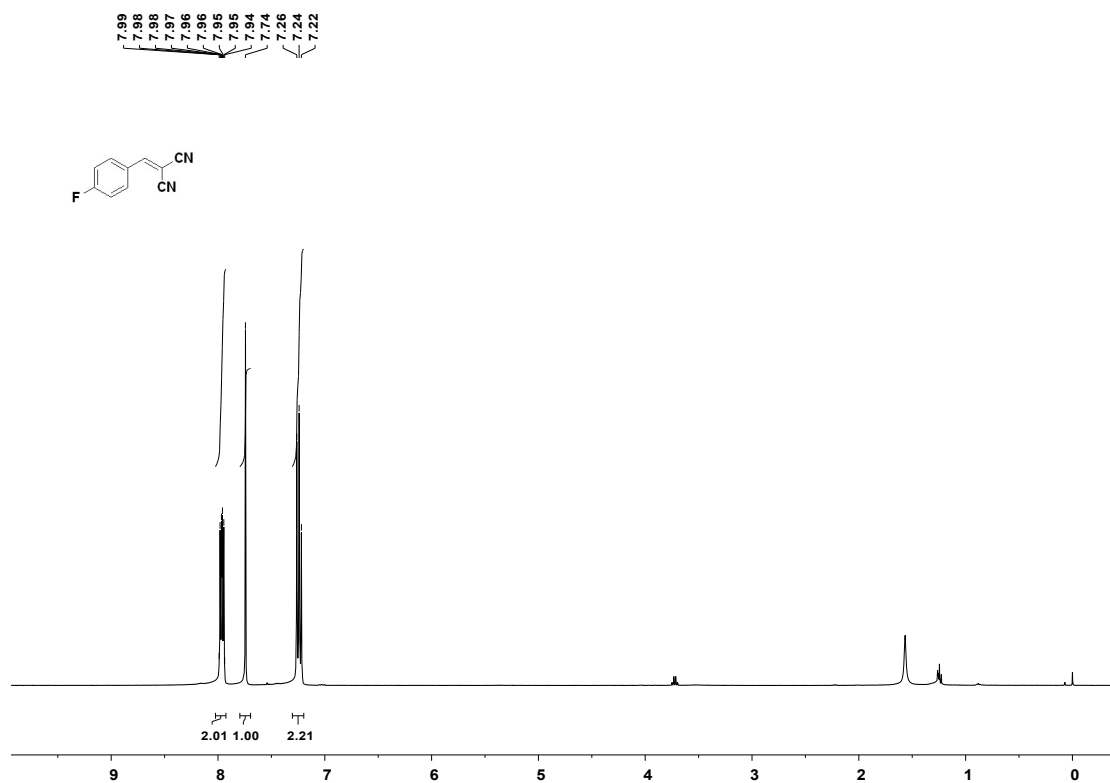


Fig. S11 ^1H NMR (400 MHz, CDCl_3) δ 8.02 – 7.93 (m, 2H), 7.74 (s, 1H), 7.30 – 7.20 (m, 2H).

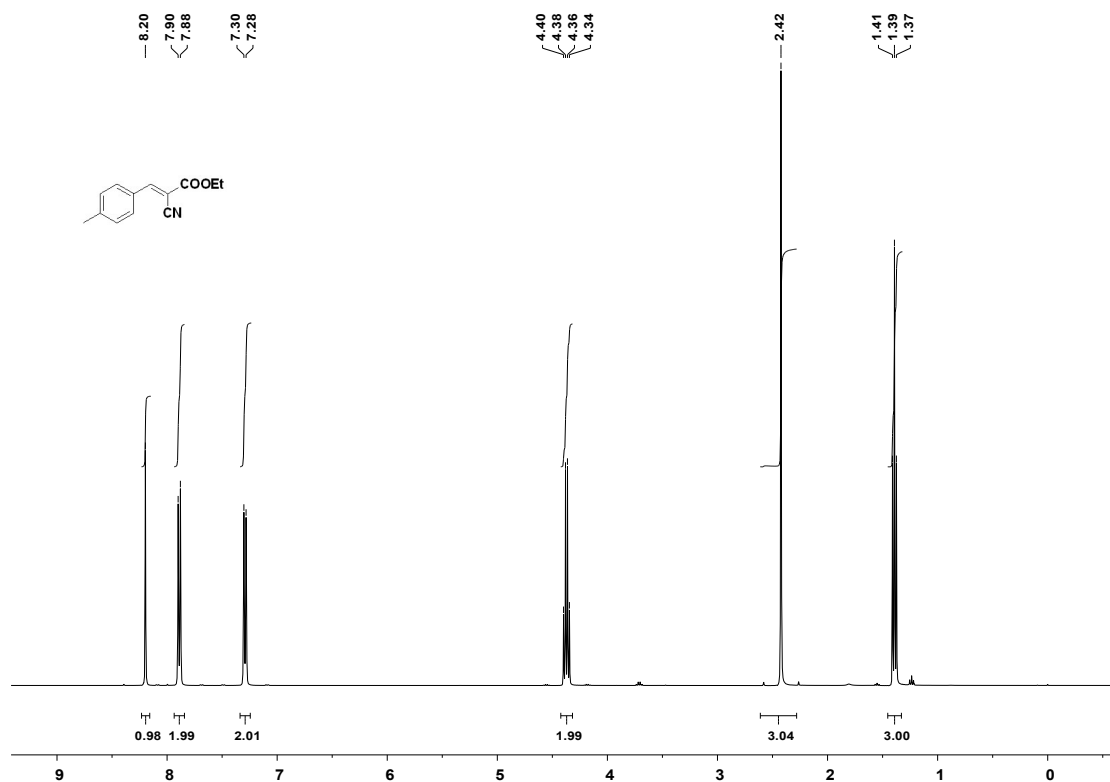


Fig. S12 ^1H NMR (400 MHz, CDCl_3) δ 8.20 (s, 1H), 7.89 (d, $J = 8.2$ Hz, 2H), 7.29 (d, $J = 7.9$ Hz, 2H), 4.37 (q, $J = 7.1$ Hz, 2H), 2.42 (s, 3H), 1.39 (t, $J = 7.1$ Hz, 3H).

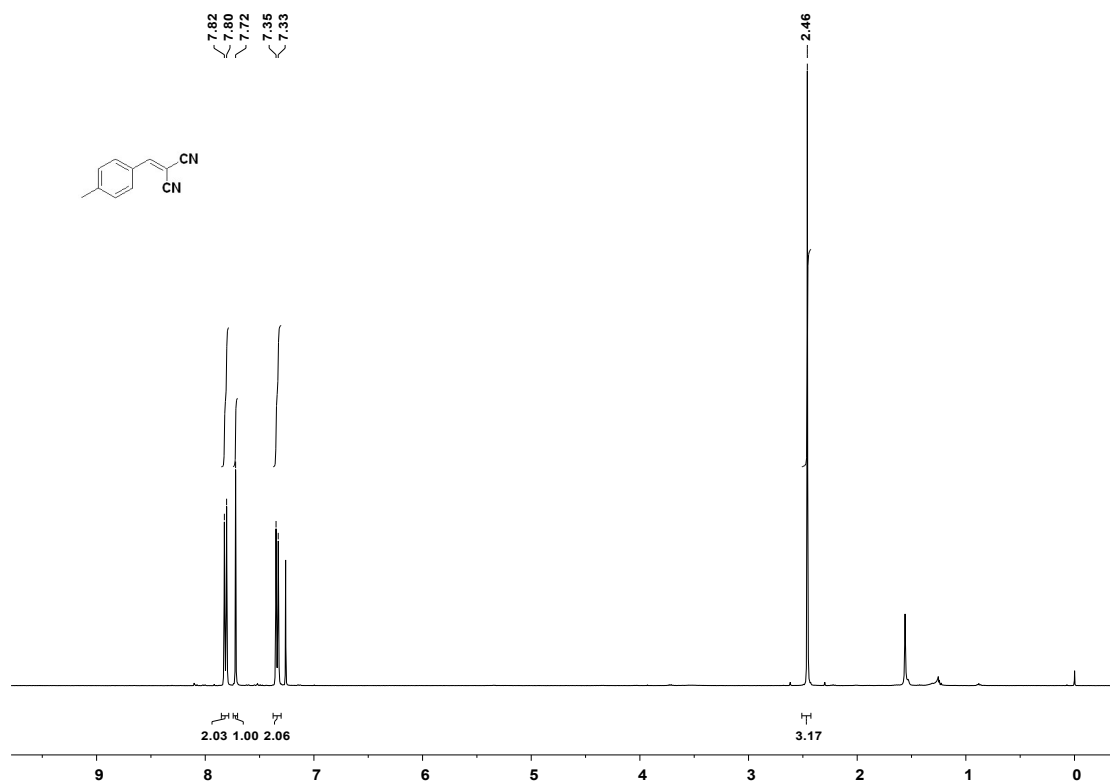


Fig. S13 ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 8.2$ Hz, 2H), 7.72 (s, 1H), 7.34 (d, $J = 8.0$ Hz, 2H), 2.46 (s, 3H).

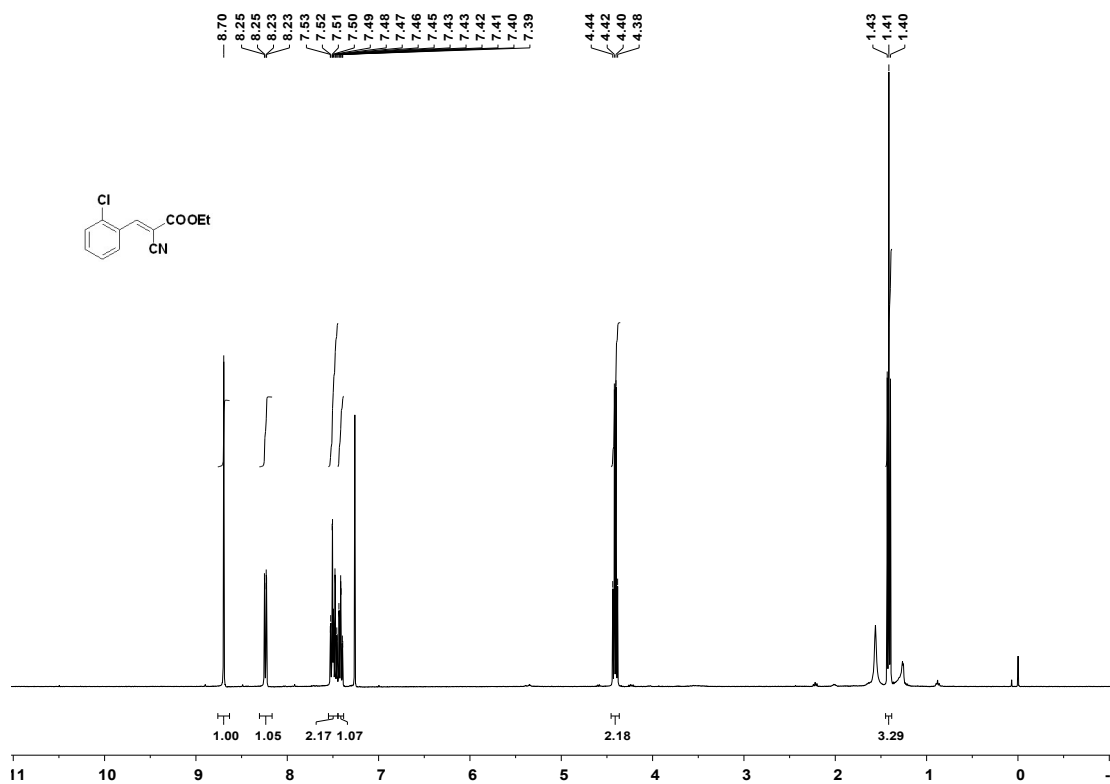


Fig. S14 ^1H NMR (400 MHz, CDCl_3) δ 8.70 (s, 1H), 8.24 (dd, $J = 7.7, 1.6$ Hz, 1H), 7.55 – 7.45 (m, 2H), 7.41 (td, $J = 7.5, 1.7$ Hz, 1H), 4.41 (q, $J = 7.1$ Hz, 2H), 1.41 (t, $J = 7.1$ Hz, 3H).

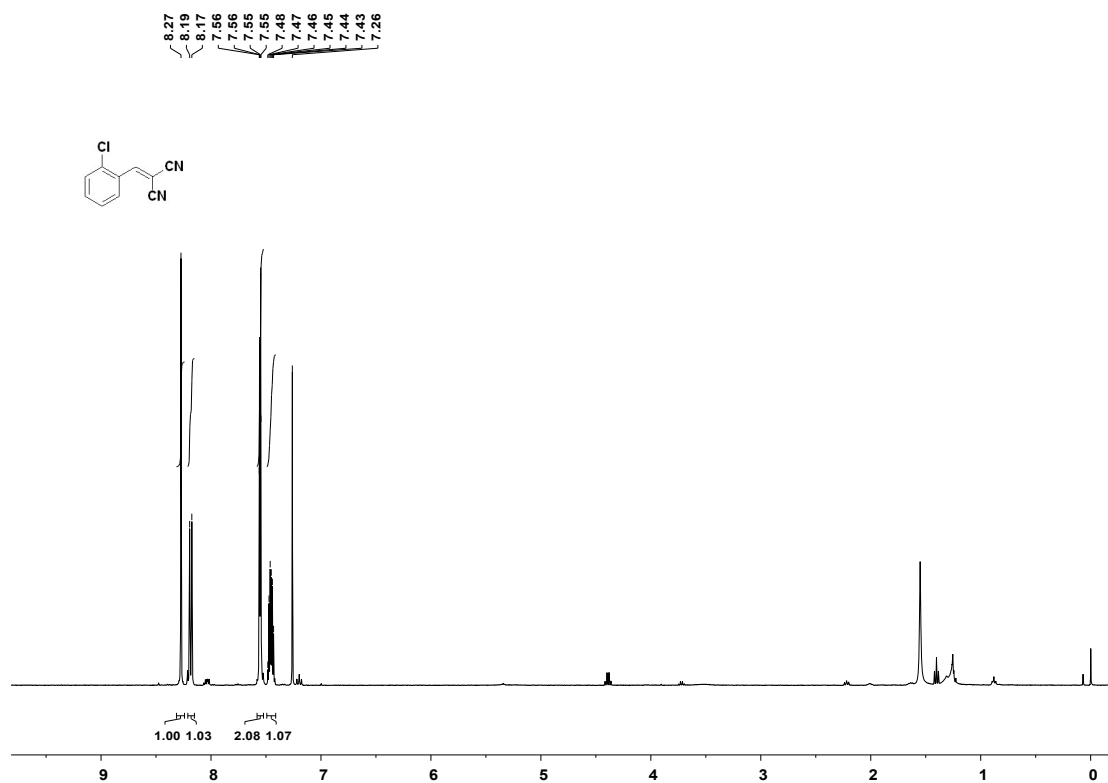


Fig. S15 ¹H NMR (400 MHz, CDCl₃) δ 8.27 (s, 1H), 8.18 (d, J = 7.9 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.49 – 7.41 (m, 1H).

4. References

1. J. Dopta, L. K. Mahnke and W. Bensch, New pronounced progress in the synthesis of group 5 polyoxometalate, *CrystEngComm*, 2020, **22**, 3254–3268.
2. Q. F. Xu, Y. J. Niu, G. Wang, Y. G. Li, Y. Zhao, V. Singh, J. Y. Niu and J. P. Wang, Polyoxoniobates as a superior Lewis base efficiently catalyzed Knoevenagel condensation, *Mol. Catal.*, 2018, **453**, 93–99.
3. S. Zhao, Y. Chen and Y. F. Song, Tri-lacunary polyoxometalates of Na₈H[PW₉O₃₄] as heterogeneous Lewis base catalysts for Knoevenagel condensation, cyanosilylation and the synthesis of benzoxazole derivatives, *Appl. Catal. A Gen.*, 2014, **475**, 140–146.
4. W. L. Ge, X. C. Wang, L. Y. Zhang, L. Du, Y. Zhou and J. Wang, Fully-occupied Keggin type polyoxometalate as solid base for catalyzing CO₂ cycloaddition and Knoevenagel condensation, *Catal. Sci. Technol.*, 2016, **6**, 460–467.
5. Y. Q. Jia, Y. J. Fang, Y. K. Zhang, H. N. Miras and Y. F. Song, Classical Keggin Intercalated into Layered Double Hydroxides: Facile Preparation and Catalytic Efficiency in Knoevenagel Condensation Reactions, *Chem. Eur. J.*, 2015, **21**, 14862–14870.
6. M. J. Zhang, P. P. Zhao, Y. Leng, G. J. Chen, J. Wang and J. Huang, Schiff Base Structured Acid-Base Cooperative Dual Sites in an Ionic Solid Catalyst Lead to Efficient Heterogeneous Knoevenagel Condensations, *Chem. Eur. J.*, 2012, **18**, 12773–12782.
7. Liu K, Xu Y, Yao Z, Miras HN, Song YF, Polyoxometalate-Intercalated Layered Double Hydroxides as Efficient and Recyclable Bifunctional Catalysts for Cascade Reactions, *ChemCatChem*, 2016, **8**, 929–937.
8. Z. Y. Liu, J. P. Ye, Y. L. Li, Y. Q. Sun, X. X. Li, C. Sun and S. T. Zheng, Cadmium-containing windmill-like heteropolyoxoniobate macrocycle with high yield for catalyzing Knoevenagel condensation, *Dalton Trans.*, 2023, **52**, 1193–1197.

9. Y. T. Zhang, C. Qin, X. L. Wang, P. Huang, B. Q. Song, K. Z. Shao, Z. M. Su, High-Nuclear Vanadoniobate $\{\text{Nb}_{48}\text{V}_8\}$ Multiple-Strand Wheel, *Inorg. Chem.*, 2015, **54**, 11083–11087.