Electronic Supplementary Information (ESI)

Impact of POM's coordination mode and Mo-hybrid constituents on binding, stability, and catalytic properties of hybrid (pre)catalysts

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Contents

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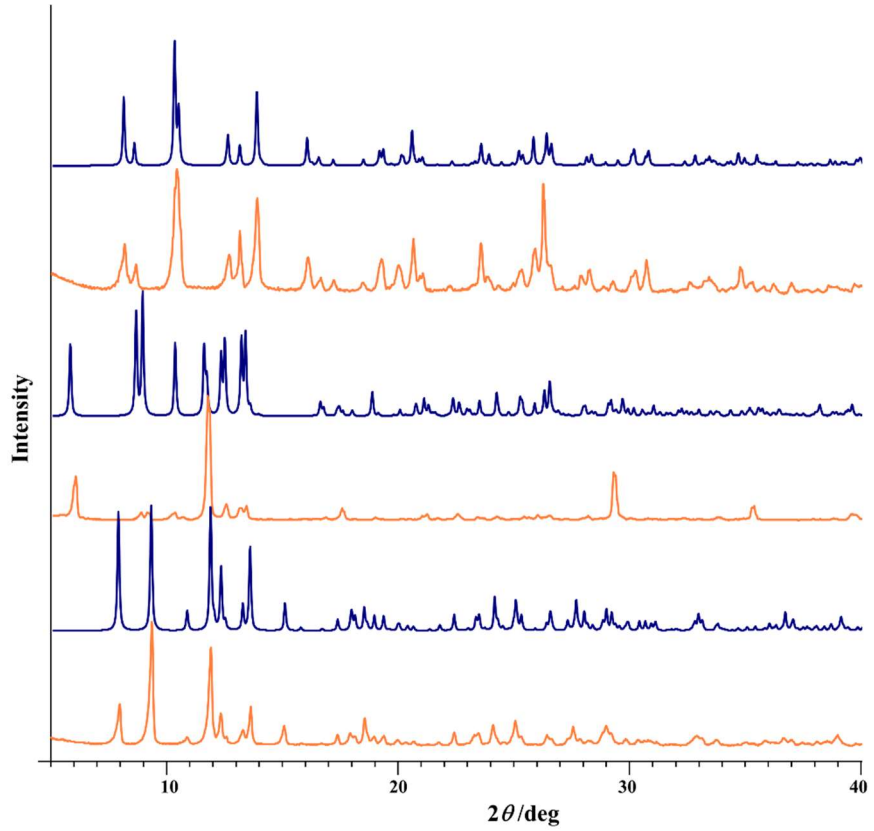
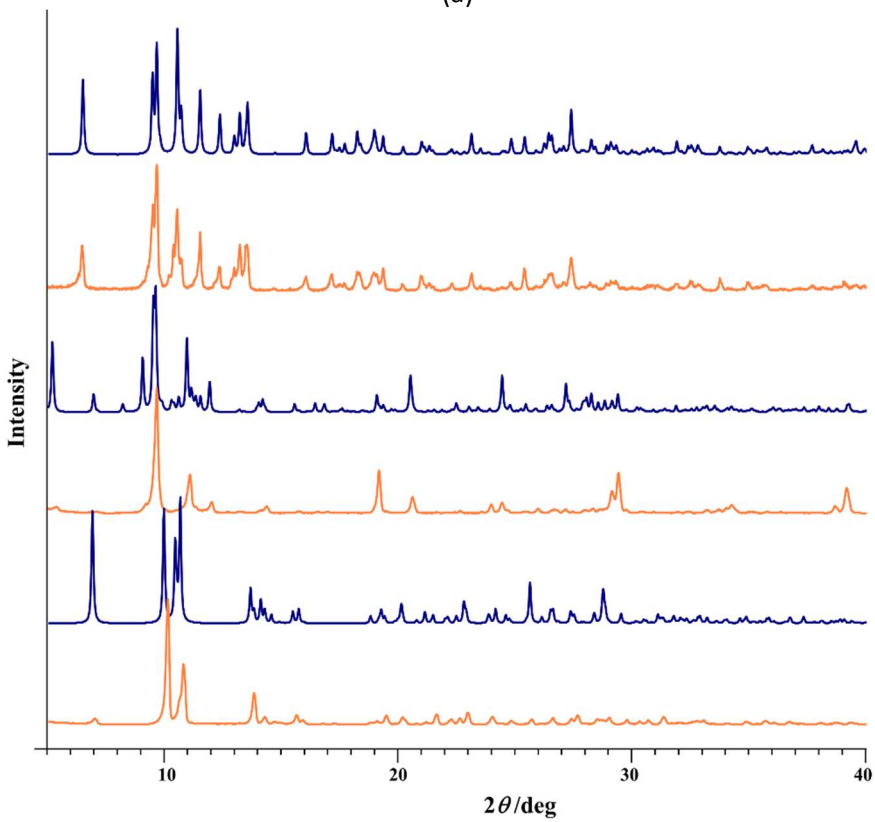
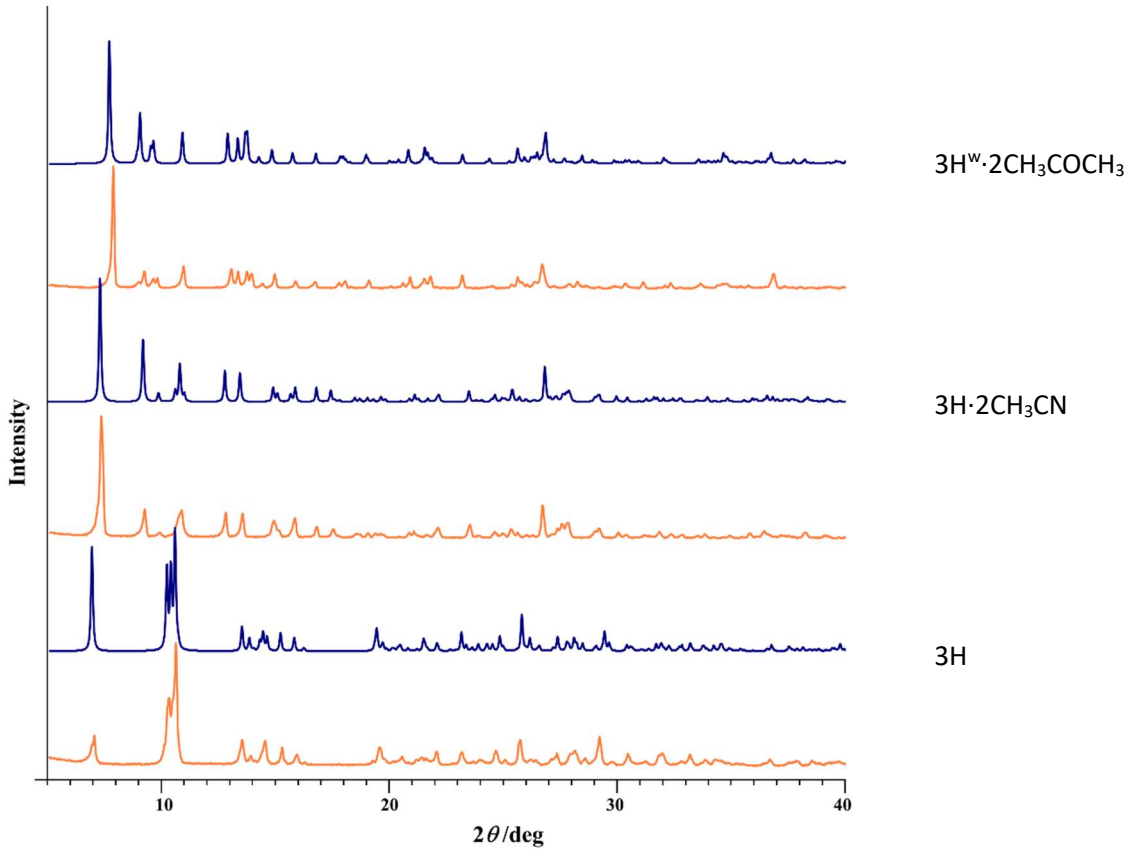
1. PXRD


Intensity
10
20
30
40
2θ/deg
1H^w
1H^a · 2CH3COCH3
1H

(a)


Intensity
10
20
30
40
2θ/deg
2H^w·2CH3COCH3
2O·CH3CN·H2O
2H

(b)



(c)

Figure S1. PXRD patterns of hybrid organic inorganic compounds: (a) **1H^{w}**, **1H^{a}** · 2CH$_3$COCH$_3$, **1H**; (b) **2H^{w}**·2CH$_3$COCH$_3$, **2O**·CH$_3$CN·H$_2$O, and **2H**; (c) **3H^{w}**·2CH$_3$COCH$_3$, **3H**·2CH$_3$CN, and **3H**. The orange lines indicate patterns obtained by powder diffraction, while the blue lines indicate patterns calculated from the X-ray single-crystal structures of the corresponding compounds.

2. IR-ATR spectra

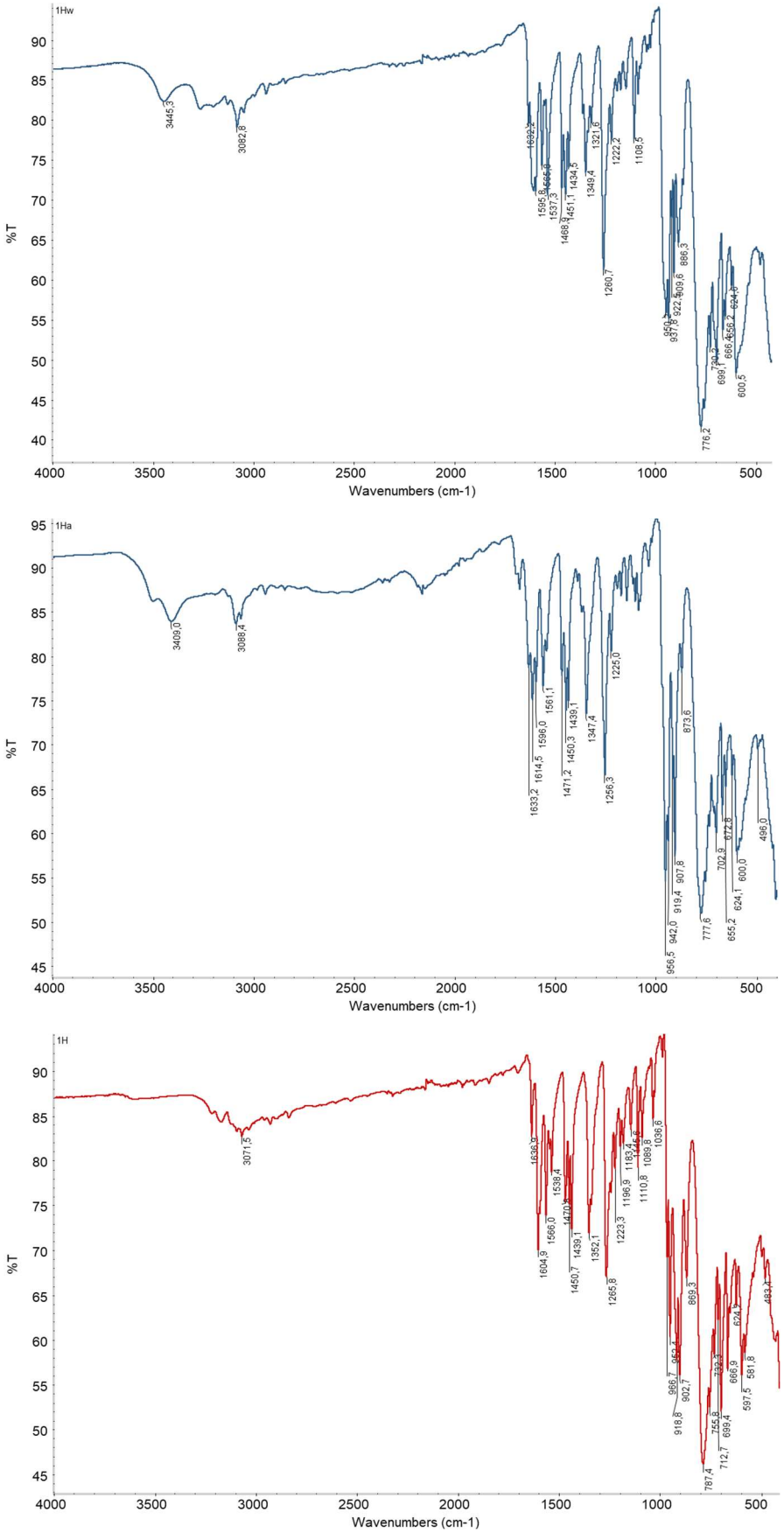


Figure S2. Comparison of IR-ATR spectra of: **1H^{w}** (top), **1H^{a}** (middle), and **1H** (bottom)

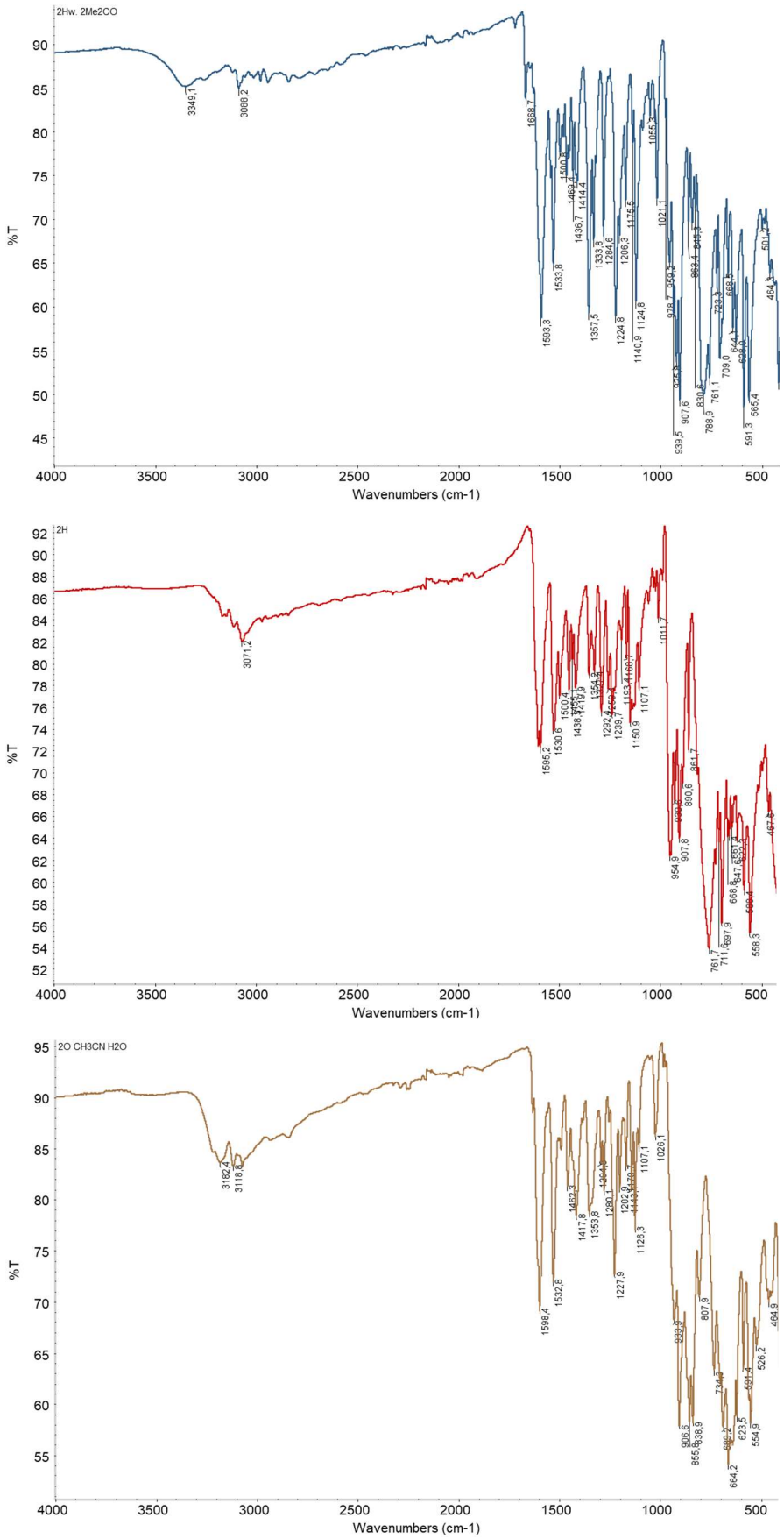


Figure S3. Comparison of IR-ATR spectra of: **2H**^{w}·2CH_3COCH_3 (top), **2H** (middle), and **2O**·2CH_3CN·H_2O (bottom)

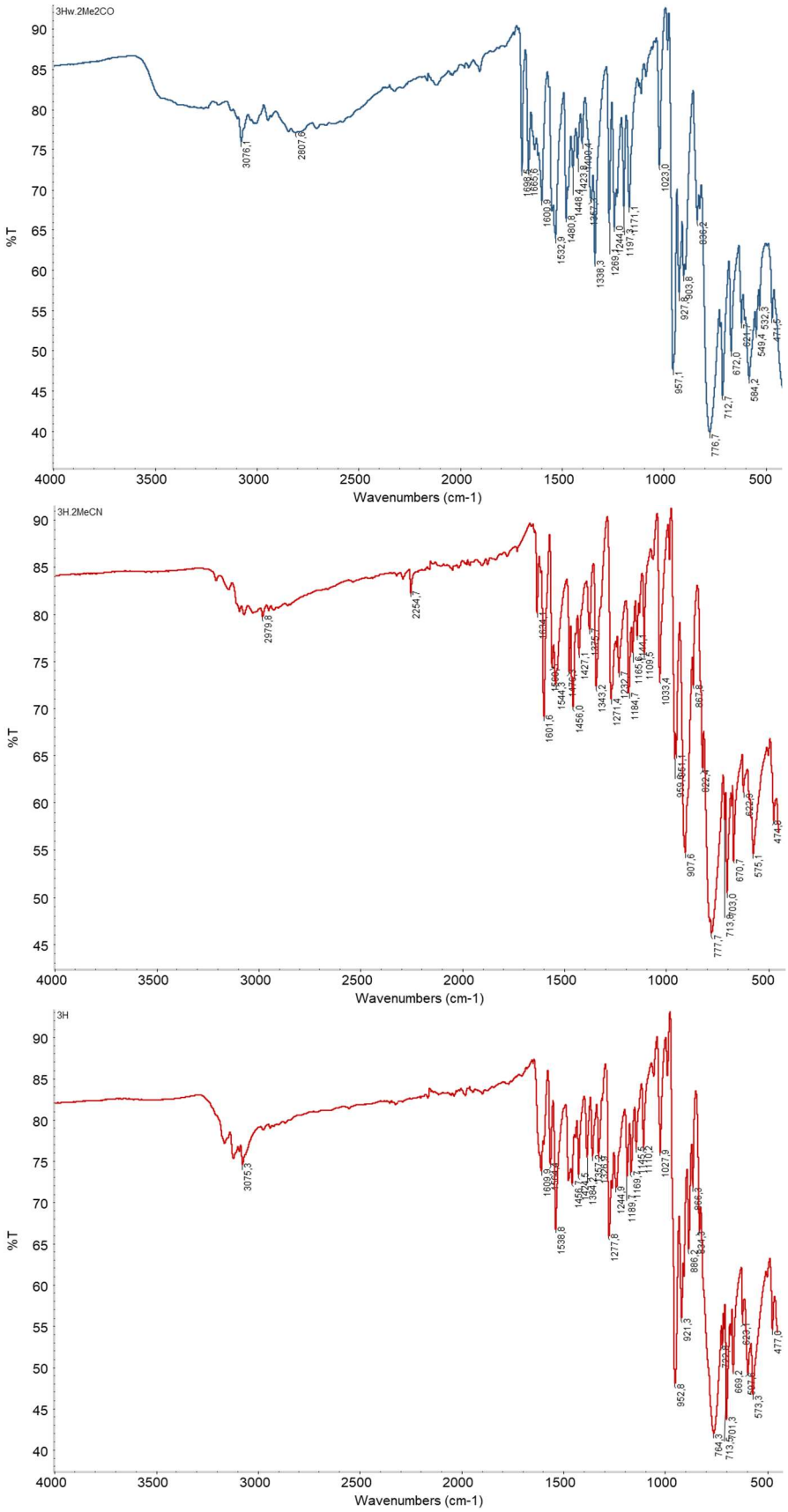
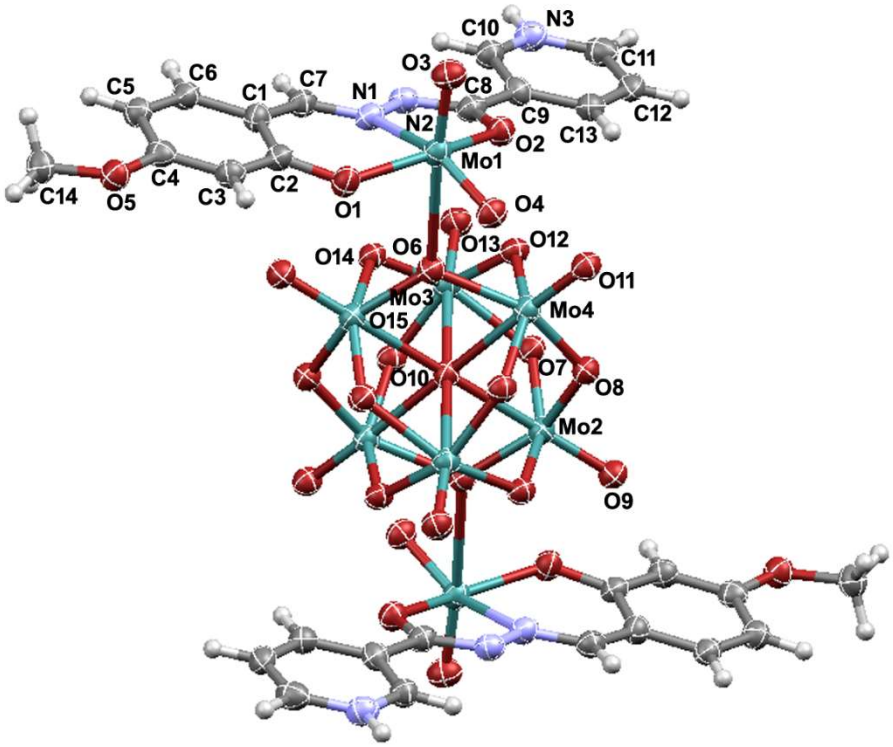
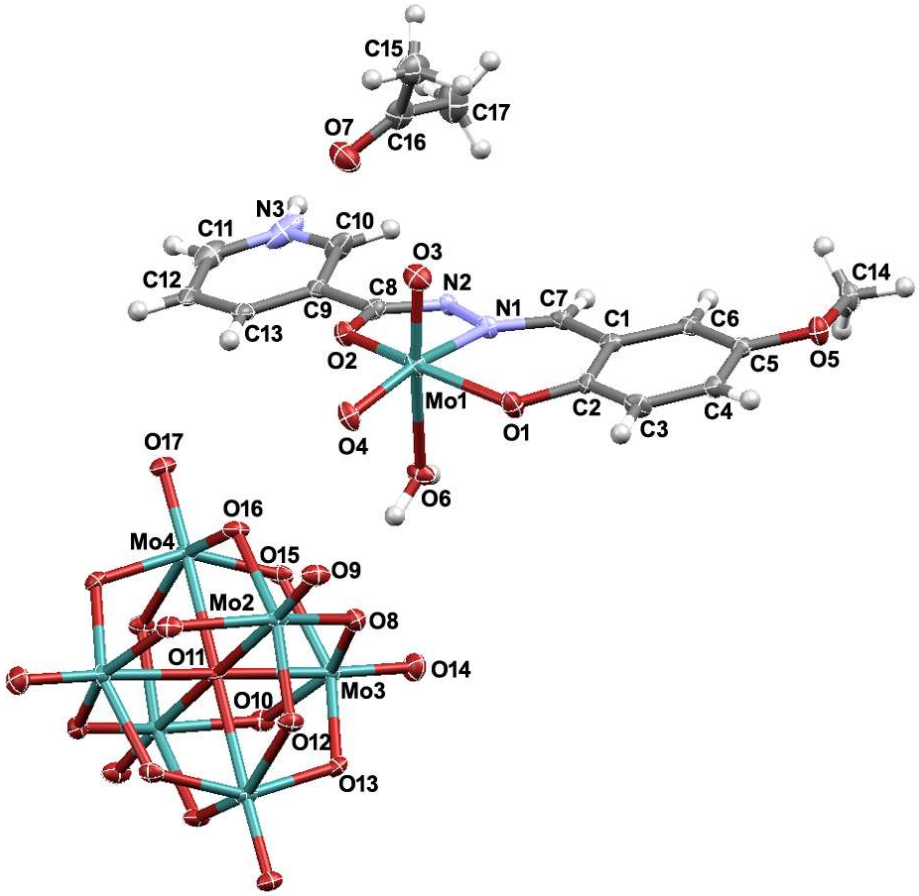


Figure S4. Comparison of IR-ATR spectra of: **3H**^{w}**·**2CH_3COCH_3 (top), **3H**·2MeCN (middle), and **3H** (bottom)

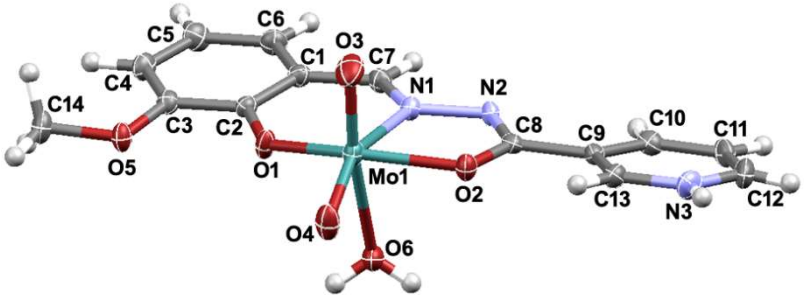
3. SCXRD

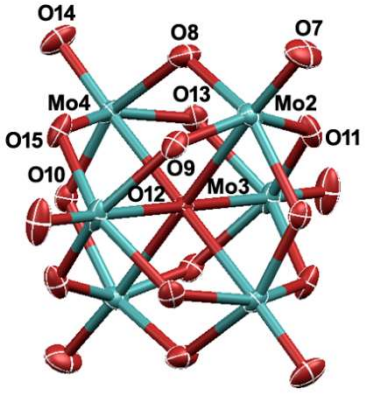

C10
N3
C11
O3
C8
C5
C6
C1
C7
N1
C9
C12
N2
C13
O2
Mo1
C14
O5
C4
C3
C2
O1
O4
O14
O6
O13
O12
O11
Mo3
Mo4
O15
O10
O7
O8
Mo2
O9

a)

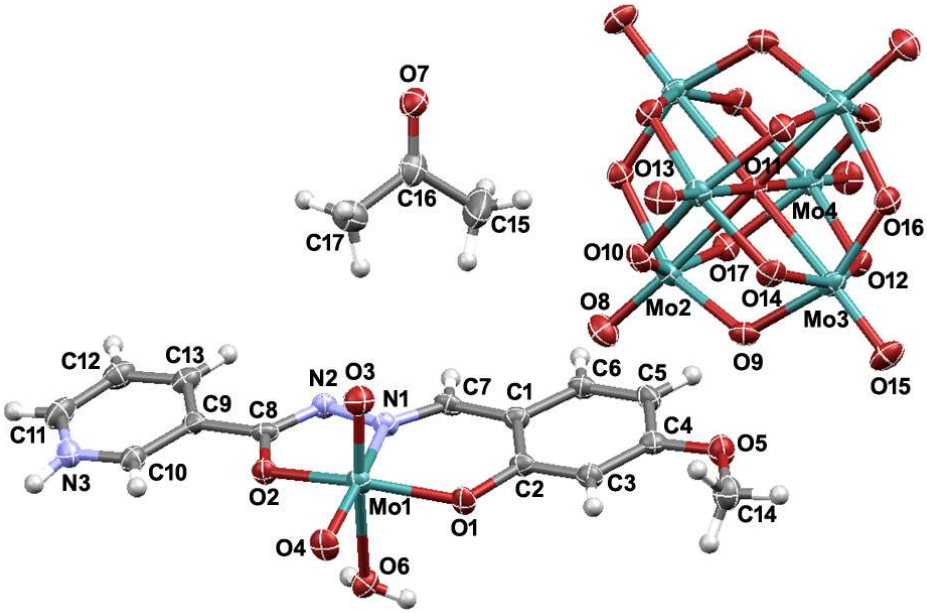

C15
C17
O7
C16
N3
C11
C10
O3
C12
C8
N2
C14
C9
N1
C7
C1
C6
C13
O2
C5
O5
Mo1
C2
C4
O1
C3
O4
O6
O17
O16
Mo4
O15
O9
Mo2
O8
O11
O14
Mo3
O10
O12
O13

b)

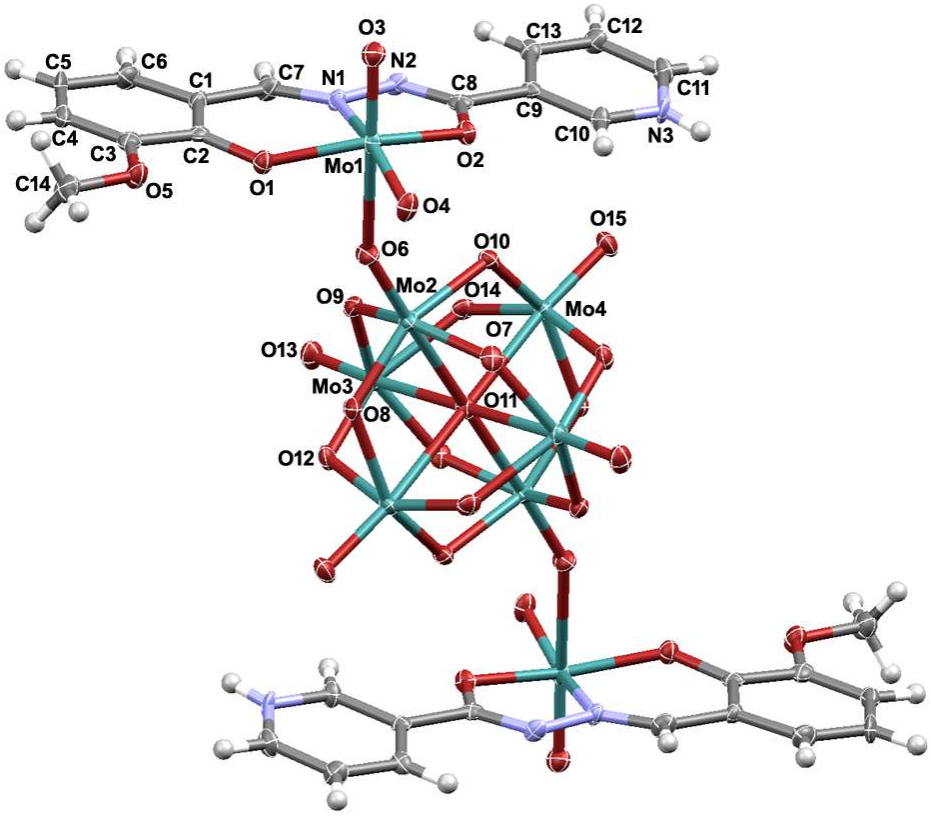

C6
C5
O3
C1
C7
C4
N1
N2
C14
C3
C2
C8
C9
C10
C11
O5
O1
Mo1
O2
C13
N3
C12
O4
O6


O14
O8
O7
Mo4
O13
Mo2
O15
O11
O10
O9
O12
Mo3

c)

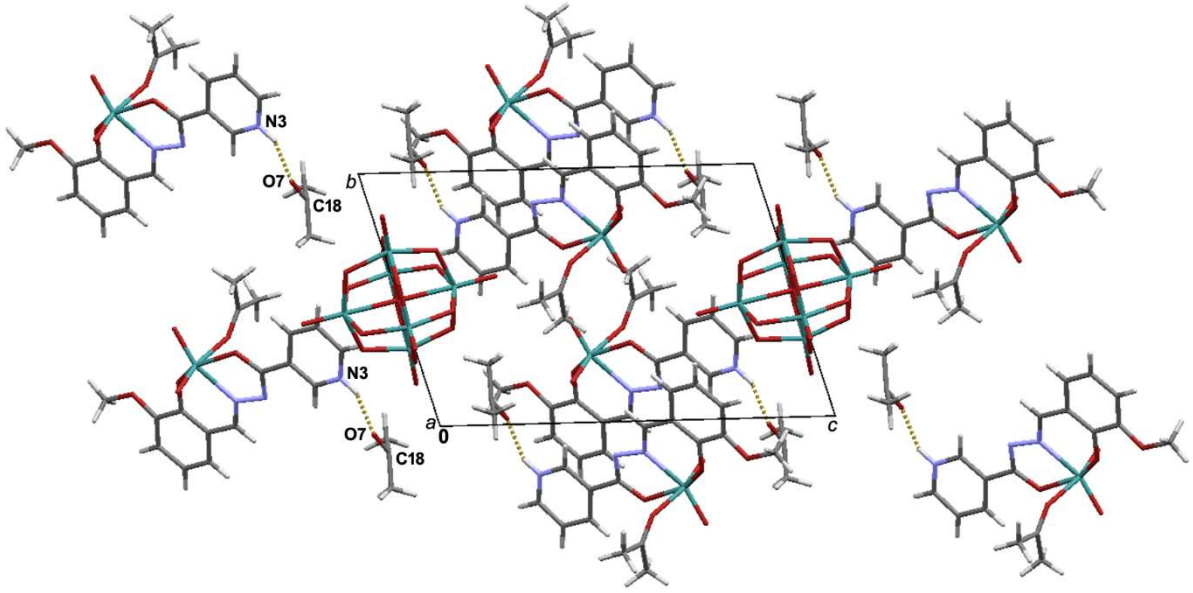

O7
C16
C17
C15
O13
O11
Mo4
O16
O10
O17
O12
O8
Mo2
O14
Mo3
O9
O15
C12
C13
N2
O3
C6
C5
C9
C8
N1
C7
C1
C11
C4
O5
N3
C10
O2
C2
C3
Mo1
C14
O1
O4
O6

d)

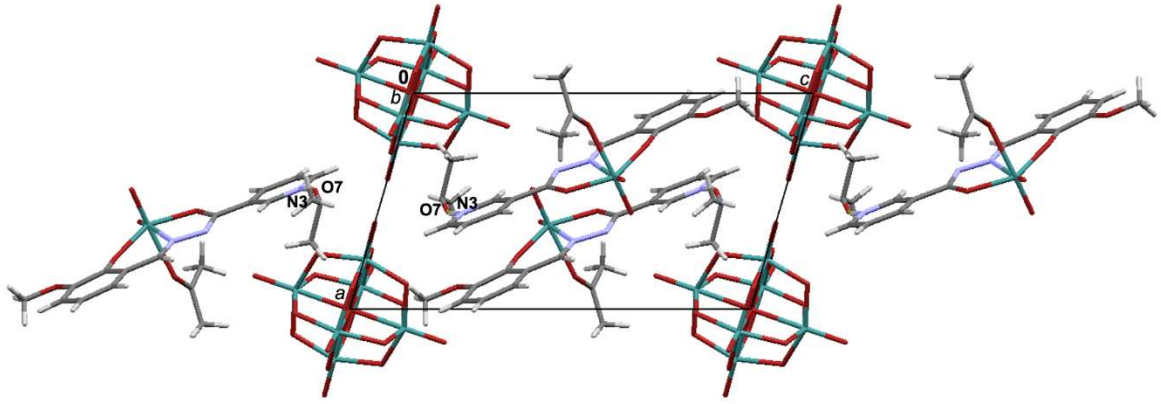


e)

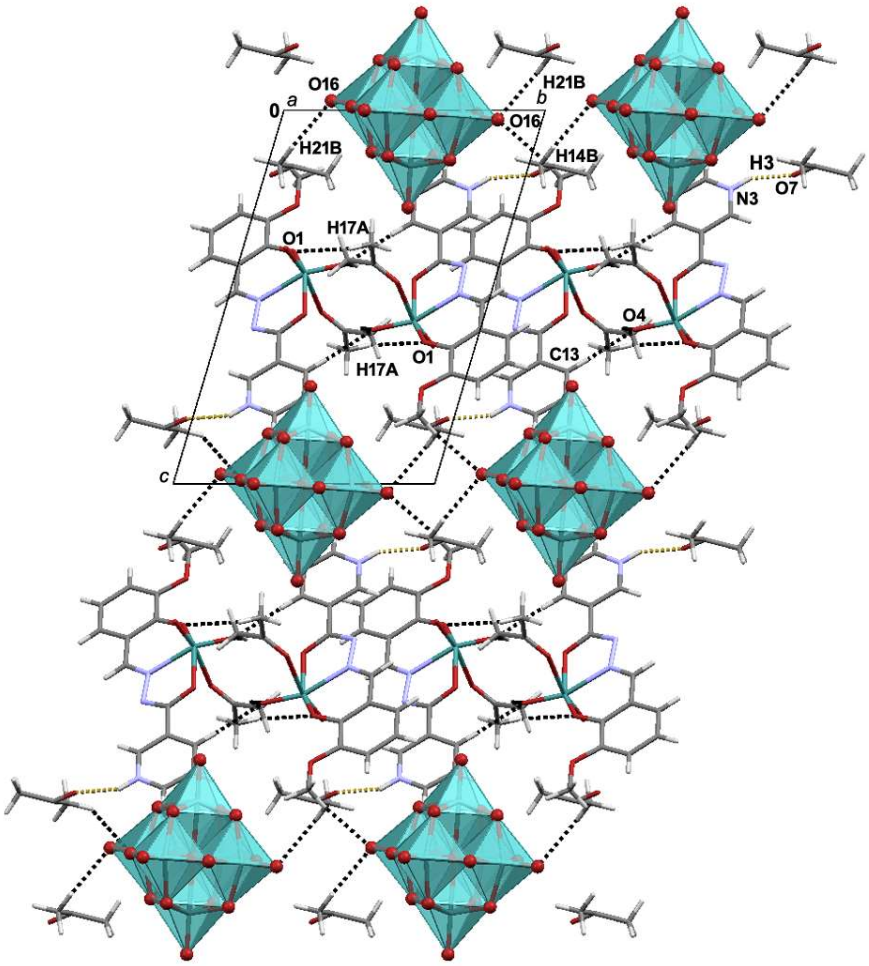
Figure S5. Molecular structures of: a) **2H** and b) **3H^{w}**·2CH_3COCH_3, c) **1H^{w}** and d) **2H^{w}**·2CH_3COCH_3 and e) **1H** with the atom labeling schemes. In a), b) and d) ellipsoids are drawn at 30% probability level, whereas in the remaining cases are drawn at 50% probability level. Hydrogen atoms are shown as spheres of arbitrary small radii. Dihedral angles between the planes of the pyridyl and the phenyl ring of the aldehyde residue amount to ca 3 ° (for **2H**), 3.6 ° (for **3H^{w}**·2CH_3COCH_3), 14.2 ° (for **1H^{w}**), 4.4 ° (for **2H^{w}**·2CH_3COCH_3) and 6.9 ° (for **1H**).



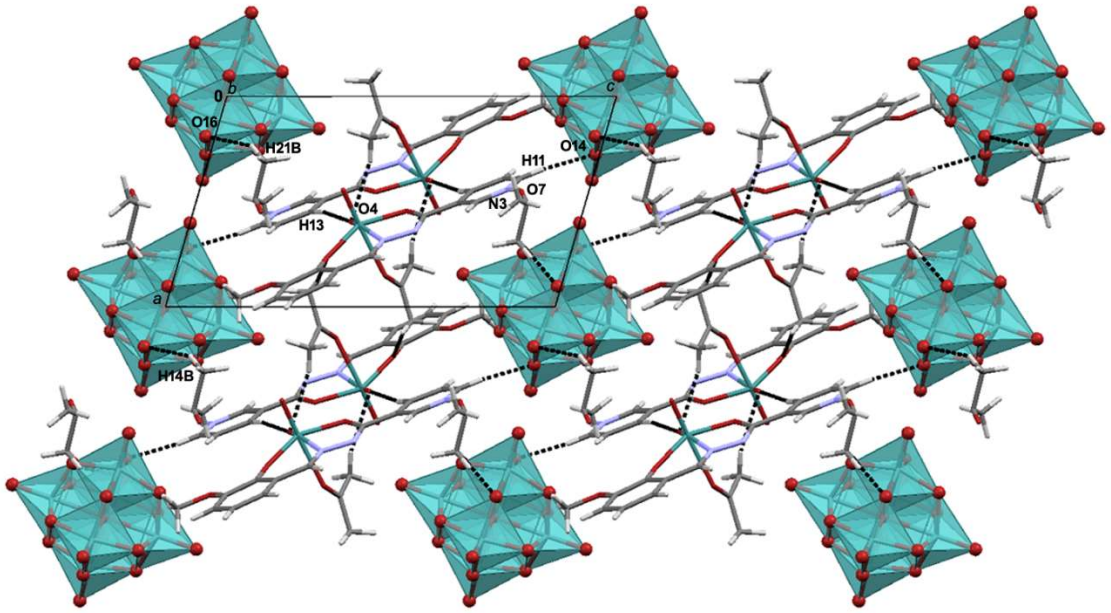
(a)



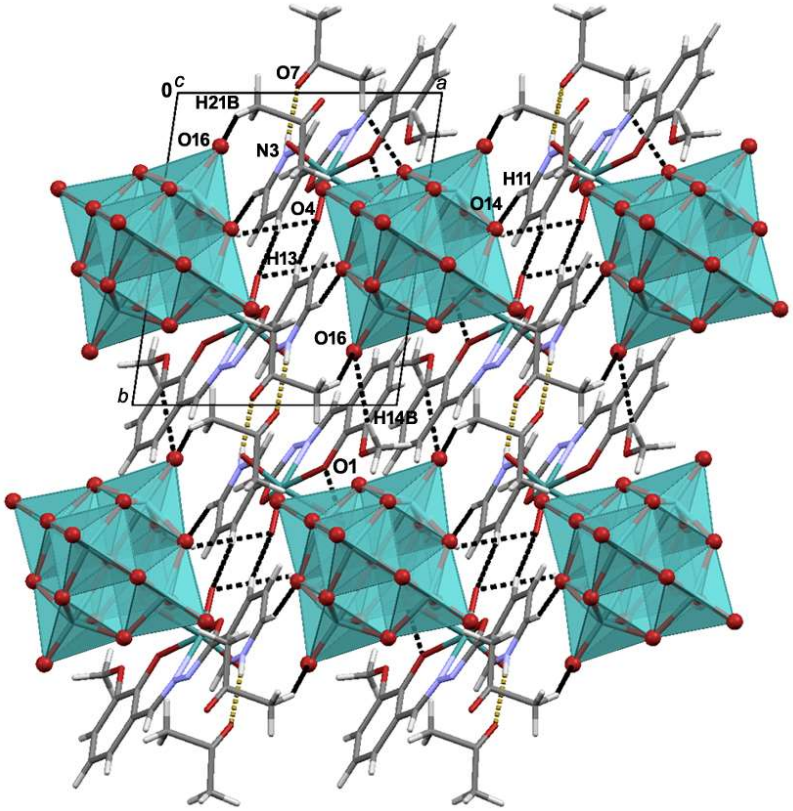
(b)


O16
H21B
0
a
b
O16
H21B
H14B
H3
O7
N3
O1
H17A
O4
O1
H17A
C13
c

(c)

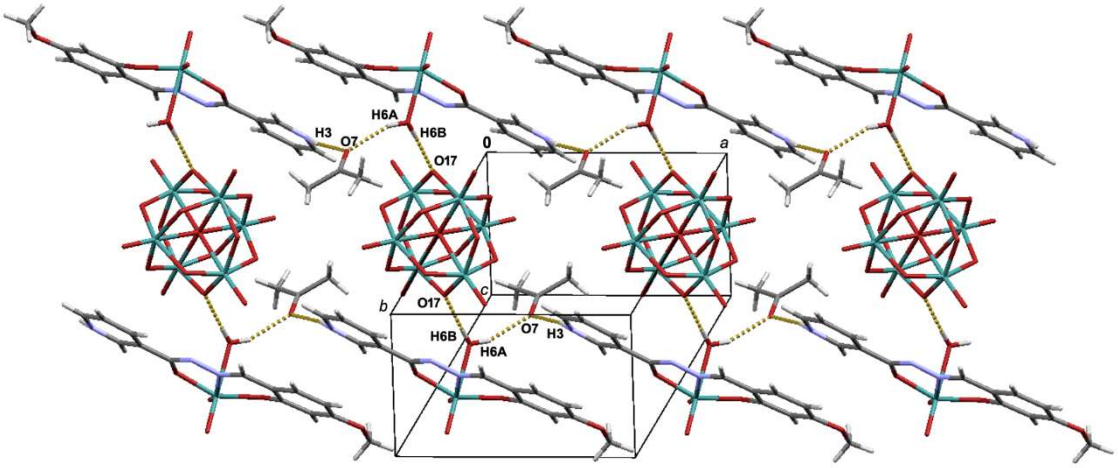

b
0
O16
H21B
c
O14
H11
O7
N3
O4
H13
a
H14B

(d)

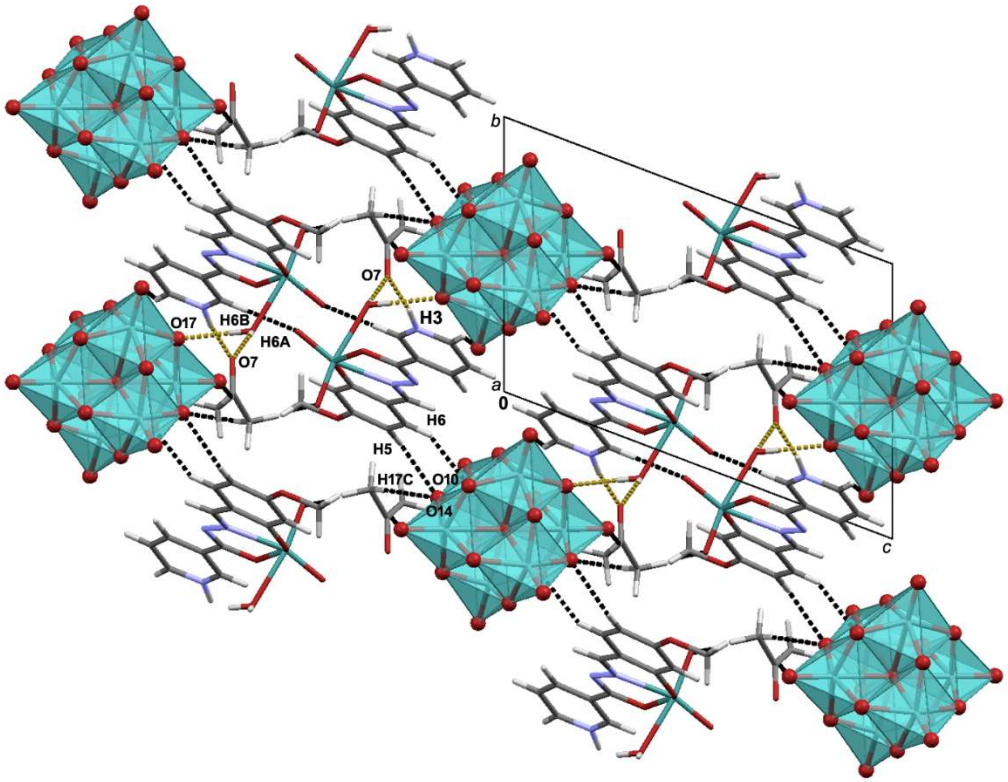


(e)

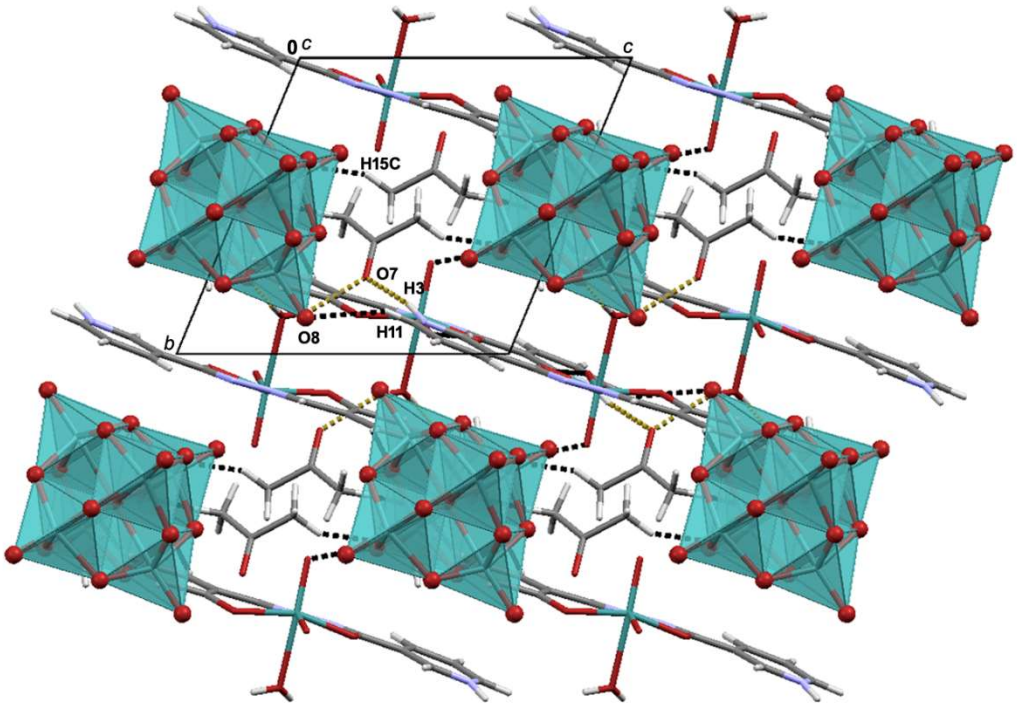
Figure S6. Hydrogen bonding motif observed in **1H**^{a}·2CH_3COCH_3 revealing discrete $D_1^1(2)$ hydrogen bond motifs involving protonated pyridine moiety and the acetone molecule (N3–H3···O7 hydrogen bond) shown down the: (a) a-axis, (b) b-axis. Crystal structure of **1H**^{a}·2CH_3COCH_3 along the: (c) *a*-axis, (d) *b*-axis and (e) *c*-axis. In (c)-(e) hydrogen bonds are shown as yellow dashed lines and C–H···O interactions as black dashed lines, while the Lindqvist anions ($Mo_6O_{19}^{2-}$) are shown in polyhedral representation.


H6A
H3
O7
H6B
O17
0
a
c
b
O17
H6B
O7
H3
H6A

(a)

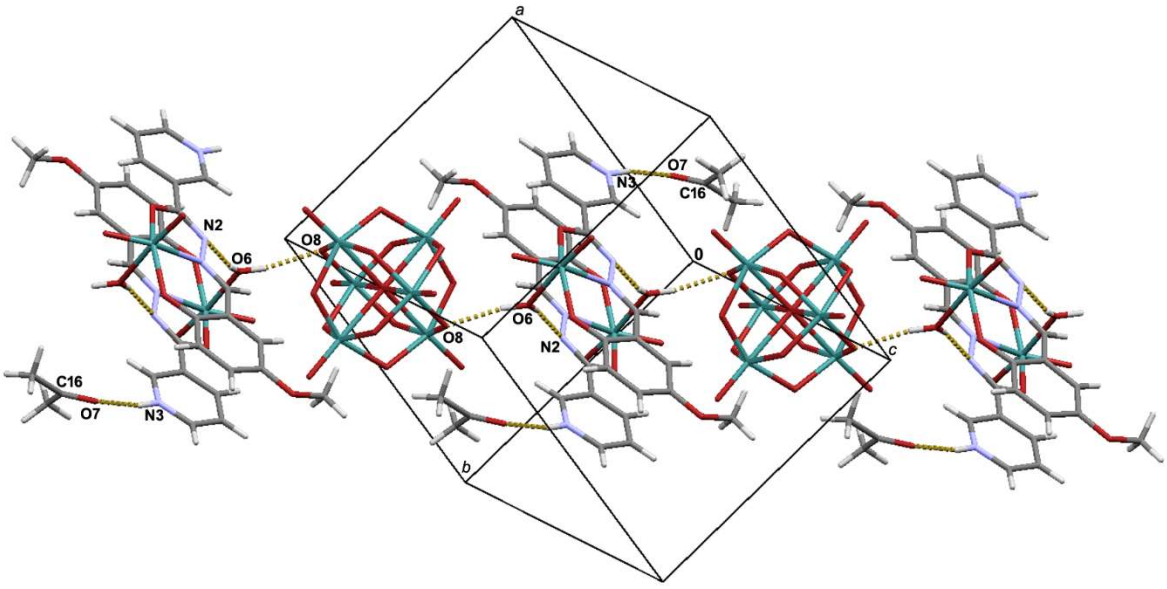

b
O7
H3
O17
H6B
H6A
O7
a
0
H6
H5
H17C
O10
O14
c

(b)

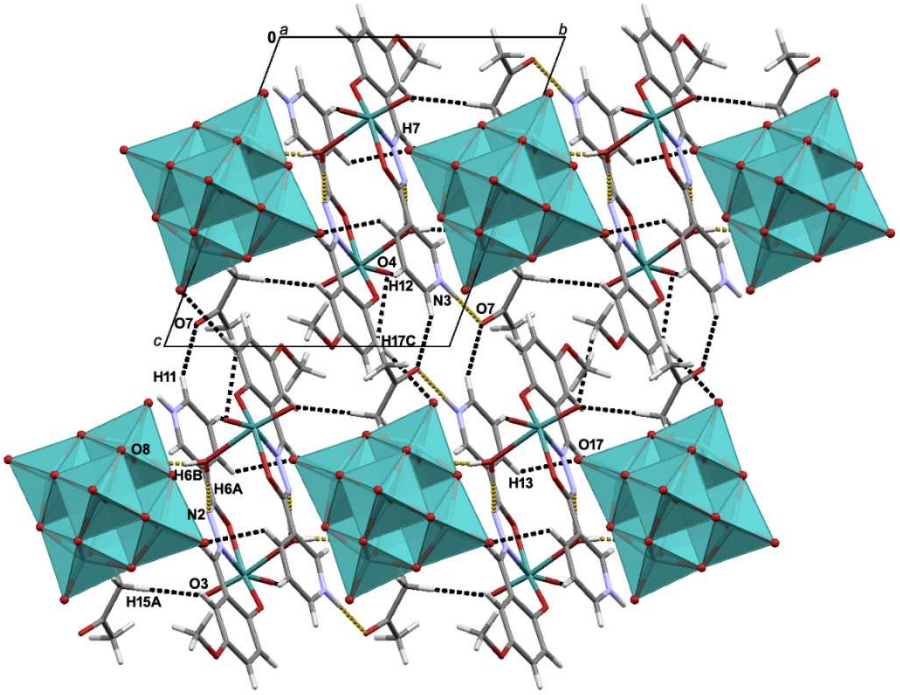


(c)

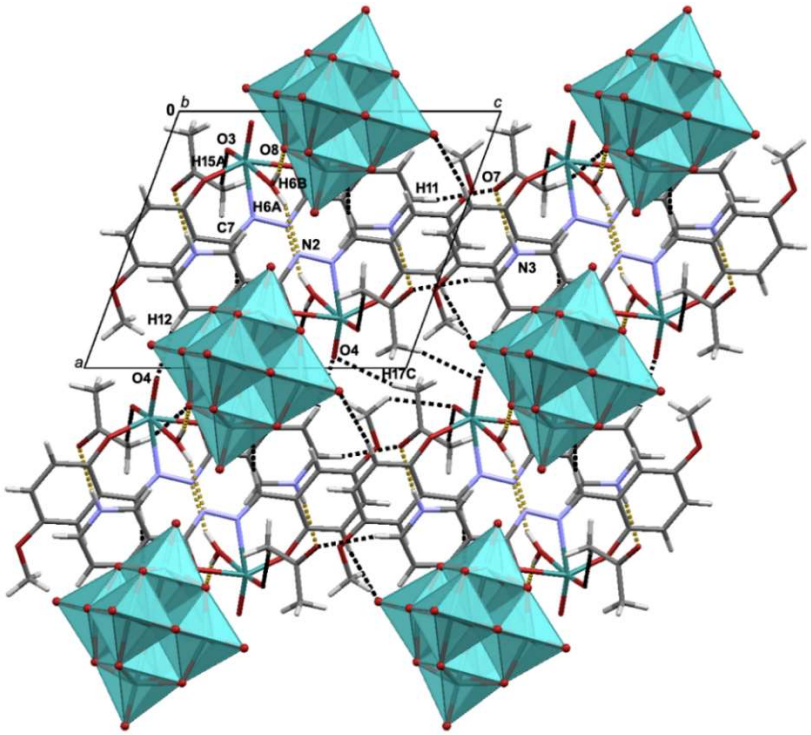
Figure S7. (a) Hydrogen bonding seen in **2H^{w}**·2CH_3COCH_3. Supramolecular chains of $[MoO_2(HL)(H_2O)]^+$ units and acetone molecules are established *via* discrete $D_1^1(2)$ motifs, namely N3–H3···O7, O6–H6A···O7 hydrogen bonds. Such supramolecular chains are further bridged by $Mo_6O_{19}^{2-}$ anions forming $D_2^2(7)$ motifs by O6–H6B···O17 hydrogen bonds. Packing in **2H^{w}**·2CH_3COCH_3 along the: (b) *a*-axis, and (c) *b*-axis. In (b) and (c) hydrogen bonds are shown as yellow dashed lines and C–H···O interactions as black dashed lines, while the Lindqvist anions ($Mo_6O_{19}^{2-}$) are shown in polyhedral representation.


a
b
c
N2
O6
O8
O8
O6
N2
N3
O7
C16
0
C16
O7
N3

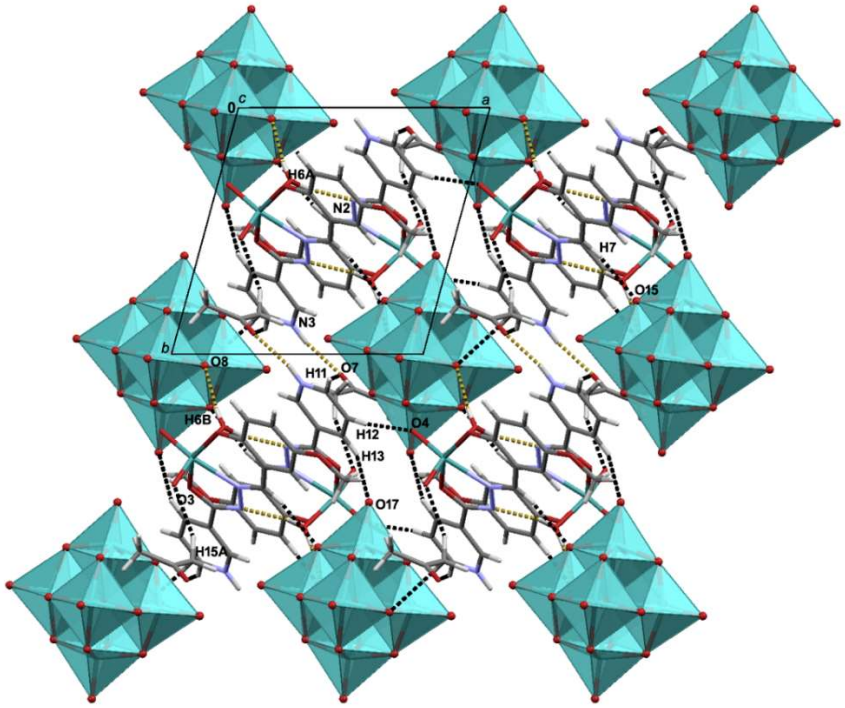
(a)


0
a
b
c
H7
O4
H12
N3
O7
O7
H17C
H11
O8
H6B
H6A
N2
O3
H15A
O17
H13

(b)

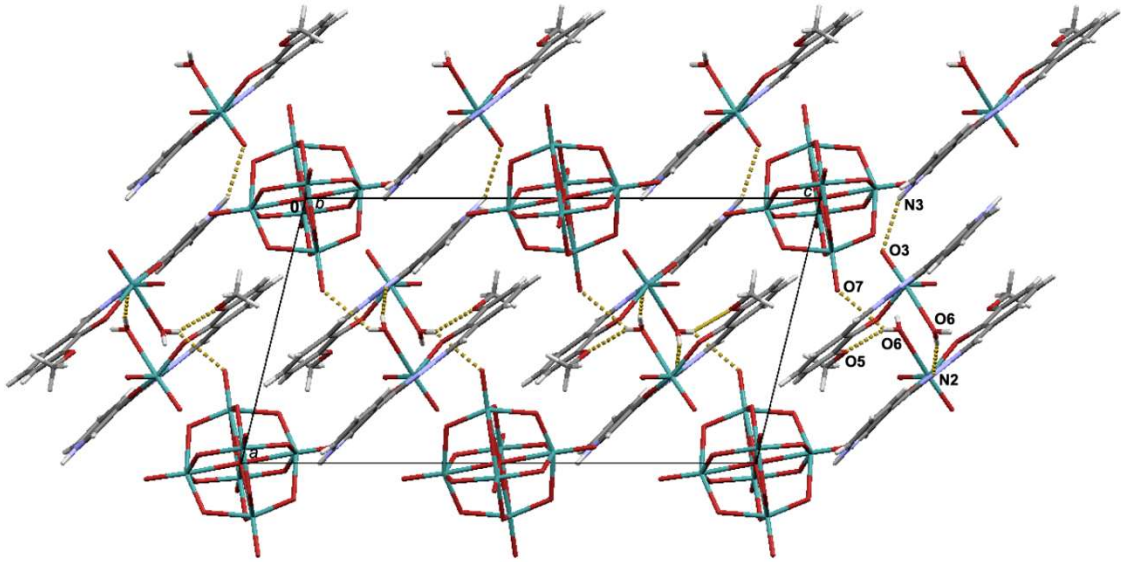


(c)

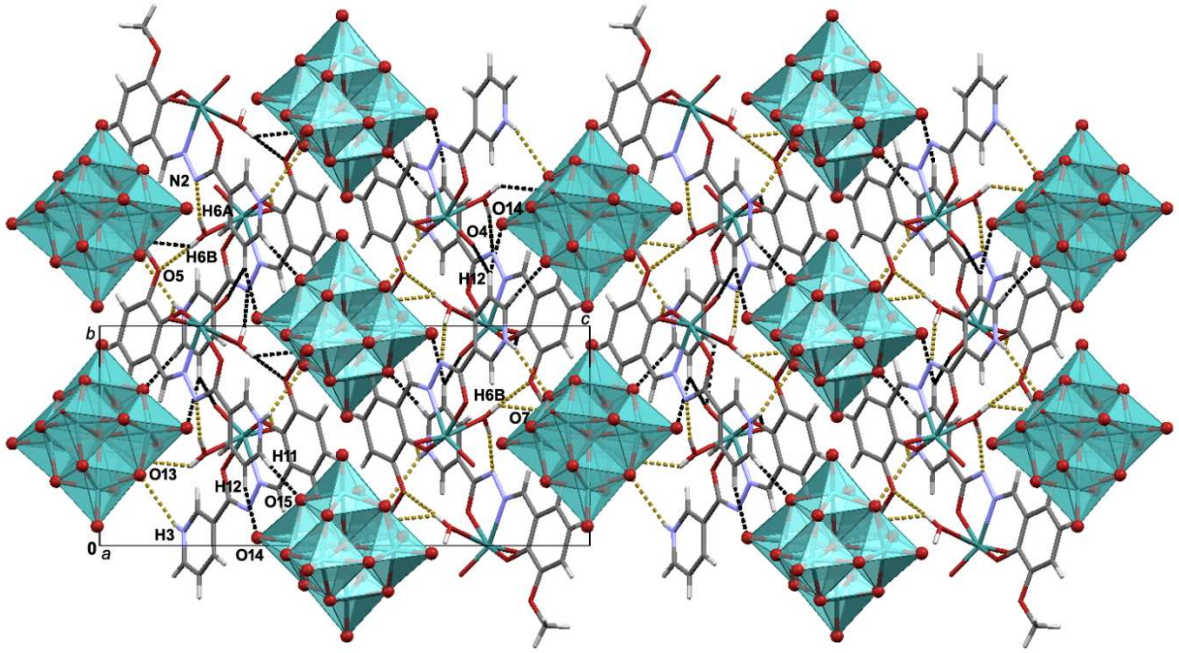


(d)

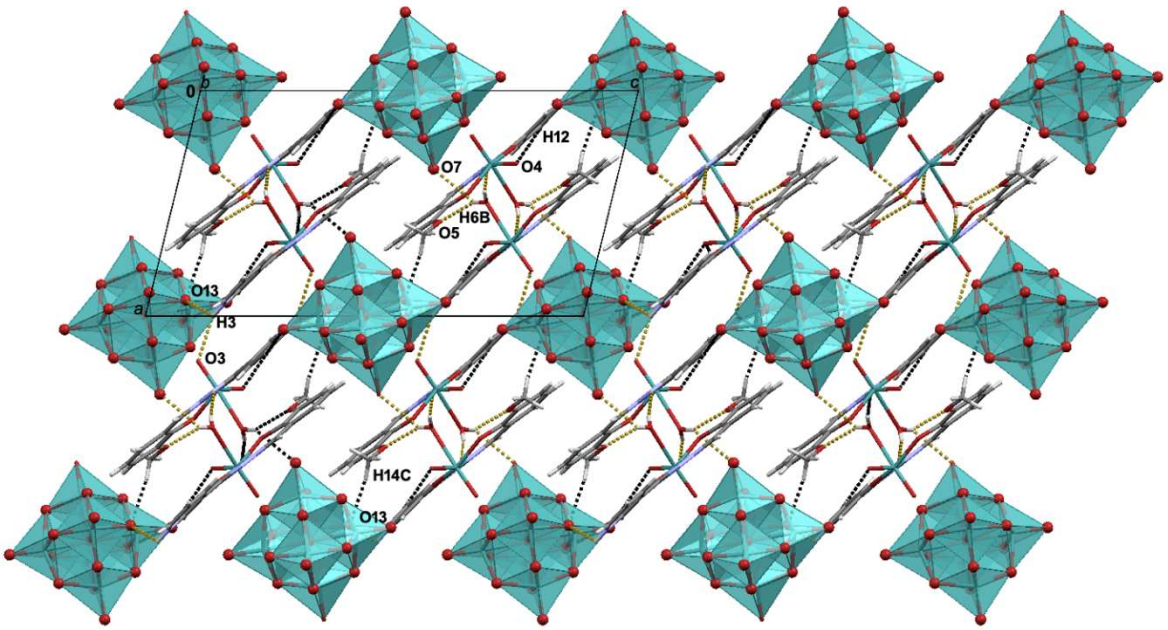
Figure S8. (a) Hydrogen bonding seen in **3H^{w}**·2CH_3COCH_3. O6–H6A···N2 hydrogen bonds associates $[MoO_2(HL)(H_2O)]^+$ units into $R_2^2(10)$ supramolecular rings, which are further associated through $Mo_6O_{19}^{2-}$ anions *via* $D_2^2(7)$ motifs. Crystal structure of **3H^{w}**·2CH_3COCH_3 along the: (b) *a*-axis, (c) *b*-axis and (d) *c*-axis. In (b)-(d) hydrogen bonds are shown as yellow dashed lines and C–H···O interactions as black dashed lines, while the Lindqvist anions ($Mo_6O_{19}^{2-}$) are shown in polyhedral representation.


0
b
c
a
N3
O3
O7
O6
O6
O5
N2

(a)

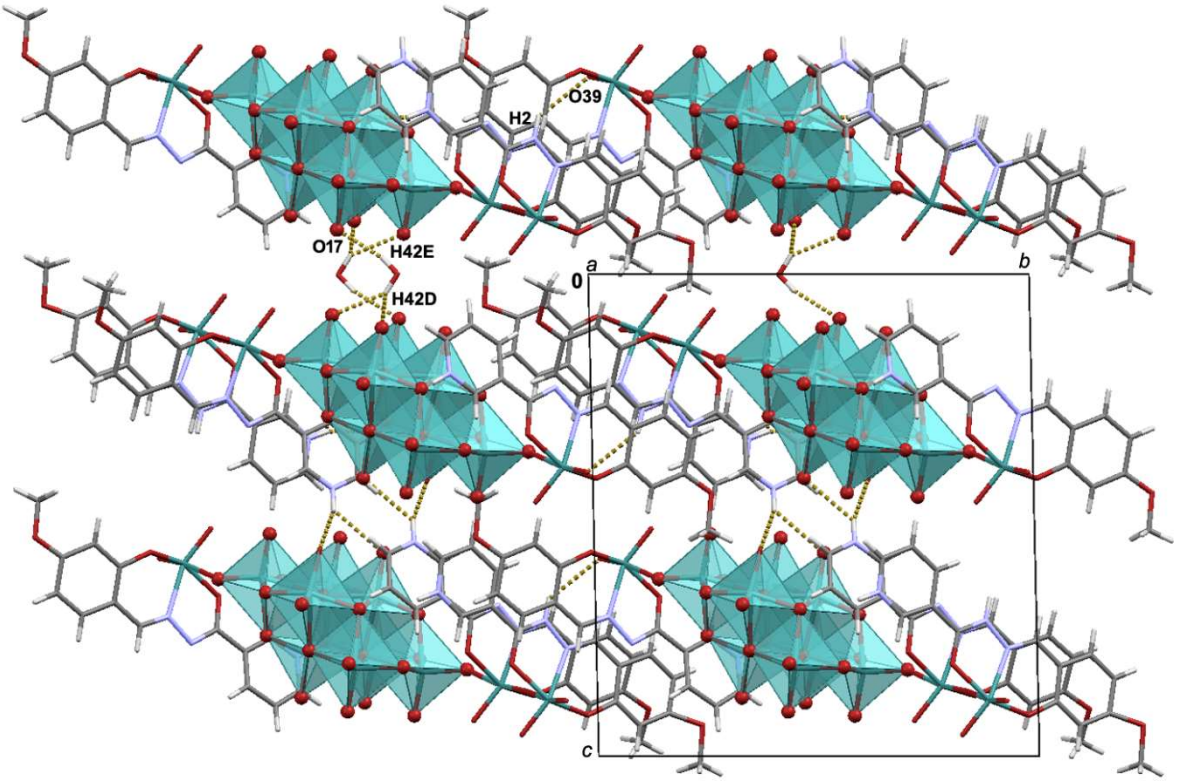

N2
H6A
H6B
O5
O14
O4
H12
b
c
H6B
O7
H11
O13
H12
O15
H3
0
a
O14

(b)

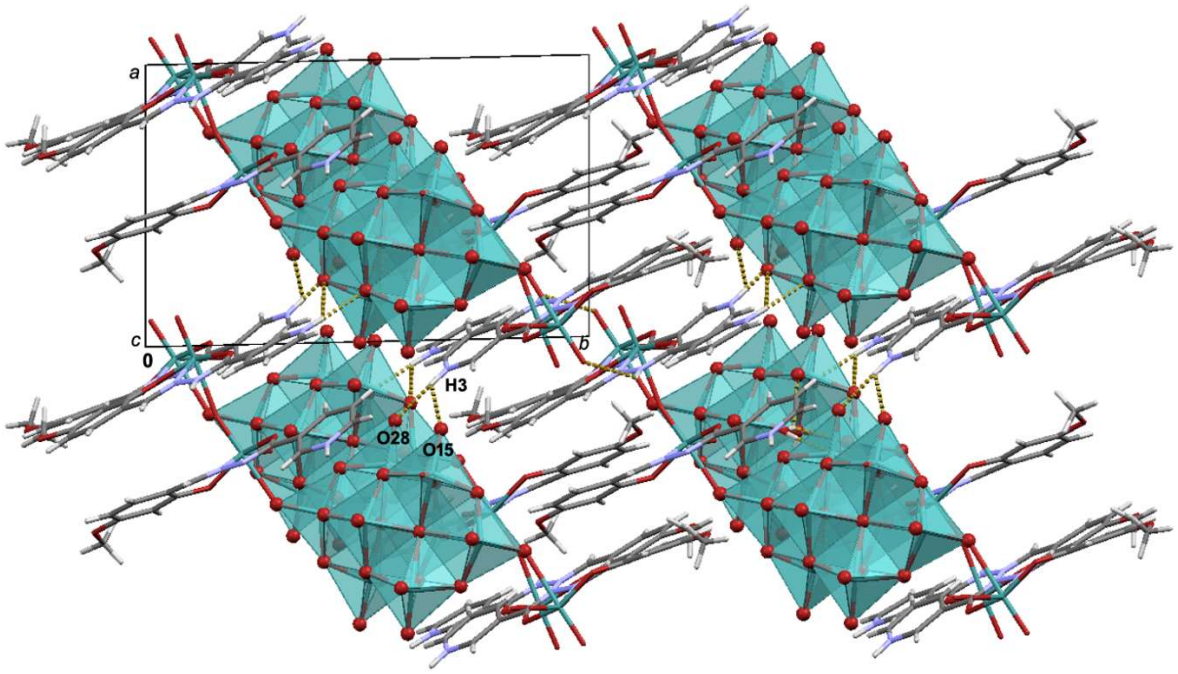


(c)

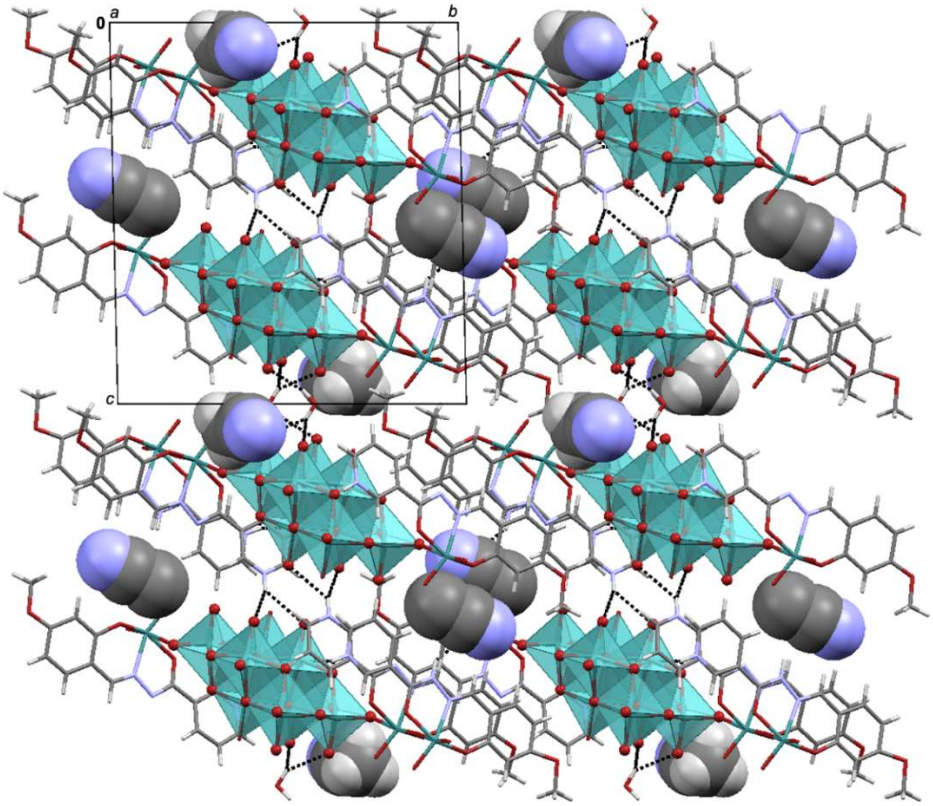
Figure S9. (a) Hydrogen bonding pattern found in **1H^{w}**. Crystal structure of **1H^{w}** along the: (a) *a*-axis, and (b) *b*-axis. In (a) and (b) hydrogen bonds are shown as yellow dashed lines and C–H···O interactions as black dashed lines, while the Lindqvist anions ($Mo_6O_{19}^{2-}$) are shown in polyhedral representation.



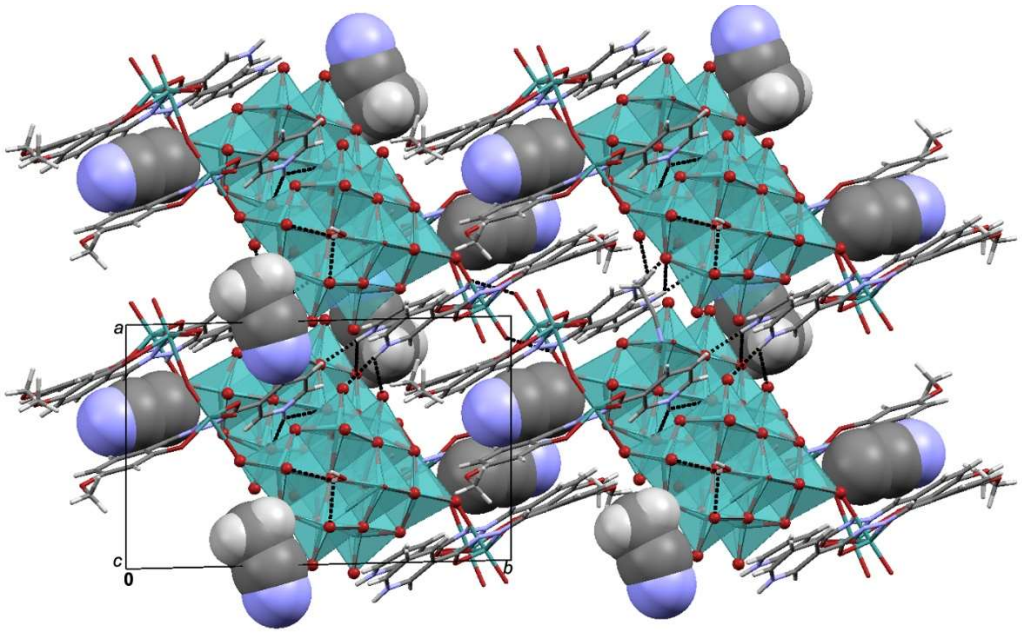
(a)



(b)

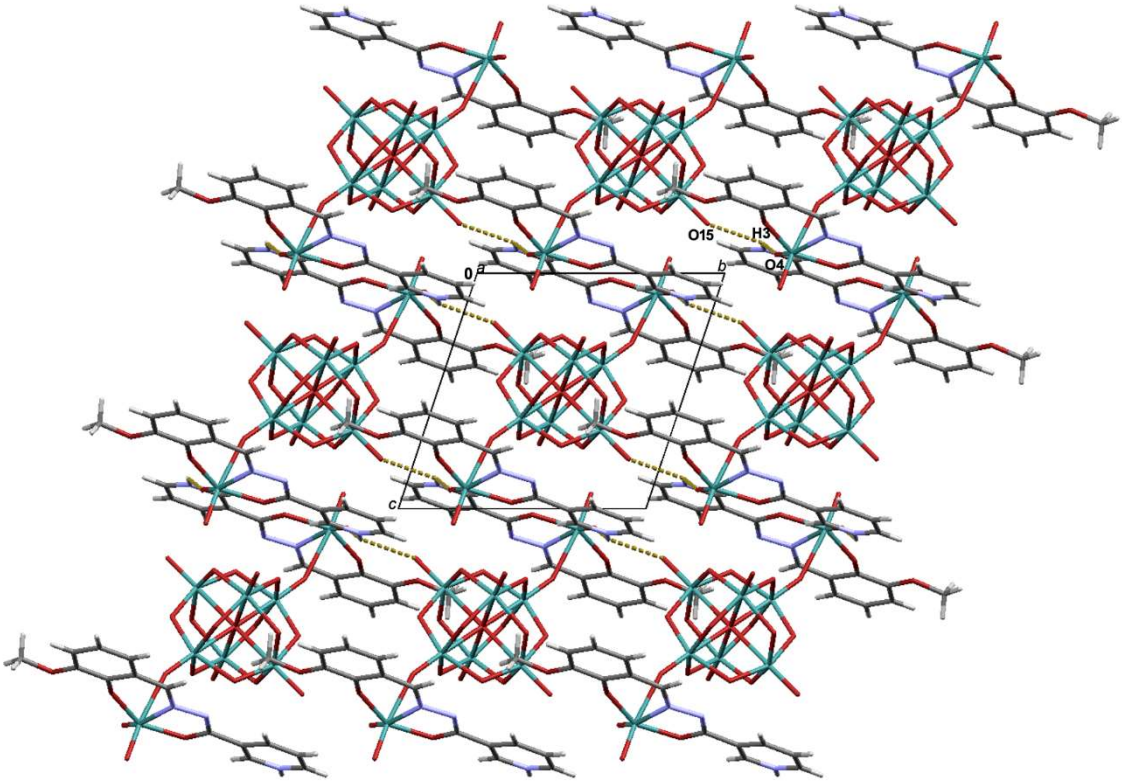


(c)

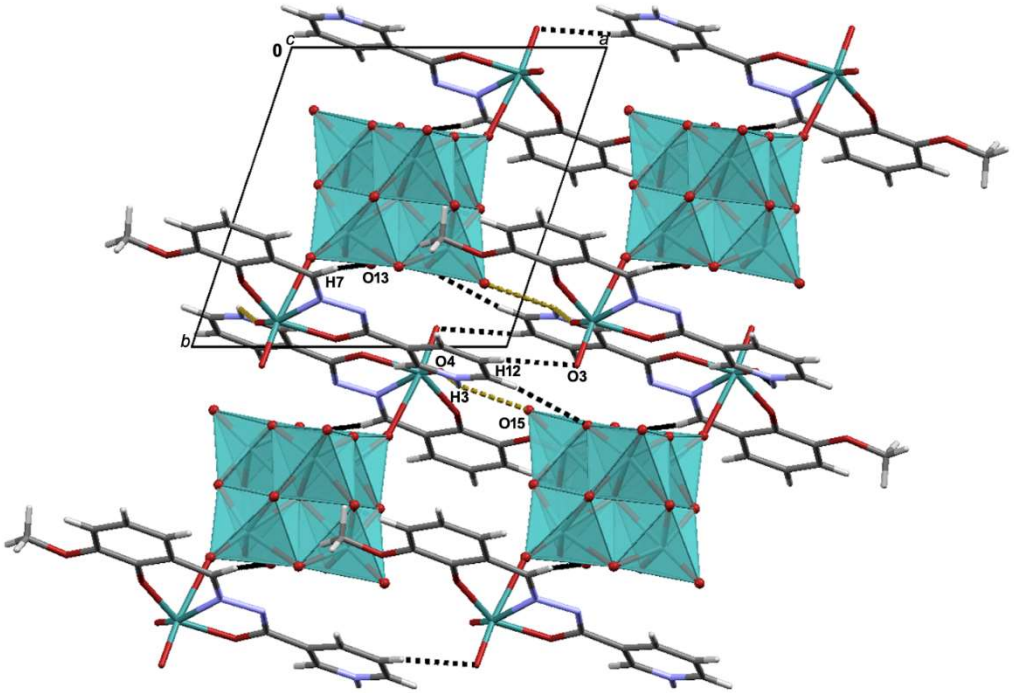


(d)

Figure S10. Complex hydrogen-bonded network observed in **2O**·2CH_3CN·H_2O shown down the: (a) *a*-axis, and (b) *c*-axis. In (c) and (d) identical fragments of crystal structure are shown down the *a*-axis and *c*-axis, respectively. In (c) and (d), solvent acetonitrile molecules are shown in a spacefill style, classical hydrogen bonds with yellow dashed lines and C–H···O interactions are shown as black dashed lines, while the octamolybdate anions ($Mo_8O_{26}^{4-}$) are shown in polyhedral representation.

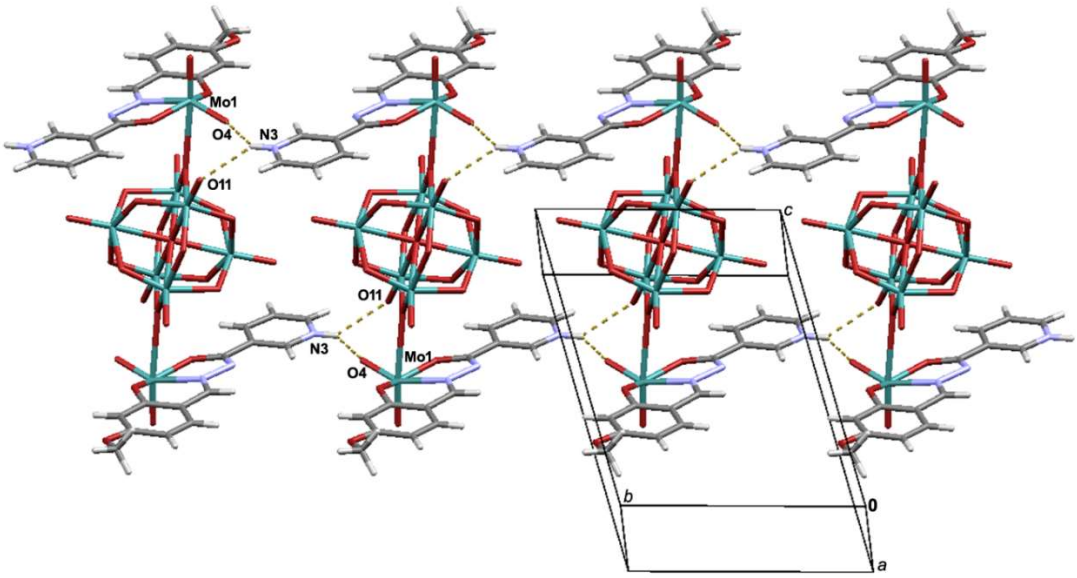


(a)



(b)

Figure S11. (a) Hydrogen-bonded supramolecular layers found in **1H** form in the *ab*-plane (view down the *c*-axis). (b) Crystal packing in **1H** shown down the *c*-axis. In (a) and (b) hydrogen bonds are shown as yellow dashed lines and in (b) C–H···O interactions are shown as black dashed lines, while the Lindqvist anions ($Mo_6O_{19}^{2-}$) are shown in polyhedral representation.



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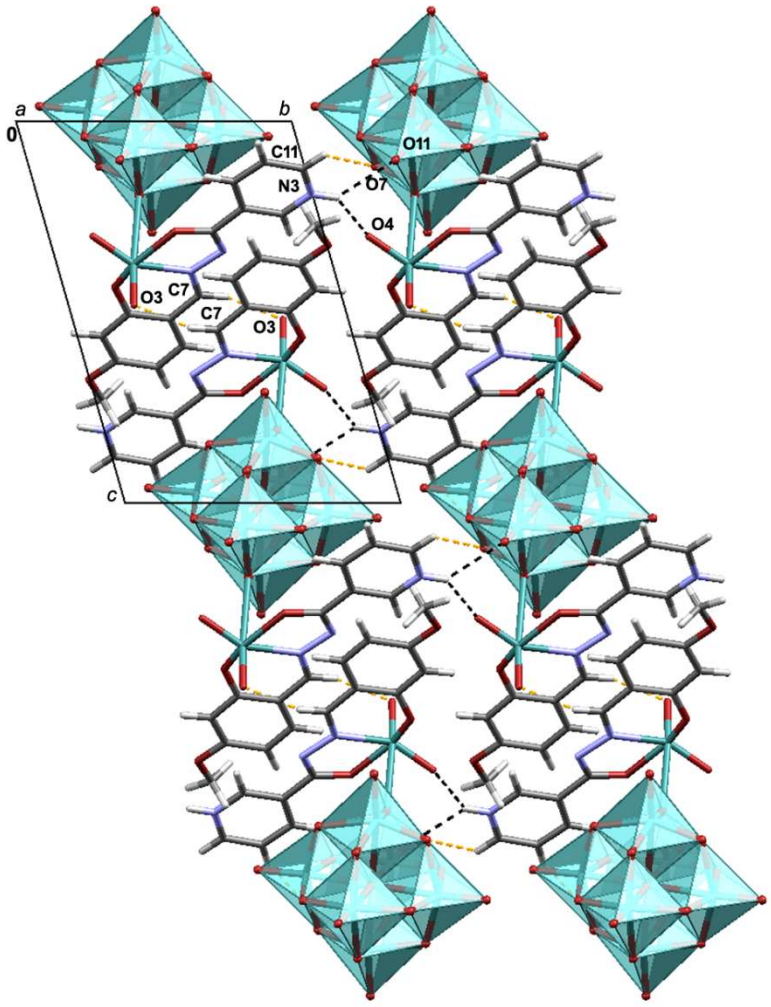
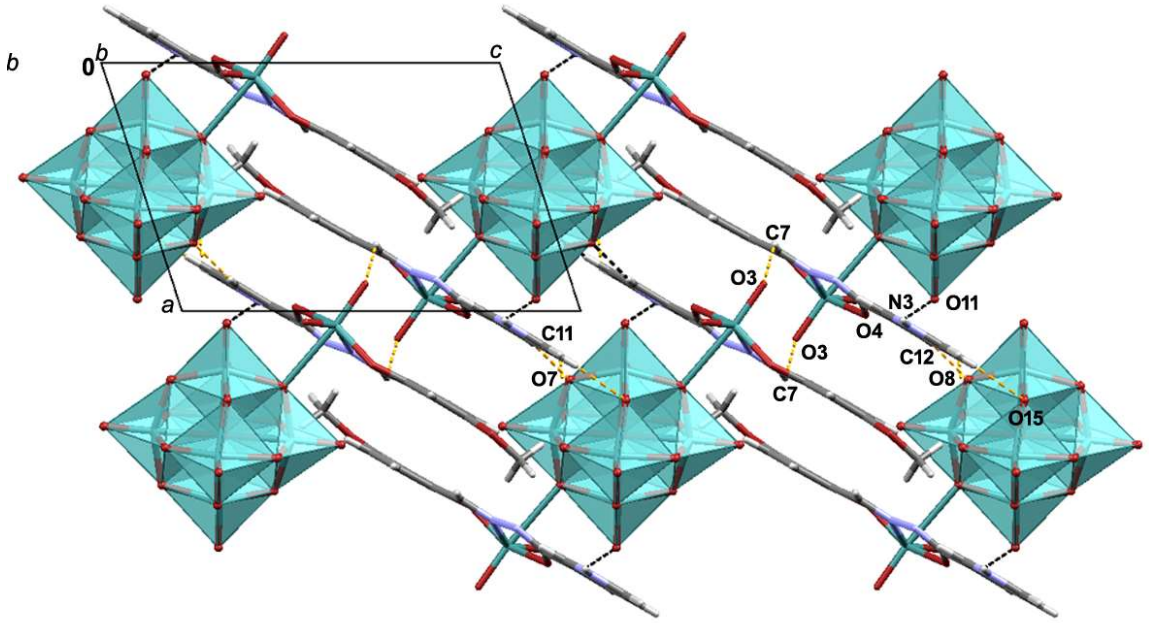
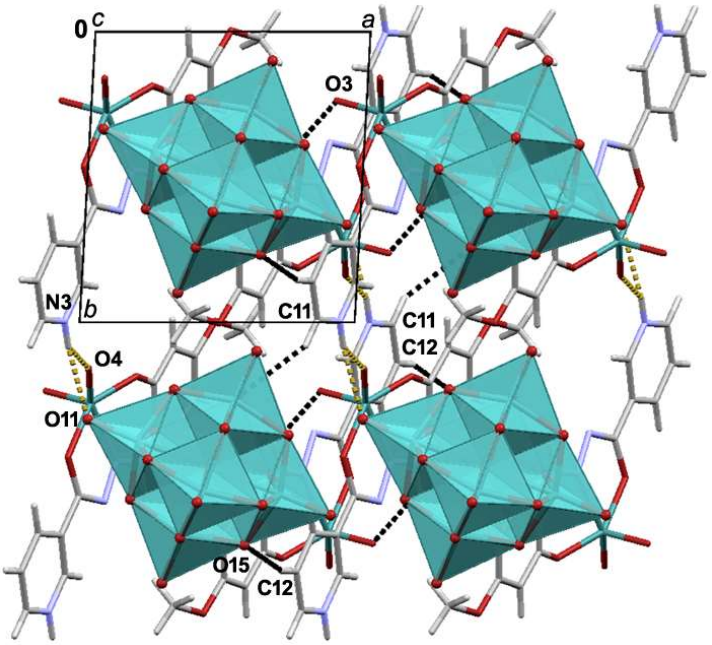


(b)

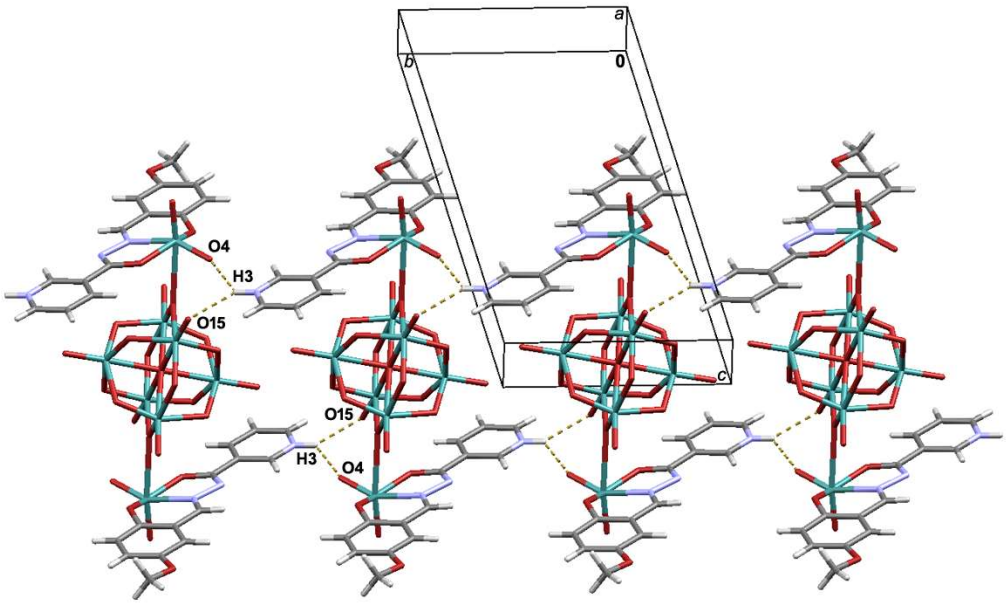


(c)

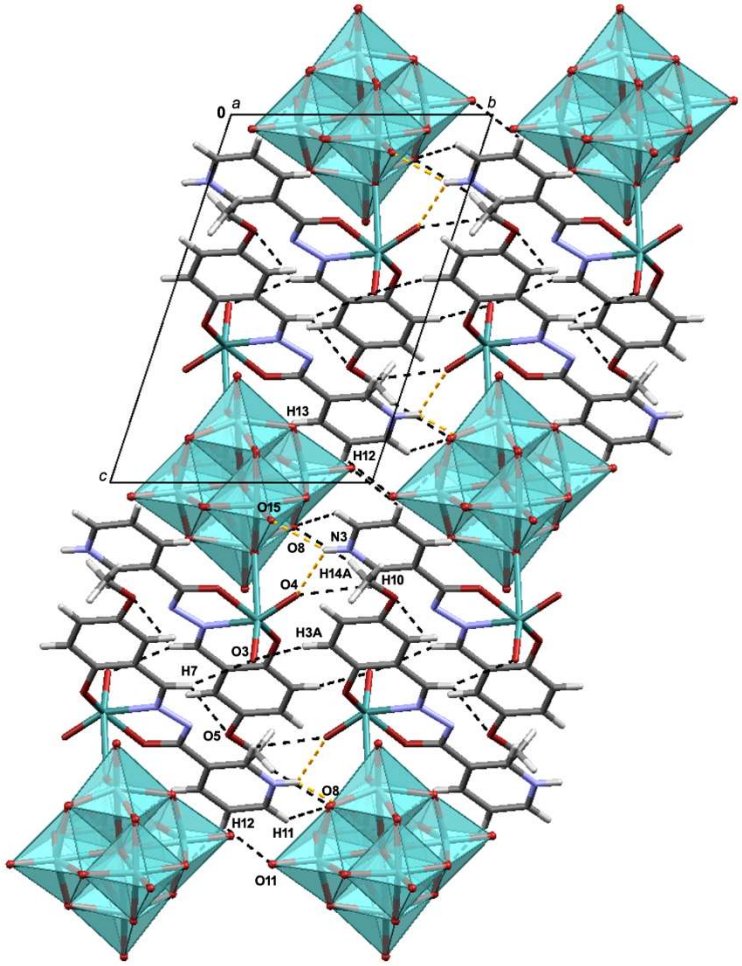


(d)

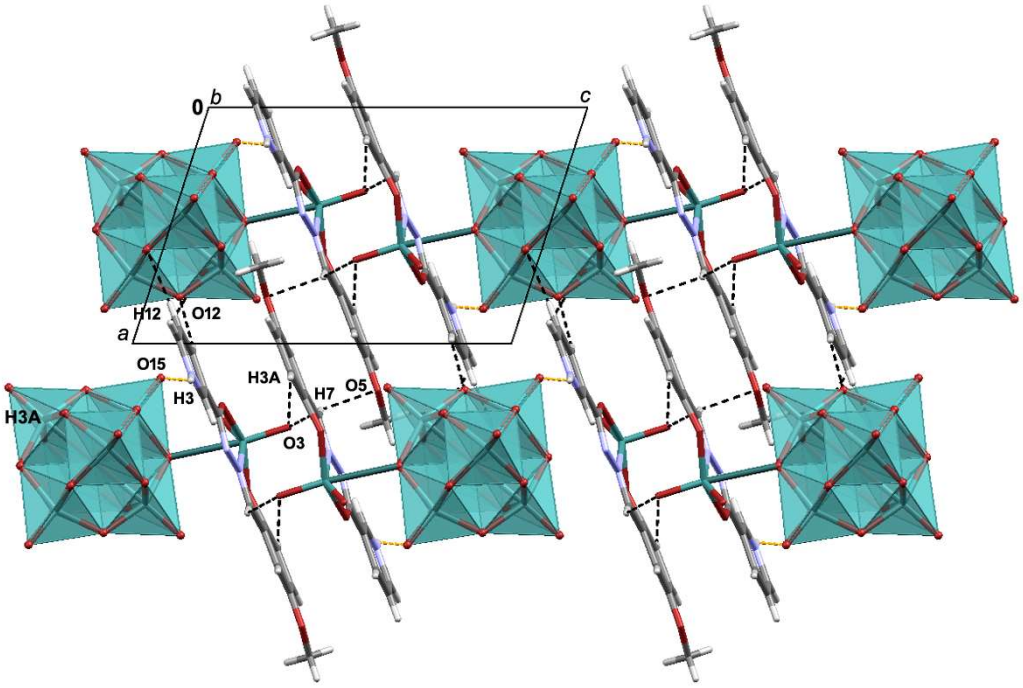
Figure S12. Fragments of crystal structures for **2H** showing: (a) hydrogen bonded chains, spreading along the *b*-axis, as a main packing motif; and the packing along the (b) *a*-axis, (c) *b*-axis and (d) *c*-axis. In (a) and (d) hydrogen bonds are shown as yellow dashed lines and C–H···O interactions as black dashed lines, whereas in (b) and (c) hydrogen bonds are shown as black dashed lines and C–H···O interactions as yellow dashed lines. In (b)-(d) Lindqvist anions ($Mo_6O_{19}^{2-}$) are shown in polyhedral representation.


a
b
0
c
O4
H3
O15
O15
H3
O4

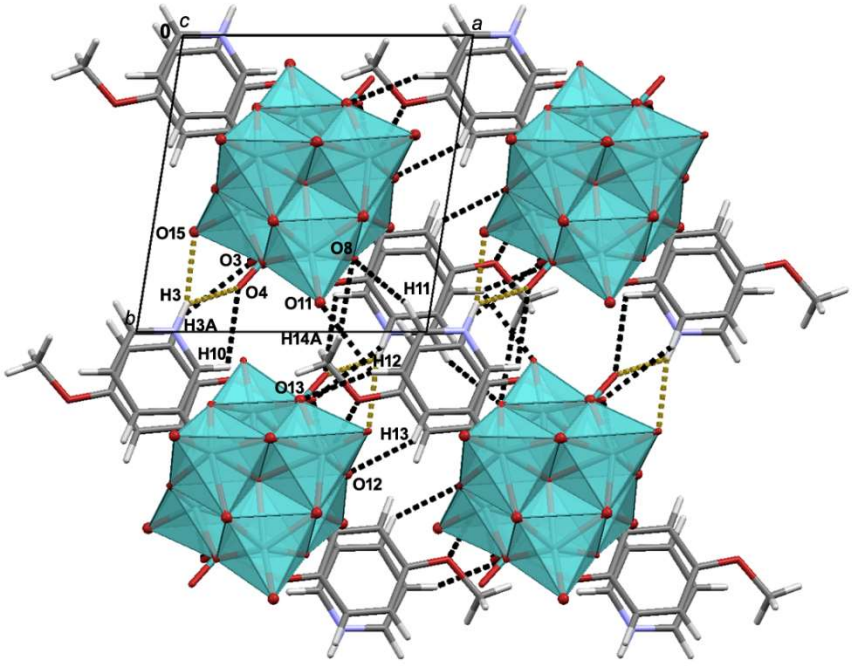
(a)


0
a
b
c
H13
H12
O15
O8
N3
H14A
H10
O4
H3A
O3
H7
O5
O8
H12
H11
O11

(b)



(c)



(d)

Figure S13. Fragments of crystal structures for **3H** showing: (a) hydrogen bonded chains, spreading along the *b*-axis, as a main packing motif; and the packing along the (b) *a*-axis, (c) *b*-axis and (d) *c*-axis. In (a)-(d) hydrogen bonds are shown as yellow dashed lines and C–H···O interactions as black dashed lines. In (b)-(d) Lindqvist anions ($Mo_6O_{19}^{2-}$) are shown in polyhedral representation.

Table S1. Selected bond lengths (Å) and angles (°) for compounds: **$1H^{a}\cdot2CH_3COCH_3$, $2H^{w}\cdot2CH_3COCH_3$, $3H^{w}\cdot2CH_3COCH_3$ and $1H^{w}$**

	$1H^{a}\cdot2CH_3COCH_3$	$2H^{w}\cdot2CH_3COCH_3$	$3H^{w}\cdot2CH_3COCH_3$	$1H^{w}$
Mo1–O1	1.920(4)	1.927(4)	1.929(5)	1.920(2)
Mo1–O2	2.014(3)	2.9(4)	2.037(5)	2.013(3)
Mo1–O3	1.698(5)	1.679(4)	1.691(5)	1.689(3)
Mo1–O4	1.696(4)	1.703(3)	1.691(5)	1.709(3)
Mo1–O6	2.398(3)	2.371(4)	2.335(5)	2.408(2)
Mo1–N1	2.238(4)	2.244(4)	2.255(5)	2.256(3)
N1–N2	1.388(6)	1.397(7)	1.388(7)	1.402(4)
C7–N1	1.295(7)	1.278(8)	1.291(9)	1.285(4)
C8–N2	1.309(7)	1.294(7)	1.313(9)	1.302(4)
C8–O2	1.307(6)	1.324(5)	1.301(9)	1.315(4)
O1–Mo1–O2	147.38(15)	147.30(13)	149.6(2)	149.67(9)
O1–Mo1–O3	1.69(19)	99.35(19)	99.6(2)	101.85(11)
O1–Mo1–O4	101.60(18)	104.07(18)	104.0(2)	103.16(10)
O1–Mo1–O6	76.95(14)	78.69(15)	81.3(2)	79.18(9)
O1–Mo1–N1	80.98(16)	82.01(16)	81.7(2)	81.20(9)
O2–Mo1–O3	98.71(19)	1.12(17)	96.3(2)	95.04(11)
O2–Mo1–O4	97.90(15)	95.74(16)	96.3(2)	96.26(11)
O2–Mo1–O6	78.93(13)	77.46(14)	78.9(2)	79.93(9)
O2–Mo1–N1	71.93(14)	71.65(16)	71.5(2)	71.50(10)
O3–Mo1–O4	106.(19)	105.39(19)	105.6(3)	105.41(13)
O3–Mo1–O6	168.78(17)	169.71(17)	170.5(2)	169.80(12)
O3–Mo1–N1	93.28(19)	91.03(18)	94.0(2)	98.24(12)
O4–Mo1–O6	85.22(14)	84.85(16)	83.2(2)	84.07(11)
O4–Mo1–N1	159.54(15)	161.05(16)	158.1(2)	154.33(11)
O6–Mo1–N1	75.54(13)	78.71(15)	76.72(19)	71.79(9)

Table S2. Selected bond lengths (Å) and angles (°) for compounds: **1H, 2H, 3H, 3H·2CH_3CN and 2O·CH_3CN·H_2O.**

	1H	**2H**	**3H**	**3H·2CH_3CN**
Mo1–O1	1.915(4)	1.934(7)	1.909(6)	1.912(3)
Mo1–O2	2.9(4)	2.026(7)	2.018(6)	2.021(2)
Mo1–O3	1.695(4)	1.707(8)	1.689(6)	1.680(4)
Mo1–O4	1.710(4)	1.715(7)	1.708(6)	1.715(3)
Mo1–O6	2.437(4)	2.723(6)	2.705(5)	2.551(3)
Mo1–N1	2.213(5)	2.213(9)	2.231(7)	2.223(3)
N1–N2	1.4(7)	1.388(12)	1.389(9)	1.389(5)
C7–N1	1.292(7)	1.299(12)	1.296(10)	1.286(5)
C8–N2	1.283(7)	1.290(12)	1.291(10)	1.295(5)
C8–O2	1.324(7)	1.326(12)	1.318(10)	1.320(5)
O1–Mo1–O2	148.65(15)	147.8(3)	147.1(2)	146.49(13)
O1–Mo1–O3	99.71(17)	101.1(3)	103.0(3)	1.54(16)
O1–Mo1–O4	101.43(17)	101.2(3)	101.1(3)	101.82(15)
O1–Mo1–O6	81.67(15)	85.4(2)	73.38(19)	80.45(11)
O1–Mo1–N1	81.(17)	80.0(3)	80.1(2)	80.52(13)
O2–Mo1–O3	99.40(17)	99.0(3)	97.7(3)	101.30(16)
O2–Mo1–O4	96.30(17)	96.9(3)	97.0(3)	95.59(15)
O2–Mo1–O6	75.46(13)	74.2(2)	95.49(19)	74.87(11)
O2–Mo1–N1	72.21(16)	71.5(3)	71.7(2)	71.75(13)
O3–Mo1–O4	107.27(18)	106.3(4)	106.7(3)	107.24(18)
O3–Mo1–O6	170.12(16)	173.2(3)	171.0(3)	172.80(15)
O3–Mo1–N1	96.92(17)	101.4(3)	98.9(3)	97.32(16)
O4–Mo1–O6	81.89(16)	74.3(3)	76.2(2)	79.39(13)
O4–Mo1–N1	154.75(18)	151.4(3)	153.3(3)	154.29(15)
O6–Mo1–N1	73.55(14)	77.3(2)	77.3(2)	75.75(11)

2O·CH_3CN·H_2O			
Mo1–O1	1.911(4)	O1–Mo1–O2	150.15(17)
Mo1–O2	2.023(4)	O9–Mo2–N4	158.82(16)
Mo1–O3	1.689(5)	O1–Mo1–O3	100.1(2)
Mo1–O4	1.693(4)	O11–Mo2–N4	78.94(13)
Mo1–O6	2.401(3)	O1–Mo1–O4	102.26(19)
Mo1–N1	2.238(4)	O11–Mo3–O12	105.47(16)
Mo2–O6	1.708(3)	O1–Mo1–O6	80.32(17)
Mo2–O7	1.918(3)	O11–Mo3–O13	90.28(14)
Mo2–O8	1.999(3)	O1–Mo1–N1	81.20(17)
Mo2–O9	1.704(4)	O11–Mo3–O14	101.69(15)
Mo2–O11	2.380(3)	O2–Mo1–O3	97.2(2)
Mo2–N4	2.222(4)	O11–Mo3–O15	104.39(14)
Mo3–O11	1.732(3)	O2–Mo1–O4	96.22(19)
Mo3–O12	1.711(4)	O11–Mo3–O20	161.03(13)
Mo3–O13	2.243(3)	O2–Mo1–O6	79.51(15)
Mo3–O14	1.911(3)	O12–Mo3–O13	164.18(14)
Mo3–O15	1.907(3)	O2–Mo1–N1	71.65(16)
Mo3–O20	2.442(3)	O12–Mo3–O14	96.61(15)
Mo4–O14	1.891(3)	O3–Mo1–O4	105.5(2)
Mo4–O16	1.700(3)	O12–Mo3–O15	98.37(15)
Mo4–O17	1.716(4)	O3–Mo1–O6	172.75(15)
Mo4–O20	2.334(3)	O12–Mo3–O20	93.44(13)
Mo4–O21	2.298(3)	O3–Mo1–N1	101.40(18)
Mo4–O25	1.999(3)	O13–Mo3–O14	78.31(13)
Mo11–O40	1.702(4)	O4–Mo1–O6	81.41(17)
Mo5–O15	1.930(3)	O13–Mo3–O15	78.73(13)
Mo5–O18	1.699(4)	O4–Mo1–N1	151.7(2)
Mo5–O19	1.708(3)	O13–Mo3–O20	70.78(11)
Mo5–O20	2.276(3)	O6–Mo1–N1	71.45(14)
Mo5–O28	2.374(3)	O14–Mo3–O15	145.07(14)
Mo5–O29	1.973(3)	O6–Mo2–O7	99.12(15)
Mo6–O13	1.753(3)	O14–Mo3–O20	74.02(12)
Mo6–O20	2.393(3)	O6–Mo2–O8	97.71(15)
Mo6–O21	1.945(3)	O15–Mo3–O20	73.74(12)
Mo6–O22	1.691(3)	O6–Mo2–O9	105.73(18)
Mo6–O27	2.127(3)	O14–Mo4–O16	102.13(15)
Mo6–O28	1.973(3)	O6–Mo2–O11	172.14(14)
Mo7–O21	2.006(3)	O14–Mo4–O17	99.64(15)
Mo7–O23	1.710(4)	O6–Mo2–N4	93.63(15)
Mo7–O24	1.708(3)	O14–Mo4–O20	77.05(12)
Mo7–O25	2.302(3)	O7–Mo2–O8	148.28(14)
Mo7–O26	1.885(3)	O14–Mo4–O21	83.48(13)
Mo7–O27	2.340(3)	O7–Mo2–O9	104.04(17)
Mo8–O27	2.297(3)	O14–Mo4–O25	146.56(14)
Mo8–O28	2.016(3)	O7–Mo2–O11	82.30(13)
Mo8–O29	2.381(3)	O16–Mo4–O17	105.36(19)
Mo8–O32	1.701(3)	O7–Mo2–N4	80.74(14)
Mo11–N7	2.215(4)	O16–Mo4–O20	161.33(15)
Mo8–O33	1.893(3)	O8 –Mo2–O9	96.95(15)
Mo8–O35	1.701(4)	O16–Mo4–O21	89.04(15)
Mo9–O20	2.174(3)	O8 –Mo2–O11	77.64(12)
Mo9–O25	1.958(3)	O16–Mo4–O25	100.03(15)
Mo9–O27	2.363(3)	O8 –Mo2–N4	71.52(13)
Mo9–O29	1.949(3)	O17–Mo4–O20	93.09(16)
Mo9–O30	1.743(3)	O9 –Mo2–O11	81.27(16)
Mo9–O31	1.694(3)	O17–Mo4–O21	164.11(16)
Mo10–O26	1.920(3)	O17–Mo4–O25	98.25(15)

Mo10–O27	2.517(3)	O21–Mo6–O22	101.86(15)
Mo10–O30	2.288(3)	O20–Mo4–O21	72.31(11)
Mo11–O38	2.013(3)	O21–Mo6–O27	78.97(13)
Mo11–O39	1.682(4)	O20–Mo4–O25	73.98(12)
Mo11–O37	1.920(4)	O21–Mo6–O28	149.60(13)
Mo10–O33	1.907(3)	O15–Mo5–O18	101.94(15)
Mo10–O34	1.703(4)	O22–Mo6–O28	101.75(14)
Mo10–O36	1.712(3)	O15–Mo5–O19	98.57(15)
		O27–Mo6–O28	78.61(12)
		O15–Mo5–O20	77.41(12)
		O21–Mo7–O23	96.10(15)
		O15–Mo5–O28	81.60(12)
		O21–Mo7–O24	99.82(15)
		O15–Mo5–O29	146.66(14)
		O21–Mo7–O25	71.93(12)
		O18–Mo5–O19	105.38(16)
		O21–Mo7–O26	146.44(14)
		O18–Mo5–O20	95.63(13)
		O21–Mo7–O27	72.82(12)
		O18–Mo5–O28	166.59(14)
		O23–Mo7–O24	104.72(16)
		O18–Mo5–O29	99.28(15)
		O23–Mo7–O25	162.37(14)
		O19–Mo5–O20	158.99(14)
		O23–Mo7–O26	101.75(15)
		O19–Mo5–O28	86.68(14)
		O23–Mo7–O27	92.26(13)
		O19–Mo5–O29	100.24(15)
		O24–Mo7–O25	90.35(14)
		O20–Mo5–O28	72.35(11)
		O24–Mo7–O26	102.74(15)
		O20–Mo5–O29	75.16(12)
		O24–Mo7–O27	162.26(14)
		O28–Mo5–O29	72.32(12)
		O25–Mo7–O26	83.36(13)
		O13–Mo6–O20	80.34(13)
		O25–Mo7–O27	72.09(11)
		O13–Mo6–O21	96.85(14)
		O26–Mo7–O27	78.26(12)
		O13–Mo6–O22	105.25(16)
		O27–Mo8–O28	73.82(12)
		O13–Mo6–O27	155.58(13)
		O27–Mo8–O29	70.88(11)
		O13–Mo6–O28	95.13(14)
		O27–Mo8–O32	157.51(15)
		O20–Mo6–O21	77.33(12)
		O27–Mo8–O33	77.64(12)
		O20–Mo6–O22	174.41(14)
		O27–Mo8–O35	97.23(16)
		O20–Mo6–O27	75.27(11)
		O28–Mo8–O29	71.49(12)
		O20–Mo6–O28	77.30(12)
		O28–Mo8–O32	100.19(15)
		O28–Mo8–O33	147.39(14)
		O27–Mo10–O30	68.74(10)
		O28–Mo8–O35	97.13(15)
		O27–Mo10–O33	71.96(12)
		O29–Mo8–O32	86.64(15)
		O27–Mo10–O34	94.93(13)
		O29–Mo8–O33	84.59(13)

		O27–Mo10–O36	159.58(13)
		O29–Mo8–O35	165.20(16)
		O30–Mo10–O33	78.32(13)
		O32–Mo8–O35	105.09(19)
		O30–Mo10–O36	91.00(14)
		O33–Mo8–O35	101.82(16)
		O33–Mo10–O34	98.54(18)
		O20–Mo9–O25	78.56(12)
		O33–Mo10–O36	102.30(15)
		O20–Mo9–O27	75.06(11)
		O34–Mo10–O36	105.37(16)
		O20–Mo9–O29	78.07(13)
		O38–Mo11–O39	98.63(16)
		O20–Mo9–O30	156.46(13)
		O38–Mo11–O40	95.42(15)
		O20–Mo9–O31	97.66(14)
		O38–Mo11–N7	71.92(13)
		O25–Mo9–O27	77.79(12)
		O37–Mo11–O38	148.53(14)
		O25–Mo9–O29	149.42(13)
		O37–Mo11–O39	101.41(17)
		O25–Mo9–O30	97.54(14)
		O37–Mo11–O40	101.57(17)
		O25–Mo9–O31	101.22(15)
		O37–Mo11–N7	80.78(14)
		O27–Mo9–O29	77.33(12)
		O39–Mo11–O40	106.95(19)
		O27–Mo9–O30	81.43(13)
		O39–Mo11–N7	100.27(16)
		O27–Mo9–O31	172.71(14)
		O40–Mo11–N7	151.50(16)
		O29–Mo9–O30	96.05(14)
		Mo1–O1 –C2	138.7(4)
		O29–Mo9–O31	101.20(15)
		Mo1–O2 –C8	119.5(3)
		O30–Mo9–O31	105.86(16)
		O26–Mo10–O33	142.59(14)
		O26–Mo10–O27	73.24(12)
		O26–Mo10–O30	76.67(13)
		Mo1–O6 –Mo2	165.57(19)
		Mo2–O7 –C16	132.3(3)

Table S3. Geometry of intermolecular hydrogen bonds (Å, °) for compounds: **$1H^{a}\cdot 2CH_3COCH_3$, $2H^{w}\cdot 2CH_3COCH_3$, $3H^{w}\cdot 2CH_3COCH_3$** and **$1H^{w}$**

	D–H···A	Symmetry code	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(D–H···A)
$1H^{a}\cdot 2CH_3COCH_3$	N3–H3···O7		0.88	1.83	2.644(8)	152
	C11–H11···O14	*1-x,1-y,-z*	0.95	2.38	3.291(7)	160
	C13–H13···O4	*1-x,1-y,1-z*	0.95	2.32	3.258(7)	169
	C14–H14B···O16	*x,1+y,1+z*	0.98	2.60	3.559(11)	167
	C17–H17A···O1	*-x,1-y,1-z*	0.98	2.51	3.474(8)	170
	C19–H19B···O16	*x,1+y,z*	0.98	2.51	3.39(3)	150
	C21–H21B···O16	*x,1+y,z*	0.98	2.53	3.411(17)	149
$2H^{w}\cdot 2CH_3COCH_3$	N3–H3···O7	*-1+x,-1+y,z*	0.85(5)	1.99(5)	2.820(7)	168(5)
	O6–H6A···O7	*x,-1+y,z*	0.81(5)	2.06(5)	2.827(6)	158(6)
	O6–H6B···O17	*-1+x,-1+y,z*	0.81(3)	2.01(3)	2.824(5)	178(8)
	C5–H5···O14		0.95	2.56	3.452(7)	157
	C6–H6···O10		0.95	2.36	3.173(6)	143
	C10–H10···O4	*-1+x,-1+y,z*	0.95	2.38	3.138(6)	136
	C11–H11···O8	*-x,-y,-z*	0.95	2.53	3.404(8)	153
	C14–H14A···O3	*1+x,y,z*	0.98	2.52	3.338(8)	141
	C15–H15C···O13		0.98	2.52	3.309(10)	137
	C17–H17C···O14	*-1+x,y,z*	0.98	2.51	3.439(8)	159
$3H^{w}\cdot 2CH_3COCH_3$	N3–H3A···O7		0.88	1.99	2.857(12)	169
	O6–H6A···N2	*1-x,1-y,1-z*	0.87	2.02	2.853(7)	160
	O6–H6B···O8		0.87	2.01	2.868(8)	168
	C7–H7···O15	*-1+x,-1+y,z*	0.95	2.38	3.288(8)	160
	C11–H11···O7	*1-x,-y,-z*	0.95	2.35	3.234(12)	154
	C12–H12···O4	*2-x,1-y,1-z*	0.95	2.06	2.955(12)	157
	C13–H13···O17	*2-x,2-y,1-z*	0.95	2.49	3.172(9)	129
	C15–H15A···O3	*1-x,-y,1-z*	0.98	2.40	3.327(12)	157
	C15–H15B···O8	*1-x,1-y,1-z*	0.98	2.55	3.464(13)	155
	C17–H17C···O4	*-1+x,-1+y,-1+z*	0.98	2.56	3.433(11)	148
$1H^{w}$	N3–H3···O3	*-x,1/2+y,3/2-z*	0.85(5)	2.39(5)	3.063(4)	136(4)
	N3–H3···O13	*x,1/2-y,1/2+z*	0.85(5)	2.58(5)	3.032(4)	114(4)
	O6–H6A···N2	*1-x,-1/2+y,3/2-z*	0.81(4)	2.11(4)	2.906(4)	169(4)
	O6–H6B···O5	*1-x,1/2+y,3/2-z*	0.81(4)	2.13(4)	2.867(3)	152(4)
	O6–H6B···O7	*1-x,1/2+y,3/2-z*	0.81(4)	2.54(4)	3.057(4)	123(3)
	C11–H11···O15	*x,3/2-y,1/2+z*	0.83(5)	2.24(4)	3.068(5)	175(3)
	C12–H12···O4	*x,1+y,z*	0.95	2.38	3.081(4)	131
	C12–H12···O14	*x,3/2-y,1/2+z*	0.95	2.59	3.347(5)	136
	C14–H14C···O13	*1-x,-y,1-z*	0.98	2.40	3.364(4)	166

Table S4. Geometry of intermolecular hydrogen bonds (Å, °) for compounds: **1H**, **2H**, **2O**·CH_3CN·H_2O, **3H** and **3H**·$2CH_3CN$

	D–H···A	Symmetry code	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(D–H···A)
1H	N3–H3···O4	*1-x,-y,-z*	0.80(3)	2.11(3)	2.790(6)	142(5)
	C4–H4···O9	*2-x,1-y,1-z*	0.93	2.44	3.331(7)	161
	C7–H7···O13	*1-x,1-y,1-z*	0.93	2.25	3.129(7)	158
	C12–H12···O3	*-1+x,y,z*	0.93	2.41	3.149(8)	137
2H	N3–H3···O4	*x,-1+y,z*	0.88	2.05	2.768(12)	138
	N3–H3···O11	*1-x,-y,2-z*	0.88	2.37	3.094(12)	140
	C7–H7···O3	*2-x,1-y,1-z*	0.95	2.33	3.034(12)	131
	C11–H11···O7	*1+x,-1+y,z*	0.95	2.60	3.388(14)	141
	C12–H12···O15	*2-x,1-y,2-z*	0.95	2.42	3.338(12)	163
	C13–H13···O8	*1+x,y,z*	0.95	2.18	2.984(12)	142
2O·CH_3CN·H_2O	N6–H6···22	*1-x,1-y,1-z*	0.88	2.59	3.174(5)	124
	N3–H3···O28	*1+x,y,z*	0.88	2.	2.846(6)	162
	N6–H6···O23	*1-x,1-y,1-z*	0.88	2.03	2.845(6)	154
	N9–H9···O16	*-1+x,y,z*	0.88	2.13	2.855(5)	139
	N9–H9···O24	*-1+x,y,z*	0.88	2.34	2.936(5)	125
	O42–H42D···O12	*1-x,1-y,-z*	0.87	2.32	3.042(6)	141
	O42–H42D···O18	*1-x,1-y,-z*	0.87	2.35	2.912(6)	123
	O42–H42E···O17		0.87	2.17	3.021(6)	166
	C3–H3A ···O3	*2-x,-y,-z*	0.95	2.56	3.5(8)	170
	C10–H10 ···O15	*1+x,y,z*	0.95	2.52	3.121(6)	121
	C11–H11 ···O35	*1-x,1-y,1-z*	0.95	2.54	3.128(7)	121
	C12–H12 ···O34	*1-x,1-y,1-z*	0.95	2.53	3.153(7)	123
	C19–H19 ···O30	*x,-1+y,z*	0.95	2.40	3.315(6)	163
	C20–H20 ···N10B	*1-x,-y,1-z*	0.95	2.61	3.54(2)	168
	C25–H25 ···O22	*1-x,1-y,1-z*	0.95	2.50	3.138(6)	125
	C26–H26 ···O32	*1+x,y,z*	0.95	2.17	3.021(6)	149
	C33–H33 ···O13	*x,1+y,z*	0.95	2.45	3.387(6)	170
	C35–H35 ···O3	*-1+x,1+y,z*	0.95	2.36	3.133(6)	138
	C39–H39 ···N11A	*1-x,-y,-z*	0.95	2.52	3.46(3)	169
	C40–H40 ···O4	*1-x,1-y,-z*	0.95	2.50	3.197(7)	130
	C45B–H45A···O15	*1-x,-y,-z*	0.98	2.54	3.273(19)	131
	C45B -- H45B···O4	*2-x,-y,-z*	0.98	2.56	3.28(2)	130
3H	N3–H3···O4	*x,1+y,z*	0.88	2.16	2.818(10)	131
	N3–H3···O15	*1-x,2-y,2-z*	0.88	2.20	2.979(10)	147
	C3–H3A···O3	*1-x,-y,1-z*	0.95	2.59	3.445(11)	149
	C7–H7···O3	*1-x,1-y,1-z*	0.95	2.54	3.278(10)	135
	C7–H7···O5	*-x,1-y,1-z*	0.95	2.59	3.310(10)	133
	C10–H10···O4	*x,1+y,z*	0.95	2.59	3.041(11)	109
	C11–H11···O8	*1+x,1+y,z*	0.95	2.49	3.228(12)	135
	C12–H12···O13	*1+x,y,z*	0.95	2.56	3.470(10)	161
	C12–H12···O11	*2-x,2-y,2-z*	0.95	2.57	3.218(11)	126
	C13–H13···O12	*1+x,y,z*	0.95	2.35	3.162(10)	143
	C14–H14A···O8	*-x,-y,1-z*	0.98	2.45	3.378(10)	157
3H·$2CH_3CN$	N3–H3···N4		0.88	2.61	3.178(6)	123
	N3–H3···O4	*1-x,1-y,1-z*	0.88	1.97	2.720(5)	143
	C7–H7···O12	*1+x,-1+y,z*	0.95	2.40	3.319(5)	163
	C11–H11···N4		0.95	2.49	3.123(7)	124

C14–H14B···O14	*1-x,-y,-z*	0.98	2.54	3.297(5)	134
C14–H14C···O15	*1+x,y,-1+z*	0.98	2.48	3.348(6)	147
C16–H16B···O9	*x,y,1+z*	0.98	2.52	3.390(9)	149
C16–H16C···O3	*-1+x,y,1+z*	0.98	2.47	3.354(9)	150

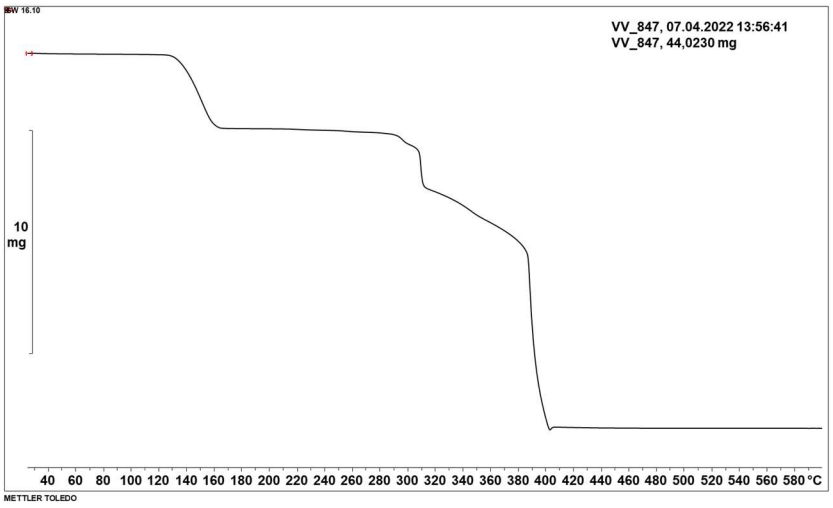
Table S5. Crystallographic data and structure refinement data for compounds: **1H^{a}**·2CH_3COCH_3, **2H^{w}**·2CH_3COCH_3, **3H^{w}**·2CH_3COCH_3, and **1H^{w}**

Identification code	**1H^{a}·2CH_3COCH_3**	**2H^{w}·2CH_3COCH_3**	**3H^{w}·2CH_3COCH_3**	**1H^{w}**
Empirical formula	$C_{40}H_{48}Mo_8N_6O_{33}$	$C_{34}H_{40}Mo_8N_6O_{33}$	$C_{34}H_{40}Mo_8N_6O_{33}$	$C_{56}H_{56}Mo_{16}N_{12}O_{62}$
Formula weight	1908.36	1828.24	1828.24	3424.16
Temperature/K	169.99	150.0	169.99(10)	150
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	P-1	P-1	P-1	$P2_1/c$
a/Å	8.9721(3)	10.1475(4)	10.6083(8)	11.2569(3)
b/Å	10.7368(2)	10.3331(5)	10.7813(6)	9.2706(2)
c/Å	16.4964(4)	14.6331(5)	12.8485(6)	21.2974(5)
α/°	104.858(2)	108.527(4)	106.660(5)	90
β/°	104.620(2)	92.219(3)	106.352(6)	103.717(2)
γ/°	94.020(2)	110.565(4)	99.224(5)	90
Volume/Å^3	1470.73(7)	1342.45(11)	1303.61(15)	2159.17(9)
Z	1	1	1	1
ρcalcg/cm^3	2.155	2.261	2.329	2.633
μ/mm^{-1}	14.380	1.907	16.182	2.359
F(0)	930.0	886.0	886.0	1644.0
Crystal size/mm^3	0.204 × 0.089 × 0.2	0.1 × 0.04 × 0.03	0.12 × 0.09 × 0.05	0.11 × 0.08 × 0.07
Radiation	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.774 to 161.044	7.954 to 58	7.656 to 160.62	8.654 to 65.854
Index ranges	-10 ≤ h ≤ 11, -13 ≤ k ≤ 13, -20 ≤ l ≤ 20	-13 ≤ h ≤ 13, -14 ≤ k ≤ 13, -19 ≤ l ≤ 19	-12 ≤ h ≤ 13, -13 ≤ k ≤ 11, -16 ≤ l ≤ 16	-16 ≤ h ≤ 12, -11 ≤ k ≤ 14, -30 ≤ l ≤ 32
Reflections collected	18183	17550	17776	15865
Independent reflections	6056 [R_{int} = 0.0485, R_{sigma} = 0.0478]	7018 [R_{int} = 0.0540, R_{sigma} = 0.0874]	5531 [R_{int} = 0.0926, R_{sigma} = 0.0792]	7131 [R_{int} = 0.0292, R_{sigma} = 0.0451]
Data/restraints/parameters	6056/1/410	7018/3/376	5531/1/374	7131/3/348
Goodness-of-fit on F^2	1.069	0.962	1.050	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0453, wR_2 = 0.1229	R_1 = 0.0517, wR_2 = 0.0789	R_1 = 0.0634, wR_2 = 0.1747	R_1 = 0.0347, wR_2 = 0.0709
Final R indexes [all data]	R_1 = 0.0477, wR_2 = 0.1252	R_1 = 0.1054, wR_2 = 0.0898	R_1 = 0.0673, wR_2 = 0.1820	R_1 = 0.05, wR_2 = 0.0793
Largest diff. peak/hole / e Å^{-3}	2.39/-2.46	0.78/-0.57	2.06/-2.04	0.88/-0.87

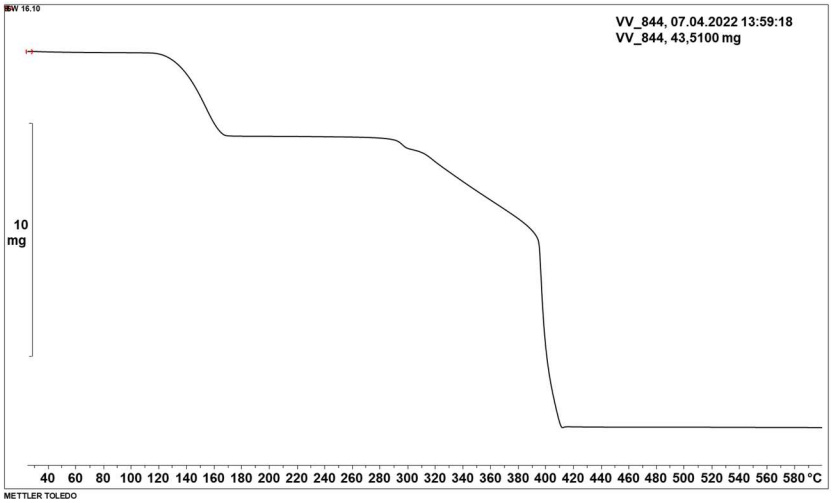
Table S6. Crystallographic data and structure refinement data for compounds: **1H**, **2H**, **2O**·CH_3CN·H_2O, **3H**, and **3H**·$2CH_3CN$

Identification code	**1H**	**2H**	**2O**·CH_3CN·H_2O	**3H**	**3H**·$2CH_3CN$
Empirical formula	$C_{28}H_{24}Mo_8N_6O_{29}$	$C_{28}H_{24}Mo_8N_6O_{29}$	$C_{46}H_{42}Mo_{11}N_{11}O_{42}$	$C_{28}H_{24}Mo_8N_6O_{29}$	$C_{32}H_{30}Mo_8N_8O_{29}$
Formula weight	1676.05	1676.05	2476.24	1676.05	1758.16
Temperature/K	150(2)	170	170	169.99(10)	169.99(10)
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1	P-1	P-1
a/Å	10.0670(6)	8.8506(5)	10.83910(10)	8.8403(2)	10.02310(10)
b/Å	10.0808(6)	9.2538(5)	17.04750(10)	9.1695(2)	10.7273(3)
c/Å	11.2764(7)	14.0175(8)	18.70750(10)	14.0494(3)	12.9277(3)
α/°	90.460(5)	74.262(5)	88.5840(10)	106.381(2)	73.422(2)
β/°	92.740(5)	72.168(5)	84.1140(10)	105.966(2)	72.752(2)
γ/°	108.443(5)	88.125(4)	88.5150(10)	93.753(2)	66.204(2)
Volume/$Å^3$	1084.03(12)	1050.34(11)	3436.54(4)	1037.78(4)	1192.60(5)
Z	1	1	2	1	1
ρcalcg/cm^3	2.567	2.650	2.393	2.682	2.448
μ/mm^{-1}	2.343	19.916	16.844	20.157	17.6
F(000)	802.0	802.0	2386.0	802.0	846.0
Crystal size/mm^3	0.23 × 0.17 × 0.08	0.09 × 0.04 × 0.01	0.123 × 0.083 × 0.073	0.097 × 0.038 × 0.022	0.166 × 0.094 × 0.031
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.208 to 66.4	6.888 to 160.024	6.956 to 160.79	10.178 to 156.2	7.292 to 155.422
Index ranges	-14 ≤ h ≤ 15, -15 ≤ k ≤ 14, -15 ≤ l ≤ 17	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -17 ≤ l ≤ 17	-13 ≤ h ≤ 13, -21 ≤ k ≤ 21, -23 ≤ l ≤ 23	-11 ≤ h ≤ 8, -11 ≤ k ≤ 11, -17 ≤ l ≤ 17	-9 ≤ h ≤ 12, -13 ≤ k ≤ 13, -16 ≤ l ≤ 16
Reflections collected	15537	13693	136522	14341	17780
Independent reflections	7115 [R_{int} = 0.0815, R_{sigma} = 0.1572]	4450 [R_{int} = 0.0635, R_{sigma} = 0.0534]	14751 [R_{int} = 0.0499, R_{sigma} = 0.0242]	4320 [R_{int} = 0.0590, R_{sigma} = 0.0529]	4996 [R_{int} = 0.0608, R_{sigma} = 0.0533]
Data/restraints/parameters	7115/1/326	4450/0/323	14751/58/1024	4320/0/323	4996/0/352
Goodness-of-fit on F^2	0.934	1.128	1.082	1.172	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0598, wR_2 = 0.0615	R_1 = 0.0829, wR_2 = 0.2175	R_1 = 0.0389, wR_2 = 0.1029	R_1 = 0.0802, wR_2 = 0.1975	R_1 = 0.0360, wR_2 = 0.0942
Final R indexes [all data]	R_1 = 0.1312, wR_2 = 0.0737	R_1 = 0.0844, wR_2 = 0.2197	R_1 = 0.0436, wR_2 = 0.1058	R_1 = 0.0818, wR_2 = 0.22	R_1 = 0.0386, wR_2 = 0.0968
Largest diff. peak/hole / e $Å^{-3}$	1.17/-1.14	2.57/-0.94	1.51/-1.81	2.55/-1.14	1.48/-1.26

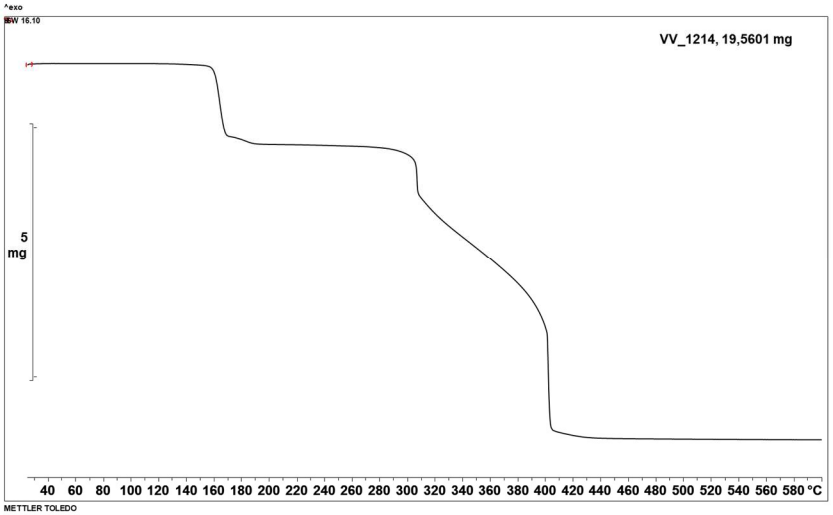
4. TGA



(a)

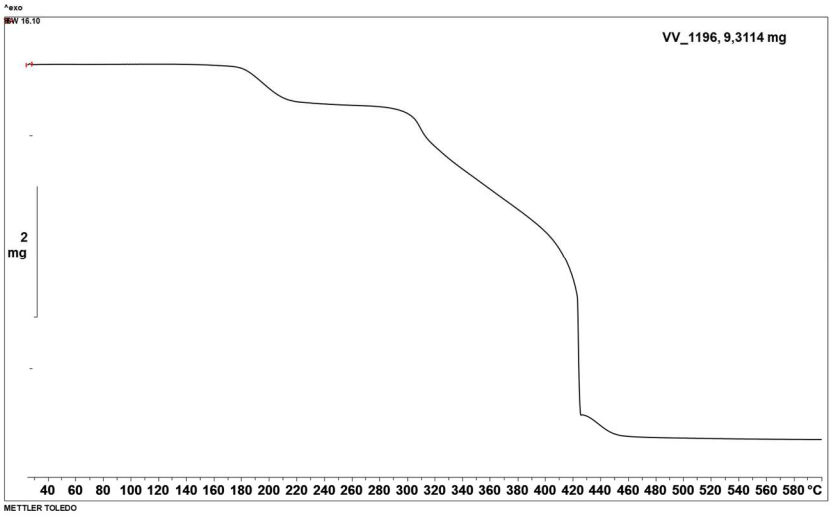


(b)

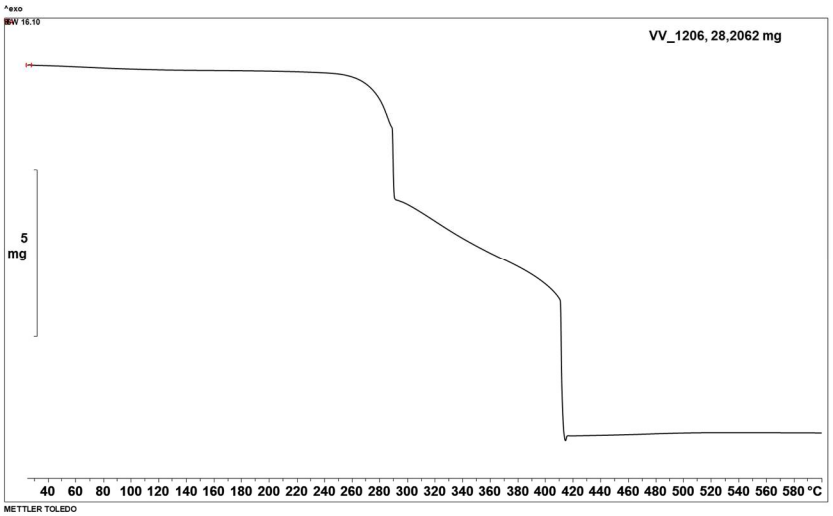


(c)

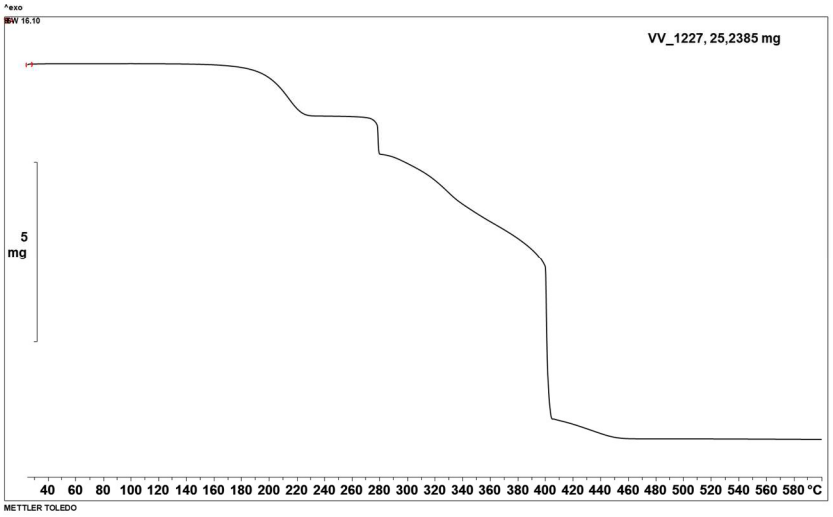
Figure S2. TG curves of (a) **1H**^{a}, (b) **2H**^{w}·2CH_3COCH_3, and (c) **3H**^{w}·2CH_3COCH_3



(a)

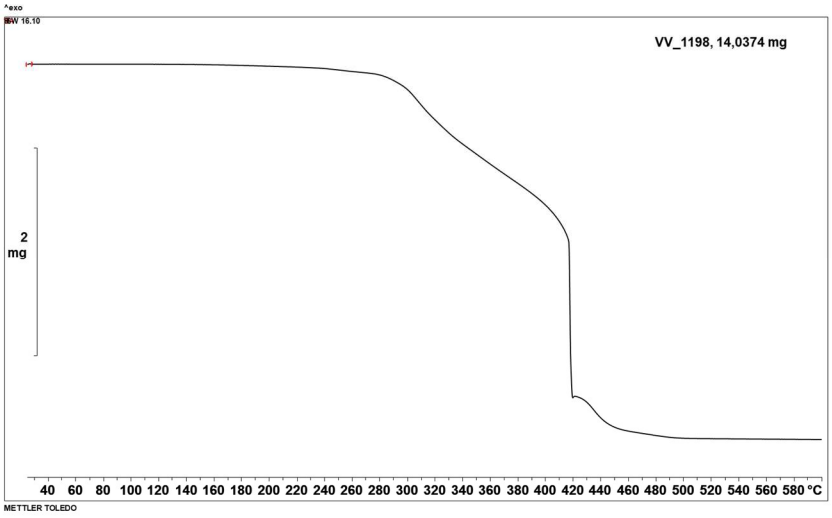


(b)

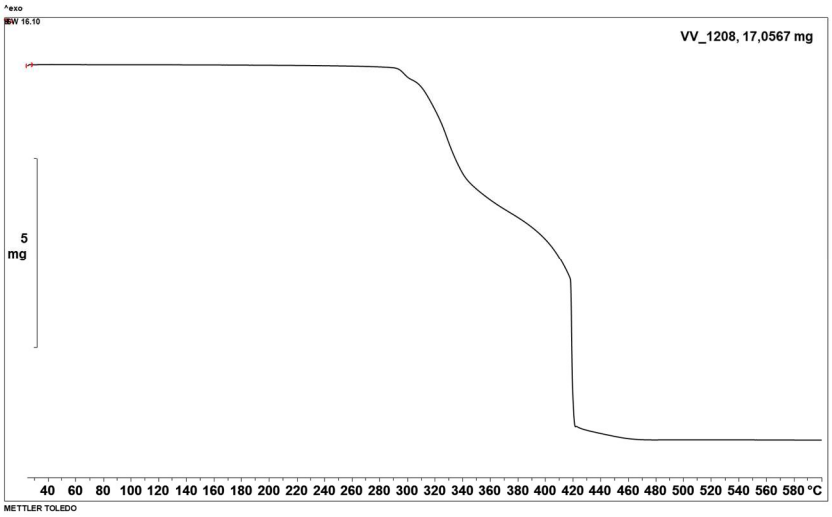


(c)

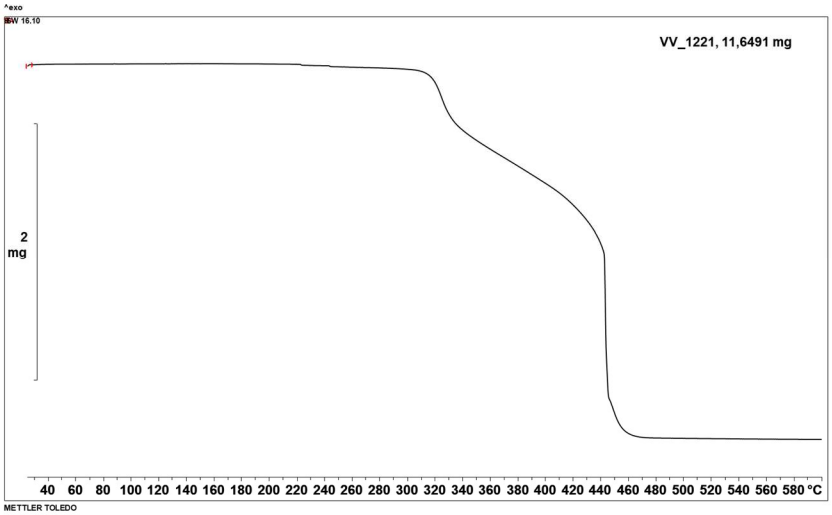
Figure S3. TG curves of (a) **1H^{w}**, (b) **2O**, and (c) **3H**·2MeCN.



(a)



(b)



(c)

Figure S4. TG curves of (a) **1H**, (b) **2H**, and (c) **3H**.

5. Catalytic studies

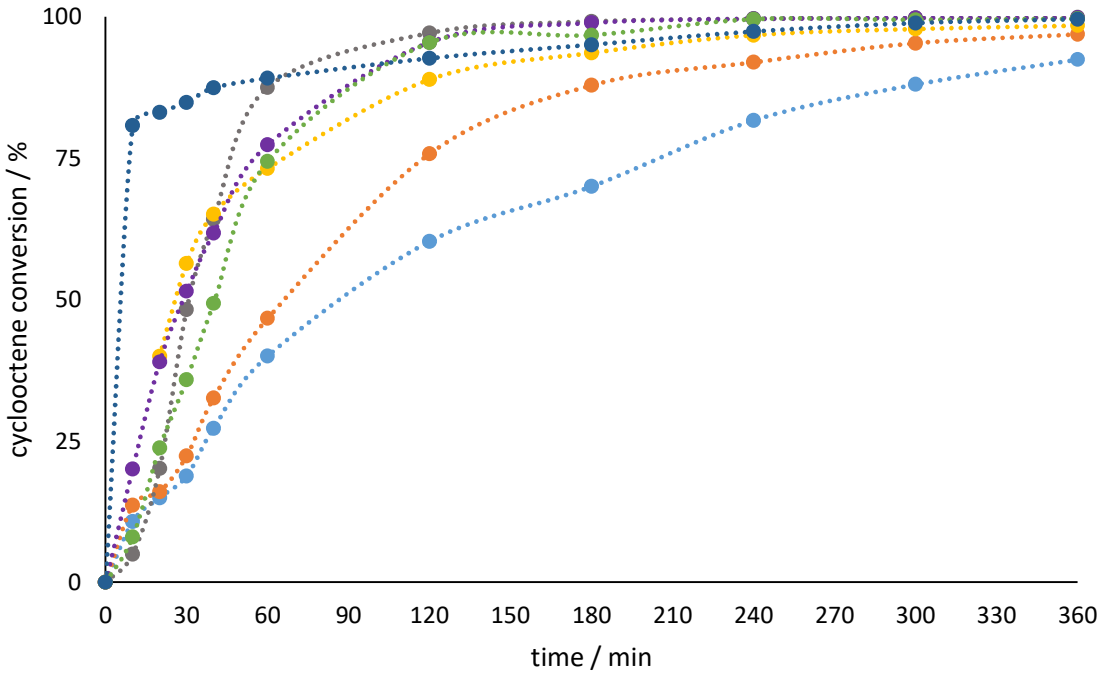
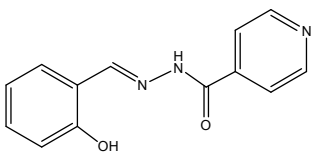


Figure S5. Catalytic profiles for all the catalyst with TBHP in decane as an oxidant: **1H**^{a} (light blue), **1H**^{w} (orange), **1H** (purple), **2H**^{w}·2CH_3COCH_3 (grey), **3H**^{w}·2CH_3COCH_3 (yellow), **3H**·2MeCN (dark blue), **3H**(brown)

Table S7. Relevant catalytic results for the cyclooctene epoxidation. Reaction conditions: time, 6 h; temperature, 80 °C.

Catalyst	**Catalyst loading % /Oxidans**	**Con/%**	**Sel/ %**	**TOF_{20min}**	**TON**	**Reference**
$[MoO_2(L)]_n$	0.25 TBHP (aq)	36	45	116	151	ref 51. *Cryst. Growth Des.* **2019**, 19, 3000–3011
$[MoO_2(L^1)]_n$		27	56	72	113	
$[MoO_2(L^2)]_n$		49	67	119	192	
$MoO_2(L^2)]_4$		78	85	151	204	
$[MoO_2(L)]_n$	0.25 TBHP (dec)	66	78	225	273	
$MoO_2(L^1)]_n$		74	85	200	305	
$[MoO_2(L^2)]_n$		79	87	221	324	
$[MoO_2(L^2)]_4$		99	94	1152	397	
$[MoO_2(L^3)]_n$	0.25 TBHP (aq)	90	84	91	360	*ref.* 26. *Int. J. Mol. Sci.* 2024, **25(3)**, 1503.



H_2L