Electronic Supplementary Information (ESI)

Molybdenum(VI) complexes of hemilabile aroylhydrazone ligands as efficient catalysts for greener cyclooctene epoxidation: An experimental and theoretical approach

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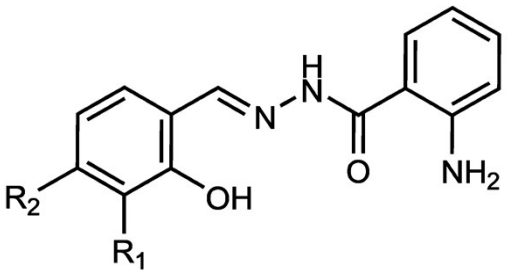
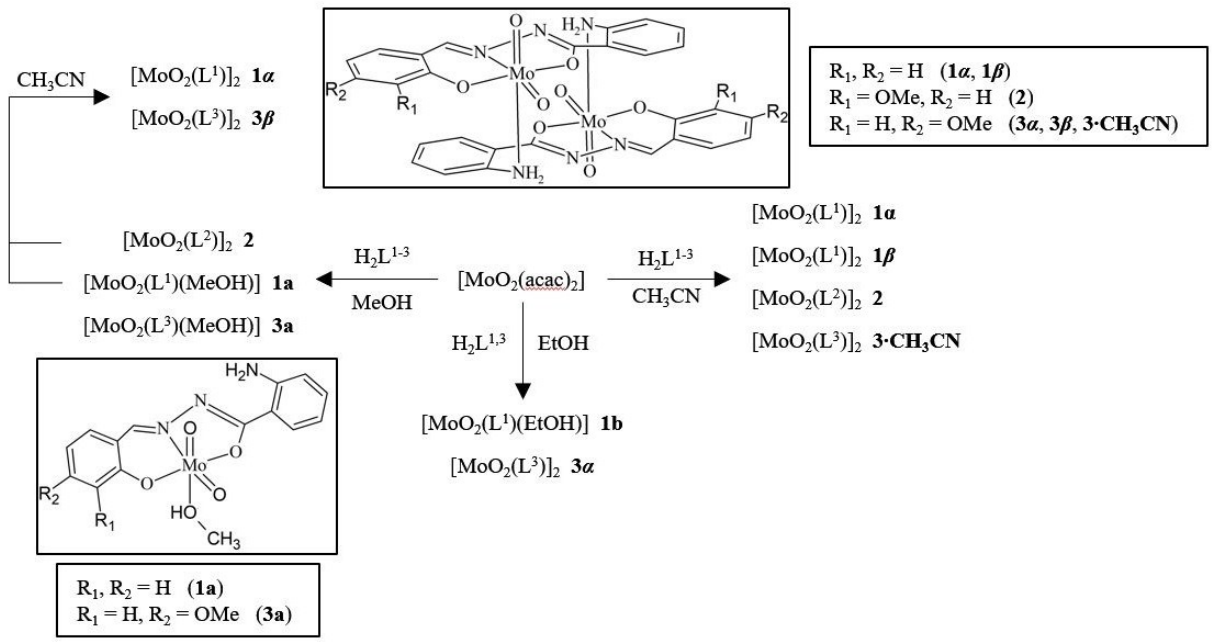
Contents

1. Schemes



H_2L^1 $R_1, R_2 = H$
H_2L^2 $R_1 = OMe, R_2 = H$
H_2L^3 $R_1 = H, R_2 = OMe$

Scheme S1 Molecular structure of the 2-aminobenhydrazones H_2L^{1-3}.



Scheme S2 Reaction pathways for the molybdenum(VI) compounds.

2. PXRD

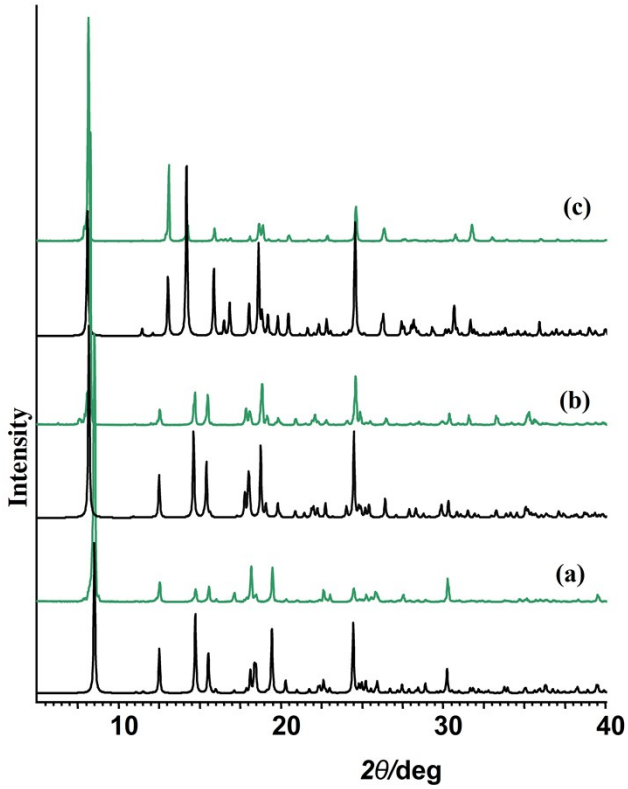


Fig. S1 Comparison of the measured PXRD patterns (green) and patterns calculated from the from the X-ray single-crystal structure (black): (a) **1a**; (b) **1b** (CSD code MUNFAC) and (c) **3a**.

3. X-Ray diffraction

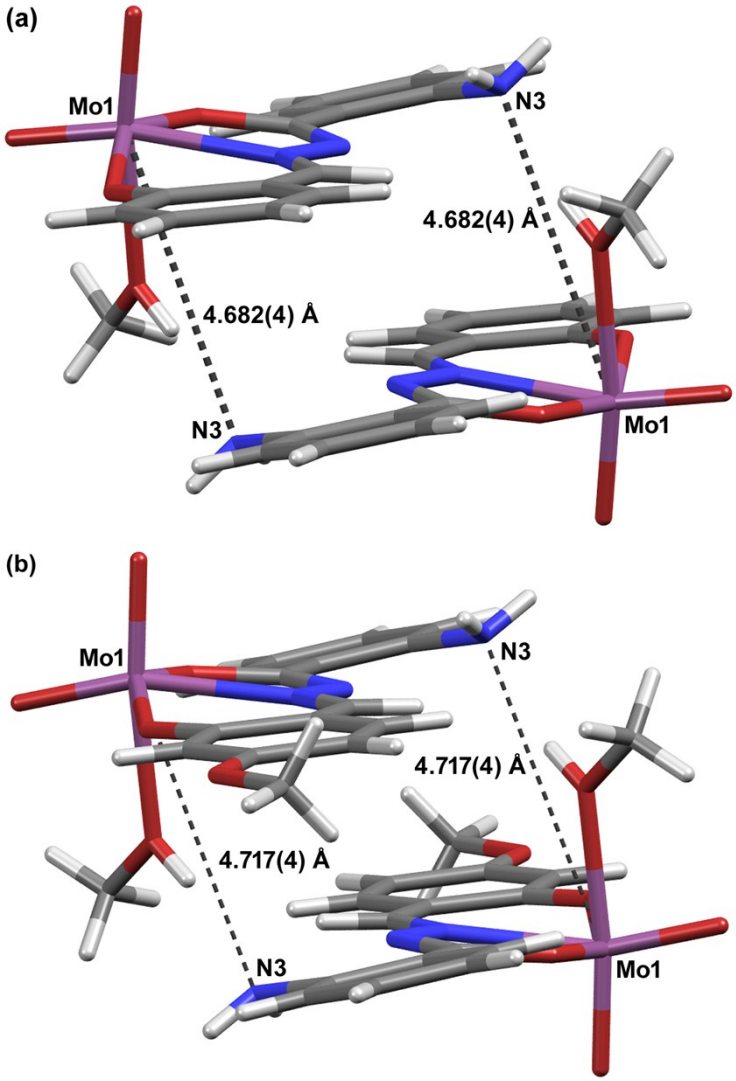
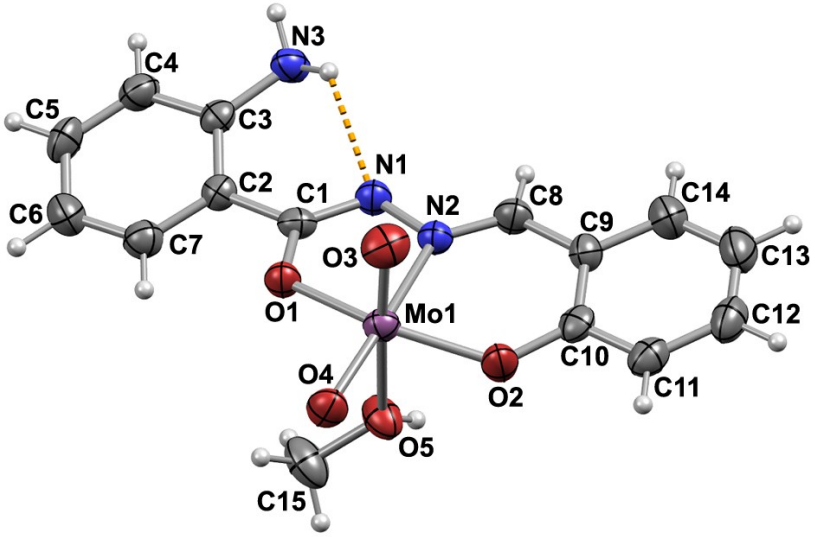
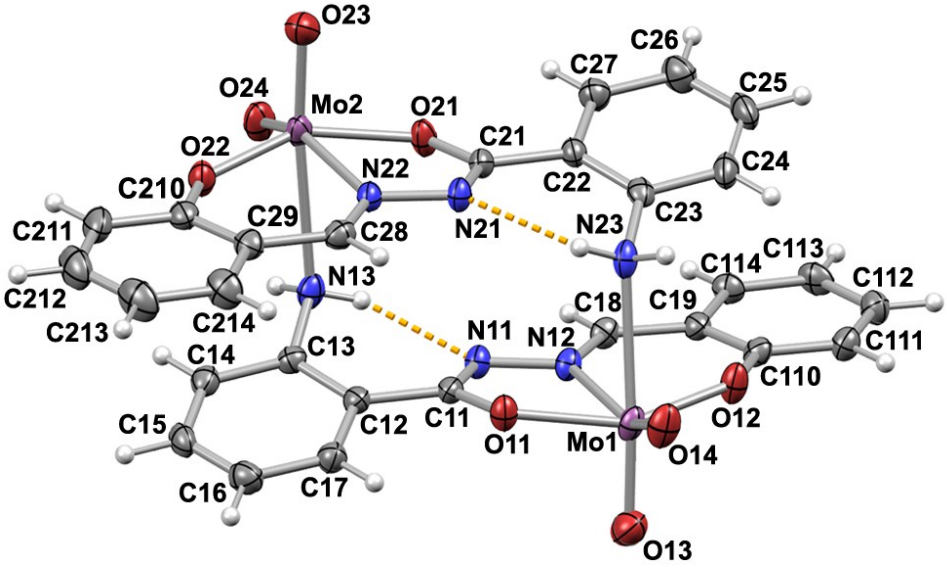


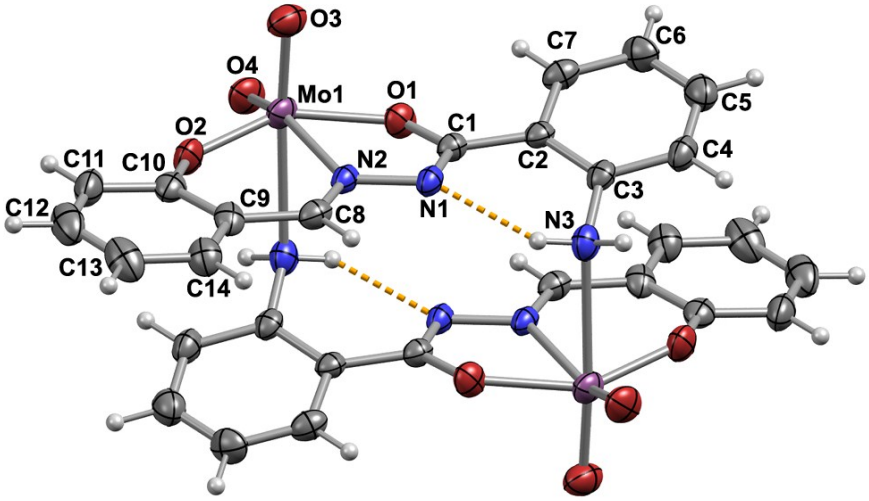
Fig. S2. The shorthes Mo···N (Å) distance between the atoms of the neighboring molecules observed in **1a** (a) and **3a** (b).


N3
C4
C5
C3
N1
C2
C1
N2
C8
C14
C6
C7
C9
O3
C13
O1
Mo1
C12
C10
O4
O2
C11
O5
C15

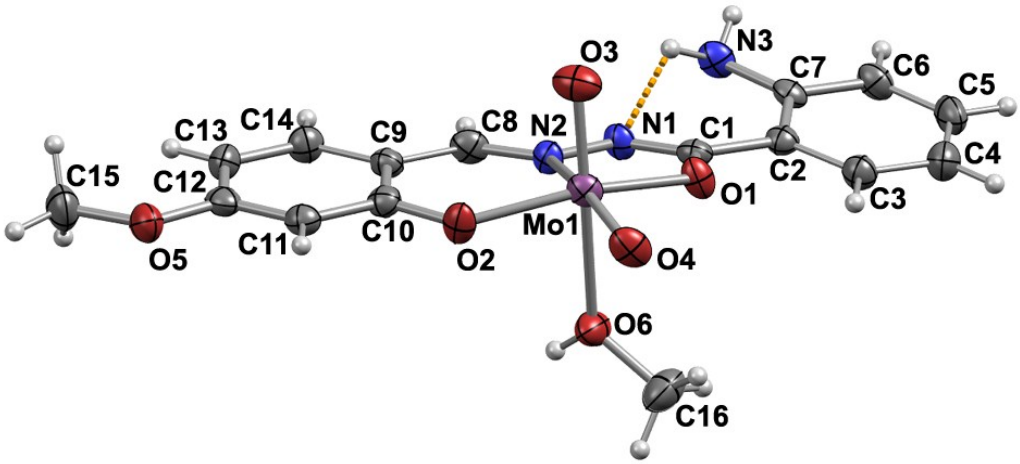
(a)


O23
C26
C27
O24
Mo2
O21
C25
C21
O22
C24
N22
C22
C210
C29
C28
N21
C23
N23
C211
C114
C113
N13
C112
C212
C18
C19
C213
C214
N11
N12
C111
C14
C13
C110
C15
C12
C11
O11
Mo1
O12
O14
C16
C17
O13

(b)


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

(c)


O3
N3
C7
C6
C5
C13
C14
C9
C8
N2
N1
C1
C4
C15
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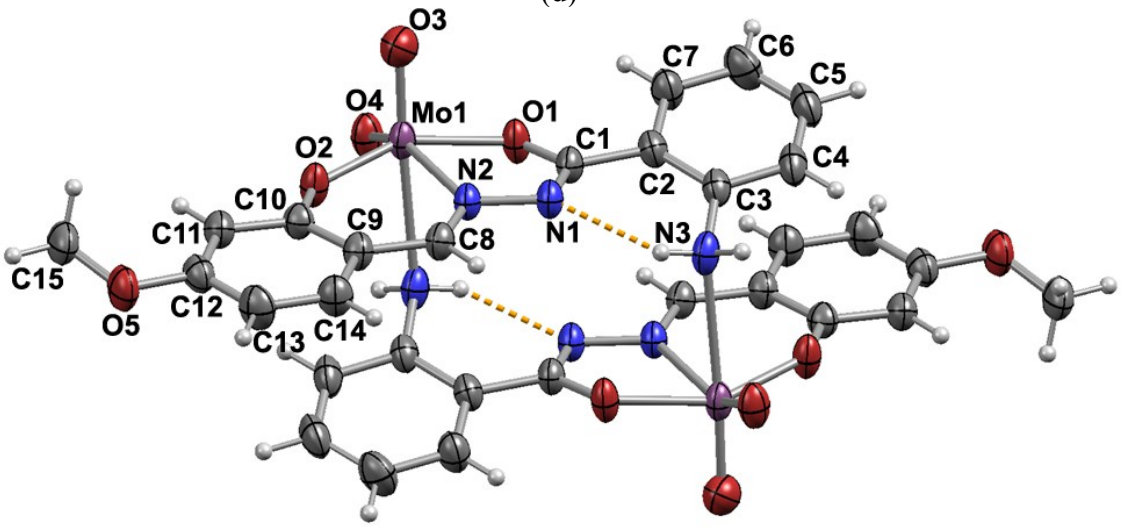
C2
O1
C3
C11
C10
Mo1
O5
O2
O4
O6
C16

(d)


O3
C7
C6
C5
O4
Mo1
O1
C1
O2
C4
N2
C2
C10
C3
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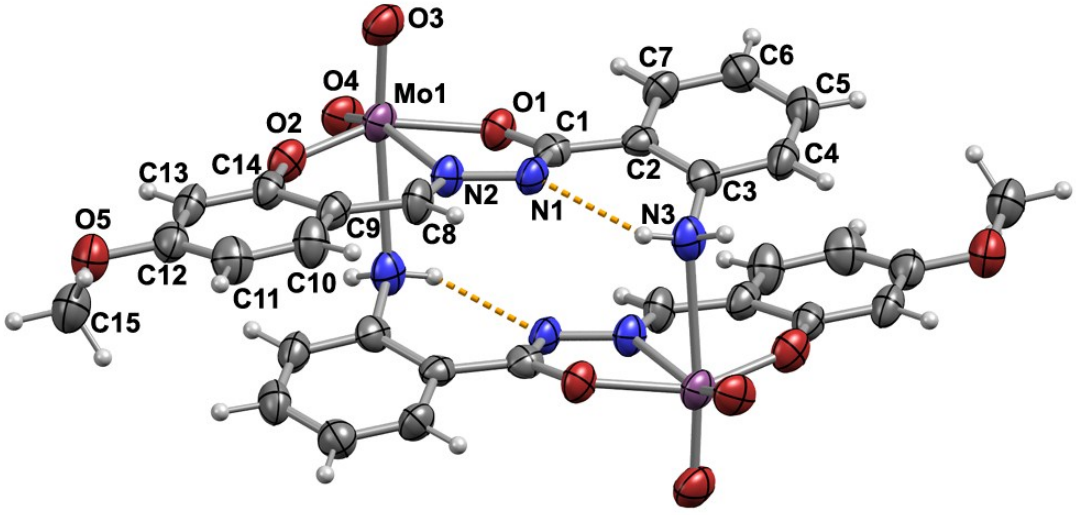
N3
C11
C8
C15
C12
O5
C13
C14

(e)


O3
C7
C6
O4
Mo1
C5
O1
C1
O2
C14
C4
C13
C2
N2
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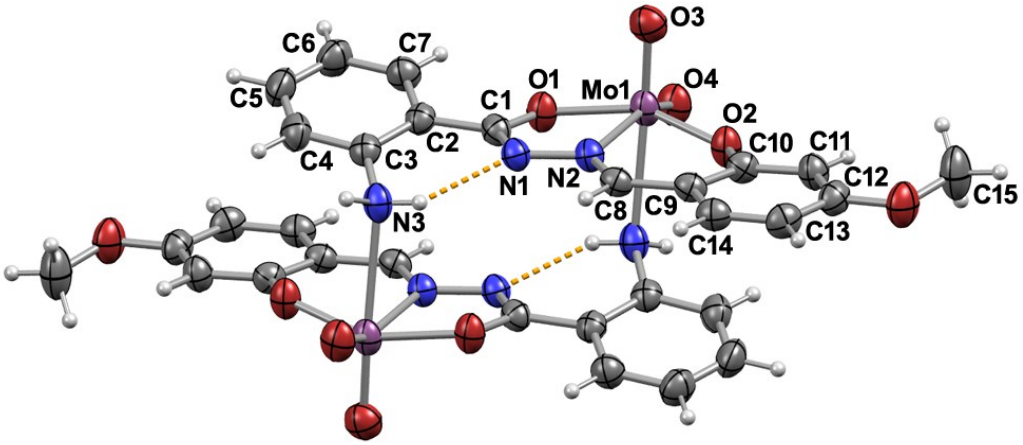
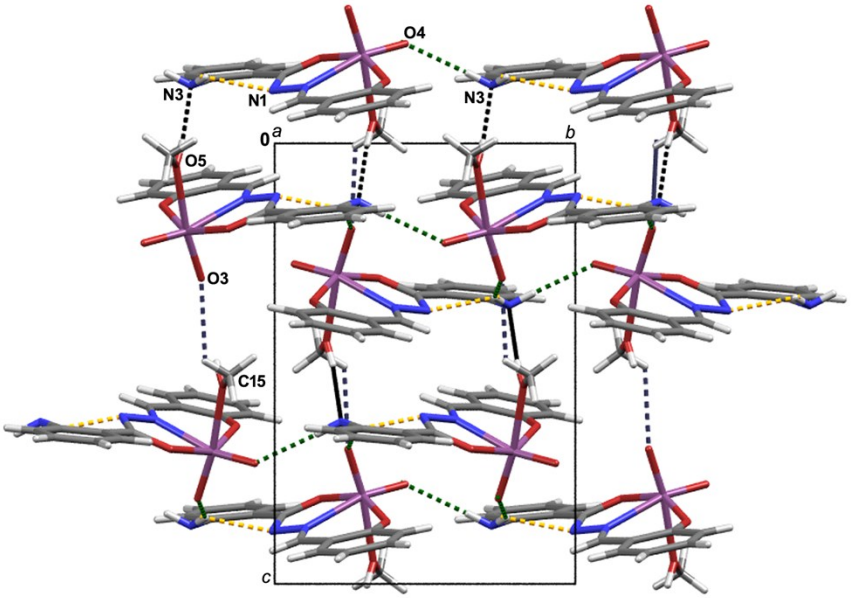
N1
N3
O5
C9
C8
C12
C10
C11
C15

(f)

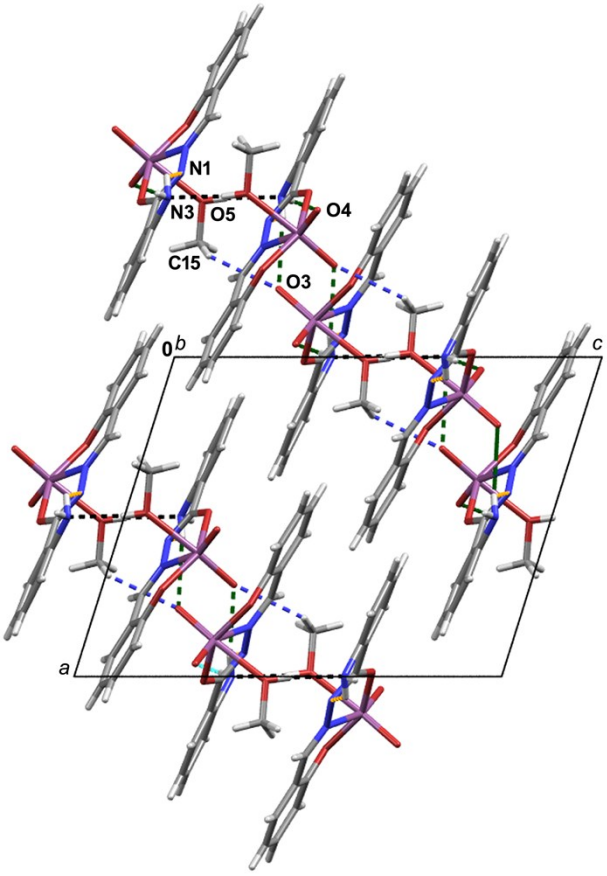


(g)

Fig. S3. Mercury-ORTEP view of molecular structures of: (a) **1a**; (b) **1-*α***; (b) **1-*β***; (d) **3a**; (e) **3-*α***, (f) **3-*β***, (g) **3**□2CH_3CN. In (g) acetonitrile molecules are omitted for clarity. The displacement ellipsoids are drawn at 50% probability level at 296 K. Hydrogen atoms are presented as spheres of arbitrary small radii. Intramolecular hydrogen bond of the N–H···N type are highlighted by orange dashed line. In the structures of **1-*β*, 3-*α***, **3-*β*** and **3·2CH_3CN**, asymmetric units contain half of the molecule presented, as the other half is generated through the center of symmetry.

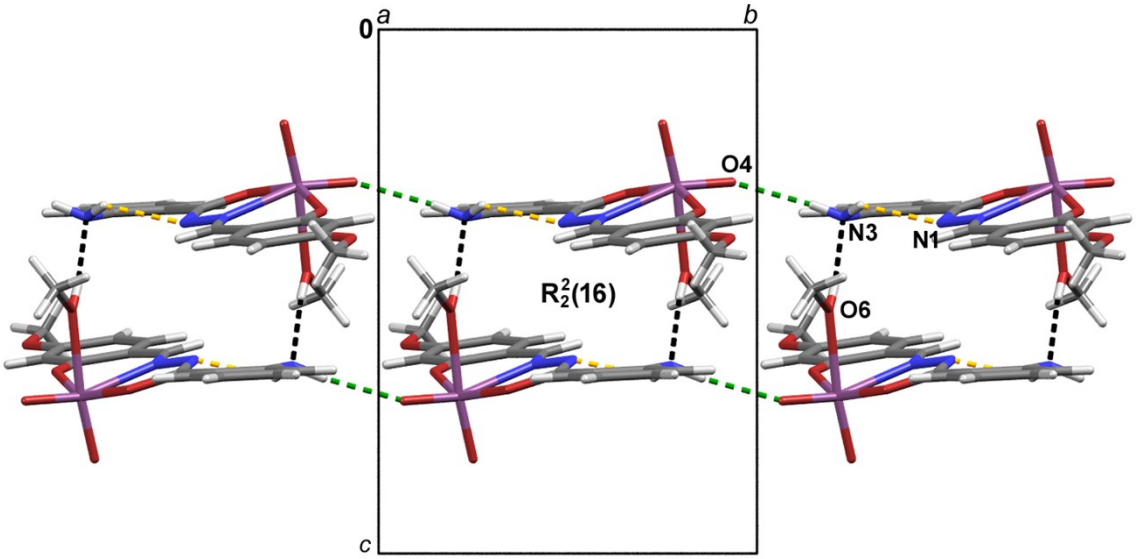


(a)

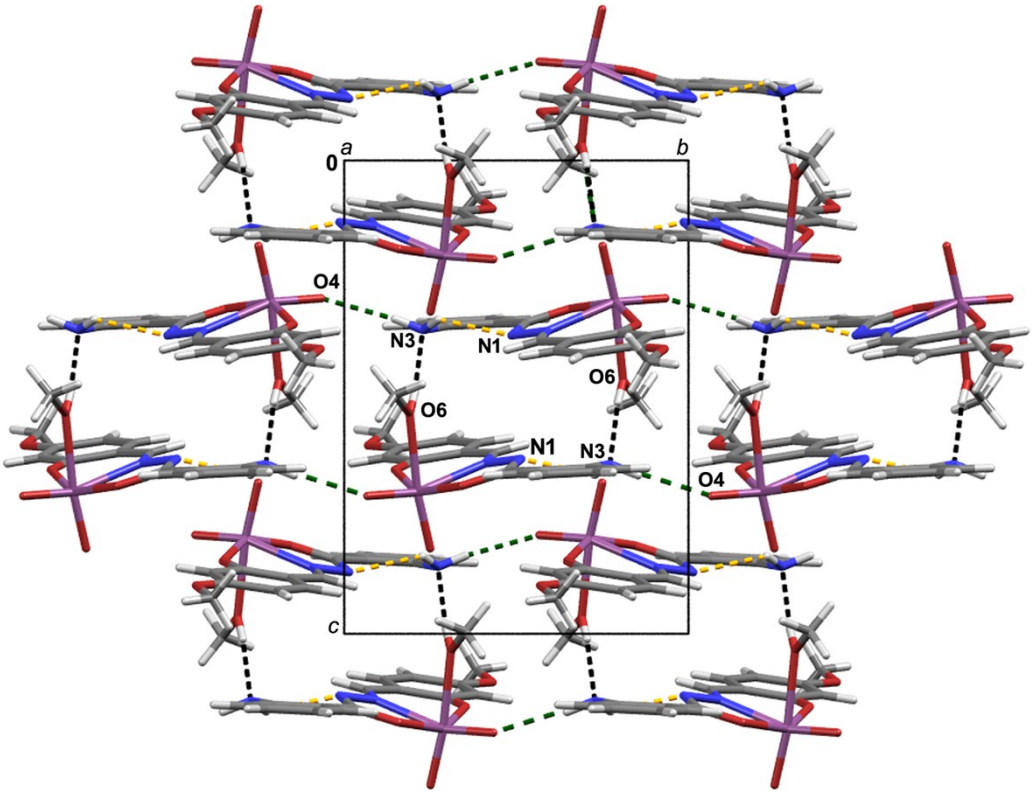


(b)

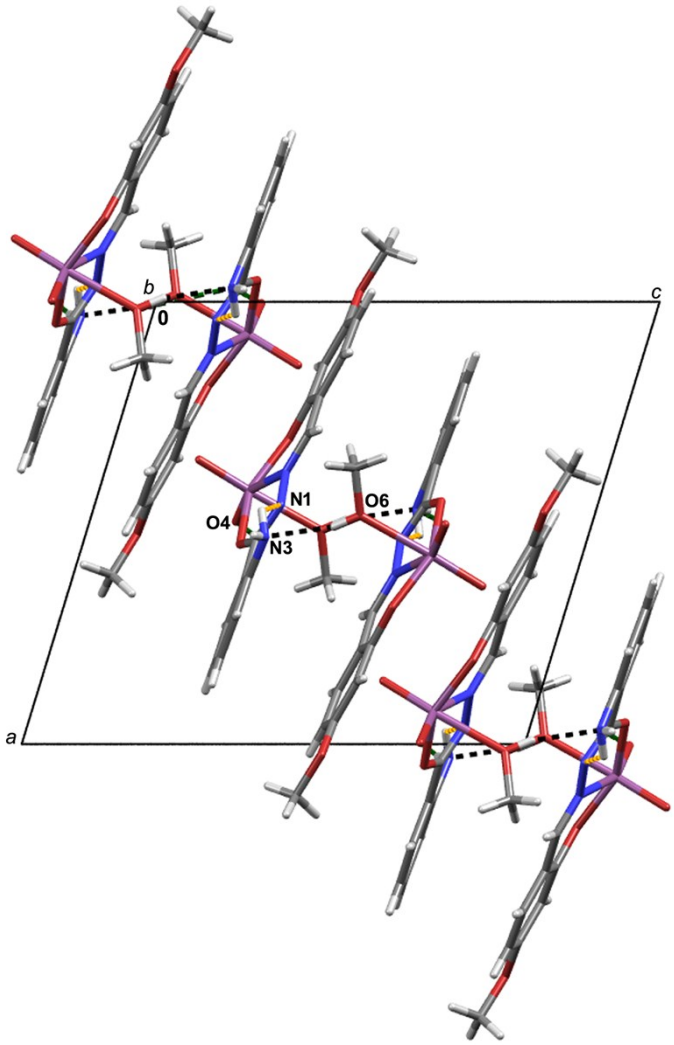
Fig. S4. Crystal packing in **1a** shown down the: (a) *a*-axis; and (b) *b*-axis. Intramolecular hydrogen bonds of the N–H···N type are presented by orange dashed lines. O–H···N hydrogen bonds are shown by black dashed lines, N–H···O hydrogen bonds by green lines, while C–H···O interactions are highlighted as blue dashed lines.



(a)

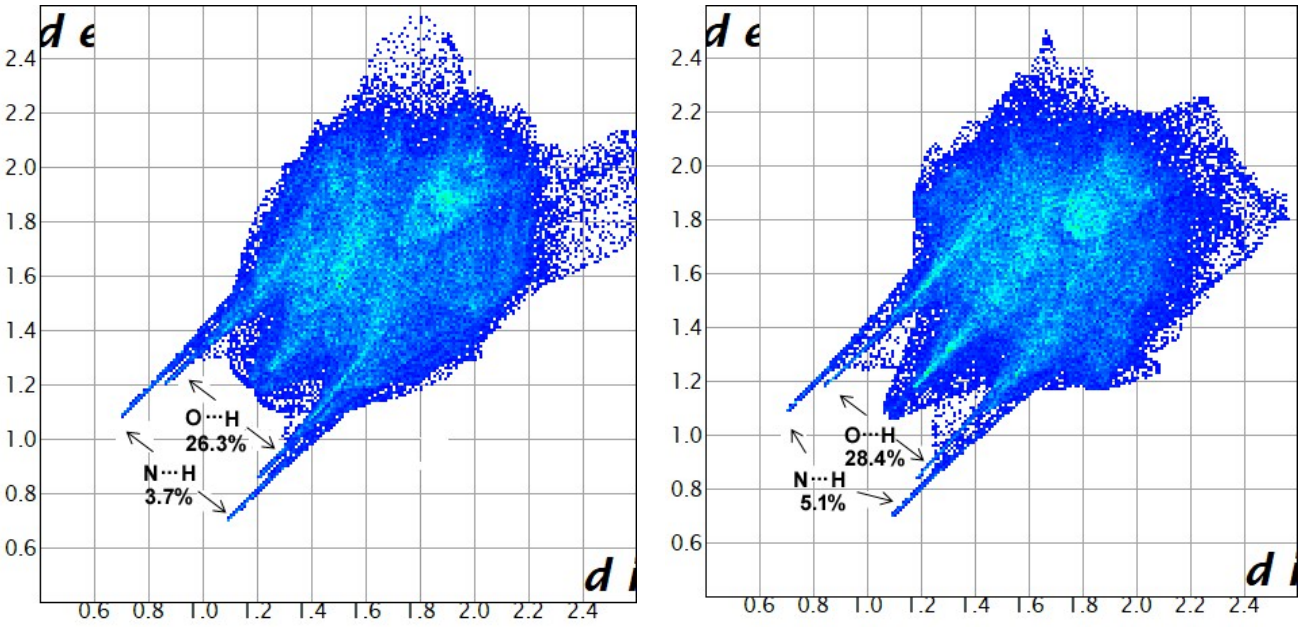


(b)



(c)

Fig. S5. Supramolecular chain-like architecture in **3a**, shown in (a), forms *via* N3–H3B···O4 and O6–H6O···N3 hydrogen bonds to produce $R_2^2(16)$ graph-set motif. Crystal packing in **3a** shown down the: (b) *a*-axis; and (c) *b*-axis. Intramolecular hydrogen bonds of the N–H···N type are presented by orange dashed lines. O–H···N hydrogen bonds are shown by black dashed lines, whereas N–H···O hydrogen bonds are highlighted as green dashed lines.



(a) (b)

Fig. S6. Fingerprint plots based on Hirshfeld surfaces for: (a) **1a** and (b) **3a**.

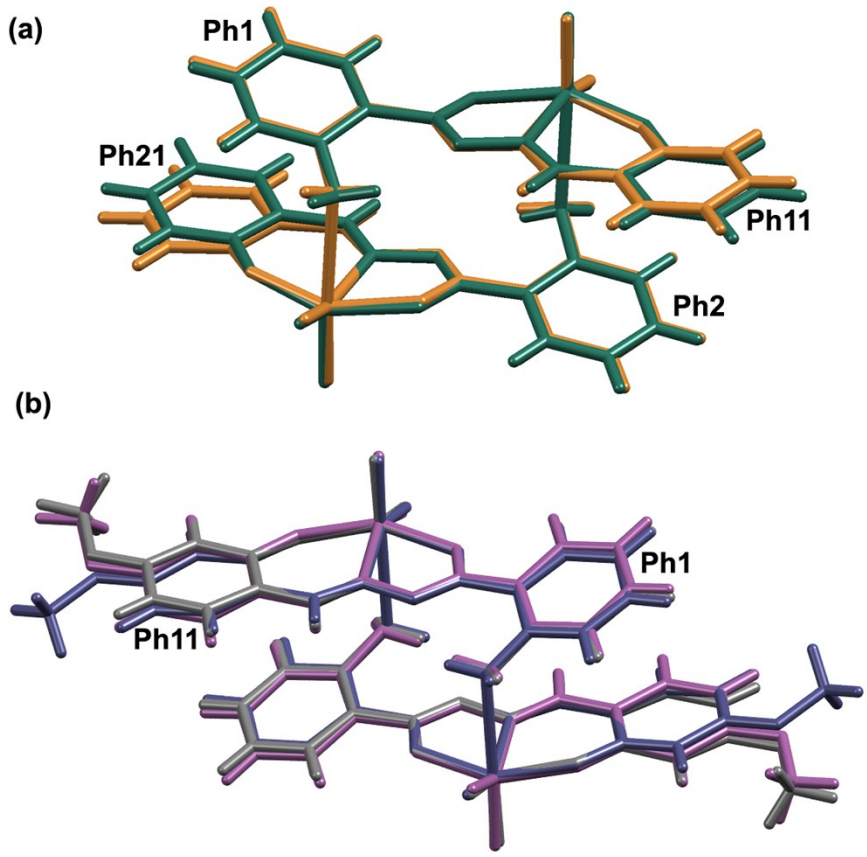
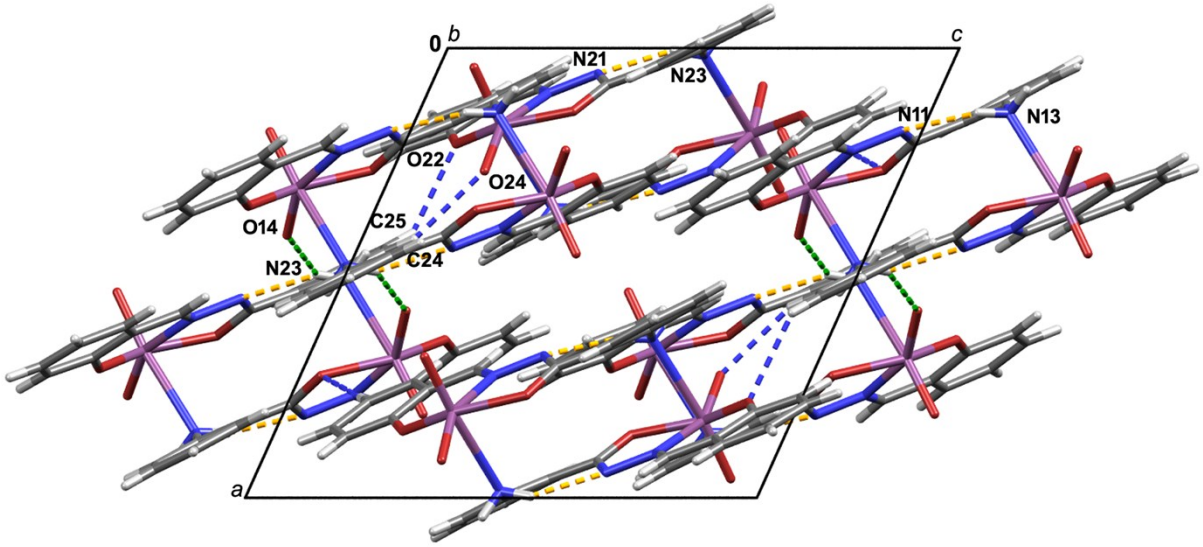


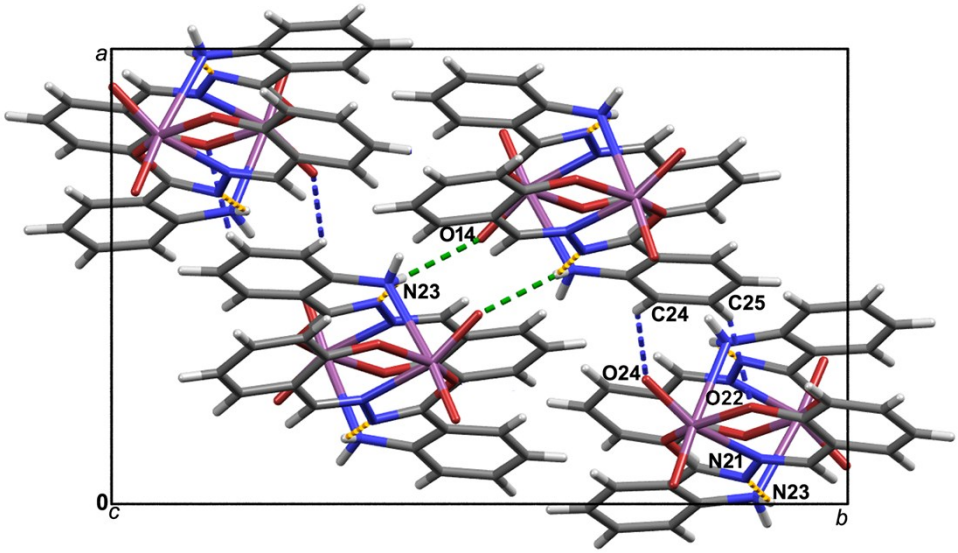
Fig. S7. Overlapping diagram for: (a) **1-*α*** (green) and **1-*β*** (orange); (b) **3-*α*** (purple)**, 3-*β*** (blue)**, 3·2CH$_3$CN** (gray), and (c) **3a** (red) and **3-*β*** (blue). The diagrams were constructed by overlapping Mo1, Mo2, N2 (for 1-*α* N12 and N22), O1 and O2 atoms (for 1-*α* O11 and O21 as well as O12 and O22).

(a) Diheadral angles for 1-*α* between the planes of the phenyl rings Ph 1 and Ph11 is 16.17(18)°, whereas for Ph2 and Ph21 dihedral angle amounts to 12.1(2)°. Planes of the phenyl rings are defined by the following atoms: Ph1-C12, C13, C14, C15, C16 and C17; Ph11-C19, C110 C111, C112, C113 and C114; Ph2-C22, C23, C24, C25, C26 and C27 and Ph21-C29, C210 C211, C212, C213 and C214. In 1-*β* dihedral angle between the planes of the Ph1 and Ph11 rings is 20.6(2)°. Planes of the phenyl rings for 1-*β* are defined by the following atoms: Ph1-C2, C3, C4, C5, C6 and C7; Ph11-C9, C10 C11, C12, C13 and C14.

(b) In 3-*α* dihedral angle between the planes of the Ph1 and Ph11 rings is 13.96(17)°, in **3-*β*** it is 15.5(4)°, while in the **3·2CH$_3$CN** is amounts to 16.29(13)°. Planes of the phenyl rings for **3-*α*, 3-*β*** and **3·2CH$_3$CN** are defined by the following atoms: Ph1-C2, C3, C4, C5, C6 and C7; Ph11-C9, C10 C11, C12, C13 and C14.

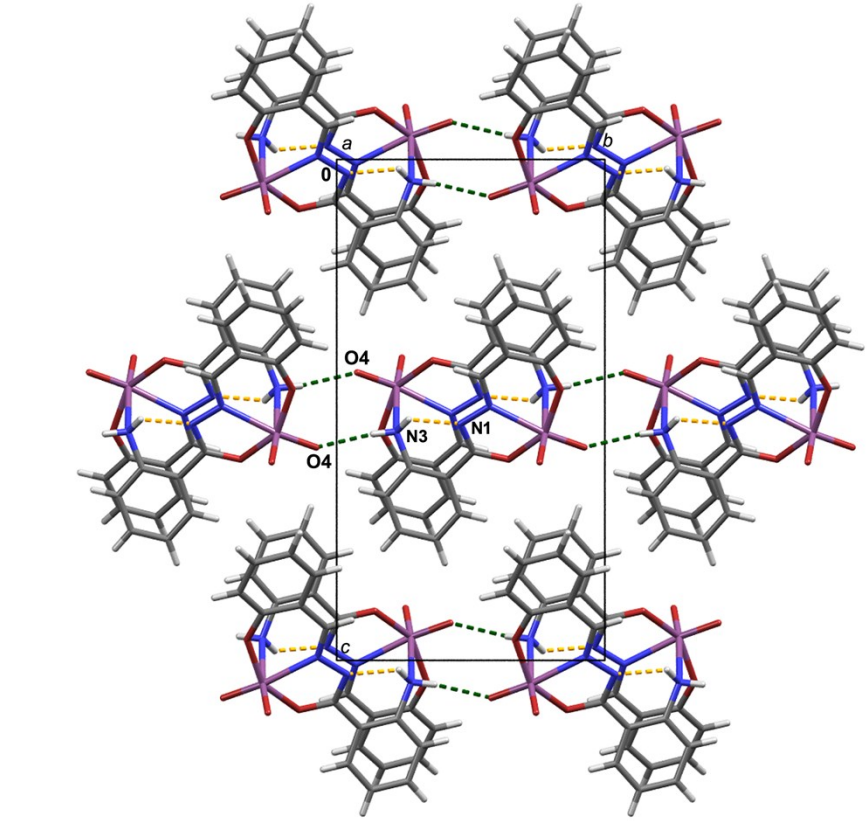


(a)

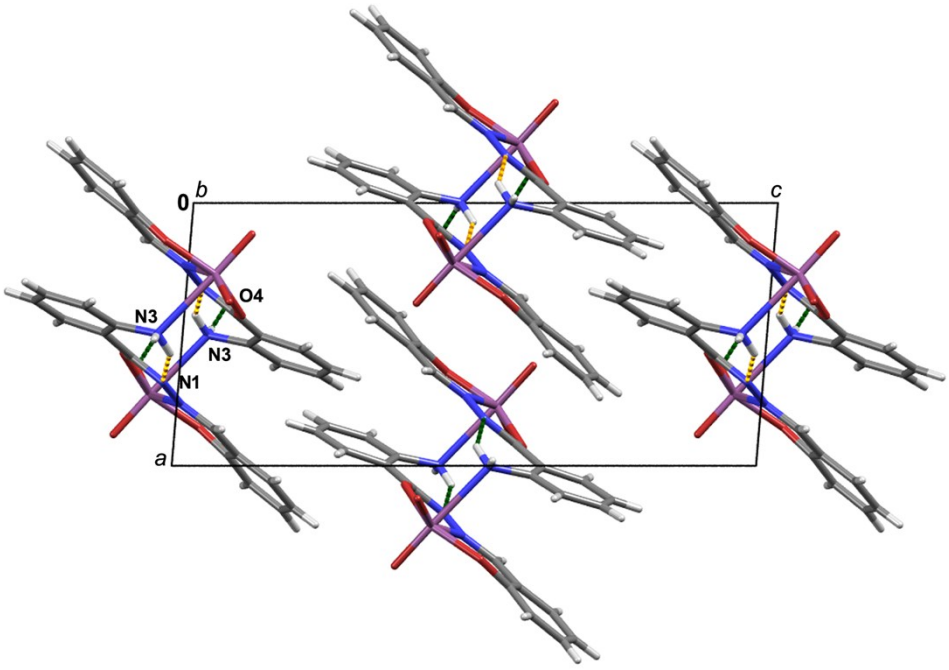


(b)

Fig. S8. Crystal packing in **1-*α*** shown down the: a) *b*-axis; and b) *c*-axis. Intramolecular hydrogen bonds of the N–H···N type are presented by orange dashed lines. N–H···O hydrogen bonds are shown by green lines, while C–H···O interactions are highlighted as blue dashed lines.

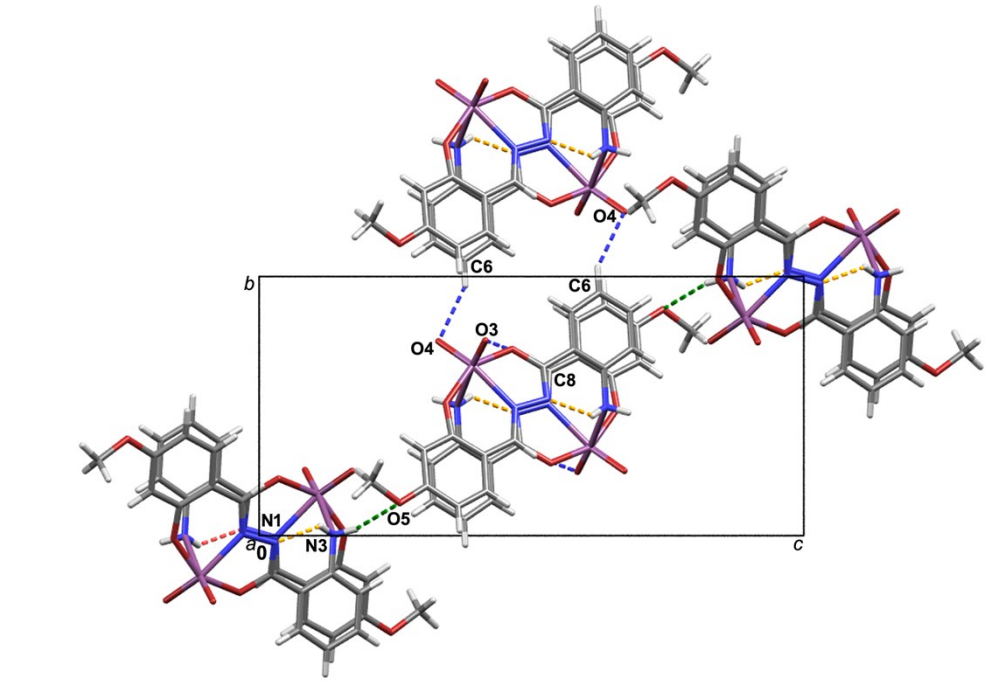


(a)

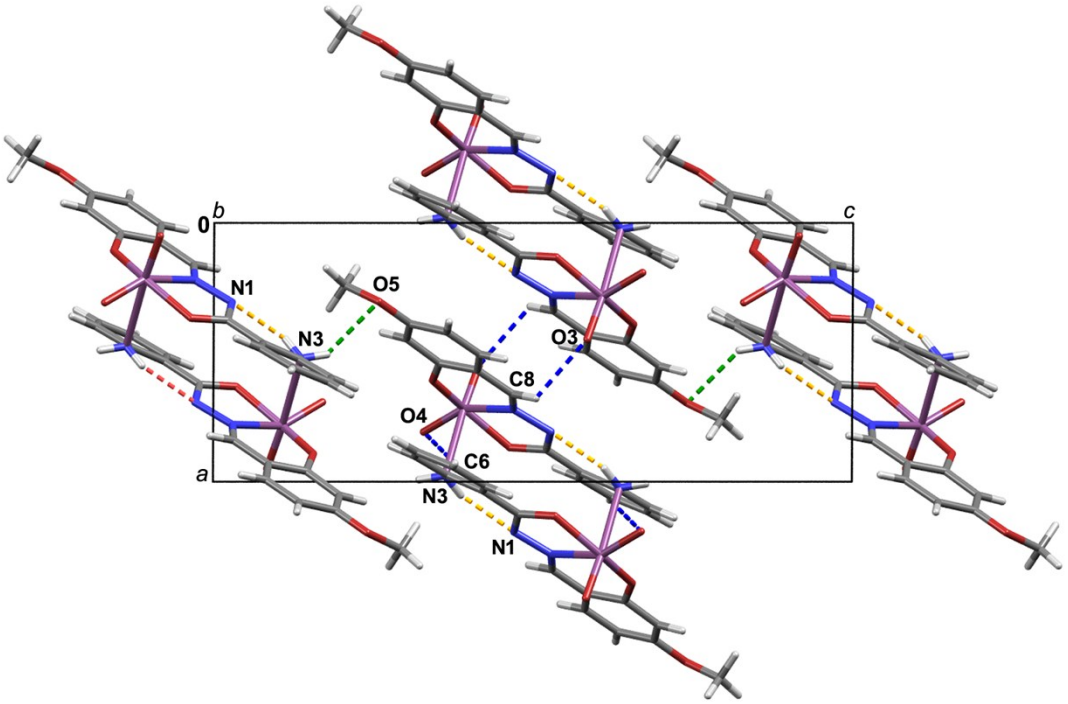


(b)

Fig. S9. Crystal packing in **1-*β*** shown down the: a) *a*-axis; and b) *b*-axis. Intramolecular hydrogen bonds of the N–H···N type are presented by orange dashed lines, whereas intermolecular N–H···O hydrogen bonds are shown by green dashed lines.

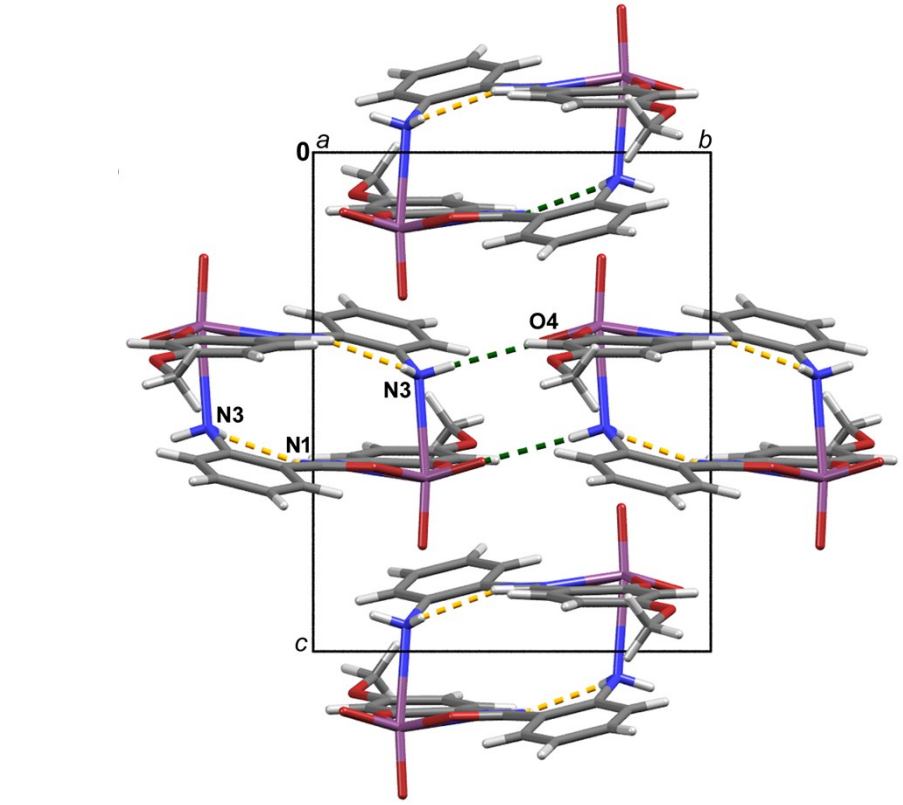


(a)

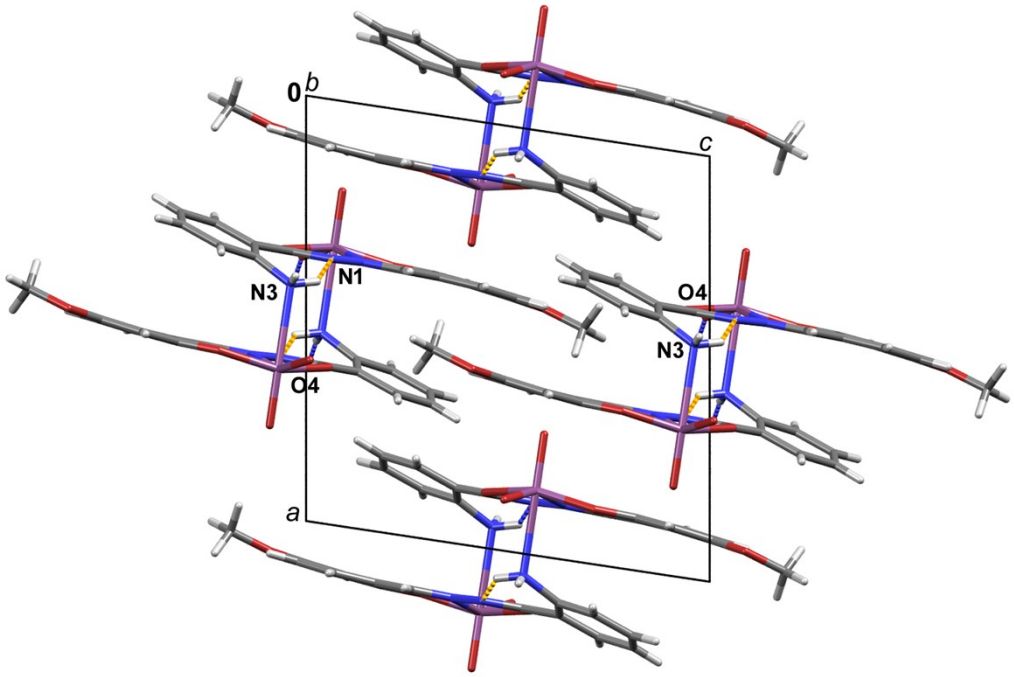


(b)

Fig. S10. Crystal packing in **3-*α*** shown down the: a) *a*-axis; and b) *b*-axis. Intramolecular hydrogen bonds of the N–H···N type are presented by orange dashed lines, whereas intermolecular N–H···O hydrogen bonds C–H···O interactions are shown by green and blue dashed lines, respectively.

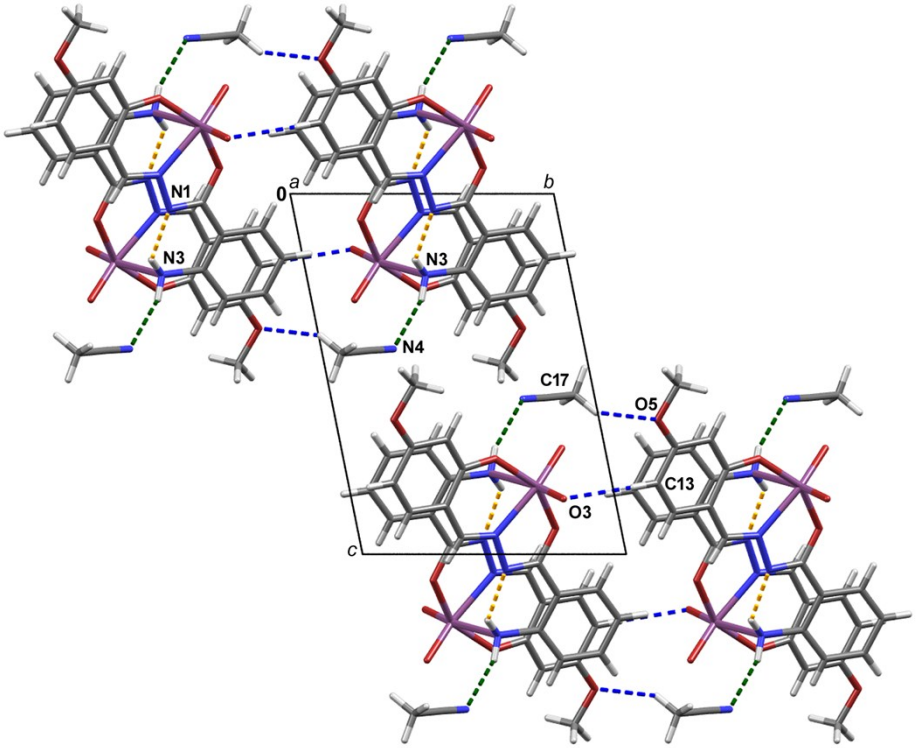


(a)

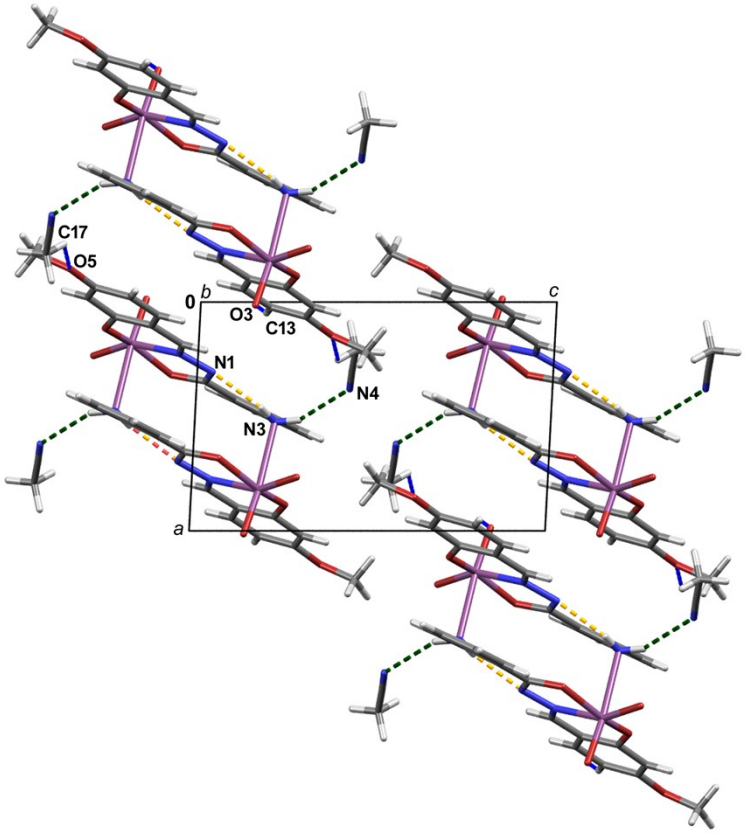


(b)

Fig. S11. Crystal packing in **3-*β*** shown down the: a) *a*-axis; and b) *b*-axis. Intramolecular hydrogen bonds of the N–H···N type are presented by orange dashed lines, whereas intermolecular N–H···O hydrogen bonds are highlighted by green dashed lines.

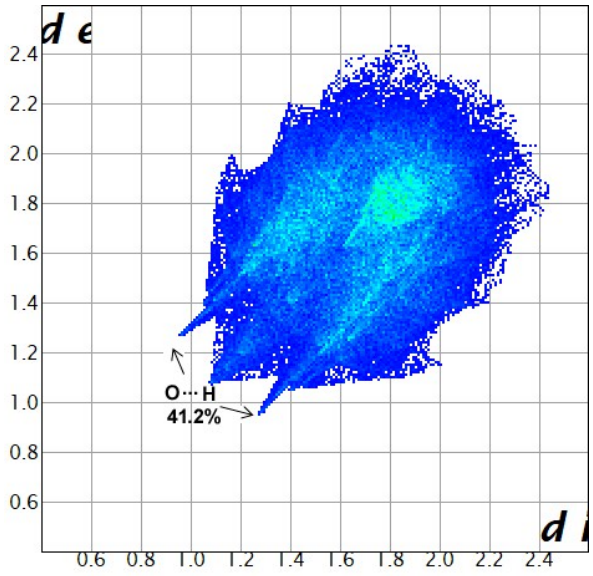


(a)

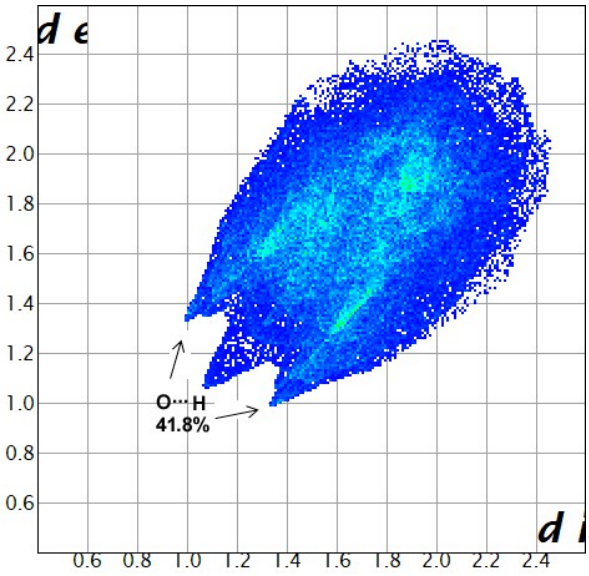


(b)

Fig. S12. Crystal packing in **3·2CH$_3$CN** shown down the: a) *a*-axis; and b) *b*-axis. Intramolecular hydrogen bonds of the N–H···N type are presented by orange dashed lines. N–H···N hydrogen bonds are highlighted by green lines, while C–H···O interactions are highlighted as blue dashed lines.



(a)



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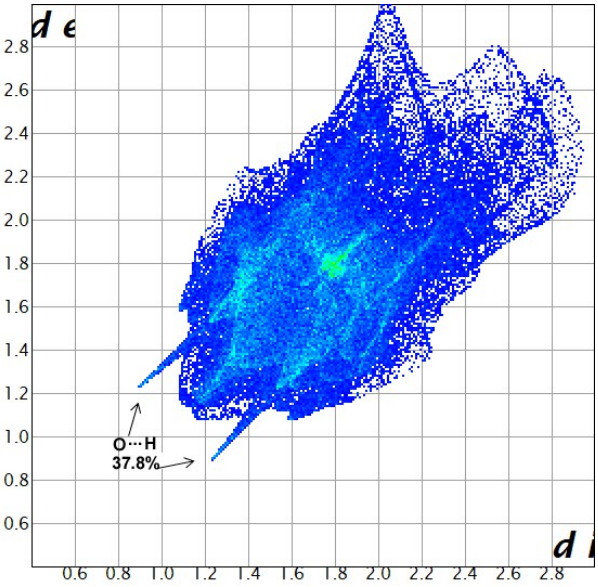
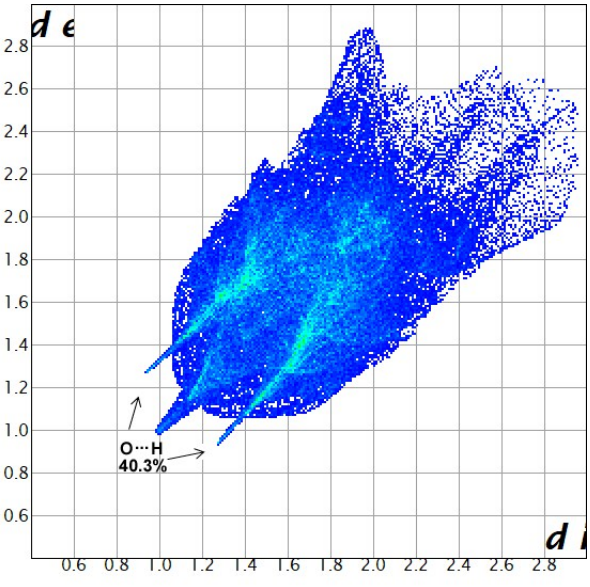
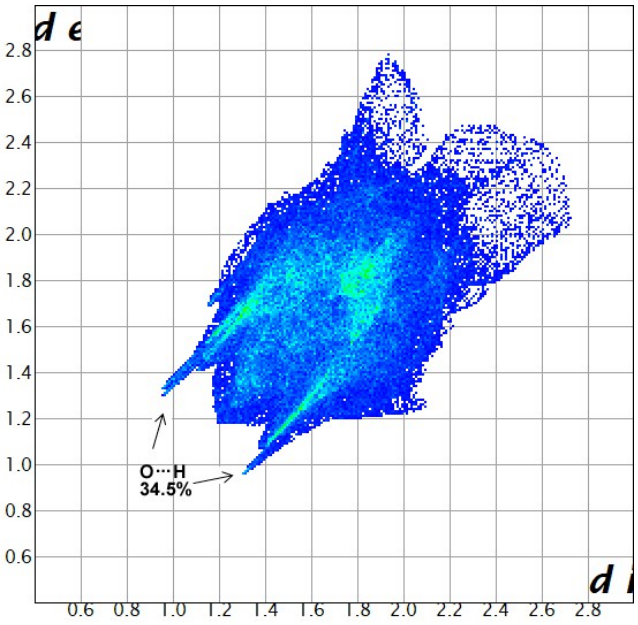


(c)



(d)



(e)

Fig. S13. Fingerprint plots based on Hirshfeld surfaces for: (a) **1**-*α,* (b) **3**-*α*, (c) **1**-*β*, (d) **3**-*β*, and (e) **3**·2CH_3CN

Table S1 Crystallographic data for compounds

Complex	**1a**	**1-*α***	**1-*β***	**3a**	**3-*α***	**3-*β***	**3·2CH$_3$CN**
Chemical formula	$C_{15}H_{15}MoN_3O_5$	$C_{28}H_{22}Mo_2N_6O_8$	$C_{14}H_{11}MoN_3O_4$	$C_{16}H_{17}MoN_3O_6$	$C_{15}H_{13}MoN_3O_5$	$C_{15}H_{13}MoN_3O_5$	$C_{17}H_{16}MoN_4O_5$
M_r	413.24	762.39	381.20	443.26	411.22	411.22	452.28
Crystal system, color and habit	Monoclinic, orange, plate	Monoclinic, orange, block	Monoclinic, prism, orange	Monoclinic, orange, plate	Monoclinic, red, prism	Monoclinic, red, plate	Monoclinic, orange, plate
Crystal dimensions / mm^3	0.02 x 0.08 x 0.31	0.08 x 0.12 x 0.30	0.04 x 0.10 x 0.23	0.02 x 0.06 x 0.26	0.12 x 0.16 x 0.43	0.03 x 0.08 x 0.58	0.06 x 0.08 x 0.45
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	P (No. 14)
Z	4	4	4	4	4	4	2
Unit cell parameters:							
a /Å	11.5800(8)	12.519(1)	8.1665(5)	12.9814(7)	8.0972(3)	12.1433(13)	8.1916(4)
b /Å	9.6323(4)	18.4290(6)	9.6856(4)	9.8022(4)	9.5153(2)	9.9365(5)	9.2854(5)
c /Å	14.7642(10)	12.9998(8)	18.1363(11)	14.1346(7)	20.0124(5)	12.6523(12)	12.5130(5)
α/°	90	90	90	90	90	90	79.025(4)
β/°	107.415(7)	114.273(8)	94.776(6)	106.969(5)	90.318(3)	98.553(9)	89.996(3)
γ/°	90	90	90	90	90	90	74.990(4)
V /Å^3	1571.34(18)	2734.1(3)	1429.55(14)	1720.27(15)	1541.88(8)	1509.7(2)	901.26(8)
D_{calc} /g cm^{-3}	1.747	1.852	1.771	1.712	1.771	1.809	1.667
μ /mm^{-1}	0.866	0.982	0.939	0.802	0.883	0.901	0.765
F(000)	832	1520	760	896	824	824	456
No. refined parameters, N_p /restraints	227, 3	409, 4	205,2	246, 3	224, 2	224, 2	252, 2
Reflections collected, unique (R_{int}), observed [$I \geq 2\sigma(I)$]	17526, 4272 (0.081), 2654	30735, 7242 (0.068), 5005	8202, 3113 (0.070), 1934	15710, 3933 (0.077), 2670	16067, 4274 (0.033), 3361	14582, 2789 (0.116), 1740	17424, 4778 (0.047), 3673
R_1[a] [$I \geq 2\sigma(I)$]	0.0531	0.0515	0.0577	0.0508	0.0364	0.0700	0.0370
g_1, g_2 in w[b]	0.0464, 0	0.0272, 0.2289	0.0111, 0	0.0106, 0	0.0640, 0	0.0896, 0	0.0373, 0
wR_2[c] (all data)	0.1216	0.0898	0.0856	0.0769	0.1196	0.1854	0.0820
Goodness of fit on F^2, S[d]	1.03	1.03	0.97	1.00	1.15	0.99	1.01

Table S2. Selected geometrical parameters (bond lengths and angles) for **1a**, **1-*α*, 1-*β*, 3a, 3-*α*, 3-*β*** and **3·2CH$_3$CN**

A−B–C	*d*(A−B)/Å	*d*(B–C)/Å	∠(A–B–C)/°
1a			
O1–Mo1–O2	1.999(3)	1.915(4)	147.70(14)
O1–Mo1–O3	1.999(3)	1.698(4)	98.04(14)
O1–Mo1–O4	1.999(3)	1.708(3)	97.24(15)
O1–Mo1–O5	1.999(3)	2.299(4)	78.52(13)
O1–Mo1–N2	1.999(3)	2.249(3)	71.86(13)
O2–Mo1–O3	1.915(4)	1.698(4)	100.12(17)
O2–Mo1–O4	1.915(4)	1.708(3)	103.57(14)
O2–Mo1–O5	1.915(4)	2.299(4)	79.69(16)
O2–Mo1–N2	1.915(4)	2.249(3)	81.00(13)
O3–Mo1–O4	1.698(4)	1.708(3)	104.83(15)
O3–Mo1–O5	1.698(4)	2.299(4)	171.58(15)
O3–Mo1–N2	1.698(4)	2.249(3)	92.03(15)
O4–Mo1–O5	1.708(3)	2.299(4)	83.31(14)
O4–Mo1–N2	1.708(3)	2.249(3)	161.24(15)
O5–Mo1–N2	2.299(4)	2.249(3)	79.61(14)
O1–C1–C2	1.341(5)	1.475(6)	115.3(4)
O1–C1–N1	1.341(5)	1.290(6)	123.1(4)
N2–N1–C1	1.402(5)	1.290(6)	109.6(3)
N1–C1–C2	1.290(6)	1.475(6)	121.6(4)
N1–N2–C8	1.402(5)	1.265(6)	117.0(3)
C8–C9–C10	1.451(6)	1.410(6)	122.0(4)
N2–C8–C9	1.265(6)	1.451(6)	124.6(4)
O2–C10–C9	1.349(6)	1.410(6)	122.4(4)
1-*α*			
O11–Mo1–O12	2.004(3)	1.915(2)	150.37(10)
O11–Mo1–O13	2.004(3)	1.688(3)	96.47(13)
O11–Mo1–O14	2.004(3)	1.700(3)	96.65(12)
O11–Mo1–N12	2.004(3)	2.232(3)	71.78(10)
O12–Mo1–O13	1.915(2)	1.688(3)	100.49(12)
O12–Mo1–O14	1.915(2)	1.700(3)	101.57(13)
O12–Mo1–N12	1.915(2)	2.232(3)	82.03(11)
O13–Mo1–O14	1.688(3)	1.700(3)	106.39(14)
O13–Mo1–N12	1.688(3)	2.232(3)	97.42(14)
O14–Mo1–N12	1.700(3)	2.232(3)	154.68(11)
O21–Mo2–O24	1.992(2)	1.700(3)	96.48(12)
O21–Mo2–N22	1.992(2)	2.231(3)	72.39(10)
O22–Mo2–O23	1.919(2)	1.695(3)	100.89(12)
O22–Mo2–O24	1.919(2)	1.700(3)	102.16(13)

O22–Mo2–N22	1.919(2)	2.231(3)	80.71(11)
O21–Mo2–O22	1.992(2)	1.919(2)	149.31(9)
O21–Mo2–O23	1.992(2)	1.695(3)	96.80(13)
O24–Mo2–N22	1.700(3)	2.231(3)	155.22(11)
O23–Mo2–O24	1.695(3)	1.700(3)	106.56(14)
O23–Mo2–N22	1.695(3)	2.231(3)	96.88(14)
O11–C11–C12	1.328(5)	1.480(5)	116.3(3)
O11–C11–N11	1.328(5)	1.303(4)	122.8(3)
N12–N11–C11	1.395(5)	1.303(4)	109.2(3)
N11–C11–C12	1.303(4)	1.480(5)	120.9(3)
N11–N12–C18	1.395(5)	1.295(4)	116.1(3)
C18–C19–C110	1.446(5)	1.393(5)	123.0(3)
N12–C18–C19	1.295(4)	1.446(5)	124.7(3)
O12–C110–C19	1.354(4)	1.393(5)	122.6(3)
O21–C21–N21	1.330(5)	1.296(4)	122.6(3)
O21–C21–C22	1.330(5)	1.472(5)	117.2(3)
N22–N21–C21	1.392(5)	1.296(4)	110.3(3)
N21–C21–C22	1.296(4)	1.472(5)	120.2(3)
N21–N22–C28	1.392(5)	1.287(4)	115.8(3)
C28–C29–C210	1.439(5)	1.388(5)	123.3(3)
N22–C28–C29	1.287(4)	1.439(5)	124.0(3)
O22–C210–C29	1.364(4)	1.388(5)	121.8(3)
1-*β*			
O1–Mo1–O2	2.010(3)	1.923(3)	149.24(13)
O1–Mo1–O3	2.010(3)	1.695(3)	96.50(14)
O1–Mo1–O4	2.010(3)	1.705(3)	97.19(14)
O1–Mo1–N2	2.010(3)	2.234(4)	71.70(13)
O2–Mo1–O3	1.923(3)	1.695(3)	99.78(15)
O2–Mo1–O4	1.923(3)	1.705(3)	102.93(15)
O2–Mo1–N2	1.923(3)	2.234(4)	80.97(13)
O3–Mo1–O4	1.695(3)	1.705(3)	106.43(16)
O3–Mo1–N2	1.695(3)	2.234(4)	95.08(14)
O4–Mo1–N2	1.705(3)	2.234(4)	156.94(16)
O1–C1–C2	1.324(6)	1.477(7)	116.6(4)
O1–C1–N1	1.324(6)	1.298(6)	123.2(4)
N2–N1–C1	1.399(5)	1.298(6)	109.2(4)
N1–C1–C2	1.298(6)	1.477(7)	120.1(4)
N1–N2–C8	1.399(5)	1.290(6)	114.9(4)
C8–C9–C10	1.446(7)	1.398(8)	122.5(5)
N2–C8–C9	1.290(6)	1.446(7)	124.0(4)
O2–C10–C9	1.360(6)	1.398(8)	122.4(5)
3a			
O1–Mo1–O2	1.999(2)	1.936(3)	148.59(10)

O1–Mo1–O3	1.999(2)	1.692(3)	97.99(14)
O1–Mo1–O4	1.999(2)	1.708(2)	96.77(11)
O1–Mo1–O6	1.999(2)	2.311(3)	79.01(11)
O1–Mo1–N2	1.999(2)	2.237(3)	71.84(12)
O2–Mo1–O3	1.936(3)	1.692(3)	99.63(15)
O2–Mo1–O4	1.936(3)	1.708(2)	103.52(11)
O2–Mo1–O6	1.936(3)	2.311(3)	80.25(13)
O2–Mo1–N2	1.936(3)	2.237(3)	81.06(11)
O3–Mo1–O4	1.692(3)	1.708(2)	104.87(14)
O3–Mo1–O6	1.692(3)	2.311(3)	172.63(13)
O3–Mo1–N2	1.692(3)	2.237(3)	94.32(13)
O4–Mo1–O6	1.708(2)	2.311(3)	82.25(12)
O4–Mo1–N2	1.708(2)	2.237(3)	159.03(12)
O6–Mo1–N2	2.311(3)	2.237(3)	78.36(11)
O1–C1–C2	1.337(4)	1.475(7)	115.9(4)
O1–C1–N1	1.337(4)	1.302(6)	122.8(4)
N2–N1–C1	1.392(5)	1.302(6)	109.3(3)
N1–C1–C2	1.302(6)	1.475(7)	121.3(4)
N1–N2–C8	1.392(5)	1.283(6)	115.9(3)
C8–C9–C10	1.435(7)	1.413(6)	122.4(4)
N2–C8–C9	1.283(6)	1.435(7)	125.0(4)
O2–C10–C9	1.342(5)	1.413(6)	122.3(4)
3-α			
O1–Mo1–O2	1.987(2)	1.913(2)	150.36(8)
O1–Mo1–O3	1.987(2)	1.689(2)	97.21(11)
O1–Mo1–O4	1.987(2)	1.699(2)	96.63(10)
O1–Mo1–N2	1.987(2)	2.221(2)	71.92(8)
O2–Mo1–O3	1.913(2)	1.689(2)	99.99(10)
O2–Mo1–O4	1.913(2)	1.699(2)	101.41(10)
O2–Mo1–N2	1.913(2)	2.221(2)	81.13(8)
O3–Mo1–O4	1.689(2)	1.699(2)	106.35(11)
O3–Mo1–N2	1.689(2)	2.221(2)	101.21(10)
O4–Mo1–N2	1.699(2)	2.221(2)	151.33(10)
O1–C1–C2	1.326(3)	1.473(4)	116.4(2)
O1–C1–N1	1.326(3)	1.301(4)	121.8(3)
N2–N1–C1	1.398(3)	1.301(4)	109.7(2)
N1–C1–C2	1.301(4)	1.473(4)	121.8(3)
C8–C9–C10	1.425(4)	1.399(4)	122.7(3)
N2–C8–C9	1.289(4)	1.425(4)	124.8(3)
O2–C10–C9	1.344(4)	1.399(4)	121.9(3)
3-β			
O1–Mo1–O2	2.010(5)	1.918(6)	150.5(2)

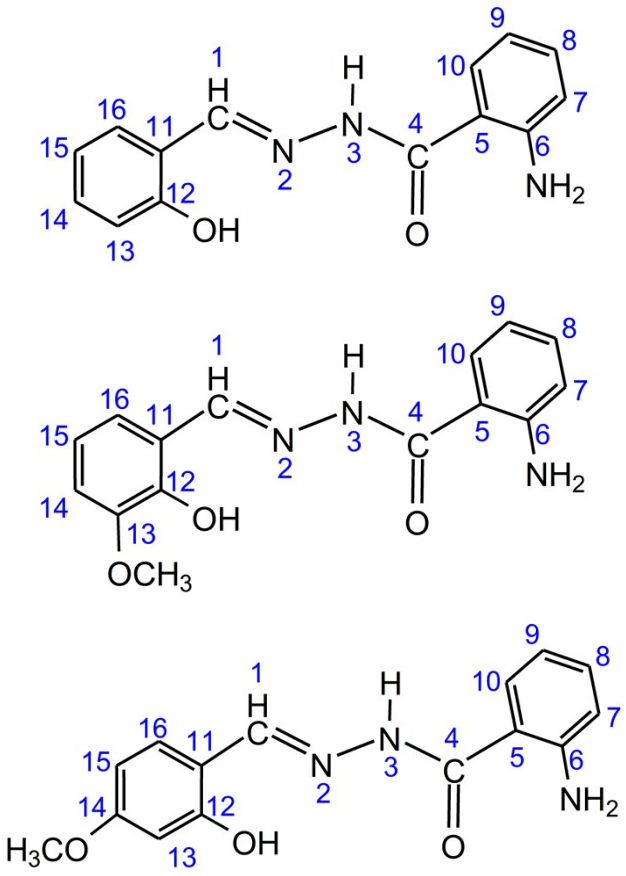
O1–Mo1–O3	2.010(5)	1.683(6)	96.1(3)
O1–Mo1–O4	2.010(5)	1.715(5)	96.3(2)
O1–Mo1–N2	2.010(5)	2.240(5)	71.7(2)
O2–Mo1–O3	1.918(6)	1.683(6)	99.9(3)
O2–Mo1–O4	1.918(6)	1.715(5)	102.8(2)
O2–Mo1–N2	1.918(6)	2.240(5)	82.2(2)
O3–Mo1–O4	1.683(6)	1.715(5)	105.9(3)
O3–Mo1–N2	1.683(6)	2.240(5)	95.7(2)
O4–Mo1–N2	1.715(5)	2.240(5)	156.4(2)
O1–C1–C2	1.333(9)	1.482(11)	116.7(7)
O1–C1–N1	1.333(9)	1.277(10)	123.5(7)
N2–N1–C1	1.388(8)	1.277(10)	110.0(5)
N1–C1–C2	1.277(10)	1.482(11)	119.8(6)
N1–N2–C8	1.388(8)	1.265(11)	117.5(6)
C8–C9–C10	1.420(11)	1.437(10)	123.5(7)
N2–C8–C9	1.265(11)	1.420(11)	126.6(7)
O2–C10–C9	1.357(10)	1.437(10)	120.0(7)
3·2CH$_3$CN			
O1–Mo1–O2	1.9907(17)	1.9255(18)	149.90(7)
O1–Mo1–O3	1.9907(17)	1.6897(18)	98.41(8)
O1–Mo1–O4	1.9907(17)	1.6994(18)	97.02(8)
O1–Mo1–N2	1.9907(17)	2.2231(19)	71.85(7)
O2–Mo1–O3	1.9255(18)	1.6897(18)	98.75(8)
O2–Mo1–O4	1.9255(18)	1.6994(18)	101.44(8)
O2–Mo1–N2	1.9255(18)	2.2231(19)	81.84(7)
O3–Mo1–O4	1.6897(18)	1.6994(18)	106.76(9)
O3–Mo1–N2	1.6897(18)	2.2231(19)	96.25(8)
O4–Mo1–N2	1.6994(18)	2.2231(19)	155.83(7)
O1–C1–C2	1.327(3)	1.484(4)	116.1(2)
O1–C1–N1	1.327(3)	1.295(3)	122.5(2)
N2–N1–C1	1.396(3)	1.295(3)	109.41(18)
N1–C1–C2	1.295(3)	1.484(4)	121.4(2)
N1–N2–C8	1.396(3)	1.297(3)	115.80(19)
C8–C9–C10	1.425(4)	1.405(4)	123.5(2)
N2–C8–C9	1.297(3)	1.425(4)	124.1(2)
O2–C10–C9	1.349(3)	1.405(4)	122.3(2)

Table S3. Geometry of hydrogen bonds and C–H···O interactions (Å, º) for **1a**, **1-*α*, 1-*β*, 3a, 3-*α*, 3-*β*** and **3·2CH$_3$CN**

D–H···A	D–H	H···A	D···A	∠D–H···A	Symmetry code
1a					
N3–H3A···N1	0.84(4)	2.21(4)	2.769(5)	125(3)	-
N3–H3A···O3	0.84(4)	2.50(4)	3.196(6)	141(3)	3/2-*x*,1/2+*y*,1/2-*z*
N3–H3B···O4	0.85(3)	2.23(3)	3.074(5)	178(5)	*x*,1+*y*,*z*
O5–H5O···N3	0.82(4)	1.95(3)	2.762(6)	171(6)	1-*x*,2-*y*,-*z*
C15–H15C···O3	0.96	2.686	3.314(7)	123.6	*x*-1/2,-*y*+3/2,+*z*-1/2
1-*α*					
N13–H13A···N11	0.86(3)	2.12(3)	2.802(5)	136(3)	-
N23–H23A···N21	0.87(3)	2.11(3)	2.752(5)	131(3)	-
N23–H23A···O14	0.87(3)	2.35(3)	3.025(4)	135(3)	2-*x*,-*y*,1-*z*
C24–H24···O24	0.9300	2.5100	3.271(6)	139.00	1/2+*x*,1/2-*y*,-1/2+*z*
C25–H25···O22	0.9300	2.5900	3.387(6)	144.00	1/2+*x*,1/2-*y*,-1/2+*z*
1-*β*					
N3–H3A···N1	0.85(3)	2.08(4)	2.767(6)	137(3)	-
N3–H3B···O4	0.85(2)	2.30(3)	3.138(6)	167(4)	*x*,1+*y*,*z*
3a					
N3–H3A···N1	0.86(3)	2.16(4)	2.723(4)	123(3)	-
N3–H3B···O4	0.86(2)	2.20(2)	3.039(4)	169(4)	*x*,-1+*y*,*z*
O6–H6O···N3	0.82(3)	1.97(3)	2.768(5)	166(3)	-*x*,-*y*,-*z*
3-*α*					
N3–H3A···N1	0.84(3)	2.12(3)	2.796(3)	137(3)	-
N3–H3B···O5	0.85(2)	2.51(3)	3.243(4)	145(3)	-1/2+x,-1/2-y,-1/2+z
C6–H6···O4	0.9300	2.4800	3.297(4)	147.00	1-x,1-y,-z
C8–H8···O3	0.9300	2.5200	3.114(4)	122.00	2-x,-y,-z
3-*β*					

N3–H3A···N1	0.87(4)	2.17(5)	2.772(8)	127(4)	-
N3–H3B···O4	0.86(3)	2.36(3)	3.215(8)	175(7)	x,1+y,z
3·2CH_3CN					
N3–H3A···N1	0.85(3)	2.11(3)	2.774(3)	134(2)	-
N3–H3B···N4	0.855(18)	2.44(2)	3.194(4)	148(2)	1-*x*,1-*y*,-*z*
C13–H13···O3	0.9300	2.4300	3.320(3)	161.00	*x*,1+*y*,*z*
C17–H17B···O5	0.9600	2.5400	3.194(5)	125.00	-1+*x*,-1+*y*,*z*

4. NMR spectroscopy



Scheme S3 The structural formulae of $H_2L^{1\text{-}3}$ with the NMR numbering scheme.

Table S4 ^{1}H and ^{13}C chemical shifts (ppm) of compounds $\mathbf{H_2L^{1-3}}$, **1**, **2** and **3**.

Atom	H_2L^1		1		H_2L^2		2		H_2L^3		3	
	δ / ppm (^{1}H)	δ / ppm (^{13}C)	δ / ppm (^{1}H)	δ / ppm (^{13}C)	δ / ppm (^{1}H)	δ / ppm (^{13}C)	δ / ppm (^{1}H)	δ / ppm (^{1}H)	δ / ppm (^{13}C)	δ / ppm (^{13}C)	δ / ppm (^{1}H)	δ / ppm (^{13}C)
1	8.60	148.22	8.99	155.44	8.59	148.09	8.97	155.43	8.49	148.65	8.88	155.16
4	–	165.48	–	170.01	–	165.45	–	170.04	–	165.42	–	168.83
5	–	112.90	–	109.83	–	112.97	–	109.86	–	113.08	–	110.05
6	–	150.81	–	149.97	–	150.79	–	149.98	–	150.71	–	149.70
7	6.80	117.01	6.80	116.50	6.78	116.98	6.80	116.50	6.77	116.95	6.79	116.38
8	7.23	133.06	7.21	133.16	7.22	133.03	7.21	133.14	7.21	132.92	7.19	132.83
9	6.60	119.76	6.58	115.40	6.59	115.09	6.58	115.39	6.58	115.08	6.57	115.35
10	7.62	130.23	7.68	130.45	7.60	128.73	7.69	130.44	7.58	128.66	7.66	130.29
11	–	119.14	–	120.84	–	119.35	–	121.08	–	112.29	–	114.15
12	–	157.97	–	159.73	–	147.66	–	149.53	–	159.91	–	161.63
13	6.95	116.90	6.96	119.06	–	148.40	–	148.98	6.50	101.67	7.56	103.54
14	7.30	131.60	7.52	135.16	7.03	114.19	7.25	117.24	–	162.36	–	165.51
15	6.93	119.76	7.08	122.04	6.86	119.43	7.02	121.88	6.52	106.86	6.69	109.83
16	7.50	130.23	7.68	134.43	7.10	121.57	7.22	125.44	7.38	131.72	7.58	135.52
OH	11.53	–	–	–	11.24	–	–	–	11.82	–	–	–
NH	11.91	–	–	–	11.86	–	–	–	11.77	–	–	–
NH_2	6.51	–	7.01	–	6.48	–	7.01	–	6.46	–	6.96	–
OMe	–	–	–	–	3.82	56.29	3.81	56.31	3.78	55.78	3.78	56.27

***** Signals belonging to MeOH (or EtOH) were also detected in ^{1}H NMR spectra in dmso solutions of the mononuclear complexes.

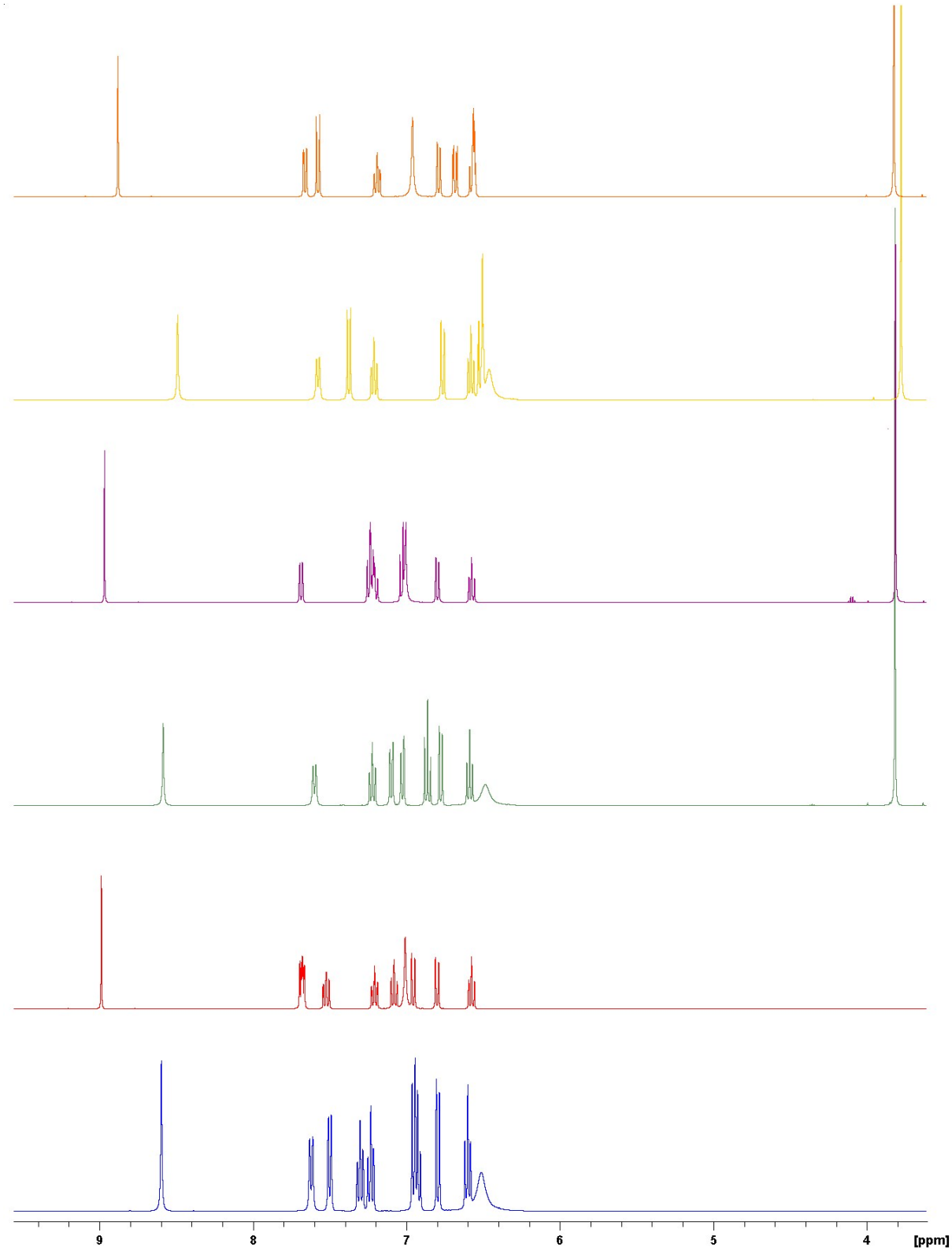


Fig. S14 A portion of the ^{1}H NMR spectra in dmso-d_6 of: (a) H_2L^1, (b) $[MoO_2(L^1)]_2$ (**1**); (c) H_2L^2, (d) $[MoO_2(L^2)]_2$ (**2**), (a) H_2L^3, (e) $[MoO_2(L^3)]_2$ (**3**)

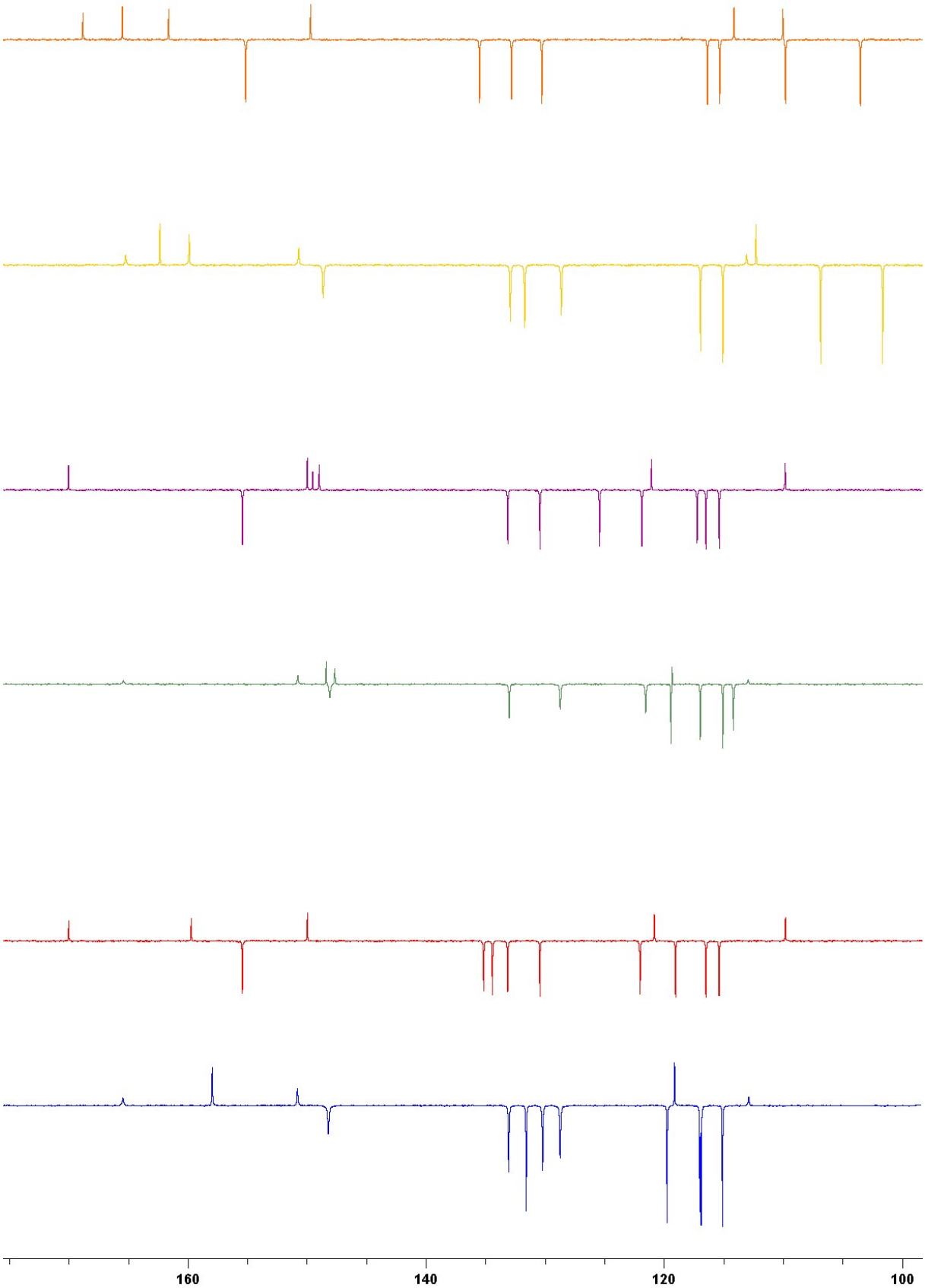


Fig. S15 A portion of the ^{13}C NMR spectra in dmso-d_6 of: (a) H_2L^1, (b) $[MoO_2(L^1)]_2$ (**1**); (c) H_2L^2, (d) $[MoO_2(L^2)]_2$ (**2**), (e) H_2L^3, (f) $[MoO_2(L^3)]_2$ (**3**)

5. Catalysis

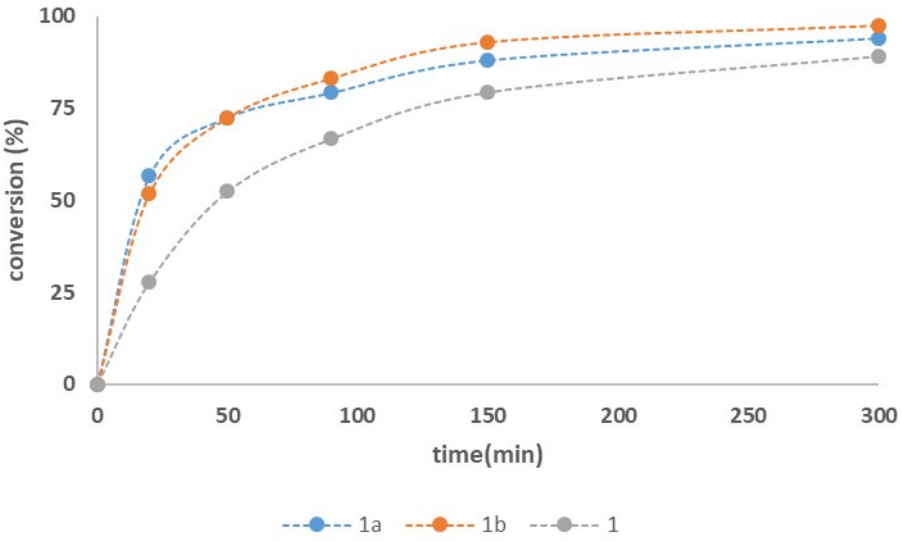


Fig. S16 Converted cyclooctene vs. time with dinuclear dioxomolybdenum(VI) complexes. Reaction conditions: catalyst/cyclooctene/TBHP molar ratio: 0.25/100/200, T = 353 K.

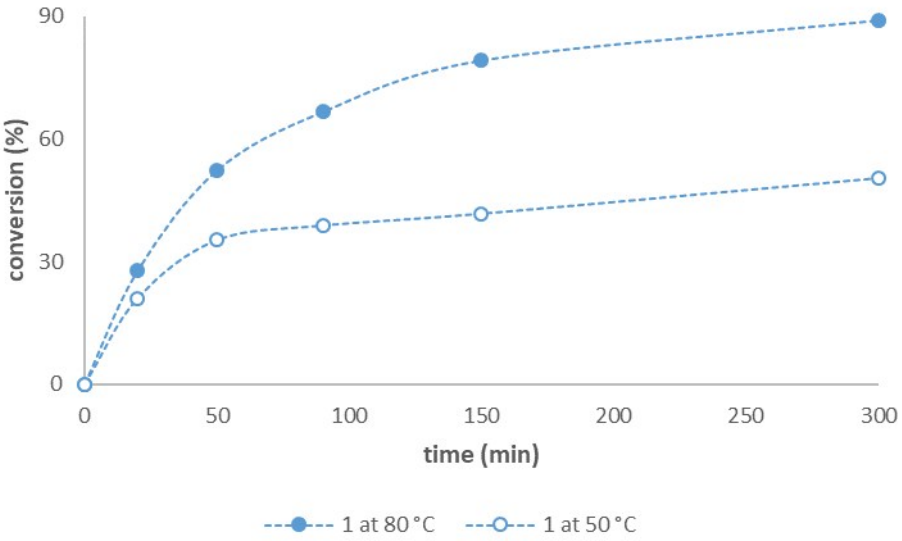


Fig. S17 Converted cyclooctene vs. time with dinuclear dioxomolybdenum(VI) complexes. Reaction conditions: catalyst/cyclooctene/TBHP molar ratio: 0.25/100/200.

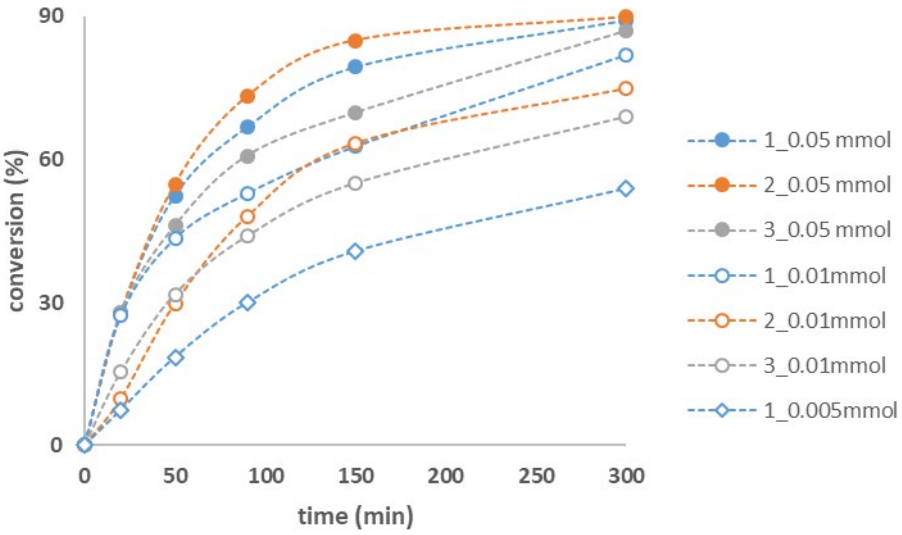
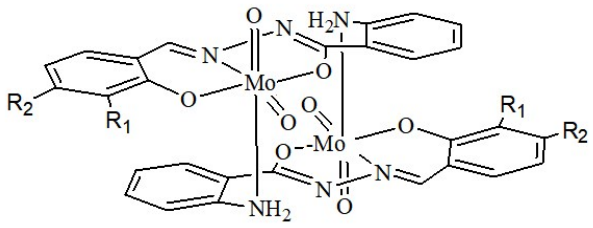
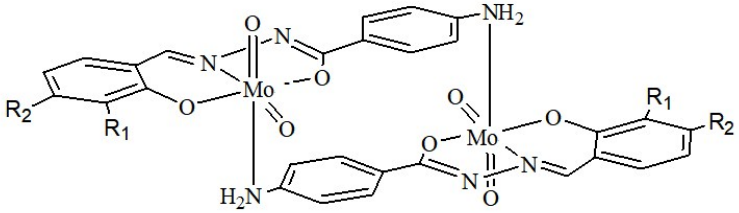


Fig. S18 Converted cyclooctene vs. time with dinuclear dioxomolybdenum(VI) complexes. Catalyst concentration is written next to the catalyst (legend), reaction T = 353 K.

6. DFT Calculations



(a)



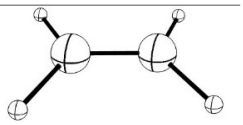
(b)

Scheme S4. (a) Complexes **1-3** with 2-aminobenzoylhydrazone ligands $\mathbf{L}^{1\text{-}3}$ and (b) complexes $\mathbf{1}^{\#}\text{-}\mathbf{3}^{\#}$ with 4-aminobenzoylhydrazone ligands $\mathbf{L}^{a\text{-}c}$

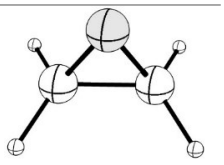
Table S5. Calculated Cartesian Coordinates (Å)

A. Organic molecules

A.1. Ethylene			
C	0.000000	0.665616	0.000000
H	0.923789	1.239603	0.000000
H	-0.923751	1.239647	0.000000
C	0.000000	-0.665616	0.000000
H	-0.923789	-1.239603	0.000000
H	0.923751	-1.239647	0.000000



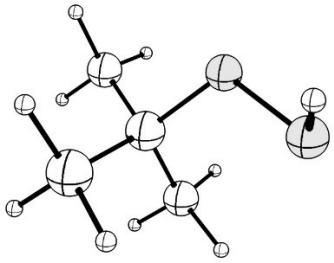
A.2. Ethylene oxide			
C	0.000000	0.823033	0.000000
C	0.663277	-0.487998	0.000000
H	-0.044284	1.406100	0.920513
H	1.105429	-0.869573	0.920803
O	-0.762744	-0.385408	0.000000
H	-0.044284	1.406100	-0.920513
H	1.105429	-0.869573	-0.920803



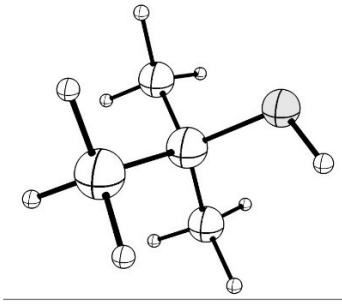
A.3. TBHP			
C	0.386165	-0.000308	0.035397
O	-0.724987	-0.046845	-0.893130
O	-1.972039	0.108498	-0.155077

A.4. tBuOH			
C	-0.005589	-0.000026	0.014420
O	0.015118	-0.000431	1.451985
H	0.945639	0.001902	1.728630

C	1.585583	-0.143167	-0.909606
C	0.308621	-1.175011	1.018102
C	0.408352	1.348581	0.762463
H	-2.332788	-0.790997	-0.249478
H	1.280940	1.416160	1.422181
H	1.183480	-1.185842	1.677386
H	2.518287	-0.108762	-0.336841
H	-0.585590	-1.096065	1.643545
H	0.276876	-2.127762	0.476787
H	1.545111	-1.094315	-1.450590
H	1.596533	0.671248	-1.640824
H	0.455018	2.168835	0.038520
H	-0.493984	1.473706	1.366836



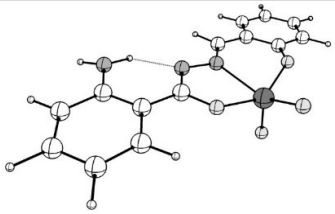
C	-1.490947	-0.005338	-0.356041
C	0.694937	-1.262772	-0.510972
C	0.685524	1.268259	-0.510112
H	0.646742	1.325318	-1.604317
H	0.656167	-1.319650	-1.605180
H	-1.623187	-0.004815	-1.443350
H	1.752964	-1.271531	-0.216357
H	0.219546	-2.158915	-0.098630
H	-1.981082	-0.894002	0.055230
H	-1.987701	0.878867	0.056897
H	0.203120	2.160551	-0.097564
H	1.743307	1.284985	-0.215007



B. Complexes

B.1. Complex **1** with ligand L^1

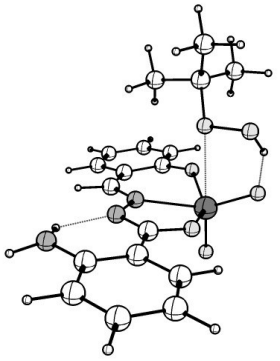
B.1.1 MoO_2L^1



Mo	-0.688732	-1.496073	0.068921
N	3.137846	2.770311	-0.059210
O	1.239734	-1.070559	-0.198333
O	-0.635409	-2.926149	-0.844564
N	0.898666	1.190183	-0.067977

C	3.824146	1.588151	-0.024848
N	-0.407263	0.752080	-0.054960
C	1.723012	0.165928	-0.112550
O	-2.484642	-0.928620	-0.432449
C	5.236725	1.608608	0.039174
H	5.737867	2.572542	0.090020
C	-3.273573	0.129522	-0.220636
O	-0.795673	-1.854600	1.723141
C	3.173710	0.316246	-0.087974
C	-3.630338	2.516102	0.135186
H	-3.216803	3.511347	0.279058
C	-5.001584	2.324430	0.116923
H	-5.674062	3.166216	0.247602
C	-1.327226	1.675122	-0.016544
H	-0.984103	2.709267	0.029613
C	3.960924	-0.857293	-0.106708
H	3.446495	-1.809860	-0.160218
C	-4.664035	-0.055620	-0.244366
H	-5.046572	-1.058482	-0.402353
C	-2.740666	1.429820	-0.024472
C	5.342135	-0.810738	-0.050424
H	5.923648	-1.726838	-0.063188
C	5.976836	0.439454	0.026993
H	7.061210	0.497169	0.076583
C	-5.513920	1.030686	-0.073502
H	-6.588721	0.872964	-0.091659
H	3.623524	3.612807	0.209389
H	2.130578	2.736818	0.045648

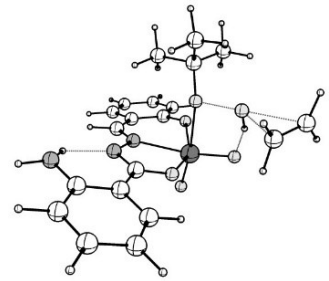
B.1.2 MoO_2L^1.TBHP



Mo	0.519849	0.050094	1.536866
N	-3.369138	-2.121911	-2.062108
O	-1.403350	0.059968	1.060537
O	0.525975	1.587812	2.297120
N	-1.109578	-1.348736	-0.723639
C	-4.034631	-1.408241	-1.104755
N	0.196783	-1.202815	-0.322629

C	-1.909476	-0.665496	0.067698
O	2.324782	0.026411	0.811586
C	-5.448048	-1.367595	-1.129001
H	-5.968109	-1.934610	-1.897769
C	3.077762	-0.874674	0.164786
O	0.594458	-1.150082	2.726519
C	-3.359075	-0.663233	-0.087901
C	3.368119	-2.694078	-1.430079
H	2.930294	-3.407476	-2.124030
C	4.739284	-2.663990	-1.231433
C	0.979331	2.871973	-1.483753
O	0.096378	2.166259	-0.561855
O	-0.556612	3.146007	0.296415
C	1.495954	1.749120	-2.388706
C	2.119178	3.542809	-0.711229
C	0.159835	3.885198	-2.290501
H	-0.171662	2.875078	1.160335
H	0.795645	4.375400	-3.036506
H	2.803513	4.048448	-1.402073
H	2.138346	2.172819	-3.168085
H	1.723415	4.288717	-0.016534
H	2.687349	2.799969	-0.141475
H	2.082897	1.021986	-1.821122
H	0.661513	1.230921	-2.872583
H	-0.662788	3.382923	-2.810341
H	-0.262015	4.650143	-1.634828
H	5.384862	-3.353651	-1.765852
C	1.095117	-1.868827	-0.987904
H	0.739652	-2.516001	-1.790469
C	-4.121782	0.098238	0.826123
H	-3.587607	0.663316	1.581001
C	4.466715	-0.843766	0.354104
H	4.875361	-0.112638	1.043832
C	2.510271	-1.813200	-0.735578
C	-5.503602	0.129124	0.776007
H	-6.066105	0.721318	1.490484
C	-6.164263	-0.618543	-0.212108
H	-7.250036	-0.611279	-0.265166
C	5.284728	-1.733004	-0.334239
H	6.358857	-1.700923	-0.174239
H	-3.888322	-2.793263	-2.607372
H	-2.370749	-2.252811	-1.948700

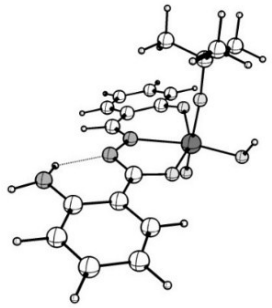
B.1.3 TS



Mo	0.327789	0.532521	1.217664
N	-3.196401	-2.000254	-2.520298
O	-1.598529	0.343562	0.688747
O	0.153892	2.014217	2.101200
N	-1.112826	-1.201721	-0.945898
C	-3.973909	-1.309595	-1.629758
N	0.155042	-0.990164	-0.461595
C	-1.984795	-0.472761	-0.279119
O	2.200048	0.440782	0.678522
C	-5.379393	-1.317092	-1.786333
H	-5.804986	-1.902493	-2.598392

C	2.981653	-0.575580	0.286692
O	0.397416	-0.691688	2.384891
C	-3.420740	-0.536896	-0.562184
C	3.391088	-2.647371	-0.928558
H	3.010563	-3.466586	-1.534110
C	4.734131	-2.600504	-0.586661
H	5.411407	-3.380649	-0.919799
C	1.104291	-1.755156	-0.902386
H	0.835253	-2.533422	-1.618401
C	-4.292560	0.189514	0.276529
H	-3.850028	0.763128	1.082881
C	4.343742	-0.531326	0.619845
H	4.697245	0.304733	1.214483
C	2.487037	-1.652818	-0.498623
C	-5.666236	0.169256	0.103399
H	-6.313414	0.732201	0.768678
C	-6.205874	-0.596708	-0.941176
H	-7.281760	-0.630001	-1.093832
C	5.206447	-1.534855	0.192439
H	-3.642900	-2.704889	-3.088309
H	-2.217941	-2.123049	-2.281382
C	0.903825	2.578908	-1.730230
H	6.257044	-1.486468	0.465627
O	0.150261	2.039625	-0.646013
O	-0.743387	3.516056	0.134285
C	1.491909	1.392403	-2.522188
C	2.032614	3.481076	-1.205866
C	-0.041901	3.360632	-2.660326
H	-0.368220	3.124761	0.973121
H	0.491705	3.701149	-3.555704
H	2.626537	3.891137	-2.031788
H	2.018647	1.769369	-3.406980
H	1.612603	4.315753	-0.636097
H	2.697772	2.912479	-0.548063
H	2.204205	0.825557	-1.920119
H	0.693304	0.722138	-2.855032
H	-0.873782	2.720893	-2.973727
H	-0.451299	4.235439	-2.149013
C	-2.252371	4.257039	0.829101
H	-2.816453	4.396718	-0.086397
H	-2.619827	3.482378	1.494430
C	-1.402450	5.241510	1.290768
H	-0.937123	5.168581	2.268584
H	-1.133608	6.087532	0.668441

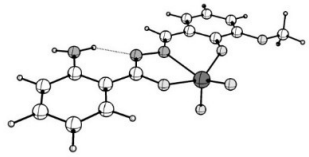
B.1.4 $MoOL^1(OH)(OtBu)$



Mo	0.550444	-0.663100	-1.052863	O	2.368373	-0.319836	-0.353296	H	-7.311292	0.553884	-0.057485
N	-3.497137	2.369317	1.602786	C	-5.541144	1.454058	0.733222	C	5.175007	1.966233	-0.111318
O	-1.413959	-0.417097	-0.896810	H	-6.089263	2.161345	1.351600	H	6.245579	1.961047	-0.297777
O	0.395563	-2.185033	-2.197941	C	3.044870	0.812202	-0.165114	H	-4.033652	3.144766	1.962260
N	-1.188848	1.360271	0.528661	O	0.914444	0.380007	-2.342367	H	-2.497491	2.491126	1.484865
C	-4.128110	1.485264	0.769252	C	-3.415553	0.553039	-0.046550	C	1.037369	-2.591011	1.571918
N	0.133717	1.128438	0.228249	C	3.195494	3.113674	0.633698	O	0.518656	-1.894839	0.447722
C	-1.956741	0.513550	-0.120782	H	2.704416	3.998684	1.031430	C	1.392391	-1.570480	2.666132
				C	4.561678	3.119185	0.403496	C	2.281718	-3.382615	1.135193
				H	5.150419	4.005465	0.617817	C	-0.066606	-3.542607	2.063323
				C	0.994364	2.025919	0.606673	H	0.164798	-2.972405	-1.673630
				H	0.600314	2.894554	1.134934	H	0.267736	-4.108979	2.940324
				C	-4.143509	-0.363881	-0.835901	H	2.702437	-3.939477	1.980540
				H	-3.581780	-1.061110	-1.447102	H	1.758924	-2.080696	3.564604
				C	4.431722	0.824728	-0.386649	H	2.022301	-4.101880	0.349711
				H	4.898018	-0.074994	-0.774635	H	3.046408	-2.705292	0.744804
				C	2.408952	1.976295	0.347585	H	2.168740	-0.884744	2.315334
				C	-5.527459	-0.378381	-0.851080	H	0.507629	-0.985270	2.939195
				H	-6.062691	-1.091101	-1.470282	H	-0.963574	-2.976758	2.335774
				C	-6.224227	0.545718	-0.057157	H	-0.336665	-4.255101	1.275977

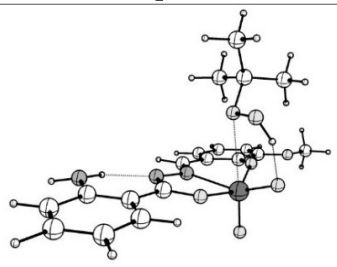
B.2.Complex **2** with ligand L^2

B.2.1 MoO_2L^2



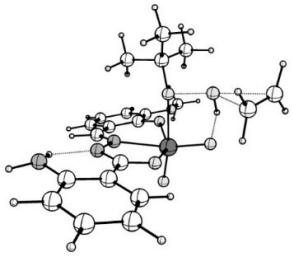
Mo	-0.328839	-1.352916	0.134445	C	2.193530	0.127237	-0.121880	C	-4.193804	0.346408	-0.146264
N	3.793961	2.623454	-0.126413	O	-2.070809	-0.659896	-0.378344	C	-2.166762	1.711181	0.012689
O	1.621810	-1.071843	-0.181507	C	5.804605	1.314001	-0.040092	C	5.734087	-1.107365	-0.097299
O	-0.387096	-2.816468	-0.724192	H	6.374348	2.239974	-0.010074	H	6.247660	-2.063310	-0.105405
N	1.447218	1.210295	-0.081843	C	-2.777091	0.449695	-0.156958	C	6.458456	0.094298	-0.046154
C	4.393547	1.394736	-0.084252	O	-0.435718	-1.640805	1.802829	H	7.544818	0.074052	-0.012425
N	0.114077	0.868753	-0.039634	C	3.652137	0.172728	-0.120327	C	-4.960139	1.497413	0.028774
				C	-2.971463	2.864550	0.177483	H	-6.042036	1.431266	0.040294
				H	-2.490400	3.830550	0.302182	H	4.342498	3.430523	0.129943
				C	-4.347416	2.752918	0.188986	H	2.788595	2.663249	-0.005268
				H	-4.967976	3.633475	0.322772	O	-4.682012	-0.906130	-0.315823
				C	-0.737887	1.854620	-0.008130	C	-6.090117	-1.085695	-0.306468
				H	-0.323543	2.863112	0.011294	H	-6.527292	-0.778936	0.652849
				C	4.352186	-1.054616	-0.133592	H	-6.571811	-0.528305	-1.120693
				H	3.769427	-1.968005	-0.166307	H	-6.252464	-2.154226	-0.453409

B.2.2 MoO_2L^2.TBHP



Mo	-0.223157	0.067500	-1.427272	C	-2.665184	-0.948208	0.067585	C	-0.690645	2.824506	1.635286
N	3.914721	-2.152804	1.851482	O	-0.328233	-1.114516	-2.633248	O	0.211796	2.166325	0.696754
O	1.722360	0.123932	-1.044370	C	3.755900	-0.598619	-0.041793	O	0.799187	3.178545	-0.171087
O	-0.297783	1.616846	-2.159874	C	-2.840006	-2.822546	1.624467	C	-1.118488	1.678771	2.557878
N	1.562320	-1.363425	0.693605	H	-2.352997	-3.549207	2.268637	C	-1.885986	3.421992	0.886129
C	4.506736	-1.375659	0.894748	C	-4.215665	-2.800154	1.498718	C	0.085126	3.889197	2.418852
N	0.232240	-1.233350	0.373520	H	-4.827361	-3.512265	2.043837	H	0.398957	2.900981	-1.026011
C	2.299505	-0.629912	-0.114055	C	-0.613969	-1.934603	1.069714	H	-0.562577	4.345615	3.176033
O	-1.971815	-0.015521	-0.593267	H	-0.201714	-2.597302	1.831291	H	-2.578057	3.898325	1.590212
C	5.917832	-1.301099	0.839099	C	4.446213	0.225550	-0.958766	H	-1.765442	2.069153	3.350798
H	6.494762	-1.892141	1.546761	H	3.855961	0.813388	-1.652002	H	-1.549170	4.181587	0.175005
				C	-4.079670	-0.927005	-0.047428	H	-2.428062	2.644082	0.338418
				C	-2.044020	-1.901383	0.903389	H	-1.675417	0.915532	2.008182
				C	5.827713	0.288676	-0.987277	H	-0.243893	1.212696	3.023454
				H	6.333547	0.929553	-1.702160	H	0.946883	3.439495	2.923338
				C	6.562083	-0.490018	-0.078528	H	0.447483	4.673399	1.750633
				H	7.648687	-0.458205	-0.088168	O	-4.576965	0.032901	-0.866348
				C	-4.837719	-1.855003	0.665446	C	-5.983891	0.101504	-1.043207
				H	-5.918464	-1.850946	0.582317	H	-6.379827	-0.827645	-1.473576
				H	4.479227	-2.841828	2.325000	H	-6.498355	0.311916	-0.096210
				H	2.914376	-2.302380	1.788124	H	-6.154482	0.924237	-1.738774

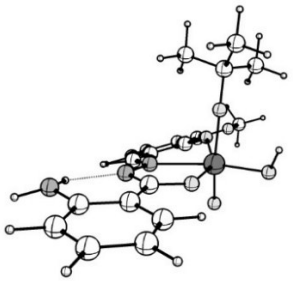
B.2.3 TS



Mo	0.801270	1.481434	-0.434656
N	-1.885029	-0.954559	-4.874458
O	-0.807363	1.627268	-1.627564
O	0.752586	3.104178	0.174451
N	-0.261173	-0.287637	-2.782350
C	-2.675596	0.070574	-4.428062
N	0.785270	-0.264047	-1.893010
C	-1.066888	0.733126	-2.568248
O	2.637961	0.875212	-0.240282
C	-3.902207	0.333357	-5.081044
H	-4.196567	-0.312861	-5.905113
C	3.197386	-0.338057	-0.214501
O	0.134781	0.514876	0.785419

C	-2.293809	0.923193	-3.346480	C	3.995641	3.402059	-2.259277
C	3.412530	-2.652461	-0.964874	C	2.617231	3.580299	-4.381423
H	3.044782	-3.474067	-1.573403	H	1.001174	4.073696	-1.149963
C	4.525752	-2.815162	-0.162035	H	3.502590	3.608572	-5.027891
H	5.044494	-3.768352	-0.130322	H	4.931475	3.496510	-2.823944
C	1.578574	-1.289041	-1.868249	H	4.208125	1.401349	-4.199607
H	1.357269	-2.116030	-2.544685	H	3.681200	4.402553	-1.945594
C	-3.143069	1.991617	-2.988520	H	4.187355	2.802614	-1.363701
H	-2.834260	2.621372	-2.162138	H	3.584658	0.713016	-2.691934
C	4.349883	-0.513147	0.596007	H	2.521388	0.847626	-4.112511
C	2.726149	-1.416364	-0.998722	H	1.788962	3.137254	-4.944655
C	-4.338179	2.233163	-3.644867	H	2.348412	4.606748	-4.119763
H	-4.974768	3.059128	-3.343340	C	-0.284447	5.593281	-2.085394
C	-4.714193	1.387768	-4.699722	H	-0.430039	5.703991	-3.154246
H	-5.650222	1.555753	-5.226636	H	-1.073619	5.069635	-1.555396
C	4.997275	-1.747448	0.618971	C	0.603843	6.404148	-1.407494
H	5.873410	-1.890241	1.241192	H	0.658665	6.393483	-0.323620
H	-2.311123	-1.657157	-5.460363	H	1.310183	7.030792	-1.940170
H	-1.105220	-1.227039	-4.285022	O	4.730763	0.585896	1.297857
C	2.897273	2.750116	-3.115141	C	5.862014	0.478934	2.146203
O	1.690128	2.618781	-2.367120	H	5.708697	-0.276753	2.928130
O	1.071221	4.389437	-2.095401	H	6.770270	0.233980	1.579151
C	3.326073	1.333314	-3.551533	H	5.978832	1.459658	2.609802

B.2.4 $MoOL^2(OH)(OtBu)$

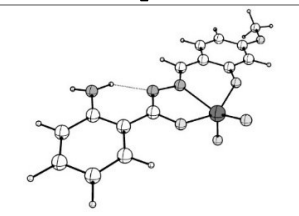


Mo	-0.213302	0.630158	-0.943099
N	4.034351	-2.326400	1.481265
O	1.765413	0.459081	-0.851524
O	-0.112336	2.154795	-2.095475
N	1.654617	-1.370272	0.520190
C	4.603500	-1.398945	0.650185
N	0.315188	-1.175512	0.273545
C	2.368214	-0.476816	-0.128166
O	-1.976615	0.209272	-0.151375
C	6.012218	-1.319596	0.560678

H	6.606987	-2.025824	1.135684	H	3.035010	-2.476999	1.398955
C	-2.603209	-0.948742	0.016064	C	-0.812787	2.600553	1.606548
O	-0.626972	-0.392920	-2.232887	O	-0.205328	1.881805	0.539964
C	3.829666	-0.468301	-0.109529	C	-1.098120	1.622108	2.758190
C	-2.657992	-3.294125	0.712602	C	-2.113116	3.249505	1.101940
H	-2.125796	-4.181696	1.043562	C	0.193894	3.674459	2.053312
C	-4.027260	-3.318161	0.538358	H	0.123886	2.942045	-1.573614
H	-4.589614	-4.226662	0.730191	H	-0.208172	4.263484	2.885839
C	-0.499680	-2.117489	0.647817	H	-2.594349	3.818974	1.905843
H	-0.055093	-2.989466	1.127885	H	-1.511027	2.154696	3.623007
C	4.495654	0.495862	-0.897009	H	-1.902251	3.940449	0.277361
H	3.887526	1.191222	-1.464317	H	-2.808288	2.485365	0.744069
C	-4.014923	-0.982868	-0.143097	H	-1.815608	0.859210	2.444654
C	-1.924390	-2.113210	0.444857	H	-0.172647	1.125165	3.068781
C	5.876870	0.557561	-0.964549	H	1.130638	3.208674	2.376968
H	6.363986	1.306023	-1.581329	H	0.419195	4.357610	1.226596
C	6.633839	-0.365778	-0.227048	O	-4.575016	0.190987	-0.539872
H	7.719777	-0.337417	-0.269315	C	-5.977289	0.223434	-0.750003
C	-4.707675	-2.163452	0.110441	H	-6.282625	-0.483763	-1.532528
H	-5.783218	-2.200449	-0.020405	H	-6.528991	0.001713	0.173639
H	4.608661	-3.094033	1.796322	H	-6.206062	1.240173	-1.072880

B.3. Complex **3** with ligand L^3

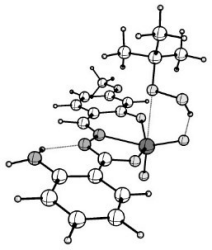
B.3.1 MoO_2L^3



H	2.516073	2.810319	0.040592
H	3.938714	3.790684	0.217381
Mo	0.003221	-1.606239	0.063559
N	1.397276	1.180051	-0.078032
N	3.517850	2.919041	-0.067719
O	1.899825	-1.049492	-0.186784
O	0.154233	-3.006350	-0.885651

N	0.124218	0.645829	-0.065722	C	5.973604	-0.495274	-0.032877
C	4.287970	1.788096	-0.023255	H	6.618756	-1.367889	-0.040014
C	2.292660	0.219917	-0.111875	C	6.517083	0.796549	0.044232
O	-6.297158	0.199012	-0.080406	H	7.594303	0.931828	0.099487
C	-4.066243	-0.450101	-0.215132	C	-7.311556	1.185620	0.071160
H	-4.407219	-1.469906	-0.350638	H	-7.232539	1.695046	1.039416
C	-2.701385	-0.171424	-0.205142	H	-8.257615	0.644819	0.022625
C	-4.569869	1.916301	0.102849	H	-7.273523	1.926102	-0.737269
H	-5.281035	2.723846	0.222720	C	-2.247475	1.168203	-0.035943
C	-0.859606	1.504683	-0.032343	C	-4.999437	0.581688	-0.058454
H	-0.584830	2.559330	0.008807	C	-3.212637	2.186611	0.106958
O	-0.065344	-2.010080	1.709866	H	-2.873204	3.212074	0.230352
O	-1.842703	-1.174667	-0.402682	C	3.730455	0.473518	-0.084535
C	5.694558	1.909969	0.048571	C	4.598850	-0.640400	-0.095532
H	6.124858	2.907666	0.098244	H	4.153920	-1.627464	-0.147693

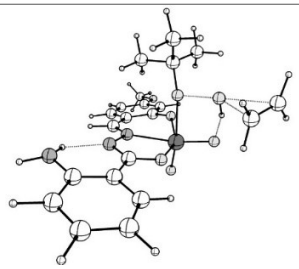
B.3.2 MoO_2L^3.TBHP



Mo	-0.004579	0.219049	-1.563078
N	3.508384	-2.454228	2.083674
O	1.894243	-0.014518	-1.049692
O	0.198452	1.778337	-2.249487
N	1.390347	-1.409965	0.694662
C	4.279083	-1.818973	1.147994
N	0.120091	-1.096746	0.265280
C	2.285595	-0.814469	-0.060748
O	-1.826720	0.387570	-0.894640
C	5.685537	-1.950535	1.204013
H	6.114981	-2.582879	1.977851

C	-2.696365	-0.424020	-0.278880	C	-0.232409	3.041117	1.509621
O	-0.184778	-0.913796	-2.807024	O	0.609138	2.222543	0.645206
C	3.722467	-0.988853	0.126069	O	1.439874	3.102707	-0.165014
C	-3.232285	-2.207813	1.281973	C	-0.967831	1.996902	2.355711
H	-2.904974	-2.977615	1.976429	C	-1.207311	3.869064	0.666702
C	-4.587592	-2.023313	1.063612	C	0.658426	3.925461	2.389156
H	-5.306595	-2.644462	1.582877	H	1.052614	2.909842	-1.048654
C	-0.868797	-1.662842	0.898232	H	0.044308	4.505670	3.087415
H	-0.608808	-2.364561	1.691673	H	-1.869079	4.455582	1.314057
C	4.591984	-0.318565	-0.762452	H	-1.597701	2.501675	3.096060
H	4.147864	0.313699	-1.522433	H	-0.661132	4.561471	0.020252
C	-4.057439	-0.226797	-0.497469	H	-1.823988	3.216223	0.039956
H	-4.386984	0.547945	-1.180092	H	-1.609439	1.366670	1.733809
C	-2.255622	-1.434895	0.622672	H	-0.253248	1.359375	2.886598
C	5.966484	-0.457070	-0.682809	H	1.355198	3.309282	2.967196
H	6.612465	0.067995	-1.379042	H	1.238343	4.618960	1.776050
C	6.508888	-1.286961	0.310787	O	-6.296560	-0.748976	-0.129580
H	7.586028	-1.412439	0.387431	C	-7.319604	-1.520235	0.489275
C	-5.002977	-1.022145	0.162026	H	-7.230684	-2.582684	0.231085
H	3.928118	-3.198812	2.619713	H	-7.302913	-1.405740	1.580277
H	2.505893	-2.470169	1.935777	H	-8.260268	-1.129779	0.098604

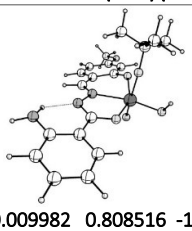
B.3.3 TS



Mo	0.460958	1.018695	0.537724
N	-3.222019	-2.167577	-2.476033
O	-1.466943	0.835030	0.026457
O	0.390181	2.687642	1.005877
N	-1.086242	-1.110331	-1.140179
C	-3.950998	-1.213422	-1.815876
N	0.193396	-0.860737	-0.701433
C	-1.907653	-0.179467	-0.703986
O	2.328732	0.669732	0.088052
C	-5.353768	-1.172176	-1.987351
H	-5.818890	-1.926207	-2.618572
C	3.042244	-0.458777	-0.018557
O	0.435944	0.137809	1.983180

C	-3.345398	-0.219903	-0.986597	C	2.422436	3.078693	-2.530724
C	3.313287	-2.784571	-0.666797	C	0.333293	2.812210	-3.944625
H	2.887736	-3.706783	-1.055105	H	-0.003841	3.518508	-0.374173
C	4.656280	-2.752268	-0.323502	H	0.889989	2.857812	-4.888310
H	5.265006	-3.639815	-0.443224	H	3.048624	3.206337	-3.422244
C	1.089646	-1.776820	-0.908290	H	2.215187	0.882177	-4.232602
H	0.766648	-2.695365	-1.401246	H	2.096454	4.067655	-2.194028
C	-4.164510	0.761662	-0.390385	H	3.030176	2.626849	-1.740320
H	-3.683258	1.501810	0.238554	H	2.305959	0.323582	-2.554441
C	4.393627	-0.418064	0.320143	H	0.787953	0.149751	-3.466397
H	4.824532	0.502906	0.695823	H	-0.565416	2.205685	-4.099319
C	2.470612	-1.666111	-0.521025	H	0.024615	3.825945	-3.677000
C	-5.537078	0.785576	-0.575245	C	-1.754461	4.762143	-0.849757
H	-6.143346	1.549289	-0.098167	H	-2.298772	4.725611	-1.786903
C	-6.128979	-0.197499	-1.382155	H	-2.202446	4.217994	-0.024450
H	-7.204955	-0.200754	-1.537977	C	-0.810630	5.742955	-0.620063
C	5.199374	-1.553782	0.177707	H	-0.359194	5.869727	0.358719
H	-3.715967	-2.973305	-2.830266	H	-0.452886	6.375893	-1.424192
H	-2.254451	-2.284426	-2.193274	O	6.495794	-1.397397	0.545582
C	1.201047	2.194972	-2.832351	C	7.375067	-2.509345	0.442872
O	0.406733	2.022630	-1.661394	H	7.040614	-3.344381	1.071239
O	-0.328884	3.730155	-1.295204	H	7.471823	-2.850592	-0.595644
C	1.655497	0.794306	-3.293663	H	8.343768	-2.154567	0.798214

B.3.4 $MoOL^3(OH)(OtBu)$

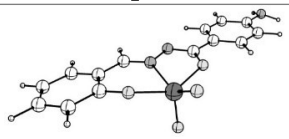


Mo	0.009982	0.808516	-1.028453
N	3.630633	-2.731756	1.609370
O	1.922742	0.291288	-0.901353
O	0.386125	2.274328	-2.199947
N	1.471869	-1.424334	0.544033
C	4.369658	-1.949203	0.761453
N	0.190768	-1.008869	0.255219
C	2.341825	-0.698227	-0.119028
O	-1.829131	0.739742	-0.287090
C	5.772941	-2.111653	0.713603
H	6.225269	-2.882268	1.333870
C	-2.656566	-0.286332	-0.100321

O	-0.544722	-0.161790	-2.306582	C	-0.194374	2.874423	1.520979
C	3.783482	-0.934950	-0.056356	O	0.234505	2.052806	0.444669
C	-3.115311	-2.542933	0.690899	C	-0.700989	1.972840	2.659332
H	-2.755670	-3.492321	1.080310	C	-1.310507	3.809239	1.024510
C	-4.473073	-2.368555	0.480574	C	1.027232	3.686919	1.983449
H	-5.161973	-3.173623	0.703675	H	0.753476	3.016634	-1.688274
C	-0.784569	-1.780572	0.641094	H	0.764600	4.343468	2.821161
H	-0.507560	-2.698142	1.161128	H	-1.655610	4.462545	1.834284
C	4.621882	-0.130997	-0.858064	H	-0.996554	2.575131	3.526486
H	4.154454	0.631702	-1.470437	H	-0.946681	4.443896	0.208112
C	-4.024238	-0.103071	-0.304114	H	-2.159499	3.226355	0.656872
H	-4.390435	0.844756	-0.681479	H	-1.565160	1.389015	2.330945
C	-2.175339	-1.533650	0.401660	H	0.088665	1.281034	2.971711
C	5.995322	-0.304812	-0.884097	H	1.831655	3.017153	2.304729
H	6.616969	0.324772	-1.512698	H	1.406298	4.309126	1.164961
C	6.566733	-1.309856	-0.089247	O	-6.230243	-0.847385	-0.274004
H	7.642576	-1.465979	-0.097799	C	-7.210914	-1.850343	-0.041617
C	-4.928556	-1.133879	-0.026319	H	-7.031126	-2.737618	-0.661296
H	4.057172	-3.575757	1.961854	H	-7.243022	-2.143508	1.015293
H	2.623013	-2.716591	1.496450	H	-8.165038	-1.400979	-0.321060

B.4. Complex **1#** with ligand L^a

B.4.1 MoO_2L^a

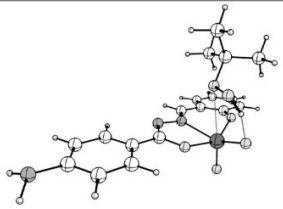


Mo	0.876212	-1.436658	0.078209
N	0.584410	0.807363	-0.053652
N	-0.721673	1.244596	-0.062725
O	-1.060216	-1.025230	-0.177678
O	2.669682	-0.863636	-0.425172
O	0.822934	-2.861778	-0.844492
C	-5.784718	0.715306	-0.021419

C	-1.530957	0.216714	-0.096729
C	-4.927734	1.834169	0.053925
H	-5.355913	2.830891	0.130319
C	-3.553441	1.671953	0.028116
H	-2.900956	2.536206	0.090112
C	-2.980676	0.389760	-0.074292
C	-3.834237	-0.724974	-0.150834
H	-3.402802	-1.717037	-0.228443
C	-5.211256	-0.567707	-0.124321
H	-5.858105	-1.439460	-0.187159
C	1.499417	1.736310	-0.023506
H	1.144912	2.766502	0.019674
C	2.914498	1.498960	-0.035011

C	3.453921	0.200305	-0.222641
C	4.845181	0.021795	-0.247357
H	5.232427	-0.980387	-0.398366
C	5.690222	1.113685	-0.087025
H	6.765819	0.961217	-0.106368
C	5.171479	2.405936	0.094329
H	5.839732	3.252398	0.216795
C	3.798993	2.590567	0.114499
H	3.380257	3.584518	0.251984
O	0.987583	-1.801895	1.731289
N	-7.158926	0.880567	-0.044720
H	-7.519328	1.746081	0.334073
H	-7.717627	0.074660	0.202309

B.4.2 MoO_2L^a.TBHP

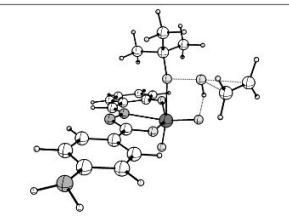


Mo	0.665796	-0.150691	1.506133
O	-1.263024	-0.091908	1.042426
O	0.663417	1.314040	2.400520
N	-0.967616	-1.317025	-0.881315
C	-3.803663	-1.413224	-1.263254
N	0.338451	-1.204543	-0.469105
C	-1.754947	-0.721532	-0.021169
O	2.467453	-0.092679	0.775488
C	-5.177758	-1.408348	-1.429050
H	-5.627180	-1.950100	-2.258057
C	3.220797	-0.917086	0.032754

O	0.747282	-1.456145	2.579632
C	-3.203639	-0.714743	-0.197976
C	3.509509	-2.551188	-1.750899
H	3.070182	-3.187441	-2.515284
C	4.881806	-2.536678	-1.556988
H	5.527129	-3.161212	-2.166634
C	1.235334	-1.790577	-1.208658
H	0.871214	-2.348748	-2.071550
C	-4.029366	-0.009159	0.694759
H	-3.576040	0.535161	1.515813
C	4.610348	-0.901912	0.218999
H	5.019780	-0.248098	0.982027
C	2.651909	-1.754853	-0.960970
C	-5.406105	-0.001531	0.532988
H	-6.030866	0.553417	1.228751
C	-6.006842	-0.701564	-0.531951
C	5.428456	-1.707366	-0.565989
H	6.503285	-1.688404	-0.408313
C	1.116429	2.977398	-1.225609

O	0.227001	2.174465	-0.395561
O	-0.437823	3.052125	0.558562
C	1.657922	1.956236	-2.231380
C	2.238489	3.576584	-0.372088
C	0.298654	4.060695	-1.938040
H	-0.052697	2.693448	1.389942
H	0.939410	4.630808	-2.620368
H	2.931673	4.148181	-0.999704
H	2.299898	2.463027	-2.959933
H	1.825792	4.250833	0.383268
H	2.801478	2.785448	0.134269
H	2.251303	1.185378	-1.732174
H	0.835648	1.475073	-2.770963
H	-0.510999	3.606374	-2.518847
H	-0.141224	4.750770	-1.214493
N	-7.377203	-0.656086	-0.725902
H	-7.941024	-0.410752	0.076925
H	-7.781384	-1.395800	-1.284488
H	-3.172690	-1.960874	-1.954908

B.4.3 TS

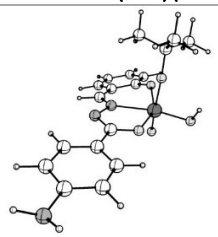


Mo	0.612028	0.077678	1.338000
O	-1.342874	0.020998	0.884590
O	0.508241	1.339350	2.524857
N	-0.962018	-1.166016	-1.060022
C	-3.763346	-1.231413	-1.581605
N	0.332075	-1.050967	-0.613746
C	-1.775794	-0.590237	-0.208862
O	2.448074	0.107384	0.684527
C	-5.130692	-1.245435	-1.802915
H	-5.531937	-1.729467	-2.690477
C	3.199072	-0.796572	0.038317
O	0.724534	-1.366368	2.213730
C	-3.222441	-0.605624	-0.443288

C	3.522301	-2.555672	-1.615402
H	3.101036	-3.226835	-2.360079
C	4.883169	-2.576857	-1.348814
H	5.534443	-3.263607	-1.880469
C	1.246992	-1.700880	-1.264028
H	0.923905	-2.308403	-2.110534
C	-4.102204	0.002403	0.467299
H	-3.695689	0.480315	1.351925
C	4.577992	-0.818229	0.295254
H	4.971013	-0.128251	1.034925
C	2.651888	-1.681382	-0.930543
C	-5.472994	-0.010500	0.252333
H	-6.139876	0.465994	0.967360
C	-6.013113	-0.634387	-0.888421
C	5.407466	-1.701797	-0.387077
H	6.472373	-1.708008	-0.170841
C	1.048864	2.718889	-1.145415
O	0.356752	1.977975	-0.144669
O	-0.399948	3.278233	1.009993
C	1.527612	1.714970	-2.215255
C	2.250572	3.459334	-0.535861

C	0.070180	3.705291	-1.808884
H	-0.003924	2.682116	1.708041
H	0.552274	4.226022	-2.644928
H	2.803676	4.015150	-1.302840
H	1.989438	2.259446	-3.047678
H	1.910130	4.168219	0.225364
H	2.933240	2.745975	-0.063194
H	2.269448	1.025019	-1.809102
H	0.681701	1.139649	-2.603805
H	-0.803422	3.166784	-2.191427
H	-0.272027	4.452699	-1.088508
N	-7.379082	-0.603784	-1.135511
H	-7.973873	-0.460876	-0.329680
H	-7.734373	-1.316883	-1.759031
H	-3.090960	-1.707284	-2.287026
C	-1.814658	3.897668	1.945744
H	-2.416023	4.278897	1.127776
H	-2.196143	3.006301	2.433643
C	-0.895981	4.709645	2.581749
H	-0.390104	4.383586	3.484853
H	-0.608874	5.667336	2.162640

B.4.4 MoOL[a](OH)(OtBu)

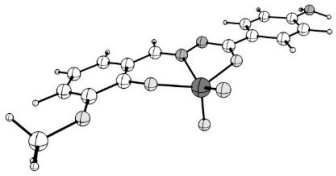


Mo	-0.690020	0.537688	-1.062797
O	1.277048	0.297305	-0.892994
O	-0.503647	1.972757	-2.315345
N	1.041290	-1.387098	0.650941
C	3.887953	-1.552746	0.918548
N	-0.278634	-1.164573	0.333700
C	1.801225	-0.588455	-0.052856
O	-2.505982	0.257819	-0.326820
C	5.268065	-1.596058	1.023026
H	5.739556	-2.308196	1.696374

C	-3.189120	-0.856817	-0.068134	C	-1.191631	2.673522	1.389137
O	-1.078567	-0.579367	-2.280399	O	-0.653475	1.885692	0.337659
C	3.259058	-0.640846	0.050482	C	-1.570150	1.748648	2.558006
C	-3.350685	-3.102714	0.872812	C	-2.424805	3.429743	0.866211
H	-2.863320	-3.963804	1.323915	C	-0.093021	3.660537	1.819729
C	-4.717737	-3.114407	0.646523	H	-0.256981	2.787324	-1.842665
H	-5.310918	-3.982217	0.917130	H	-0.440737	4.301197	2.638609
C	-1.143499	-2.030104	0.774237	H	-2.857247	4.057639	1.654024
H	-0.747718	-2.860469	1.359143	H	-1.947075	2.332379	3.406151
C	4.061994	0.222731	-0.714023	H	-2.149554	4.079333	0.027170
H	3.587266	0.927659	-1.387967	H	-3.185692	2.723817	0.522136
C	-4.576592	-0.874648	-0.285123	H	-2.344841	1.040416	2.251760
H	-5.038767	0.002013	-0.727198	H	-0.693351	1.182436	2.890282
C	-2.558347	-1.990305	0.514468	H	0.795765	3.116732	2.156679
C	5.444822	0.181813	-0.614617	H	0.195908	4.302354	0.979864
H	6.052275	0.853590	-1.216545	N	7.456780	-0.807353	0.322061
C	6.074256	-0.728208	0.256821	H	7.845656	-1.223267	1.157895
C	-5.325984	-1.992374	0.062450	H	7.969599	0.007171	0.011464
H	-6.397066	-1.992448	-0.121432	H	3.274219	-2.222899	1.510771

B.5. Complex **2[#]** with ligand L[b]

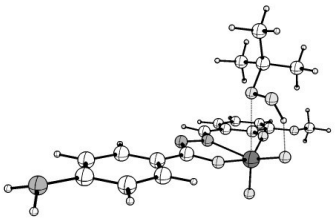
B.5.1 MoO_2L^b



Mo	0.478306	-1.293780	0.144921
N	0.058203	0.929043	-0.039736
N	-1.269897	1.290030	-0.076254
O	-1.476301	-0.998119	-0.152858
O	2.226479	-0.623114	-0.376077
O	0.511358	-2.754415	-0.721593
O	0.591168	-1.587822	1.812434

O	4.835592	-0.896408	0.317294	C	2.945097	0.481056	0.164947
C	-2.017433	0.215656	-0.100444	C	4.360413	0.363186	0.156744
C	-3.475493	0.305492	-0.098620	C	5.139609	1.507258	0.006574
C	-4.262202	-0.857961	-0.161772	H	6.220797	1.429880	0.015405
H	-3.772889	-1.824488	0.213474	C	4.540146	2.770088	0.158518
C	-5.646421	-0.780545	-0.154611	H	5.169996	3.645424	0.283309
H	-6.240885	-1.689551	0.206744	C	3.165166	2.895542	0.150357
C	-6.294238	0.468671	-0.085500	H	2.694022	3.867144	0.269123
C	-5.504437	1.636493	-0.023736	C	6.241427	-1.089377	-0.309662
H	-5.990576	2.608017	0.026788	H	6.727067	-0.543901	-1.129740
C	-4.122636	1.553965	0.029925	H	6.393444	-2.160701	-0.447586
H	-3.522081	2.455741	0.021660	H	6.684300	-0.778440	0.645784
C	0.920150	1.907133	-0.018880	N	-7.675928	0.553504	-0.128648
H	0.510338	2.917268	0.002908	H	-8.089155	1.403438	0.231204
C	2.347948	1.749703	0.003248	H	-8.188795	-0.278250	0.131902

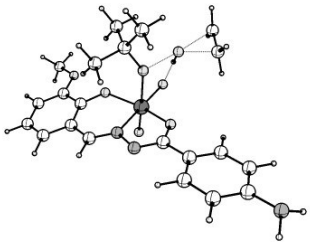
B.5.2 MoO_2L^b.TBHP



Mo	0.347748	-0.121535	-1.398575
O	1.600606	-0.041382	-1.015638
O	-0.397642	1.351513	-2.278164
N	1.410850	-1.340451	0.873818
C	4.263635	-1.426693	1.106196
N	0.085667	-1.229190	0.529060
C	2.148735	-0.705198	-0.002177
O	-2.100148	-0.094242	-0.567998
C	5.644439	-1.413790	1.203516
H	6.139650	-1.986272	1.984433
C	-2.806992	-0.947745	0.181285

O	-0.462615	-1.416785	-2.481765	C	-1.978895	3.473455	0.571947
C	3.604894	-0.689766	0.103708	C	-0.008202	4.069613	2.060004
C	-3.008379	-2.652583	1.918624	H	0.299439	2.738495	-1.280882
H	-2.531197	-3.315517	2.634800	H	-0.654225	4.599787	2.769106
C	-4.383333	-2.628728	1.784651	H	-2.671208	4.014015	1.227798
H	-5.004800	-3.275730	2.395980	H	-1.870135	2.353898	3.154408
C	-0.770568	-1.847805	1.289329	H	-1.635693	4.163573	-0.203857
H	-0.363045	-2.431429	2.115089	H	-2.522846	2.651237	0.095438
C	4.378367	0.063425	-0.796866	H	-1.789507	1.082710	1.921115
H	3.879193	0.637751	-1.569469	H	-0.355948	1.458311	2.906133
C	-4.220519	-0.923062	0.058271	H	0.848904	3.662761	2.607034
C	-2.199471	-1.817487	1.112444	H	0.361270	4.785435	1.322365
C	5.761390	0.079569	-0.703295	N	7.799538	-0.607160	0.425426
H	6.345619	0.671421	-1.403884	H	8.318313	-0.323142	-0.394931
C	6.421032	-0.659579	0.298440	H	8.237103	-1.368464	0.927059
C	-4.991846	-1.766118	0.857370	H	3.672808	-2.010504	1.803726
H	-6.072133	-1.758895	0.768914	O	-4.704829	-0.044396	-0.855251
C	-0.789010	2.941082	1.376810	C	-6.110178	0.023923	-1.040772
O	0.111528	2.192269	0.508708	H	-6.517982	-0.937673	-1.379216
O	0.695818	3.110182	-0.460275	H	-6.623061	0.331914	-0.119835
C	-1.226587	1.888187	2.400083	H	-6.270279	0.776924	-1.813649

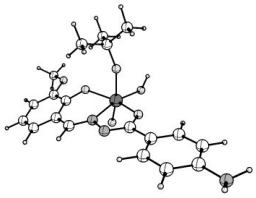
B.5.3 TS



Mo	1.164818	1.535480	-0.300650
O	-0.436111	2.004659	-1.422647
O	1.218842	3.024545	0.588558
N	-0.006442	0.304625	-2.926702
C	-2.308333	1.048150	-4.435926
N	1.041640	0.104154	-2.061200
C	-0.737915	1.309014	-2.508534
O	2.961678	0.798624	-0.249161
C	-3.449852	1.417389	-5.128733
H	-3.713927	0.906692	-6.052075
C	3.452766	-0.426035	-0.465788
O	0.438666	0.407051	0.731878
C	-1.944251	1.700969	-3.243997

C	3.534845	-2.558283	-1.653534	H	5.402345	3.725730	-2.330813
H	3.118348	-3.224337	-2.404125	H	4.560156	1.961501	-4.065154
C	4.641603	-2.933452	-0.915279	H	4.203823	4.524999	-1.291286
H	5.107274	-3.900692	-1.077749	H	4.617475	2.819623	-1.015541
C	1.775929	-0.948412	-2.247511	H	3.910884	1.046522	-2.695431
H	1.500901	-1.611572	-3.068688	H	2.846295	1.488397	-4.050620
C	-2.768040	2.734620	-2.769021	H	2.252719	3.932619	-4.459431
H	-2.501470	3.237352	-1.845724	H	2.881916	5.194064	-3.379692
C	4.596092	-0.817652	0.278899	N	-5.393597	2.858581	-5.370904
C	2.918594	-1.304277	-1.436709	H	-6.106998	3.347622	-4.845946
C	-3.915164	3.105905	-3.456167	H	-5.781724	2.174698	-6.007566
H	-4.542300	3.907963	-3.073388	H	-1.679636	0.246066	-4.806902
C	-4.276702	2.454509	-4.650611	C	0.294642	5.904116	-1.175596
C	5.174927	-2.065296	0.050949	H	0.149781	6.213815	-2.204816
H	6.045436	-2.373264	0.618864	H	-0.513608	5.322648	-0.743441
C	3.329680	3.159206	-2.735644	C	1.203816	6.557471	-0.365921
O	2.116316	2.959412	-2.015042	H	1.258363	6.349431	0.697801
O	1.593025	4.679974	-1.413988	H	1.930857	7.245739	-0.781826
C	3.679863	1.823813	-3.425697	O	5.040635	0.100595	1.176880
C	4.461548	3.582539	-1.784876	C	6.166248	-0.233053	1.971666
C	3.099383	4.220950	-3.827159	H	5.974323	-1.120532	2.589400
H	1.514528	4.199520	-0.540563	H	7.058664	-0.407676	1.355484
H	3.988722	4.321918	-4.460709	H	6.337592	0.627866	2.619716

B.5.4 MoOL[b](OH)(OtBu)

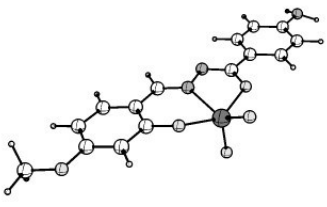


Mo	-0.332012	0.518569	-0.951874
O	1.647526	0.335280	-0.835412
O	-0.184270	1.962503	-2.203427
N	1.502178	-1.411765	0.648704
C	4.359026	-1.511891	0.824648
N	0.168240	-1.211405	0.379283
C	2.219327	-0.568544	-0.047810
O	-2.102565	0.173860	-0.138218
C	5.742644	-1.527348	0.880694
H	6.252241	-2.247531	1.516742
C	-2.745822	-0.964233	0.094834
O	-0.760784	-0.573013	-2.178333

C	3.680976	-0.590046	0.005626	C	0.059375	3.782159	1.810069
C	-2.834975	-3.261238	0.932238	H	0.064992	2.774326	-1.727561
H	-2.315791	-4.133359	1.319973	H	-0.349589	4.431943	2.592681
C	-4.203728	-3.278194	0.751926	H	-2.722181	3.911902	1.630531
H	-4.779062	-4.165949	0.995657	H	-1.662850	2.381543	3.476859
C	-0.660673	-2.117429	0.809398	H	-2.023681	3.898929	0.000100
H	-0.224748	-2.959200	1.347238	H	-2.932775	2.487884	0.580782
C	4.438207	0.312551	-0.760149	H	-1.938309	0.993659	2.400496
H	3.925366	1.025645	-1.396535	H	-0.307537	1.324276	3.023094
C	-4.156686	-0.989788	-0.070531	H	0.995622	3.345916	2.173935
C	-2.084251	-2.108697	0.597324	H	0.287278	4.401196	0.934885
C	5.824366	0.299193	-0.709705	N	7.888855	-0.671191	0.127772
H	6.395932	1.001016	-1.312558	H	8.314536	-1.099422	0.939156
C	6.503042	-0.620800	0.112697	H	8.371871	0.164308	-0.174986
C	-4.866895	-2.143217	0.250419	H	3.780669	-2.212123	1.417707
H	-5.942198	-2.174376	0.116065	O	-4.699029	0.165672	-0.541712
C	-0.940317	2.672945	1.439946	C	-6.099040	0.202565	-0.764244
O	-0.320867	1.875203	0.439160	H	-6.408560	-0.548686	-1.502873
C	-1.232776	1.786537	2.662386	H	-6.660381	0.046951	0.167118
C	-2.238310	3.278141	0.877890	H	-6.312296	1.199713	-1.152507

B.6. Complex **3[#]** with ligand L[c]

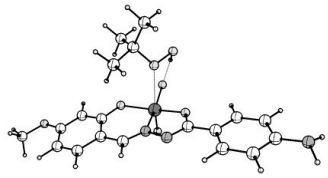
B.6.1 MoO_2L^c



Mo	-0.184926	1.565403	0.074256
O	1.723839	1.034360	-0.163051
O	-2.025193	1.114051	-0.395233
O	-0.261955	1.977025	1.718867
O	-0.043197	2.960634	-0.884935
O	-6.465617	-0.312621	-0.096639
N	-0.038005	-0.683049	-0.057698

N	1.238871	-1.207704	-0.066302	C	-2.872899	0.099742	-0.204304
C	2.112916	-0.236900	-0.092373	C	-4.241040	0.362560	-0.219497
C	3.549897	-0.503174	-0.070948	H	-4.593350	1.378631	-0.354208
C	4.473222	0.554517	-0.138181	C	-5.162597	-0.680417	-0.069341
H	4.106456	1.572818	-0.208157	C	-4.718152	-2.009668	0.091474
C	5.837812	0.308750	-0.112362	H	-5.420128	-2.825879	0.207150
H	6.539185	1.137903	-0.168101	C	-3.357351	-2.263959	0.100926
C	6.327746	-1.008552	-0.019103	H	-3.005973	-3.285412	0.223917
C	5.400689	-2.070122	0.046513	C	-7.467518	-1.312069	0.048327
H	5.763682	-3.093029	0.114962	H	-7.387144	-1.822247	1.016197
C	4.039210	-1.819712	0.021144	H	-8.420520	-0.783801	-0.004319
H	3.332635	-2.640922	0.075647	H	-7.416064	-2.051352	-0.760638
C	-1.011394	-1.554204	-0.028227	N	7.690150	-1.261777	-0.043059
H	-0.718349	-2.603673	0.013633	H	7.990715	-2.149126	0.337891
C	-2.403824	-1.234441	-0.036387	H	8.295304	-0.494795	0.218645

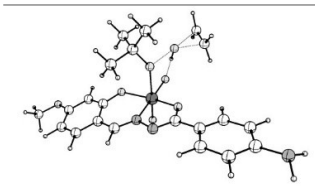
B.6.2 MoO_2L^c.TBHP



Mo	0.147306	0.069856	1.547197
O	-1.760645	-0.077249	1.028100
O	-0.022079	1.568948	2.366881
N	-1.289531	-1.362677	-0.818435
C	-4.094035	-1.748912	-1.271682
N	-0.012977	-1.101100	-0.374965
C	-2.156898	-0.805106	-0.014682
O	1.961915	0.269762	0.868887
C	-5.457327	-1.887250	-1.469670
H	-5.828258	-2.507843	-2.282152
C	2.815578	-0.512200	0.193589
O	0.317208	-1.168985	2.687552
C	-3.594932	-0.947337	-0.227838

C	3.315589	-2.191759	-1.488496	C	-0.415337	4.137165	-2.070468
H	2.972870	-2.906101	-2.232916	H	-0.792755	2.843611	1.280585
C	4.674979	-2.044275	-1.264670	H	0.213181	4.720831	-2.752834
H	5.381434	-2.639426	-1.829742	H	2.180653	4.390684	-1.067546
C	0.961513	-1.637509	-1.054850	H	1.699405	2.616897	-2.990953
H	0.679861	-2.275853	-1.892851	H	1.036717	4.462460	0.286169
C	-4.510052	-0.286833	0.610058	H	2.096021	3.047239	0.094360
H	-4.135296	0.335478	1.415210	H	1.666018	1.366526	-1.734166
C	4.180554	-0.352152	0.418790	H	0.274441	1.568392	-2.824305
H	4.524949	0.368288	1.151723	H	-1.185828	3.626659	-2.657880
C	2.354106	-1.451332	-0.772565	H	-0.907663	4.822920	-1.377210
C	-5.876292	-0.422694	0.415912	N	-7.739831	-1.324686	-0.855621
H	-6.571342	0.098935	1.069593	H	-8.343468	-1.105006	-0.074360
C	-6.376030	-1.226063	-0.627468	H	-8.051617	-2.131339	-1.380031
C	5.110358	-1.115106	-0.298332	H	-3.393553	-2.262731	-1.921202
C	0.437384	3.116787	-1.307861	O	6.410188	-0.883568	0.005498
O	-0.429640	2.289876	-0.479067	C	7.416702	-1.629387	-0.667952
O	-1.172161	3.155416	0.427622	H	7.310076	-2.705116	-0.480835
C	1.056640	2.098615	-2.271156	H	7.398456	-1.442698	-1.749
C	1.504351	3.795586	-0.443272	H	8.365822	-1.282521	-0.256866

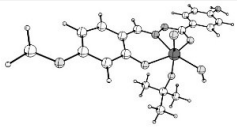
B.6.3 TS



Mo	0.784444	0.913658	0.521626
O	-1.175186	0.855983	0.099650
O	0.799495	2.530454	1.153001
N	-0.926696	-0.978059	-1.280068
C	-3.733665	-0.987175	-1.791534
N	0.382430	-0.809520	-0.892081
C	-1.676597	-0.072575	-0.704848
O	2.610331	0.559411	-0.068343
C	-5.102642	-0.970568	-2.004326
H	-5.556365	-1.695375	-2.676599
C	3.278102	-0.568583	-0.346107
O	0.799142	-0.106855	1.872103
C	-3.125209	-0.054283	-0.931993
C	3.430981	-2.811483	-1.265357
H	2.951683	-3.671515	-1.726736

C	4.792830	-2.854253	-1.006402	H	2.276323	1.250559	-4.343556
H	5.362515	-3.738401	-1.263818	H	2.377901	4.204034	-1.971912
C	1.232621	-1.721899	-1.254348	H	3.282740	2.697849	-1.715406
H	0.844444	-2.566811	-1.825153	H	2.460878	0.521282	-2.740384
C	-3.938924	0.893456	-0.290426	H	0.882399	0.472956	-3.559670
H	-3.480816	1.610815	0.381702	H	-0.429936	2.625445	-3.924845
C	4.648018	-0.602504	-0.090894	H	0.222844	4.174548	-3.352891
H	5.131406	0.258306	0.356721	N	-7.284456	0.030437	-1.612252
C	2.636923	-1.694676	-0.943235	H	-7.849076	0.481915	-0.904305
C	-5.311305	0.913066	-0.497243	H	-7.702521	-0.826581	-1.950667
H	-5.926443	1.654410	0.007889	H	-3.112637	-1.725261	-2.287359
C	-5.918786	-0.018811	-1.359646	C	-1.349538	4.845547	-0.352420
C	5.405213	-1.735652	-0.410558	H	-1.927611	4.950232	-1.264059
C	1.391300	2.433948	-2.752920	H	-1.790931	4.213983	0.412092
O	0.650103	2.158262	-1.568543	C	-0.377042	5.771331	-0.026427
O	0.007606	3.840247	-0.974582	H	0.109391	5.755254	0.943588
C	1.776590	1.078604	-3.382631	H	-0.026095	6.495248	-0.753068
C	2.654521	3.246665	-2.424263	O	6.726928	-1.656118	-0.111648
C	0.491055	3.190974	-3.747046	C	7.560777	-2.770191	-0.399175
H	0.369325	3.511139	-0.102292	H	7.241667	-3.663661	0.152271
H	1.004842	3.330522	-4.705799	H	7.578171	-2.992642	-1.473738
H	3.242624	3.448262	-3.328013	H	8.561825	-2.482876	-0.073570

B.6.4 MoOL^c(OH)(OtBu)



Mo	-0.135759	0.719599	-1.029440
O	1.791679	0.259049	-0.864708
O	0.246981	2.119023	-2.282872
N	1.365022	-1.412499	0.649601
C	4.175346	-1.919764	0.897052
N	0.079275	-1.029467	0.338521
C	2.211806	-0.696105	-0.040014
O	-1.975402	0.649797	-0.282753
C	5.541700	-2.123396	0.996334
H	5.928533	-2.904915	1.646352
C	-2.782305	-0.383119	-0.050295
O	-0.677541	-0.312575	-2.262765
C	3.655037	-0.916968	0.058230
C	-3.196327	-2.609966	0.842803

H	-2.817557	-3.533106	1.274716	H	0.610049	2.886498	-1.806782
C	-4.557443	-2.472168	0.625791	H	0.436715	4.567297	2.543716
H	-5.230329	-3.279676	0.885909	H	-1.955114	4.534617	1.472501
C	-0.881459	-1.802758	0.759022	H	-1.297671	2.820215	3.346364
H	-0.580777	-2.687538	1.320462	H	-1.191129	4.394442	-0.122997
C	4.551704	-0.128083	-0.681672	H	-2.386332	3.186917	0.392816
H	4.160716	0.646490	-1.332522	H	-1.800882	1.520930	2.241739
C	-4.153688	-0.236542	-0.261386	H	-0.165800	1.512399	2.935048
H	-4.538666	0.685724	-0.681080	H	1.553340	3.234198	2.169342
C	-2.276649	-1.596406	0.507565	H	1.127982	4.414783	0.914145
C	5.921270	-0.328853	-0.586510	N	7.807845	-1.568883	0.314767
H	6.601639	0.287672	-1.169376	H	8.142945	-2.047070	1.140728
C	6.442172	-1.330263	0.255142	H	8.408247	-0.804762	0.034061
C	-5.037190	-1.271165	0.063885	H	3.488955	-2.532950	1.471059
C	-0.443067	2.967213	1.344767	O	-6.345305	-1.021899	-0.194791
O	0.043645	2.067429	0.359661	C	-7.305020	-2.031359	0.088468
C	-0.962103	2.154127	2.542674	H	-7.110249	-2.943590	-0.489225
C	-1.565703	3.823471	0.734538	H	-7.328194	-2.275335	1.158137
C	0.741401	3.851678	1.771068	H	-8.268885	-1.614517	-0.207788