Electronic Supplementary Information (ESI)

Dioxotungsten(VI) complexes with isoniazid-related hydrazones as (pre)catalysts for olefin epoxidation: solvent and ligand substituent effects

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X-Ray Crystallography. Single crystal diffraction.

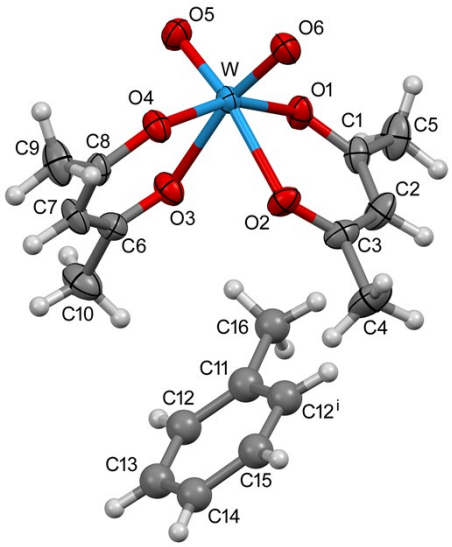
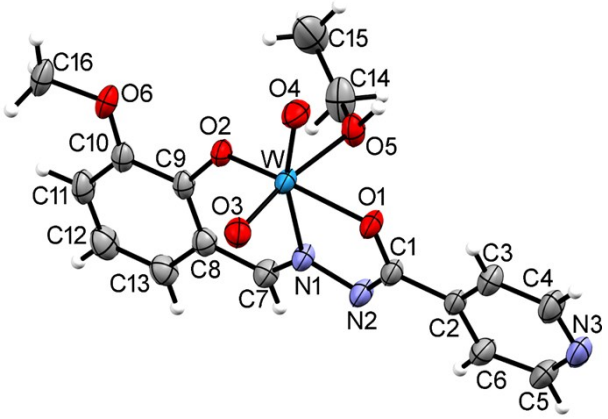
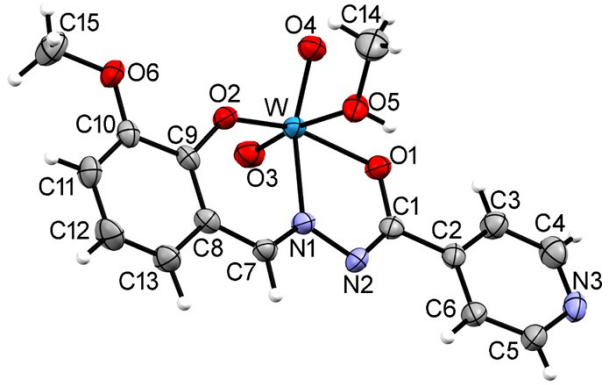


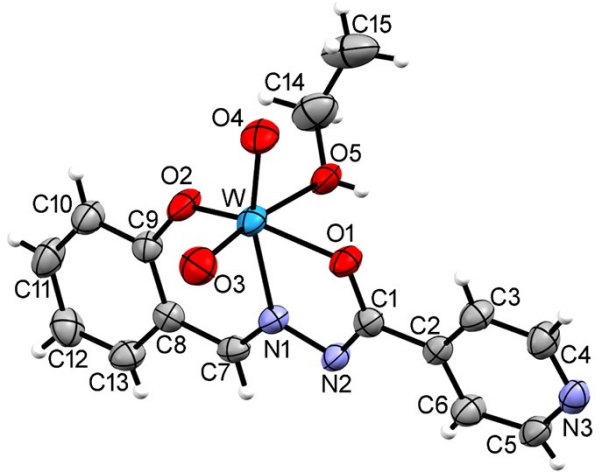
Fig. S1 ORTEP drawings of the $[WO_2(acac)_2]\cdot 0.5C_6H_5Me$ with the atom-labeling scheme (displacement ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level).



1a



1b



3a

Fig. S2 ORTEP drawings of **1a**, **1b** and **3a** with the atom-labeling scheme (displacement ellipsoids of non-hydrogen atoms are drawn at the 50% probability level).

Table S1 Selected bond lengths (Å) and angles (°) for compound **[**$WO_2(acac)_2]\cdot 0.5C_6H_5Me$

	[$WO_2(acac)_2]\cdot 0.5C_6H_5Me$
W−O1	1.989(4)
W−O2	2.166(3)
W−O3	2.170(4)
W−O4	1.971(4)
W−O5	1.718(4)
W−O6	1.712(4)
O1−C1	1.296(7)
C1−C2	1.355(9)
C2−C3	1.386(9)
C3−O2	1.267(7)
O3−C6	1.247(8)
C6−C7	1.415(8)
C7−C8	1.350(9)
C8−O4	1.296(8)
O1−W−O2	80.97(14)
O1−W−O3	82.27(17)
O1−W−O4	159.45(17)
O1−W−O5	92.67(18)
O1−W−O6	98.84(19)
O2−W−O3	75.54(17)
O2−W−O4	83.15(17)
O2−W−O5	164.71(17)
O2−W−O6	90.27(19)
O3−W−O4	81.19(17)
O3−W−O5	89.89(19)
O3−W−O6	165.5(2)
O4−W−O5	99.4(2)
O4−W−O6	94.18(19)
O5−W−O6	104.5(2)

Table S2 Angle between the phenyl and the pyridine moieties, φ (˚) and angle between the five- and six-membered chelate rings, ψ (˚) for compounds **1a**, **1b** and **3a**

	φ /°	ψ /°
1a	7.39(11)	10.94(17)
1b	5.20(14)	9.34(19)
3a	8.94(12)	16.87(16)

Table S3 Geometry of intra- and intermolecular hydrogen bonds (Å, °) for compounds **1a**, **1b** and **3a**

	D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	D−H···A(°)
1a	O5−H50···N3[a]	0.83	1.9	2.723(4)	172
	C5−H5···O4[b]	0.93	2.47	3.097(4)	125
	C7−H7···O3[c]	0.93	2.49	3.097(4)	123
	C15−H18b···O4[d]	0.96	2.52	3.374(5)	148
1b	O5−H50···O1	0.83	2.38	2.811(4)	113
	O5−H50···N3[e]	0.83	2.01	2.692(4)	139
	C4−H4···O4[f]	0.93	2.58	3.421(5)	151
	C7−H7···O3[g]	0.93	2.35	3.253(4)	165
	C15−H15b···O4[h]	0.96	2.57	3.408(5)	146
3a	O5−H50···N3[i]	0.72(3)	1.98(3)	2.700(4)	175(4)
	C3−H3···O2[j]	0.93	2.51	3.380(4)	156
	C7−H7···O4[h]	0.93	2.57	3.461(4)	161

[a] 2-x,2-y,2-z; [b]x,1+y,z; [c]2-x,1-y,1-z; [d]2-x,1-y,2-z ; [e]-x,-y,1-z; [f]1-x,-y,1-z; [g]-1+x,y,z; [h] -1/2+x,1/2-y,-1/2+z; [i]1-x,-y,-z; [j] 1/2-x,-1/2+y,1/2-z

Table S4 Geometry of $\pi\cdots\pi$ interactions involved in the formation of dimers and between neighbouring dimer molecules for compounds **1a**, **1b** and **3a**

	d$(\pi\cdots\pi)$ /Å
1a	d(Cg3···Cg3)[i] =3.608(2)
	d(Cg1···Cg4)[ii]=4.2013(18)
1b	d(Cg3···Cg3)[iii] =3.549(2)
	d(Cg1···Cg3) [iv] =4.284(2)
3a	d(Cg3···Cg3)[v]=3.5516(19)
	(Cg4···Cg4)[vi]=3.9292(19)

[i] 2−*x*,2−*y*,2−*z*; [ii] 2−x,1−y,1−z; [iii]–*x*, −*y*, 1−*z*; [iv] 1−*x*,−*y*,−*z*; [v]–*x*, 1−*y*, 2−*z*; [vi]–*x*, 1−*y*,−*z*;
Cg1 is the centroid of the ring W, O1, C1, N1 and N2, Cg3 is the centroid of the ring N3, C2−C5 and Cg4 is the centroid of the ring C8 −C13 in **1a**, **1b** and **3a**.

Powder X-ray diffraction patterns

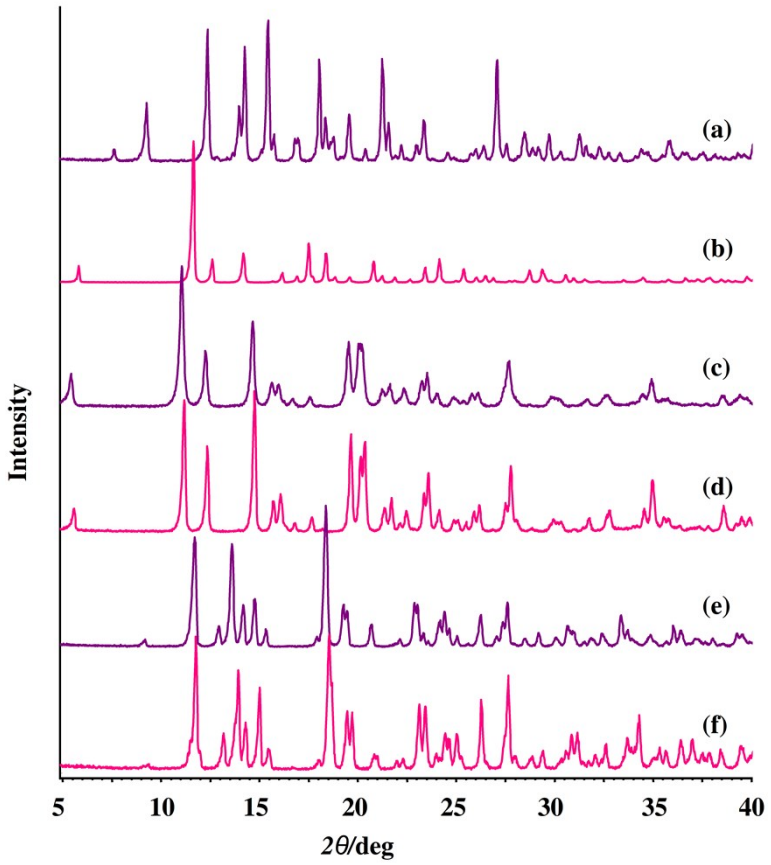
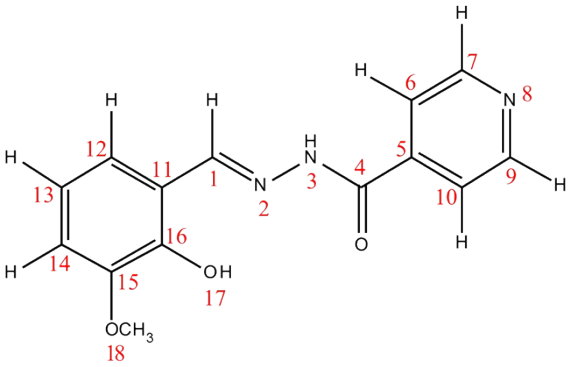
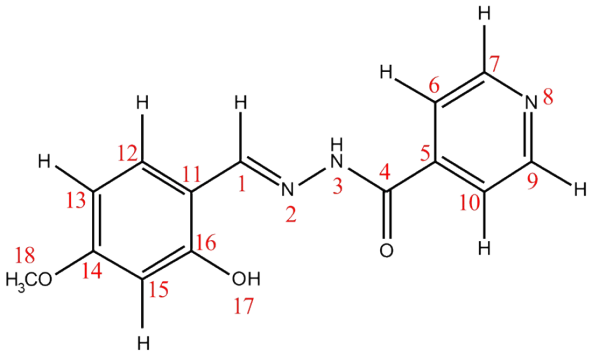


Fig. S3 Powder X-ray diffraction patterns of **1a** (a), **1b** (b), **2a** (c), **2b** (d), **3a** (e) and **3b** (f).

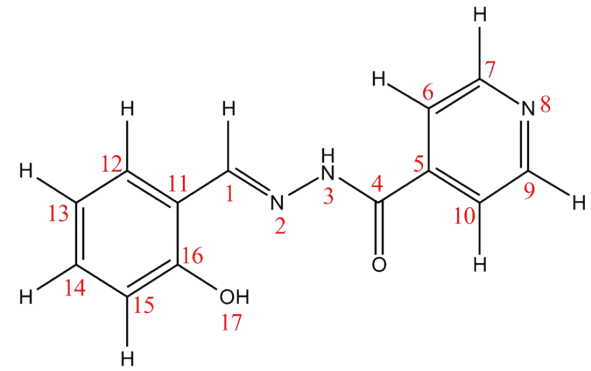
NMR numbering scheme



H_2L^{3OMe}



H_2L^{4OMe}



H_2L^{H}

Scheme S1 The structural formula of H_2L^R with the NMR numbering scheme.

NMR spectroscopy

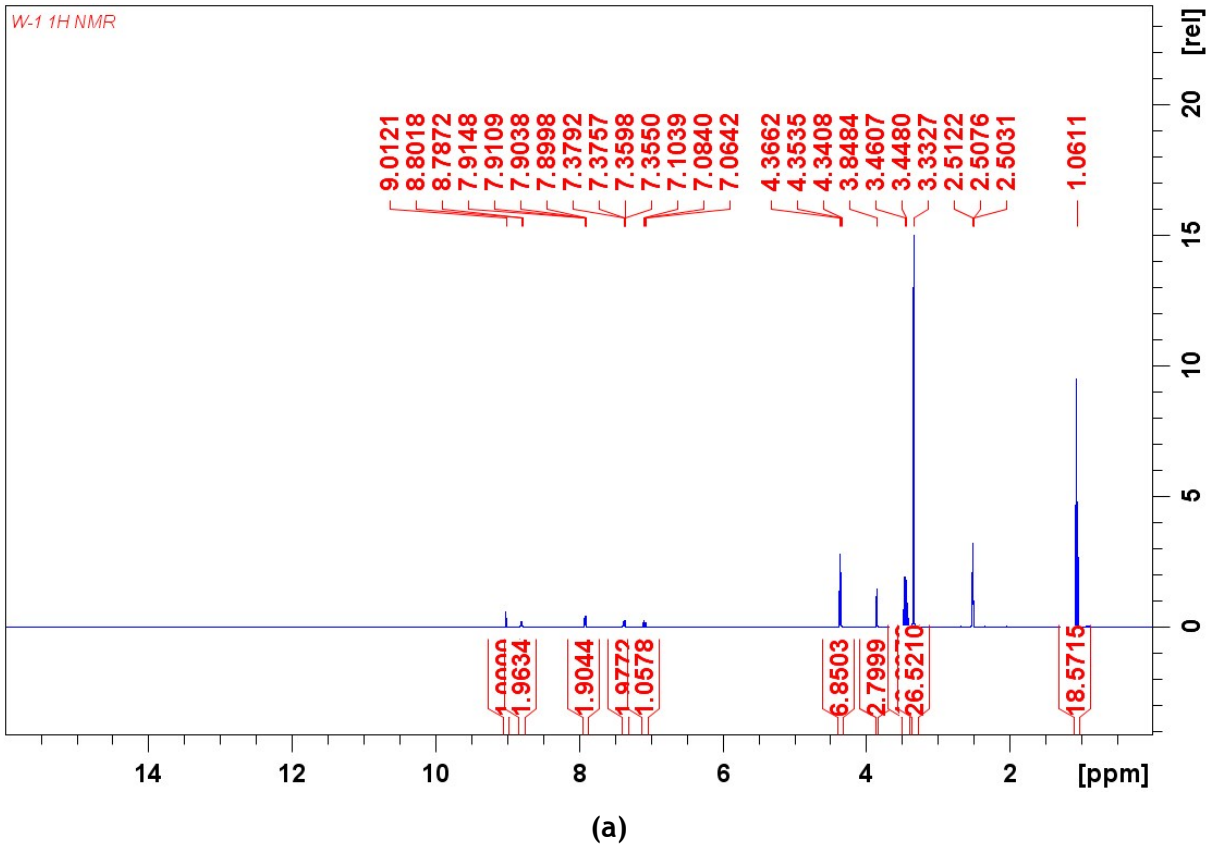
Table S5 ^{1}H and ^{13}C chemical shifts (ppm) of H_2L^{3OMe}, H_2L^{4OMe} and H_2L^{H}

Atom	H_2L^{3OMe}		H_2L^{4OMe}		H_2L^{H}	
	δ / ppm (^{1}H)	δ / ppm (^{13}C)	δ / ppm (^{1}H)	δ / ppm (^{13}C)	δ / ppm (^{1}H)	δ / ppm (^{13}C)
1	8.71	149.30	8.59	150.06	8.70	149.46
2	-	-	-	-	-	-
3	12.27	-	12.20	-	12.30	-
4	-	161.78	-	161.55	-	161.81
5	-	140.60	-	140.57	-	140.45
6	7.85	121.57	7.84	121.93	7.85	121.97
7	8.80	150.85	8.80	150.83	8.81	150.86
8	-	-	-	-	-	-
9	8.80		8.80	150.83	8.81	150.86
10	7.85	121.97	7.84	121.93	7.85	121.97
11	-	119.45	-	112.17	-	119.16
12	7.21	120.90	7.48	131.50	7.61	129.70
13	6.88	119.45	6.53	107.09	6.94	119.90
14	7.05	114.45	-	162.83	7.32	132.21
15	-	148.46	6.51	101.64	6.95	116.92
16	-	147.65	-	159.93	-	157.95
17	10.71	-	11.43	-	11.09	-
18	3.83	56.31	3.79	55.81	-	-

Table S6 ^{1}H and ^{13}C chemical shifts (ppm) of complexes **1a**−**3a** and **1b** −**3b**

Atom	**1a** and **1b**		**2a** and **2b**		**3a** and **3b**	
	δ / ppm (^{1}H)	δ / ppm (^{13}C)	δ / ppm (^{1}H)	δ / ppm (^{13}C)	δ / ppm (^{1}H)	δ / ppm (^{13}C)
1	9.01	159.64	8.91	159.03	9.04	159.62
2	-	-	-	-	-	-
3	-	-	-	-	-	-
4	-	167.30	-	165.98	-	167.28
5	-	137.51	-	137.62	-	137.50
6	7.91	122.05	7.88	121.92	7.97	122.06
7	8.80	151.19	8.77	151.12	8.79	151.18
8	-	-	-	-	-	-
9	8.80	151.19	8.77	151.12	8.79	151.18
10	7.91	122.05	7.88	121.92	7.91	122.06
11	-	121.18	-	114.32	-	120.94
12	7.36	126.18	7.70	136.51	7.80	135.35
13	7.08	122.39	6.74	110.42	7.14	122.55
14	7.36	118.58	-	166.62	7.64	136.53
15	-	149.75	6.66	104.54	7.06	120.06
16	-	148.40	-	160.91	-	158.76
17	-	-	-	-	-	-
18	3.85	56.48	3.86	56.48	-	-

* Signals belonging to EtOH and MeOH were also detected in ^{1}H NMR spectra in dmso solutions.



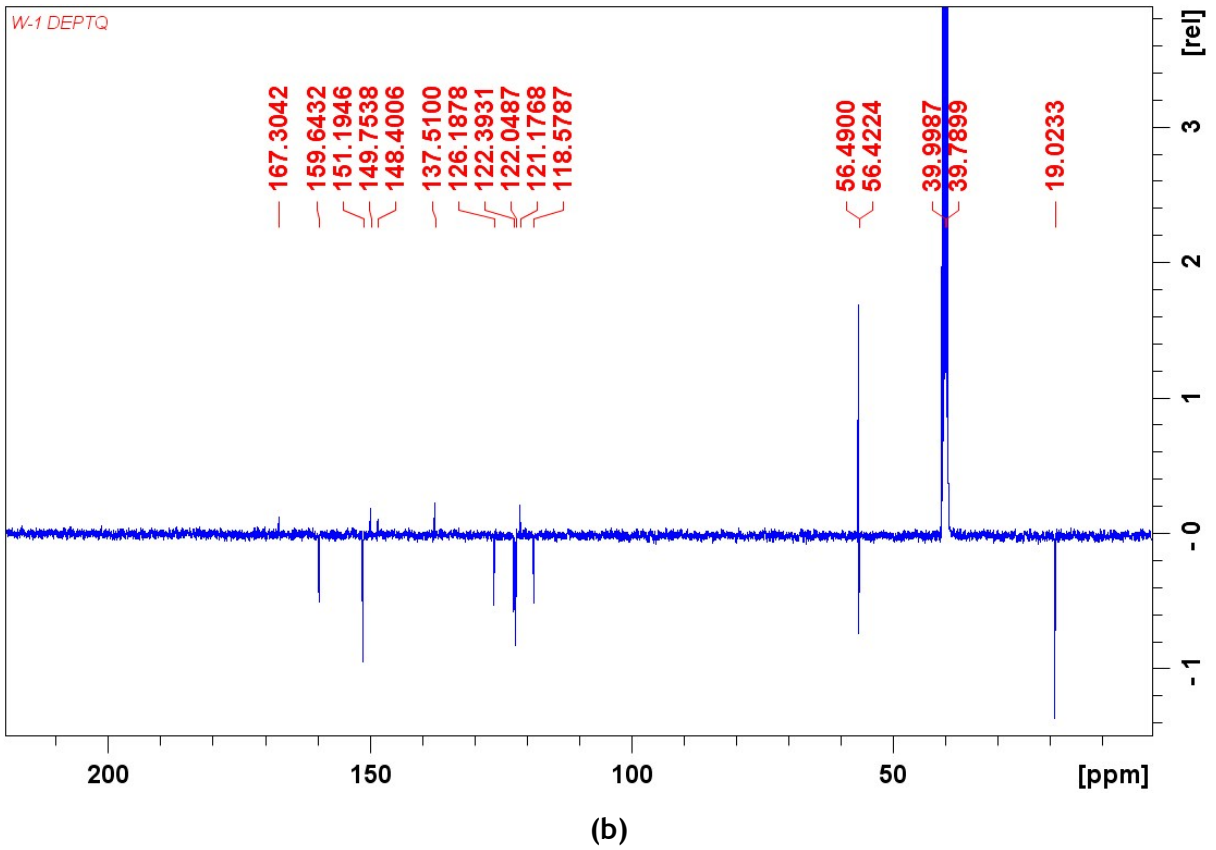
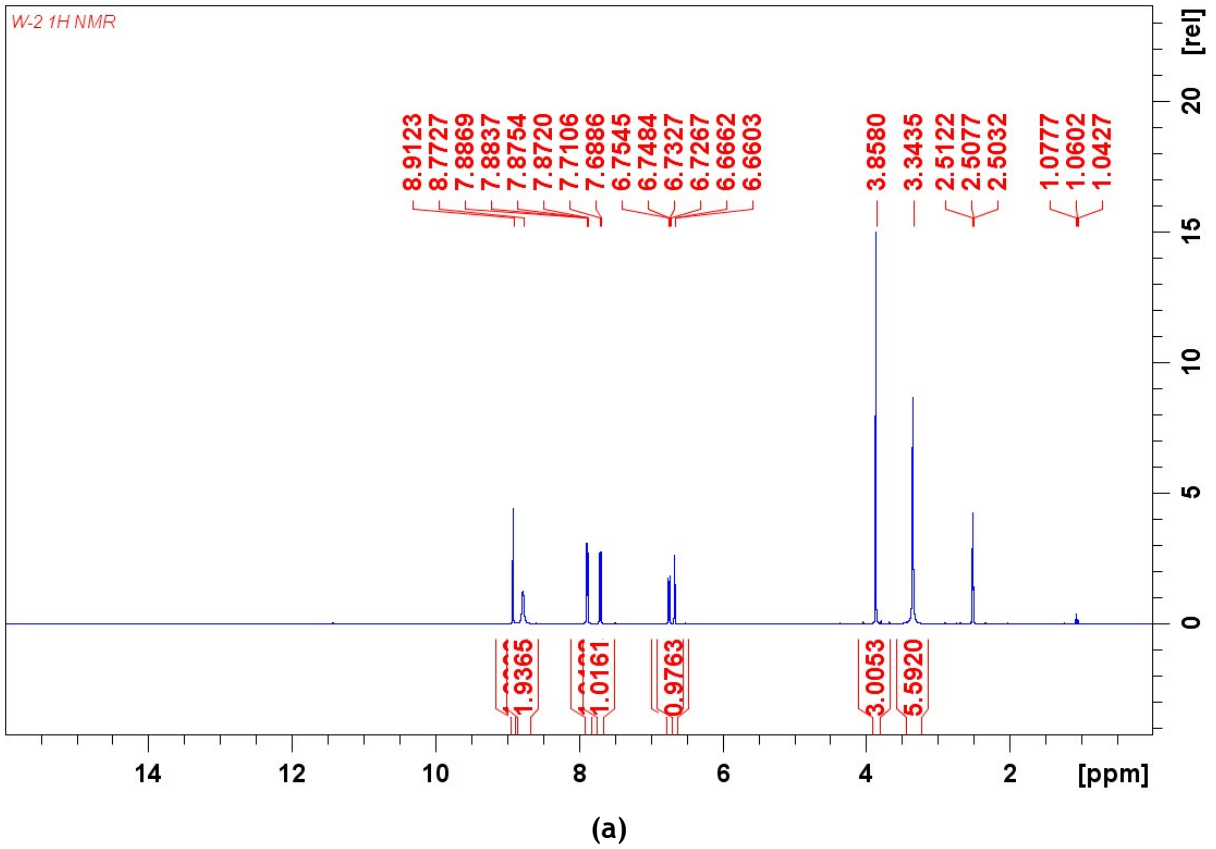
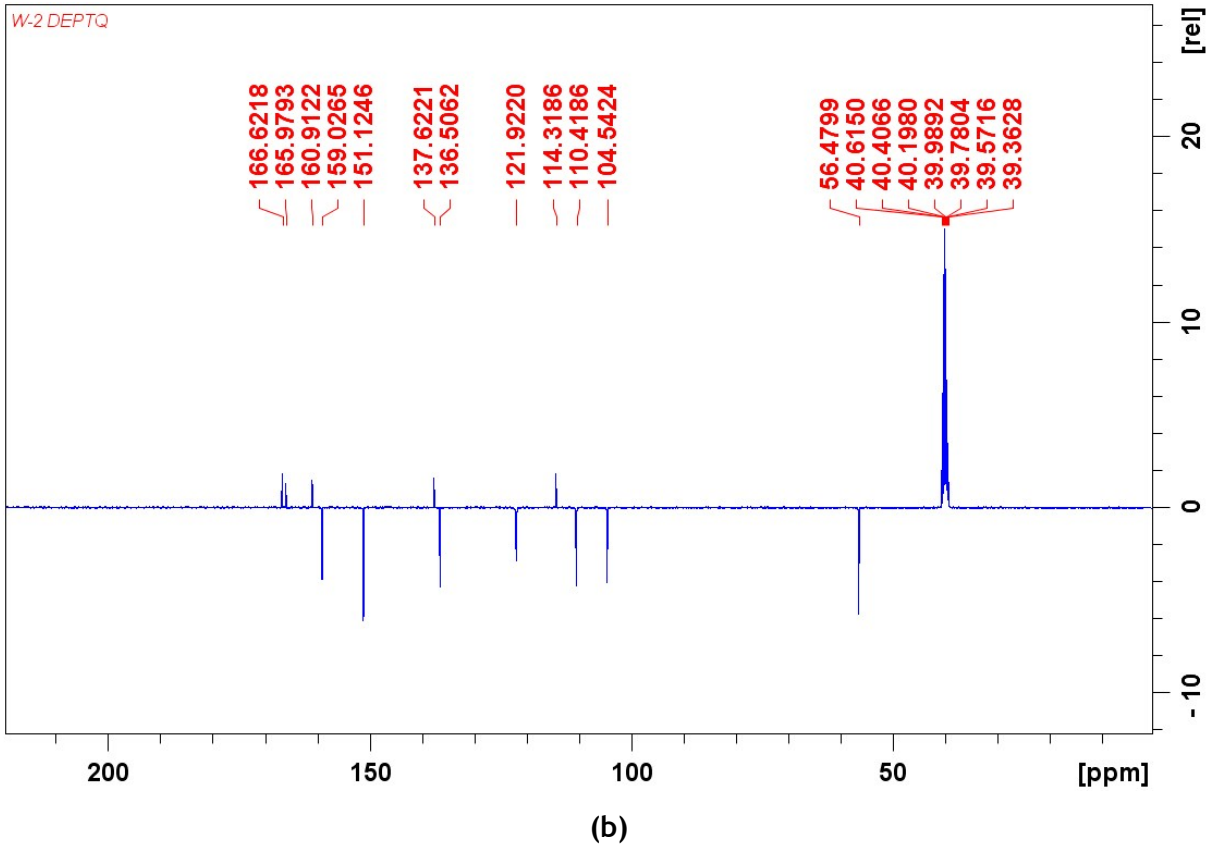


Fig S4 ^{1}H (a) and ^{13}C NMR (b) spectra of complex **1a** in DMSO-d_6

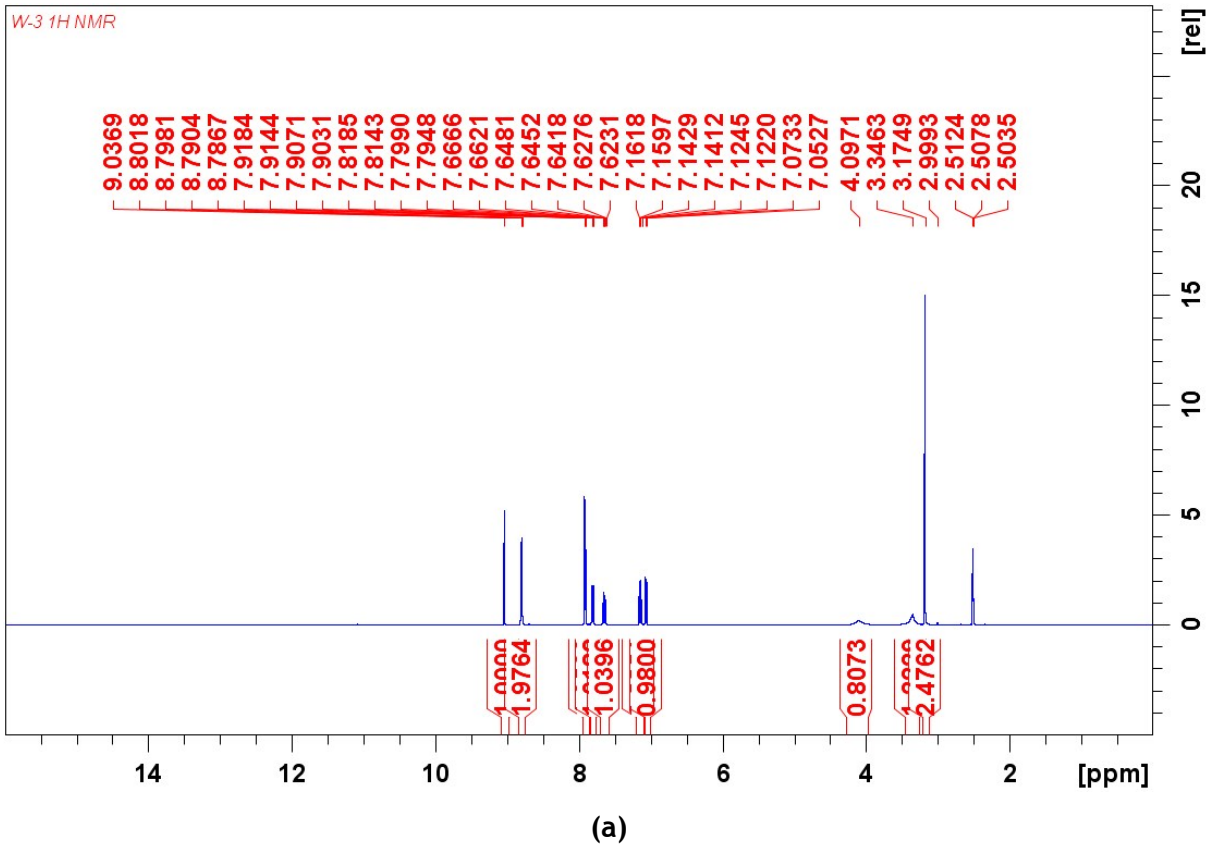


(a)



(b)

Fig S5 ^{1}H (a) and ^{13}C NMR (b) spectra of complex **2a** in DMSO-d_6



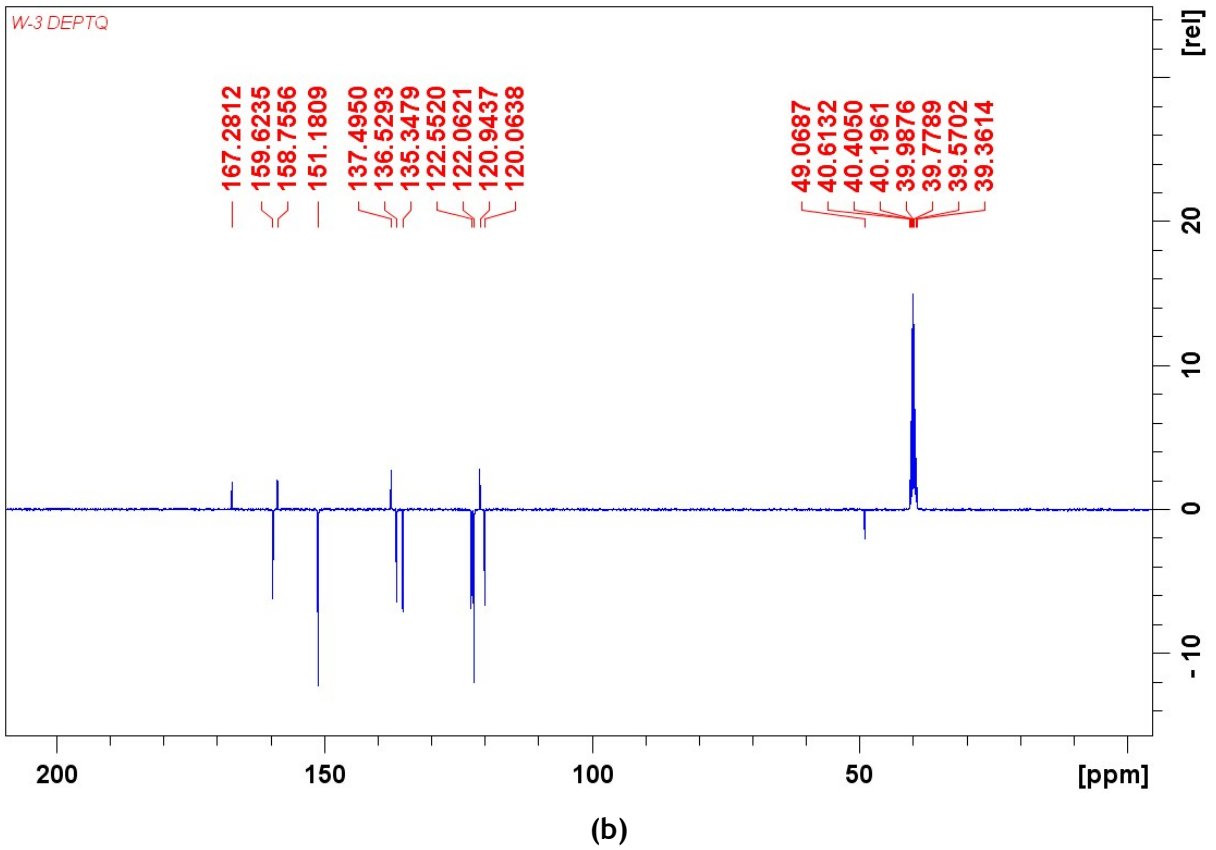


Fig S6 ^{1}H (a) and ^{13}C NMR (b) spectra of complex **3a** in DMSO-d_6

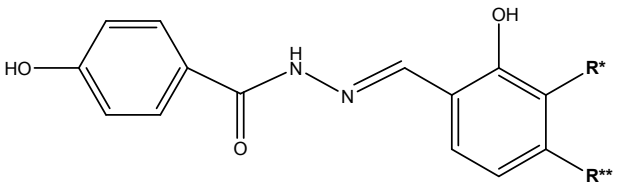
Table S7 Relevant catalytic results for the cyclooctene epoxidation by aqueous TBHP[a] taken from Ref.12**.**

*H_2L^{3OMe} is 3-methoxysalicylaldehyde 4-hydroxybenzhydrazone

**H_2L^{4OMe} is 4-methoxysalicylaldehyde 4-hydroxybenzhydrazone

Compound	Conversion[b]	TOF_{20min}[c]/h^{-1}	TON[d]
$[WO_2(L^{3OMe*})(EtOH)]$	17	190	70
$[WO_2(L^{4OMe*})(EtOH)]$	31	260	128

[a] Reaction conditions: time, 5 h; temperature, 80 °C; [W]/cyclooctene/TBHP molar ratio: 0.25/100/200 for all compounds. [b] For cyclooctene, calculated after 5 h. [c]*n*(cyclooctene transformed)/*n*(catalyst)/time at 20 minutes. [d]*n*(cyclooctene transformed)/n(catalyst at 5 h).



R*	R**	
OCH_3	H	H_2L^{3OMe}
H	OCH_3	H_2L^{4OMe}

Scheme S2 The structural formula of ligands H_2L taken from Ref.12.