Electronic supporting information

Catalytic oxidation of tetralin by dioxomolybdenum complexes: design, synthesis, characterization and DFT investigations

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Experimental section

Crystal structure determination

Single crystals of complexes **1a, 2a** and **4a** appropriate for diffraction studies were grown in DMSO solvent. Suitable crystals were selected and mounted on the goniometer in a nylon loop on a Rigaku XtaLAB Synergy, Dualflex, HyPix3000 diffractometer. The data were corrected for Lorentz and polarization effects and multi-scan absorption correction was applied. Using Olex^2 [1], the structures were solved with the SHELXT[2] structure solution program using Intrinsic Phasing and refined with the SHELXL[3] refinement package using Least Squares minimization. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined with isotropic displacement parameters. All hydrogen atoms on carbon were fixed geometrically with U_{iso} values of 1.2 and 1.5 times the U_{iso} values of phenylene and methyl carbons and the hydrogen on phenolic oxygen and water molecule were located from difference fourier map and refined with fixed distances (0.85 Å) with U_{iso} values of 1.5 times the U_{iso} values of their carrier atoms. CCDC 2494735, 2494733, and 2494734 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/structures. The CIF, report and molecular graphics were generated using Olex^2 crystallographic suite. Table S1 shows the crystal data and structural refinement parameters for the compounds. Tables S2 and S3 provide a summary of the selected bond lengths and bond angles, respectively.

Table S1 Crystal data and structure refinement for complexes **1a**, **2a** and **4a**.

Identification code	Complex 1a	Complex 2a	Complex 4a
Empirical formula	$C_{18}H_{20}MoN_2O_7S$	$C_{19}H_{22}MoN_2O_8S$	$C_{18}H_{19}ClMoN_2O_7S$
Formula weight	504.36	534.38	538.80

Temperature/K	293	293	293
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/c$	P-1
a/Å	8.57400(10)	9.21100(10)	8.4494(2)
b/Å	16.43340(10)	8.01890(10)	11.4162(3)
c/Å	14.39460(10)	29.0172(2)	12.3491(3)
α/°	90	90	65.537(2)
β/°	93.9080(10)	93.2880(10)	79.809(2)
γ/°	90	90	83.735(2)
Volume/Å^3	2023.48(3)	2139.74(4)	1066.30(5)
Z	4	4	2
ρ_{calc}g/cm^3	1.656	1.659	1.678
μ/mm^{-1}	6.657	6.369	7.487
F(000)	1024.0	1088.0	544.0
Crystal size/mm^3	0.3 × 0.2 × 0.16	0.28 × 0.22 × 0.16	0.32 × 0.24 × 0.18
Radiation	Cu/K_α (λ = 1.54184)	Cu/K_α (λ = 1.54184)	Cu/K_α (λ = 1.54184)
2θ range/°	8.176 to 136.178	6.102 to 136.14	7.95 to 136.176
Index ranges	$-9 \le h \le 10$, $-19 \le k \le 19$, $-17 \le l \le 16$	$-11 \le h \le 11$, $-9 \le k \le 9$, $-24 \le l \le 34$	$-10 \le h \le 10$, $-13 \le k \le 13$, $-14 \le l \le 14$
Reflections collected	28038	21524	20146
Independent reflections	3692 (R_{int} = 0.0347)	3882 (R_{int} = 0.0312)	3872 (R_{int} = 0.0415)
Data/restraints/parameters	3692/86/285	3882/0/286	3872/0/276
Goodness-of-fit on F^2	1.048	1.060	1.053
Final R indexes [I ≥ 2σ (I)]	R_1 = 0.0214, wR_2 = 0.0570	R_1 = 0.0246, wR_2 = 0.0634	R_1 = 0.0291, wR_2 = 0.0783
Final R indexes [all data]	R_1 = 0.0229, wR_2 = 0.0579	R_1 = 0.0284, wR_2 = 0.0654	R_1 = 0.0302, wR_2 = 0.0793
Largest diff. peak/hole/e Å^{-3}	0.31/-0.35	0.27/-0.43	0.76/-0.65
CCDC No.	**2494735**	**2494733**	**2494734**

Table S2 Selected bond lengths for Complex **1a**, **2a** and **4a**.

Bond Length [A^0]		**Complex 1a**		**Complex 2a**		**Complex 4a**	
		Obs.	**Calc.**	**Obs.**	**Calc.**	**Obs.**	**Calc.**
Mo1	O1	1.9998(14)	1.963	2.0218(15)	2.0012	1.9917(18)	1.9569
Mo1	O2	1.9314(15)	1.9339	1.9385(16)	2.1399	1.9236(18)	1.9464
Mo1	O3	1.7060(16)	1.7172	1.7062(16)	1.7349	1.7019(19)	1.716
Mo1	O4	1.6928(16)	1.7151	1.6987(18)	1.7294	1.697(2)	1.716
Mo1	O5	2.3061(15)	2.9123	2.2932(17)	2.9206	2.2806(17)	2.925
Mo1	N1	2.2363(17)	1.9411	2.2223(17)	1.8793	2.245(2)	1.9672
O1	C9	1.326(2)	1.4678	1.327(3)	1.4987	1.335(3)	1.4467
O2	C12	1.347(3)	1.4472	1.351(3)	1.5708	1.347(3)	1.4385
N1	N2	1.395(2)	1.385	1.395(2)	1.323	1.401(3)	1.3872
N1	C10	1.285(3)	1.2792	1.291(3)	1.1044	1.279(3)	1.2878
N2	C9	1.297(3)	1.319	1.299(3)	1.4677	1.297(3)	1.298
O6	C3	1.363(3)	1.4293	1.367(3)	1.4343	1.366(3)	1.43
O7	C4	1.360(2)	1.4312	1.358(3)	1.4504	1.360(3)	1.43
O8	C13	-	-	1.364(3)	1.4284	-	-
O8	C14	-	-	-	-	-	-

Table S3 Selected bond angles for Complex **1a**, **2a** and **4a**.

Bond angle [^{0}]	Complex 1a		Complex 2a		Complex 4a	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
O(1)- Mo(1)- O(5)	80.34(6)	-	81.51(6)	122.109	80.05(7)	92.7363
O(1)- Mo(1)- N(1)	71.70(6)	81.9344	71.77(6)	69.8006	71.64(7)	80.01
O(2)- Mo(1)- O(1)	151.07(6)	94.1327	149.97(7)	110.0503	149.48(8)	-
O(2)- Mo(1)- O(5)	80.82(6)	85.8013	80.12(6)	73.1095	79.30(7)	91.7612
O(2)- Mo(1)- N(1)	82.47(6)	87.0462	81.64(6)	82.7126	82.28(7)	95.6075
O(3)- Mo(1)- O(1)	96.22(7)	89.2277	95.00(7)	68.7996	96.61(9)	90.5282
O(3)- Mo(1)- O(2)	103.84(7)	-	106.25(8)	143.3591	103.54(9)	85.7917
O(3)- Mo(1)- O(5)	85.13(7)	90.8507	83.50(7)	77.3309	84.61(8)	89.8699
O(3)- Mo(1)- N(1)	158.64(7)	90.1299	159.78(8)	126.5268	160.48(9)	92.1657
O(4)- Mo(1)- O(1)	96.95(7)	96.8552	97.40(8)	133.8676	97.52(9)	93.3196
O(4)- Mo(1)- O(2)	97.21(8)	95.2166	97.11(8)	107.1484	99.14(9)	90.5705
O(4)- Mo(1)- O(3)	106.19(8)	87.68	105.40(9)	95.9694	104.86(10)	-
O(4)- Mo(1)- O(5)	168.62(7)	82.9389	171.09(7)	77.3309	170.48(9)	87.3744
O(4)- Mo(1)- N(1)	92.99(7)	-	91.72(8)	89.1751	92.36(9)	91.0406
N(1)- Mo(1)- O(5)	75.65(6)	98.2747	79.52(6)	155.4912	78.13(7)	-

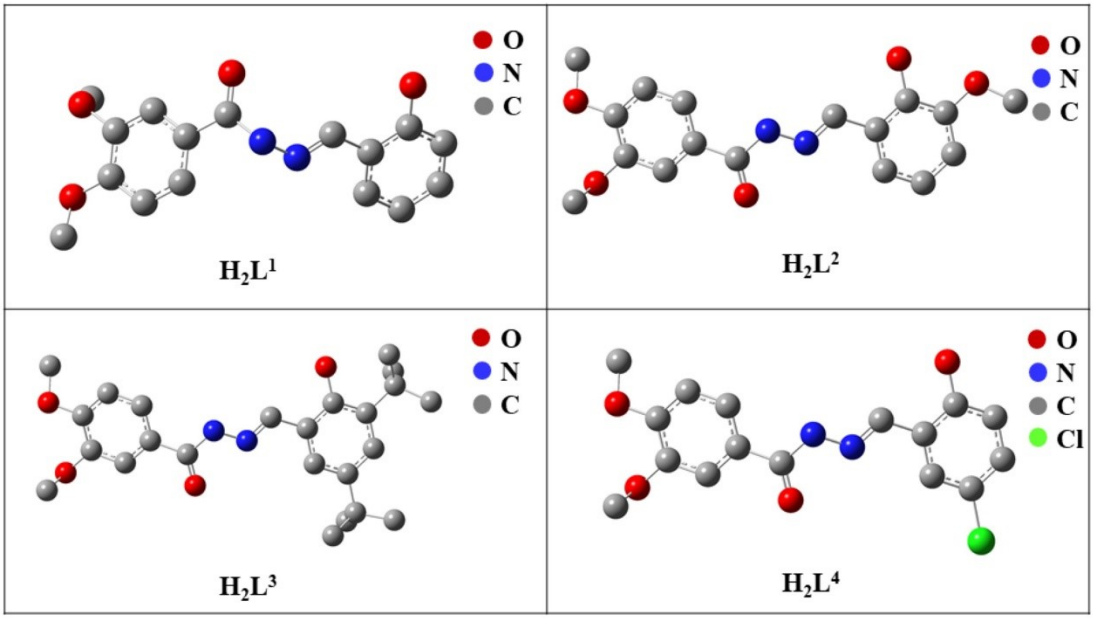


Fig. S1 Geometry optimised structure of the ligands.

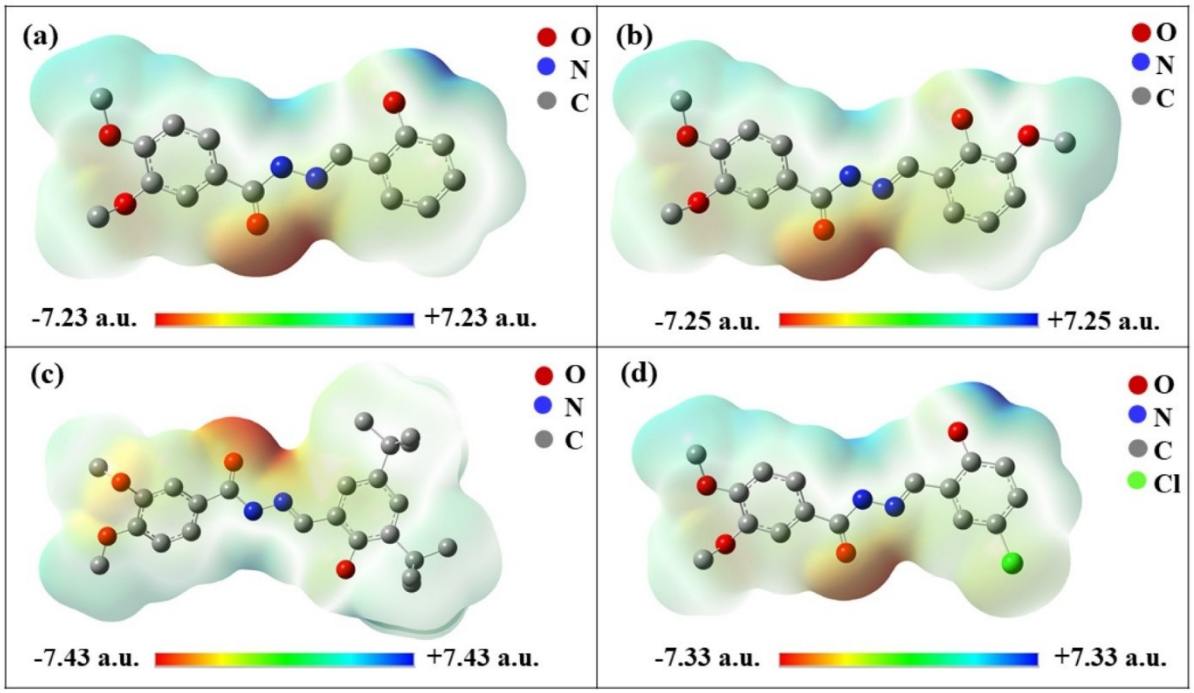


Fig. S2 The MEP maps of ligands (a) H_2L^1, (b) H_2L^2, (c) H_2L^3, (d) H_2L^4

Table S4 The stretching frequency (in cm^{-1}) values for ligands and their complexes.

Compound	ν(N-H)		ν(C=O)		ν(C=N)		ν(Mo-N)		ν(Mo-O)		$\nu_{asymm.}$ (O=M=O)		$\nu_{symm.}$ (O=M=O)	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
H_2L_1	3245	3225	1664	1652	1637	1628	-	-	-	-	-	-	-	-
H_2L_2	3256	3212	1666	1652	1640	1648	-	-	-	-	-	-	-	-
H_2L_3	3249	3225	1661	1671	1632	1628	-	-	-	-	-	-	-	-
H_2L_4	3251	3247	1659	1659	1631	1610	-	-	-	-	-	-	-	-
$[MoO_2L^1.H_2O]$ **1**	-	-	-	-	1605	1631	488	490	564	570	943	944	907	927
$[MoO_2L^2.H_2O]$ **2**	-	-	-	-	1606	1641	471	477	576	580	950	947	903	926
$[MoO_2L^3.H_2O]$ **3**	-	-	-	-	1606	1611	470	480	575	577	950	941	910	913
$[MoO_2L^4.H_2O]$ **4**	-	-	-	-	1600	1618	473	476	577	580	943	952	906	907

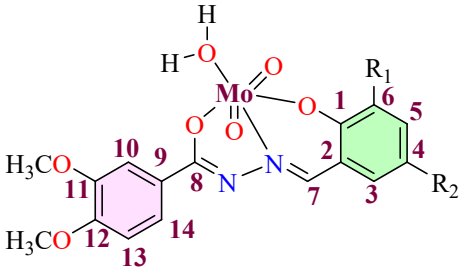
Table S5 UV-Visible data of the synthesized complexes.

S.No.	Compounds	λ_{max}/nm (ε/M^{-1} cm^{-1})
1	H_2L^1	301 (386), 327 (353)
2	H_2L^2	300 (381), 329 (547)
3	H_2L^3	307 (486), 339 (459)
4	H_2L^4	302(365), 312(356), 359(194)
5	$[MoO_2L^1.H_2O]$ **1**	273(427), 327(534), 411(181)
6	$[MoO_2L^2.H_2O]$ **2**	275 (318), 330(441), 416(144)
7	$[MoO_2L^3.H_2O]$ **3**	273(419), 328(304), 419(125)
8	$[MoO_2L^4.H_2O]$ **4**	262(404), 346(544), 442 (113)

Table S6 The chemical shifts(δ) values in ppm of the ligands and their complexes as determined by ^{1}H NMR in DMSO-d_6.

Compounds	Phenolic (–OH)	–NH	–CH=N–	Aromatic protons
H_2L^1	12.06 (1H, Br)	11.36 (1H, s)	8.56 (1H, s)	7.49- 7.54 (3H, m), 7.44 (1H, s), 7.27- 7.31 (1H, t), 7.04 -7.07 (1H, d), 6.89 -6.93 (1H, t), 3.79(6H, s)
H_2L^2	11.96 (1H, Br)	11.06 (1H, s)	8.64 (1H, s)	7.57- 7.59 (1H, d), 7.51 (1H, s), 7.08-7.14 (2H, q), 7.02-7.04 (1H, d), 6.84- 6.88 (1H, t), 3.84 (3H, s), 3.81 (3H, s), 3.17 (3H, s)
H_2L^3	12.29 (1H, Br)	12.06 (1H, s)	8.57 (1H, s)	7.57- 7.59 (1H, d), 7.50 (1H, s), 7.31(1H, s), 7.21 (1H, s), 7.11-7.13 (1H, d), 3.84 (3H, s), 1.41 (9H, s), 1.28 (9H, s)
H_2L^4	12.00 (1H, Br)	10.60 (1H, s)	8.49 (1H, s)	7.51- 7.54 (1H, d),7.44 (1H, s), 7.03-7.05 (1H, d), 6.95 (1H, s), 6.73 (2H, s), 3.78 (6H, s)
$[MoO_2(L^1).H_2O]$ 1	-	-	8.94 (1H, s)	7.71- 7.74 (1H, d), 7.60-7.63 (1H, d), 7.51-7.55 (2H, t), 7.07-7.11 (2H, t), 6.94-6.96 (1H, dd), 3.84 (3H, s), 3.83 (3H, s)
$[MoO_2(L^2).H_2O]$ 2	-	-	8.89 (1H, s)	7.59- 7.61 (1H, d), 7.49 (1H, s), 7.21-7.29 (2H, q), 7.01-7.09 (2H, t), 4.17 (3H, s), 3.82 (3H, s), 3.16 (3H, s)
$[MoO_2(L^3).H_2O]$ 3	-	-	8.90 (1H, s)	7.59-7.61 (2H, d), 7.48 (2H, s), 7.07-7.09 (1H, d), 3.83 (3H, s), 3.82 (3H, s), 1.35 (9H, s), 1.29 (9H, s)
$[MoO_2(L^4).H_2O]$ 4	-	-	8.91 (1H, s)	7.82 (1H, d), 7.62-7.63 (1H, s), 7.54-7.55 (2H, d), 7.08-7.10 (1H, s), 6.98-7.00 (1H, d), 3.84 (3H, s), 3.83 (3H, s)

Table S7 ^{13}C-NMR chemical shift for ligands and their complexes recorded in DMSO-d_6.



Group	Complex
R_1=R_2=H	1
R_1=OCH_3,R_2=H	2
R_1=R_2=tert but	3
R_1=H, R_2=Cl	4

Compounds	C1	C7	C8	Carbon values
H_2L^1	163.95	152.75	158.04	149.32, 149.13, 132.53, 130.61, 125.16, 122.10, 120.51, 119.26, 117.24, 111.87, 111.29
H_2L^2	162.44	148.51	152.03	148.03, 147.79, 147.19, 124.87,

				121.20, 120.91, 119.17, 119.04 113.78, 111.16, 110.90, 55.89, 55.78, 48.71
H_2L^3	185.13	167.27	175.38	158.22, 155.12, 151.22, 149.20, 145.48, 141.67, 140.88, 136.11, 126.12, 121.59, 111.57, 50.17, 36.13, 34.34, 31.76, 31.16
H_2L^4	163.84	150.92	152.61	150.30, 149.01, 148.46, 125.15, 121.99, 119.86, 119.61, 117.93, 114.85, 111.73, 111.18, 56.34, 56.24
$[MoO_2(L^1).H_2O]$ 1	168.75	155.15	159.31	152.18, 148.59, 134.82, 134.20, 122.05, 121.96, 121.71, 120.49, 118.59, 111.48, 110.40, 55.73, 55.55, 48.70
$[MoO_2(L^2).H_2O]$ 2	156.45	148.49	155.25	148.01, 147.49, 147.09, 133.14, 122.05, 120.81, 119.16, 118.05, 113.46, 111.08, 110.49, 55.82, 54.82, 48.79
$[MoO_2(L^3).H_2O]$ 3	179.25	148.93	152.45	137.92, 129.35, 111.85, 110.79, 103.00, 55.93, 36.39, 34.57, 31.59, 31.16
$[MoO_2(L^4).H_2O]$ 4	169.34	154.06	158.10	152.40, 148.65, 134.06, 132.75, 124.97, 122.19, 121.93, 121.87, 120.60, 111.53, 110.51, 55.77, 55.60

Powder X-ray studies

P-XRD analyses of complexes **1**, **2**, and **4** were performed to assess their bulk phase purity, with the experimental patterns equated with the simulated pattern resultant from SC-XRD data. The strong agreement between the experimental and simulated patterns verifies that the bulk materials possess the same crystalline phases as those determined by single-crystal analysis (Fig. S3, ESI). This consistency confirms that the single-crystal structures are representative of the overall bulk composition. The relative diffraction profiles of all complexes are presented in Fig. S3(ESI).

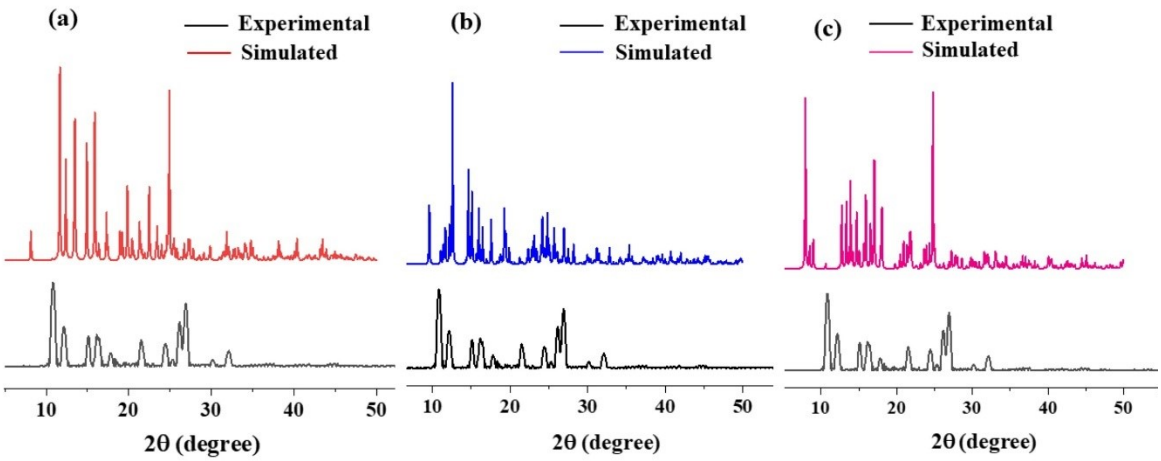


Fig. S3 P-XRD patterns of complexes (a) **1**, (b) **2** and (c) **4**.

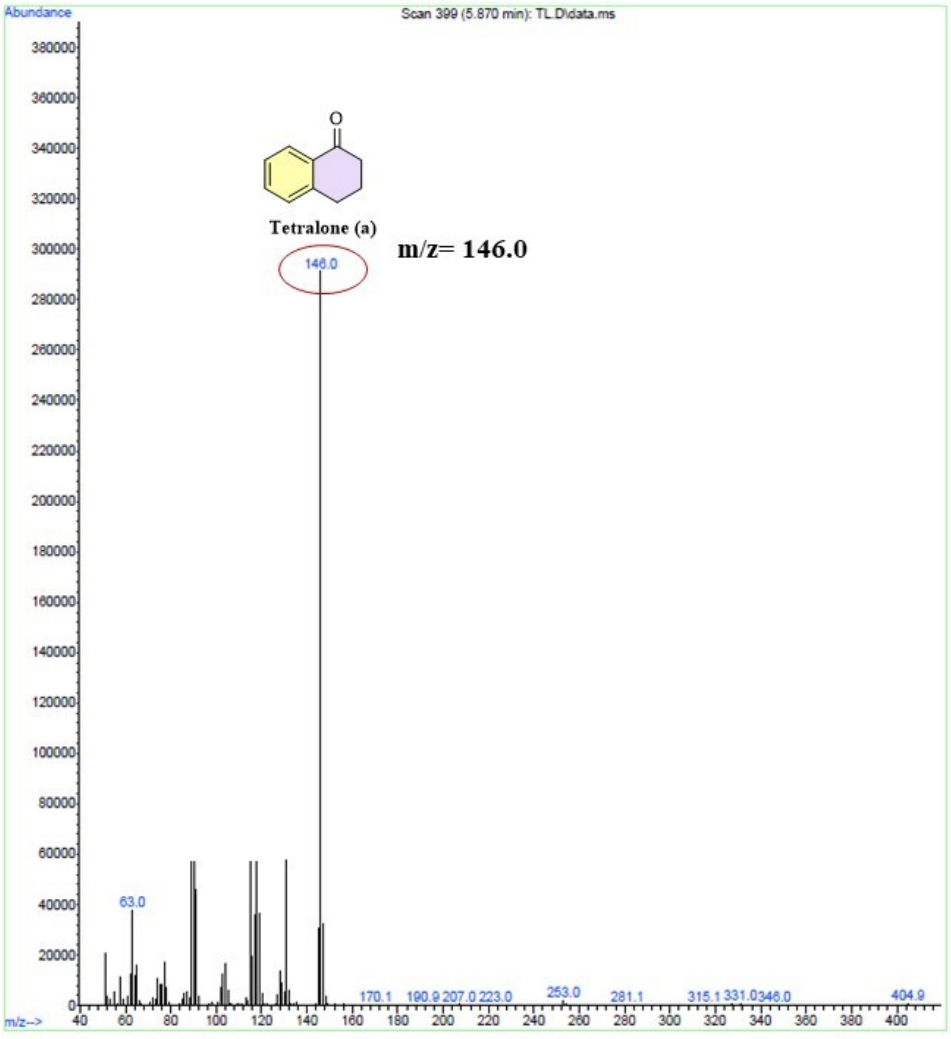


Fig. S4 GC-MS chromatogram of oxidized product tetralone (a).

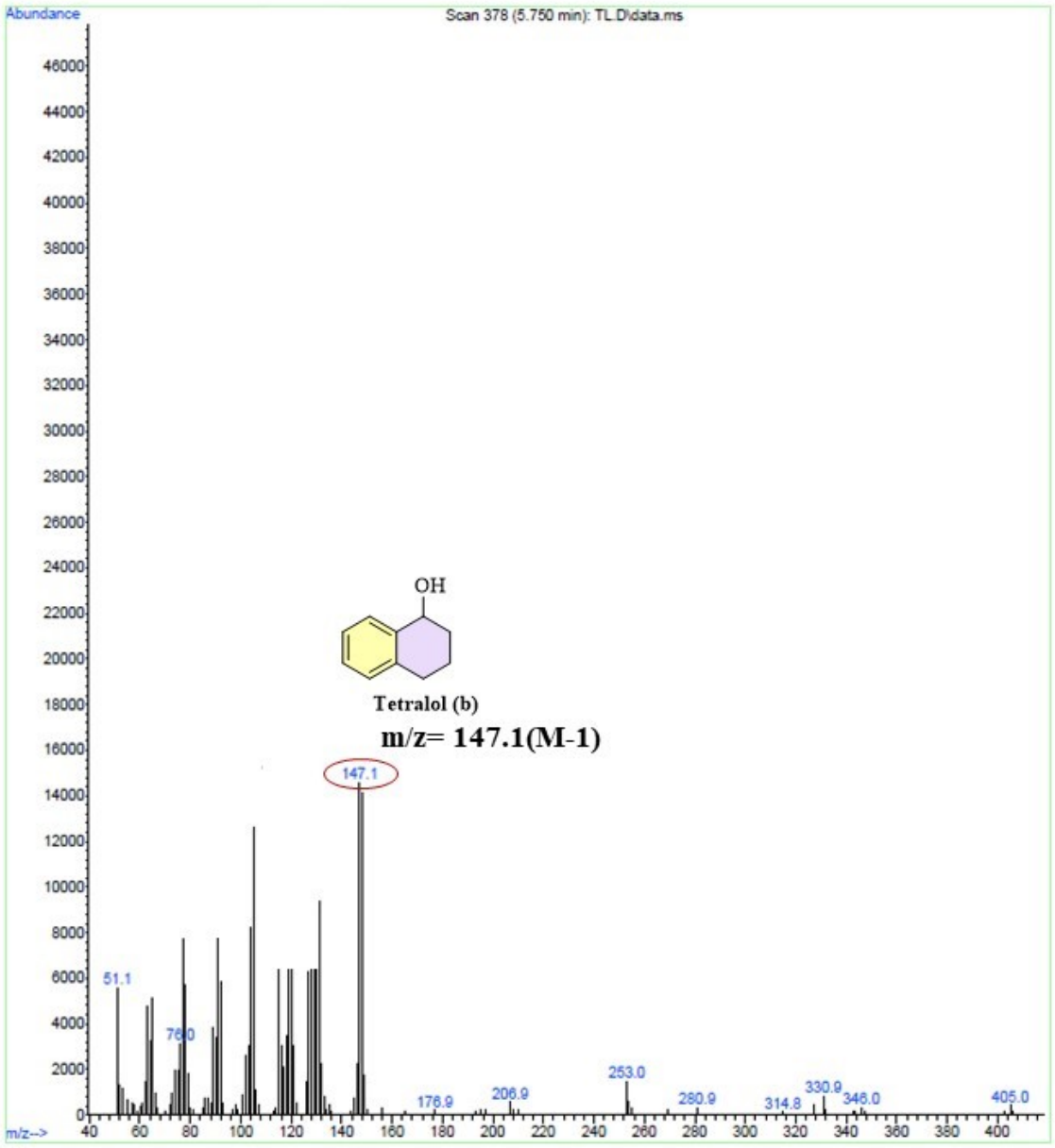


Fig. S5 GC-MS chromatogram of oxidized product tetralol (b).

References

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. AK. Howard and H. Puschmann, *OLEX2*: a complete structure solution, refinement and analysis program, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.
2. G. M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Cryst.*, 2015, **A71**, 3–8.

3. G.M. Sheldrick, Crystal Structure Refinement with SHELXL. *Acta Crystallogr., Sect. C: Struct. Chem*, 2015, **71**, 3–8.