Supplementary Materials

Alcohol Oxidation Assisted by Molybdenum Hydrazonato Catalysts Employing Hydroperoxide Oxidants

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Table of content :

Crystal and molecular structure of $[MoO_2(L^3)]_n \cdot H_2O$

Table S1. Selected bond lengths (Å) and angles (°) for **3·H₂O.**

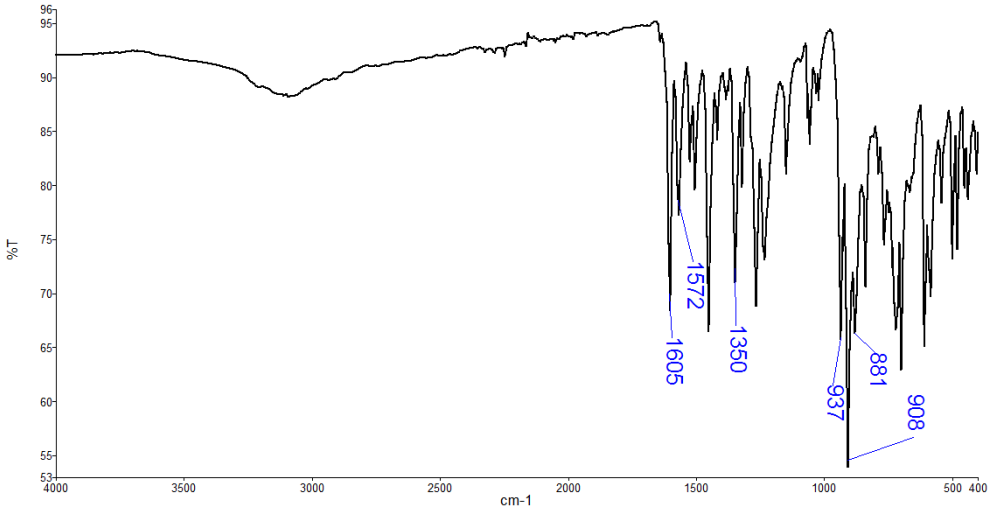
	bond lengths (Å)
Mo1–O1	1.723(2)
Mo1–O2	1.694(2)
Mo1–O3	1.933(2)
Mo1–O4	2.019(2)
Mo1–N1	2.219(2)
Mo1–N3	2.427(2)
C1–N1	1.294(4)
C2–N2	1.291(4)
N1–N2	1.395(3)
	angles (°)
O1–Mo1–O2	106.3(1)
O1–Mo1–O3	105.13(9)
O1–Mo1–O4	95.32(9)
O1–Mo1–N1	160.93(9)
O1–Mo1–N3	83.69(9)
O2–Mo1–O3	97.60(9)
O2–Mo1–O4	99.33(9)
O2–Mo1–N1	90.05(9)
O2–Mo1–N3	169.96(9)
O3–Mo1–O4	148.51(8)
O3–Mo1–N1	81.71(8)
O3–Mo1–N3	80.22(8)
O4–Mo1–N1	71.94(8)
O4–Mo1–N3	78.50(8)
N1–Mo1–N3	79.94(8)

Table S2. Geometry of intermolecular hydrogen bonds (Å, °) for $[MoO_2(L)]_n \cdot H_2O$ **(3·H₂O)**

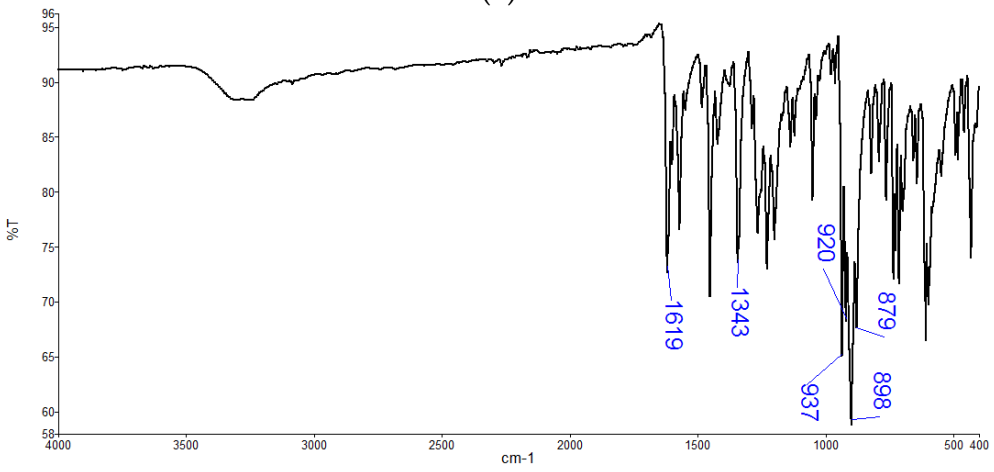
D–H···A	D–H / Å	H···A / Å	D···A / Å	D–H···A /°
O5–H5···O1[a]	0.84	1.93	2.770(3)	175.5
C12–H12···N2[b]	0.95	2.40	3.311(4)	160.6
C1–H1···O5[c]	0.95	2.65	3.368(4)	132.3

[a] x,1/2-y,1/2+z; [b]-x-1/2, y-1/2, z; [c]-x-1/2, y+1/2, z

IR-ATR spectra of $[MoO_2(L^{1-4})]_n$



(a)



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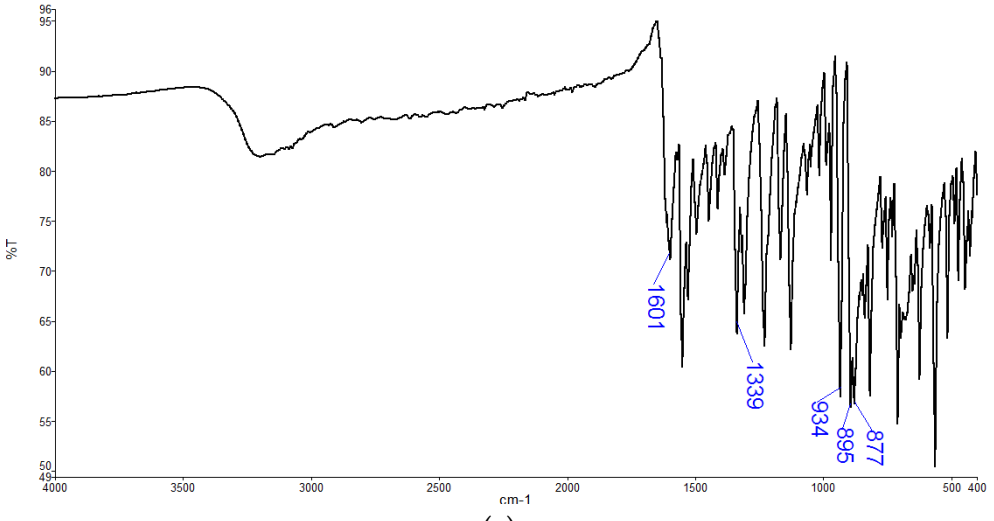
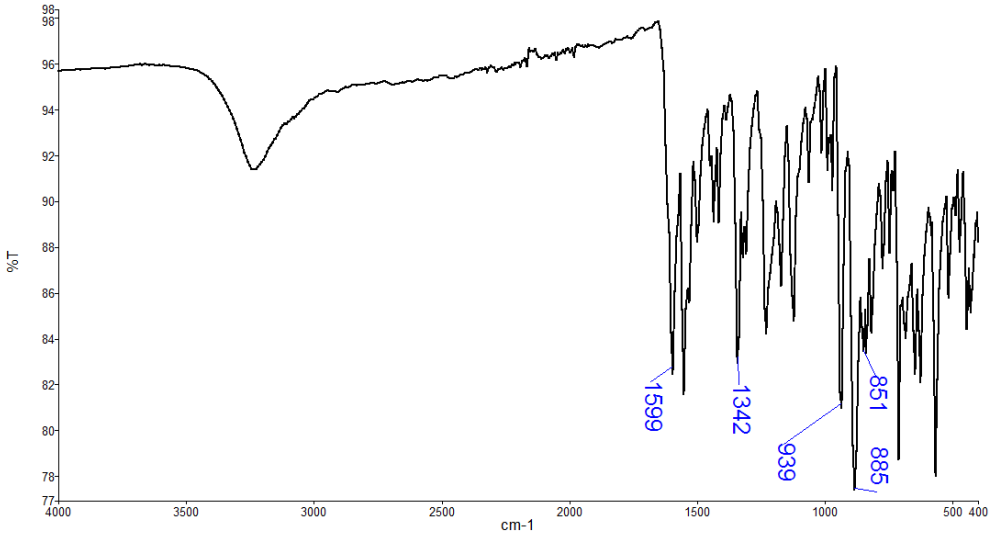
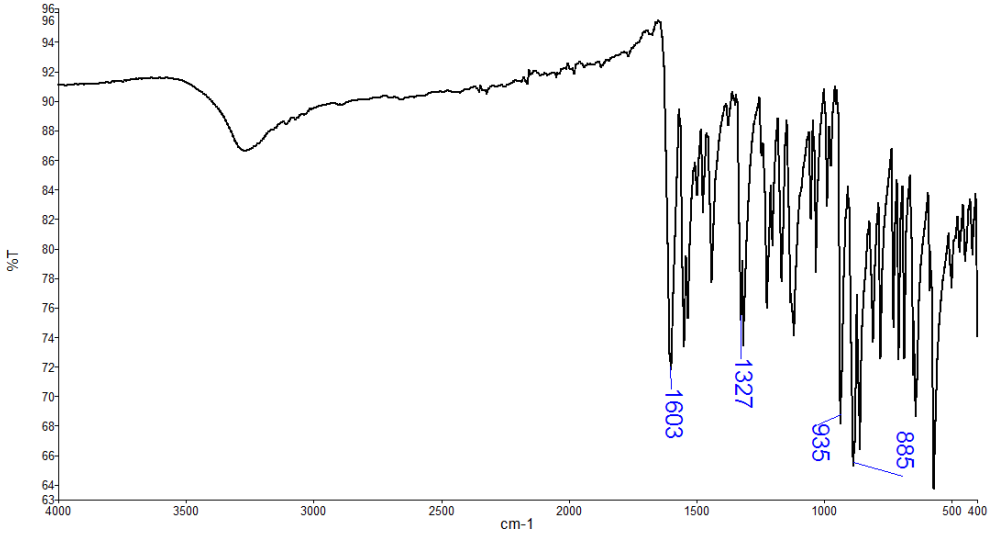


(c)



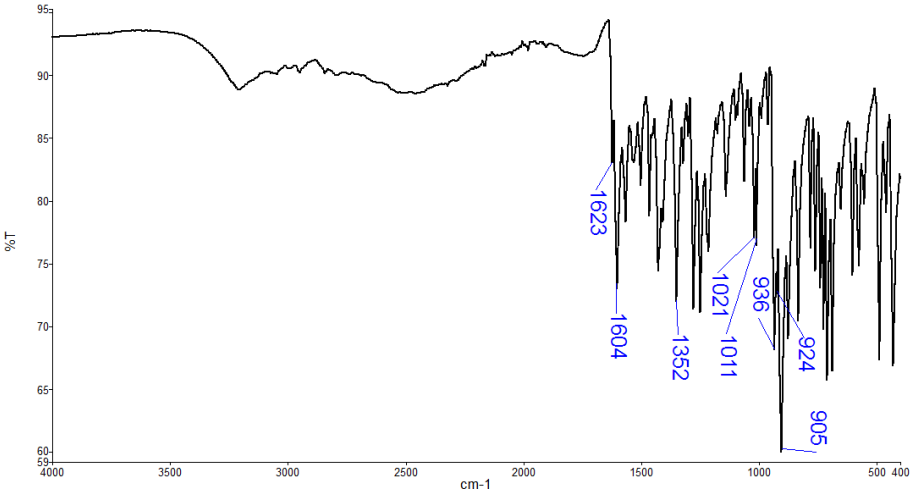
(d)



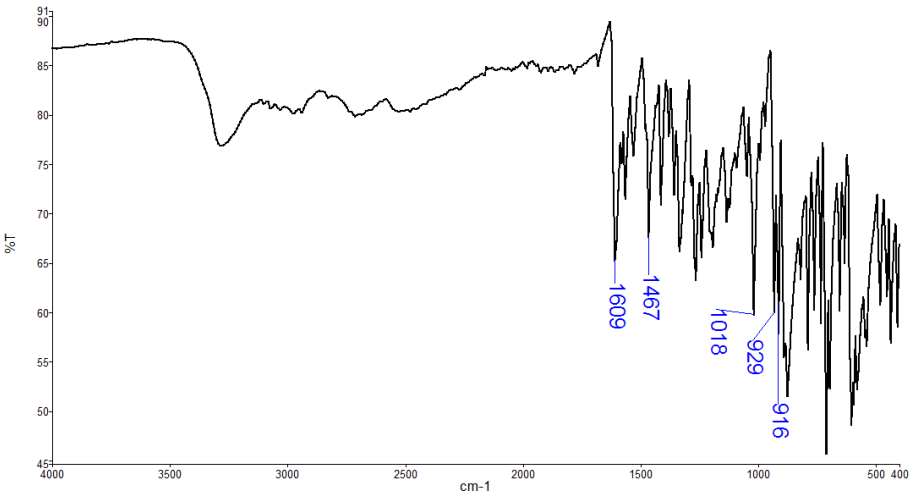
(e)

Figure S1. IR-ATR spectra of polymers (a) **1**, (b) **2**, (c) **3**, (d) **3**·H_2O, and (e) **4**.

IR-ATR spectra of [$MoO_2(L^{1-4})(MeOH)$]



(a)



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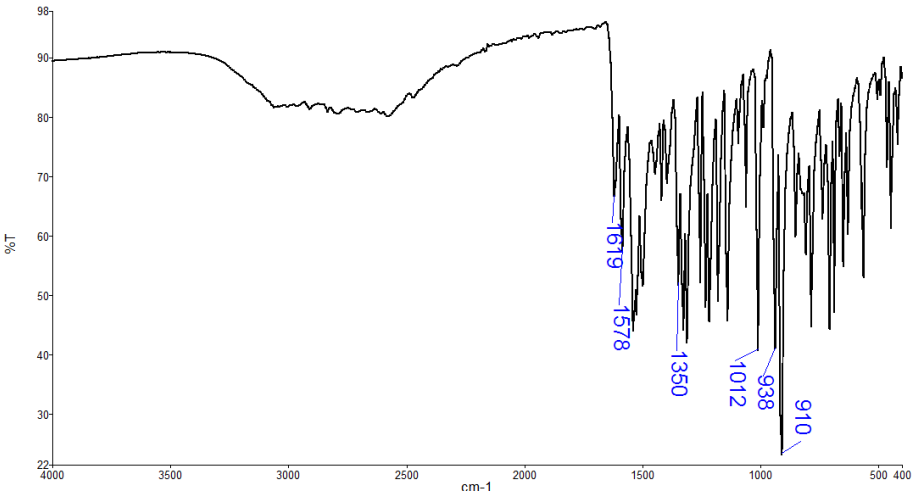

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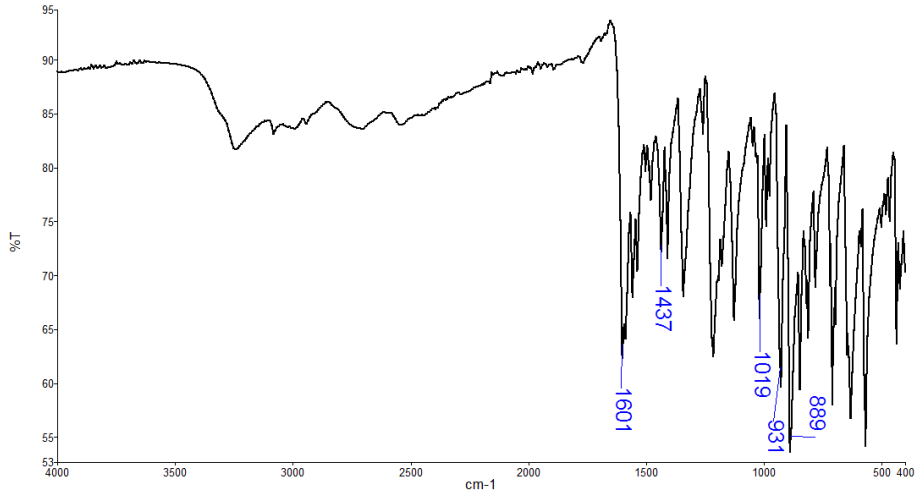
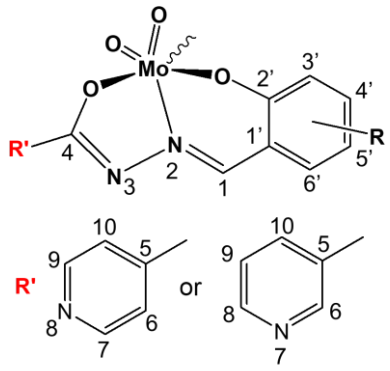


(d)

Figure S2. IR-ATR spectra of **1a**, **2a**, **3a** and **4a** (from top to bottom).

NMR spectroscopy of $[MoO_2(L)]_n$



3′-OH	1	3
4′-OH	2	4

The **Table S3**, **S4**, **Figure S1** and **S2** are according to the scheme and numeration used above.

Table S3 ^{1}H and ^{13}C chemical shifts (ppm) of H_2L^1, **1,** and H_2L^2 and **2**

	H_2L^1		**1**		**H_2L^2**		**2**	
Atom	^{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	^{13}C δ / ppm
1	8.65	150.22	8.97	158.23	8.54	150.37	8.85	157.63
4	–	161.77	–	167.43	–	161.40	–	165.87
5	–	140.41	–	138.05	–	140.60	–	138.08
6	7.86	121.98	7.88	121.99	7.83	121.92	7.84	121.81
7	8.81	150.87	8.77	151.02	8.79	150.82	8.74	150.95
8	–	–	–	–	–	–	–	–
9	8.81	150.87	8.77	151.02	8.79	150.82	8.74	150.95
10	7.86	121.98	7.88	121.99	7.83	121.92	7.84	121.81
1'	–	119.27	–	121.02	–	110.92	–	112.83
2'	–	146.65	–	148.69	–	159.99	–	162.01
3'	–	146.12	–	146.71	6.34	103.10	6.33	105.12
4'	6.89	118.07	7.10	121.90	–	161.50	–	165.34
5'	6.76	119.72	6.93	122.38	6.38	108.33	6.55	111.04
6'	7.03	120.27	7.22	125.15	7.37	131.66	7.58	136.77
N–H	12.31	–	–	–	12.12	–	–	–
2'–OH	10.86	–	–	–	11.26	–	–	–
3'–OH	9.31	–	9.51	–	10.01	–	10.71	–

Table S4 ^{1}H and ^{13}C chemical shifts (ppm) of H_2L^3, **3,** and H_2L^4 and **4**

	H_2L^3		**3**		H_2L^4		**4**	
Atom	^{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	^{13}C δ / ppm
1	8.62	149.80	8.94	157.38	8.52	149.96	8.82	156.86
4	–	161.87	–	167.52	–	161.53	–	165.97
5	–	129.13	–	126.69	–	129.30	–	126.73
6	9.10	149.09	9.15	149.20	9.08	149.01	9.11	149.00
7	–	–	–	–	–	–	–	–
8	8.79	152.94	8.76	152.79	8.77	152.77	8.73	152.50
9	7.59	124.13	7.57	124.44	7.58	124.09	7.54	124.39
10	8.29	135.94	8.31	135.85	8.26	135.83	8.27	135.61
1'	–	119.25	–	121.09	–	110.93	–	112.88
2'	–	146.60	–	148.56	–	159.97	–	161.85
3'	–	146.10	–	146.68	6.34	103.11	6.32	105.10
4'	6.88	117.99	7.09	121.66	–	161.38	–	165.07
5'	6.76	119.69	6.92	122.32	6.38	108.27	6.54	110.94
6'	7.02	120.36	7.21	124.99	7.36	131.71	7.57	136.55
N–H	12.26	–	–	–	12.07	–	–	–
2'–OH	10.96	–	–	–	11.33	–	–	–
3'–OH	9.29	–	9.49	–	10.00	–	10.66	–

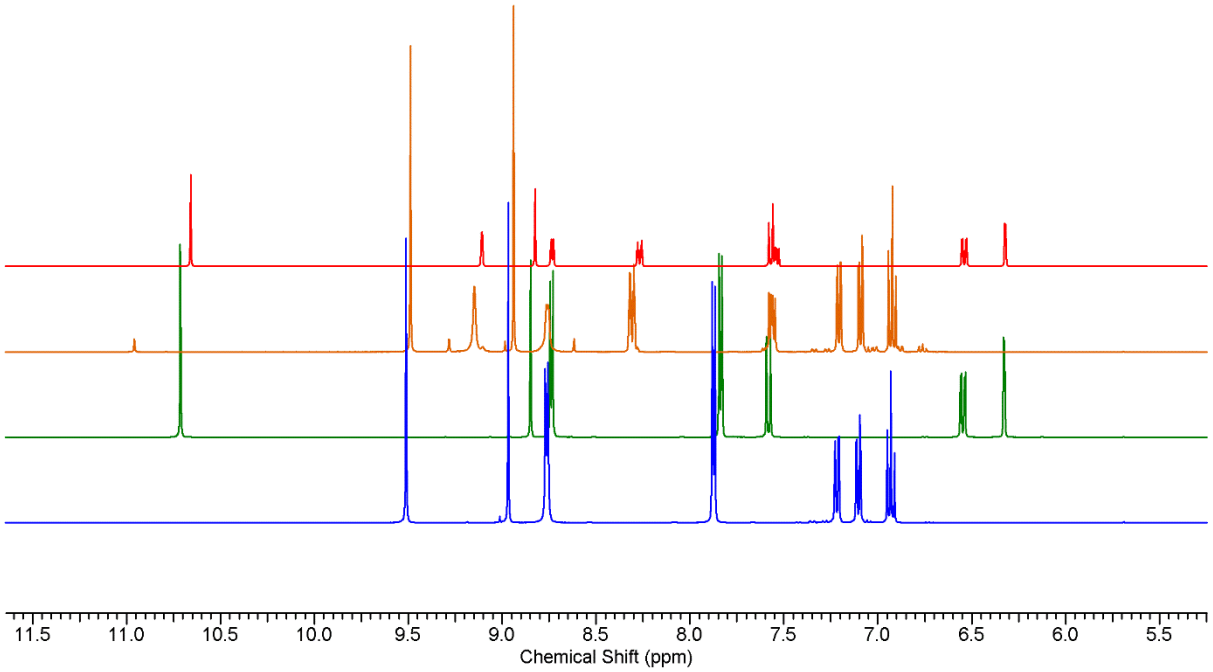


Figure S1. ^{1}H NMR spectra of **1–4** in dmso-d_6 (form botom to top).

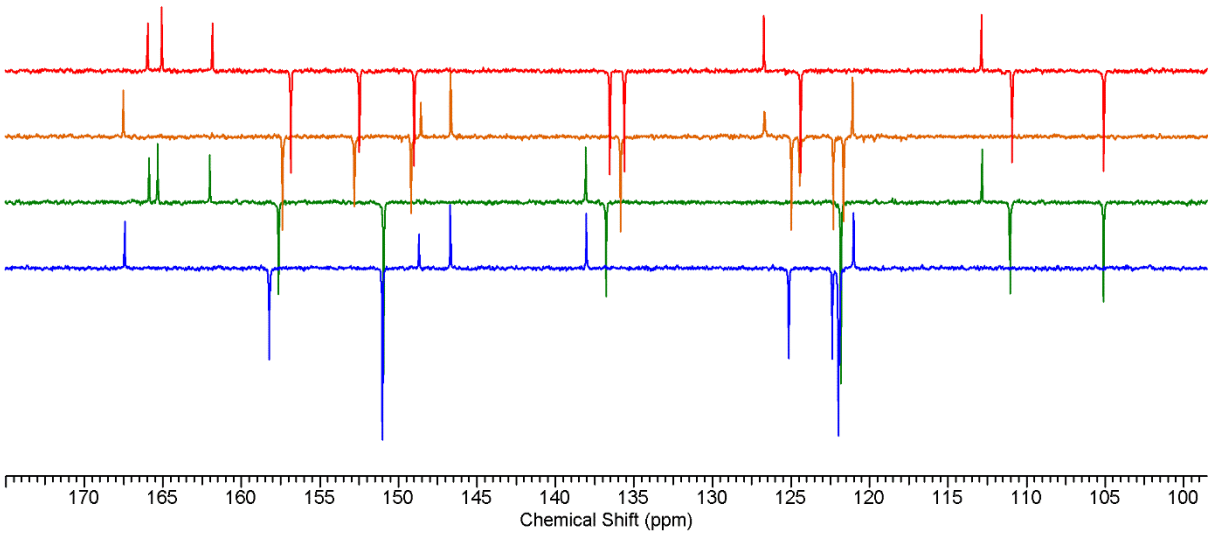
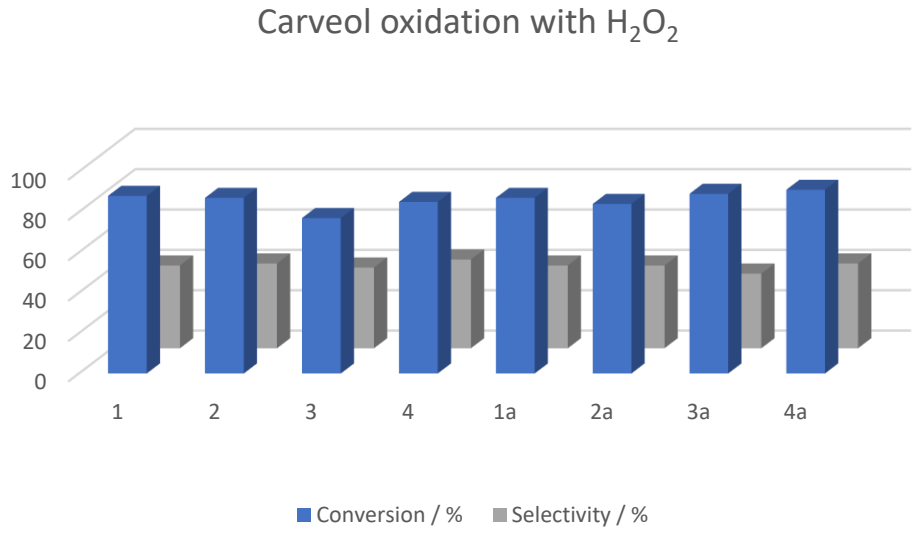
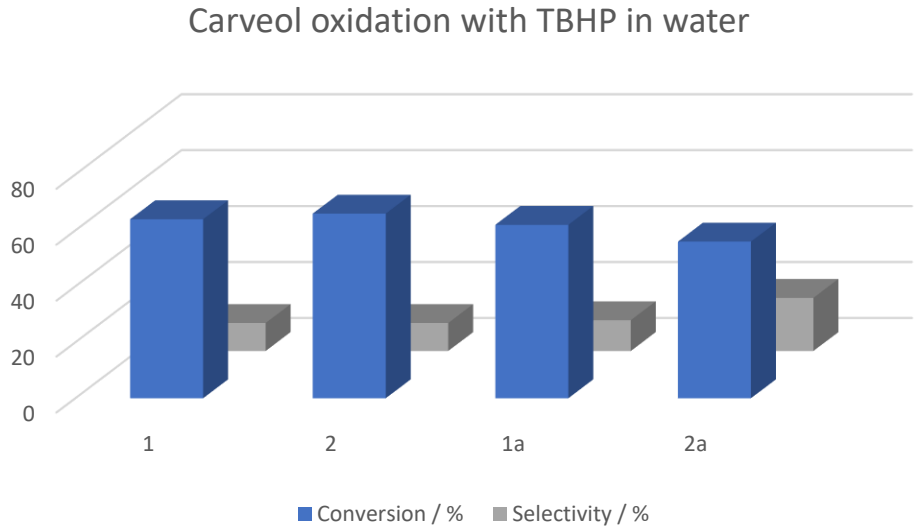
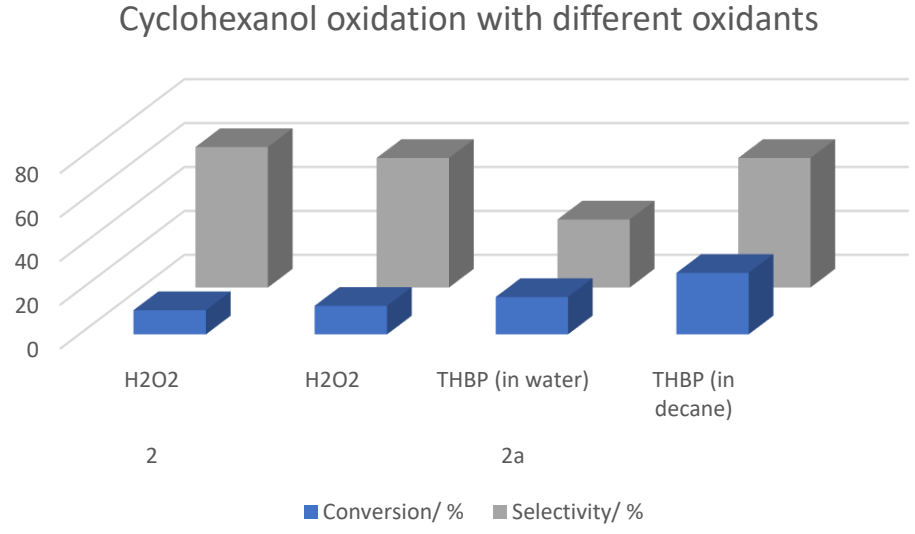


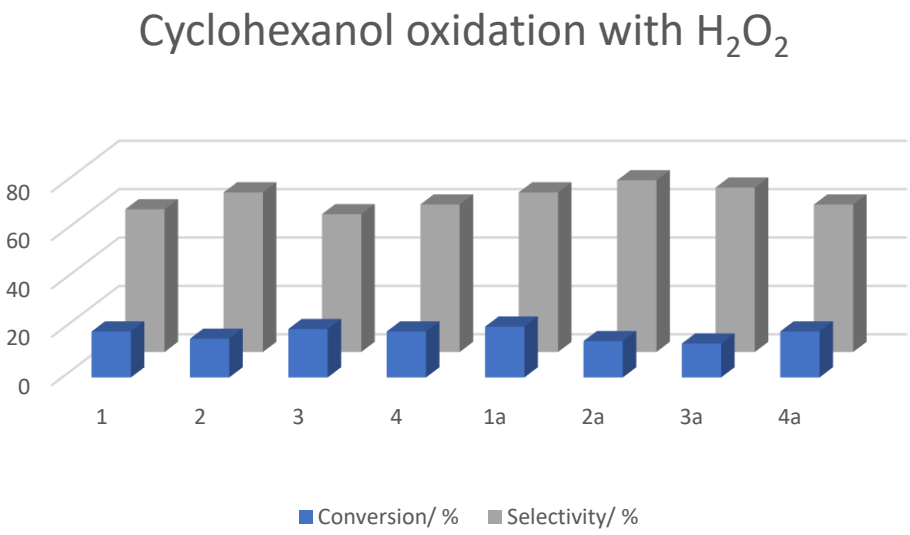
Figure S2. ^{13}C NMR spectra of **1–4** in dmso-d_6 (form botom to top).

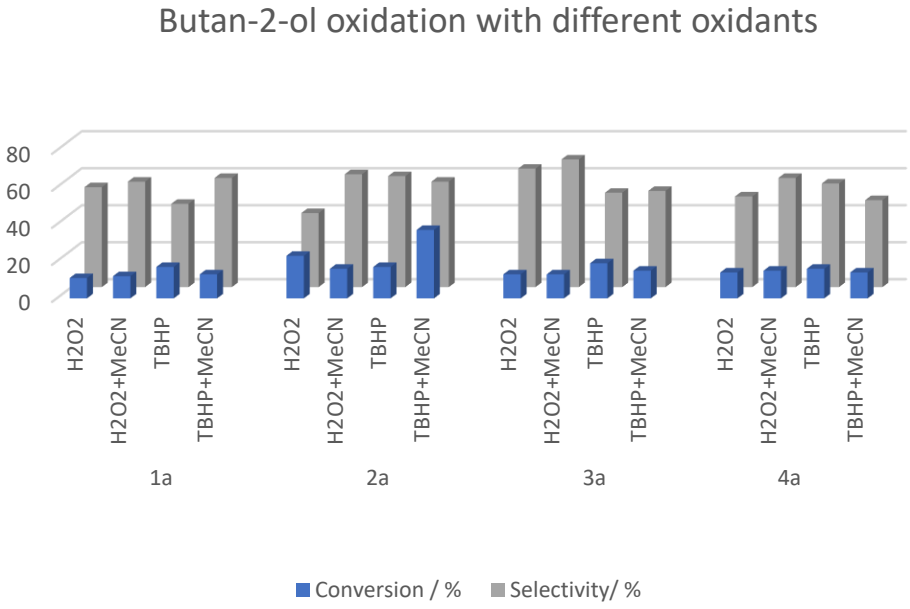
Visual presentation of catalytic results











Carveol oxidation – discussion part

GC and NMR spectra indicated more than two by-products in all types of reaction. In order to identify by-products, several experiments were performed. After purification of the reaction mixtures with H_2O_2 and aqueous THBP by column chromatography[1], the obtained fractions were analyzed by GC-MS, NMR, and GC. Even with those methods, it was not possible to identify the unknown product **A** with certainty. In GC-MS experiment the product **A** was identified as limonene diepoxide, but the presence was not confirmed in the NMR

[1]Conditions for CC: Stationary phase: silica gel. Mobile phase: 250 mL of the mixtures of hexane and diethyl ether with different polarities (diethyl ether content: 5 %, 10 %, 10 %, 30 %, 50 %, 100 %). The composition of the eluent flow was monitored with TLC and visualized with UV lamp, iodine or permanganate.

spectra. Besides, the fraction in which product **A** was isolated was contaminated with other by-products and due to overlapping of the NMR signals, no identification was possible. GC-MS spectral data additionally confirmed the previously assumed stereoselectivity of the reaction towards *cis*-carveol in the case of H_2O_2 and towards *trans*-carveol in the case of aqueous THBP.