Selective oxidation of alcohols promoted by *cis-Dioxomolybdenum (VI) ONO Complexes*

Xiaoxia Liu[a], Shuya Yang[b], Lan Yang[b], Honglei Yu[b], Tao Zhang[*,c], Weili Wang[*,b]
[a]Zibo Linzi District Environmental Monitoring Station, ZiBo 255400, China
[b] School of Chemistry and Material Science, Ludong University, 186 Hongqi Middle Road, Yantai, 264025, China,
[c] Environmental Monitoring Station of Zibo National High-tech Industrial Development Zone, ZiBo, Shandong, 255400, China

Oxidació selectiva d'alcohols promoguda per complexos ONO cis-Dioxomolibdè (VI)

Oxidación selectiva de alcoholes promovida por complejos cis-dioxomolibdeno (VI) ONO

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SUMMARY

Selective oxidation of alcohols to aldehydes in mild conditions remains an important reaction in organic synthesis, in this regard the use of molybdenum complexes of Schiff bases results in an effective improvement of the catalysis of this reaction. Several ONO Schiff bases were synthesized by condensation of o-aminophenol and the corresponding 5-substituted salicylaldehyde derivatives, further complexation with bis(acetylacetonato)dioxomolybdenum(VI) afforded the corresponding cis-dioxomolybdenum(VI) complexes which were fully characterized. These complexes were used as catalysts for the oxidation of several alcohols under solvent-free condition using H_2O_2 as oxidant with outstanding results. The electronic effects of the substituents in the catalytic process were studied concluding that strong electron withdrawing groups indeed facilitates the catalytic reaction. Furthermore, the scope of the methodology was evaluated showing good tolerance to other functional groups.

Keywords: Schiff base; alcohol; oxidation; molybdenum complex; catalysis.

RESUMEN

La oxidación selectiva de alcoholes a aldehídos en condiciones suaves sigue siendo una reacción importante en la síntesis orgánica, en este sentido el uso de complejos de molibdeno de bases de Schiff da como resultado una mejora efectiva de la catálisis de esta reacción. Se sintetizaron varias bases ONO Schiff por condensación de o-aminofenol y los derivados de salicilaldehído sustituidos en 5 correspondientes, la complejación adicional con bis (acetilacetonato) dioxomolibdeno (VI) proporcionó los correspondientes complejos de cis-dioxomolibdeno (VI) que se caracterizaron por completo. Estos complejos se utilizaron como catalizadores para la oxidación de varios alcoholes en condiciones libres de solventes utilizando H2O2 como oxidante con resultados sobresalientes. Se estudiaron los efectos electrónicos de los sustituyentes en el proceso catalítico y se concluyó que los grupos atractores de electrones fuertes facilitan la reacción catalítica. Además, se evaluó el alcance de la metodología mostrando buena tolerancia a otros grupos funcionales.

Paraules clau: base de Schiff; alcohol; oxidación; complejo de molibdeno; catálisis

RESUM

L'oxidació selectiva d'alcohols a aldehids en condicions suaus segueix sent una reacció important en la síntesi orgànica, en aquest sentit l'ús de complexos de molibdè de bases de Schiff dóna com a resultat una millora efectiva de la catàlisi d'aquesta reacció. Es van sintetitzar diverses bases ONO Schiff mitjançant la condensació d'o-aminofenol i els derivats de salicilaldehid substituïts en 5 corresponents, la complexació addicional amb bis (acetilacetonato) dioxomolibdè (VI)

***Corresponding author :wangweilishou@163.com**

va proporcionar els complexos cis-dioxomolibdè (VI) corresponents que es van caracteritzar completament. Aquests complexos es van utilitzar com a catalitzadors per a l'oxidació de diversos alcohols en condicions sense dissolvents utilitzant H2O2 com a oxidant amb resultats excel·lents. Es van estudiar els efectes electrònics dels substituents en el procés catalític i es van concloure que els forts grups d'extracció d'electrons faciliten efectivament la reacció catalítica. A més, es va avaluar l'abast de la metodologia mostrant una bona tolerància a altres grups funcionals.

Paraules clau: base Schiff; alcohol; oxidació; complex de molibdè; catàlisi

1. INTRODUCTION

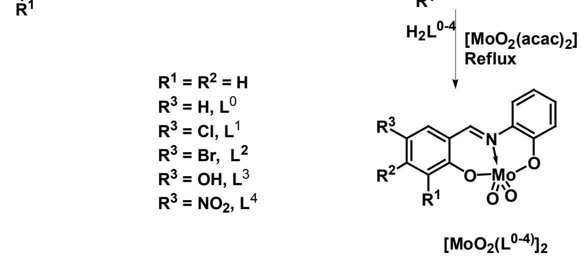
Carbonyl compounds are important building blocks and products within chemical industry [1], in fact, the application of carboxylic acids [2-5] and aldehydes [6-9] as starting materials or intermediaries in almost every field of basic and applied research is customary, show the importance of their availability. On another hand, aldehydes and ketones are mainly produced by oxidizing alcohols [10] in organic solvents and in the presence of inorganic oxidants (NaClO, $KMnO_4$, CrO_3, etc.) which are commonly used combinations [11] in the traditional oxidation processes. However, these methodologies have resulted either expensive, or toxic, or cumbersome operation, including the low selectivity due to side reactions and exhaustive oxidation of the initial alcohols, thus generating a lot of byproducts. This is no longer recommended in the context of green chemistry principles.

According a green chemistry approach, new synthetic approaches have been developed including the use of greener, safer and environmentally friendly oxidants such as TBHP [12], H_2O_2 [13], O_2 [14], etc., in this regard, catalytic process are highly valuable alternatives to achieve oxidation reactions in mild conditions. Besides, in terms of solvent selection, solvent free protocols have been developed and widely preferred. Compared with the use of solvents, solvent free reactions have the advantages of being safer, environmentally friendlier, simpler separation process.

Recently, significant efforts have been redirected to the development of better and efficient catalytic oxidation systems for alcohols [15]. In this regard, the development of suitable ligands for this application is an important research field for catalysis. Among the important class of ligands, Schiff bases are known and have been extensively used for many applications such as adsorbent to remove toxic metal ion from aqueous solution [16-18], or as ligands in transition metal based catalysts [19-22], particularly, Schiff bases as ligands have been found in the development of highly efficient catalysts with good selectivity and activity for oxidation of alcohols, such as Schiff base manganese(III) complex [15], MoO_3/Cu Schiff base nanoparticles [23], amide-functionalized metal (Co(II) and Zn(II)) organic frameworks (MOFs) [24].

In recent years, several Schiff base molybdenum(VI) complexes have been used as catalysts for important oxidation reactions, such as epoxidation of olefins [25-26], oxidation of sulfides [27] and oxidation of alcohols [14], concerning oxidation of alcohols, various of Schiff base molybdenum complexes have been reported for the reaction of oxidizing alcohols with TBHP or H_2O_2 as oxidant to the corresponding aldehydes or ketones, such as Mo–V bimetallic organosilicon [28], μ-O{MoO_2}$_2$ binuclear μ-oxidobis{dioxidomolybdenum(VI)} complexes [29], magnetic recoverable molybdenum(VI) nanocatalyst [30]. Less dioxomolybdenum(VI) complexes [31] than oxoperoxo-molybdenum(VI) complexes have been reported for the oxidation of alcohols [32-33]. However, as far as we know, only a few reports have studied the influence between the electronic environment due to the nature and position of the substituents within the ligand and the outcome of catalytic activity of molybdenum–based dioxomolybdenum(VI).

In previous work, our research group have reported and studied several [MoO_2L(L = ONO ligands)]$_2$ type cis-dioxomolybdenum(VI) Schiff base complexes, particularly, as catalysts in solvent-free olefin epoxidation reactions, showing high catalytic activity [34-36]. The electron density delocalization has been studied by introducing electron donor (-NEt_2) and/or acceptor (-NO_2) substituents into the aromatic ring, the observed results have yield interesting conclusions about the relation between geometry, electron density distribution and the proposed catalytic olefin oxidation mechanism [34]. Additionally, the relative position of a given substituent (OH) on the ligand backbone has proven to exhibit an impact on the catalytic performance of epoxidation of olefins (R1> R3> R2) (Scheme 1) [36]. Conceptual DFT studies allowed us to propose a catalytic mechanism that fits with the experimental results. To continue our research on molybdenum catalysis, herein we report the synthesis and study of the influence of different substituents on 5-position of ONO cis-dioxomolybdenum(VI) complexes (R3, Scheme 1) as catalysts for alcohol oxidation. The substitution pattern was selected to maximize the influence of the ligand on the molybdenum center, as explained by the inductive effect exerted by the substituents due to the relative position within the hydrocarbon backbone.



Scheme 1 Synthesis of cis-dioxomolybdenum Schiff base complexes

2. MATERIAL AND METHODS

2.1 Materials

All preparations were carried out in air. Water was distilled before use. Organic solvents (ethanol, methanol, diethylether and acetrontrile) and organic compounds such as benzylic alcohol (99%), benzaldehyde (99%), 2-aminophenol (99%), 5-chloro-2-hydroxybenzaldehyde (98%), 5-bromo-2-hydroxybenzaldehyde (99%), 2,5-dihydroxybenzaldehyde (99%), 5-nitro-2-hydroxybenzaldehyde (98%)) and other alcohols were used as received without further purification, H_2O_2 (30% in water) was used as received. The thermogravimetric analyses were performed on a thermal analyzer. The sample was placed into a nickel/platinum alloy crucible and heated at 0.83 °C s^{-1} in a reconstituted air flow from 15 °C to 700 °C. An empty crucible was used as a reference. Infrared spectra were recorded at room temperature with a MAGNA550 spectrometer. ^{1}H NMR spectra were recorded on 300, 400 or 500 MHz Bruker spectrometer. Catalytic reactions were followed by gas chromatography on a chromatograph equipped with FID detector and a HF-5 column (30 m * 0.32 mm * 0.5 μm).

The GC parameters were quantified with authentic samples of the reactants and products. The conversion of benzylic alcohol, and the formation of benzaldehyde were calculated from calibration curves (r^2 = 0.999) relatively to an internal standard (acetophenone).

2.2 Methods

2.2.1 General procedure for synthesis of the ligands

In a 100 mL Erlenmeyer flask, 2 mmol of the 5-substituted-2-hydroxybenzaldehyde was dissolved in 20 mL of ethanol and then 2 mmol of 2-amino-phenol was added. The mixture was stirred at reflux temperature for 4 h. The resulting precipitate was filtered and washed with ethanol to obtain the corresponding Schiff bases, as red colored powders, namely, H_2L.

General procedure for synthesis of the molybdenum complexes

In a 100 mL Erlenmeyer flask, the ligand H_2L^{0-4} (1.42 mmol) was dissolved in 20 mL of ethanol and then $[MoO_2(acac)_2]$ (1.42 mmol) was added. The mixture was stirred at reflux temperature for 4 h leading to $[MoO_2L]_2$ precipitated as brown powder. The precipitate was dried (80 °C) under reduced pressure for 24 hours.

(a) $[MoO_2L^1]_2$ [37] {4-Chloro-2-[(2-hydroxy-phenylimino)-methyl]-phenolato}dioxido-molybdenum(VI)

Brown powder, yield: 77.2%; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1613 (s) (C=N), 924 (Mo=O), 807 (Mo–O–Mo).

^{1}H NMR (400 MHz, DMSO-d_6, (ppm)): δ = 9.25 (s, 1H, CH=N), 7.85 (d, 1H, J = 2.8 Hz, Ar-H), 7.77 (d, 1H, J = 8.2 Hz, Ar-H), 7.55 (dd, 1H, J = 8.8, 2.8 Hz, Ar-H), 7.26 (t, 1H, J = 7.8 Hz, Ar-H), 6.97 (dd, 2H, J = 8.6, 5,7 Hz, Ar-H), 6.87 (d, 1H, J = 8.2 Hz, Ar-H).

^{13}C NMR (100 MHz, DMSO-d_6, (ppm)): δ = 160.6, 160.3, 156.1, 135.8, 135.1, 134.0, 131.0, 124.3, 123.6, 121.4, 121.0, 117.9, 116.9.

TGA: 38.3% MoO_3 residue (requires 38.5%); elemental analysis Calcd (%) for $C_{13}H_8ClMoNO_4$ (Mr = 373.60): C 41.79, H 2.16, N 3.75; found: C 40.76, H 2.19, N 3.73%.

(b) $[MoO_2L^2]_2$ [37] {4-Bromo-2-[(2-hydroxy-phenylimino)-methyl]-phenolato}dioxido-molybdenum(VI)

Brown powder, yield: 85%, ^{1}H NMR (500 MHz, DMSO-d_6, (ppm)): δ = 9.28 (s, 1H, CH=N), 7.82-7.77 (m, 2H, Ar-H), 7.25 (t, 1H, J = 10 Hz, Ar-H), 7.14 (d, 1H, J = 10 Hz, Ar-H), 7.07 (s, 1H, Ar-H), 6.96 (t, 1H, J = 10 Hz, Ar-H), 6.87 (d, 1H, J = 10 Hz, Ar-H).

^{13}C NMR (125 MHz, DMSO-d6, (ppm)) δ = 160.2, 160.1, 155.6, 137.5, 136.5, 135.3, 130.5, 123.7, 121.3, 120.5, 117.4, 116.5, 111.3.

TGA: 34.3% MoO_3 residue (requires 34.4%); elemental analysis Calcd (%) for $C_{13}H_8BrMoNO_4$ (Mr = 418.05): C 37.35, H 1.93, N 3.35; found: C 37.36, H 1.95, N 3.31%.

(c) $[MoO_2L^3]_2$ [36] {4-Hydroxy-2-[(2-hydroxy-phenylimino)-methyl]-phenolato}dioxido-molybdenum(VI)

Yield: 87%. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1613 (C=N), 912 (Mo=O), 804 (Mo-O-Mo). ^{1}H NMR (300 MHz, DMSO-d_6, (ppm)): δ = 9.43 (s, 1 H, Ar-OH), 9.15 (s, 1 H, CH=N), 7.78-8.82 (m, 1 H, Ar-H), 6.75-7.24 (m, 6 H, Ar-H).

^{13}C NMR (DMSO-d_6, (ppm)): δ = 160.6 (Cq-O), 156.9 (CH-N), 155.0 (Cq-O),151.4 (Cq-O), 136.0 (Cq-N), 130.6 (CH-Ar), 123.8 (CH-Ar), 122.5 (Cq), 120.6 (CH-Ar), 119.7 (CH-Ar), 119.4 (CH-Ar), 117.8 (CH-Ar), 116.9 (CH-Ar).

TGA: 41.3% MoO_3 residue (requires 40.5%). Anal. Calcd. for $C_{13}H_9MoNO_5$ (Mr = 355.15): C, 43.96; H, 2.55; N, 3.90 %. Found: C, 43.84; H, 1.83; N, 3.84 %.

(d) $[MoO_2L^4]_2$ [38] {4-Nitro-2-[(2-hydroxy-phenylimino)-methyl]-phenolato}dioxido-molybdenum(VI)

Yield: 89%. IR (ATR, cm^{-1}) 1603 (C=N), 941 (Mo=O), 780 (Mo–O–Mo).

^{1}H NMR (500 MHz, DMSO-d_6, (ppm)): δ = 9.48 (s, 1H, CH=N), 8.81 (d, 1H, J = 2.9 Hz, Ar-H), 8.34 (dd, 1H, J = 9.2, 3.0 Hz, Ar-H), 7.85 (dd, 1H, J = 8.2, 1.3 Hz, Ar-H), 7.31 (t, 1H, J = 8.4 Hz, Ar-H), 7.13 (d, 1H, J = 9.2 Hz, Ar-H), 7.04 (t, 1H, J = 8.4 Hz, Ar-H) , 6.92 (dd, 1H, J = 8.2, 1.2 Hz, Ar-H).

^{13}C NMR (125 MHz, DMSO-d_6, (ppm)) δ = 166.2, 160.5, 156.5, 140.5, 135.7, 131.7, 131.3, 130.2, 122.0, 121.5, 121.0, 117.9, 117.3.

TGA: 37.2% MoO_3 residue (requires 37.4%). Anal. Calc. For $C_{13}H_8MoN_2O_6$ (Mr = 384.15): C, 40.65; H, 2.10; N, 7.29. Found: C, 40.63; H, 2.12; N, 7.30%.

2.2.2 Catalytic alcohol oxidation with H_2O_2 under solvent-free condition

The oxidation of benzyl alcohol by $[MoO_2L]_2$ was carried out according to the following general procedures. The optimized condition was as follow: to the alcohol (2 mmol), complex (0.01 mmol), acetophenone (0.2 mmol, 0.0240 g, internal standard) and H_2O_2 (4 mmol, 30% in water, 0.4 mL) were added in a 50 mL two neck flask. While for volatile products, the reaction was performed in closed schlenk tube. The reaction mixture was stirred at 65 °C for 4 h. The crude of the reaction was introduced and quantified by GC-FID or NMR periodically. After the complication of the reaction, the products were isolated by column chromatography with Petroleum ether / ethyl acetate = 5:1 as eluent.

Benzaldehyde (2a): ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.03 (s, 1H), 7.89 (d, J = 8.4 Hz, 2H), 7.64 (t, J = 7.2, 1H), 7.54 (t, J = 7.5, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.39, 136.42, 134.47, 129.75, 129.01.

4-Chloro-benzaldehyde (2b): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.99 (s, 1H, CHO), 7.88-7.80 (m, 2H), 7.55-7.42 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.87, 140.96, 134.72, 130.92, 129.47, 129.34.

2-Hydroxy-benzaldehyde (2c): ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.02 (s, 1H, OH), 9.89 (s, 1H, CHO), 7.59-7.49 (m, 2H), 7.07-6.96 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.63, 161.64, 137.01, 133.75, 120.68, 119.87, 117.63.

4-Hydroxy-benzaldehyde (2d): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.87 (s, 1H), 8.04-7.67 (m, 2H), 7.17-6.83 (m, 2H), 6.17 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.28, 161.55, 132.56, 129.90, 116.03.

4-Methoxy-benzaldehyde (2e): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.88-7.81 (m, 2H), 7.04-6.97 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.83, 164.63, 132.01, 129.98, 114.33, 55.60.

4-Nitro-benzaldehyde (2f): ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.17 (s, 1H, CHO), 8.41-8.40 (m, 2H), 8.11-8.07 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.28, 151.16, 140.06, 130.50, 129.47, 124.34.

Pyridine-2-carbaldehyde (2g): ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.09 (s, 1H), 8.81 (m, 1H), 8.04-7.95 (m, 1H), 7.94-7.86 (m, 1H), 7.55 (m, J = 7.6, 4.8, 1.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.40, 152.78, 150.20, 137.07, 127.87, 121.69.

Furan-2-carbaldehyde (2h): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.68 (s, 1H), 7.72-7.68 (m, 1H), 7.26 (dd, J = 3.7, 0.8 Hz, 1H), 6.61 (dd, J = 3.6, 1.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.90, 153.02, 148.07, 120.95, 112.59.

Diphenyl-methanone (2i): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86-7.77 (m, 4H), 7.61-7.54 (m, 2H), 7.47 (t, J = 7.7 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.76, 137.62, 132.44, 130.08, 128.31.

1,2-Diphenyl-ethane-1,2-dione (2j): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23-8.16 (m, 1H), 7.78 (dt, J = 6.4, 3.2 Hz, 1H), 7.58-7.49 (m, 2H), 7.41-7.30 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.46, 141.19, 138.99, 130.05, 129.88, 129.19, 128.88, 128.31.

Butyraldehyde (2k): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.77 (t, J = 1.9 Hz, 1H), 2.41 (td, J = 7.2, 1.8 Hz, 2H), 1.67 (q, J = 7.3 Hz, 2H), 0.99-0.95 (m, 3H).

Decanal (2l): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.76 (d, J = 2.0 Hz, 1H), 2.42 (td, J = 7.4, 1.9 Hz, 2H), 1.63 (m, 2H), 1.29 (d, J = 14.7 Hz, 12H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.99, 43.93, 31.86, 29.39, 29.36, 29.24, 29.17, 22.66, 22.10, 14.10.

2-Methyl-butyraldehyde (2m): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.63 (s, 1H), 2.28 (m, 1H), 1.79-1.72 (m, 1H), 1.44 (dt, J = 14.3, 7.2 Hz, 1H), 1.12-1.07 (m, 3H), 0.97-0.94 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.43, 47.76, 23.52, 12.86, 11.35.

Acetone (2n): ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.17 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.88, 30.85.

Oct-2-enal (2o): 1H NMR (500 MHz, $CDCl_3$) δ 9.51 (d, J = 8.1 Hz, 1H), 6.86 (dt, J = 15.7, 6.8 Hz, 1H), 6.17-6.07 (m, 1H), 2.38-2.29 (m, 2H), 1.59-1.47 (m, 2H), 1.34 (tq, J = 7.4, 3.8 Hz, 4H), 0.95-0.86 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.18, 159.07, 132.98, 32.70, 31.30, 27.52, 22.39, 13.94.

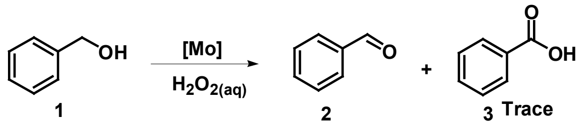
3. RESULTS AND DISCUSSION

3.1 Characterization

The ligands H_2L^0 [22, 39] and H_2L^{1-4} compounds were synthesized according to literature (see experimental part). $[MoO_2(acac)_2]$ was synthesized as previously described [40] and used freshly prepared. Complex $[MoO_2L^0]_2$ was prepared as described earlier [22]. The complexes were fully characterized by IR, NMR, TG analysis or elemental analysis. The above ligands exhibit the typical imine (CH=N) resonance signals at around 9.0 ppm, which shift downfield due to the coordination with $\{MoO_2\}^{2+}$ core. The iminic (CH=N) signal shifts due to the electron withdrawing ability of the different substituents, in fact, even without nitro the iminic signal is slightly shifted downfield, as Lewis acids make the coordination bond and polarizes towards the metallic center reduce the electronic density of the imine. The two signals assigned to the protons from free OH groups in the ligand also disappeared after coordination. On another hand, FT-IR spectroscopy is also relevant for characterization, the broad signal corresponding to the C=N stretching vibration is also shown at around 1603-1613 cm^{-1}, the signal is sharper than the ligand as the rigidity of the structure is somehow increased by the coordination with the metallic center. There are two other relevant signals appearing at the expected region between at 941-912 and 807-780 cm^{-1} respectively which were assigned to the vibrations of cis-dioxomolybdenum and the Mo-O-Mo vibration as referred in literature. Concerning other structural features, the complex $[MoO_2L^0]_2$ as obtained from the reaction gives a monomeric complex from ethanol solution, namely $[MoO_2(L^0)(EtOH)]$ (orange needles), as seen by TGA coordinated ethanol is loosed at higher temperature obtaining the corresponding dimeric $[MoO_2(L^0)]_2$ (red powder) [36], the monomeric-dimeric equilibrium is observed in the presence of σ donor ligands and is described elsewhere.

3.2 Oxidation of benzyl alcohol catalyzed by cis-dioxomolybdenum(VI) complexes

The catalytic ability of the synthesized cis-dioxomolybdenum(VI) complexes were tested in alcohols oxidation. All the results were obtained by GC, while benzyle alcohol (Fig. 1) and oct-2-en-1-ol were also compared by NMR, the results were very close to that measured by GC. Benzyl alcohol was used as a model substrate, and 30% H_2O_2 aqueous was used as an oxidant without any added organic solvent. Blank experiments were carried out and have the expected results, in the absence of catalyst, no significant benzaldehyde or benzoic acid was observed, showing the catalytic effect of the complexes. The catalytic oxidation reaction produced benzoic acid product only after 24 hours of reaction. In addition, the catalytic oxidation of alcohol strongly depends on the reaction temperature. No benzoic acid was observed at room temperature. When we observe the conversion of more than 50% at 65°C, we can conclude that the reaction starts at higher temperature. The optimized catalytic experiments were performed using two equivalents of H_2O_2 per benzyl alcohol and a 0.5% Mo/ benzyl alcohol / ratio at 65 °C. Each complex showed good catalytic activity. The kinetic study was shown in Fig. 2 with different catalysts. The reactions show fast speed at the beginning, then get slower with the lapse of time. The conversions are already very high after 3-4 hours.



Scheme 2 *Oxidation of benzyl alcohol*

It is well known that the modification of the ligand backbone will affect the electrochemical performance of the molybdenum complexes [38]. As shown in Table 1, the influence of the presence of substituents (-Cl, -Br, -OH, $-NO_2$) on the backbone of tridentate ligand is observed. Among them, $[MoO_2L^0]_2$ is also active (conversion: 68%, selectivity: 99%), but it is the lowest one. To its framework the electron withdrawing group was introduced showing higher catalytic activity than the complex $[MoO_2(L^0)]_2$ (all conversions > 81%, up to 93% for $[MoO_2L^4]_2$). This may be due to the fact that the electron withdrawing groups in the benzene ring backbone of these ligands reduce the electron density of the aromatic ring of the parent salicylaldehyde reducing the coordination ability of the coordinating O atom which is in para relative position to the molybdenum atom [31], whicch making the metal center more active to get coordinated with the oxidant setting the start of our proposed catalytic cycle (Scheme 3). That is because it forms the deshielding effect on the metal center. For X = NO_2, this is expected since the nitro group is a strong electron acceptor. The electron withdrawing group exert a long-range electronic effect withdrawing electron density away from the metal center allowing the metal to coordinate with the oxidant. These were in accordance with Kuhn and coworkers reported that aromatic N-based ligand coordinated with the metal center reducing the catalyst's Lewis acidity and additionally accelerating the catalytic oxidation [41-42]. The catalytic conversions are in accordance with the electron withdrawing ability of the substitute in the order as follow: $[MoO_2L^4]_2$ (NO_2) > $[MoO_2L^1]_2$ (Cl) > $[MoO_2L^2]_2$ (Br) > $[MoO_2L^3]_2$ (OH) > $[MoO_2L^0]_2$.

Table 1 *Solvent-free oxidation of benzyl alcohol with different molybdenum complexes*[a]

Complex	Ligand	Conversion [%]	Selectivity [%]	TON	TOF $[h^{-1}]$[d]
$[MoO_2(L^0)]_2$	L^0	68	99	57	108
$[MoO_2L^1]_2$	L^1 (5-Cl)	88, 87.8[b], 82[c]	98	171	129
$[MoO_2L^2]_2$	L^2 (5-Br)	85	99	120	99
$[MoO_2L^3]_2$	L^3 (5-OH)	81	98	83	76
$[MoO_2L^4]_2$	L^4 (5-NO_2)	93	98	214	148

[a] Conditions: Mo/ benzyl alcohol / H_2O_2 = 0.5/100/200; T = 65 °C; t = 4 h.
[b] Calculated by ^1H NMR
[c] Isolated result
[d] TOF is calculated on the time interval with maximum slope for the conversion plot.

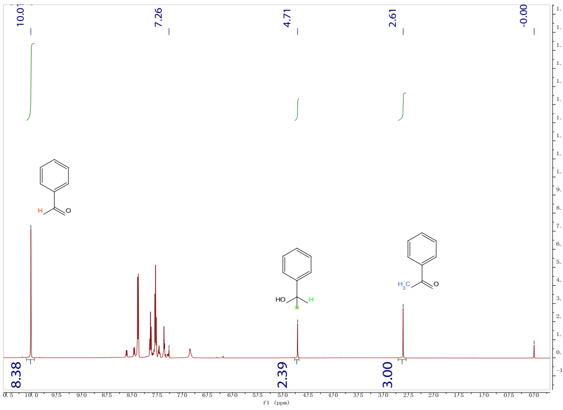


Fig. 1 *^1H NMR of the crude reaction mixture with $[MoO2L^1]_2$ as catalyst in the 4th hour*

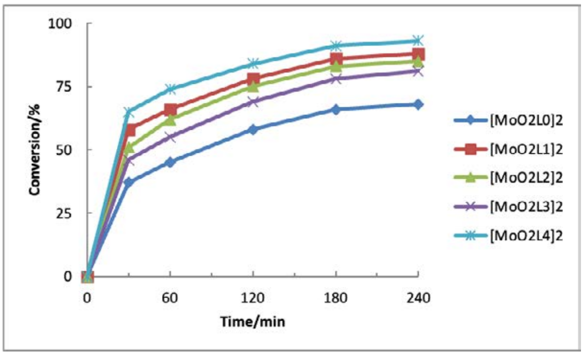
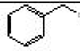
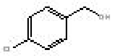
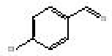
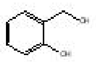
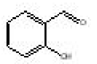
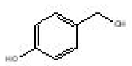
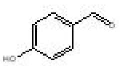
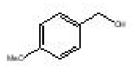
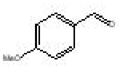
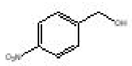
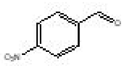
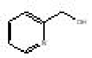
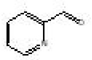
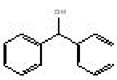
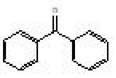
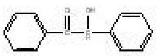
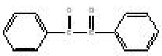
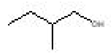
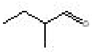
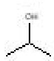
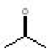


Fig. 2 *Conversion vs time for alcohol oxidation with dioxomolybdenum(VI) complexes*

Having performed the selective oxidation of benzyl alcohol to afford the corresponding benzaldehyde we get inspired to further investigate the versatility of the dioxomolybdenum(VI) complexes under aqueous conditions. The oxidation of a variety of primary and secondary alcohols was performed under the optimized reaction conditions with $[MoO_2L^4]_2$ as catalyst (Table 2). Methoxy, chloro and hydroxybenzyl alcohols were oxidized to corresponding aldehydes (Table 2, entries 1-6) in high isolated yields (81-98%). Substrates containing electron withdrawing functionalities like nitro afforded their corresponding aldehydes (Table 2, entries 6) in moderate yields. Several substituted benzyl alcohols with either electron donor or withdrawing groups were also converted to their related aldehydes in good to excellent yields (entries 1-6) by this catalyst, even benzylic alcohols were oxidized selectively in the presence of an hydroxyl group in the aromatic ring, in this regard, oxidation of phenols to quinones is a known oxidation reaction, despite this fact the quinone was not isolated, showing the selectivity of this catalytic system. Furthermore, good yields were observed for heteroaromatic alcohols which are difficult to oxidize in most transition-metal catalytic conditions (entry 7-8, Table 2). Hindered benzyl alcohols were also oxidized to aldehydes with high yields (entries 9-10). Linear alcohols also gave lower yield aldehydes (entries 11-13), while secondary alcohols produced the corresponding ketones in high yields (entries 14). It is worth to point out that the alkenols, especially conjugate ones (oct-2-en-1-ol, entry 15) are selective oxidized to aldehyde while with the double band remain. We have found that these kinds of dioxomolybdenum(VI) complexes do not work for alkenes with H_2O_2 as oxidatnt. Thus, all the above mentioned functional groups were found to be tolerated. A preliminary mechanistic study is provided in a later section.

Table 2 *Oxidation of alcohols with H_2O_2 catalyzed by the $[MoO_2L^4]_2$ complex under solvent-free conditions*[a]

Entry	Substrate (1)	Product (2)[b]	Conv.[c]	Selectivity[e] (%)	TON
1			93	98	214
2			91	96	205
3			86	94	201
4			97	95	227
5			98	96	235
6			81	93	146
7			95	92	218
8			89	90	198
9			86	87	221
10			85	93	215
11			87[f]	93	186
12			84	88	171
13			88[f]	92	199
14			86[f]	85	187
15			91, 91.4[d]	97	197

[a] Conditions: Mo/ benzyl alcohol / H_2O_2 (aq.) = 0.5/100/200; T = 65 °C; t = 4 h.

[b] The products were identified by comparison of physical and spectroscopic properties with authentic compounds.

[c] Obtained from GC

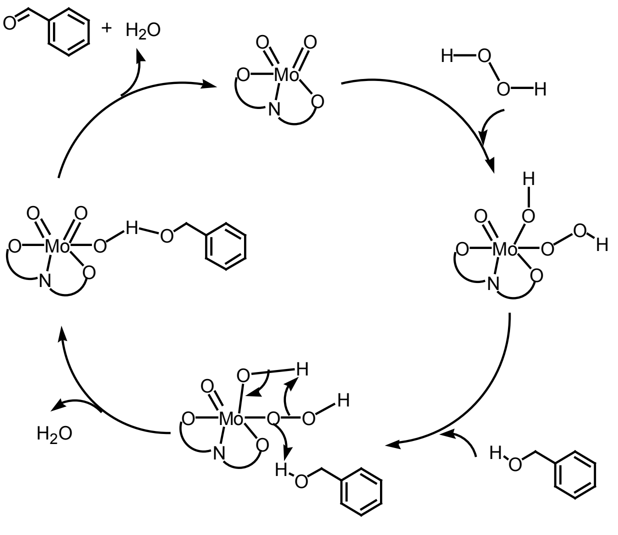
[d] Calculated by ^1H NMR

[e] Aldehyde selectivity.

[f] Performed in closed schlenk tube at 65 °C

3.3 Plausible mechanism

Concerning a plausible mechanism, it is known that the dimeric complexes of the type $[MoO_2L]_2$ dissociate to give monomers while in solution, particularly in the presence of σ donor solvents [36] (Wang et al., 2016) in this case, the hydrogen peroxide is a σ donor capable of disrupt the dimeric structure therefore activating the oxygen atom. The mechanism for oxidation of alcohols by oxidometal complexes in the presence of H_2O_2 is not clear yet but based on both, existing literature [43-44] (Burke, 2008; Hatefi-Ardakani et al., 2016) and previous results of our group, we propose that the alcohol oxidation starts with the formation of peroxido-molybdenum-Schiff base intermediate as the active species that oxidize the substrate. The first step of the catalytic cycle involves a H_2O_2 proton exchange in the presence of one of the cis Mo=O and the HOO- coordinated to the Lewis-acidic metal center, giving the peroxo intermediate. Then, the intermediate oxidizes alcohol and loses one molecule H_2O, giving an intermediate that releases aldehyde and H_2O and finally regenerates the dioxomolybdenum(VI) complex.



Scheme 3 *Probable mechanism of catalytic cycle for benzyl alcohol oxidation catalyzed by dioxomolybdenum(VI) complex*

4. CONCLUSIONS

Several dioxomolybdenum Schiff base complexes were synthesized from o-aminophenol and 5-substituted salicylaldehydes. These molybdenum Schiff base complexes were used as catalysts to catalyze the oxidation of alcohols in solvent free condicionts. $[MoO_2L]_2$ resulted in good catalytic ability to oxidize the selected alcohols, the reaction turned to be highly selective to the aldehydes, thus, the full oxidation to carboxylic acids or other side reaction products were not observed. Experiments have shown that the molybdenum Schiff base complexes have good conversion and selectivity for the oxidation of alcohols, and the different substituents at 5-position have slightly different catalytic activities due to their electrochemical performance derived from different electron withdrawing groups. The catalytic activities follow the trend of the electron acceptor ability of the substituents (NO_2>Cl>Br>OH). This type of dioxomolybdenum catalyst may turn into versatile and viable complexes for a wide range of alcohols.

5. ACKNOWLEDGEMENTS

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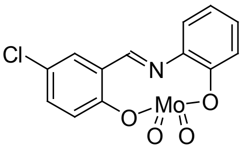
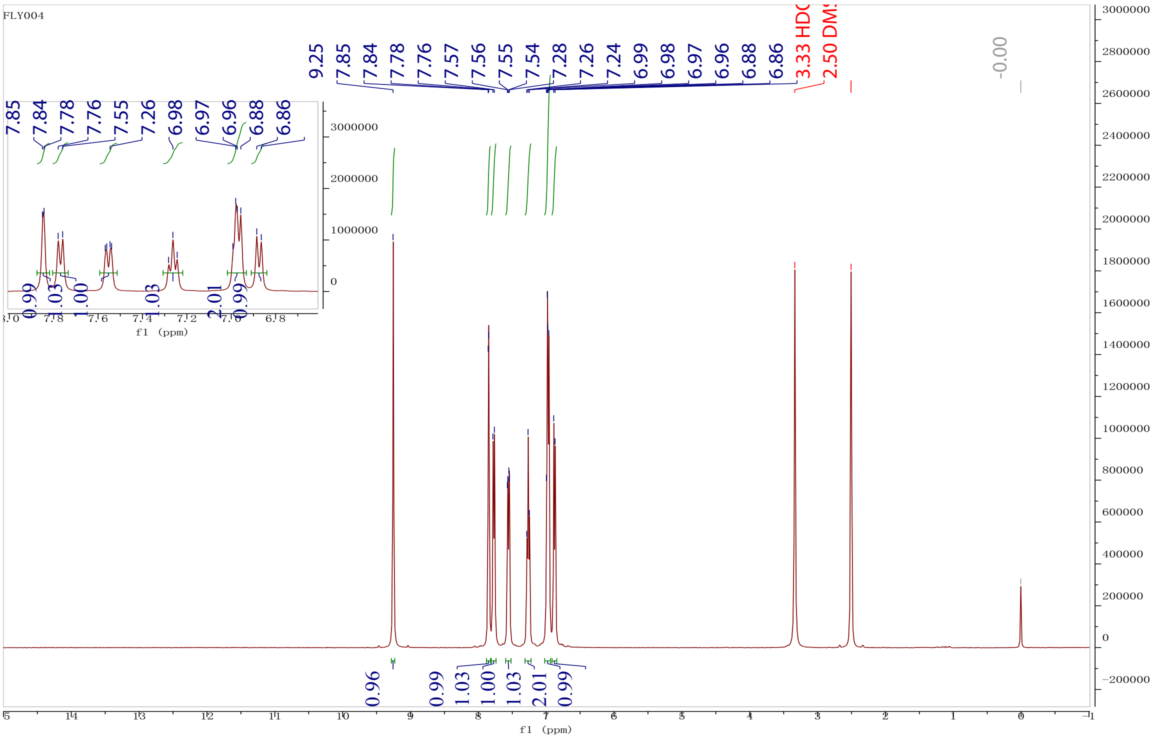
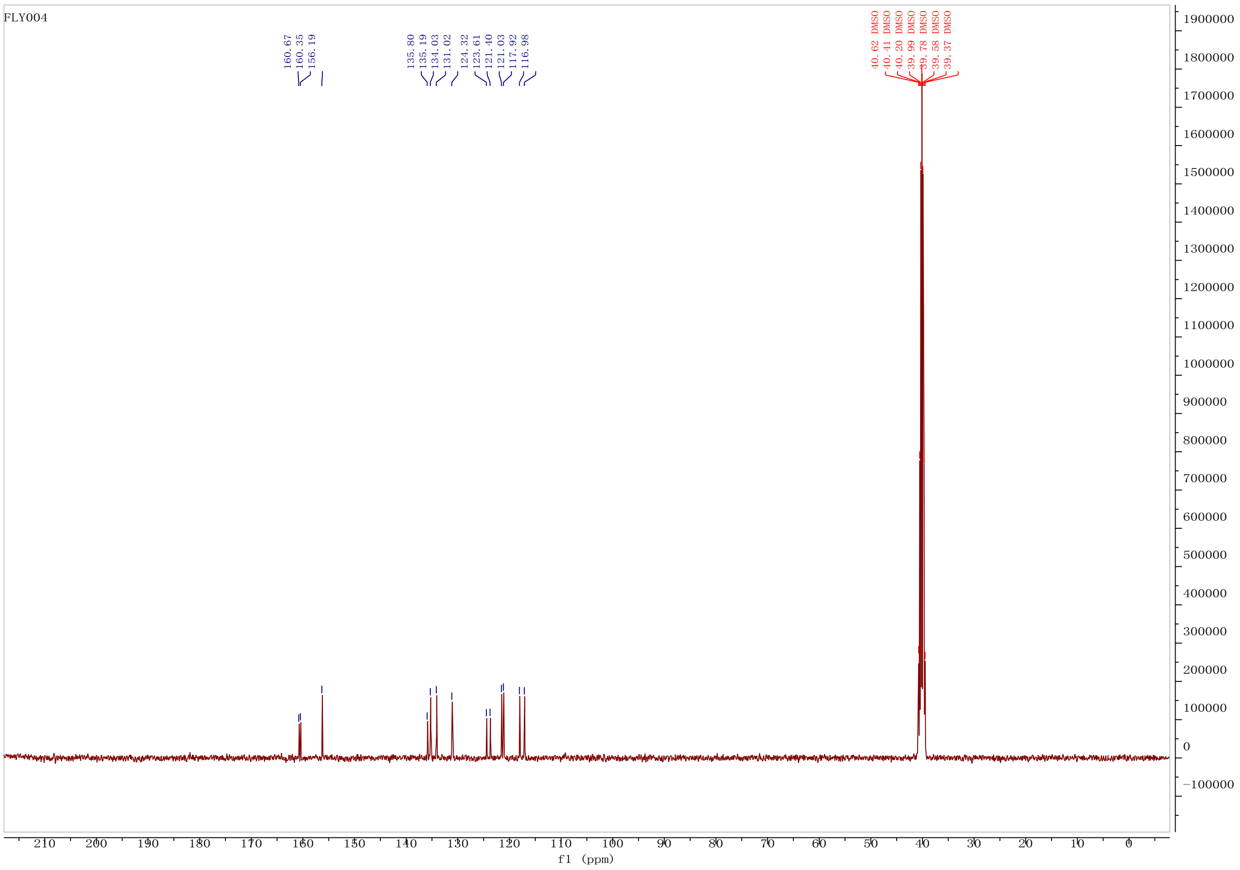
SUPPLEMENTARY DATA

[MoO$_2$L^1]$_2$



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116.98
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40.41 DMSO
40.20 DMSO
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39.78 DMSO
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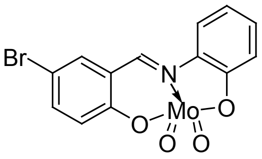
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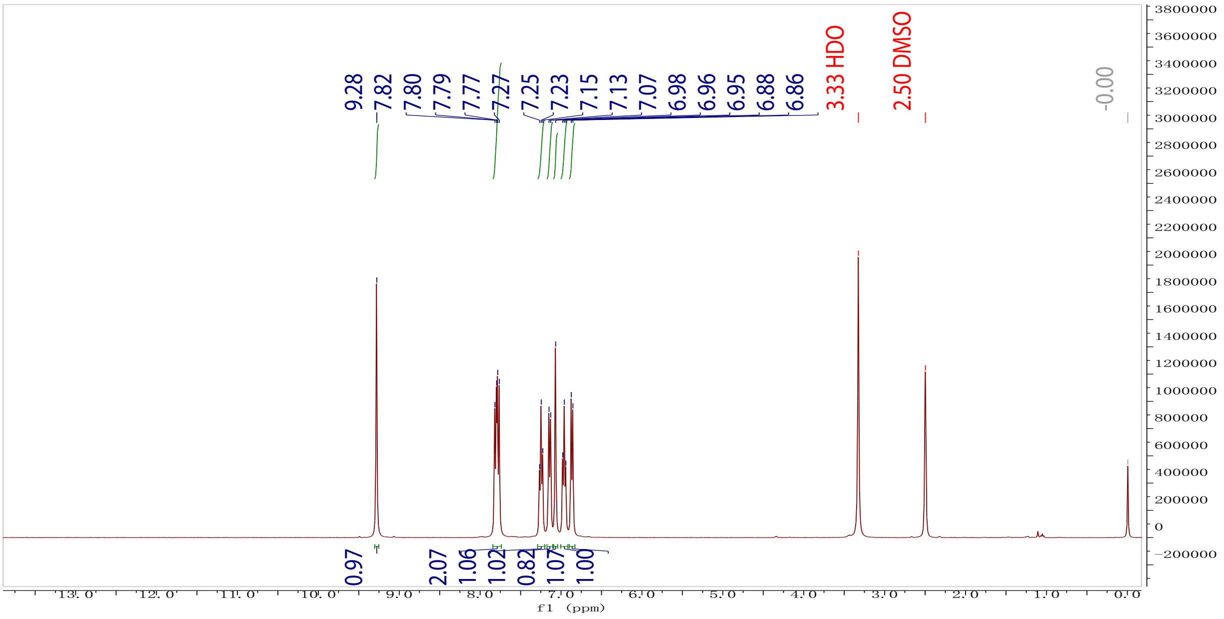
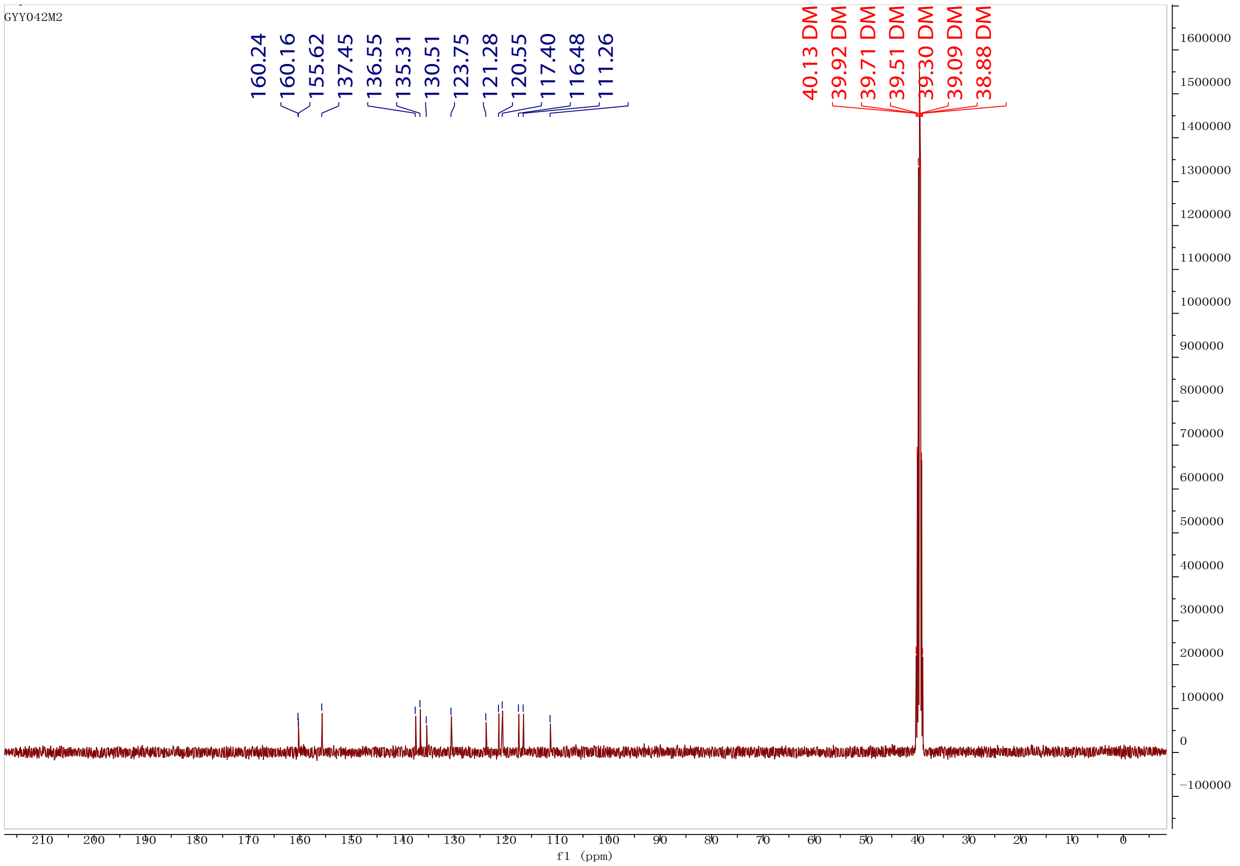
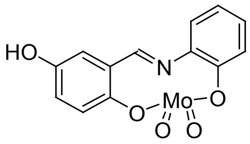
O
O

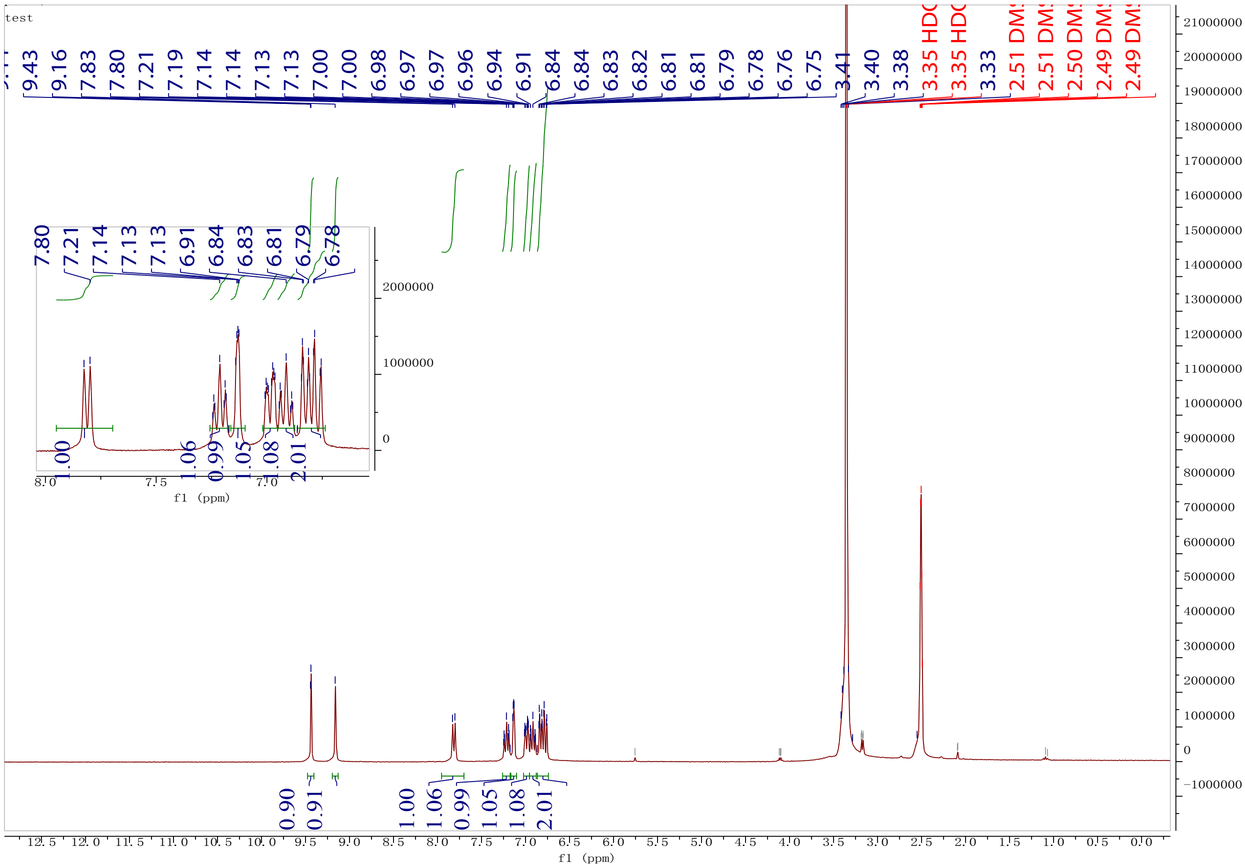
[MoO$_2$L^2]$_2$

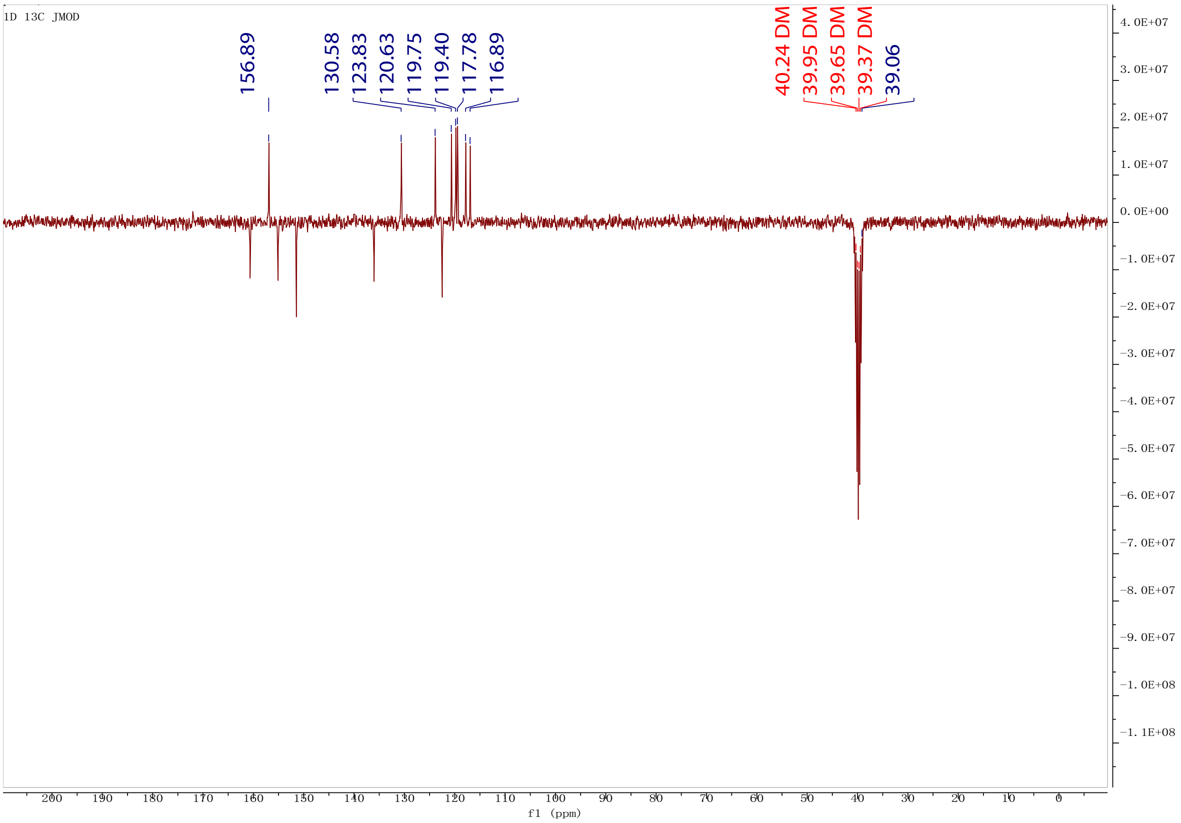

9.28
7.82
7.80
7.79
7.77
7.27
7.25
7.23
7.15
7.13
7.07
6.98
6.96
6.95
6.88
6.86
3.33 HDO
2.50 DMSO
-0.00
0.97
2.07
1.06
1.02
0.82
1.07
1.00
3800000
3600000
3400000
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
−200000
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


GYY042M2
160.24
160.16
155.62
137.45
136.55
135.31
130.51
123.75
121.28
120.55
117.40
116.48
111.26
40.13 DM
39.92 DM
39.71 DM
39.51 DM
39.30 DM
39.09 DM
38.88 DM
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
−100000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

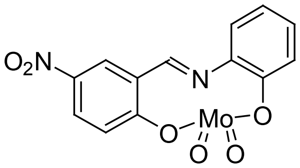
[MoO$_2$L^3]$_2$

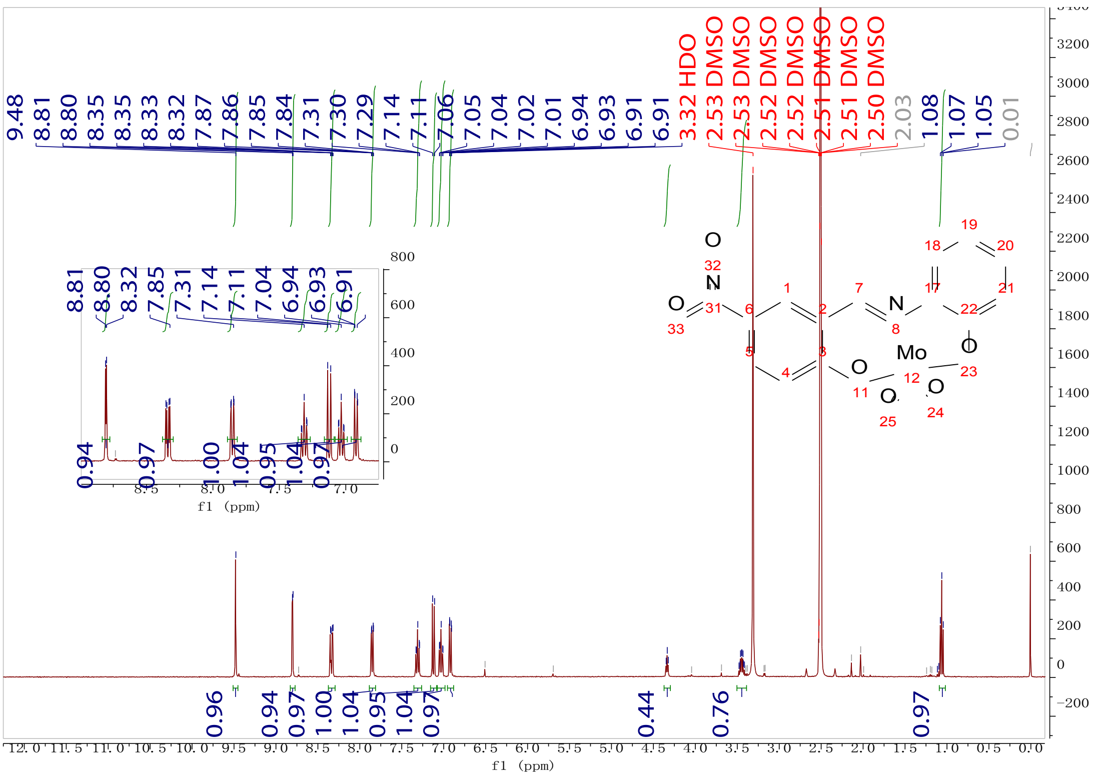

HO
N
O
Mo
O
O
O

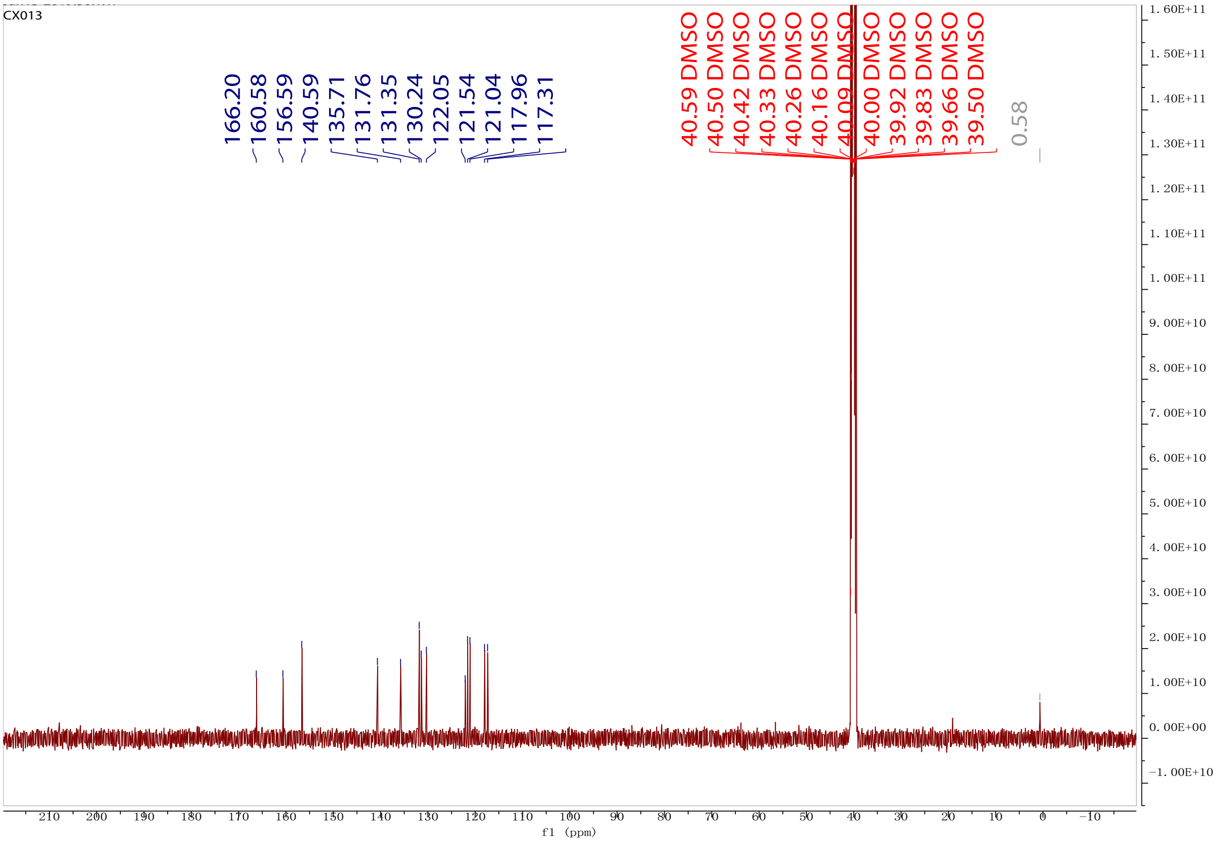

test
9.43
9.16
7.83
7.80
7.21
7.19
7.14
7.14
7.13
7.13
7.00
7.00
6.98
6.97
6.97
6.96
6.94
6.91
6.84
6.84
6.83
6.82
6.81
6.81
6.79
6.78
6.76
6.75
3.41
3.40
3.38
3.35 HDC
3.35 HDC
3.33
2.51 DM
2.51 DM
2.50 DM
2.49 DM
2.49 DM
7.80
7.21
7.14
7.13
7.13
6.91
6.84
6.83
6.81
6.79
6.78
2000000
1000000
0
1.00
1.06
0.99
1.05
1.08
2.01
8.0 7.5 7.0
f1 (ppm)
0.90
0.91
1.00
1.06
0.99
1.05
1.08
2.01
21000000
20000000
19000000
18000000
17000000
16000000
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
−1000000
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


1D 13C JMOD
156.89
130.58
123.83
120.63
119.75
119.40
117.78
116.89
40.24 DM
39.95 DM
39.65 DM
39.37 DM
39.06
f1 (ppm)

$[MoO_2L^4]_2$

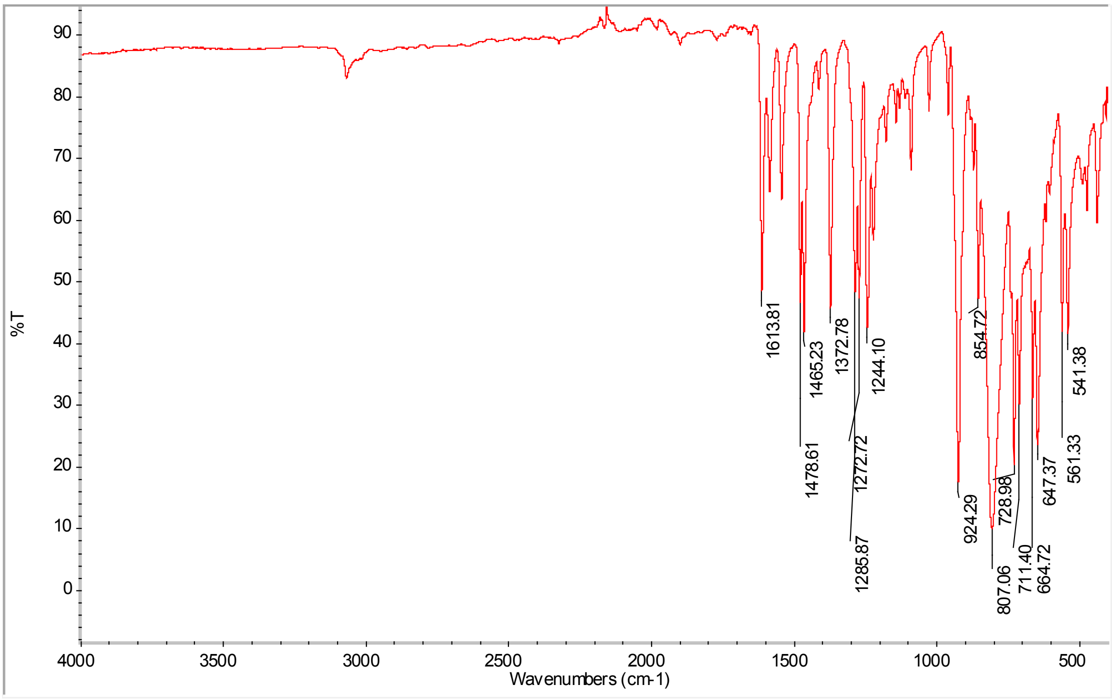

O2N
N
Mo
O
O
O
O

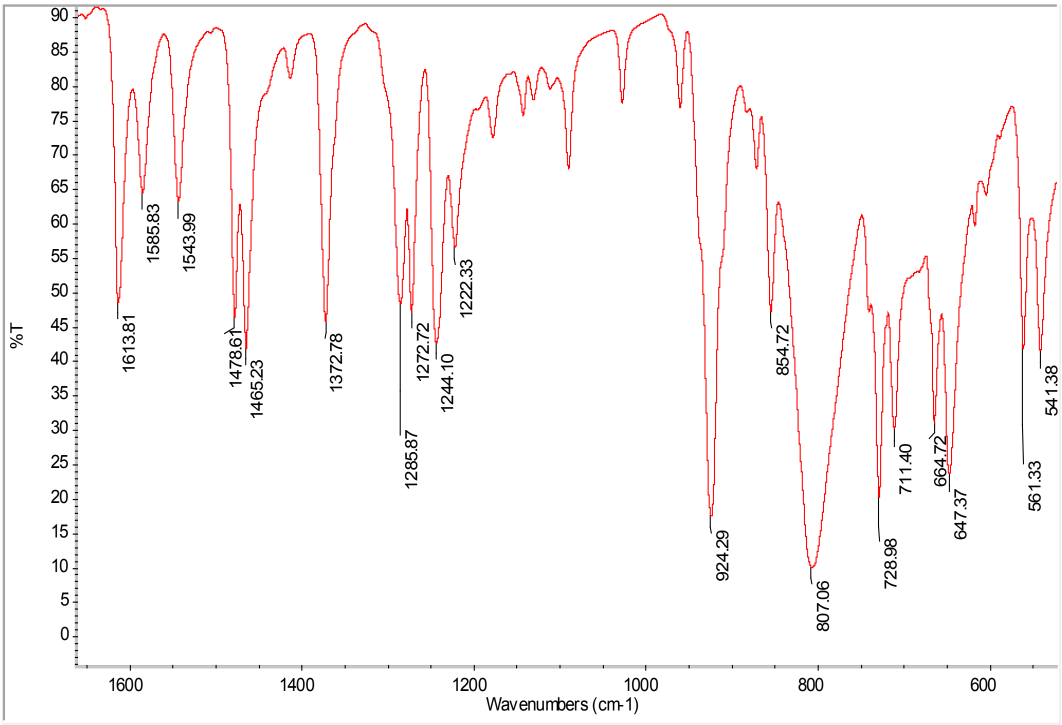

9.48
8.81
8.80
8.35
8.35
8.33
8.32
7.87
7.86
7.85
7.84
7.31
7.30
7.29
7.14
7.11
7.06
7.05
7.04
7.02
7.01
6.94
6.93
6.91
6.91
3.32 HDO
2.53 DMSO
2.53 DMSO
2.52 DMSO
2.52 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.03
1.08
1.07
1.05
0.01
0.96
0.94
0.97
1.00
1.04
0.95
1.04
0.97
0.44
0.76
0.97
f1 (ppm)


CX013
166.20
160.58
156.59
140.59
135.71
131.76
131.35
130.24
122.05
121.54
121.04
117.96
117.31
40.59 DMSO
40.50 DMSO
40.42 DMSO
40.33 DMSO
40.26 DMSO
40.16 DMSO
40.09 DMSO
40.00 DMSO
39.92 DMSO
39.83 DMSO
39.66 DMSO
39.50 DMSO
0.58
f1 (ppm)

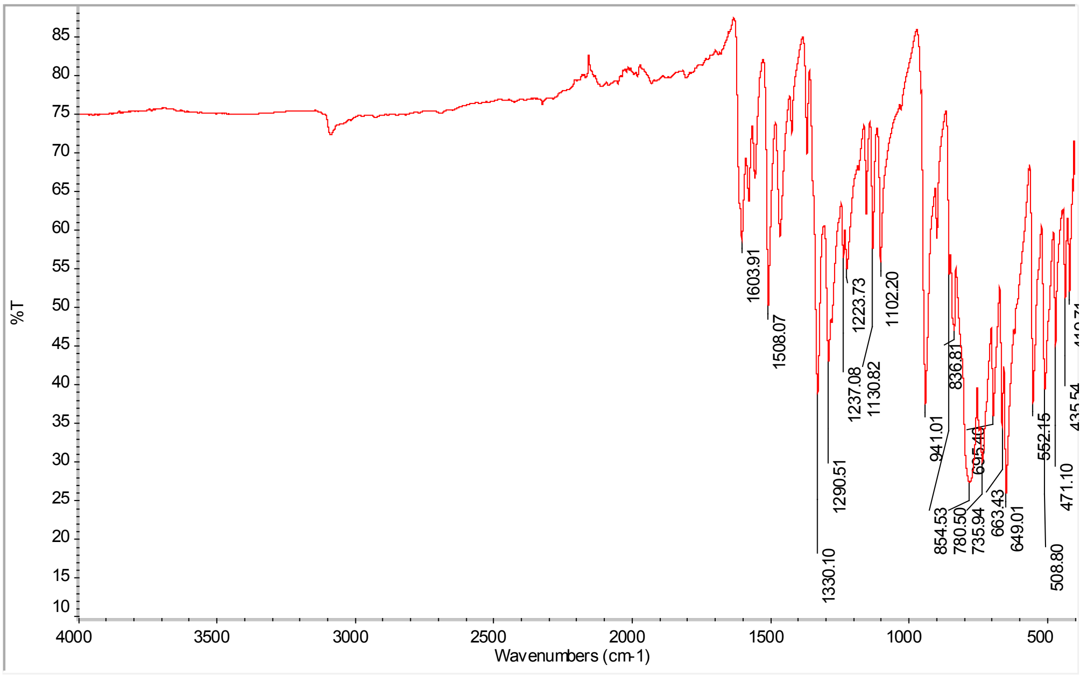
IR

[MoO$_2$L^1]$_2$

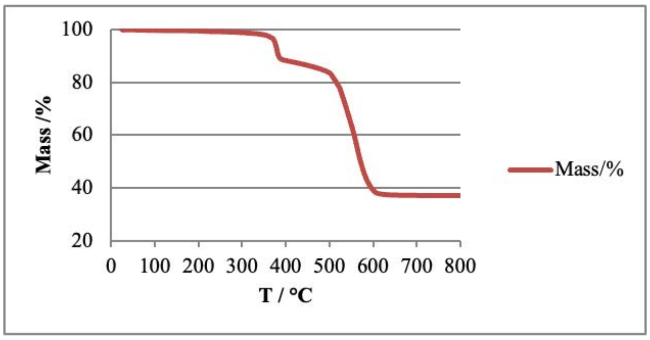

%T
Wavenumbers (cm-1)
1613.81
1478.61
1465.23
1372.78
1285.87
1272.72
1244.10
924.29
854.72
807.06
728.98
711.40
664.72
647.37
561.33
541.38

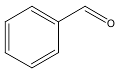


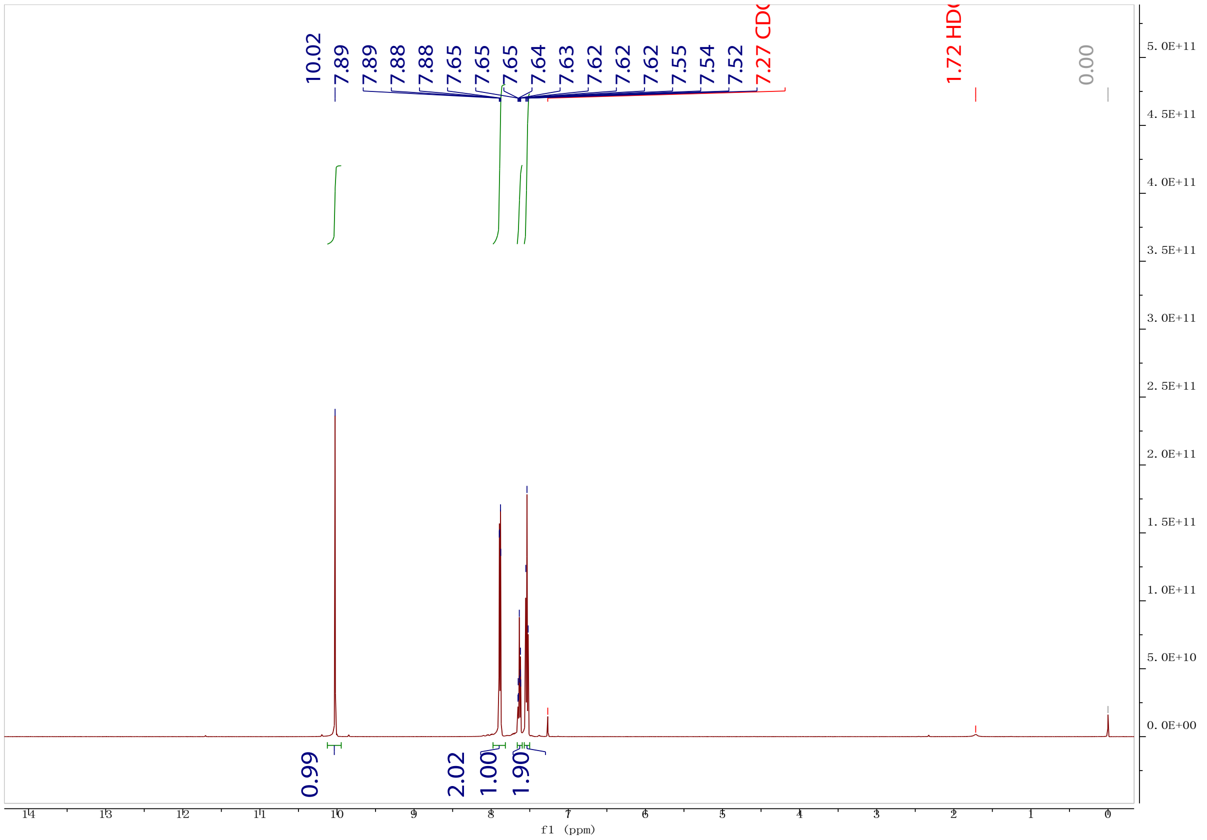
$[MoO_2L^4]_2$

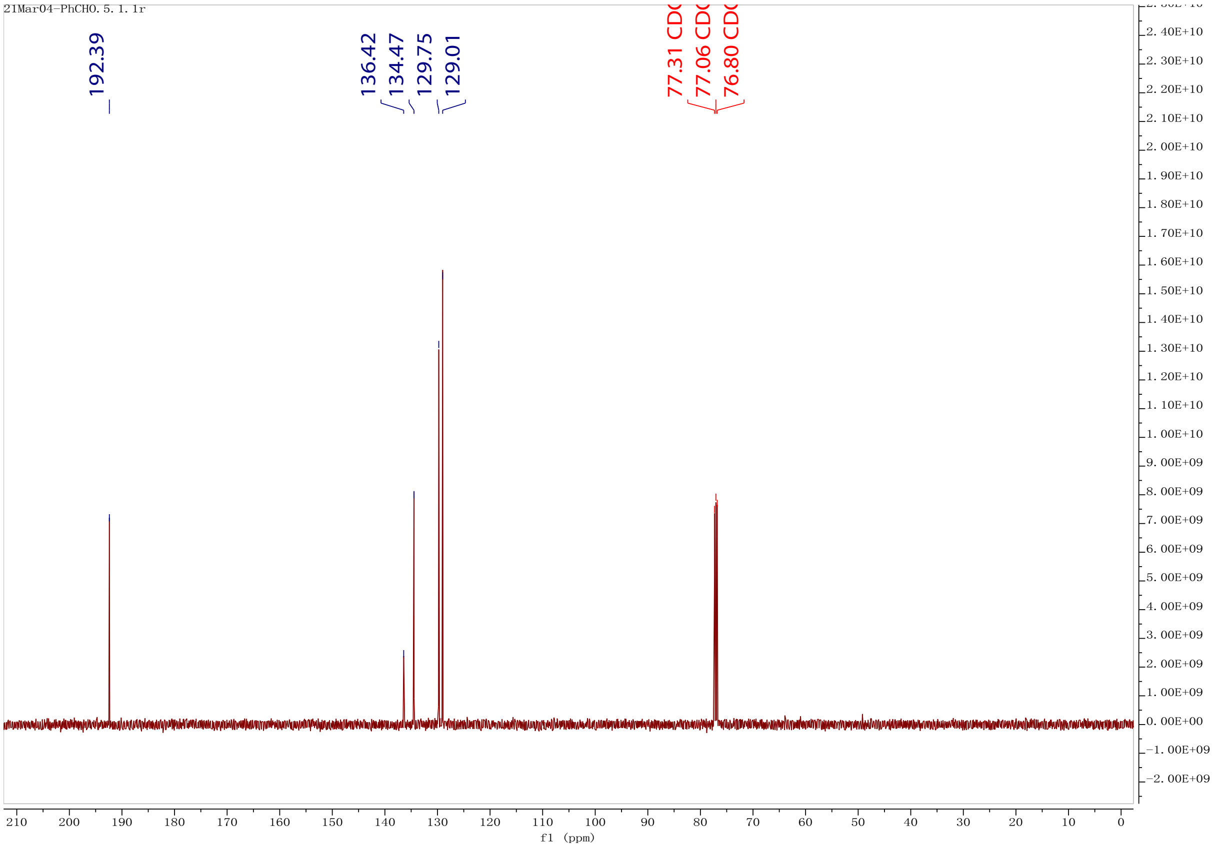


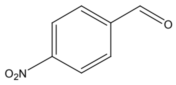
TGA
$[MoO_2L^4]_2$

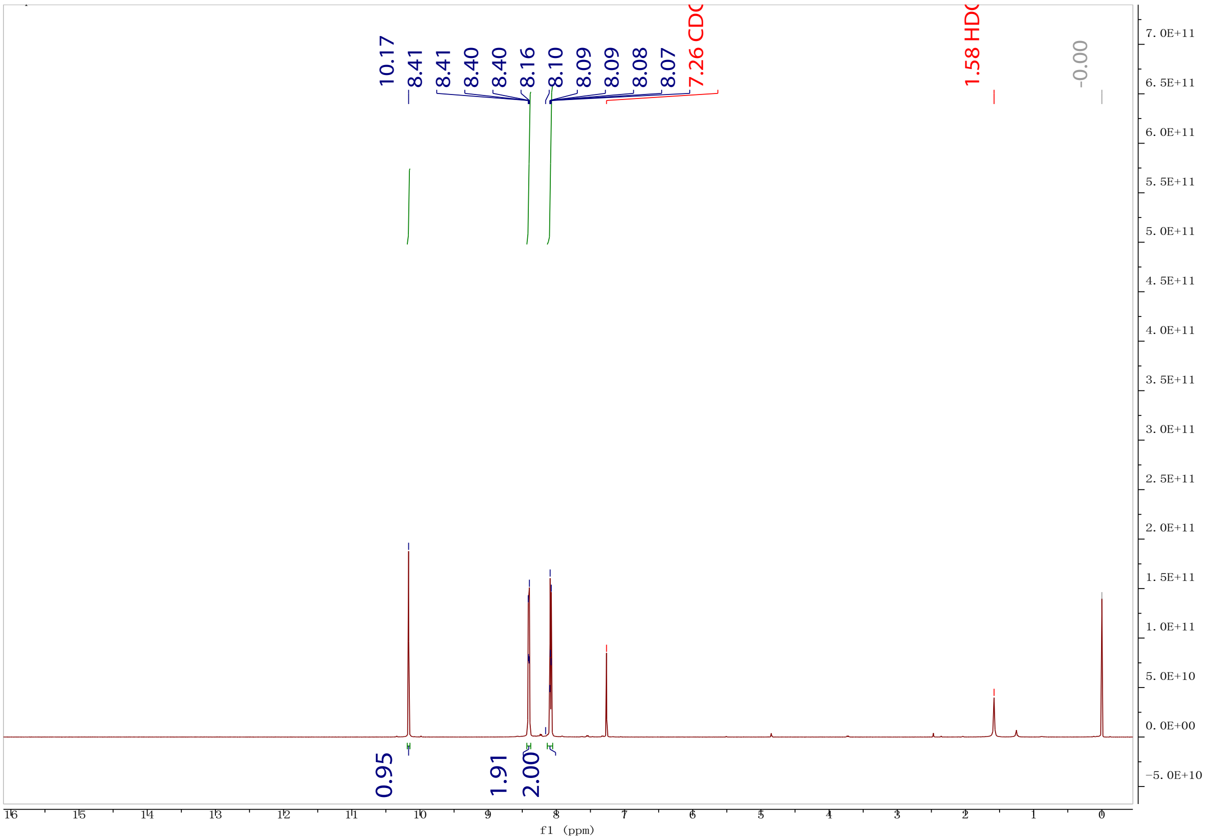


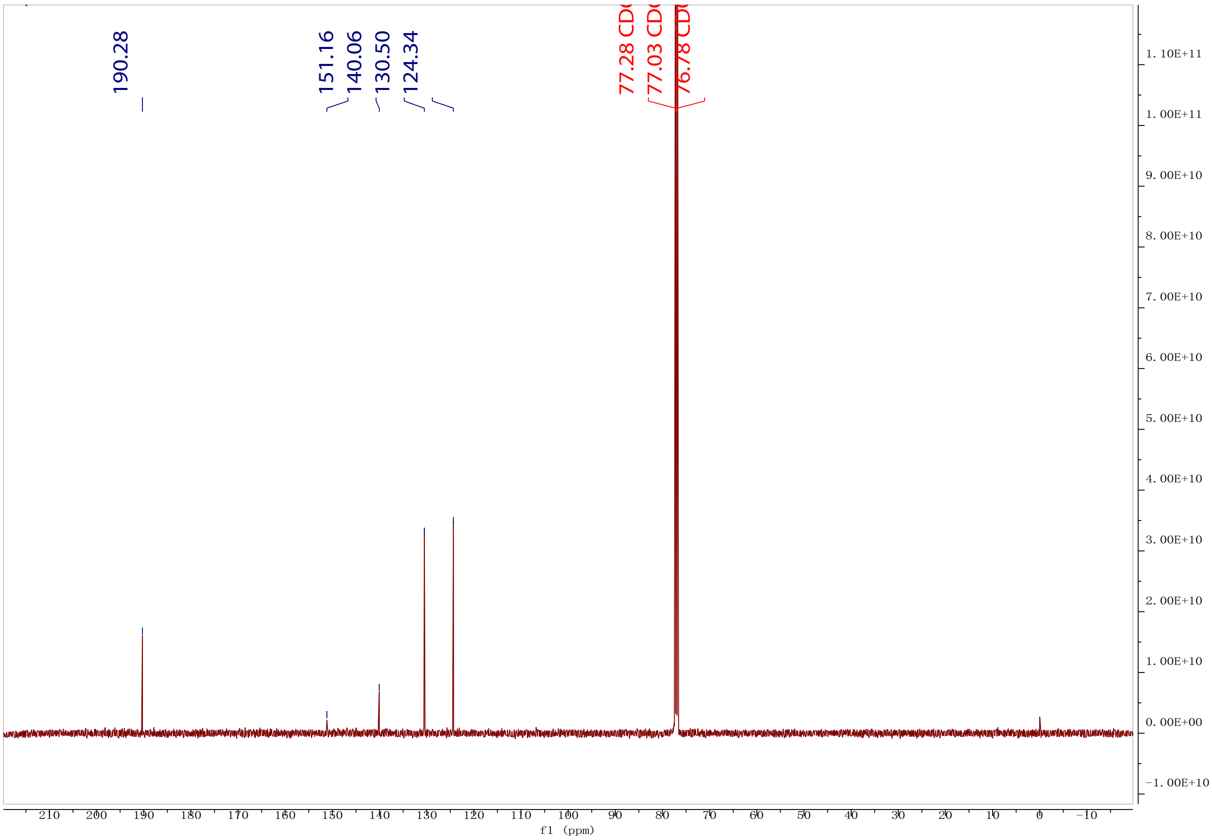

O


10.02
7.89
7.89
7.88
7.88
7.65
7.65
7.65
7.64
7.63
7.62
7.62
7.62
7.55
7.54
7.52
7.27 CDC
1.72 HDC
0.00
0.99
2.02
1.00
1.90
5. 0E+11
4. 5E+11
4. 0E+11
3. 5E+11
3. 0E+11
2. 5E+11
2. 0E+11
1. 5E+11
1. 0E+11
5. 0E+10
0. 0E+00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


21Mar04-PhCHO. 5. 1. 1r
192.39
136.42
134.47
129.75
129.01
77.31 CDC
77.06 CDC
76.80 CDC
2. 40E+10
2. 30E+10
2. 20E+10
2. 10E+10
2. 00E+10
1. 90E+10
1. 80E+10
1. 70E+10
1. 60E+10
1. 50E+10
1. 40E+10
1. 30E+10
1. 20E+10
1. 10E+10
1. 00E+10
9. 00E+09
8. 00E+09
7. 00E+09
6. 00E+09
5. 00E+09
4. 00E+09
3. 00E+09
2. 00E+09
1. 00E+09
0. 00E+00
-1. 00E+09
-2. 00E+09
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O2N


10.17
8.41
8.41
8.40
8.40
8.16
8.10
8.09
8.09
8.08
8.07
7.26 CDC
1.58 HDO
-0.00
0.95
1.91
2.00
7.0E+11
6.5E+11
6.0E+11
5.5E+11
5.0E+11
4.5E+11
4.0E+11
3.5E+11
3.0E+11
2.5E+11
2.0E+11
1.5E+11
1.0E+11
5.0E+10
0.0E+00
-5.0E+10
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


190.28
151.16
140.06
130.50
124.34
77.28 CDC
77.03 CDC
76.78 CDC
1.10E+11
1.00E+11
9.00E+10
8.00E+10
7.00E+10
6.00E+10
5.00E+10
4.00E+10
3.00E+10
2.00E+10
1.00E+10
0.00E+00
-1.00E+10
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)