

Synthesis and Characterization of Water Stable η^3 -Allyl Dicarbonyl Complexes of Molybdenum(II)

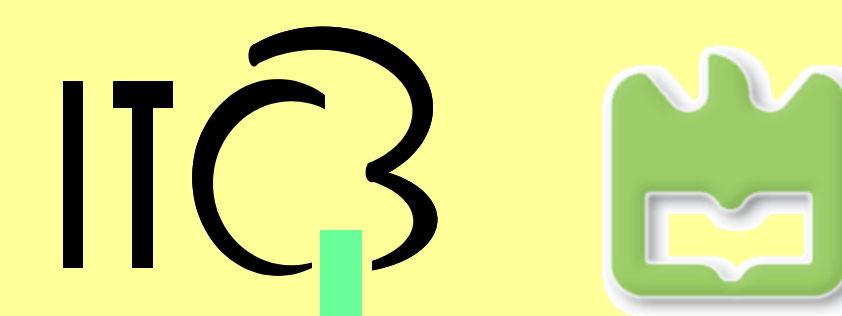
Carla A. Gamelas¹, Ana C. Gomes², Martyn Pillinger², Carlos C. Romão^{3,4}, Isabel S. Gonçalves²

¹Escola Superior de Tecnologia de Setúbal, Instituto Politécnico de Setúbal, Campus do IPS, Estefanilha, Setúbal, Portugal

²Department of Chemistry, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal

³Instituto de Tecnologia Química e Biológica, UNL, Av. da República, EAN, Apt 127, 2781-901 Oeiras, Portugal

⁴Alfama Ltd., Taguspark, Núcleo Central 267, 2740-122, Porto Salvo, Portugal



I. INTRODUCTION

The family of η^3 -allyldicarbonyl complexes of Mo(II) has been studied in coordination chemistry and catalysis, due to its facile preparation and introduction of a variety of ligands. Investigations in our laboratories have focused on new methods to prepare bent metallocene complexes of molybdenum and tungsten containing substituted cyclopentadienyl ligands or other h^5 -cyclic analogues, and we used $[\text{Mo}(\eta^3\text{-allyl})\text{Cl}(\text{CO})_2(\text{NCMe})_2]$ as starting material [1]. The acetonitrile ligands in pseudo-octahedral molybdenum(II) complexes of the type $[\text{Mo}(\eta^3\text{-allyl})\text{X}(\text{CO})_2(\text{NCMe})_2]$ (X = halide) can be readily replaced by other monodentate or bidentate ligands. The resultant complexes have been successfully used as catalysts or catalyst precursors for imine aziridination, oxidation of triphenylphosphine with molecular oxygen, allylic alkylations, and recently for the oxidation of olefins [2].

Here we report the aqueous syntheses of complexes $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{CO})_2(\text{L})]$ [L = 2,2'-bipyridine (1), 4,4'-di-*tert*-butyl-2,2'-bipyridine (2), 2,2'-bipyridine-5,5'-dicarboxylate (3)] and their oxidative decarbonylation reactions. Complexes 1-3 have been characterized by FTIR, NMR (including COSY and HMQC) and EA.

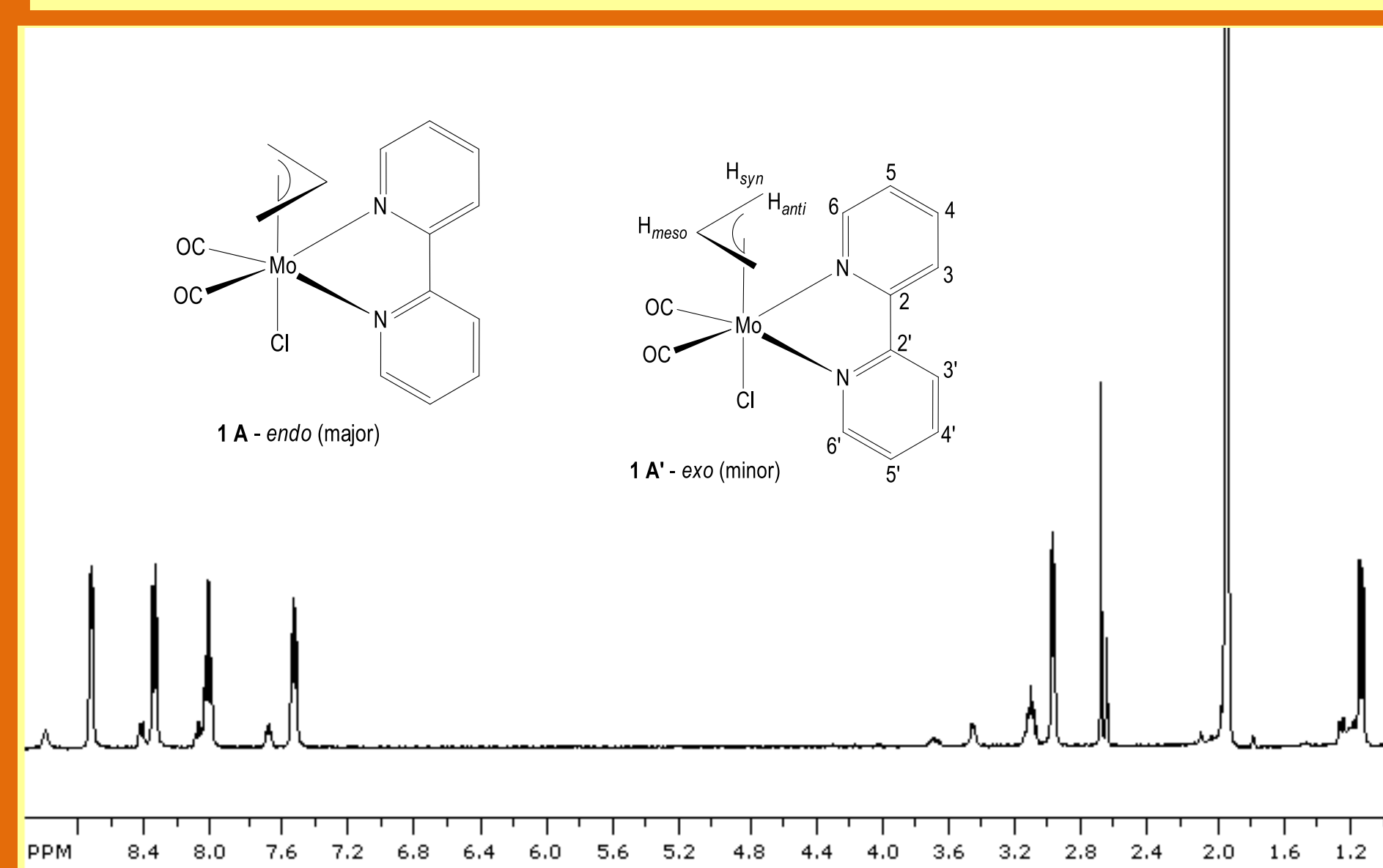
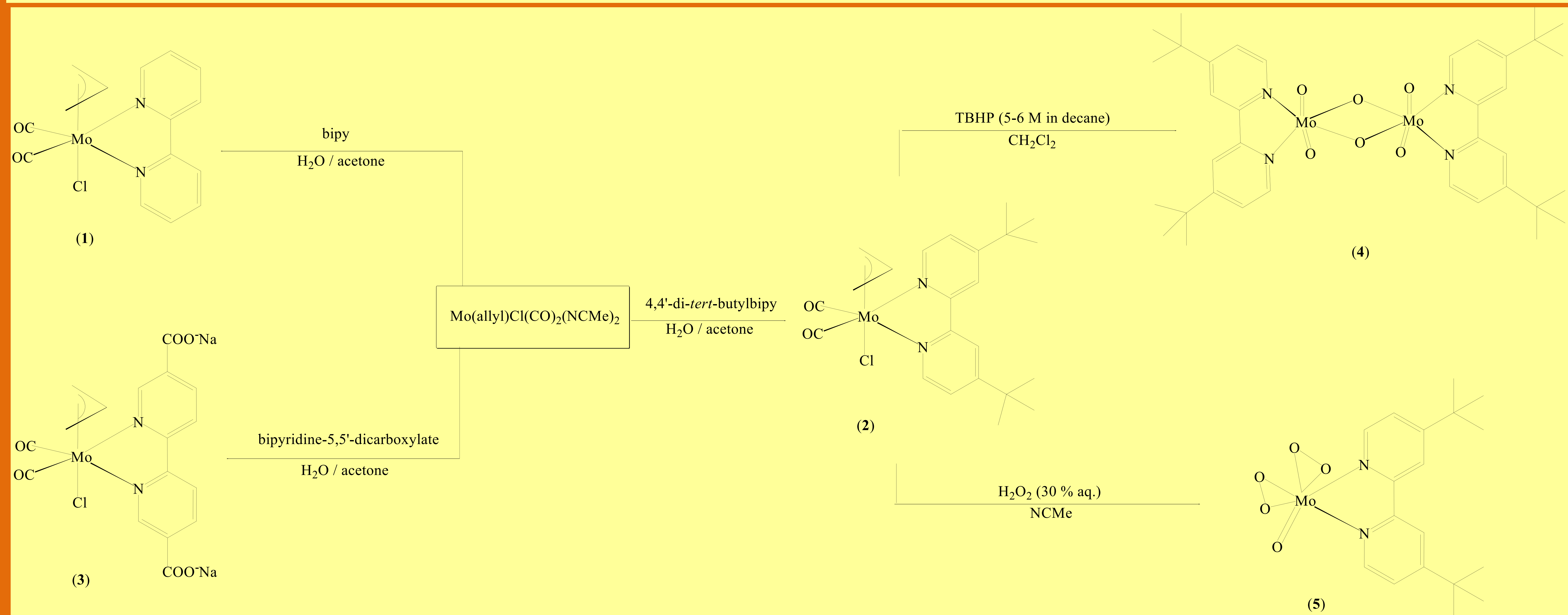


Figure 1. ¹H NMR spectrum of (1) in acetone-*d*₆ at r.t.

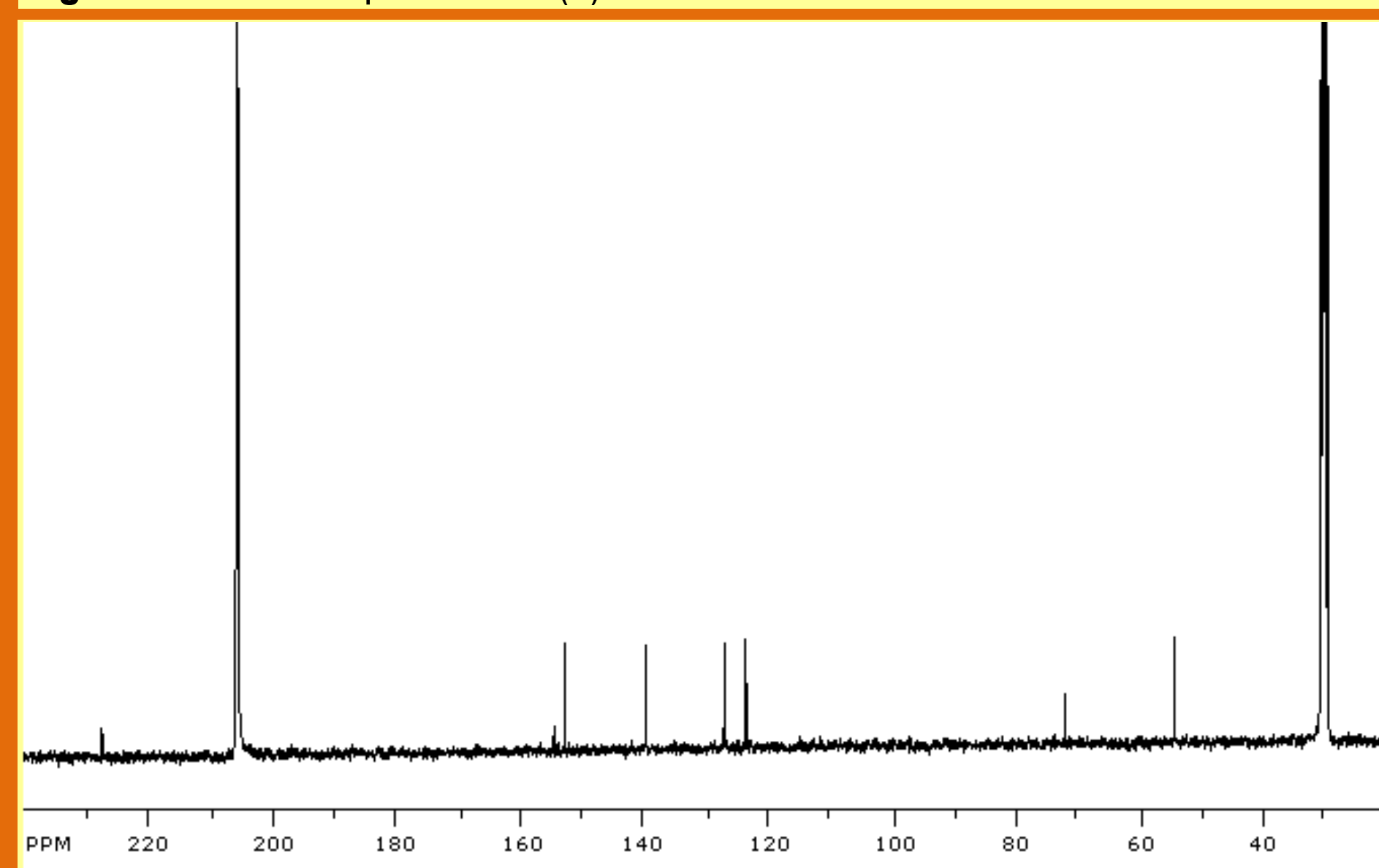


Figure 2. ¹³C NMR spectrum of (1) in acetone-*d*₆ at r.t.

Complexes (1) and (3): Each isomer has only three allyl signals in the ¹H NMR. Both isomers are therefore symmetrical (with bipy ligand in an equatorial position, *trans* to the two carbonyls).

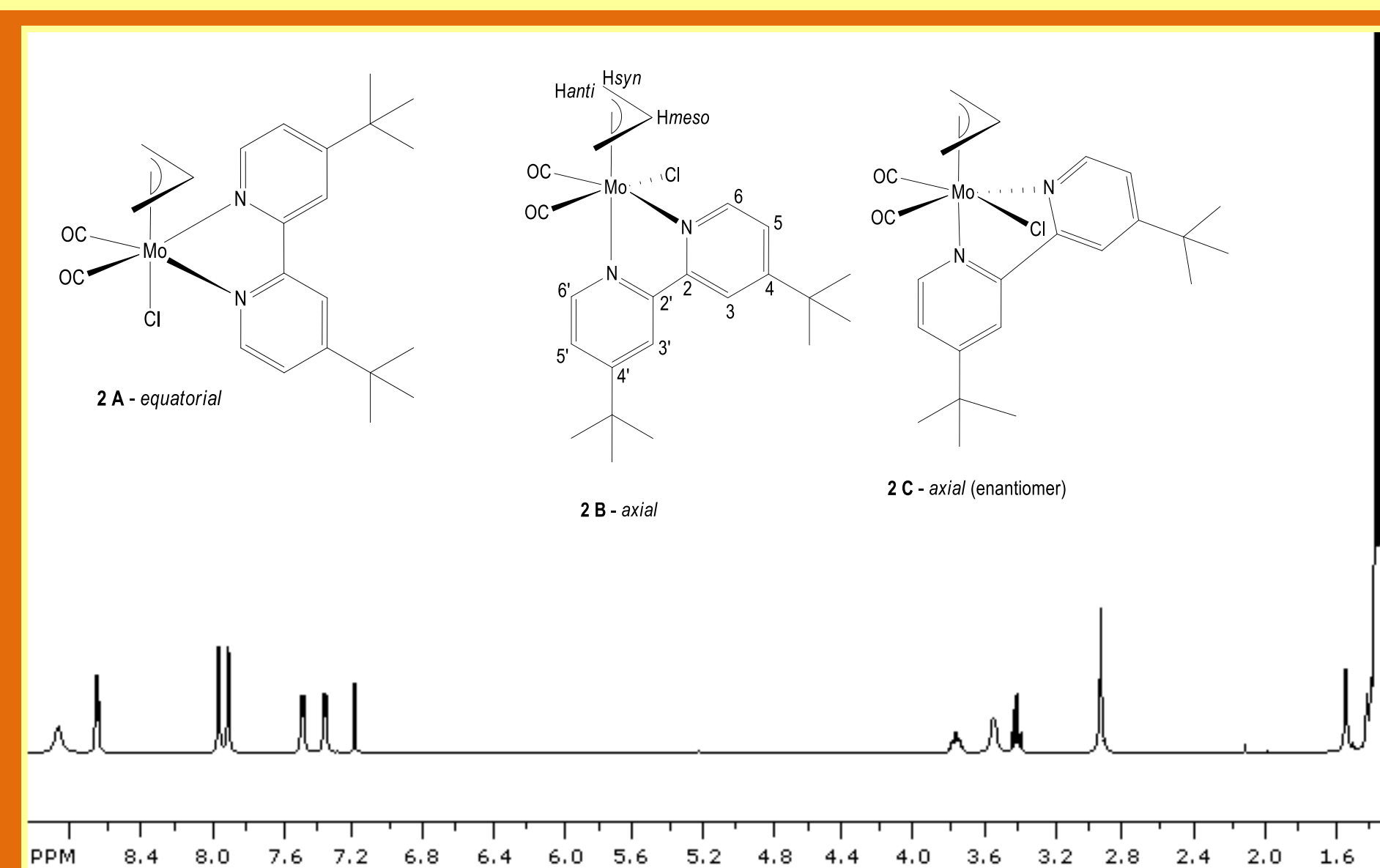


Figure 3. ¹H NMR spectrum of (2) in CDCl₃ at r.t.

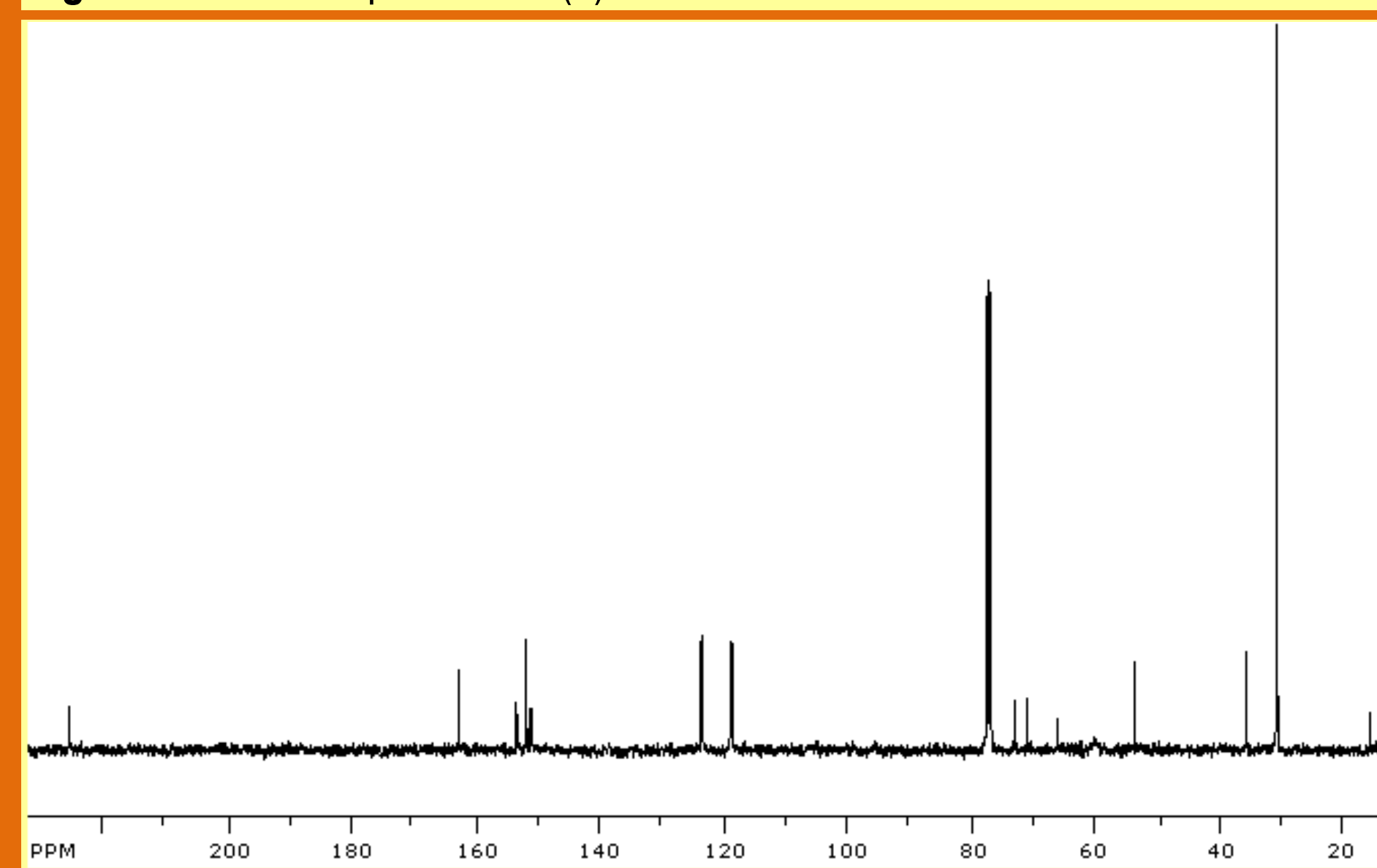


Figure 4. ¹³C NMR spectrum of (2) in CDCl₃ at r.t.

Complex (2): Two sets of signals for both the di-*tert*-butylbipyridine and the allyl ligands are reported in the literature.³

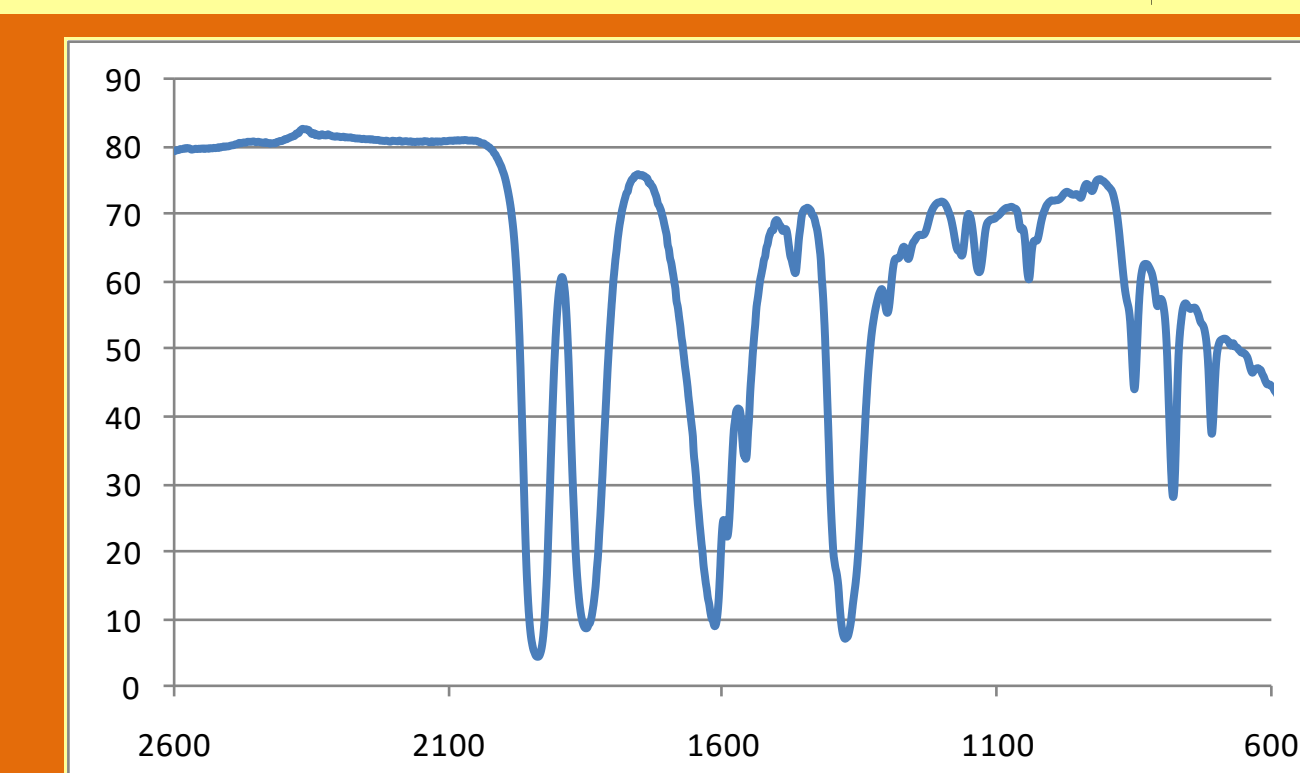


Figure 5. Infrared spectrum of (3)

Complex	IR (cm ⁻¹)
1	1938 (s), 1838 (s), $\nu(\text{CO})$ 1601 (m), 1615 (m), $\nu(\text{C=C})$ and $\nu(\text{C=N})$
2	1943 (s), 1852 (s), $\nu(\text{CO})$ 1615 (m), 1547 (w), $\nu(\text{C=C})$ and $\nu(\text{C=N})$
3	1938 (s), 1847 (s), $\nu(\text{CO})$ 1615 (s), 1592 (sh), 1561 (m), 1378 (s), $\nu(\text{COO}^-)$

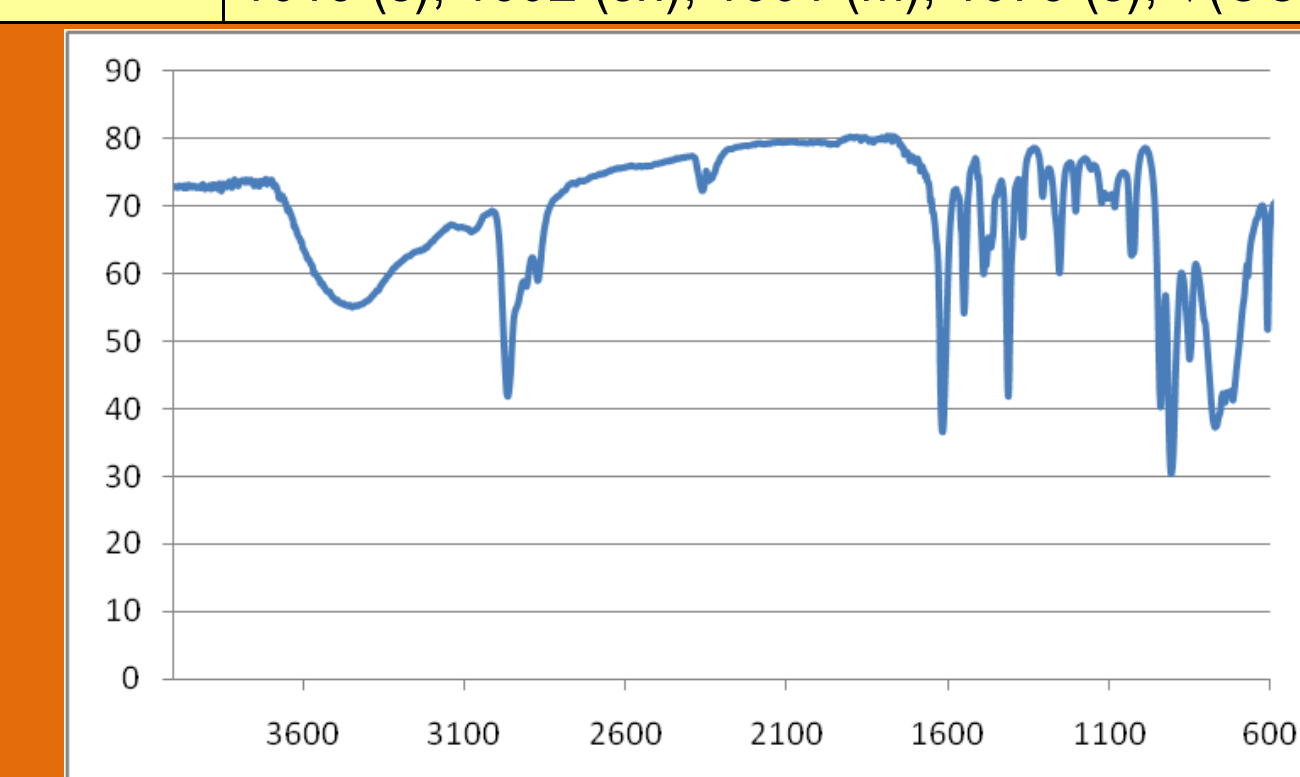


Figure 6. Infrared spectrum of dimer (4)

Complex	IR (cm ⁻¹)
4	1614 (m), 1550 (w), $\nu(\text{C=C})$ and $\nu(\text{C=N})$ 939 (s), $\nu_{\text{sym}}(\text{Mo=O})$, 907 (s), $\nu_{\text{asym}}(\text{Mo=O})$ 771 (s), 744 (s), 711 (sh), $\nu(\text{Mo-O-Mo})$
5	1618 (s), 1450 (w), $\nu(\text{C=C})$ and $\nu(\text{C=N})$ 948 (s), $\nu_{\text{sym}}(\text{Mo=O})$ 874 (sh), 862 (s), $\nu(\text{O-O})$

CONCLUSIONS

This study reports the synthesis and characterization of η^3 -allyldicarbonyl molybdenum(II) complexes 1-3 and their oxidation reactions. The results reveal the potential application of these complexes in aqueous catalysis (which is presently being investigated), due to their high stability in water.

REFERENCES

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