

Supporting Information

Oxidation of secondary alcohols by conventional and microwave-assisted methods using molybdenum complexes of ONO donor ligands

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¹H and ¹³C NMR spectral studies

Table S1 provides ¹H NMR spectral data of ligands and complexes. Fig S1 presents representative ¹H NMR spectra of a ligand and the respective complex. The broad signal appearing at $\delta = 12.21$ - 12.34 ppm, owing to the phenolic OH group, disappears in the spectra of the complexes due to coordination of the phenolic oxygen to the molybdenum. The appearance of two signals due to azomethine proton (each equivalent to 1H) in complexes, one at nearly same position as of ligand and other at significantly down field with a coordination-induced shifts [$\Delta\delta = [\delta(\text{complex}) - \delta(\text{free ligand})]$] of 0.21 –0.35 ppm demonstrates the coordination of only one of the azomethine nitrogen atom. Similarly, signal equivalent to two protons due to the –NH– remains at nearly same position with one equivalent of proton, supports the enolization of only one of the NH groups and consequent replacement of H by the metal ion. Aromatic and aliphatic protons appear in the expected regions in spectra of the ligands as well as of the complexes, with slight shifts in their positions.

Table S1 ¹H NMR chemical shifts^a [δ in ppm] of ligands and complexes recorded in DMSO-d₆

Compounds	–CH=N–	Aromatic H	–OH	–NH	–CH ₃
I	8.73(s, 2H)	7.57(m, 6H), 7.64(m, 2H), 7.95(d, 4H)	12.34(s, 1H)	12.15(s, 2H)	2.31(s, 3H)
1	8.94(s, 1H), 8.82(s, 1H)	7.59(m, 4H), 7.65(m, 3H), 8.02(d, 5H)	-	12.03(s, 1H)	2.36(s, 3H)
$\Delta\delta$	(0.21)				
II	8.74(s, 2H)	7.61(s, 2H), 7.86(d, 4H), 8.81(b, 4H)	12.21(s, 1H)	12.43(s, 2H)	2.39(s, 3H)
2	9.02(s, 1H), 8.81(s, 1H)	7.63(s, 1H), 7.88(d, 4H), 7.97(s, 1H)	-	12.21(s, 1H)	2.37(s, 3H)
$\Delta\delta$	(0.28)	8.79(b, 4H)			
III	8.75 (s, 2H)	7.69(d, 4H), 8.34(s, 2H), 8.82(s, 2H), 9.28(s, 2H)	12.21(s, 1H)	12.42(s, 2H)	2.37(s, 3H)

3	9.10(s, 1H), 8.80(s, 1H)	7.56(s, 2H), 7.58(s, 1H), 7.97(s, 1H),	-	12.15(s, 1H)	2.36(s, 3H)
$\Delta\delta$	(0.35)	8.32(m, 2H), 8.77(d, 3H), 8.98(s, 1H)			

^aLetters given in parentheses indicate the signal structure: s = singlet, m = multiplet, d = doublet, br = broad (unresolved).

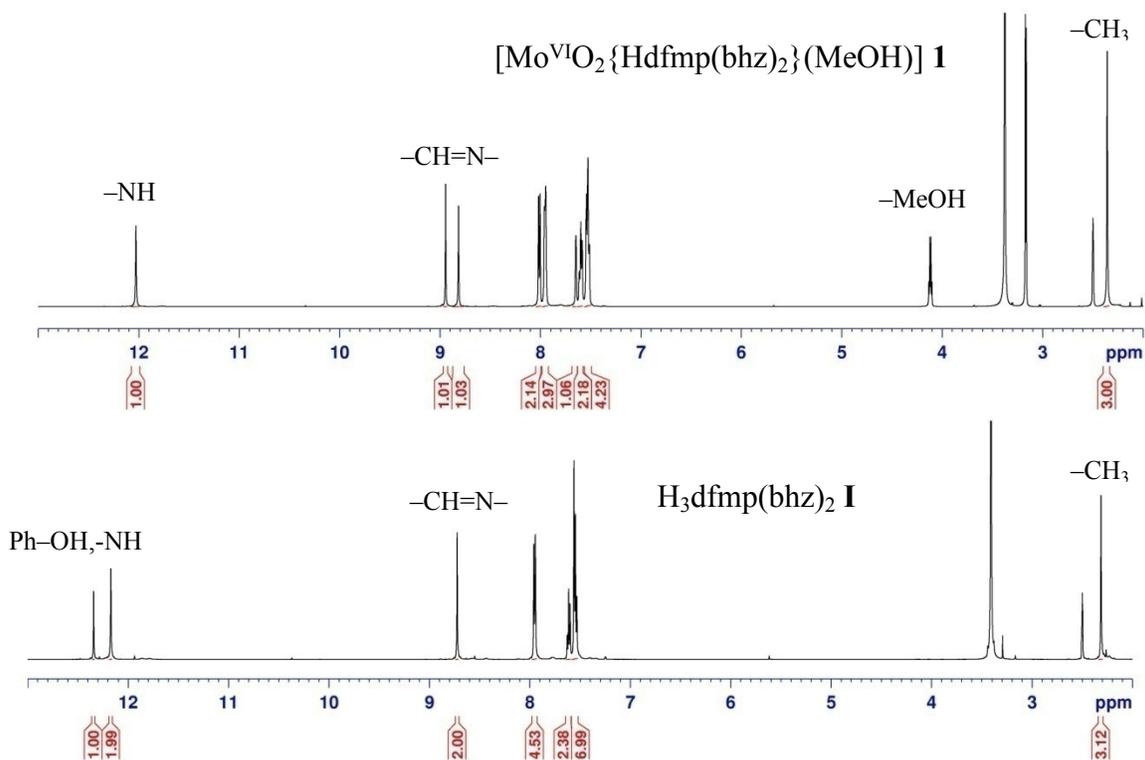


Fig. S1 ¹H NMR spectra of H₃dfmp(bhz)₂ **I** and [Mo^{VI}O₂{Hdfmp(bhz)₂}(MeOH)] **1**.

Fig S2 presents representative spectra of ligand **I** and its complex. Ligands **I**, **II** and **III** display 11, 10 and 12 signals corresponding to the 23, 21 and 21 carbon atoms, respectively due to the presence of a centre of symmetry. A total of 18, 16 and 20 signals were observed for complexes **1**, **2** and **3**, respectively due to asymmetry generated after coordination of the ligands to the molybdenum. All ligands display single signal each for azomethine (C8 and C9) and the enolate (C10 and C11) carbon atoms. Appearance of two distinct signals each due to azomethine (C8 and C9) and the enolate carbons (C10 and C11) with significant coordination-induced shifts ($\Delta\delta$) against one of the signal each for these two different carbons of the ligands suggest the involvement of only one set of the azomethine nitrogen and the enolate oxygen atoms in coordination. In addition, these complexes show one signal each for coordinated MeOH.

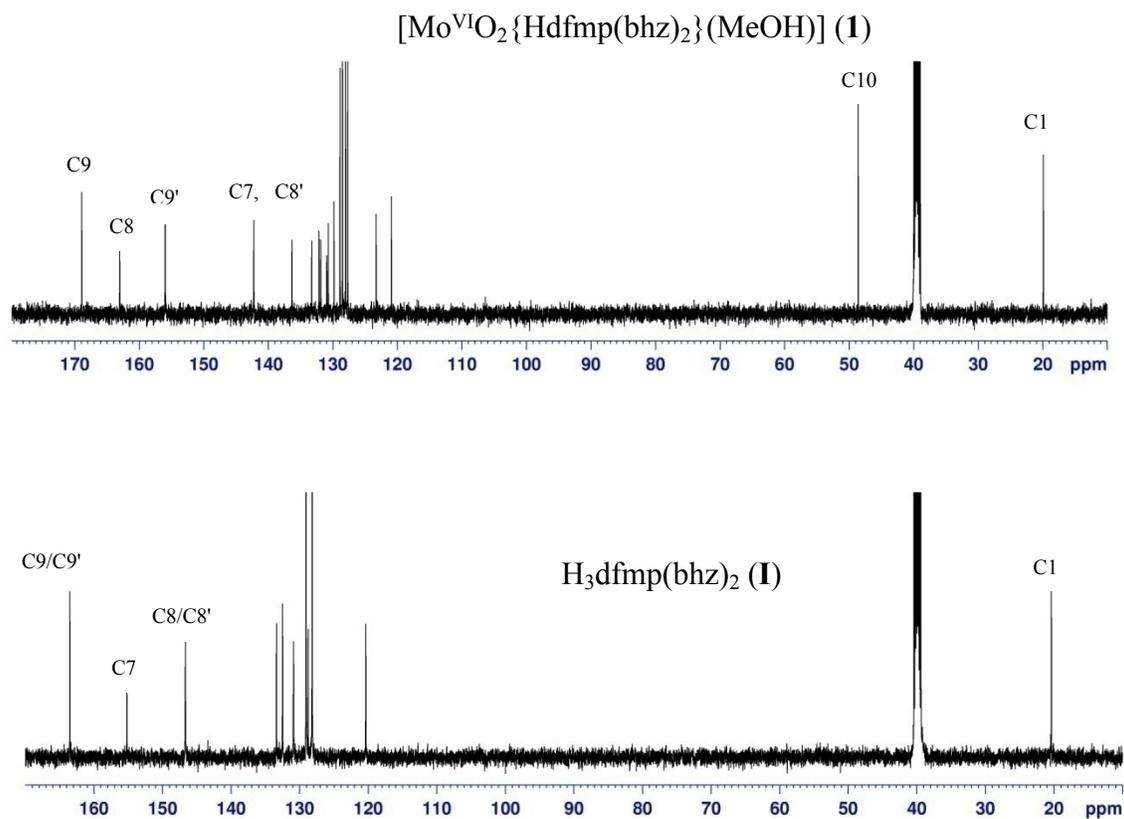


Fig. S2 ^{13}C NMR spectra of $\text{H}_3\text{dfmp}(\text{bhz})_2$ **I** and complex $\text{Mo}^{\text{VI}}\text{O}_2\{\text{Hdfmp}(\text{bhz})_2\}(\text{MeOH})$ **1**.
For numbering of carbons see Table 7.