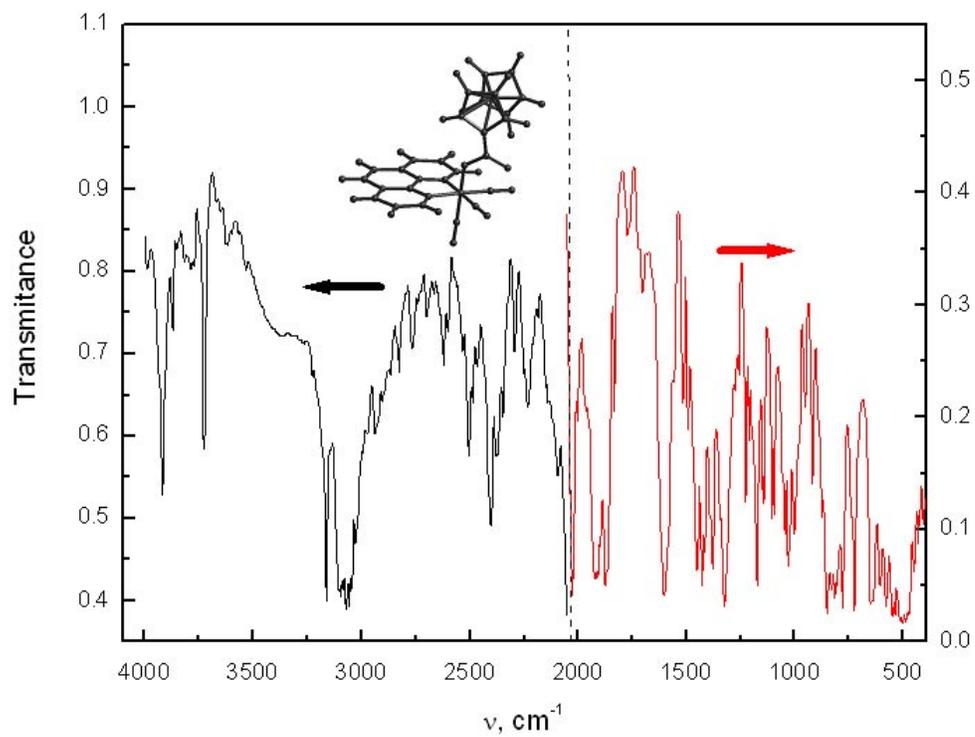
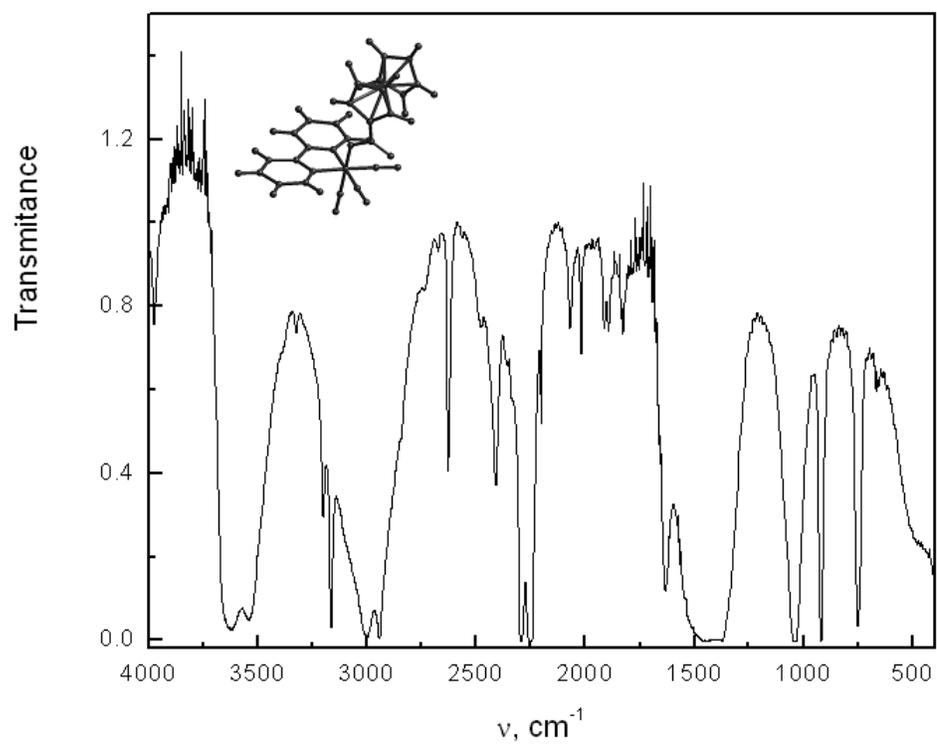


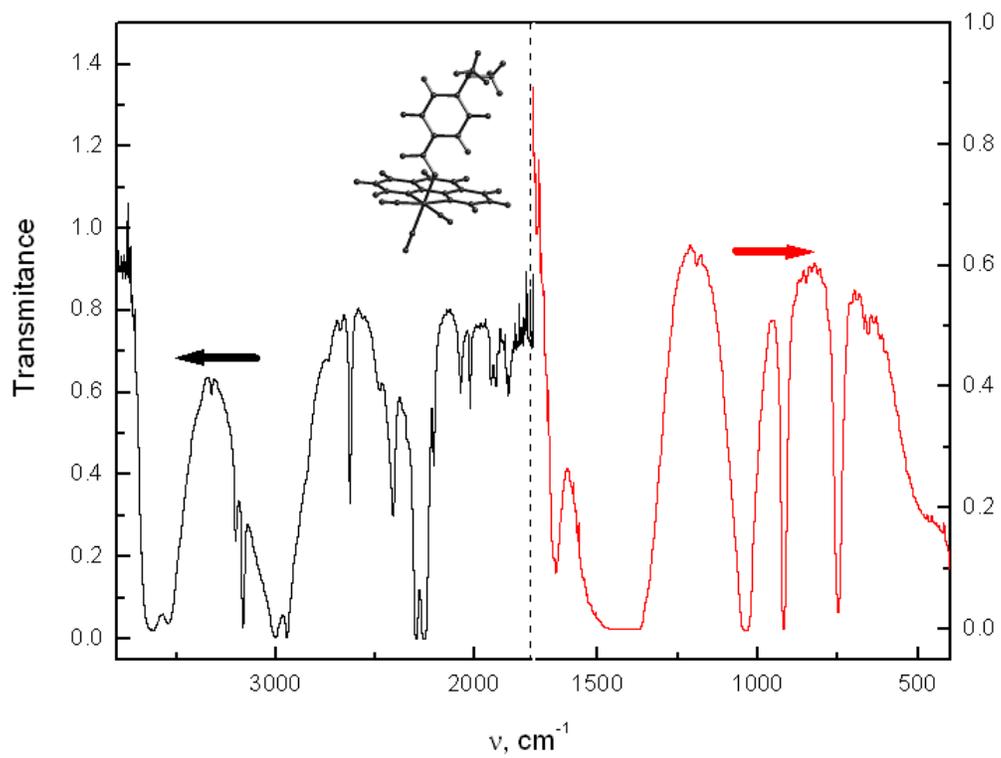
## Supporting Information



**Figure 1S.** FTIR spectrum of fac-(ferroceneCO<sub>2</sub>)Re(CO)<sub>3</sub>(phen).



**Figure 2S** . FTIR spectrum of  $3 \times 10^{-3}$  M fac-(ferroceneCO<sub>2</sub>) Re(CO)<sub>3</sub>(2,2'-bpy) in CH<sub>3</sub>CN.



**Figure 3S.** FTIR spectrum of  $2.8 \times 10^{-3}$  M  $\text{fac}-(\text{DMABCO}_2)\text{Re}(\text{CO})_3(\text{phen})$  in  $\text{CH}_3\text{CN}$ .

### *Interpretation of the NMR spectra*

<sup>1</sup>H-NMR spectra of the complexes in CD<sub>3</sub>CN solutions, Fig. 4S - 6S, were recorded with a Bruker AC 250 Spectrometer (at 250.13). Chemical shifts (in ppm), were calibrated from a residual solvent signal (CH<sub>3</sub>CN 1.94 ppm) and they are reported relative to Me<sub>4</sub>Si.

The protons in the ligands of the complexes are identified in the structures attached to the spectra. <sup>1</sup>H NMR data for the complexes are also listed at the bottom of this section.

Protons in the (CH<sub>3</sub>)<sub>2</sub>N group of the 4-DMABCO<sub>2</sub> ligand and the non substituted cyclopentadienyl (cp) in the ferrocene-CO<sub>2</sub> ligand appear as a singlet signal to high field in the spectra of the respective complexes. The AB system generated by Ha and Hb protons in the p-substituted aromatic ring of 4-DMABCO<sub>2</sub> appears as a two doublet in the NMR spectra. Similarly, the Ha and Hb protons in substituted cp in the ferrocene (Fc) ligand appears as a two pseudo-triplet signal (related to a dd pattern) in the high field.

The H5 of the phen ligand in both phen complexes appears as a singlet. Three signals due to AXM systems generated by three H2, H3 and H4 protons coupled among themselves are observed in the aromatic region of the spectra. The dd signal with a pattern of two 3J coupling is assigned to H3 in accordance with its position in the molecule. The other signals are assigned to systems generated for a 3J and 4J coupling as it is expected for the H2 and H4 protons. The final assignment for these protons was realized by comparison with fac-[ClRe(CO)<sub>3</sub>(phen)] and considering the deshielding generated by CO ligands placed in the equatorial plane of complex on the **H2** signal.

The spectra of the bpy ligand in the aromatic region shows two signals with the ddd multiplicity expected for H4 (doublet pseudo-triplet) and H5 protons, and two signals with a dd multiplicity expected for H3 and H6 protons. The chemical shift of these protons may be established on the same structural consideration given to the protons in the Phen ligand because of the proximity to carbonyl ligands (H6) and the analysis of the coupling constants to other protons.

**fac-(4-DMABCO<sub>2</sub>)Re<sup>I</sup>(CO)<sub>3</sub>(phen):**

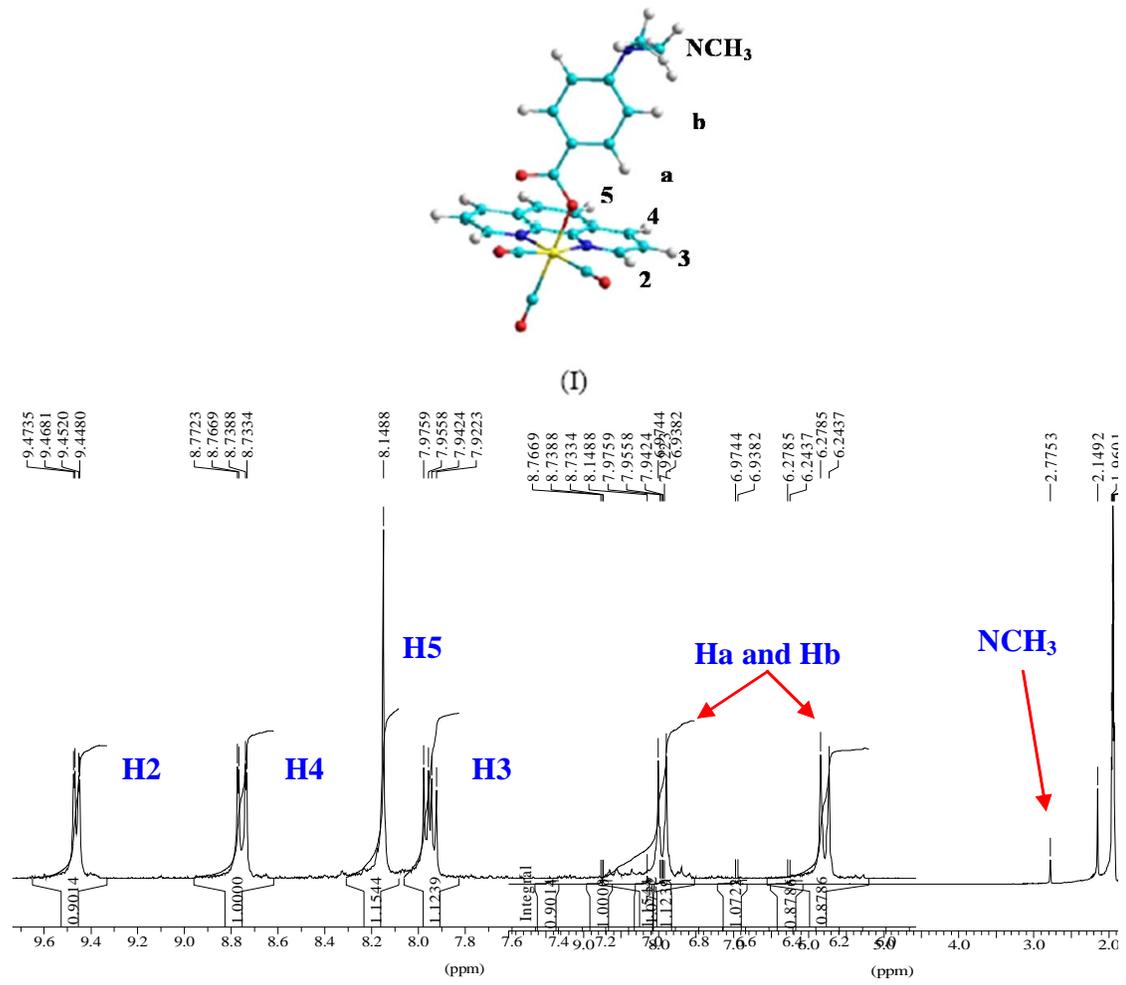
$^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , in ppm): 9.46 (2H, dd,  $\text{H}_2$ ), 8.75(2H,dd,  $\text{H}_4$ ), 8.15(2H,s,  $\text{H}_5$ ), 7.95(2H, dd,  $\text{H}_3$ ), 2.78 (6H, s,  $\text{H}_6$ ) for Phen ligand. 6.96 (2H, d), 6.26 (2H, d) for Ha and Hb of the DMA ligand.

**fac-(FerroceneCO<sub>2</sub>)Re<sup>I</sup>(CO)<sub>3</sub>(phen):**

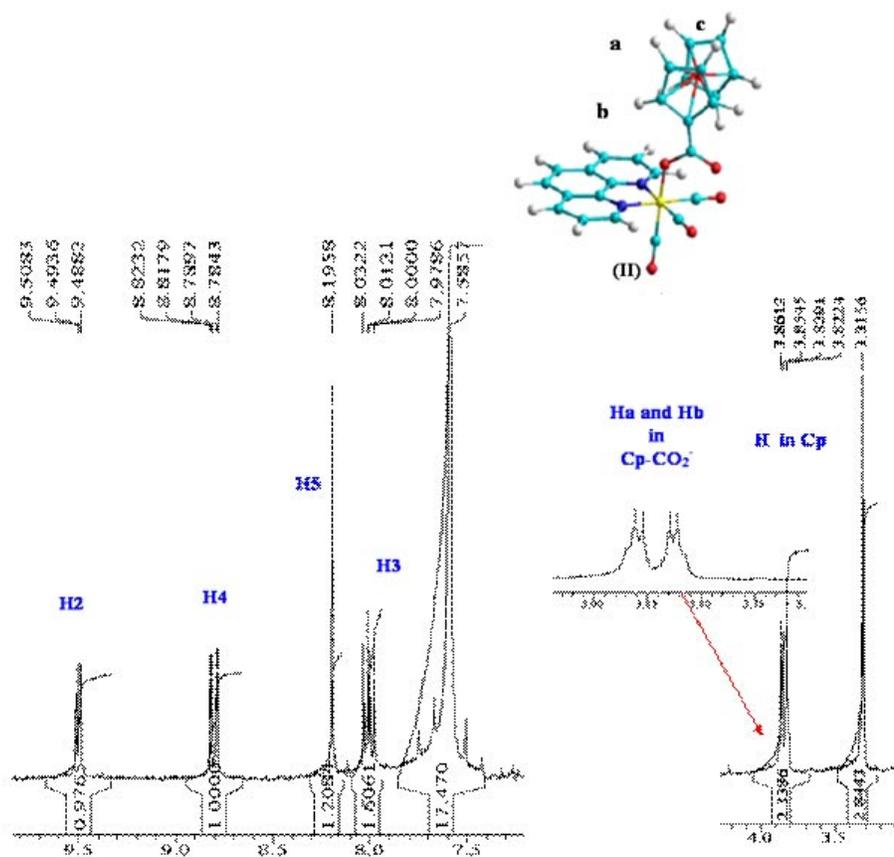
$^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , in ppm): 9.50 (2H, dd,  $\text{H}_2$ ), 8.80 (2H,dd,  $\text{H}_4$ ), 8.20 (2H,s,  $\text{H}_5$ ), 8.0 (2H, dd,  $\text{H}_3$ ) for Phen ligand. 3.85 (2H,dd), 3.82 (2H,dd) for Cp-sust. and 3.32 (5H,s) for Cp of the FerroceneCO<sub>2</sub> ligand.

**fac-(FerroceneCO<sub>2</sub>)Re<sup>I</sup>(CO)<sub>3</sub>(2,2'-bpy):**

$^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , in ppm): 9.12 (2H, dd,  $\text{H}_6$ ), 8.50 (2H,dd,  $\text{H}_3$ ), 8.24 (2H,ddd,  $\text{H}_4$ ), 7.66 (2H, ddd,  $\text{H}_5$ ) for bpy ligand. 4.06(2H,dd), 3.98 (2H,dd) for Cp-sust. and 3.65 (5H,s) for Cp of the FerroceneCO<sub>2</sub> ligand.



**Figure 4S**



**Figure 5S**

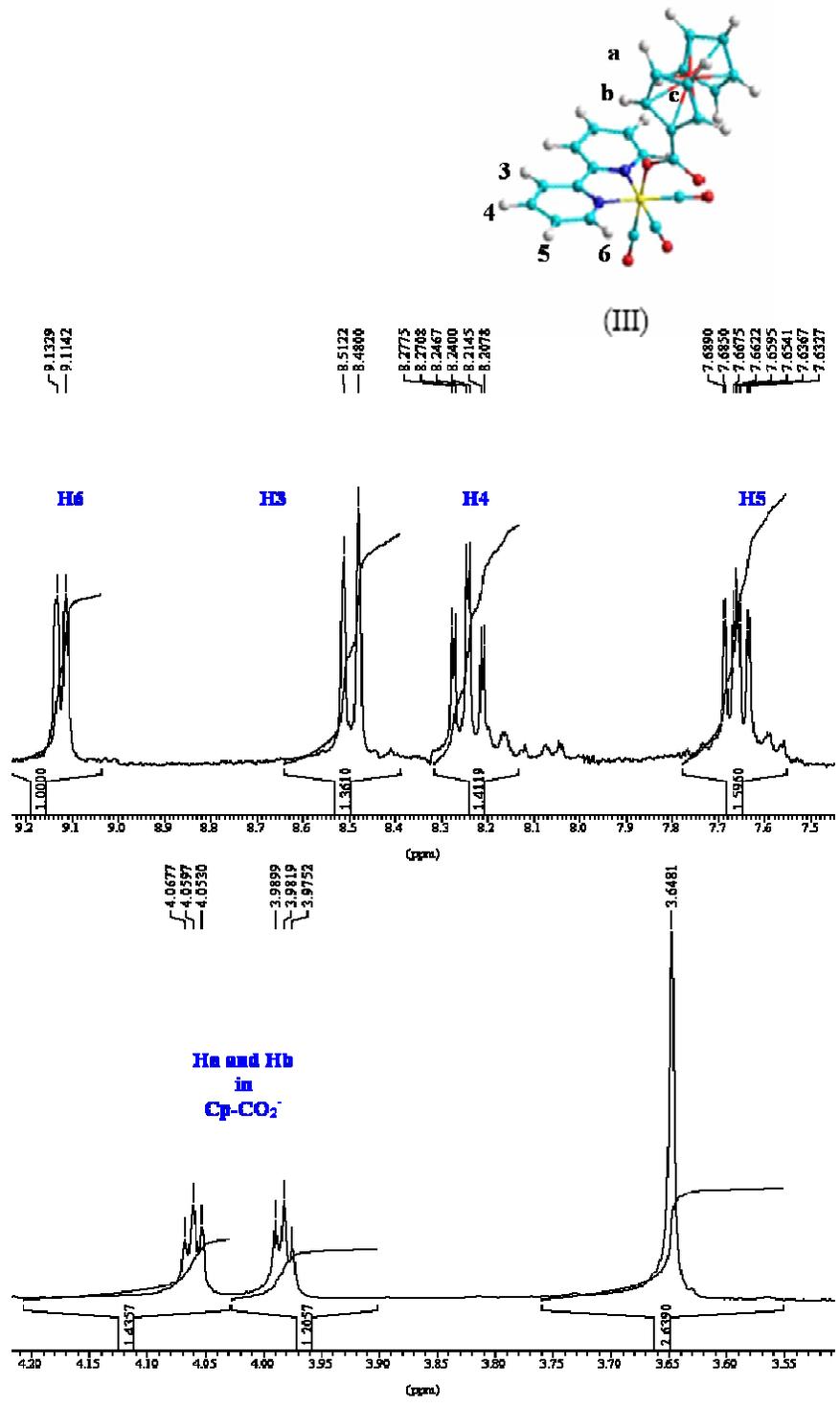


Figure 6S