Synthesis and Photochemical Properties of Re(I) Tricarbonyl Complexes Bound to Thione and Thiazole-2-ylidene Ligands

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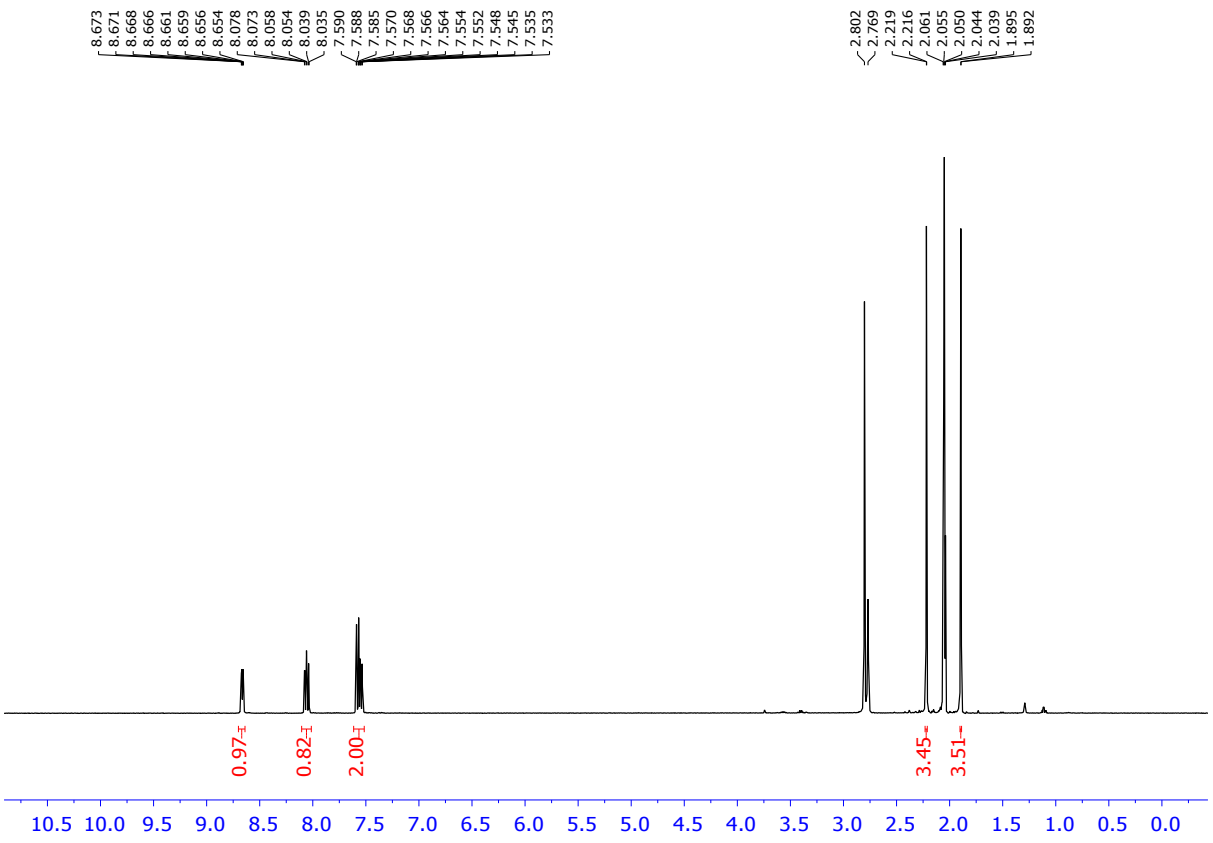
Supporting Information



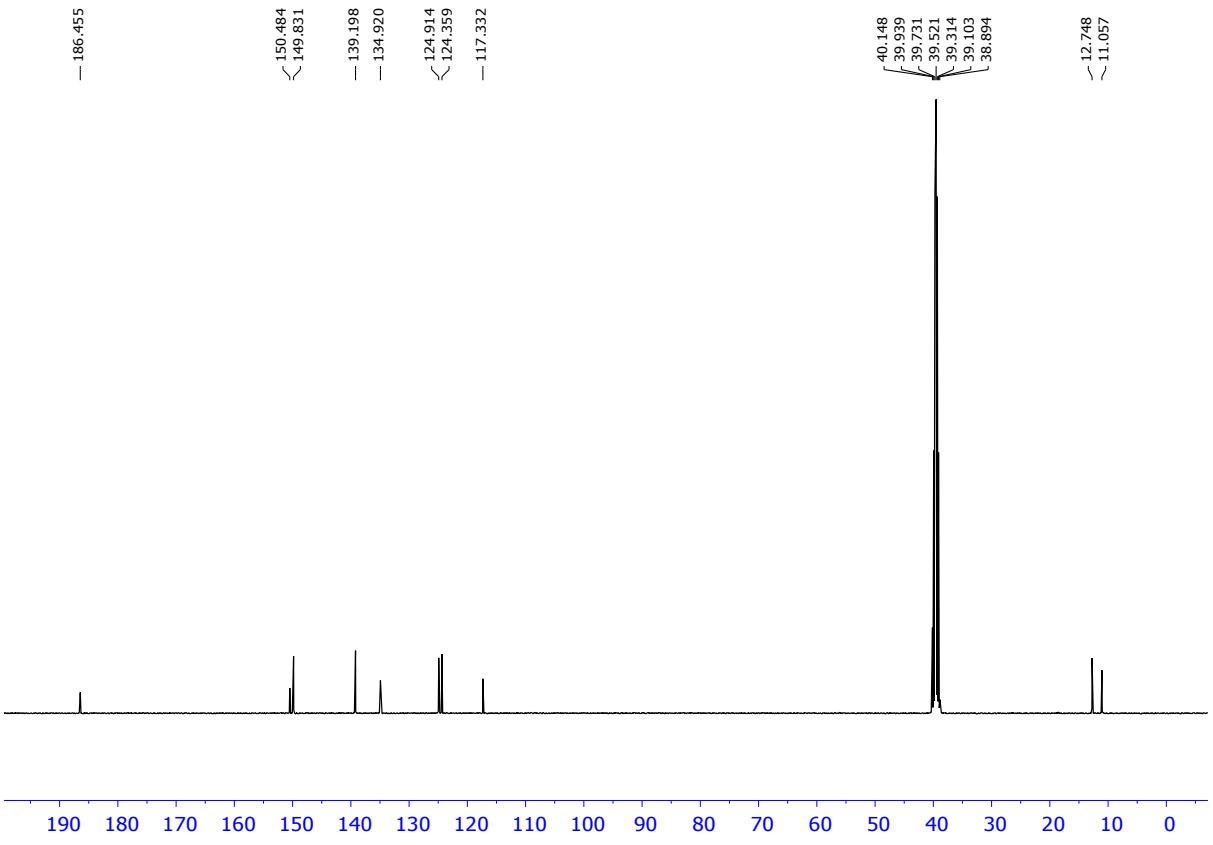


Figure S1 and S2: ^{1}H and ^{13}C-NMR of **1** in acetone-d_6 dimethylsulfoxide-d_6, respectively.

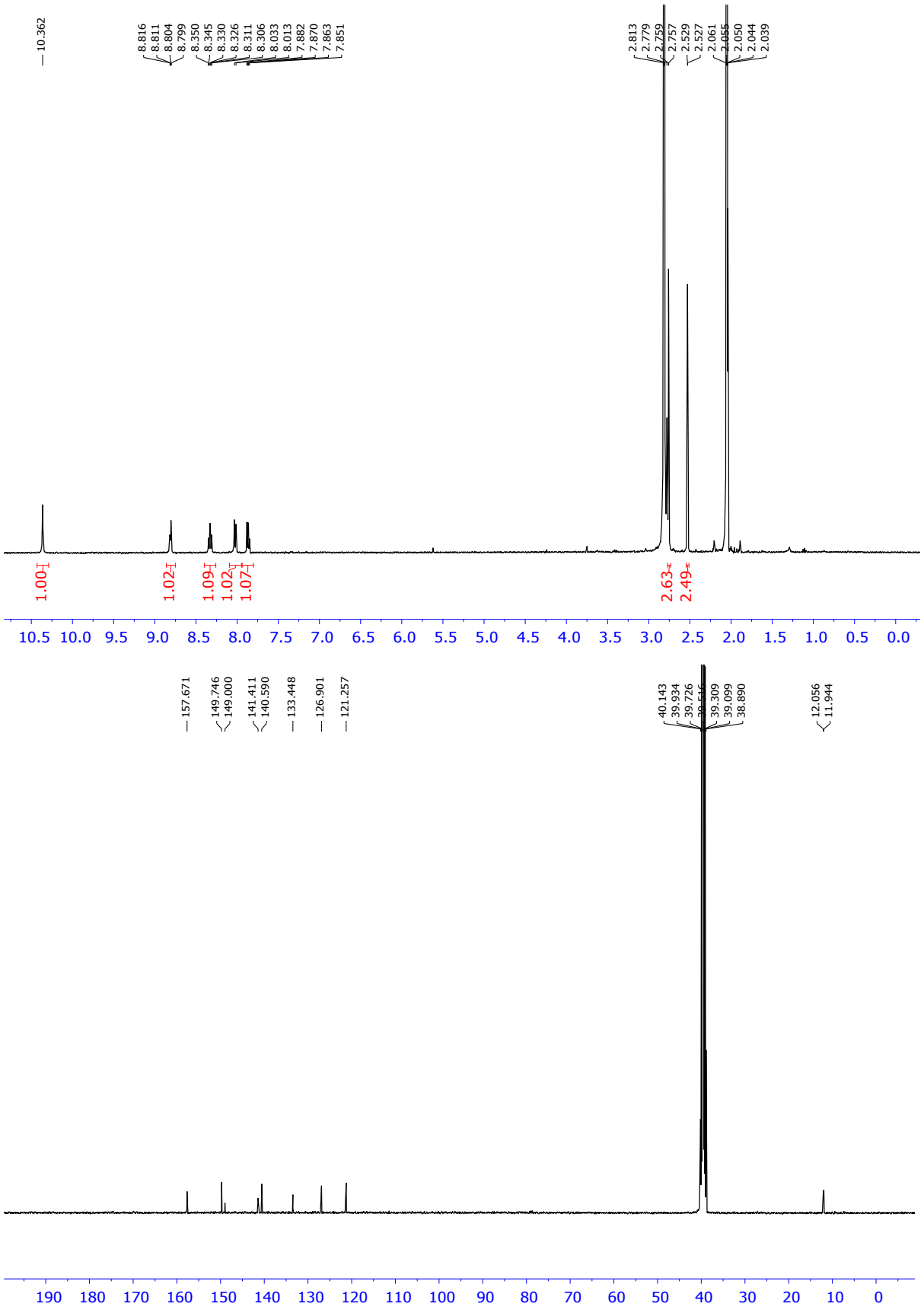
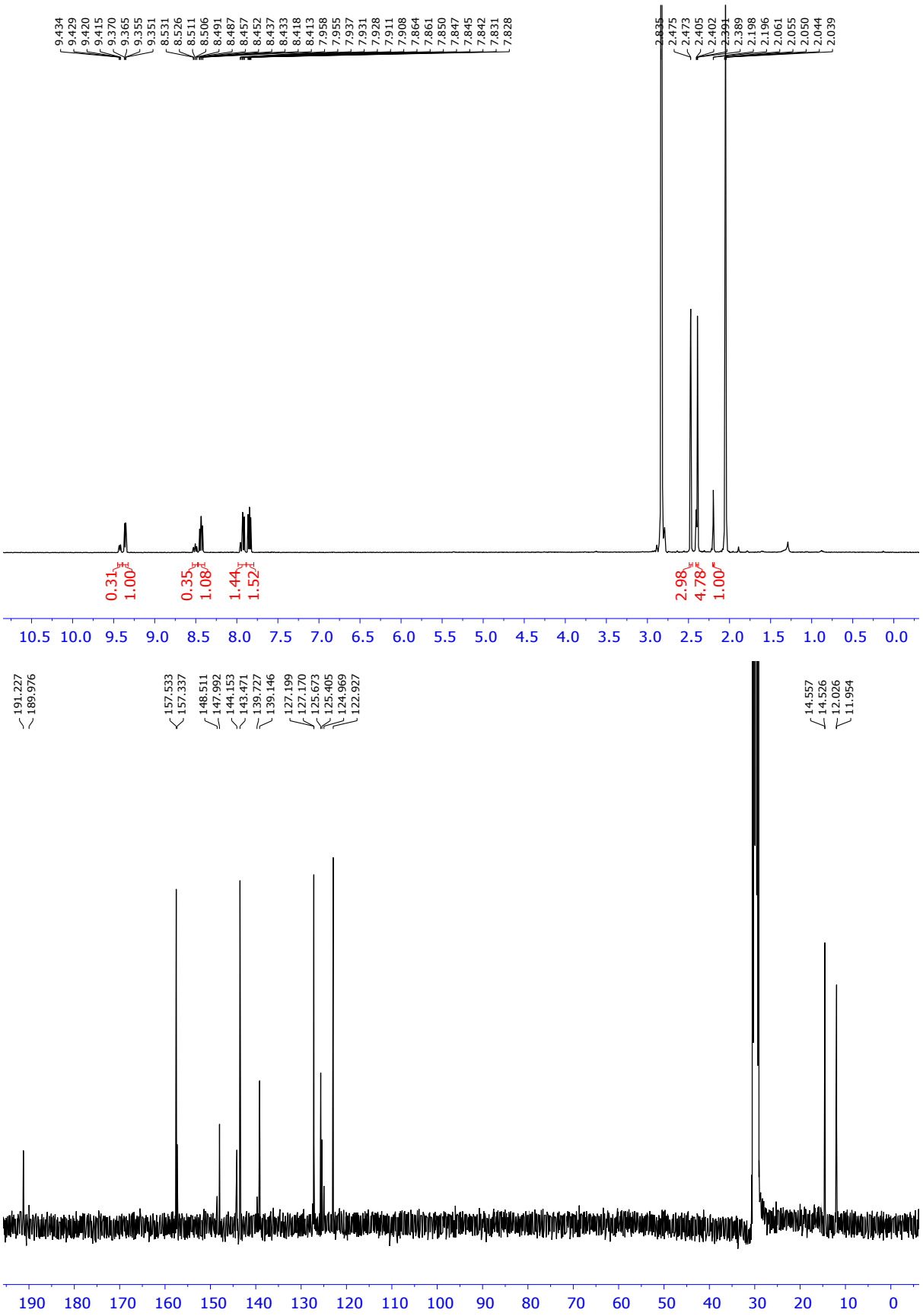
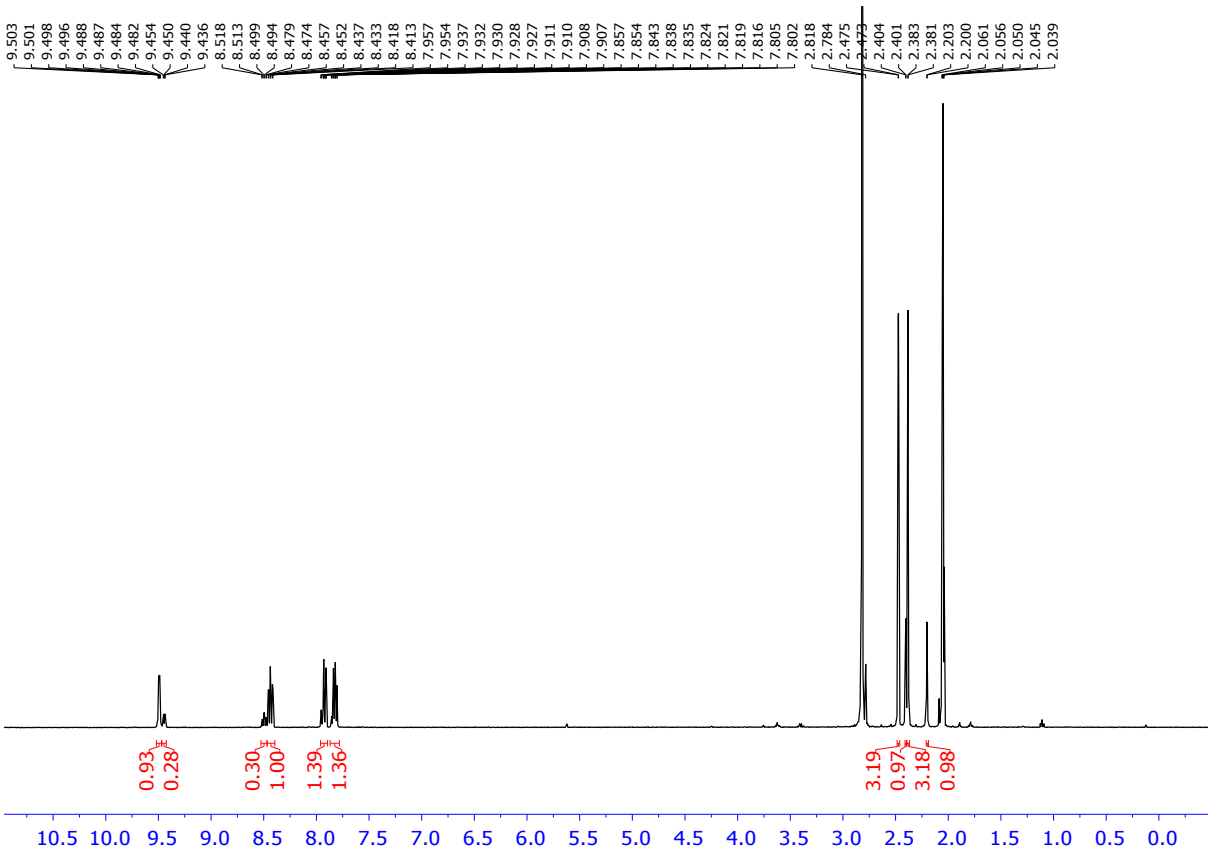
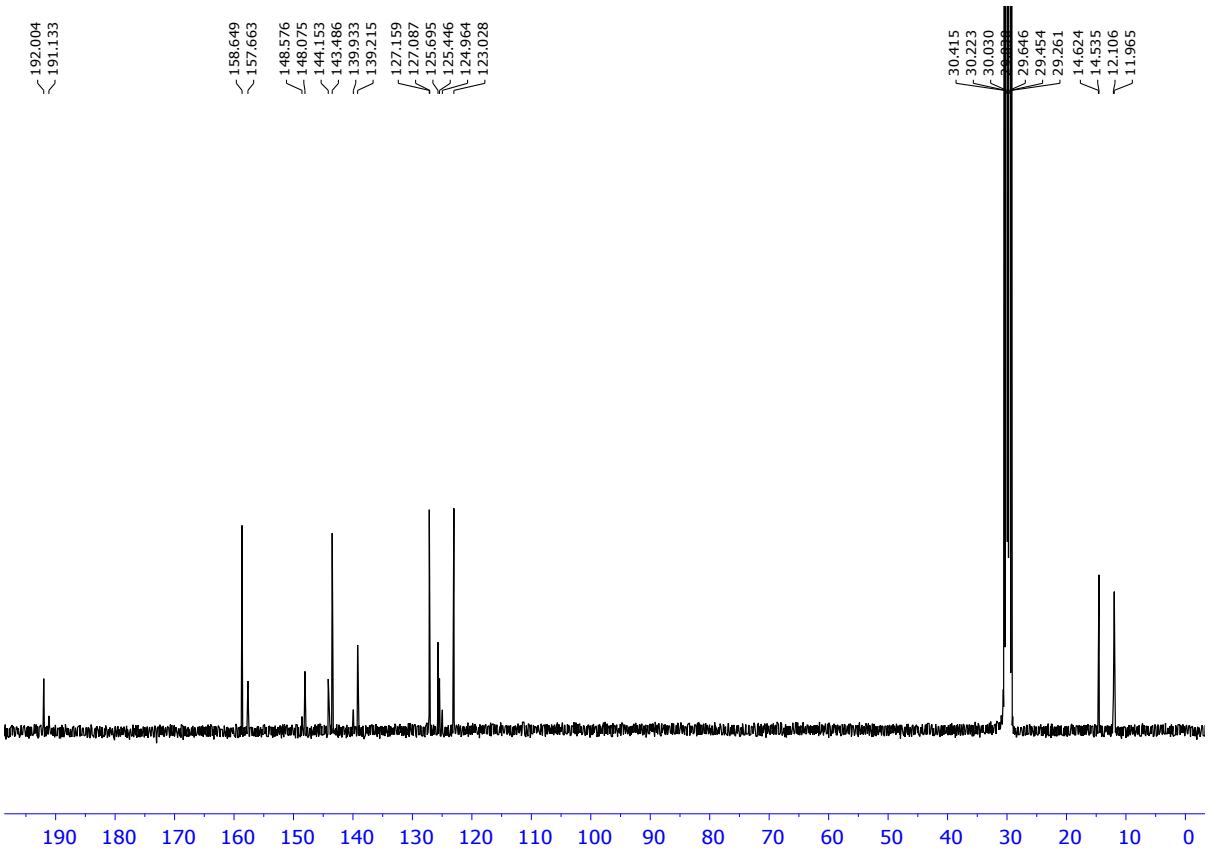


Figure S3 and S4: ^{1}H and ^{13}C-NMR of **2**H[PF_6] in acetone-d_6 dimethylsulfoxide-d_6, respectively.

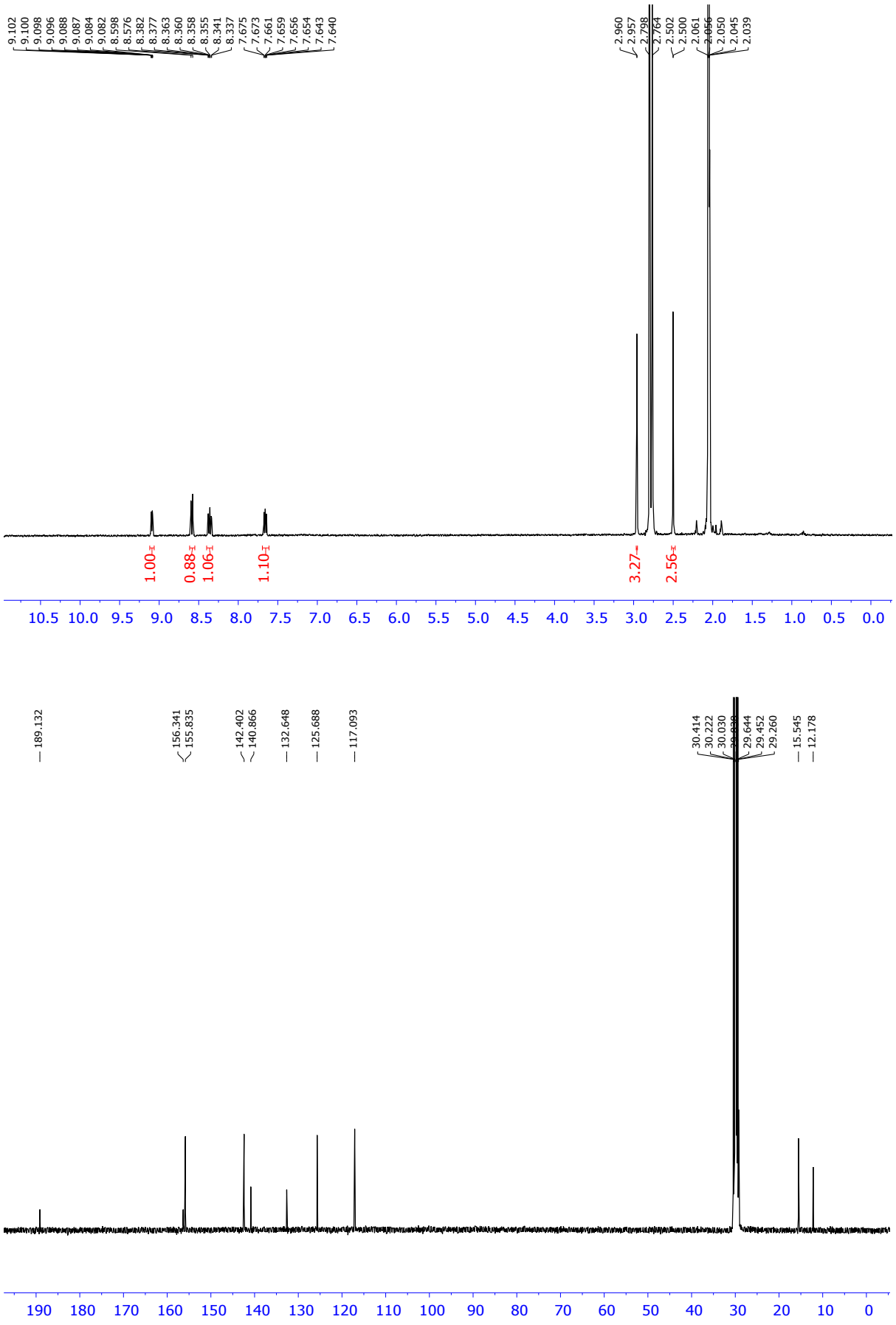


Figures S5 and S6: ^{1}H and ^{13}C-NMR of Re(**1**)$(CO)_3$Cl in acetone-d_6.





Figures S7 and S8: ^{1}H and ^{13}C-NMR of Re(**1**)$(CO)_3$Br in acetone-d_6.



Figures S9 and S10: ^{1}H and ^{13}C-NMR of Re(**2**)$(CO)_3$Br in acetone-d_6.

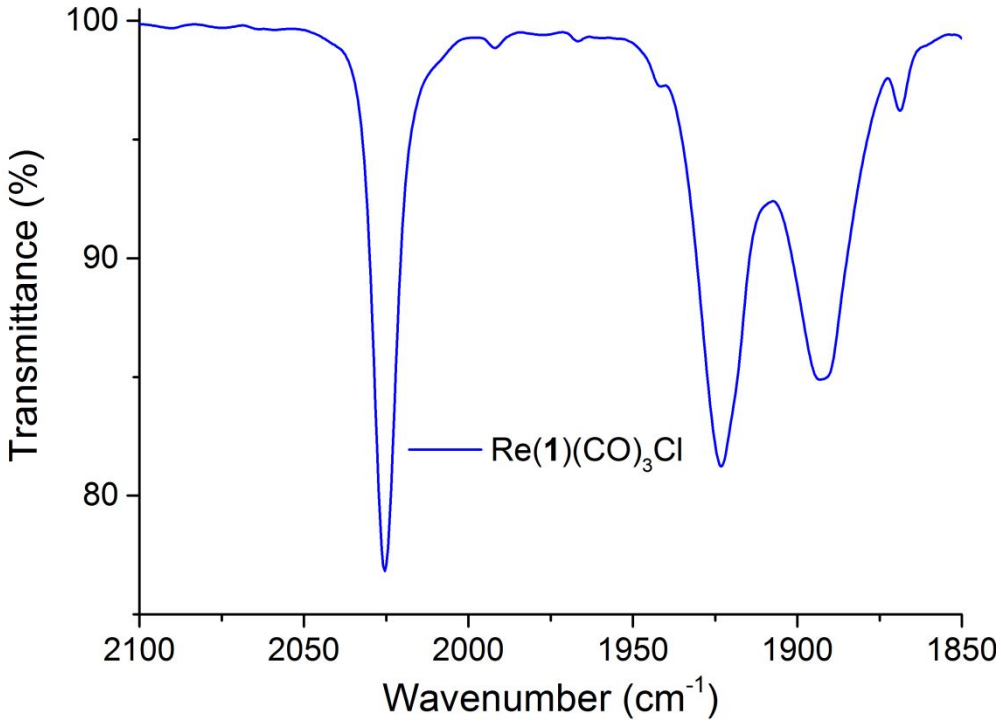


Figure S11: FT-IR spectrum of Re(**1**)$(CO)_3$Cl in dichloromethane.

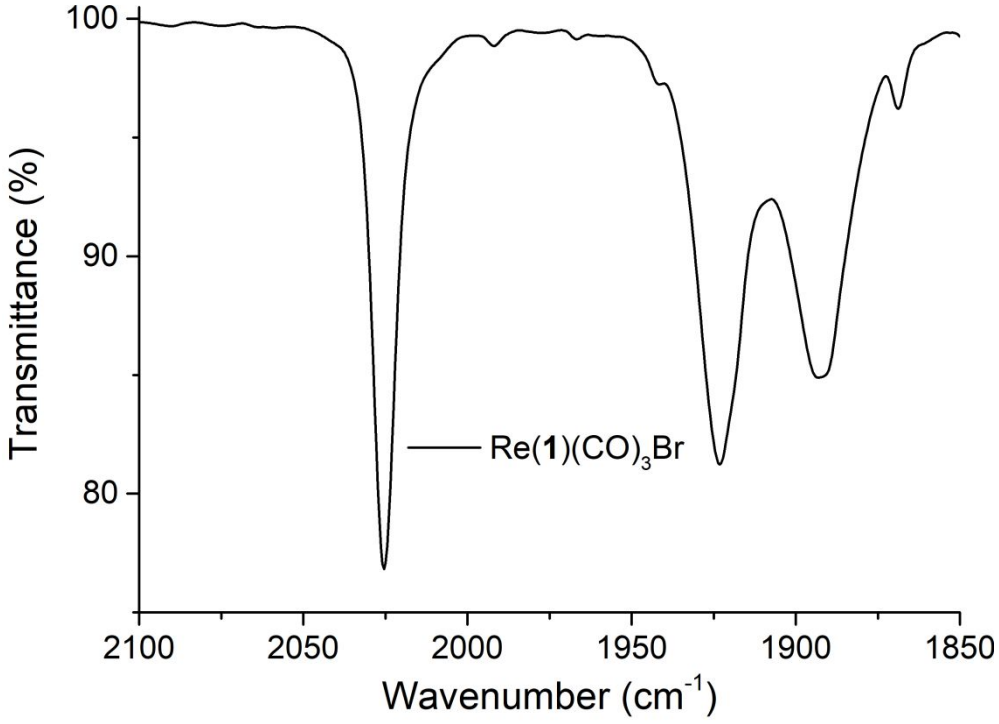


Figure S12: FT-IR spectrum of Re(**1**)$(CO)_3$Br in dichloromethane.

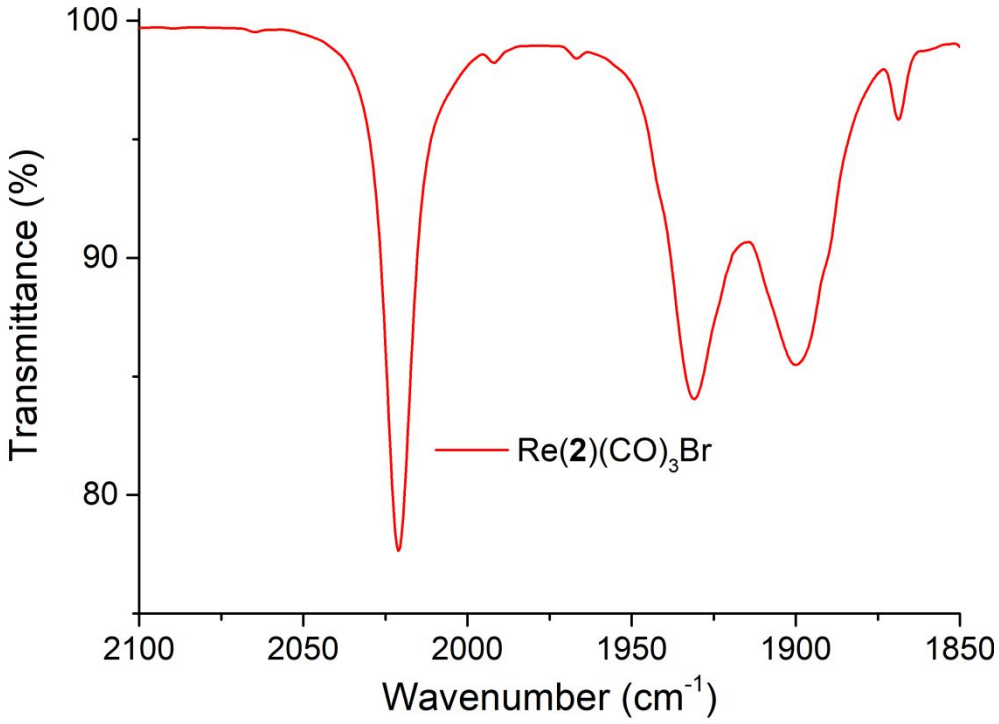


Figure S13: FT-IR spectrum of Re(**2**)$(CO)_3$Br in dichloromethane.

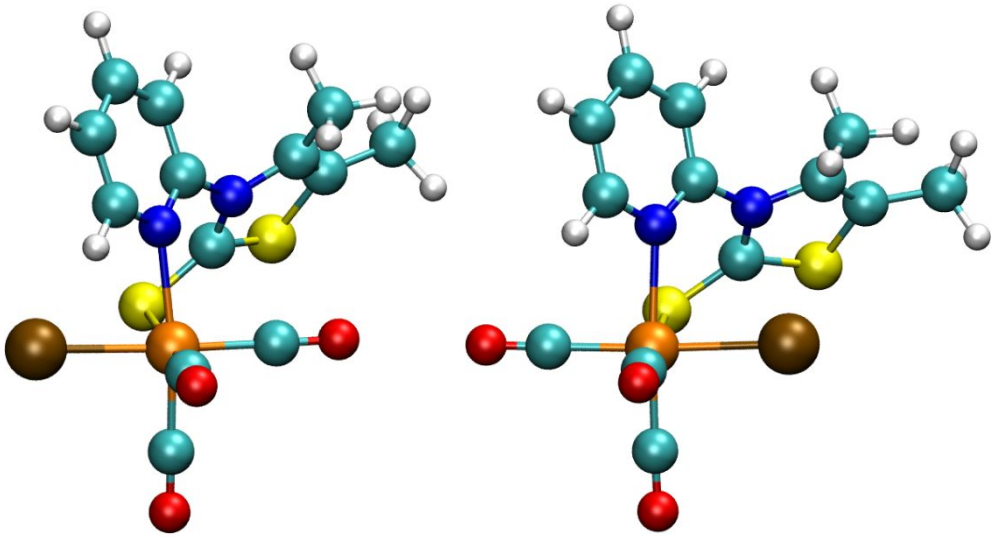


Figure S14: DFT relaxed structures of the two diastereomers of the Re(**1**)$(CO)_3$Br in acetone.

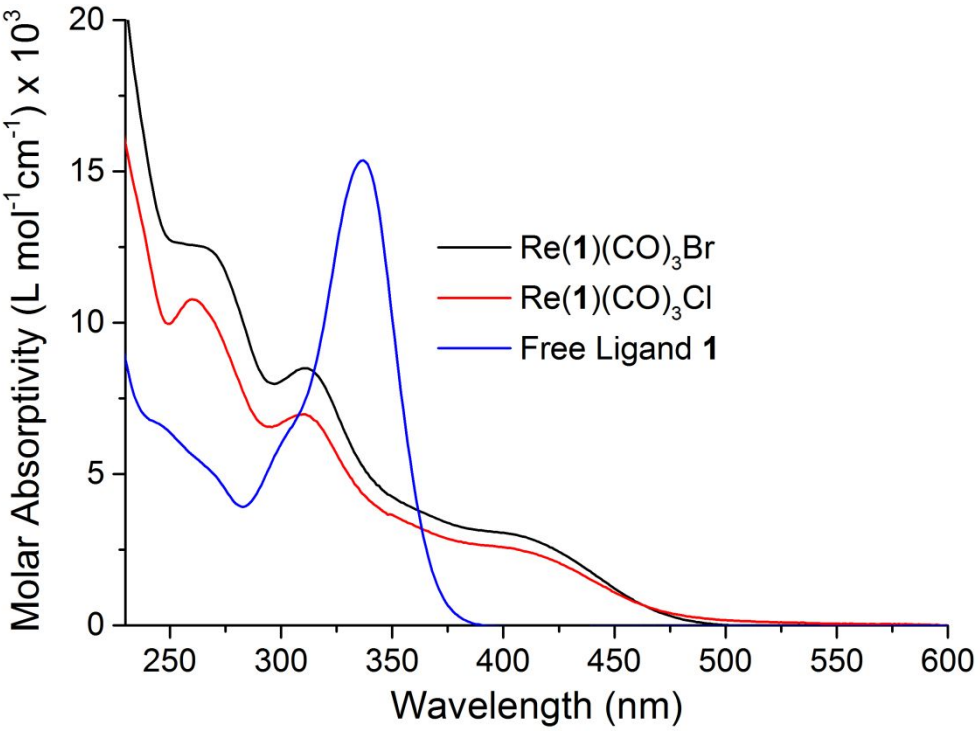


Figure S15. UV-Vis absorption spectra of Re(**1**)$(CO)_3$Cl, Re(**1**)$(CO)_3$Br and free ligand **1** from diluted dichloromethane solutions.

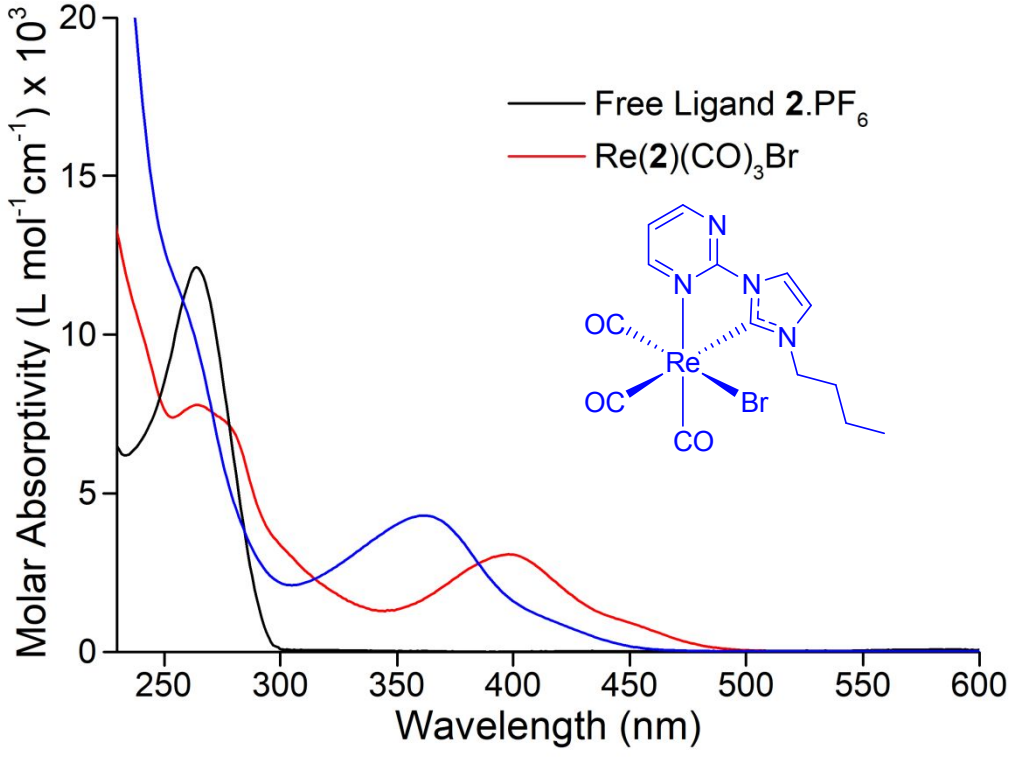


Figure S16. UV-Vis absorption spectra of Re(**2**)$(CO)_3$Br, free ligand **2**H[PF_6] and reference Re-NHC complex (blue trace) from diluted dichloromethane solutions.

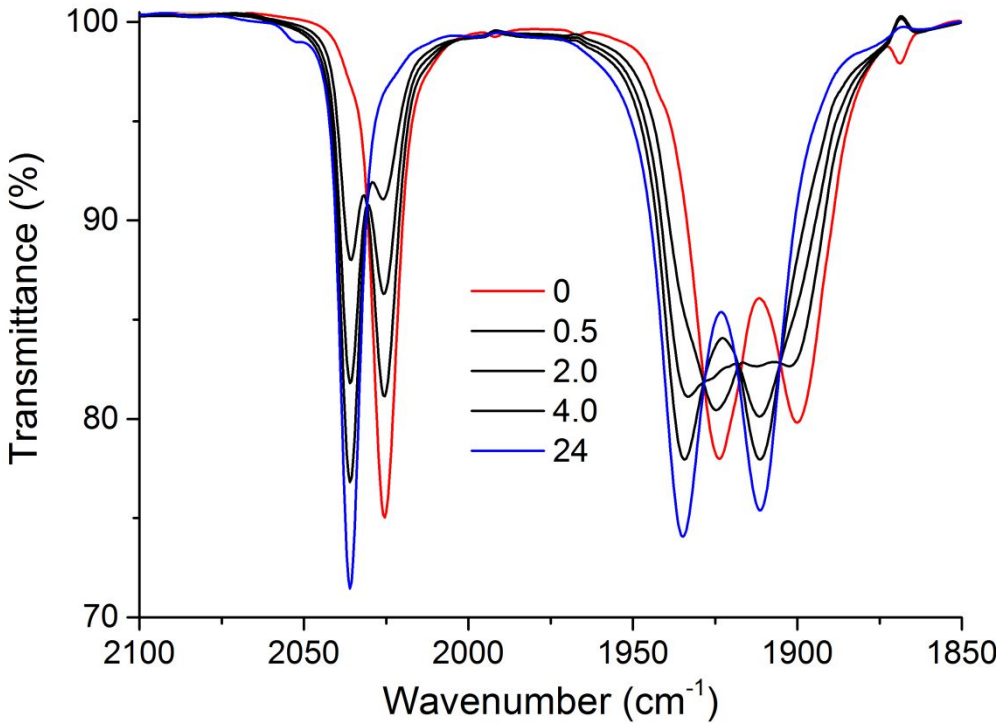


Figure S17: FT-IR spectra monitoring the carbonyl collapse of Re(**1**)$(CO)_3$Br and the simultaneous carbonyl formation of Re$(NCMe)_2(CO)_3$Br in acetonitrile.

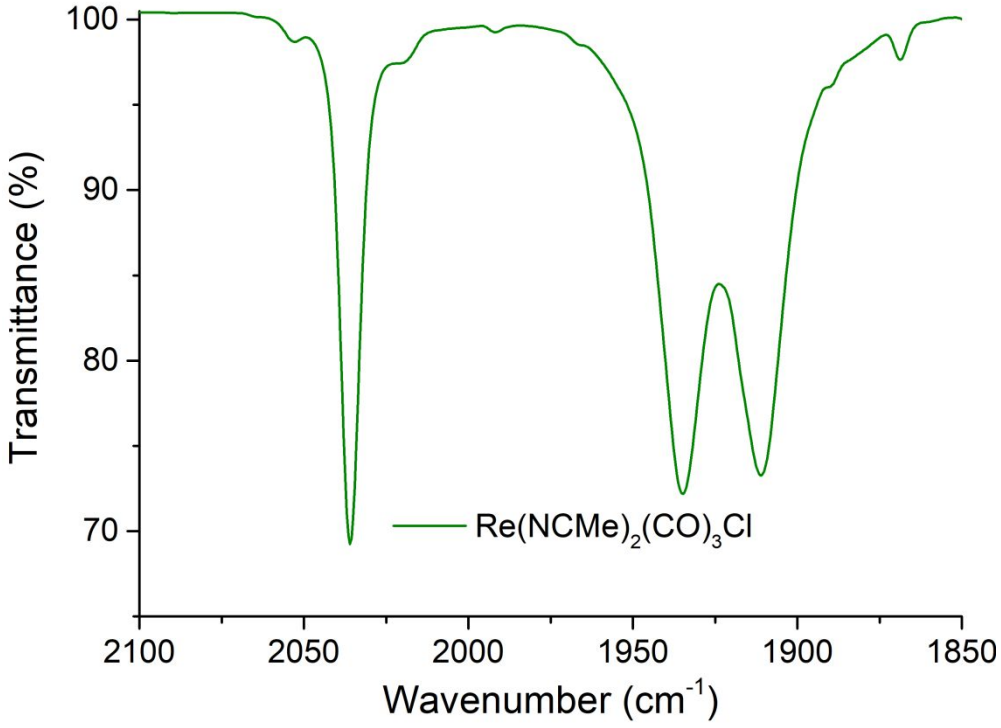


Figure S18: FT-IR spectra of synthesised Re$(NCMe)_2(CO)_3$Cl in acetonitrile.

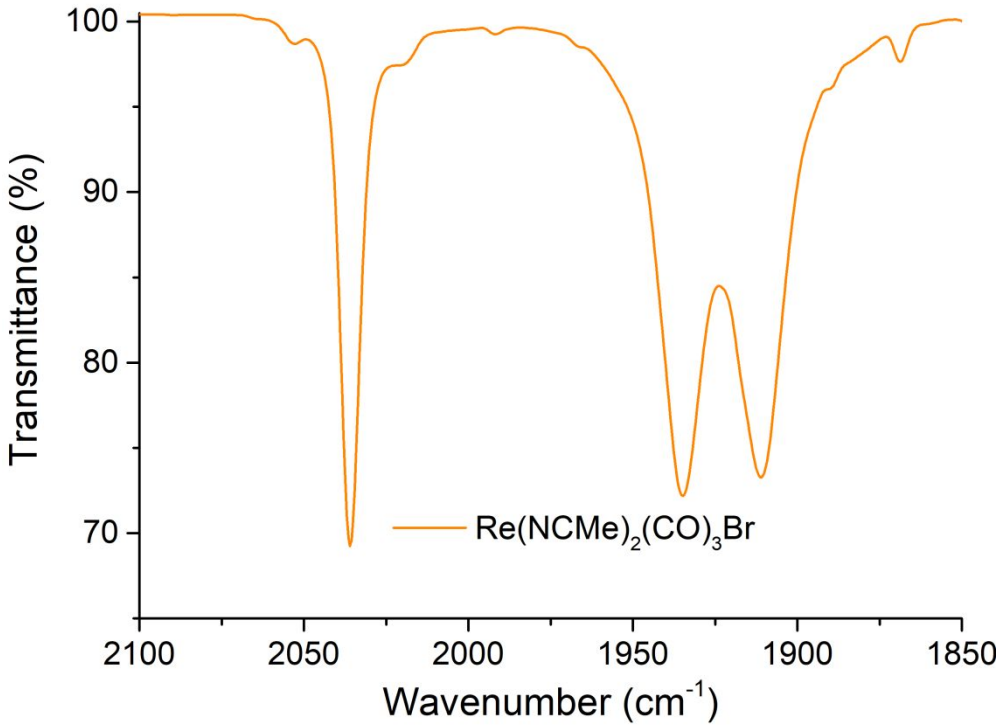


Figure S19: FT-IR spectra of synthesised $Re(NCMe)_2(CO)_3Br$ in acetonitrile.

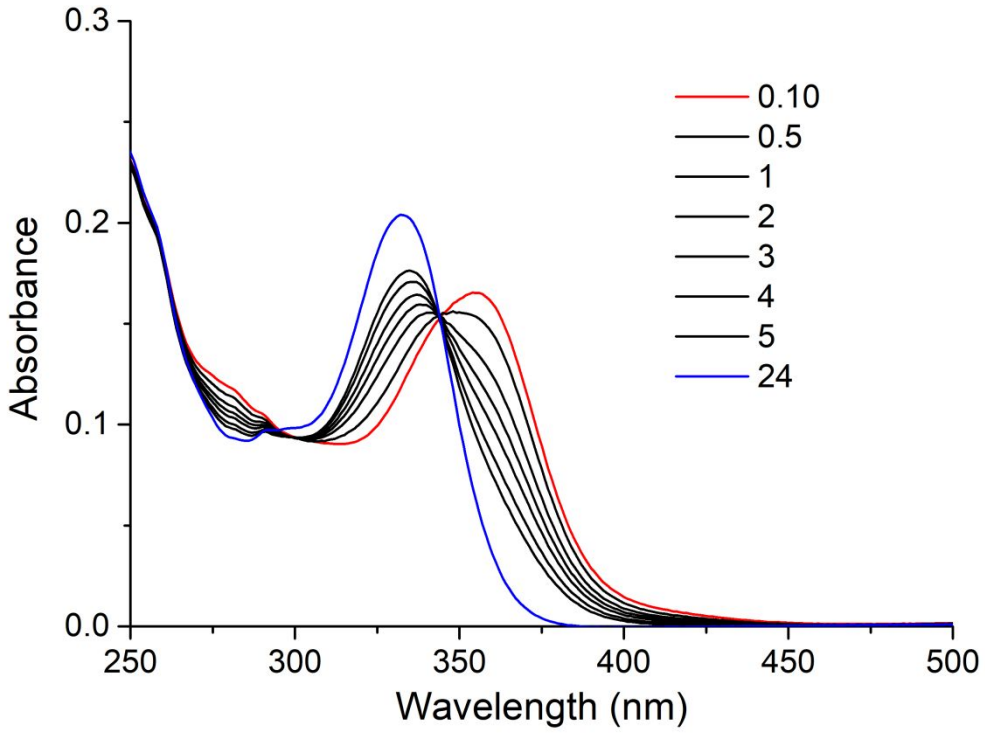


Figure S20: UV-Vis spectra of Re(**1**)$(CO)_3$Br complex dissolved in acetonitrile and kept in the dark. No change was observed beyond 24 h scan. Legend time intervals in hours.

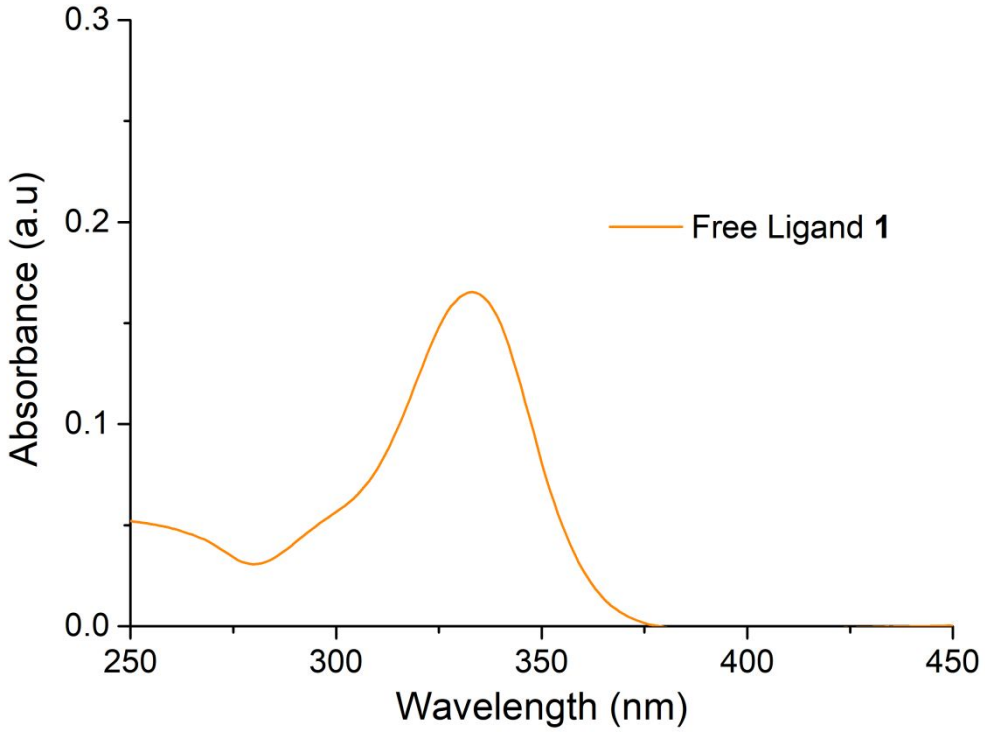


Figure 21: Free Ligand **1** UV-VIS spectrum in diluted acetonitrile.

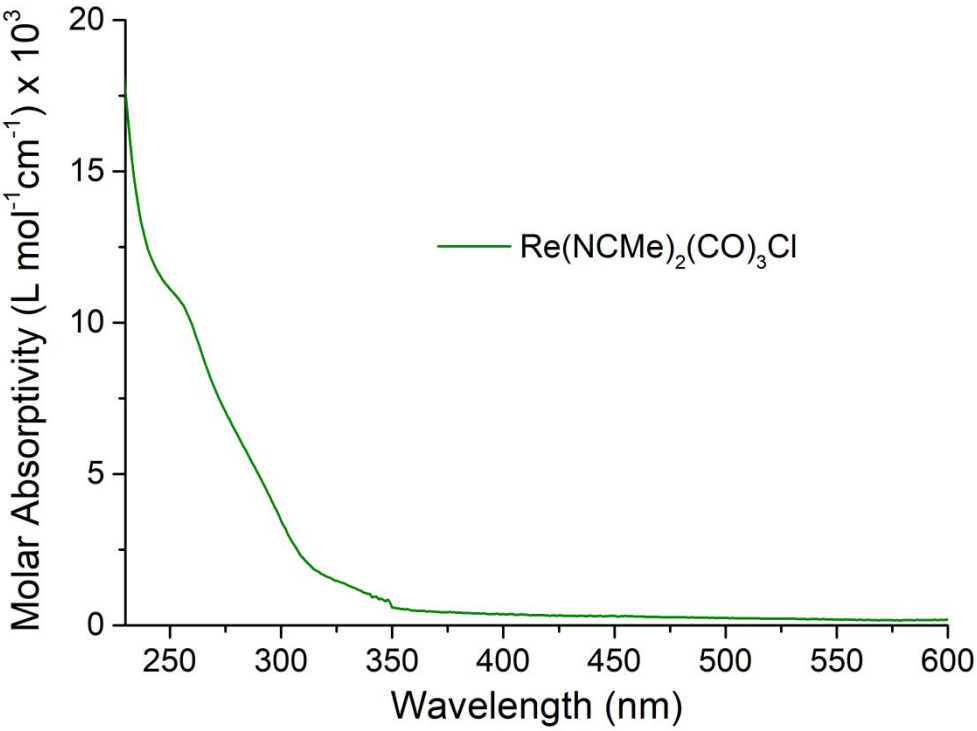


Figure 22: $Re(NCMe)_2(CO)_3Cl$ UV-VIS spectrum in diluted acetonitrile.

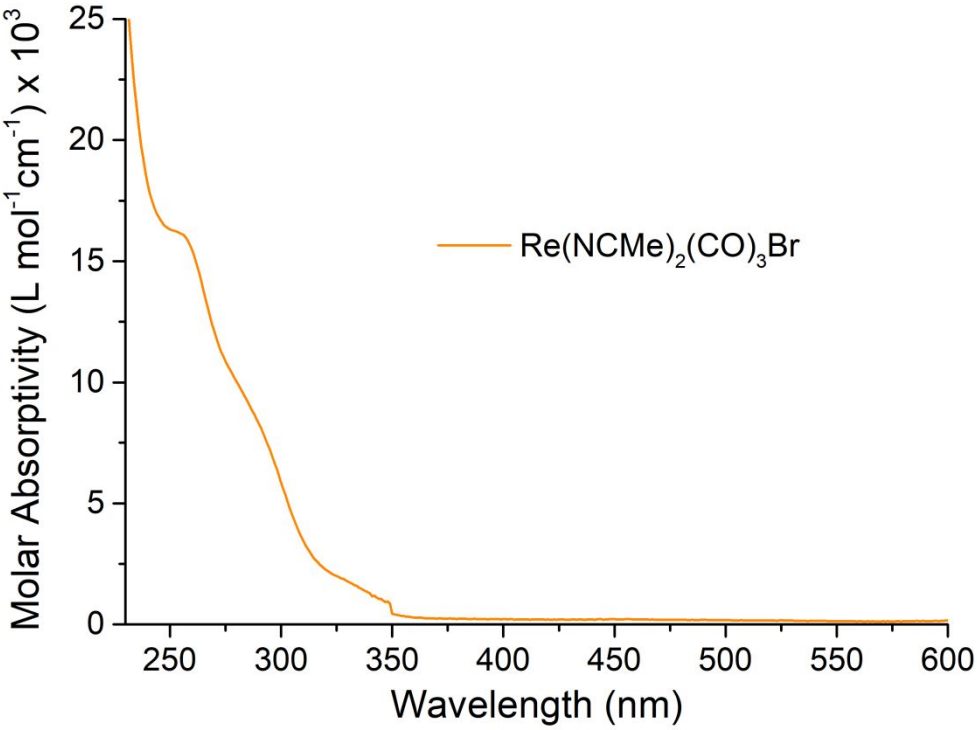


Figure 23: $Re(NCMe)_2(CO)_3Br$ UV-VIS spectrum in diluted acetonitrile.

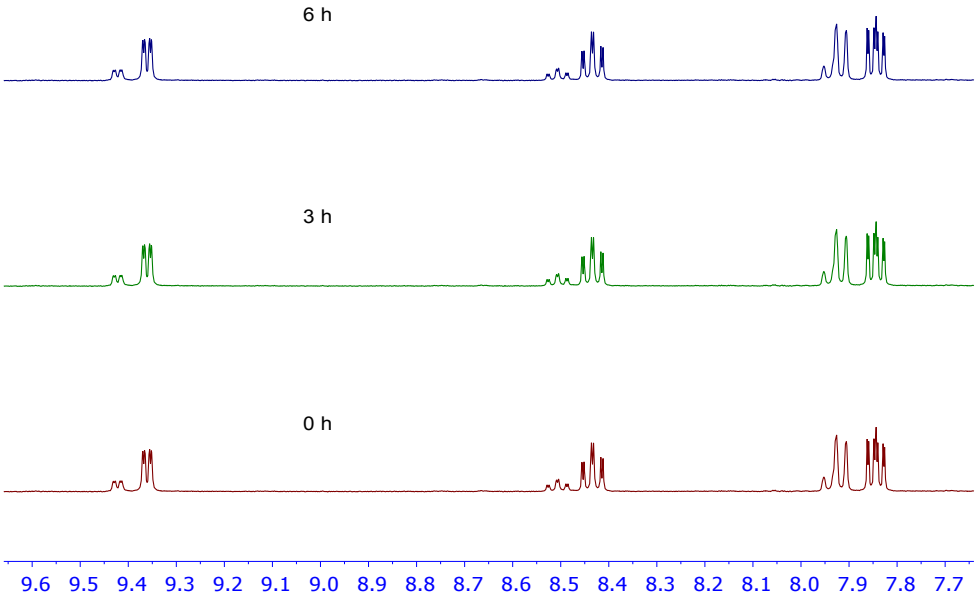


Figure S24: ^{1}H-NMR spectra of Re(**1**)$(CO)_3$Cl in acetone-d_6 kept in the dark.

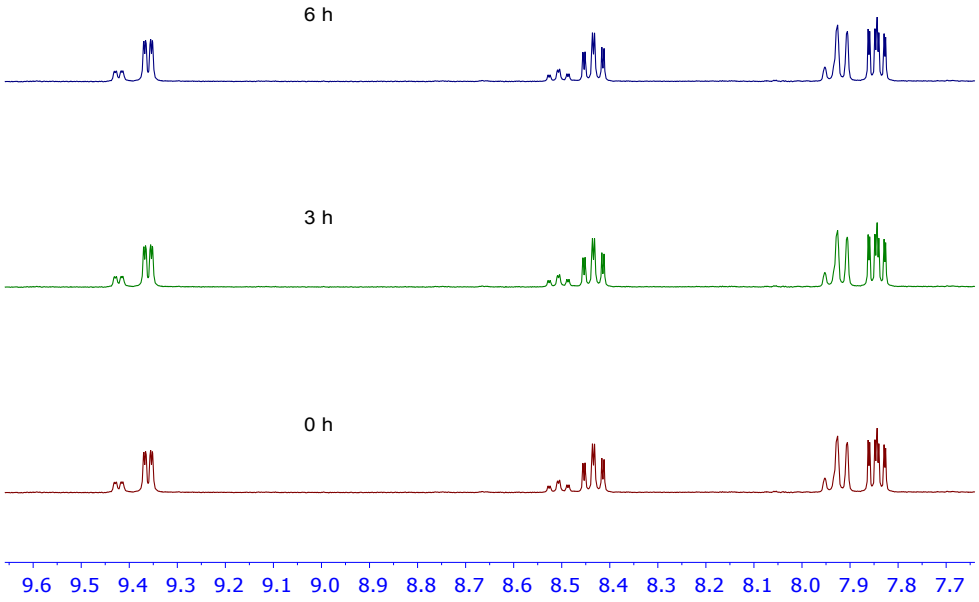


Figure S25: ^{1}H-NMR spectra of Re(**1**)$(CO)_3$Cl in acetone-d_6 exposed to radiation at 365 nm.

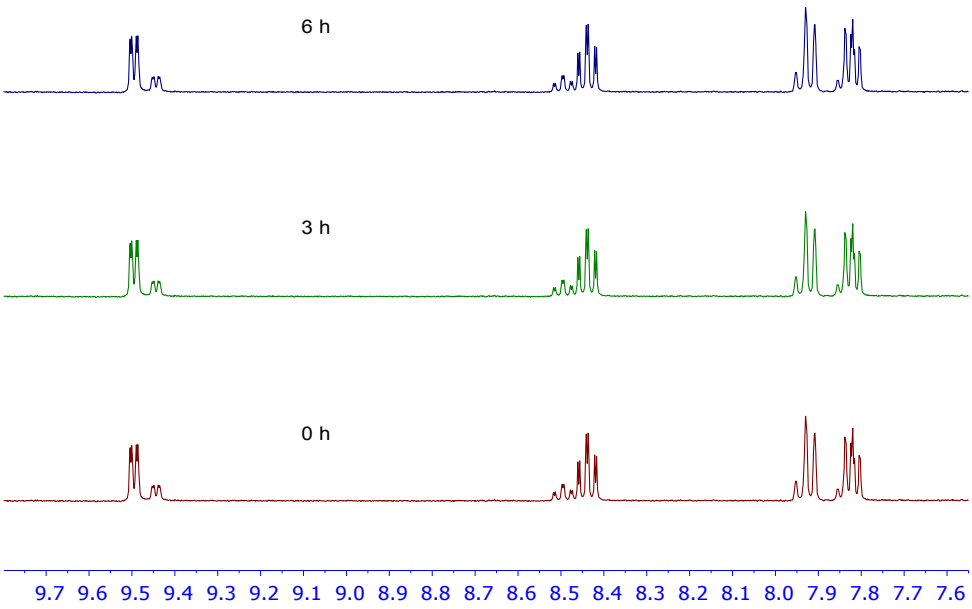


Figure S26: ^{1}H-NMR spectra of Re(**1**)$(CO)_3$Br in acetone-d_6 kept in the dark.

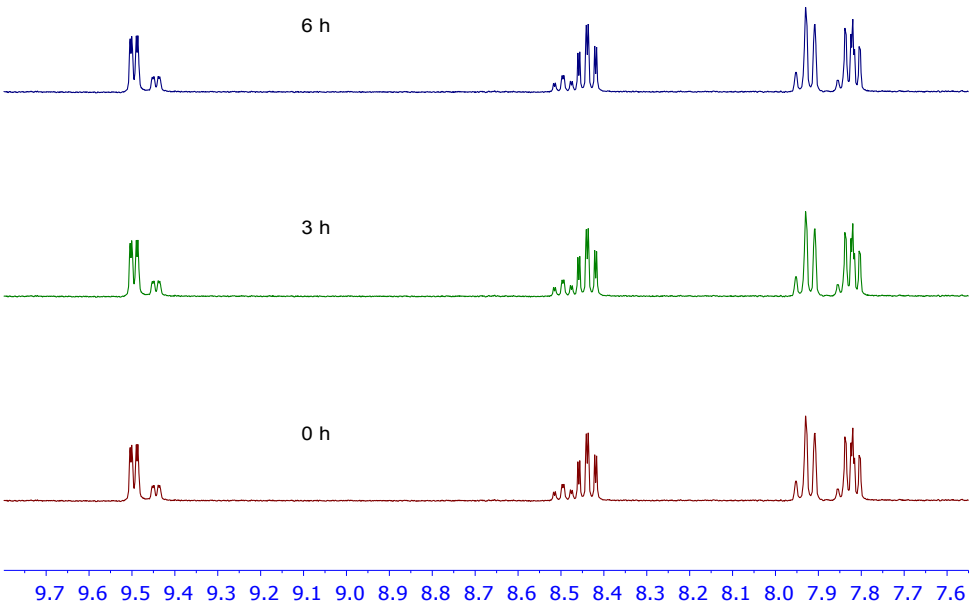


Figure S27: ^{1}H-NMR spectra of Re(**1**)$(CO)_3$Br in acetone-d_6 exposed to radiation at 365 nm.

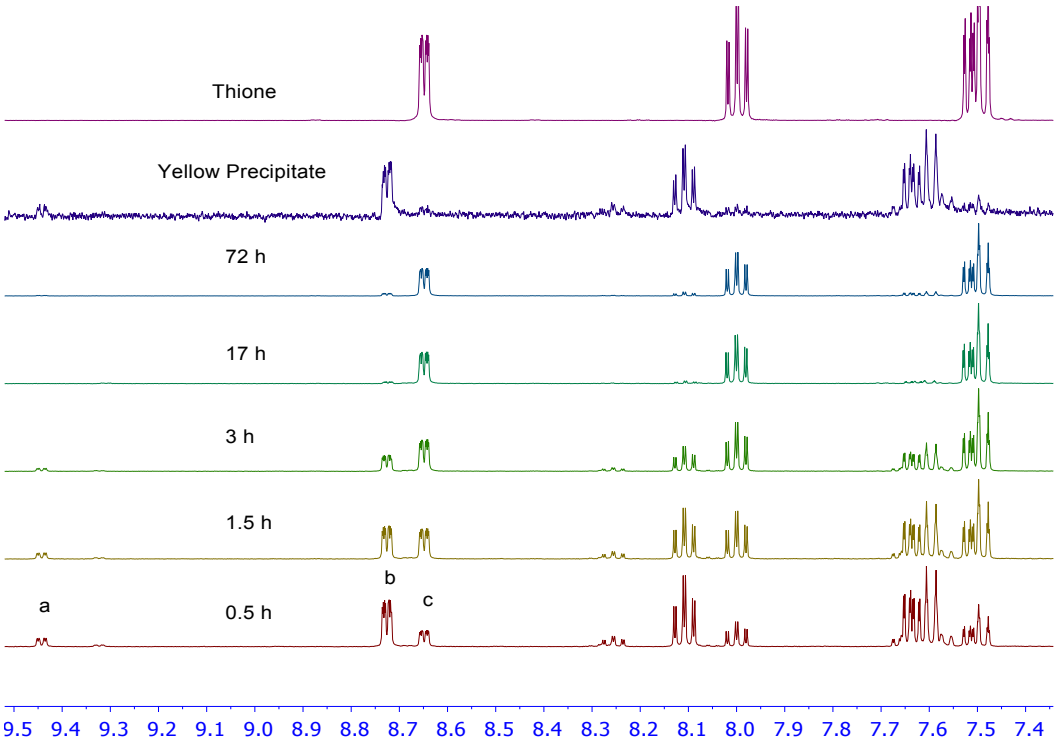


Figure S28: ^{1}H-NMR spectra of Re(**1**)$(CO)_3$Br in acetonitrile-d_6 left in the dark along with the spectrum of the yellow precipate formed by addition of diethyl ether.

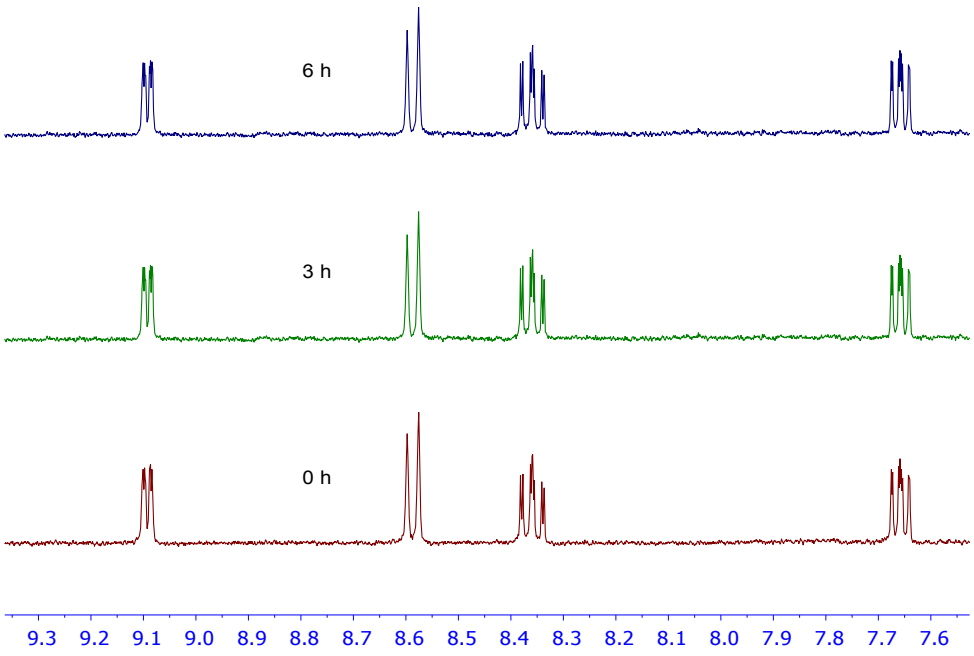


Figure S29: ^{1}H-NMR spectra of Re(**2**)$(CO)_3$Br in acetone-d_6 kept in the dark.

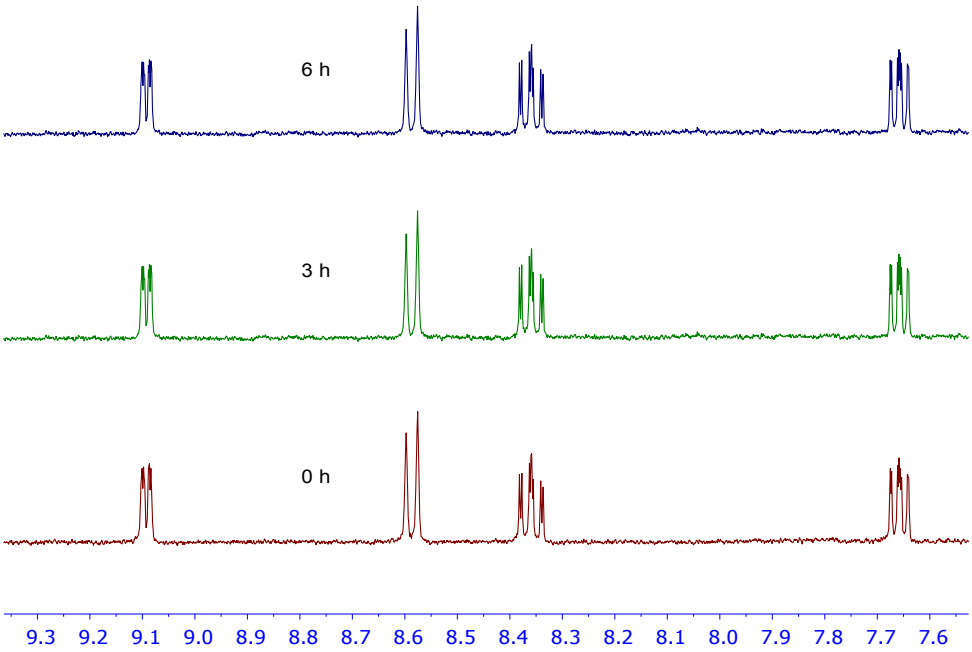


Figure S30: ^{1}H-NMR spectra of Re(**2**)$(CO)_3$Br in acetone-d_6 exposed to radiation at 365 nm.

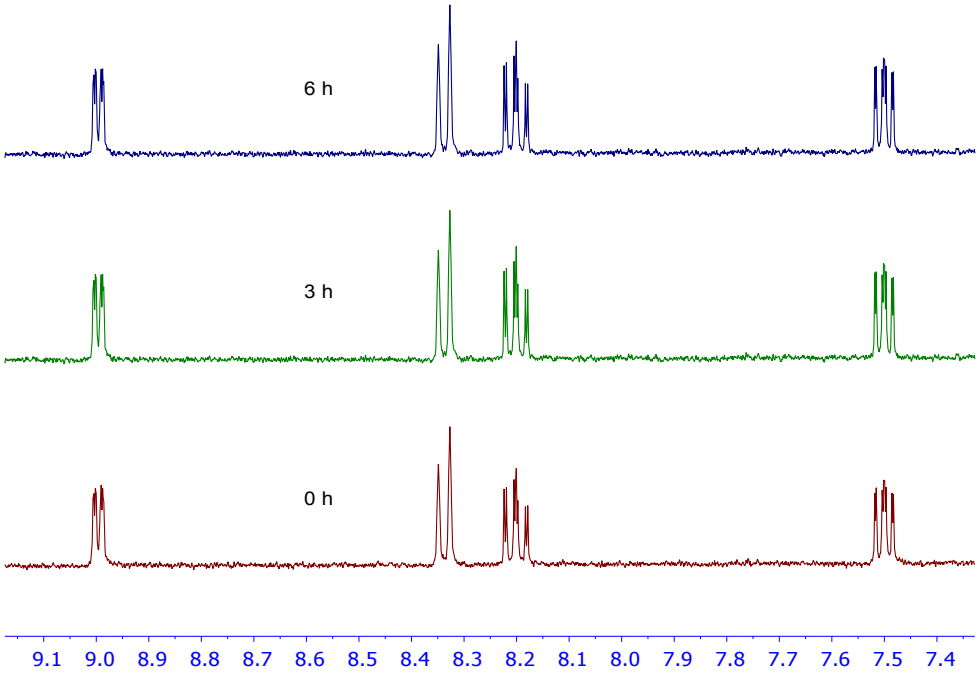


Figure S31: ^{1}H-NMR spectra of Re(**2**)$(CO)_3$Br in acetonitrile-d_3 kept in the dark.

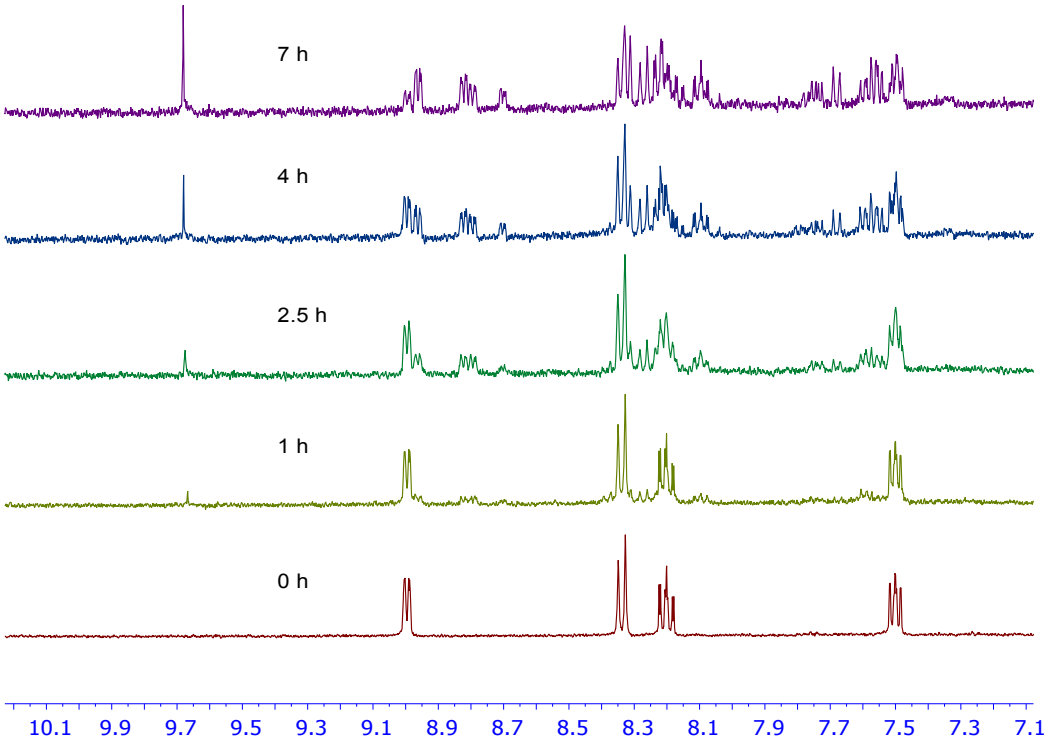


Figure S32: ^{1}H-NMR spectra of Re(**2**)$(CO)_3$Br in acetonitrile-d_3 exposed to radiation at 365 nm.