Synthesis and Characterization of Pd(II) and Ru(II) Complexes of *Tetradentate N,N,N,N*-(diphosphinomethyl)amine Ligands: Catalytic Properties in Transfer Hydrogenation and Heck Coupling Reactions

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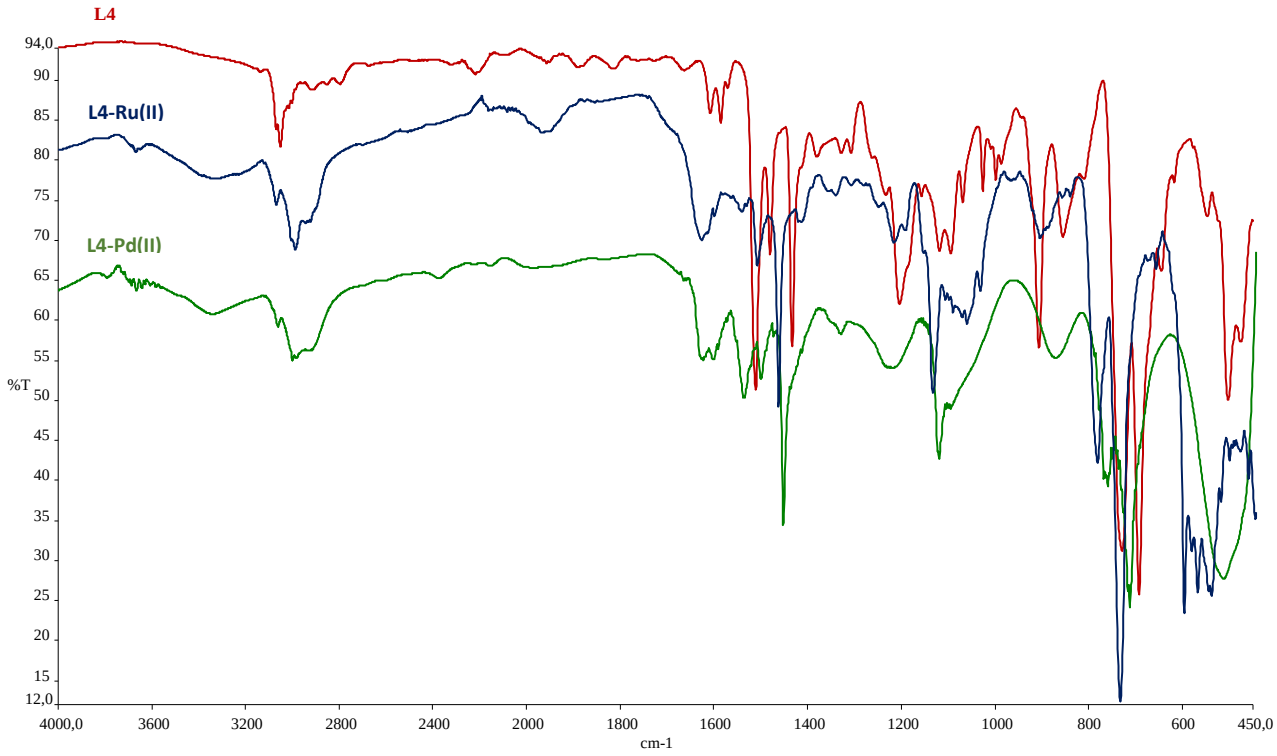
Spectral Characterization

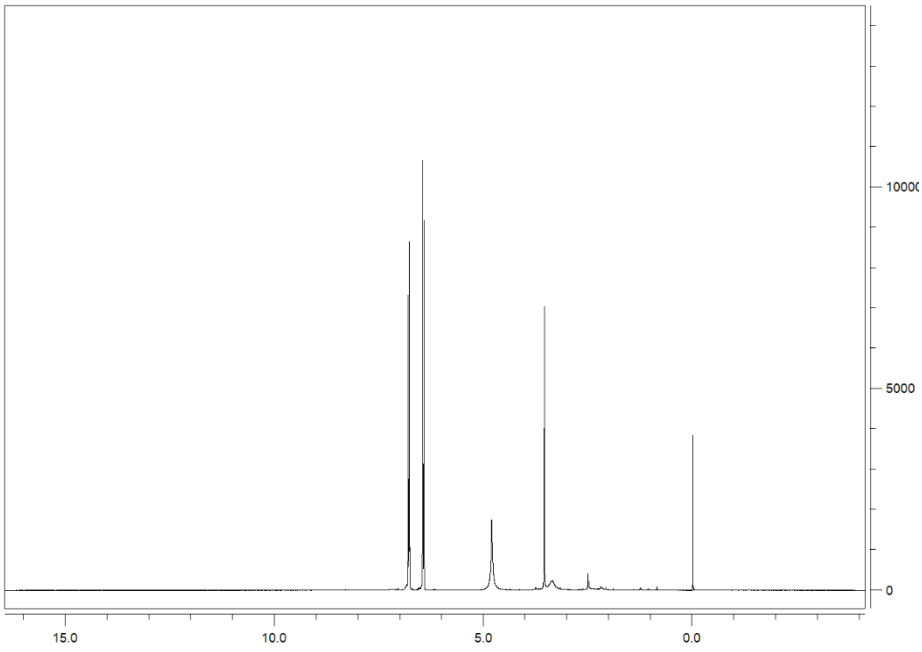
Doublet peaks from N-H stretches from a primary amine must be observed around 3500-3300 cm^{-1} in FT-IR spectrum. These doublet peaks were removed after the reaction of diamine and phosphonium salt. Thus, it can be said that, all of the di-substituted primary amines were reacted with $[Ph_2P(CH_2OH)_2]Cl$ and the desired products were obtained according to the FT-IR spectra. Aromatic and aliphatic C-H stretches were assigned to around 3100-3000 cm^{-1} and 2950-2900 cm^{-1} in FT-IR spectra of the ligands. Aromatic C=C bendings were observed at about 1650-1500 cm^{-1} and in the FT-IR spectra. Sharp peaks about 1450-1400 cm^{-1} were because of P-Ph stretches. Tertiary amine C-N stretches were collected about 1100-1090 cm^{-1}. Thus, it can be said that, all the primary amine were reacted to phosphonium salt and given the desired products.[1,2,6-18] There are not significant differences between the ligands and Pd(II) and Ru(II) complexes in FT-IR spectra (Supplementary 1). After the complexation of the ligand and a metal ion, P-Ph stretches were shifted to higher region recorded about 1460 cm^{-1}.



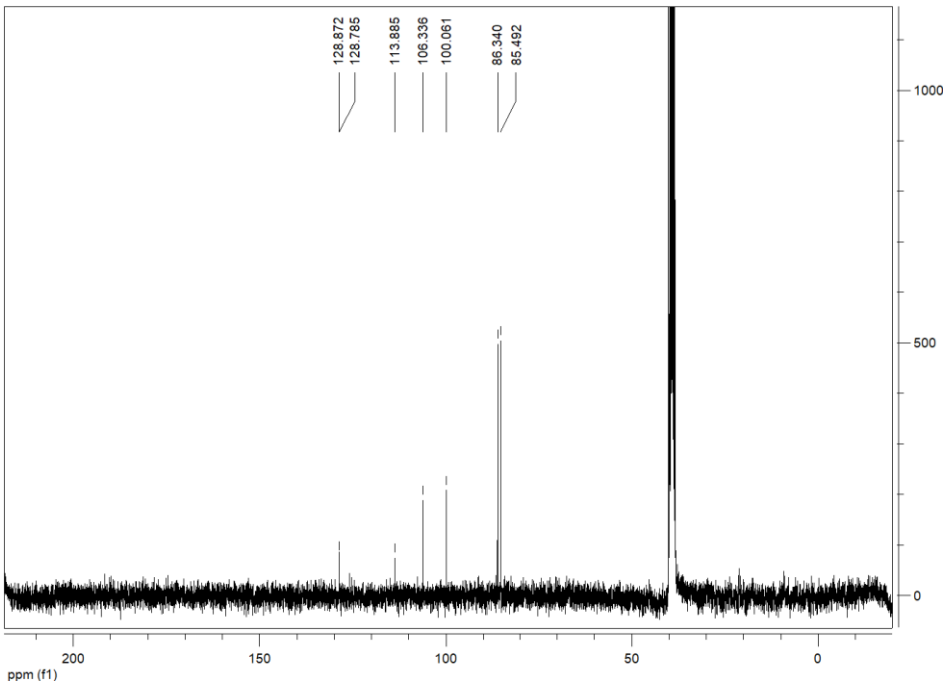
Supplementary 1. FT-IR spectra of L4 and its complexes.

Symmetric structure of all the *N*,*N*,*N*,*N*-(diphosphinomethyl)amine type ligands were observed in ^{1}H-NMR spectra (Supplementary 2). The aromatic protons' resonances of L4 which was the novelly synthesized ligand were recorded at two different area; multiplets between 7.44-7.20 ppm for two phenyl rings bound to one phosphorus and multiplet peaks between 7.10-6.93 ppm from the phenyl groups of basic diamine structure. Ph-C$\underline{H}_2$-Ph resonances of aminomethylphosphine groups were observed at 3.95 ppm as a singlet signal. Aryl-CH_2-N protons were observed as a singlet peak at 3.76 ppm. The metal complexes showed the similar proton resonances in ^{1}H-NMR spectra with the ligands. Proton resonances of NEt_3 in the complexes were observed in two different areas as N-CH_2-C$\underline{H}_3$ and N-C$\underline{H}_2$-CH_3 in ^{1}H-NMR spectra. In addition, it can be said that, *p*-cymene ligands were removed while synthesizing the Ru(II) complexes due to fact that secondary C-H resonances of *p*-cymene were not observed in ^{1}H-NMR of Ru(II) complexes. Besides, integrations of the resonances proved the removing of *p*-cymene while the synthesizing of Ru(II) complexes. L4 showed three type resonances of ^{13}C that belong to aromatic structures, N-CH_2-P and Ar-CH_2-N in ^{13}C-NMR spectra. Aromatic carbons from P-Ph and the Ar-CH_2-N backbone were resonanced as five peaks at 128.87, 128.78, 113.88, 106.34, 100.06 ppm. ^{13}C Resonances of two type of methylene bridges (N-CH_2-P and Ar-CH_2-N) were observed at 86.34 and 85.49 ppm respectively (Supplementary 2). Phosphorus resonances were shifted from negative region to positive region after metal-

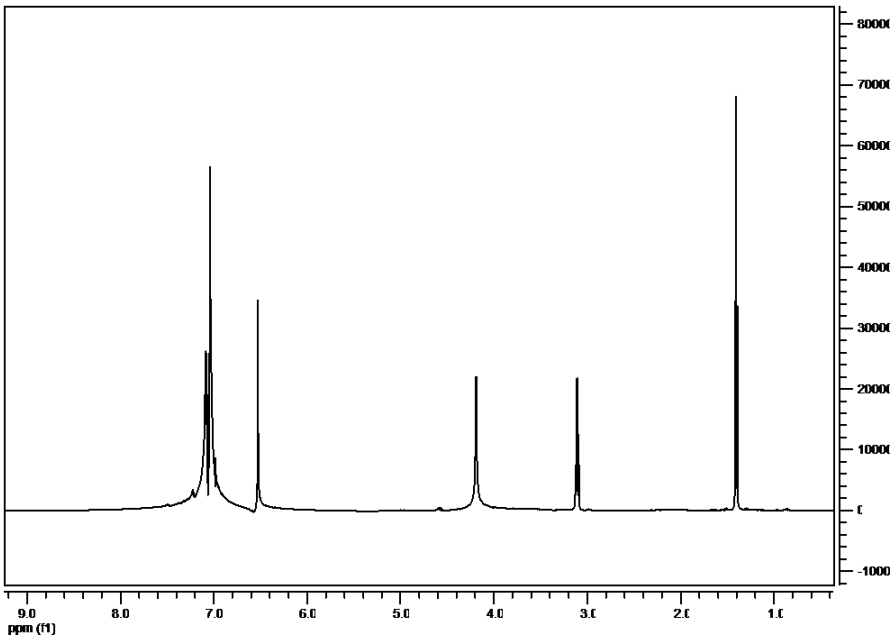
phosphorus complexation. Aminomethylphosphine ligand L4 has a single ^{31}P peak at -27.57 ppm in ^{31}P-NMR spectrum (Supplementary 3). Phosphorus resonances were shown as singlet signals at 28.21 ppm and 77.56 ppm for L4-Pd(II) and L4-Ru(II) complexes respectively. Since, metal-phosphorus complexations were proved with the shielding of the resonances of ^{31}P nuclei to the positive region in ^{31}P-NMR spectra for all the complexes. The small peaks were possibly due to the the resonances of oxidized phoshine ligands. [1,2,6-18]



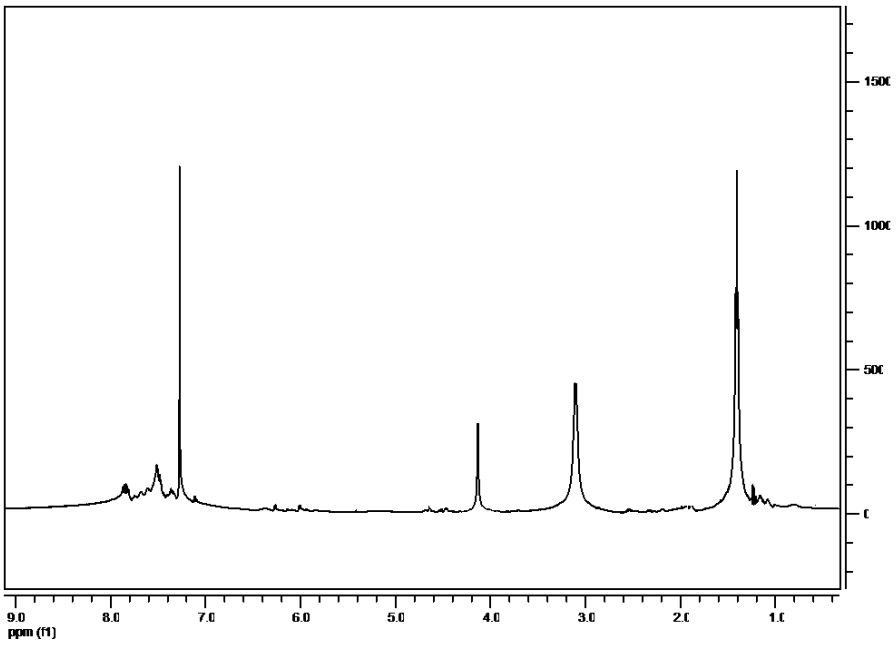
^{1}H-NMR of L4



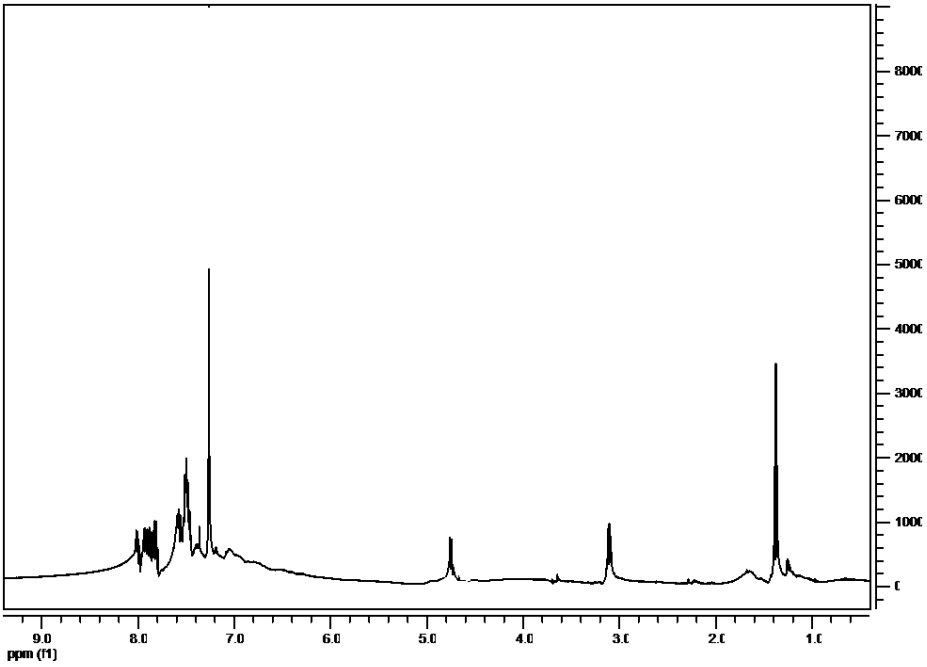
^{13}C-NMR of L4



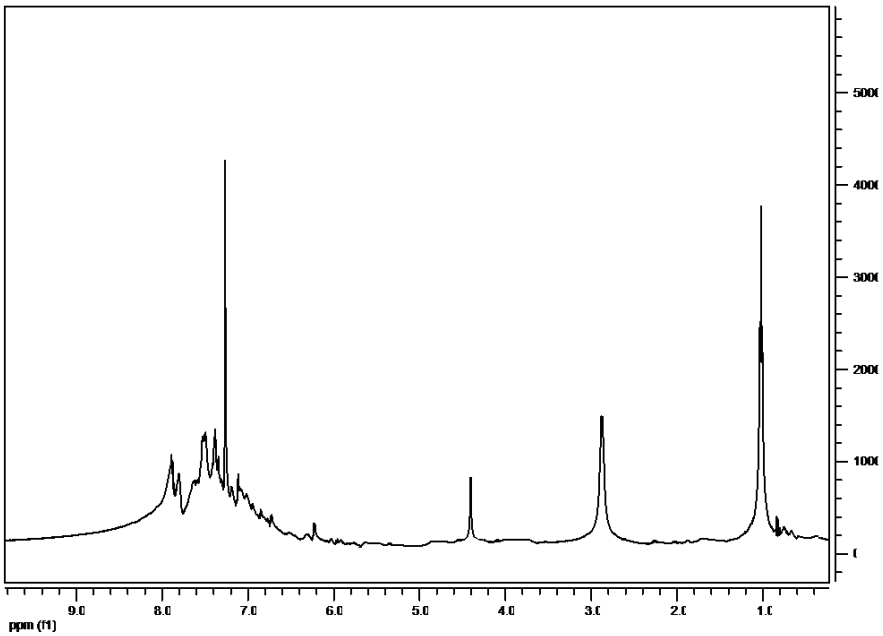
L1-Pd(II)



L1-Ru(II)



L2-Pd(II)



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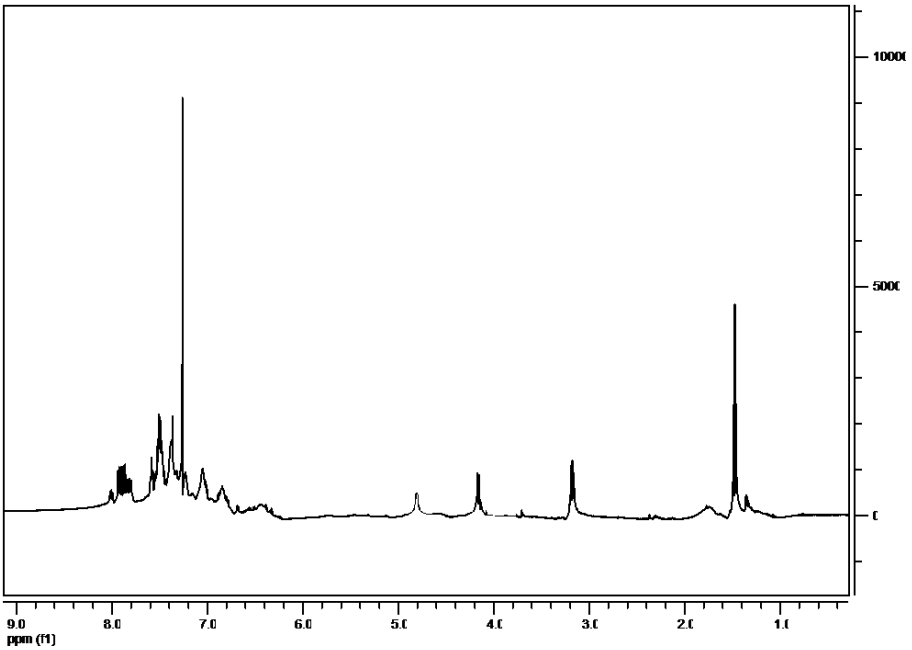
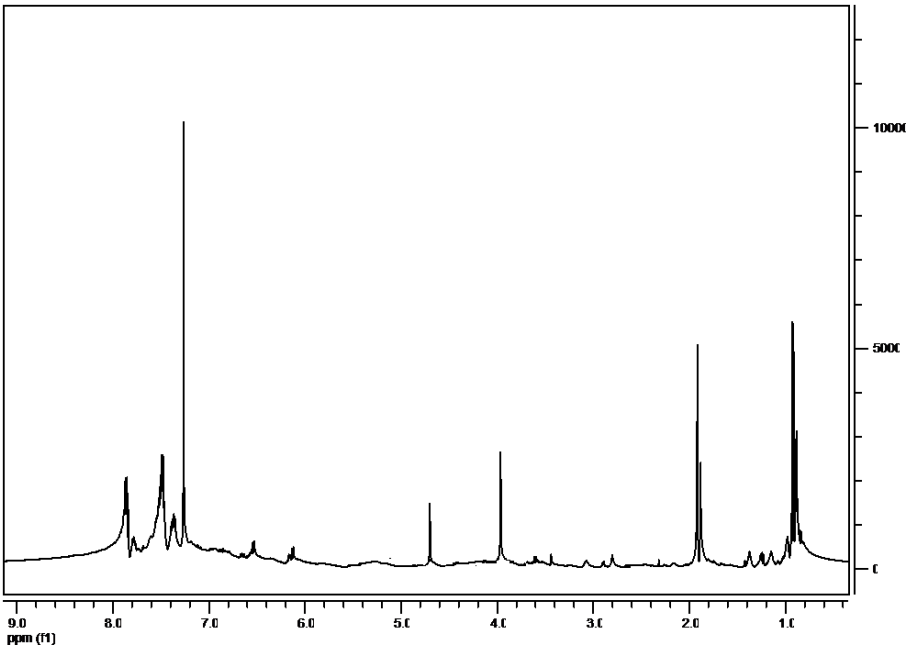


L3-Pd(II)



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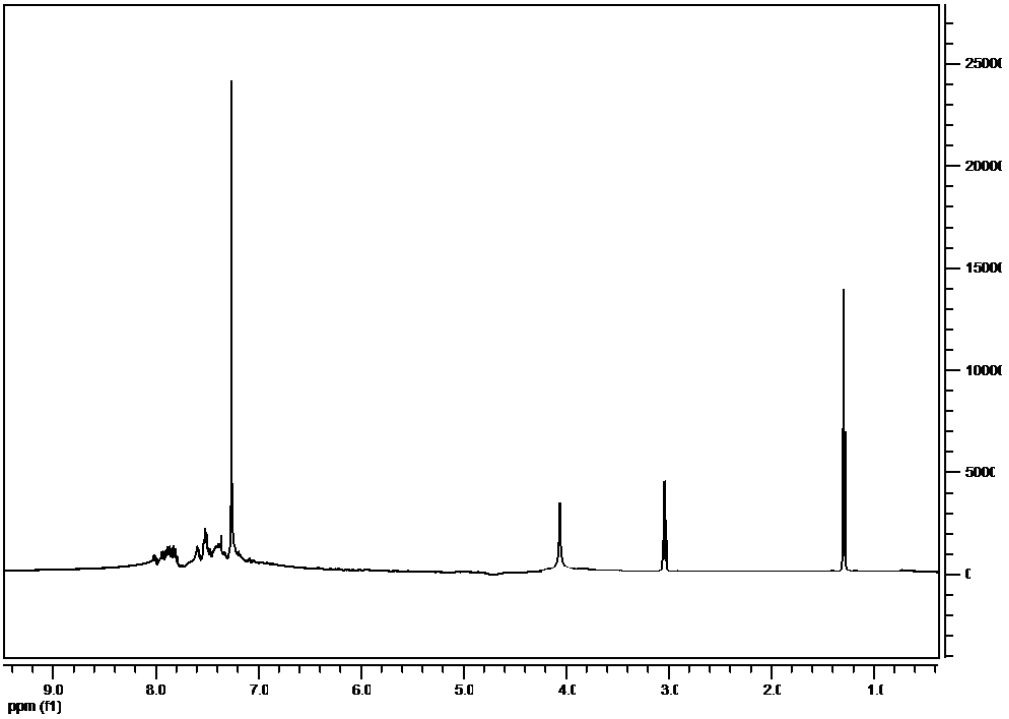

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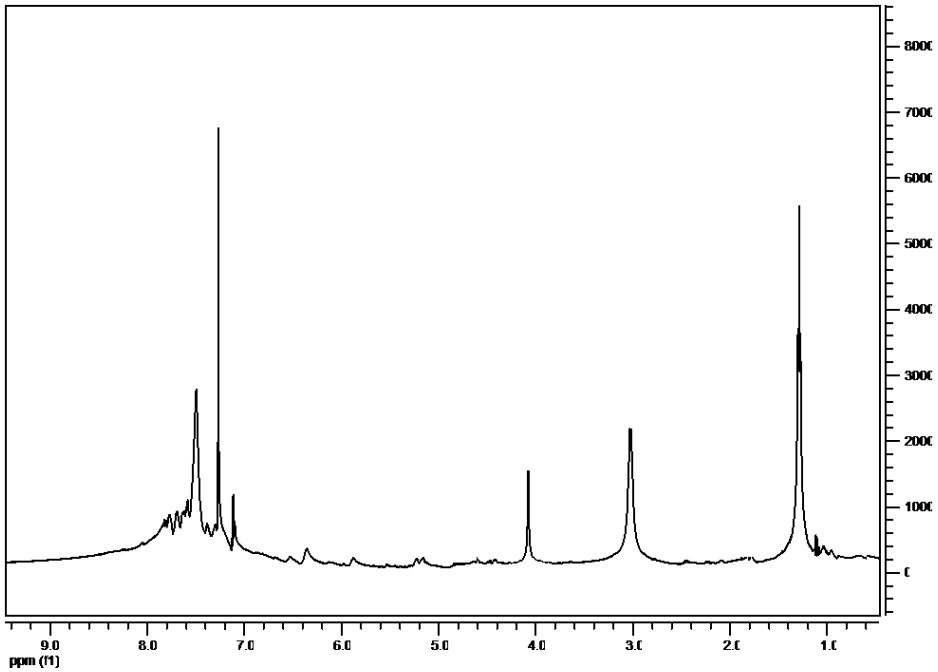
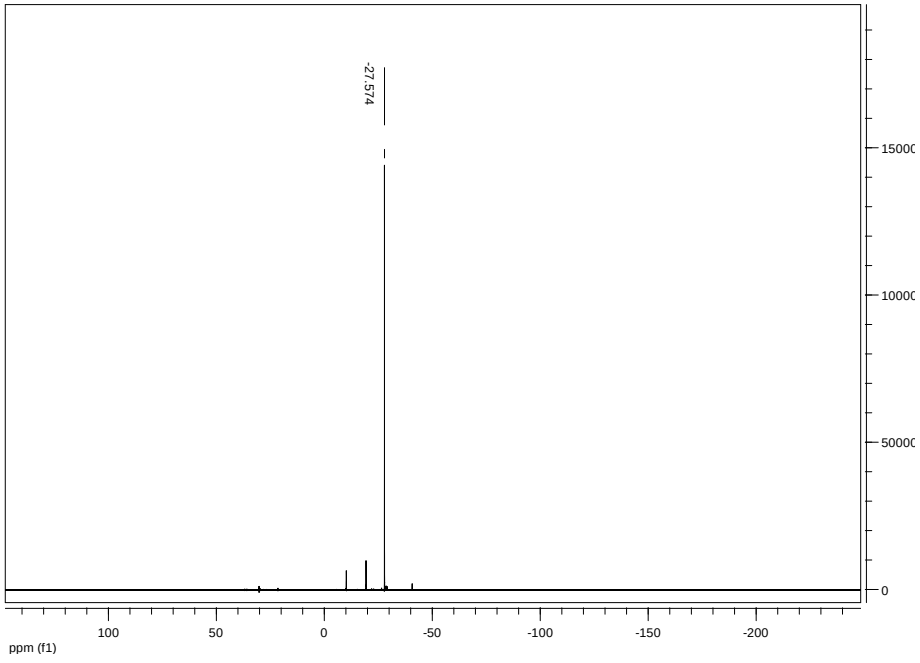
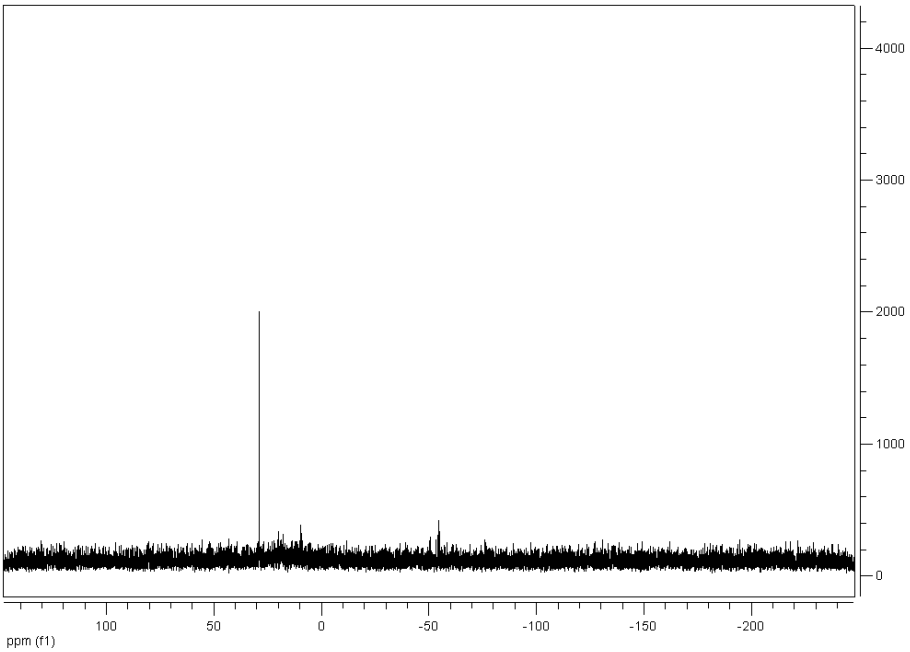


L4-Ru(II)

Supplementary 2. ^{1}H-NMR and ^{13}C-NMR spectra of the novelly synthesized ligand and ^{1}H-NMR spectra of the complexes.



L4



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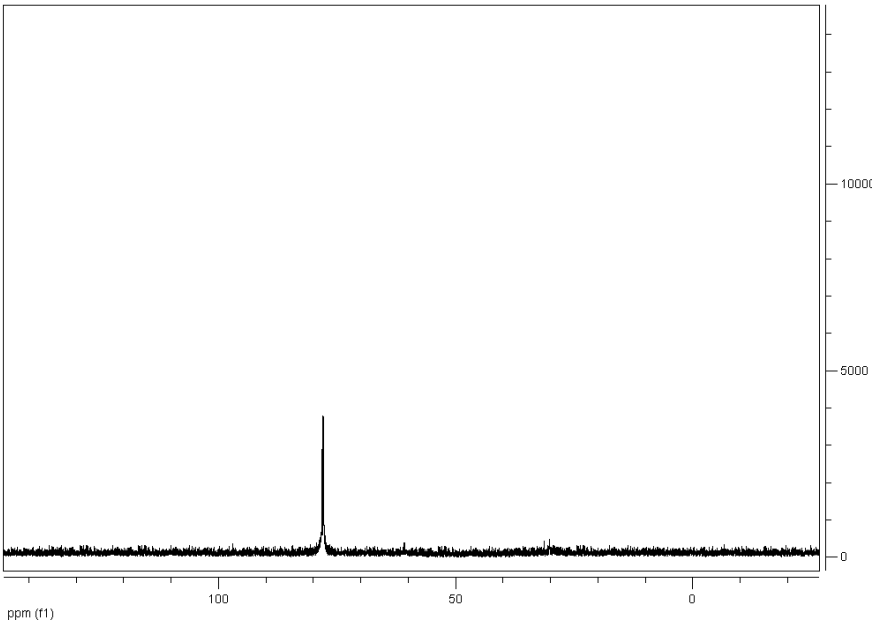

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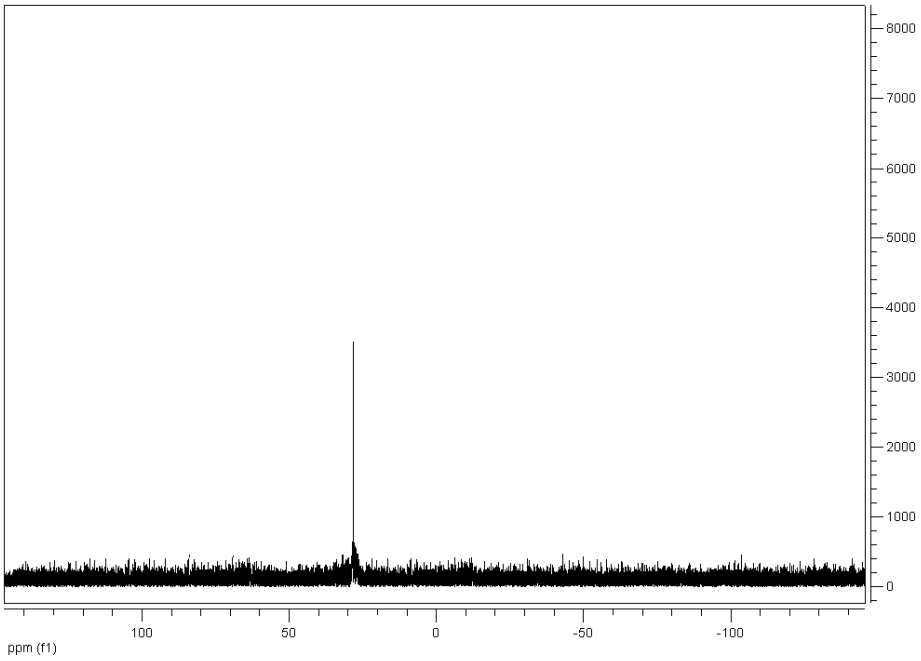
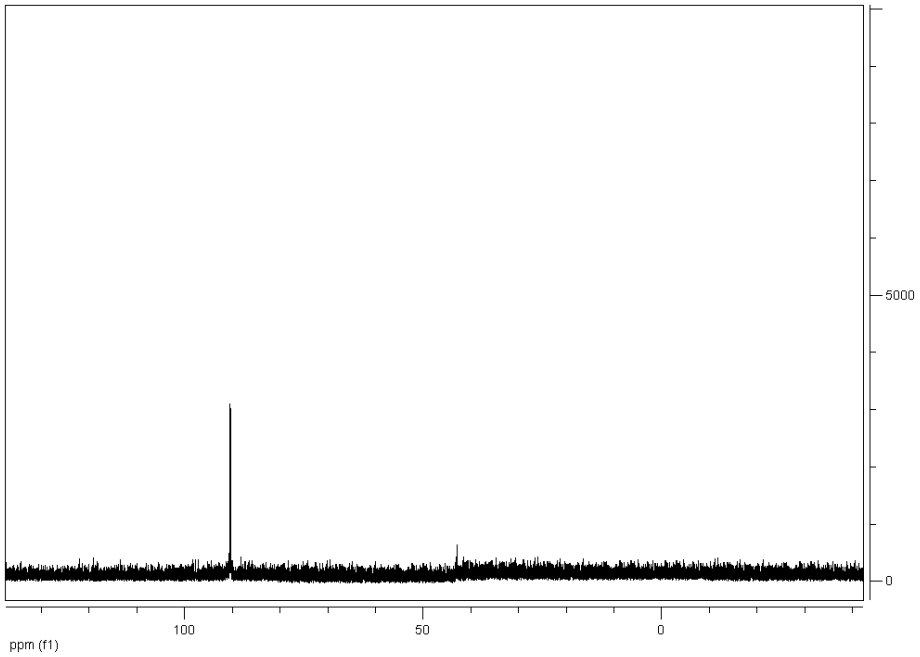


L2-Pd(II)



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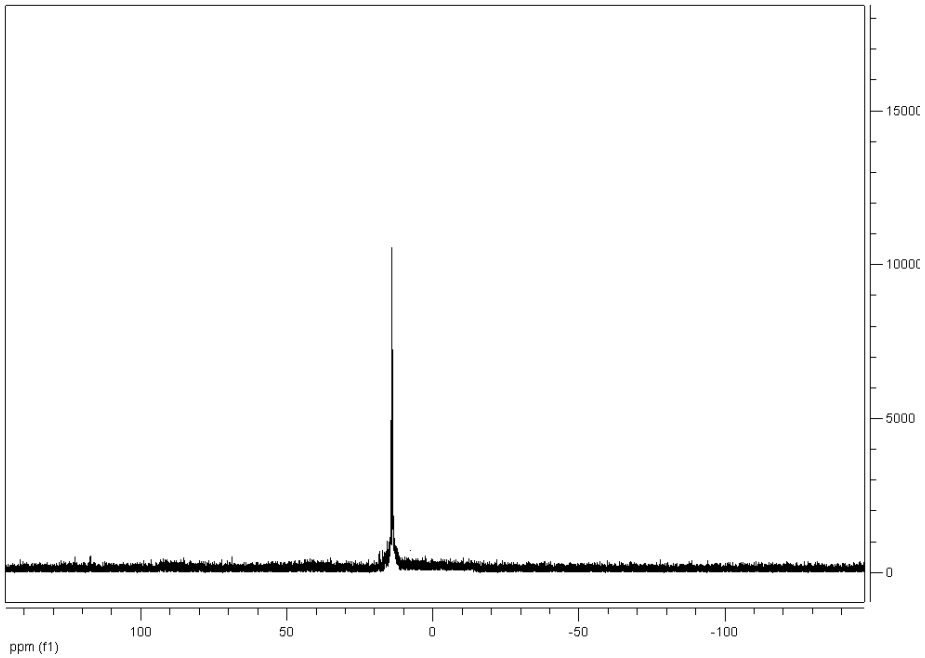

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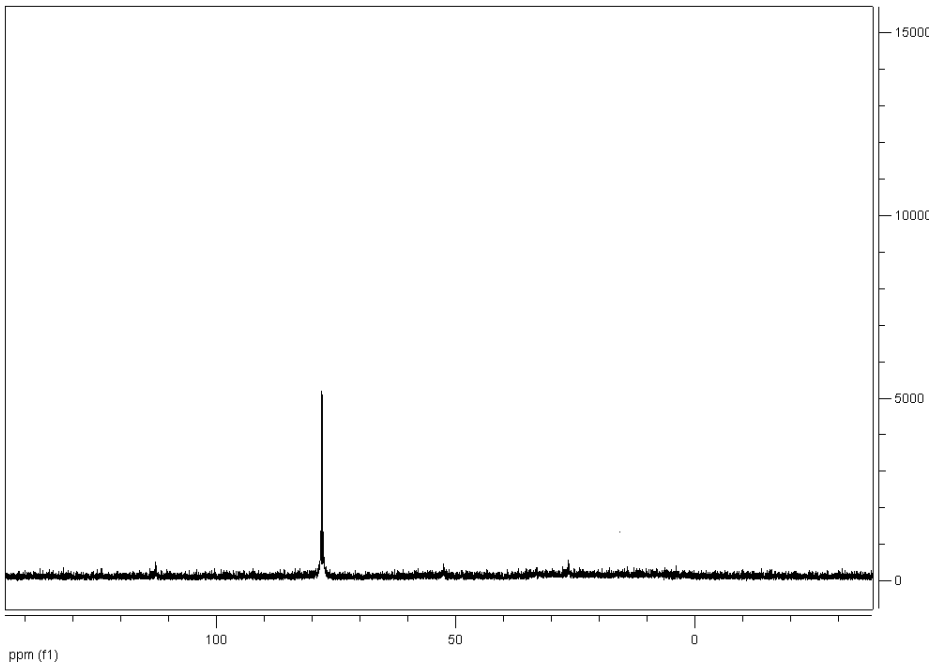

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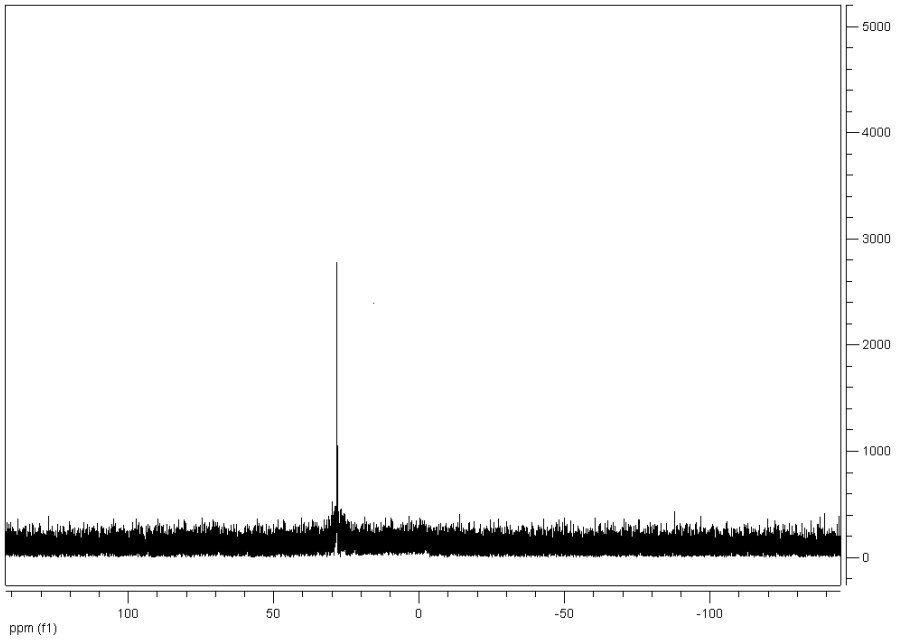
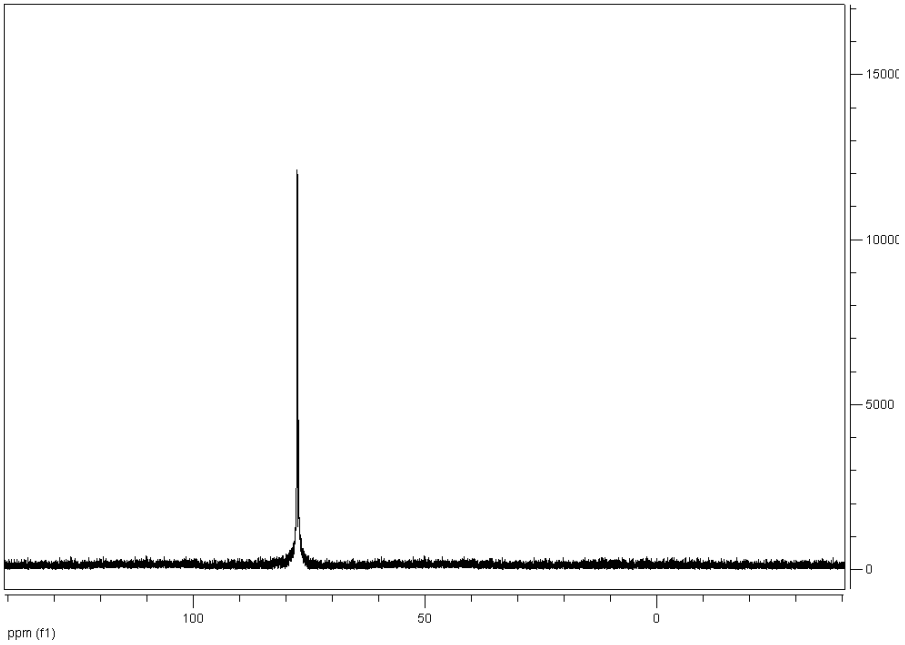
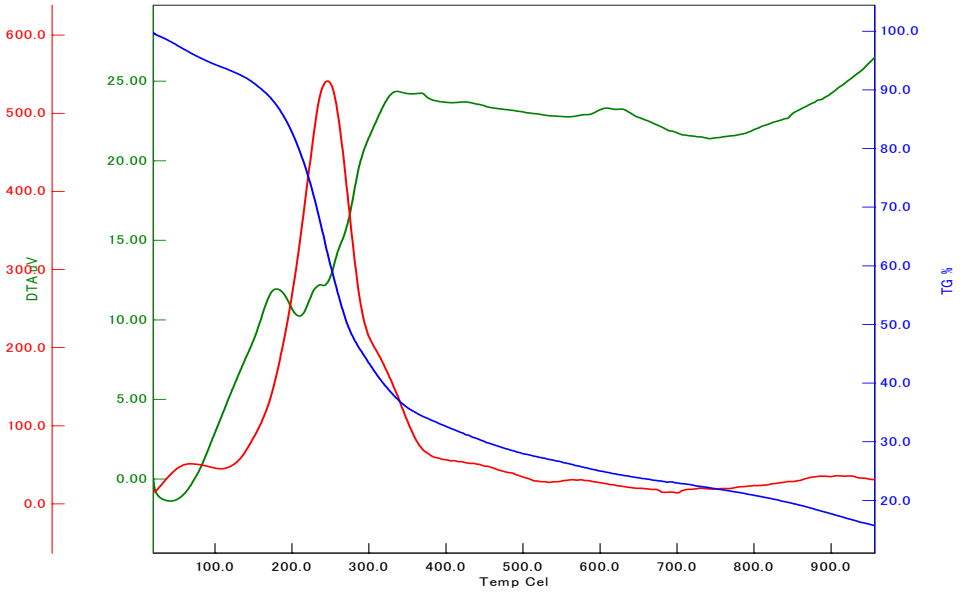


L4-Pd(II)



L4-Ru(II)

Supplementary 3. $^{31}P\{H\}$-NMR spectra of the novelly synthesized ligand and the complexes.



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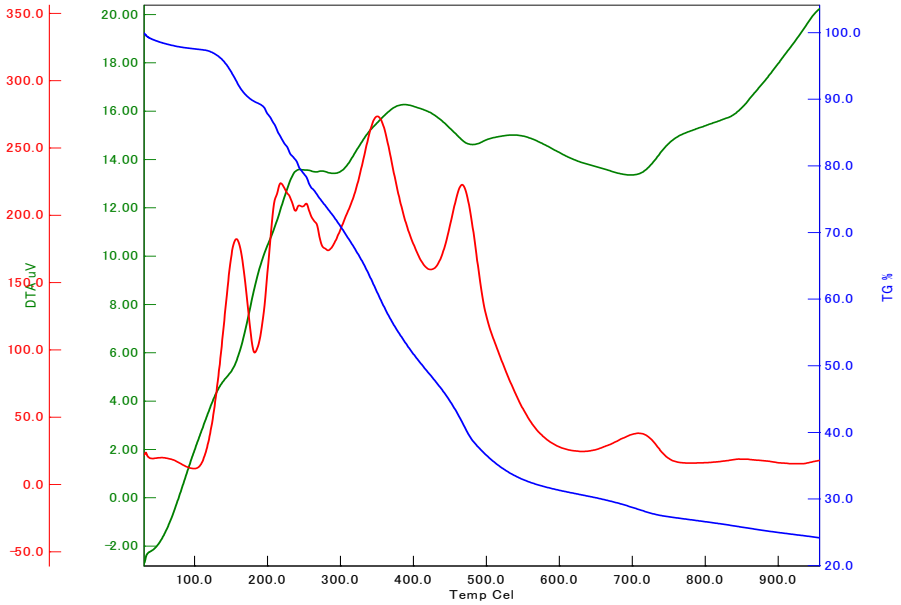
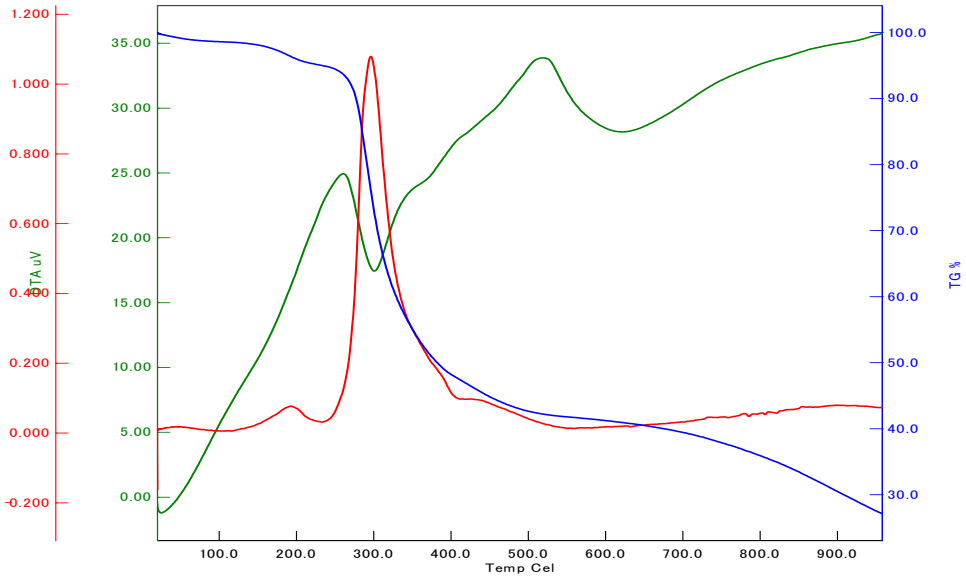
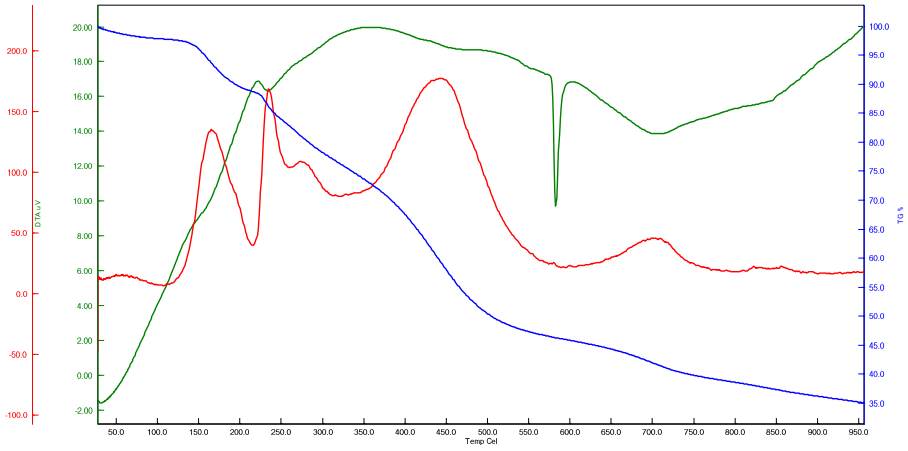


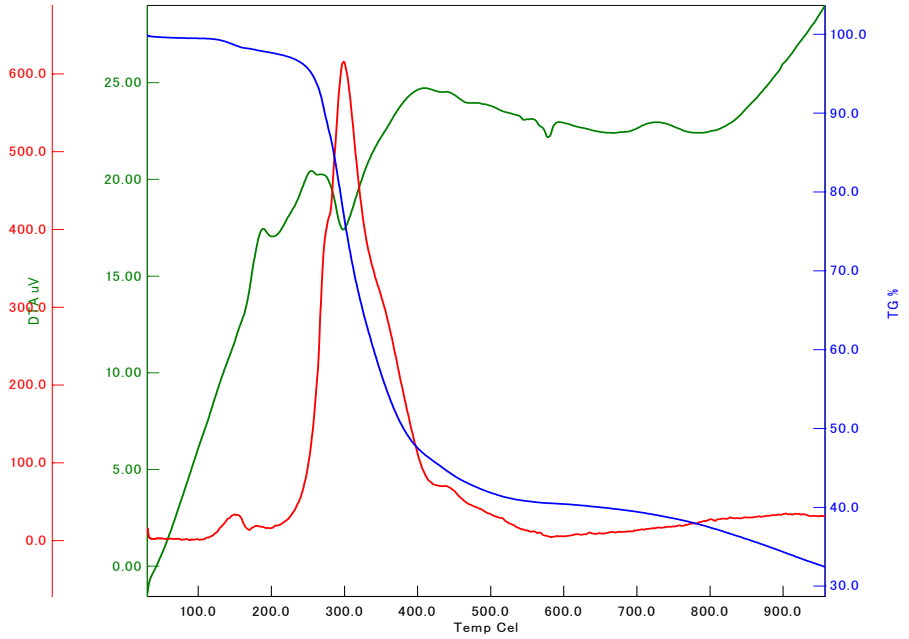
L1-Ru(II)



L2-Pd(II)



L2-Ru(II)



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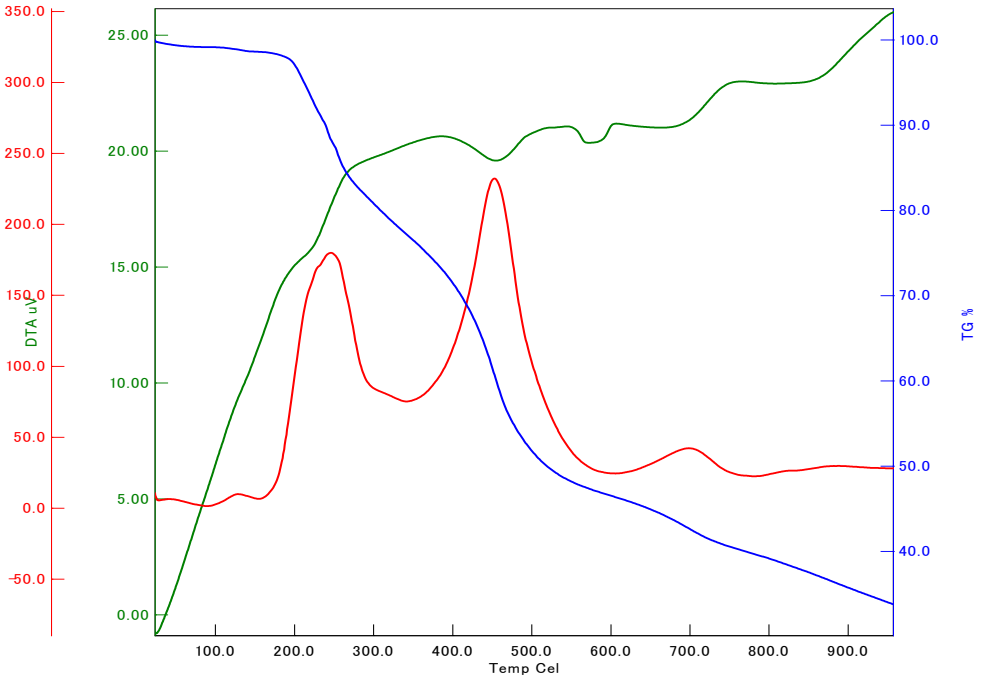

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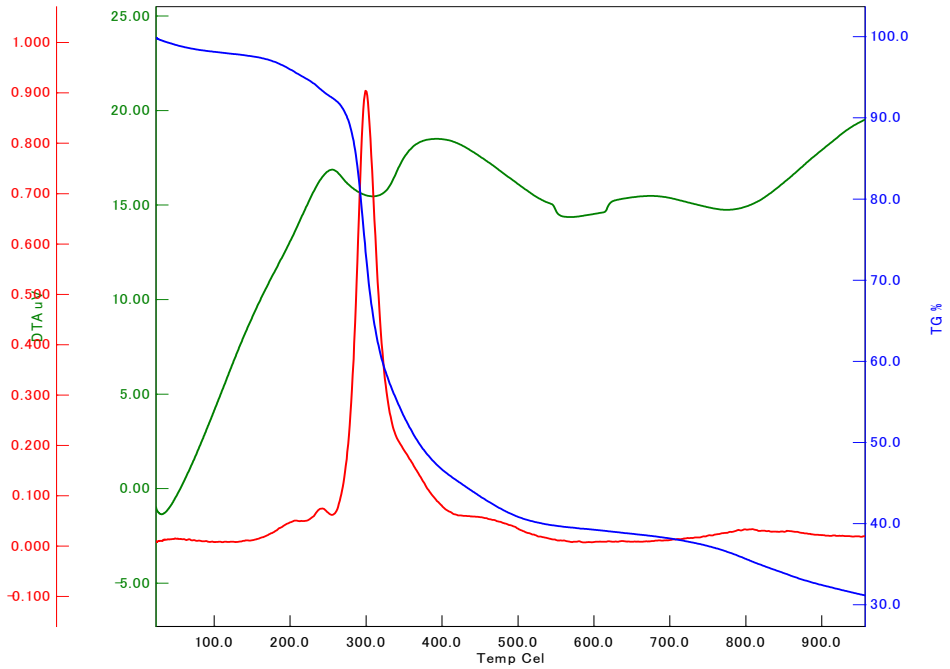
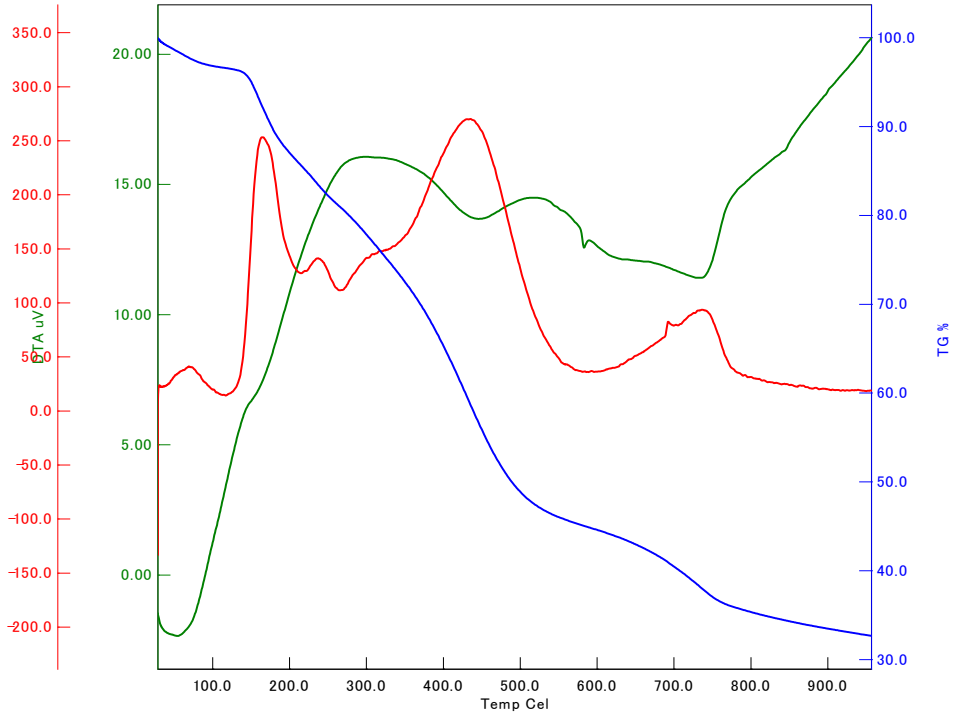


L4-Pd(II)



L4-Ru(II)

Supplementary 4. TG/DTA/DTG Curves of the complexes.