Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Effect of free rotation in polypyridinic ligands of Ru(II) complexes applied in light-emitting electrochemical cells.

Paulina Dreyse,[a] Bárbara Loeb,[*,a] Marco Soto-Arriaza,[a] Daniel Tordera,[b] Enrique Ortí,[b]

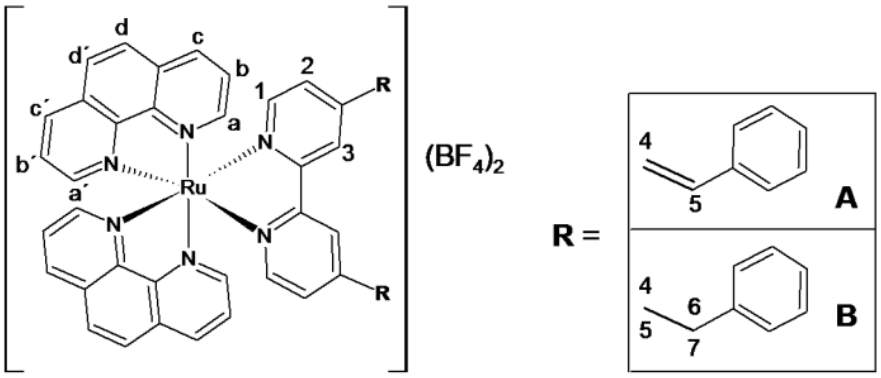
Juan J. Serrano-Pérez,[b] and Henk Bolink[*,b]

[a]*Facultad de Química, Pontificia Universidad Católica de Chile. Vicuña Mackenna 4860, Macul, Santiago, Chile.*

[b]*Instituto de Ciencia Molecular, Universidad de Valencia, 46980, Paterna, España.*

^{1}H-NMR Characterization

The ^{1}H-NMR and 2-dimensional ^{1}H-NMR (COSY) spectra of the complexes $[Ru(phen)_2LH](BF_4)_2$ and $[Ru(phen)_2Lhydro](BF_4)_2$ are shown below. The labels used in the following scheme (Fig. 1 in the main text) have been employed in the analysis of the ^{1}H NMR spectra.



*Chemical structures of the polypyridinic complexes $[Ru(phen)_2LH][BF_4]_2$ (**A**) and $[Ru(phen)_2Lhydro][BF_4]_2$ (**B**). Numbering of protons used for ^{1}H NMR analysis.*

$[Ru(phen)_2LH](BF_4)_2$ complex

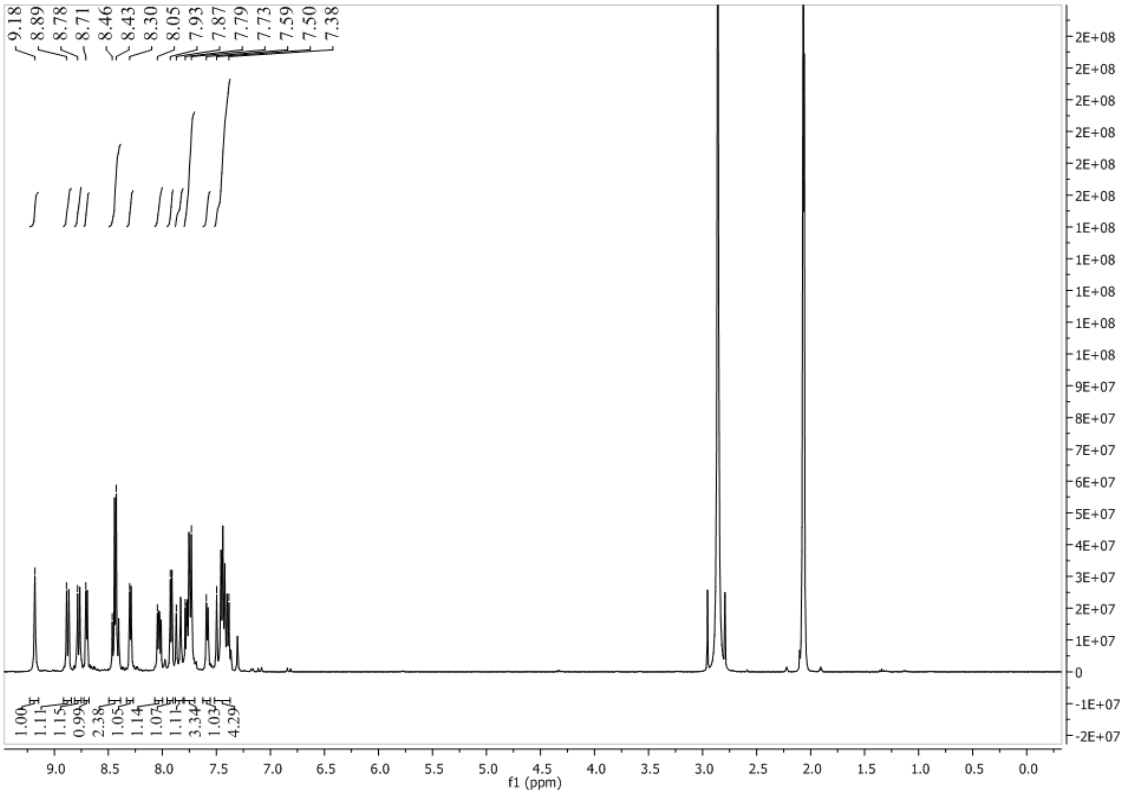


Figure 1. *Full ^{1}H-NMR spectrum of $[Ru(phen)_2LH](BF_4)_2$ complex (400 MHz, acetone-D_6).*

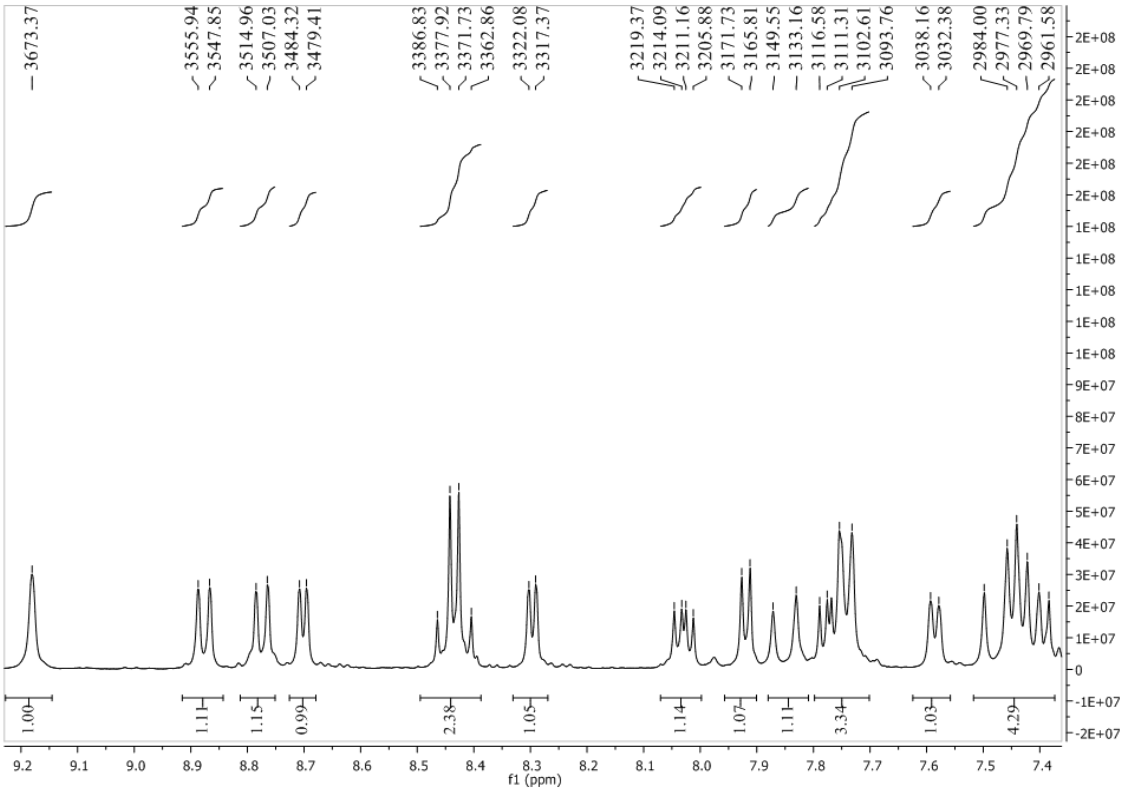


Figure 2. *Down field region ^{1}H-NMR spectrum of $[Ru(phen)_2LH](BF_4)_2$ complex (400 MHz, acetone-D_6).*

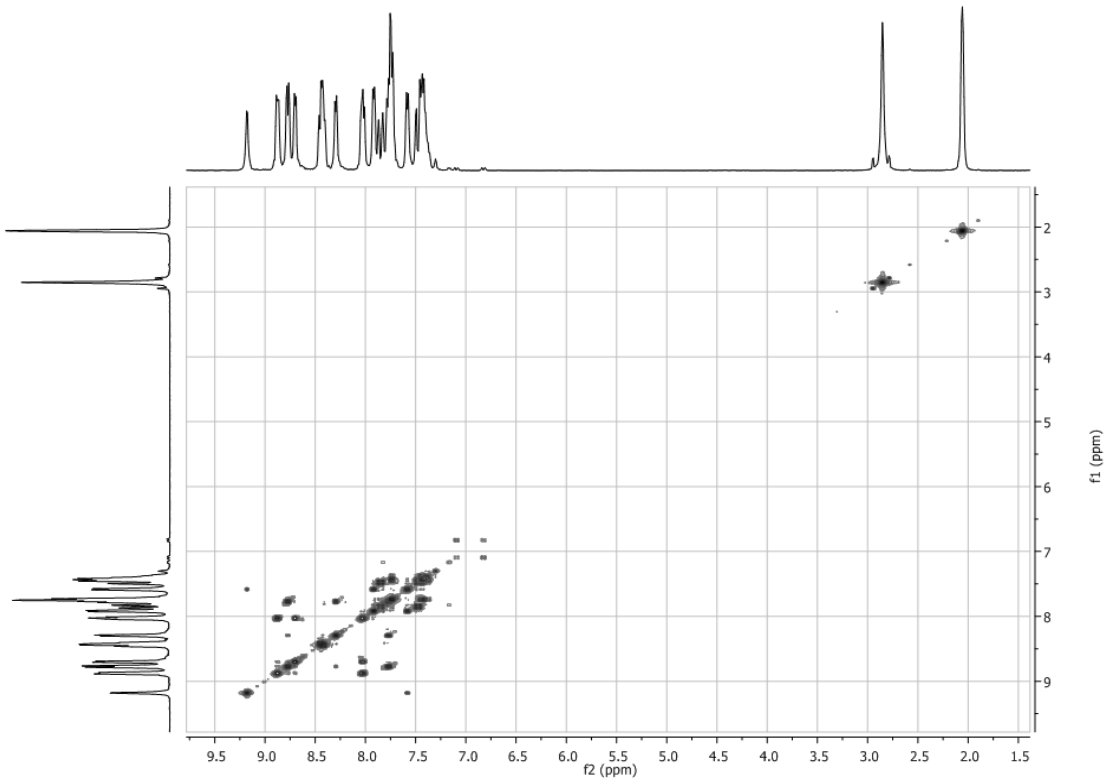


Figure 3. *Full 2D-^{1}H-NMR spectrum of $[Ru(phen)_2LH](BF_4)_2$ complex (400 MHz, acetone-D_6).*

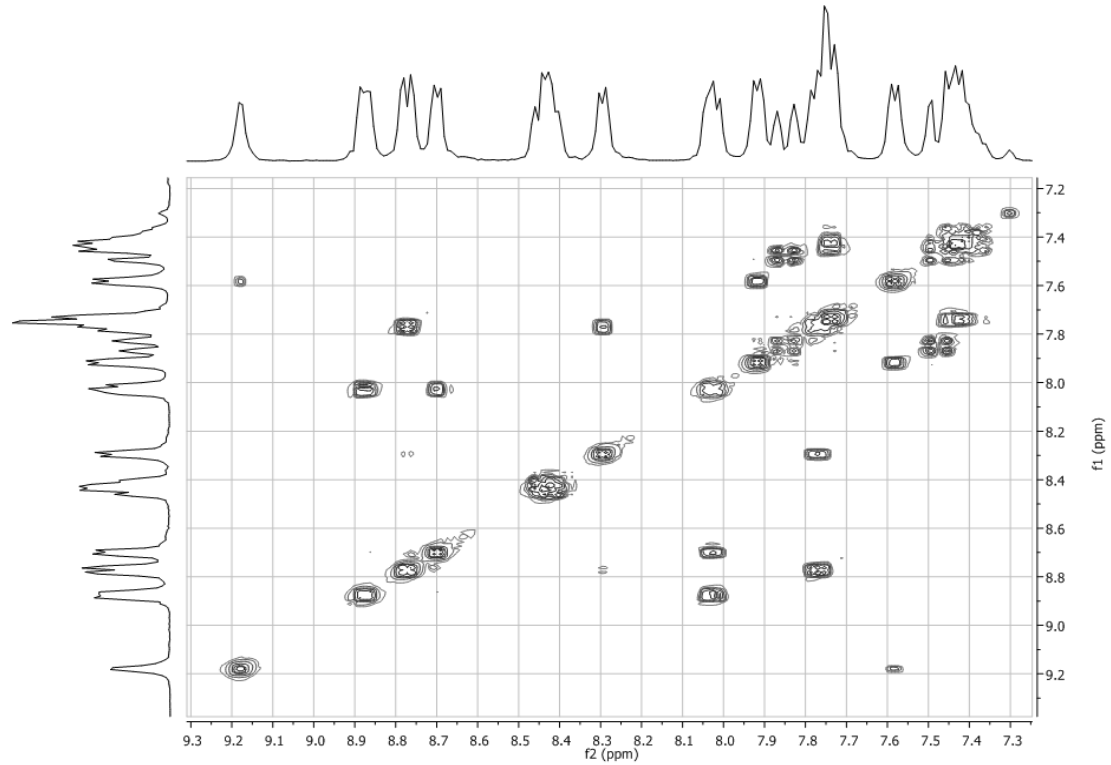


Figure 4. *Down field region of the 2D-^{1}H-NMR spectrum of $[Ru(phen)_2LH](BF_4)_2$ complex (400 MHz, acetone-D_6).*

According to the spectra depicted the chemical shift and coupling constant values are:

δ 9.18 (s, H_3), 8.89 (d, J_{ab} = 8.09 Hz, H_a), 8.78 (d, $J_{a'b'}$ = 7.93 Hz, $H_{a'}$), 8.71 (d, J_{cb} = 4.91 Hz, H_c), 8.46 (d, $J_{dd'}$ = 8.91 Hz, H_d), 8.43 (d, $J_{d'd}$ = 8.87 Hz, $H_{d'}$), 8.30 (d, $J_{c'b'}$ = 4.71 Hz, $H_{c'}$), 8.05 (dd, J_{ba} = 8.21 Hz, J_{bc} = 5.28 Hz, H_b), 7.93 (d, J_{12} = 5.92 Hz, H_1), 7.87 (d, J_{45} = 16.39 Hz, H_4), 7.79-7.73 (m, $H_{b'}$, $2H_{phenyl}$), 7.59 (d, J_{21} = 5.78 Hz, H_2), 7.50-7.38 (m, H_5, $3H_{phenyl}$).

The spectra and the values of the coupling constants demonstrate the formation of the $[Ru(phen)_2LH](BF_4)_2$ complex.

$[Ru(phen)_2Lhydro](BF_4)_2$ complex

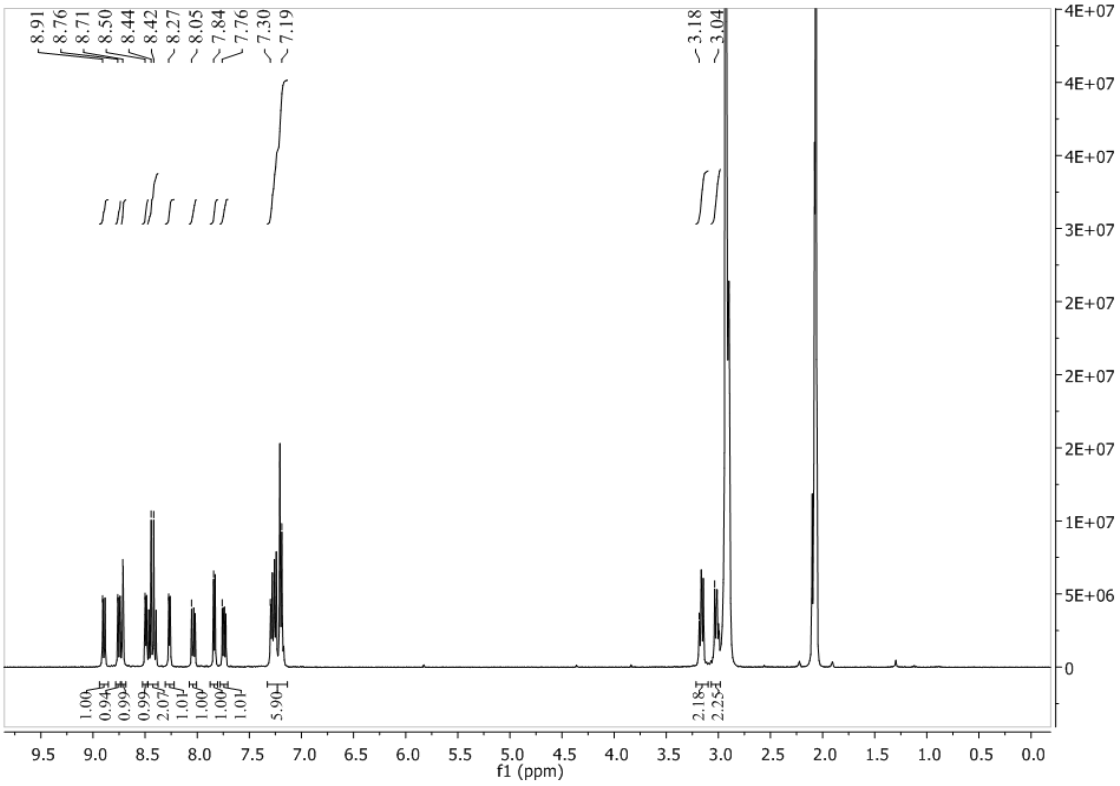


Figure 5. *Full ^{1}H-NMR spectrum of $[Ru(phen)_2Lhydro](BF_4)_2$ complex (400 MHz, acetone-D_6).*

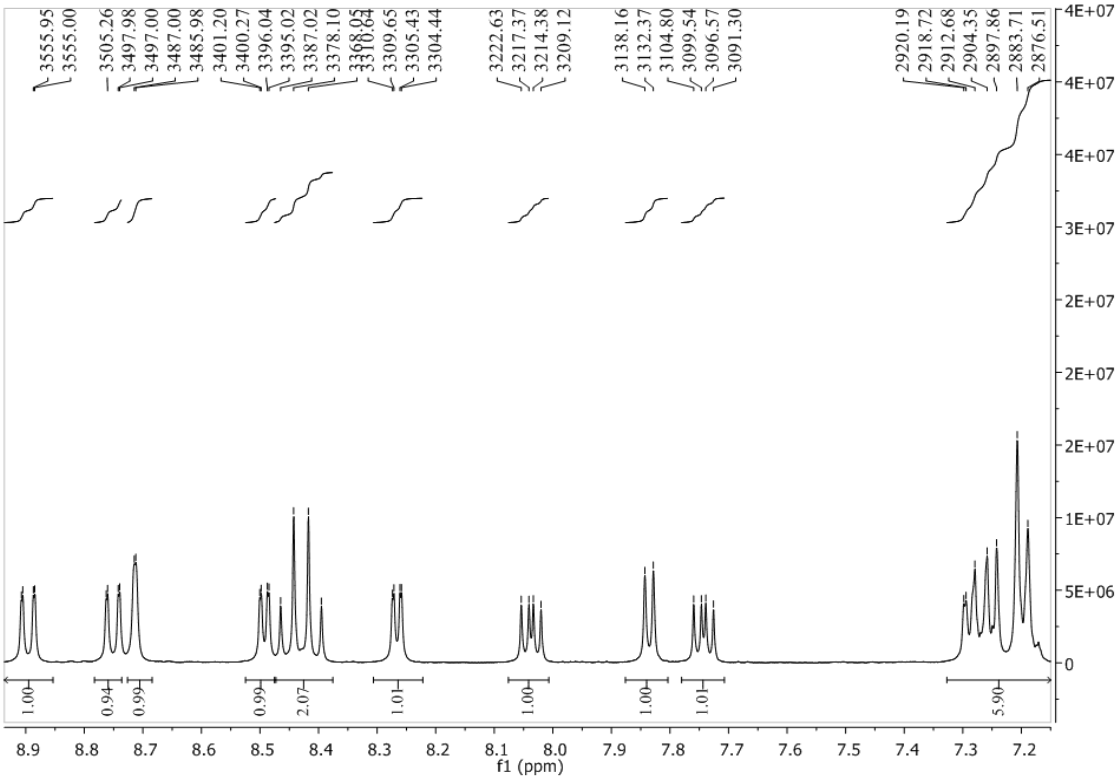


Figure 6. *Down field region ^{1}H-NMR spectrum of $[Ru(phen)_2Lhydro](BF_4)_2$ complex (400 MHz, acetone-D_6).*

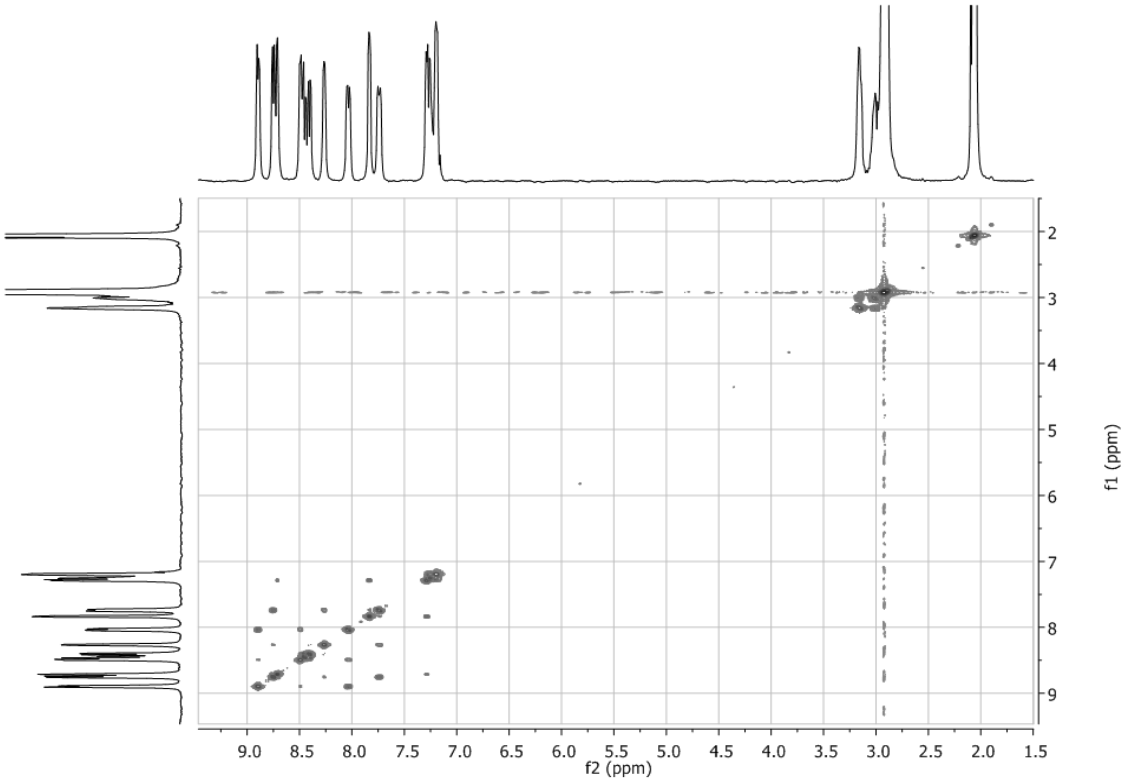


Figure 7. *Full 2D-^{1}H-NMR spectrum of [Ru(phen)$_2$Lhydro](BF$_4$)$_2$ complex (400 MHz, acetone-D$_6$).*

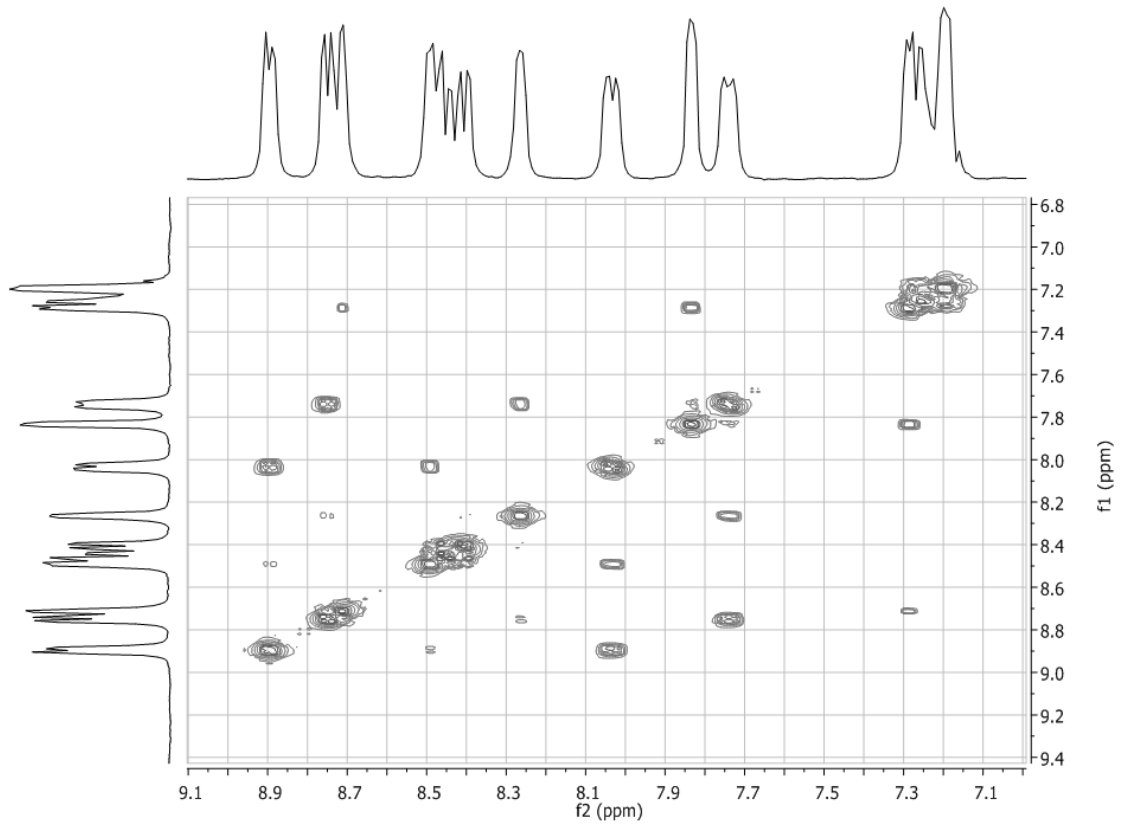


Figure 8. *Down field region of the 2D-^{1}H-NMR spectrum of [Ru(phen)$_2$Lhydro](BF$_4$)$_2$ complex (400 MHz, acetone-D$_6$).*

According to the spectra depicted the chemical shift and coupling constant values are:

δ 8.91 (d, J_{ab} = 8.25 Hz, H_a), 8.76 (d, $J_{a'b'}$ = 8.26 Hz, $H_{a'}$), 8.71 (s, H_3), 8.50 (d, J_{cb} = 5.25 Hz, H_c), 8.44 (d, $J_{dd'}$ = 8.92 Hz, H_d), 8.42 (d, $J_{d'd}$ = 8.90 Hz, $H_{d'}$), 8.27 (d, $J_{c'b'}$ = 5.21 Hz, $H_{c'}$), 8.05 (dd, J_{ba} = 8.25 Hz, J_{bc} = 5.26 Hz, H_b), 7.84 (d, J_{12} = 5.79 Hz, H_1), 7.76 (dd, $J_{b'a'}$ = 8.23 Hz, $J_{b'c'}$ = 5.26 Hz, $H_{b'}$), 7.30-7.19 (m, H_2, $5H_{phenyl}$), 3.18 (t, H_4, H_5), 3.04 (t, H_6, H_7).

The spectra and the values of the coupling constants demonstrate the formation of the $[Ru(phen)_2Lhydro](BF_4)_2$ complex.

MS Characterization

To corroborate that the complexes were effectively obtained, MS spectrometry was utilized according to the description given below.

The samples of $[Ru(phen)_2LH](BF_4)_2$ and $[Ru(phen)_2Lhydro](BF_4)_2$ complexes were diluted in 200 µL of acetonitrile and were measure using ESI and MALDI mass spectrometry.

Analysis of spectrum/Identification of signals: In the case of the samples analyzed, the molecular mass of the intact complex is not easy observed, however, the signals observed clearly correspond to the molecular mass of complex without counteranions. According to the spectra of the complexes, the signals m/z pseudo molecular and the isotopic distributions are similar to the theoretical data (see table 1).

On the other hand, in both analysis ESI and MALDI MS, it is possible to observe some signals that do not have assignation. In the case of the ESI MS, this behavior can be attributed to formation of adducts between the complex and ligands that have been ionized, which could be interacting with the molecules of the solvent used for preparing the samples. In the case of the MALDI MS analysis it is possible to observe signals that can be attributed to interference due to matrix cluster formation, in this case matrix of α-ciane-4-hydroxycinamic (CHCA), observed as signals dominating in the range below m/z 1200; this type of effect has been reported earlier in literature.[1] In spite of the behavior described, the mass analysis is conclusive in order to affirm the effective obtaining of the synthesized complexes since that the interfering signals do not overlap with the signals of the complexes that described below.

Table 1. *Analysis of signals.*

$[Ru(phen)_2Lhydro](BF_4)_2$		Experimental	
	Theoretical	ESI-MS	MALDI-MS
$Ru(C_{12}H_8N_2)_2(C_{26}H_{24}N_2)(BF_4)_2$	1000.2416	-	-
$-(BF_4)_1$	913.2381	913.3	913.2272
$-(BF_4)_2-H$	825.2280	825.3	825.2476
$[Ru(phen)_2LH](BF_4)_2$		Experimental	
	Theoretical	ESI-MS	MALDI-MS
$Ru(C_{12}H_8N_2)_2(C_{26}H_{20}N_2)(BF_4)_2$	996.2103	-	-
$-(BF_4)_1$	909.2069	909.3	909.2162
$-(BF_4)_2$	822.2039	821.3(-H)	822.1932

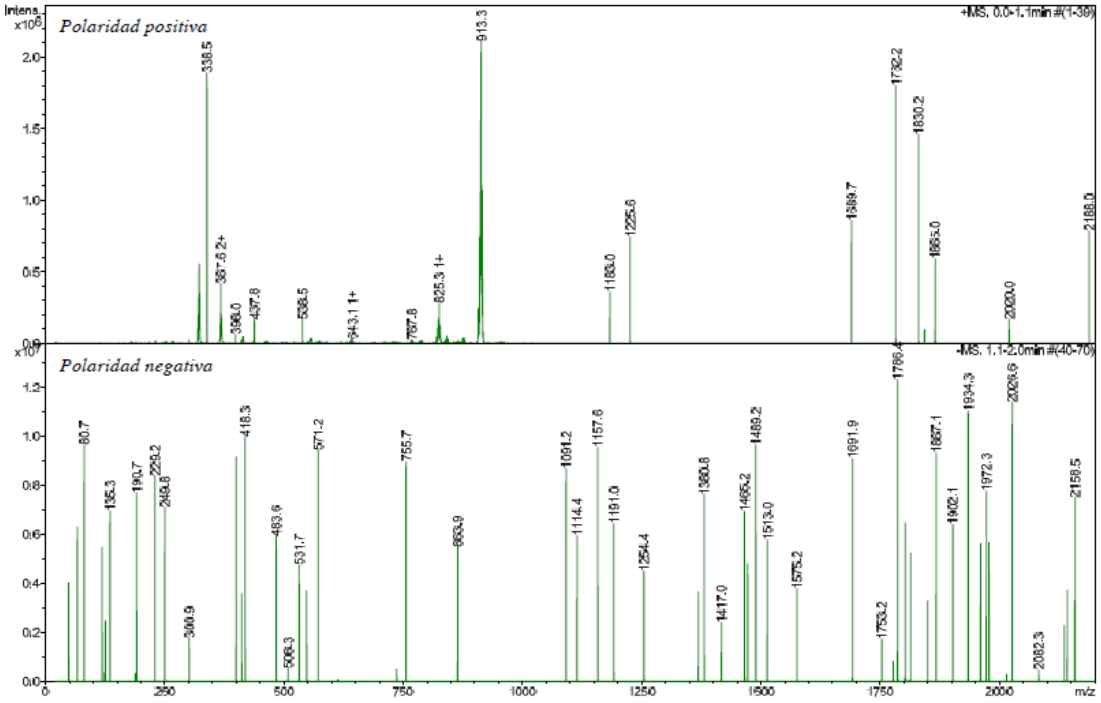


Figure 1. *ESI-MS spectrum of [Ru(phen)$_2$Lhydro](BF$_4$)$_2$ complex.*

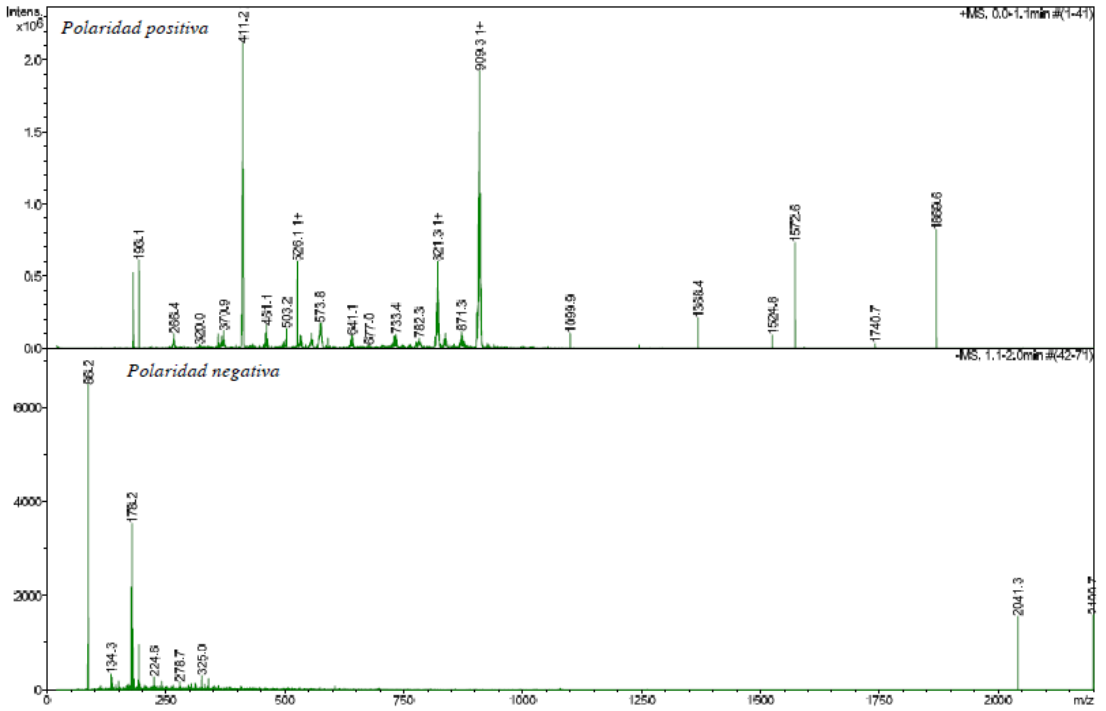


Figure 2. *ESI-MS spectrum of [Ru(phen)$_2$LH](BF$_4$)$_2$ complex.*

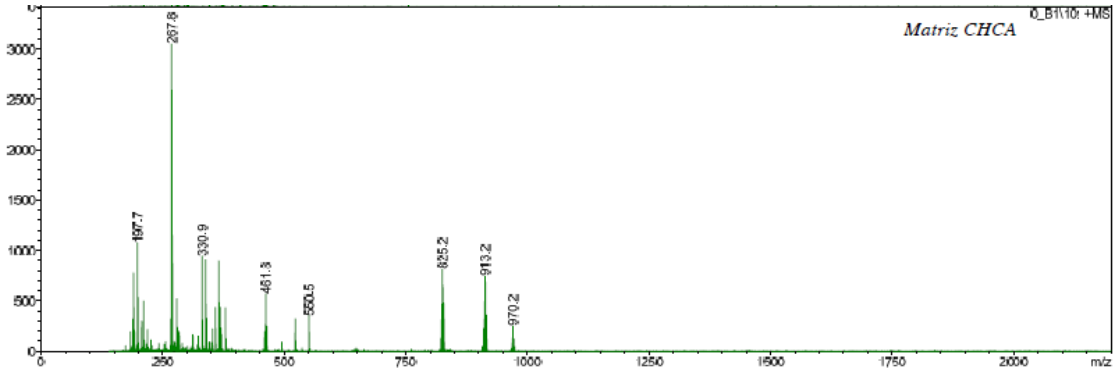


Figure 3. *MALDI-MS spectrum of [Ru(phen)$_2$Lhydro](BF$_4$)$_2$ complex.*

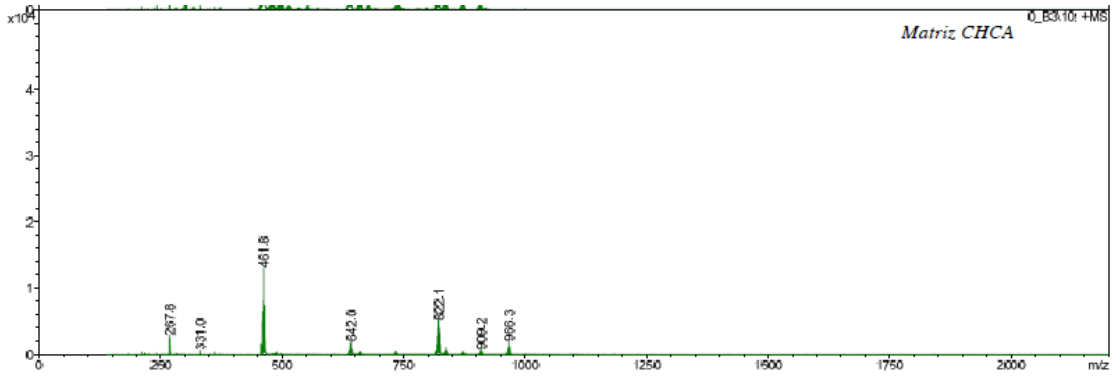


Figure 4. *MALDI-MS spectrum of [Ru(phen)$_2$LH](BF$_4$)$_2$ complex.*

REFERENCE

1. I. P. Smirnov, X. Zhu, T. Taylor, Y. Huang, P. Ross, I. A. Papayanopoulos, S. A. Martin and D. J. Pappin, *Anal. Chem.*, 2004, **76**, 2958.