

SYNTHESIS AND ^1H NMR CHARACTERIZATION OF NOVEL Ru(II) COMPLEX

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ABSTRACT

A novel Ru(II) complex has been successfully synthesized. Firstly, the new synthetic ligands composing an anchor 1,10-phenanthroline-5-carboxylic acid (compound D) and an antenna ligand [5-(9,9-dihexylfluoren-2-yl)]-phenanthroline (compound H) were synthesized. After that, novel Ru(II) complex was designed by association of two antenna ligands, one anchor and Ru(II) salt. All compounds in these synthetic steps were analyzed by ^1H NMR spectra and elemental analysis.

Keywords: Ru(II) complex; antenna ligands; anchor; luminescence; quantum dot.

TÓM TẮT

Tổng hợp và đặc trưng bằng phổ ^1H NMR phức chất mới của Ru(II)

Một hợp chất phức mới của Ru(II) đã được tổng hợp thành công. Trước tiên, các phối tử mới gồm phối tử móc (móc liên kết) 1,10-phenanthroline-5-carboxylic axit (hợp chất D) và phối tử tín hiệu [5-(9,9-dihexylfluoren-2-yl)]-phenanthroline (hợp chất H) được điều chế. Sau đó, phức mới của Ru(II) được tạo ra bằng các phản ứng kết hợp giữa các phối tử và hợp chất muối Ru(II). Các hợp chất trong quá trình tổng hợp được đặc trưng bằng phổ ^1H NMR và phương pháp phân tích nguyên tố.

Từ khóa: phức Ru(II), phối tử tín hiệu, phối tử móc, anchor, phát quang, chấm lượng tử.

1. Introduction

Ruthenium has several oxidation states: Ru(II), Ru(III), and Ru(IV). Most of these oxidation states are accessible under physiological conditions.

Recent literature present the use of ruthenium(IV) complexes as a catalyst or pre-catalyst. Allylic ruthenium(IV) complexes as pre-catalyst in transition metal-catalyzed reactions. The most domination is in the nucleophilic substitution reactions, where they appear either as initial catalysts or are generated upon oxidative addition of allylic substrates to ruthenium(II) pre-catalysts [1]. Whereas, bis(allyl) ruthenium(IV) complexes containing water-soluble phosphane ligands can apply as catalysts in the selective hydration of nitriles into amides in pure aqueous medium and neutral conditions [2].

Ru(III) complexes serve as precursors to Ru(II) by a reduction *in vivo* by biological reductants such as glutathione and ascorbic acid [3].

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Among ruthenium complexes, ruthenium(II) complexes are still being the most attracted for scientific researchers. They have indisputable advantages, for a wide range of applications such as optical power limiting [4-6], optical data processing, biological imaging [7], photosensitizers (PS) in the conversion of solar energy [8] and PS for application in photodynamic therapy (PDT) [9-11]. For example, ruthenium(II) complexes containing a benzimidazole ligand have important applications in optoelectronic devices, efficient sensitizers for molecular photovoltaics [12]. A series of Ru(II) complexes of polyphosphine ligands has been used as catalyst precursors in the homogeneous hydrogenation of cyclohexene, cyclohexanone, propanal and 2-cyclohexen-1-one [13]. These polyphosphine Ru(II) complexes show enhanced catalytic activities compared to monodentate, bidentate phosphine, arsine analog. From another point of view, tetraamine-based ruthenium(III) and (II) complexes constitute is very interesting class of compounds for medicinal chemistry studies because of their water solubility, stability in an aqueous medium, and low cytotoxicity [3]. Furthermore, ruthenium(II) complexes possess many interesting properties such as luminescent property, high stability with a large number of potential ligands [6], allowing their use in practical applications.

In this study, we focused on novel Ru(II) complex (Fig. 1). This is heteroleptic Ru(II) complex involving three bidentate ligands: two ligands (abbreviate: L) playing an important role for linear and nonlinear optical properties and a third ligand such as an anchor (abbreviate: A) for connecting with the quantum dots. This report presents about synthesis and characterization of this novel Ru(II) complex.

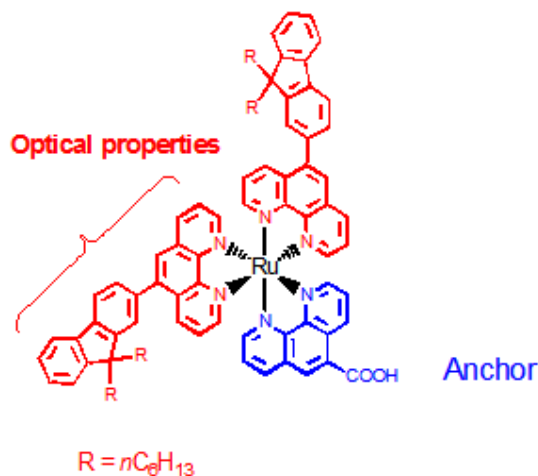


Figure 1. Molecular structure of novel Ru(II) complex

2. Materials and method

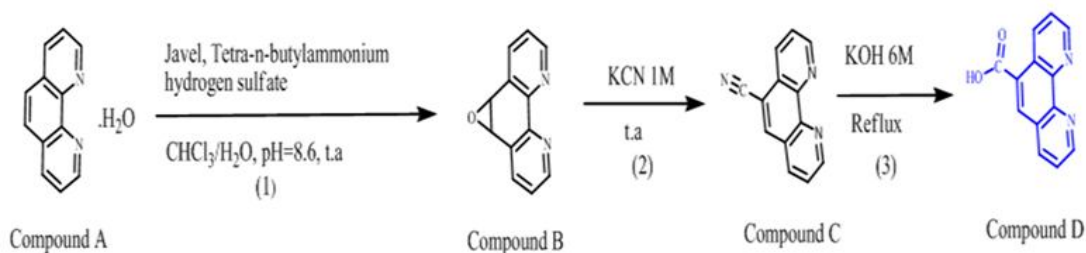
2.1. Materials

Main chemical reagents used such as: Javel water Lacroix; 1,10-phenanthroline monohydrate, Sigma-Aldrich, $\geq 99\%$; Potassium cyanide, Sigma-Aldrich, $\geq 96\%$; Potassium hydroxide, Sigma-Aldrich, $\geq 90\%$; Bromohexane, Sigma-Aldrich, $\geq 98\%$; n-Butyllithium solution 2.5M in hexane, Sigma-Aldrich; Triisopropyl borate, Sigma-Aldrich, $\geq 98\%$; 2-bromofluorene, Sigma-Aldrich, 95%; $\text{RuCl}_2(\text{DMSO})_4$, Sigma-Aldrich, 98%; 5-bromo-1,10-phenanthroline, Sigma-Aldrich, 99%.

2.2. Synthesis

2.2.1. Synthesis of the new anchor

From 1,10-phenanthroline monohydrate (compound A), anchor D was synthesized following the scheme 1.



Scheme 1. Synthesis of the Phen-COOH ligand

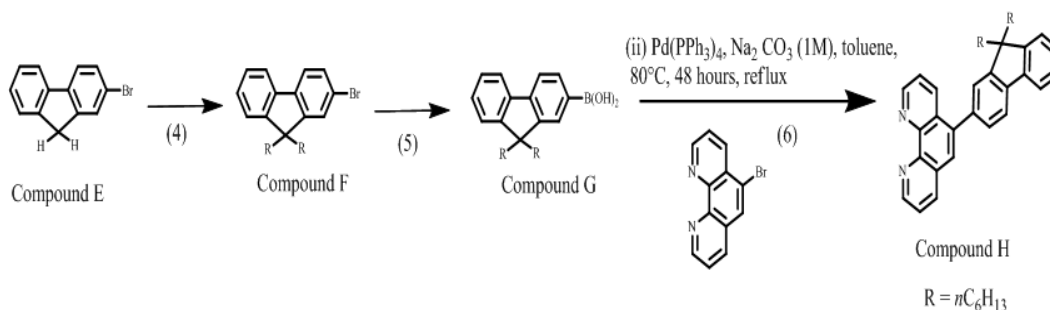
In a 500 ml round bottom flask, adding to 125 ml of Javel water (NaClO and NaCl aqueous solution) and 60 ml of distilled water. Then, 1 g (5.05×10^{-3} mol) of 1,10-phenanthroline monohydrate (compound A) and 0.8 g of tetra-n-butylammonium hydrogen sulfate (2.36×10^{-3} mol) were dissolved in 100 ml of chloroform. Controlling the temperature $T^\circ\text{C} = 20^\circ\text{C}$ and the $\text{pH} = 8.6$ (by NaOH 6M and HCl solution 2M) for 2 hours 40 minutes. The organic phase was separated. Washing this organic phase with distilled water (3×100 ml), saturated sodium chloride (1×100 ml) to collect organic phase. Drying a small water inside organic phase by sodium sulfate anhydrous, filtering and, evaporating off solvent to collect the crude product. Then, washing this crude product with cold acetone (3×10 ml). 5,6-epoxy-5,6-dihydro-1,10-phenanthroline compound (compound B) was obtained as hygroscopic solid (90% yield).

To synthesize compound C, put 1.95 g (9.95×10^{-3} mol) of 5,6-epoxy-5,6-dihydro-(1,10-phenanthroline) (compound B) inside a 50 ml round bottom flask. Adding to 25 ml of potassium cyanide 1M solution. Agitating for 1 night. Then, making the filtration to collect precipitate and washing with a small amount of cold distilled water. Solubilizing the precipitate in chloroform and drying with sodium sulfate anhydrous to collect organic phase. Continuing to filter and evaporate the solvent. 5-cyano-1,10-phenanthroline compound (compound C) was obtained as a white powder (20% yield).

In a 50 ml round bottom flask, put inside 0.804g (0.004 mol) of 5-cyano-1,10-phenanthroline (compound C) and 23 ml of potassium hydroxide KOH 6M. This suspension was agitated under reflux system and heating at 80°C for 1 night. After the reaction came back to ambient temperature, we added to 100 ml of distilled water to obtain a solution. Then, washing with chloroform solvent (3x25ml) to collect aqueous phase and concentrate this phase to get 20 ml of volume. Then, adjusting pH up to 5.4 to re-precipitate, continuing to centrifuge and washing with a small amount of cold distilled water and acetone. 790 mg of compound D were obtained (88% yield).

2.2.2. Synthesis of the new photon antenna ligand

Scheme 2 describes the synthetic steps of antenna ligand (compound H).



Scheme 2. Synthesis of [5-(9,9-dihexylfluoren-2-yl)]-phenanthroline ($R = C_6H_{13}$)

In 100 ml round bottom flask under argon atmosphere, 4 g (16.3×10^{-3} mol, 1 equivalent) of 2-bromofluorene (compound E) was dissolved in 18 ml of DMSO (dimethyl sulfoxide). Adding to 0.206g (0.9×10^{-3} mol, 5.5%) of bezyl triethylammonium chloride, 10 ml (11.41×10^{-3} mol, 7 equivalents) of sodium hydroxyl 12.5M and 7 ml (48.9×10^{-3} mol, 3 equivalents) of bromohexane. Stirring at room temperature for one hour and at 60 °C for two hours. Then, adding to ethyl acetate in excess (approximately 40 ml). Filtering to collect solution. Continuing to wash solution with diluted hydrochloric acid (HCl 1M) then, distilled water, and saturated sodium chloride. A small amount of water in the organic phase was dried with sodium sulfate anhydrous. Filtering and evaporating the solvent. After that, using chromatographic (silica column, the eluent is *n*-hexane) to purify crude product. The compound 2-bromo-(9,9-dihexylfluorene) (compound F) was obtained as a liquid (yield around 65% after a second alkylation of the mono-hexyl-substituted compound firstly obtained).

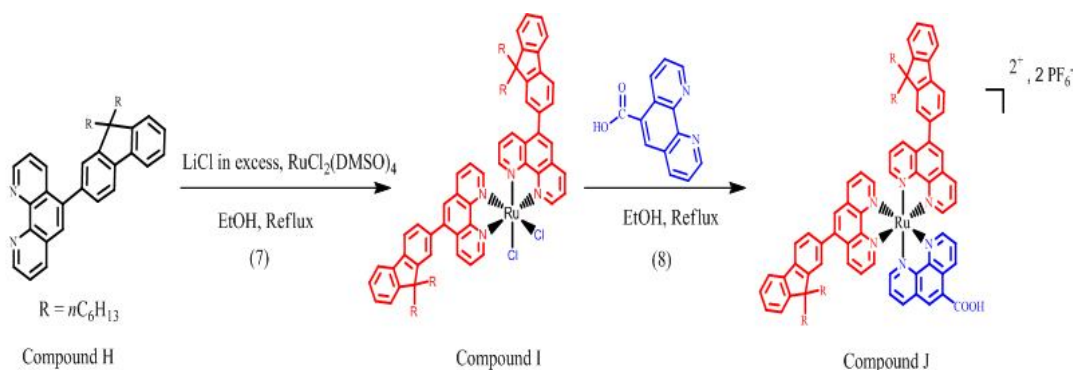
In one round bottom flask (100 ml of volume), 1.6g (3.87×10^{-3} mol, 1 equivalent) of 2-bromo-(9,9-dihexylfluorene) (compound F) was dissolved with 40 ml of dried tetrahydrofuran (THF) under argon atmosphere. Put round bottom flask inside cooling bath. At -78°C, add to 2 ml (5.418×10^{-3} mol, 1.4 equivalents) of *n*-butyl lithium 2.65M, drop by drop. The reaction was rotated for 2 hours and 30 minutes. Continuing to add 3.5 ml (0.015 mol, 4 equivalents) of triisopropyl borate, drop by drop. Let reaction go back to ambient temperature and continue to agitate for 12 hours. Then, adding to 12

ml of hydrochloric acid 2M. The organic phase was collected and washed with 50 ml of distilled water and drying with sodium sulfate anhydrous. After evaporating the solvent to collect crude product, the crude product was purified by chromatographic technique (silica column, using 200 ml of dichloromethane at the beginning, then changing to 200 ml of mixture solvent including dichloromethane 90% and acetone 10%, and mixture solvent of dichloromethane 85% and acetone 15%), the pure product (compound G) was obtained as a white solid (30% yield).

For compound H, In one round bottom flask (50 ml of volume) under argon atmosphere, 0.450 g of 2-(9,9-dihexylfluorenyl) boronic acid (compound G) (0.119×10^{-2} mol, 1 equivalent) and 0.308 g of 5-bromo-1,10-phenanthroline (0.119×10^{-2} mol, 1 equivalent) were dissolved in 6 ml of toluene and 6 ml of sodium carbonate solution 1M (0.0059 mol, 5 equivalents). Then added to 0.055 g of tetrakis-phenylphosphine palladium (0). The reaction was kept under reflux and agitation for 3 days. Then, extracting more organic phase by adding dichloromethane to the aqueous phase. The organic phase was dried with sodium sulfate anhydrous and evaporated the solvent. After that using the chromatographic technique (alumina column, the eluent is a mixture of dichloromethane 80%, acetone 19%, and triethylamine 1%) to purify the crude product. Then, washing the product several times with a small amount of pentane solvent, then evaporating the solvent. Ligand L1 was obtained as a white solid (25% yield).

2.2.3. Synthesis of the novel ruthenium complex

Related ruthenium complex $\text{RuCl}_2(\text{L})_2$ was obtained by reaction under reflux of 2 equivalents of ligand L (in ethanol) with 1 equivalent of ruthenium dichloride tetra(dimethylsulfoxide) (in ethanol) and precipitated in dichloromethane (compound I). Novel ruthenium complex was synthesized by reaction under reflux of one equivalent of $\text{RuCl}_2(\text{L})_2$ with 1 equivalent of 1,10-phenanthroline-5-carboxylic acid (compound D: anchor) and precipitated by ammonium hexafluorophosphate (NH_4PF_6) (compound J) (see Scheme 3).



Scheme 3. Synthesis of the ruthenium(II) complex (J)

In one round bottom flask (50 ml of volume) under argon atmosphere, 37.81 mg (7.81×10^{-5} mol, 1 equivalent) of $\text{RuCl}_2(\text{DMSO})_4$ and 33.2 mg (7.81×10^{-4} mol, 10 equivalents) of lithium chloride were dissolved in minimum volume of ethanol. In one erlenmeyer flask, 80 mg (1.56×10^{-4} mol, 2 equivalents) of ligand L1 (compound H) was also dissolved in minimum volume of ethanol. Put this solution inside the round bottom flask. The reaction was kept under reflux and heating (80 degree Celsius, rotating (570 rpm) for 1 night. Let the round bottom flask go back to room temperature, added to distilled water to precipitate, drop by drop. Centrifuging to collect the precipitate. The precipitate was dissolved in dichloromethane, then, added a small amount of distilled water to separate the two phases easily. Collecting the organic phase, and drying with sodium sulfate anhydrous and evaporate the solvent. 100 mg of product were obtained (around 100% of yield), as a solid (compound I).

In one round bottom flask (50 ml of volume) under argon atmosphere, 100 mg (8.36×10^{-5} mol, 1 equivalent) of $\text{RuCl}_2(\text{L})_2$ (compound I) and 28.92 mg (8.36×10^{-5} mol, 1 equivalent) of one compound (involved of 1 molecular of 1,10-phenanthroline-5-carboxylic + 2.5 molecules of sodium hydroxyl) were dissolved in minimum volume of ethanol (around 2 ml). The reaction was kept under reflux, heating at 80-degree celsius and stirring for one night. Then saturated ammonium hexafluorophosphate was added to get a precipitate. The collected solid was solubilized in dichloromethane, and distilled water. The organic layer was dried by sodium sulfate anhydrous, then filtered, and evaporated to dry. The product was obtained as a red-orange/brownish solid (around 40% yield) (compound J: novel Ru(II) complex).

2.3. Instrument and characteristic

All synthesized compounds including B, C, D, F, G, H, I and J were checked by ^1H NMR spectra on a Bruker 250 MHz spectrometer or elemental analysis on AAS spectrometer.

3. Results and discussion

3.1. ^1H NMR of compound B (5,6-epoxy-5,6-dihydro-1,10-phenanthroline)

^1H NMR (250MHz, CDCl_3): δ (ppm) : 8.89 - 8.95 ppm (2H, dd, $J = 4.8$ Hz, $J = 9.8$ Hz); 8.0 - 8.1 ppm (2H, dd, $J = 6$ Hz, $J = 10.5$ Hz), 7.42 - 7.47 ppm (2H, dd, $J = 4.5$ Hz, $J = 7.5$ Hz); 4.65 ppm (2H, s).

3.2. ^1H NMR of compound C [5-cyano-(1,10-phenanthroline)]

^1H NMR (250 MHz, CDCl_3): δ (ppm) : 9.30 - 9.35 ppm (2H, dd, $J = 6$ Hz, $J = 4.2$ Hz); 8.64 - 8.67 ppm (1H, dd, $J = 6.5$ Hz, $J = 1.7$ Hz); 8.34 - 8.37 ppm (1H, dd, $J = 6.5$ Hz, $J = 3$ Hz); 7.93 ppm (1H, s); 7.74 - 7.86 ppm (2H, dd, $J = 16.2$ Hz, $J = 8.2$ Hz, $J = 4.5$ Hz).

3.3. Elemental analysis of compound D (1,10-phenanthroline-5-carboxylic acid)

Compound D was analyzed by elemental analysis (due to the difficulty to solubilize). Elemental analysis calculated for $\text{C}_{13}\text{H}_8\text{F}_{12}\text{N}_2\text{O}_2$ ($224,2 \text{ g}\cdot\text{mol}^{-1}$) with (%):

C 69.0; H 3.6; N 12.5 (in theory), and C 68.7; H 3.5; N 12.4 (in experiment). The deviation of elemental analysis results from experiment and theory belongs to the accepted value.

3.4. ^1H NMR of compound F (2-bromo-9,9-dihexylfluorene)

^1H NMR (250 MHz, CDCl_3): δ (ppm) : 7.67 ppm (m, 1H); 7.57 ppm (d, 1H, $J = 8.5$ Hz); 7.45 ppm (d, 2H, $J = 6.7$ Hz); 7.32 ppm (m, 3H); 1.96 ppm (t, 4H, $J = 6$ Hz); 1.05 ppm (m, 12H); 0.77 ppm (t, 6H, $J = 6.8$ Hz); 0.59 ppm (m, 4H).

3.5. ^1H NMR of compound G [Acid 2 – (9,9-dihexylfluorenyl) boronic]

^1H NMR (250MHz, CDCl_3): δ (ppm) : 8.33 ppm (d, 1H, $J = 7.5$ Hz); 8.22 ppm (s, 1H); 7.83-7.91 ppm (m, 2H); 7.38 - 7.41 ppm (m, 3H); 2.06 - 2.12 ppm (m, 4H); 1.07 - 1.2 ppm (m, 12H); 0.72 - 0.78 ppm (m, 10H).

3.6. ^1H NMR of compound H

^1H NMR (250MHz, CDCl_3): δ (ppm): 9.24 ppm (m, 2 H); 8.30-8.36 ppm (m, 2 H); 7.85-7.90 ppm (m, 1 H); 7.70 ppm (s, 1 H); 7.60-7.70 ppm (m, 1H); 7.56 ppm (m, 1 H); 7.48 ppm (m, 1H); 7.40 (s, 1H); 7.39 ppm (d, 1H, $J = 2.3$ Hz); 7.27-7.37 ppm (m, 1H); 7.48 ppm (m, 1H); 7.40 (s, 1H); 7.39 ppm (d, 1H, $J = 2.3$ Hz); 7.27-7.37 ppm (m, 3H); 2.0 ppm (m, 4H, H alkyl); 1.10 ppm (m, 12H, H alkyl); 0.75-0.80 ppm (m, 10H, H alkyl).

3.7. Elemental analysis of compound I: $\text{RuCl}_2(\text{L})_2$

Elemental analysis of $\text{RuC}_{74}\text{H}_{80}\text{N}_4\text{Cl}_2$ ($1200 \text{ g}\cdot\text{mol}^{-1}$) (%) in theory and experiment was (C 66.0 ; H 7.1 ; N 3.9) and (C 65.8; H 7; N 3.8) respectively. The deviation of elemental analysis results from experiment and theory belongs to the accepted value.

3.8. ^1H NMR of compound J: Ru(II) complex

^1H NMR spectrum (at 250MHz) in CDCl_3 is too complicated to analyze in detail. The ratio between hydrogen alkyl and hydrogen aromatic from the molecular structure is $52/35=1.5$. The ratio between hydrogen alkyl and hydrogen aromatic from ^1H NMR spectra in the experiment is $5.67/2.93=1.9$. It seems to be similar (Fig. 2). More hydrogen alkyl in the spectra is assigned to solvent or impurity.

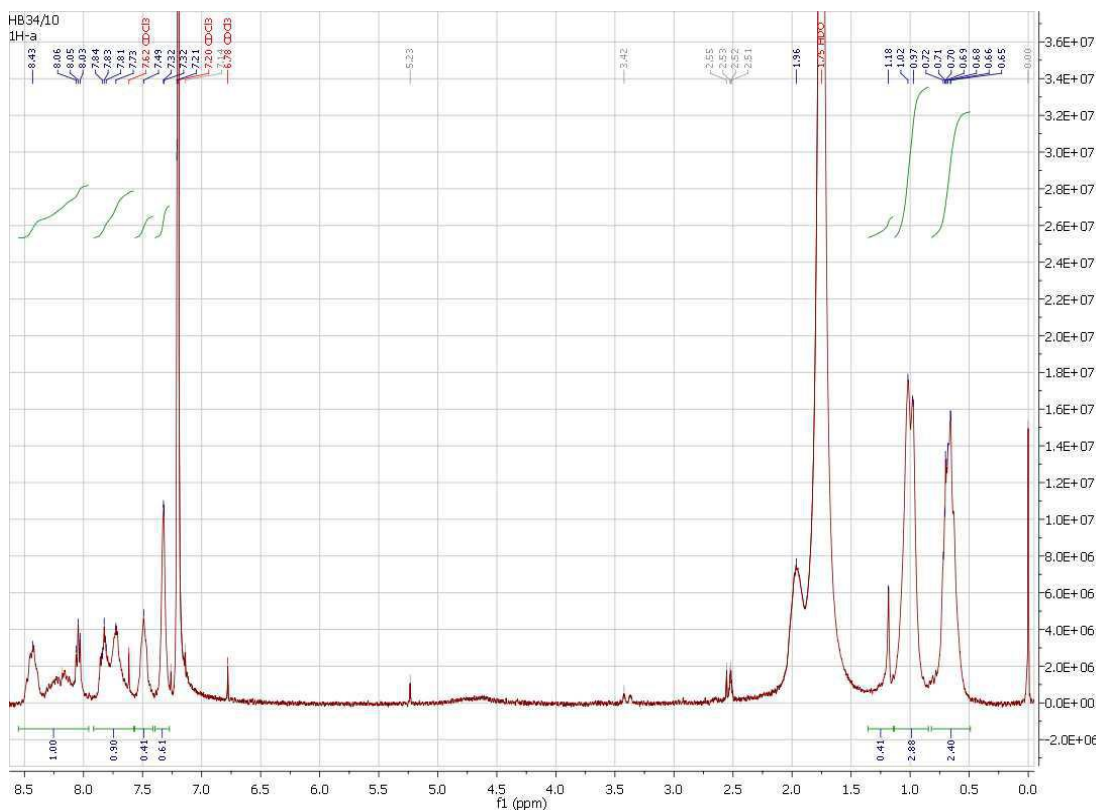


Figure 2. ^1H NMR (250MHz, CDCl_3) spectra of final compound J:
 $\{[\text{RuPhenCOOH}(\text{L1})_2], 2\text{PF}_6\}$

4. Conclusion and perspective

A novel Ru(II) complex has been successfully synthesized by association of the new synthetic ligands and Ru(II) salt. This contains two antenna ligands and one anchor. ^1H NMR spectra and elemental analysis of the all compounds were recorded. The novel Ru(II) complex will be checked its optical properties and capacity of grafting to quantum dots for (bio)-imaging applications in the next study.

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(Received: 22/10/2016; Revised: 21/11/2016; Accepted: 16/12/2016)