

Electronic Supplementary Information

**Isolated *facial* and *meridional* Ru^{II}(bipy)₃ for STM
studies on Au(111)**

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Materials and Instruments

All chemicals for synthesis were purchased from Sigma-Aldrich or Alfa-Aesar and were used as received without further purification. THF was dried over Na/ benzophenone, DIEA over CaH₂ and freshly distilled under nitrogen prior to use.¹ TLC was carried out on Merck silica gel 60 F₂₅₄ plates and column chromatography using Merck silica gel 60 (0.040–0.063 mm). The solvents used for spectroscopy and deposition on the Au-surface (CH₃CN) were of spectroscopic grade.

Dichlorotetrakis(dimethyl sulfoxide)ruthenium(II) has been prepared following standard reported procedure.²

5-bromo-2,2'-bipyridine³ was received from Dr. Frank Schramm and was further purified by column chromatography. 4-(thioacetyl)-iodobenzene⁴ was received from Mr. Matthias Fischer. These compounds have been prepared following standard reported procedures.^{3, 4}

Characterizations were performed with the following instruments:

¹H (300MHz) and ¹³C NMR (75MHz) spectroscopic data were recorded with a Bruker Ultra Shield DPX300 spectrometer with the solvent-proton signal used as an internal standard. ¹H and ¹³C NMR spectra are calibrated to the signals of the deuterated solvents reported in literature.⁵ The assignment of ¹H and ¹³C signals was accomplished with the help of DEPT 135 experiments and by two-dimensional correlation experiments (COSY, HMQC). The chemical shifts, δ are given in ppm.

Melting points were measured with a Büchi Melting Point B-540 apparatus.

Mass spectra were obtained with a MALDI-ToF-MS PerSeptive Biosystems Voyager-DE PRO mass spectrometer. Electrospray ionization (ESI) spectrum was measured on a Bruker microTOF-Mass spectrometer QII.

Infrared spectra were recorded using KBr pressed pallets with a Perkin Elmer GX FT-IR spectrophotometer in the range 4000-400 cm⁻¹.

UV-vis spectra were recorded on Varian Cary 500 Scan spectrophotometer. Emission spectra were measured on a Varian Fluorescence spectrometer Cary Eclipse apparatus using a (1 cm x 1 cm) quartz cell in aerated solutions.

Elemental analyses were performed using the Vario Micro Cube CHNS Analyzer.

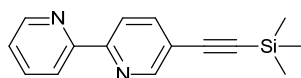
Single crystal X-ray Crystallography data of *fac* [RuL₃](PF₆)₂ were collected on a STOE IPDS II diffractometer with graphite monochromated Mo-K α radiation ($\lambda=0.71073$ Å). The structure was solved by direct methods and refined against F^2 by least square techniques using the SHELXS-97 and SHELXL-97 programs.⁶ Non-hydrogen atoms were refined with anisotropic displacement parameters (disordered atoms were refined isotropically); hydrogen atoms were calculated on idealized positions.

The STM measurements were carried out with a modified Omicron VT UHV STM. A Au(111) crystal was cleaned in situ by several cycles of Ar⁺ sputtering and annealing to $T=770$ - 800 K. The crystal was transferred to the load lock of the UHV chamber, which was flooded with nitrogen and opened. A solution of metal-complex (ca 7 μ l with $c\approx 2\cdot 10^{-6}$ mol/l in CH₃CN) was dropped onto the crystal under nitrogen flow to avoid surface contaminations. The chamber was closed and pumped immediately. The crystal was annealed in UHV for 10 minutes at $T\approx 323$ K to remove remaining solvent from the surface. Finally, the crystal was transferred to the STM and cooled down to temperatures of 30 K. At this temperature the molecules are immobilized and STM imaging is possible.

Synthesis

*5-ethynyl-2,2'-bipyridine*⁷ was synthesised by Sonogashira cross-coupling reaction with TMSA followed by deprotection of trimethylsilyl group using a slightly modified procedure. The spectra agree with literature data.^{7,8}

*5-((trimethylsilyl)-ethynyl)-2,2'-bipyridine*⁷



A solution of 5-bromo-2,2'-bipyridine³ (1.093 g, 4.65 mmol) in THF/ N,N-Diisopropylethylamine (DIEA) anh. (40 mL, 1/1) was degassed 1h under N₂. [PdCl₂(PPh₃)₂] (163 mg, 0.233 mmol), CuI (44.0 mg, 0.233 mmol) and (trimethylsilyl)-acetylene (1.827 g, 18.6 mmol) were added. After stirring overnight at rt, the reaction mixture was diluted with CH₂Cl₂ (400 mL) then washed with H₂O (200 mL). The aqueous layer was extracted with CH₂Cl₂ (3x200 mL). The combined organic layers were dried over MgSO₄ and the solvent was removed in vacuum. Purification by column chromatography (SiO₂, hexane/EtOAc, 10/0 to 9/1) afforded the 5-((trimethylsilyl)-ethynyl)-2,2'-bipyridine (1.09 mg, 93%) as a yellowish oil.

R_f (SiO₂, hexane/EtOAc, 8/2): 0.37;

¹H NMR (CDCl₃): δ (ppm) 0.28 (s, 9H, TMS), 7.32 (ddd, ³J = 7.5 Hz, ³J = 4.8, ⁴J = 1.2 Hz, 1H, H-5'), 7.80-7.89 (m, 2H, H-4,4'), 8.33 – 8.45 (m, 2H, H-3,3'), 8.61 – 8.70 (m, 1H, H-6'), 8.73 (d, ⁴J = 2.1 Hz, 1H, H-6)

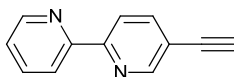
¹³C NMR (CDCl₃): δ (ppm) 0.0 (TMS), 99.4 (C \equiv), 101.9 (C \equiv), 120.3 (q = quaternary), 120.4, 121.7, 124.1, 137.3, 140.0, 149.2, 152.2, 154.8 (q), 155.8 (q);

¹³C DEPT 135 NMR (CDCl₃): δ (ppm) 0.2 (TMS), 120.3, 121.6, 124.0, 137.2, 139.9, 149.0,

152.0;

MALDI-TOF (1,8,9-anthracenetriol), m/z (%): 252.9 (100) $[M+H]^+$;

5-ethynyl-2,2'-bipyridine^{7,8}



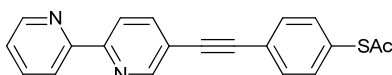
To a N_2 degassed solution of 5-((trimethylsilyl)-ethynyl)-2,2'-bipyridine (1.093 g, 4.33 mmol) in CH_3OH/CH_2Cl_2 (80 mL, 1/1), K_2CO_3 (2.992 g, 21.65 mmol) was added as a solid. After stirring for 1h at rt, the solution was concentrated by rotary evaporation. Purification by flash chromatography (SiO_2 , hexane/EtOAc, 10/0 to 8/2) afforded the 5-ethynyl-2,2'-bipyridine (708 mg, 91%) as a white solid.

R_f (SiO_2 , hexane/EtOAc, 8/2): 0.30;

1H NMR ($CDCl_3$): δ (ppm) 3.29 (s, 1H, $\equiv CH$), 7.29 (ddd, $^3J = 7.5$, $^3J = 4.8$, $^4J = 1.1$ Hz, 1H, H-5'), 7.80 (td, $^3J = 7.7$, $^4J = 1.8$ Hz, 1H, H-4'), 7.88 (dd, $^3J = 8.2$, $^4J = 2.1$ Hz, 1H, H-4), 8.38 (dd, $^3J = 8.1$, $^4J = 3.5$ Hz, 2H, H-3/3'), 8.66 (d, $^3J = 4.7$ Hz, 1H, H-6'), 8.75 (d, $^4J = 1.8$ Hz, 1H, H-6);

^{13}C NMR ($CDCl_3$): δ (ppm) 80.8 ($C\equiv$), 81.5 ($C\equiv$), 119.2, 120.4, 121.5, 124.2, 137.1, 140.1, 149.3, 152.3, 155.3, 155.4;

Ligand L



5-ethynyl-2,2'-bipyridine⁷ (708 mg, 3.93 mmol), and 4-(thioacetyl)-iodobenzene⁴ (1.201 g, 4.322 mmol) were dissolved in THF/DIEA anhydrous (35 mL, 2.5/1) and degassed 1h under N_2 . $Pd(PPh_3)_2Cl_2$ (138 mg, 0.196 mmol) and CuI (37 mg, 0.196 mmol) were added. After stirring overnight at rt, the reaction mixture was diluted with CH_2Cl_2 (300 mL) then washed with H_2O (200 mL). The aqueous layer was extracted with CH_2Cl_2 (3x200 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed in vacuum. Twofold purification by column chromatography (SiO_2 , hexane/EtOAc, 1/0 to 1/1) afforded the pure ligand (650 mg, 50%) as a white-yellowish solid.

R_f (SiO_2 , hexane/EtOAc, 8/2): 0.23; M.p. 136°C.

Anal. calc. for $C_{20}H_{14}N_2OS$ ($M_r = 330.40$): C, 72.70; H, 4.27; N, 8.48; S, 9.70; Found: C, 72.66; H, 4.33; N, 8.42; S, 9.64;

^1H NMR (CDCl_3): δ (ppm) 2.44 (s, 3H, CH_3), 7.35 (ddd, $^3J = 7.5$, $^3J = 4.9$, $^4J = 1.0$ Hz, 1H, H-5'), 7.43 (d, $^3J = 8.5$ Hz, 2H, Ph), 7.59 (d, $^3J = 8.5$ Hz, 2H, Ph), 7.86 (td, $^3J = 7.9$, $^4J = 1.8$ Hz, 1H, H-4'), 7.95 (dd, $^3J = 8.3$, $^4J = 2.1$ Hz, 1H, H-4), 8.45 (dd, $^3J = 8.5$, $^4J = 3.3$ Hz, 2H, H-3/3'), 8.71 (d, $^3J = 4.3$ Hz, 1H, H-6'), 8.82 (d, $^4J = 1.6$ Hz, 1H, H-6);

^{13}C NMR (CDCl_3): δ (ppm) 30.5 (CH_3), 88.0 ($\text{C}\equiv$), 93.0 ($\text{C}\equiv$), 120.3 (q), 120.7 (C-3/3'), 121.7 (C-3/3'), 123.9 (C-5'), 124.2 (q), 128.9 (q), 132.4 (Ph), 134.4 (Ph), 137.5 (C-4'), 139.7 (C-4), 149.1 (C-6'), 151.8 (C-6), 154.7 (q C-2/2'), 155.3 (q C-2/2'), 193.4 (C=O);

^{13}C DEPT135 NMR (CDCl_3): δ (ppm) 30.3 (CH_3), 120.5 (C-3/3'), 121.5 (C-3/3'), 124.1 (C-5'), 132.3 (Ph), 134.3 (Ph), 137.3 (C-4'), 139.5 (C-4), 149.1 (C-6'), 151.7 (C-6);

Selected IR (KBr pellet): $\tilde{\nu}$ (cm^{-1}) 2217w, 1696, 1584, 1570, 1539, 1497, 1457, 1432, 1398, 1368, 1352, 1120, 1092, 1017, 955, 828, 796, 747, 629, 621, 613, 545;

MALDI-TOF (no matrix), m/z (%): 330.8 (100) $[\text{M}+\text{H}]^+$;

UV-vis (CH_3CN), λ , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 336 sh (35640), 320 (45870);

Fac and mer [RuL₃](PF₆)₂

$\text{Ru}(\text{DMSO})_4\text{Cl}_2 \cdot 2$ (195 mg, 0.40 mmol) was added to a solution of the ligand **L** (412 mg, 1.25 mmol) in EtOH (60 mL). After stirring for 48 h at reflux under Ar, the solvent was removed under vacuum. The *mer* isomer exhibited higher R_f values than the *fac* isomer in the TLC conditions (SiO_2 , MeCN/ H_2O / KNO_3). The preparative thick layer chromatography silica plates in the same conditions lead in our case only to a partial separation of the two isomers. The crude brown solid was separated by flash column chromatography under Ar (SiO_2 , 50 cm, MeCN/ H_2O / KNO_3 (0.4M), 1/0/0 to 95/5/2). The first red-orange fraction contains the meridional isomer followed by a second fraction containing the facial isomer. The solvent was evaporated to dryness, the solid dissolved in MeCN and filtered to remove the insoluble KNO_3 . The fractions were dissolved in MeCN/ H_2O (50 mL, 4/1) and were treated separately with KPF_6 aq. (500 mg, 2.717 mmol, 10 mL). They were allowed to stir for 2 h at rt under Ar. The MeCN was evaporated under vacuum. The precipitates were centrifuged, filtered off and washed with H_2O (4x150 mL). Anion exchange metathesis was carried out twice to assure the complete removing of nitrate salts. Recrystallization in CH_2Cl_2 /hexane gave the *fac* (141 mg, 26%) and *mer* (52 mg, 10%) Ru(II) complex as orange-red powders. The isolated yields of the two isomers were calculated in respect to the amount of the ligand (3.125 eq.).

As an indication of purity of the two isomers the TLC after separation demonstrated two very distinct single spots.

fac [RuL₃](PF₆)₂

Crystals suitable for single crystal X-ray diffraction were grown from a MeCN solution of complex by slow diffusion of Et₂O.

R_f (SiO₂, MeCN/H₂O/KNO₃, 98/2/2%) = 0.05;

Anal. calc. for [C₆₀H₄₂N₆O₃S₃Ru](PF₆)₂•0.5H₂O: C, 51.80; H, 3.12; N, 6.04; S, 6.91. Found: C, 51.73; H, 3.30; N, 6.10; S, 6.66;

¹H NMR (CD₂Cl₂): δ (ppm) 2.39 (s, 9H, CH₃), 7.38 (d, ³J = 8.4 Hz, 6H, Ph), 7.46 – 7.53 (m, 9H, Ph, H-5'), 7.62 (d, ³J = 4.8 Hz, 3H, H-6'), 7.86 (d, ⁴J = 1.6 Hz, 3H, H-6), 8.10 (td, ³J = 8.0, ⁴J = 1.4 Hz, 3H, H-4'), 8.16 (d, ³J = 8.3 Hz, 3H, H-4), 8.49 (d, ³J = 8.5 Hz, 6H, H-3,3');

¹³C NMR (CD₂Cl₂): δ (ppm) 30.3 (CH₃), 84.9 (C≡), 97.2 (C≡), 122.0 (q), 124.2 (C-3/3'), 124.7 (q), 125.2 (C-3/3'), 128.7 (C-5'), 130.8 (q), 132.4 (Ph), 134.5 (Ph), 138.7 (C-4), 140.7 (C-4'), 151.5 (C-6'), 152.7 (C-6), 155.7 (q C-2/2'), 156.0 (q C-2/2'), 192.9 (C=O);

¹³C DEPT135 NMR (CD₂Cl₂): δ (ppm) 30.2 (CH₃), 124.1 (C-3/3'), 125.1 (C-3/3'), 128.6 (C-5'), 132.3 (Ph), 134.4 (Ph), 138.6 (C-4), 140.6 (C-4'), 151.4 (C-6'), 152.6 (C-6);

¹H NMR (CD₃CN): δ (ppm) 2.43 (s, 9H, CH₃), 7.34 – 7.48 (m, 9H, Ph, H-5'), 7.53 (d, ³J = 8.4 Hz, 6H, Ph), 7.63 (d, ³J = 4.9 Hz, 3H, H-6'), 7.96 – 8.13 (m, 6H), 8.23 (dd, ³J = 8.5, ⁴J = 1.7 Hz, 3H, H-4), 8.44 (d, ³J = 8.1 Hz, 3H), 8.54 (d, ³J = 8.5 Hz, 3H);

ESI mass spectrum (CH₃CN), *m/z* (%), positive: 546.1 (100) [RuL₃]²⁺, 1237.2 (2) [(RuL₃)₂(PF₆)₂]²⁺; negative: 144.9 [PF₆]¹⁻ (100);

Selected IR (KBr pellet): $\tilde{\nu}$ (cm⁻¹) 3446, 2223m, 2185w, 1702, 1598, 1495, 1465, 1437, 1121, 842, 786, 558;

UV-vis (CH₃CN, aerated), λ, nm (ε, M⁻¹cm⁻¹): 471 (11650, ¹MLCT), 325 (102000), 274 sh (48900);

mer [RuL₃](PF₆)₂

R_f (SiO₂, MeCN/H₂O/KNO₃, 98/2/2%) = 0.11;

Anal. calc. for [C₆₀H₄₂N₆O₃S₃Ru](PF₆)₂•H₂O: C, 51.47; H, 3.17; N, 6.00; S, 6.87. Found: C, 51.22; H, 3.40; N, 6.12; S, 6.49;

^1H NMR (CD_2Cl_2) δ (ppm) 2.39 and 2.40 (2s partially overlapped, 9H, 2 CH_3 , CH_3), 7.40 (dd, J = 8.3, 1.9 Hz, 6H, Ph), 7.47-7.52 (m, 9H, Ph, H-5'), 7.68–7.79 (m, 6H, H-6,6'), 8.06 – 8.19 (m, 6H, H-4,4'), 8.46 – 8.54 (m, 6H, H-3,3');

^{13}C NMR (CD_2Cl_2): δ (ppm) 30.3 (CH_3), 84.8 ($\text{C}\equiv$), (97.1, 97.2, 97.3) ($\text{C}\equiv$), (121.9, 122.0) (q), (124.3, 124.4) (C-3/3'), (124.7, 124.8, 124.9) (C-3/3'), 125.2 (q), (128.5, 128.7) (C-5'), (130.8, 130.9) (q), 132.4 (Ph), 134.5 (Ph), 138.7 (C-4), (140.7, 140.7, 140.8) (C-4'), (151.3, 151.5, 151.7) (C-6), (152.5, 152.6, 152.8) (C-6'), (155.6, 155.6, 155.7) (q), (156.1, 156.2) (q), 192.9 (C=O);

^1H NMR (CD_3CN): δ (ppm) 2.43 (3s partially overlapped, 9H, 3 CH_3), 7.41 – 7.49 (m, 9H, Ph, H-5'), 7.54-7.58 (m, 6H, Ph), 7.74 (d, J = 4.9 Hz, 1H), 7.77 – 7.90 (m, 4H), 7.97 (d, J = 1.6 Hz, 1H), 8.07- 8.14 (m, 3H), 8.16 – 8.25 (m, 3H), 8.62 – 8.48 (m, 6H);

^{13}C NMR (CD_3CN) δ (ppm) 30.7 (CH_3), (86.4, 86.5, 86.6) ($\text{C}\equiv$), (96.4, 96.4, 96.5) ($\text{C}\equiv$), (123.3, 123.4, 123.4) (q), 124.7 (q), (125.0, 125.2, 125.3) (C-3/3'), (125.9, 126.0, 126.1) (C-3/3'), (128.9, 129.0) (C-5'), 131.5 (q), 133.2 (Ph), 135.7 (Ph), 139.2 (C-4), 141.1 (C-4'), (153.1, 153.2, 153.4) (C-6'), (154.4, 154.6, 154.7) (C-6), (157.1, 157.2, 157.2) (q), (157.4, 157.5) (q), 194.1 (C=O);

^{13}C DEPT135 NMR (CD_3CN) δ (ppm) 30.5 (CH_3), (124.8, 124.9, 125.0) (C-3/3'), (125.6, 125.8, 125.9) (C-3/3'), (128.7, 128.8) (C-5'), 133.0 (Ph), 135.5 (Ph), 139.0, 140.9, (152.8, 152.9, 153.1) (C-6'), (154.2, 154.4, 154.5) (C-6);

ESI mass spectrum (CH_3CN), m/z (%), positive: 546.1 (100) $[\text{RuL}_3]^{2+}$, 1237.2 (4) $[(\text{RuL}_3)_2(\text{PF}_6)_2]^{2+}$; negative: 144.9 $[\text{PF}_6]^{1-}$ (100);

Selected IR (KBr pellet): $\tilde{\nu}$ (cm^{-1}) 3433, 2223m, 2185w, 1705, 1598, 1494, 1465, 1437, 1122, 842, 787, 558;

UV-vis (CH_3CN aerated), λ , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 471 (11000, $^1\text{MLCT}$), 335 (97050), 274 sh (44320);

Spectroscopic analysis

In the ^1H NMR spectrum of the *fac* isomer, the signal of thioacetyl protons is located at 2.39 ppm as a singlet, while for the *mer* isomer appears as two superimposed signals in approximately 2:1 intensity. The coordination of Ru(II) ion results to a significant upfield shift (≈ -1 ppm) of the 6 and 6' protons (α position to the coordinating nitrogen atoms) compared to the free ligand. This strong shift is induced by the interaction of the 6 and 6' hydrogen atoms with the ring current of the pyridine rings of the neighboring legs as observed by crystallographic analysis.^{9,10} For the *fac* isomer, these protons appear as two distinct tight doublets keeping the same coupling constants as in the ligand, while for the *mer* isomer a multiplet is formed, a result of the protons proximity to different heterocyclic rings. The 3 and 3' protons keep almost the same chemical shift, while 4 and 4' protons present a downfield shift (0.23 ppm) in comparison to the ligand. The 5' proton observed in literature^{11,12} to give a distinct set of signals for the two isomers, is overlapped in our case for the both isomers by the phenyl signal.

ESI mass spectra of the both *fac* and *mer* isomers show a dominant peak at 546.1 amu with the expected isotopic distribution pattern of the $[\text{RuL}_3]^{2+}$ molecular ion. Additionally, in very low intensity an aggregation as $[(\text{RuL}_3)_2(\text{PF}_6)_2]^{2+}$ at 1237.2 is present. The counter ion $(\text{PF}_6)^{1-}$ is observed at 144.9 amu in negative acceleration mode.

The found chemical composition of the *fac* and *mer* isomers correlates to molecular formulation of $[\text{RuL}_3](\text{PF}_6)_2 \cdot x\text{H}_2\text{O}$ ($x = 0, 5$ or 1) comprising the presence of water molecule in the solid state. The complexes were observed to retain water despite drying in vacuum, as presented in literature for other Ru-complexes which are supposedly hygroscopic.^{11,13}

The IR spectra of the two *fac* and *mer* isomers are essentially the same. Characteristic weak stretching vibration bands assigned to acetylene bonds in both isomers are identified at 2223 cm^{-1} with a shoulder around 2180 cm^{-1} . In the free ligand this vibration appears as a very weak band at 2217 cm^{-1} . For the free ligand the stretching vibration (C=O) corresponding to the thioacetyl functionality is observed at 1696 cm^{-1} ,¹⁴ while a slightly shifted frequency is observed for *fac* and *mer* complexes to 1702 and 1705 cm^{-1} respectively. The ring frequencies of the free *bipy* ligand are assigned to 1457 and 1584 cm^{-1} bands. Upon coordination these values are shifted to 1465 and 1598 cm^{-1} .¹⁵ The presence of PF_6 counter ions in each isomer is evidenced by a very intense band at 842 cm^{-1} which refers to the (P-F) stretching mode.

Spectroscopic data

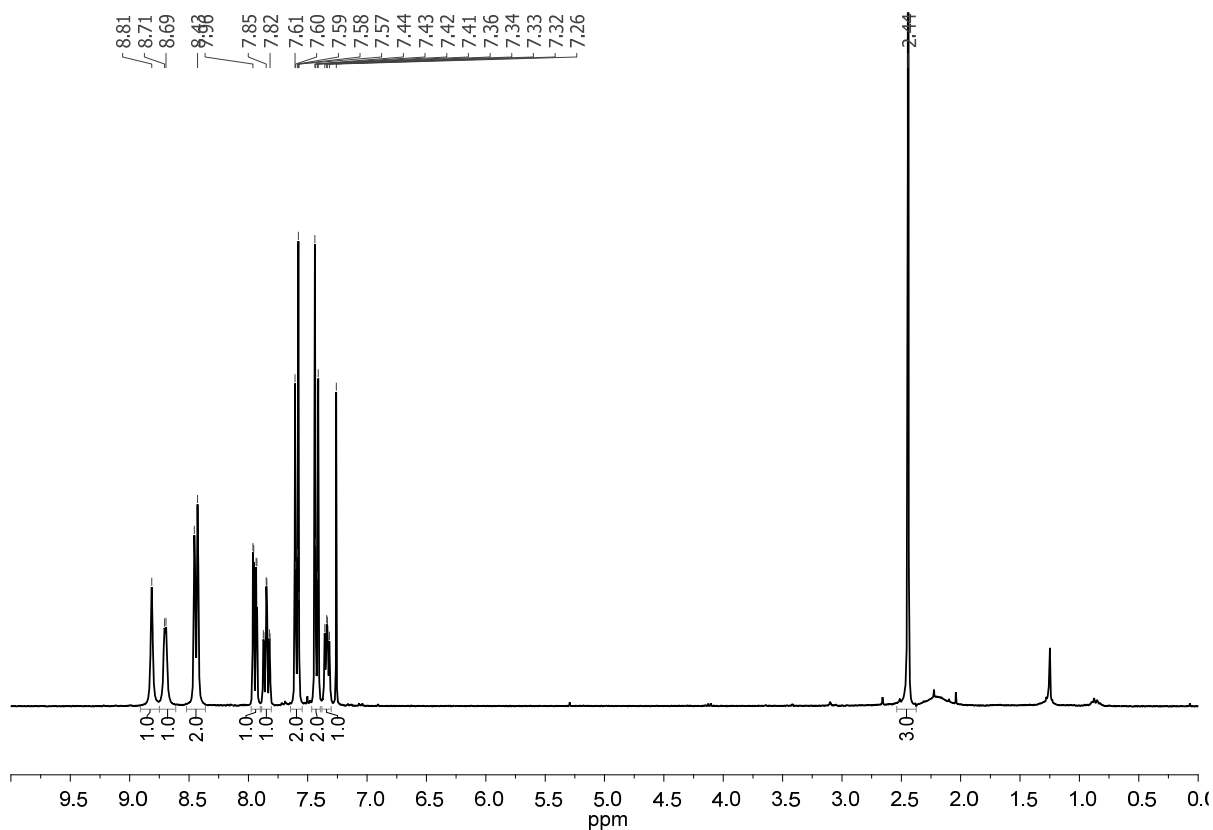


Fig. SI.1. ^1H NMR spectrum in CDCl_3 of the ligand **L**

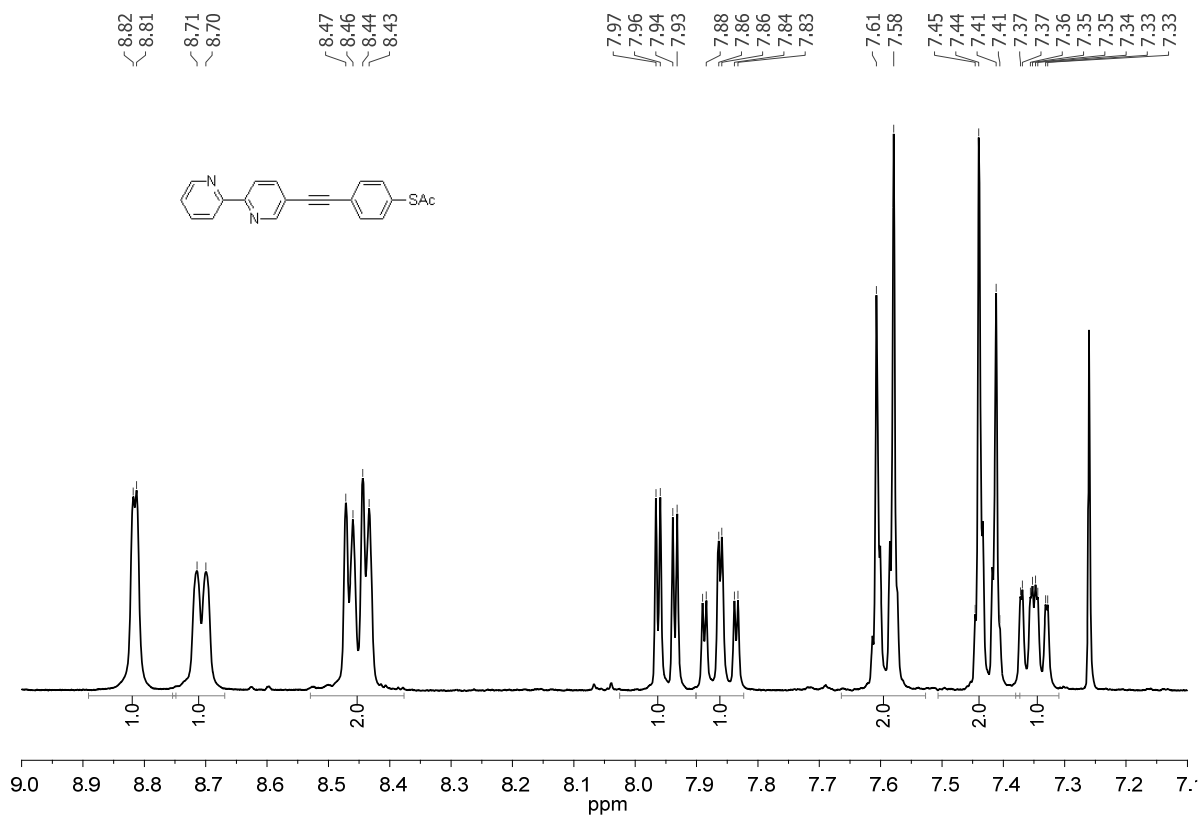


Fig. SI.1a. Zoom of the ^1H NMR spectrum in CDCl_3 of the ligand **L**

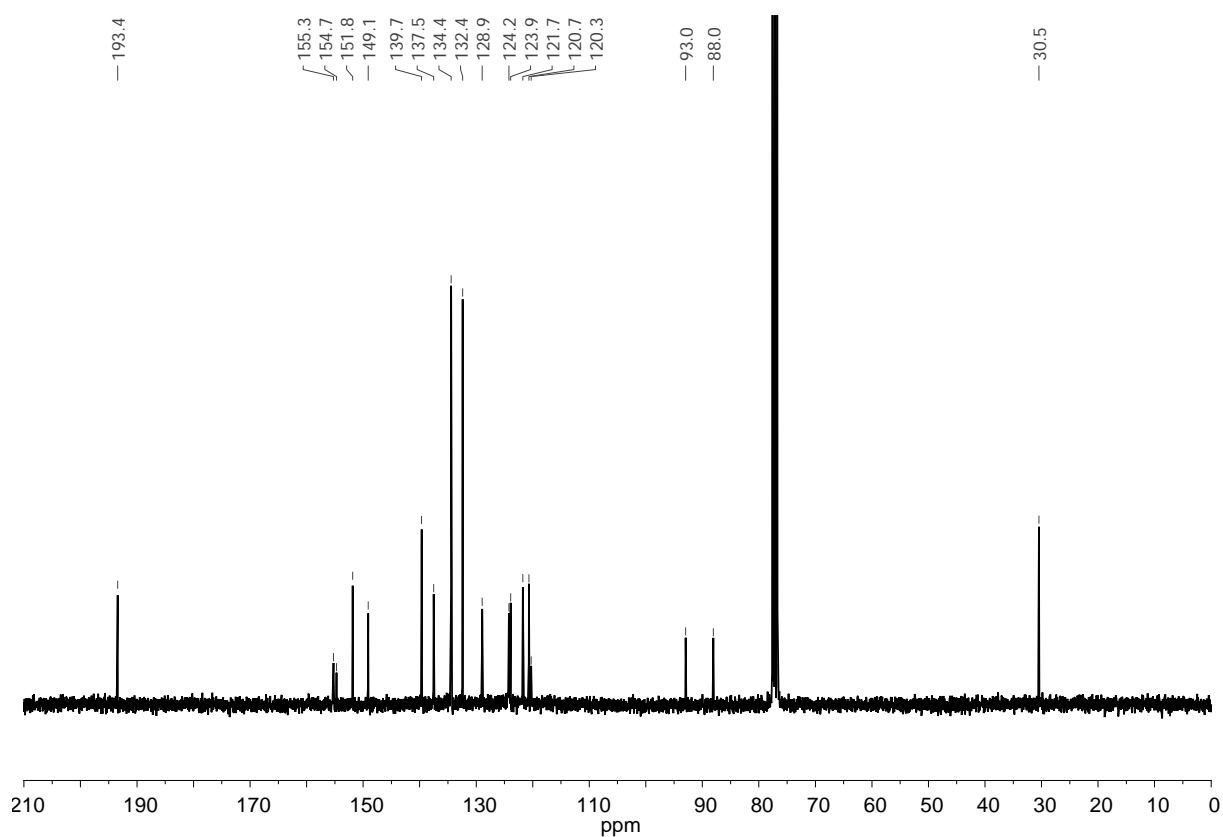


Fig. SI.2. ^{13}C NMR spectrum in CDCl_3 of the ligand **L**

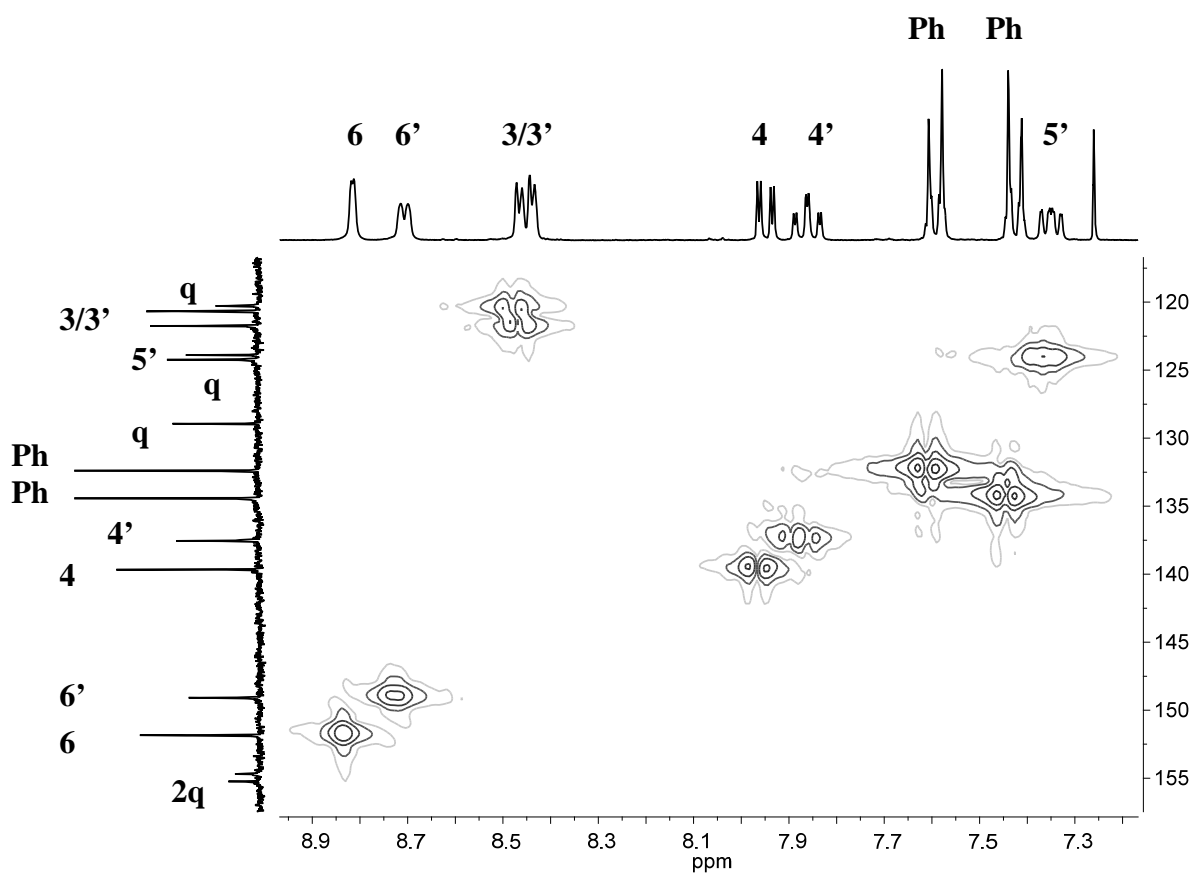


Fig. SI.3. ^1H ^{13}C NMR spectrum in CDCl_3 of the ligand **L**

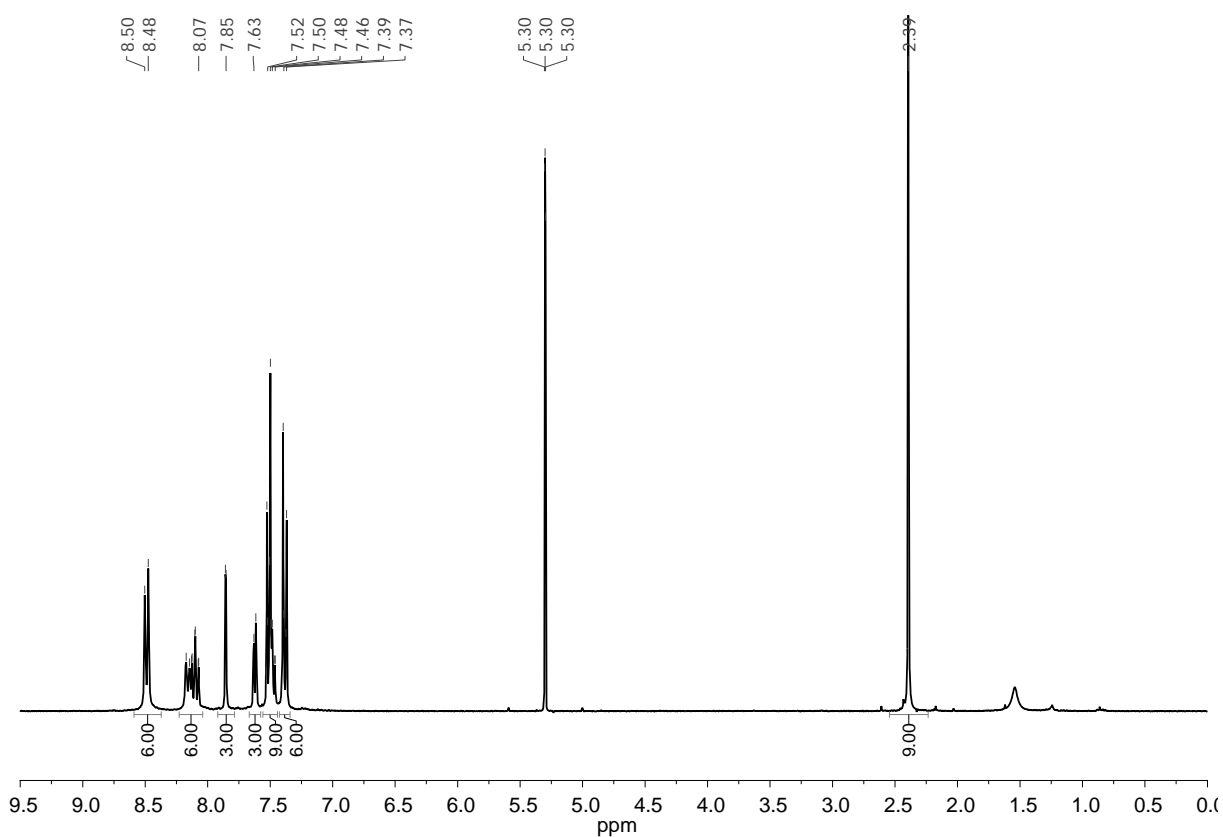


Fig. SI. 4. ^1H NMR spectrum in CD_2Cl_2 of the *fac* Ru(II) complex

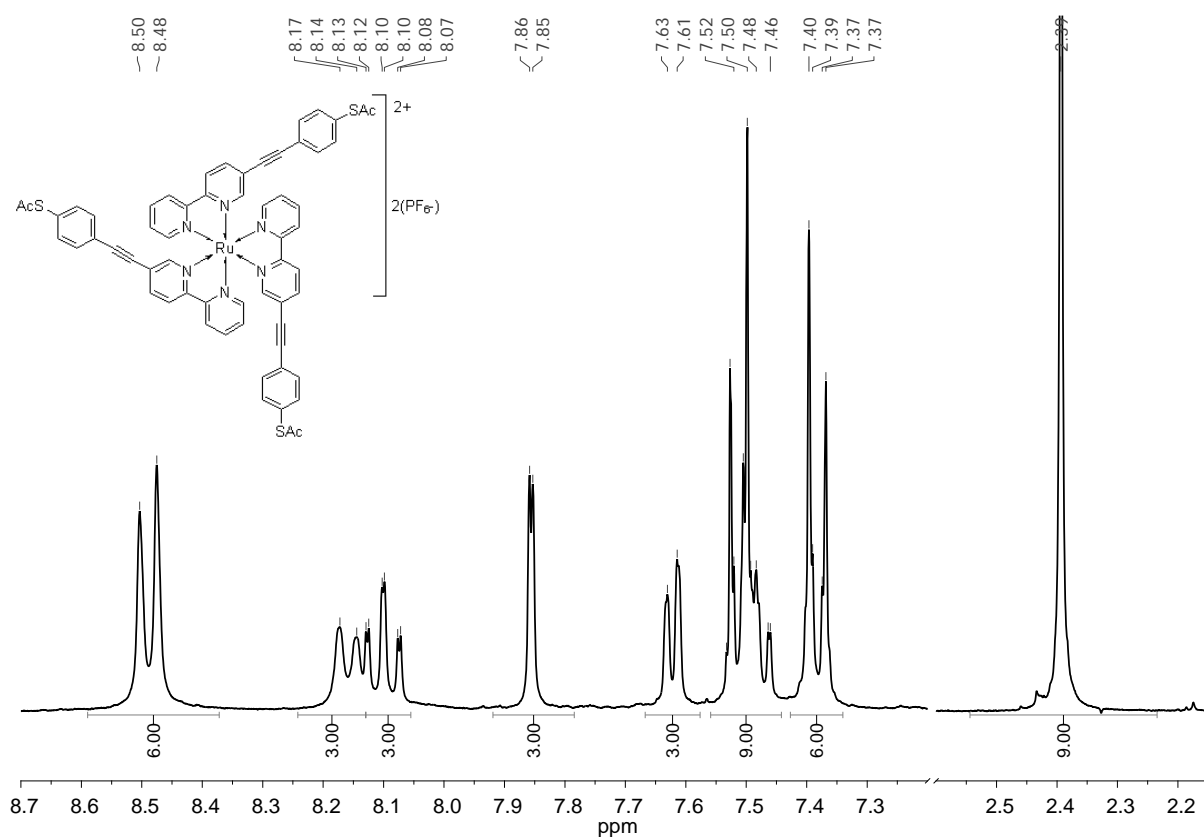


Fig. SI.4a. Zoom of the ^1H NMR spectrum in CD_2Cl_2 of the *fac* Ru(II) complex

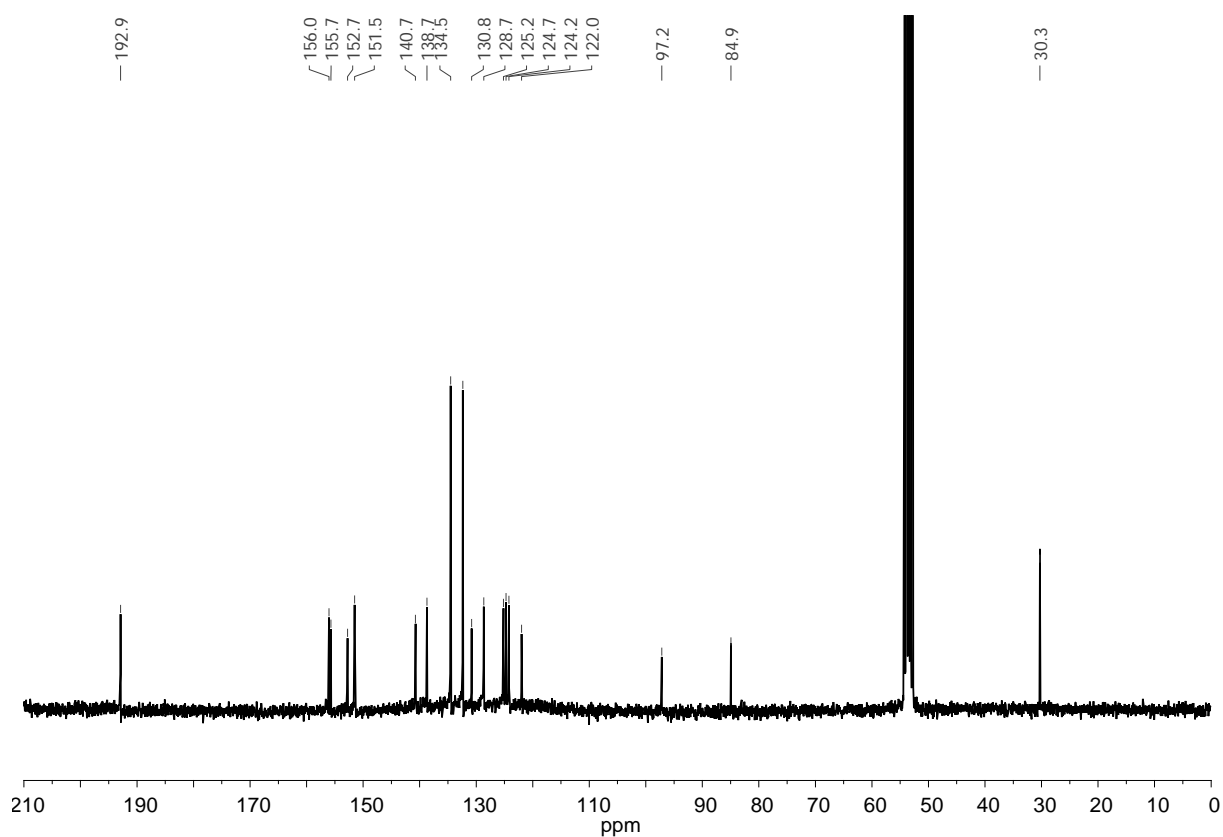


Fig. SI.5. ^{13}C NMR spectrum in CD_2Cl_2 of the *fac* Ru(II) complex

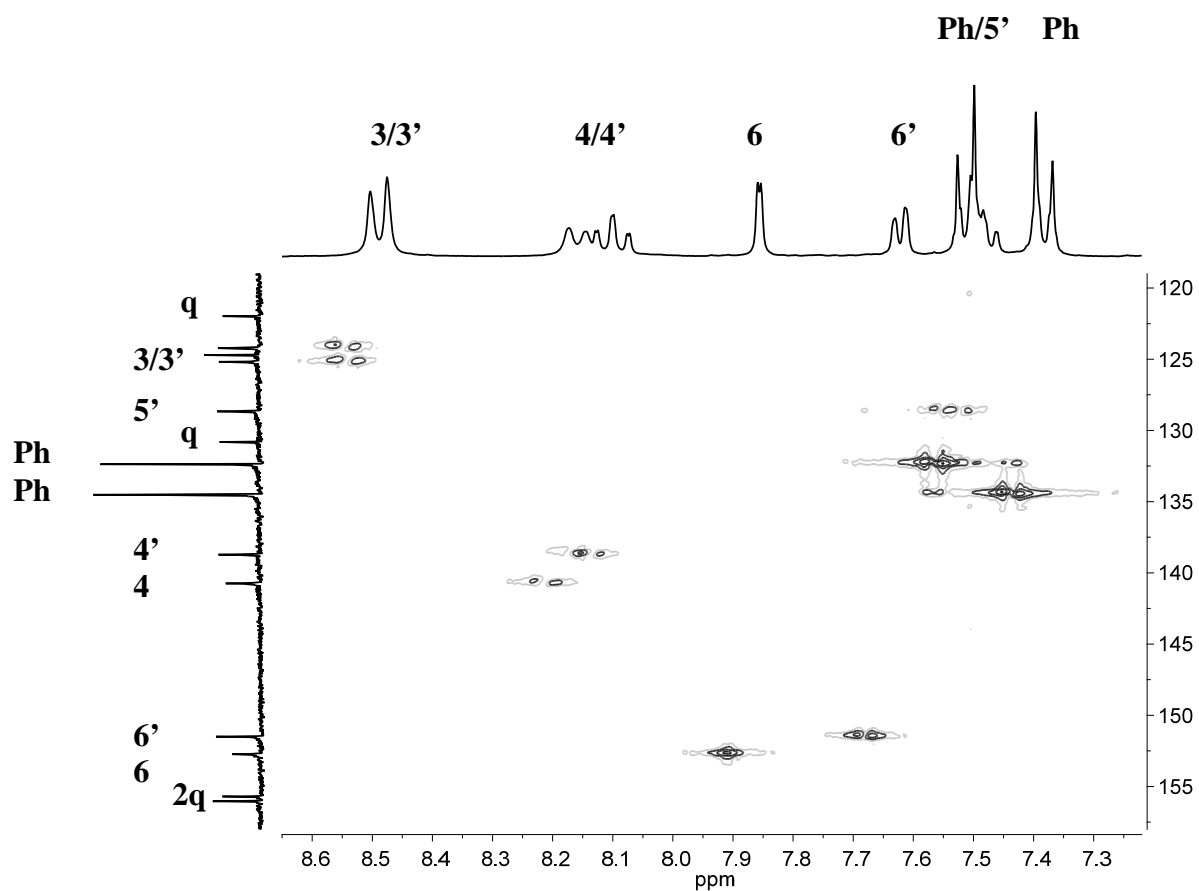


Fig. SI.6. ^1H ^{13}C NMR spectrum in CD_2Cl_2 of the *fac* Ru(II) complex

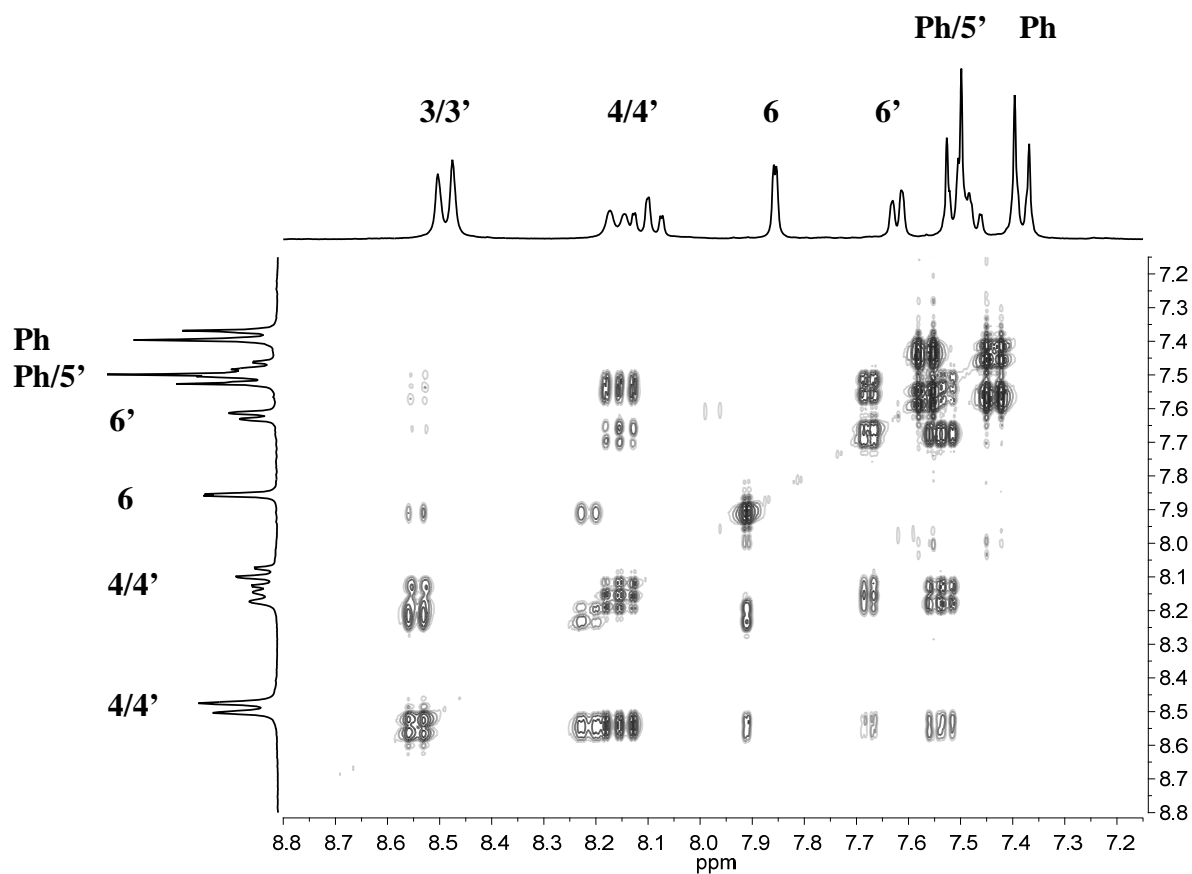


Fig. SI.7. ^1H ^1H COSY90 NMR spectrum in CD_2Cl_2 of the *fac* Ru(II) complex

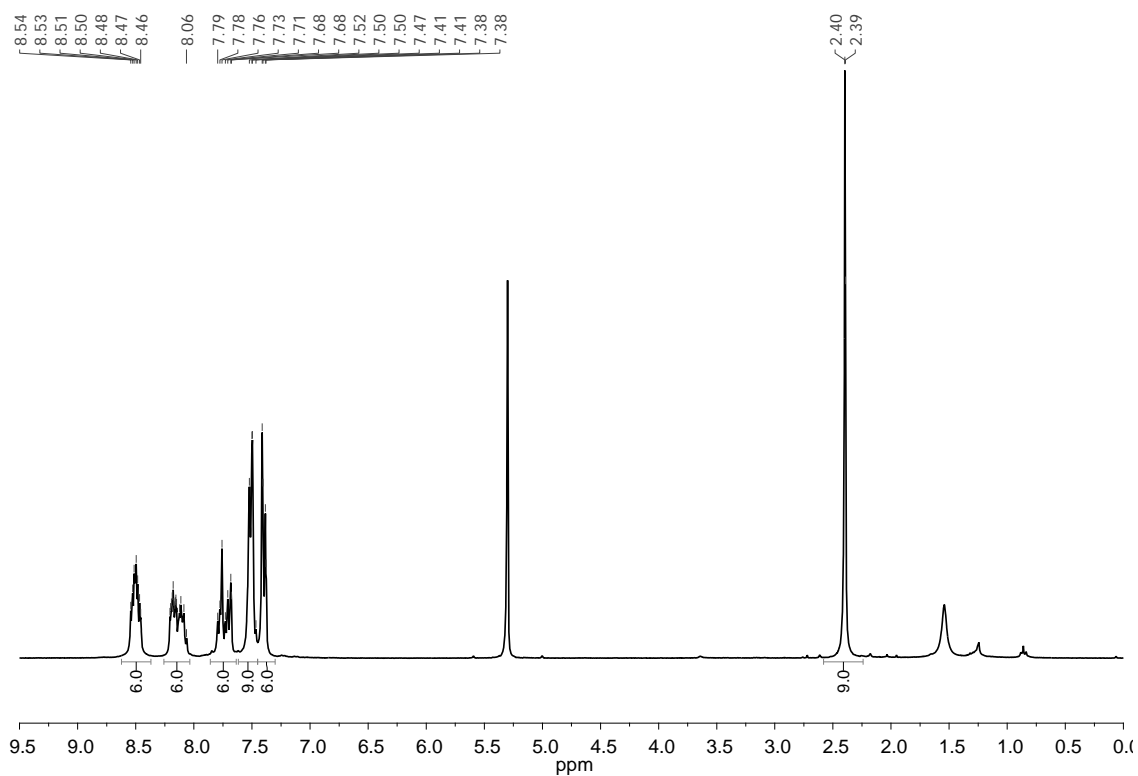


Fig. SI.8. ^1H NMR spectrum in CD_2Cl_2 of the *mer* Ru(II) complex

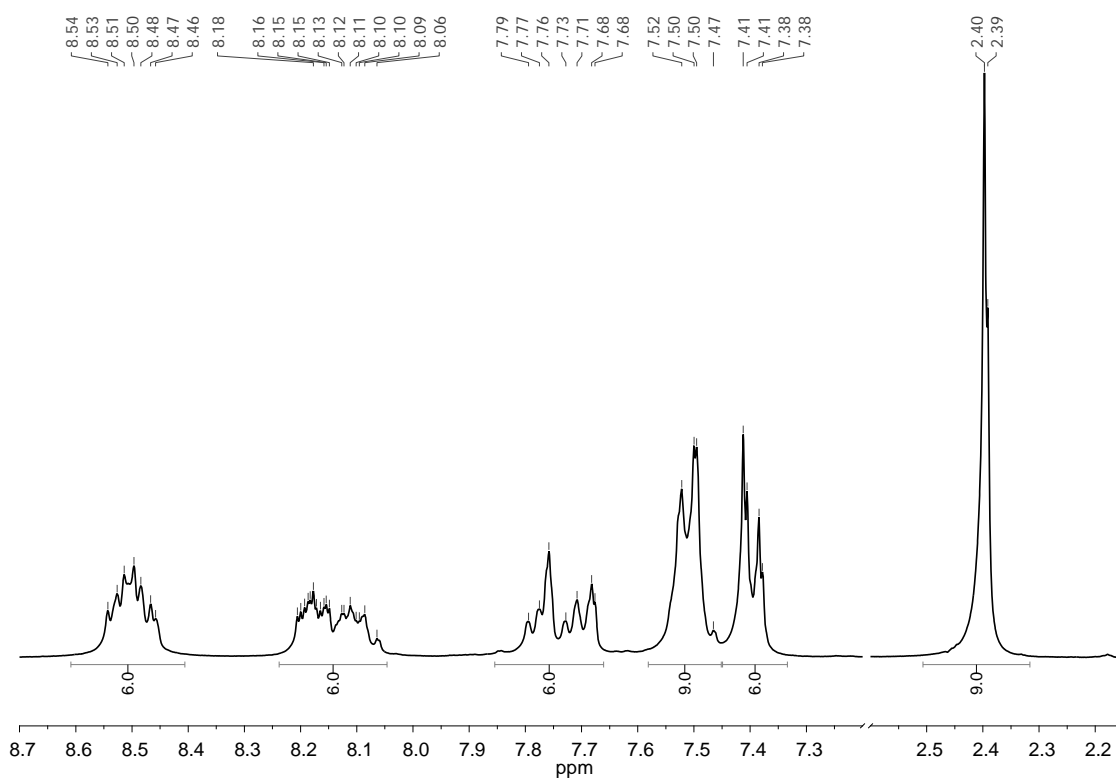


Fig. SI.8a. Zoom of the ^1H NMR spectrum in CD_2Cl_2 of the *mer* Ru(II) complex

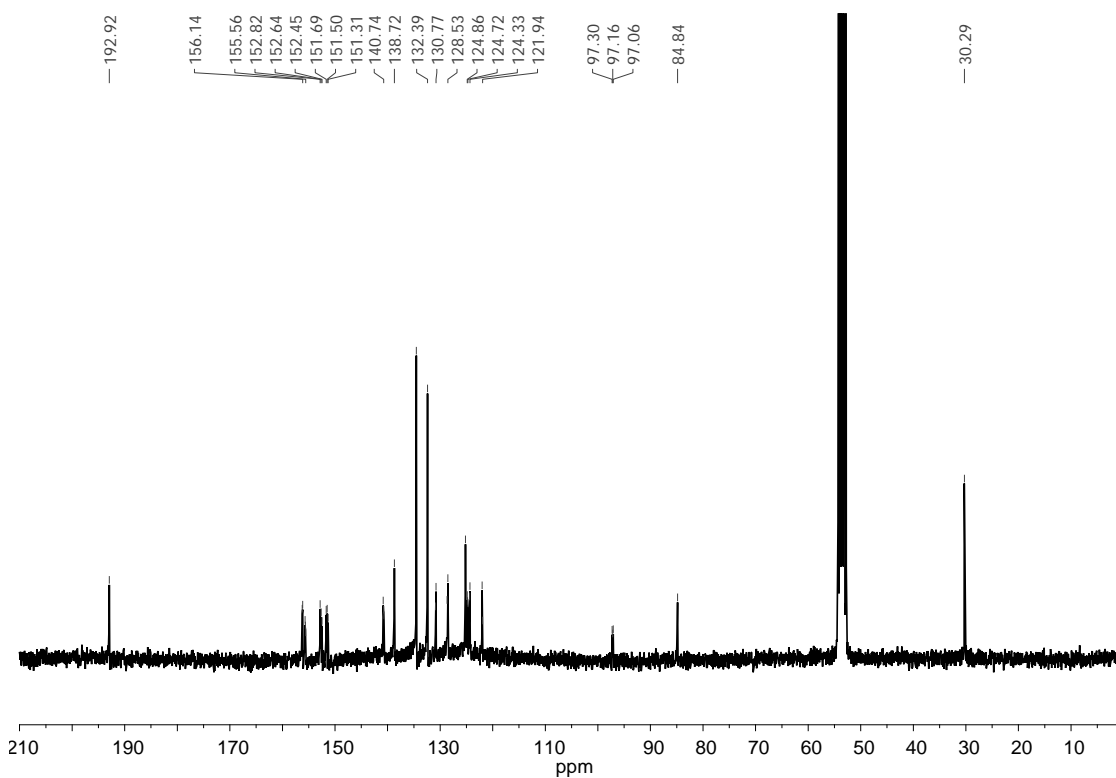


Fig. SI.9. ^{13}C NMR spectrum in CD_2Cl_2 of the *mer* Ru(II) complex

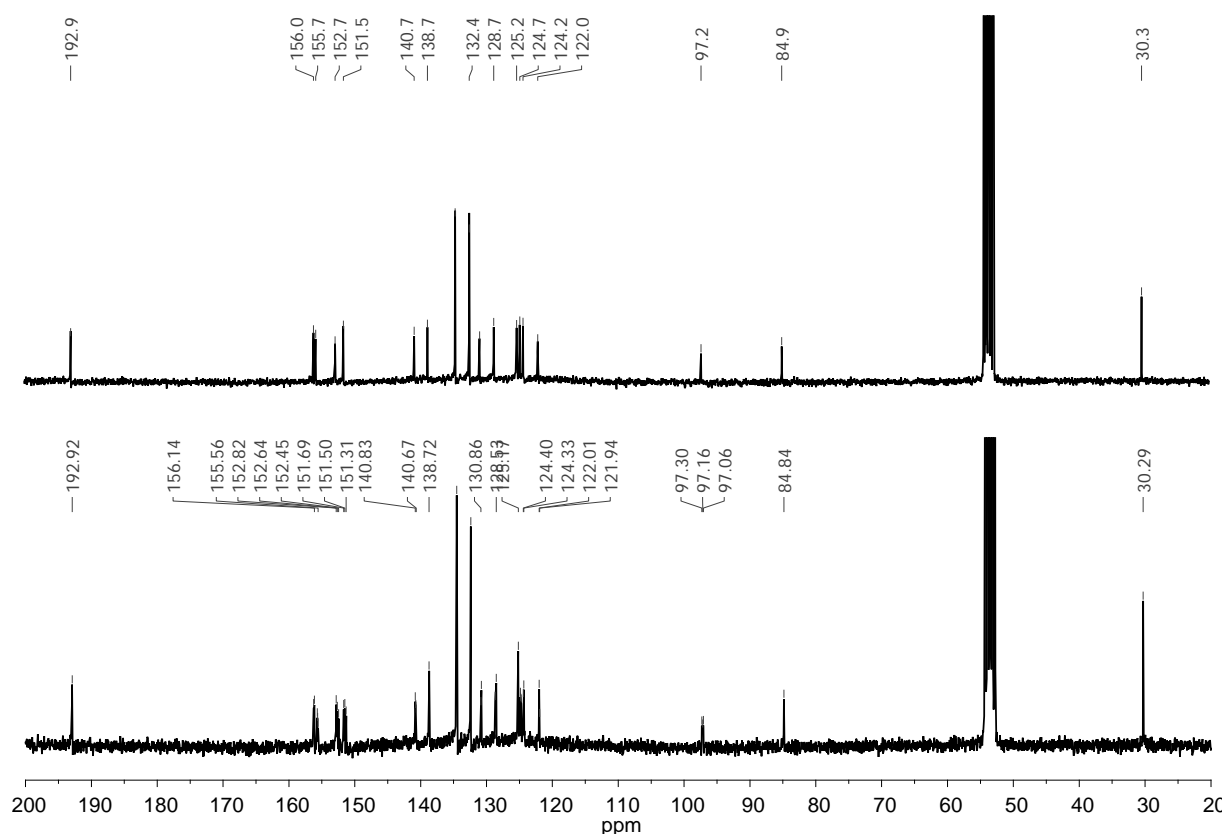


Fig. SI.10. ^{13}C NMR spectra comparison in CD_2Cl_2 of the *fac* (up) and *mer* (down) Ru(II) complex

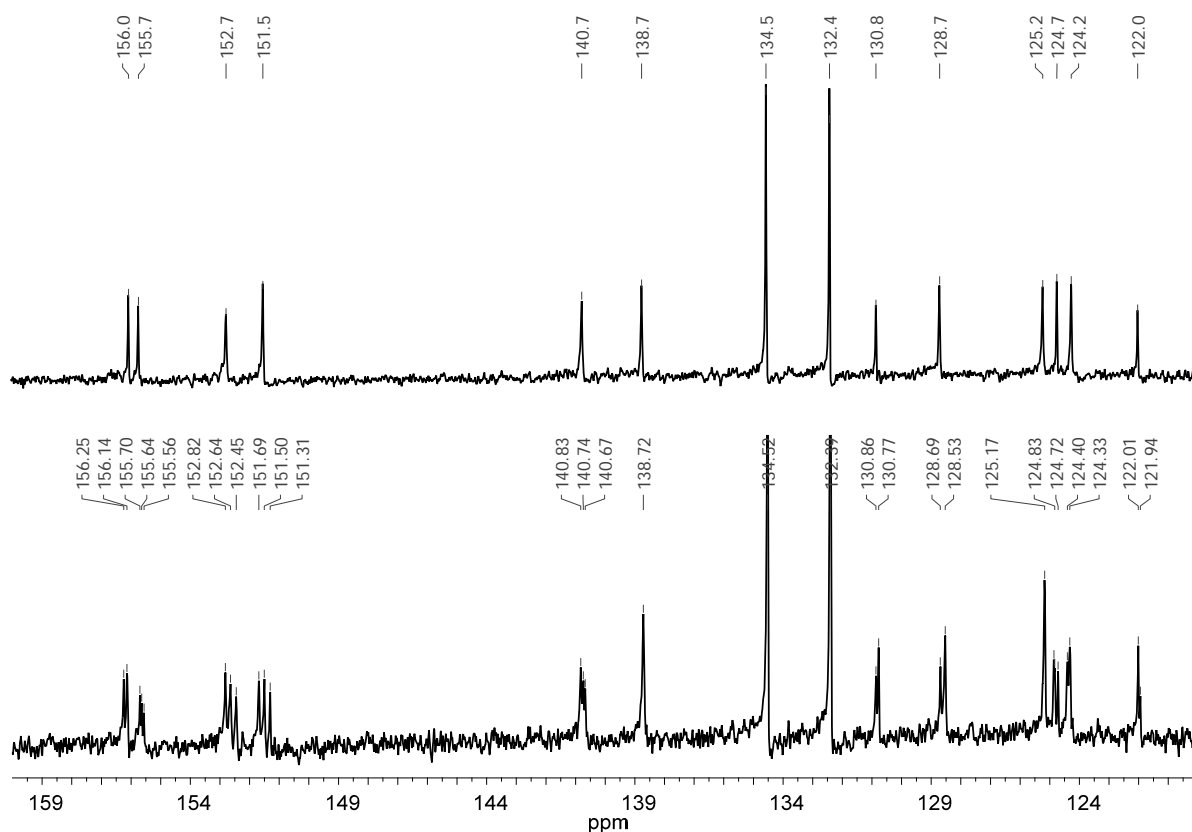


Fig. SI.10a. Zoom of the ^{13}C NMR spectra in CD_2Cl_2 of the *fac* (up) and *mer* (down) Ru(II) complex

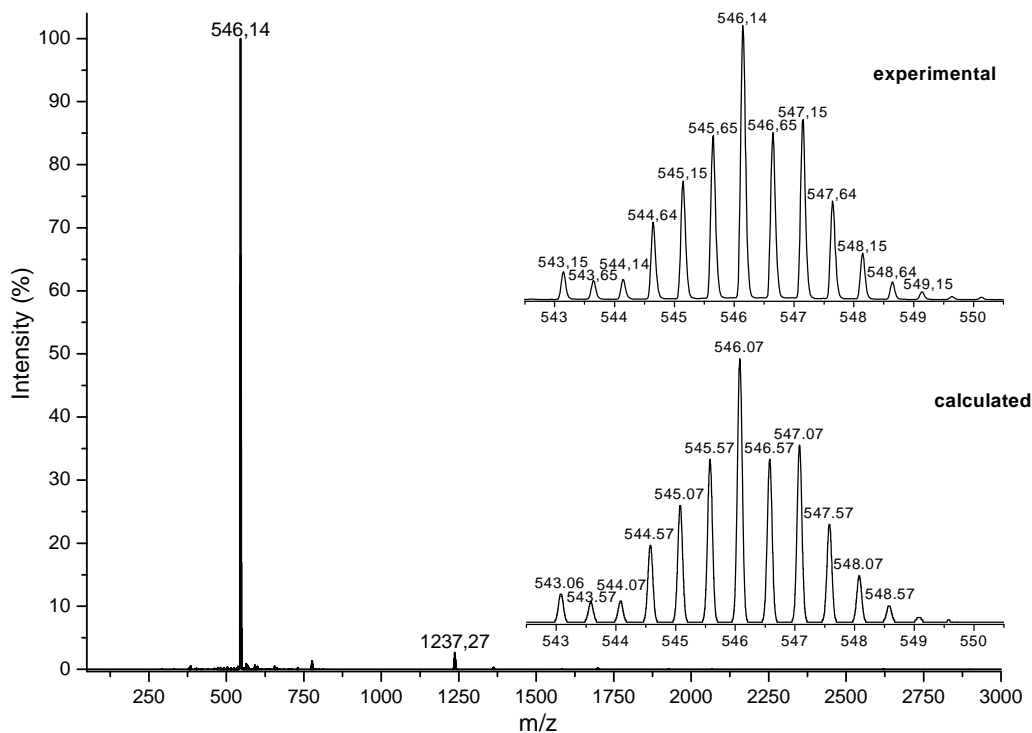


Fig. SI.11. ESI mass spectrum of *fac* Ru(II) complex. Inset: experimental and calculated isotopic pattern of $[\text{RuL}_3]^{2+}$

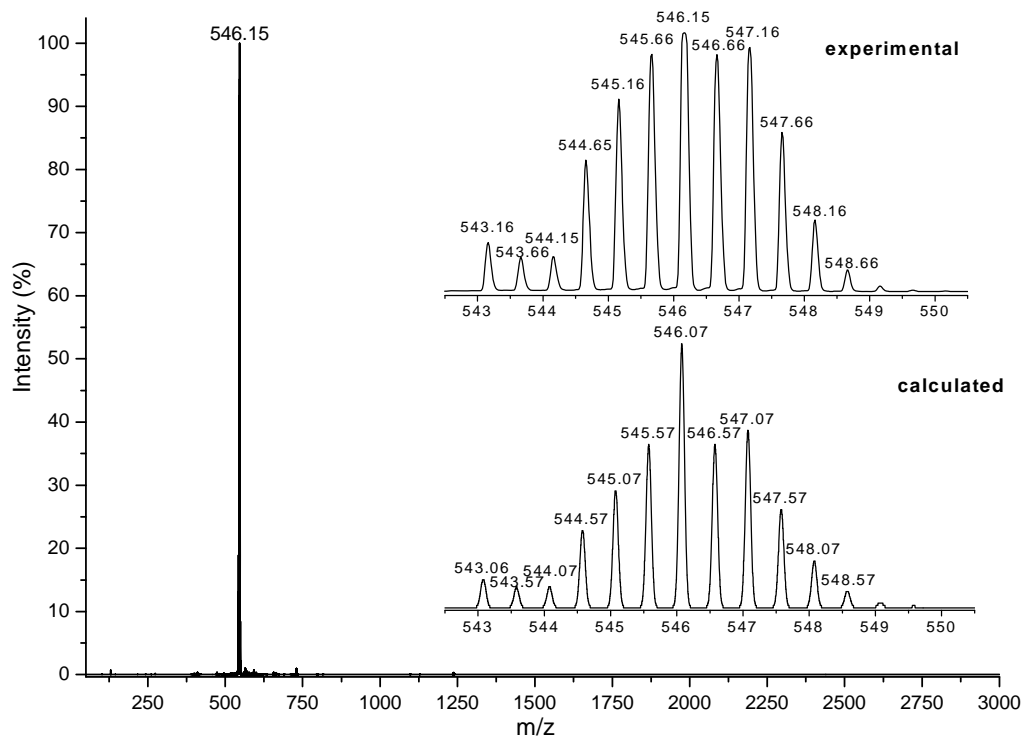
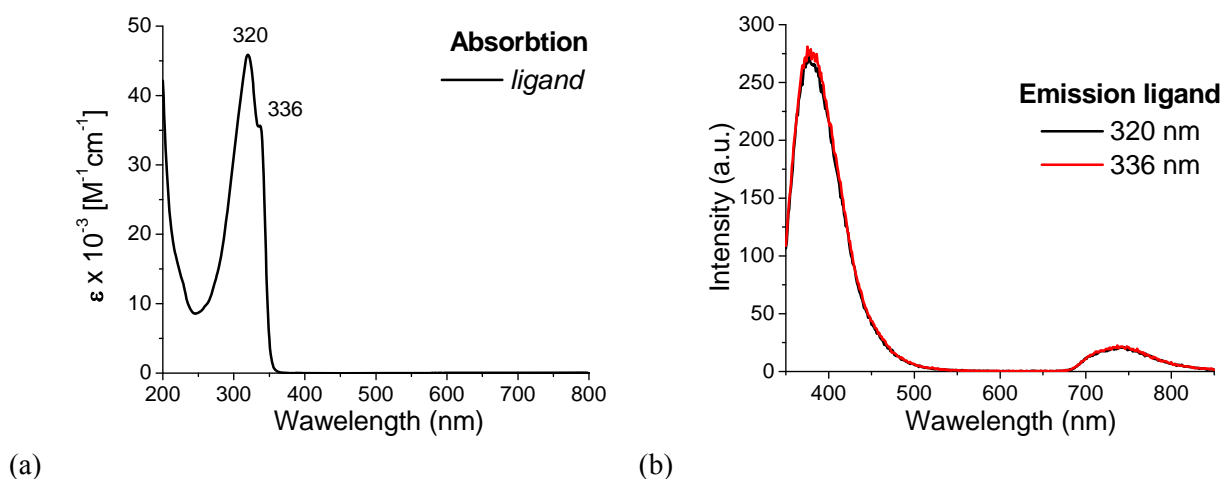
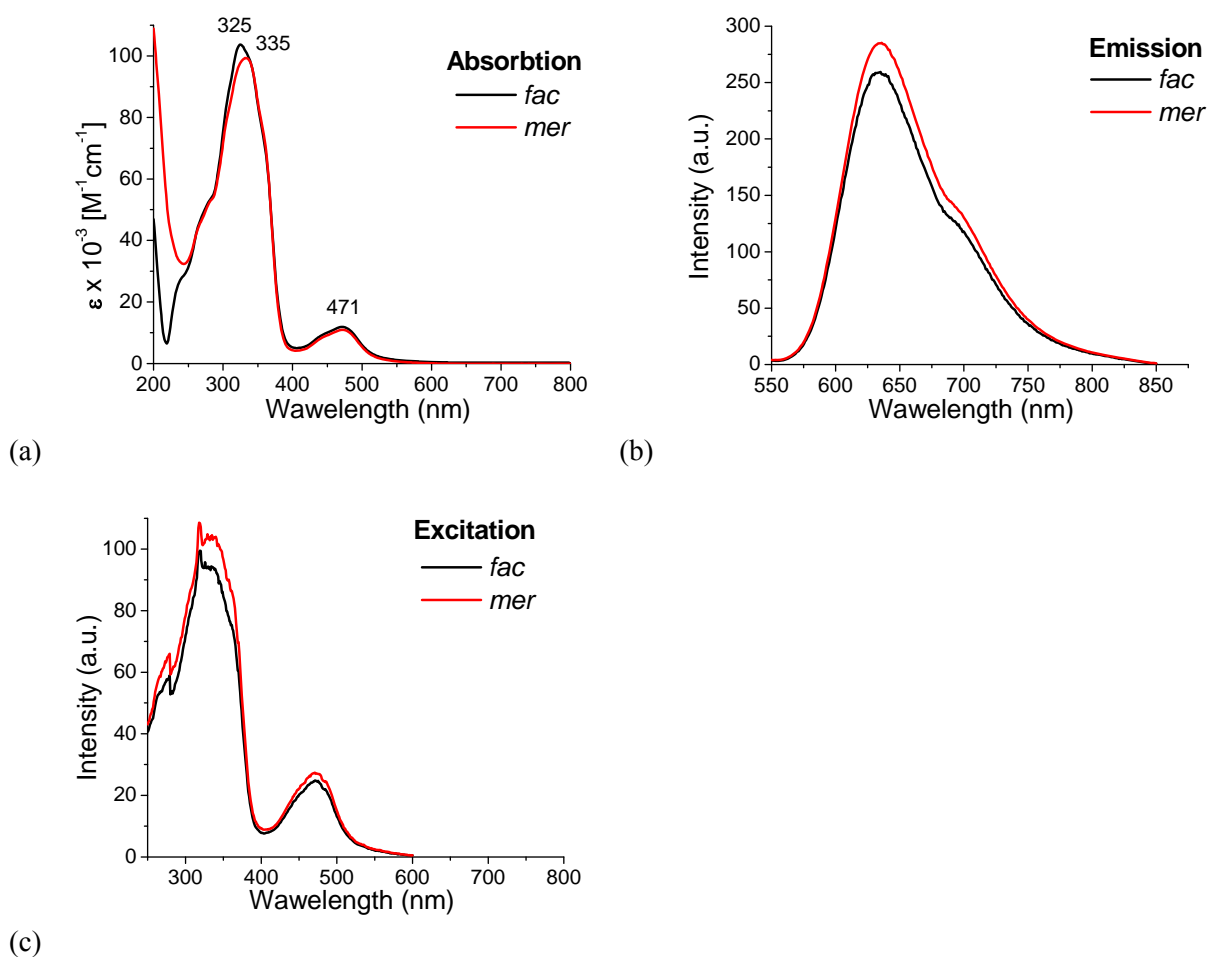


Fig. SI.12. ESI mass spectrum of *mer* Ru(II) complex. Inset: experimental and calculated isotopic pattern of $[\text{RuL}_3]^{2+}$



Figs. SI.13. Electronic spectra of the ligand **L** recorded in aerated CH₃CN at rt under normal atmosphere; (a) absorption spectrum (b) emission spectra by excitation at 320 and 336 nm;



Figs. SI.14. Electronic spectra of the *fac* and *mer* [RuL₃](PF₆)₂ recorded in aerated CH₃CN at rt under normal atmosphere; (a) absorption spectrum (b) emission spectra by excitation at 471 nm; (c) emission-excitation spectra of the 635 nm emission signal.

Table SI.1. Absorption and emission properties recorded in aerated MeCN at rt; the emission spectra are uncorrected; ^a reported values; ^b excited at 471 nm; ^c excited at 320 and 336 nm.

Compound	Absorption λ /nm ($\epsilon \times 10^{-3}/M^{-1}cm^{-1}$)			Emission $\lambda (\pm 1)$ /nm
Ligand L	320 (45.87)	336sh (35.64)	-	376 ^c
^a [Ru(bipy) ₃](PF ₆) ₂	286 (102.30)		452 (16.10)	610
<i>fac</i> [RuL ₃](PF ₆) ₂	274sh (48.90)	325 (102.00)	471 (11.65)	635 ^b
<i>mer</i> [RuL ₃](PF ₆) ₂	274sh (44.32)	335 (97.05)	471 (11.00)	635 ^b

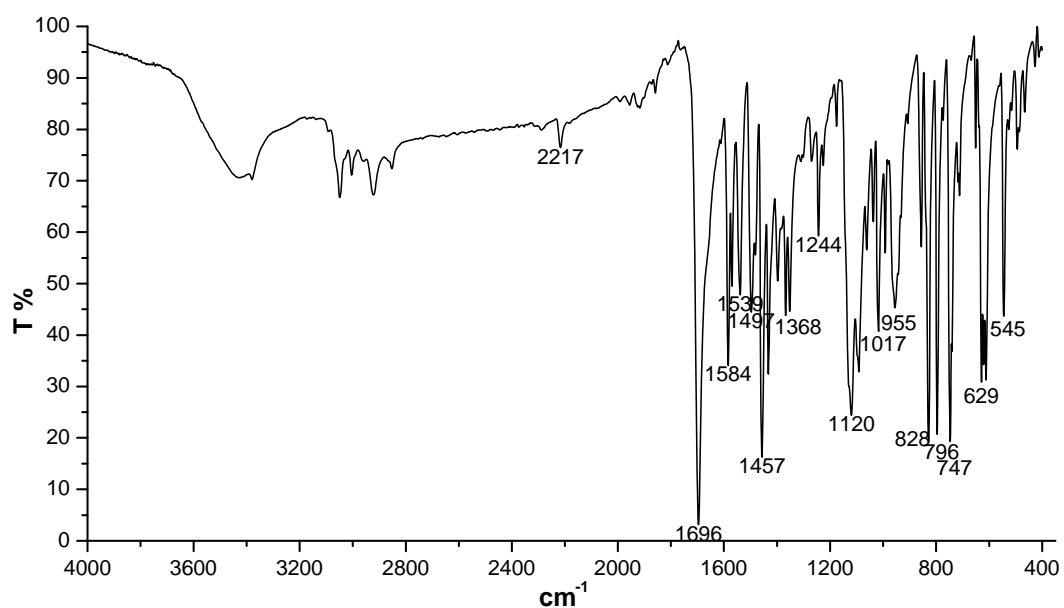


Fig. SI.15. IR spectrum of **L** in KBr pellet.

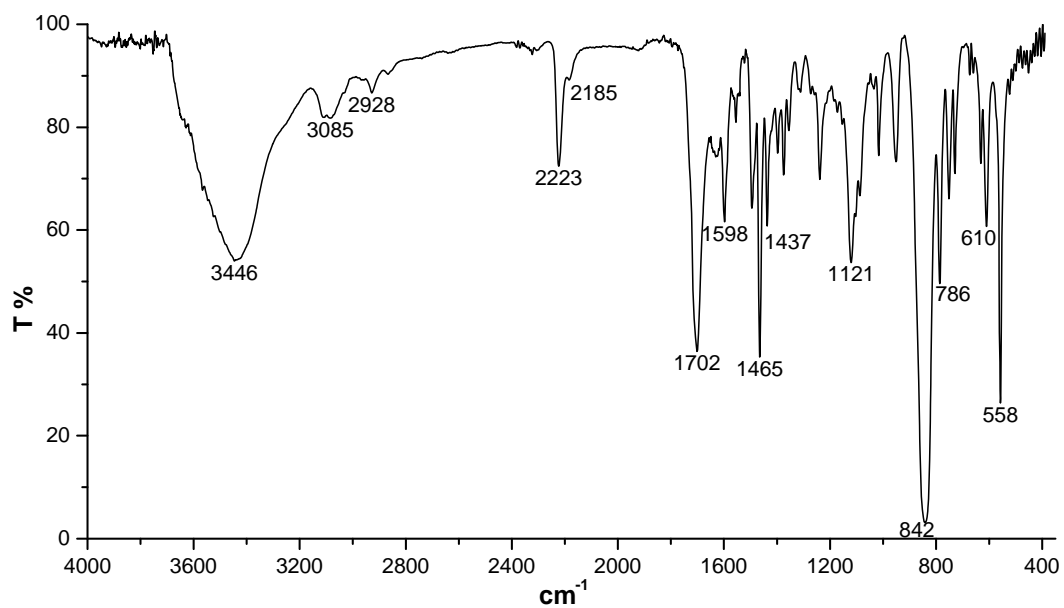


Fig. SI.16. IR spectrum of *fac* [RuL₃](PF₆)₂ in KBr pellet.

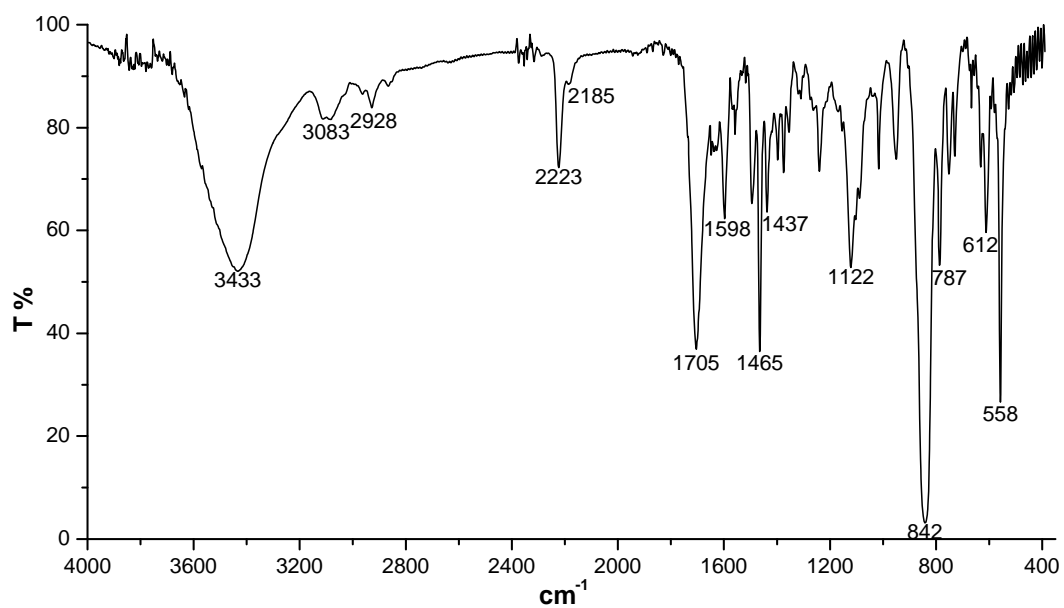


Fig. SI.17. IR spectrum of *mer* [RuL₃](PF₆)₂ in KBr pellet.

Crystallographic data

Table SI.2. Main bond lengths [\AA] and angles [$^\circ$] for *fac* $[\text{RuL}_3](\text{PF}_6)_2 \cdot 1,5(\text{CH}_3\text{CN})$; standard deviations are given in parentheses.

<i>fac</i> $[\text{RuL}_3](\text{PF}_6)_2 \cdot 1,5(\text{CH}_3\text{CN})$	
Bond atoms	Distance / \AA
Ru(1)-N(6)	2.058(6)
Ru(1)-N(5)	2.058(6)
Ru(1)-N(2)	2.065(6)
Ru(1)-N(1)	2.065(6)
Ru(1)-N(3)	2.065(6)
Ru(1)-N(4)	2.066(5)
Angle atoms	Bond Angles / $^\circ$
N(6)-Ru(1)-N(5)	78.6(2)
N(6)-Ru(1)-N(2)	99.0(2)
N(5)-Ru(1)-N(2)	174.4(2)
N(6)-Ru(1)-N(1)	89.9(2)
N(5)-Ru(1)-N(1)	96.3(2)
N(2)-Ru(1)-N(1)	78.6(2)
N(6)-Ru(1)-N(3)	171.0(2)
N(5)-Ru(1)-N(3)	93.6(2)
N(2)-Ru(1)-N(3)	89.2(2)
N(1)-Ru(1)-N(3)	95.4(2)
N(6)-Ru(1)-N(4)	96.3(2)
N(5)-Ru(1)-N(4)	88.2(2)
N(2)-Ru(1)-N(4)	97.1(2)
N(1)-Ru(1)-N(4)	172.9(2)
N(3)-Ru(1)-N(4)	78.8(2)

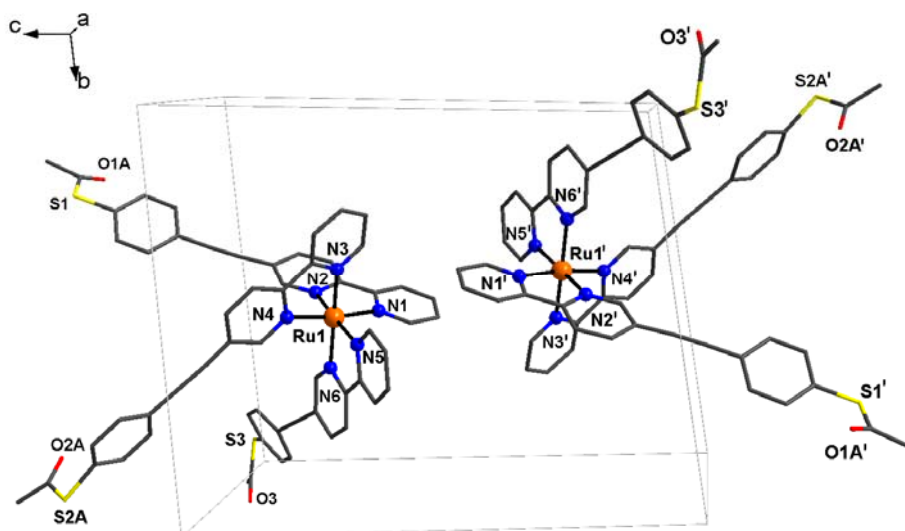


Fig. SI.18. Unit cell of *fac* [RuL₃](PF₆)₂ determined by single crystal X-ray diffraction with the two enantiomers Δ and Λ. The hydrogen atoms, PF₆⁻ counter ions and CH₃CN solvate molecules were omitted for clarity (sticks drawn). The molecule at the right-hand-side is at equivalent position '(1-x, 1-y, 1-z).

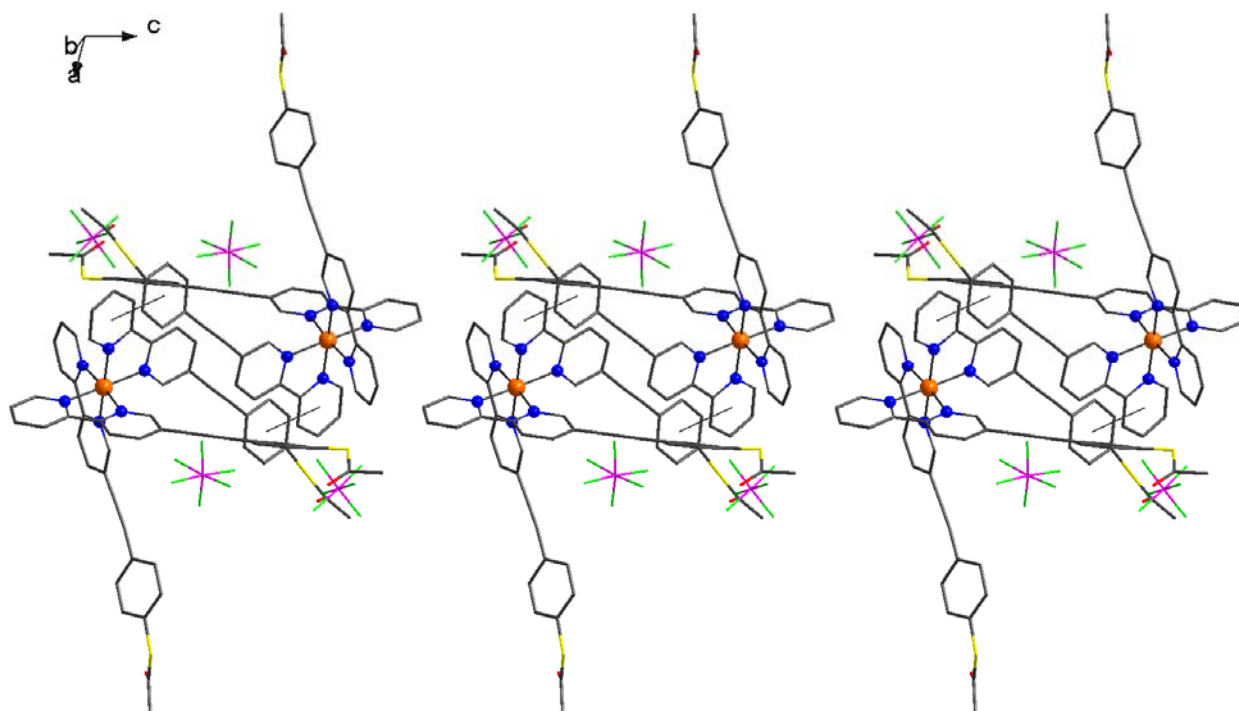


Fig. SI.19. Crystal packing along *c* axis of the *fac* [RuL₃](PF₆)₂ showing the intermolecular π···π stacking interactions (grey line) between two neighbour molecules (pyridine and phenyl rings, 3.86 Å centroid - centroid) and the position of PF₆ counter ions. The hydrogen atoms and MeCN solvate molecules were omitted for clarity (sticks drawn); *a* = 13.081 Å, *b* = 15.083 Å, *c* = 18.470 Å.

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