SUPPORTING INFORMATION

An Efficient Access to a Versatile 5,6-Dithio-1,10-Phenanthroline Building-Block and Corresponding Organometallic Complexes

Bertrand Chesneau, Angélique Passelande and Piétrick Hudhomme*

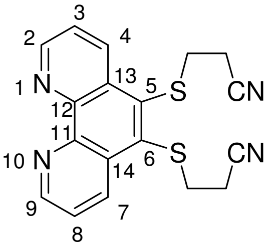
List of contents of the Supporting Information :

Experimental procedures and spectroscopic data :

General procedures : The following chemicals were obtained commercially and were used without any purification. Dry toluene was obtained by distillation over Na/benzophenone. Thin-layer chromatography (TLC) was performed on aluminium sheets coated with silica gel 60 F_{254} and neutral aluminium oxide 60 F_{254}. Column chromatography was carried out on silica gel 60A (40-60 µm) or deactivated neutral alumina [deactivation by addition of H_2O (7g) in neutral aluminium oxide 50-200µm (100g)]. Melting points were determined using a Reichert-Jung microscope and are uncorrected. ^{1}H (500 MHz), ^{13}C (125 MHz) and ^{19}F (470 MHz) NMR spectra were recorded on spectrometer (Brucker Avance DRX 500). Chemical shifts are reported as δ values in ppm using $CHCl_3$ or CH_3CN as the reference. Infra-red spectra were performed on a Perkin Elmer 841. Mass spectra were recorded on a MALDI-TOF Brucker Biflex III or DSQ tune (Thermo Electron Corporation) for EI spectra. Cyclic voltammetry was performed in a three-electrode cell equipped with a platinum millielectrode and a platinum wire counter-electrode. A silver wire served as pseudo-reference electrode and its potential was checked against the ferricinium/ ferrocene couple (Fc^+/Fc) before and after each experiment. The electrolytic media involved CH_2Cl_2 and CH_3CN (HPLC grade), and 0.1 M of tetrabutylammonium hexafluorophosphate (TBAHP - puriss quality). All experiments were performed in a glove box containing dry, oxygen-free (< 1ppm) argon, at room temperature. Electrochemical experiments were carried out with an EGG PAR 273A potentiostat.

***5,6-Bis(2-cyanoethylsulfanyl)-1,10-phenanthroline* 1 :**

To a solution of 5,6-dibromo-1,10-phenanthroline **3** (0.5 g; 1.48 mmol) in anhydrous toluene (15 mL) was added $Pd(PPh_3)_4$ (0.5 g; 0.44 mmol). A solution of 3-(tributylstannylsulfanyl)propanenitrile (2.66 g ; 12 mmol) in anhydrous toluene (25 mL) was added. The reaction mixture was refluxed for 36h under nitrogen atmosphere. After the solution was cooled to room temperature, the solution was filtered and the precipitate was washed with CH_2Cl_2. The filtrate was partially concentrated *in vacuo*. Then the solution containing compound **1** in few mL of toluene was stored in the fridge overnight. The precipitate was filtered giving compound **1** as a beige solid which was recrystallized from toluene (0.328 g; 63% yield).

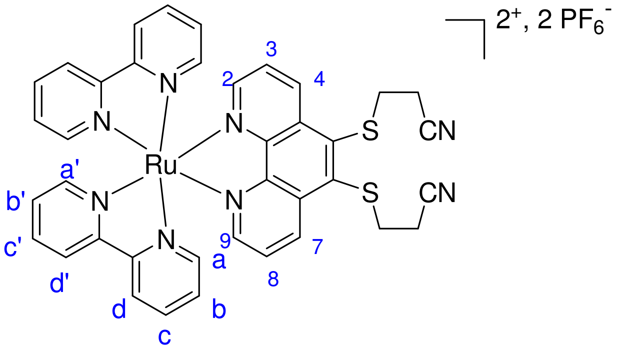


M.p = 169°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 9.26 (dd, 2H, H_2 and H_9, ^{3}J = 4.5 Hz and ^{4}J = 1.5 Hz), 9.21 (dd, 2H, H_4 and H_7, ^{3}J = 8.5 Hz and ^{4}J = 1.5 Hz), 7.78 (dd, 2H, H_3 and H_8, ^{3}J = 4.5 Hz and ^{3}J = 8.5 Hz), 3.29 (t, 4H, S-$\underline{CH_2}$-CH_2, ^{3}J = 7 Hz), 2.54 (t, 4H, CH_2-$\underline{CH_2}$-CN, ^{3}J = 7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 151.7 (C_2 and C_9), 146.7 (C_5 and C_6), 138.5 (C11 and C12), 136.0 (C_4 and C_7), 130.2 (C13 and C14), 124.2 (C_3 and C_8), 117.8 (CH_2-CH_2-$\underline{CN}$), 33.2 ($\underline{CH_2}$-CH_2-CN), 18.5 (CH_2-$\underline{CH_2}$-CN); IR (KBr, cm^{-1}) ν = 2244 (CN); MS (MALDI-TOF, dithranol, CH_2Cl_2) : 373 (M + Na^+); *elemental analysis for* $C_{18}H_{14}N_4S_2$ (350.46) calcd. C 61.69, H 4.03, N 15.99; found C 58.41, H 4.17, N 15.01.

(Traces of resulting organotin impurities could be responsible of the weak quality of elemental analysis)

***Ruthenium(II)bis(2,2'-bipyridine)(5,6-bis(2-cyanoethylsulfanyl)-1,10-phenanthroline)* 2 :**

To a solution of compound **1** (120 mg; 0.34 mmol) in ethanol (55 mL) was added *cis*-dichloro*bis*(2,2'-bipyridine)ruthenium [Ru(2,2'-bpy)$_2$Cl$_2$] (167 mg; 0.34 mmol). The reaction mixture was refluxed for 18h under nitrogen atmosphere. After the solution was cooled to room temperature, a saturated aqueous solution of KPF_6 was added. The precipitate was filtered affording compound **2** as an orange solid (240 mg; 67% yield).

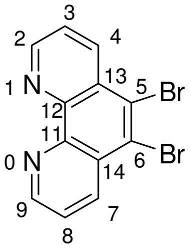


M.p = 159°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 9.24 (dd, 2H, H_4 and H_7, ^{3}J = 8 Hz and ^{4}J = 1.0 Hz), 8.50 (d, 2H, ^{3}J = 8.0 Hz), 8.46 (d, 2H, ^{3}J = 8.0 Hz) (Hd and Hd')*, 8.12 (dd, 2H, H_2, ^{3}J = 5.0 Hz and ^{4}J = 1.0 Hz), 8.07 (ddd, 2H, ^{3}J = 8.0 Hz, ^{3}J =

7.0 Hz and ^{4}J = 1.0 Hz) and 7.97 (ddd, 2H, ^{3}J = 8.0 Hz, ^{3}J = 7.0 Hz and ^{4}J = 1.0 Hz) (Hc and Hc’), 7.78 (m, 4H, H_3 and Ha or Ha’), 7.49 (d, 2H, Ha or Ha’, ^{3}J = 5.0 Hz), 7.42 (ddd, 2H, ^{3}J = 7.0 Hz, ^{3}J = 5.0 Hz and ^{4}J = 1.0 Hz) and 7.19 (ddd, 2H, ^{3}J = 7.0 Hz, ^{3}J = 5.0 Hz and ^{4}J = 1.0 Hz) (Hb and Hb’)*, 3.31 (t, 4H, S-$\underline{CH_2}$-CH_2, ^{3}J = 7 Hz), 2.63 (t, 4H, CH_2-$\underline{CH_2}$-CN, ^{3}J = 7 Hz);* the reversibility of the coupling constant between (Hb, Hb’ and Hd, Hd’) and (Hc, Hc’ and Ha, Ha’) is not completely observed; ^{13}C NMR (125 MHz, $CDCl_3$) δ= 158.1(Ce’), 157.9 (Ce), 154.2 (C2), 153.0 (Ca’), 152.9 (Ca), 149.3 (C5), 141.9 (C12), 138.9 (Cc’), 138.8 (Cc), 137.7 (C4), 134.0 (C11), 128.6 (Cb’), 128.4 (Cb), 127.6 (C3), 125.3 (Cd’), 125.2 (Cd), 119.6 (CH_2-CH_2-$\underline{CN}$), 33.9 ($\underline{CH_2}$-CH_2-CN), 19.5 (CH_2-$\underline{CH_2}$-CN); ^{19}F NMR (470 MHz, CD_3CN) δ= -70.6, -72.1; IR (KBr, cm^{-1}) ν = 2251(CN); MS (MALDI-TOF, dithranol, CH_2Cl_2) : 909 ($[M-PF_6^-]^+$) ; 764 ($[M-2PF_6^-]^+$); MS (ESI) : 382 ($[M-2PF_6^-]^{2+}$; *elemental analysis for* $C_{38}H_{30}F_{12}N_8P_2S_2Ru$ (1053.83) calcd. C 43.31, H 2.87, N 10.63; found C 40.88, H 2.89, N 10.11.
(Traces of resulting organotin impurities could be responsible of the weak quality of elemental analysis)

5,6-Dibromo-1,10-phenanthroline **3 :**

To a solution 1,10-phenanthroline (1.8 g; 10 mmol) in a Schlenk tube were added 20% oleum (17.5 mL) and bromine (1mL; 20 mmol). The reaction mixture was heated at 150°C for 60 h. After the solution was cooled to room temperature, the solution was poured on crushed ice (400g). An aqueous 25% solution of ammonia was cautiously added until pH = 3-4. The solution was filtered and the precipitate was dissolved with CH_2Cl_2. The solvent was removed *in vacuo* and the residue was purified by column chromatography on deactivated alumina using CH_2Cl_2 as the eluent to afford compound **3** as a white solid (2.1 g; 62% yield).



M.p = 221°C (litterature = 223°C,[17] 221-223°C[18]); ^{1}H NMR (500 MHz, $CDCl_3$) δ= 7.20 (dd, 2H (H_3 and H_8), ^{3}J = 4.5 Hz and ^{3}J = 8.5 Hz), 8.75 (dd, 2H (H_4 and H_7), ^{3}J = 8.5Hz and ^{4}J = 1.5 Hz), 9.2 (dd, 2H, H_2 and H_9), ^{3}J = 4.5Hz and ^{4}J = 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 151.1 (C2 and C9), 145.7 (C11 and C12), 137.2 (C4 and C7), 128.6 (C13 and C14), 125.2 (C5 and C6), 124.5 (C3 and C8); IR (KBr, cm^{-1}) ν = 732 (C-Br); MS (MALDI-TOF, dithranol, CH_2Cl_2) : 339 ($M+H^+$).

5,6-Bis(pentylsulfanyl)-1,10-phenanthroline **4 :**

To a solution of compound **1** (40 mg, 0.115 mmol) in DMF (2 mL) was added at 0°C *t*-BuOK (30 mg, 0,29 mmol). After stirring for 15 min at 0°C, 1-iodopentane (23 mg, 0.116 mmol) was added. The reaction mixture was stirred at room temperature for 1h. After addition of diethyl ether, the organic layer was washed with brine, dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was purified by column chromatography on deactivated alumina using CH_2Cl_2 as the eluent to afford compound **4** as a colorless oil which crystallizes by freezing to give a white solid (25 mg; 57% yield).
^{1}H NMR (500 MHz, $CDCl_3$) δ= 9.15 (m, 4H), 7.68 (dd, 2H, ^{3}J = 4.5 Hz and ^{3}J = 8.5 Hz), 2.91 (t, 4H, ^{3}J = 7.5 Hz), 1.51 (quint, 4H, ^{3}J = 7.5 Hz), 1.34 (m, 4H), 1.21 (m, 4H), 0.79 (t, 6H, ^{3}J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 150.6, 146.5, 140.0, 136.4, 130.4, 123.5, 38.0, 31.0, 29.4, 22.2, 13,9; MS (EI) : 384 ($M^{+\cdot}$, 100%), 314 (45%), 244 (39%); *elemental analysis for* $C_{22}H_{28}N_2S_2$ (384.60) calcd. C 68.70, H 7.34; found C 69.06, H 8.41.

5-(2-Cyanoethylsulfanyl)-6-(pentylsulfanyl)-1,10-phenanthroline **5 :**

To a solution of compound **1** (130 mg, 0.37 mmol) in DMF (3 mL) was added at 0°C *t*-BuOK (38 mg, 0,37 mmol). After stirring for 15 min at 0°C, 1-iodopentane (74 mg, 0.37 mmol) was added. The reaction mixture was stirred at room temperature for 1h. After purification by column chromatography on deactivated alumina using CH_2Cl_2 as the eluent, compound **4** was precipitated with addition of ether and petroleum ether. The precipitate was filtered to give a white solid (112 mg; 82% yield).
^{1}H NMR (500 MHz, $CDCl_3$) δ= 9.23 (dd, 1H, ^{3}J = 4.5 Hz and ^{4}J = 1.5 Hz), 9.22 (dd, 1H, ^{3}J = 4.5 Hz and ^{4}J = 1.5 Hz), 9.20 (dd, 1H, ^{3}J = 8.5 Hz and ^{4}J = 1.5 Hz), 9.19 (dd, 1H, ^{3}J = 8.5 Hz and ^{4}J = 1.5 Hz), 7.76 (dd, 1H, ^{3}J = 4.5 Hz and ^{3}J = 8.5 Hz), 7.74 (dd, 1H, ^{3}J = 4.5 Hz and ^{3}J = 8.5 Hz), 3.26 (t, 2H, ^{3}J = 7 Hz), 2.98 (t, 2H, ^{3}J = 7.5 Hz), 2.52 (t, 2H, ^{3}J = 7 Hz), 1.55 (quint, 2H, ^{3}J = 7.5 Hz), 1.37 (m, 2H), 1.24 (sext, 2H, ^{3}J = 7.5 Hz), 0.83 (t, 3H, ^{3}J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 151.3, 151.1, 146.7, 146.5, 141.6 137.0, 136.6, 136.0, 130.4, 130.3, 124.0, 123.8, 118.0, 38.4, 33.0, 31.0, 29.4, 22.2, 18.6, 14.0; IR (KBr, cm^{-1}) ν = 2240 (CN); MS (EI) : 367 ($M^{+\cdot}$, 88%), 314 (72%), 244 (100%); *elemental analysis for* $C_{20}H_{21}N_3S_2$ (367.53) calcd. C 65.36, H 5.76; found C 64.39, H 5.79.

5-(Methylsulfanyl)-6-(pentylsulfanyl)-1,10-phenanthroline **6** ***:***

To a solution of compound **5** (70 mg, 0.19 mmol) in DMF (2 mL) was added at 0°C *t*-BuOK (30 mg, 0,29 mmol). After stirring for 15 min at 0°C, 1-iodopentane (27 mg, 0.19 mmol) was added. The reaction mixture was stirred at room temperature for 1h. After addition of diethyl ether, the organic layer was washed with brine, dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was purified by column chromatography on deactivated alumina using CH_2Cl_2 as the eluent to afford compound **4** as a colorless oil which crystallizes by freezing to give a white solid (46 mg; 74% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ= 9.16 (dd, 1H, ^{3}J = 4.5 Hz and ^{4}J = 1.5 Hz), 9.15 (dd, 1H, ^{3}J = 4.5 Hz and ^{4}J = 1.5 Hz), 9.12 (dd, 1H, ^{3}J = 8.5 Hz and ^{4}J = 1.5 Hz), 9.11 (dd, 1H, ^{3}J = 8.5 Hz and ^{4}J = 1.5 Hz), 7.69 (m, 2H), 2.92 (t, 2H, ^{3}J = 7.5 Hz), 2.46 (s, 3H), 1.51 (quint, 2H, ^{3}J = 7.5 Hz), 1.33 (m, 2H), 1.21 (m, 2H), 0.79 (t, 3H, ^{3}J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 150.7, 150.6, 146.6, 146.5, 141.2, 139.6, 136.4, 136.2, 130.4, 129.7, 123.7, 123.6, 38.1, 31.0, 29.5, 22.2, 20.9, 14.0; MS (EI) : 329 (MH^+, 100%), 313 (11%), 258 (34%), 243 (14%); *elemental analysis for* $C_{18}H_{20}N_2S_2$ (328.49) calcd. C 65.81, H 6.14; found C 61.36, H 6.19.

[1,3]Dithiolo[4,5-f][1,10]phenanthroline-2-one **7 :**

To a solution of compound **1** (185 mg; 0.53 mmol) in a mixture of DMF (3 mL) and MeOH (3 mL) was added at 0°C *t*-BuOK (165 mg; 1.59 mmol). After the solution was stirred at 0°C for 2h under nitrogen atmosphere, phosgene was added (278 μL; 0.53 mmol). The reaction mixture was stirred overnight at room temperature. The precipitate was filtered and washed with MeOH affording compound **7** as a white solid (94 mg; 66% yield).

^{1}H and ^{13}C NMR spectra could not be recorded due to the low solubility of compound **7** in usual deuterated solvents.

M.p = > 260°C; IR (KBr, cm^{-1}) ν = 1616 (C=O); MS (EI) : 270 ($M^{+\cdot}$, 90%), 242 (100%)

Compound **7** is insoluble in common solvents used for NMR spectroscopy

[1,3]Dithiolo[4,5-f][1,10]phenanthroline-2-thione **8 :**

To a solution of compound **1** (185 mg; 0.53 mmol) in a mixture of DMF (3 mL) and MeOH (3 mL) was added at 0°C. *t*-BuOK (165 mg; 1.59 mmol). After the solution was stirred at 0°C for 2h under nitrogen atmosphere, thiophosgene was added (41 μL; 0.53 mmol). The reaction mixture was stirred overnight at room temperature. The precipitate was filtered and washed with MeOH affording compound **8** as a pale yellow solid (105 mg; 69% yield).

^{1}H and ^{13}C NMR spectra could not be recorded due to the low solubility of compound **8** in usual deuterated solvents.

M.p = 238°C; IR (KBr, cm^{-1}) ν = 1071 (C=S); MS (EI) : 286 ($M^{+\cdot}$, 100%)

Compound **8** is insoluble in common solvents used for NMR spectroscopy

Ruthenium(II)bis(2,2'-bipyridine)(5-(2-cyanoethylsulfanyl)-6-(pentylsulfanyl)-1,10-phenanthroline) **9 :**

To a solution of compound **2** (100 mg, 0.094 mmol) in DMF (3 mL) was added at 0°C *t*-BuOK (10 mg, 0,98 mmol). After stirring for 30 min at 0°C, 1-iodopentane (19 mg, 0.96 mmol) was added. The reaction mixture was stirred at room temperature for 3h. After addition of diethyl ether, the precipitate was filtered then dissolved using CH_2Cl_2. After purification by column chromatography on deactivated alumina using CH_2Cl_2/CH_3CN (5/1 : v/v) as the mixture of eluents, compound **9** was isolated as an orange solid (73 mg; 73% yield).

M.p = 151°C; ^{1}H NMR (500 MHz, CD_3CN) δ= 9.22 (dd, 1H, ^{3}J = 8.5 Hz and ^{4}J = 1.5 Hz), 9.21 (dd, 1H, ^{3}J = 8.5 Hz and ^{4}J = 1.5 Hz), 8.50 (d, 2H, ^{3}J = 8.5 Hz), 8.47 (d, 1H, ^{3}J = 4 Hz), 8.45 (d, 1H, ^{3}J = 4 Hz), 8.07 (m, 4H), 7.97 (m, 2H), 7.79 (m, 2H), 7.76 (m, 2H), 7.49 (m, 2H), 7.42 (m, 2H), 7.19 (m, 2H), 3.29 and 3.28 (2t, 2H, ^{3}J = 7 Hz), 3.06 and 3.04 (2t, 2H, ^{3}J = 7 Hz), 2.61 (t, 2H, ^{3}J = 7 Hz), 1.55 (m, 4H), 136 (m, 2H), 1.22 (m, 2H), 0.78 (t, 3H, ^{3}J = 7 Hz) ; ^{13}C NMR (125 MHz, CD_3CN) δ= 157.2, 156.9, 153.1, 152.8, 152.1, 152.0, 151.9 ; 148.3, 148.1, 143.3, 139.5, 137.9, 137. 8, 137.0, 136.7, 133.0, 132.8, 127.6, 127.4, 126.5, 124.3, 124.2, 118.8, 32.8, 30.1, 30.5, 29.1, 21.9, 18.5, 13.2; ^{19}F NMR (470 MHz, CD_3CN) δ= -72.6, -74.1; MS (MALDI-TOF, dithranol, CH_2Cl_2) : 927 (M - PF_6, 74%), 782 (M - 2PF_6, 100%); *elemental analysis for* $C_{40}H_{37}N_7S_2RuP_2F_{12}$(1070.90) calcd. C 44.86, H 3.48; found C 44.74, H 3.94.

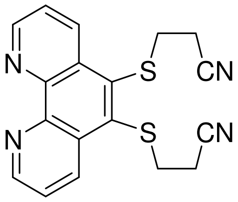
Ruthenium(II)bis(2,2'-bipyridine)([1,3]dithiolo[4,5-f][1,10]phenanthroline-2-thione) **10 :**

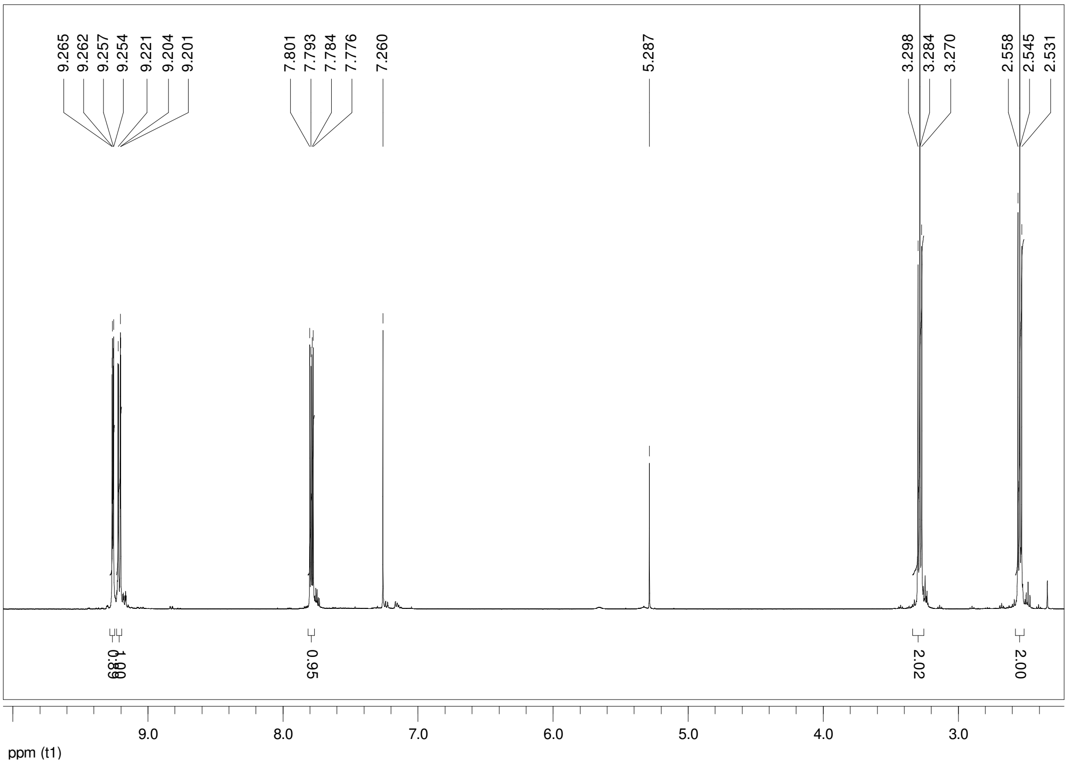
To a solution of compound **2** (240 mg; 0.23 mmol) in a mixture of DMF (5 mL) and MeOH (5 mL) was added at 0°C. *t*-BuOK (80 mg; 0.77 mmol). After the solution was stirred at 0°C for 2h under nitrogen atmosphere, thiophosgene was added (16 μL; 0.25 mmol). The reaction mixture was stirred overnight at room temperature. After addition of diethyl ether, the precipitate was filtered. The solid was dissolved in CH_3CN and purified by chromatography on deactivated alumina using CH_3CN/H_2O/saturated solution of NH_4PF_6 (5/3/1 : v/v/v) as the mixture of eluents to afford compound **10** as an orange solid (139 mg; 60% yield).

^{1}H and ^{13}C NMR spectra could not be recorded due to the low solubility of compound **10** in usual deuterated solvents.

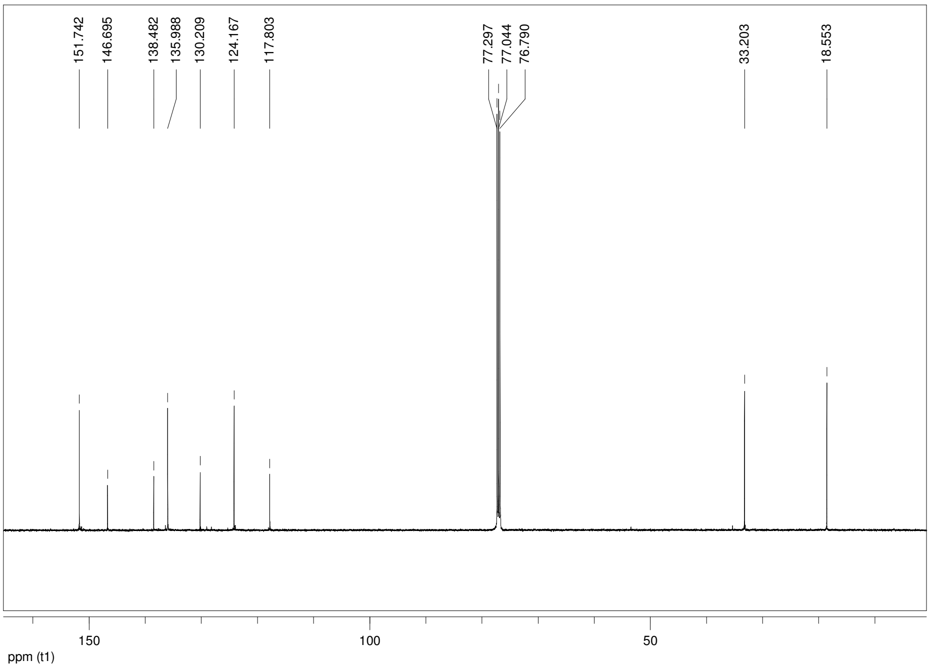
M.p = > 260°C; IR (KBr, cm^{-1}) ν = 1070 (C=S); MS (MALDI-TOF, dithranol, CH_2Cl_2) : 845 ($[M\text{-}PF_6^-]^+$) ; 700 ($[M\text{-}2PF_6^-]^+$); MS (ESI) : 350 ($[M\text{-}2PF_6^-]^{2+}$) ; 144,5 (PF_6^-); *elemental analysis for* $C_{33}H_{22}N_6S_3RuP_2F_{12}$(989.76) calcd. C 40.05, H 2.24; found C 38.11, H 2.69.

^{1}H NMR spectrum of 5,6-bis(2-cyanoethylsulfanyl)-1,10-phenanthroline 1 :

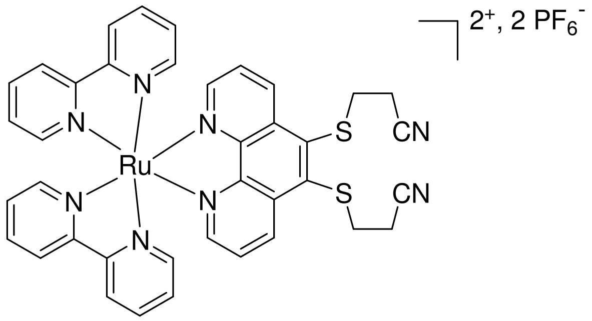




^{13}C NMR spectrum of 5,6-bis(2-cyanoethylsulfanyl)-1,10-phenanthroline 1 :



^{1}H NMR spectrum of ruthenium(II)bis(2,2'-bipyridine)(5,6-bis(2-cyanoethylsulfanyl)-1,10-phenanthroline) 2 :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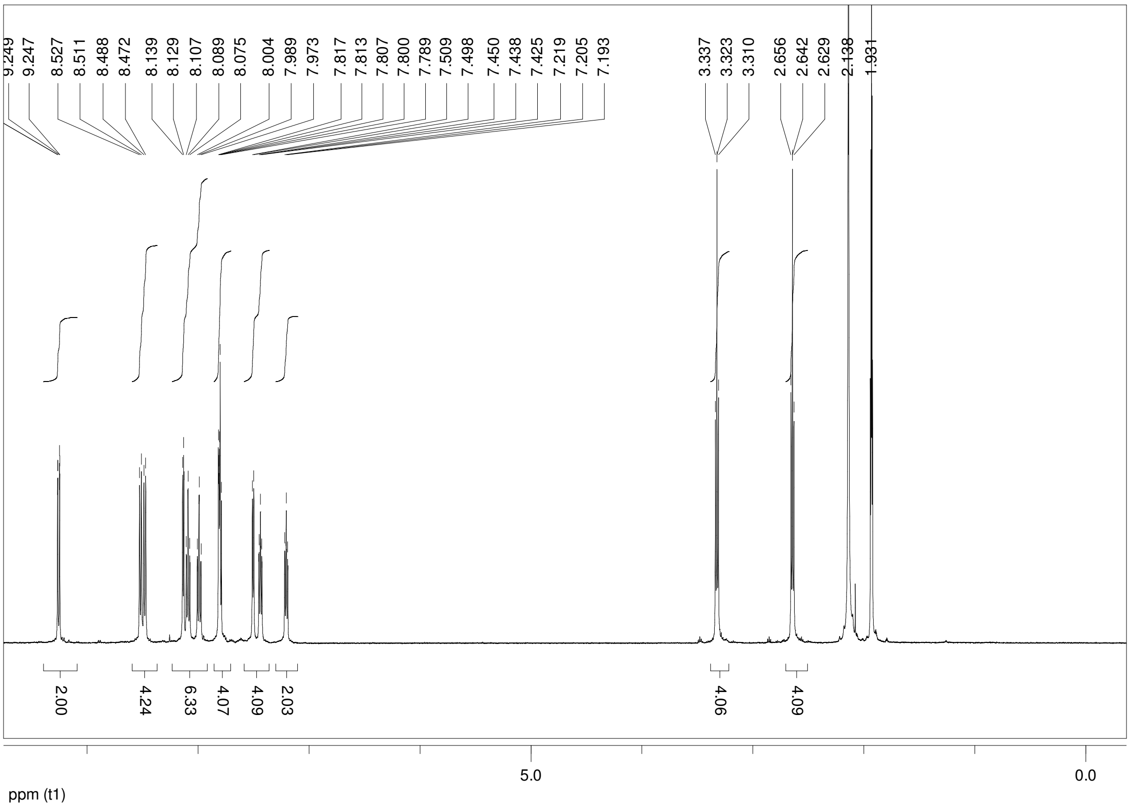
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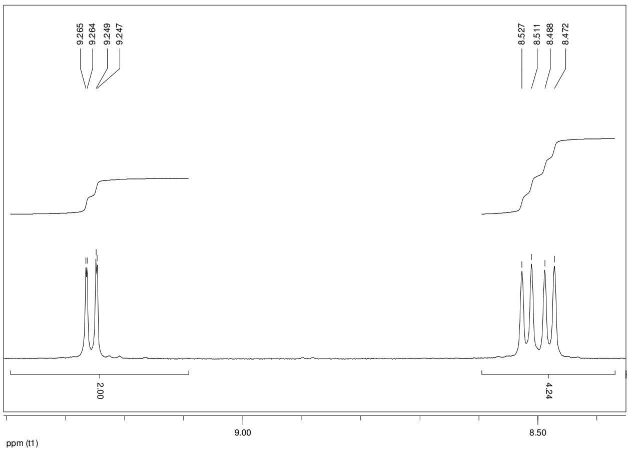
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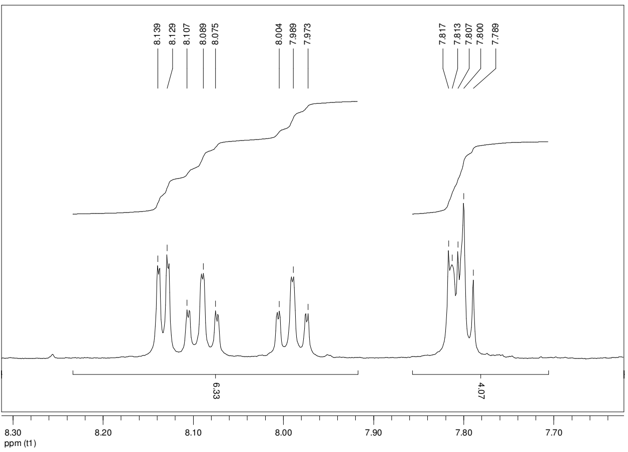
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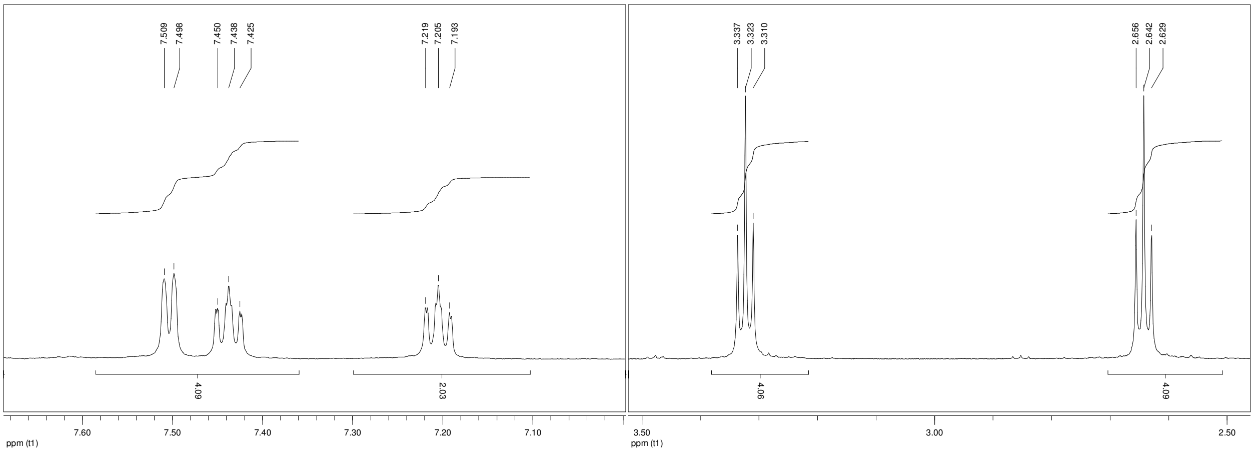
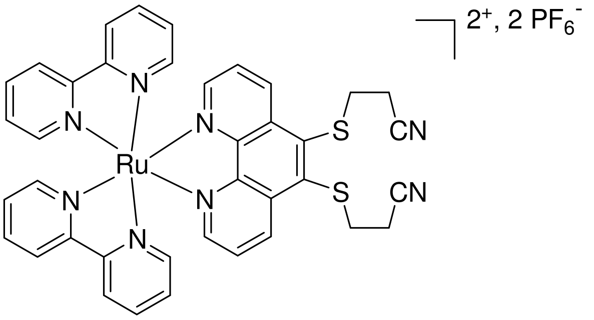
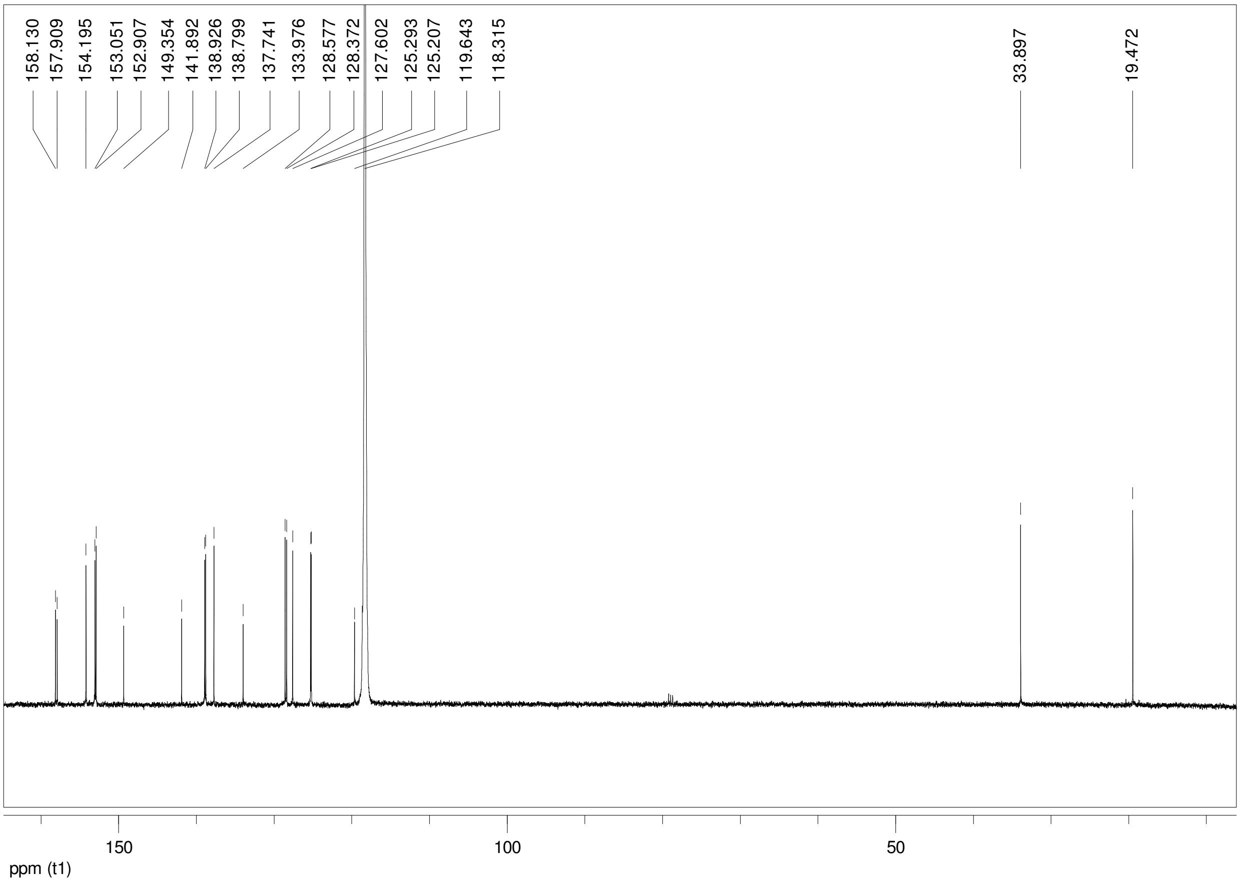
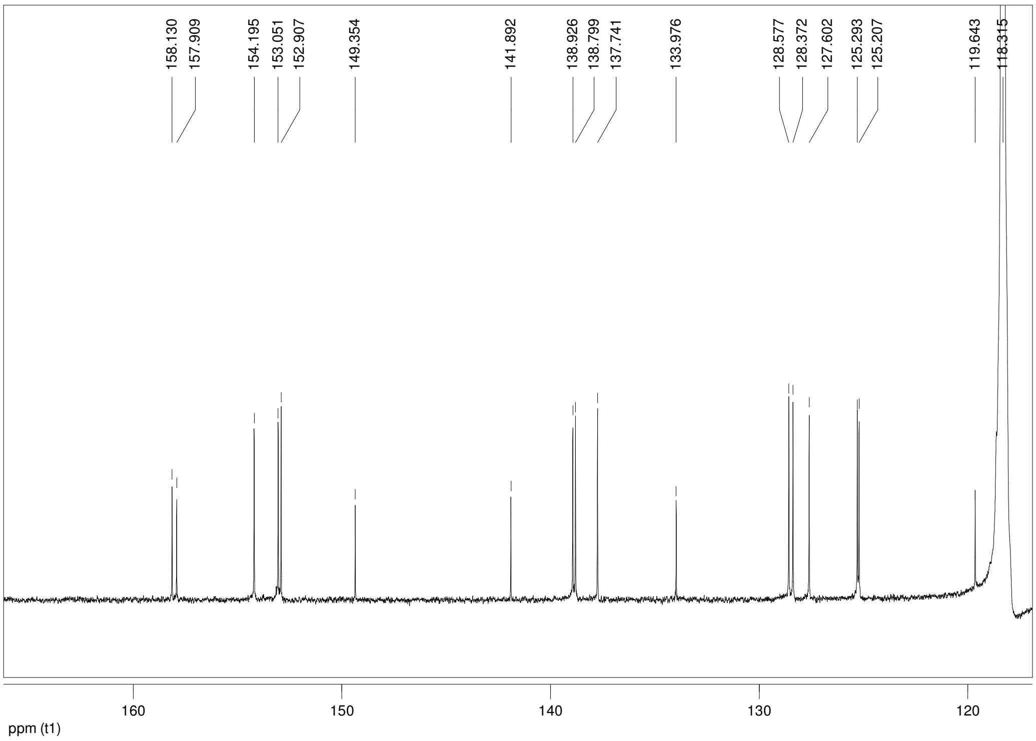


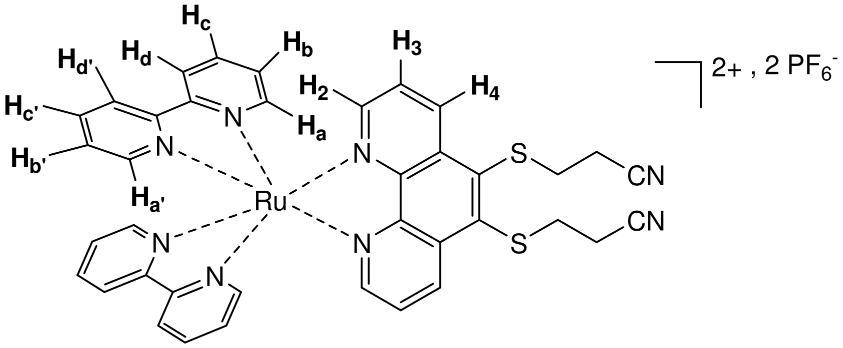
^{13}C NMR spectrum of ruthenium(II)bis(2,2'-bipyridine)(5,6-bis(2-cyanoethylsulfanyl)-1,10-phenanthroline) 2 :

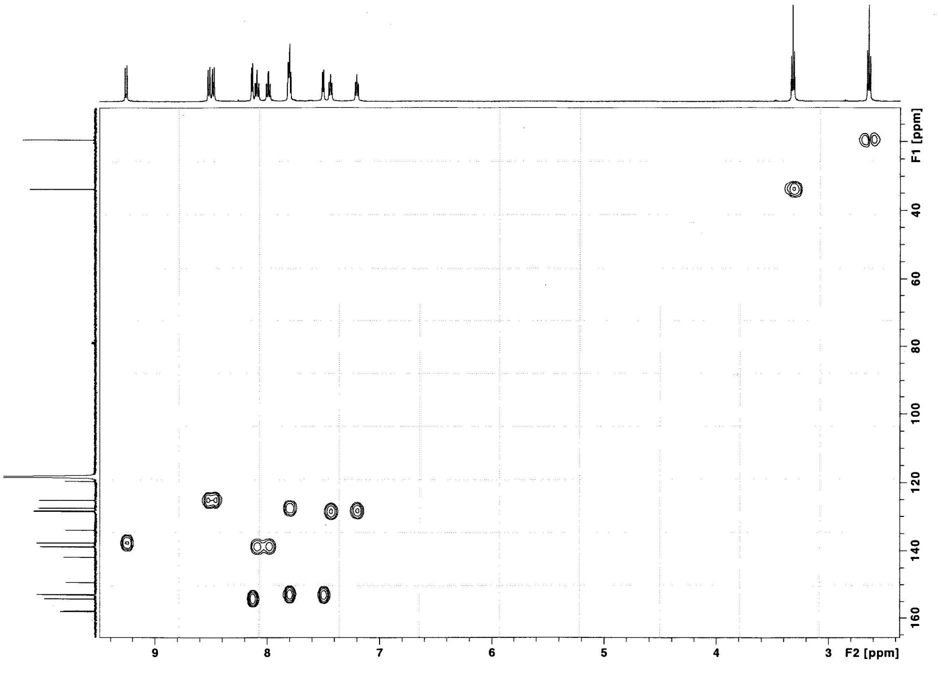


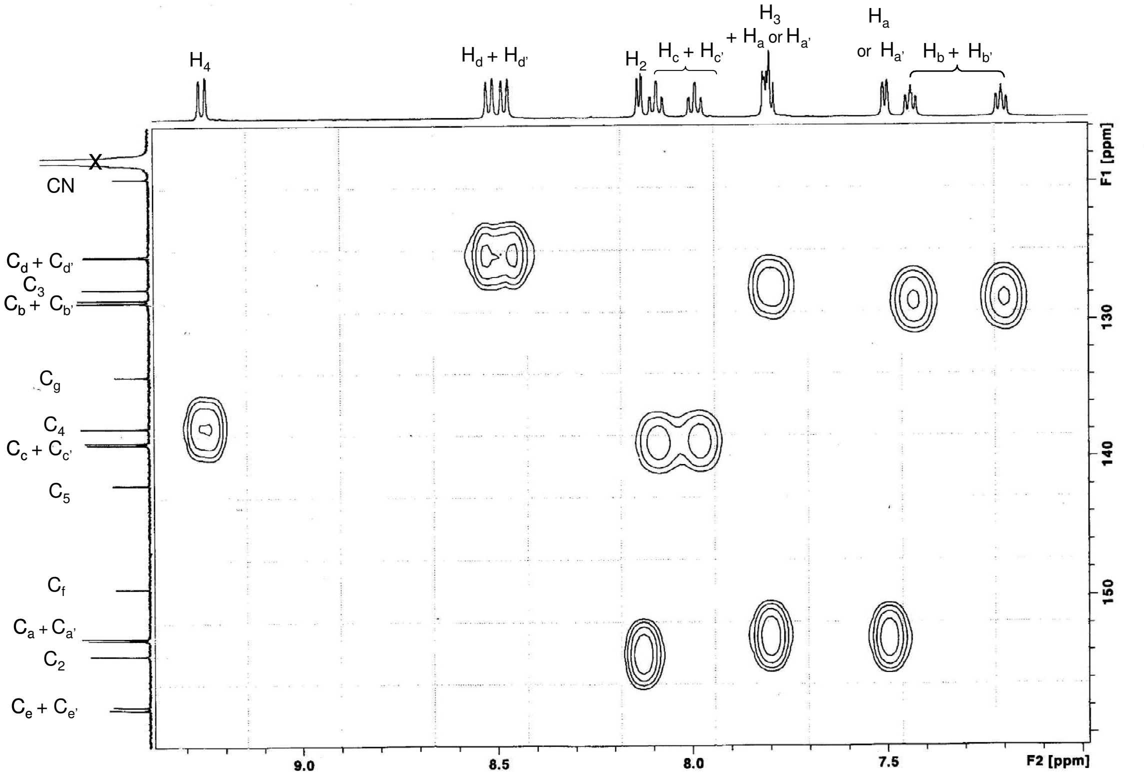




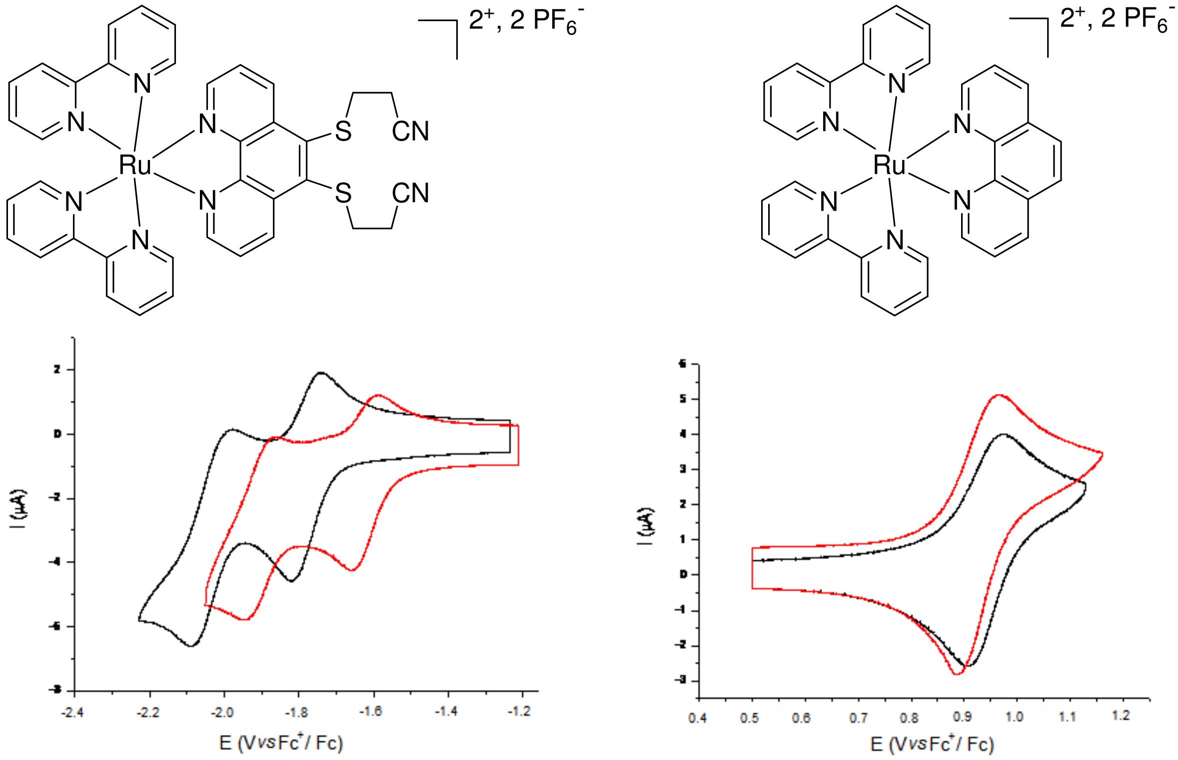
HMQC compound 2 (CD_3CN) :







Cyclic voltammograms of compound 2 (in red line) **and [Ru(phen)(bpy)$_2$] (PF$_6$)$_2$** (in black line) recorded in Bu_4NPF_6 0.1 M in CH_2Cl_2/CH_3CN (9:1) solution as the supporting electrolyte, platinum wires as counter and working electrodes. C = 5.10^{-4} M; Scan rate: 100 mV/s. V *versus* Fc$^+$/Fc.



E^0_{red1} = - 1.61 V and E^0_{red2} = - 1.88,
E^0_{ox1} = + 0.95 V (*vs* Fc$^+$/Fc)

E^0_{red1} = - 1.74 V and E^0_{red2} = - 1.98 V,
E^0_{ox1} = + 0.97 V (*vs* Fc$^+$/Fc)