Electronic Supporting Information for:

Synthesis and Electrochemical Evaluation of Ruthenium(II) Complexes Containing Functionalised β-diketonate Ligands: Developing a Ferrocene Mimic for Biosensing Applications

Yeng Ying Lee,[a] D. Barney Walker,[a] J. Justin Gooding*[a] and Barbara A. Messerle.*[a]

[a] School of Chemistry, The University of New South Wales, Kensington, Sydney, NSW 2052, Australia

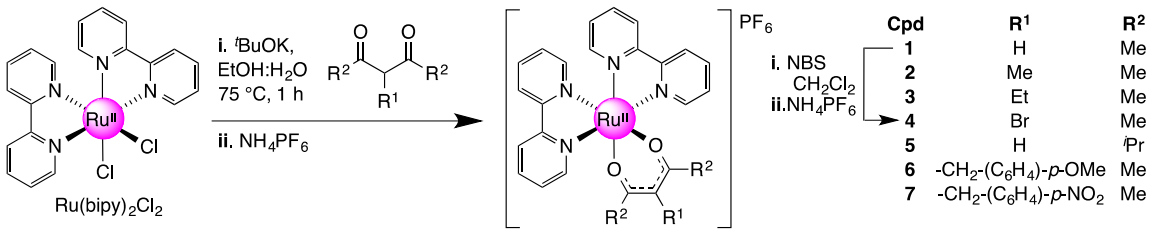
Phone: +61 2 9385 4653 Fax: +61 2 9385 4161

Email: b.messerle@unsw.edu.au

Table of Contents

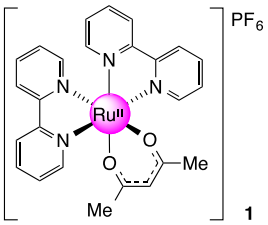
Synthetic Procedures

Series I: Ruthenium Mono(β-diketonato) complexes, [Ru(bpy)$_2$(β-diketonato)][PF$_6$]



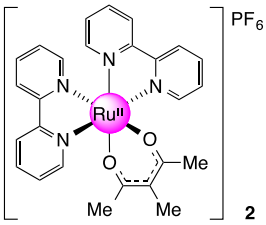
Unless otherwise noted, complexes of Series I, [Ru(bpy)$_2$(β-diketonato)][PF$_6$] (**1** – **7**), were prepared using the following method adapted from a literature procedure:[1] Ru(bpy)$_2$Cl$_2$·2H$_2$O (1 equiv.) was dissolved in degassed water or a 1:1 water : ethanol mix and heated to 75 °C for 30 minutes. The appropriate β-diketone was added to the solution followed by *t*-BuOK (1 – 1.5 equiv). The mixture was then stirred at 75 °C for 1 h and cooled to room temperature before NH_4PF_6 (5.5 equiv.) was added to precipitate the products. The solids were collected, washed with water and diethyl ether or recrystallised from CH_2Cl_2/hexane to give the products as dark solids.

The ligands 3-(4-methoxybenzyl)-2,4-pentanedione[2] (mbpd) and 3-(4-nitrobenzyl)-2,4-pentanedione[3] (nbpd) were prepared according to literature procedures. Metal complexes previously reported in the literature were characterised using ^{1}H NMR spectroscopy and ESI-MS and a reference is provided. The absolute composition of novel compounds was confirmed by elemental microanalysis.



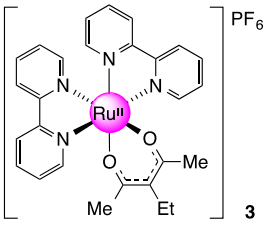
[Ru(bpy)$_2$(acac)][PF$_6$], **1**.[1, 4, 5]

Prepared with 1.00 mL (9.38 mmol, 10 equiv.) of 2,4-pentanedione (acac). Yield: 0.39 g, 57%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.78 (s, 6H), 5.36 (s, 1H), 7.23 (m, 2H), 7.70 (m, 2H), 7.75 (m, 2H), 7.86 (m, 2H), 8.18 (m, 2H), 8.64 (m, 4H), 8.75 (m, 2H) ppm. MS (ESI): *m/z* 513.0804 ([M]$^+$ required 513.0859).



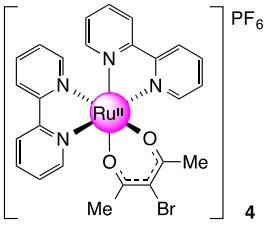
[Ru(bpy)$_2$(macac)][PF$_6$], **2**[6]

Prepared with 1.12 g (9.81 mmol, 10 equiv.) of 3-methyl-2,4-pentanedione (macac). Yield: 0.60 g, 90%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.81 (s, 3H), 1.89 (s, 6H), 7.21 (m, 2H), 7.65 (m, 2H), 7.75 (m, 2H), 7.83 (m, 2H), 8.17 (m, 2H), 8.62 (m, 4H), 8.75 (m, 2H) ppm. MS (ESI): *m/z* 527.0954 ([M]$^+$ required 527.1016).



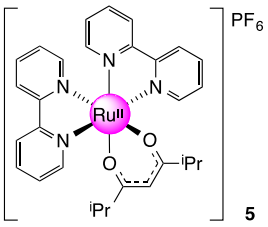
[Ru(bpy)$_2$(eacac)][PF$_6$], **3**.

Prepared with 0.100 g (0.780 mmol, 1.5 equiv.) of 3-ethyl-2,4-pentanedione (eacac). Purified by column chromatography (silica gel, CH_2Cl_2/MeCN 4:1). Yield: 0.05 g, 15%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.92 (t, J = 6.8 Hz, 3H), 1.90 (s, 6H), 2.21 (q, J = 6.8 Hz, 2H), 7.21 (m, 2H), 7.66 (m, 2H), 7.74 (m, 2H), 7.83 (m, 2H), 8.16 (m, 2H), 8.62 (m, 4H), 8.75 (m, 2H) ppm. ^{13}C NMR (150.90 MHz, DMSO-d_6): δ 15.32, 23.51, 27.02, 109.61, 123.34, 123.45, 125.61, 126.37, 134.60, 136.44, 149.77, 152.73, 157.34, 158.76, 184.99 ppm. MS (ESI): *m/z* 541.1166 ([M]$^+$ required 541.1172). Anal. Calcd. for $C_{27}H_{27}F_6N_4O_2PRu$: C, 47.30; H, 3.97; N, 8.17; Found: C, 46.93; H, 3.94; N, 7.91. CV (MeCN, 0.1 M NBu_4PF_6, 0.1 V s^{-1}, *vs* $FcH^{+/0}$) $E_{1/2}$ ($Ru^{2+/3+}$) = 0.181 V, |ΔE| = 0.066V.



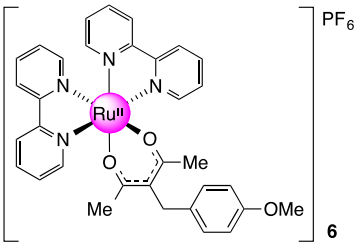
[Ru(bpy)$_2$(Br-acac)][PF$_6$], **4**.[1]

N-bromosuccinimide (0.040 g, 0.225 mmol) was added to a CH_2Cl_2 solution of [Ru(bpy)$_2$(acac)](PF$_6$) (0.140 g, 0.213 mmol). The mixture was stirred for an hour under nitrogen followed by the addition of NH_4PF_6 (0.200 g, 1.22 mmol) before the CH_2Cl_2 was evaporated. The complex was purified by chromatography (silica gel, CH_2Cl_2/MeCN 4:1) to give the product as a black solid. Yield: 0.07 g, 40%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.14 (s, 6H), 7.24 (m, 2H), 7.68 (m, 2H), 7.80 (m, 2H), 7.87 (m, 2H), 8.22 (m, 2H), 8.66 (m, 4H), 8.78 (m, 2H) ppm. MS (ESI): *m/z* 590.9890 ([M]$^+$ required 590.9890 for ^{79}Br), *m/z* 592.9882 ([M]$^+$ required 592.9949 for ^{81}Br).



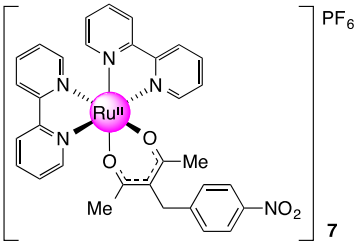
[Ru(bpy)$_2$(dmhd)][PF$_6$], **5**.

Prepared with 0.100 g (0.640 mmol, 1.2 equiv.) of 2,6-dimethyl-3,5-heptanedione (dmhd). Yield: 0.37 g, 60%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.58 (d, J = 6.8 Hz, 6H), 0.79 (d, J = 6.8 Hz, 6H), 2.25 (qq, J = 6.8, 6.8 Hz, 2H), 5.34 (s, 1H), 7.23 (ddd, J = 7.3, 7.3, 1.3 Hz, 2H), 7.73 (ddd, J = 7.3, 7.3, 1.3 Hz, 2H), 7.83-7.90 (m, 4H), 8.16 (ddd, J = 7.3, 7.3, 1.5 Hz, 2H), 8.50 (dd, J = 7.3, 1.3 Hz, 2H), 8.64 (dd, J = 7.3, 1.3 Hz, 2H), 8.75 (dd, J= 7.3, 1.5 Hz, 2H) ppm. ^{13}C NMR (150.90 MHz, DMSO-d_6): δ 19.98, 38.18, 94.27, 123.01, 123.21, 125.40, 126.03, 134.74, 136.35, 149.63, 153.11, 157.46, 158.75, 192.85 ppm. MS (ESI): *m/z* 569.1547 ([M]$^+$ 569.1485). Anal. Calcd. for $C_{29}H_{31}F_6N_4O_2PRu$: C, 48.81; H, 4.38; N, 7.85. Found: C, 48.15; H, 4.52; N, 7.70. CV (MeCN, 0.1 M NBu_4PF_6, 0.1 V s^{-1}, *vs* $FcH^{+/0}$) $E_{1/2}$ ($Ru^{2+/3+}$) = 0.201 V, |ΔE| = 0.070 V.



[Ru(bpy)$_2$(mbpd)][PF$_6$], **6**

Prepared with 0.111 g (0.503 mmol, 1.2 equiv.) of mbpd. Yield: 0.20 g, 53%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.79 (s, 6H), 3.57 (s, 2H), 3.73 (s, 3H), 6.86 (m, 4H), 7.22 (m, 2H), 7.71 (m, 2H), 7.80 – 7.88 (m, 4H), 8.22 (m, 2H), 8.67 (m, 4H), 8.78 (m, 2H) ppm. ^{13}C NMR (100.64 MHz, DMSO-d_6): δ 27.56, 34.70, 54.99, 106.26, 113.76, 123.38, 123.44, 125.57, 126.37, 128.03, 133.26, 134.64, 136.51, 149.74, 152.79, 157.28, 157.36, 158.68, 185.82 ppm. MS (ESI): *m/z* 633.1420 ([M]$^+$ required 633.1434). Anal. Calcd for $C_{33}H_{31}F_6N_4O_3PRu$: C, 50.97; H, 4.02, N, 7.20. Found: C, 50.34; H, 4.04; N, 7.24. CV (MeCN, 0.1 M NBu_4PF_6, 0.1 V s^{-1}, *vs* $FcH^{+/0}$) $E_{1/2}$ ($Ru^{2+/3+}$) = 0.167 V, |ΔE| = 0.066 V.



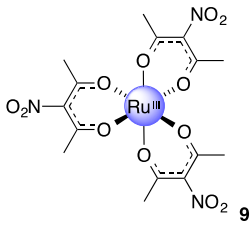
[Ru(bpy)$_2$(nbpd)][PF$_6$], **7**

Prepared with 0.113 g (0.480 mmol, 1 equiv.) of nbpd. Yield: 0.20 g, 27%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.79 (s, 6H), 3.81 (s, 2H), 7.23 (m, 2H), 7.28 (m, 2H), 7.72 (m, 2H), 7.84-7.88 (m, 4H), 8.16 (m, 2H), 8.23 (m, 2H), 8.65

(m, 2H), 8.71 (m, 2H), 8.78 (m, 2H) ppm. ^{13}C NMR (100.64 MHz, DMSO-d_6): δ 27.74, 35.82, 105.25, 123.42, 123.46, 123.52, 125.61, 126.49, 128.39, 134.73, 136.65, 145.84, 149.77, 150.49, 152.85, 157.29, 158.68, 185.96 ppm. MS (ESI): *m/z* 648.1188 ([M]$^+$ required 648.1179). Anal. Calcd for $C_{32}H_{28}F_6N_5O_4PRu$: C, 48.49; H, 3.56, N, 8.84. Found: C, 47.85; H, 3.53; N, 8.80. CV (MeCN, 0.1 M NBu_4PF_6, 0.1 V s^{-1}, *vs* $FcH^{+/0}$) $E_{1/2}$ ($Ru^{2+/3+}$) = 0.194 V, |ΔE| = 0.070 V.

Ru(β-diketonato)$_3$ Complexes

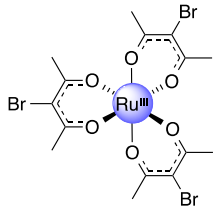
Complexes Ru(acac)$_3$ (**8**),[7] and Ru (dbm)$_3$ (**12**)[8, 9] (dbm = dibenzoylmethane) were prepared according to literature procedures.



9

Ru(NO_2-acac)$_3$, **9**

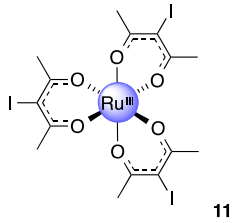
Based on a similar procedure for Co(III):[10] Acetic anhydride (30 mL) was added to $Cu(NO_3)_2 \cdot 3H_2O$ (2.35 g, 9.73 mmol) to give a light blue suspension. The contents were stirred at 0 °C for 15 min after the flask was fitted with a calcium chloride drying tube. **8** (1.20 g, 3.01 mmol) was added to the cold deep blue solution. The mixture was stirred at 0 °C for 2 h and a further 2 h at room temperature. Ice (100 g), deionised water (100 g) and anhydrous sodium acetate (2.14 g, 26.1 mmol) were added to the now reddish brown mixture. The colour immediately turned greenish blue. The solution was left to stir until a gummy substance was no longer present in the mixture. The contents were filtered to give bright red powder. The solid was washed with water to give product as a bright red powder. Yield: 1.12 g, 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ -3.55 (s, 18H) ppm. MS (ESI): *m/z* 556.9813 ([M + Na]$^+$ required 556.9826). Anal. Calcd for $C_{15}H_{18}N_3O_{12}Ru$: C, 33.78; H, 3.40; N, 7.88. Found: C, 33.01; H, 3.54; N, 7.65. CV (MeCN, 0.1 M NBu_4PF_6, 0.1 V s^{-1}, *vs* $FcH^{+/0}$) $E_{1/2}$ ($Ru^{2+/3+}$) = -0.389 V, |ΔE| = 0.068 V.



10

Ru(Br-acac)$_3$, **10** [11]

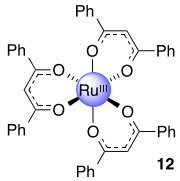
N-bromosuccinimide (1.18 g, 6.63 mmol) was added to **8** (0.800 g, 2.00 mmol) followed by CH_2Cl_2 (30 mL). The mixture turned dark violet instantly. The mixture was left to stir at room temperature overnight before solvent was removed under vacuum. The dark solids were then redissolved in a minimum amount of CH_2Cl_2 before passing through a column of silica gel to remove unidentified dark purple (top) and pink (middle) bands. The dark violet solvent collected was evaporated to give dark solids which upon recrystallisation by CH_2Cl_2 /pentane gave product **10**. Yield: 0.82 g, 64%. ^{1}H NMR (400 MHz, $CDCl_3$): δ -7.78 (s) ppm. MS (ESI): *m/z* 655.7571 ([M + Na]$^+$ required for ^{79}Br 655.7567), 661.7544 ([M + Na]$^+$ required for ^{81}Br 661.7559).



11

Ru(I-acac)$_3$, **11** [11]

N-iodosuccinimide (2.03 g, 9.02 mmol) was added to Ru(acac)$_3$ (**8**) (0.402 g, 1.01 mmol) dissolved in toluene (50 mL). The reaction heated at reflux for 2 h. The toluene was removed at reduced pressure and the resultant solid purified using flash chromatography (silica, CH_2Cl_2). A major dark violet band was collected and solvent evaporated. The solids were recrystallised with CH_2Cl_2 /pentane to give **11** as a dark solid. Yield: 0.65 g, 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ -7.54 (s) ppm. MS (ESI): *m/z* 776.7279 ([M]$^+$ required 776.7275).



12

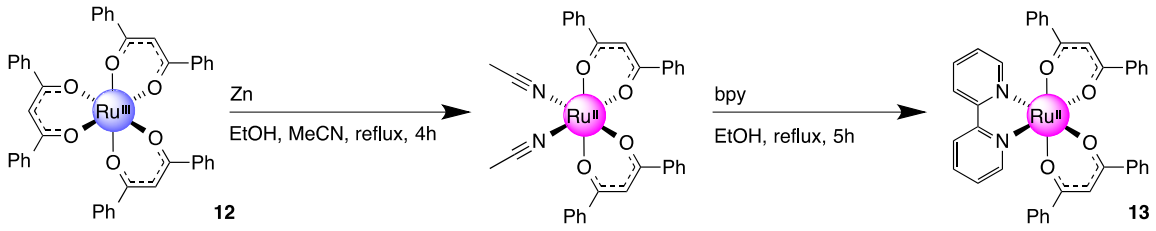
Ru(dbm)$_3$ **12**[8, 9]

$RuCl_3 \cdot 3H_2O$ (1.31 g, 5.01 mmol) was dissolved in a mixture of EtOH (100 mL) and degassed water (25 mL) resulting in a dark brown solution. The solution was refluxed for 4 h, during which time a colour change of the solution from dark brown to dark blue was observed. Dibenzoylmethane (dbm) (3.70 g, 16.5 mmol) was added to the dark blue solution after cooling down to room temperature. The reaction was refluxed for a further 1.5

h before cooling again. $KHCO_3$ (0.860 g, 8.59 mmol) was added to the now black green solution and the mixture was refluxed again for another 1.5 h, during which time gas evolution was observed. A second portion of $KHCO_3$ (0.860 g, 8.59 mmol) was added to the cooled yellow-green solution. The reaction was refluxed for a further 2 h, the colour of which was now black. After cooling a dark precipitate was formed and separated from the brown solution. The precipitate was washed with cold EtOH and hexane before being purified by silica gel column chromatography (CH_2Cl_2 /hexane 3:7 to 1:1). An insoluble layer remained on top of column while a dark red, later dark brown fraction was collected. The collected fraction was dried *in vacuo*, which upon recrystallisation in CH_2Cl_2/pentane gave the product as a black solid. Yield: 0.96 g, 25%. ^{1}H NMR (300 MHz, $CDCl_3$): δ -32.56 (br s, 3H), 6.72 (m, 12 H), 9.20 (m, 6H), 11.78 (m, 12H) ppm. MS (ESI): *m/z* 794.1187 ([M + Na]$^+$ required 794.1213).

Series II. Ruthenium Bis(β-diketonato) Complexes, Ru(β-diketonato)$_2$(bpy)

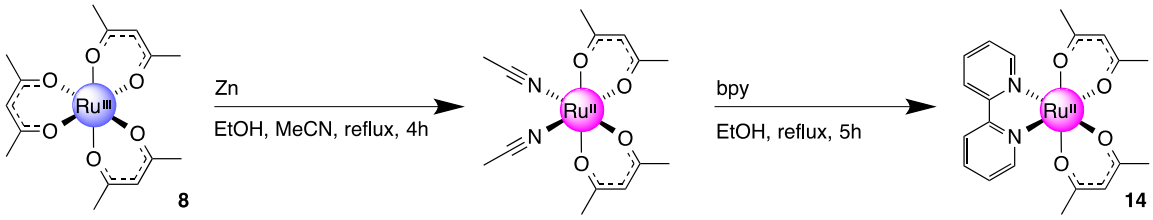
$Ru(acac)_2(MeCN)_2$ was prepared according to a literature procedure.[12]



(a) **12** (0.581 g, 0.752 mmol) was added to a flask containing activated zinc dust (0.5 g) followed by EtOH (15 mL). The suspension was refluxed for 1 h, during which time a colour change from black to dark blue was observed. MeCN (10 mL) was added to the mixture under nitrogen and colour changed from dark blue, to brown, to green, to dark green, then red to dark red was observed over 2 h of reflux. The dark red reaction mixture was refluxed for a further 3.5 h before being filtered through a bed of celite to give a clear red solution. The solution was dried *in vacuo*

to give a dark red powder. The powder was purified by silica gel column chromatography with CH_2Cl_2 to firstly remove dbm, followed by pure EtOAc to elute complex **13** as a dark red powder. Yield: 0.25 g, 50%. ^{1}H NMR (400 MHz, C_6D_6): δ 2.69 (s, 6H), 6.77 (s, 2H), 7.24 – 7.36 (m, 6H), 7.39 – 7.50 (m, 6H), 7.88 (m, 4H), 8.05 (m, 4H) ppm. MS (ESI): *m/z* 630.1082 ([M]$^+$ required 630.1087).

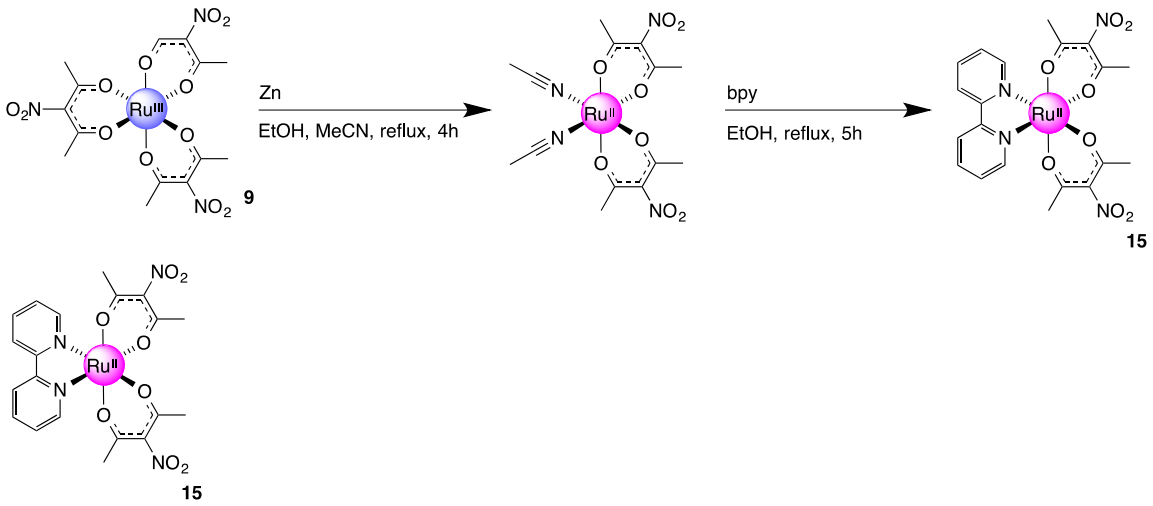
(b) The intermediate isolated in part (a) (0.065 g, 0.102 mmol) and bpy (0.0170 g, 0.109 mmol) were added to a flask followed by EtOH (20 mL). The reaction mixture was refluxed for 3 h during which a colour change from brown to black was observed in the first 30 min. The reaction was cooled to room temperature, solvent removed and solids redissolved in a minimal amount of CH_2Cl_2 before being added dropwise to excess pentane to precipitate the product as a black solid. The solid was filtered, washed twice with pentane and dried *in vacuo* to give the title compound.[13] Yield: 0.050 g, 70%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.72 (s, 2H), 7.28 (m, 4H), 7.35 – 7.49 (m, 10H), 7.60 (m, 4H), 7.79 (m, 2H), 8.02 (m, 4H), 8.59 (m, 2H), 8.84 (m, 2H) ppm. MS (ESI): *m/z* 704.1217 ([M]$^+$ 704.1244). CV (MeCN, 0.1 M NBu_4PF_6, 0.1 V s^{-1} *vs* $FcH^{+/0}$) $E_{1/2}$ ($Ru^{2+/3+}$) = -0.416 V, |ΔE|= 0.059 V.



Ru(acac)$_2$(bpy), **14**[14]

Using a recently reported procedure,[15] Ru(acac)$_2$(MeCN)$_2$(0.096 g, 0.252 mmol) and bpy (0.0395 g, 0.253 mmol) were dissolved in EtOH (10 mL). The reaction was refluxed overnight. The initially orange mixture turned deep green. Ethanol was removed to give dark solids. The solids were subjected to column chromatography (silica gel, CH_2Cl_2 /MeOH 9:1) to give the product 15 as a dark solid. Yield: 0.12 g, 66%. ^{1}H NMR (400 MHz, C_6D_6): δ 1.60 (s, 6H), 2.21 (s, 6H), 5.38 (s, 2H), 6.41 (m, 2H),

6.61 (m, 2H), 7.08 (m, 2H), 9.17 (m, 2H) ppm. MS (ESI): *m/z* 479.0512 ([M + Na]$^+$ required 479.0515).

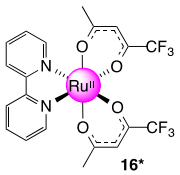


Ru(NO_2-acac)$_2$(bpy), **15**

(a) Compound **9** (0.574 g, 1.08 mmol) was stirred in EtOH with activated zinc dust (0.5 g) for 1 h, during which time the colour changed from bright red to brown. MeCN (5 mL) was added to the brown mixture and refluxed for 4 h. The mixture was filtered through a bed of celite on which a brown layer remained. The crude product was subjected to silica gel column chromatography to first elute unreacted **9** with CH_2Cl_2 followed by EtOAc to flush the product out from the column as an orange fraction. Solvent was removed to give the title product as an orange solid. Yield: 0.46 g, 92%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.09 (s, 6H), 2.11 (s, 6H), 2.73 (s, 6H) ppm. ^{13}C NMR (100.64 MHz, DMSO-d_6): δ 3.83, 26.59, 26.83, 128.46, 139.13, 183.15, 184.52 ppm. MS (ESI): *m/z* 495.0052 ([M + Na]$^+$ 495.0060).

(b) The Ru(acac-NO_2)$_2$($MeCN$)$_2$ intermediate isolated in (a) (0.200 g, 0.424 mmol) and bpy (0.0660 g, 0.423 mmol) were added to a Schlenk flask followed by EtOH (~15 mL). The reaction was refluxed for 5 h before solvent was removed under reduced pressure to give a dark brown solid. The solid was purified by column chromatography (silica gel, $MeCN/CH_2Cl_2$ 1:5) to give a dark brown solid. Yield:

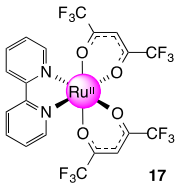
0.030 g, 13%. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.76 (s, 6H), 2.28 (s, 6H), 7.52 (m, 2H), 7.90 (m, 2H), 8.59 (m, 2H), 8.68 (m, 2H) ppm. ^{13}C NMR (100.64 MHz, DMSO-d_6): δ 26.57, 27.11, 122.74, 125.21, 128.44, 134.66, 152.07, 159.82, 182.14, 184.49 ppm. MS (ESI): *m/z* 569.0209 ([M + Na]$^+$ required 569.0217). Anal. Calcd for $C_{20}H_{20}N_4O_8Ru$: C, 44.04; H 3.70; N 10.27. Found: C, 44.17; H, 3.77; N, 10.04. CV (MeCN, 0.1 M NBu_4PF_6, 0.1 V s^{-1} *vs* $FcH^{+/0}$) $E_{1/2}$ ($Ru^{2+/3+}$) = -0.054 V, |ΔE|= 0.071 V.



16*

Ru(tfac)$_2$(bpy), **16**[16]

$Ru(bpy)(Cl)_4$ (0.200 g, 0.500 mmol) was added to a flask containing activated zinc dust (0.5 g) followed by EtOH – degassed water (15 mL each). The mixture was stirred for 15 min to result in a deep violet colour. Colour changed to maroon upon addition of trifluoroacetylacetone (tfac) (0.900 mL, 7.42 mmol) and Na_2CO_3 (0.583 g, 5.50 mmol). The reaction was refluxed for 3 h. The maroon mixture was filtered; the filtrate was reduced to 5 mL and extracted by CH_2Cl_2 (20 mL x 3). The CH_2Cl_2 layer was washed with water, dried with $MgSO_4$ and solvent removed *in vacuo* to give a dark solid. The solid was purified by column chromatography (silica gel, MeCN/toluene 1:5) to give the product as a dark maroon solid. Yield: 0.070 g, 25%. ^{1}H NMR (400 MHz, C_6D_6), a mixture of three isomers: δ 1.34 (s, 3H), 1.39 (s, 3H), 1.96 (s, 3H), 1.97 (s, 3H), 5.89 (s, 2H), 6.23 – 6.32 (m, 4H), 6.52 – 6.61 (m, 4H), 6.86 (m, 2H), 6.91 (m, 2H), 8.69 (m, 1H), 8.78 (m, 1H), 8.91 (m, 1H), 9.00 (m, 1H) ppm. ^{19}F NMR (376 MHz, C_6D_6): δ -73.16, -73.17, -73.31, -73.40 ppm. MS (ESI): *m/z* 586.9939 ([M]$^+$ required 586.9939). CV (MeCN, 0.1 M NBu_4PF_6, 0.1 V s^{-1} *vs* $FcH^{+/0}$) $E_{1/2}$ ($Ru^{2+/3+}$) = -0.087 V, |ΔE|= 0.073 V.



17

Ru(hfac)$_2$(bpy), **17**[17]

$Ru(bpy)(Cl)_4$ (0.201 g, 0.502 mmol) was added to a flask containing activated Zn dust followed by EtOH (15 mL) and degassed water (15 mL). The mixture was left to stir at room temperature for 15 min

whereupon its colour changed from dark to deep purple. Hexafluoroacetylacetone (hfac) (0.970 mL, 6.85 mmol) was added to the stirring mixture followed immediately by Na_2CO_3 (0.581 g, 5.48 mmol). The reaction was refluxed for one hour. The resulting maroon mixture was filtered, the filtrate reduced to 5 mL and extracted with CH_2Cl_2 (50 mL, 30 mL × 3). The combined organic extracts was then dried with $MgSO_4$, filtered and solvent removed to give a reddish brown solid. The solid was purified by column chromatography (silica gel, MeCN/toluene 1:5) to give reddish brown solids. Yield: 0.11 g, 33%. ^{1}H NMR (400 MHz, C_6D_6): δ 6.12 (m, 2H), 6.45 (s, 2H), 6.52 (m, 2H), 6.71 (m, 2H), 8.44 (m, 2H) ppm. MS (ESI): *m/z* 694.9374 ($[M + Na]^+$ required 694.9385).

Cyclic Voltammetry Data

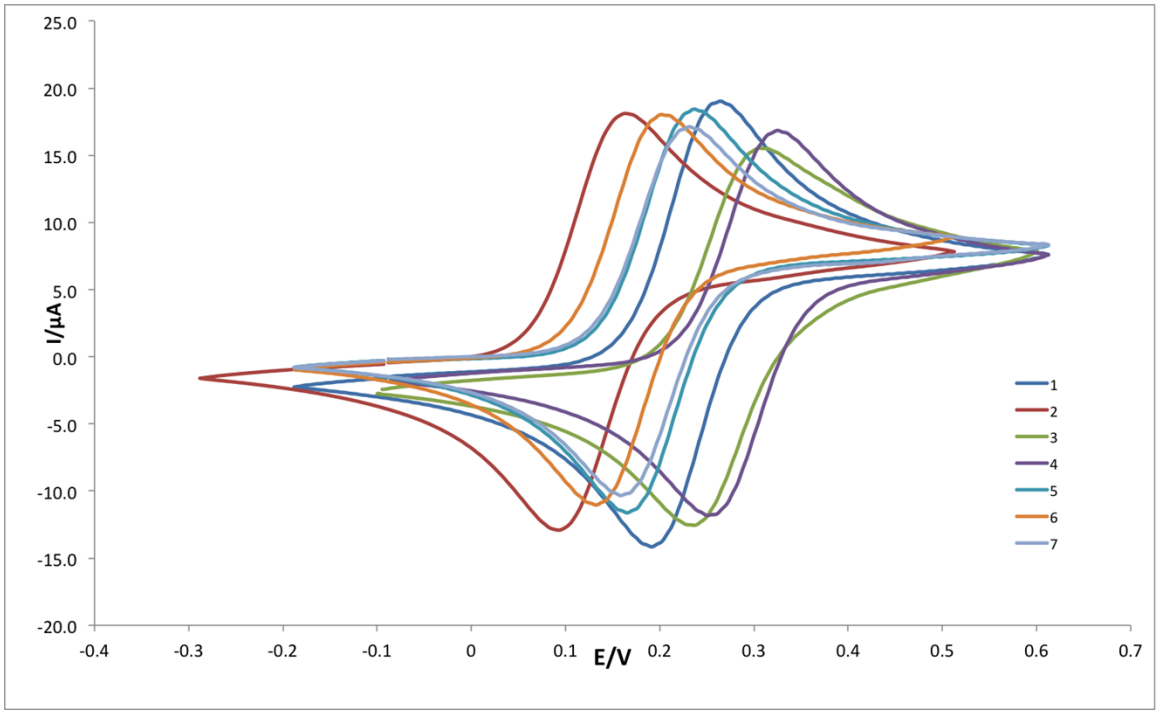


Figure S1. Cyclic voltammograms of complexes **1** – **7**

Table S1 E_{pa}, E_{pc} and ΔE for Series I Ru(bpy)$_2$(β-diketonato) complexes.

Complex	E_{pa}/V	E_{pc}/V	ΔE/mV	I_{pa}/I_{pc}
1 (R^1=H, R^2=Me)	0.263	0.193	70	0.9798
2 (R^1=Me, R^2=Me)	0.161	0.095	66	0.9736
3 (R^1=Et, R^2=Me)	0.215	0.149	66	0.9625
4 (R^1=Br, R^2=Me)	0.325	0.259	66	0.9634
5 (R^1=H, R^2=^{i}Pr)	0.236	0.166	70	1.0093
6 (R^1=*p*-MeOBn, R^2=H)	0.200	0.134	66	0.9866
7 (R^1=*p*-NO_2Bn, R^2=H)	0.229	0.159	70	0.9972

Collected in MeCN with 0.1 M NBu_4PF_6, ν = 0.1 V s^{-1}

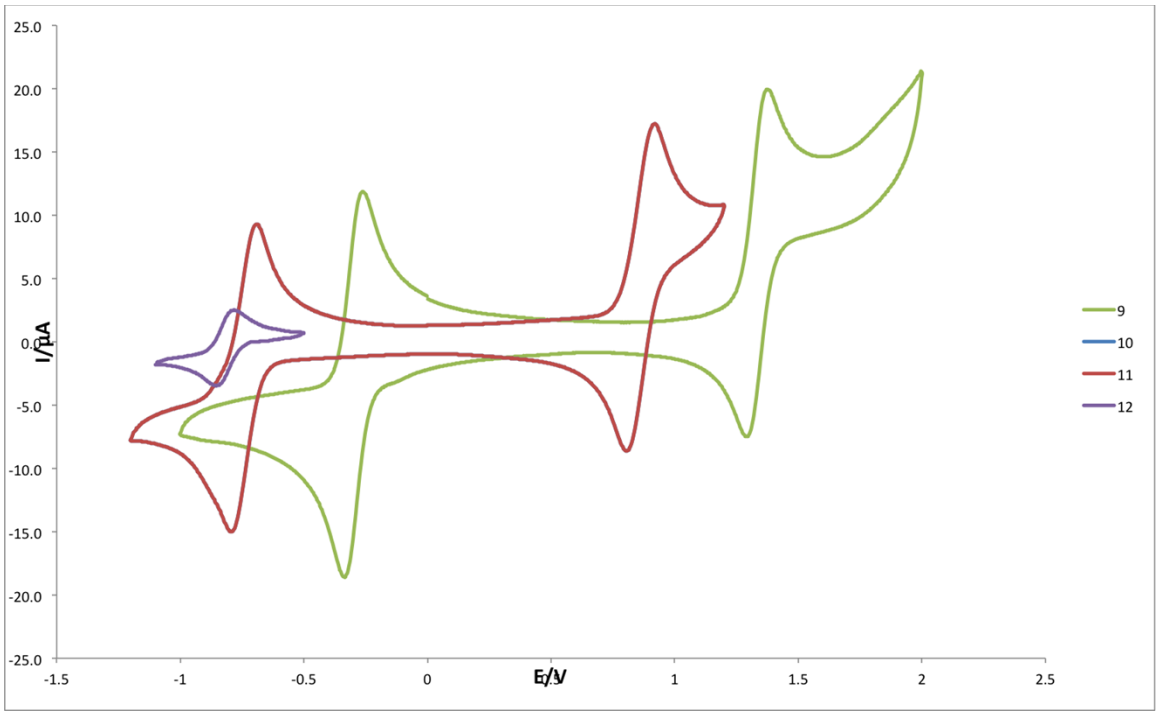


Figure S2. Cyclic voltammograms of complexes **9-12.***

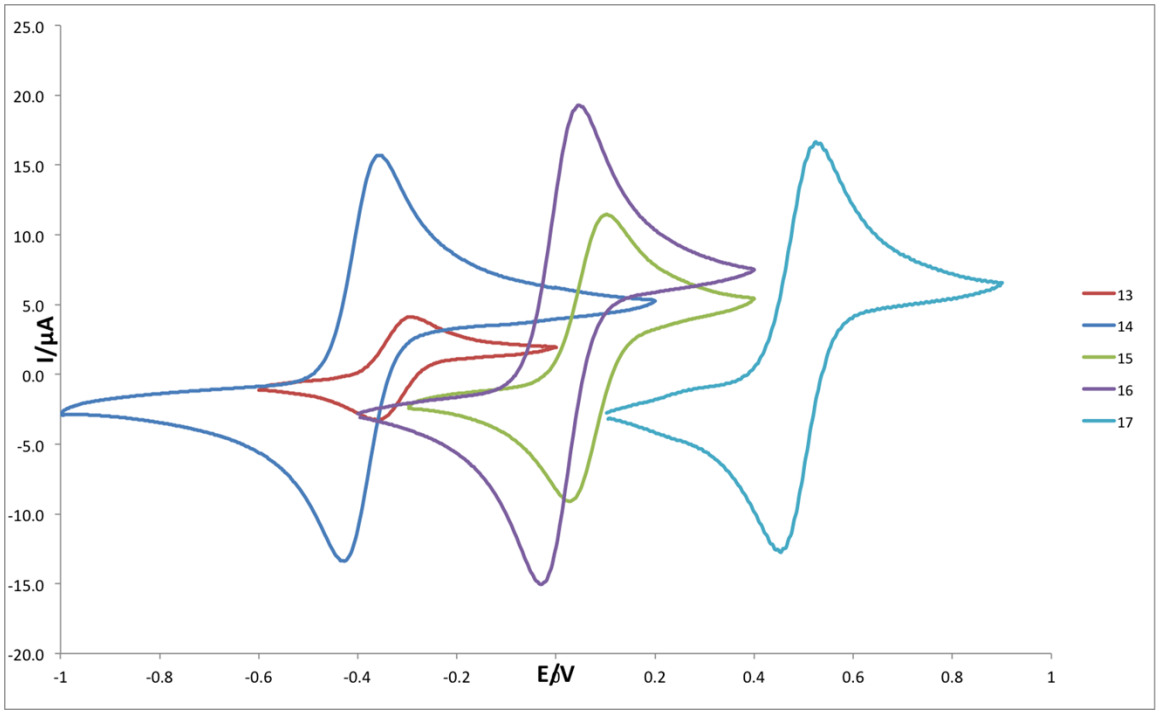


Figure S3. Cyclic voltammograms of complexes **13-17**.*

*Compounds 12 and 13 were less soluble in the electrolyte than the other compounds resulting in a lower observed current.

Table S2 E_{pa}, E_{pc} and ΔE for Series II and III complexes.

Series II	E_{pa}/V	E_{pc}/V	ΔE/V	I_{pa}/I_{pc}
8 (acac)	-1.032	-1.095	63	-
9 (NO_2-acac)	-0.355	-0.424	69	0.9556
10 (Br-acac)	-0.784	-0.877	93	1.0139
11† (I-acac)	-0.782	-0.877	95	1.0843
12 (dbm)	-0.870	-0.941	71	1.0406
Series III	E_{pa}/V	E_{pc}/V	ΔE/V	I_{pa}/I_{pc}
13 (dbm)	-0.387	-0.445	59	1.0204
14 (acac)	-0.446	-0.510	63	0.9828
15 (NO_2-acac)	-0.019	-0.089	71	0.9686
16 (tfac)	-0.050	-0.123	73	0.9884
17 (hfac)	0.433	0.396	73	0.9999

Analysis using Hammett Constants

The sum of Hammett constants for β-diketones in a complex can be calculated using the following equation:

$\Sigma\sigma_{pmp} = n[\sigma_p(R) + \sigma_m(R') + \sigma_p(R'')]$

where n = number of β-diketones in complex.[18]

Using available literature data,[19] the sums of Hammett constants ($\Sigma\sigma_{pmp}$) for ruthenium complexes were compiled and the data are shown in Table 4.[1]

[1] For complexes **6** and **7** the substituent constants are only an approximation using a 4-substituted phenyl ring as a model as there is no data available for a para-substituted benzyl ring.

Table S3 Sums of the Hammett constants, $\Sigma\sigma_{pmp}$, for complexes **1**-**17**.

$[Ru(bpy)_2((R^2C(O))_2CR^1))]PF_6$	$\sigma_p(R)$	$\sigma_m(R')$	$\sigma_p(R'')$	$\Sigma\sigma_{pmp}$
1 (R^1=H, R^2=Me)	-0.07	0	-0.07	-0.14
2 (R^1=Me, R^2=Me)	-0.07	-0.17	-0.07	-0.31
3 (R^1=Et, R^2=Me)	-0.07	-0.15	-0.07	-0.29
4 (R^1=Br, R^2=Me)	-0.07	0.23	-0.07	0.09
5 (R^1=H, R^2=*i*Pr)	-0.06	0	-0.06	-0.12
6 (R^1=*p*-MeOBn, R^2=H)	-0.07	-0.08*	-0.07	-0.22
7 (R^1=*p*-NO_2Bn, R^2=H)	-0.07	0.26*	-0.07	0.12
Series II ([Ru(β-diketonato)$_3$]				
8 (acac)	-0.07	0	-0.07	-0.42
9 (NO_2-acac)	-0.07	0.78	-0.07	1.92
10 (Br-acac)	-0.07	0.23	-0.07	0.27
11† (I-acac)	-0.07	0.18	-0.07	0.12
12 (dbm)	0.06	0	0.06	0.36
Series III [Ru(bpy)(β-diketonato)$_2$]				
13 (dbm)	0.06	0	0.06	0.24
14 (acac)	-0.07	0	-0.07	-0.28
15 (NO_2-acac)	-0.07	0.78	-0.07	1.28
16 (tfac)	0.43	0	-0.07	0.72
17 (hfac)	0.43	0	0.43	1.72

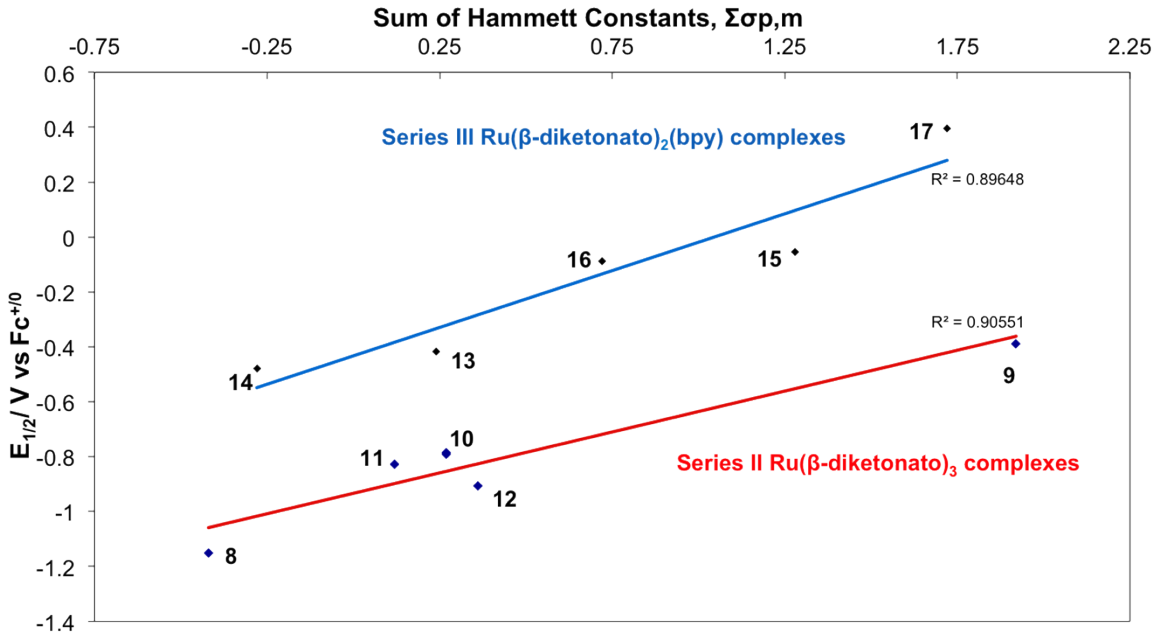


Figure S4 $E_{1/2}$ vs the sum of the Hammett constants (Σσpmp) for Series II and Series III complexes.

It was expected that the increase in $\Sigma\sigma_{pmp}$ would be inversely proportional to the strength of the donor character of the substituent according to the Hammett constants.

Given that the correlation between $\Sigma\sigma_{p,m}$ and $E_{1/2}$ is derived entirely from substituents on the β-diketone ligands it was anticipated that Series II complexes, of the form Ru(β-diketonato)$_3$, would display the most linear relationship in this analysis. As expected a strong linear correlation between between $\Sigma\sigma_{pmp}$ and $E_{1/2}$ was observed for Series II (Figure 1). However, the data recorded for Series III complexes (wherein one β-diketonato ligand is substituted for a bpy) also showed a pronounced linear relationship. No correlation was established for the data derived from the Series I complexes.

Table S4 $\Sigma E_{(L)}$ of selected complexes and their $E_{1/2}$ (*vs* NHE)

Series I	$E_{1/2}$/V	$\Sigma E_{(L)}$/V
1 (R^1=H, R^2=Me)	-0.314	0.438
2 (R^1=Me, R^2=Me)	-0.414	0.408
4 (R^1=Br, R^2=Me)	-0.361	0.488
5 (R^1=H, R^2=^{i}Pr)	-0.341	0.388
Series II		
8 (acac)	-1.602	-0.24
10 (Br-acac)	-1.372	-0.09
11(I-acac)	-1.371	-0.09
12 (dbm)	-1.448	0.36
Series III		
13 (dbm)	-0.958	0.179
14 (acac)	-1.020	0.099
16 (tfac)	-0.146	0.319
17 (hfac)	-0.629	0.599

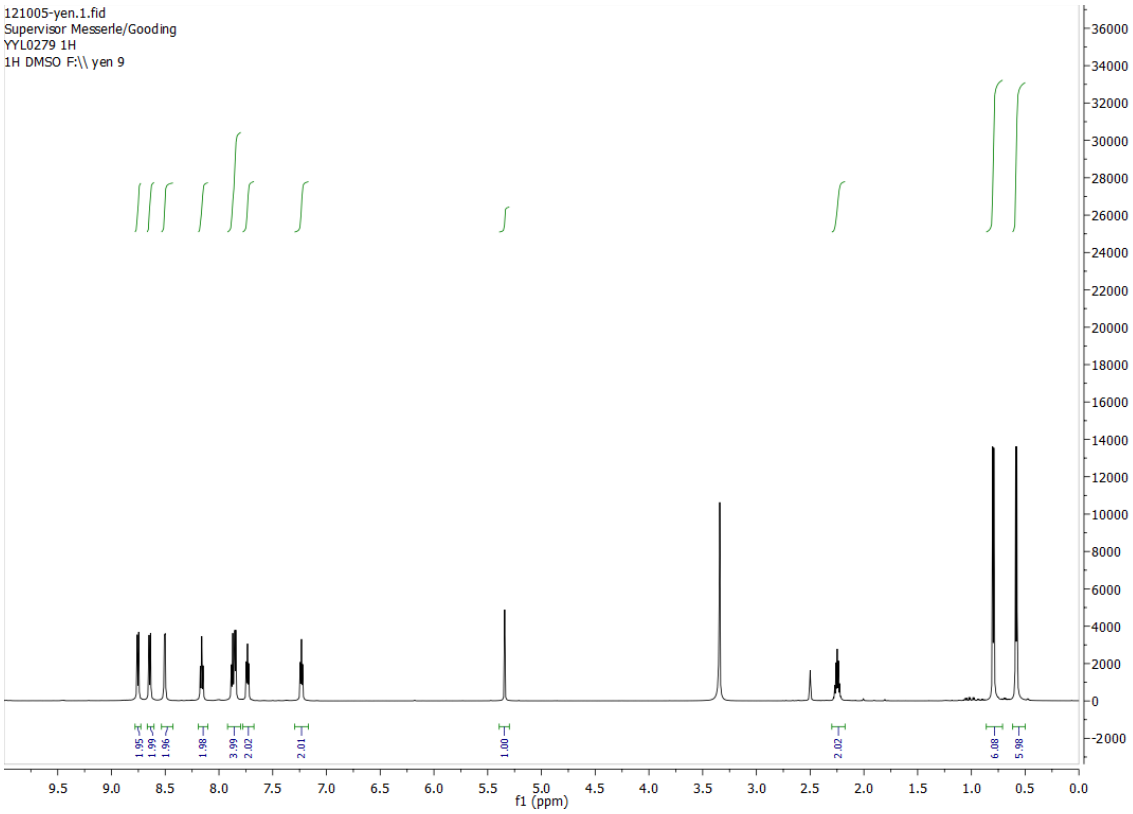


Figure S5 ^{1}H NMR spectrum of compound **5**.

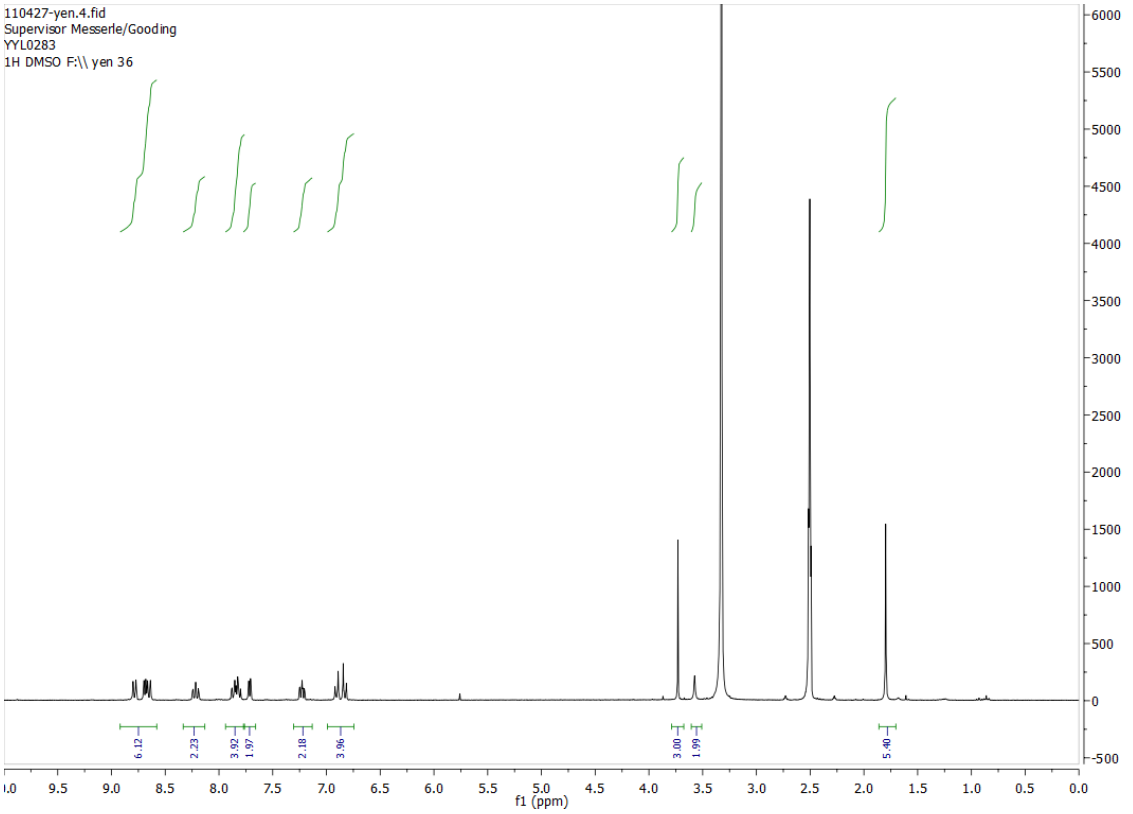


Figure S6 ^{1}H NMR spectrum of compound **6**.

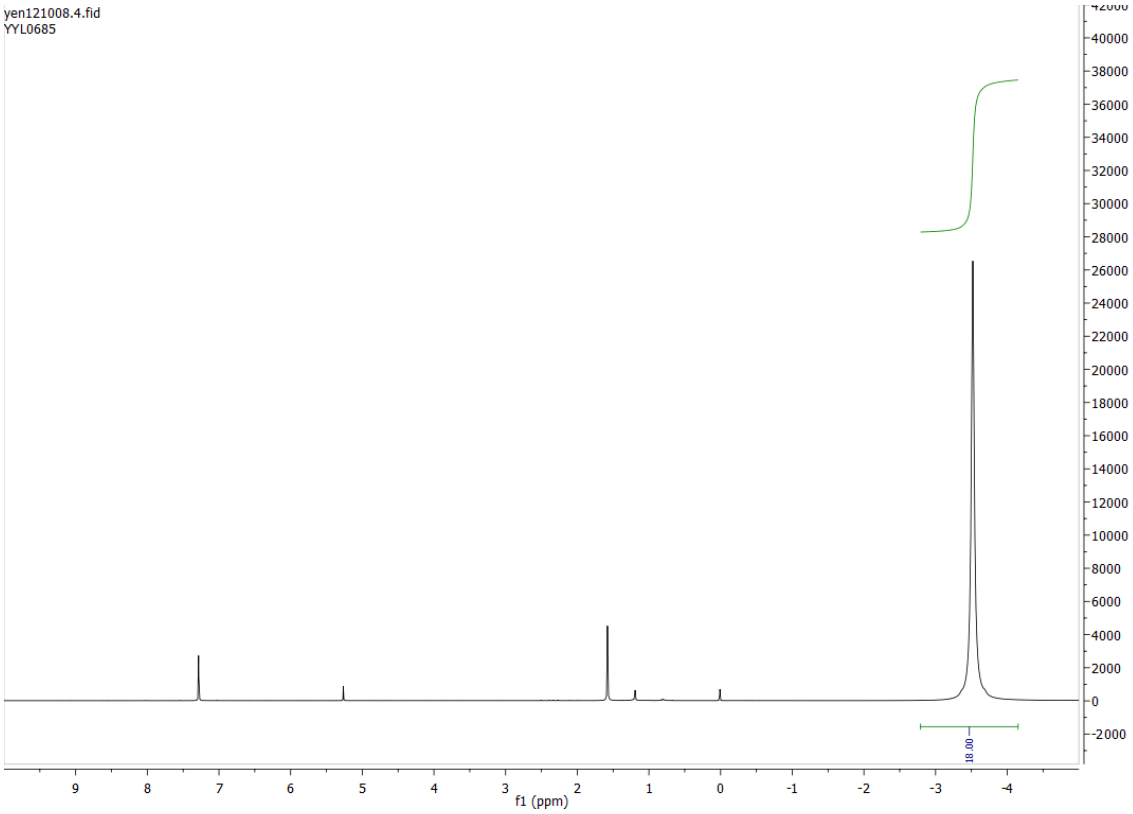


Figure S7 ^{1}H NMR spectrum of compound **9**.

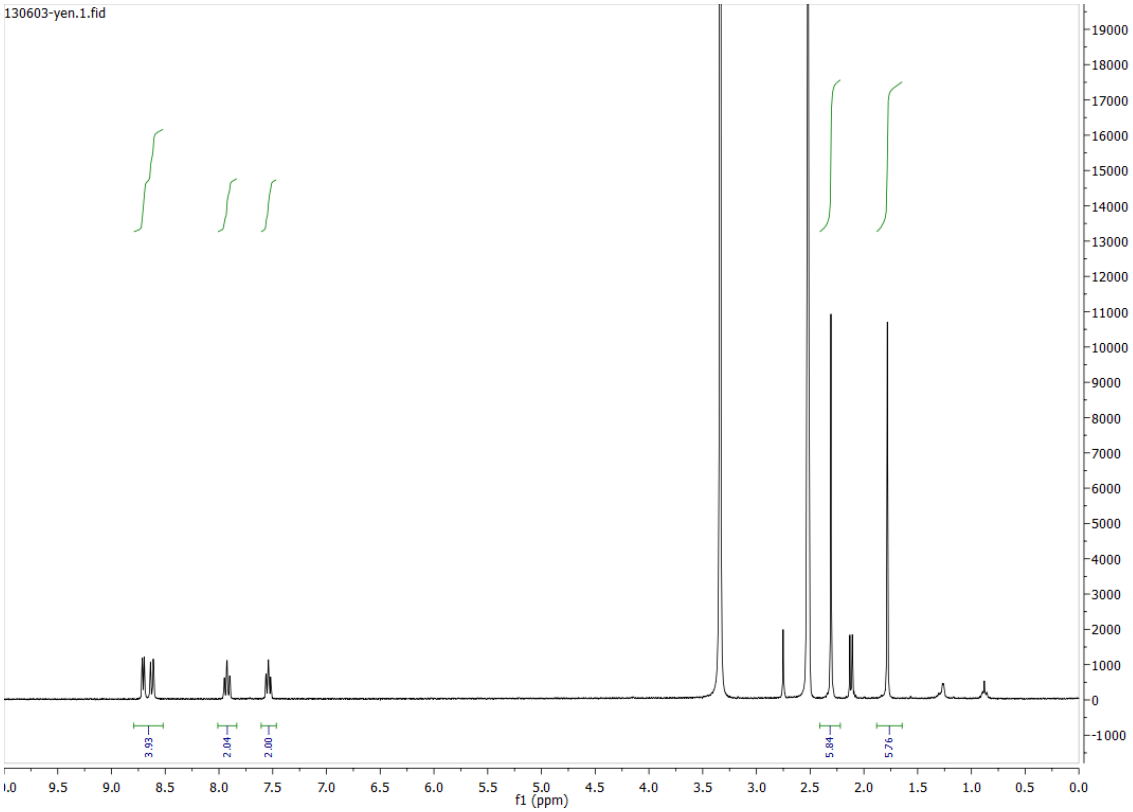


Figure S8 ^{1}H NMR spectrum of compound **15**.

References:

1. S. Munery, J. Jaud and J. Bonvoisin, *Inorg. Chem. Commun.*, 2008, 11, 975-977.
2. U. Jana, S. Biswas and S. Maiti, *Tetrahedron Lett.*, 2007, 48, 4065-4069.
3. A. A. Tregubov, K. Q. Vuong, E. Luais, J. J. Gooding and B. A. Messerle, *J. Am. Chem. Soc.*, 2013, 135, 16429-16437.
4. M. S. Chan and A. C. Wahl, *J. Phys. Chem.*, 1985, 89, 5829-5831.
5. A. M. El-Hendawy, A. H. Al-Kubaisi and H. A. Al-Madfa, *Polyhedron*, 1997, 16, 3039-3045.
6. M. M. Allard, O. S. Odongo, M. M. Lee, Y.-J. Chen, J. F. Endicott and H. B. Schlegel, *Inorg. Chem.*, 2010, 49, 6840-6852.
7. T. S. Knowles, M. E. Howells, B. J. Howlin, G. W. Smith and C. A. Amodio, *Polyhedron*, 1994, 13, 2197-2203.
8. L. Wolf, E. Butter and H. Weinelt, *Z. Anorg. Allg. Chem.*, 1960, 306, 87-93.
9. A. Endo, M. Kajitani, M. Mukaida, K. Shimizu and G. P. Sato, *Inorg. Chim. Acta*, 1988, 150, 25-34.
10. J. P. Collman and W. L. Young, III, *Inorg. Syn. (Jacob Kleinberg, editor. McGraw)*, 1963, 7, 205-207.
11. A. Endo, K. Shimizu and G. P. Satô, *Chem. Lett.*, 1985, 1985, 581-584.
12. T. Kobayashi, Y. Nishina, K. Shimizu and G. P. Satô, *Chem. Lett.*, 1988, 1137-1140.
13. X. Xiao, J. Sakamoto, M. Tanabe, S. Yamazaki, S. Yamabe and T. Matsumura-Inoue, *J. Electroanal. Chem.*, 2002, 527, 33-40.
14. F. P. Dwyer, H. A. Goodwin and E. C. Gyarfas, *Aust. J. Chem.*, 1963, 16, 42-50.
15. A. K. Gupta and R. K. Poddar, *Indian J. Chem.*, 2000, 39A, 457-460.
16. M. M. Allard, O. S. Odongo, M. M. Lee, Y. Chen, J. F. Endicott and H. B. Schlegel, *Inorg. Chem.*, 2010, 49, 6840-6852.
17. A. M. El-Hendawy, S. Y. Alqaradawi and H. A. Al-Madfa, *Transition Met. Chem. (Dordrecht, Neth.)*, 2000, 25, 572-578.
18. A. Endo, M. Kajitani, S. Mukaida, K. Shimizu and G. P. Satô, *Inorg. Chim. Acta*, 1988, 150, 25-34.
19. C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, 91, 165-195.