Supporting Information

Heteromultimetallic compounds based on polyfunctional carboxylate linkers

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S1. Experimental

General Comments. Unless otherwise stated, all experiments were carried out in the air, and the complexes obtained appear stable towards the atmosphere, whether in solution or the solid-state. Reagents and solvents were used as received from commercial sources. Petroleum ether is the fraction boiling in the 40–60 °C range. The following complexes were prepared following literature routes: *cis*-[$RuCl_2$(dppm)$_2$],[S1] [Ru(CH=CHC_6H_4Me4)Cl(CO)(BTD)(PPh_3)$_2$],[S2] [Ru(C(C≡CPh)=CHPh)Cl(CO)(PPh_3)$_2$],[S3] [ReCl(CO)$_3$(dcbpy)],[S4] (HC≡CC_5H_4)Fe($C_5H_4CO_2H$),[S5] [OsHCl(CO)(BTD)(PPh_3)$_2$] (M = Ru,[S6] Os[S7]), [AuCl(PPh_3)][S8] and [(dppf)$AuCl_2$].[S9] Electrospray (ES) and Fast Atom Bombardment (FAB) mass data were obtained using Micromass LCT Premier and Autospec Q instruments, respectively. Infrared data were obtained using a Perkin-Elmer Spectrum 100 FT-IR spectrometer employing an ATR method, and characteristic triphenylphosphine-associated infrared data are not reported. NMR spectroscopy was performed at 25 °C using Bruker AV400 or AV 500 spectrometers in $CDCl_3$ unless stated otherwise. All coupling constants are in Hertz. Resonances in the ^{31}P{^{1}H} NMR spectrum due to the hexafluorophosphate counteranion were observed where the formulation indicates but are not included below. Elemental analysis data were obtained from London Metropolitan University. Solvates were confirmed by integration of the ^{1}H NMR spectra. The procedures given provide materials of sufficient purity for synthetic and spectroscopic purposes.

[{Ru(CH=CHC_6H_4Me-4)(CO)(PPh_3)$_2$}$_2$(*μ*-dcbpy)] (1)

A solution of 2,2'-bipyridine-4,4'-dicarboxylic acid (10.0 mg, 0.041 mmol) and sodium methoxide (6.7 mg, 0.123 mmol) in methanol (10 mL) was stirred at room temperature for 30 minutes. A dichloromethane (20 mL) solution of [Ru(CH=CHC$_6$H$_4$Me–4)Cl(CO)(BTD)(PPh$_3$)$_2$] (77 mg, 0.082 mmol) was added and stirred for another 2 h at room temperature. All the solvent was removed under vacuum and the crude product was dissolved in dichloromethane (10 mL) and filtered through Celite to remove NaCl, NaOMe and excess ligand. The solvent was again removed using rotary evaporator. Diethyl ether (10 mL) was added, and the resulting mixture triturated in the ultrasonic bath. The dark brown precipitate obtained was filtered under vacuum, washed with diethyl ether (10 mL) and dried. Yield: 34 mg (47%). The product can be recrystallised from dichloromethane-diethyl ether mixtures. IR: 1928 (ν_{CO}), 1573, 1544 (ν_{OCO}), 1481, 1433, 1185, 1090, 979, 875, 836, 741, 692 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.23 (s, 6H, CH$_3$), 5.89 (d, 2H, Hβ, J_{HH} = 15.2 Hz), 6.35, 6.82 (AB, 8H, C$_6$H$_4$, J_{AB} = 7.8 Hz), 6.92 (dd, 2H, bpy, J_{HH} = 4.9, 1.4 Hz), 7.30 – 7.43, 7.50 (m x 2, 60H, C$_6$H$_5$), 7.66 (m, 2H, bpy), 7.82 (dt, 2H, Hα, J_{HH} = 15.2 Hz, J_{HP} = 2.7), 8.46 (d, 2H, bpy, J_{HH} = 4.9) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 38.2 (s, PPh$_3$) ppm. MS (ES +ve) *m/z* (abundance): 1894 (4) [M+4Na+H$_2$O]$^+$, 1543 (3) [M–PPh$_3$+Na]$^+$, 1113 (50) [M–vinyl–CO–2PPh$_3$]$^+$, 991 (100) [M–CO–3PPh$_3$+Na]$^+$. Elem. Anal. Calcd. for C$_{104}$H$_{84}$N$_2$O$_6$P$_4$Ru$_2$·2.5CH$_2$Cl$_2$ (M$_W$ = 1996.16): C 64.1, H 4.5, N 1.4%. Found: C 63.7, H 4.2, N 1.8%

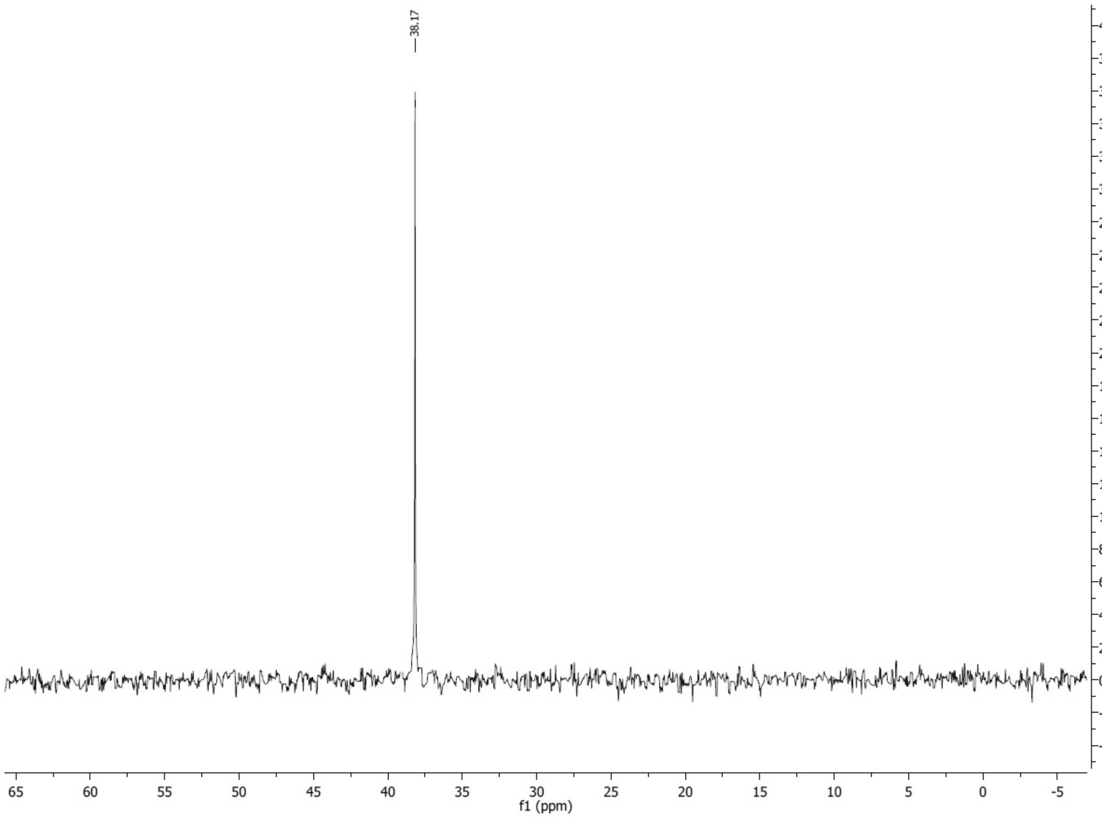

Figure S1-1. ^{31}P{^{1}H} NMR spectrum of compound **1** in CDCl$_3$.

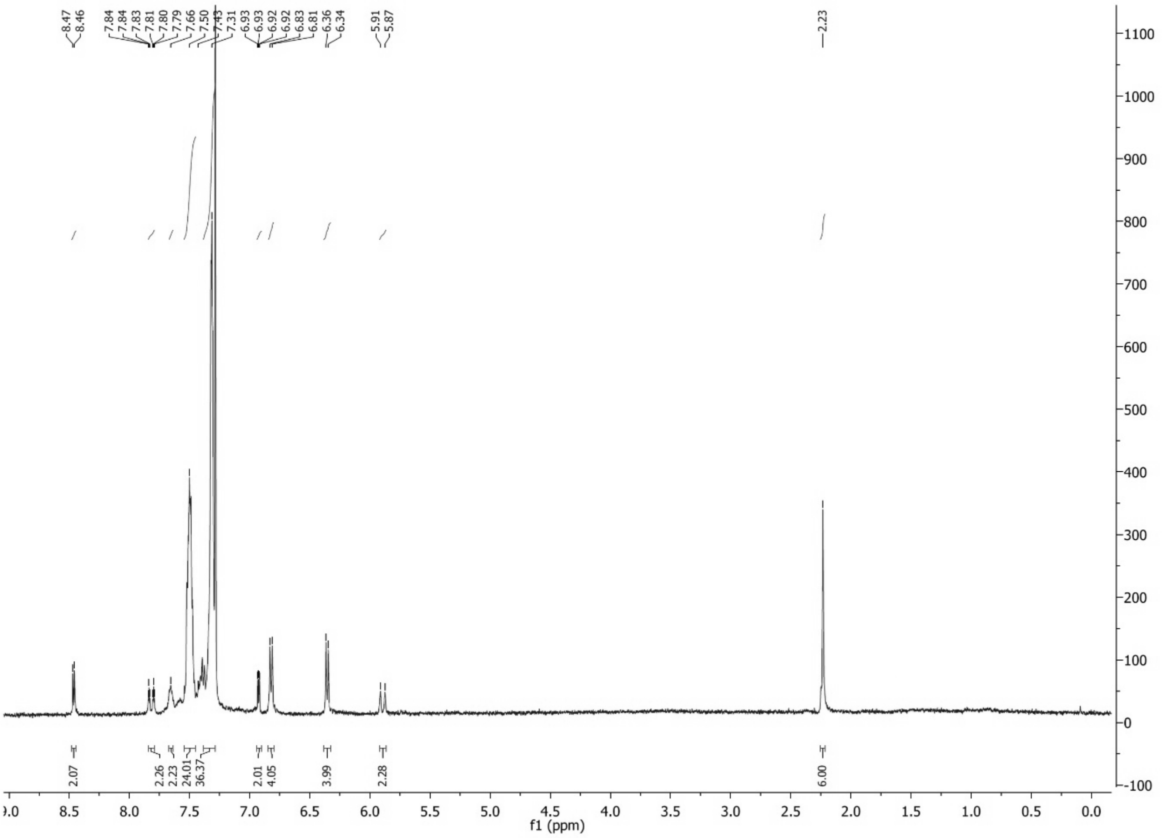

Figure S1-2. ^1H NMR spectrum of compound **1** in $CDCl_3$.

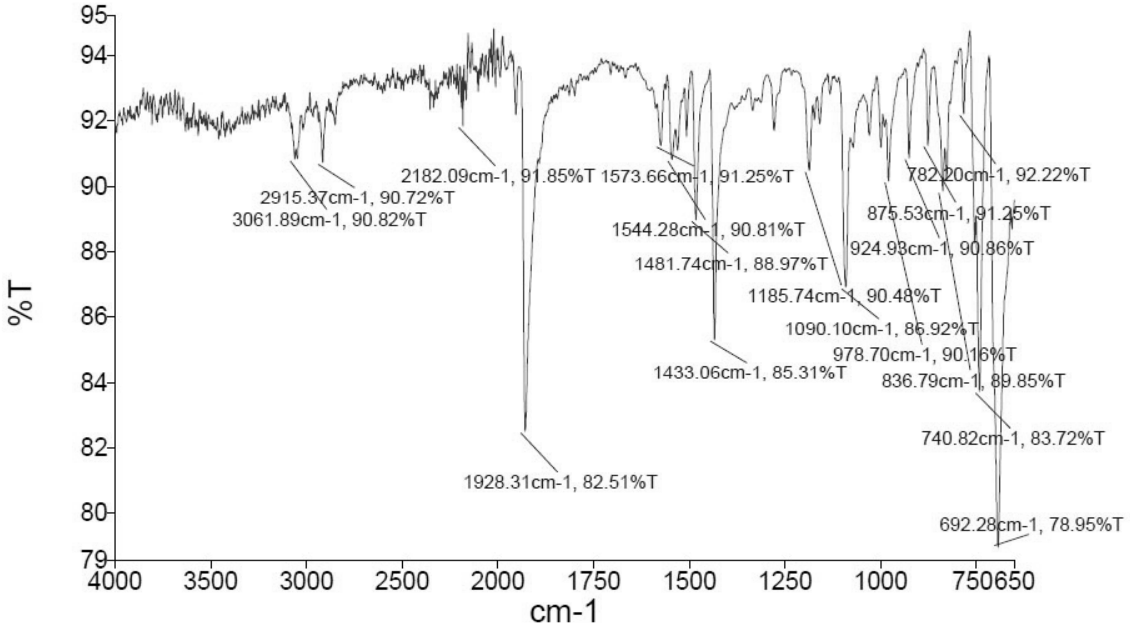

Figure S1-3. Solid-state infrared spectrum of compound **1**.

[{Ru(C(C≡CPh)=CHPh)(CO)(PPh$_3$)$_2$}$_2$(*μ*-dcbpy)] (2)

A methanolic solution (10 ml) of 2,2'-bipyridine-4,4'-dicarboxylic acid (20 mg, 0.082 mmol) and sodium methoxide (13.3 mg, 0.246 mmol) was stirred for 30 minutes at room temperature and treated with a dichloromethane solution (10 mL) of [Ru(C(C≡CPh)=CHPh)Cl(CO)(PPh$_3$)$_2$] (146.3 mg, 0.164 mmol). The reaction was stirred for 2h at room temperature. The solvent was removed under vacuum (rotary evaporator) and the resulting red product was dissolved in the minimum amount of dichloromethane. This was filtered through Celite and the solvent removed by rotary evaporation. Diethyl ether (10 mL) was added, and subsequent ultrasonic titruration provided a dark red precipitate, which was filtered, washed with diethyl ether (10 mL) and dried. Yield: 80 mg (50%). The product is slightly soluble in diethyl ether. IR: 2163 ($\nu_{C\equiv C}$), 1929 (ν_{CO}), 1522 (ν_{OCO}), 1482, 1432, 1186, 1094, 877, 743, 691 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 6.01 (s(br), 2H, Hβ), 6.92 (dd, 2H, bpy, J_{HH} = 6.2), 7.00 (m, 6H, C_6H_5), 7.09 (t, 6H, CC_6H_5, J_{HH} = 7.5 Hz), 7.20 - 7.22 (m, 34H, PC_6H_5), 7.35 (m, 4H, CC_6H_5), 7.42 (t, 4H, CC_6H_5, J_{HH} = 7.5 Hz), 7.54 - 7.59 (m, 26H, PC_6H_5), 7.78 (m, 2H, bpy), 8.46 (dd, 2H, bpy) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 38.2 (s, PPh$_3$) ppm. MS (ES +ve) *m/z* (abundance): 1980 (10) [M+H+Na]$^+$, 897 (100) [M–4PPh$_3$–CO+H$_2$O]$^+$. Elem. Anal. Calcd. for $C_{118}H_{88}N_2O_6P_4Ru_2$ (M_W = 1956.01): C 72.4, H 4.5, N 1.4%. Found: C 72.3, H 4.3, N 1.6%.

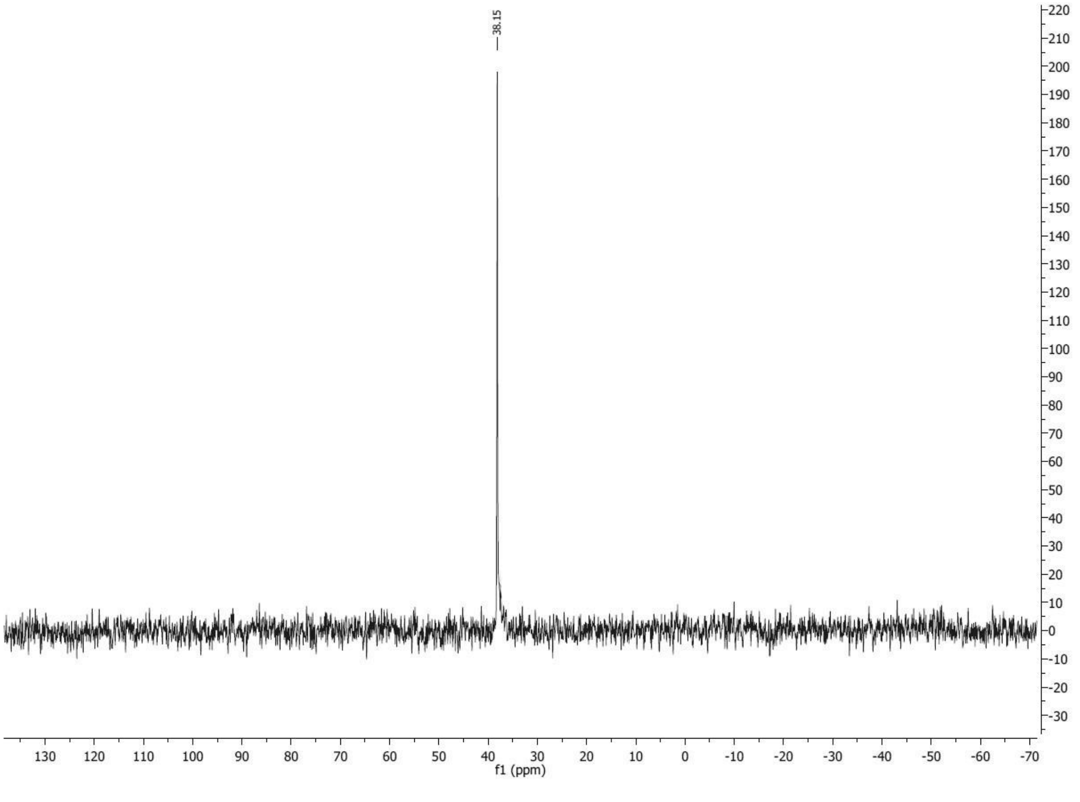

Figure S1-4. ^{31}P{^{1}H} NMR spectrum of compound **2** in CDCl$_3$.

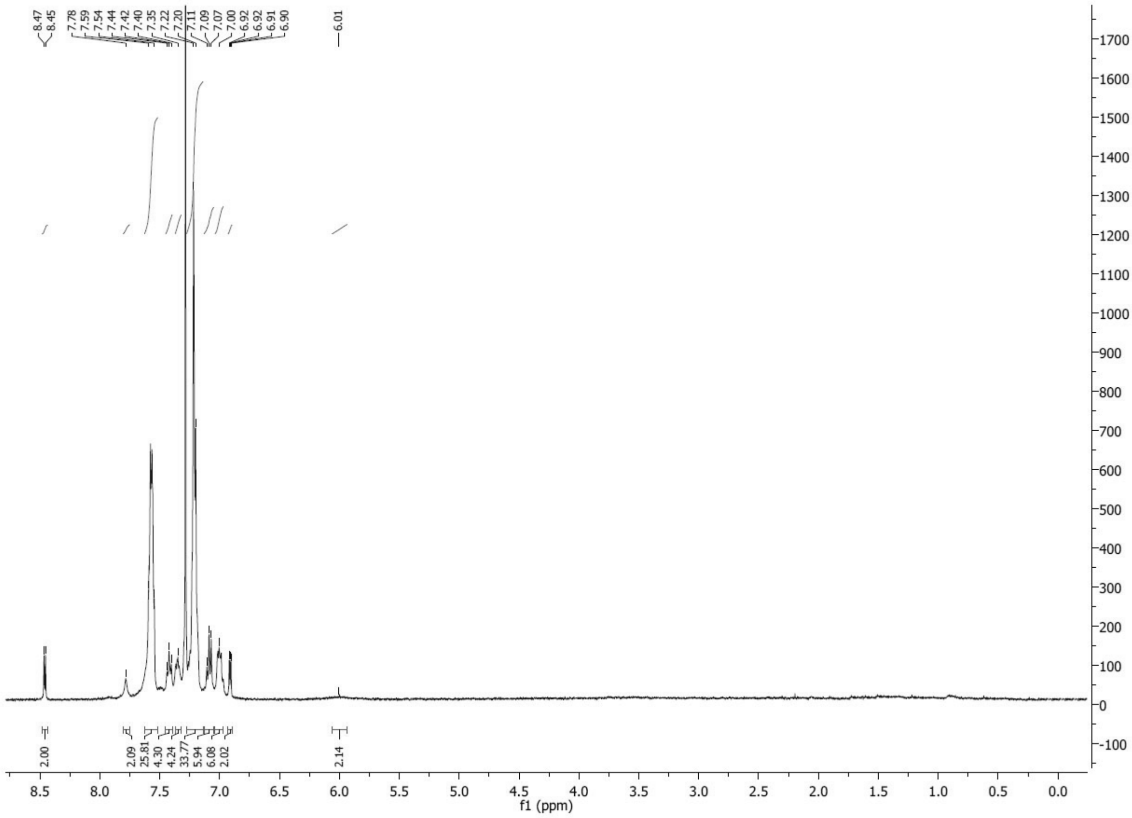

Figure S1-5. ^{1}H NMR spectrum of compound **2** in CDCl$_3$.

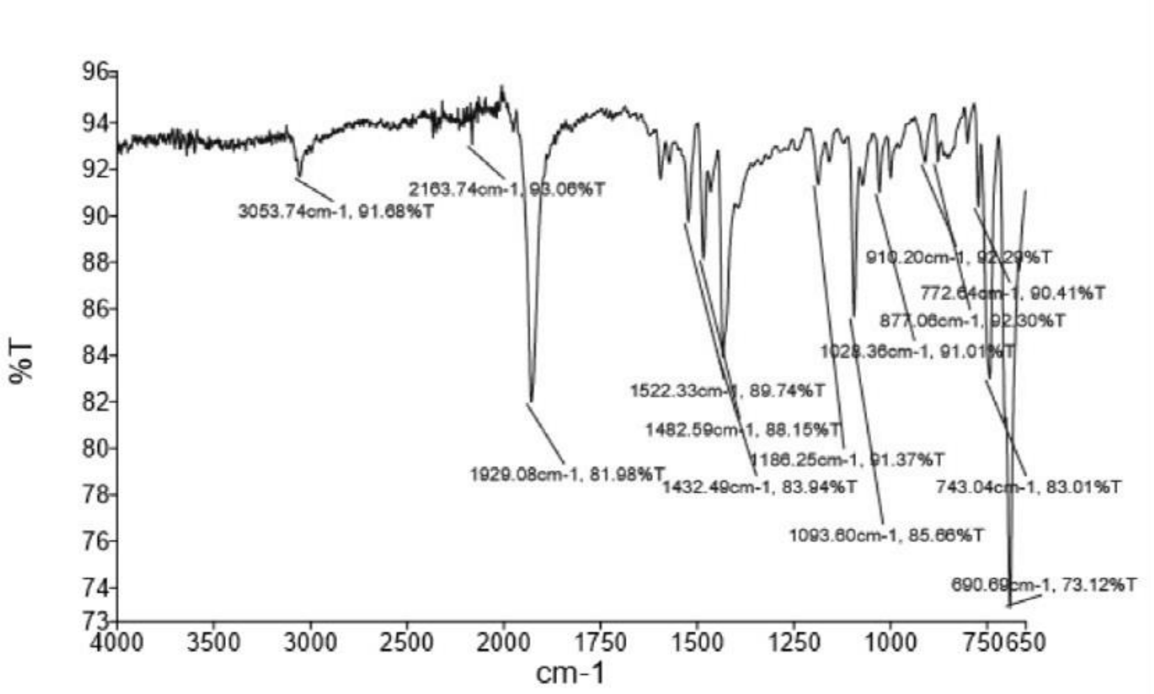

Figure S1-6. Solid-state infrared spectrum of compound **2**.

[{Ru(dppm)$_2$}$_2$(μ-dcbpy)](PF$_6$)$_2$ (3·2PF$_6$)

A solution of 2,2'-bipyridine-4,4'-dicarboxylic acid (10.0 mg, 0.041 mmol) and sodium methoxide (8.9 mg, 0.164 mmol) in methanol (10 mL) was stirred for 30 minutes at room temperature. A solution of *cis*-[RuCl$_2$(dppm)$_2$] (77 mg, 0.082 mmol) in dichloromethane (20 mL) was then added along with ammonium hexafluorophosphate (22.6 mg, 0.123 mmol). The reaction mixture was stirred for 2 h at room temperature. All the solvent was then removed using a rotary evaporator and the crude product was re-dissolved in dichloromethane (10 mL) and filtered through Celite. Ethanol (20 mL) was added and the solvent volume slowly reduced on a rotary evaporator until the formation of a brown solid. The precipitate was filtered, washed with petroleum ether (10 mL) and dried under vacuum. The product is partially soluble in ethanol, contributing to a reduced yield. Yield: 48 mg (51%). IR: 1593, 1521 (ν_{OCO}), 1482, 1426, 1186, 1093, 835 (ν_{PF}) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 4.16, 4.76 (m x 2, 2 x 4H, PCH$_2$P), 6.26 (m, 8H, C$_6$H$_5$), 6.99 − 7.54 (m, 56H + 2H, C$_6$H$_5$ + bpy), 7.65, 7.80 (m x 2, 2 x 8H, C$_6$H$_5$), 8.55 (s, 2H, bpy), 8.91 (d, 2H, bpy, J_{HH} = 4.3 Hz) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ −11.9, 8.7 (pseudotriplet x 2, dppm, J_{PP} = 38.8 Hz) ppm. MS (MALDI +ve) *m/z* (abundance): 2128 (12) [M+H+PF$_6$]$^+$, 1981 (11) [M+H]$^+$. Elem. Anal. Calcd. for $C_{112}H_{94}F_{12}N_2O_4P_{10}Ru_2 \cdot CH_2Cl_2$ (M$_W$ = 2356.75): C 57.6, H 4.1, N 1.2%. Found: C 57.3, H 4.2, N 1.0%. **[{Ru(dppm)$_2$}$_2$(μ-dcbpy)](PF$_6$)$_2$ (3·2BPh$_4$)** was prepared in an identical manner, using sodium tetraphenylborate. Spectroscopic data for the cation were found to be identical to those for **3·2PF$_6$**.

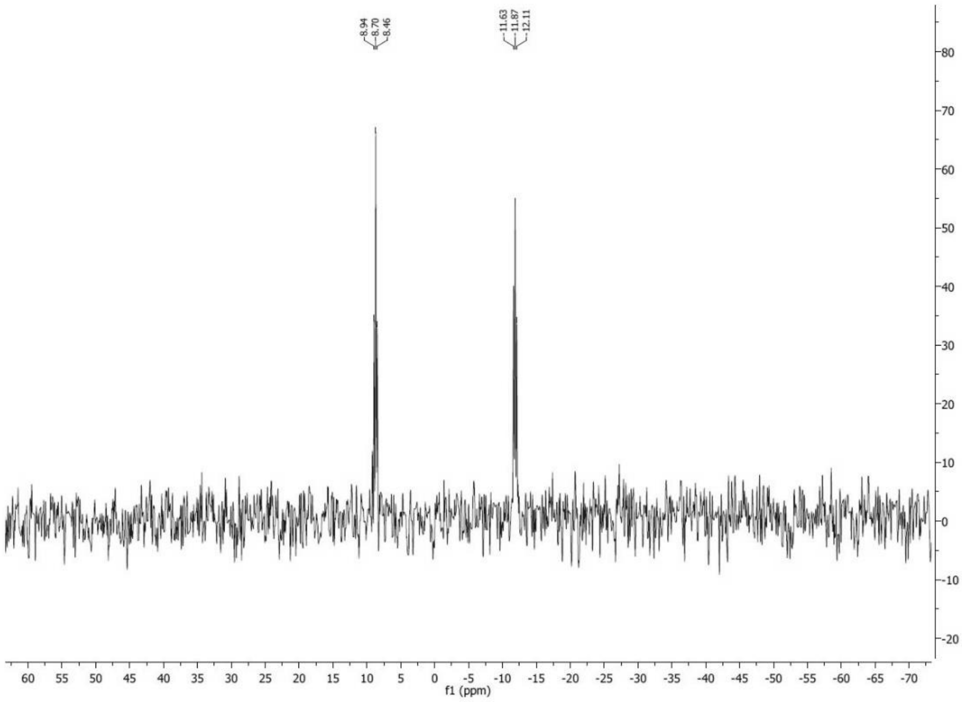

Figure S1-7. ^{31}P{^{1}H} NMR spectrum of compound **3·2PF$_6$** in CDCl$_3$.

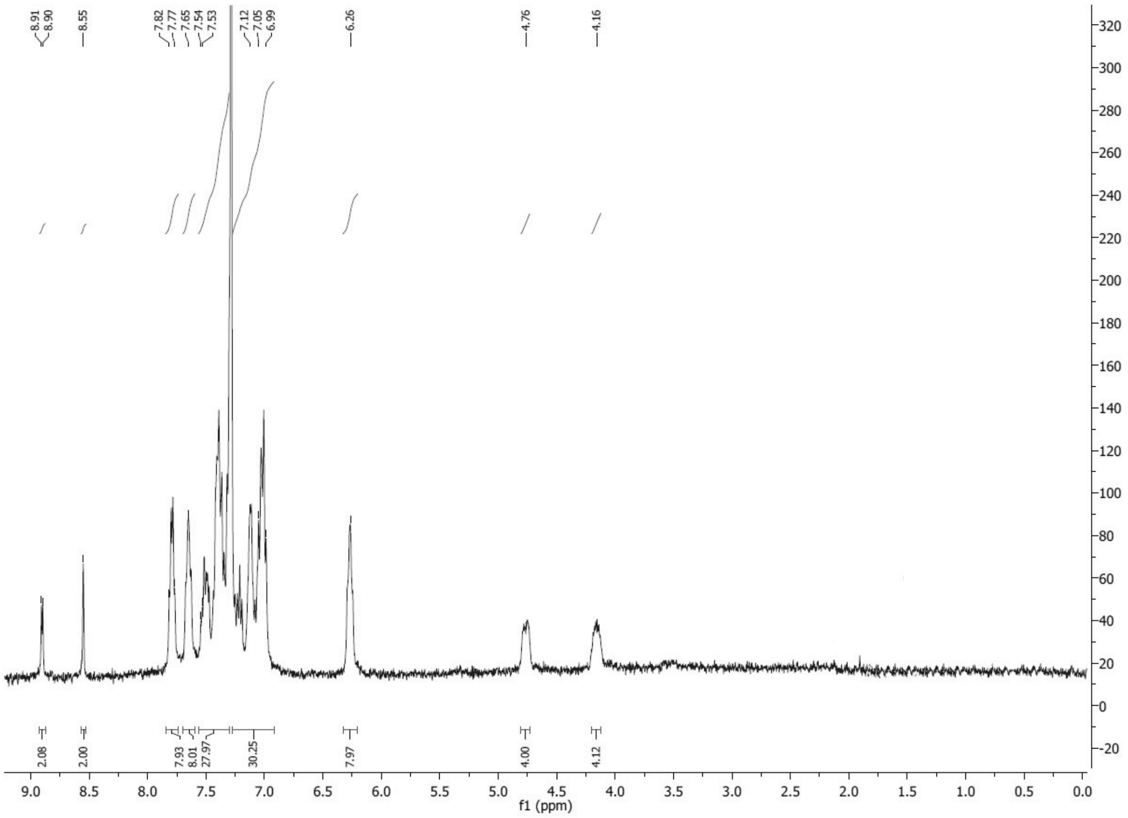

Figure S1-8. ^{1}H NMR spectrum of compound **3·2PF$_6$** in CDCl$_3$.

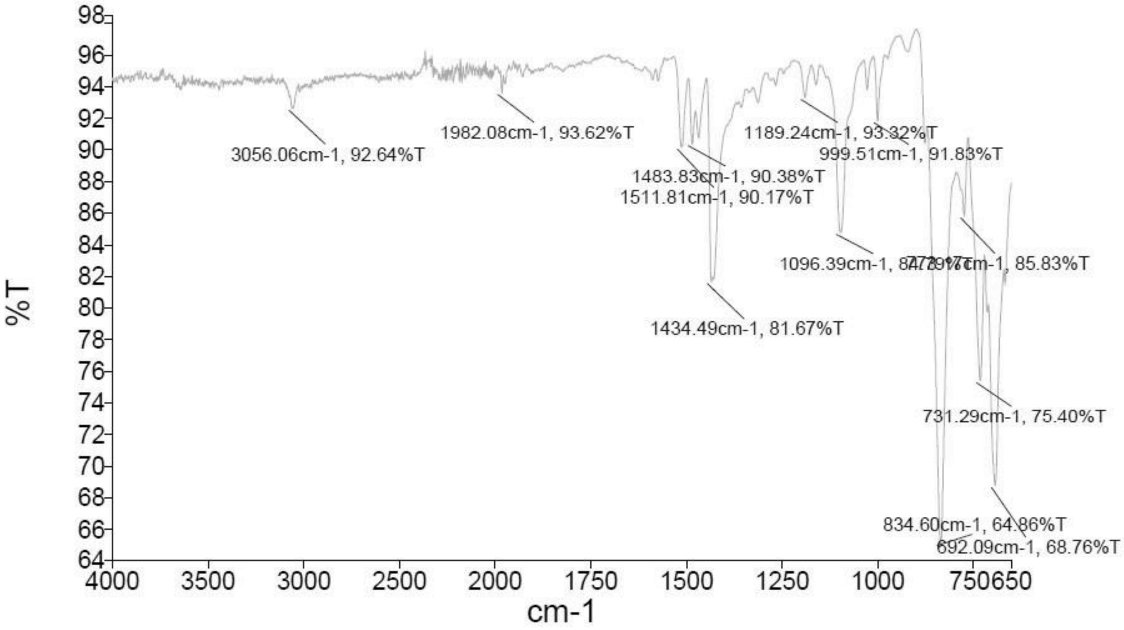

Figure S1-9. Solid-date IR spectrum of compound **3·2PF$_6$**.

[ReCl(CO)$_3$(μ-H$_2$dcbpy)] (4)

Re(CO)$_5$Cl (193 mg, 0.53 mmol) was dissolved in an hot toluene (50 mL) and methanol (20 mL). 4,4'-dicarboxyl-2,2'-bipyridine (130 mg, 0.53 mmol) was added to the solution, and the reaction mixture was stirred under reflux for 1h. During this time, the colour of the solution changed from colourless to orange. The solution was kept at –20 degrees for 1h to precipitate the unreacted starting material which was then filtered. The resulting orange solution was evaporated to dryness to yield the product. Yield: 233 mg (80 %). IR: 2030 (ν_{CO}), 1902 (ν_{CO}), 1875 (ν_{CO}), 1734, 1511 (ν_{OCO}), 1426, 1214, 1095, 832, 772, 731, 691, 663 cm^{-1}. ^{1}H NMR (d_6-DMSO): δ 8.14 (dd, 2H, bpy, J_{HH} = 5.7, 1.7 Hz), 9.15 (dd, 2H, bpy, J_{HH} = 1.7, 0.8 Hz), 9.22 (dd, 2H, bpy, J_{HH} = 5.7, 0.8 Hz), 14.39 (s(br), 2H, CO$_2$H) ppm. The data obtained were found to be in good agreement with those reported in the literature.[S4]

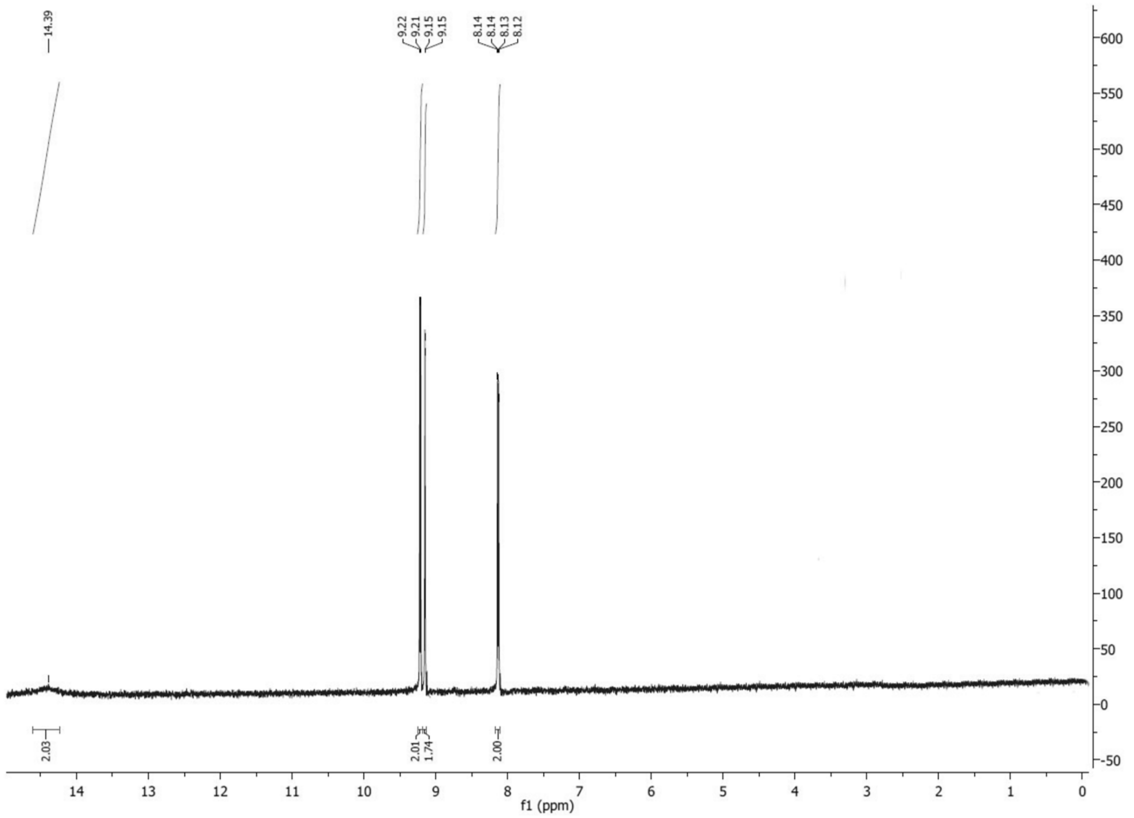

Figure S1-10. ^{1}H NMR spectrum of compound **4** in DMSO (solvent peaks removed).

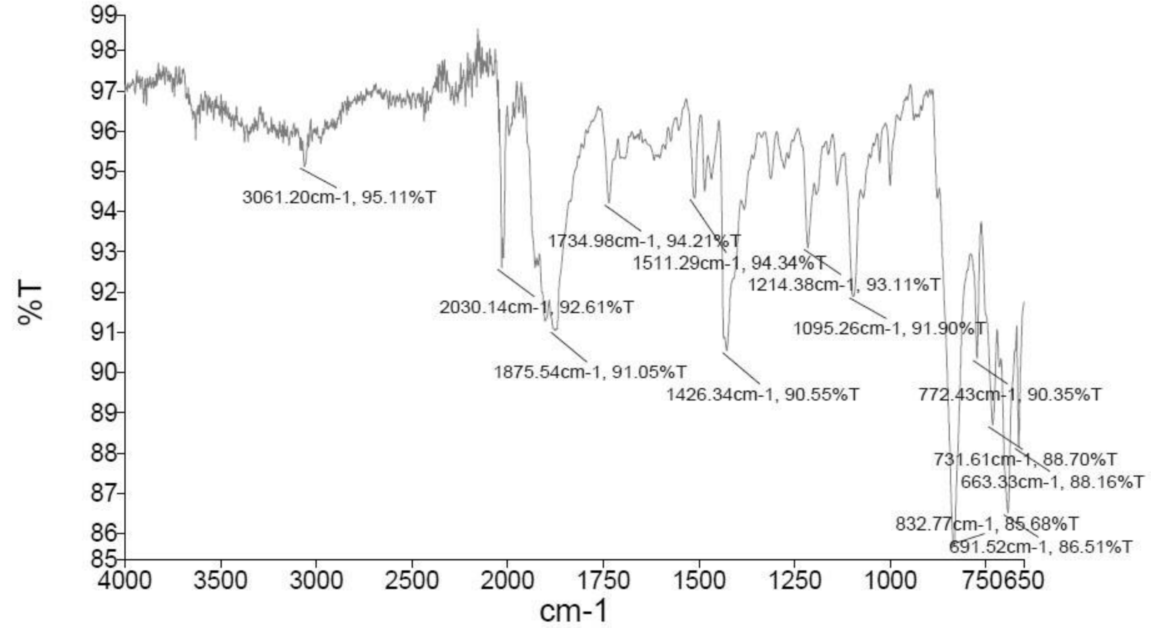

Figure S1-11. Solid-state IR spectrum of compound **4**.

[{Ru(CH=CHC$_6$H$_4$Me-4)(CO)(PPh$_3$)$_2$}$_2$(*μ*-dcbpy)ReCl(CO)$_3$] (5)

A solution of **4** (30 mg, 0.055 mmol) and sodium methoxide (11.9 mg, 0.22 mmol) in methanol (10 mL) was stirred for 30 minutes at room temperature. A solution of [Ru(CH=CHC$_6$H$_4$Me–4)Cl(CO)(BTD)(PPh$_3$)$_2$] (102.7 mg, 0.109 mmol) in dichloromethane (10 mL) was added and stirred for another 2h. Ethanol (10 mL) was added and the solvent volume slowly reduced on a rotary evaporator until the formation of a brown solid was complete. The precipitate was filtered, washed with ethanol (10 mL) and dried under vacuum. Yield: 79 mg (69 %). IR: 2019 (ν_{CO}), 1918 (ν_{CO}), 1890 (ν_{CO}), 1531 (ν_{OCO}), 1481, 1433, 1391, 1184, 1090, 979, 827, 743, 692 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.23 (s, 6H, CH$_3$), 5.94 (d, 2H, Hβ, J_{HH} = 15.0 Hz), 6.38, 6.82 (AB, 8H, C$_6$H$_4$, J_{AB} = 7.7 Hz), 7.01 (dd, 2H, bpy, J_{HH} = 5.6, 1.4 Hz), 7.26 (m, 2H, bpy), 7.36, 7.52 (m x 2, 60H, C$_6$H$_5$), 7.84 (dt, 2H, Hα, J_{HH} = 15.0 Hz, J_{HP} = 2.8 Hz), 8.68 (d, 2H, bpy, J_{HH} = 5.6 Hz) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 206.4 (t, RuCO, J_{PC} = 15.0 Hz), 197.8 (s, 2 x ReCO), 197.6 (s, ReCO), 172.8 (s, CO$_2$), 155.1, 152.6 (s x 2, 2 x bpy), 151.0 (t, Cα, J_{PC} = 11.5 Hz), 142.4 (s, bpy), 138.0 (s, *ipso/p*-C$_6$H$_4$), 134.7 (t^v, *o/m*-C$_6$H$_5$, J_{PC} = 5.4 Hz), 133.7 (s, Cβ), 132.2 (s, *ipso/p*-C$_6$H$_4$), 131.1 (t^v, *ipso*-C$_6$H$_5$, J_{PC} = 22.0 Hz), 130.7 (s, *p*-C$_6$H$_5$), 128.7 (t^v, *o/m*-C$_6$H$_5$, J_{PC} = 5.5 Hz), 128.4 (s, *o/m*-C$_6$H$_4$), 125 (s, bpy), 124.6 (s, *o/m*-C$_6$H$_4$), 121.5 (s, bpy), 21.0 (s, *p*-C$_6$H$_4$) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 38.1 (s, PPh$_3$) ppm. MS (ES +ve) *m/z* (abundance): 1244 (12) [M–3PPh$_3$–3CO+H+Na]$^+$, 1303 (4) [M–3PPh$_3$]$^+$. Elem. Anal. Calcd. for C$_{107}$H$_{84}$N$_2$O$_9$P$_4$ReRu$_2$ (M$_W$ = 2089.51): C 61.5, H 4.1, N 1.3%. Found: C 61.4, H 3.9, N 1.4%.

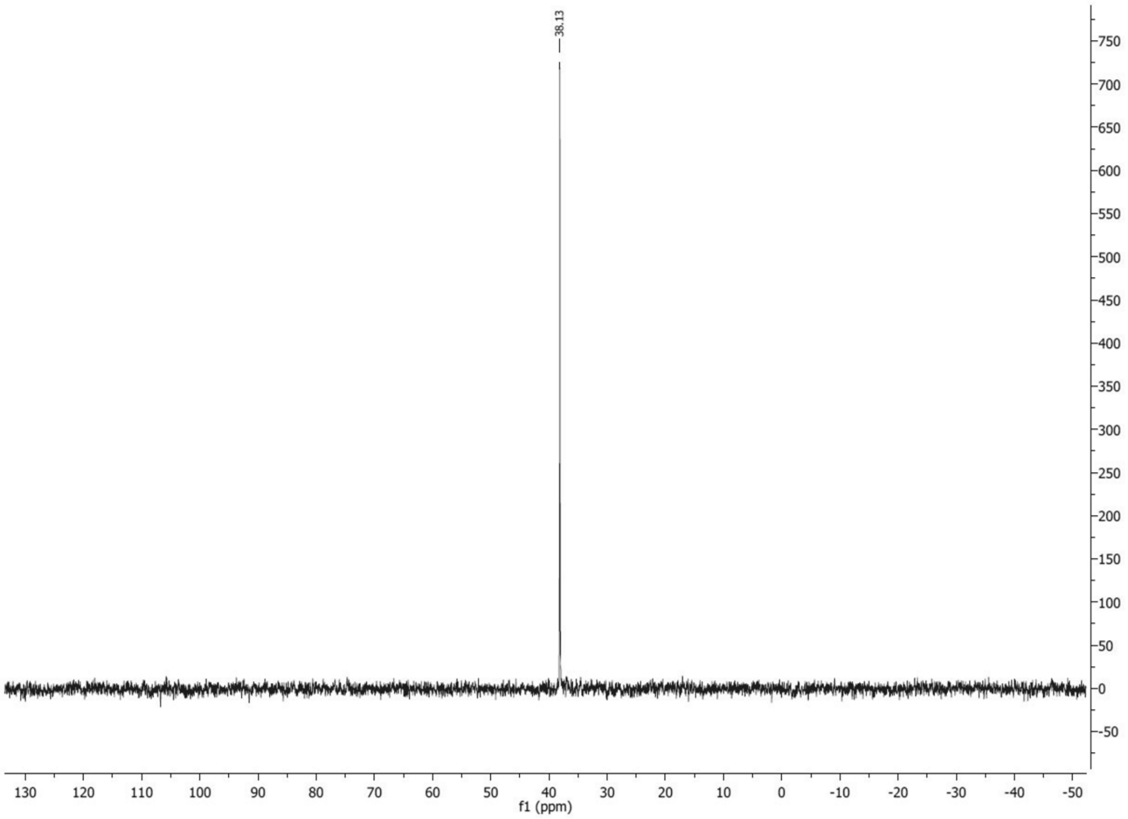

Figure S1-12. $^{31}P\{^{1}H\}$ NMR spectrum of compound **5** in $CDCl_3$.

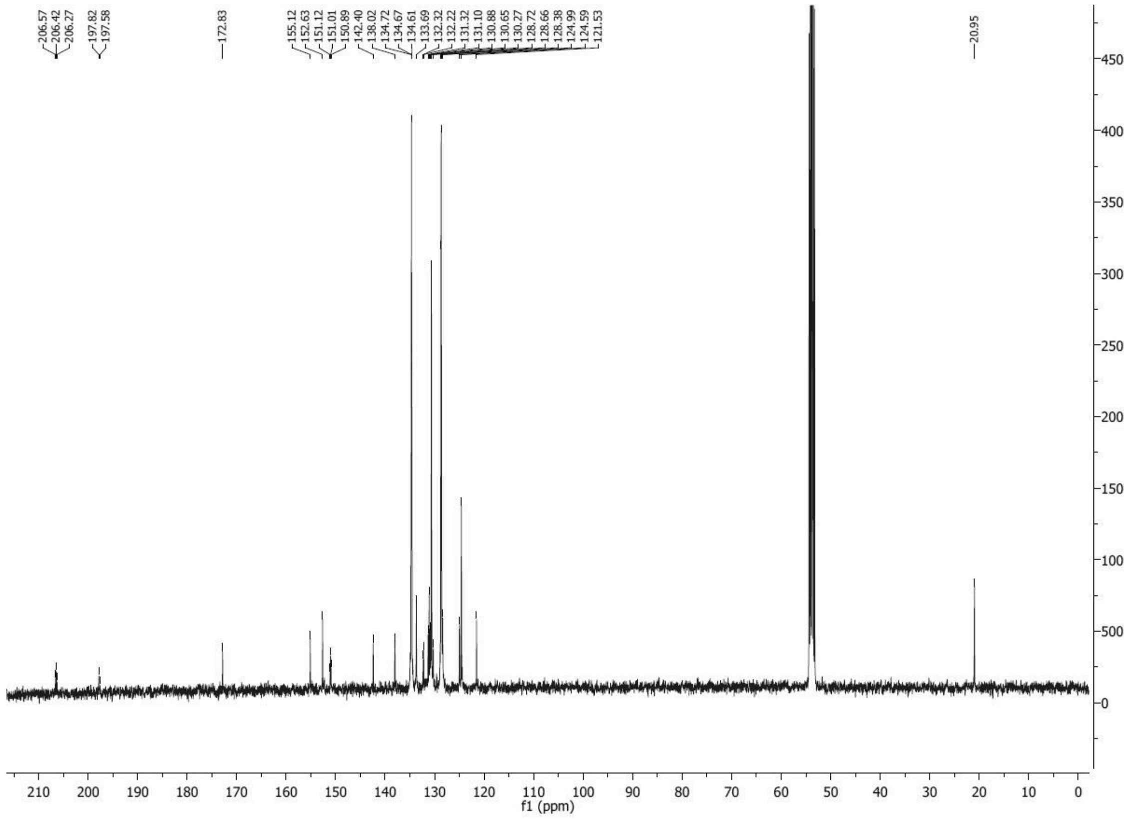

Figure S1-13. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5** in $CDCl_3$.

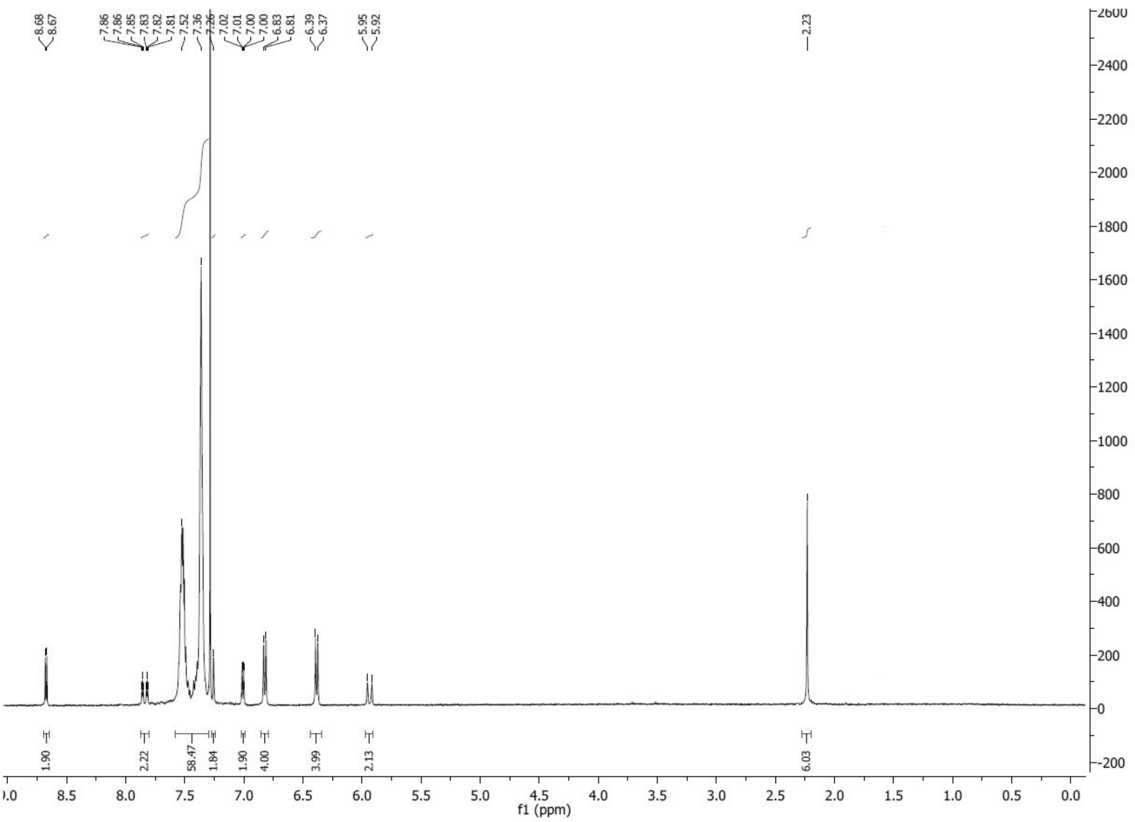

Figure S1-14. ^{1}H NMR spectrum of compound **5** in $CDCl_3$.

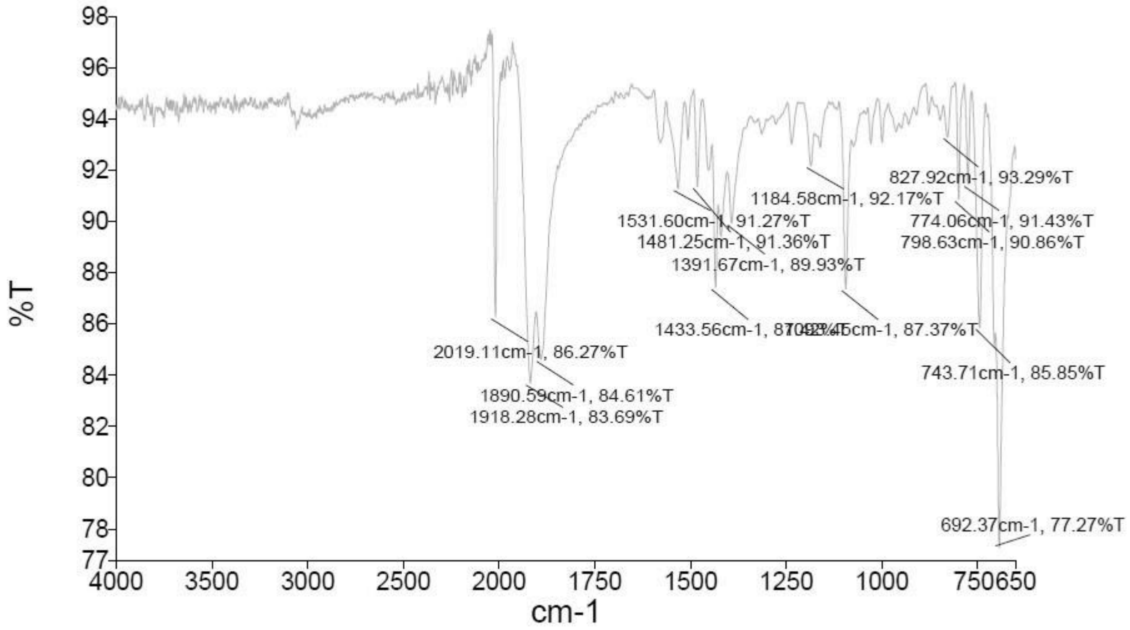

Figure S1-15. Solid-state IR spectrum of compound **5**.

$[\{Ru(C(C{\equiv}CPh)=CHPh)(CO)(PPh_3)_2\}_2(\mu\text{-dcbpy})ReCl(CO)_3]$ (6)

A solution of **4** (30 mg, 0.055 mmol) and sodium methoxide (11.9 mg, 0.22 mmol) in methanol (10 ml) was stirred for 30 minutes at room temperature. A brown solution of $[Ru(C(C{\equiv}CPh)=CHPh)Cl(CO)(PPh_3)_2]$ (97.3 mg, 0.109 mmol) in dichloromethane (10 mL) was added and stirred for another 2h. Ethanol (10 mL) was added and the solvent volume slowly reduced on a rotary evaporator until the formation of a brown solid was complete. The precipitate was filtered, washed with ethanol (10 mL) and dried under vacuum. Yield: 82 mg (66 %). IR: 2019 (ν_{CO}), 1917 (ν_{CO}), 1890 (ν_{CO}), 1531 (ν_{OCO}), 1481, 1433, 1185, 1094, 826, 743, 691 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.12 (s(br), 2H, Hβ), 6.89 (d, 2H, bpy, J_{HH} = 5.6 Hz), 7.04 (m, 6H, CC_6H_5), 7.12 (t, 6H, CC_6H_5, J_{HH} = 7.4 Hz), 7.21 - 7.35 (m, 36H, PC_6H_5), 7.39 -7.46 (m, 8H, CC_6H_5), 7.59 (m, 24H + 2H, PC_6H_5 + bpy), 8.66 (d, 2H, bpy, J_{HH} = 5.6 Hz) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 37.9 (s, PPh_3) ppm. MS (ES +ve) *m/z* (abundance): 1245 (4) $[M–3PPh_3–CO–enynyl]^+$, 898 (100) $[(M–PPh_3–enynyl)/2]^+$. Elem. Anal. Calcd. for $C_{121}H_{88}ClN_2O_9P_4ReRu_2$ (M_W = 2261.70): C 64.3, H 3.9, N 1.2%. Found: C 64.1, H 3.8, N 1.2%.

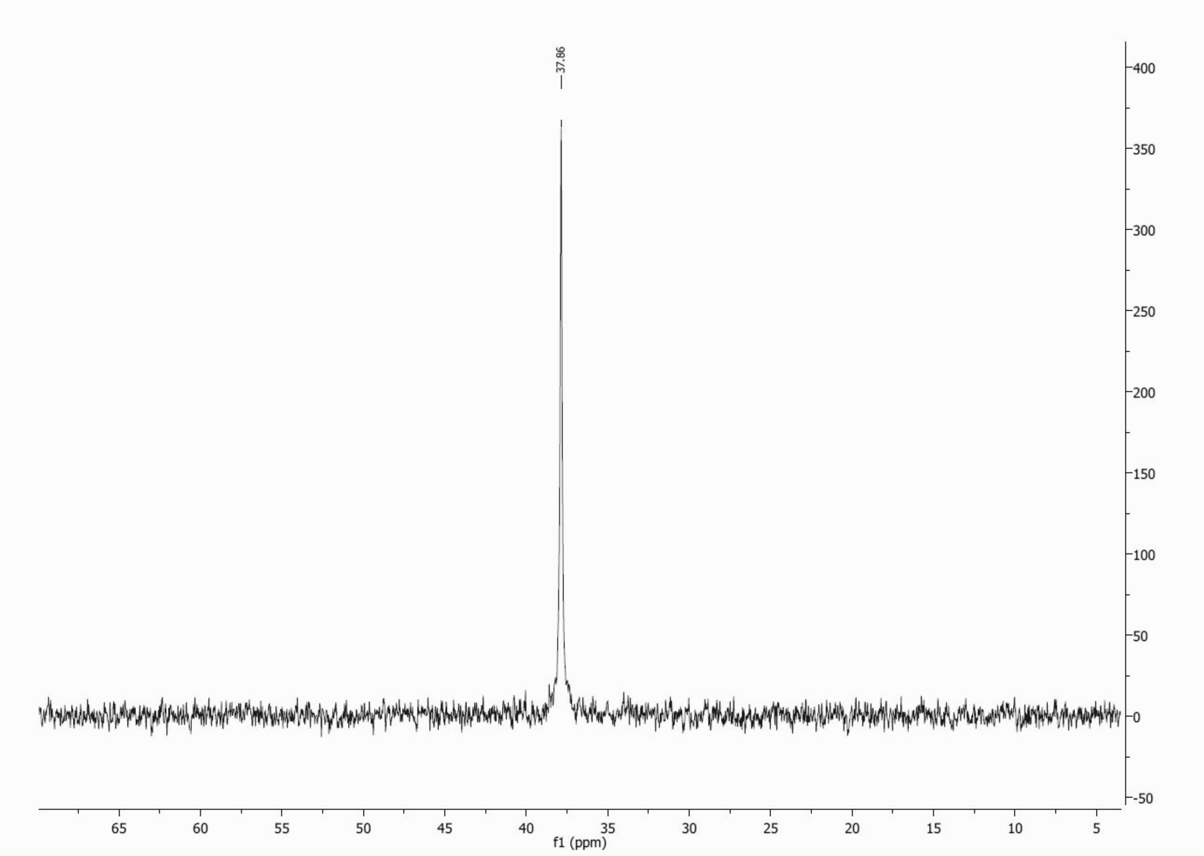

Figure S1-16. $^{31}P\{^1H\}$ NMR spectrum of compound **6** in $CDCl_3$.

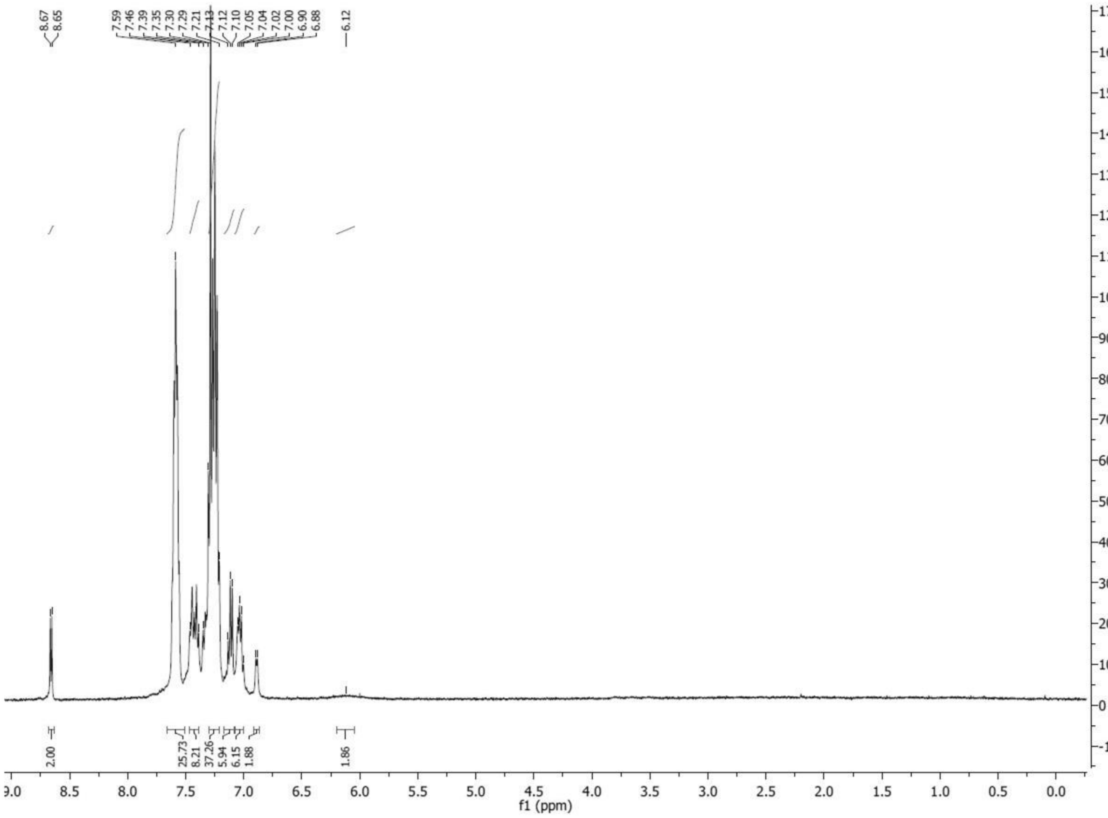

Figure S1-17. ^{1}H NMR spectrum of compound **6** in $CDCl_3$.

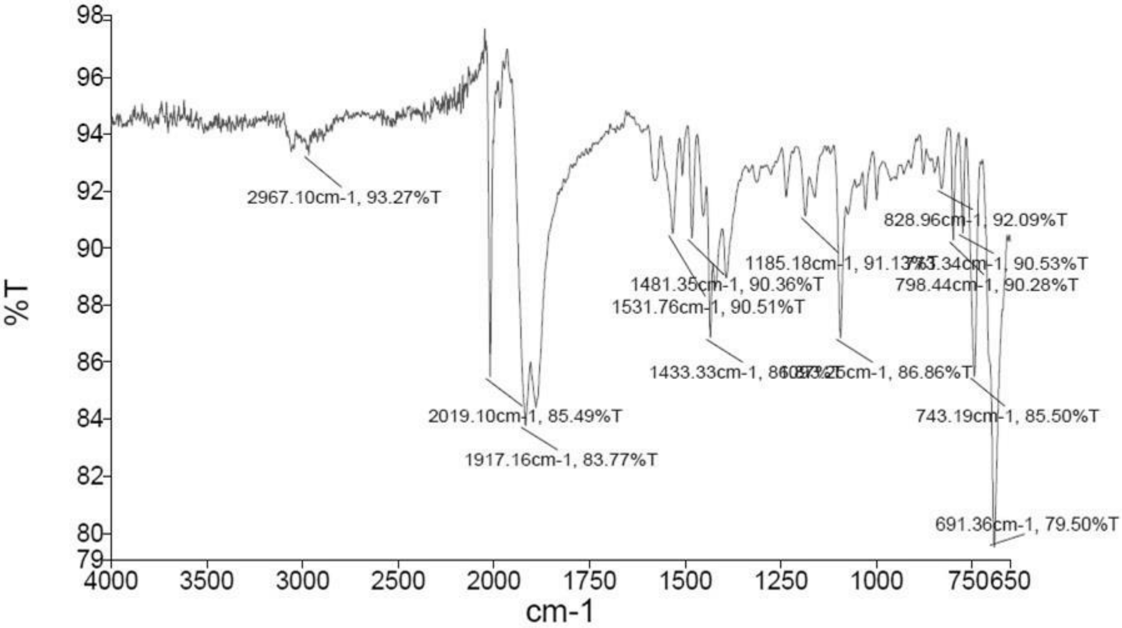

Figure S1-18. Solid-state IR spectrum of compound **6**.

$[\{Ru(dppm)_2\}_2(\mu\text{-dcbpy})ReCl(CO)_3](PF_6)_2$ (7)

An orange solution of **4** (30 mg, 0.055 mmol) and sodium methoxide (11.9 mg, 0.22 mmol) in methanol (10 mL) was stirred for 30 minutes at room temperature. A yellow solution of *cis*-$[RuCl_2(dppm)_2]$ (102.5 mg, 0.11 mmol) in dichloromethane (10 mL) was added to the mixture leading to an immediate colour change to orange. Potassium hexafluorophosphate (40.5 mg, 0.22 mmol) was added and the reaction mixture was stirred for another 1 h at room temperature. All the solvent was removed under vacuum and the crude product was dissolved in dichloromethane (10 mL) and filtered through Celite to remove NaCl, NaOMe and excess ligand. Ethanol (10 mL) was added and the solvent volume was slowly reduced on a rotary evaporator until the formation of an orange solid. The precipitate was filtered, washed with ethanol (10 mL) and dried under vacuum. Yield: 85 mg (60%). IR: 2020 (ν_{CO}), 1919 (ν_{CO}), 1892 (ν_{CO}), 1515 ($\nu_{C\text{-}O}$), 1482, 1434, 1092, 839, 741, 692 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 4.25, 4.80 (m x 2, 2 x 4H, PCH_2P), 6.28 (m, 8H, C_6H_5), 7.03 − 7.93 (m, 72H + 2H, C_6H_5 + bpy), 7.92 (d, 2H, bpy, J_{HH} = 8.9 Hz), 9.18 (dd, 2H, bpy, J_{HH} = 11.2, 5.2 Hz) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −11.5, 9.3 (pseudotriplet x 2, dppm, J_{PP} = 38.9 Hz) ppm. MS (ES +ve) *m/z* (abundance): 1144 (100) $[M/2]^+$. Elem. Anal. Calcd. for $C_{115}H_{94}ClF_{12}N_2O_7P_{10}ReRu_2{\cdot}2CH_2Cl_2$ (M_W = 2747.37): C 51.1, H 3.6, N 1.0%. Found: C 50.9, H 3.3, N 1.3%.

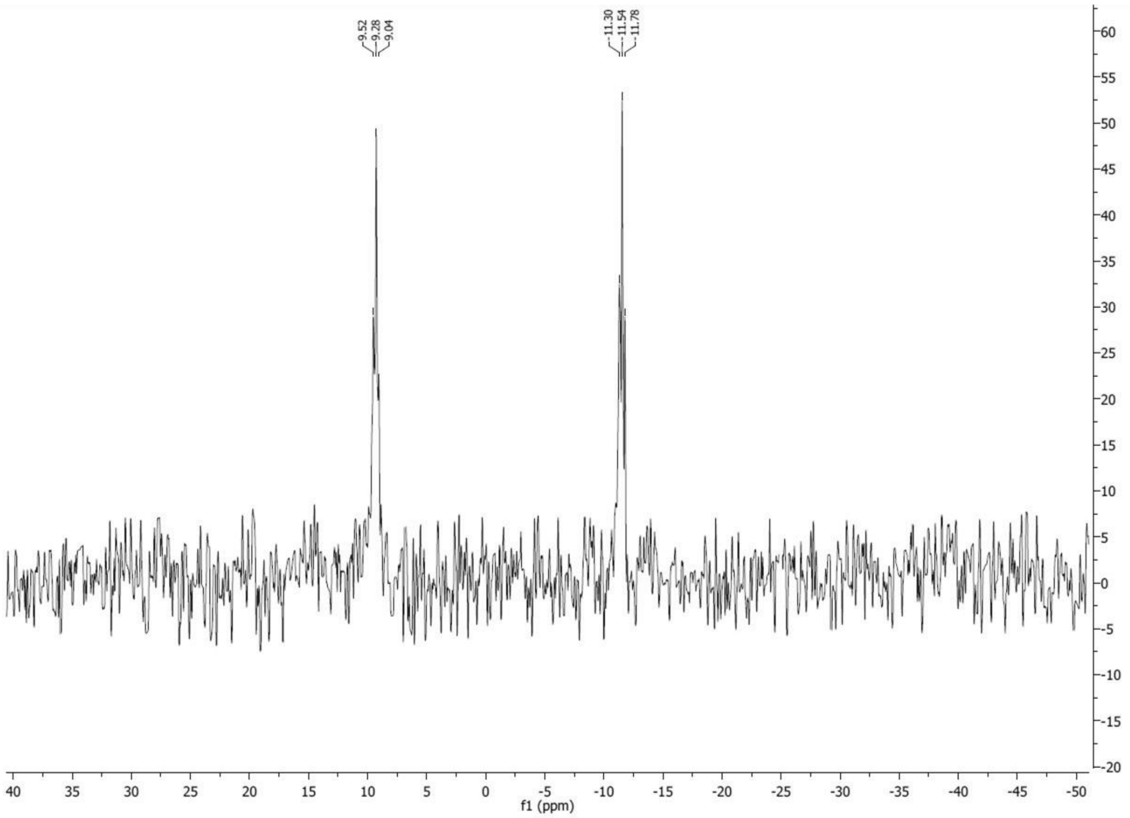

Figure S1-19. $^{31}P\{^1H\}$ NMR spectrum of compound **7** in CD_2Cl_2.

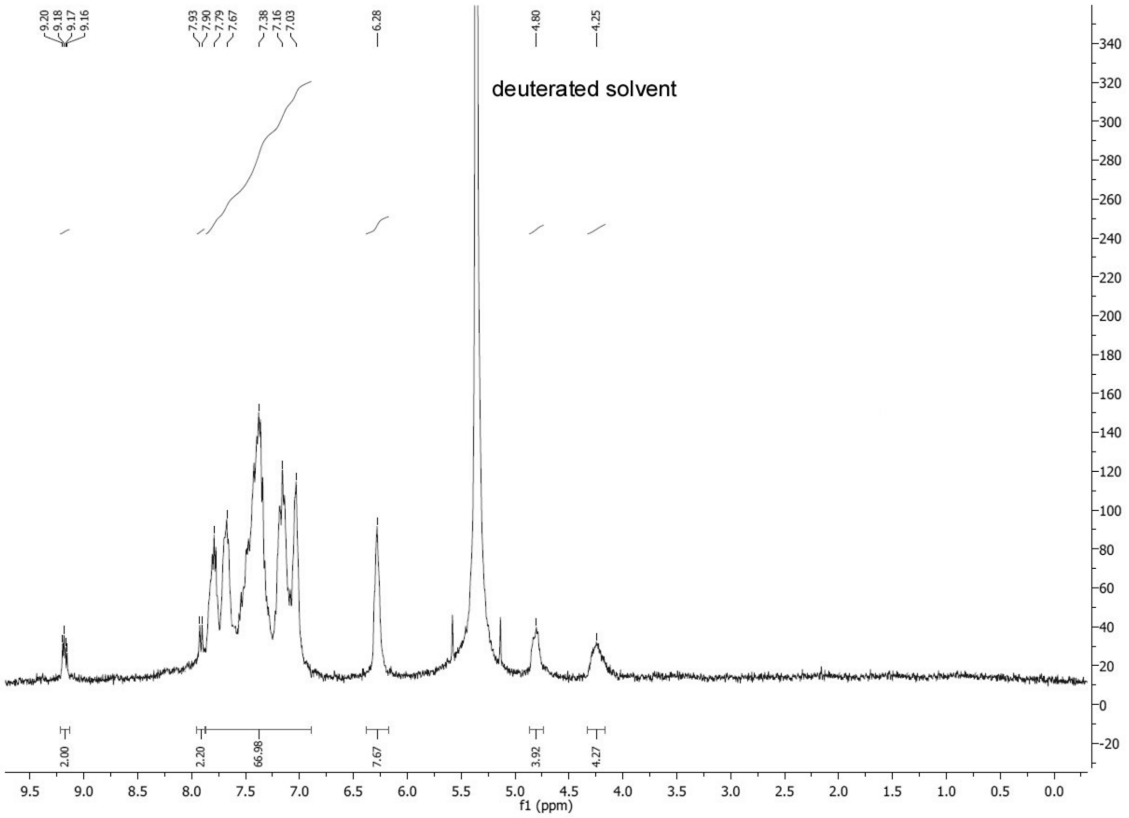

Figure S1-20. ^{1}H NMR spectrum of compound **7** in CD_2Cl_2.

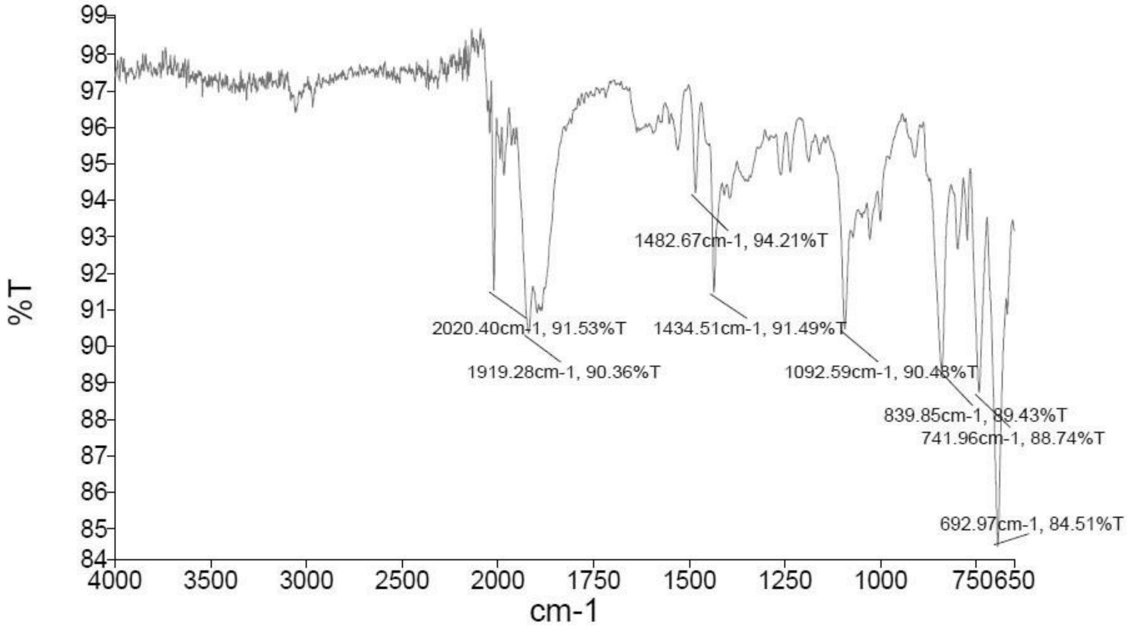

Figure S1-21. Solid-state IR spectrum of compound **7**.

$[Ru\{C(C\equiv CPh)=CHPh\}(O_2CC_5H_4FeC_5H_4C\equiv CH)(CO)(PPh_3)_2]$ (8)

1,1'-Ethynylferrocene carboxylic acid (132 mg, 0.520 mmol) was suspended in dichloromethane (100 mL) and triethylamine (0.3 mL, 2.15 mmol) added. The reaction was stirred until complete dissolution had occurred (30-45 minutes). $[RuCl\{C(C\equiv CPh)CHPh\}(CO)(BTD)(PPh_3)_2]$ (489 mg, 0.420 mmol) was added and the mixture stirred for a further three hours. All solvent was removed under reduced pressure and the resultant crude product dissolved in a minimum volume of dichloromethane and filtered through Celite. Ethanol (100 mL) was added and the solvent volume was reduced (rotary evaporation) to form a bright orange product. This was washed with cold ethanol (20 mL) and *n*-hexane (20 mL) and dried under vacuum. Yield: 330 mg (69%). IR: 3298, 2143 ($\nu_{C\equiv C}$), 2100 ($\nu_{C\equiv C}$), 1908 (ν_{CO}), 1501 (ν_{OCO}), 1433, 1187, 1093 cm^{-1}. ^1H NMR (d^6-acetone): δ 3.23 (s, 1H, $C\equiv CH$); 3.38, 3.88, 4.01, 4.12 (s(br) x 4, 4 x 2H, C_5H_4), 5.61 (s(br), 1H, $H\beta$), 6.94 - 7.80 (m, 30H + 10H, PC_6H_5 + CC_6H_5) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 207 (t, CO, J_{PC} = 16.5 Hz), 181.3 (s, CO_2), 144.2 (t, $C\alpha$, J_{PC} unresolved), 140.2 (s, $C\beta$), 135.1 (t^v, *o/m*-PC_6H_5, J_{PC} = 5.6 Hz), 131.9 (s, C_6H_5), 131.5 (t^v, *ipso*-C_6H_5, J_{PC} = 21.5 Hz), 130.4 (s, C_6H_5), 130.2 (s, *p*-C_6H_5), 130.1 (s, C_6H_5), 128.5 (s, C_6H_5), 128.2 (t^v, *o/m*-C_6H_5, J_{PC} = 4.8 Hz), 127.3 (s, C_6H_5), 126.7 (s, $\underline{C}\equiv CPh$), 124.9 (s, C_6H_5), 109.9 (s, $C\equiv\underline{C}Ph$), 82.2 (s, $\underline{C}\equiv CH$), 77.2 (s, $C\equiv\underline{C}H$), 74.0 (s, C^1-C_5H_4), 72.3, 72.2, 70.5, 70.0 (s x 4, C^{2-4}-C_5H_4), 64.4 (s, C^1-C_5H_4) ppm. $^{31}P\{^1H\}$ NMR (d^6-acetone): δ 35.5 (s, PPh_3) ppm. MS (ES +ve) *m/z* (abundance) = 1149 (6) $[M+K]^+$. Anal. Calcd. for $C_{66}H_{50}FeO_3P_2Ru$ (M_W = 1109.96): C 71.4, H 4.5%. Found: C 71.3, H 4.4%.

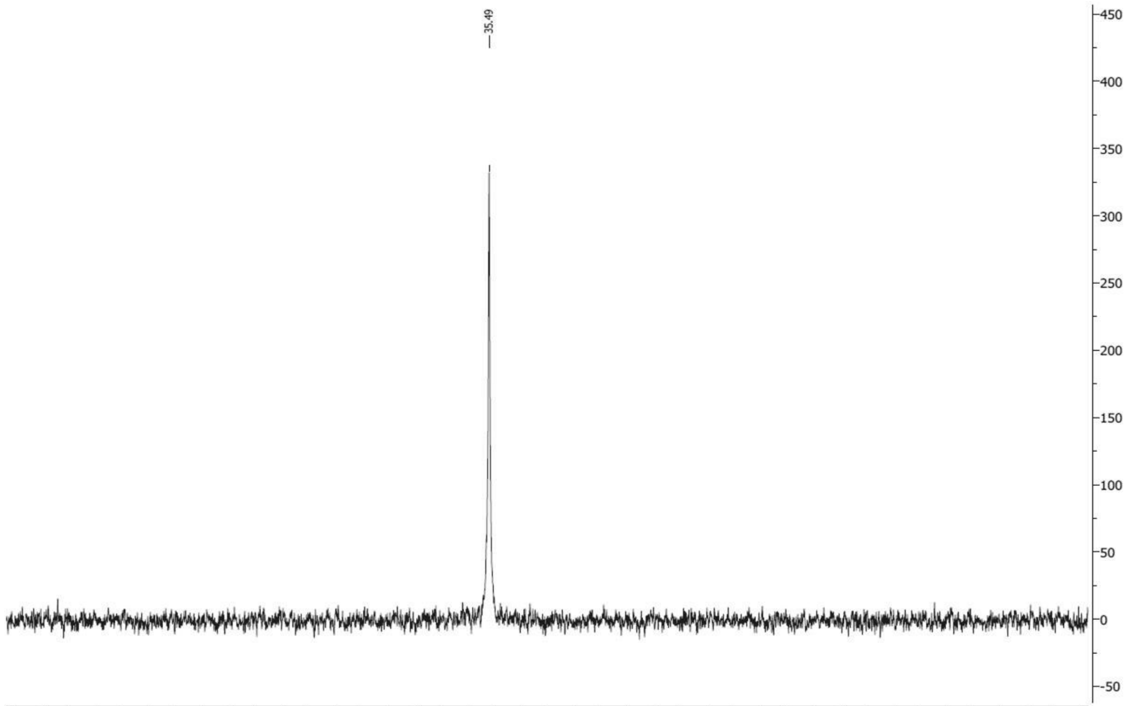

Figure S1-22. $^{31}P\{^1H\}$ NMR spectrum of compound **8** in d^6-acetone.

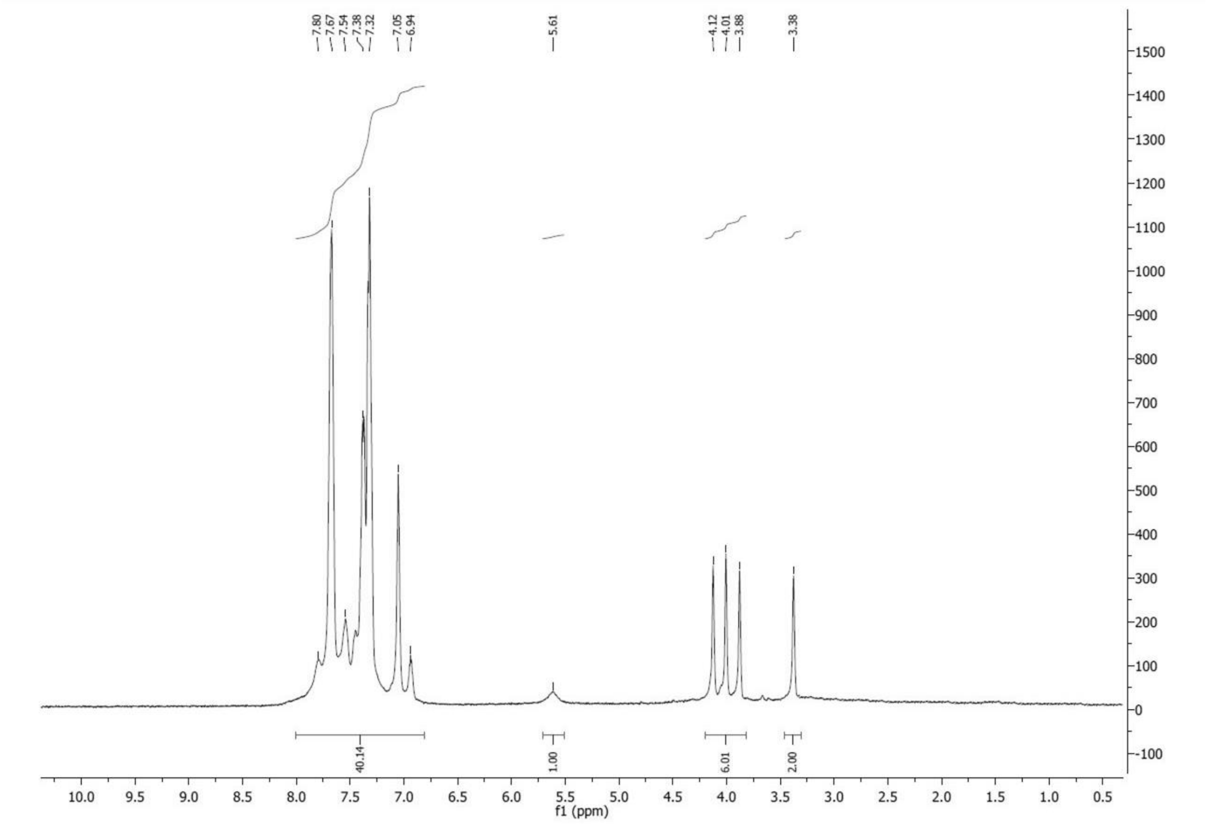

Figure S1-23. ^{1}H NMR spectrum of compound **8** in d^{6}-acetone.

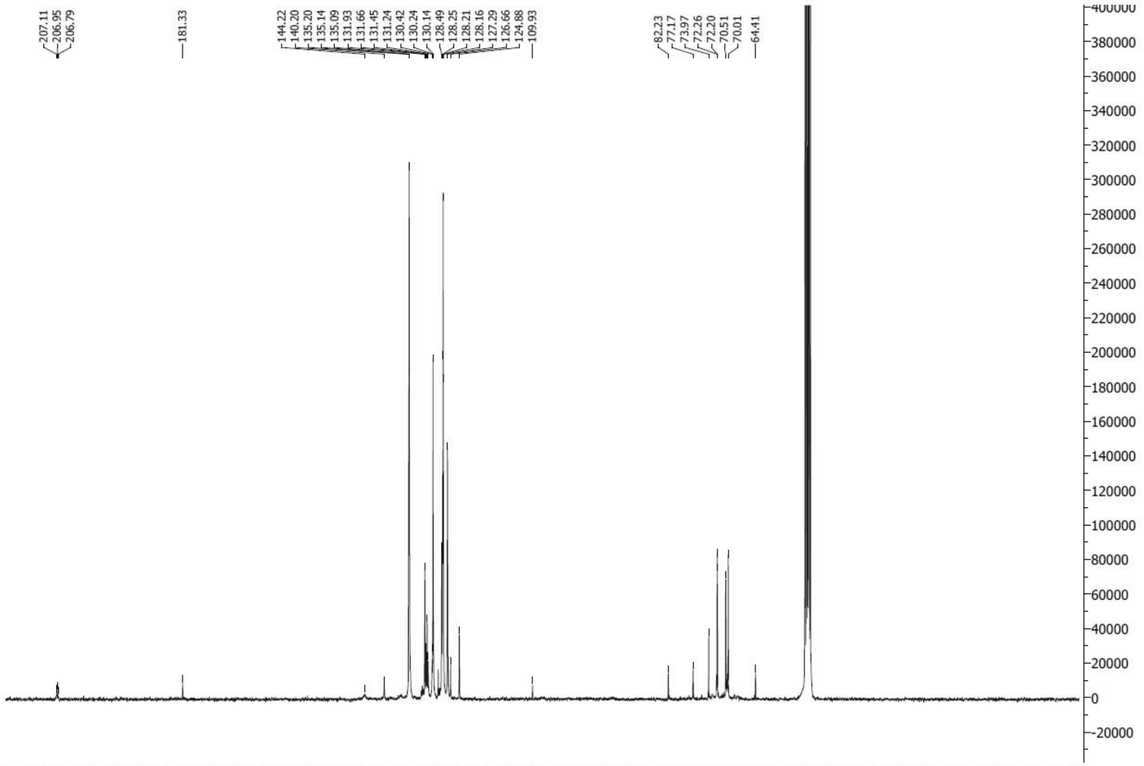

Figure S1-24. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8** in CD_2Cl_2.

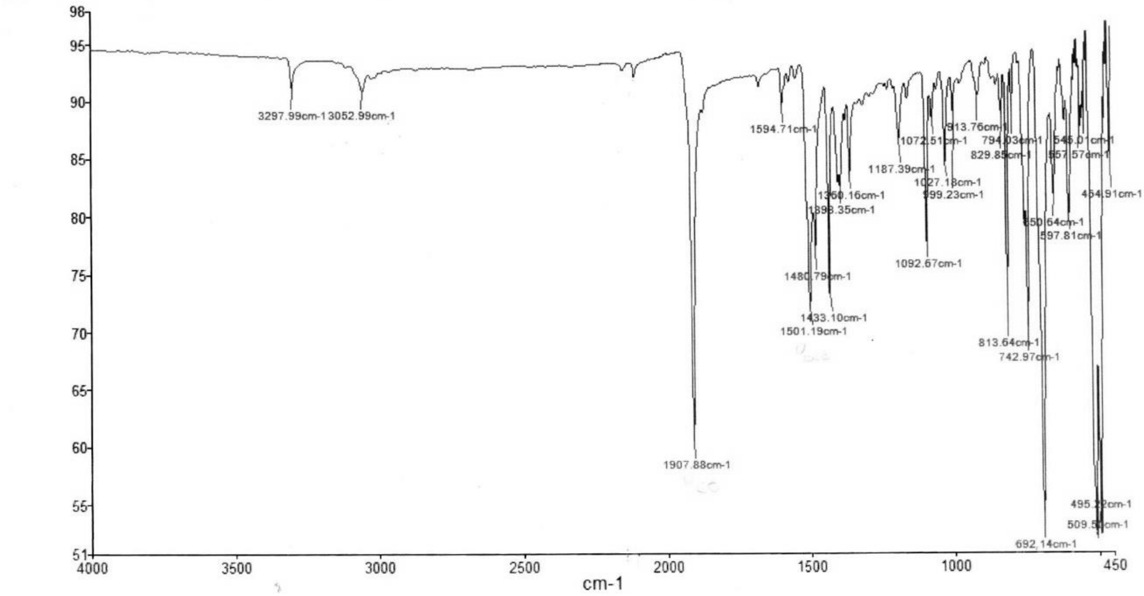

Figure S1-25. Solid-state IR spectrum of compound **8**.

[Ru{C(C≡CPh)=CHPh}($O_2CC_5H_4FeC_5H_4C≡CAuPPh_3$)(CO)($PPh_3$)$_2$] (9)

[Ru{C(C≡CPh)=CHPh}($O_2CC_5H_4FeC_5H_4C≡CH$)(CO)(PPh_3)$_2$] (50 mg, 0.045 mmol) was dissolved in dichloromethane (20 mL) and [AuCl(PPh_3)] (22 mg, 0.045 mmol) and a few drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were added. The mixture was stirred in the dark for 18 hours after which time ethanol (20 mL) was added and the product obtained as a pale yellow solid by rotary evaporation. This was washed with cold ethanol (10 mL) and *n*-hexane (10 mL) and dried under vacuum. Yield: 37 mg (52%). The product is partially soluble in ethanol and a second crop could be obtained on further evaporation of solvent. IR: 2182 ($\nu_{C≡C}$), 1920 (ν_{CO}), 1593, 1500 (ν_{OCO}), 1435, 1095, 1027, 813 cm^{-1}. ^{1}H NMR (d^6-acetone): δ 3.26, 3.76, 3.94, 4.1 (s x 4, 4 x 2H, C_5H_4), 5.63 (s(br), 1H, Hβ), 6.92 (t, 1H, *p*-CC_6H_5, J_{HH} = 7.3 Hz), 7.06 (m, 4H, CC_6H_5), 7.28 - 7.26 (m, 18H, PC_6H_5), 7.51 (m, 3H, CC_6H_5), 7.55 - 7.67 (m, 28H, PC_6H_5), 7.81 (m, 2H, CC_6H_5) ppm. ^{31}P{^{1}H} NMR (d^6-acetone): δ 35.3 (s, $RuPPh_3$), 42.0 (s, $AuPPh_3$) ppm. MS (MALDI +ve) *m/z* (abundance) = 1306 (11) [M–PPh_3]$^+$. Anal. Calcd. for $C_{84}H_{64}AuFeO_3P_3Ru$ (M_W = 1568.21): C 64.3, H 4.1%. Found: C 64.4, H 4.0%.

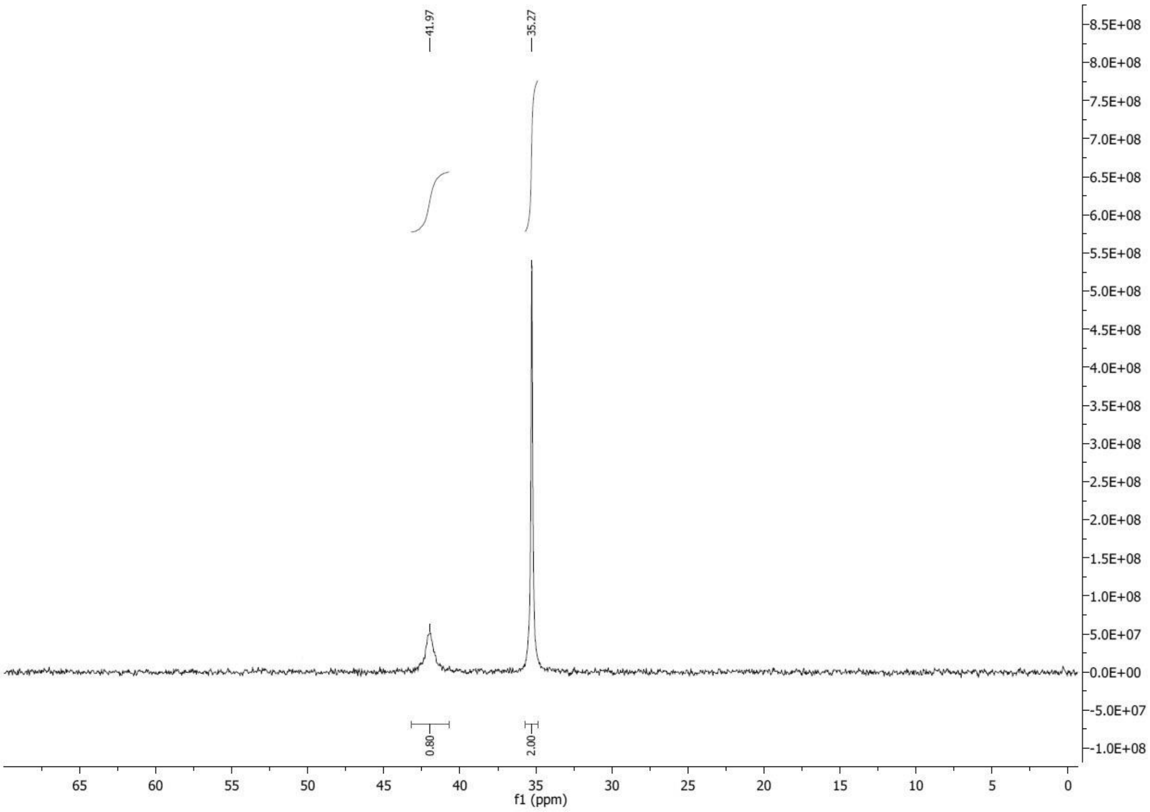

Figure S1-26. $^{31}P\{^{1}H\}$ NMR spectrum of compound **9** in d^{6}-acetone.

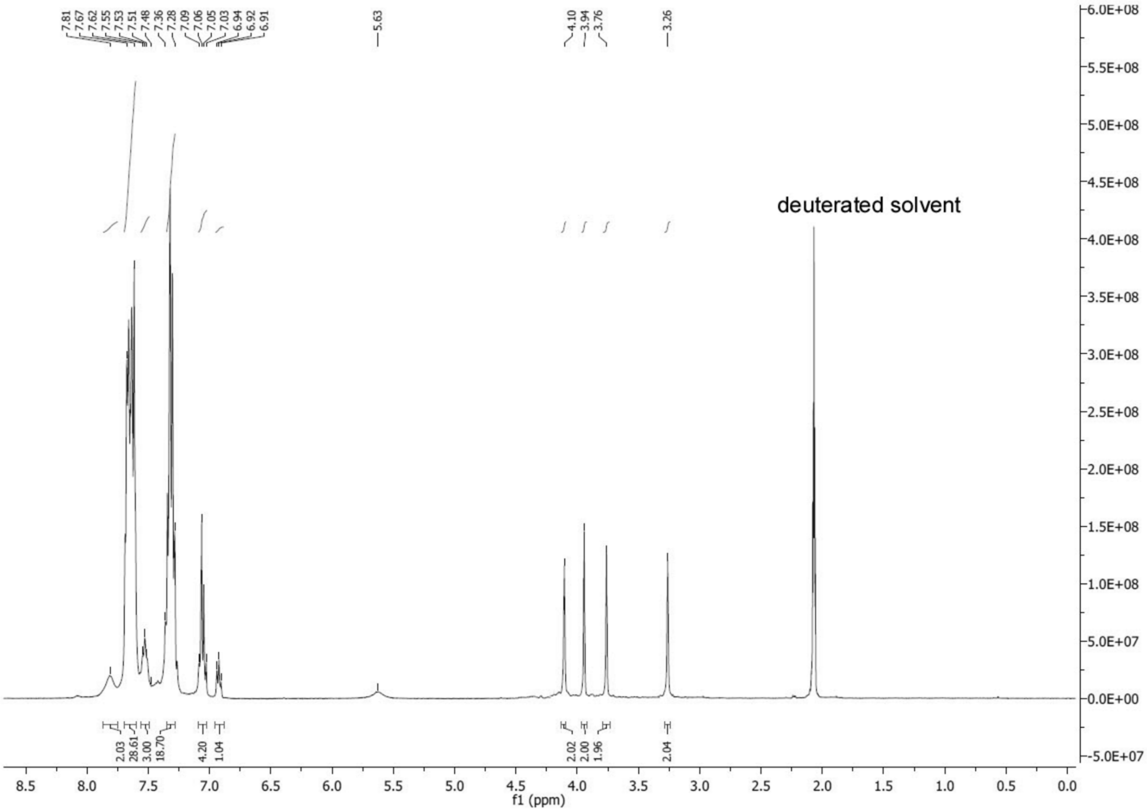

Figure S1-27. ^{1}H NMR spectrum of compound **9** in d^{6}-acetone.

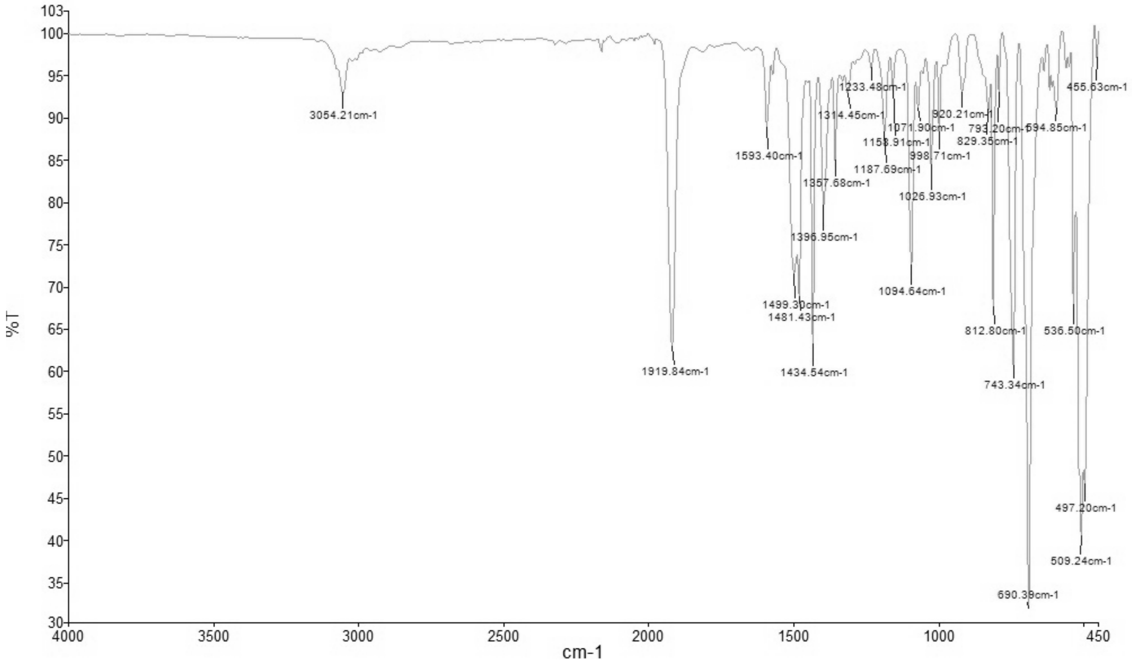

Figure S1-28. Solid-state IR spectrum of compound **9**.

[Ru{C(C≡CPh)=CHPh}($O_2CC_5H_4FeC_5H_4C$≡C)(CO)(PPh_3)$_2$]$_2$(Au_2dppf) (10)

Compound **8** (50 mg, 0.045 mmol) and [dppf($AuCl$)$_2$] (23 mg, 0.023 mmol) were dissolved in dichloromethane (20 mL). To this was added a few drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and the reaction was stirred in the dark at room temperature for 18 hours. Ethanol (20 mL) was then added and the solvent volume reduced to provide a pale yellow solid. This was washed with cold ethanol (10 mL) and *n*-hexane (10 mL) and dried under vacuum. Yield: 40 mg (56%). IR (solid state): 2160 ($\nu_{C\equiv C}$), 1921 (ν_{CO}), 1594, 1500 (ν_{OCO}), 1482, 1435, 1094 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 3.22 (s, 4H, C_5H_4), 3.87, 3.98, 4.15 (t x 3, 3 x 4H, C_5H_4, J_{HH} = 1.7 Hz), 4.32, 4.80 (s x 2, 2 x 4H, C_5H_4), 5.58 (s(br), 1H Hβ), 6.97 (m, 6H, CC_6H_5), 7.08 (m, 4H, CC_6H_5), 7.26 - 7.38 (m, 40H, PC_6H_5), 7.46 – 7.67 (m, 50H, PC_6H_5 + CC_6H_5) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 35.7 (s, RuPPh_3), 36.6 (s, Au-dppf) ppm. MS (MALDI +ve) *m/z* (abundance) = 2642 (8) [M–2PPh_3]$^+$, 2462 (15) [M–enynyl–PPh_3+Na]$^+$. Anal. Calcd. for $C_{166}H_{126}Au_2Fe_3O_6P_6Ru_2$ (M_W = 3166.22): C 63.0, H 4.0%. Found: C 63.0, H 3.9%.

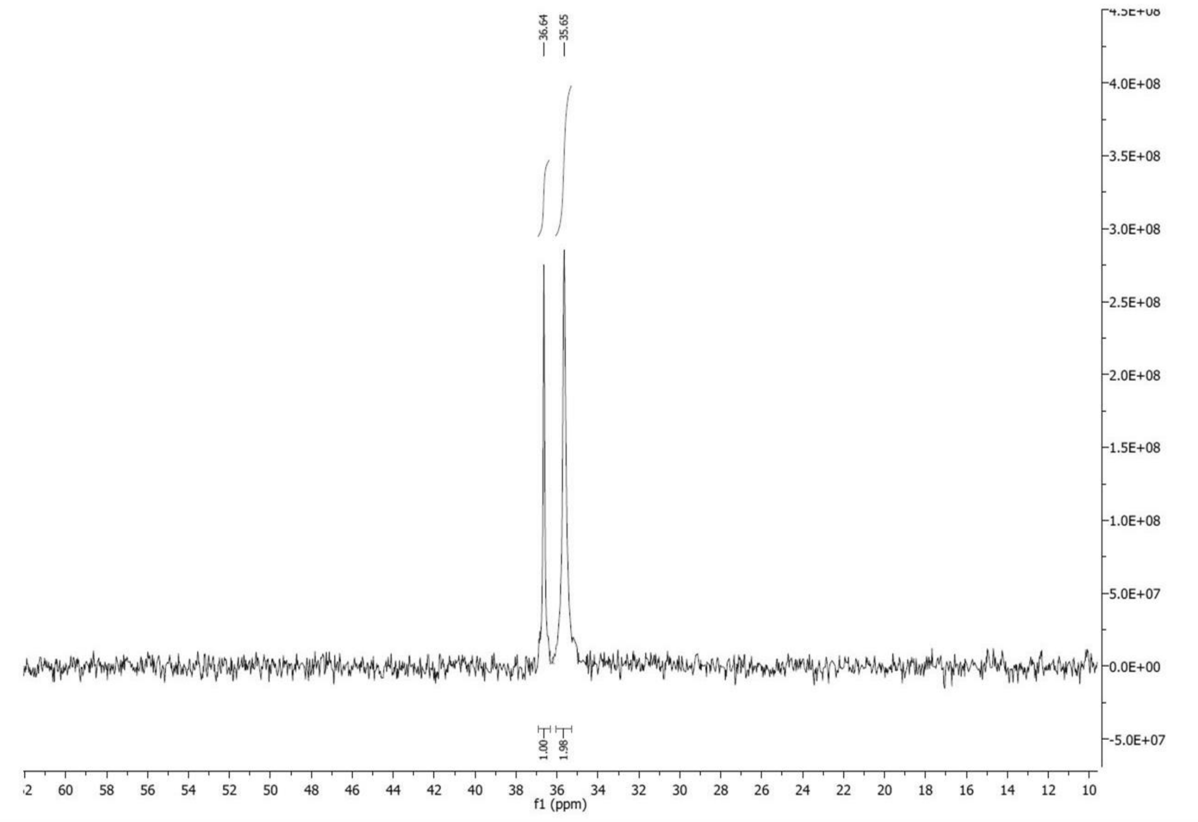

Figure S1-29. $^{31}P\{^{1}H\}$ NMR spectrum of compound **10** in CD_2Cl_2.

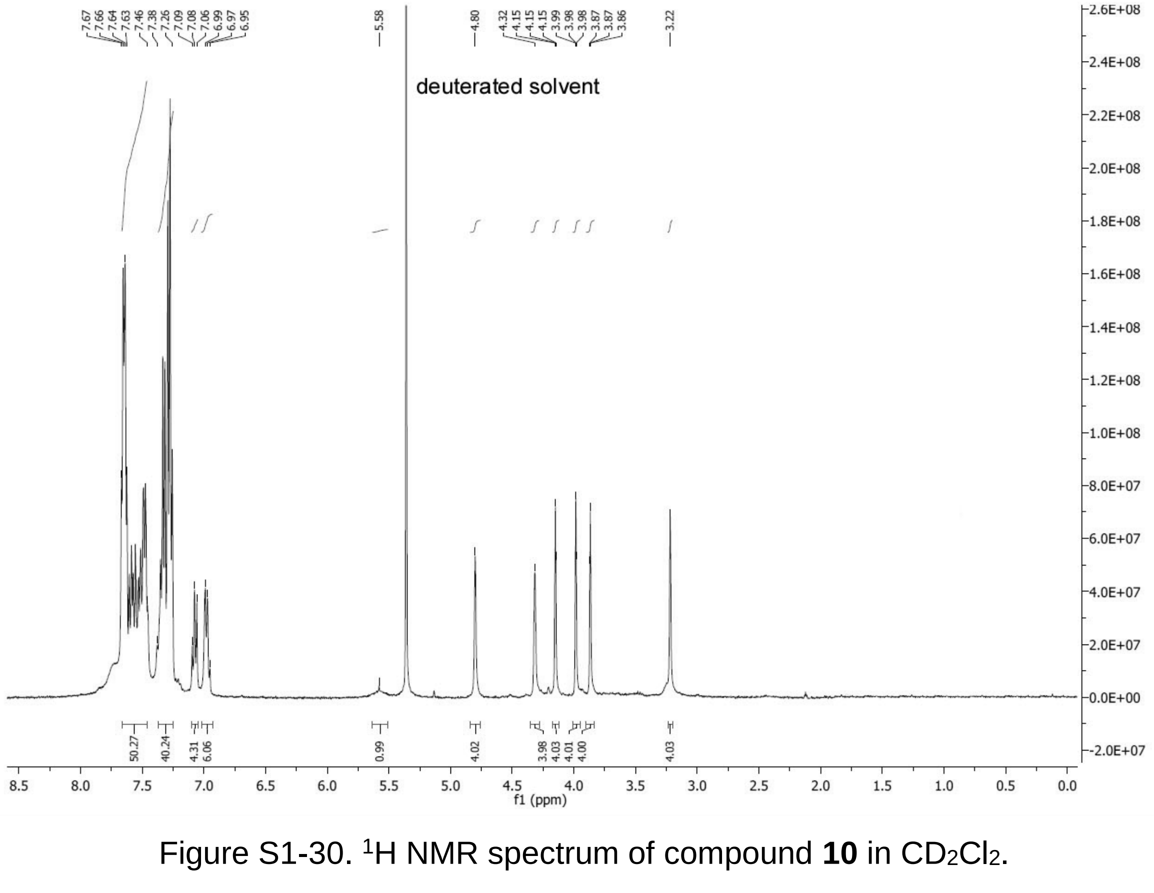

Figure S1-30. ^{1}H NMR spectrum of compound **10** in CD_2Cl_2.

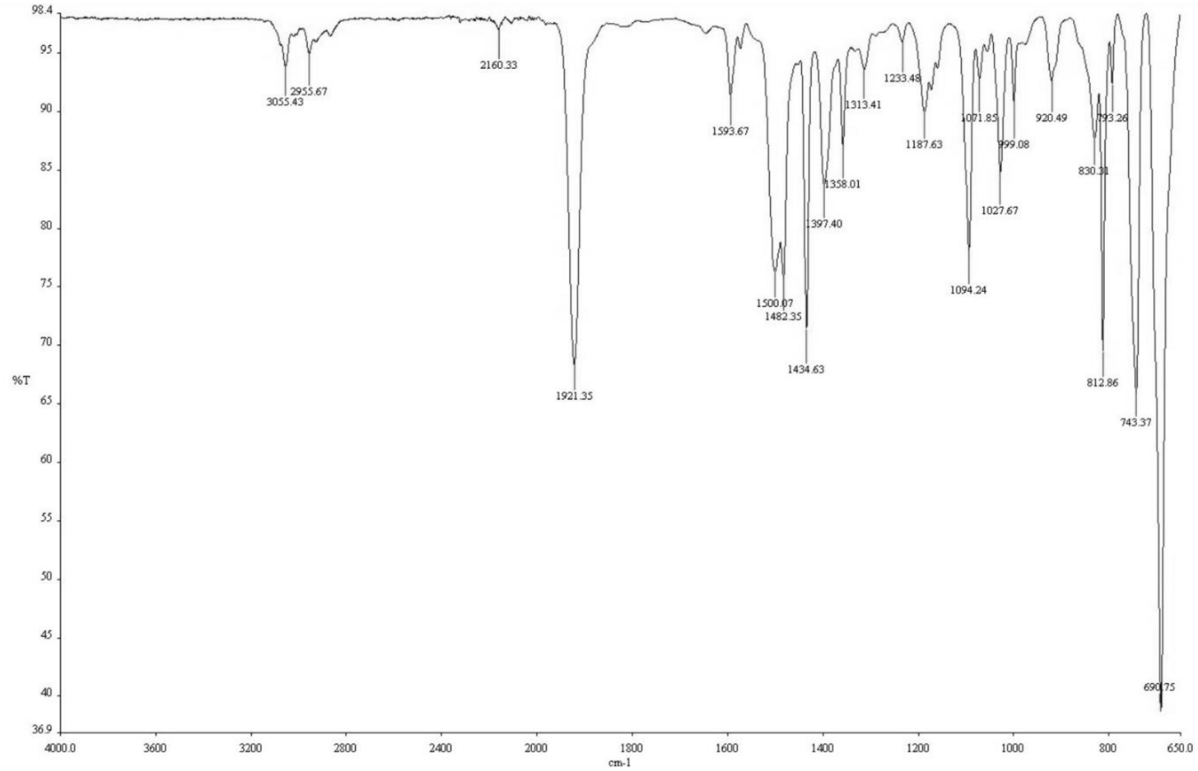

Figure S1-31. Solid-state IR spectrum of compound **10**.

$[Ru\{C(C{\equiv}CPh){=}CHPh\}\{O_2CC_5H_4FeC_5H_4CH{=}CH(RuCl(CO)(BTD)(PPh_3)_2)\}(CO)(PPh_3)_2]$ (11)

$[Ru\{C(C{\equiv}CPh)CHPh\}(O_2CFcC{\equiv}CH)(CO)(PPh_3)_2]$ (62 mg, 0.056 mmol) was dissolved in dichloromethane (25 mL) and $[RuHCl(CO)(BTD)(PPh_3)_2]$ (40 mg, 0.057 mmol) added. The mixture was stirred for 30 minutes after which time ethanol (25 mL) was added and the product obtained as a dark red solid by rotary evaporation. This was washed with cold methanol (5 mL), cold ethanol (5 mL) and petroleum ether (10 mL) and dried under vacuum. Yield: 57 mg (56%). IR (solid state): 2162 ($\nu_{C{\equiv}C}$), 1918 (ν_{CO}), 1593, 1572, 1500 (ν_{OCO}), 1481, 1433, 1092 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 3.08, 3.32, 3.52, 3.86 (s(br) x 4, 4 x 2H, C_5H_4), 5.41 (d, 1H, RuCH=C$\underline{H}$, J_{HH} = 14.5 Hz), 5.55 (s(br), 1H, RuC(C≡CPh)=C*H*Ph), 6.99 (m, 3H, CC_6H_5), 7.09 (m, 2H, CC_6H_5), 7.24 - 7.52 (m, 50H, PC_6H_5 + PC_6H_5), 7.55 (m, 2H, BTD), 7.64 (m, 15H, PC_6H_5 + PC_6H_5), 7.85 (d, 1H, RuC$\underline{H}$=CH, J_{HH} = 14.5 Hz), 7.96 (s(br), 2H, BTD) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 26.9 (s, vinyl-RuPPh_3), 35.4 (s, enynyl-RuPPh_3) ppm. MS (MALDI +ve) *m/z* (abundance) = 1801 (7) $[M{-}BTD{+}H]^+$, 1538 (11) $[M{-}BTD{-}PPh_3]^+$. Anal. Calcd. for $C_{109}H_{85}ClFeN_2O_4P_4Ru_2S$ (M_W = 1936.25): C 67.6, H 4.4, N 1.5%. Found: C 67.7, H 4.6, N 1.6%.

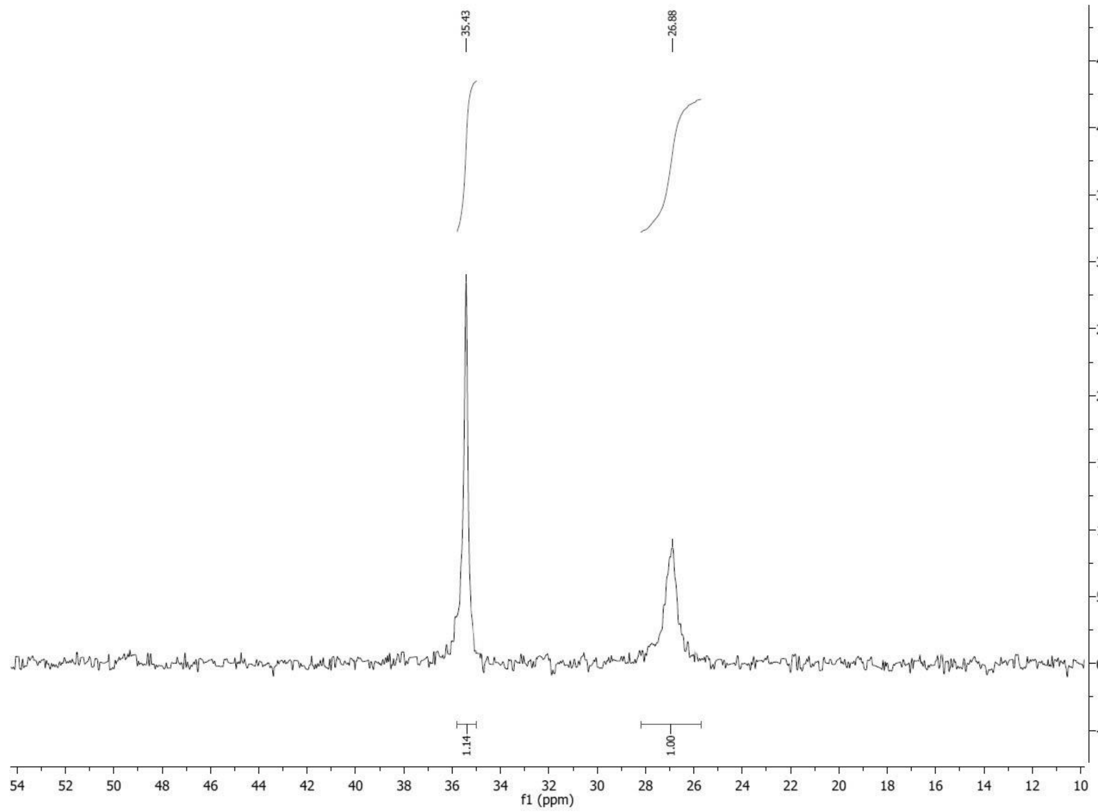

Figure S1-32. $^{31}P\{^{1}H\}$ NMR spectrum of compound **11** in CD_2Cl_2.

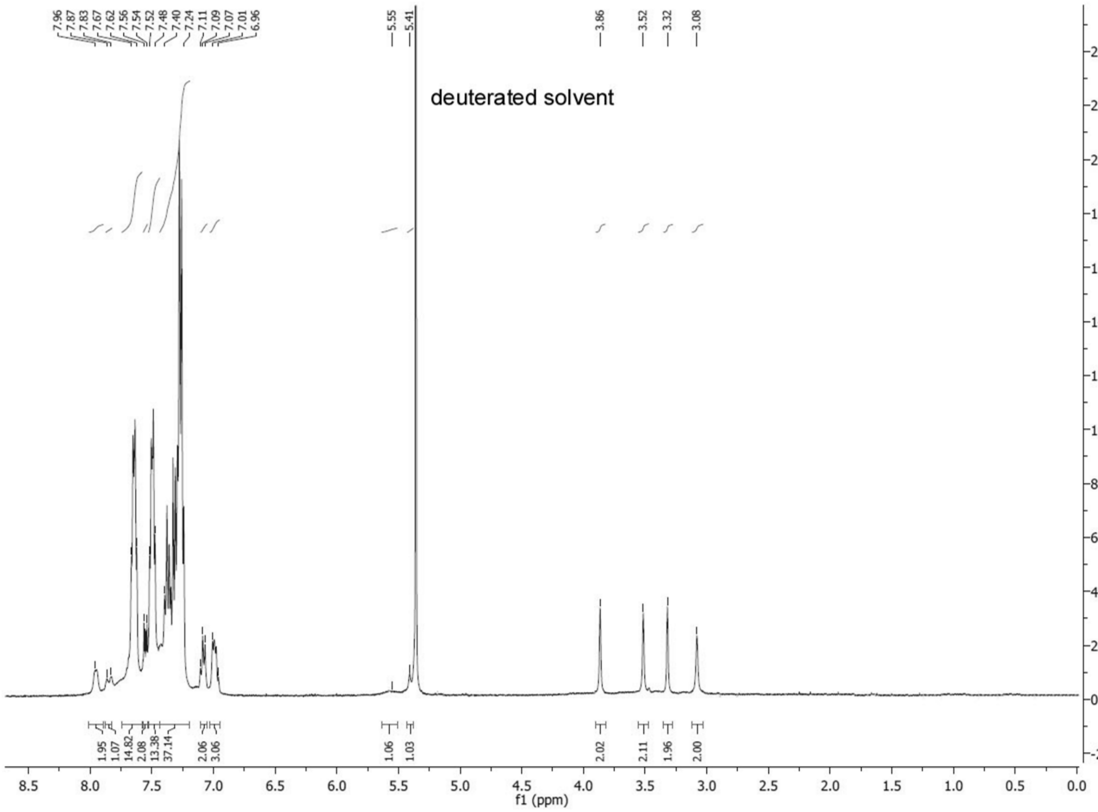

Figure S1-33. ^{1}H NMR spectrum of compound **11** in CD_2Cl_2.

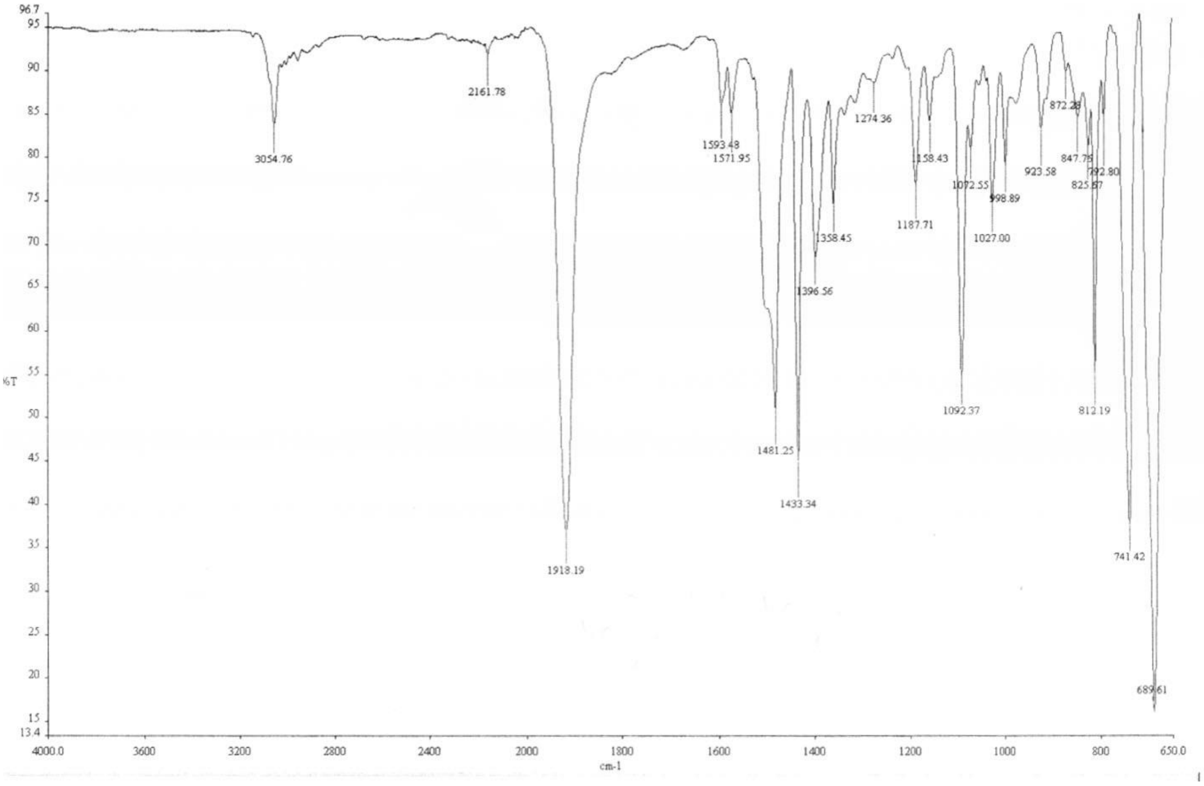

Figure S1-34. Solid-state IR spectrum of compound **11**.

[Ru{C(C≡CPh)=CHPh}{O$_2$CC$_5$H$_4$FeC$_5$H$_4$CH=CH(OsCl(CO)(BTD)(PPh$_3$)$_2$)}(CO)(PPh$_3$)$_2$] (12)

[Ru{C(C≡CPh)CHPh}(O$_2$CFcC≡CH)(CO)(PPh$_3$)$_2$] (61 mg, 0.055 mmol) was dissolved in dichloromethane (25 mL) and [OsHCl(CO)(BTD)(PPh$_3$)$_2$] (48 mg, 0.052 mmol) was added. The reaction was stirred for one hour after which time ethanol (20 mL) was added and a dark purple solid was obtained on reduction of the solvent volume (rotary evaporation). This was washed with cold ethanol (10 mL) and petroleum ether (10 mL) and dried under vacuum. Yield: 60 mg (54%). IR: 1921 ($^{\mathrm{Ru}}\nu_{\mathrm{C\equiv O}}$), 1898 (sh, $^{\mathrm{Os}}\nu_{\mathrm{C\equiv O}}$), 1594, 1573, 1503 ($\nu_{\mathrm{OCO}}$), 1482, 1434, 1395, 1093 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 3.08, 3.28, 3.63, 3.88 (s x 4, 4 x 2H, C$_5$H$_4$), 5.55 (s, 1H, RuC=CH), 5.61 (d, 1H, OsC=CH, J_{HH} = 16.8 Hz), 6.99 - 7.66 (m, 70H + 2H, C$_6$H$_5$ + BTD), 8.08 (m, 2H, BTD), 8.48 (d, 1H, OsCH, J_{HH} = 16.8 Hz) ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ -3.1 (s, OsPPh$_3$), 35.4 (s, RuPPh$_3$) ppm. MS (MALDI +ve) *m/z* (abundance): 1890 (5) [M–BTD]$^+$, 1524 (8) [M–2PPh$_3$+Na]$^+$. Anal. Calcd. for C$_{109}$H$_{85}$ClFeN$_2$O$_4$OsP$_4$RuS (M$_{\mathrm{W}}$ = 2025.41): C 64.6, H 4.2, N 1.4%. Found: C 64.7, H 4.4, N 1.5%.

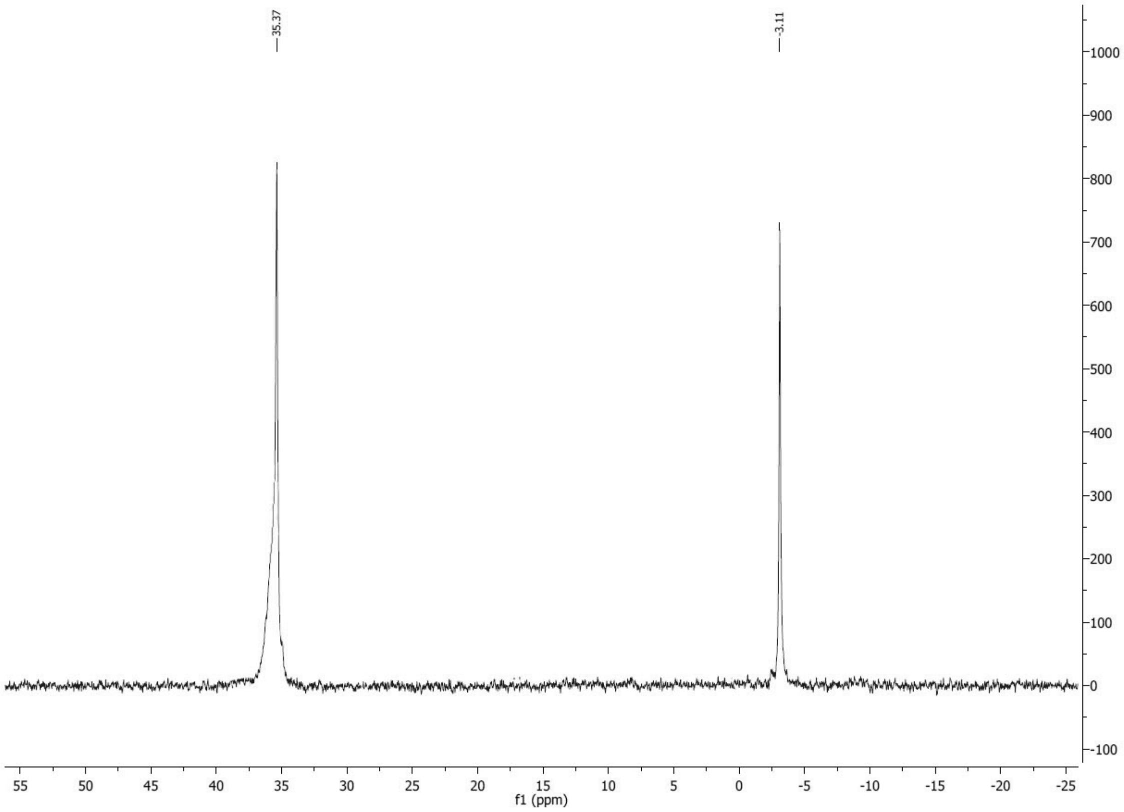

Figure S1-35. $^{31}P\{^1H\}$ NMR spectrum of compound **12** in CD_2Cl_2.

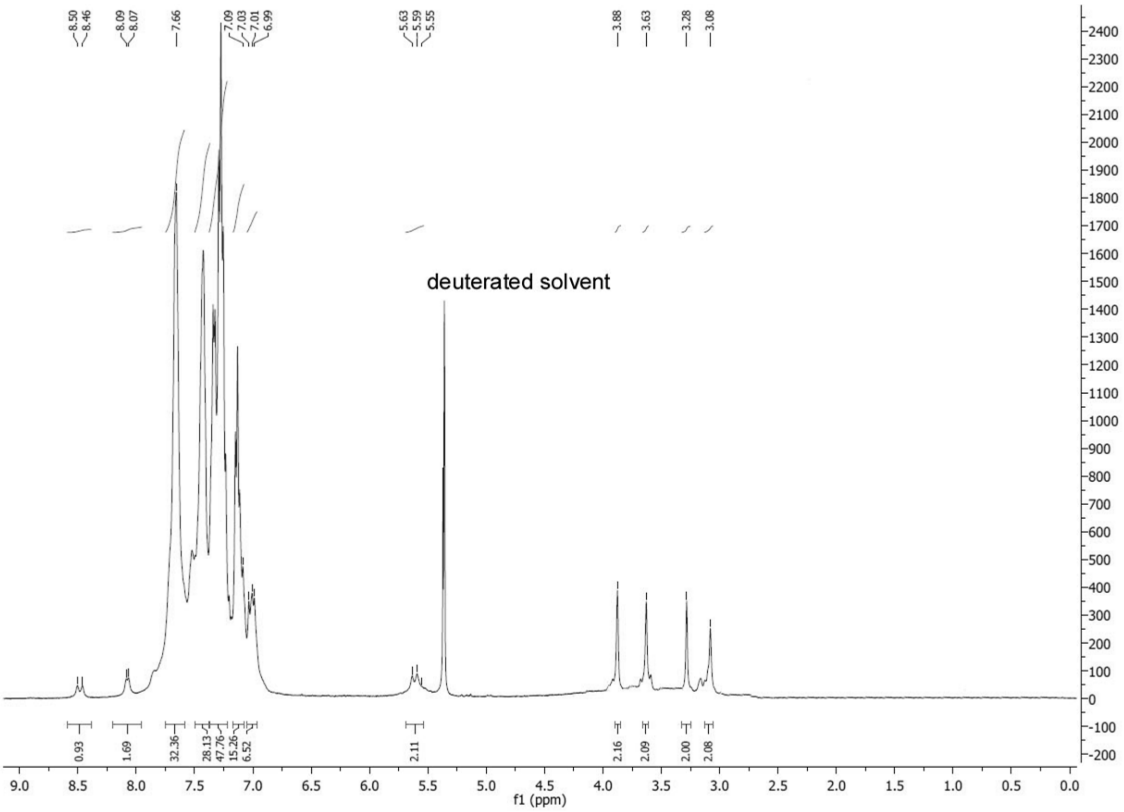

Figure S1-36. ^1H NMR spectrum of compound **12** in CD_2Cl_2.

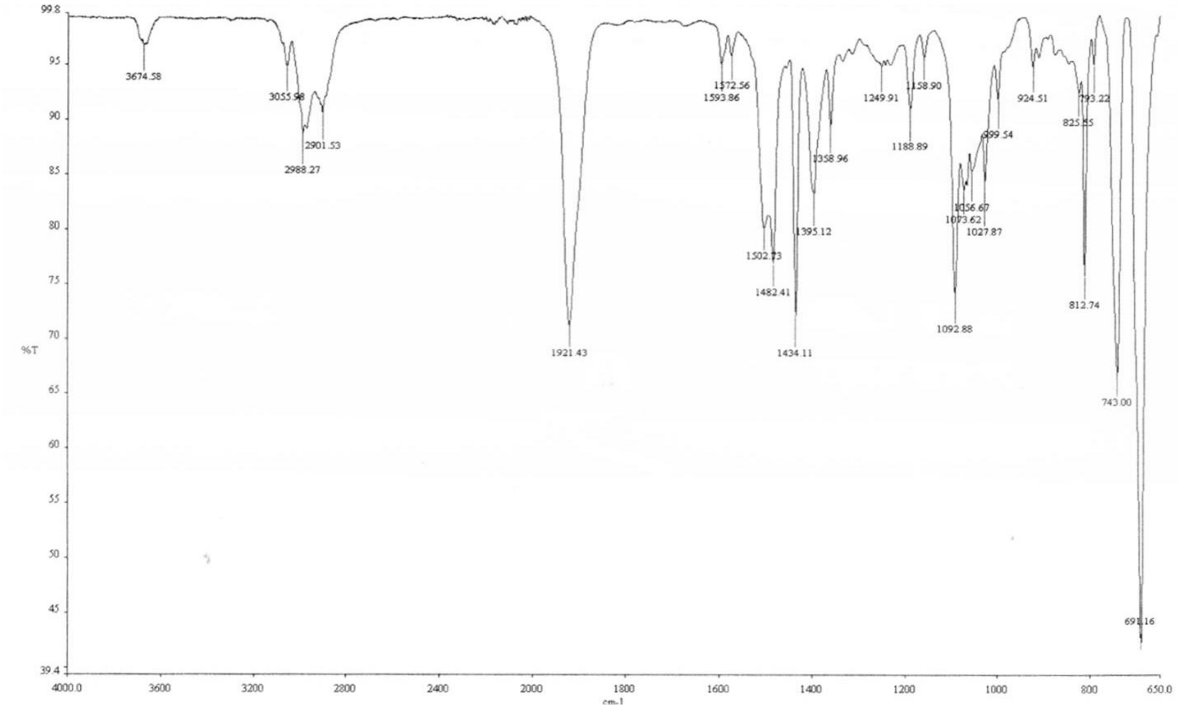

Figure S1-37. Solid-state IR spectrum of compound **12**.

S2. Crystallography

The X-ray crystal structure of 3·2BPh4

Crystal data for **3·2BPh4**: $[C_{112}H_{94}N_2O_4P_8Ru_2](C_{24}H_{20}B)_2\cdot 5CHCl_2$, $M = 3044.83$, monoclinic, $P2_1/c$ (no. 14), a = 11.3803(4), b = 21.7537(9), c = 30.4002(14) Å, β = 92.572(4)°, V = 7518.4(5) Å^3, Z = 2 [C_i symmetry], D_c = 1.345 g cm^{-3}, μ(Mo-Kα) = 0.519 mm^{-1}, T = 173 K, yellow blocky needles, Agilent Xcalibur 3 E diffractometer; 15010 independent measured reflections (R_{int} = 0.0412), F^2 refinement,[S10,S11] R_1(obs) = 0.1000, wR_2(all) = 0.1925, 10657 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, completeness to θ_{full}(25.2°) = 98.8%], 886 parameters. CCDC 1840500.

The di-ruthenium complex in the structure of **3·2BPh4** sits across a centre of symmetry at the middle of the C6–C6A bond linking the two pyridyl rings. The asymmetric unit was found to contain three distinct sites occupied by dichloromethane solvent molecules, but inspection of their thermal parameters showed the sites to be only partially occupied, something that was unsurprising given that the crystal was seen to partially desolvate on the slide before mounting. When refined freely the occupancies of the C100-, C110-, and C120-based dichloromethane molecules settled to *ca*. 0.85, 0.88 and 0.77 respectively, and so for simplicity the combined occupancy was subsequently set to total exactly 2.5 molecules per asymmetric unit (*i.e.* 5 per metal complex). All of the non-hydrogen atoms across all three molecules were refined anisotropically.

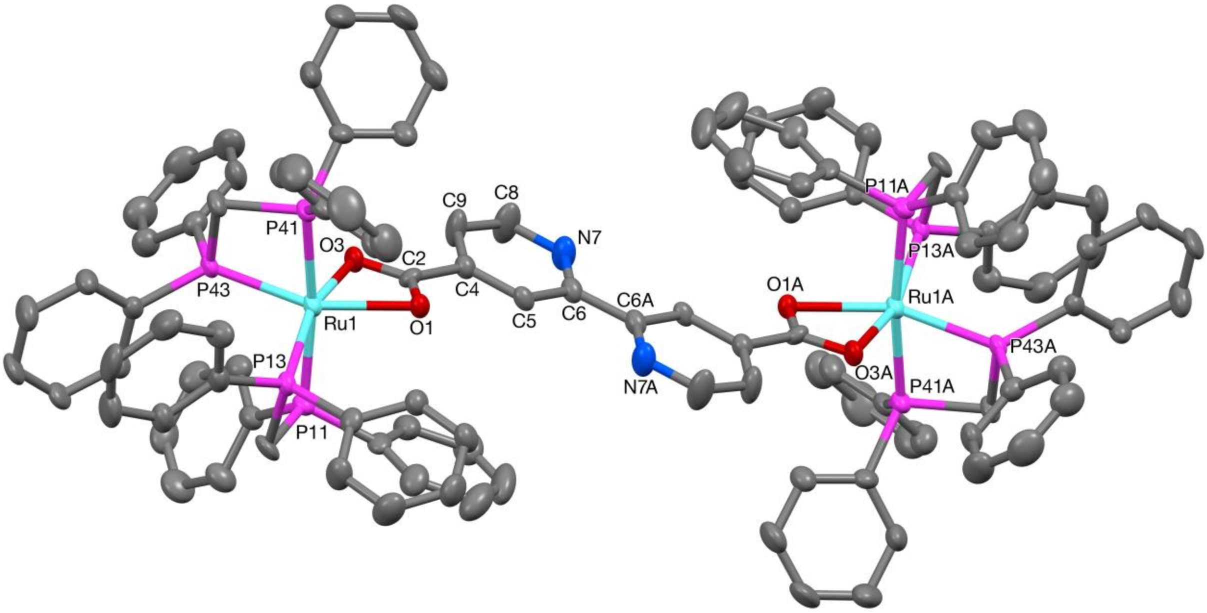

Figure S2-1. The structure of the C_i-symmetric complex present in the crystal of **3·2BPh₄** (50% probability ellipsoids).

S3. Photophysics

Absorption spectra were recorded at room temperature using a Perkin Elmer Lambda 35 UV-vis spectrometer. Uncorrected steady-state emission and excitation spectra were recorded on an Edinburgh FLSP920 spectrometer equipped with a 450 W xenon arc lamp, double excitation and single emission monochromators, and a Peltier-cooled Hamamatsu R928P photomultiplier tube (185−850 nm). Emission and excitation spectra were acquired with a cut-off filter (395 nm) and corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by a calibration curve supplied with the instrument. The wavelengths for the emission and excitation spectra were determined using the absorption maxima of the MLCT transition bands (emission spectra) and at the maxima of the emission bands (excitation spectra). Quantum yields (Φ) were determined using the optically dilute method by Crosby and Demas[S12] at an excitation wavelength obtained from absorption spectra on a wavelength scale [nm] and compared to the reference emitter by the following equation:[S13]

$$\phi_s = \phi_r \left[\frac{A_r(\lambda_r)}{A_s(\lambda_s)}\right] \left[\frac{I_r(\lambda_r)}{I_s(\lambda_s)}\right] \left[\frac{n_s^2}{n_r^2}\right] \left[\frac{D_s}{D_r}\right]$$

where A is the absorbance at the excitation wavelength (λ), I is the intensity of the excitation light at the excitation wavelength (λ), n is the refractive index of the solvent, D is the integrated intensity of the luminescence, and Φ is the quantum yield. The subscripts r and s refer to the reference and the sample, respectively. A stock solution with an absorbance > 0.1 was prepared, then two dilutions were obtained with dilution factors of 20 and 10, resulting in absorbances of about 0.02 and 0.08 respectively. The Beer-Lambert law was assumed to remain linear at the concentrations of the solutions. The degassed measurements were obtained after passing a stream of argon through the solutions for 10 minutes using a septa-sealed quartz cell. An air-equilibrated $[Ru(bpy)_3]Cl_2/H_2O$ solution ($\Phi = 0.028$)[S14] was used as the reference. The quantum yield determinations were performed at identical excitation wavelengths for the sample and the reference, therefore deleting the I(λr)/I(λs) term in the equation. Emission lifetimes (τ) were determined with the single photon counting technique (TCSPC) with the same Edinburgh FLSP920 spectrometer using pulsed picosecond LED (EPLED 360, FWHM < 800ps) as the excitation source, with repetition rates between 1 kHz and 1 MHz, and the above-mentioned R928P PMT as detector. The goodness of fit was assessed by minimizing the reduced χ^2 function and by visual inspection of the weighted residuals. To record the 77 K luminescence spectra, the samples were put in quartz tubes (2 mm diameter) and inserted in a special quartz Dewar filled with liquid nitrogen. The solvent used in the preparation of the solutions for the photophysical investigations was of spectrometric grade. Experimental uncertainties are estimated to be ±8% for lifetime determinations, ±20% for quantum yields, and ±2 nm and ±5 nm for absorption and emission peaks, respectively.

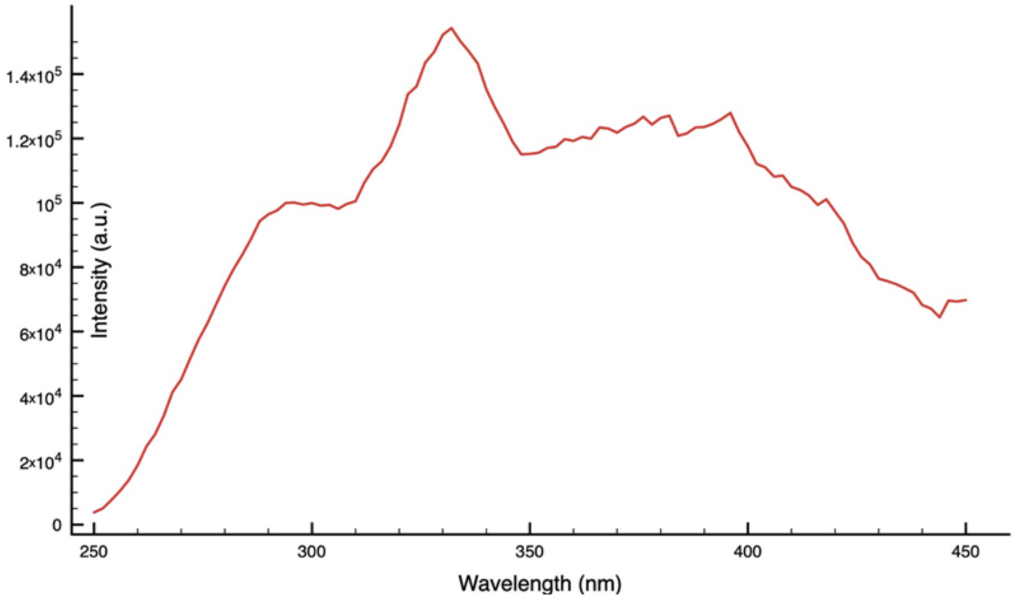

Figure S3-1. Excitation profile of compound **4** in an oxygenated solution of CH_3CN (10^{-5}M).

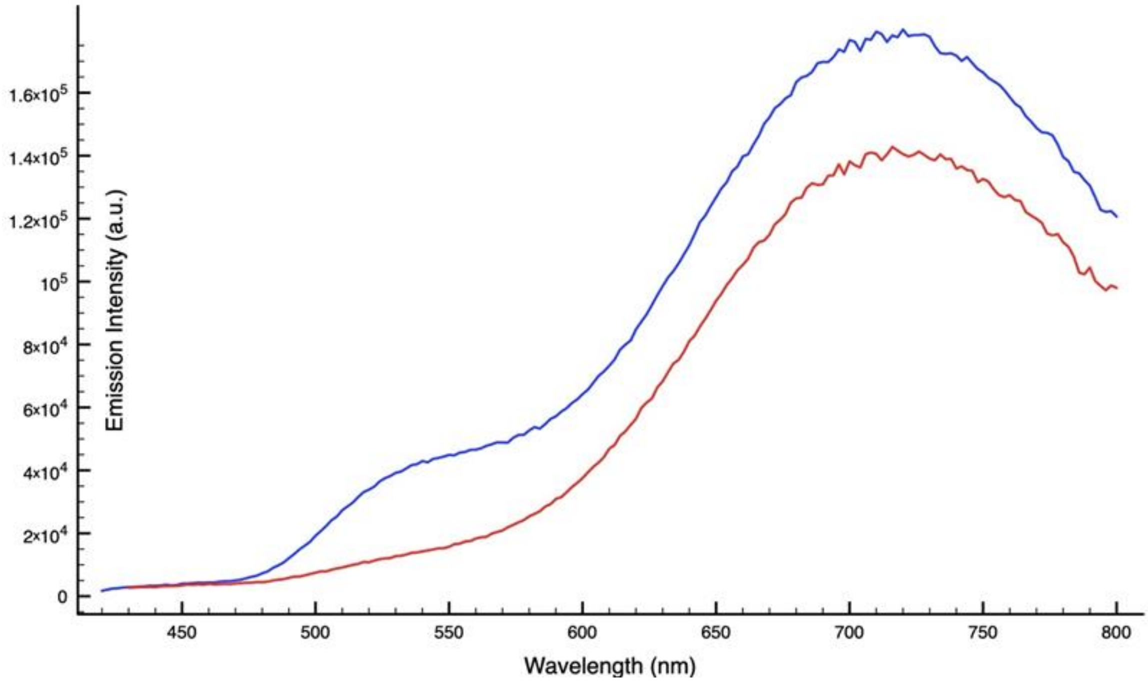

Figure S3-2. Emission profile of compound **4** in an oxygenated solution (red trace) and deoxygenated solution (blue trace) of CH_3CN (10^{-5} M).

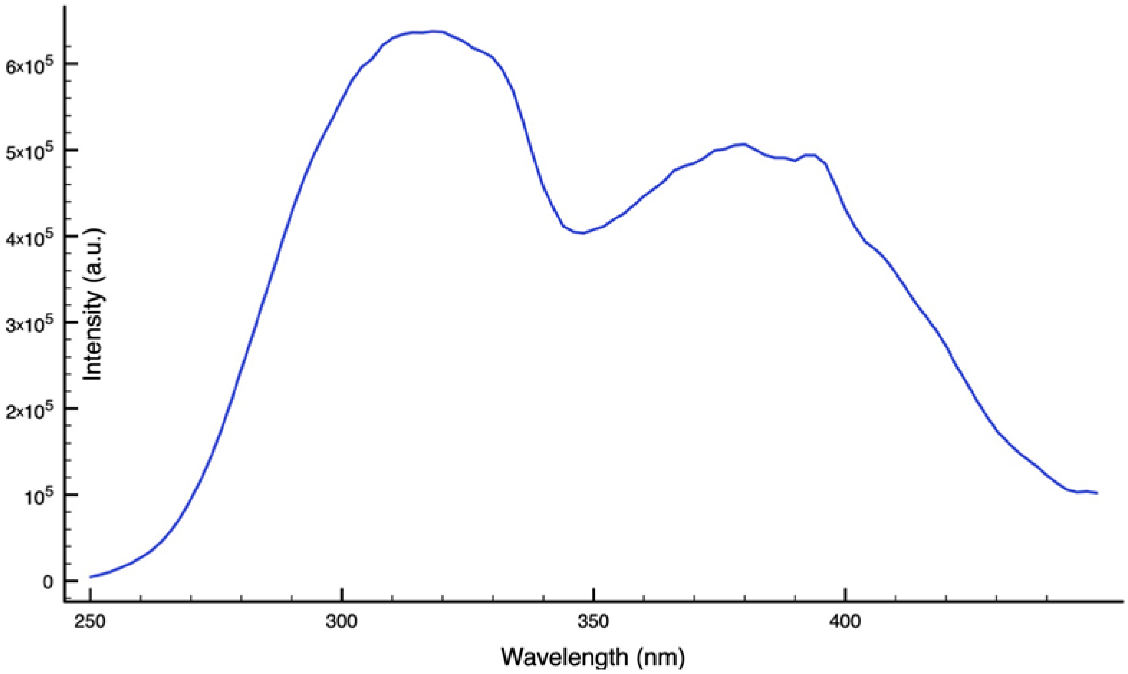

Figure S3-3. Excitation profile of compound **7** in an oxygenated solution of CH_3CN (10^{-5} M).

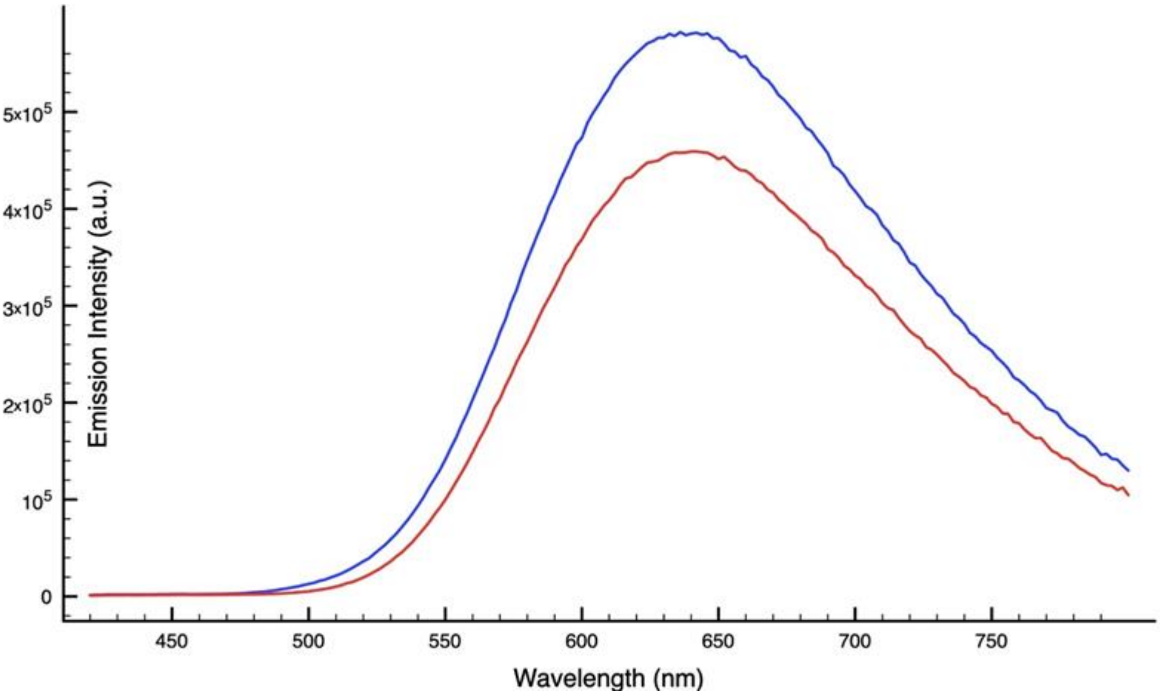

Figure S3-4. Emission profile of compound **7** in an oxygenated solution (red trace) and deoxygenated solution (blue trace) of CH_3CN (10^{-5} M).

S4. Electrochemistry

Electrochemical measurements were obtained on a Gamry Reference 600^{TM} (Gamry Instruments, Warminter, PA, USA) using a standard three-electrode cell with a glassy carbon disk working electrode (3 mm diameter), Pt wire counter electrode and a Pt wire pseudoreference electrode. The analyte was dissolved in a 0.1 M solution of NBu_4PF_6 in CH_2Cl_2 and purged with argon prior to, and between scans. At the end of each experiment, ferrocene was added as an internal standard. The values reported herein are relative to the Fc/Fc^+ couple and corrected for solution resistance (R_s) using R_s values obtained from ac impedance spectroscopy. NBu_4PF_6 was obtained from Fluorochem and ferrocene was obtained from Tokyo Chemical Industry. Both were used as received.

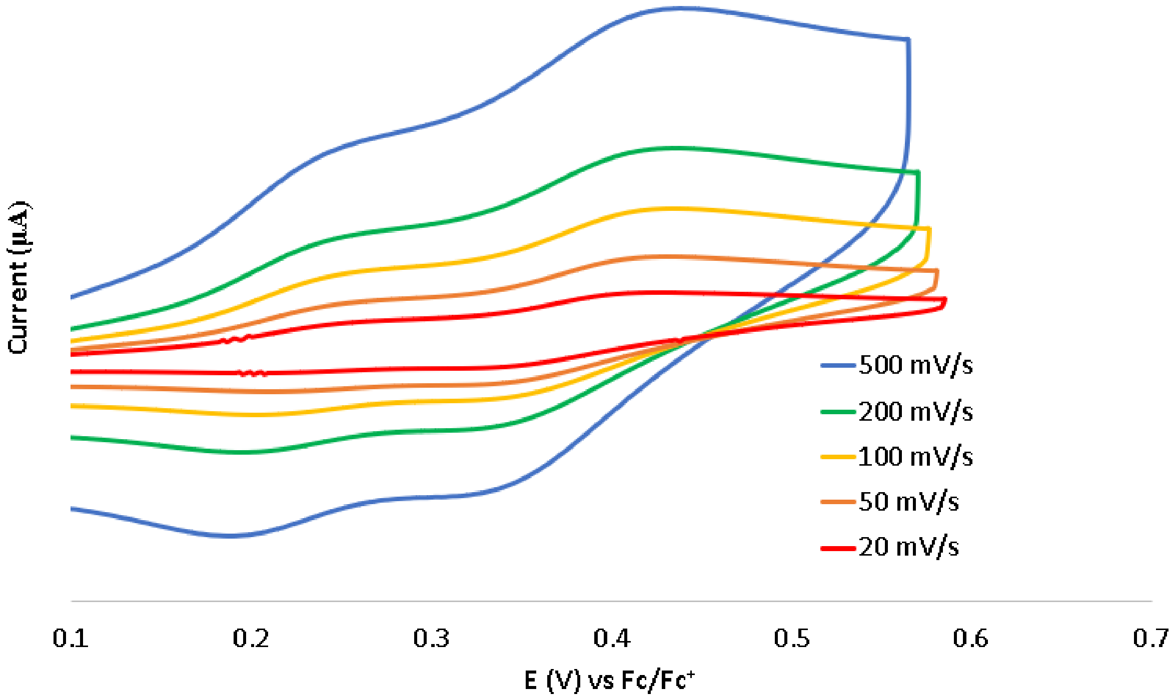

Figure S4-1: The scan rate dependent cyclic voltammogram of **8**

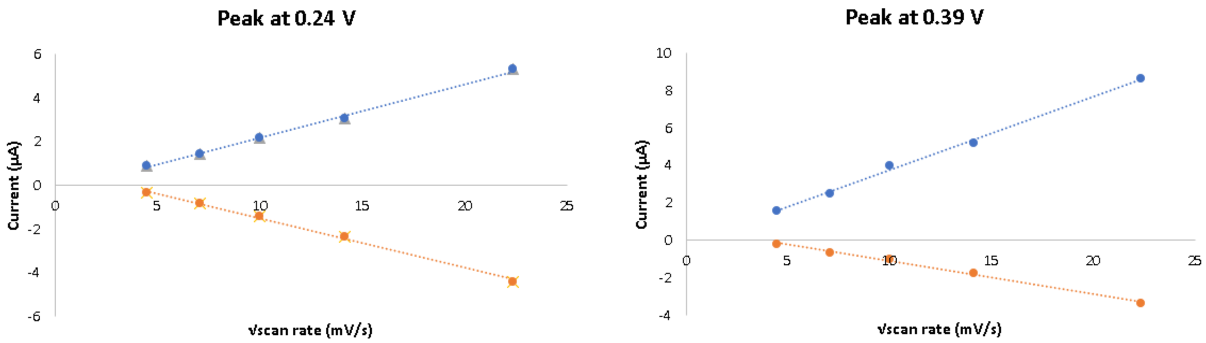

Figure S4-2: Plots of i_{pa} (top, blue) and i_{pc} (bottom, orange) vs the square root of the scan rate for the two redox processes of **8** in figure S4-1.

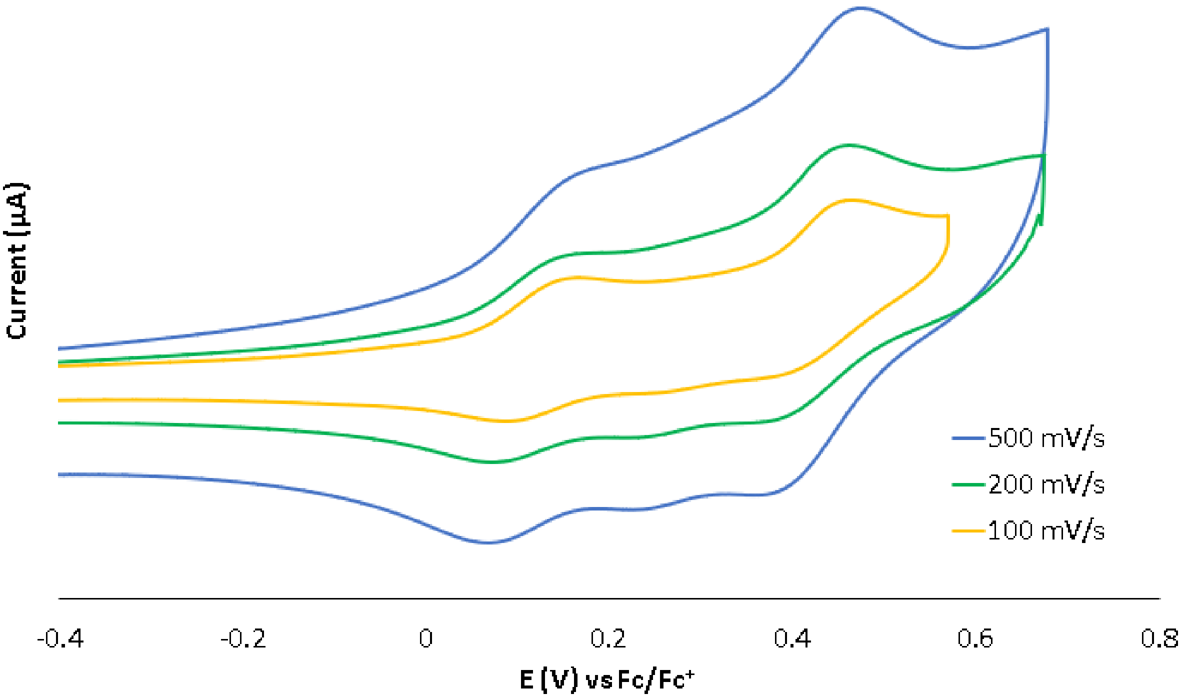

Figure S4-3: The scan-rate dependent voltammogram of **10**

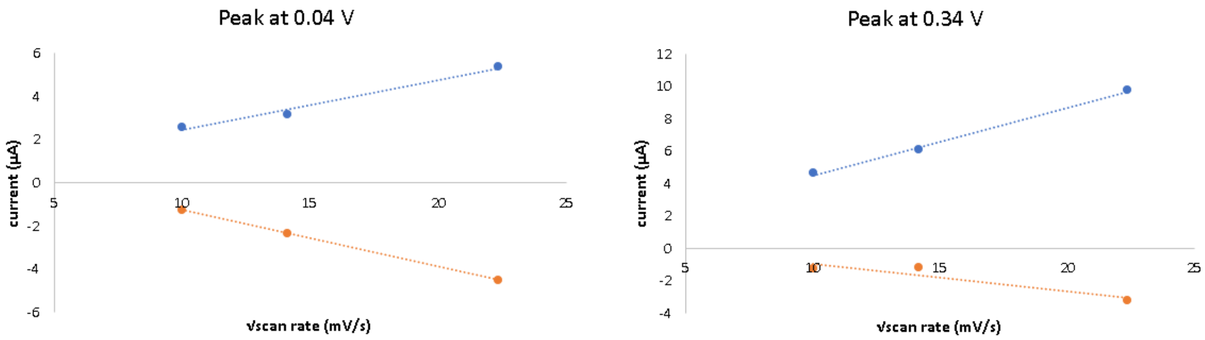

Figure S4-4: Plots of i_{pa} (top, blue) and i_{pc} (bottom, orange) vs the square root of the scan rate for the two redox processes of **10** in figure S4-3.

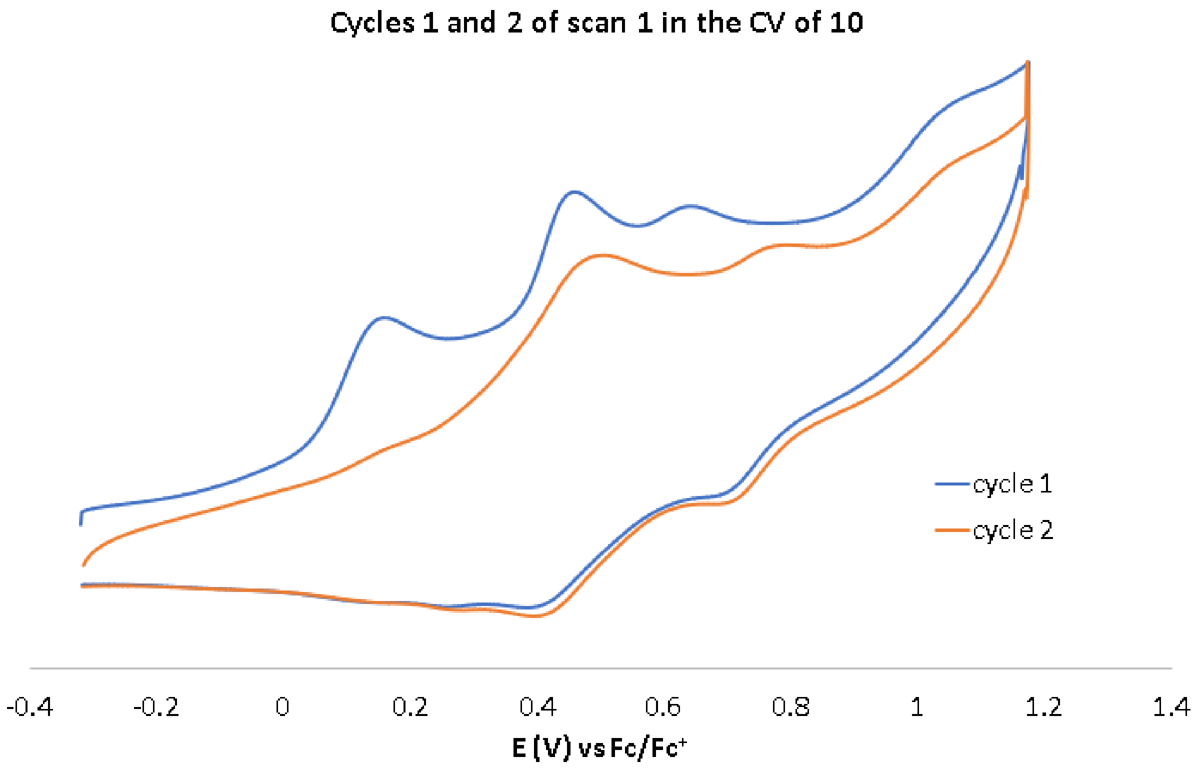

Figure S4-5: The CV of **10** showing decomposition of the material after scanning to higher potentials. The second cycle of the scan (orange) shows a loss of the signal at around 0.2 V (blue) and a shift in the signal at around 0.6 V (blue) to around 0.8 V.

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