Electronic Supplementary Information

$[Re(\eta^6\text{-arene})_2]^+$ As a Highly Stable Ferrocene-like Scaffold for Ligands and Complexes

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1. General Information

a. Materials

All reactions were carried out under nitrogen atmosphere on a standard nitrogen/vacuum line. The glassware was dried by the use of a heat gun or in an oven at 130°C. Commercially available reagents were purchased reagent-grade and used without further purification. All chemicals were purchased from Sigma Aldrich (Switzerland), except potassium perrhenate (>99%, Chempur, Germany). The chemicals were used without further purification. Deuterated NMR solvents were obtained from Armar Chemicals (Switzerland).

b. Characterization

FT-IR spectra were acquired on a Perkin Elmer Spectrum Two spectrophotometer equipped with a Specac Golden Gate single reflection diamond accessory. ^{1}H-NMR, ^{13}C{^{1}H}-NMR and DEPT-NMR spectra were recorded on a BrukerDRX 500 MHz spectrometer. ^{1}H and ^{13}C chemical shifts were referenced with the residual solvent resonance relative to TMS.

Preparative HPLC was performed on a Varian ProStar 320 system, using a Dr. Maisch Reprosil C18 100-7 (40 x 250mm) column. The solvents (HPLC grade) were 0.1% trifluoroacetic acid (solvent A) and acetonitrile (solvent B). Analytical HPLC was performed on a VWR HITACHI Chromaster system, using a Macherey-Nagel Nucleosil C18 100-5 column. HPLC solvents were 0.1% trifluoroacetic acid (solvent A) and acetonitrile (solvent B).

Electrospray-ionisation mass spectrometry (ESI-MS) was performed on a Bruker esquireTM/LC spectrometer or on a Bruker esquireTM/HCTTM spectrometer. High-resolution mass spectrometry (HR-ESI-MS) was performed on a Bruker maXis QTof high-resolution mass spectrometer (Bruker GmbH, Bremen, Germany).

Electrochemical measurements were carried out in acetonitrile and dimethylformamide containing 0.1M TBA[PF_6] as a conducting electrolyte. A Metrohm 757VA Computrace electrochemical analyzer was used with a standard three-electrode setup of glassy carbon working electrode (i.d.= 3mm), platinum auxiliary electrode and Ag/AgCl reference electrode. All potentials are given vs Ag/AgCl and are referenced with Fc/Fc^{+} at 450mV. Elemental Analysis (EA) measurements were performed on a LecoCHNS-932 elemental analyzer.

UPLC-ESI-MS was performed on a Waters Acquity UPLC System coupled to a Bruker HCTTM, using an Acquity UPLC BEH C18 1.7µm (2.1 x 50mm) column. UPLC solvents were formic acid (0.1% in millipore water) (solvent A) and acetonitrile HPLC grade (solvent B). Applied UPLC gradient: 0-0.5 minutes: 95% A, 5% B; 0.51-4.0 minutes: linear gradient from 95% A (5% B) to 0% A (100% B); 4-5 minutes: 100% B. The flow rate was 0.6 ml/min. Detection was performed between 250nm and 480nm (DAD).

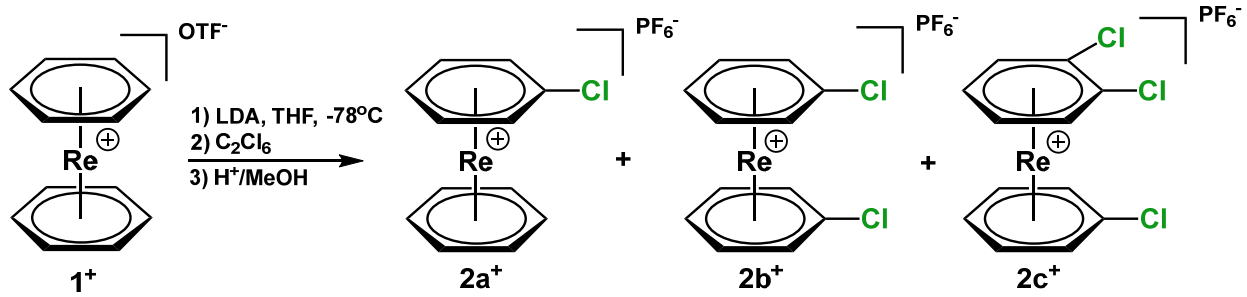
X-ray Crystallographic data were collected at either 160.0(1) or 183(1)K with either Mo Kα radiation (λ = 0.7107Å) or Cu Kα radiation (λ = 1.54184Å). Compounds [**2a**](PF_6), [**2b**](PF_6) and [**4a**](PF_6) were measured on an Oxford Diffraction CCD Xcalibur system with a Ruby detector while compounds [**5a**](PF_6), [**6b**](PF_6), [**7a**](PF_6), [**7b**](PF_6), decomposition of [**7b**](PF_6) and [**12a**]OTf were measured on a Rigaku-Oxford Diffraction, dual source, XtaLAB Synergy system with Dectris Pilatus3 R 200K. Suitable crystals were covered with oil (Infineum V8512, formerly known as Paratone N), placed on a nylon loop that is mounted in a CrystalCap Magnetic™ (Hampton Research) and immediately transferred to the diffractometer. Data were corrected for Lorentz and polarisation effects as well as for absorption (numerical). The program suite CrysAlis^{Pro} was used for data collection, multi-scan absorption correction and data reduction.[1] The structures were solved with direct methods using ShelxT[2] and were refined by full-matrix least-squares methods on F^2 with with SHELXL-2014.[3] The structures were checked for higher symmetry with help of the program Platon.[4] Supplementary crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures (CCDC nr. 1957333 to 1957341).

2. Synthetic procedures

$[Re(\eta^6\text{-}C_6H_6)_2](OTf)$ ([1](OTf))

Synthesis according to literature.[5]

$[Re(\eta^6\text{-}C_6H_5Cl)(\eta^6\text{-}C_6H_6)](PF_6)$ ([2a](PF_6)) and $[Re(\eta^6\text{-}C_6H_5Cl)_2](PF_6)$ ([2b](PF_6))



Synthesis: 300mg (0.61mmol) of [**1**](OTf) was dissolved in 30mL dry THF and cooled to -78°C. 1.5mL (1.53mmol, 2.5 eq.) of a 1M LDA in THF/hexane solution was slowly added to the yellow suspension. The reaction was stirred for 1.5h at -78°C and then 721.9mg (3.05mmol, 5 eq.) hexachloroethane was added to the dark orange solution. Stirring was continued for 7 h at -78°C and monitored by UPLC-MS. The colour of the solution changed from orange to yellow. The reaction was quenched with MeOH/HCl solution and the volume of mixture reduced under vacuum to 5mL. The orange solution was extracted with hexane (3 x 2.5mL) and evaporated in

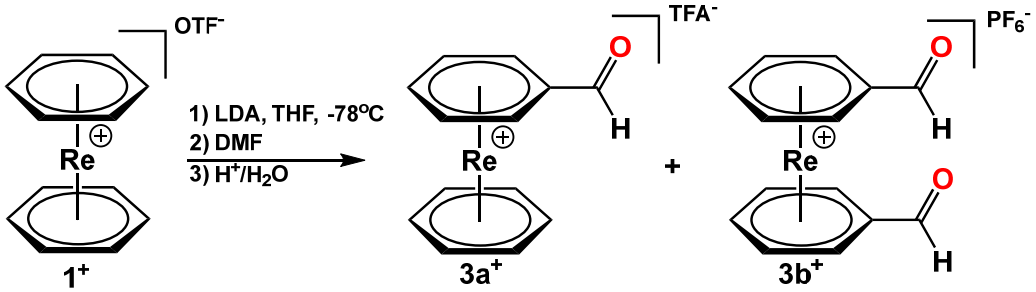
vacuum. The residue was purified by *preparative HPLC* (Reprosil 100 C18, 250mm x 40mm, 0.1% TFA/CH_3CN, linear gradient: 15-30% CH_3CN in 45min, 40mL/min, detection at 270nm). The products were precipitated upon addition of NH_4PF_6 to yield analytically pure, yellow [**2a**](PF_6), [**2b**](PF_6) and [**2c**](PF_6). Suitable crystals for X-ray for all compounds were obtained by slow evaporation from CH_3CN/H_2O (1:1). Yields: 151.7mg (0.28mmol, 47.6%) for [**2a**](PF_6), 52.3mg (0.09 mmol, 15%) for [**2b**](PF_6) and 9.2mg (0.015mmol, 2.5%) [**2c**](PF_6).

Analysis: [Re(η^6-C_6H_5Cl)(η^6-C_6H_6)](PF_6) ([**2a**](PF_6)): ^{1}H NMR (500MHz, CD_3CN) δ [ppm]: 6.51 (d, 2H, *o*-CH_{arom}), 6.04 (t, 2H, *m*-CH_{arom}), 6.02 (s, 6H, CH_{arom}), 5.83 (t, 1H, *p*-CH_{arom}), ^{13}C NMR (125MHz, CD_3CN) δ [ppm]: 100.05 (*C*Cl), 80.77 (*C*H_{arom}), 79.74 (*o*-*C*H_{arom}), 77.00 (*p*-*C*H_{arom}), 75.82 (*m*-*C*H_{arom}), IR ν [cm^{-1}]: 3097 (m), 1475 (m), 1430 (m), 1397 (w), 1082 (m), 926 (w), 807 (s), HR-ESI-MS $C_{12}H_{11}ClRe$ $[M]^+$: calculated, 377.0101; found, 377.0096.

[Re(η^6-$C_6H_5Cl)_2$](PF_6) ([**2b**](PF_6)): ^{1}H NMR (500MHz, CD_3CN) δ [ppm]: 6.49 (d, 4H, *o*-CH_{arom}), 6.11 (t, 4H, *m*-CH_{arom}), 5.90 (t, 2H, *p*-CH_{arom}), ^{13}C NMR (125MHz, CD_3CN) δ [ppm]: 101.65 (*C*Cl), 82.25 (*o*-*C*H_{arom}), 79.53 (*p*-*C*H_{arom}), 78.68 (*m*-*C*H_{arom}), IR ν [cm^{-1}]: 3097 (m), 1498 (w), 1428 (m), 1396 (m), 1278 (w), 1088 (m), 1026 (w), 928 (m), 904 (w), 839 (s), 813 (s), 705 (m)cm^{-1}. HR-ESI-MS $C_{12}H_{10}Cl_2Re$ $[M]^+$: calculated, 410.9711; found, 410.9702.

[Re(η^6-$C_6H_4Cl_2$)(η^6-C_6H_5Cl)](PF_6) ([**2c**](PF_6)): ^{1}H NMR (500MHz, CD_3CN) δ [ppm]: 6.71 (dd, 2H, *o*-CH_{arom}), 6.42 (d, 2H, *o*-CH_{arom}), 6.19 (t, 2H, *m*-CH_{arom}), 6.01 (dd, 2H, *m*-CH_{arom}), 5.95 (t, 1H, *p*-CH_{arom}). ^{13}C NMR (125MHz, CD_3CN) δ [ppm]: 103.5 (*C*Cl), 102.59 (*C*Cl), 84.77 (*o*-*C*H_{arom}), 81.0 (*p*-*C*H_{arom}), 80.9 (*m*-*C*H_{arom}), 80.4 (*o*-*C*H_{arom}), 78.4 (*m*-*C*H_{arom}). IR ν [cm^{-1}]: 3092 (m), 2923 (m), 2851 (w), 1429 (m), 1404 (m), 1383 (m), 1112 (w), 1085 (w), 1029 (w), 821 (s), 737 (m)cm^{-1}. HR-ESI-MS $C_{12}H_9Cl_3Re$ $[M]^+$: calculated, 444.9327; found, 444.9305.

[Re(η^6-C_6H_5COH)(η^6-C_6H_6)](TFA) ([3a](TFA)) and [Re(η^6-$C_6H_5COH)_2$](PF_6) ([3b](PF_6))



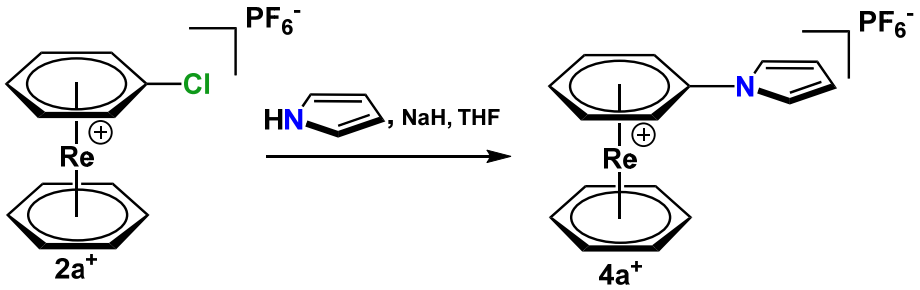
Synthesis: 200mg (0.41mmol) of [**1**](OTf) was dissolved in 20mL dry THF and cooled to -78°C. 0.62 mL (0.62mmol, 1.5 eq.) of a 1M LDA in THF/hexane solution was slowly added to the yellow suspension. The reaction was stirred for 1.5h at -78°C and then 2mL (25.9mmol, 63eq.) dry dimethylformamide was added to the dark orange solution. Stirring was continued for 4h at -78°C and monitored by UPLC-MS. The colour of the solution changed to light orange. The

reaction was quenched with acidic water (H_2O/TFA, 0.1%) and the volume of mixture reduced under vacuum to 5mL. The residue was purified by *preparative HPLC* (Reprosil 100 C18, 250x40mm, 0.1% TFA/CH_3CN, isocratic gradient: 5% CH_3CN in 45min, 40mL/min, detection at 270nm). Product [**3a**](TFA) was obtained analytically pure as an orange oil. [**3b**]TFA was not totally pure. It was then redissolved in water, and NH_4PF_6 was added to change the counter ion. A continuous liquid-liquid extraction (DCM/water) was performed to get the product in the organic phase. After evaporation of the solvent, the solid was washed with a minimum amount of cold water to get an orange solid analytically pure. Yields: 74mg (0.153mmol, 37.8%) for [**3a**](TFA) and 13.2mg (0.0243mmol, 5.9%) for [**3b**](PF_6).

Analysis: [Re(η^6-C_6H_5COH)(η^6-C_6H_6)](TFA) ([**3a**](TFA)): ^{1}H NMR (500MHz, CD_3CN) δ [ppm]: 9.76 (s, 1H, CO*H*), 6.46 (d, 2H, *o*-CH_{arom}), 6.17 (t, 2H, *m*-CH_{arom}), 6.11 (t, 1H, p-CH_{arom}), 6.07 (s, 6 H, CH_{arom}). ^{13}C NMR (125MHz, CD_3CN) δ [ppm]: 194.95 (*C*OH), 82.63 (C_{arom}), 80.75 (*C*H$_{arom}$), 77.83 (*C*H$_{arom}$), 76.82 (*C*H$_{arom}$), 76.57 (*C*H$_{arom}$) IR ν [cm^{-1}]: 3076 (m), 1708 (s), 1684 (s), 1435 (m), 1406 (m), 1258 (s), 1194 (s), 1117 (s), 1029 (s), 861 (m), 812 (m), 800 (m), 716 (m), 636 (s). HR-ESI-MS $C_{13}H_{12}ORe$ $[M]^+$: calculated, 371.04402; found, 371.04345 and 403.06938 (mass of the corresponding hydrate).

[Re(η^6-$C_6H_5COH)_2$](PF_6) ([**3b**](PF_6)): ^{1}H NMR (500MHz, CD_3CN) δ [ppm]: 9.75 (s, 1H, CO*H*), 6.56 (d, 2H, *o*-CH_{arom}), 6.30 (t, 2H, *m*-CH_{arom}), 6.24 (t, 1*H*, *p*-CH_{arom}). ^{13}C NMR (500 MHz, CD_3CN) δ [ppm]: 193.31 (*C*OH), 85.11 (C_{arom}), 80.81 (*C*H$_{arom}$), 80.02 (*C*H$_{arom}$), 79.51 (*C*H$_{arom}$). IR ν [cm^{-1}]: 3097 (w), 3061 (w), 2920 (w), 2852 (w), 1707 (s), 1523 (w), 1491 (w), 1395 (w), 1374 (w), 1286 (w), 1191 (m), 1050 (w), 1001 (w), 933 (w), 828 (s), 632 (m). HR-ESI-MS $C_{14}H_{12}O_2Re$ $[M]^+$: calculated, 399.03893; found, 399.03848.

[Re(η^6-C_6H_5-NC_4H_5)(η^6-C_6H_6)](PF_6) ([4a](PF_6))

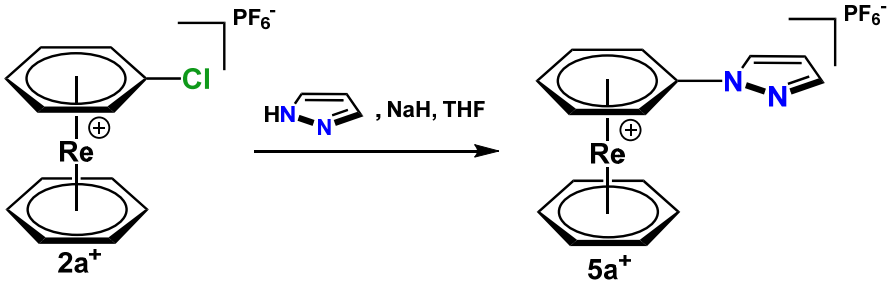


Synthesis: 21mg (0.88mmol, 15 eq.) of NaH was added to 100 µL of pyrrole (1.44mmol, 25 eq.) and the mixture was stirred for 2h at 60°C in 5ml of dry THF. Afterwards, 30mg of [**2a**](PF_6) (0.057mmol) was added to the mixture. The solution was stirred for 3h at 60°C. The mixture was cooled to room temperature, quenched with 1mL of acidic water (H_2O/TFA 0.1%) and neutralized with a solution of trifluoroacetic acid (2mol/L). The solvent was evaporated in

vacuum. The residue was washed with hexane (3 x 5mL), water (2 x 3mL) and isolated after preparative HPLC (Reprosil 100 C18, 250mm x 40mm, 0.1% TFA/CH_3CN, linear gradient: 15-100% CH_3CN in 45 min, 40mL/min, detection at 285nm). Analytically pure yellow [Re(η^6-C_6H_5-NC_4H_5)(η^6-C_6H_6)](PF_6) was precipitated from the HPLC eluent upon addition of NH_4PF_6. Single crystals, suitable for X-ray diffraction analysis were obtained by slow evaporation of an acetonitrile solution of [Re(η^6-C_6H_5-NC_4H_5)(η^6-C_6H_6)](PF_6). Yield: 7.5mg (0.014mmol, 23.8%) of [Re(η^6-C_6H_5-NC_4H_5)(η^6-C_6H_6)](PF_6).

Analysis: [Re(η^6-C_6H_5-NC_4H_5)(η^6-C_6H_6)](PF_6) ([**4a**](PF_6)): ^{1}H NMR (500MHz, CD_3CN) δ [ppm]: 7.03 (t, 2H, C$H_{pyrrole}$), 6.69 (d, 2H, *o*-CH_{arom}), 6.27 (t, 2H, C$H_{pyrrole}$), 6.13 (t, 2H, *m*-CH_{arom}), (5.89 (s, CH_{arom}) and 5.86 (t, *p*-CH_{arom}) 7 H). ^{13}C NMR (125MHz, CD_3CN δ [ppm]: 121.11 (C$H_{pyrrole}$), 112.29 (C$H_{pyrrole}$), 78.71 (CH_{arom}), 77.23 (CH_{arom}), 74.78 (CH_{arom}), 72.41 (CH_{arom}). IR ν cm^{-1}: 3100 (w), 2956 (w), 2921 (s), 2851 (w), 1662 (w), 1631 (w), 1522 (m), 1495 (m), 1479 (m), 1433 (m), 1320 (m), 817 (s), 731 (s). HR-ESI-MS $C_{16}H_{15}NRe$ $[M]^+$: calculated, 408.07620; found, 408.07563.

[Re(η^6-C_6H_5-NC_3H_4N)(η^6-C_6H_6)](PF_6) ([5a](PF_6))

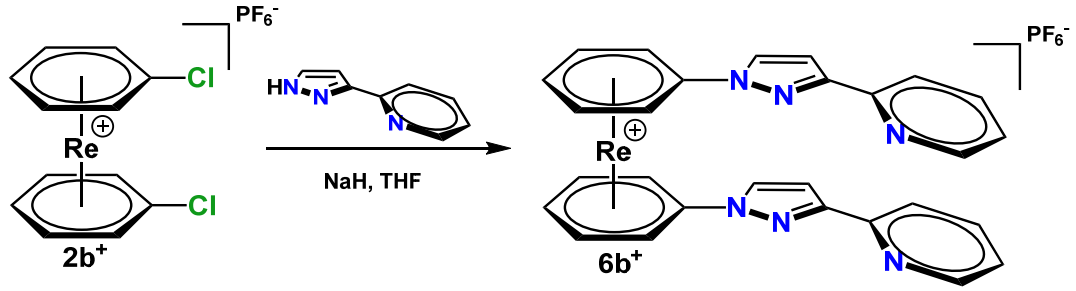


Synthesis: 21mg (0.88mmol, 15 eq.) of NaH, 98mg of pyrazole (1.44mmol, 25 eq.) was added to 5mL of dry THF and the mixture was stirred for 2h at 60°C. Afterwards, 30mg of [**2a**](PF_6) (0.057mmol) was added to the mixture. The yellowish solution was stirred for 3h at 60°C. The mixture was cooled to room temperature, quenched with 1mL of acidic water (H_2O/TFA 0.1%) and neutralized with a solution of trifluoroacetic acid (2mol/L). The solvent was evaporated in vacuum. The residue was washed with hexane (3 x 5mL) and water (2 x 3mL). Analytically pure yellow [Re(η^6-C_6H_5-NC_3H_4N)(η^6-C_6H_6)](PF_6) was precipitated from the aqueous solution by the addition of NH_4PF_6. Single crystals, suitable for X-ray diffraction analysis were obtained by slow evaporation of an acetonitrile solution of [Re(η^6-C_6H_5-NC_3H_4N)(η^6-C_6H_6)](PF_6). Yield: 30.9mg (0.053mmol, 98.2%) of [Re(η^6-C_6H_5-NC_3H_4N)(η^6-C_6H_6)](PF_6).

Analysis: ^{1}H NMR (500MHz, CD_3CN) δ [ppm]: 7.98 (d, 1H, C$H_{pyrazole}$), 7.68 (d, 1H, C$H_{pyrazole}$), 6.97 (d, 2H, *o*-CH_{arom}), 6.48 (t, 1H, C$H_{pyrazole}$), 6.18 (t, 2H, *m*-CH_{arom}), 5.91 (t, 1H, *p*-CH_{arom}), 5.87 (s, 6H, CH_{arom}). ^{13}C NMR (125MHz, CD_3CN δ [ppm]: 143.30 (C$H_{pyrazole}$), 129.86 (C$H_{pyrazole}$),

109.90 (*C*H$_{pyrazole}$), 79.32 (*C*H$_{arom}$), 77.77 (*C*H$_{arom}$), 75.09 (*C*H$_{arom}$), 71.36 (*C*H$_{arom}$). IR ν cm^{-1}: 3088 (w), 1529 (w), 1518 (w), 1455 (w), 1433 (w), 700 (s), 762 (s). HR-ESI-MS $C_{15}H_{14}N_2Re$ [M]$^+$: calculated, 409.07145; found, 409.07110.

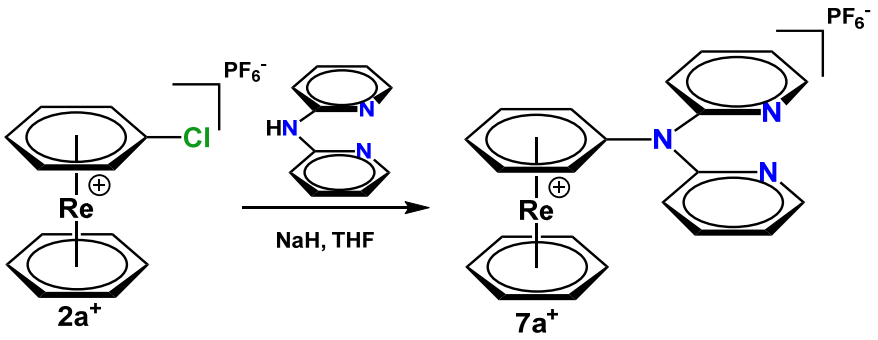
[Re(η^6-C$_6$H$_5$-C$_8$H$_6$N$_3$)$_2$](PF$_6$) ([6b](PF$_6$))



Synthesis: 20.1mg (0.88mmol, 16 eq.) of NaH, 160mg of pyrazole-pyridine (1.10mmol, 20 eq.) was added to 5mL of dry THF and the mixture was stirred for 2h at 60°C. Afterwards, 30,9mg of [**2b**](PF$_6$) (0.056mmol) was added to the mixture. The yellowish solution was stirred for 3h at 60°C. The mixture was cooled to room temperature, quenched with 1mL of acidic water (H$_2$O/TFA 0.1%) and neutralized with a solution of trifluoroacetic acid (2mol/L). The solvent was evaporated in vacuum. The residue was washed with hexane (3 x 5mL), water (2 x 3mL) and isolated after preparative HPLC (Reprosil 100 C18, 250 mm x 40 mm, 0.1% TFA/CH$_3$CN, linear gradient: 15-100% CH$_3$CN in 45min, 40mL/min, detection at 285nm). NH$_4$PF$_6$ was added and the product was extracted by continuous liquid-liquid extraction (DCM/water) over night. The Organic phase was evaporated which afforded [Re(η^6-C$_6$H$_5$-C$_8$H$_6$N$_3$)$_2$](PF$_6$) as analytically pure, yellow crystalline powder. Single crystals, suitable for X-ray diffraction analysis were obtained by vapour diffusion Acetone/diethyl ether. Yield: 41.8mg (0.054mmol, 96.4%) of [Re(η^6-C$_6$H$_5$-C$_8$H$_6$N$_3$)$_2$](PF$_6$).

Analysis: ^{1}H NMR (500MHz, CD$_3$CN) δ [ppm]: 8.48 (d, 1H, C*H*$_{pyridine}$), 7.83 (m, 3H, C*H*$_{pyridine}$, C*H*$_{pyrazole}$), 7.39 (t, 1H, C*H*$_{pyridine}$), 7.01 (d, 2H, *o*-C*H*$_{arom}$), 6.73 (d, 1H, C*H*$_{pyrazole}$), 6.29 (t, 2H, *m*-C*H*$_{arom}$), 5.96 (t, 1H, *p*-C*H*$_{arom}$). ^{13}C NMR (125MHz, CD$_3$CN δ [ppm]: 152.52 (*C*$_{pyridine}$), 149.53 (*C*$_{pyrazole}$), 148.15 (*C*H$_{pyridine}$), 140.39 (*C*H$_{pyridine}$), 131.14 (*C*H$_{pyrazole}$), 124.97 (*C*H$_{pyridine}$), 122.03 (*C*H$_{pyridine}$), 108.81 (*C*H$_{pyrazole}$), 103.23 (*C*$_{arom}$), 78.56 (*C*H$_{arom}$), 76.83 (*C*H$_{arom}$), 72.36 (*C*H$_{arom}$). IR ν cm^{-1}: 3100.8 (w), 2960 (w), 2924 (w), 2856 (w), 1591 (w), 1543 (m), 1531 (m), 1487 (w), 1459 (m), 1366 (m), 1274 (m), 1045 (m), 832 (s), 756 (s). HR-ESI-MS $C_{28}H_{22}N_6Re$ [M]$^+$: calculated, 629.14572; found, 629.14549.

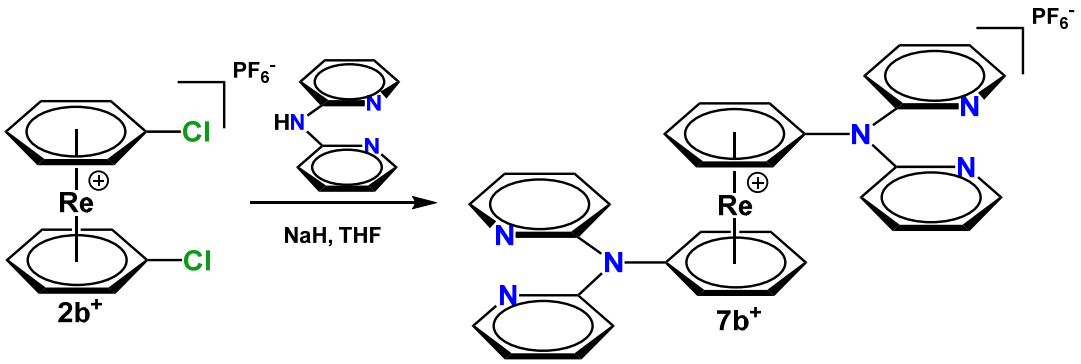
[Re(η^6-C$_6$H$_5$-N(C$_5$H$_5$N)$_2$)(η^6-C$_6$H$_6$)](PF$_6$) ([7a](PF$_6$))



Synthesis: 21mg (0.88mmol, 15 eq.) of NaH and 220mg (1.285 mmol, 22 eq.) of 2,2'-dipyridylamine were added to 5 mL of dry THF and the mixture was stirred for 2h at 60°C. Afterwards, 30.8mg of [**2b**](PF$_6$) (0.059mmol) was added to the mixture. The solution was stirred for 3h at 60°C. The mixture was cooled to room temperature, quenched with 1 mL of acidic water (H$_2$O/TFA 0.1%) and neutralized with a solution of trifluoroacetic acid (2 mol/L). The solvent was evaporated in vacuum. The residue was washed with hexane (3 x 5mL), water (2 x 3mL) and isolated after preparative HPLC (Reprosil 100 C18, 250 mm x 40mm, 0.1% TFA/CH$_3$CN, linear gradient: 25-75% CH$_3$CN in 45min, 40mL/min, detection at 290nm). Analytically pure yellow [Re(η^6-C$_6$H$_5$-N(C$_5$H$_5$N)$_2$)(η^6-C$_6$H$_6$)](PF$_6$) was precipitated from the HPLC eluent by the addition of NH$_4$PF$_6$. Single crystals, suitable for X-ray diffraction analysis were obtained by slow evaporation of an acetonitrile solution of [Re(η^6-C$_6$H$_5$-N(C$_5$H$_5$N)$_2$)(η^6-C$_6$H$_6$)](PF$_6$). Yield: 28.7mg (0.043mmol, 74.1%) of [Re(η^6-C$_6$H$_5$-N(C$_5$H$_5$N)$_2$)(η^6-C$_6$H$_6$)](PF$_6$).

Analysis: ^{1}H NMR (500MHz, CD$_3$CN) δ [ppm]: 8.49 (dd, 2H, C*H*$_{pyridine}$), 7.78 (dt, 2H, C*H*$_{pyridine}$), 7.24 (dt, 2H, C*H*$_{pyridine}$), 6.91 (d, 2H, C*H*$_{pyridine}$), 6.14 (d, 2H, *o*-C*H*$_{arom}$), 5.97 (t, 2H, *m*-C*H*$_{arom}$), (5.82 (s, C*H*$_{arom}$), 5.78 (t, 7H, *p*-C*H*$_{arom}$). ^{13}C NMR (125MHz, CD$_3$CN δ [ppm]: 156.65 (*C*$_{pyridine}$), 149.89 (*C*H$_{pyridine}$), 140.06 (*C*H$_{pyridine}$), 122.17 (*C*H$_{pyridine}$), 120.69 (*C*H$_{pyridine}$), 113.12 (*C*$_{arom}$), 77.89 (*C*H$_{arom}$), 76.74 (*C*H$_{arom}$), 75.32 (*C*H$_{arom}$), 72.43 (*C*H$_{arom}$). IR ν cm^{-1}: 3089 (w), 2961 (w), 2926 (w), 1578 (m), 1513 (m), 1466 (m), 1427 (m), 1316 (m), 1264 (m), 828 (s), 774 (s), 741 (m). HR-ESI-MS C$_{22}$H$_{19}$N$_3$Re [M]$^+$: calculated, 512.11322; found, 512.11319. Elem. Anal. calculated C: 40.24, H: 2.92, N: 6.40; found C: 39.85, H: 3.017, N: 6.060.

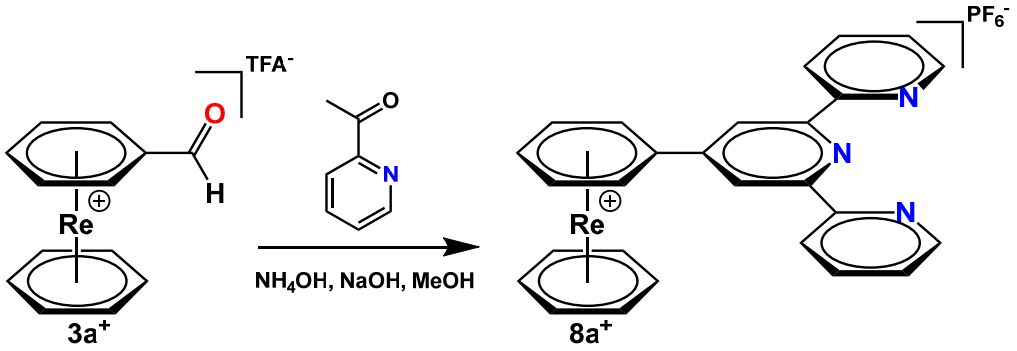
[Re(η^6-C_6H_5-N(C_5H_5N)$_2$)$_2$](PF$_6$) ([7b](PF$_6$))



Synthesis: 31.2 mg (1.30mmol, 16 eq.) of NaH and 365mg (2.13mmol, 26 eq.) of 2,2'-dipyridylamine were added to 5mL of dry THF and the mixture was stirred for 2h at 60°C. Afterwards, 45.5mg of [**2b**](PF$_6$) (0.081 mmol) was added to the mixture. The solution was stirred for 3h at 60°C. The mixture was cooled to room temperature, quenched with 1mL of acidic water (H_2O/TFA 0.1%) and neutralized with a solution of trifluoroacetic acid (2mol/L). The solvent was evaporated in vacuum. The residue was washed with hexane (3 x 5mL), water (2 x 3mL) and isolated after preparative HPLC (Reprosil 100 C18, 250mm x 40mm, 0.1% TFA/CH_3CN, linear gradient: 25-75% CH_3CN in 45min, 40mL/min, detection at 300nm). Analytically pure yellow [Re(η^6-C_6H_5-N(C_5H_5N)$_2$)$_2$](PF$_6$) was precipitated from the HPLC eluent upon addition of NH_4PF_6. Single crystals, suitable for X-ray diffraction analysis were obtained by vapor diffusion DCM/cyclopentane. Yield: 16mg (0.019mmol, 23.7%) of [Re(η^6-C_6H_5-N(C_5H_5N)$_2$)$_2$](PF$_6$).

Analysis: ^{1}H NMR (500MHz, CD_3CN) δ [ppm]: 8.37 (dd, 4H, C*H*$_{pyridine}$), 7.72 (dt, 4H, C*H*$_{pyridine}$), 7.18 (dt, 4H, C*H*$_{pyridine}$), 6.89 (d, 4H, C*H*$_{pyridine}$), 6.01 (d, 4H, *o*-C*H*$_{arom}$), 5.87 (t, 4H, *m*-C*H*$_{arom}$), 5.73 (t, 2H, *p*-C*H*$_{arom}$). ^{13}C NMR (125MHz, CD_3CN δ [ppm]: 156.72 (*C*$_{pyridine}$), 149.71 (*C*H$_{pyridine}$), 140.00 (*C*H$_{pyridine}$), 122.01 (*C*H$_{pyridine}$), 120.61 (*C*H$_{pyridine}$), 113.12 (*C*$_{arom}$), 77.94 (*C*H$_{arom}$), 75.90 (*C*H$_{arom}$), 72.79 (*C*H$_{arom}$). IR ν cm^{-1}: 3064 (w), 2960 (w), 2920 (w), 1587 (w), 1563 (w), 1503 (w), 1467 (w), 1423 (m), 1319 (m), 834 (s), 780 (m), 748 (m). HR-ESI-MS $C_{32}H_{26}N_6Re$ [M]$^+$: calculated, 681.17730; found, 681.17717.

[Re(η^6-C_6H_5-terpy)(η^6-C_6H_6)](PF$_6$) ([8a](PF$_6$))

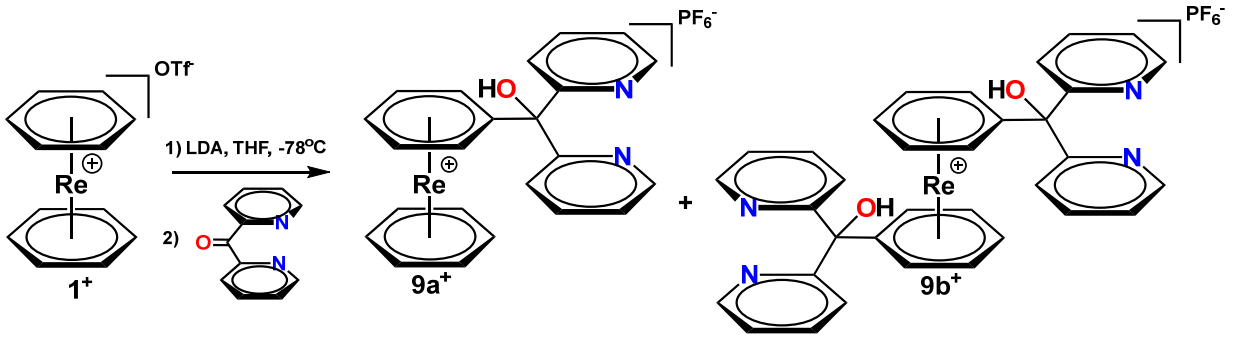


Synthesis: 74mg (0.15mmol) of [**3a**](TFA), 10 mL of NH_4OH solution 25% in mass, high excess of NaOH (1 pellet) and 52µL of acetyl pyridine (0.46mmol, 3 eq.) was dissolved in 10 mL of MeOH. The reaction mixture was stirred for 3h at room temperature. The solvent was then evaporated and the solid was redissolved in water. The product was precipitated upon addition of NH_4PF_6. The solid was filtered and washed with cold water to get a light orange-brownish solid. Yield: 46mg (0.064mmol, 41.8 %) of [Re(η^6-C_6H_5-terpy)(η^6-C_6H_6)](PF_6).

Analysis: ^{1}H NMR (500MHz, CD_3CN) δ [ppm]: 9.18 (d, 2H, C*H*$_{terpy}$), 8.86 (d, 2H, C*H*$_{terpy}$), 8.65 (t, 2H, C*H*$_{terpy}$), 8.58 (s, 2H, C*H*$_{terpy}$), 8.08 (t, 2H, C*H*$_{terpy}$), 6.84 (d, 2H, *o*-C*H*$_{arom}$), 6.31 (t, 2H, *m*-C*H*$_{arom}$), 6.15 (t, 1H, *p*-C*H*$_{arom}$), 6.02 (s, 6H, C*H*$_{arom}$). ^{13}C NMR (125MHz, CD_3CN) δ [ppm]: 151.85 (*C*$_{terpy}$), 150.61 (*C*$_{terpy}$), 149.16 (*C*$_{terpy}$), 146.79 (*C*H$_{terpy}$), 145.49 (*C*H$_{terpy}$), 128.80 (*C*H$_{terpy}$), 125.81 (*C*H$_{terpy}$), 123.91 (*C*H$_{terpy}$), 88.78 (*C*$_{arom}$), 80.59 (*C*H$_{arom}$), 77.72 (*C*H$_{arom}$), 77.05 (*C*H$_{arom}$), 76.96 (*C*H$_{arom}$). IR ν [cm^{-1}]: 3089 (w), 1584 (m), 1565 (w), 1555 (w), 1467 (w), 1435 (w), 1410 (w), 993 (w), 833 (s), 792 (m), 740 (m). HR-ESI-MS $C_{27}H_{21}N_3Re$ $[M]^+$: calculated, 574.12875; found, 574.12825.

[Re(η^6-$C_6H_5C(C_5H_5N)_2(OH)$)(η^6-C_6H_6)](PF_6) ([9a](PF_6))

[Re(η^6-$C_6H_5C(C_5H_5N)_2(OH))_2$]($PF_6$) ([9b]($PF_6$))



Synthesis: 25.6mg (0.05mmol) of [**1**](OTf) was dissolved in 6mL of dry THF and cooled to -78°C. Afterward, 0.15mL (0.15mmol, 3 eq.) of a 1M LDA solution (THF/hexane) was added slowly to the yellow suspension. The reaction was stirred for 1.5h at -78°C, and 95mg (0.52mmol, 10 eq.) of 2,2′-dipyridyl ketone was added to the clear orange solution. Stirring was

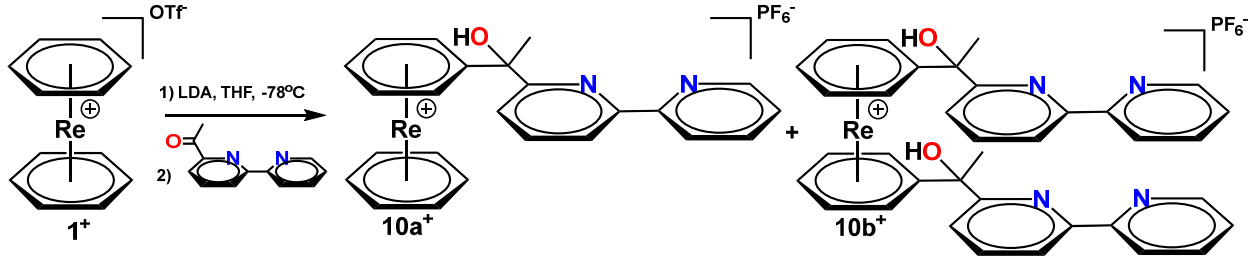
continued for 5h at -78°C. The color of the solution changed from orange to dark blue. The reaction was quenched with acidified H_2O (H_2O/TFA 0.1%) and the volume of the mixture was reduced under N_2 flow. The solution was extracted with diethylether (3 x 10mL) and the remaining solvent was evaporated in vacuum. The residue was purified by preparative HPLC (Reprosil 100 C18, 250 mm x 40mm, 0.1% TFA/CH_3CN, linear gradient 25-75% CH_3CN in 60min, 40mL/min, detection at 270nm). Analytically pure yellow [Re(η^6-$C_6H_5C(C_5H_5N)_2(OH)$)(η^6-C_6H_6)](PF_6) and [Re(η^6-$C_6H_5C(C_5H_5N)_2(OH))_2$]($PF_6$) precipitated from the solution upon addition of NH_4PF_6. Yields: 6.8mg (0.01mmol, 19.4%) for [Re(η^6-$C_6H_5C(C_5H_5N)_2(OH)$)(η^6-C_6H_6)](PF_6) and 20.5mg (0.024 mmol, 46.1%) for [Re(η^6-$C_6H_5C(C_5H_5N)_2(OH))_2$]($PF_6$).

Analysis: [Re(η^6-$C_6H_5C(C_5H_5N)_2(OH)$)(η^6-C_6H_6)](PF_6) (**[9a]**(PF_6)): ^{1}H NMR (500MHz, CD_3CN) δ [ppm]: 8.59 (d, 2H, C*H*$_{pyridine}$), 7.81 (m, 4H, C*H*$_{pyridine}$), 7.36 (m, 2H, C*H*$_{pyridine}$), 6.33 (m, 2H, *m*-C*H*$_{arom}$), 5.90 (m, 3H, *o,p*-C*H*$_{arom}$), 5.72 (s, 6H, C*H*$_{arom}$). ^{13}C NMR (125MHz, CD_3CN) δ [ppm]: 161.09 (*C*$_{pyridine}$), 148.78 (*C*H$_{pyridine}$), 138.49 (*C*H$_{pyridine}$), 124.56 (*C*H$_{pyridine}$), 122.91 (*C*H$_{pyridine}$), 105.21 (*C*$_{arom}$), 79.34 (*C*$_{sp3}$), 78.09 (*C*H$_{arom}$), 78.04 (*C*H$_{arom}$), 76.47 (*C*H$_{arom}$), 76.37 (*C*H$_{arom}$). IR (as a [10a]TFA) ν [cm^{-1}]: 3381 (w), 3076 (w), 1678 (m), 1587 (w), 1433 (m), 1197 (m), 1175 (m), 1121 (s), 831 (w), 800 (w), 779 (w), 719 (w). HR-ESI-MS $C_{23}H_{20}N_2ORe$ $[M]^+$: calculated, 527.11277; found, 527.11261.

[Re(η^6-$C_6H_5C(C_5H_5N)_2(OH))_2$]($PF_6$) (**[9b]**($PF_6$)): ^{1}H NMR (500MHz, CD_3CN) δ [ppm]: 8.59 (dt, 4H, C*H*$_{pyridine}$), 7.88 (td, 4H, C*H*$_{pyridine}$), 7.76 (d, 4H, C*H*$_{pyridine}$), 7.43 (qd, 4*H*, C*H*$_{pyridine}$), 6.12 (d, 4*H*, *o*-C*H*$_{arom}$), 5.76 (t, 2*H*, *p*-C*H*$_{arom}$), 5.68 (t, 4*H*, *m*-C*H*$_{arom}$). ^{13}C NMR (125MHz, CD_3CN) δ [ppm]: 160.06 (*C*$_{pyridine}$), 148.16 (*C*H$_{pyridine}$), 139.58 (*C*H$_{pyridine}$), 125.02 (*C*H$_{pyridine}$), 123.39 (*C*H$_{pyridine}$), 104.66 (*C*$_{arom}$), 79.07 (*C*$_{sp3}$), 78.48 (*C*H$_{arom}$), 77.46 (*C*H$_{arom}$), 77.33 (*C*H$_{arom}$). IR ν [cm^{-1}]: 3369 (w), 3301 (w), 2033 (w), 1808 (w), 1655 (w), 1471 (m), 1390 (m), 1182 (w), 1150 (w), 820 (s). HR-ESI-MS $C_{34}H_{28}O_2N_4Re$ $[M]^+$: calculated, 711.17656; found, 711.17640.

[Re(η^6-$C_6H_5CCH_3C_{10}H_7N_2(OH)$)($\eta^6$-$C_6H_6$)]($PF_6$) ([10a]($PF_6$))

[Re(η^6-$C_6H_5CCH_3(C_{10}H_7N_2)_2(OH)$]($PF_6$) ([10b]($PF_6$))



Synthesis: 200mg (0.41mmol) of [**1**](OTf) was dissolved in 20mL of dry THF and cooled to -78°C. Afterward, 1.2mL (1.2mmol, 3 eq.) of a 1M LDA solution (THF/hexane) was added slowly to the yellow suspension. The reaction was stirred for 1.5h at -78°C, and 406mg (2.05mmol, 5 eq.) of 1-(2,2'-bipyridin-6-yl)ethanone was added to the clear orange solution. Stirring was continued for 5 h at -78°C. The reaction was quenched with acidified H_2O (H_2O/TFA 0.1%) and the volume of the mixture was reduced under N_2 flow. The solution was extracted with diethylether (3 x 10mL) and the remaining solvent was evaporated in vacuum. The residue was purified by preparative HPLC (Reprosil 100 C18, 250mm x 40mm, 0.1% TFA/CH_3CN, linear gradient 10-30% CH_3CN in 45 min, 40mL/min, detection at 310nm). Analytically pure yellow $[Re(\eta^6\text{-}C_6H_5CCH_3C_{10}H_7N_2(OH))(\eta^6\text{-}C_6H_6)](PF_6)$ and $[Re(\eta^6\text{-}C_6H_5CCH_3(C_{10}H_7N_2)_2(OH)](PF_6)$ precipitated from the solution upon addition of NH_4PF_6. Yields: 31.2mg (0.046mmol, 11.2%) for $[Re(\eta^6\text{-}C_6H_5CCH_3C_{10}H_7N_2(OH))(\eta^6\text{-}C_6H_6)](PF_6)$ and 31.3mg (0.035mmol, 8.7%) for $[Re(\eta^6\text{-}C_6H_5CCH_3(C_{10}H_7N_2)_2(OH)](PF_6)$.

Analysis:

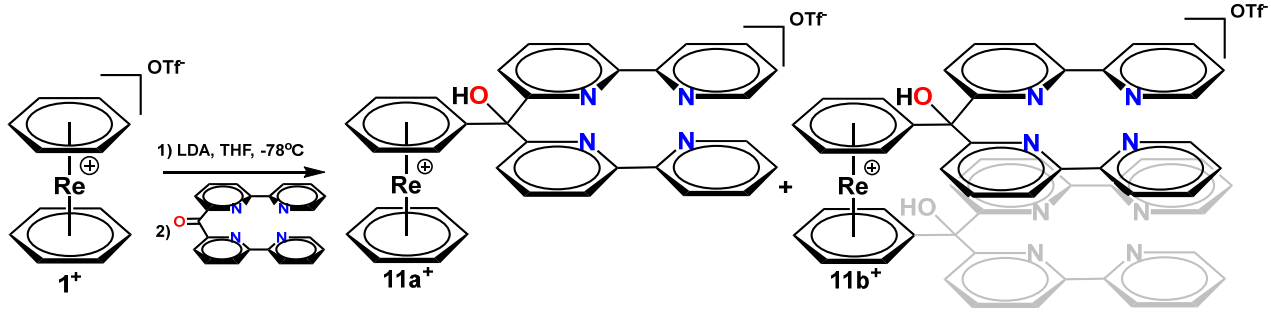
$[Re(\eta^6\text{-}C_6H_5CCH_3C_{10}H_7N_2(OH))(\eta^6\text{-}C_6H_6)](PF_6)$ ([**10a**](PF$_6$)): ^{1}H NMR (500 MHz, CD_3CN) δ [ppm]: 8.68 (dt, 1H, C$H_{pyridine}$), 8.49 (d, 1H, C$H_{pyridine}$), 8.37 (d, 1H, C$H_{pyridine}$), 7.97 (t, 1*H*, C$H_{pyridine}$), 7.93 (td, 1*H*, C$H_{pyridine}$), 7.69 (d, 1*H*, C$H_{pyridine}$), 7.43 (qt, 1*H*, C$H_{pyridine}$), 6.55 (d, 1*H*, *o*-CH_{arom}), 6.22 (d, 1*H*, *o*-CH_{arom}), 5.98 (t, 1*H*, *p*-CH_{arom}), 5.86 (m, 2*H*, *m*-CH_{arom}), 5.82 (s, 6*H*, CH_{arom}), 5.00 (s, OH), 1.89 (s, 3H, CH_3). ^{13}C NMR (125MHz, CD_3CN) δ [ppm]: 163.14 ($C_{pyridine}$), 155.98 ($C_{pyridine}$), 155.43 ($C_{pyridine}$), 150.39 (C$H_{pyridine}$), 139.59 (C$H_{pyridine}$), 138.20 (C$H_{pyridine}$), 125.34 (C$H_{pyridine}$), 121.86 (C$H_{pyridine}$), 120.92 (C$H_{pyridine}$), 120.86 (C$H_{pyridine}$), 106.86 (C_{arom}), 77.88 (CH_{arom}), 77.03 (CH_{arom}), 76.56 (CH_{arom}), 76.49 (CH_{arom}), 76.35 (CH_{arom}), 76.17 (CH_{arom}), 75.64 (C_{sp3}), 30.14 (CH_3). IR ν [cm^{-1}]: 3092 (w), 2984 (w), 1579 (w), 1563 (w), 1429 (m), 831 (s), 785 (m). HR-ESI-MS $C_{24}H_{22}ON_2Re$ $[M]^+$: calculated, 541.12842; found, 541.12764.

$[Re(\eta^6\text{-}C_6H_5CCH_3(C_{10}H_7N_2)_2(OH)](PF_6)$ ([**10b**](PF$_6$)) (mixture of 3 estereosiomers): ^{1}H NMR (500MHz, CD_3CN) δ [ppm]: 8.67 (m, 2H, C$H_{pyridine}$), 8.48 (m, 2H, C$H_{pyridine}$), 8.35 (m, 2H, C$H_{pyridine}$), 7.96 (m, 4*H*, C$H_{pyridine}$), 7.69 (m, 2*H*, C$H_{pyridine}$), 7.43 (m, 2*H*, C$H_{pyridine}$), (6.52 (m, CH_{arom}), 6.39 (d, CH_{arom}), 6.23 (d, CH_{arom}), 6.20 (d, CH_{arom}), 5.87 (m, CH_{arom}), 5.82 (m, CH_{arom}), 5.78 (t, CH_{arom}), 5.74 (t, CH_{arom}), 5.69 (d, CH_{arom}), 5.59 (d, CH_{arom}), total integration 10H), 2.19 (s broad, O*H*), (1.91 (s, CH_3), 1.85 (s, CH_3), total integration 6H). ^{13}C NMR (125MHz, CD_3CN) δ [ppm]: 163.16 ($C_{pyridine}$), 162.84 ($C_{pyridine}$), 155.85 ($C_{pyridine}$), 155.80 ($C_{pyridine}$), 155.25 ($C_{pyridine}$), 155.20 ($C_{pyridine}$), 150.25 (C$H_{pyridine}$), 150.20 (C$H_{pyridine}$), 139.71 (C$H_{pyridine}$), 139.60 (C$H_{pyridine}$), 138.40 (C$H_{pyridine}$), 125.39 (CH_{arom}), 125.38 (CH_{arom}), 121.98 (CH_{arom}), 121.95 (CH_{arom}), 120.97 (CH_{arom}), 120.91 (CH_{arom}), 120.85 (CH_{arom}), 120.76 (CH_{arom}), 106.89 (C_{arom}), 106.57 (C_{arom}), 78.40 (CH_{arom}), 78.38 (CH_{arom}), 78.32 (CH_{arom}), 77.34 (CH_{arom}), 77.28 (CH_{arom}), 77.13 (CH_{arom}),

77.02 (CH_{arom}), 76.98 (CH_{arom}), 76.90 (CH_{arom}), 76.86 (CH_{arom}), 76.84 (CH_{arom}), 76.81 (CH_{arom}), 76.45 (CH_{arom}), 75.94 (C_{sp3}), 75.86 (C_{sp3}), 30.37 (CH_3), 30.01 (CH_3). IR v [cm^{-1}]: 3092 (w), 2924 (w), 1579 (w), 1563 (w), 1429 (m), 834 (s), 783 (m), 752 (w). HR-ESI-MS $C_{36}H_{32}O_2N_4Re$ $[M]^+$: calculated, 739.20773; found, 739.20789.

[Re(η^6-C$_6$H$_5$C(C$_{10}$H$_7$N$_2$)$_2$OH)(η^6-C$_6$H$_6$)](OTf) ([11a](OTf))

[Re(η^6-C$_6$H$_5$C(C$_{10}$H$_7$N$_2$)$_2$OH))$_2$](OTf) ([11b](OTf))



Synthesis: 161.1mg (0.33mmol) of [**1**](OTf) was dissolved in 15mL of dry THF and cooled to -78°C. Afterward, 0.95mL (0.95mmol, 2.9 eq.) of a 1M LDA solution (THF/hexane) was added slowly to the yellow suspension. The reaction was stirred for 1.5h at -78°C, and 111mg (0.33 mmol, 1 eq.) of di([2,2′-bipyridin]-6-yl)methanone was added to the clear orange solution. Stirring was continued for 5 h at -78°C. The reaction was quenched with acidified H_2O (H_2O/TFA 0.1%) and the crude was dried under N_2 flow. The solid was suspended in mixture ACN:H_2O (3:2) and filtrated or decanted. The filtrate was purified by preparative HPLC (Reprosil 100 C18, 250mm x 40mm, 0.1% TFA/CH_3CN, linear gradient 15-50% CH_3CN in 45min, 50-100% CH_3CN in 60min 40mL/min, detection at 270nm). Excess of lithium triflate was added to the filtrate and the product was extracted several times (DCM/H_2O). Analytically pure yellow [Re(η^6-C$_6$H$_5$C(C$_{10}$H$_7$N$_2$)$_2$(OH)(η^6-C$_6$H$_6$)](OTf) and [Re(η^6-C$_6$H$_5$C(C$_{10}$H$_7$N$_2$)$_2$(OH))$_2$](OTf) was obtained. Yields: 42.5mg (0.051mmol, 15.6%) for [Re(η^6-C$_6$H$_5$C(C$_{10}$H$_7$N$_2$)$_2$(OH)(η^6-C$_6$H$_6$)](OTf) and 13.6mg (0.012mmol, 3.6%) for [Re(η^6-C$_6$H$_5$C(C$_{10}$H$_7$N$_2$)$_2$(OH))$_2$](OTf).

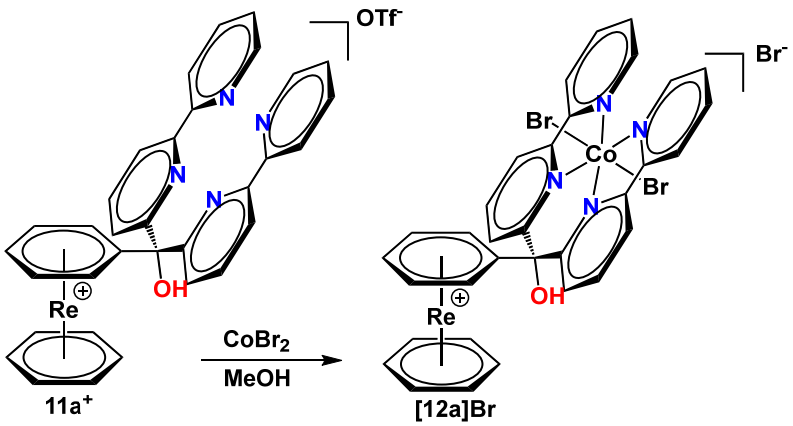
Analysis:

[Re(η^6-C$_6$H$_5$C(C$_{10}$H$_7$N$_2$)$_2$(OH)(η^6-C$_6$H$_6$)](OTf) ([**11a**](OTf)): ^{1}H NMR (500MHz, CD_3CN) δ [ppm]: 9.10 (d, 2H, C*H*$_{pyridine}$), 8.49 (d, 2H, C*H*$_{pyridine}$), 8.39 (td, 2H, C*H*$_{pyridine}$), 8.30 (dd, 2*H*, C*H*$_{pyridine}$), 8.10 (m, 4*H*, C*H*$_{pyridine}$), 7.86 (qd, 2*H*, C*H*$_{pyridine}$), 6.45 (d, 2*H*, *o*-C*H*$_{arom}$), 5.94 (m, 4*H*, *m,p*-C*H*$_{arom}$), 5.77 (s, 6*H*, C*H*$_{arom}$). ^{13}C NMR (125MHz, CD_3CN) δ [ppm]: 162.52 (*C*$_{pyridine}$), 151.18 (*C*$_{pyridine}$), 149.28 (*C*$_{pyridine}$), 145.94 (*C*H$_{pyridine}$), 144.99 (*C*H$_{pyridine}$), 140.25 (*C*H$_{pyridine}$), 127.40 (*C*H$_{pyridine}$), 125.71 (*C*H$_{pyridine}$), 124.56 (*C*H$_{pyridine}$), 122.59 (*C*H$_{pyridine}$), 103.36 (*C*$_{arom}$), 80.89 (*C*$_{sp3}$), 78.28 (*C*H$_{arom}$), 77.96 (*C*H$_{arom}$), 76.53 (*C*H$_{arom}$), 76.34 (*C*H$_{arom}$). IR (as a [12a](PF$_6^-$)) ν [cm^{-1}]: 3108 (w), 1676 (w), 1612 (w), 1587 (w), 1535 (w), 1451 (w), 1435 (w), 1194 (w), 1133 (w), 829 (s), 768 (s). HR-ESI-MS $C_{33}H_{26}O_1N_4Re$ [M]$^+$: calculated, 681.16599; found, 681.16587.

[Re(η^6-C$_6$H$_5$C(C$_{10}$H$_7$N$_2$)$_2$(OH))$_2$](OTf) ([**11b**](OTf)): ^{1}H NMR (500MHz, CD_3CN) δ [ppm]: 8.97 (d, 4H, C*H*$_{pyridine}$), 8.37 (d, 4H, C*H*$_{pyridine}$), 8.25 (m, 8H, C*H*$_{pyridine}$), 7.96 (m, 8*H*, C*H*$_{pyridine}$), 7.76 (t,

4*H*, C*H*$_{pyridine}$), 6.22 (d, 4*H*, *o*-C*H*$_{arom}$), 5.84 (m, 2*H*, *m*,*p*-C*H*$_{arom}$). ^{13}C NMR (125MHz, CD_3CN) δ [ppm]: 162.03 (*C*$_{pyridine}$), 151.93 (*C*$_{pyridine}$), 150.24 (*C*$_{pyridine}$), 146.76 (*C*H$_{pyridine}$), 143.65 (*C*H$_{pyridine}$), 139.99 (*C*H$_{pyridine}$), 126.99 (*C*H$_{pyridine}$), 125.15 (*C*H$_{pyridine}$), 123.95 (*C*H$_{pyridine}$), 122.26 (*C*H$_{pyridine}$), 104.05 (*C*$_{arom}$), 80.71 (*C*$_{sp3}$), 78.51 (*C*H$_{arom}$), 77.59 (*C*H$_{arom}$), 77.40 (*C*H$_{arom}$). IR (as a [12b]PF_6^-) ν [cm^{-1}]: 3081 (w), 2924 (w), 2852 (w), 1584 (w), 1560 (w), 1451 (w), 1427 (m), 836 (s), 773 (s), 744 (w). HR-ESI-MS $C_{54}H_{40}O_2N_8Re$ $[M]^+$: calculated, 1019.28297; found, 1019.28275.

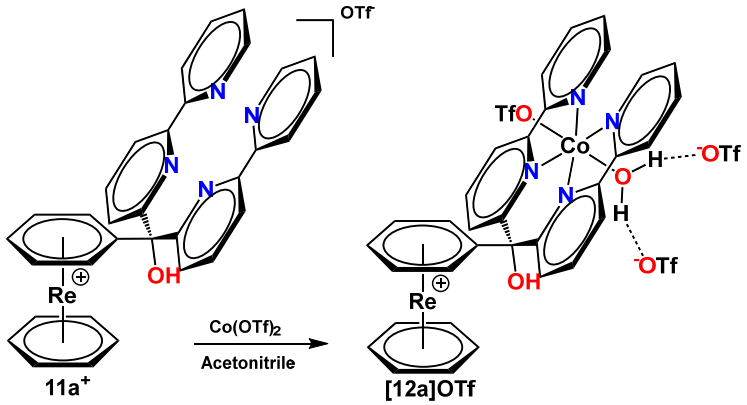
[Re(η^6-C_6H_5C((OH)($C_{20}H_{14}N_4$)Co(Br_2))(η^6-C_6H_6)](Br) ([12a]Br)



Synthesis: To a solution of [**11a**](OTf) (18.6mg, 0.023mmol) in 5ml of MeOH was added 102.4mg (0.468mmol, 20 eq.) of $CoBr_2$. The solution changed the color immediately from light yellow to pink. The reaction was controlled by UPLC-MS. After 40min, the peak in the chromatogram corresponding to complex [**11a**](OTf) disappeared and a new peak with a m/z corresponding to complex [**12a**]Br appeared. The solvent was evaporated in vacuum and the solid was washed multiple times with Et_2O until all remaining $CoBr_2$ was removed. The brownish solid was then dried under high vacuum to give analytically pure [Re(η^6-C_6H_5C((OH)($C_{20}H_{14}N_4$)Co)(η^6-C_6H_6)](Br_3). Yield: 21.4mg (0.022mmol, 93.2%) of [Re(η^6-C_6H_5C((OH)($C_{20}H_{14}N_4$)Co)(η^6-C_6H_6)](Br_3).

Analysis: ^{1}H NMR (400MHz, CD_3OD) δ [ppm]: broad signals (see Figure S15) 79.80 (C*H*$_{pyridine}$), 71.74 (C*H*$_{pyridine}$), 63.79 (C*H*$_{pyridine}$), 52.46 (C*H*$_{pyridine}$), 31.64 (C*H*$_{pyridine}$), 16.55 (C*H*$_{pyridine}$) , -9.34 (C*H*$_{pyridine}$). IR ν [cm^{-1}]: 3282 (w), 3067 (w), 1604 (w), 1450 (m), 1411 (w), 1301 (w), 1251 (w), 773 (m). HR-ESI-MS $C_{35}H_{27}N_4O_5NaReCo$ $[M]^{1+}$: calculated, 852.07632; found, 852.07654; $C_{35}H_{27}N_4O_5NaReCo$ $[M]^{2+}$: calculated, 426.54180; found, 426.54176; $C_{34}H_{27}N_4O_3ReCo$ $[M]^{2+}$: calculated, 392.54808; found, 392.54801; $C_{33}H_{25}N_4OReCo$ $[M]^{2+}$: calculated, 369.54535; found, 369.54527.

[Re(η^6-C_6H_5C((OH)($C_{20}H_{14}N_4$)Co(H_2O)(OTf))(η^6-C_6H_6)](OTf)$_2$ ([Co(11a)(H_2O)OTf](OTf)$_2$)



Synthesis: To a solution of [**11a**](OTf) (5.50mg, 0.007mmol) in 4ml of acetonitrile was added 2.38mg (0.007mmol, 1 eq.) of Co(OTf)$_2$. The solution changed the color immediately from light to dark yellow. The reaction was controlled by UPLC-MS. After 40min, the peak in the chromatogram corresponding to complex [**11a**](OTf) disappeared and a new peak with a m/z corresponding to complex [**12a**]OTf appeared. The solvent was evaporated in vacuum to give analytically pure yellow [Re(η^6-C_6H_5C((OH)($C_{20}H_{14}N_4$)Co)(η^6-C_6H_6)](H_2O)(OTf)$_3$ in quantitative yield. Single crystals, suitable for X-ray diffraction analysis were obtained by slow evaporation from acetonitrile.

Analysis: IR ν [cm^{-1}]: 3340 (w), 1605 (w), 1450 (w), 1284 (m), 1259 (m), 1172 (m), 1029 (m), 774 (m). HR-ESI-MS $C_{35}H_{26}N_4O_7F_6S_2ReCo$ $[M]^+$: calculated, 1038.00296; found, 1038.00464; $C_{34}H_{25}N_4O_4F_3SReCo$ $[M]^+$: calculated, 888.04271; found, 888.04326; $C_{33}H_{25}N_4OReCo$ $[M]^{2+}$: calculated, 369.54535; found, 369.54554

3. Cyclic voltammetry

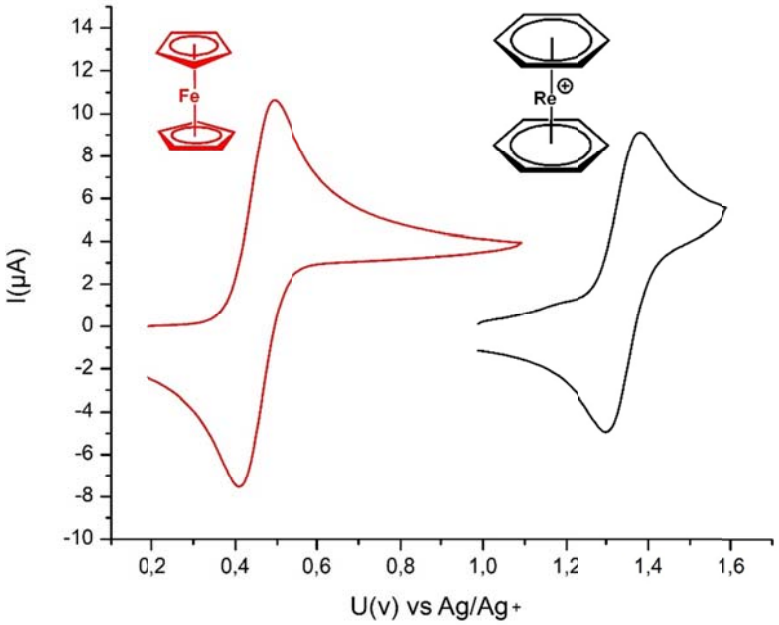


Figure S1. Cyclic voltammograms (positive potentials) of ferrocene (red) and $[Re(benzene)_2]^+$ **1**$^+$ (black). Acetonitrile, 0.1M [TBA][PF_6] as electrolyte, glassy carbon working electrode (inside diameter of 3mm), Pt counter electrode, and Ag/AgCl reference electrode. Analyte concentrations of 1mM, voltage step of 6mV, sweep rate of 0.1V/s.

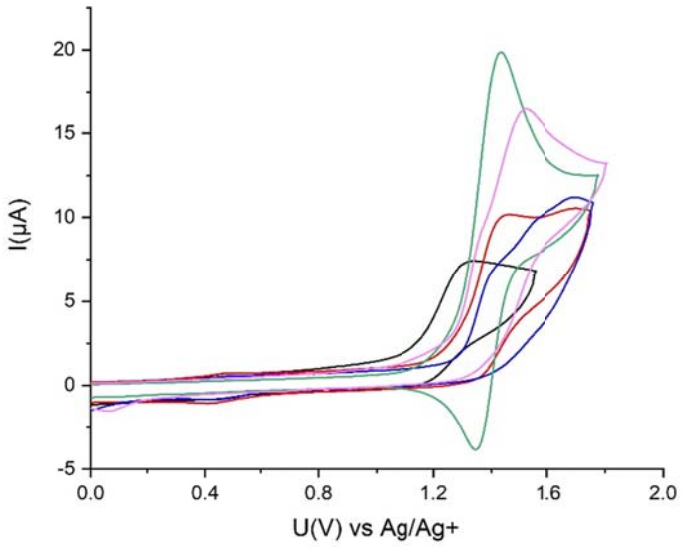


Figure S2. Cyclic voltammograms (positive potentials) of complexes **6b**$^+$ (blue), **7a**$^+$ (black), **8a**$^+$ (pink), **10a**$^+$ (green) and **11a**$^+$ (red). Acetonitrile, 0.1M [TBA][PF_6] as electrolyte, glassy carbon working electrode (inside diameter of 3mm), Pt counter electrode, and Ag/AgCl reference electrode. Analyte concentrations of 1mM, voltage step of 6mV, sweep rate of 0.1V/s.

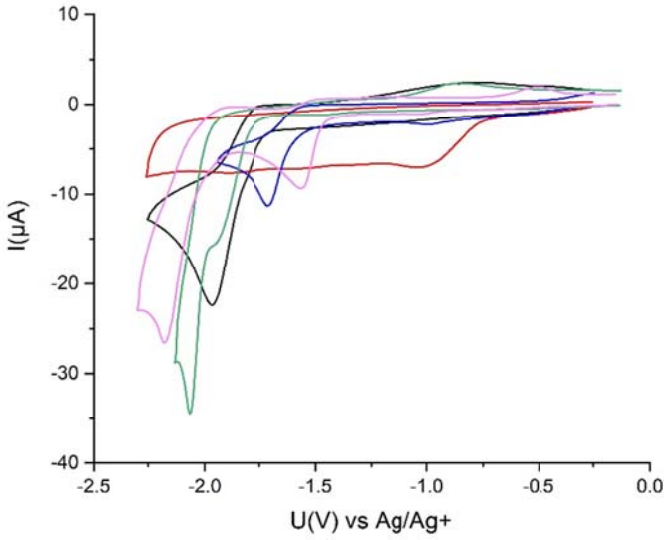
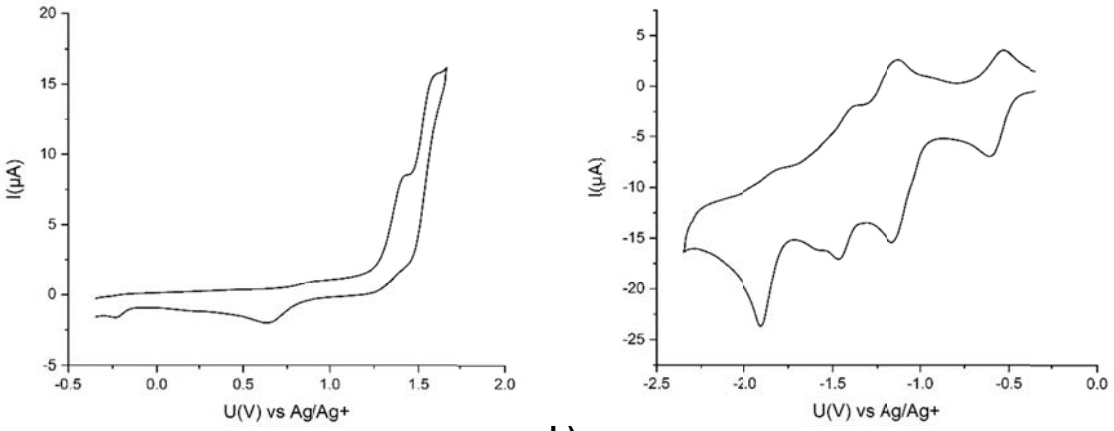


Figure S3. Cyclic voltammograms (negative potentials) of complexes **6b**$^+$ (blue), **7a**$^+$ (black), **8a**$^+$ (pink), **10a**$^+$ (green) and **11a**$^+$ (red). Acetonitrile, 0.1M [TBA][PF_6] as electrolyte, glassy carbon working electrode (inside diameter of 3 mm), Pt counter electrode, and Ag/AgCl reference electrode. Analyte concentrations of 1mM, voltage step of 6mV, sweep rate of 0.1V/s.



a) **b)**

Figure S4. Cyclic voltammograms of complex [**12a**]OTf. a) positive potentials, b) negative potentials. Acetonitrile, 0.1M [TBA][PF_6] as electrolyte, glassy carbon working electrode (inside diameter of 3mm), Pt counter electrode, and Ag/AgCl reference electrode. Analyte concentrations of 1mM, voltage step of 6mV, sweep rate of 0.1V/s.

4. UPLC chromatograms

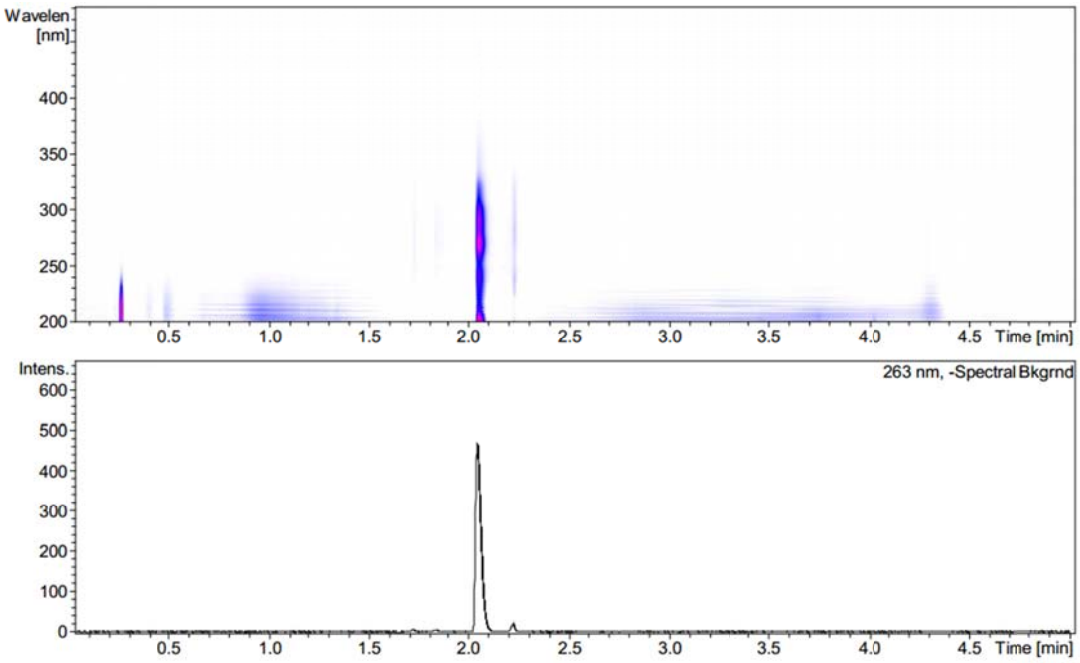


Figure S5. UV trace of pure complex **11a**$^{+}$ before synthesis of complex [**12a**]Br

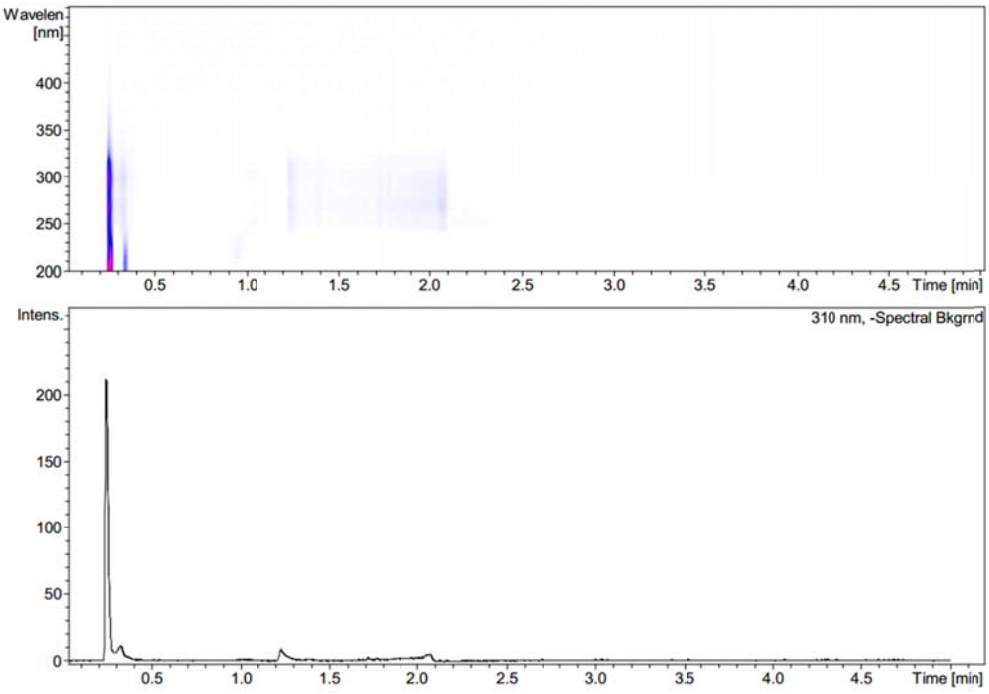


Figure S6. UV trace, reaction control after 40min of synthesis of [**12a**]Br

5. NMR spectra

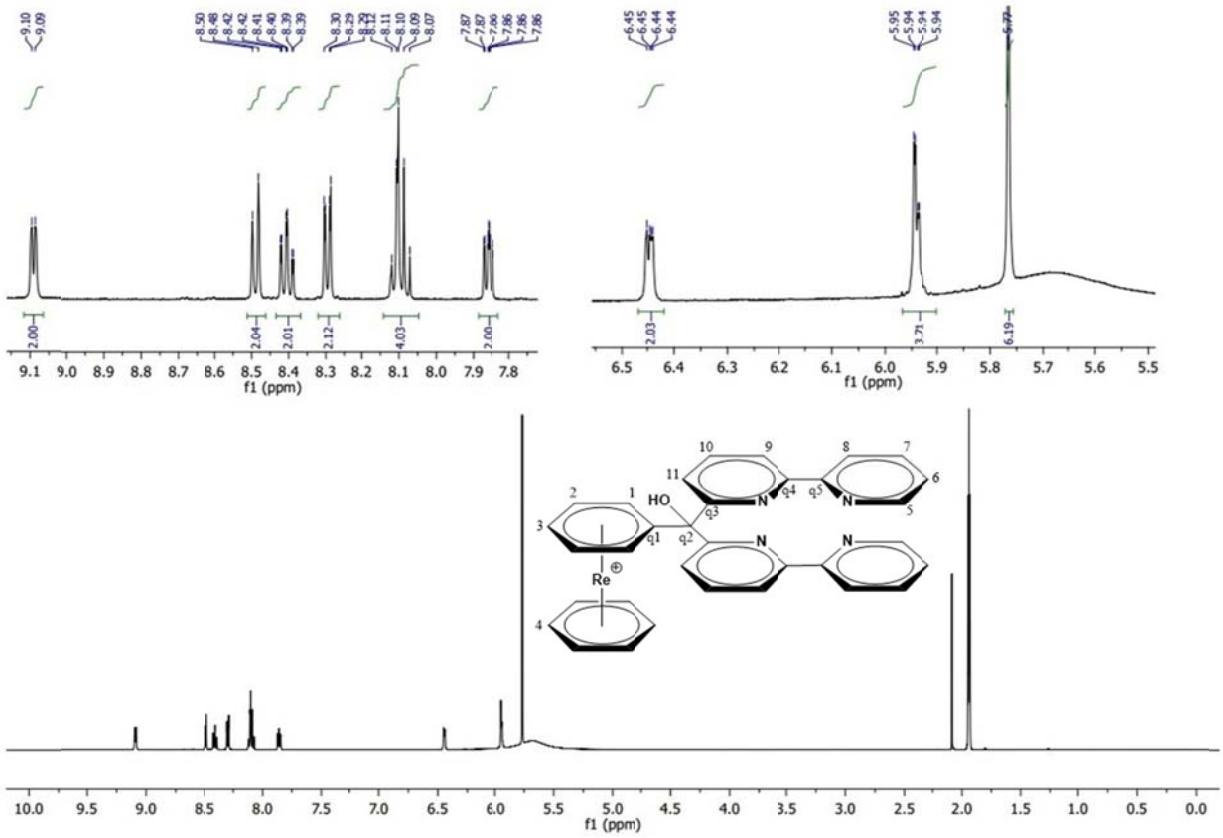


Figure S7. ^{1}H-NMR of complex **11a^{+}**. 500MHz, CD_3CN, 295K.

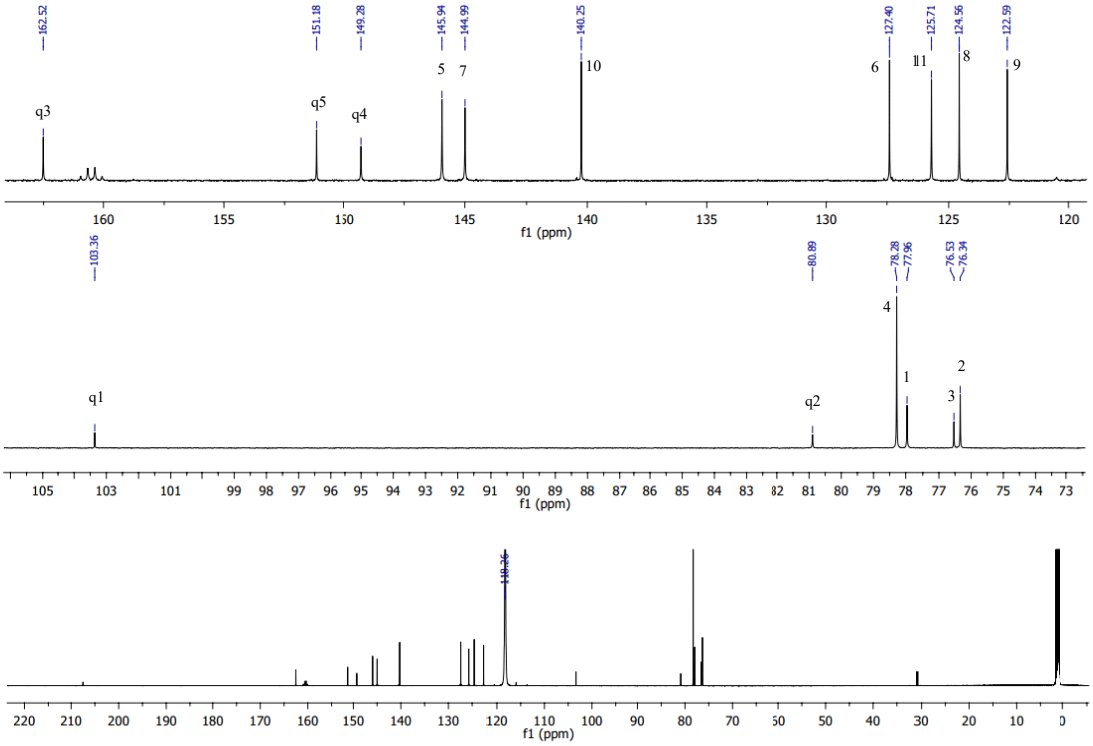


Figure S8. ^{13}C-NMR of complex **11a^{+}**. 125MHz, CD_3CN, 295K.

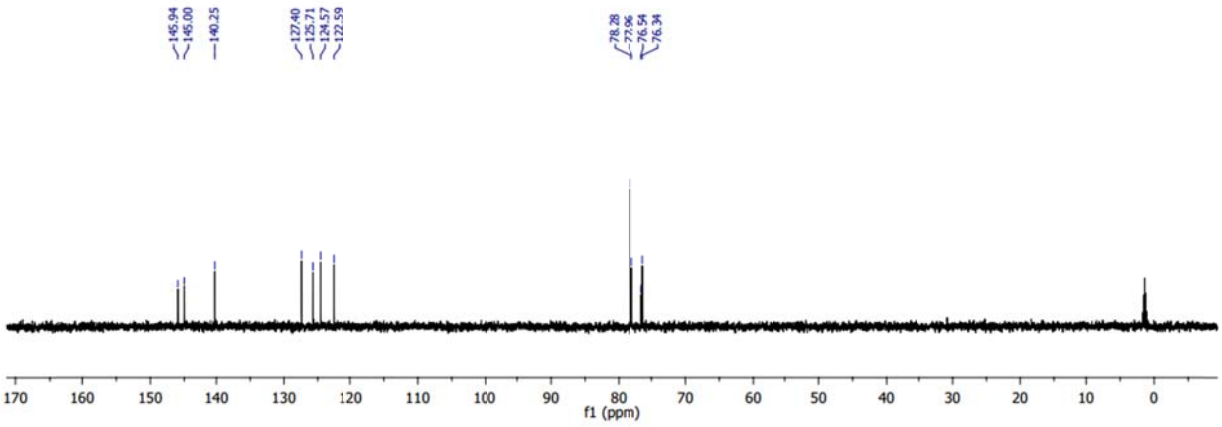


Figure S9. ^{13}C-NMR DEPT-135 of complex **11a^{+}**. 125MHz, CD_3CN, 295K.

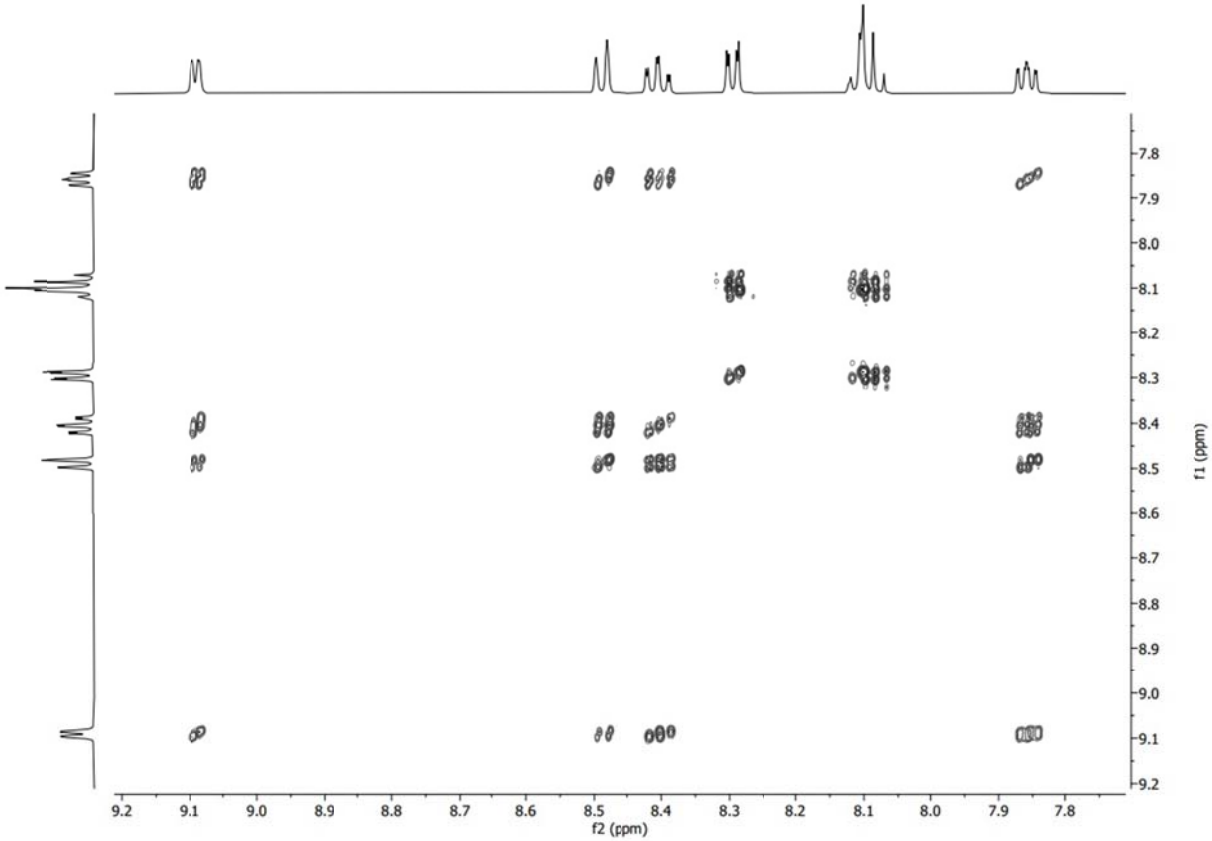


Figure S10. ^{1}H-COSY of complex **11a^{+}**. 500MHz, CD_3CN, 295K.

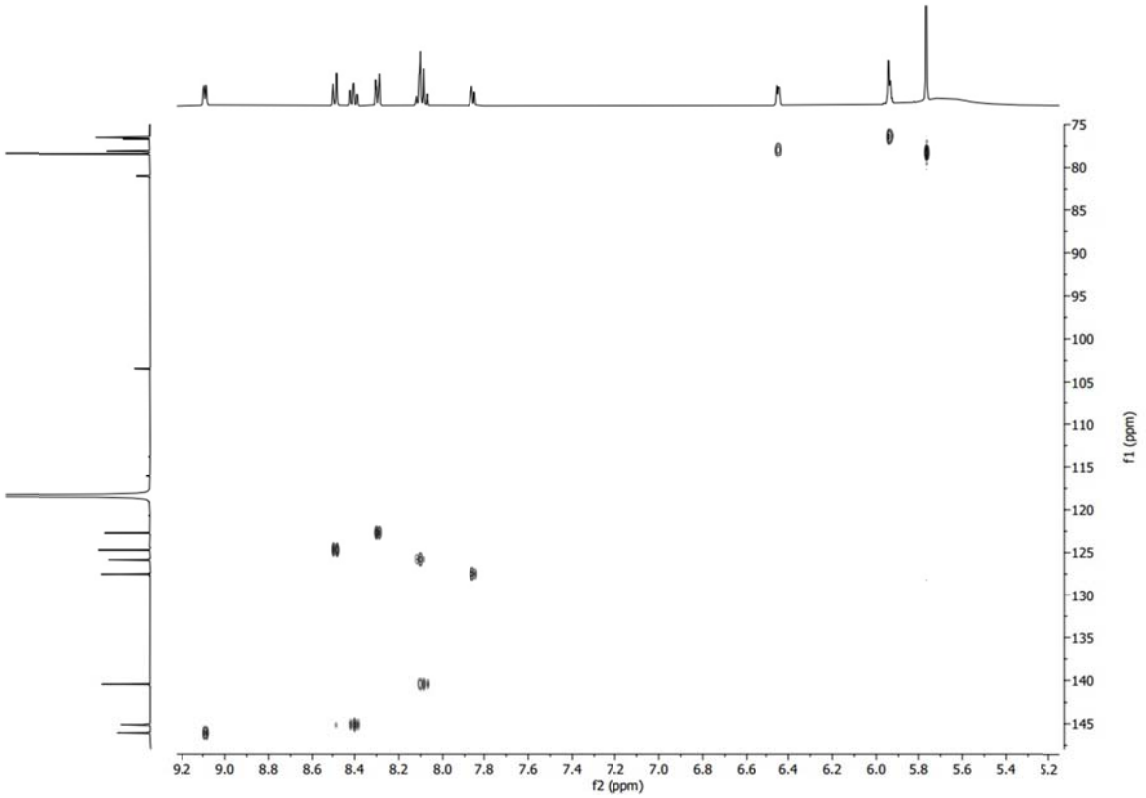


Figure S11. HSQC of complex **11a**$^{+}$. 500MHz, CD_3CN, 295K.

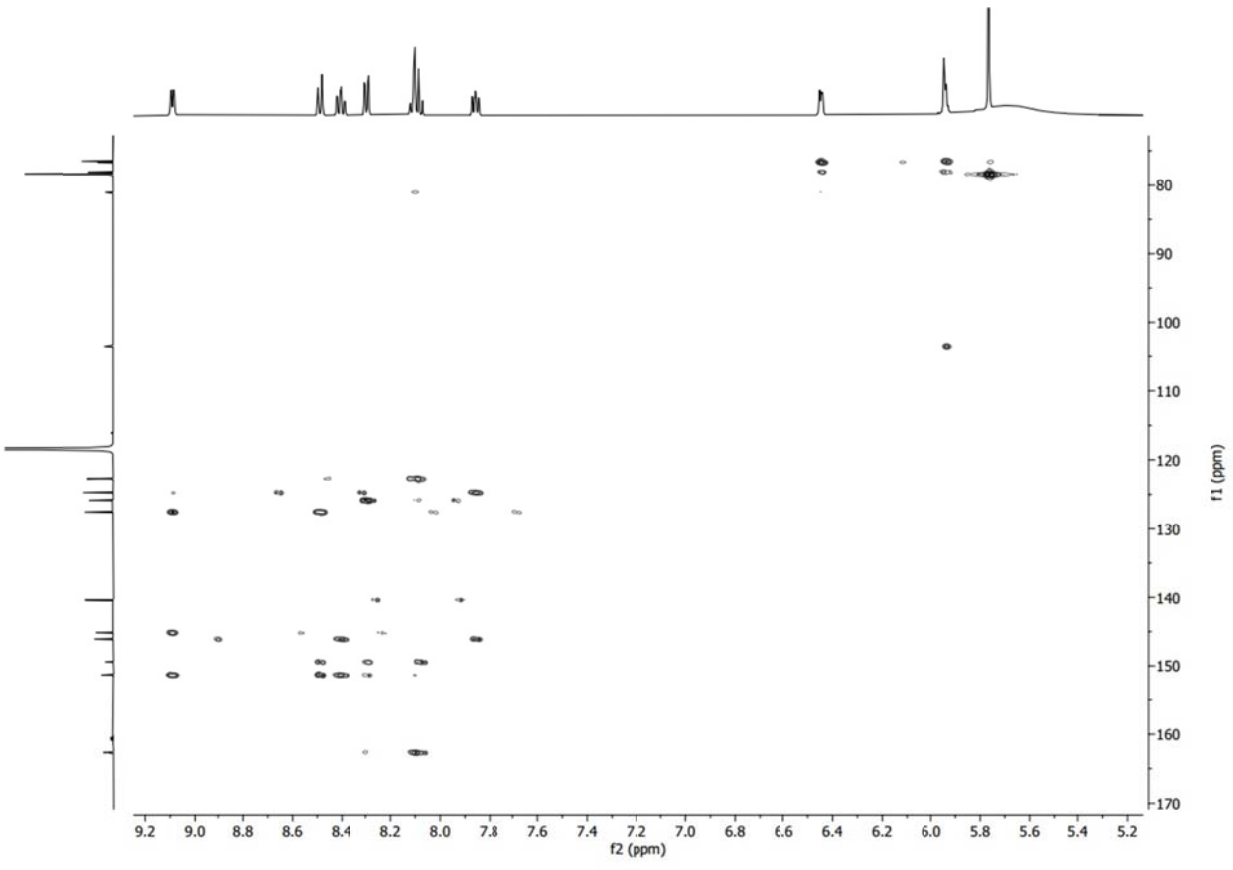


Figure S12. HMBC of complex **11a**$^{+}$. 500MHz, CD_3CN, 295K.

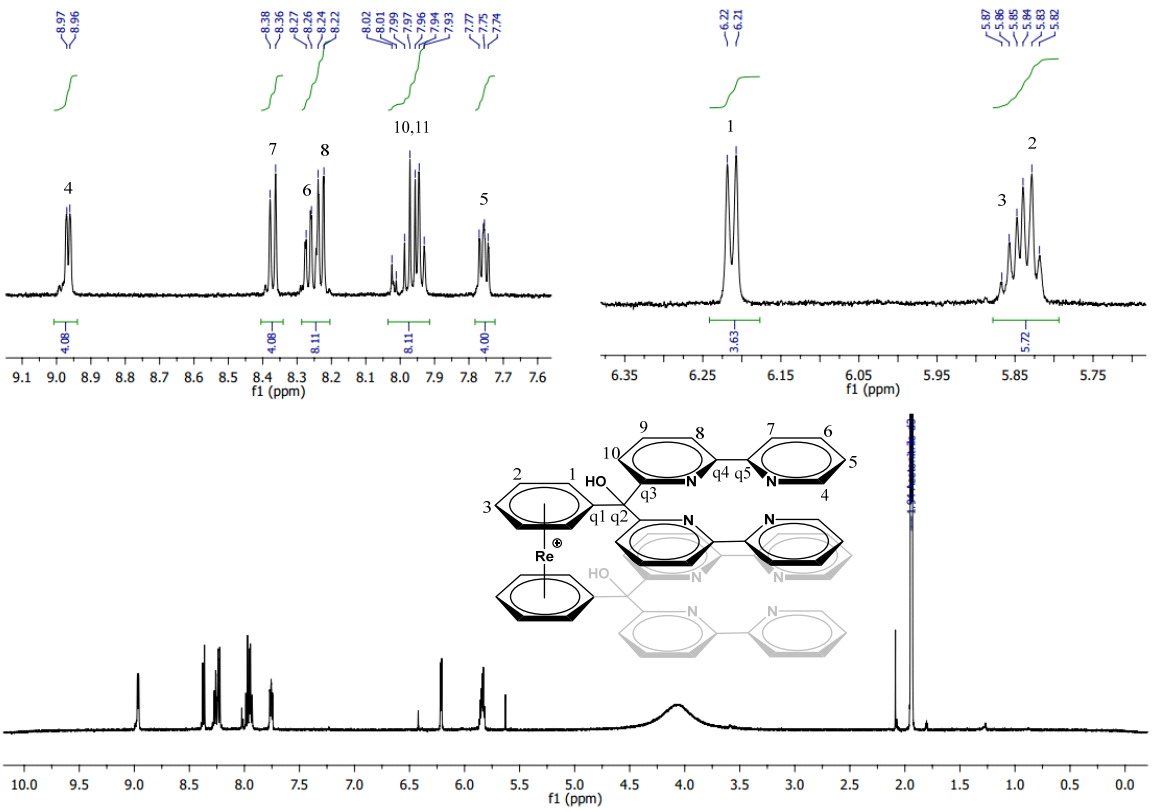


Figure S13. ^{1}H-NMR of complex **11b^{+}**. 500MHz, CD_3CN, 295K.

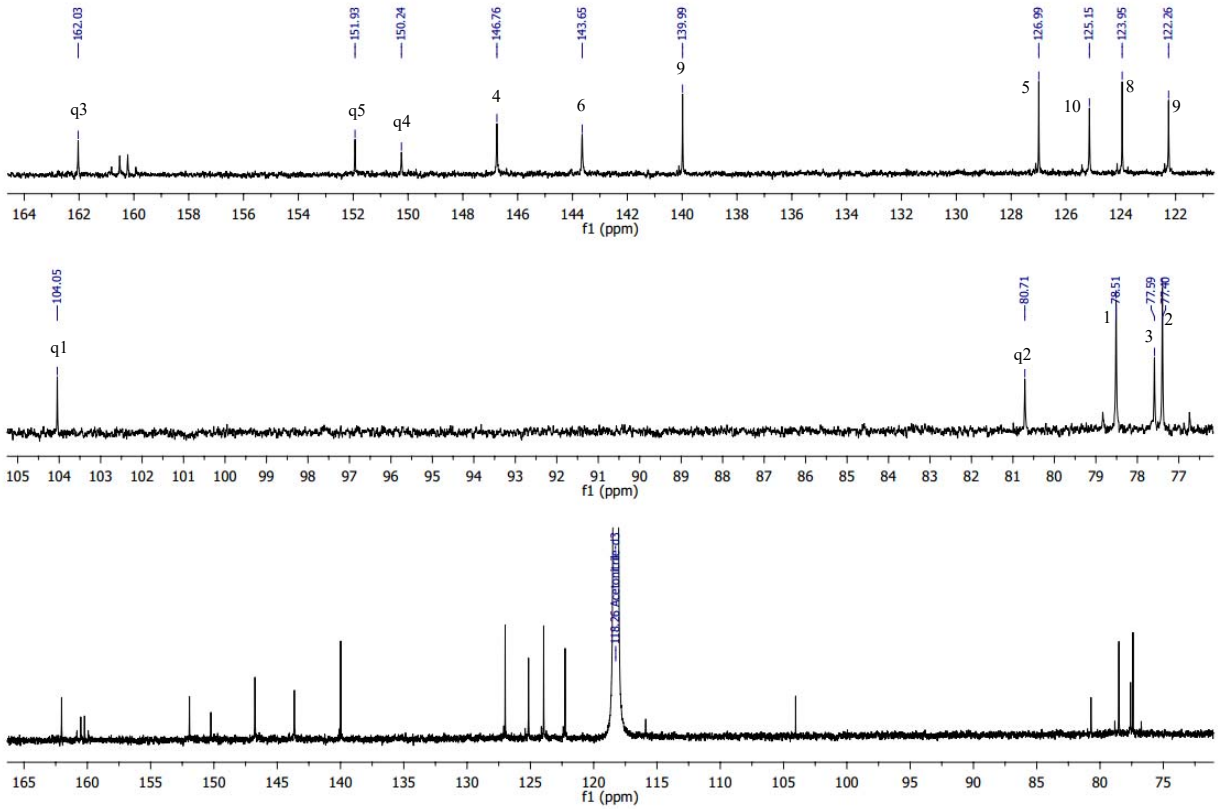


Figure S14. ^{13}C-NMR of complex **11b^{+}**. 125MHz, CD_3CN, 295K.

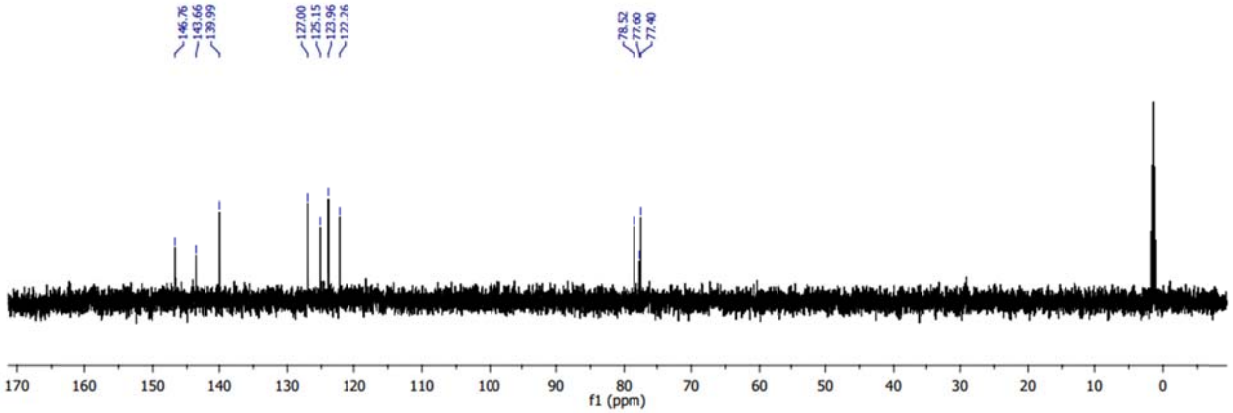


Figure S15. ^{13}C-NMR DEPT-135 of complex **11b^{+}**. 125MHz, CD_3CN, 295K.

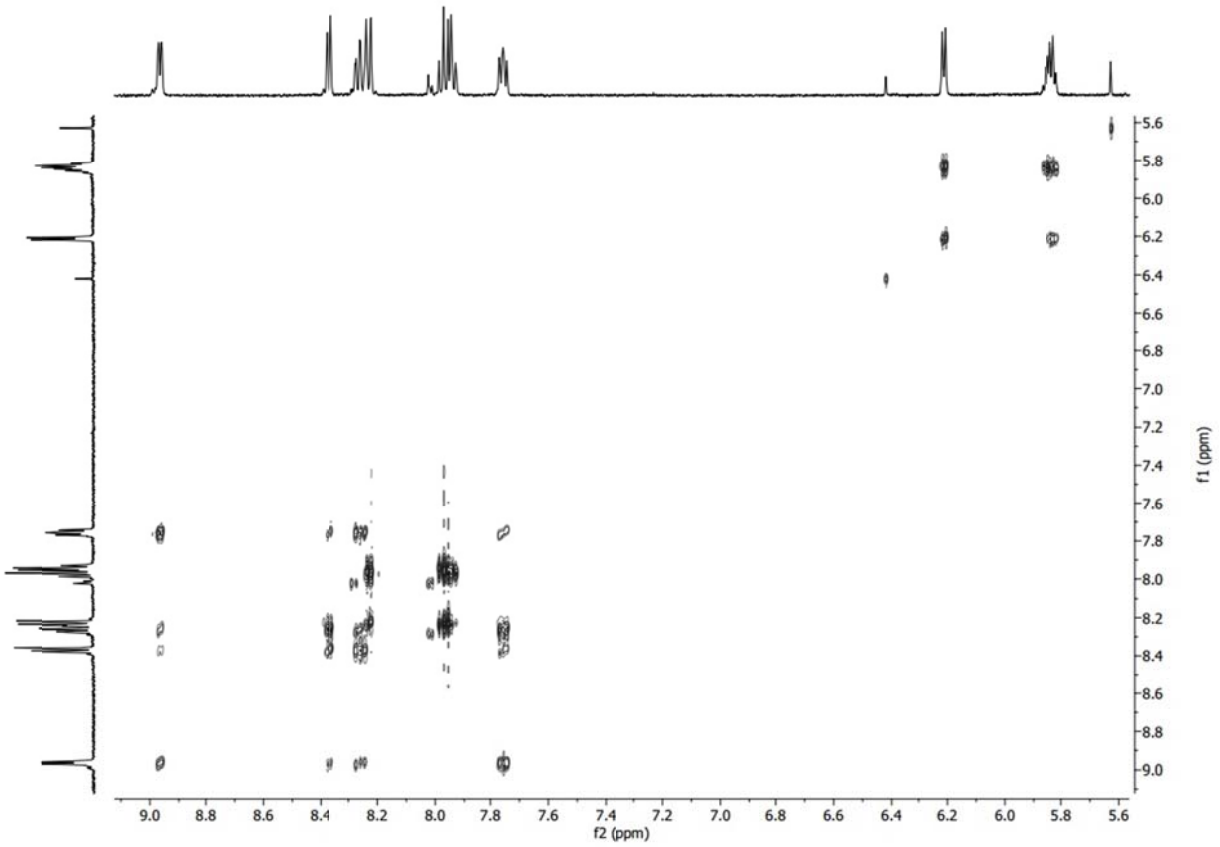


Figure S16. ^{1}H-COSY of complex **11b^{+}**. 500MHz, CD_3CN, 295K.

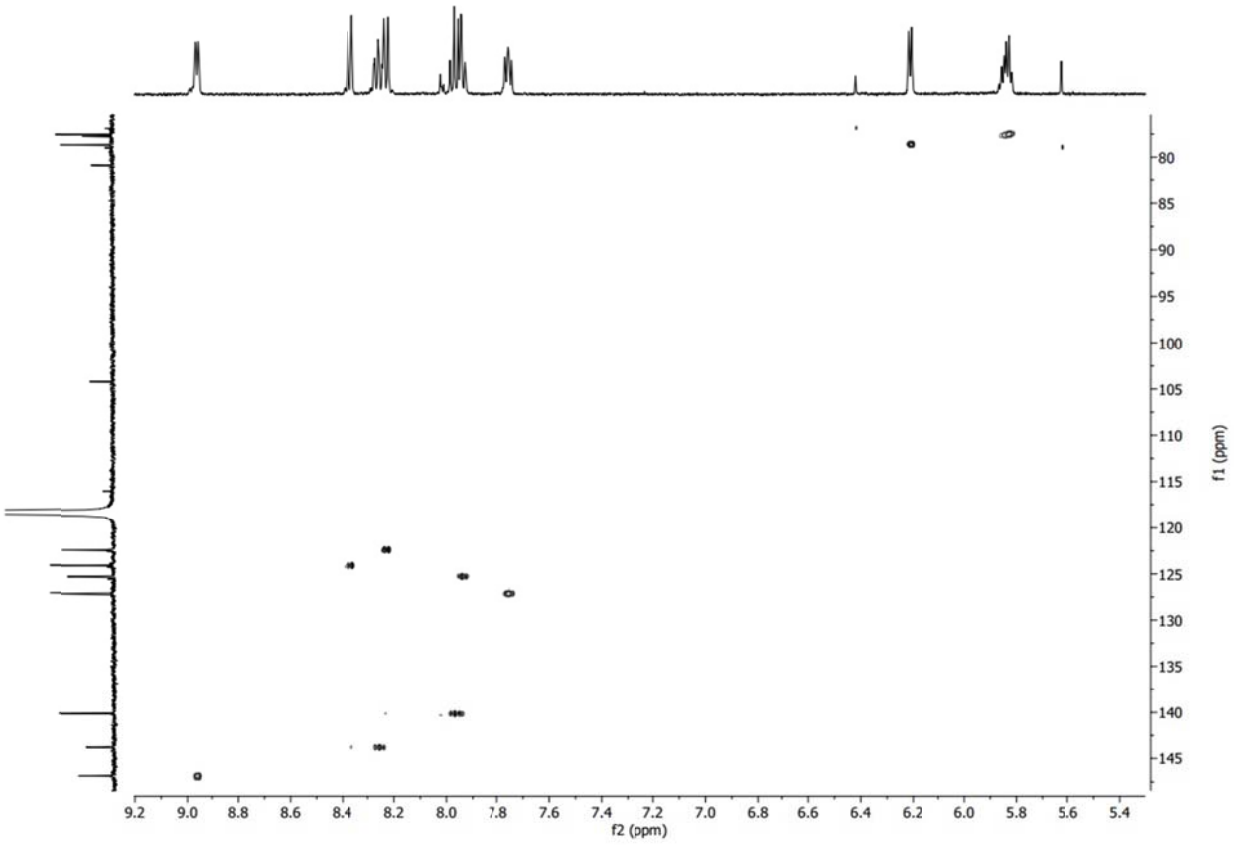


Figure S17. HSQC of complex **11b**$^{+}$. 500MHz, CD_3CN, 295K.

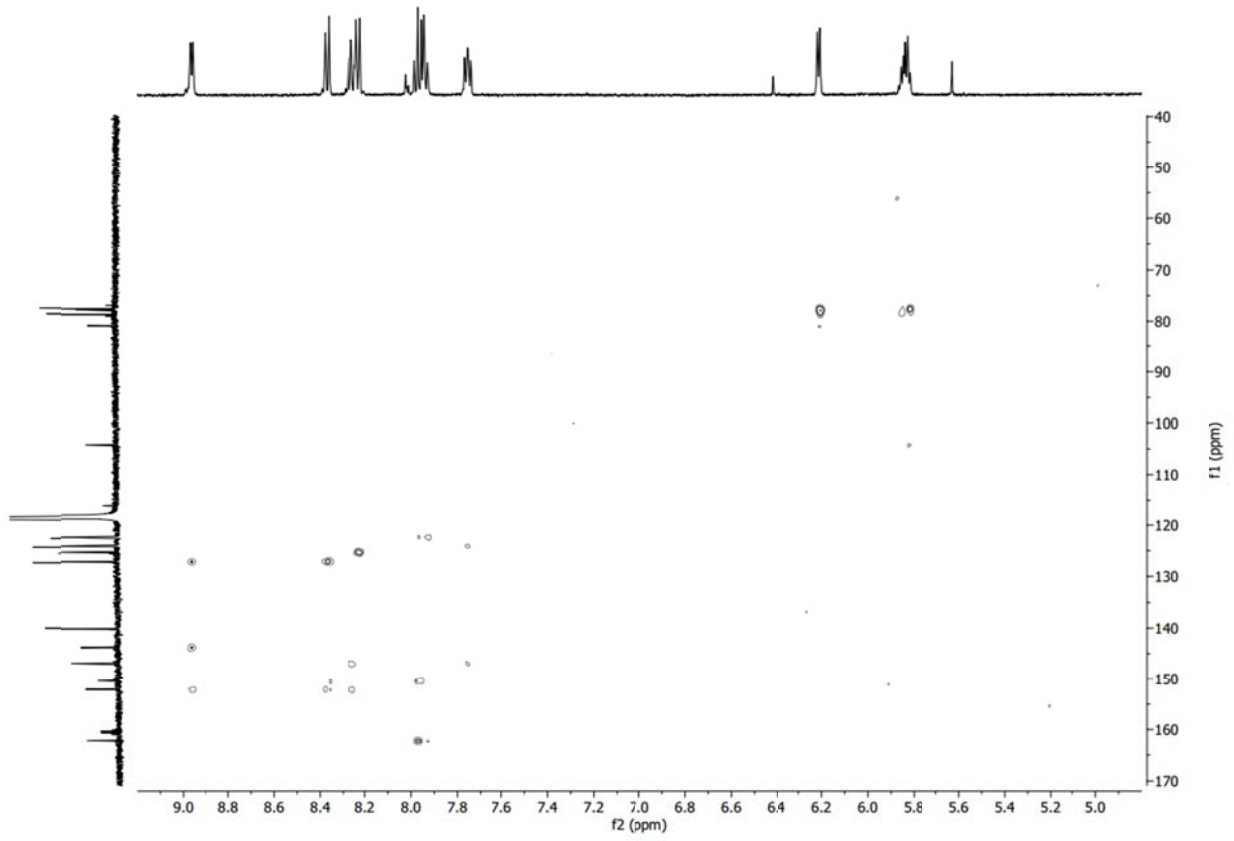


Figure S18. HMBC of complex **11b**$^{+}$. 500MHz, CD_3CN, 295K.

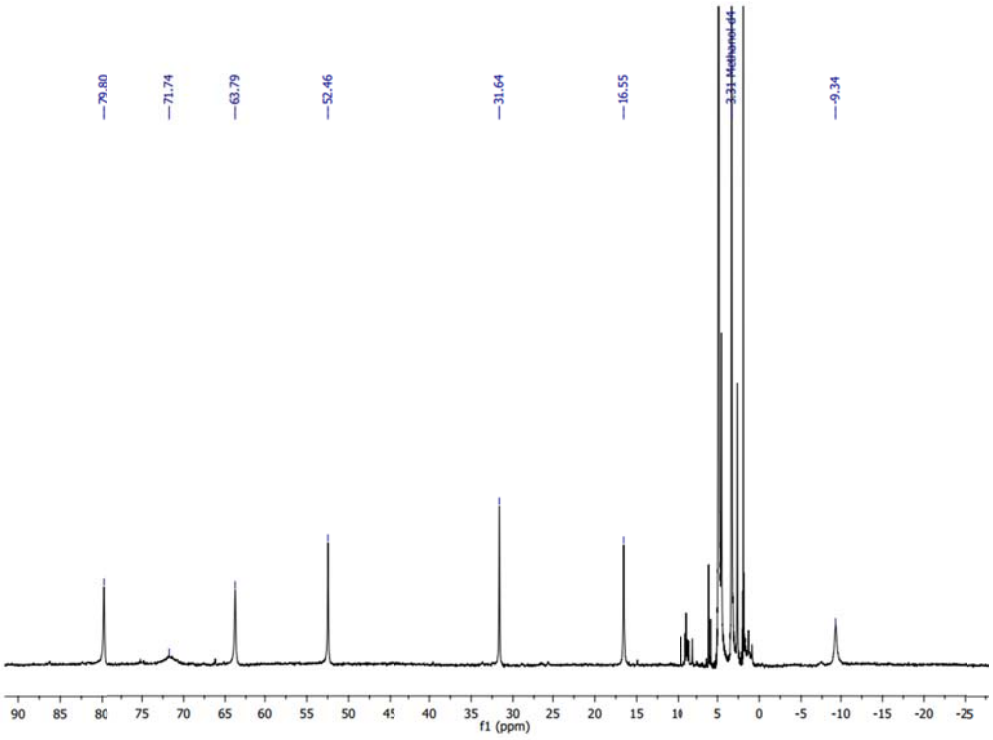


Figure S19. ^{1}H-NMR of complex [**12a**]Br. Signals highlighted in the spectrum are the most affected by the Co(II) centre and presumably related with the polypyridyl system.

6. Photo and pH stability

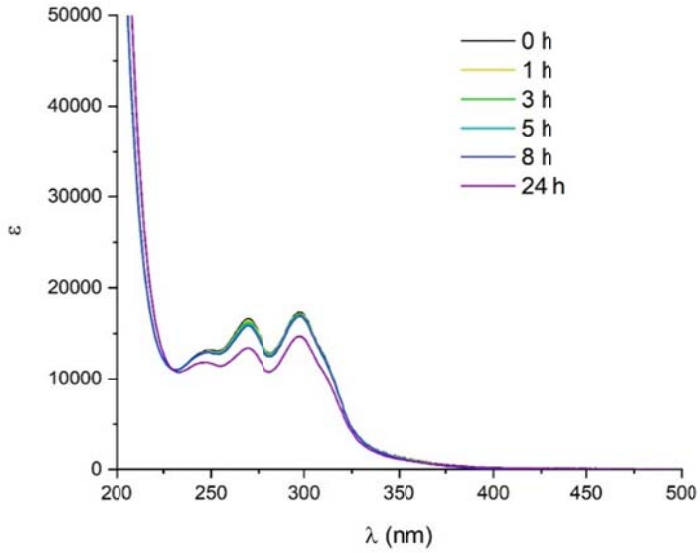


Figure S20. Light stability experiment. UV/Vis of complex [**12a**]Br over time in water during continuous irradiation at 453nm LED, photon flux 0.35μE/s, 20μM [**12a**]Br, 3mL total volume.

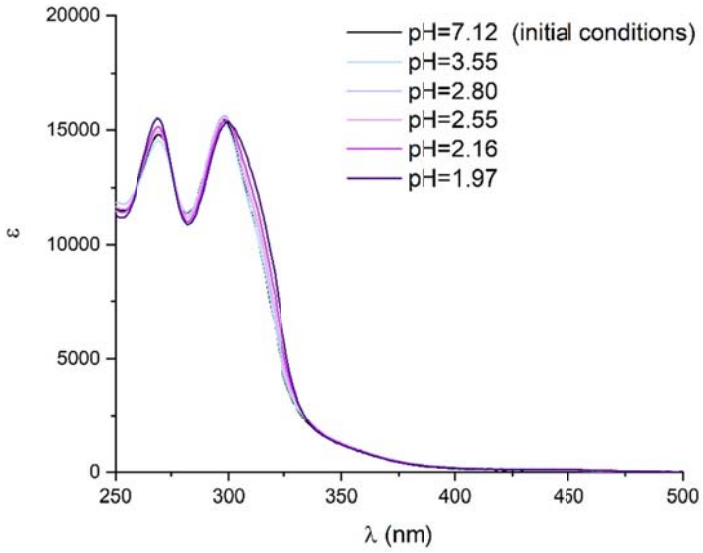


Figure S21. Stability experiment under acidic conditions. A fresh solution of [**12a**]Br was prepared (20μM, 3mL total volume). Concentrate TFA solution (1M) was added stepwise and the UV-spectra were immediately recorded.

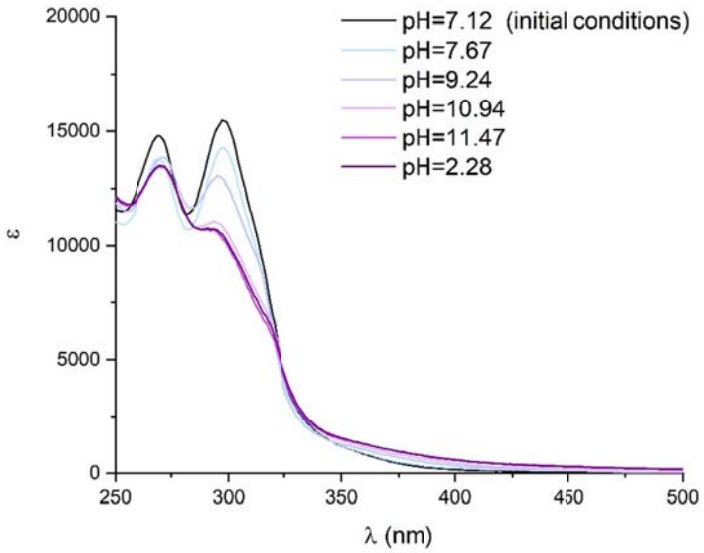
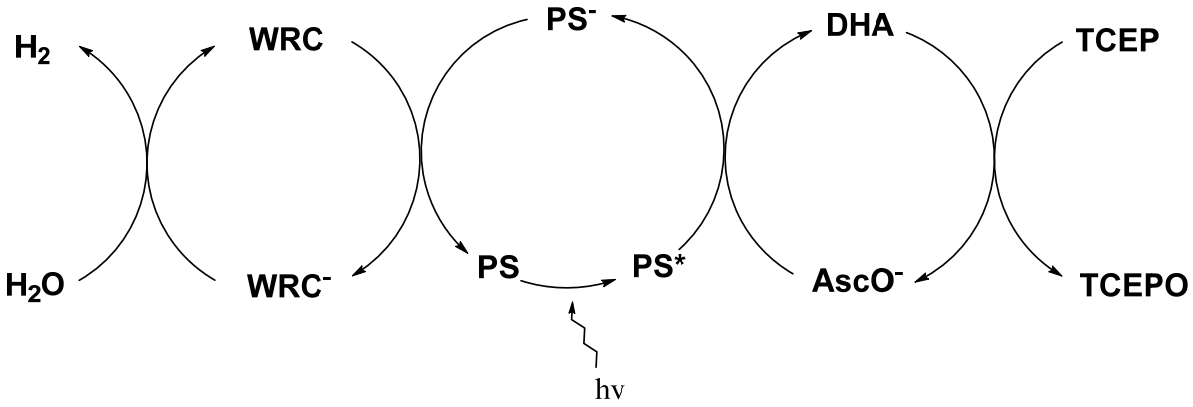


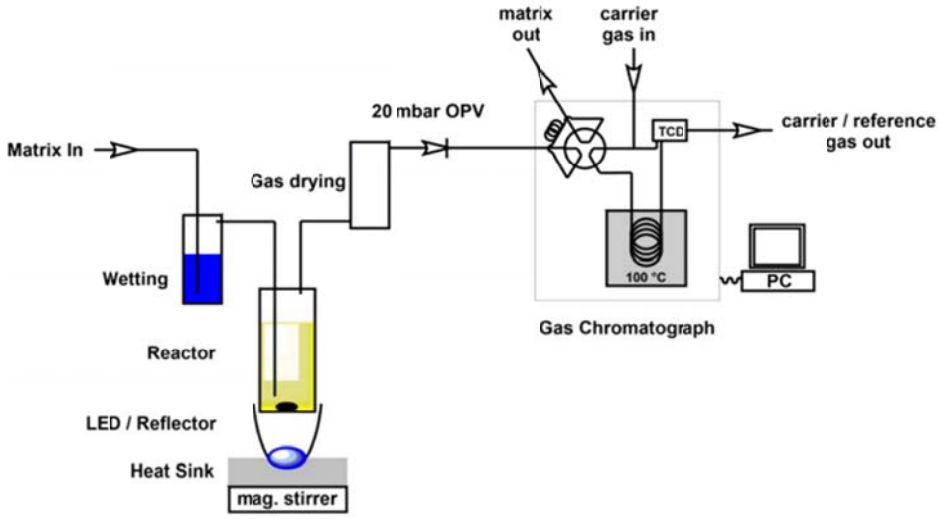
Figure S22. Stability experiment under basic conditions. A fresh solution of [**12a**]Br was prepared (20μM, 3mL total volume). Concentrate NaOH solution (1M) was added stepwise and the UV-spectra were immediately recorded. Upon basification, change in UV spectra are observed. Re-acidification of the sample does not show reversibility.

7. Photocatalysis experiments and in-line H_2 detection



Scheme S1. Half-reaction (proton reduction) water-splitting system with $[Ru(bpy)_3]^{2+}$ as photosensitizer, ascorbic acid as electron relay and TCEP as a sacrificial electron donor.

The samples for catalysis were prepared by mixing the photosensitizer $[Ru(bpy)_3]Cl_2 \cdot 5 H_2O$ (PS, µM), sodium ascorbate (NaAsc, 0.1M), tris(2-carboxyethyl) phosphine hydrochloride (TCEP, 0.1 M) and the corresponding WRC [**12a**]Br (with final concentrations of 1, 5, 10, 20 and 100µM, respectively) in water (approximately 5mL). The mixture was titrated (pH-meter from Mettler Toledo SevenEasy with an InLab Semi-Micro pH electrode) with NaOH (2M) to a pH of 5.00 (variation between pH 4.99 and 5.01). Finally, the samples were filled up with H_2O to a total reaction volume of 10mL. The catalytic solution was connected to the argon line with a controlled flow of 6.0 ± 0.15mL/min and directly dried and degassed under stirring until oxygen and nitrogen have been vanished. After degassing, irradiation was started from the bottom with an LED lamp (453nm, 80 ± 5mW, photon flux of 0.35 ± 0.02µE/s). Gas chromatograms were recorded on a Bruker 450 or Bruker 456 GC gas chromatograph by using argon as carrier gas (20 mL/min for both reference and sample), a column of 3m x 2mm packed with molecular sieves 13X 80-100, an oven operated isothermally at 100°C and a thermal conductivity detector operated at 150°C. Automated measurements were performed using a home made in-line setup (Scheme 2)



Scheme S2. Representation of the setup for photocatalysis experiments with in-line H_2 detection

Table S1. Summary of photocatalysis experiments. In line H_2 detection, total volume 10mL, 0.5mM $[Ru(bpy)_3Cl_2]$, 0.1M NaAsc, 0.1M TCEP, pH=5.00. Different concentrations of [**12a**]Br and different light intensities.

WRC	Conc. WRC (μM)	Photon flux (μE/s)	total H_2 (μmol)	Max. rate (nmol/s)	TON_{Co} (H_2/Co)	Max. TOF_{Co} (H_2/Co/h)
-[a]	0	0.35	1.00±0.50	0.03±0.01	-	-
$CoBr_2$	5	0.35	3.46±0.54	0.15±0.01	69±11	10±1
$CoBr_2$, bpy[b]	5	0.35	4.39±0.56	0.94±0.05	88±11	68±4
[**12a**]Br	1	0.35	8.87±0.77	1.45±0.08	887±77	521±28
[**12a**]Br	5	0.35	131.2±13.9	7.29±0.72	2624±277	525±52
[**12a**]Br	10	0.35	546.8±36.0	14.38±0.93	5468±360	518±33
[**12a**]Br	20	0.35	776.7±65.8	18.22±1.51	3884±323	328±27
[**12a**]Br	100	0.35	975.2±38.0	10.13±0.39	975±38	36±1
[**12a**]Br**, Hg**[c]	5	0.35	140.5±9.7	6.52±0.42	2809±195	469±30
[**12a**]Br	10	0.88	193.1±16.3	20.41±1.70	1931±163	735±61
[**12a**]Br	10	1.75	265.5±26.7	42.23±4.20	2655±267	1520±151
[**12a**]Br	10	2.63	235.1±15.4	52.60±3.39	2351±154	1894±122
[**12a**]Br	10	3.51	234.3±13.0	69.01±3.70	2343±130	2484±133

[a]Blank experiment, no Cobalt containing species.
[b]Blank experiment, 5μM $CoBr_2$, 20μM 2,2'-bipyridine.
[c]Mercury poisoning experiment, 5μM [**12a**]Br, 293mg Hg per 10mL of catalytic solution. No decrease in catalytic activity compare to experiment without Hg, thus no nanoparticles formed.

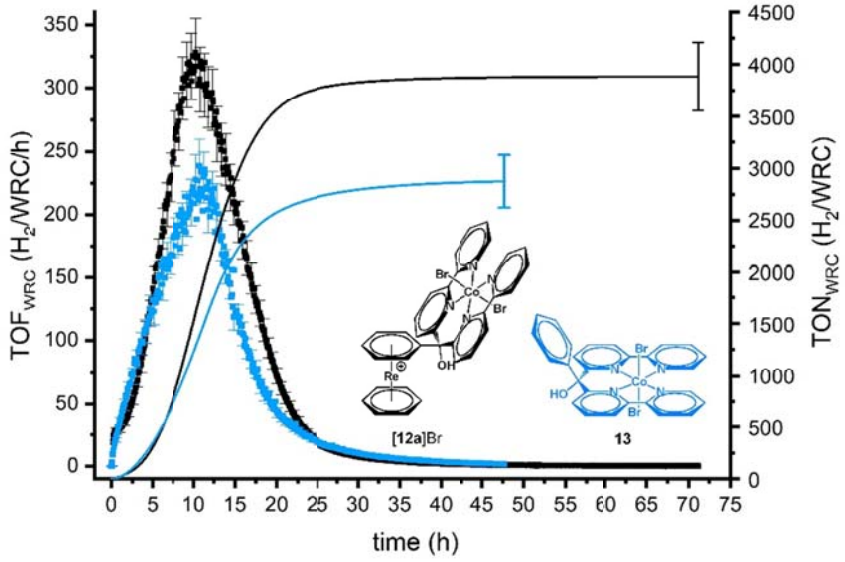


Figure S23. Photocatalysis experiment with [**12a**]Br, in black and the parent catalyst. TOF (dots) (H_2/WRC/h) and TON (lines) (H_2/WRC) formed as a function of time for 5μM catalyst. Experimental conditions: 10mL solution, 0.5mM $[Ru(bpy)_3]Cl_2$, 0.1M NaAsc, 0.1M TCEP, pH 5.0, 453nm LED irradiation.

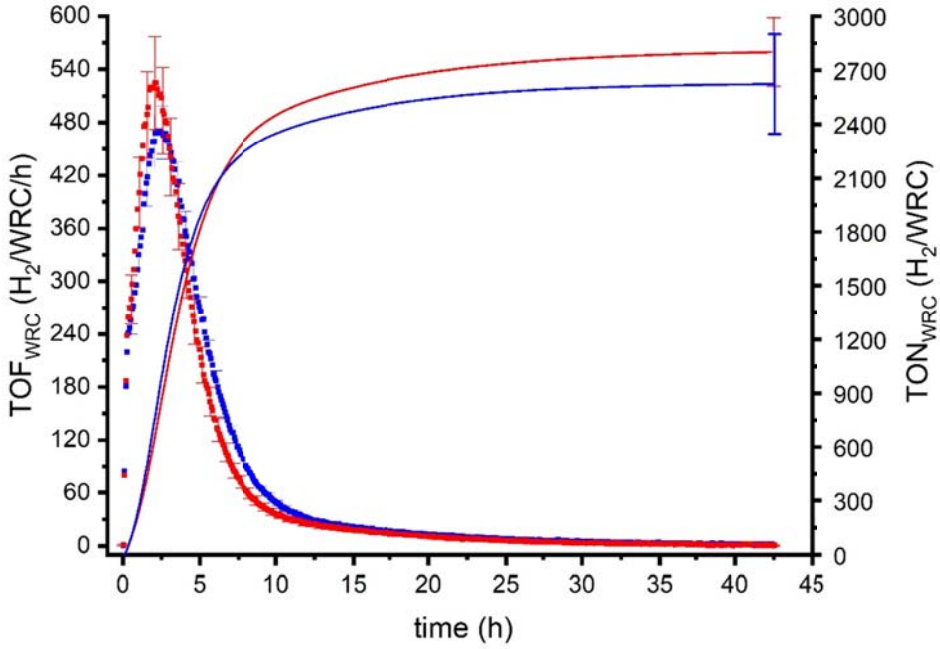
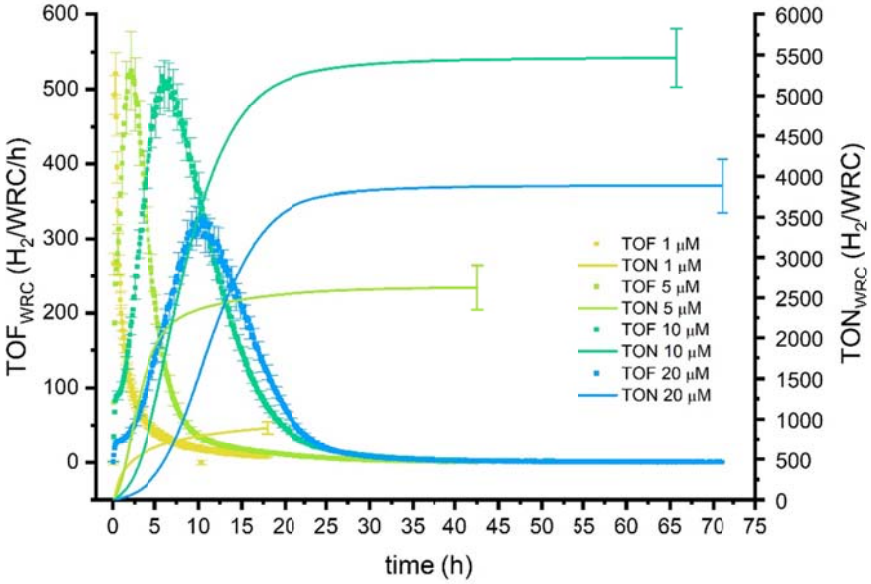
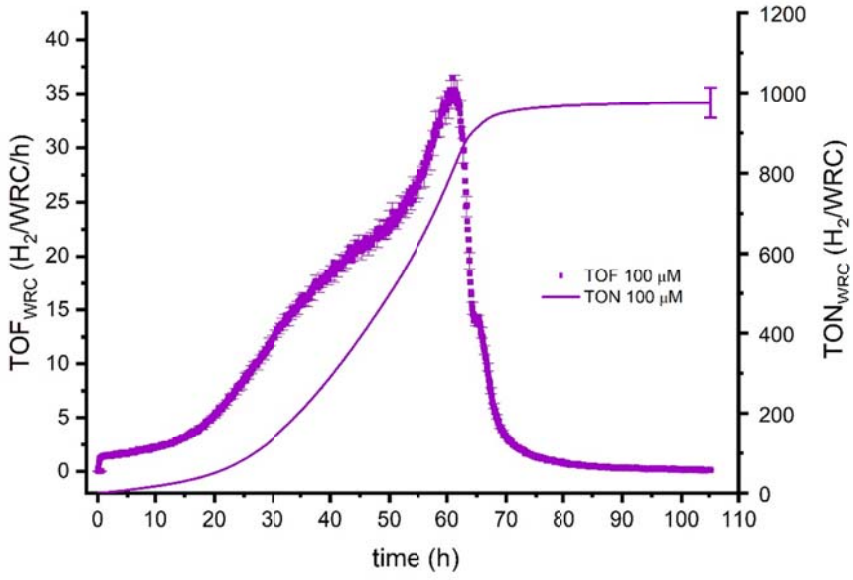


Figure S24. Mercury-poisoning experiment. Blue trace: reference experiment containing 5μM WRC ([**12a**]Br), 500μM $[Ru(bpy)_3]Cl_2$, 0.1M NaAsc, 0.1M TCEP, pH=5.00, 453nm LED

with a photon flux of 0.35μE/s. Red trace: experiment under the same conditions containing 293mg of Hg/10mL of catalytic solution.



a)



b)

Figure S25. H_2 profile as a function of time for [**12a**]Br, a) 1, 5, 10, 20μM of catalyst, b) 100μM of catalyst. Conditions: 500μM $[Ru(bpy)_3]Cl_2$, 0.1M NaAsc, 0.1M TCEP, pH=5.00, 453nm LED with a photon flux of 0.35μE/s. Dots represent TOF and lines TON. Error bars for TON were omitted for clarity

8. Crystallographic data

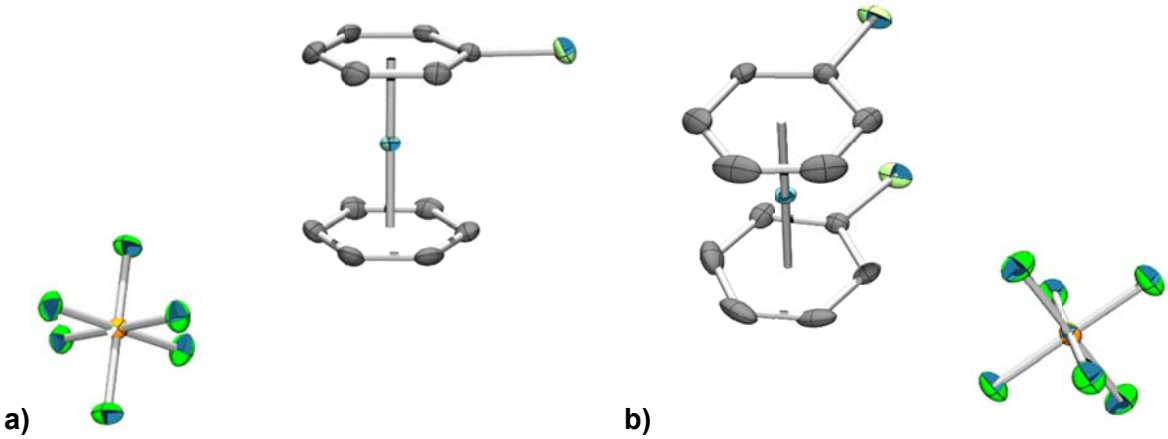


Figure S26. ORTEP representation. a) complex [**2a**](PF_6) and b) complex [**2b**](PF_6). Hydrogen atoms are omitted for clarity; thermal ellipsoids represent 50% probability.

Table S2. Crystal data and data collection of complexes [**2a**](PF_6) and [**2b**](PF_6)

	[Re(η^6-C_6H_5Cl)(η^6-C_6H_6)](PF_6) ([**2a**](PF_6))	[Re(η^6-C_6H_5Cl)$_2$](PF_6) ([**2b**](PF_6))
Empirical formula	$C_{12}H_{11}ClF_6PRe$	$C_{12}H_{10}Cl_2F_6PRe$
Diffractometer	Xcalibur, Ruby	Xcalibur, Ruby
Wavelength (Å)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
mol. weight (g/mol)	521.83	556.27
Crystal system	triclinic	monoclinic
Space group	P-1	C2/c
a (Å)	6.93330(15)	8.7827(4)
b (Å)	9.2527(2)	11.5752(3)
c (Å)	10.8291(2)	14.4118(5)
α (°)	93.0017(18)	90
β (°)	96.8379(18)	95.847(3)
γ (°)	96.4142(18)	90
Volume (Å^3)	683.93(3)	1457.50(9)
Z	2	4
Dens.(calc.) (g/cm^3)	2.534	2.535
Abs. coeff. (mm^{-1})	9.253	8.870
F(000)	488.0	1040.0
Crystal size (mm^3)	0.364 × 0.1 × 0.076	0.472 × 0.261 × 0.149
Crystal description	Light yellow needle	Light yellow
2θ range (°)	5.648 to 76.896	5.684 to 72.626
Index ranges	-11 ≤ h ≤ 11, -15 ≤ k ≤ 16, -18 ≤ l ≤ 18	-14 ≤ h ≤ 14, -19 ≤ k ≤ 19, -24 ≤ l ≤ 22
Refl. collected	27367	11219
Indep. reflections	7057 [Rint = 0.0391]	3528 [Rint = 0.0385]
Reflections obs.	6456	3314
Criterion for obs.	>2sigma(I)	>2sigma(I)
Completeness to θ	99.10 to 36.23o	99.97 to 36.23
Absorption corr.	Analytical	Analytical
Max. and min. transm.	0.565 and 0.121	0.312 and 0.084
Data / restraints / param.	7057/0/190	3528/0/102
Goodness-of-fit on F^2	1.050	1.110
Fin. R ind. [I>2sigma(I)]	R1 = 0.0218, wR2 = 0.0458	R1 = 0.0236, wR2 = 0.0548
R indices (all data)	R1 = 0.0265, wR2 = 0.0478	R1 = 0.0263, wR2 = 0.0560
Fin. diff. ρ_{max} (e$^-$/Å^3)	1.51 and -1.04	0.70 and -1.70
CCDC Nr.	1957333	1957334

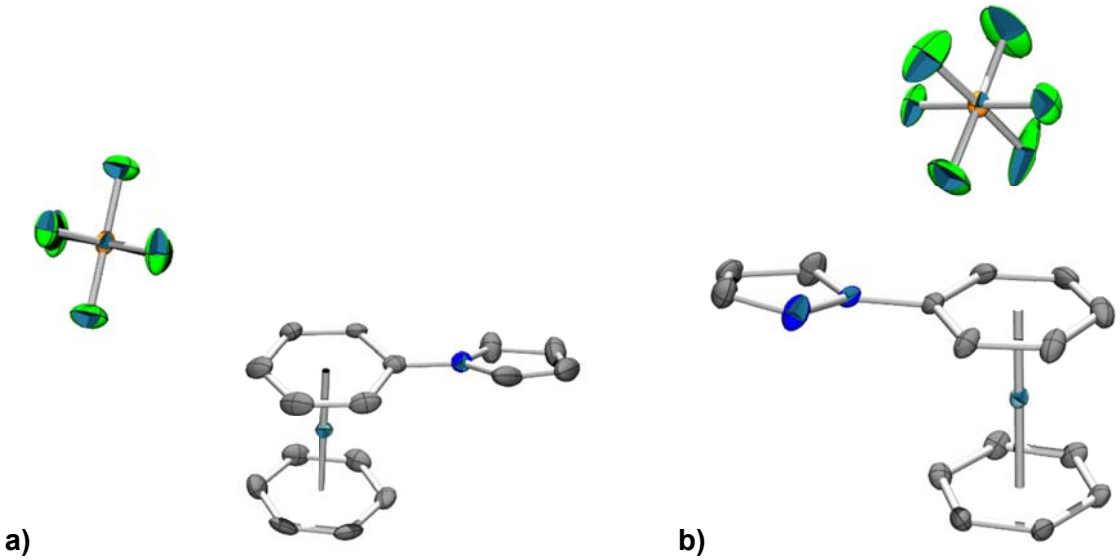


Figure S27. ORTEP representation. a) complex [**4a**](PF_6) and b) complex [**5a**](PF_6). Hydrogen atoms are omitted for clarity; thermal ellipsoids represent 50% probability.

Table S3. Crystal data and data collection of complexes [**4a**](PF_6) and [**5a**](PF_6).

	[Re(η^6-C_6H_5-NC_4H_5)(η^6-C_6H_6)](PF_6) ([**4a**](PF_6))	[Re(η^6-C_6H_5-NC_3H_4N)(η^6-C_6H_6)](PF_6) ([**5a**](PF_6))
Empirical formula	$C_{16}H_{15}F_6NPRe$	$C_{15}H_{14}F_6N_2PRe$
Diffractometer	Xcalibur, Ruby	XtaLAB Synergy, Dualflex, Pilatus 200 K
Wavelength (Å)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
mol. weight (g/mol)	552.46	553.45
Crystal system	triclinic	orthorhombic
Space group	P-1	Pbcm
a (Å)	7.4498(3)	8.25941(9)
b (Å)	8.9441(3)	16.80045(20)
c (Å)	12.4750(4)	11.25367(14)
α (°)	87.943(3)	90
β (°)	81.378(3)	90
γ (°)	81.589(3)	90
Volume ($Å^3$)	812.92(5)	1561.58(3)
Z	2	4
Dens.(calc.) (g/cm^3)	2.257	2.354
Abs. coeff. (mm^{-1})	7.635	7.951
F(000)	524.0	1048.0
Crystal size (mm^3)	0.229 × 0.143 × 0.051	0.337 × 0.084 × 0.024
Crystal description	Yellow plate	Yellow needle
2θ range (°)	4.604 to 67.152	4.85 to 75.856
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -18 ≤ l ≤ 18	-13 ≤ h ≤ 14, -28 ≤ k ≤ 28, -19 ≤ l ≤ 18
Refl. collected	20046	90440
Indep. reflections	5833 [Rint = 0.0495]	4278 [Rint = 0.0473]
Reflections obs.	5330	3831
Criterion for obs.	>2sigma(I)	>2sigma(I)
Completeness to θ	99.80 to 30.44	99.93 to 36.23
Absorption corr.	analytical	gaussian
Max. and min. transm.	0.696 and 0.319	1.000 and 0.335
Data / restraints / param.	5833/0/226	4278/18/217
Goodness-of-fit on F^2	1.042	1.091
Fin. R ind. [I>2sigma(I)]	R1 = 0.0286, wR2 = 0.0604	R1 = 0.0196, wR2 = 0.0385
R indices (all data)	R1 = 0.0327, wR2 = 0.0634	R1 = 0.0249, wR2 = 0.0396
Fin. diff. ρ_{max} ($e^-/Å^3$)	1.07 and -1.24	1.05 and -1.37
CCDC Nr.	1957336	1957339

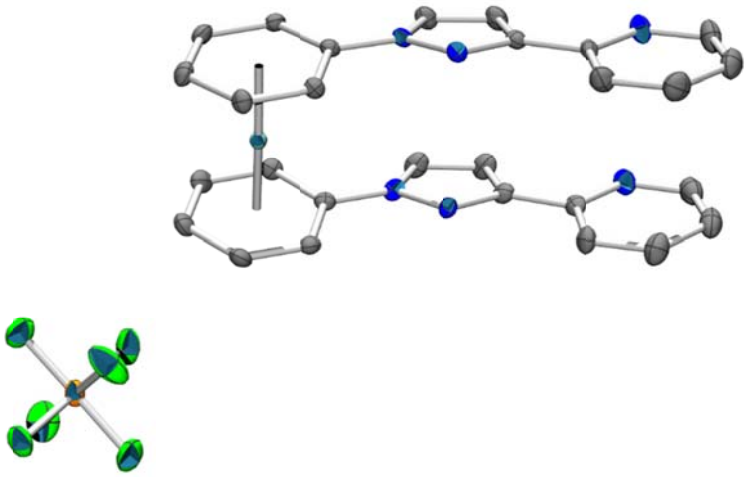


Figure S28. ORTEP representation of complex [**6b**](PF_6). Hydrogen atoms are omitted for clarity; thermal ellipsoids represent 50% probability.

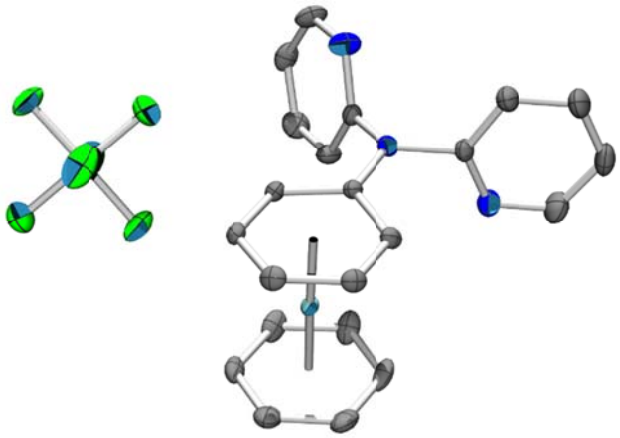


Figure S29. ORTEP representation of complex [**7a**](PF_6). Hydrogen atoms are omitted for clarity; thermal ellipsoids represent 50% probability.

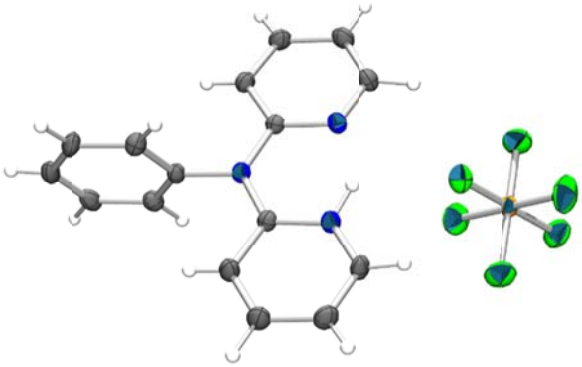


Figure S30. ORTEP representation of the decomposition product of complex [**7a**](PF_6). Thermal ellipsoids represent 50% probability.

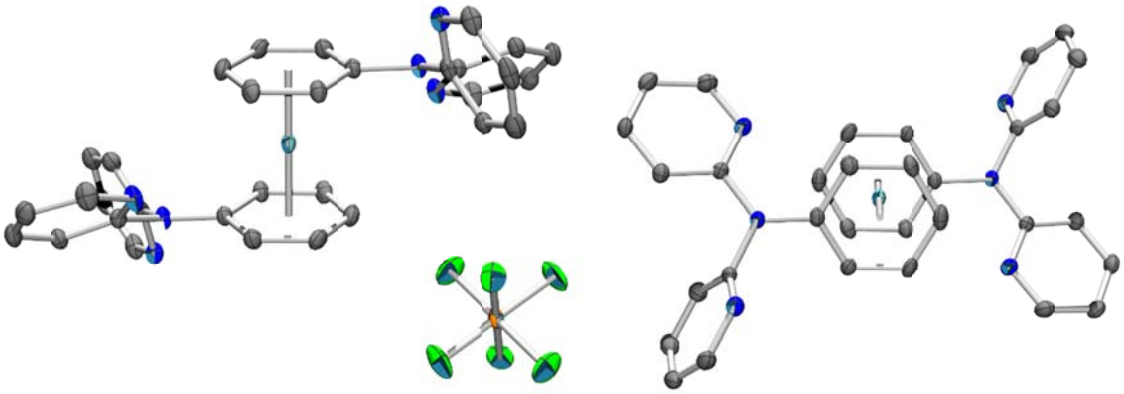


Figure S31. ORTEP representation of complex [**7b**](PF_6). a) Side view and b) Top view. Hydrogen atoms in both views and PF_6^- in the Top view are omitted for clarity; thermal ellipsoids represent 50% probability.

Table S4. Crystal data and data collection of complexes [**6b**](PF_6) and [**7a**](PF_6).

	[Re(η^6-C_6H_5-$C_8H_6N_3$)$_2$](PF_6) ([**6b**](PF_6))	[Re(η^6-C_6H_5-N(C_5H_5N)$_2$)(η^6-C_6H_6)](PF_6) ([**7a**](PF_6))
Empirical formula	$C_{28}H_{22.5}F_6N_6O_{0.25}PRe$	$C_{22}H_{19}F_6N_3Pre$
Diffractometer	XtaLAB Synergy, Dualflex, Pilatus 200 K	XtaLAB Synergy, Dualflex, Pilatus 200 K
Wavelength (Å)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
mol. weight (g/mol)	778.19	656.57
Crystal system	triclinic	monoclinic
Space group	P-1	P21/n
a (Å)	9.12699(16)	10.70728(14)
b (Å)	11.2066(2)	16.7513(2)
c (Å)	13.6865(2)	12.06921(17)
α (°)	88.3898(15)	90
β (°)	71.1433(16)	103.9768(14)
γ (°)	86.0932(15)	90
Volume (Å^3)	1321.65(4)	2100.65(5)
Z	2	4
Dens.(calc.) (g/cm^3)	1.955	2.076
Abs. coeff. (mm^{-1})	4.734	5.930
F(000)	757.0	1264.0
Crystal size (mm^3)	0.103 × 0.058 × 0.027	0.311 × 0.126 × 0.035
Crystal description	Yellow plate	Yellow plate
2θ range (°)	4.726 to 66.6	4.244 to 66.834
Index ranges	-14 ≤ h ≤ 13, -16 ≤ k ≤ 16, -20 ≤ l ≤ 19	-15 ≤ h ≤ 16, -25 ≤ k ≤ 25, -17 ≤ l ≤ 18
Refl. collected	31350	69825
Indep. reflections	8740 [Rint = 0.0396]	7539 [Rint = 0.0387]
Reflections obs.	7847	6559
Criterion for obs.	>2sigma(I)	>2sigma(I)
Completeness to θ	96.93 to 30.44	99.97 to 30.44
Absorption corr.	gaussian	gaussian
Max. and min. transm.	0.911 and 0.552	1.000 and 0.202
Data / restraints / param.	8740/0/423	7539/1/301
Goodness-of-fit on F^2	1.050	1.018
Fin. R ind. [I>2sigma(I)]	R1 = 0.0235, wR2 = 0.0479	R1 = 0.0207, wR2 = 0.0456
R indices (all data)	R1 = 0.0291, wR2 = 0.0491	R1 = 0.0276, wR2 = 0.0474
Fin. diff. ρ_{max} (e$^-$/Å^3)	0.68 and -0.75	1.66 and -0.70
CCDC Nr.	1957340	1957337

Table S5. Crystal data and data collection of complex [**7b**](PF_6) and decomposition product of [**7b**](PF_6).

	Decomposition product of ([**7b**](PF_6))	[Re(η^6-C_6H_5-N(C_5H_5N)$_2$)$_2$](PF_6) ([**7b**](PF_6))
Empirical formula	$C_{16}H_{14}F_6N_3P$	$C_{32}H_{26}F_6N_6PRe$
Diffractometer	XtaLAB Synergy, Dualflex, Pilatus 200 K	XtaLAB Synergy, Dualflex, Pilatus 200 K
Wavelength (Å)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
mol. weight (g/mol)	393.27	825.76
Crystal system	monoclinic	monoclinic
Space group	P21/n	C2/c
a (Å)	9.25190(8)	14.62401(13)
b (Å)	8.61633(7)	7.99651(7)
c (Å)	21.15676(20)	25.03769(19)
α (°)	90	90
β (°)	101.9367(9)	102.4340(8)
γ (°)	90	90
Volume (Å^3)	1650.09(2)	2859.26(4)
Z	4	4
Dens.(calc.) (g/cm^3)	1.583	1.918
Abs. coeff. (mm^{-1})	2.142	9.513
F(000)	800.0	1616.0
Crystal size (mm^3)	0.295 × 0.079 × 0.038	0.151 × 0.061 × 0.035
Crystal description	Colourless plate	Orange plate
2θ range (°)	8.544 to 159.314	7.23 to 158.682
Index ranges	-11 ≤ h ≤ 11, -10 ≤ k ≤ 10, -24 ≤ l ≤ 26	-18 ≤ h ≤ 17, -10 ≤ k ≤ 9, -31 ≤ l ≤ 31
Refl. collected	27074	15828
Indep. reflections	3462 [Rint = 0.0263]	3055 [Rint = 0.0191]
Reflections obs.	3257	2976
Criterion for obs.	>2sigma(I)	>2sigma(I)
Completeness to θ	97.54 to 74.33	99.81 to 74.33
Absorption corr.	gaussian	gaussian
Max. and min. transm.	1.000 and 0.487	1.000 and 0.383
Data / restraints / param.	3462/0/239	3055/0/211
Goodness-of-fit on F^2	1.091	1.179
Fin. R ind. [I>2sigma(I)]	R1 = 0.0506, wR2 = 0.1462	R1 = 0.0277, wR2 = 0.0748
R indices (all data)	R1 = 0.0522, wR2 = 0.1475	R1 = 0.0282, wR2 = 0.0752
Fin. diff. ρ_{max} (e$^-$/Å^3)	0.68 and -0.57	1.88 and -0.90
CCDC Nr.	1957338	1957335

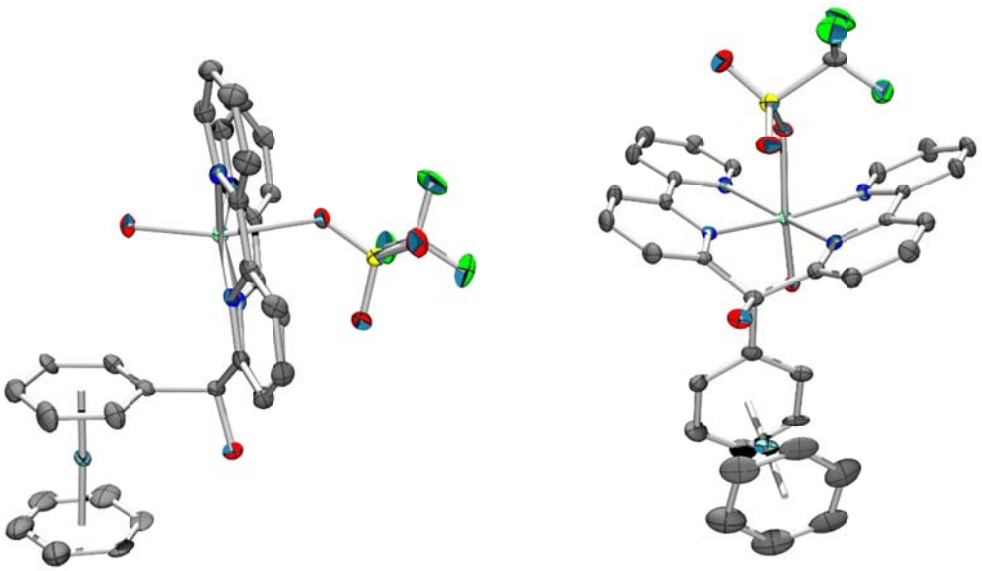


Figure S32. ORTEP representation of the crystal structure of [**12a**]OTf. Hydrogen atoms and two OTf^- anions have been omitted for clarity; thermal ellipsoids represent 40% probability.

Table S6. Crystal data and data collection of complex [**12a**]OTf.

	[Re(η^6-C_6H_5C((OH)($C_{20}H_{14}N_4$)Co(H_2O)(OTf))(η^6-C_6H_6)](OTf)$_2$ ([**12a**]Br)
Empirical formula	$C_{36}H_{28}CoF_9N_4O_{11}ReS_3$
Diffractometer	XtaLAB Synergy, Dualflex, Pilatus 200 K
Wavelength (Å)	Cu Kα (λ = 1.54184)
mol. weight (g/mol)	1204.93
Crystal system	monoclinic
Space group	P2/n
a (Å)	24.24000(10)
b (Å)	8.25330(10)
c (Å)	42.2847(2)
α (°)	90
β (°)	92.7090(10)
γ (°)	90
Volume (Å3)	8450.03(12)
Z	8
Dens.(calc.) (g/cm3)	1.894
Abs. coeff. (mm-1)	10.914
F(000)	4728.0
Crystal size (mm3)	0.267 × 0.093 × 0.066
Crystal description	Brown needle
2θ range (°)	7.112 to 159.142
Index ranges	-30 ≤ h ≤ 30, -10 ≤ k ≤ 10, -53 ≤ l ≤ 53
Refl. collected	172912
Indep. reflections	18124 [Rint = 0.0494]
Reflections obs.	17358
Criterion for obs.	>2sigma(I)
Completeness to θ	99.65 to 74.33
Absorption corr.	gaussian
Max. and min. transm.	0.945 and 0.114
Data / restraints / param.	18124/103/1180
Goodness-of-fit on F2	1.354
Fin. R ind. [I>2sigma(I)]	R1 = 0.0692, wR2 = 0.1587
R indices (all data)	R1 = 0.0712, wR2 = 0.1594
Fin. diff. ρmax (e–/Å3)	2.85 and -2.67
CCDC Nr.	1957341

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4. Spek, A., Single-crystal structure validation with the program PLATON. *Journal of Applied Crystallography* **2003,** *36* (1), 7-13.

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